A semi–phenomenological approach to the structure and transport properties of macromolecules in solution

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von

Aliaksandr Uvarau
(Alexander Uvarov)
aus Minsk, Belarus

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1. Gutachter: PD Dr. Stephan Fritzsche
2. Gutachter: Prof. Dr. Burkhard Fricke

weitere Miglieder der Prüfungskommission:

Prof. Dr. Martin E. Garcia
Prof. Dr. Arno Ehresmann

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Zusammenfassende deutsche Darstellung der in englischer Sprache abgefassten Doktorarbeit:

EINE SEMIPHÄNOMENOLOGISCHE NÄHERUNG ZUR BESCHREIBUNG DER STRUKTUR UND TRANSPORTEIGENSCHAFTEN VON MAKROMOLEKÜLEN IN LÖSUNGEN

Motiviert durch die Lebenswissenschaften *(Life sciences)* haben sich Untersuchungen zur Dynamik von Makromolekülen in Lösungen in den vergangenen Jahren zu einem zukunftsweisenden Forschungsgebiet etabliert, dessen Anwendungen von der Biophysik über die physikalische Chemie bis hin zu den Materialwissenschaften reichen. Neben zahlreichen experimentellen Forschungsprogrammen zur räumlichen Struktur und den Transporteigenschaften großer Moleküle, wie sie heute praktisch an allen (Synchrotron–) Strahlungsquellen und den Laboren der Biophysik anzutreffen sind, werden gegenwärtig daher auch umfangreiche theoretische Anstrengungen unternommen, um das Diffusionsverhalten von Makromolekülen besser zu erklären.

Um neue Wege für eine *quantitative* Vorhersagen des Translations– und Rotationsverhaltens großer Moleküle zu erkunden, wurde in dieser Arbeit ein *semi–phänomenologischer* Ansatz verfolgt. Dieser Ansatz erlaubte es, ausgehend von der Hamiltonschen Mechanik des Gesamtsystems 'Molekül + Lösung', eine Mastergleichung für die Phasenraumdichte der Makromoleküle herzuleiten, die den Einfluß der Lösung mittels effektiver Reibungstensoren erfaßt. Im Rahmen dieses Ansatzes gelingt es z.B. (i) sowohl den Einfluß der Wechselwirkung zwischen den makromolekularen Gruppen (den sogenannten molekularen *beads*) und den Lösungsteilchen zu analysieren als auch (ii) die Diffusionseigenschaften für veschiedene thermodynamische Umgebungen zu untersuchen. Ferner gelang es auf der Basis dieser Näherung, die Rotationsbewegung von großen Molekülen zu beschreiben, die einseitig auf einer Oberfläche festgeheftet sind.

Im Vergleich zu den aufwendigen molekulardynamischen (MD) Simulationen großer Moleküle zeichnet sich die hier dargestellte Methode vor allem durch ihren hohen 'Effizienzgewinn' aus, der für komplexe Systeme leicht mehr als fünf Größenordnungen betragen kann. Dieser Gewinn an Rechenzeit erlaubt bspw. Anwendungen, wie sie mit MD Simulationen wohl auch zukünftig nicht oder nur sehr zögerlich aufgegriffen werden können. Denkbare Anwendungsgebiete dieser Näherung betreffen dabei nicht nur *dichte* Lösungen, in denen auch die Wechselwirkungen der molekularen *beads* zu benachbarten Makromolekülen eine Rolle spielt, sondern auch Untersuchungen zu ionischen Flüssigkeiten oder zur Topologie großer Moleküle.

Keywords: Diffusion, Fokker–Planck Gleichung, hydrodynamische Wechselwirkung, Makromolekül, molekulare beads, Reibung, Transporteigenschaften von Molekülen.

Abstract:

A SEMI–PHENOMENOLOGICAL APPROACH TO THE STRUCTURE AND TRANSPORT PROPERTIES OF MACROMOLECULES IN SOLUTION

Being very important in life, the macromolecules are the point of interest of a lot of disciplines including biophysics, chemical physics, material science, etc. During the last few years, therefore, a novel *semi–phenomenological* approach has been developed starting from the microscopic view point on the system 'macromolecule+solvent' and using the Hamiltonian mechanics as well as the master equations for the phase–space distribution functions of the macromolecules. Since then, the phenomenological approach has been employed very succesfully to investigate the structure and transport properties of macromolecules in solution. Within the framework of the semi–phenomenological approach, in particular, (i) the role of the macromolecule–solvent interaction on the translational motion of macromolecules in solution as well as (ii) the diffusion properties of the various macromolecules have been investigated for different thermodynamic regimes of the solvent. Apart our investigations in the translational motion of the macromolecules in solution, however, (iii) the properties of the rotational (orientational) motion of macromolecules, which is immobilized on a surface, have been also studied with respect to the various intermolecule and macromolecule–surface interactions.
Compared with often expensive MD calculations, a great gain in efficiency is obtained *by several orders of magnitude* and may thus allow investigations on more complex systems for which other numerical techniques will remain unfeasible in the near future. Special attention of this thesis work, moreover, was placed on the flexibility of our approach which makes it possible to implement future investigations in the field of the macromolecular solution.

Keywords: bead, diffusion, Fokker–Planck equation, friction, hydrodynamic interaction, macromolecules, transport.

Preface

This thesis is based on seven papers which have been completed at the University of Kassel during the last three years. These manuscripts are the main source of this thesis and are referred in the text by roman numbers. These papers are appended below.

- PAPER I: *Effects of the bead–solvent interaction on the dynamics of macromolecules, 1 The dumbbell molecule.*
  A. Uvarov and S. Fritzsche,
  MACROMOLECULAR THEORY AND SIMULATIONS, **13**(3), 241–256, (2004)

- PAPER II: *Effects of the bead–bead interaction on the restricted rotational diffusion of the nonrigid macromolecules.*[1]
  A. Uvarov and S. Fritzsche,
  JOURNAL OF CHEMICAL PHYSICS, **121**(13), 6561–6572, (2004)

- PAPER III: *A semi–phenomenological approach to the transport and diffusion of small spherical macromolecules in solution.*
  A. Uvarov and S. Fritzsche,
  CHEMICAL PHYSICS LETTERS, **401**(3), 296–301, (2005)

- PAPER IV: *Friction of N–beads macromolecules in solution: effects of the bead–solvent interaction.*[2]
  A. Uvarov and S. Fritzsche,
  PHYSICAL REVIEW, **E73**(1), 011111—1–12, (2006)

- PAPER V: *Restricted rotational diffusion of non–rigid macromolecules on surfaces: Effects of the bead–bead and bead–surface interaction.*
  A. Uvarov and S. Fritzsche,
  PROGRESS IN COLLOID & AND POLYMER SCIENCE, **133**, 95–99, (2006)

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[1] This article has been selected for the VIRTUAL JOURNAL OF BIOLOGICAL PHYSICS RESEARCH, **8**(7), (2004).

[2] This article has been selected for the VIRTUAL JOURNAL OF BIOLOGICAL PHYSICS RESEARCH, **11**(3), (2006).

- <u>PAPER VI:</u> *Restricted rotational diffusion of nonrigid dumbbell macromolecules on a surface: Interplay of the bead–bead and bead–surface interactions.*
  A. Uvarov and S. Fritzsche,
  CHEMICAL PHYSICS LETTERS, `in print` (2006)

- <u>PAPER VII:</u> *High–order correlation contributions to the friction of macromolecules in solution: A semi–phenomenological Fokker–Planck approach*
  A. Uvarov and S. Fritzsche,
  PHYSICAL REVIEW LETTER, `submitted`, (2006)

In addition, I have also contributed to the following papers, which are not included in this thesis.

1. *Orientation relaxation of macromolecules immobilized on a surface.*
   A.P. Blokhin, M.F. Gelin and A.V. Uvarov,
   NONLINEAR PHENOMENA IN COMPLEX SYSTEMS, **2**(3), 72–82, (1999)

2. *Does the harmonic oscillator bath induce dissipative dynamics of dumbbells?*
   A.V. Uvarov, A.P. Blokhin and M.F. Gelin,
   MAX PLANCK INSTITUTE FOR THE PHYSICS OF COMPLEX SYSTEMS,
   PREPRINT, **mpi-pks/0105004**, (2000)

3. *Polarized fluorescence of nonrigid macromolecules in the solution.*
   A.V. Uvarov, A.P. Blokhin and M.F. Gelin,
   LASER PHYSICS AND PHOTONICS. SARATOV, RUSSIA. REFEREED PROC. SPIE INT. SOC. OPT. ENG. **4002**, 255–260, (2000)

4. *Dynamics of macromolecules in the bath of harmonic oscillators.*
   A. V. Uvarov, M.F. Gelin and A.P. Blokhin,
   NONLINEAR PHENOMENA IN COMPLEX SYSTEMS, **6**(1), 572–576, (2003)

5. *Radical Transport Modelling in NANOJET.*
   O.Rabinovych, A. Uvarov, D. Filenko and I. W. Rangelow,
   APPLIED PHYSICS, **A81**(8), 1661–1666, (2005)

Contents

Chapter 1

Introduction

A better understanding the dynamical behaviour of macromolecules, i.e. translational and rotational motion of macromolecules, or formation and deformation of macromolecular shape, remains a central problem for the study of proteins and DNA in solution. Apart from the fundamental research, of course, the knowledge of structural and dynamical properties of macromolecules in solutions are really important both in the medical and pharmaceutical applications as well as in industrial applications in order to build so called 'designer enzymes' for biocatalysis, or the biological purification of industrial waste water, ect. During the past decay, therefore, a large number of experimental techniques have been developed in order to describe and analyze the statical and dynamical properties of macromolecular solutions. For instance, the dynamic light– , X–ray– and neutron–scattering experiments have been carried out in order to describe the translational motion of the macromolecule, which determines the motion of the macromolecule as whole (Sorlie and Pecora 1990; Harnau *et al* 1996; Yardimcii *et al* 2005). In order to describe the formation and deformation of the macromolecular shape, i.e. internal configurational changes of macromolecules, the dielectric relaxation (Gaiduk 1999) as well as fluorescence depolarization techniques have been successfully used (Chirico *et al* 1999; Krishna *et al* 2000).

On the theoretical side, the evolution of the investigations of the statical and dynamical properties of the macromolecules has crucially been influenced by the *phenomenological* models of Rouse (1953) and Zimm (1956). By making use the fact that macromolecule is large molecules containing many *repeat* units (Doi and Edwards; Grosberg and Khokhlov 1989), Rose (1953) considered macromolecule as *a set of* (identical) *beads* which are coupled to each other by the pairwise Hookean potential. The solvent was modeled by a Newtonian viscous fluid, i.e. unstructured and incompressible medium. On moving through this solvent, moreover, the beads experience a hydrodynamic drag given by Stokers (Grossberg and Khokhlov 1989) law in which the drag force on the bead and solvent is proportional to the relative velocity with the proportionality (friction) constant ξ . Finally, the macromolecular solution was presumed to be sufficiently *dilute* that different macromolecules did not interact with each other. Although the *Rouse* model of the macromolecular solution looks oversimple, it have been widely and successfully used by a lot of scientist in order to analyze the experimental data as well as predict some statical and transport properties of the macromolecular solutions (Doi and Edwards 1986). Nevertheless, the Rouse model has several drawbacks and variances with the experiments (Öttinger 1986).

In order to overcome the drawbacks, Zimm (1956) extended the Rouse model by taking into account the (so–called) hydrodynamic interaction (Kirkwood and Riseman 1948) between the beads of the macromolecule which 'arises' due to any moving beads of the macromolecule disturbs the solvent flow which, in its turn, influence on the motion of another beads. Let us note, that, by including the hydrodynamic interaction, the Rouse model has been considerably improved. In contrast to the Rouse model, for example, the *Rose–Zimm* model of the macromolecular solution reproduced the experimentally observed dependence of the intrinsic viscosity on the macromolecular weight even with hydrodynamical interaction tensor in the *preaveraged* form when the equations of motion for the beads may be linearize. (Doi and Edwards 1986). In fact, the Rouse–Zimm theory has been a very successful theory of macromolecular dynamics.

Unfortunately, both Rouse as well as Zimm (phenomenological) methods are based on the assumption that the solvent is a *non–discrete* and *incompressible* medium. However, the need for taking the discrete (atomistic) structure of the solvent into account has been recognized mainly due to molecular dynamic simulations (MDS) of Dünweg and Kremer (1993), Polson and Galant (2006) ect. Often, the discrete nature of the solvent leads moreover to rather remarkable deviations from a pure Brownian behaviour of the macromolecular beads and hence, may play an important role also in studying the dynamics of macromolecules (Ould–Kaddour and Levesque 2001, 2003; Schmidt and Skinner 2003, 2004). In fact, the discrete nature of the solvent can change both the (conformational) static as well as the dynamical properties of the macromolecules dramatically. (Shirayev *et al* 2005)

Molecular dynamic simulation (MDS) is really powerful method for the investigation of the statical and transport properties of the macromolecules in solution which bases on pure *microscopic* view point of the overall system 'macromolecules+solvent'. In contrast to the *phenomenological* theories, the discrete structures of the solvent as well as macromolecule are taken into account in MD simulation from the very beginning (cf. Figure 1.1). In principle, the MDS approach is very attractive: Simply solving Newtons equations of motion both for the beads of the macromolecule as well as for the solvent particles numerically provides us, *per definition*, with correct statical as well as transport properties of the macromolecular solution. During the past decade, therefore, a

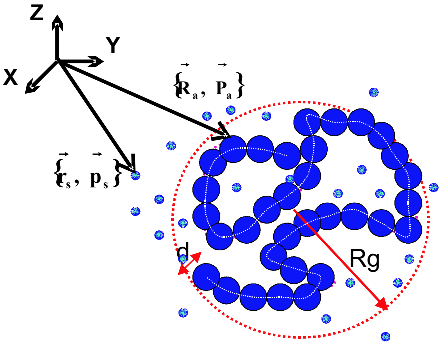

Figure 1.1: Microscopic model of the classical system 'N–bead (chain) macromolecule+solvent': Macromolecule is a set of the beads which are specified by their position and momentum coordinates $\{\mathbf{R}_a,\, \mathbf{P}_a,\, a = 1, \ldots, N\}$. Similarly, the solvent is taken as a set of n ($\gg N$) spherical particles of mass m and with coordinates $\{\mathbf{r}_s,\, \mathbf{p}_s,\, s = 1, \ldots, n\}$.

lot of MDS have been performed in order to analyze the dynamical behaviour of the macromolecules in solution. Extended molecular dynamics simulations were done by Dünweg and Kremer together with coworker (1990, 1993, 1999, 2003), Schmidt and Skiner (2003, 2004), Polson and Gallant (2006) and others, dealing with questions such as the transport properties and (de–) formation of the shape of the macromolecules in solution, structure factors, and shorttime diffusion. However, each MD simulation is really a valuable tool since it often requires larger–scale computations, and hence,cannot be 'repeated' so easily for different interactions or chemical solutions. Indeed, the smallest time step in MD simulations has to be short compared to the fastest timescale of the relevant physical processes involved (typically few femtoseconds) (Dünweg and Kremer 1993; Binder 1995). Therefore, the MD simulations are typically limited to a few nanoseconds. The (asymptotic) relaxation processes of the larger macromolecules, however, takes much more time. For instance, the relaxation time of the end-to-end vector, which can easily be of the order of 10^{-5} seconds are out of reach for present day MD simulations and probably remain unaccessible for near future computer generations (Binder 1995, Znamenskiy and Kobrak 2004).

The aim of this thesis is therefore to gain a better understanding the statical as well as the transport properties of macromolecules in solution by using a *semi–phenomenological* approach. This approach is based on the microscopic view point on the system 'macromolecule+solvent' (cf. Fig. 1.1) and starts from the Hamiltonian mechanics and the master equations for the phase–space distribution functions of the macromolecules. The semi–phenomenological approach have been recently derived and presented by us in the Papers I, III, IV, VII which are main results of my research performed at the Kassel University. Therefore, this thesis contains two part. In the first part, we present the short introduction (Section 2.1) to the semi–phenomenological approach as well as two applications (Section 2.2) of the approach to the translational motion of the macromolecules immersed in the solvent. In addition to the translational motion, we present (Chapter 3) the properties of the rotational (orientational) motion of macromolecules in solutions which have be also investigated by us during the last years (Papers II, V, VI). A special place of this thesis is reserved for the description of the possible future applications of the semi–phenomenological approach. In particular, in Chapter 4, four scenarios for future studies is presented. In final of the first part of this thesis, a short summary are given in Chapter 5. In addition, as second part of the thesis, the original papers are added.

Chapter 2

A semi–phenomenological approach

2.1 Fokker–Planck equation and friction tensors

To understand the dynamical behaviour of macromolecules in solution, one may start most generally from Hamiltonian mechanics and the master equations (PAPER I) for the phase–space distribution functions of the overall system "macromolecule+solvent". Taking such a *microscopic viewpoint*, for instance, we were recently able to derive a Fokker–Planck type equation (FPE) for the time evolution of the phase–space distribution function of a dumbbell–type molecule (PAPER I), which where later (PAPER IV) also generalized for the macromolecule consisting out of a N pairwise interacting molecular components (the so–called *beads* of the macromolecule). In a slightly simplified form, this Fokker–Planck equation reads

$$\frac{\partial \rho_N(\mathbf{\Gamma};\mathbf{t})}{\partial t} + \sum_{a=1}^{N} \frac{\mathbf{P}_a}{M} \frac{\partial \rho_N(\mathbf{\Gamma};\mathbf{t})}{\partial \mathbf{R}_a} - \sum_{a,b=1}^{N} \frac{\partial\, U\left(|\mathbf{R}_a - \mathbf{R}_b|\right)}{\partial \mathbf{R}_a} \frac{\partial \rho_N(\mathbf{\Gamma};\mathbf{t})}{\partial \mathbf{P}_a}$$

$$= \sum_{a,b=1}^{N} \frac{\partial}{\partial \mathbf{P}_a}\, \xi^{\,(\mathbf{ab})} \left(\frac{\partial}{\partial \mathbf{P}_b} + \frac{1}{k_B T\, M}\, \mathbf{P}_b \right) \rho_N(\mathbf{\Gamma};\mathbf{t}) \tag{2.1}$$

where M denotes the mass of the beads, $\mathbf{R}_a$ and $\mathbf{P}_a$, $a = 1, \ldots, N$ the positions and the momenta of the individual beads, respectively, and where $\mathbf{\Gamma} \equiv \{\mathbf{R}_1, \ldots \mathbf{R}_N;\, \mathbf{P}_1, \ldots \mathbf{P}_N\}$ has been utilized in order to refer to the phase–space coordinates altogether. For each pair (a, b) of beads, there is associated also a friction tensor $\xi^{\,(ab)}$ which characterizes the (thermodynamically averaged) interaction of these two beads with the surrounding particles from the solvent. Finally, k_B denotes the Boltzmann constant and T the temperature of the overall system 'macromolecule + solvent'.

The FPE (2.1) has be derived from the (*exact*) Liouville equation (Landau and Lifshitz 1980) for the phase–space distribution of overall system 'macromolecule+solvent' by using the techniques of projection operators (Paper I; Szamel 1998; Evans and Morriss 1990) as well as the two assumptions, that (i) the macromolecule and the solvent particles did not interact *before* some initial time, $t < t_{\rm in} = 0$, and that (ii) the solvent starts at $t = 0$ from an Boltzmann equilibrium state with the distribution function

$$\Phi_{eq}\left(\{\mathbf{r}_s, \mathbf{p}_s\}\right. \;=\; \frac{1}{z}\, e^{-H_S/k_B T} \;,$$

where H_S is the Hamiltonian of the solvent which depend on the all the position and momenta, $\{\mathbf{r}_s, \mathbf{p}_s\}$, $s = 1 \ldots n$ of the solvent particles, and $z = \int d\{\mathbf{r}_s, \mathbf{p}_s\}\; e^{-\beta H_S}$ denotes the proper normalization integral for the phase–space distribution.

In the frame of the two basic assumptions from above, the FPE (2.1) describes the time evolution of the phase–space distribution $\rho_N(\mathbf{\Gamma}; \mathbf{t})$ and, hence, includes all the information about the dynamics of the N–bead macromolecule in solution. From this (probability density) function, in fact, the probability to find the macromolecule at time t within a small volume $d\mathbf{\Gamma}$ around the point $\mathbf{\Gamma}$ in phase space is simply given by $\rho_N(\mathbf{\Gamma}; \mathbf{t})\, d\mathbf{\Gamma}$. For this to be right, of course, the distribution function should be normalized,

$$\int d\mathbf{\Gamma}\; \rho_N(\mathbf{\Gamma}; \mathbf{t}) \;=\; 1\,, \tag{2.2}$$

by taking the integral over the complete phase–space of the macromolecule. In practise, the knowledge of the phase–space distribution (or, at least, of some of its properties) plays a *key* role for studying the dynamical behaviour of molecules in solution. As discussed previously in the literature (Doi and Edwards 1986; Cortes *et al* 1985; Paper II), this distribution function help calculate for instance the *translational* as well as *rotational* properties of macromolecules. Moreover, knowing once the phase–space distribution $\rho_N(\mathbf{\Gamma}; \mathbf{t})$ of a macromolecule, the time average $\langle \ldots \rangle$ of *any* function $A \equiv A(\{\mathbf{\Gamma}\})$ can be easily derived from the integral

$$\langle A \rangle \;=\; \int d\,\mathbf{\Gamma} A(\mathbf{\Gamma})\, \rho_N(\mathbf{\Gamma}; \mathbf{t})\,. \tag{2.3}$$

The FPE (2.1), moreover, has the nice feature that the friction tensors, $\widehat{\xi}^{(ab)}$, whose off–diagonal elements describe the hydrodynamic interaction between beads a and b, contain in fact all information about influence of the solvent on the macromolecular behaviour. As shown recently in Paper VII, the *exact* expression for the friction tensor of a $N-$bead macromolecule

$$\begin{aligned}
\widehat{\xi}^{(ab)}(\mathbf{R}_a, \mathbf{R}_b) \;=\; & \sum_{j=0}^{\infty} \int_0^{\infty} d\tau\, \frac{\tau^j}{j!} n_0 \int \frac{d\mathbf{k}_1 d\,\mathbf{k}_2}{(2\pi)^6}\, \mathbf{k}_1\, W(\mathbf{k_1}) W(\mathbf{k_2}) e^{i\mathbf{k_1}\mathbf{R}_a} e^{\widehat{L}_B \tau} e^{i\mathbf{k_2}\mathbf{R}_b}\, \mathbf{k}_2 \\
& \times \frac{1}{n} \sum\!\!\!\!\!\!\int_{s,t} d\{\mathbf{r}_s, \mathbf{p}_s\} e^{-i\mathbf{k_1}\mathbf{r}_s} e^{\widehat{L}_S \tau} e^{-i\mathbf{k_2}\mathbf{r}_t} \left(\sum_{a',s'} \frac{\partial\, W}{\partial\, \mathbf{R}_{a'}} \left[-\frac{\partial}{\partial \mathbf{p}_{s'}} \right] \right)^j \Phi_{eq}
\end{aligned} \tag{2.4}$$

can be written as an (infinite) series of terms which depend on the number density (concentration) n_0 of the solvent and on the Fourier transform $W(\mathbf{k}) = \int d\mathbf{r}\, e^{-i\,\mathbf{kr}}\, W(\mathbf{r})$ of the *bead–solvent* interaction $W(\mathbf{r})$ with $\mathbf{k}$ being the wave vector. Of course, the friction terms in (2.4) also contain the Liouville operators $\widehat{L}_B$ for the 'free macromolecule', respectively, $\widehat{L}_S$ of the solvent. Instead of the Liouville operators, moreover, the each friction term in the series expansion (2.4) for the friction tensor of a macromolecule can be written in terms of the bead–solvent interaction potential W and the $(j+2)-$point correlation functions of the solvent (Papers IV and Papers VI) which, as defined in the framework of the kinetic theory of the liquids (van Zon and Schofield 2001; Zaccarelli *et al* 2001; Hansen and McDonald 1990) contain all the information about the solvent including, for example, its relaxation time back into the equilibrium, temperature, viscosity, and many further properties. The friction tensor $\widehat{\xi}^{\,(ab)}(\mathbf{R}_a, \mathbf{R}_b)$ in Eq. (2.4) should be one of the *key* ingredient for studying the dynamical properties of macromolecules in solutions.

While, however, the infinite series (2.4) for the friction tensor can not be used directly in the calculations of the dynamical properties of the macromolecule in solutions, this equation gives rise to a *series* of approximations owing to the powers in the Fourier shape of the bead–solvent interaction potential.

To obtain further insight into the behaviour of macromolecules in solutions, let us note that the each term of the friction tensors $\widehat{\xi}^{\mathbf{(ab)}}_{[j]\,\alpha\beta}$ are symmetric in the cartesian indices α and β and of rank 2 in the wave vector and, as shown in the Papers I and IV, may have just six independent components. Furthermore, since these components only depend on the positions of the *two* beads, these tensors can always be parameterized in terms of two parameters (Grosberg and Khokhlov, Paper IV)

$$\widehat{\xi}^{\mathbf{(ab)}}_{[j]} \;=\; A_{[j]}(\Delta_{ab})\,\mathbf{I} + B_{[j]}(\Delta_{ab})\;\mathbf{q}^{(ab)}\,\mathbf{q}^{(ab)} \qquad (2.5)$$

with $\mathbf{I}$ being the 3×3 unit tensor. In the expression (2.5), $\Delta_{ab} = |\mathbf{R}_a - \mathbf{R}_b|$ is the distance between the beads a and b and $\mathbf{q}^{(ab)} = \frac{\mathbf{R}_a - \mathbf{R}_b}{\Delta_{ab}}$ denotes a unit vector which points from bead b to bead a. The parameters $A_{[j]}$ and $B[j]$ still contain all information about the solvent. If we consider only the first ($j \equiv 0$) term of the series (2.4) for the friction tensor $\widehat{\xi}^{\,(ab)}(\mathbf{R}_a, \mathbf{R}_b)$ of the macromolecule immersed in the solvent (the so–called *zero–order* approximation), for example, we obtain the friction tensor (parameters) which are appropriate in particular for a *weak* interaction of the macromolecule with the solvent particles (Paper IV). Figure 2.1, for example, shows a quite different behaviour of the 'zero–order' friction tensor parameters $A(\Delta_{ab})\,/\,\xi_0$ and $B(\Delta_{ab})\,/\,\xi_0$ for the high–density as well as *critical* thermodynamic regimes of the solvent if we assume a Yukawa– or Born–Mayer–type bead–solvent interactions.

As seen from this figure, moreover, the beads do not affect each other anymore for a

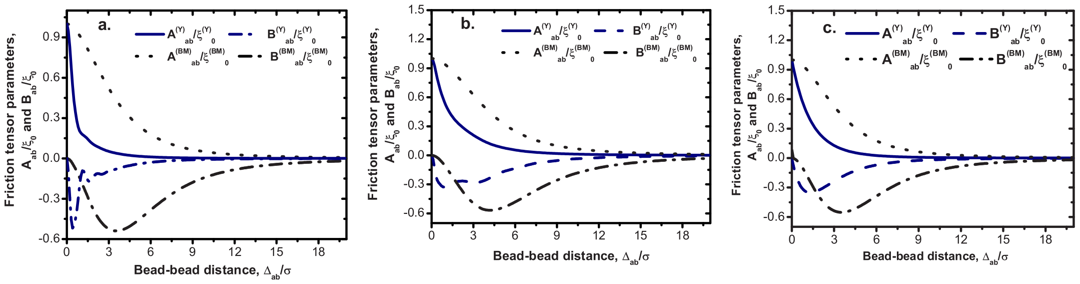

Figure 2.1: Friction tensor parameters $A_{[0]}$ and $B_{[0]}$ normalized on the single–bead friction coefficient ξ_0 as function of the bead–bead distance Δ_{ab}. They are shown for a Yukawa (Y) and Born–Mayer (BM) bead–solvent potential. These friction parameters are shown for three cases: (a) the long–wave part ($k \to 0$) of the statical structure factor of the high–density solvent $g(k)$ was taken into account; (b) the same like (a) but for the solvent at the critical point; (c) only short–wave part ($k \gg 0$) of the statical structure factor of the high–density solvent ($g(k) = 1$) was taken into account. See text and PAPER IV for further discussion.

distance of say 6σ for the Yukawa bead–solvent potential. In contrast, however, they will interact at this or even larger distances in the case of a Born–Mayer potential.

The Figure 2.1 also demonstrates that the friction parameters depend rather strongly on the oscillating nature of the "two–point" correlation function $g(k)$ of the solvent (so–called the structure factor or scattering function) for $k \leq 20\sigma$ of the solvent, i.e. on the discrete nature of the solvent (Dünweg and Kremer 1993). As seen from Figure 2.1, the oscillating of $g(k)$ for small values of k leads to the *qualitative* different behaviour [sf. Fig. 2.1 (a), (b)] than obtained if the solvent is considered as uniform and unstructured medium, i.e. the (so–called) 'high–frequency' approximation of the static factor $g(k) = 1$ is assumed constant (Figure 2.1 (c)). Moreover, Fig. 2.1 clearly shows the role of the various thermodynamical regimes of the solvent on the behaviour of the macromolecule. In particular, we will consider the solvent at the *critical point* (Drozdov and Ticker 2001; Yamaguchi *et al* 2002) as well as the high–density solvent which is far from criticality. [compare, for example, Fig. 2.1 (a) and (b), in which the friction tensor parameters of the macromolecule have been calculated (PAPER IV) for the solvent in the critical point (cp) (the temperature $k_B T_{cp} \approx 1.2\epsilon_B$ and the number density $n_{0_{cp}} \approx 0.30/\sigma^3$) and for the high–density of the solvent ($k_B\, T \approx 1.2\, \epsilon_B$, $n_0\, \sigma^3 \approx 0.86$), respectively.]

Apart from its explicit dependence on the bead–solvent potential, the friction tensor parameters can be also used to analyze the effects of the various part of the bead–solvent interactions. As shown in the PAPER IV, for instance, only the *repulsive* part of the van der Waals interaction is generally responsible for the behaviour of the friction tensor parameters. This results is fully in agreements with the molecular dynamic simulations of Dünweg and Kremer (1993).

Beside of a simplified scenario of zero–order approximation, however, expression (2.4) enables one also to analyze the first– and higher–order *corrections* to the friction tensor. For instance, by utilizing the well–known property $-\frac{\partial}{\partial \mathbf{p}_t}\Phi_{eq} = \frac{\beta}{m}\mathbf{p}_t\Phi_{eq}$ of the equilibrium distribution of the solvent (Bird *et al* 1987; Grosberg and Khokhlov 1989) and by restricting the summation to $j \leq 1$, the friction tensor (2.4) of a $N-$bead macromolecule read as (PAPER VI)

$$\begin{aligned}
\widehat{\xi}^{(ab)} &= n_0 \int_0^\infty d\tau \left[\int \frac{d\mathbf{k}_1}{(2\pi)^3} (\mathbf{k}_1\mathbf{k}_1) W(\mathbf{k}_1) W(\mathbf{k}_1)\, e^{i\mathbf{k}_1\mathbf{R}_a}\, e^{-i\mathbf{k}_1\mathbf{R}_b} g^{(0)}(\mathbf{k}_1;\tau)\right] \\
&\quad - \beta n_0 \int_0^\infty d\tau \left[\tau \int \frac{d\mathbf{k}_1 d\mathbf{k}_2}{(2\pi)^6} (\mathbf{k}_1\mathbf{k}_2) W(\mathbf{k}_1)\, W(\mathbf{k}_2)\, e^{i\mathbf{k}_1\mathbf{R}_a}\, e^{i\mathbf{k}_2\mathbf{R}_b} \right. \\
&\qquad\qquad \left. \times \sum_{c=1}^{N} e^{-i(\mathbf{k}_1+\mathbf{k}_2)\,\mathbf{R}_c}\, W(\mathbf{k}_1+\mathbf{k}_2)\, g^{(1)}(\mathbf{k}_1,\mathbf{k}_2;\tau) \right] \qquad (2.6)
\end{aligned}$$

where

$$g^{(0)}(\mathbf{k}_1;\tau) = \frac{1}{n} \sum\!\!\!\!\!\!\int_{s,t} d\{\mathbf{r},\mathbf{p}\} e^{-i\mathbf{k}_1\mathbf{r}_s}\, e^{\widehat{L}_S\,\tau}\, e^{-i\mathbf{k}_2\mathbf{r}_t}\, \Phi_{eq} \qquad (2.7)$$

is the two–point correlation function (CF) of the solvent, known also as the dynamic structure factor (Grosberg and Khokhlov 1989), and

$$g^{(1)}(\mathbf{k}_1,\mathbf{k}_2;\tau) = \frac{1}{n} \sum\!\!\!\!\!\!\int_{s,t,u} d\{\mathbf{r},\mathbf{p}\} e^{-i\mathbf{k}_1\mathbf{r}_s}\, e^{\tau\widehat{L}_S}\widehat{L}_S\; e^{-i\mathbf{k}_2\mathbf{r}_t} e^{i(\mathbf{k}_1+\mathbf{k}_2)\mathbf{r}_u}\, \Phi_{eq} \qquad (2.8)$$

the three–point correlation function. Both of these correlation functions, Eq. (2.7) and (2.8), are well–known from the theory of liquids (van Zon and Schofield 2001; Zaccarelli *et al* 2001; Hansen and McDonald 1990) and contain all information about the solvent as, for example, its relaxation time back into the equilibrium, the temperature, viscosity, and many further properties which could be determined experimentally.

As mentioned above, the friction tensor is one of the *key* ingredient for studying the dynamical properties of macromolecules in solutions. It affects not only the relaxation time (which is needed for the macromolecule in order to return back from a non–equilibrium into the equilibrium state) or the center–of–mass and internal velocity autocorrelation functions of the macromolecule but also its end–to–end vector and radius of gyration (PAPER I; Doi and Edwards 1986). In addition to the internal properties of the macromolecular behaviour, the friction tensors affects also the dynamical behaviour of the macromolecule as a whole. In the next subsections, for example, we shall indicate how the expression for the friction tensors can be utilized in order to calculate and analyze the center–of–mass (cm) diffusion coefficient for a wide range of mass ratios as well as for different macromolecules with different number of beads. Information about this coefficient will help us understand the motion of the macromolecule as a whole within the solvent.

2.2 Applications of the approach to the translational motion of macromolecules

Various (large-scale) molecular–dynamic computations have been carried out during the last decade in order to understand the dynamical properties of macromolecules in solution including case studies on the dynamical and statical structure factors (Ahrichs and Dünweg (1999); Liu and Dünweg (2003); Yamaguchi *et al* 1999, 2002), the velocity and force autocorrelation functions (Ould–Kaddour and Levesque 2001, 2003), the diffusion coefficients (Schmidt and Skinner J L 2003, 2004; Srinivas *et al* 1999; Heyes *et al* 1998; Easteal and Woolf 1990), and various other properties. Apart from the interaction parameters, these investigations differ by the size and mass of the macromolecules, as well as by the internal structure of the macromolecule. A lot of MD simulations, in particular, were devoted to investigate the behaviour of macromolecules immersed in a (so–called) Lennard–Jones solvent for which the interaction among the solvent particles is modeled by a "truncated" Lennard–Jones (LJ) potential

$$V(r) \;=\; \begin{cases} 4\epsilon_S \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] & \text{if } \; r \le r_S \\ 0 \qquad \text{otherwise} \end{cases} \tag{2.9}$$

where ϵ_S is the interaction strength and r_S the cut–off radius beyond which the potential becomes zero. Moreover, similar shape of the interaction has been assumed also for the macromolecule–solvent potential

$$W(r) \;=\; \begin{cases} 4\,\epsilon_M \left[\left(\frac{\sigma}{r-l_M}\right)^{12} - \left(\frac{\sigma}{r-l_M}\right)^{6} \right] S(r-l_M) & \text{if } \;\; l_M \le r \le r_M \\ 0 \qquad \text{otherwise}\,, \end{cases} \tag{2.10}$$

but with independent parameters ϵ_M, r_M for the strength and the cut–off, and where the (additional) length l_M defines a 'hard–sphere like' boundary condition for the macromolecule at small distances: $W(r \rightarrow l_M) \longrightarrow \infty$. In addition, the 'switching' function $S(r)$ was introduced into the expression (2.10) in order to 'non–linearly' vary the attraction force between macromolecule and solvent particle if the interaction strength ϵ_M of the bead–solvent interaction W is increased.

Let us note that the model of LJ solvent is very popular and useful since it gives many general information about the statical as well as dynamical properties of the various macromolecules immersed in the LJ solvent. To facilitate the comparison of the various computations, however, a common 'unit system' is typically applied which is based on the parameters of the Lennard–Jones potential (2.9) among the solvent particles. In these (LJ) units ($m = \sigma = \epsilon_S = 1$), all lengthes are measured in units of σ and energies in units of ϵ_S. For the other quantities, this leads to the *derived* units: $\tau_{\rm LJ} = (m\,\sigma^2/\epsilon_S)^{1/2}$ (time); $\xi_{\rm LJ} = (\epsilon_S m/\sigma^2)$ (friction); $D_{\rm LJ} = (m/(\epsilon_S\,\sigma^2))^{-1/2}$ (diffusion coefficients); $\eta_{\rm LJ} = (m\,\epsilon_S)^{1/2}/\sigma^2$ (viscosity); etc. For the sake of convenience, we will use the same unit system in order to allow for a direct comparison with MDS data.

2.2.1 Single–bead macromolecules

In a first application of this semi–phenomenological approach, which was presented in the previous subsection, we shall focus on the dynamical properties of a single–bead macromolecule ($N \equiv 1$) which interacts isotropically [cf. Figure 2.2] with the surrounding LJ solvent (2.9). For such a molecule, the friction tensor $\widehat{\xi}^{\,\rm (aa)} = \xi\,\mathbf{I}$ just depends on a single (friction) coefficient ξ as obtained by making use of the general expression (2.6) for $a = b$,

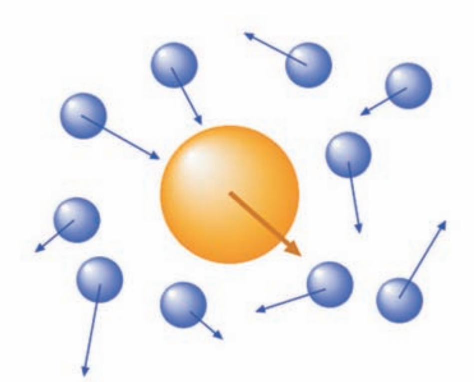

Figure 2.2: Single–bead macromolecule which interacts isotropically with the surrounding solvent.

$$\begin{aligned}\xi &= \frac{1}{3}\,n_0 \int_0^\infty d\tau \left[\int \frac{d\mathbf{k}_1}{(2\pi)^3}\,\mathbf{k}_1^2 W(\mathbf{k}_1)^2\, g^{\,(0)}(\mathbf{k}_1;\tau)\right] \\ &\quad - \int_0^\infty d\tau \left[\tau\,\frac{1}{3}\beta n_0 \int \frac{d\mathbf{k}_1 d\mathbf{k}_2}{(2\pi)^6}\,(\mathbf{k}_1\mathbf{k}_2)W(\mathbf{k}_1)\,W(\mathbf{k}_2)\;W(\mathbf{k}_1+\mathbf{k}_2)\,g^{\,(1)}(\mathbf{k}_1,\mathbf{k}_2;\tau)\right] . \quad (2.11)\end{aligned}$$

Similar to the $N-$bead macromolecule, this friction coefficient now depends on the two– and three–point CF of the solvent. The functions $g^{\,(0)}$ and $g^{\,(1)}$ contain all information about the solvent and can be calculated, at least in the limit of $\tau \to \infty$, by using the (so–called) Mode Coupling Theory (MCT) of liquids (van Zon and Schofield 2001; Zaccarelli *et al* 2001; Hansen and McDonald 1990). Here, we shall not discuss how one can calculate these CF of the LJ solvent but simply note that they can be evaluated numerically by using the mode–coupling formalism as described, for instance, by Ali *et al* (2001).

Having the Fourier transform $W(k)$ of the LJ bead–solvent potential (2.10) and the two and three point correlation functions of the solvent, we can — by inserting these functions into Eq. (2.11) — calculate immediately the friction coefficient ξ of the macromolecule for different values M/m of the macromolecule–to–solvent mass ratio if we assume an equal (and constant) mass density of the macromolecule and the solvent particles, i.e $\frac{M}{R^3} = \frac{m}{(\sigma/2)^3}$, independent of radius R of the macromolecule. As known from the general *phenomenological* Stokes–Einstein (SE) theory (Doi and Edwards 1986; Grosberg and Khokholov 1998), the friction ξ is closely related to the diffusion coefficient D of the macromolecule

$$D\xi \;=\; k_B T\,. \tag{2.12}$$

Below, on figure 2.3, we display the translational diffusion coefficient of the single–bead molecule as function of the mass ratio of the macromolecule relative to the mass of the solvent particle. Moreover, we compare our results with MD simulations of Schmidt and Skinner (2003) and Brey and Ordóñez (1982). In both these simulations, a spherical–symmetric macromolecule was assumed which interacts with the solvent particles due to the LJ potential (2.10) with 'switching' function $S(r) = 1$ and with the interaction strength $\epsilon_M = \epsilon_S$ as well as with the cut–off parameters $r_S = 2.5\,\sigma$ for the solvent–solvent potential (2.9) and $r_M = 2.5\,\sigma + l_M$ for the macromolecule–solvent interaction (2.10), respectively. The computations of Schmidt and Skinner (2003) and Brey and Ordóñez (1982) differed however with respect to their temperatures T, viscosities η, and the number densities n_0 of the solvents. While Schmidt and Skinner applied the values $k_B T \approx \epsilon_S$, $\eta \approx 2.83\,\eta_{\mathrm{LJ}}$, $n_0 \approx 0.85$, Brey and Ordóñez simulated the macromolecular motion when $k_B T \approx 2.95\,\epsilon_S$, $\eta \approx 7.7\,\eta_{\mathrm{LJ}}$, $n_0 \approx 0.6$, respectively. For all further details in the initial set–up of the MDS, we refer the reader to the literature.

As seen from figure 2.3, an excellent agreements with the MDS simulations is obtained for all medium and larger mass ratio M/m (and with minor deviation only for small ratios), but independent on the particular choice of the temperature and the viscosity of the solvent (Paper III).

Instead of the friction and/or diffusion coefficients of the macromolecule, the boundary condition coefficient is sometimes used in order to describe the properties of macromolecules in solution. This coefficient

$$c \;=\; \frac{\xi}{\pi\,\eta\,R_{\mathrm{hydr}}}\,, \tag{2.13}$$

which depends on the *hydrodynamic* radii of the macromolecule, is usually utilized to specify the boundary conditions (BC) for the velocity of the solvent particles at the surface of the macromolecule (Doi and Edvards 1986; Schmidt and Skinner 2003, 2004). Figure 2.4 displays the BC coefficient for a single–bead macromolecule with mass $M =$

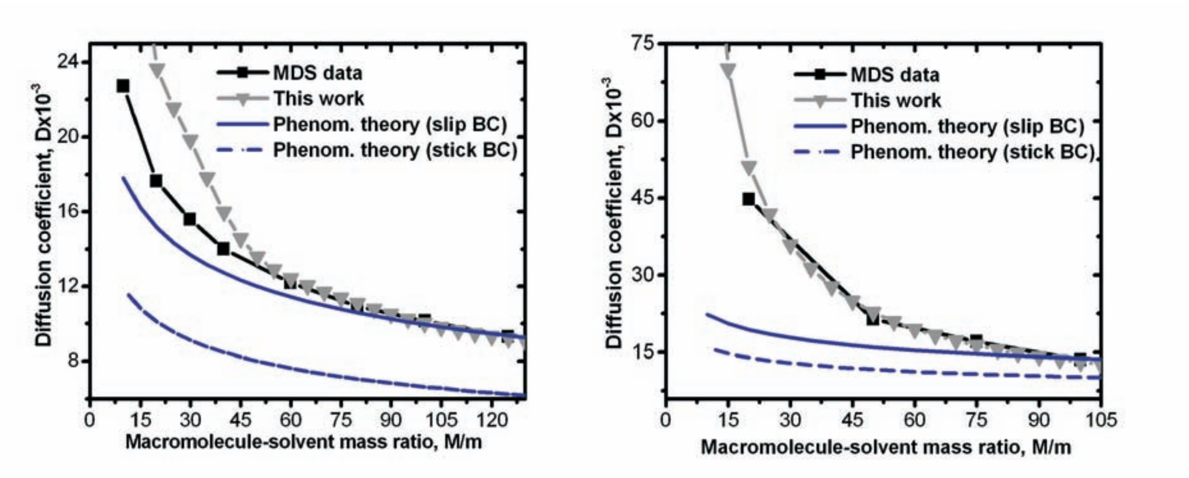

Figure 2.3: Diffusion coefficient D of macromolecules in solution as function of the macromolecule–to–solvent mass ratio M/m. The results from our semi–phenomenological theory, calculated for a "truncated" Lennard–Jones potential (2.10) between the macromolecule and the solvent particles. See the text and Paper III for further discussion.

$100\,m$ as function of the relative interaction strength $\epsilon_{\mathrm{BS}}/\epsilon_S$ of the LJ potentials (2.9) and (2.10). In order to model strong but short-range attraction interaction between macromolecule and solvent particles, however, we use the 'switching' function

$$S(r) \quad = \quad \begin{cases} 1 & \text{if } r \leq a = \sqrt[6]{2}\sigma \\ \frac{(b^2-r^2)^2\,(b^2+2r^2-3a^2)}{(b^2-a^2)^3} & \text{if } a \leq r \leq b = \frac{3\sigma}{2} \\ 0 & \text{otherwise} \end{cases} \tag{2.14}$$

which was introduced by Schmidt and Skinner (2004) in into the expression (2.10) in order to ensure that the solvent particles remain attracted to the macromolecule if the interaction strength ϵ_M of the bead–solvent interaction is increased.
The computations of the boundary condition coefficient c were based on expression (2.11) for the friction coefficient and the two– and three-point CF which were evaluated numerically. The hydrodynamical radius $R_{\mathrm{hydr}} \;=\; l_M \,+\, (1+\sqrt[6]{2})$ has been used for the macromolecule by making use of the criteria of Schmidt and Skinner (2004) that the particles of the first shell of solvation correspond to the minimum of the LJ macromolecule–solvent potential (2.10) with switching function (2.14) and, hence, sit directly on the surface of the macromolecule (Paper III).

Apart from our (semi–empirical) zero– and first–order computations of the BC coefficient, Figure 2.4 displays also the results of the MD simulations by Schmidt and Skinner (2004) as well as the constant coefficients for the stick and slip boundary condition, i.e. for a purely phenomenological treatment of the properties of the solvent (Doi and Edwards 1986). Excellent agreement are found with the MD data by Schmidt and Skinner for all

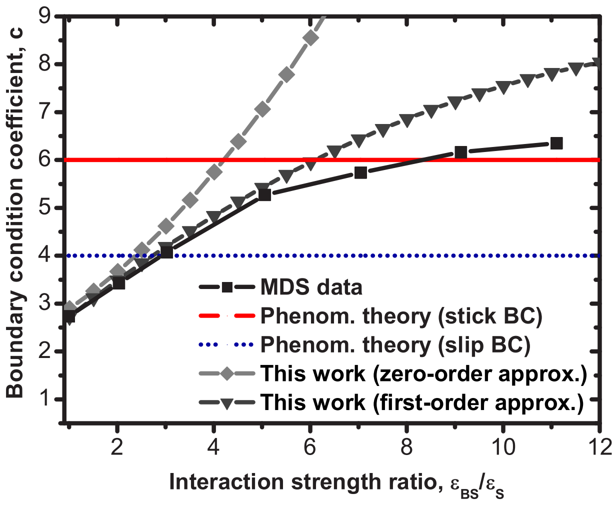

Figure 2.4: Boundary condition coefficient c of a single–bead macromolecule in solution with mass $M = 100\,m$ as function of the bead–to–solvent interaction strength ratio ϵ_{BS}/ϵ_S. See text and Paper VII for further discussion.

small and medium ratios of the LJ interaction strengthes. However, while the zero–order approach starts to deviate from the numerical values already for ratios $\epsilon_{\mathrm{BS}}/\epsilon_S \approx 2$, the first–order approximation (2.11) remains accurate up to $\epsilon_{\mathrm{BS}}/\epsilon_S \approx 6$ and is larger by only 25 % for a ratio of about 8.7 of the bead–solvent to the solvent–solvent interaction. As seen from the figure 2.4, moreover, the purely phenomenological theory behaves quite differently and is appropriate only for very large ratios of the interaction strength and if, for the present choice of interaction parameters, the stick boundary conditions are applied.

Apart from the dependence of the diffusion coefficient from of the mass of the molecules as well as from the bead–solvent interaction strength, we also investigated the transport properties of macromolecule immersed in the LJ solvent with regards to different thermodynamical properties of the solvent, such as their temperature T, number density n_0, or the viscosity η (Paper III). For these properties, good agreement with MD simulations is usually found as far as theoretical data are available at all from the literature.

2.2.2 N–bead macromolecular chains

Apart from the single–bead molecule, the semi–phenomenological approach may be utilized in order to understand the effects of the influence of the solvent on the transport properties of large macromolecule with internal structure. In particular, the expressions for the internal and center–of–mass frictions was recently derived in Paper I for the dumbbell–type molecule under the assumption that bead–solvent interaction is weak

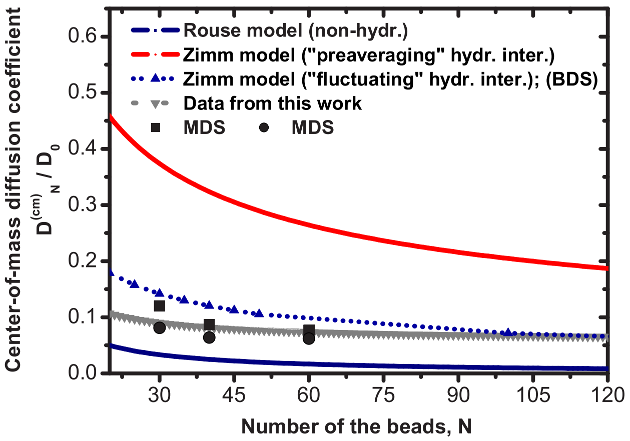

Figure 2.5: Center–of–mass diffusion coefficient $D_N^{(\mathrm{cm})}$ as function of N, the number of beads in the macromolecule. The results from this work for ”truncated” Lennard–Jones potential (2.10) (triangles) are compared with the MDS data (Dünweg and Kremer 1993) (squares) and MCS data (Ahrichs and Dünweg 1999) (circles) as well as with the theoretical data from the Rouse model (solid line) and from the Zimm model with ”preaveraging” (dots line) and ”fluctuating” hydrodynamic interactions (BDS data) from (Liu and Dünweg 2003) (triangles+dots line). See text and Paper IV for further discussion.

and, therefore, the zero–order approach for the general friction tensor (2.4) may be used. In Paper IV, moreover, we extend the result from Paper Ifor the center–of–mass friction tensor on the case of general N–beads macromolecule. The particular feature of the derived expression for the center–of–mass friction tensor

$$\xi_N^{(\mathrm{cm})} = \frac{n_0}{3}\, N \int_0^\infty \frac{d\mathbf{k}}{(2\pi)^3} \left[\int_0^\infty d\tau\, \mathbf{k}^2\, W(\mathbf{k})^2\, S_N(\mathbf{k},\tau)\, g(\mathbf{k},\tau) \right] \qquad (2.15)$$

is that it can be expressed in terms of the measurable parameters of the system ’macromolecule+solvent’ (Paper IV). As seen from the expression (2.15), the center–of–mass friction coefficient depends on the structure factor $S_N(\mathbf{k},\tau) = \frac{1}{N} \left\langle \sum_{a,\,b=1}^{N} e^{i\mathbf{k}\mathbf{R}_a}\, e^{-i\mathbf{k}\mathbf{R}_b(\tau)} \right\rangle$ describing both the geometrical configuration as well as dynamical properties of the macromolecule (Doi and Edwards 1986). This cm friction coefficient also depends on the dynamic structure factor $g(\mathbf{k},\tau)$ which contain all the information about the solvent. This is the key results of the present section since the knowledge of the center–of–mass friction coefficient plays a quite central role for understanding the motion of macromolecules in solution (Doi and Edwards 1986; Grosberg and Khokhlov 1989; Kenward and Slater 2004). In figure 2.5, for example, the center–of–mass diffusion coefficient is shown as function of the length of the chain N. Obviously, a very good agreement is found again for any length of the macromolecular chain, when compared to the ’pure’ MD simulations by Dünweg and Kremer (1993) and as well as to the Monte Carlo Simulations (MCS) by Ahrichs and Dünweg (1999). In addition, as seen from the Figure 5, the data, which calculated from the Rouse (*non–hydrodynamic*) phenomenological theory (Kirkwood and Riseman 1948; Rouse 1953) are always smaller than simulation data and can give only a *qualitative* understanding of the behaviour of the cm diffusion coefficient for the N–bead macromolecule. Similarly, the Zimm model with "preaveraging" hydrodynamic interactions (Zimm 1956; Bixon 1973; Zwanzig 1974; Barkley and Zimm 1979) predicts the result which is also far from the MDS data, the Zimm model with "fluctuating" hydrodynamic interactions ((so–called) Brownian dynamic simulation (BDS) data by Liu and Dünweg (2003)) lead to a reasonable appears for the cm diffusion coefficient for the N–bead macromolecule, but only if the number of the beads ≥ 110.

The semi–phenomenological description of the structure and transport properties of the macromolecular solutions, as derived in this thesis,has several advantages when compared with MD simulations. While the treatment of (all) the particles from the macromolecules *and* the solvent is typically unfeasible (or would be very expensive even for a restricted size of the overall system), the phenomenological theory can be utilized efficiently in order to explore the effects of additional interactions as well as for determining some suitable parameterizations for the interaction potentials involved. For this reason, the use of our semi–phenomenological methods may help understand a number of properties of the macromolecular solutions without that large–scale MD studies become necessary. In addition, in order to facilitate a further analysis of our semi–phenomenological approach, several computer codes were developed during the last years and are now available for calculating the transport properties of different macromolecules solutions. We therefore believe that these method will be very powerful also for calculating and analyzing the statical and dynamical properties of the macromolecules, clusters and nanoparticles in solutions.

Chapter 3

Rotation diffusion of macromolecules

Apart our researches in the translational motion of the macromolecules in solution (PAPERS I, III, IV, VII), the properties of the rotational (orientational) motion of macromolecules have been also investigated by us during the last years. In fact, accurate studies on the rotational dynamics of macromolecules in solutions are still a challenge for the modern polymer, protein and DNA research. Of course, the reason for this interest is that a better understanding of the rotational properties of the macromolecules in solutions may help illuminate the *nature* of the coupling between macromolecules and their solvent environment as well as the internal structure of the macromolecules. During the past decade, therefore, a number of the experimental methods have been developed and utilyzed in order to investigate the rotational properties not only *free* macromolecules in solutions but also macromolecules which immobilized on a surface, i.e the macromolecules with *restricted* mobility. In particular, attention has been paid by the dielectric relaxation, the dynamic scattering (Díaz-Leyva *et al* 2004) and the fluorescence depolarization experiments especially upon the *rotational* diffusion coefficient as well as the various combinations of the first and second rank of the orientational correlation functions [cf. Section 4.2 of the next Chapter]. On the theoretical side, in addition, several — often quite large — Molecular (Satoh 2006; Kaznessis *et al* 1998a, 1998b; Dove and Pawley 1983;) and Brownian dynamical simulations (Tao *et al* 2005; Diaz *et al* 1987; Ermak and McCammon 1978) have been carried out in order to study the (restricted) rotational diffusion of the free as well as immobilized macromolecules immersed in the solvent. Both the experiments as well as the dynamical simulations have been moreover supplemented by a number of analytical case studies including the work of Kinosita *et al* (1977) and Wang and Pecora (1980) on the (restricted) rotational diffusion of rigid rod–like molecule. This work was later extended by Kumar and coworkers (1986, 1989) as well as by Fujiware and Nagayama (1985), who explored the restricted rotational diffusion of symmetric top molecules as well as of flexible molecules which were modeled as a set of the beads connected by the rigid rods. Moreover, the rotational behaviour of the spherical and rigid–rod molecules in strong electric fields was investigated by Kalmuck and Déjardin in 1999 as well as Koenderink with coworkers (2002), respectively. In all these investigations, however, the macromolecules were considered so far as rigid particles without any 'internal' motion, that is without any changes in the distances between neighboured beads [cf. Figure 3.1].

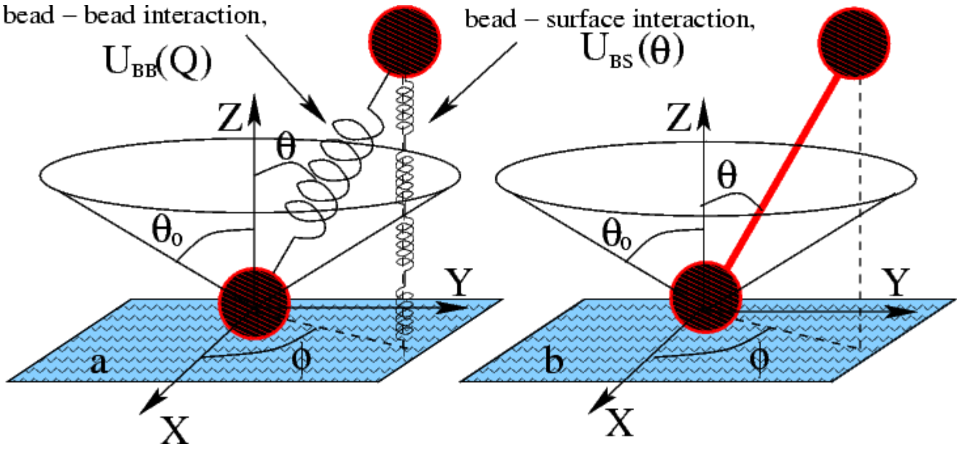

Figure 3.1: Two models of the macromolecule immobilized on a surface: (a) the non–rigid dumbbell and (b) the rigid–rod model.

Therefore, starting from Paper II, we pay attention to the (restricted) rotational motion of *nonrigid* macromolecules and analyze the effect of the bead–bead interaction potentials and the values of the restriction angle on the rotational diffusion coefficient as well as on the *configuration* distribution function. By starting from the microscopic theory of the macromolecular motion, i.e. from a Fokker–Planck equation (2.1) for the phase–space distribution function of the nonrigid macromolecule, we derived an explicit expression for the configuration–space distribution function of a *non*–rigid dumbbell–type molecule which is immobilized on a surface [cf. Figure 3.1]. This function contains all the information about the interaction among the beads as well as the effects from the surface and the surrounding solvent. As derived in Paper II, moreover, this configuration–space distribution

$$\begin{aligned}\psi(Q,\theta,\varphi;t) &= \sum_{n=1}^{\infty}\sum_{m=-\infty}^{\infty} e^{-\nu_n^m(\nu_n^m+1)D_R\,t} \\ &\qquad \times \left(A_n^m \cos m\varphi + B_n^m \sin m\varphi\right) P_{\nu_n^m}^m(\cos\theta)\Psi_{\nu_n^m}(Q), \qquad (3.1)\end{aligned}$$

can be written in terms of the *rotational* diffusion coefficient of the dumbbell

$$D_R \;=\; D\left\langle \frac{1}{Q^2}\right\rangle , \tag{3.2}$$

as well as the radial distribution functions $\Psi_{\nu_n^m}(Q)$. In expression (3.1), moreover, A_n^m, B_n^m are expansion coefficients and $P_{\nu_n^m}^m(\cos\theta)$ denote the *associated* Legendre function of degree ν_n^m which is *noninteger* and strongly depends on the restriction angle θ_0. In PAPER II we numerically determined the values of $\nu_1^m \;<\; \nu_2^m \;<\; \nu_3^m \ldots$ (i.e. the sequence of ν's which satisfy the (restricted) boundary conditions $\theta \le \theta_0$ for a given m) and found that the values of ν_n^m increase when the maximal angle θ_0 decrease, i.e. when the *cone* for the rotational motion of the molecule becomes smaller.

To obtain further insight into the rotational behaviour of the molecules, we considered several particular cases for the most of the commonly applied bead–bead interaction potentials including (i) a Hookean (Grosberg and Khokhlov 1989), (ii) a finitely–extensible nonlinear elastic (FENE) (Kaznessis 1998a, 1998b), (iii) a Frenkel (Doi and Edwards 1986) as well as (iv) a DNA–type (Bustamante *et al* 1992; Vologodskii 1994) bead–bead potential. All these potentials have their origin in the field of physical chemistry where they were constructed in order to simulate the chemical bonds and transport coefficients of the macromolecules in different (chemical) environments. In addition to the bead–bead interaction potential U_{BB}, moreover, we assumed the (bead–surface) potential U_{BS} which describes the interaction between "upper" beads and the surface [cf. Figure 3.1]. In particular, we took the *Cone* (PAPER II) as well as the effective double well (*Sin*) bead–surface interaction potential (Tirado *et al* 1984; PAPERS V and VI).

Having selected a bead-bead and bead-surface potentials, we calculated the (set of) radial distribution functions $\Psi_{\nu_n^m}(Q)$ which are the *keys* for studying the configurational and relaxation properties of the rotational motion of nonrigid macromolecules in solution. It was found, in particular, that all distribution functions with order $m \neq 0$ are rather sensitive both to the opening angle of the cone θ_0 as well as to the particular choice of the bead–bead potential. Moreover, the structure of the radial distribution functions becomes less pronounced for, say, $40^\circ \le \theta_0 \le 90^\circ$ (PAPER V).

Apart from its dependence on the restricted angle θ_0, the Radial distribution functions $\Psi_{\nu_n^m}(Q)$ should be used in order to calculate and analyze both the rotational diffusion coefficient D_R and the orientational correlation function

$$P_2(t) \;=\; \frac{1}{2}\left(3\left\langle \cos\theta(t)\right\rangle - 1\right) \tag{3.3}$$

which is often used in order to characterize the rotational motion of macromolecules in solution, if immobilized on a surface (Uvarov, Gelin and Blokhin 1999; Ermak and McCammon 1978;). Let us now note, however, that in order to calculate the rotational diffusion coefficient or *any* other measurable function for the macromolecule we — at least in principle — need to calculate the *infinite* set of the radial distribution functions $\Psi_{\nu_n^m}(Q)$. Fortunately, it was found that maximal values of the radial distribution functions decreases with increasing of the n and m quite quickly. As following from Paper V, in particular, the radial distribution functions $\Psi_{\nu_n^m}(Q)$ is almost zero for any values θ_0 and Q when, in particular, $n \geq 4$ and $m \geq 4$.

Having available the radial distribution functions $\Psi_{\nu_n^m}(Q)$, we may evaluate now (Paper VI) the time behaviour of the OCF for *any* restricted angles. Figure 3.2 shows the normalized orientational correlation function (OCF) for two of such angles, $\theta_0 = 30^o$ and 66.4^o,

$$C_{(\mathrm{orien})}(t) \quad = \quad \langle P_2(t)/P_2(0) \rangle \tag{3.4}$$

as function of time t and compares them with those from the Brownian dynamical simulations by Carrasco and de la Torre (1984).

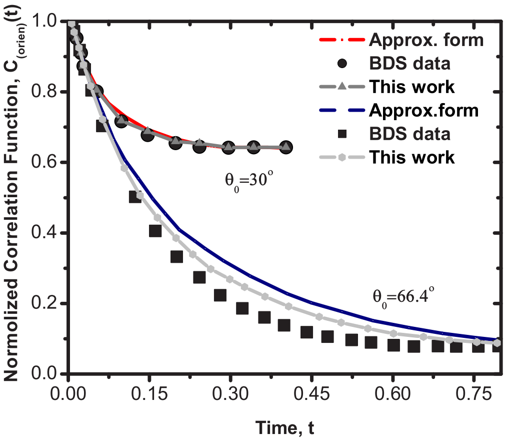

Figure 3.2: Time behaviour of the orientational correlation function (OCF), $C_{(\mathrm{orien})}(t)$, of a nonrigid dumbbell macromolecule which interacts with the surface via the effective double well (Sin) potential. OCF from our semi–phenomenological theory are compared with the BDS by Carrasco and de la Torre (1984). See text and Paper VI for further discussion.

This figure 3.2 shows a very good agreement of our calculations with the BDS data is found in for $\theta_0 = 30^o$ and with some minor deviations also for $\theta_0 = 66.4^o$. As seen from Figure 3.2, moreover, the OCF from the *triexponential* approximation by Carrasco and de la Torre (1984) are always larger than our computations, especially for rather large values of θ_0. Apart from orientational correlation function $C_{(\mathrm{orien})}$, moreover, we also used the derived Radial distribution functions $\Psi_{\nu_n^m}(Q)$ in order to analyze the properties of the rotational diffusion coefficient D_R with regards to the different bead–bead and bead–surface potentials. For this coefficient, good agreement with Brownian dynamic simulation (BDS) as far as theoretical data are available from the literature. [cf., for example, Table 1 in PAPER VI].

This demonstrates that our approach enables one to understand and calculate the rotational (and further) properties of macromolecules without that extensive Brownian dynamical simulations are always necessary. In the future, moreover, we hope that the Radial distribution functions from above will help to interprete (NMR) experiments from dielectric relaxation and correlation spectroscopy as carried out, for instance, for biological molecules. In addition, we are presently also continue this work to better understand the rotational dynamics of N–bead chains or other macromolecular structures.

Chapter 4

Outlook: Scenarios for future studies

4.1 Towards dense macromolecular solutions

As discussed in the previous chapters 2 and 3, the dynamical behavior of the macromolecular solutions can be described and analyzed in terms of the *microscopic* Fokker–Planck equation (2.1). This equation describes for the time evolution of the phase–space distribution function of the macromolecule while all information about surrounding solvent is accumulated into the friction tensors, which appear in the rhs. of the FPE. Until now, however, we have considered only the case of the dilute or semi–dilute macromolecular solutions. For such solutions the *inter*–molecular interaction, i.e. interaction between different macromolecules, may be disregarded and, hence, all statical and dynamical properties of the solutions can be described in terms of an (*isolated*) single macromolecule. In contrast to the dilute solutions, however, the dense solutions is characterized by several addition affects which comes due to the interaction between different macromolecules as well as due to the fact that macromolecules can not intersect each other. It was found by using the microrheology experimental techniques (Amblard *et al* 1996; Helfer 2000), for example, that even at moderate concentrations of the macromolecules, they start to interpenetrate each other and to become entangled. This 'entanglements' gives rise the unusual (anomalous) dynamics as well as to some novel viscoelastic effects of the macromolecular solutions. These anomalous have been observed experimentally by measuring the time–dependent correlation functions of entangled polymer melts. These experiments showed the appearance of 'plateaus' in the center–of–mass mean–square displacement (Lodge *et al* 1990), and in the shear moduli (Ferry 1980; Graessley 1974).

Up to now, the most fruitful theoretical treatment of the dynamical behaviour of the macromolecules in the high–density solutions is the (so–called) reptation model of the polymers which was firstly suggested by de Gennes (1979). The basic idea of this model is that the entanglements between a chain and its neighbors *prevent* any large–scale motions perpendicular to its local direction and, therefore, the chains can only reptate in a snakelike motion parallel to their own curve. In other words, the local beads of the macromolecule can only diffuse longitudinally along the line of the chain. Doi and Edwards (1986) have expressed these ideas in mathematically well–defined form which allowed a calculation of aa dynamical properties of the macromolecular solutions. Let us note, moreover, that the reptation theory of the macromolecular solution has been found useful to predict the statical and dynamical properties of entangled polymers which were later established in the Monte Carlo (Kolinski *et al* 1987; Paul *et al* 1991; Shaffer 1994) and molecular dynamic simulations (Kremer and Grest 1990; Pütz *et al* 2000; Bulacua and van der Giessen 2005) as well as in the experiments (Lodge *et al* 1990; Helfer 2000).

In spite of several theoretical, MDS as well as experimental works, were devoted to the reptation theory, a *microscopic* foundation of the reptation model is still lacking. Such a microscopic theory should be able to *derive* from first principles the existence of the reptative motion of the macromolecule as a consequence of the repulsive interactions. As mentioned in the chapter 2 of this work, our semi–phenomenological approach is based on such a microscopic view point of the macromolecular solutions from the beginning and, therefore, can be utilized in order to describe and analyze the behaviour of the macromolecule in the dense solutions. Let us note that the Fokker–Planck equation for the distribution function of the high–density macromolecular solutions have been recently derived by us (Uvarov and Fritzsche 2006e). Similar to the dilute solutions, the rhs. of this FPE contains the friction tensor of the macromolecule which describes all possible effects coming from the neighboring macromolecule as well as solvent particles. In these works, it was found that starting from some 'critical' number density n_{crit} of the macromolecules in solution, the hydrodynamic interaction starts to be strongly screened, i.e. the effect of solvent on the macromolecular friction becomes negligible for any particular choice of the bead–solvent interaction and the friction is determined by the critical number density n_{crit} and the interactions between macromolecules only. In contrast to the reptation theory, which is *assumed* such property of the fiction and diffusion of the macromolecules in the dense solution, we *derived* this result by starting from the microscopic view point and by using the semi–phenomenological approach. Actually, this extension of our semi–phenomenological approach for studying the statical and dynamical properties of the 'entangled' macromolecules in the semi– and high–density solutions is currently under way in our group and will be published soon (Uvarov and Fritzsche 2006e).

4.2 Behaviour of time–dependent correlation functions

As follows from the statistical physics (Landau and Lifshitz 1980; Kreuzer 1981), several properties corresponding the time–behaviour of the macromolecules in solutions can be described and understand in terms of the time–dependent correlation functions (CF). These CFs describe the relaxation of the macromolecule from non–equilibrium to the equilibrium states by indicating the effects of the 'memory' in the behaviour of the same or different quantities (Berne 1977; Cortes *et al* 1985; Uvarov *et al* 1999). The behaviour of the correlation functions, moreover, can be directly measured in the experiments which make the study of the CFs properties are really important. In particular, the self–density equilibrium time CF, which is defined as probability for finding a selected test macromolecule at a position within $d\mathbf{r}$ of $\mathbf{r}(t)$ at a time within dt of t given that it was initially located at $\mathbf{r}(0)$, is nothing else like the Fourier shape of the intermediate scattering function which may be directly obtained from the scattering experiments (Lindenberg and Cukier 1977; Rathgeber *et al* 2004). Moreover, dielectric relaxation, dynamic light scattering and fluorescence depolarization experiments measure various combinations of the first and second rank of the CFs

$$C(t) \;=\; \left\langle \mathbf{W}^{(j_1)}_{k_1\,k_2}(\mathbf{\Omega}(0))\,\mathbf{W}^{(j_2)}_{k_3\,k_4}(\mathbf{\Omega}(t)) \right\rangle \tag{4.1}$$

of the orientation of some vector fixed to the macromolecule as defined in various papers (cf. for example, Wang and Pecora 1980; Szabo 1984; Kumar 1986, 1989; Blokhin *et al* 1999). In equation 4.1, the solid angle $\mathbf{\Omega}(t)$ determines the orientation of the vector fixed to the macromolecule at time t and $\mathbf{W}^{(j_1)}$ refers to the Wigner rotation matrix of rank j_1 (Varshalovich *et al* 1989; Boas 1983).

As known from the theoretical investigations, however, the behaviour of correlation functions closely relates to the transport properties of macromolecular solution. In particular, by using the Mori–Zwanzig projection operator formalism (Mori 1965a, 1965b; Zwanzig 1961), several so–called *Kubo* or *Green–Kubo* relations for the transport coefficients may be derived in terms of the autocorrelation functions (ACFs), including viscosity (in terms of the ACF of the off–diagonal elements of the instantaneous pressure tensor), thermal conductivity (in terms of the ACF of the internal energy density of the solution) and diffusion coefficient (in terms of the velocity ACF) as well as many further transport coefficients (Evans and Morriss 1990). As found by Dünweg and Kremer (1991), moreover, the hydrodynamic diffusion *tensor* can be described in terms of autocorrelation function of transversal velocity field modes. The Green–Kubo relations between transport coefficients of the macromolecular solution and the correlation functions, in fact, are very general results and independent on the microscopic mechanism of the energy dissipation and friction in the system 'macromolecule+solvent' (Evans and Morriss 1990).

Recently, in Paper I, we have considered the long–time behaviour of the autocorrelation function (ACF) for the center–of–mass, $C^{(\mathrm{cm})}_{\alpha\beta}(t)$, and the internal momenta, $C^{(\mathrm{int})}_{\alpha\beta}(t)$ for a dumbbell–type macromolecule as defined by:

$$C^{(\mathrm{i})}(t) \;\equiv\; \left\langle \mathbf{P}^{(\mathrm{i})}(0)\, \mathbf{P}^{(\mathrm{i})}(t) \right\rangle ; \qquad \mathrm{i} \;=\; \mathrm{cm,\ int}\,. \tag{4.2}$$

where $\mathbf{P}^{(\mathrm{i})}(t)$ refer to the center–of–mass (cm) or the internal (Q) momentum of the dumbbell at the time t. In this case study, in particular, we found that the internal momentum (auto–) correlation function $C^{(\mathrm{int})}(t)$, which is closely related to the internal friction tensor $\widehat{\xi}^{(\mathrm{int})}$ of the macromolecule (Paper I; Uvarov *et al* 1999), decays *algebraically* both for Yukawa and Born–Mayer bead–solvent interactions but with different decay rate. From our analyses, in particular, it was found that the asymptotic time behaviour ($\rightarrow \infty$) of the internal momentum ACF decays like $C^{(\mathrm{int;\,BM})}(t \rightarrow \infty) \sim t^{-3}$ for the Born–Mayer (BM) potential. In contrast to the BM interaction potential, the decay rate increases, $C^{(\mathrm{int;\,Y})}(t \rightarrow \infty) \sim t^{-3/2}$, for the Yakawa (Y) bead–solvent potential which becomes more stronger than Born–Mayer potential for large distance between the beads of the dumbbell macromolecule. Let us note, that such behaviour of *algebraic tail* of ACF was predicted empirically from molecular dynamics simulations and theoretical works by several authors (cf. for example, Erpenbeck 1982 1985; Hoef *et al* 1992; Gelin and Kosov 2006) in contrast to the (unphysical) exponential decay as known from the phenomenological theory (Doi and Edwards 1986; Grossberg and Khokhlov 1989). Up to now, however, the investigations of these CFs was not the general focus of our work. Therefore, all our studies of in the topic of CF was restricted by the (simplest) dumbbell–type molecule but should be extended to deal with the (general) N–bead case of the macromolecule in order to better understand the dynamics of macromolecular chain and other macromolecular structures.

4.3 Nanoparticles and macromolecules immersed into ionic liquids

In the past years much attention was paid for studying the properties of ionic liquids (IL) which have great potential in fundamental researches in physical chemistry and chemical engineering (Wasserscheid and Welton 2002). Although many characteristics of ionic liquids are similar to those found for (conventional) macromolecular solvent, they shows a number of 'anomalous' properties. One of this properties, for example, is that each molecule within the liquids still appear as ion, giving rise to solutions with high polarity and viscosity as well as rather low vapor pressure. Despite of the potentials application of IL, however, a detailed understanding of their structure and dynamical properties is still missing and a challenge of present–day research. During the past decade, therefore, a number of theoretical and experimental techniques have been developed in order to analyze and describe the physical and chemical properties of IL in the solid, liquid as well as gas phase (Wasserscheid and Welton 2002; Dupon 2004; Giernoth *et al* 2005). On the theoretical side, in particular, many of these case studies were based on the molecular dynamic (MD) simulations which often required large–scale computations and, hence, can not be 'repeated' so easily for different interactions and solutions (Znamenskiy and Kobrak 2004; Del Pópolo and Voth 2004). Much less attention, in contrast, has been paid to analytical investigations among the molecular components of ILs and to their statical and transport properties of nanoparticles and macromolecules if immersed in ILs.

Therefore, another future applications of the semi–phenomenological approach is extension of our theory to support also analytical investigations of the dynamical properties complex macromolecules, colloids as well as nanoparticles immersed into the solvents with 'specific' properties such as ionic liquids, polar and non–polar solutions ect. By using, for example, the fact, that the microscopic friction $\widehat{\xi}$ is explicitly expressed in term of the bead–solvent interaction potential [cf. equations (2.6), (2.11) as well as (2.15)], it is possible to investigate and analyze the effect of each interaction (Coulomb, van der Waals, hydrogen–bonds ect) on the structural and transport properties of the macromolecules immersed in specific solvent. When combining with the MD simulation data, moreover, the semi–phenomenological approach help to 'restrict' the possible values in the *parametrization* of the interactions in order to *qualitatively* predict the formation and deformation properties of dissolved particles (macromolecules, colloids, . . .).

Apart from the structure and transport properties of macromolecules dissolved in IL, additional task refer to the extention of our semi–phenomenological approach in order to investigate the *orientational* (rotational) properties of free macromolecules in IL or if macromolecule (in such liquids) are immobilized to some surface. In fact, experiments and MD simulations on the re–orientation of macromolecules in IL have gained both a lot of interest over the years (Morrow and Maginn 2002; Ito *et al* 2004; Mali *et al* 2005). Of course, the reason for this interest is that a better understanding of the orientational properties of the immersed macromolecules may help illuminate the *nature* of the coupling between macromolecules and their ionic environment. Actually, the is extention of our semi–phenomenological approach for studying the *translational* as well as *rotational* properties of the macromolecule immersed in IL is currently under way in our group. Several computer codes, which are now available for calculating, have been developed during the last years in order to analyze the effects of the each interaction (Coulomb, van der Waals, hydrogen–bonds ect) on the structural, translational as well as rotational properties of the macromolecules immersed in specific solvent.

4.4 Internal structure and transport properties of macromolecule in solutions. Topological effects

Of course, the possible applications of the semi–phenomenological approach are not restricted to the examples from above but can be used also to study other tasks in the field of the macromolecular physics. For instance, this approach can be used in order to investigate the influence of the different internal geometrical structures of macromolecule on the statical and dynamical (rotational&translational) properties of macromolecules in solution. As known from literature (cf. for example, Doi and Edwards 1986; Paper I, Paper IV), the internal geometrical structure of the macromolecule is fully determined by the interaction potential among the beads of the macromolecule. Therefore, by using a similar *ansatz* for macromolecules we shall be able to analyze the coupling between rotational and translational motion of macromolecules (Beloborodov *et al* 1998) as well as to calculate friction tensor, diffusion coefficient and time–dependent correlation functions for rings (Doi and Edwards 1986), dendrimers (Satmarel *et al* 2004; Gurtovenko *et al* 2003), or even for 'fractal'–shape macromolecules (Jurjiu *et al* 2002; Blumen *et al* 2003) immersed into different solvents.

Chapter 5

Summary

The influence of the bead–solvent interaction on the dynamics of macromolecules, which are immersed into a solution, has been investigated by using Hamiltonian mechanics and master equations for the phase–space distribution functions. In this approach, the macromolecules is taken as a *set of beads* which are coupled to each other by a force and which are surrounded by — a large number of — solvent particles. Starting from the Hamiltonian of the overall system 'macromolecule + solvent', then, a Fokker–Planck equation (FPE) was derived for the time evolution of the phase–space distribution function of the (N–bead) macromolecule. In this derivation, three realistic assumptions were made: (i) The macromolecule and the solvent particles did not interact *before* some initial time up to which the solvent stayed in the equilibrium; (ii) The interaction between the beads and the solvent particles is considered to be weak when compared to the bead–bead interaction, which keep the macromolecule together; (iii) The relaxation of the solvent proceeds much faster in time than those of the beads. These three assumptions are made very frequently in studying the translational as well as rotational properties behaviour of macromolecules in solutions.

For the basic assumptions from above, the dynamics of the macromolecule is determined purely by the friction tensors that appear on the right–hand side of the FPE and which can be expressed in terms of the bead–solvent interaction potential as well as the dynamic structure factor of the solvent. Using the explicit expression, as obtained earlier for the friction tensors of the molecule in solution, we showed that the behaviour of the friction tensor parameters depend on the distance between the beads as well as on the thermodynamic regime of the solvent. From our analysis of the friction tensors, moreover, the discrete nature of the solvent can be seen clearly at small distances between the bead and solvent particles.

For a moderate bead–solvent interaction, all coefficients obtained agree excellent with Brownian and molecular dynamic (MD) simulations carried out over the years. We therefore conclude that our semi–phenomenological approach can be utilized also for studying other dynamical properties of macromolecules in solution. Compared with often expensive MD calculations, a great gain in efficiency is obtained *by several orders of magnitude* and may thus allow investigations on more complex systems for which other numerical techniques will remain unfeasible in the near future.

Special attention of this thesis work was placed on the flexibility of our approach which makes it possible to implement future investigations in the field of the macromolecular solution, as described in Chapter 4. These implementation is very reasonable, because few steps of the possible future applications are already realized in the frame of the semi–phenomenological approach. In particular, we derived the Fokker–Planck equation (FPE) for the phase–space distribution function of the high–density macromolecular solution (cf. Section 4.1). Together with the FPE, we also derived the friction tensors in terms of the macromolecule–solvent and macromolecule–macromolecule interactions. Moreover, first step has been made in order to analyze the influence of the bead–solvent interaction on the time evolution of the center–of–mass and internal correlation functions of the macromolecules immersed in the solvent (Section 4.2). Finally, we would like to mention that the ability of the semi–phenomenological approach is not exhausted by applications, mentioned in those thesis work only.

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To my family I dedicate this thesis.

Kassel, July 2006

A. Uvarov

Curiculum Vitae

Personal Data:

Name :	**Aliaksandr Uvarau (Alexander Uvarov)**
Date of Birth:	September 9, 1975
Place of Birth:	Nesvish, Minsk region, Belarus

Education:

01/ 09/ 1982 — 30/ 05/ 1985	Primary school, Borisov, Belarus
01/ 09/ 1985 — 30/ 05/ 1990	Secondary school, Borisov, Belarus
01/ 09/ 1990 — 25/ 06/ 1992	Higher school, Borisov, Belarus
01/ 09/ 1992 — 13/ 06/ 1997	Physical Department of the Belarussian State University, Minsk, Belarus

Diploma: 13/ 06/ 97, speciality "Physics", major "Theoretical Physics" by the Belarussian State University, Minsk, Belarus;

Diploma Subject: *"Investigation of changing of the amplitude as well as shape of the magnetic induction at the non–uniform magnetized ferromagnetic"*

Nov. 1996 — June 1997	Institute of Applied Physics, National Academy of Sciences of Belarus, Minsk, Belarus

Employment:

11/ 11/ 1997 — 01/ 03/ 2002	Junior Scientist at the Institute of Molecular and Atomic Physics (IMAPh), National Academy of Sciences of Belarus (NASB), Minsk, Belarus
27/ 05/ 2002 — 18/ 07/ 2006	Scientific collaborator and PhD student at University of Kassel, Germany

Erklärung

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July, 2005, Kassel

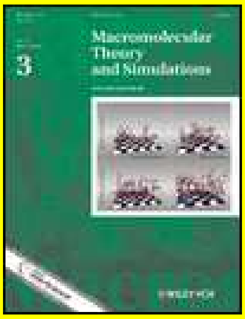
Aliaksandr Uvarau (Alexander Uvarov)

PAPER I

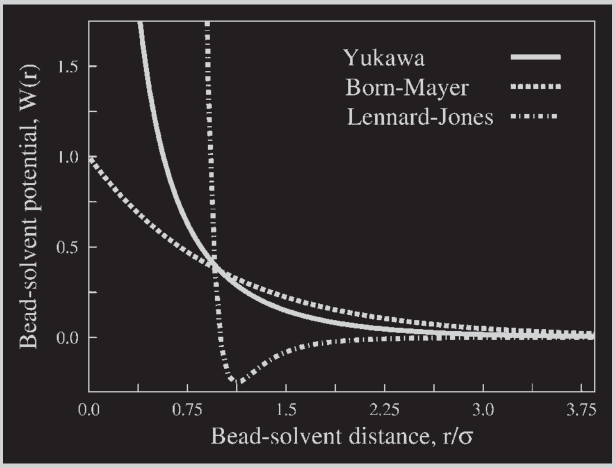
Effects of the Bead–Solvent Interaction on the Dynamics of Macromolecules, 1

The Dumbbell Molecule

2004, Macromolecular Theory and Simulations, **13**, 241–256.



Summary: Hamiltonian dynamics and a chain model are used to study the dynamics of macromolecules immersed in a solution. From the Hamiltonian of the overall system, ‘‘macromolecule + solvent,’’ a master and a Fokker-Planck equation are then derived for the phase-space distribution of the macromolecule. In the Fokker-Planck equation, all the information about the interaction among the beads of the macromolecule as well as the effects of the surrounding solvent is described by friction tensors, which are expressed in terms of the bead-solvent interaction and the dynamic structure factor of the solvent. To explore the influence of the bead-solvent potential on the dynamics of macromolecules, the friction tensors are calculated for a dumbbell molecule and for three choices of the interaction (Yukawa, Born-Mayer, and Lennard-Jones). Expressions are derived, in particular, for the friction tensor coefficients of the center-of-mass and the relative coordinates of the dumbbell. For the long-term behaviour of the internal momentum autocorrelation function, moreover, an ‘‘algebraic decay’’ is found, in contrast to the (unphysical) exponential decay as known from phenomenological theory.



Yukawa, Born-Mayer and Lennard-Jones bead-solvent interaction potentials.

Effects of the Bead-Solvent Interaction on the Dynamics of Macromolecules, 1

The Dumbbell Molecule

Alexander Uvarov, Stephan Fritzsche*

Fachbereich Physik, Universität Kassel, Heinrich-Plett-Str. 40, D-34132 Kassel, Germany
Fax: 0049 5618044006; E-mail: uvarov@physik.uni-kassel.de

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Introduction

In the past two decades, one of the main goals of kinetic theory has been to derive master equations for the phase-space distribution function by starting from *first principles*, i.e., from the Hamiltonian of the overall system. From these equations, the hope (and research program) is then to obtain non-phenomenological expressions for the transport coefficients, including information about the relaxation of the system towards its equilibrium state. Until now, this program has been realized successfully for a system of (i) rigid spherical particles with allowed binary collisions[1] (Boltzmann-type equations); (ii) point-like charged particles with either a truncated Coulomb potential[2] (Landau equations) or a full Coulomb interaction[3] (Lennard-Balesku equations); or (iii) for weakly interacting spherical particles (Fokker-Planck-type equations). Apart from being a – more or less – realistic gas model, the latter case (iii) of weakly interacting particles also incorporates the motion of a Brownian particle in a bath.[4] In addition to these cases, some effort has also been undertaken to derive (iv) a Fokker-Planck equation for non-spherical particles, including the rotational degrees of freedom.[5,6] Obviously, all these approaches go beyond the phenomenological theory for

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an ensemble of an interacting particle, which has just been immersed into an uncompressible and unstructured bath.

To understand the dynamics of macromolecules, they are often described in terms of a few – or even some larger number – of (molecular) subsystems, called the *beads* of the (macro-)molecule. If immersed in a solution, of course, the dynamic behaviour of the macromolecules is determined not only by the interaction among the (neighboured) beads, but also by the interaction of the beads with the surrounding solvent particles. In the past, this *bead-solvent* interaction has often been treated theoretically in terms of *stochastic forces* which only include the (time-)averaged interaction with the solution.[7,8] As known from molecular dynamic simulations (MDS), however, the discrete (atomistic) structure of the solvent leads to clear deviations from a pure Brownian behaviour of the beads[9–12] and, hence, may play an important role in studying the macromolecular dynamics. In the last few years, therefore, several attempts were made to derive a Fokker-Planck equation (FPE) for the phase-space distribution of the interacting beads, starting from the *first principles* of statistical Hamiltonian mechanics.[13–18] Until today, however, such Fokker-Planck (-type) equations are difficult to apply to any particular system in practice, since they usually contain terms (projection operators) which refer to the total Hamiltonian of the system and which are known as the generalized friction tensors in the literature.

In a previous case study,[19] we first considered a macromolecule in solution which interacts with the surrounding medium by a harmonic potential. For such a potential, it was shown that the center-of-mass of the macromolecule follows a generalized Langevin equation, whereas a set of *deterministic* equations were derived for all the internal coordinates. In practice, of course, this means that a *dissipative motion of the molecule cannot be obtained by using only a harmonic bead-solvent interaction* owing to the – somehow oversimplified – coupling of the solvent particles to the molecular beads.[20,21] In the present paper, therefore, we study the effects of the bead-solvent potential on the dynamic behaviour of macromolecules for a more realistic choice of the interaction. We exclusively assume below that the bead-solvent interaction is *weak* when compared to the coupling among the beads. With this assumption in mind, we are able to derive a Fokker-Planck equation for the time evolution of the phase-space distribution function of the macromolecule. In this equation, the dynamics purely depend on the friction tensors (i.e., the right-hand sides of the FPE), which now contain all the information about the interaction of the macromolecule with the particles of the solvent. For a *weak* interaction with the solvent, explicit expressions for the friction tensors are derived in terms of the bead-solvent potential as well as the dynamic structure factor of the solvent. They will be discussed below and compared with those from phenomonological theory.

In the next section, we will start from Liouville's equation for the time evolution of the phase-space distribution function of the overall system "macromolecule + solvent." Using the case of a simple 2-bead *dumbbell* molecule, we are able then to reduce this Liouville equation to a Fokker-Planck(-type) equation, which, in turn again, can be generalized for a chain of *N* pairwise interacting beads. Below, we discuss these FPE along with the (included) friction or diffusion tensors, which can be calculated for any bead-solvent potential. To explore the dependence of this interaction in greater detail for a single dumbbell molecule, the section on the effects of the bead-solvent interaction on the behavior of the friction tensors provides the friction tensor components for three different types of bead-solvent interactions, including a Yukawa, a Born-Mayer, and a Lennard-Jones potential. In addition, several further properties such as the center-of-mass and internal momentum correlation functions are also discussed. Finally, a few conclusions are given.

Fokker-Planck Equation and Friction Tensors for Isolated Macromolecules

To describe the *dynamics* of macromolecules in solution, let us start from a microscopic view point and first, derive a Fokker-Planck equation (FPE) for an isolated molecule, which has been immersed in of a bath of solvent particles. For the sake of simplicity, we assume here that the molecule just consists of N spheric-symmetrical particles of mass, M. As usual, these (so-called) beads of the macromolecule are specified by their position and momentum coordinates $\{\mathbf{R}_a, \mathbf{P}_a, a = 1,\ldots, N\}$ and are supposed to interact with each other through a spherical potential, $U(|\mathbf{R}_a - \mathbf{R}_b|)$. Similarly, the solvent is taken as a set of $n(\gg N)$ spherical particles of mass m and with coordinates $\{\mathbf{r}_s, \mathbf{p}_s, s = 1,\ldots, n\}$. In addition to the bead-bead interaction, U, we also assume a (pair-wise) spherical potential, $V(|\mathbf{r}_s - \mathbf{r}_t|)$, between all the solvent particles as well as the potential, $W(|\mathbf{R}_a - \mathbf{r}_s|)$, between any bead, a, and the particles, s, from the solvent. To keep the macromolecule *alive* within the bath over a longer time, obviously, the bead-solvent potential, W, has to be *weak* when compared with the (attractive) bead-bead interaction potential, U. For such an overall system "molecule + solvent," the Hamiltonian is simply given by:

$$H = H_B + H_S + H_{BS} \tag{1}$$

where

$$H_B = \sum_{a=1}^{N} \frac{\mathbf{P}_a^2}{2M} + \sum_{a<b}^{N} U(|\mathbf{R}_a - \mathbf{R}_b|) \tag{2}$$

$$H_S = \sum_{s=1}^{n} \frac{\mathbf{p}_s^2}{2m} + \sum_{s<t}^{n} V(|\mathbf{r}_s - \mathbf{r}_t|) \tag{3}$$

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$$H_{BS} = \sum_{a=1}^{N} \sum_{s=1}^{n} W(|\mathbf{R}_a - \mathbf{r}_s|) \tag{4}$$

describe the kinetic and the interaction energies of the bead (B) and solvent (S) particles, respectively. As for the Hamiltonian, we may write down a similar equation also for the Liouville operator:

$$\frac{\partial \rho}{\partial t} = \hat{L}\rho = (\hat{L}_B + \hat{L}_S + \hat{L}_{BS})\rho \tag{5}$$

which, to the right, acts on the phase-space distribution function, ρ. Apart from the time, t, of course, this distribution function $\rho(\{\mathbf{R}_a, \mathbf{P}_a\}, \{\mathbf{r}_s, \mathbf{p}_s\}; t)$ will depend on the position and momentum coordinates of all the particles. Similar to in Equation (1), the (total) Liouville operator, $\hat{L}$, consists of three parts:

$$\hat{L}_B = \sum_{a=1}^{N} \left[\left\{ \sum_{b=1,\, b\neq a}^{N} \frac{\partial U(|\mathbf{R}_a - \mathbf{R}_b|)}{\partial \mathbf{R}_a} \right\} \frac{\partial}{\partial \mathbf{P}_a} - \frac{\mathbf{P}_a}{M} \frac{\partial}{\partial \mathbf{R}_a} \right] \tag{6}$$

$$\hat{L}_S = \sum_{s=1}^{n} \left[\left\{ \sum_{t=1,\, t\neq s}^{n} \frac{\partial V(|\mathbf{r}_s - \mathbf{r}_t|)}{\partial \mathbf{r}_t} \right\} \frac{\partial}{\partial \mathbf{p}_s} - \frac{\mathbf{p}_s}{m} \frac{\partial}{\partial \mathbf{r}_s} \right] \tag{7}$$

$$\hat{L}_{BS} = \sum_{a=1}^{N} \sum_{s=1}^{n} \frac{\partial W(|\mathbf{R}_a - \mathbf{r}_s|)}{\partial \mathbf{R}_a} \left[\frac{\partial}{\partial \mathbf{P}_a} - \frac{\partial}{\partial \mathbf{p}_s} \right] \tag{8}$$

owing to the bead-bead, solvent-solvent, and bead-solvent interaction, respectively.

In general, of course, beads of various sizes and masses will be present in a macromolecule. However, to simplify our further treatments, we assume (i) that all beads have an equal mass M (much) larger than the mass of the solvent particles: $M \gg m$ and (ii) that the macromolecule and the solvent particles did not interact in the past before some *initial time*, $t < t_{\text{in}} = 0$, until which the solvent was in equilibrium. Under these circumstances, namely, we are able to derive a Fokker-Planck type equation for the phase-space distribution (function) of the macromolecule:

$$\rho_N(\{\mathbf{R}_a, \mathbf{P}_a\}; t) \equiv \int d\{\mathbf{r}_s, \mathbf{p}_s\} \rho(\{\mathbf{R}_a, \mathbf{P}_a\}, \{\mathbf{r}_s, \mathbf{p}_s\}; t)\,, \tag{9}$$

by starting from Equation (5). In this reduced form, the distribution function $\rho_N(\{\mathbf{R}_a, \mathbf{P}_a\}; t)$ just depends on the coordinates of the N beads of the macromolecule but not on the coordinates of the solvent particles.

As seen from Equation (9) for the reduced distribution function, however, the *separation* of the bead and solvent particles requires integration over all the coordinates of the solvent and, hence, can be carried out explicitly, only if the (full) phase space distribution factorizes at some time $t_{\text{in}} = 0$ (in the past) into a product of two distribution functions for the solvent and the macromolecule, respectively. As usual, we may assume a Boltzmann-like distribution function for the initial state of the solvent, $\Phi_{eq}(\{\mathbf{r}_s, \mathbf{p}_s\} = \frac{1}{z} e^{-\beta H_S}$, where H_S is the Hamiltonian of the solvent, $\beta = \frac{1}{k_B T}$ the (inverse) temperature of the system, and $z = \int d\{\mathbf{r}_s, \mathbf{p}_s\} e^{-\beta H_S}$ denotes the proper normalization integral for the phase-space distribution. Having, however, with the factorization, $\rho(\{\mathbf{R}_a, \mathbf{P}_a\}, \{\mathbf{r}_s, \mathbf{p}_s\}; 0) = \rho_N(\{\mathbf{R}_a, \mathbf{P}_a\}; 0)\Phi_{eq}(\{\mathbf{r}_s, \mathbf{p}_s\})$, at some given initial time $t_{\text{in}} = 0$, we can also separate the coordinates of the beads (from those of the solvent particles) for all later times. This can be seen, for instance, by introducing the projection operator $\hat{P} = \Phi_{eq}(\{\mathbf{r}_s, \mathbf{p}_s\}) \int d\{\mathbf{r}_s, \mathbf{p}_s\}$ and its complement $\hat{Y} \equiv 1 - \hat{P}$ into the Liouville Equation (5) from which then follows:[12,17]

$$\begin{aligned} \Phi_{eq} \frac{\partial \rho_N(t)}{\partial t} \equiv \frac{\partial \hat{P} \rho(t)}{\partial t} &= (\hat{L}_B + \hat{P}\hat{L}_{BS})\hat{P}\rho(t) \\ &+ \hat{P}\hat{L}_{BS} \int_0^t d\tau e^{(\hat{L}_B + \hat{L}_S + \hat{Y}\hat{L}_{BS})\tau} \hat{Y}\hat{L}_{BS}\hat{P}\rho(t-\tau) \end{aligned} \tag{10}$$

i.e., the well-known master equation for the phase-space distribution function of the macromolecule.

Despite *averaging* over the solvent coordinates, however, the master Equation (10) is – by itself – of little help for exclusively analyzing the *time evolution*, $\rho_N(t)$, of the macromolecule, since all three parts of the Liouville operator, $\hat{L}$, still appear on the rhs of this equation. Therefore, in order to continue the separation of the coordinates, we first need to return to the (previous) assumption of a *weak* bead-solvent potential, W, when compared with the bead-bead interaction, U. With this assumption in mind, we may omit the third term $\hat{Y}\hat{L}_{BS}$ from the exponent and rewrite Equation (10) in a form, in which the interaction of the macromolecule with the surrounding solvent particles can be treated in terms of the (so-called) "bath operators." These operators only depend on the bead-solvent potential, W, and, thus, can be used to derive a master equation for any number of beads in the macromolecule. However, since such a derivation of a *(reduced) master equation* is quite tedious for the general case of N interacting beads, we first consider a (much simpler) 2-bead *dumbbell* molecule from which the (correct) result for N beads can be obtained later also by a proper generalization of the final expressions.

For a *dumbbell* model of the macromolecule ($N = 2$), the notation is considerably simplified; using namely the Liouville operators [Equation (6)–(8)] for just two beads with the coordinates, (R_1, P_1) and (R_2, P_2), respectively, and by omitting the third term in the exponent, the master

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Equation (10) becomes:

$$\frac{\partial f(t)}{\partial t}+\frac{\mathbf{P}_1}{M}\frac{\partial f(t)}{\partial \mathbf{R}_1}+\frac{\mathbf{P}_2}{M}\frac{\partial f(t)}{\partial \mathbf{R}_2}-\frac{\partial U}{\partial \mathbf{R}_1}\frac{\partial f(t)}{\partial \mathbf{P}_1}-\frac{\partial U}{\partial \mathbf{R}_2}\frac{\partial f(t)}{\partial \mathbf{P}_2}$$
$$=\frac{\partial}{\partial \mathbf{P}_1}\int_0^t d\tau[\hat{I}^{(11)}(\tau)+\hat{I}^{(21)}(\tau)]f(t-\tau)$$
$$+\frac{\partial}{\partial \mathbf{P}_2}\int_0^t d\tau[\hat{I}^{(12)}(\tau)+\hat{I}^{(22)}(\tau)]f(t-\tau) \qquad (11)$$

where, as a short-hand notation, we introduce $f(t) \equiv \rho_2(\mathbf{R}_1, \mathbf{R}_2, \mathbf{P}_1, \mathbf{P}_2; t)$ to refer to the (phase-space) distribution function of the two beads and where the (four) *bath operators*:

$$\hat{I}^{(ab)}=\sum_{s,s'=1}^{n}\int d\{\mathbf{r}_s,\mathbf{p}_s\}\frac{\partial W(|\mathbf{R}_a-\mathbf{r}_s|)}{\partial \mathbf{R}_a}e^{(\hat{L}_B+\hat{L}_S)\tau}$$
$$\times\frac{\partial W(|\mathbf{R}_b-\mathbf{r}_{s'}|)}{\partial \mathbf{R}_b}\left[\frac{\partial}{\partial \mathbf{P}_b}-\frac{\partial}{\partial \mathbf{p}_{s'}}\right] \quad a,b=1,2 \qquad (12)$$

describe the influence of the solvent on the dynamics of the dumbbell. In Equation (12), the bath operators still contain a (double) summation over all the solvent particles and, therefore, require further consideration. A simplification of these operators can be achieved, for instance, for a particular choice of the equilibrium distribution function, Φ_{eq} (see below), and if, as usual, the bead-solvent potential, $W(|\mathbf{R}_a-\mathbf{r}_s|)$, is assumed to be spheric-symmetrical. For such a potential, of course, the Fourier transform in terms of the *wave vector* $\mathbf{k}$ is given by:

$$W(|\mathbf{R}_a-\mathbf{r}_s|)=\frac{1}{V}\sum_{\mathbf{k}}W(\mathbf{k})e^{i\,\mathbf{k}(|\mathbf{R}_a-\mathbf{r}_s|)} \qquad (13)$$

where $V=L^3$ represents the (finite) volume of the whole system "macromolecule + bath," given within a box of size L, and where $\mathbf{k}=(k_x,k_y,k_z)=\frac{2\pi}{L}(n_x,n_y,n_z)$ cycles over all possible (integer) triples with $-\infty<n_i<\infty$ and $i=x, y, z$. Substituting Equation (13) into Equation (12), the bath operators (a, $b=1$, 2) then become:

$$\hat{I}^{(ab)}=\frac{1}{V^2}\sum_{\mathbf{k},\mathbf{k}'}\sum_{s,s'}\mathbf{k}W(\mathbf{k})W(\mathbf{k}')\int d\{\mathbf{r}_s,\mathbf{p}_s\}e^{i\mathbf{k}(\mathbf{R}_a-\mathbf{r}_s)}$$
$$\times e^{(\hat{L}_B+\hat{L}_S)\tau}e^{i\mathbf{k}(\mathbf{R}_b-\mathbf{r}_{s'})}\mathbf{k}'\left[\frac{\partial}{\partial \mathbf{P}_b}-\frac{\partial}{\partial \mathbf{p}_{s'}}\right] \qquad (14)$$

For a spherical-symmetric potential, moreover, the Fourier components $W(\mathbf{k})$ in Equation (13) are known to be real and symmetrical:

$$W(\mathbf{k})=W^*(\mathbf{k})=W(-\mathbf{k}) \qquad (15)$$

and, thus, the bath operators in Equation (14) are nonzero, only if $\mathbf{k}+\mathbf{k}'=0$ or $\mathbf{k}=-\mathbf{k}'$, respectively. This is seen, for instance, from the fact that the bath operators are just multiplied by a factor $e^{-i\mathbf{k}\cdot\mathbf{a}}$, if all the solvent particles are *shifted* by a constant amount, $\mathbf{r}_s\rightarrow\mathbf{r}_s+\mathbf{a}$. In addition to the properties of the Fourier transform of the bead-solvent potential, W, we may also use the well-known relation $-\frac{\partial\Phi_{eq}}{\partial \mathbf{p}_s}=\frac{\beta\,\mathbf{p}_s\,\mathbf{\Phi}_{eq}}{m}$ for the (solvent) equilibrium distribution function, in order to bring the bath operators in Equation (14) into the form:

$$\hat{I}^{(ab)}=\frac{1}{V^2}\sum_{\mathbf{k}}W^2(\mathbf{k})e^{i\,\mathbf{k}\cdot\mathbf{R}_a}\,e^{\hat{L}_B\,\tau}\,e^{-i\,\mathbf{k}\cdot\mathbf{R}_b}$$
$$\times\left\langle\left(\sum_s e^{-i\,\mathbf{k}\cdot\mathbf{r}_s}\right)e^{\hat{L}_S\,\tau}\sum_s e^{i\,\mathbf{k}\cdot\mathbf{r}_s}\mathbf{k}\left[\frac{\partial}{\partial \mathbf{P}_b}+\frac{\beta\,\mathbf{p}_s}{m}\right]\right\rangle_{eq} \qquad (16)$$

where the brackets $\langle\ldots\rangle_{eq}$ refer to the average over all the solvent particles in the bath. However, we may still proceed one step further in simplifying these operators, using a second relation for the Liouville operator of the solvent and the corresponding equilibrium distribution function:

$$e^{\hat{L}_S\tau}\sum_s e^{i\mathbf{k}\cdot\mathbf{r}_s}\frac{\beta\mathbf{p}_s}{m}=i\frac{\partial}{\partial\tau}e^{\hat{L}_S\,\tau}\sum_s e^{i\mathbf{k}\cdot\mathbf{r}_s} \qquad (17)$$

to obtain the bath operators in their final form:

$$\hat{I}^{(ab)}=\frac{n}{V^2}\sum_{\mathbf{k}}W^2(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}_a}e^{\hat{L}_B\,\tau}e^{-i\mathbf{k}\cdot\mathbf{R}_b}$$
$$\times\left[g(\mathbf{k},\tau)\mathbf{k}\frac{\partial}{\partial \mathbf{P}_b}+i\beta\frac{g(\mathbf{k},\tau)}{\partial\tau}\right] \qquad (18)$$

where:

$$g(\mathbf{k},\tau)=\frac{1}{n}\left\langle\left(\sum_s e^{-i\mathbf{k}\cdot\mathbf{r}_s}\right)e^{\hat{L}_S\,\tau}\sum_s e^{i\mathbf{k}\cdot\mathbf{r}_s}\right\rangle_{eq}$$
$$=\frac{1}{n}\left\langle\sum_{ss'}e^{-i\mathbf{k}\cdot(\mathbf{r}_s(0)-\mathbf{r}'_s(\tau))}\right\rangle_{eq} \qquad (19)$$

is known as the *dynamic structure factor* or the *scattering function* of the solution. We shall return later to this function and discuss its properties in more detail. For the moment, let us just mention that the bath operators $\hat{I}^{(ab)}$ still include – via the scattering function $g(\mathbf{k},\tau)$ – the effects of the solvent on the dynamics of the macromolecule. By summarizing all the steps of the derivation above, we now recognize that the bath operators can be expressed in terms of the Fourier transform of the bead-solvent potential as well as the scattering function of the bath. Since the (same) scattering function also arises independently as the Fourier transform of the density distribution of the solvent particles, Equation (18) and (19) help simplify the study of the bead-solvent interaction and its influence on the dynamic behaviour of the molecules. On the other hand, however, the "bead operator" $\hat{L}_B$ still appears explicitly in Equation (18). To also remove this part of the Liouville operator from the expressions of the bath operators, we also have to separate – additionally – the center-of-mass motion of the overall macromolecule from the internal motion of the beads, as will be shown below.

Instead of the individual coordinates, $\mathbf{R}_i$, and momenta, $\mathbf{P}_i (i = 1, \ldots, N)$, of the beads, of course, we may use the center-of-mass and internal coordinates to describe the molecular motion as a whole. For a dumbbell molecule with just two beads, such a definition of the center-of-mass (C) and internal (Q) coordinates is particularly simple:

$$\mathbf{R}_C = \frac{\mathbf{R}_1 + \mathbf{R}_2}{2}, \quad \mathbf{Q} = \mathbf{R}_1 - \mathbf{R}_2 \tag{20}$$

$$\mathbf{P}_C = \frac{\mathbf{P}_1 + \mathbf{P}_2}{2}, \quad \mathbf{P}_Q = \mathbf{P}_1 - \mathbf{P}_2 \tag{21}$$

and leads immediately to a Liouville operator, $\hat{L}_B$, of the (two) beads that also consists of two parts:

$$\hat{L}_B = \hat{L}_B^C + \hat{L}_B^Q \tag{22}$$

with

$$\hat{L}_B^C = -\frac{\mathbf{P}_C}{M}\frac{\partial}{\partial \mathbf{R}_C} \quad \text{and} \quad \hat{L}_B^Q = -\frac{\mathbf{P}_Q}{M}\frac{\partial}{\partial \mathbf{Q}} + 2\frac{\partial U|\mathbf{Q}|}{\partial \mathbf{Q}}\frac{\partial}{\partial \mathbf{P}_Q} \tag{23}$$

Apart from the operators, we now must also treat the phase-space distribution $\rho_2(\mathbf{R}_1, \mathbf{R}_2, \mathbf{P}_1, \mathbf{P}_2; t) \rightarrow f(t) \equiv f(\mathbf{R}_C, \mathbf{Q}, \mathbf{P}_C, \mathbf{P}_Q; t)$ in terms of the new coordinates where, for the sake of simplicity, we make use of the same symbol $f(t)$ as before.

There are various simplifications of the master Equation (11) and the bath operators in Equation (18), which can be made within the center-of-mass coordinates. Taking Equation (18), for instance, we see that the Liouville operator, $\hat{L}_B$, of the two beads only appears in the exponent, i.e.,

$$e^{\hat{L}_B \tau} \rightarrow e^{\hat{L}_B^C \tau} \cdot e^{\hat{L}_B^Q \tau} \tag{24}$$

from which the first part, $e^{\hat{L}_B^C \tau}$, needs to be eliminated from the master Equation (11) to separate the internal dynamics of the macromolecule from its overall motion. Since this first part, which includes a partial derivative with respect to the center-of-mass coordinate, $\mathbf{R}_C$, acts to the right in Equation (18) on both, $e^{-i\mathbf{k}\cdot\mathbf{R}_C}$ as well as the phase-space distribution function of the dumbbell, $f(\mathbf{R}_C, \mathbf{Q}, \mathbf{P}_C, \mathbf{P}_Q, t)$, we can only eliminate this term when the distribution function is replaced by its Fourier transform (with respect to $\mathbf{R}_C$):

$$f(\mathbf{R}_C, \mathbf{Q}, \mathbf{P}_C, \mathbf{P}_Q, t) = \frac{1}{V}\sum_{\mathbf{l}} f(\mathbf{l}, \mathbf{Q}, \mathbf{P}_C, \mathbf{P}_Q, t)\, e^{i\mathbf{l}\cdot\mathbf{R}_C} \tag{25}$$

from which, finally $e^{i\mathbf{k}\cdot\mathbf{R}_C} e^{\hat{L}_b^C \tau} e^{-i(\mathbf{k}-\mathbf{l})\cdot\mathbf{R}_C} = e^{i\mathbf{l}\cdot\mathbf{R}_C} e^{i(\mathbf{k}-\mathbf{l})\cdot\frac{\mathbf{P}_C \tau}{M}}$ and

$$\begin{aligned} \hat{I}_{\mathbf{l}}^{(ab)} &= \frac{n}{V^2}\sum_{\mathbf{k}} W^2(\mathbf{k}) e^{i\mathbf{l}\cdot\mathbf{R}_C} e^{i(\mathbf{k}-\mathbf{l})\cdot\frac{\mathbf{P}_C\tau}{M}} e^{\varepsilon(a)\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} e^{\hat{L}_B^Q \tau} e^{-\varepsilon(b)\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} \\ &\times \left[g(\mathbf{k},\tau)\mathbf{k}\left(\frac{1}{2}\frac{\partial}{\partial \mathbf{P}_C} + \varepsilon(b)\frac{\partial}{\partial \mathbf{P}_Q}\right) + i\beta\frac{g(\mathbf{k},\tau)}{\partial \tau}\right], \\ & a, b = 1, 2 \end{aligned} \tag{26}$$

is obtained. In Equation (26), we make use of the function $\varepsilon(x) = (-1)^{x-1}$. In the thermodynamic limit, $n \rightarrow \infty$, $V \rightarrow \infty$, $\frac{n}{V} \rightarrow n_0$, and $\frac{1}{V}\sum_{\mathbf{k}}(\ldots) \rightarrow \int \frac{d\mathbf{k}}{(2\pi)^3}(\ldots)$, therefore, the master Equation (11) of the dumbbell can be written in terms of an (infinite) system of equations:

$$\begin{aligned} \frac{\partial f(\mathbf{l}; t)}{\partial t} &+ i\frac{\mathbf{P}_C}{M} f(\mathbf{l}; t) - \hat{L}_S^Q f(\mathbf{l}; t) \\ &= \frac{1}{2}\frac{\partial}{\partial \mathbf{P}_C}\int_0^t d\tau\, \hat{I}_{\mathbf{l}}^{(C)}(\tau) f(\mathbf{l}; t-\tau) \\ &+ \frac{\partial}{\partial \mathbf{P}_Q}\int_0^t d\tau\, \hat{I}_{\mathbf{l}}^{(Q)}(\tau) f(\mathbf{l}; t-\tau) \end{aligned} \tag{27}$$

which now contains both the Fourier components of the phase-space distribution function, $f(\mathbf{l}; t)$ as well as those of the bath operators, $\hat{I}_{\mathbf{l}}^{(C,Q)}(\tau)$, respectively. In practice, of course, we are interested only in the asymptotic form of these equations, i.e., we expand the function $e^{i\mathbf{l}\mathbf{R}_C}$ in Equation (27) in the series and neglect all terms of an order higher than the first one. For the bath operators, $\hat{I}^{(C)}$ and $\hat{I}^{(Q)}$, the Fourier components, $\hat{I}_{\mathbf{l}}^{(C,Q)}(\tau)$, can then be written in terms of four (sub-)operators:

$$\hat{I}_{\mathbf{l}}^{(C)} = \hat{I}_{\mathbf{l}}^{(11)} + \hat{I}_{\mathbf{l}}^{(12)} + \hat{I}_{\mathbf{l}}^{(21)} + \hat{I}_{\mathbf{l}}^{(22)} \tag{28}$$

$$\hat{I}_{\mathbf{l}}^{(Q)} = \hat{I}_{\mathbf{l}}^{(11)} + \hat{I}_{\mathbf{l}}^{(12)} - \hat{I}_{\mathbf{l}}^{(21)} - \hat{I}_{\mathbf{l}}^{(22)} \tag{29}$$

where the two superscripts, 1 and 2, refer to the (two) beads of the dumbbell. In detail, these four (sub-)operators are given by:

$$\begin{aligned} \hat{I}_{\mathbf{l}}^{(11)}(\tau) &= n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W^2(\mathbf{k}) e^{i(\mathbf{k}-\mathbf{l})\cdot\frac{\mathbf{P}_C\tau}{M}} e^{\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} e^{\hat{L}_B^Q \tau} e^{-\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} \\ &\times \left[g(\mathbf{k},\tau)\mathbf{k}\left(\frac{1}{2}\frac{\partial}{\partial \mathbf{P}_C} + \frac{\partial}{\partial \mathbf{P}_Q}\right) + i\beta\frac{\partial g(\mathbf{k},\tau)}{\partial \tau}\right] \end{aligned} \tag{30}$$

$$\begin{aligned} \hat{I}_{\mathbf{l}}^{(12)}(\tau) &= n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W^2(\mathbf{k}) e^{i(\mathbf{k}-\mathbf{l})\cdot\frac{\mathbf{P}_C\tau}{M}} e^{\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} e^{\hat{L}_B^Q \tau} e^{\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} \\ &\times \left[g(\mathbf{k},\tau)\mathbf{k}\left(\frac{1}{2}\frac{\partial}{\partial \mathbf{P}_C} - \frac{\partial}{\partial \mathbf{P}_Q}\right) + i\beta\frac{\partial g(\mathbf{k},\tau)}{\partial \tau}\right] \end{aligned} \tag{31}$$

$$\begin{aligned} \hat{I}_{\mathbf{l}}^{(21)}(\tau) &= n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W^2(\mathbf{k}) e^{i(\mathbf{k}-\mathbf{l})\cdot\frac{\mathbf{P}_C\tau}{M}} e^{-\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} e^{\hat{L}_B^Q \tau} e^{-\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} \\ &\times \left[g(\mathbf{k},\tau)\mathbf{k}\left(\frac{1}{2}\frac{\partial}{\partial \mathbf{P}_C} + \frac{\partial}{\partial \mathbf{P}_Q}\right) + i\beta\frac{\partial g(\mathbf{k},\tau)}{\partial \tau}\right] \end{aligned} \tag{32}$$

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$$\hat{I}_{\mathbf{l}}^{(22)}(\tau) = n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k}\, W^2(\mathbf{k}) e^{i(\mathbf{k}-\mathbf{l})\cdot\frac{\mathbf{P}_C \tau}{M}} e^{-\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} e^{\hat{L}_S^Q \tau} e^{\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} \times \left[g(\mathbf{k},\tau)\mathbf{k}\left(\frac{1}{2}\frac{\partial}{\partial \mathbf{P}_C} - \frac{\partial}{\partial \mathbf{P}_Q}\right) + i\beta \frac{\partial g(\mathbf{k},\tau)}{\partial \tau}\right] \tag{33}$$

With Equation (27), of course, we are still at the level of a master equation for the (Fourier components of the) phase space distribution function. To finally arrive at a Fokker-Planck(-type) equation for the macromolecule, we first need to remove the explicit dependence of the bath operators in Equation (30)–(33) on the scattering function $g(\mathbf{k},\ \tau)$ and, particularly, on its time derivative [as found within the square brackets]. For this purpose, we may consider the time behaviour of $g(\mathbf{k},\ \tau)$ which is determined by the relaxation time, τ_R as required to bring the solvent back into its equilibrium state[7,22] and, hence, is *non-negligible* only within a short time interval $[0..\tau_R]$.[23,24] On such a short time-scale, in contrast, the internal positions of the (massive) beads of the macromolecule will not be able to change much, i.e., we may assume in good approximation $e^{\hat{L}_S^Q \tau} \sim 1$ for all times, $0 \le \tau \le \tau_R$, within the relaxation of the solvent. With these two assumptions on the shape of the scattering function, $g(\mathbf{k},\ \tau)$, and the internal dynamics of the macromolecule in mind, we are now able also to separate the time integration in Equation (27) from the coordinates and the momenta of the beads and, especially, to remove the (unknown) time derivative of the scattering function. For the sake of brevity, however, we cannot display all the steps in the manipulation of the master Equation (27) in detail here; instead, since all the *bath operators* in Equation (30)–(33) have a very similar structure, we may discuss the main steps just for the first term, $\hat{I}_{\mathbf{l}}^{(11)}(\tau)$, and leave similar manipulations for the other terms to the reader.

Substituting Equation (30) into the set of master equations [Equation (27)], we obtain:

$$\int_0^t d\tau \hat{I}_{\mathbf{l}}^{(11)}(\tau) f(\mathbf{l}; t-\tau) = n_0 \int_0^t d\tau \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W^2(\mathbf{k}) e^{i(\mathbf{k}-\mathbf{l})\cdot\frac{\mathbf{P}_C \tau}{M}} e^{\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} e^{\hat{L}_B^Q \tau} e^{-\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} \times \left[g(\mathbf{k},\tau)\mathbf{k}\left(\frac{1}{2}\frac{\partial}{\partial \mathbf{P}_C} + \frac{\partial}{\partial \mathbf{P}_Q}\right) + i\beta \frac{\partial g(\mathbf{k},\tau)}{\partial \tau}\right] f(\mathbf{l}; t-\tau) \tag{34}$$

which, in practice, includes two terms due to the scattering function and its time derivative. For the second term, we can perform an integration by parts (over the time) to bring Equation (34) into the form:

$$\begin{aligned}
& i\beta n_0 \int_0^t d\tau \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W^2(\mathbf{k}) e^{i(\mathbf{k}-\mathbf{l})\cdot\frac{\mathbf{P}_C \tau}{M}} e^{\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} e^{\hat{L}_B^Q \tau} e^{-\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} \frac{\partial g(\mathbf{k},\tau)}{\partial \tau} f(\mathbf{l};\ t-\tau) \\
& = i\beta n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W^2(\mathbf{k}) \left[g(\mathbf{k},t) e^{i(\mathbf{k}-\mathbf{l})\frac{\mathbf{P}_C t}{M}} e^{\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} e^{\hat{L}_B^Q t} e^{-\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} f(\mathbf{l};\ 0) - g(\mathbf{k},\ 0) f(\mathbf{l};\ t)\right] \\
& \quad - i\beta n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W^2(\mathbf{k}) \left[\left[\int_0^t d\tau g(\mathbf{k},\ \tau) \frac{\partial}{\partial \tau} \left\{ e^{i(\mathbf{k}-\mathbf{l})\frac{\mathbf{P}_C \tau}{M}} e^{\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} e^{\hat{L}_B^Q \tau} e^{-\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} f(\mathbf{l};\ t-\tau)\right\}\right]\right] \\
& = i\beta n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W^2(\mathbf{k}) \left[g(\mathbf{k},t) e^{i(\mathbf{k}-\mathbf{l})\frac{\mathbf{P}_C t}{M}} e^{\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} e^{\hat{L}_B^Q t} e^{-\frac{i\mathbf{k}\mathbf{Q}}{2}} f(\mathbf{l};\ 0) - g(\mathbf{k},0) f(\mathbf{l};\ t)\right] \\
& \quad - i\beta n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W^2(\mathbf{k}) \left[\int_0^t d\tau g(\mathbf{k},\tau) e^{i(\mathbf{k}-\mathbf{l})\frac{\mathbf{P}_C \tau}{M}} e^{\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} e^{\hat{L}_B^Q \tau} e^{-\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} \frac{\partial f(\mathbf{l};\ t-\tau)}{\partial \tau}\right] \\
& \quad + \beta n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W^2(\mathbf{k}) \int_0^t d\tau g(\mathbf{k},\tau) e^{i(\mathbf{k}-\mathbf{l})\cdot\frac{\mathbf{P}_C \tau}{M}} e^{\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} e^{\hat{L}_B^Q \tau} e^{-\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} \\
& \quad \times \left[(\mathbf{k}-\mathbf{l})\cdot\frac{\mathbf{P}_C}{M} + \frac{1}{2}\mathbf{k}\cdot\frac{\mathbf{P}_Q}{M}\right] f(\mathbf{l};\ t-\tau)
\end{aligned} \tag{35}$$

which now includes only a time integration $\int_0^t d\tau g(\mathbf{k},\tau)$... over the scattering function. As discussed above, we can carry out this time integration by assuming that (i) the scattering function $g(\mathbf{k},\tau)$ is zero for all times $\tau > \tau_R$ and (ii) the macromolecule does not change its internal shape on such a short time scale, i.e., by adopting a δ-like behaviour for $g(\mathbf{k},\ \tau)$ we obtain $\int_0^t d\tau g(\mathbf{k},\tau)\hat{I}_{\mathbf{l}}^{(11)}(\tau) f(\mathbf{l}; t-\tau) \rightarrow \hat{I}_{\mathbf{l}}^{(11)}(0) f(\mathbf{l}; t) \int_0^\infty d\tau g(\mathbf{k},\tau)$.

In addition, by taking into account the symmetry properties for both, the scattering function, $g(\mathbf{k},\tau) = g(-\mathbf{k},\ \tau)$ [cf. Equation (19) and ref.[8]] and of the bead-solvent potential, $W(\mathbf{k}) = W(-\mathbf{k})$, we obtain $\int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W(\mathbf{k})^2 g(\mathbf{k},\tau) = 0$. That is, only the third term of Equation (35) will survive finally:

$$\begin{aligned} & i\beta n_0 \int_0^t d\tau \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W^2(\mathbf{k}) e^{i(\mathbf{k}-\mathbf{l})\cdot\frac{\mathbf{P}_C\tau}{M}} e^{\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} e^{\hat{L}_B^Q \tau} e^{-\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} \\ & \quad \times \frac{\partial g(\mathbf{k},\tau)}{\partial \tau} f(\mathbf{l};\, t-\tau) \\ & \quad = \beta n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W^2(\mathbf{k}) \int_0^t d\tau g(\mathbf{k},\tau) e^{i(\mathbf{k}-\mathbf{l})\cdot\frac{\mathbf{P}_C\tau}{M}} e^{\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} e^{\hat{L}_B^Q \tau} e^{-\frac{i\mathbf{k}\cdot\mathbf{Q}}{2}} \\ & \qquad \times \left[(\mathbf{k}-\mathbf{l}) \frac{\mathbf{P}_C}{M} + \frac{1}{2} \mathbf{k} \frac{\mathbf{P}_Q}{M} \right] f(\mathbf{l};\, t-\tau) \end{aligned} \tag{36}$$

Similar manipulations can be applied to all other (sub-)components in Equation (31)–(33) of the bath operators. Sorting out these details, therefore, we may write the asymptotic form of the two *bath operators* in Equation (28) and (29) as:

$$\begin{aligned} \hat{I}_{\mathbf{l}}^{(C)} = {} & n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W^2(\mathbf{k}) [2 + e^{i\mathbf{k}\cdot\mathbf{Q}} + e^{-i\mathbf{k}\cdot\mathbf{Q}}] \\ & \times \left[\int_0^\infty d\tau g(\mathbf{k},\tau) \right] \mathbf{k} \left[\frac{1}{2} \frac{\partial}{\partial \mathbf{P}_C} + \beta \frac{\mathbf{P}_C}{M} \right] \end{aligned} \tag{37}$$

$$\begin{aligned} \hat{I}_{\mathbf{l}}^{(Q)} = {} & n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} \mathbf{k} W^2(\mathbf{k}) [2 - (e^{i\mathbf{k}\cdot\mathbf{Q}} + e^{-i\mathbf{k}\cdot\mathbf{Q}})] \\ & \times \left[\int_0^\infty d\tau g(\mathbf{k},\tau) \right] \mathbf{k} \left[\frac{\partial}{\partial \mathbf{P}_Q} + \frac{1}{2} \beta \frac{\mathbf{P}_Q}{M} \right] \end{aligned} \tag{38}$$

Combining the (system of) master Equation (27) with the bath operators in Equation (37) and (38), we may now return to the (original) phase-space distribution function, $f(t) \equiv f(\mathbf{R}_C, \mathbf{Q}, \mathbf{P}_C, \mathbf{P}_Q; t)$, of the dumbbell and will arrive at a Fokker-Planck (FPE) equation of the macromolecule:

$$\begin{aligned} \frac{\partial f}{\partial t} + \frac{\mathbf{P}_C}{M} \frac{\partial f}{\partial \mathbf{R}_C} - \hat{L}_B^Q f = {} & \frac{1}{2} \frac{\partial}{\partial \mathbf{P}_C} \hat{\xi}^{(C)}(Q) \left(\frac{1}{2} \frac{\partial}{\partial \mathbf{P}_C} + \beta \frac{\mathbf{P}_C}{M} \right) f \\ & + \frac{\partial}{\partial \mathbf{P}_Q} \hat{\xi}^{(Q)}(Q) \left(\frac{\partial}{\partial \mathbf{P}_Q} + \frac{1}{2} \beta \frac{\mathbf{P}_Q}{M} \right) f \end{aligned} \tag{39}$$

where $\hat{\xi}^{(C)}(Q)$ and $\hat{\xi}^{(Q)}(Q)$ are called the *friction tensors* for the center-of-mass and internal coordinate of the dumbbell, respectively. As seen from Equation (37) and (38), moreover, these tensors have the components:

$$\begin{aligned} \hat{\xi}_{\alpha\alpha'}^{(C)} = {} & n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} k_\alpha k_{\alpha'} W^2(\mathbf{k}) \\ & \times [2 + e^{i\mathbf{k}\cdot\mathbf{Q}} + e^{-i\mathbf{k}\cdot\mathbf{Q}}] \left[\int_0^\infty d\tau g(\mathbf{k},\tau) \right] \end{aligned} \tag{40}$$

$$\begin{aligned} \hat{\xi}_{\alpha\alpha'}^{(Q)} = {} & n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} k_\alpha k_{\alpha'} W^2(\mathbf{k}) \\ & \times [2 - (e^{i\mathbf{k}\cdot\mathbf{Q}} + e^{-i\mathbf{k}\cdot\mathbf{Q}})] \left[\int_0^\infty d\tau g(\mathbf{k},\tau) \right] \end{aligned} \tag{41}$$

Instead of the internal coordinates, $\mathbf{R}_C$ and $\mathbf{Q}$, of course, the FPE can also be expressed in the phase-space coordinates of the individual beads.

$$\begin{aligned} & \frac{\partial f}{\partial t} + \frac{\mathbf{P}_1}{M} \frac{\partial f}{\partial \mathbf{R}_1} + \frac{\mathbf{P}_2}{M} \frac{\partial f}{\partial \mathbf{R}_2} - \frac{\partial U}{\partial \mathbf{R}_1} \frac{\partial f}{\partial \mathbf{P}_1} - \frac{\partial U}{\partial \mathbf{R}_2} \frac{\partial f}{\partial \mathbf{P}_2} \\ & \quad = \frac{\partial}{\partial \mathbf{P}_1} \hat{\xi}^{(+)} \left(\frac{\partial}{\partial \mathbf{P}_1} + \frac{\beta}{M} \mathbf{P}_1 \right) f + \frac{\partial}{\partial \mathbf{P}_2} \hat{\xi}^{(+)} \left(\frac{\partial}{\partial \mathbf{P}_2} + \frac{\beta}{M} \mathbf{P}_2 \right) f \\ & \qquad + \frac{\partial}{\partial \mathbf{P}_1} \hat{\xi}^{(-)} \left(\frac{\partial}{\partial \mathbf{P}_2} + \frac{\beta}{M} \mathbf{P}_2 \right) f + \frac{\partial}{\partial \mathbf{P}_2} \hat{\xi}^{(-)} \left(\frac{\partial}{\partial \mathbf{P}_1} + \frac{\beta}{M} \mathbf{P}_1 \right) f \end{aligned} \tag{42}$$

where the friction tensor components are given by:

$$\begin{aligned} \hat{\xi}_{\alpha\alpha'}^{(+)} & = \frac{1}{4} \left(\hat{\xi}_{\alpha\alpha'}^{(C)} + \hat{\xi}_{\alpha\alpha'}^{(Q)} \right) \\ & = n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} k_\alpha k_{\alpha'} W^2(\mathbf{k}) \left[\int_0^\infty d\tau g(\mathbf{k},\tau) \right] \end{aligned} \tag{43}$$

$$\begin{aligned} \hat{\xi}_{\alpha\alpha'}^{(-)} = \frac{1}{4} \left(\hat{\xi}_{\alpha\alpha'}^{(C)} - \hat{\xi}_{\alpha\alpha'}^{(Q)} \right) = {} & n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} k_\alpha k_{\alpha'} W^2(\mathbf{k}) \\ & \times \left[\frac{e^{i\mathbf{k}\cdot\mathbf{Q}} + e^{-i\mathbf{k}\cdot\mathbf{Q}}}{2} \right] \left[\int_0^\infty d\tau g(\mathbf{k},\tau) \right] \end{aligned} \tag{44}$$

Equation (39) and (42) represent two FPE which describe the time evolution of the phase-space distribution function for a dumbbell molecule. In these equations, all the effects of the solvent onto the beads of the molecule are now incorporated into the (two) frictions tensors in Equation (40) and (41) in the center-of-mass and relative coordinates [cf. Equation (39)] or into Equation (43) and (44), respectively, if the distribution function given in terms of the cartesian coordinates of the individual beads [cf. Equation (42)].

Equation (42)–(44) can easily be generalized for a macromolecule, which is formed by N beads:

$$\begin{aligned} & \frac{\partial \rho_N}{\partial t} + \sum_{a=1}^{N} \frac{\mathbf{P}_a}{M} \frac{\partial \rho_N}{\partial \mathbf{R}_a} - \sum_{a,b=1}^{N} \frac{\partial U(|\mathbf{R}_a - \mathbf{R}_b|}{\partial \mathbf{R}_a} \frac{\partial \rho_N}{\partial \mathbf{P}_a} \\ & \quad = \sum_{a,b=1}^{N} \frac{\partial}{\partial \mathbf{P}_a} \hat{\xi}^{ab}(|\mathbf{R}_a - \mathbf{R}_b|) \left(\frac{\partial}{\partial \mathbf{P}_b} + \frac{\beta}{M} \mathbf{P}_b \right) \rho_N \end{aligned} \tag{45}$$

if friction tensors, $\hat{\xi}^{(ab)}$, with components:

$$\begin{aligned} \hat{\xi}_{\alpha\alpha'}^{(ab)} = {} & n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} k_\alpha k_{\alpha'} W^2(\mathbf{k}) \\ & \times \left[\frac{e^{i\mathbf{k}\cdot\mathbf{R}_a} + e^{-i\mathbf{k}\cdot\mathbf{R}_b}}{2} \right] \left[\int_0^\infty d\tau g(\mathbf{k},\tau) \right] \end{aligned} \tag{46}$$

are introduced for the center-of-mass of the macromolecule and for each pair of interacting beads. These friction tensors, $\hat{\xi}_{\alpha\alpha'}^{(ab)}$, contain [via the bead-solvent potential, W, and the dynamic structure factor of the solvent, $g(\mathbf{k},\tau)$] all

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information about the influence of the solvent on the dynamic behaviour of the macromolecule. In fact, a detailed knowledge of the friction tensor plays a *key* role in studying the dynamic properties of the macromolecule. For example, the behaviour of the friction tensor does not affect only the end-to-end vector or the radius of gyration of the macromolecule, but also its momentum correlation functions. In the next section, therefore, we will consider a few of these properties of the friction tensors in more detail.

Effects of the Bead-Solvent Interaction on the Behavior of the Friction Tensors

Having derived the Fokker-Planck equations [Equation (39) and (42)] for the dumbbell molecule (in two different sets of coordinates), we see that – for a *weak* bead-solvent interaction – the dynamics of the macromolecule is determined entirely by the friction tensors in Equation (40) and (41) [or the two tensors in Equation (43) and (44), respectively]. Therefore, to gain further insight into the behaviour of the molecules, we shall investigate the properties of these friction tensors. In the following subsection, we start with analysis of the (two) limits of a zero and very large separation of the two beads in the dumbbell to obtain a proper parametrization of the friction tensor components. Such a parametrization helps calculate, for instance, various derived quantities such as the (normalized) correlation functions of the center-of-mass or internal momenta. The main emphasis of this section, however, will be placed later on the question, how the bead-solvent potential, W, effects the friction tensor components, if taken as functions of the internal separation of the beads. To this end, we consider three particular choices of the bead-solvent interaction in more detail. However, all of our discussions here will be restricted to the case of a (2-bead) dumbbell molecule. The generalization of these results for larger macromolecules and other (chain) structures is presently underway and will be presented elsewhere.

General Properties of the Friction Tensors

We start our discussion by considering a dumbbell in the two limits of a zero and a large separation of the two beads. If we assume, for instance, that the interaction potential $U \to 0$ for both, a small ($Q \to 0$) and a very large ($Q \to \infty$) separation of the two beads, the friction tensor $\hat{\xi}^{(-)}_{\alpha\alpha'}$ in Equation (44) vanishes, and the Fokker-Planck equation [Equation (42)] becomes either an equation for a single particle:

$$\frac{\partial f}{\partial t} + \frac{\mathbf{P}}{M}\frac{\partial f}{\partial \mathbf{R}} = \frac{\partial}{\partial \mathbf{P}}\hat{\xi}^{\text{single}}\left(\frac{\partial}{\partial \mathbf{P}} + \frac{\beta}{M}\mathbf{P}\right)f \tag{47}$$

with mass, $2M$, and a (scalar) friction coefficient, $\hat{\xi}^{\text{single}}$, or, respectively, a Fokker-Planck-type equation for two *free* particles:

$$\frac{\partial f}{\partial t} + \frac{\mathbf{P}_1}{M}\frac{\partial f}{\partial \mathbf{R}_1} + \frac{\mathbf{P}_2}{M}\frac{\partial f}{\partial \mathbf{R}_2} = \frac{\partial}{\partial \mathbf{P}_1}\hat{\xi}\left(\frac{\partial}{\partial \mathbf{P}_1} + \frac{\beta}{M}\mathbf{P}_1\right)f + \frac{\partial}{\partial \mathbf{P}_2}\hat{\xi}\left(\frac{\partial}{\partial \mathbf{P}_2} + \frac{\beta}{M}\mathbf{P}_2\right)f \tag{48}$$

where, again, the friction tensor components become constant, i.e., they do not depend on the bead-bead distance of the macromolecule [cf. Equation (43) and (44)]:

$$\hat{\xi}_{\alpha\alpha'} = n_0 \int \frac{d\mathbf{k}}{(2\pi)^3} k_\alpha k_{\alpha'} W(\mathbf{k})^2 \left[\int_0^\infty d\tau g(\mathbf{k},\tau)\right] \tag{49}$$

Both cases, therefore, describe a (dumbbell) macromolecule *without* a hydrodynamic interaction among the beads and have been discussed frequently in the literature.[4,20,21]

In general, however, the friction tensors [Equation (40) and (41)] are rank 2, symmetrical tensors and, thus, may have six independent components. Since for a dumbbell, these components may depend only on the distance $|\mathbf{Q}|$ of the two beads, they can be written always in terms of just two parameters[7]

$$\hat{\xi}^{(i)}_{\alpha\alpha'} = A^{(i)}\delta_{\alpha\alpha'} + B^{(i)}q_\alpha q_{\alpha'} \tag{50}$$

where $q_\alpha = \frac{Q_\alpha}{|\mathbf{Q}|}$ denotes the (normalized) components of the vector, which points from bead 1 to bead 2, and where $i = [C, Q, -]$ refers to the various types (or representations) of the friction tensors above. Independent of the particular type, the parameters, $A^{(i)}$ and $B^{(i)}$, can be determined from the two equations:

$$\sum_\alpha \hat{\xi}^{(i)}_{\alpha\alpha} = 3A^{(i)} + B^{(i)} \tag{51}$$

and

$$\sum_{\alpha,\alpha'} \hat{\xi}^{(i)}_{\alpha\alpha'} q_\alpha q_{\alpha'} = A^{(i)} + B^{(i)} \tag{52}$$

We can utilize the parametrization [Equation (50)] of the friction tensors to simplify their expressions in Equation (40) and (41) which were given in terms of the Fourier transform of the bead-solvent interaction potential and the scattering function, respectively. Concerning the scattering function, $g(\mathbf{k},\tau)$, we just note that – owing to the veryÂdifferent masses of the bead and solvent particles – we may adopt an exponential dependence, $g(\mathbf{k},\tau) = e^{-\mathbf{k}^2 D_B \tau}$ on the diffusion coefficient, D_B, of the solvent.[23,24] Of course, this simple dependence of the scattering function on the property of the surrounding bath reflects the fact that the solvent particles relax much faster to equilibrium than the beads of the macromolecule. But by assuming such an approximation for the scattering function, we also have

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$\int_0^\infty d\tau g(\mathbf{k},\tau) = \frac{1}{k^2 D_\mathrm{B}}$, which now enables us to reduce the 3-dimensional integration in the friction tensors [Equation (40) and (41)] to a 1-dimensional integral, taken over the modulus of the wave vector. Using polar coordinates and by carrying out the integration over the angles, $\vartheta_\mathbf{k}$ and $\varphi_\mathbf{k}$, explicitly, these two friction tensors become:

$$\begin{aligned}\hat{\xi}^{(C)}_{\alpha\alpha'} &= \frac{n_0}{(2\pi)^2 D_\mathrm{B}} \int_0^\infty dk k^2 W_k^2 \\ &\quad \times \left[4\left(\frac{1}{3} + \frac{\sin(kQ) - kQ\cos(kQ)}{(kQ)^3}\right)\delta_{\alpha\alpha'} \right. \\ &\quad \left. + 4\left(\frac{\sin(kQ)}{kQ} - 3\frac{\sin(kQ) - kQ\cos(kQ)}{(kQ)^3}\right) q_\alpha q_{\alpha'}\right]\end{aligned} \tag{53}$$

$$\begin{aligned}\hat{\xi}^{(Q)}_{\alpha\alpha'} &= \frac{n_0}{(2\pi)^2 D_\mathrm{B}} \int_0^\infty dk k^2 W_k^2 \\ &\quad \times \left[4\left(\frac{1}{3} - \frac{\sin(kQ) - kQ\cos(kQ)}{(kQ)^3}\right)\delta_{\alpha\alpha'} \right. \\ &\quad \left. + 4\left(3\frac{\sin(kQ) - kQ\cos(kQ)}{(kQ)^3} - \frac{\sin(kQ)}{kQ}\right) q_\alpha q_{\alpha'}\right]\end{aligned} \tag{54}$$

For a slow relaxation of the beads, when compared to the solvent particles, these tensors still incorporate all the influence of the solvent on the dynamic behaviour of the macromolecule. However, before we analyze the dependence of the friction tensors for a few particular choices of the bead-solvent interaction potential, let us first consider the (normalized) correlation functions (CF) for the center-of-mass, $C^{(C)}_{\alpha\beta}(t)$, and the internal momenta, $C^{(Q)}_{\alpha\beta}(t)$, respectively. These (auto-)correlation functions are defined by:[14]

$$C^{(i)}_{\alpha\beta}(t) \equiv \left\langle P^{(i)}_\alpha(0) P^{(i)}_\beta(t)\right\rangle = \frac{1}{2}\left\langle \left(e^{(-\hat{\xi}^{(i)} t)}\right)_{\alpha\beta}\right\rangle, \quad i = C, Q \tag{55}$$

where the angular brackets, $\langle\ldots\rangle$, refer to the average over the equilibrium state of the macromolecule. If, for example, we take Γ to denote all the coordinates and momenta of the macromolecule, this bracket can be written as:

$$\langle\ldots\rangle \equiv h^{-1}\int d\Gamma \ldots f_{eq}(\Gamma;\, t), \quad f_{eq}(\Gamma;\, t) = e^{-\beta H_B} \tag{56}$$

where $h = \int d\Gamma f_{eq}(\Gamma;\, t)$ accounts for the proper normalization of the average. As seen from Equation (55), moreover, such a momentum CF describes the correlation between some current momentum, $\mathbf{P}(t)$, and the corresponding momentum, $\mathbf{P}(0)$, at the initial time. Substituting the friction tensors in Equation (50) into the autocorrelation function in Equation (55), we therefore obtain:

$$C^{(i)}_{\alpha\beta}(t) \equiv C^{(i)}(t)\delta_{\alpha\beta} = \frac{1}{6}\left\langle e^{\left(-A^{(i)}(Q)t\right)}\left(2 + e^{\left(-B^{(i)}(Q)t\right)}\right)\right\rangle \delta_{\alpha\beta} \tag{57}$$

for the parametrization of the CFs.

In general, of course, we are more interested in the asymptotic form of the correlation functions instead of their explicit time behaviour. We can derive the asymptotic behaviour for any bead-solvent potential by using a Taylor expansion at $Q = 0$ from which, for $t \to \infty$, only the first (non-vanishing) term will survive. For example, if we consider the center-of-mass momentum correlation function, $C^{(C)}(t)$, and truncate the Taylor expansion after the first term [cf. Equation (53)], we obtain $A^{(C)}(Q) = A^{(C)}(0) + O(Q)$, $B^{(C)}(Q) = O(Q)$, independent of the particular bead-solvent interaction potential, and thus:

$$C^{(C)}(t) \approx \frac{1}{3} e^{-A^{(C)}(0)\, t} \tag{58}$$

for its asymptotic behaviour ($t \to \infty$). In this equation, $A^{(C)}(0) = \frac{4}{3}\frac{n_0}{(2\pi)^2 D_B}\int_0^\infty dk k^2 W_k^2$ is called the *decay parameter* of the center-of-mass momentum CF; it shows that the correlation function, $C^{(C)}_{\alpha\beta}(t)$, always decays exponentially. A similar behaviour is found for the internal momentum CF, $C^{(Q)}_{\alpha\beta}(t)$, for the center-of-mass momentum, $\mathbf{P}_C$, which tends to zero also for any choice of the bead-solvent interaction potential, but with a different decay rate. Therefore, a more detailed investigation of the bead-solvent potential and their effects on the friction tensors is needed to understand the dynamics of the macromolecules and their relaxation, when immersed in a solvent. In the following, we consider three realistic choices for such an interaction potential and calculate both the friction tensors [Equation (53) and (54)] as functions of the bead-bead separation as well as the asymptotic behaviour of the internal momentum auto-correlation function.

Yukawa and Born-Mayer Potential

There are several bead-solvent interaction potentials known from the literature which have been used to describe the dynamics of macromolecules. They often have their roots in the field of physical chemistry to help simulate the chemical bonding in different (chemical) environments. Three frequently applied interaction potentials are the screened Coulomb (Yukawa), Born-Mayer, as well as the Lennard-Jones potential (Figure 1). While the Yukawa (Y) potential has been found useful to describe the (repulsive) interaction between charged particles, the Born-Mayer (BM) potential is used for dilute solutions, and the Lennard-Jones (LJ) potential is useful for modelling long-range van-der-Waals interaction between neutral particles.

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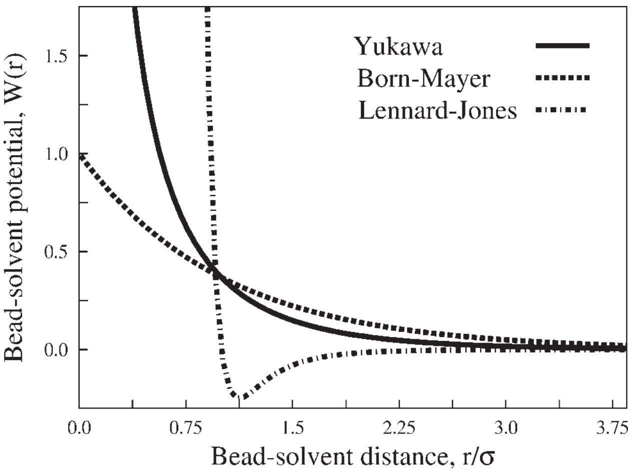

Figure 1. The bead-solvent interaction potentials as defined by Equation (59), (70), and (79), respectively. For discussion see text.

We start with the Yukawa potential:

$$W^{\mathrm{Y}}(r) = \frac{e^{-\varepsilon_{\mathrm{Y}} r}}{r} \tag{59}$$

which describes a $1/r$ Coulomb repulsion for a small distance, r, between the bead and solvent particles, while, due to the exponential dependence of the nominator, the interaction is screened for larger r. The constant, ε_{Y}, is called the screening parameter and provides, by its inverse $1/\varepsilon_{\mathrm{Y}}$, a characteristic length for the screening.

To calculate the friction tensors [Equation (53) and (54)], we first have to evaluate the Fourier transform of the bead-solvent interaction:

$$W_k = \frac{4\pi}{k} \int_0^\infty dr W(r) r \sin kr \tag{60}$$

which, for the Yukawa potential, simplifies to:

$$W_k^{\mathrm{Y}} = \frac{4\pi}{\varepsilon_{\mathrm{Y}}^2 + k^2} \tag{61}$$

and can be used to evaluate the integrals over k analytically for both tensors, Equation (53) and (54), respectively. Using, moreover, the general parametrization [Equation (50)] of the friction tensors for a dumbbell molecule, we can express the friction tensor parameters $A^{(..)}$ and $B^{(..)}$ explicitly:

$$A^{(Q;\mathrm{Y})}(Q) = \left(\frac{16\pi^3\gamma}{3\varepsilon_Y}\right) \times \frac{-6 + Q^3\varepsilon_{\mathrm{Y}}^3 + 3Q^2\varepsilon_Y^2 e^{-Q\varepsilon_{\mathrm{Y}}} + 6Q\varepsilon_{\mathrm{Y}} e^{-Q\varepsilon_{\mathrm{Y}}} + 6e^{-Q\varepsilon_{\mathrm{Y}}}}{Q^3\varepsilon_{\mathrm{Y}}^3} \tag{62}$$

$$B^{(Q;\mathrm{Y})}(Q) = \left(\frac{16\pi^3\gamma}{\varepsilon_{\mathrm{Y}}}\right) \times \frac{6 - Q^3\varepsilon_{\mathrm{Y}}^3 e^{-Q\varepsilon_{\mathrm{Y}}} - 3Q^2\varepsilon_{\mathrm{Y}}^2 e^{-Q\varepsilon_{\mathrm{Y}}} - 6Q\varepsilon_{\mathrm{Y}} e^{-Q\varepsilon_{\mathrm{Y}}} - 6e^{-Q\varepsilon_{\mathrm{Y}}}}{Q^3\varepsilon_{\mathrm{Y}}^3} \tag{63}$$

$$A^{(C;\mathrm{Y})}(Q) = \left(\frac{16\pi^3\gamma}{3\varepsilon_{\mathrm{Y}}}\right) \times \frac{6 + Q^3\varepsilon_{\mathrm{Y}}^3 - 3Q^2\varepsilon_Y^2 e^{-Q\varepsilon_{\mathrm{Y}}} - 6Q\varepsilon_{\mathrm{Y}} e^{-Q\varepsilon_{\mathrm{Y}}} - 6e^{-Q\varepsilon_{\mathrm{Y}}}}{Q^3\varepsilon_{\mathrm{Y}}^3} \tag{64}$$

$$B^{(C;\mathrm{Y})}(Q) = \left(\frac{16\pi^3\gamma}{\varepsilon_{\mathrm{Y}}}\right) \times \frac{-6 + Q^3\varepsilon_{\mathrm{Y}}^3 e^{-Q\varepsilon_{\mathrm{Y}}} + 3Q^2\varepsilon_{\mathrm{Y}}^2 e^{-Q\varepsilon_{\mathrm{Y}}} + 6Q\varepsilon_{\mathrm{Y}} e^{-Q\varepsilon_{\mathrm{Y}}} + 6e^{-Q\varepsilon_{\mathrm{Y}}}}{Q^3\varepsilon_{\mathrm{Y}}^3} \tag{65}$$

$$\xi^{(C;\mathrm{Y})}(0) = \frac{32\pi^3\gamma}{3\varepsilon_{\mathrm{Y}}} \tag{66}$$

where $\gamma = n_0/(2\pi)^2 D_{\mathrm{B}}$, and an additional superscript, Y, now refers to the particular choice of the Yukawa potential. In Figure 2 and 3, these parameters are displayed as function of the distance Q between the two beads of the dumbbell. To facilitate the comparison of the friction tensor parameters for the different choices of the bead-solvent potential, we give the distance Q here in terms of the characteristic length $\sigma = 1/\varepsilon$ of the potential and normalize all friction tensor parameters onto the scalar friction coefficient $\xi^{(C)}(Q = 0)$. As seen from Figure 2, the two diagonal parameters, $A^{(Q;\mathrm{Y})}(Q)$ and $A^{(C;\mathrm{Y})}(Q)$, are always positive. For the

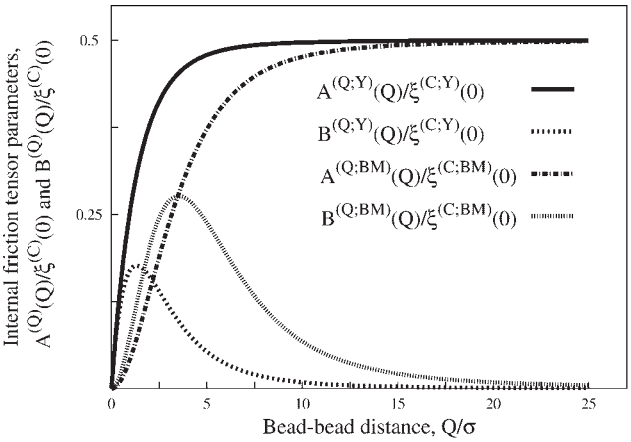

Figure 2. Normalized friction tensor parameters, $A^{(Q)}/\xi^{(C)}(0)$ and $B^{(Q)}/\xi^{(C)}(0)$, for the internal coordinate as function of the bead-bead separation. These parameters are shown for a Yukawa (Y) and Born-Mayer (BM) bead-solvent potential; see text for discussion.

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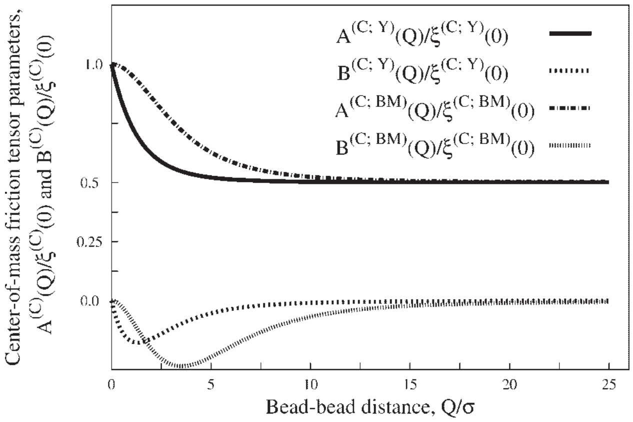

Figure 3. Normalized center-of-mass friction tensor parameters, $A^{(C)}/\xi^{(C)}(0)$ and $B^{(C)}/\xi^{(C)}(0)$, for the internal coordinate as function of the bead-bead separation. These parameters are shown for a Yukawa (Y) and Born-Mayer (BM) bead-solvent potential; see text for discussion.

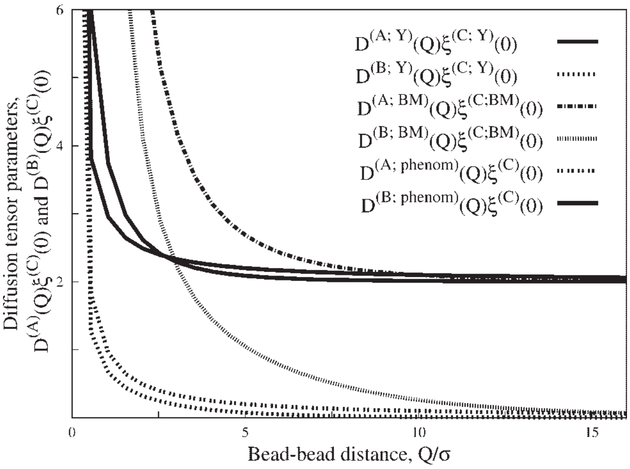

Figure 4. Normalized diffusion tensor parameters, $D^{(A)}/\xi^{(C)}(0)$ and $D^{(B)}/\xi^{(C)}(0)$, for the internal coordinate as function of the bead-bead separation. These parameters are shown for a Yukawa (Y) and Born-Mayer (BM) bead-solvent potential.

friction tensor of the internal coordinate, moreover, the $A^{(Q;\mathrm{Y})}(Q)$ parameter increases from zero up to 1/2, when one follows along Q from $Q=0$ (single-particle case) to the case of two *free* particles. At a distance of about $10/\varepsilon_\mathrm{Y}$, there is then no correlation left between the two beads of the dumbbell. The non-diagonal parameter, $B^{(Q;\mathrm{Y})}(Q)$, in contrast, first increases up to about $2/\varepsilon_\mathrm{Y}$ and then decreases quickly to zero. We can interpret this behaviour in the following way: the two beads affects each other strongly at small distances and then become less correlated as the separation increases. Figure 3 shows, in contrast, the $A^{(C;\mathrm{Y})}(Q)$ parameter for the center-of-mass friction tensor which decreases from 1 to 1/2 at a separation of about $Q > 5/\varepsilon_\mathrm{Y}$ where the two beads do not longer "feel" each other anymore.

Instead of the (internal) friction tensor, which refers to the relative coordinate $\mathbf{Q}=\mathbf{R}_1-\mathbf{R}_2$, the diffusion tensor $\hat{D}^{(Q)}_{\alpha\alpha'}$ is often used within phenomenological theory. In practice, of course, the diffusion tensor is not much more than the *inverse* of the friction tensor and, hence, can be used alternatively. As known from phenomenological theory,[7,8] the diffusion tensor (for the relative coordinate) depends approximately like $\frac{1}{Q}$ (known as Oseen tensor) on the distance between the beads. From the parametrization of the friction tensor [Equation (50)], we easily see that an analogue form must also apply for the diffusion tensor:

$$\hat{D}^{(Q)}_{\alpha\alpha'} = D^{(A)}\delta_{\alpha\alpha'} + D^{(B)}q_\alpha q_{\alpha'} \tag{67}$$

where $D^{(A)}$ and $D^{(B)}$ are used as the corresponding parameters. Figure 4 compares the diffusion tensor parameters, $D^{(A;Y)}$ and $D^{(B;Y)}$ calculated for the Yukawa potential, with the corresponding parameters of the (phenomenological) Oseen tensor; apparently, the largest deviations from the phenomenological theory arise at small distances between the beads. This can be understood quite easily as – at such small distances – the discrete (molecular) character of the solvent, which is not included of course in any phenomenological theory, becomes especially pronounced. In a phenomenological approach, instead, the solvent around the macromolecule always appears as an uncompressible and unstructured medium, giving rise to a random Brownian force between the solvent particles and the beads.[7] For large distances between the beads, however, the discrete structure of the solvent becomes negligible and our results for the diffusion tensor (components) agree well with the phenomenological theory.

Apart from the shape of the friction or diffusion tensor parameters of the dumbbell, we are interested also in the long-term behaviour of the CF for the internal momentum of the two beads. Similar as for the center-of-mass momentum CF, the asymptotic behaviour for the internal momentum CF, $C^{(Q)}(t)$, is determined only by the first (non-vanishing) term in the Taylor expansion of the corresponding friction tensor parameters, $A^{(Q)}$ and $B^{(Q)}$ In the case of a Yukawa potential, therefore, we may expand these parameters, $A^{(Q;Y)}$ and $B^{(QY)}$, as given by Equation (62) and (63), respectively, and truncate the Taylor series after the first non-vanishing term

$$\begin{aligned} A^{(Q;\mathrm{Y})}(Q) &\approx -\mu_\mathrm{Y} Q + O(Q^2), \\ B^{(Q;\mathrm{Y})}(Q) &\approx -\nu_\mathrm{Y} Q + O(Q^2) \end{aligned} \tag{68}$$

where the constants, $\mu_\mathrm{Y} = \partial A^{(Q;\,\mathrm{Y})}/\partial Q$ and $\nu_\mathrm{Y} = \partial B^{(Q;\,\mathrm{Y})}/\partial Q$, are taken at $Q=0$. With this parametrization of the friction tensor and by making use of an integration by parts [cf. Equation (56) and (57)], the asymptotic form of the internal momentum CF [Equation (57)] for a Yukawa potential becomes:

$$C^{(Q;\,\mathrm{Y})}(t\to\infty) \approx \frac{1}{3} f_{eq}(0)\left[2\mu_\mathrm{Y}^{-3} + (\mu_\mathrm{Y}+\nu_\mathrm{Y})^{-3}\right]t^{-3} \tag{69}$$

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where a more detailed derivation has been moved to Appendix A. This is indeed a very interesting result. The internal momentum correlation function remains its *algebraic* tail even for long times, a result which cannot be obtained from the (traditional) phenomenological theory of the dynamics of macromolecules. In phenomenological theory, namely, the internal momentum CF always decays exponentially and, hence, must vanish must faster.[7,25]

Beside of the Yukawa potential, we may also assume a Born-Mayer potential:

$$W^{\mathrm{BM}}(r) = e^{-\varepsilon_{\mathrm{BM}} r} \tag{70}$$

for the bead-solvent interaction which decays exponentially from one to zero (Figure 1). Again, the inverse of the (Born-Mayer) parameter, $\sigma_{\mathrm{BM}} = \frac{1}{\varepsilon_{\mathrm{BM}}}$, describes a characteristic decay length. By using the Fourier transform [Equation (60)] of this potential:

$$W_k^{\mathrm{BM}} = \frac{8\pi\varepsilon_{\mathrm{BM}}}{(\varepsilon_{\mathrm{BM}}^2 + k^2)^2} \tag{71}$$

we can follow similar lines as before and evaluate the corresponding parameters of the friction tensors:

$$\begin{aligned}A^{(Q;\mathrm{BM})}(Q) = {} & \left(\frac{8\pi^3\gamma}{3\varepsilon_{\mathrm{BM}}^3 Q^3 \varepsilon_{\mathrm{BM}}^3}\right) \\ & \times \left[-48 + Q^3\varepsilon_{\mathrm{BM}}^3 + 24Q^2\varepsilon_{\mathrm{BM}}^2 e^{-Q\varepsilon_{\mathrm{BM}}} + 48Q\varepsilon_{\mathrm{BM}} e^{-Q\varepsilon_{\mathrm{BM}}}\right. \\ & \left. + 7Q^3\varepsilon_{\mathrm{BM}}^3 e^{-Q\varepsilon_{\mathrm{BM}}} + Q^4\varepsilon_{\mathrm{BM}}^4 e^{-Q\varepsilon_{\mathrm{BM}}} + 48e^{-Q\varepsilon_{\mathrm{BM}}}\right]\end{aligned} \tag{72}$$

$$\begin{aligned}B^{(Q;\mathrm{BM})}(Q) = {} & \left(-\frac{8\pi^3\gamma}{\varepsilon_{\mathrm{BM}}^3 Q^3 \varepsilon_{\mathrm{BM}}^3}\right) \\ & \times \left[-144 + 6Q^4\varepsilon_{\mathrm{BM}}^4 e^{-Q\varepsilon_{\mathrm{BM}}} + 144\varepsilon_{\mathrm{BM}} Q e^{-Q\varepsilon_{\mathrm{BM}}}\right. \\ & + 72\varepsilon_{\mathrm{BM}}^2 Q^2 e^{-Q\varepsilon_{\mathrm{BM}}} + 24\varepsilon_{\mathrm{BM}}^3 Q^3 e^{-Q\varepsilon_{\mathrm{BM}}} \\ & \left. + Q^5\varepsilon_{\mathrm{BM}}^5 e^{-Q\varepsilon_{\mathrm{BM}}} + 144e^{-Q\varepsilon_{\mathrm{BM}}}\right]\end{aligned} \tag{73}$$

$$\begin{aligned}A^{(C;\mathrm{BM})}(Q) = {} & \left(-\frac{8\pi^3\gamma}{3\varepsilon_{\mathrm{BM}}^3 Q^3 \varepsilon_{\mathrm{BM}}^3}\right) \\ & \times \left[-48 - Q^3\varepsilon_{\mathrm{BM}}^3 + 24Q^2\varepsilon_{\mathrm{BM}}^2 e^{-Q\varepsilon_{\mathrm{BM}}} + 48Q\varepsilon_{\mathrm{BM}} e^{-Q\varepsilon_{\mathrm{BM}}}\right. \\ & \left. + 7Q^3\varepsilon_{\mathrm{BM}}^3 e^{-Q\varepsilon_{\mathrm{BM}}} + Q^4\varepsilon_{\mathrm{BM}}^4 e^{-Q\varepsilon_{\mathrm{BM}}} + 48e^{-Q\varepsilon_{\mathrm{BM}}}\right]\end{aligned} \tag{74}$$

$$\begin{aligned}B^{(C;\mathrm{BM})}(Q) = {} & \left(\frac{8\pi^3\gamma}{\varepsilon_{\mathrm{BM}}^3 Q^3 \varepsilon_{\mathrm{BM}}^3}\right)\left[-144 + 6Q^4\varepsilon_{\mathrm{BM}}^4 e^{-Q\varepsilon_{\mathrm{BM}}}\right. \\ & + 144\varepsilon_{\mathrm{BM}} Q e^{-Q\varepsilon_{\mathrm{BM}}} + 72\varepsilon_{\mathrm{BM}}^2 Q^2 e^{-Q\varepsilon_{\mathrm{BM}}} + 24\varepsilon_{\mathrm{BM}}^3 Q^3 e^{-Q\varepsilon_{\mathrm{BM}}} \\ & \left. + Q^5\varepsilon_{\mathrm{BM}}^5 e^{-Q\varepsilon_{\mathrm{BM}}} + 144e^{-Q\varepsilon_{\mathrm{BM}}}\right]\end{aligned} \tag{75}$$

$$\xi^{(C;\mathrm{BM})}(0) = \frac{16\pi^3\gamma}{3\varepsilon_{\mathrm{Y}}^3} \tag{76}$$

They are shown, again as functions of the characteristic length, $\sigma = 1/\varepsilon$, in Figure 2 for the internal parameters of the friction tensor and in Figure 3 for the center-of-mass friction tensor parameters. From Figure 2 and 3, we see that – although similar in their qualitative behaviour – these parameters have a quite different quantitative behaviour, when compared to the parameters for the Yukawa potential. While, for example, the two beads do virtually not ‘‘feel’’ each other anymore at a distance of about 8 σ in the case of a Yukawa potential, they still interact and are affected at this and even larger distances with a Born-Mayer potential. Concerning the diffusion parameters, $D^{(A;\mathrm{BM})}$ and $D^{(B;\mathrm{BM})}$, the deviations from the phenomenological theory are even more pronounced in this case as seen from Figure 4.

Like for the Yukawa potential, we may calculate the long-term behaviour of the internal momentum correlation function, $C^{(Q;\mathrm{BM})}(t)$. By expanding the friction tensor parameters [Equation (72) and (73)] and truncating their Taylor expansions after the first non-vanishing term, the asymptotics of the friction tensor parameters become:

$$\begin{aligned}A^{(Q;\mathrm{BM})} &= \mu_{\mathrm{BM}} Q^2 + O(Q^3), \\ B^{(Q;\mathrm{BM})} &= \nu_{\mathrm{BM}} Q^2 + O(Q^3)\end{aligned} \tag{77}$$

leading to a long-term behaviour of the relative momentum CF like [cf. Appendix A for details of the derivation]:

$$\begin{aligned}C^{(Q;\mathrm{BM})}(t \to \infty) \approx {} & \frac{\sqrt{\pi}}{24} f_{eq}(0) \\ & \times \left[2\mu_{\mathrm{BM}}^{-3/2} + (\mu_{\mathrm{BM}} + \nu_{\mathrm{BM}})^{-3/2}\right] t^{-3/2}\end{aligned} \tag{78}$$

where $\mu_{\mathrm{BM}} = (1/2!)\partial^2 A^{(Q;\mathrm{BM})}/\partial Q^2$ and $\nu_{\mathrm{BM}} = (1/2!)\partial^2 B^{(Q;\mathrm{BM})}/\partial Q^2$, taken at $Q = 0$. As with the asymptotic behaviour [Equation (69)] for the Yukawa potential, the internal momentum CF, $C^{(Q;\mathrm{BM})}(t)$, decays algebraically for the Born-Mayer potential, i.e., with a so-called *algebraic tail*, but with a different decay rate. In practice, this rate increases when the bead-solvent potential becomes stronger for large distances among the beads. Again, such a result could not be derived from phenomenological theory, but has been found *numerically* in a number of molecular dynamics simulations.[26–28]

Lennard-Jones Potential

In the previous section, we got a (first) impression how the bead-solvent interaction, W, may influence the dynamics of macromolecules, if immersed in a solution. To obtain a deeper insight into the effects of the bead-solvent interaction, we shall now analyze the Lennard-Jones (LJ) potential which has, very frequently in the past, been applied to model the long-range van-der-Waals interactions between neutral particles (Figure 1). Using the characteristic interaction strength, ε, and the decay length, σ_{LJ}, for the parametrization, the Lennard-Jones potential is given by:

$$W^{\mathrm{LJ}}(r) = \varepsilon\left[\left(\frac{\sigma_{\mathrm{LJ}}}{r}\right)^{12} - \left(\frac{\sigma_{\mathrm{LJ}}}{r}\right)^{6}\right] \tag{79}$$

including a strong repulsive part $\sim \frac{1}{r^{12}}$ for short distances between the particles and a far-ranging attractive part $\sim \frac{1}{r^6}$.

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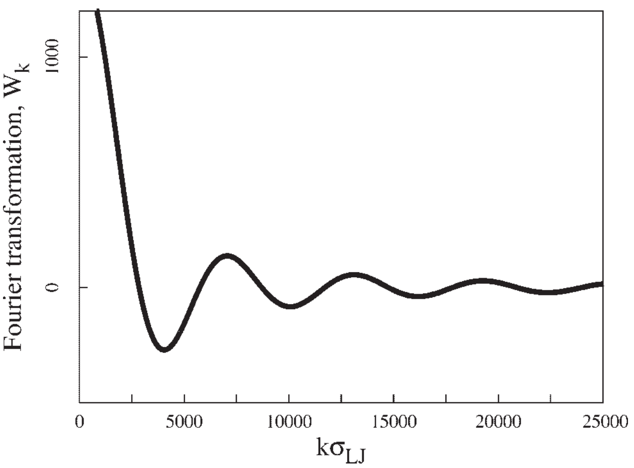

Figure 5. Fourier transform of the Lennard-Jones potential in Equation (79) as function of the modulus of *k*.

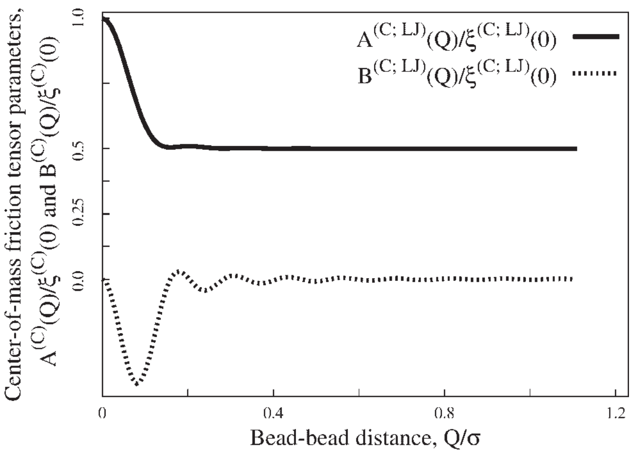

Figure 7. Center-of-mass friction tensor parameters, $A^{(C;\mathrm{LJ})}/\xi^{(C;\mathrm{LJ})}(0)$ and $B^{(C;\mathrm{LJ})}/\xi^{(C;\mathrm{LJ})}(0)$, for the internal coordinate and for the Lennard-Jones interaction potential as function of the bead-bead separation.

Due to computational problems, instead of the Lennard-Jones potential [Equation (79)] one often uses some potential which behaves similar to the LJ potential but which is more appropriate for the theoretical and numerical works (such as SHRAT potential or Gaussian like potential).[29–31] Figure 5 displays the Fourier transform of the Lennard-Jones potential, which was calculated numerically as function of the modulus of the wave vector, *k*. This function was then utilized to compute the friction tensor parameters for both, the center-of-mass [Equation (53)] and the relative coordinates [Equation (54)], respectively.

For the Lennard-Jones potential, the parameters of the friction tensor components, $A^{(..;\mathrm{LJ})}(Q)$ and $B^{(..;\mathrm{LJ})}(Q)$, are shown in Figure 6 and 7, respectively; they have been determined numerically along a 1-dimensional grid and are shown as a function of the separation, Q, of the two beads. When compared with the corresponding parameters for the Yukawa and Born-Mayer potential (cf. Figure 2 and 3), the shape of the friction tensor (parameters) is quite different. If we compare, for example, the parameter, $A^{(Q;\mathrm{LJ})}(Q)$, for the internal momentum friction tensor components in Figure 2 and 6, we can see that, for any given potential, these parameters increases from zero (single-particle case) up to 1/2 (the case of two free particles). However, the distance, at which the two beads can be considered free, is very different for a Yukawa, Born-Mayer and Lennard-Jones potential. From Figure 6, we see that the two beads of the dumbell "feel" each other only at very small distances, say, $Q \le \sigma_{\mathrm{LJ}}$, i.e., that the behaviour of the friction tensor parameters of the center-of-mass and internal coordinates are purely determined by the repulsive part of the Lennard-Jones potential. The far-ranging attractive part, in contrast, does not matter much, a fact which has been found *empirically* in molecular dynamics computations[9,10] before, where one often takes into account only the repulsive part of the Lennard-Jones (bead-solvent) potential.

Instead of the friction tensor of the internal coordinate, as mentioned before, the diffusion tensor, $\hat{D}^{(Q)}_{\alpha\alpha'}$, is often used in phenomenological theory. To analyze the influence of the bead-solvent interaction on the diffusion of macromolecules, Figure 8 displays the parameters of the diffusion tensor dependent on the bead-bead separation and compares them with the behaviour of the Oseen tensors from phenomenological theory. As seen from this figure again, the discrete nature of the solvent becomes important for a small separation of the two beads, say, for $Q \le 2\sigma_{\mathrm{LJ}}$, and leads to a clear reduction in the diffusion parameters, $D^{(A;\mathrm{LJ})}$ and $D^{(B;\mathrm{LJ})}$. Obviously, this discrete structure of the solvent has to be taken into account explicitly, if the statistical and dynamic properties of macromolecules in solution are to be

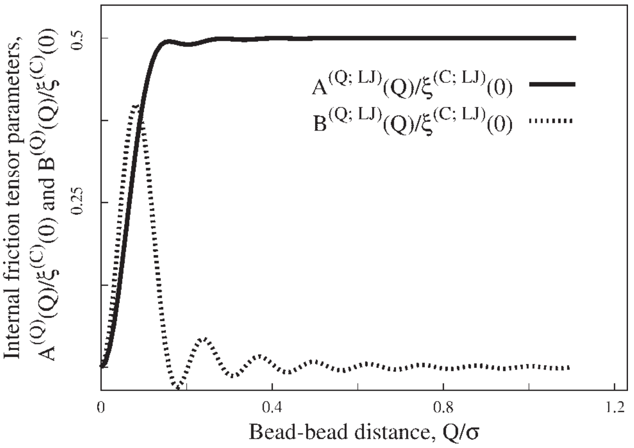

Figure 6. Friction tensor parameters, $A^{(Q;\mathrm{LJ})}/\xi^{(C;\mathrm{LJ})}(0)$ and $B^{(Q;\mathrm{LJ})}/\xi^{(C;\mathrm{LJ})}(0)$, for the internal coordinate and for the Lennard-Jones interaction potential as function of the bead-bead separation.

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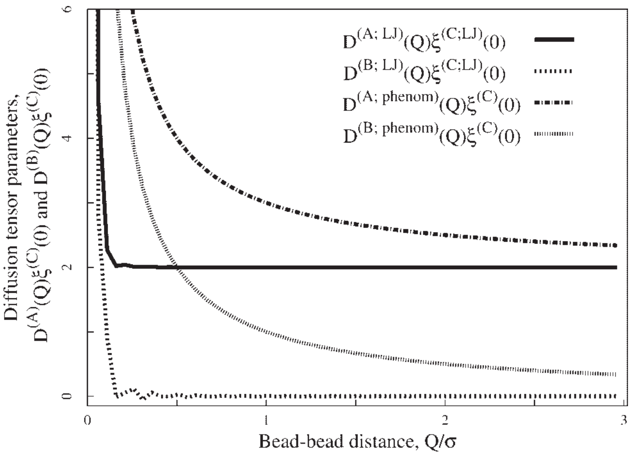

Figure 8. Normalized diffusion tensor parameters, $D^{(A)}/\xi^{(C)}(0)$ and $D^{(B)}/\xi^{(C)}(0)$, for the internal coordinate as function of the bead-bead separation. These parameters are shown for a Lennard-Jones interaction potential.

described properly. At large bead distances, however, the phenomenological theory provides a reasonable approach and can be used to model the relaxation and the diffusion of macromolecules.

Conclusion

The influence of the bead-solvent interaction on the dynamics of macromolecules, which are immersed in a solution, has been investigated by using Hamiltonian mechanics and master equations for the phase-space distribution functions. In such a model, the macromolecules are taken as a *chain of beads* which are coupled to each other by a force and which are surrounded by – a large number of – solvent particles. Starting from the Hamiltonian of the overall system "macromolecule + solvent," a Fokker-Planck equation (FPE) is then derived for the time evolution of the phase-space distribution function of the (*N*-bead) macromolecule. In this derivation, three realistic assumptions were made: (i) the interaction between the beads and the solvent particles is considered to be weak when compared to the bead-bead interaction, which keeps the macromolecule together; (ii) the relaxation of the solvent proceeds much faster in time than those of the beads; and (iii) the dynamics of the solvent is described properly in terms of a diffusion equation. The dynamics of the macromolecule is then determined purely by the "friction tensors" that appear on the right-hand side of the FPE and that can be expressed in terms of the bead-solvent interaction potential as well as the dynamic structure factor of the solvent.

To understand the effects of the bead-solvent interaction on the dynamic behaviour of macromolecules in detail, we have considered a few typical bead-solvent interaction potentials for a dumbbell molecule here; the generalization of this work to larger molecules will be considered in the future. Apart from a few general properties of the friction tensors, which are independent on the bead-solvent potential, the influence of the interaction has been studied for the three cases of a Yukawa, a Born-Mayer as well as a Lennard-Jones potential. For these cases, the behaviour of the friction tensors dependent on the bead-bead separation has been analyzed and compared with results from phenomenological theory. Analytic expressions for the friction tensor parameters are obtained, in particular, for a Yukawa and Born-Mayer potential, whereas they had to be determined numerically for a Lennard-Jones potential. Moreover, the asymptotic time behaviour ($t \to \infty$) of the internal momentum (auto-)correlation function is investigated and an *algebraic tail*, i.e., a non-exponential decay of the correlation between the two beads, is confirmed as known empirically from molecular dynamics simulations. For the Lennard-Jones potential, in addition, the internal and center-of-mass friction coefficients were computed numerically which show that only the repulsive part of the potential determines the behaviour of the friction tensor parameters.

From our analysis of the friction tensors, the discrete nature of the solvent can be seen clearly at small distances between the bead and solvent particles. Of course, this behaviour has to be compared with that from of the phenomenological theory, where the solvent is always treated as an incompressible and viscous fluid. The use of Fokker-Planck-(type) equations in the description of the dynamic behaviour of macromolecules may, therefore, help combine the various physical models which have been applied in the past for both, the solvent and the macromolecules. In addition, we are presently continuing this work to better understand the dynamics of *N*-bead chains or other macromolecular structures.

Appendix A: Asymptotic Behavior of the Relative Momentum Correlation Function

Using Equation (56) for the definition of the phase-space average, we may re-write the internal momentum correlation function [Equation (57)] of the dumbbell macromolecule in the integral form:

$$C^{(Q)}(t) = \frac{1}{6}h^{-1}\int d\Gamma\Big\{e^{(-A^{(Q)}(Q)t)}\ \Big(2\ +\ e^{(-B^{(Q)}(Q)t)}\Big)\Big\}e^{-\beta H_d} \tag{A1}$$

where $h = \int d\Gamma f_{eq}(\Gamma;t)$ denotes the normalization integral of the (equilibrium) distribution function, and H_d is the Hamiltonian of the dumbbell:

$$H_d = \frac{\mathbf{P}_C^2}{2M} + \frac{\mathbf{P}_Q^2}{2M} + U(|\mathbf{Q}|) \tag{A2}$$

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given in terms of the relative coordinates, $\Gamma = \{\mathbf{R}_C, \mathbf{Q}, \mathbf{P}_C, \mathbf{P}_Q\}$. We can evaluate the integral in Equation (A1), since the two friction tensor parameters, $A^{(Q)}(Q)$ and $B^{(Q)}(Q)$ [cf. Equation (54) and (53)] do not depend on either the center-of-mass coordinate $\mathbf{R}_C$, or the momenta, $\mathbf{P}_C$ and $\mathbf{R}_Q$, or the orientation of the relative coordinate, $\mathbf{Q} = \mathbf{R}_1 - \mathbf{R}_2$. In fact, these two parameters are simply functions of the bead-bead separation. Therefore, by carrying out the integration over the center-of-mass and the two momentum coordinates of the dumbbell, we first obtain:

$$C^{(Q)}(t) = \frac{1}{6}\left[\int d\mathbf{Q} e^{-\beta U(Q)}\right]^{-1} \times \int d\mathbf{Q}\left\{e^{(-A^{(Q)}(Q)t)}\left(2 + e^{(-B^{(Q)}(Q)t)}\right)\right\}e^{-\beta U(Q)} \tag{A3}$$

and, finally,

$$C^{(Q)}(t) = \frac{1}{6}h_Q^{-1}\int_0^\infty dQ\left\{e^{(-A^{(Q)}(Q)\,t)}\left(2 + e^{(-B^{(Q)}(Q)\,t)}\right)\right\}Q^2\rho_{eq}(Q) \tag{A4}$$

if we introduce polar coordinates, $\mathbf{Q} = (Q, \vartheta_\mathbf{Q}, \varphi_\mathbf{Q})$, and if the integral is taken over the polar angles (i.e., $\int \ldots \sin \vartheta_\mathbf{Q} d\vartheta_\mathbf{Q} d\varphi_\mathbf{Q}$). In this expression for the internal momentum CF, $\rho_{eq}(Q) = e^{-\beta U(Q)}$ and $h_Q = \int_0^\infty dQ Q^2 \rho_{eq}(Q)$ denotes the normalization integral. As mentioned before, the asymptotic behaviour of this CF for $t \to \infty$ is determined by the first (non-vanishing) term in the Taylor expansion of the friction tensor [Equation (54)]. We can perform this Taylor expansion, for instance in the case of a Yukawa interaction potential, for the friction tensor parameters [Equation (62) and (63)], respectively; if we truncate the expansion after the first non-vanishing term and denote the constant coefficient of the expansion by $\mu_\mathrm{Y} = \partial A^{(Q;\mathrm{Y})}/\partial Q\big|_{Q=0}$ and $\nu_\mathrm{Y} = \partial B^{(Q;\mathrm{Y})}/\partial Q\big|_{Q=0}$, the friction tensor parameters become:

$$\begin{aligned} A^{(Q;\mathrm{Y})}(Q) &= \mu_Y Q + O(Q^2), \\ B^{(Q;\mathrm{Y})}(Q) &= \nu_Y Q + O(Q^2) \end{aligned} \tag{A5}$$

For longer times and a Yukawa-type bead-solvent potential, therefore, the relative momentum correlation function (A4) takes the form:

$$C^{(Q;\mathrm{Y})}(t \to \infty) \approx \frac{1}{6}h_Q^{-1} \times \int_0^\infty dQ\left\{e^{(-\mu_\mathrm{Y}Qt)}\left(2 + e^{(-\nu_\mathrm{Y}Qt)}\right)\right\}Q^2\rho_{eq}(Q) \tag{A6}$$

We still can simplify this expression by integrating it by parts:

$$\begin{aligned} C^{(Q;\mathrm{Y})}(t \to \infty) &\approx \frac{1}{6}h_Q^{-1} \times \int_0^\infty dQ\left\{e^{(-\mu_\mathrm{Y}Q\,t)}\left(2 + e^{(-\nu_\mathrm{Y}Q\,t)}\right)\right\}Q^2\rho_{eq}(Q) \\ &= \frac{1}{6}h_Q^{-1}\int_0^\infty Q^2\rho_{eq}(Q)\frac{d}{dQ}\{\ldots\}dQ \\ &= \frac{1}{6}h_Q^{-1}\left[Q^2\rho_{eq}(Q)\{\ldots\}\right]_0^\infty + \frac{1}{6}h_Q^{-1}\int_0^\infty\{\ldots\}d(Q^2\rho_{eq}(Q)) \end{aligned} \tag{A7}$$

where $\{\ldots\} = \{e^{(-\mu_\mathrm{Y}Qt)}(-\frac{2}{\mu_\mathrm{Y}t} - \frac{1}{(\mu_\mathrm{Y}+\nu_\mathrm{Y})t}e^{(-\nu_\mathrm{Y}Q\,t)})\}$ is used as a short-hand notation in the second and third line above. The internal momentum CF now consists of two terms, from which the first term $[Q^2\rho_{eq}(Q)\{\ldots\}]_0^\infty = 0$ vanishes identically. The second term is

$$C^{(Q;\mathrm{Y})}(t \to \infty) \approx \frac{1}{6}h_Q^{-1} \times \int_0^\infty\left\{e^{(-\mu_\mathrm{Y}Qt)}\left(-\frac{2}{\mu_\mathrm{Y}t} - \frac{1}{(\mu_\mathrm{Y}+\nu_\mathrm{Y})t}e^{(-\nu_\mathrm{Y}Qt)}\right)\right\}d(Q^2\rho_{eq}(Q)) \tag{A8}$$

and can be simplified further by means of a second integration by parts to the final form:

$$C^{(Q;\mathrm{Y})}(t \to \infty) \approx \frac{1}{3}h_Q^{-1}\rho_{eq}(0)\left[2\mu_\mathrm{Y}^{-3} + (\mu_\mathrm{Y} + \nu_\mathrm{Y})^{-3}\right]t^{-3} \tag{A9}$$

of the asymptotic behaviour of the internal momentum CF in the case of a Yukawa-type bead-solvent interaction potential. The same steps [Equation (A5)–(A9)] can be carried out for the Born-Mayer interaction potential and finally yields:

$$C^{(Q;\mathrm{BM})}(t \to \infty) \approx \frac{\sqrt{\pi}}{24}f_{eq}(0) \times \left[2\mu_\mathrm{BM}^{-3/2} + (\mu_\mathrm{BM} + \nu_\mathrm{BM})^{-3/2}\right]t^{-3/2} \tag{A10}$$

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PAPER II

Effects of the bead–bead potential on the restricted rotational diffusion of nonrigid macromolecules

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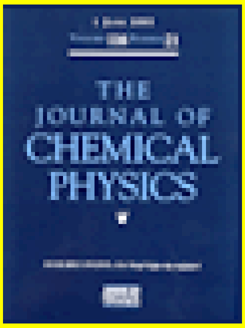

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Effects of the bead-bead potential on the restricted rotational diffusion of nonrigid macromolecules

Alexander Uvarov[a] and Stephan Fritzsche
Fachbereich Physik, Universitat Kassel, Heinrich-Plett-Strasse 40, D-34132 Kassel, Germany

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The influence of the bead-bead interaction on the rotational dynamics of macromolecules which are immersed into a solution has been investigated by starting from the microscopic theory of the macromolecular motion, i.e., from a Fokker-Planck equation for the phase-space distribution function. From this equation, we then derived an explicit expression for the configuration-space distribution function of a *non*rigid molecule which is immobilized on a surface. This function contains all the information about the interaction among the beads as well as the effects from the surrounding solvent particles and from the surface. For the restricted rotational motion, the dynamics of the macromolecules can now be characterized in terms of a rotational diffusion coefficient as well as a radial distribution functions. Detailed computations for the rotational diffusion coefficient and the distribution functions have been carried out for HOOKEAN, finitely extensible nonlinear elastic, and a DNA type bead-bead interaction. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1787831]

I. INTRODUCTION

Understanding the dynamical behavior of macromolecules, i.e., translational and rotational motion of macromolecules, or formation and deformation of their shape, remains a central problem for the study of proteins and DNA in solution. During the last years, therefore, a large number of experiments and molecular dynamic simulations have been carried out in order to describe the statical and the dynamical properties of macromolecules.[1–18] For instance, the dynamic light scattering experiments have been carried out in order to describe the translational motion of the macromolecule, which determines the motion of the macromolecule as whole.[1–3] In order to describe the formation and deformation of the macromolecular shape, i.e., internal configurational changes of macromolecules, the dielectric relaxation as well as fluorescence depolarization techniques have been successfully used.[4–11]

To understand the properties of the macromolecules by means of theoretical methods, they are often treated in terms of a several number of molecular subsystems which are usually referred to as the *beads* of the macromolecule. When immersed into a solvent, of course the shape and the dynamical behavior of the macromolecules will be determined not only by the interaction of the beads with the surrounding solvent but also by the interaction among their (neighboring) beads. Various models have been developed in the past for studying the translational motion of macromolecules in solution.[19–23] Apart from the translational motion of the molecules, their rotational properties have been studied by various authors, including the work of Wang and Pecora[24] on the restricted rotational diffusion of rigid rodlike molecule. This was later extended by Kumar and co-workers as well as by Fujiwara and Nagayama, who explored the restricted rotational diffusion of symmetric top molecules[25,26] as well as of flexible molecules which were modeled as a set of the beads connected by the rigid rods.[27] Moreover, the rotational behavior of the spherical and rigid-rod molecules in strong electric fields was investigated by Koenderink *et al.*[28] and Kalmykov and Déjardin,[29,30] respectively. In addition, the (restricted) rotational diffusion was investigated also by using Brownian dynamics simulation techniques.[31] For instance, de la Torre and co-workers as well as Peters and Ying considered the rotational properties of dimer-type and trimer-type macromolecules.[32–36] In all these investigations, however, the macromolecules were considered so far as rigid particles without any ''internal'' motion, that is without any changes in the distances between neighbored beads.

In the present paper, we pay attention to the *internal* dynamics of macromolecules which are immersed in a solution. For this part of the overall dynamics, we analyze the effects of the bead-bead interaction potential as well as the interaction with the particles from solvent. In particular, we will consider the (restricted) rotational motion of *nonrigid* macromolecules and derive an expression for the *rotational diffusion coefficient* of the macromolecules. Apart from the properties of the solvent and its interaction with the molecules, of course, this coefficient is affected also by the bead-bead interaction potential. Detailed computations for the rotational diffusion coefficient are carried out for a HOOKEAN,[19,20] a finitely extensible nonlinear elastic (FENE) (Refs. 17, 18, and 21) as well as a (so-called) DNA-type potential[37–39] among the beads. All of these potentials have their roots originally in physical chemistry where they have been utilized in molecular dynamic simulations in order to describe the chemical bonds in various types of (chemical) environments. Results from our theory are then compared with other computations from Doi-Edwards theory[19–21,32,40]

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[a] Electronic mail: uvarov@physik.uni-kassel.de

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which are based, however, on a *rigid-rod model* of the macromolecules.

The paper is organized as follows: In the following section, we will start from the most basic equation, the Fokker-Planck equation for the time evolution of the phase-space distribution function, in order to deal with a *N*-bead macromolecule which is immersed in a solution. Since this equation contains the full dynamical information about the macromolecule, it could be used immediately—at least in principle—for describing the molecular motion in the solvent. By assuming, however, that the mass of the macromolecule is (much) larger than the mass of the solvent particles, it is more convenient to *reduce* this Fokker-Planck equation to a (noninertial) diffusion equation (DE) which, in turn, describes the time evolution of the *coordinate-space* distribution function of the *N*-bead macromolecule. For this diffusion equations, a remarkable feature is that the generalized diffusion tensor, which accounts for the effects of the solvent on the dynamical behavior of the macromolecule, now depends explicitly on its end-to-end vector. In Sec. II B, therefore, we make use of the diffusion equation to analyze first the internal dynamics of just a two-bead *dumbbell* molecule in some detail. For such a dumbbell, an expression for the diffusion tensor is then obtained in terms of the (self-) diffusion tensors of the two beads as well as the tensor which arises from their hydrodynamic interaction. In this subsections, in addition, we also discuss a few further properties of a dumbbell such as its anisotropic diffusion in the case of nonspherical beads, or the proper choice of a single anisotropy parameter for describing the mobility of the macromolecule in the solution. In Sec. III, later, we will investigate the rotational motion of a dumbbell molecule which is immobilized on a surface. A general expression for the configuration-space distribution function of the macromolecule is derived and discussed, which can be calculated for any given bead-solvent and/or bead-surface potential, respectively. However, in order to obtain some deeper insight in how the interaction among the beads will influence the rotational motion of the macromolecule, a particular choice has to be made for the bead-bead potential. Therefore, detailed computations for the rotational diffusion coefficient of the macromolecules have been carried out in Sec. III B for the linear HOOKEAN potential, the nonlinear FENE as well as for a DNA-like bead-bead potential and are compared with calculations from Doi-Edwards theory.[19–21,32,40] Finally, a few conclusions are given in Sec. IV.

II. BASIC MODEL EQUATIONS

A. General diffusion equation for a *N*-bead macromolecule

In the microscopic theory, the *dynamical* behavior of a *N*-bead macromolecule in solution is described most generally in terms of a Fokker-Planck equation (FPE) for the time evolution of its phase-space distribution function $\rho_N(\mathbf{\Gamma};\mathbf{t})$ (Refs. 19, 22, and 41)

$$\frac{\partial \rho_N(\mathbf{\Gamma};t)}{\partial t}=\hat{\mathbf{L}}\rho_N(\mathbf{\Gamma};t). \tag{1}$$

In this equation, the Fokker-Planck operator $\hat{\mathbf{L}}$ has the form

$$\hat{\mathbf{L}}=-\sum_{a=1}^{N}\frac{\mathbf{P}_a}{M}\frac{\partial}{\partial \mathbf{R}_a}+\sum_{a,b=1}^{N}\frac{\partial U(|\mathbf{R}_a-\mathbf{R}_b|)}{\partial \mathbf{R}_a}\frac{\partial}{\partial \mathbf{P}_a} +\sum_{a,b=1}^{N}\frac{\partial}{\partial \mathbf{P}_a}\hat{\xi}^{(ab)}\left(\frac{\partial}{\partial \mathbf{P}_b}+\frac{1}{k_BTM}\mathbf{P}_b\right), \tag{2}$$

if we assume an equal mass M and a pairwise interaction $U(|\mathbf{R}_a-\mathbf{R}_b|)$ for all the N beads of the molecule. Here, as usual, $\mathbf{R}_a$, $\mathbf{R}_b,\ldots$ and $\mathbf{P}_a$, $\mathbf{P}_b,\ldots$ $(a,b=1,\ldots,N)$ are taken to denote the positions or, respectively, the momenta of the individual beads, while $\mathbf{\Gamma}\equiv\{\mathbf{R}_1,\ldots,\mathbf{R}_N;\mathbf{P}_1,\ldots,\mathbf{P}_N\}$ will be used below as an abbreviation to describe the phase-space coordinates alltogether. For each pair (a,b) of beads, moreover, there is a friction tensor $\hat{\xi}^{(ab)}$ which characterizes the (thermodynamical averaged) interaction of these two beads with the surrounding particles from the solvent. In Eq. (2), moreover, k_B is the Boltzmann constant and T the temperature of the overall system ''macromolecule+solvent.''

The FPE (1) enables one to describe in fact all the dynamical properties of a *N*-bead molecule which is immersed in the solvent. In practise, however, it appears rather unfeasible to deal with the coordinates and the momenta of all the beads simultaneously. Since the molecular beads usually have a much larger mass and size than the particles from the solvent, we may use instead a very good approximation for the momentum distribution in order to simplify the FPE (1) to a diffusion equation which just depends on the coordinates of the beads. For most solutions, namely, we may assume that the relaxation to the equilibrium (values) happens much faster for the momenta of the molecular beads rather than for their positions and, hence, that the phase-space distribution function $\rho_N(\mathbf{\Gamma};\mathbf{t})$ can be factorized

$$\rho_N(\mathbf{\Gamma};t)=\varrho_N(\{\mathbf{R}_a\};t)\cdot p_{N;eq}(\{\mathbf{P}_a\}) \tag{3}$$

into a coordinate-space distribution $\varrho_N(\{\mathbf{R}_a\};t)$ and the momentum-space distribution function $p_{N;eq}(\{\mathbf{P}_a\})$, taken at the equilibrium. Owing to the factorization (3), moreover, both the distribution functions ϱ_N and $p_{N;eq}$ should be normalized independently to one as, for instance, by

$$\int d\{\mathbf{R}_a\}\varrho_N(\{\mathbf{R}_a\};t)=1. \tag{4}$$

With the Eqs. (1)–(3) in mind and by using the techniques of projection operators, now an equation of motion can be derived for the coordinate-space distribution function[22,42]

$$\frac{\partial \rho_N(\{\mathbf{R}_a\};t)}{\partial t} =\sum_{a,b=1}^{N}\frac{\partial}{\partial \mathbf{R}_a}\hat{\mathbf{D}}^{(ab)}\left(\frac{\partial}{\partial \mathbf{R}_b}-\frac{1}{k_BT}\frac{\partial U}{\partial \mathbf{R}_b}\right)\rho_N(\{\mathbf{R}_a\};t), \tag{5}$$

which is called the noninertial diffusion equation (DE) and where the configuration-dependent diffusion tensor of the macromolecule, $\hat{\mathbf{D}}^{(ab)}\equiv\hat{\mathbf{D}}^{(ab)}(\{\mathbf{R}_a\})$, is closely related to the friction tensor

$$\hat{\mathbf{D}}^{(ab)}\hat{\xi}^{(ab)}=k_BT\mathbf{I},$$

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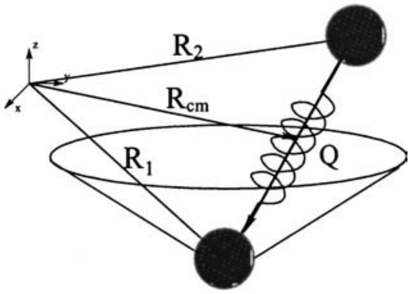

FIG. 1. Model of the nonrigid dumbbell molecule. For each bead of the macromolecule, the anisotropic diffusion tensor (14) can generally be described in terms of two parameters $D_\parallel$ for the diffusion along the end-to-end vector $\mathbf{Q}$ and $D_\perp$ for the diffusion in its perpendicular plane.

with $\mathbf{I}$ being the 3×3 unit tensor. In fact, a detailed knowledge of the configuration-space distribution function plays a *key* role in studying the various properties of macromolecules in solution. In particular, the coordinate-space distribution function can be used to analyze and/or to calculate the *translational* and *rotational* dynamics of macromolecules. In practice, of course, such computations may become rather tedious if either N represents a large number of interacting beads or, in particular, if the rotational motion of macromolecules is concerned. For all further considerations below, we therefore restrict ourselves to the much simpler two-bead dumbbell molecule which enables us to study the basic features of the rotational motion of macromolecules in more detail.

B. Rotational diffusion equation for the dumbbell-type molecule

Since, in the following, we are interested only in the dynamics of the dumbbell molecule, let us first separate from each other the center-of-mass (c.m.) and the internal (Q) motion (cf. Fig. 1). Instead of the Cartesian coordinates $\mathbf{R}_a$, $a=1$, 2 of the two beads, we then make better use of the center-of-mass and the relative coordinates,

$$\mathbf{R}_{c.m.}=\frac{\mathbf{R}_1+\mathbf{R}_2}{2}, \tag{6}$$

$$\mathbf{Q}=\mathbf{R}_2-\mathbf{R}_1, \tag{7}$$

where the latter one is known also as the *end-to-end vector* of the (dumbbell) molecule. If we assume, furthermore, that the internal dynamics of the macromolecule does not depend on its particular position within the solution, we may factorize (once more) the coordinate-space distribution function $\rho_2(\{\mathbf{R}_a\};t)$ of the dumbbell into

$$\rho_2(\{\mathbf{R}_a\};t)=\phi(\mathbf{R}_{c.m.};t)\,\psi(\mathbf{Q};t), \tag{8}$$

where $\phi(\mathbf{R}_{c.m.};t)$ denotes the distribution function of the center-of-mass coordinate and $\psi(\mathbf{Q};t)$ the distribution function for the internal motion, sometimes briefly referred to as (again) the configuration-space distribution function. In accordance with Eq. (4), these functions are taken to be normalized due to

$$\int d\mathbf{R}_{c.m.}\,\phi(\mathbf{R}_{c.m.};t)=1 \tag{9}$$

and

$$\int d\mathbf{Q}\,\psi(\mathbf{Q};t)=1, \tag{10}$$

respectively.

Owing to the separation (8) of the configuration-space distribution function $\rho_2(\{\mathbf{R}_a\};t)$, it can be shown that the distribution function $\psi(\mathbf{Q};t)$ obeys a diffusion equation similar to Eq. (5) above. Inserting Eq. (8) into this equation and by making use of the chain rule for a few times, we then find that the (internal) configuration-space distribution function, $\psi=\psi(\mathbf{Q};t)$, fulfills the equation

$$\frac{\partial\psi}{\partial t}=\frac{\partial}{\partial\mathbf{Q}}\hat{\mathbf{D}}^{(\mathbf{Q})}(\mathbf{Q})\left(\frac{\partial}{\partial\mathbf{Q}}-\frac{\mathbf{F}(\mathbf{Q})}{k_BT}\right)\psi, \tag{11}$$

which is called below the diffusion equation for the internal motion of the dumbbell. In Eq. (11), moreover, the vector $\mathbf{F}(\mathbf{Q})=-\partial U/\partial\mathbf{Q}$ denotes the force, which acts on the beads of the dumbbell, and $\hat{\mathbf{D}}^{(\mathbf{Q})}(\mathbf{Q})$ is the generalized diffusion tensor for the relative (internal) motion of the two beads. For a dumbbell molecule, this latter tensor can be written as

$$\hat{\mathbf{D}}^{(\mathbf{Q})}(\mathbf{Q})=\hat{\mathbf{D}}^{(11)}+\hat{\mathbf{D}}^{(22)}-\hat{\mathbf{D}}^{(12)}-\hat{\mathbf{D}}^{(21)}, \tag{12}$$

i.e., in terms of the diffusion tensors of the individual beads $\hat{\mathbf{D}}^{(aa)}$ $(a=1,2)$ and the tensors $\hat{\mathbf{D}}^{(ab)}$ $(a\neq b)$ which describe the hydrodynamic interaction among them.

The generalized diffusion tensor (12) contains all the information about the influence of the solvent on the *internal* motion of the dumbbell molecule. In the following, therefore, let us analyze this tensor in more detail and discuss how it can be parametrized in terms of just a single parameter.

1. Properties of the diffusion tensor for the internal motion of the dumbbell

As seen from Eq. (12), the generalized diffusion tensor for the internal motion of a dumbbell molecule depends first of all on the diffusion tensors of the individual beads which, in turn, may depend on their particular shape. For a spherical bead, for instance, the influence of the solvent should not depend on the direction in which it moves[19–21] and, therefore, the diffusion tensor is expected to be a function of just a single parameter,

$$\hat{\mathbf{D}}^{(aa)}=D\mathbf{I}, \tag{13}$$

which is called the *self-diffusion coefficient* of the bead. For a nonspherical bead, in contrast, such as a spheroid, rod, ellipsoid, or some other shape, its motion in the solvent will be quite different for different directions. In the most general case, the moments of inertia are different for all of the three principal axes of the macromolecule and, hence, three parameters might be needed to characterize the diffusion tensor for a nonspherical bead completely.[19,40] If the moments of inertia are equal for any two of the principal axes, we may use the parameters $D_\parallel$ and $D_\perp$ in order to describe the mobility of the bead along its symmetry axis or, respectively, along any other direction which is perpendicular to it. For such a (nonspherical) symmetry top, then, the *anisotropic* diffusion tensor becomes[42–47]

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$$\hat{\mathbf{D}}^{(aa)} = D_{\parallel}\mathbf{u}^{a}\otimes\mathbf{u}^{a} + D_{\perp}(\mathbf{I}-\mathbf{u}^{a}\otimes\mathbf{u}^{a}), \tag{14}$$

where $\mathbf{u}^a$ is the unit vector in parallel to the main symmetry axis of the bead. In addition, here we use the operation $\otimes$ to denote a tensor (dyadic) product which turns two vectors into a second-rank tensor. Since, for (almost) spherical beads, we may assume $D_{\parallel} \simeq D_{\perp} \equiv D$, we find—as expected—that the diffusion tensor of a spherical bead (13) appears just a particular case of the anisotropic diffusion tensor (14). Apart from the tensors of the two individual beads, however, the generalized diffusion tensor (12) of the internal motion of the dumbbell still depends on the hydrodynamic interaction as described by the diffusion tensors $\hat{\mathbf{D}}^{(ab)}$, $a \neq b$, $a,b = 1,2$. There are various explicit tensor expressions known from the literature which describe the hydrodynamic interaction of the beads.[22,31,48–52] All of them can be represented in the form,

$$\hat{\mathbf{D}}_{h}(\mathbf{Q}) = \hat{\mathbf{D}}^{(12)} + \hat{\mathbf{D}}^{(21)} = 2D_{h;1}(Q)\mathbf{I} + 2D_{h;2}(Q)\mathbf{q}\otimes\mathbf{q}, \tag{15}$$

where $D_{h;1}(Q)$ and $D_{h;2}(Q)$ are two functions which depend purely on the bead-bead distance Q. These functions contain all the information about the solvent in which the macromolecule is immersed (for instance, about its viscosity or the bead-solvent interaction potential). In the second term of Eq. (15), the vector $\mathbf{q} = \mathbf{Q}/|\mathbf{Q}|$ denotes the normalized end-to-end vector $\mathbf{Q}$ which points from bead 2 to bead 1. If, moreover, one of the principal axes of the two beads is parallel to $\mathbf{q}$, i.e., $\mathbf{u}^a \| \mathbf{q}\ (a = 1,2)$, then, the diffusion tensor (12) of the internal motion of the dumbbell becomes

$$\hat{\mathbf{D}}^{(\mathbf{Q})}(\mathbf{Q}) = D_{\parallel}^{(Q)}(Q)\mathbf{q}\otimes\mathbf{q} + D_{\perp}^{(Q)}(Q)(\mathbf{I}-\mathbf{q}\otimes\mathbf{q}), \tag{16}$$

where the function $D_{\parallel}^{(Q)}(Q)$ is introduced to describe the mobility of the dumbbell along the direction $\mathbf{q}$,

$$D_{\parallel}^{(Q)}(Q) = 2[D_{\parallel} - D_{h;1}(Q) - D_{h;2}(Q)]. \tag{17}$$

Similarly, in this case, the function $D_{\perp}^{(Q)}(Q)$ is used to characterize the mobility of the dumbbell along any direction perpendicular to $\mathbf{q}$,

$$D_{\perp}^{(Q)}(Q) = 2[D_{\perp} - D_{h;1}(Q)]. \tag{18}$$

As seen from Eqs. (16)–(18), the diffusion of a macromolecule has *always* an anisotropic nature, a well-known feature which was considered before in Refs. 42–47 by introducing an anisotropy parameter $\Lambda \leqslant 1$ which is generally a function of the distance Q of the two beads,

$$\Lambda^{(Q)}(Q) = \frac{D_{\parallel}^{(Q)}(Q)}{D_{\perp}^{(Q)}(Q)} \tag{19}$$

owing to the hydrodynamic interaction.

To deal with the hydrodynamic interaction in the case of two spherical-symmetric beads with radius σ and a self-diffusion coefficient D, two approximations are often used. In the first one, which was formulated originally by Oseen and later modified by Burger,[31,50,51] it is assumed that the radius σ of the beads is much smaller than their distance Q,

$$\mathbf{D}_{h}^{OB}(\mathbf{Q}) = \frac{3}{4}D\,\frac{2\sigma}{Q}\,\frac{Q^2}{Q^2+\sigma^2}\mathbf{I} + \frac{3}{4}D\,\frac{2\sigma}{Q}\,\frac{Q^2}{Q^2+\sigma^2}\mathbf{q}\otimes\mathbf{q}, \tag{20}$$

i.e., the Oseen tensor is valid only for $Q \gg \sigma$. A second and more general approximation for the hydrodynamic interaction (tensor) was given by Rotne and Prager[48] and by Yamakawa[49] for beads of equal size,

$$\mathbf{D}_{h}^{RPY}(\mathbf{Q}) = \frac{3}{4}D\,\frac{2\sigma}{Q} \times \begin{cases} \left[\left(1+\dfrac{2\sigma^2}{3Q^2}\right)\mathbf{I} + \left(1-\dfrac{2\sigma^2}{Q^2}\right)\mathbf{q}\otimes\mathbf{q}\right] & \text{if } Q \geqslant 2\sigma \\ \left[\dfrac{Q}{2\sigma}\left(\dfrac{8}{3}-\dfrac{3Q}{4\sigma}\right)\mathbf{I} + \dfrac{Q}{4\sigma}\mathbf{q}\otimes\mathbf{q}\right] & \text{if } Q < 2\sigma \end{cases} \tag{21}$$

and can be applied for any bead-bead distance Q. For a first comparison of these approximations, Fig. 2 displays the anisotropy parameter $\Lambda^{(Q)}(Q)$ as a function of the distance Q of the beads which, for the sake of simplicity, is taken in terms of their radius σ. As seen from this figure—and, in fact, if a hydrodynamic interaction is at all assumed for the dumbbell—the anisotropic parameter $\Lambda^{(Q)}(Q)$ is always positive and less than 1. We can interpret this behavior of $\Lambda^{(Q)}(Q)$ in the way that the dumbbell can rotate more easily than it would move along its axis $\mathbf{q}$, in particular, for rather small distances of the two beads. Only when the bead-bead distance becomes larger than, say, 8σ (i.e., in the case of the so-called extended macromolecule), we may neglect the hydrodynamic interaction among the beads. In this latter case, we have $\Lambda^{(Q)}(Q) = 1$, the same value as for an (equilibrium) *isotropic* Brownian motion of each spherical bead of the dumbbell.

Let us now return to the diffusion equation (11) for the internal motion of the dumbbell which describes the time evolution of the configuration-space distribution function $\psi(\mathbf{Q};t)$. This equation still depends—via the force $\mathbf{F}(\mathbf{Q})$—on the interaction potential $U_B(\mathbf{Q})$ among the beads as well as, if appropriate, on the interaction with some external field $U_{\text{ext}}(\mathbf{Q})$. We shall return later to the influence of these potentials on the motion of the dumbbell and shall discuss their properties in more detail. For the moment, we just mention that the full interaction $U = U_B(\mathbf{Q}) + U_{\text{ext}}(\mathbf{Q})$ depends on the end-to-end vector $\mathbf{Q}$, but does not depend explicitly on the time t or the momenta of the individual

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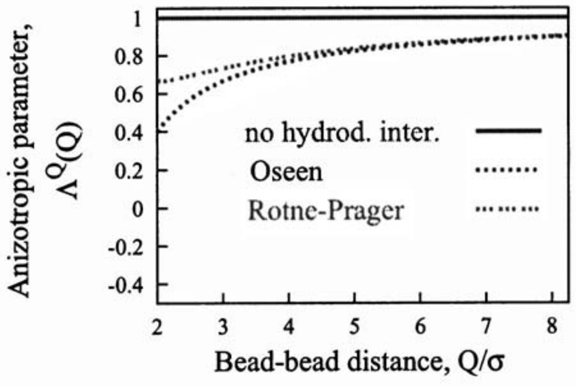

FIG. 2. Anisotropy parameter $\Lambda^{(Q)}$ [Eq. (19)] for a nonrigid dumbbell molecule as function of the (dimensionless) distance Q/σ of the two beads. This parameter is shown for three cases: (i) no hydrodynamic interaction among the beads, (ii) the Oseen hydrodynamic tensor [Eq. (20)], and (iii) the Rotne-Prager tensor [Eq. (21)].

beads. In the following subsection, we make use of Eq. (11) to describe the (restricted) *rotational* motion of the dumbbell which is immobilized on a surface. For such a molecule, the rotation of the "free end" does influence not only the dielectrical relaxation[17,18,29,30] of the molecule but may cause also a depolarization of the fluorescence light.[5–8,53,54]

2. General diffusion equation for a dumbbell molecule in polar coordinates

To describe the restricted *rotational* motion of a dumbbell macromolecule, it is convenient to use polar coordinates. In the following, therefore, we take the second bead (with index 2), which is sticked to the surface, as the origin O of the coordinates and use θ and φ to denote the azimuth and polar angles of the end-to-end vector $\mathbf{Q}$. Then, as usual, the differential operator $\partial/\partial\mathbf{Q}$ is given by[55]

$$\frac{\partial}{\partial\mathbf{Q}}=\mathbf{q}\frac{\partial}{\partial Q}+\mathbf{e}_{\theta}\frac{1}{Q}\frac{\partial}{\partial\theta}+\mathbf{e}_{\varphi}\frac{1}{Q\sin\theta}\frac{\partial}{\partial\varphi}, \tag{22}$$

where $\mathbf{q}\equiv\mathbf{e}_Q$ is (still) the unit vector along the internal coordinate $\mathbf{Q}$, while $\mathbf{e}_\theta$ and $\mathbf{e}_\varphi$ are the unit vectors of the corresponding angles. In order to rewrite the diffusion equation (11) in terms of the polar coordinates, moreover, we make use of two known properties of the dyadic product of the unit vector $\mathbf{q}$,[56] namely,

$$(\mathbf{q}\otimes\mathbf{q})\cdot\mathbf{q}=(\mathbf{q}\cdot\mathbf{q})\mathbf{q}=\mathbf{q}, \tag{23}$$

$$\frac{\partial}{\partial\mathbf{Q}}\cdot(\mathbf{q}\otimes\mathbf{q})=\frac{2}{Q}\mathbf{q}. \tag{24}$$

By using the expressions (22)–(24) and inserting the diffusion tensor (16) for the internal motion of the dumbbell, the diffusion equation (11) now becomes

$$\begin{aligned}\frac{\partial\psi}{\partial t}=&D_{\perp}^{(Q)}\left(\Delta\psi+\frac{1}{k_BT}\psi\Delta U+\frac{1}{k_BT}\nabla\psi\cdot\nabla U\right)\\&+(D_{\parallel}^{(Q)}-D_{\perp}^{(Q)})\left[\frac{\partial^2\psi}{\partial Q^2}+\frac{1}{k_BT}\frac{\partial^2 U}{\partial Q^2}\psi+\frac{1}{k_BT}\frac{\partial U}{\partial Q}\frac{\partial\psi}{\partial Q}\right]\\&+\left(\frac{\partial D_{\parallel}^{(Q)}}{\partial Q}+\frac{2(D_{\parallel}^{(Q)}-D_{\perp}^{(Q)})}{Q}\right)\left(\frac{\partial\psi}{\partial Q}+\frac{1}{k_BT}\frac{\partial U}{\partial Q}\psi\right),\end{aligned} \tag{25}$$

where Δ denotes the Laplacian in a coordinate-free notation.[55] This equation is the basic result of this section, and we will refer to it below as the internal diffusion equation for the (internal) motion of a dumbbell molecule which is immersed in a solvent. Like in the general case (11), the diffusion equation (25) describes the time evolution of the configuration-space distribution function of the dumbbell with an anisotropic diffusion tensor. While, however, Eq. (11) is described in terms of the end-to-end vector $\mathbf{Q}$ and the force $\mathbf{F}(\mathbf{Q})$ onto the dumbbell, the internal diffusion equation (25) only depends on the bead-bead distance Q but not on the polar angles θ and φ of the vector $\mathbf{Q}$. The use of polar coordinates, therefore, makes Eq. (25) much more convenient in order to describe the rotational motion of a *nonrigid* dumbbell molecule. In the following section, we will utilize the internal diffusion equation (25) to derive expressions for the configuration-space distribution (function) of the dumbbell as well as the rotational diffusion coefficient. In the past, this coefficient has played a key role in studying the rotational properties of macromolecules since it does determine not only their relaxation time to return back from a nonequilibrium into the equilibrium state[28–30,57] but also provides information about fluorescence anisotropy decay due to rotational diffusion of the macromolecule.[5–8,53,54]

III. INFLUENCE OF THE BEAD-BEAD POTENTIAL ON THE RESTRICTED MOTION OF NONRIGID MACROMOLECULES

During the last decades, the rotational motion of macromolecules has often been studied within a (so-called) *rigid-rod model*.[19,24–27,29,30,53,54,57–59] In this model, the macromolecule is taken usually as a set of spherical beads of mass M which are connected to each other by rigid rods of length L in order to form a chain. Various correlation functions have been calculated within this model to describe, for instance, the reorientation of macromolecules in solution. Since for rigid rods, however, the distance between any two neighbored beads is fixed from the very beginning, this model cannot be used (of course) to analyze the dynamical behavior of *nonrigid* macromolecule for which the distance between the beads may depend on time. To better understand the rotational motion of such macromolecules, therefore, we consider a nonrigid dumbbell molecule with spherical beads and with one of them (bead no. 2) attached to a surface. In fact, this is perhaps the simplest model for a nonrigid macromolecule which is immobilized on a surface. The two models of the nonrigid and the rigid-rod dumbbell molecule, both immobilized on some surface, are shown in Fig. 3. For the

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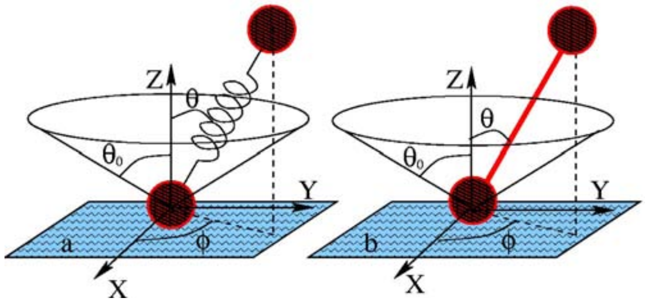

FIG. 3. Two models of the macromolecule immobilized on a surface: (a) the nonrigid dumbbell and (b) the rigid-rod model.

nonrigid dumbbell, obviously, the dynamical behavior will depend not only on the polar angle θ and azimuth angle φ (like in the rigid-rod model) but also on the variable distance Q among the beads. In the following, therefore, we first need to analyze the internal diffusion equation (25) for the *nonrigid* dumbbell molecule.

A. Configuration-space distribution function of the nonrigid macromolecule

As mentioned before, the isotropic diffusion tensor (13) is appropriate to describe an "extended dumbbell" for which the bead-bead separation is much larger than the radii of the beads. In this case, the internal diffusion equation (25) can be further simplified to

$$\begin{aligned}\frac{\partial\psi}{\partial t}&=D\Delta\psi+\frac{D}{k_BT}\boldsymbol{\nabla}\cdot(\psi\boldsymbol{\nabla}U)\\&=D\Delta\psi+\frac{D}{k_BT}\psi\Delta U+\frac{D}{k_BT}\boldsymbol{\nabla}\psi\cdot\boldsymbol{\nabla}U,\end{aligned}\tag{26}$$

where Δ denotes again the Laplacian and D is the self-diffusion coefficient of the "free" beads of the dumbbell. Since, of course, any solution to this equation will depend on the interaction $U(\mathbf{Q})=U(Q,\theta,\varphi)$ among the beads, we shall first consider the bead-bead potential in some more detail before we continue our discussion of ψ to which we will refer below as the configuration-space distribution function of the dumbbell molecule. Note that any potential $U=U(\mathbf{Q})$, which does not depend explicitly on time ($\partial U/\partial t=0$), gives rise to a stationary solution of the internal diffusion equation (26) or, in other words, $U(\mathbf{Q})$ determines the solution of Eq. (26) completely whenever $t\to\infty$. Moreover, such a stationary solution must correspond to an equilibrium configuration distribution function of the macromolecule $\psi_{\mathrm{eq}}(\mathbf{Q})$ and, therefore, must reflect its configuration properties at the equilibrium state,

$$\psi_{\mathrm{eq}}(\mathbf{Q})=e^{-U(\mathbf{Q})/(k_BT)}.\tag{27}$$

There is a further simplification possible if, instead of the equilibrium distribution function (27), we make use of the radial (equilibrium) configuration distribution of the macromolecule, $\Psi_{\mathrm{eq}}(Q)$. This radial distribution function only depends on the bead-bead distance Q and describes the equilibrium distance between the two beads of the dumbbell. In general, of course, the full interaction $U(\mathbf{Q})$ may contain both, the bead-bead potential $U_B(\mathbf{Q})$ as well as some external potential $U_{\mathrm{ext}}(\mathbf{Q})$ which, for a immobilized macromolecule on some surface (cf. Fig. 3) is given by the interaction of the "upper" bead of the dumbbell with the surface. Below, we use the symbol U_{BS} to denote this external *bead-surface* interaction. In this paper, the aim is to consider the rotational motion of a nonrigid macromolecule as function of the solid angle $\Omega=(\theta,\varphi)$ and if the polar angle is restricted by some upper bound, $\theta\leqslant\theta_0\leqslant\pi/2$. In the literature, such a restricted rotational motion is sometimes called also the diffusion-in-a-cone. To model this restricted rotation, we assume that (i) the bead-bead interaction only depends on the distance Q of the two beads—but not on the angles θ and φ—and that, for a sufficiently small angle θ_0, (ii) due to the symmetry of the system "dumbbell+surface" (cf. Fig. 3), the bead-surface interaction is supposed to be a function of only the polar angle θ, i.e., $U_{\mathrm{BS}}=U_{\mathrm{BS}}(\theta)$. With these two assumptions in mind, we may write the bead-surface potential for the diffusion-in-a-cone model as

$$U_{\mathrm{BS}}=\begin{cases}U_{\mathrm{BS}}(\theta) & \text{if}\quad \theta\leqslant\theta_0\\ \infty & \text{if}\quad \theta>\theta_0.\end{cases}\tag{28}$$

Using, moreover, the explicit form (43) of the bead-surface potential, we are able to rewrite the boundary conditions for the angles θ and φ of the molecular motions as

$$0\leqslant\theta\leqslant\theta_0,\quad 0\leqslant\varphi\leqslant 2\pi.\tag{29}$$

In addition, we assume some boundary condition also for the separation of the two beads

$$0\leqslant Q\leqslant Q_0,\tag{30}$$

where Q_0 is taken as the maximal distance beyond which the beads of the dumbbell cannot be stretched. In practice, of course, this maximum is finally determined always by the bead-bead interaction potential U_B itself. Since the configuration-space distribution function $\psi(Q,\theta,\varphi;t)$ is taken as a continuous functions, and especially when it comes close to the boundaries (29) and (30), it must satisfy for the polar angle θ the reflection (or von Neumann) condition,

$$\left.\frac{\partial\psi(Q,\theta,\varphi;t)}{\partial\theta}\right|_{\theta=\theta_0}=0\tag{31}$$

and for the azimuthal angle φ the periodic boundary condition,

$$\psi(Q,\theta,\varphi=0;t)=\psi(Q,\theta,\varphi=2\pi;t).\tag{32}$$

For the bead-bead distance Q, moreover, the distribution function $\psi(Q,\theta,\varphi;t)$ must satisfy the boundary condition,

$$\left.\frac{\partial\psi(Q,\theta,\varphi;t)}{\partial Q}\right|_{Q=Q_0}=0.\tag{33}$$

Using these three boundary conditions (31)–(33), we are able then to derive the internal diffusion equation (26) for the configuration distribution function $\psi=\psi(Q,\theta,\varphi;t)$ of a nonrigid dumbbell molecule. Inserting the Laplacian in polar coordinates,

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$$\Delta = \frac{1}{Q^2}\frac{\partial}{\partial Q}\left\{Q^2\frac{\partial}{\partial Q}\right\} + \frac{1}{Q^2 \sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta\frac{\partial}{\partial\theta}\right\} + \frac{1}{Q^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}, \tag{34}$$

into Eq. (26), this diffusion equation becomes

$$\frac{\partial\psi}{\partial t} = \hat{R}(Q)\psi + \hat{O}(\theta)\psi + \frac{D}{Q^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}, \tag{35}$$

where, if we make use of the new variable $\mu = \cos\theta$, polar diffusion operator takes the form,

$$\hat{O}(\mu) = \frac{d}{d\mu}\left[(1-\mu^2)\frac{d}{d\mu}\right] + \frac{d}{d\mu}\left[(1-\mu^2)\frac{dU_{\mathrm{BS}}(\mu)}{d\mu}\right] + \frac{1}{k_BT}\frac{dU_{\mathrm{BS}}(\mu)}{d\mu}\frac{d}{(d\mu)}, \tag{36}$$

while the radial diffusion operator $\hat{R}(Q)$ is given by

$$\hat{R}(Q) = D\frac{\partial}{\partial Q}\left(Q^2\frac{\partial\psi}{\partial Q}\right) + \frac{D}{k_BT}\psi\frac{\partial}{\partial Q}\left(Q^2\frac{\partial U_B}{\partial Q}\right)\frac{D}{k_BT}Q^2\frac{\partial\psi}{\partial Q}\frac{\partial U_B}{\partial Q}. \tag{37}$$

Solutions for the diffusion equation (35) can be obtained by a separation of the variables. If we simply try for the phase-space distribution function $\psi(Q,\theta,\varphi;t)$ the separation ansatz

$$\psi(Q,\theta,\varphi;t) = \Psi(Q)\Theta(\theta\Phi(\varphi)T(t), \tag{38}$$

and the internal diffusion equation (35) split into four ordinary differential equations, one for each of the variables

$$\frac{dT(t)}{dt} = -\lambda D T(t), \tag{39}$$

$$\frac{d^2\Phi(\varphi)}{d\varphi} = -m^2\Phi(\varphi), \tag{40}$$

$$\hat{O}(\mu)\Theta(\mu) + \left[\nu(\nu+1) + \frac{m^2}{1-\mu^2}\right]\Theta(\mu) = 0, \tag{41}$$

and

$$\frac{1}{D}\hat{R}(Q)\Psi(Q)[\lambda Q^2 - \nu(\nu+1)]\Psi(Q) = 0, \tag{42}$$

where the operators $\hat{O}(\mu)$ and $\hat{R}(Q)$ are taken from Eqs. (36) and (37), respectively, and where m, ν, and λ are the corresponding separation constants. We shall return later to these constants and discuss their properties in more detail. For the moment, we just mention that these constants are closely related to the boundary conditions (31)–(33) which restrict the internal motion of the dumbbell. The four Eqs. (39)–(42) above fully describe the behavior of the configuration-space distribution function $\psi(Q,\theta,\varphi;t)$ of the dumbbell molecule if immobilized on the surface. These equations, derived in this work, make it possible to obtain the configuration-space distribution function $\psi(Q,\theta,\varphi;t)$ of the dumbbell molecule in the presence of both, the bead-bead U_B and bead-solvent U_{BS} interaction. While the first Eq. (39) determines the (trivial) time evolution of the distribution function $\psi(Q,\theta,\varphi;t)$, the second and third one (40)–(44) are the two "angular equations" which only depend on the *orientation* of the molecule, i.e., the direction of the end-to-end vector $\mathbf{Q}$. In addition to these angular equations, we have to consider also the *radial* Eq. (42) which describe the behavior of the configuration-space distribution function $\psi(Q,\theta,\varphi;t)$ as function of the distance of the two beads.

Having obtained the Eqs. (39)–(42) for a dumbbell molecule, we see that the *orientational* dynamics of such molecules is entirely determined by the bead-solvent interaction potential $U_{\mathrm{BS}}(\theta)$. To obtain further insight into the behavior of the molecules, let us now consider the particular case for the bead-solvent interaction potential as given by

$$U_{\mathrm{BS}} = \begin{cases} 0 & \text{if } \theta \leqslant \theta_0 \\ \infty & \text{if } \theta > \theta_0. \end{cases} \tag{43}$$

In the literature, such a interaction potential is sometimes called also the "pure" cone potential. From a physical viewpoint, of course, this potential can be used only by assuming that the bead-surface interaction is negligible when compared with the bead-bead interaction, $|U_B| \gg |U_{\mathrm{BS}}|$ and, therefore, the total interaction potential $U \approx U_B(Q)$ is just determined by the bead-bead interaction for all the polar angles $\theta \leqslant \theta_0$ under consideration. With this assumption in mind and by using the cone bead-solvent potential (43), the orientational equation (41) can be simplified considerably and now becomes

$$\frac{d}{d\mu}\left[(1-\mu^2)\frac{d\Theta(\mu)}{d\mu}\right] + \left[\nu(\nu+1) + \frac{m^2}{1-\mu^2}\right]\Theta(\mu) = 0. \tag{44}$$

The configuration-space distribution function $\psi(Q,\theta,\varphi;t)$ of the molecule, as mentioned before [cf. Eq. (38)], can be obtained from the solution of the (set of) the Eqs. (39), (40), (42), and (44). Here, we need not to go into further details concerning the solution of the Eqs. (39), (40), (42), and (44) from above. Instead, we may display the general solution of the configuration-space distribution,

$$\psi(Q,\theta,\varphi;t) = \sum_{n=1}^{\infty}\sum_{m=-\infty}^{\infty} e^{-\lambda_n^m Dt}(A_n^m\cos m\varphi + B_n^m\sin m\varphi) \times P_{\nu_n^m}^m(\mu)\Psi_{\lambda_n^m,\nu_n^m}(Q), \tag{45}$$

in terms of the radial distribution functions $\Psi_{\lambda_m^n,\nu_n^m}(Q)$ which must obey Eq. (42) for any given set of separation constants λ and ν. The functions $P_{\nu_n^m}^m(\mu)$ in Eq. (45) are called the associated Legendre function of degree ν_n^m and order m and are well known as solutions of the angular equation (44).

As said before, the separation constants must be obtained from the three boundary conditions (31)–(33). Since the azimuthal angle φ is not restricted in the rotational motion of the dumbbell, the configuration-space distribution should have a period of 2π and, hence, the constant m must be an integer. In order to find also the values of ν_n^m, i.e., the

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TABLE I. Values of the separation constants ν_n^m, which obey the boundary condition $dP^m_{\nu_n^m}/d\mu|_{\mu=\mu_0}=0$, and given as a function of the maximal polar angle θ_0 of the cone.

$\nu_n^m \backslash \theta_0$	30°	50°	70°	90°
ν_1^0	0.00	0.00	0.00	0.00
ν_1^1	2.90	1.63	1.12	1.00
ν_1^2	5.60	3.37	2.30	2.00
ν_2^0	6.65	3.75	2.53	2.00
ν_2^1	9.45	5.41	3.65	3.00
ν_2^2	12.15	7.21	4.53	4.00
ν_3^0	12.32	7.19	5.10	4.00
ν_3^1	15.56	9.22	6.30	5.00
$\nu_3^2=\nu_4^0$ [a]	18.53	10.49	7.60	6.00
ν_4^1	21.60	12.71	9.03	7.00
$\nu_4^2=\nu_5^0$ [a]	24.62	14.73	10.28	8.00
ν_5^1	27.30	16.44	11.47	9.00

[a] In this table, the following properties apply: $\nu_n^m=\nu_{n-1}^{m+2}$ for $n\geqslant 4$, for any m and θ_0; cf. Ref. 24 for more details.

sequence of ν's which satisfy the boundary conditions for a given value of m, we may utilize the condition (31) for the polar angle in terms of the variable $\mu_0=\cos\theta_0$,

$$\left.\frac{\partial P^m_{\nu_n^m}(\mu)}{\partial\mu}\right|_{\mu=\mu_0=0} \tag{46}$$

and by using the ordering $\nu_1^m<\nu_2^m<\nu_3^m\cdots$. Equation (46) determines the number and the values of the separation constants ν completely for any given m. Note that, in contrast to a free (i.e., nonrestricted) diffusion of the dumbbell, these constants are in general no longer integers and that, for any fixed m and n, they are functions of the angle θ_0. Such type equations [such as Eq. (46)] are often obtained in the topic of the restriction rotational diffusion [cf. Eq. (6) in Ref. 24 or Eq. (38) in Ref. 25]. The general difference between Eq. (46) and mentioned above equations is that Eq. (46) is just only the particular case of the choice of both the boundary condition (31) as well as the bead-surface interaction potential (43). Unfortunately, however, the roots of the Eq. (46) cannot be obtained analytically but have to be determined numerically. In Table I, therefore, we display these roots ν_n^m ($m=0$, 1, and 2) for a few values of n and for several maximal angles θ_0 which may restrict the rotational diffusion of the molecules. These roots are numerically derived by following the method of the solution of such type equations which is described in Ref. 24 in detail. As seen from Table I, the value of the roots ν_n^m increases when the maximal angle θ_0 decreases, i.e., when the *cone* for the rotational motion of the molecule becomes smaller. A more detailed discussion about these roots and the properties of the associated Legendre function with a noninteger degree can be found in Refs. 24–27. From this discussion, here we only summarize those properties as needed in the following calculations. As known from the hydrogen atom, for instance, the roots ν_n^m are symmetric with respect to a sign change of the order m,

$$\nu_n^m=\nu_n^{-m}. \tag{47}$$

In addition, the associated Legendre function obey the symmetry,

$$P^m_{\nu_n^m}(\mu)=P^m_{-\nu_n^m-1}(\mu), \tag{48}$$

even if ν_n^m has a noninteger value. In the general form (45) of the configuration-space distribution $\psi(Q,\theta,\varphi;t)$, moreover, there arise the coefficients A_n^m and B_n^m which have to be derived from the initial condition $\psi(\mathbf{Q};0)=\delta[\mathbf{Q}-\mathbf{Q}(0)]$ as well as normalization condition (10) and which are given by[24]

$$A_n^m=\frac{\cos m\varphi(0)}{\pi H_n^m\epsilon}P^m_{\nu_n^m}[\mu(0)] \tag{49}$$

and

$$B_n^m=\frac{\sin m\varphi(0)}{\pi H_n^m}P^m_{\nu_n^m}[\mu(0)], \tag{50}$$

where $\mu(0)=\cos\theta(0)$ and $\varphi(0)$ is the polar and azimuthal angle at the initial time $t_{\text{in}}=0$, respectively, and

$$\epsilon=\begin{cases}2 & \text{if } m=0\\ 1 & \text{otherwise.}\end{cases} \tag{51}$$

In Eqs. (49) and (50), furthermore, H_n^m denotes a normalization factor which follows from the known orthogonality properties of the associated Legendre functions[24,27]

$$\int_{\mu_0}^{1}d\mu P^m_{\nu^m_{n_1}}(\mu)P^m_{\nu^m_{n_2}}(\mu)=H^m_{n_1}\delta_{n_1n_2} \tag{52}$$

and with

$$\delta_{n_1n_2}=\begin{cases}1 & \text{if } n_1=n_2\\ 0 & \text{if } n_1\neq n_2,\end{cases} \tag{53}$$

being the usual Kronecker symbol. Instead of the associated Legendre functions $P^m_{\nu_n^m}(\mu)$, we could use also the generalized spherical harmonics $Y^m_{\nu_n^m}(\mathbf{\Omega})$ with the solid angle $\mathbf{\Omega}=\{\theta,\varphi\}$ and a noninteger degree ν_n^m in order to describe the restricted rotational diffusion of the macromolecules immersed in the solvent. These generalized harmonics are simply related to the associated Legendre functions $P^m_{\nu_n^m}(\mu)$ by[24,27]

$$Y^m_{\nu_n^m}(\mathbf{\Omega})=\sqrt{\frac{1}{2\pi H_n^m}}e^{im\varphi}P^m_{\nu_n^m}(\mu). \tag{54}$$

As discussed in Ref. 24, the degree ν_n^m of the associated Legendre functions has the form

$$\nu_n^m=2(n-1)+m \tag{55}$$

when θ may take the full range of the polar angle, i.e., $0\leqslant\theta\leqslant\theta_0=\pi/2$. Therefore, the generalized spherical harmonics (54) will always approach to the *standard* spherical harmonics where both, the degree and order are proper integers.[55] Using the generalized spherical harmonics (54), we can now rewrite the configuration-space distribution function (45) for the nonrigid macromolecule in the form,

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$$\psi(Q,\theta,\varphi;t)=\sum_{n=1}^{\infty}\sum_{m=-\infty}^{\infty} e^{-\lambda_n^m D t} Y^m_{\nu_n^m}[\Omega(0)] \times Y^m_{\nu_n^m}[\Omega(t)]\Psi_{\lambda_n^m,\nu_n^m}(Q). \tag{56}$$

Apart from the two separation constants m and ν_n^m, we have to determine of course also the constants λ_n^m before we may use the configuration-space distribution function (56) for analyzing the *time evolution* of the macromolecule. Similar as above for the constants m and the ν, the separation constants λ_n^m should be obtained from the corresponding boundary conditions (30) and (33) which restrict the distance between the two beads of the dumbbell. To find these constants, we first introduce the *radial* equilibrium distribution function $\Psi_{\mathrm{eq}}(Q)$ as the integral about the configuration-space equilibrium function of the macromolecule, $\psi_{\mathrm{eq}}(Q,\theta,\varphi)$, taken over the polar angles θ and φ,

$$\Psi_{\mathrm{eq}}(Q)=\int_0^{2\pi} d\varphi \int_0^{\theta_0} \sin\theta d\theta \psi_{\mathrm{eq}}(Q,\theta,\varphi). \tag{57}$$

Obviously, this radial function only depends on Q and just describes the distribution of the bead-bead distance within the equilibrium. Inserting the function (57) into the radial diffusion equation (35) and by carrying out the integration over Q, we find that this radial equilibrium function must, for any given bead-bead potential $U_B(Q)$, obey (i) the condition

$$\int_0^{Q_0} \hat{R}(Q)\Psi_{\mathrm{eq}}(Q)=0, \tag{58}$$

and that it (ii) fulfills the equation,

$$\lambda \int_0^{Q_0} dQ Q^2 \Psi_{\mathrm{eq}}(Q)=\nu(\nu+1)\int_0^{Q_0} dQ \Psi_{\mathrm{eq}}(Q). \tag{59}$$

Since, however,

$$\frac{\int_0^{Q_0} dQ \Psi_{\mathrm{eq}}(Q)}{\int_0^{Q_0} dQ Q^2 \Psi_{\mathrm{eq}}(Q)}=\left\langle \frac{1}{Q^2}\right\rangle_{\mathrm{eq}} \tag{60}$$

is just the average of the function $1/Q^2$ at the equilibrium, Eq. (59) simplifies to

$$\lambda=L^2\nu(\nu+1), \tag{61}$$

where $L=\sqrt{\langle 1/Q^2\rangle_{\mathrm{eq}}}$ is the inverse (parameter) of the equilibrium distance Q of the two beads. We may now combine the general form of the configuration-space distribution function (56) with the expression (61) for the constant λ to finally obtain the internal configuration-space distribution function $\psi(Q,\theta,\varphi;t)$ of the nonrigid dumbbell.

$$\psi(Q,\theta,\varphi;t)=\sum_{n=1}^{\infty}\sum_{m=-\infty}^{\infty} e^{-\nu_n^m(\nu_n^m+1)D_R t} Y^m_{\nu_n^m}[\Omega(0)] \times Y^m_{\nu_n^m}[\Omega(t)]\Psi_{\nu_n^m}(Q), \tag{62}$$

where

$$D_R=D\left\langle \frac{1}{Q^2}\right\rangle_{\mathrm{eq}} \tag{63}$$

is the diffusion coefficient for the *rotational* motion or, for short, the rotational diffusion coefficient of the dumbbell. The expression for the rotation coefficient of the nonrigid dumbbell is one of the important result of this section. As seen from the Eq. (63), the rotational coefficient contains—via the self-diffusion coefficient D of each bead and the bead-bead potential U_B—all the information about the influence of the solvent as well as influence of the bead-bead interaction on the rotational motion of the macromolecule. Therefore, a detailed knowledge about the rotational coefficient and the radial distribution function $\Psi_{\lambda_n^m,\nu_n^m}(Q)$ are the *keys* for studying the configurational and relaxation properties of the rotational motion of macromolecules in solution. In the following section, therefore, we will consider a few of these properties of the rotational diffusion coefficient and the radial distribution function in detail.

B. Bead-bead interaction potentials

Having derived the internal diffusion equation (35) for a dumbbell molecule, we see that the dynamics of such molecules is determined entirely by the interaction potential $U_B(Q)$ among the beads. To obtain further insight into the behavior of the molecules, let us now consider three particular cases for the bead-bead interaction. In all the following, however, we will restrict our considerations to a (two-bead) dumbbell molecule. A generalization of these results to more complex macromolecules $(N>2)$ and other chain structure is presently under work and will be presented elsewhere.

As mentioned before, most of the commonly applied bead-bead potentials have their origin in the field of physical chemistry where they were constructed in order to simulate the chemical bonds in different (chemical) environments. In the following, we will consider (i) a HOOKEAN potential[19,20]

$$U_B^H(Q)=\tfrac{1}{2}k_H Q^2, \tag{64}$$

(ii) a finitely extensible nonlinear elastic (FENE) potential[17,18,21]

$$U_B^{\mathrm{FENE}}(Q)=-\frac{1}{2}k_{\mathrm{FENE}}Q_0^2 \ln\left(1-\frac{Q^2}{Q_0^2}\right), \tag{65}$$

as well as (iii) a DNA-type bead-bead potential[37–39]

$$U_B^{\mathrm{DNA}}(Q)=k_{\mathrm{DNA}}\left(\frac{1}{4\left(1-\dfrac{Q}{Q_0}\right)}-\frac{1}{4}Q+\frac{Q^2}{2Q_0}-\frac{1}{4}\right). \tag{66}$$

In all these potentials, the constant $k\ldots$, which is known also as the "spring" constant, determines the strength of the interaction. In the FENE and DNA potentials, moreover, we use Q_0 as the maximal lengths beyond which the beads of the dumbbell cannot be stretched out. Figure 4 displays these given choices of the bead-bead interaction potential as functions of distance Q. While the HOOKEAN (H) potential has been found useful for treating small perturbations in the internal dynamics of the macromolecules from the equilibrium, the more realistic FENE and DNA potentials have been frequently applied in molecular dynamic (MD) simula-

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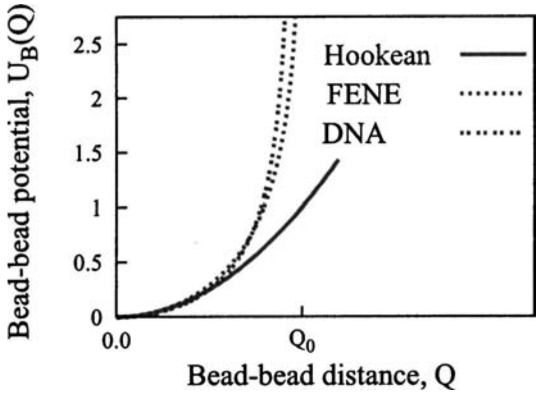

FIG. 4. Three choice of the bead-bead potential U_B as function of the bead-bead distance Q.

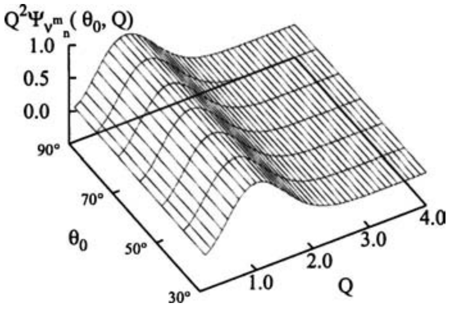

FIG. 6. Normolized radial distribution function $Q^2\Psi_{\nu_n^m}$ of the macromolecule with HOOKEAN bead-bead potential (64) for the ν_1^0 as function of the bead-bead distance Q and restricted angle θ_0.

tions[12–18,60,61] in order to calculate the dynamical properties of nonrigid macromolecules in a solvent. Let us note that the DNA bead-bead interaction potential (66) was first applied in Ref. 60 in the analysis of the measurements[61] which presents the ''extension'' of individual DNA molecules when some force is applied to the free end of the DNA.

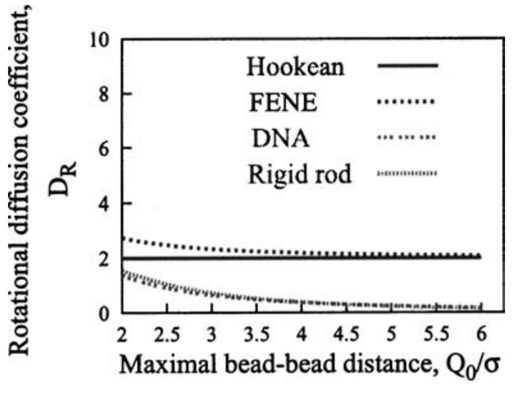

FIG. 5. Rotational diffusion coefficient D_R/D as a function of the maximal separation of the dumbbell molecule Q_0 for the HOOKEAN $Q_0=\infty$, FENE, and DNA bead-bead potential U_B, respectively.

Using the expression (63), we may compute the rotational diffusion coefficient D_R of the macromolecule for any of the bead-bead interaction potentials (64)–(66). This has been carried out in Fig. 5, for instance, where the (relative) rotational diffusion coefficient is shown as function of the bead-bead distance, given in terms of the dimensionless length Q_0/σ. As seen from this figure, a quite different behavior of the rotational diffusion coefficient arises for the different interaction potentials and, in particular, if the maximal distance of the beads is, say, $Q_0 \leqslant 6\sigma$. For a large maximal separation Q_0, in contrast, the diffusion coefficient approaches either to $D_R \approx 2D$ for the HOOKEAN and FENE potential, while it goes smoothly to zero for the DNA potential similarly as for a rigid-rod model of the macromolecule.[4] Apart from the rotational diffusion coefficient D_R of the dumbbell, we may also evaluate and compare the radial distribution function $\Psi_{\nu_n^m}(Q)$. To this end, we have to solve Eq. (42) for the different choices of the bead-bead interaction potential. As seen from Eqs. (37) and (42), the radial distribution functions does not only depend on the distance of the beads but, of course, parametrically also on the bead-bead potential U_B as well as the (maximal) polar angle θ_0 of the cone. For the HOOKEAN potential (64), the configuration-space distribution function can still be obtained in analytical form,

$$\Psi_{\nu_n^m}(Q) = Z_n^m \frac{e^{-(1/2)(k_H/k_BT)Q^2}}{Q^{3/2}} M(\gamma_{n;1}^m, \gamma_{n;2}^m, \gamma_{n;3}^m), \quad (67)$$

where $Z_n^m = \int dQ Q^2 \Psi_{\nu_n^m}(Q)$ denotes the proper normalization integral due to normalization condition (10) and $M(\mu,\nu,z)$ denotes the Whittaker function in the variable z and where the three arguments of this function are given by

$$\gamma_{n;1}^m = \left(\frac{3}{4k_BT} + \frac{1}{2}(\nu_n^m)^2 + \frac{1}{2}\nu_n^m \right) k_BT, \quad (68)$$

$$\gamma_{n;2}^m = \tfrac{1}{2}\nu_n^m + \tfrac{1}{2}, \quad (69)$$

and

$$\gamma_{n;3}^m = \frac{k_H}{k_BT} Q^2. \quad (70)$$

The Whittaker function $M(\cdots)$ can be expressed also in terms of the hypergeometric function $F(x_1, x_2, z)$ Ref. 56 by

$$M(\mu,\nu,z) = e^{-z/2} z^{1/2+\nu} F\left(\left[\frac{1}{2} + \nu - \mu \right], \left[1 + \frac{2}{\nu} \right], z \right), \quad (71)$$

which has been used in the computations below. For the HOOKEAN bead-bead potential, Figs. 6–8 show the behavior of the radial distribution function (67) for a few values of the separation constant ν_n^m. From these three figures, we

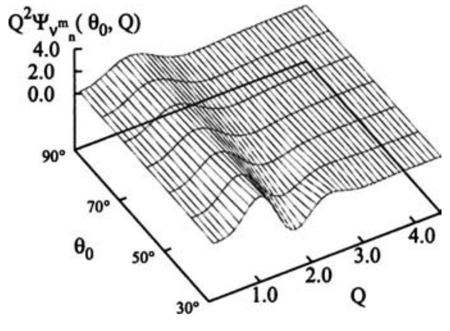

FIG. 7. The same as in Fig. 6 but only for ν_1^1.

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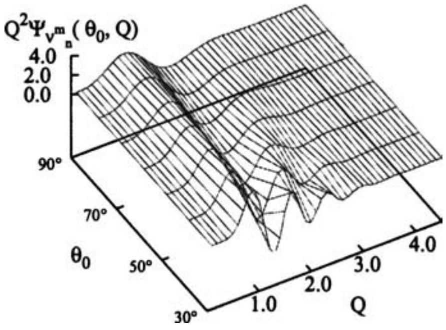

FIG. 8. The same as in Fig. 6 but only for ν_0^2.

may observe that—apart from the distribution function $\Psi_{\nu_1^0}$ in Fig. 6, which is just the equilibrium distribution function and, hence, is independent of the θ_0—the radial distribution functions $\Psi_{\nu_n^{m\neq 0}}$ are very sensitive to the value of the θ_0, i.e., to the angle of the cone. As seen from Figs. 7 and 8, moreover, the structure of the distribution functions becomes less for, say, $70° < \theta_0 \leqslant 90°$, where these functions smoothly approaches the radial distribution of a *unrestricted* (or ''free'') rotational motion. In contrast to the HOOKEAN potential, however, no analytical solution for the radial diffusion equation (42) could be obtained for neither the FENE-type nor the DNA-type bead-bead interaction potential. For these potentials, Eq. (42) has to be solved numerically. Although we have carried out these computations, we will delay their further discussion to some later time and only mention for the moment, that the radial distribution function appears very sensitive to the angle θ_0 also for these two choices of the interaction. In contrast to the HOOKEAN potential, however, the radial functions approaches much faster to the corresponding distribution for an unrestricted rotational motion which is obtained at ≈50° for the FENE and already at ≈35° for a DNA bead-bead potential.

IV. CONCLUSION

The influence of the bead-bead interaction on the dynamics of macromolecules, which are immersed into a solution, has been investigated by starting from a Fokker-Planck equation for the phase-space distribution function. Within such a model, the macromolecules is taken as a *chain of beads* which are coupled to each other by some pairwise potential and surrounded by (a large number of) solvent particles. From the Fokker-Planck equation of the overall system ''macromolecule+solvent,'' we then derived an internal diffusion equation for the time evolution of the configuration-space distribution function of the (two-beads) dumbbell macromolecule. There are three realistic assumptions which have been made in our derivation: Since (i) the mass of the each bead of the macromolecule is considered to be larger when compared to the mass of the solvent particles, we may assume (ii) that the momenta of the beads relax much faster to their equilibrium values than the coordinates. For this reason, (iii) the dynamics of the solvent can be well described in terms of a diffusion equation or, equivalently, in terms of the ''diffusion tensors'' which occur on the r.h.s. of the diffusion equation for the internal coordinates. These three assumptions are made very frequently in studying the behavior of macromolecules in solutions.[19–23]

For the three basic assumptions from above, the diffusion tensor contains all the information about the internal motion of the molecules. Apart from the diffusion tensors of the individual beads, of course, this tensor also contains the hydrodynamic interaction among the various beads of the macromolecule. To explore the effects of this hydrodynamic interaction, we derived and analyzed an expression for the anisotropy parameter for the Oseen and Rotne-Prager hydrodynamic diffusion tensors. The results of our computations clearly show the anisotropic nature of the diffusion tensor and, in particular, at small distances of the molecular beads. To further analyze the behavior of macromolecules in solution, this behavior of the diffusion tensor has to be compared nonhydrodynamical limit of diffusion theory in which the hydrodynamical tensor is set to zero.

To further understand the effects of the bead-bead interaction on the rotational motion of macromolecules, which are sticked to some surface, we have studied a few realistic bead-bead interaction potentials for a dumbbell molecule including a HOOKEAN, FENE, and DNA type potential; the generalization of this work to larger macromolecules will be considered in the future. For the given three interaction potentials, the behavior of the rotational diffusion coefficient has been calculated in detail; these computations reveal that the rotational diffusion coefficient depend on the maximal separation of the beads as possible for a given potential. For the HOOKEAN potential, moreover, an analytic expression was derived for the radial distribution function.

From our analysis of the rotational diffusion coefficient and the radial distribution functions of the macromolecule, a clear dependence of the rotational motion is found also for the bead-bead interaction potential and for the maximal value of the polar angle θ_0, i.e., for the case of a rotational diffusion in a cone. Of course, this dependence has to be compared with that from the rigid-rod macromolecular theory. The use of diffusion (type) equations in the description of the rotational dynamics may therefore help combine different physical models concerning the behavior of the macromolecules in the solution.

The results from this work might useful also to interprets dielectric relaxation, the correlation spectroscopy and NMR relaxation experiments which are carried out on the diffusion coefficients and the cone restricted angles for biological molecules (such as DNA).[4–11] Moreover, the theory is applicable, at least in principle, for analyzing the role of the bead-surface interaction for the rotational behavior of immobilized macromolecules.

In addition, we are presently also continue this work to better understand the rotational dynamics of *N*-bead chains or other macromolecular structures.

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PAPER III

A semi–phenomenological approach to the transport and diffusion of small spherical macromolecules in solution.

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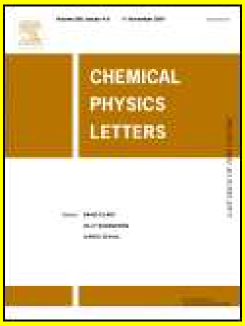

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A semi-phenomenological approach to the transport and diffusion of small spherical macromolecules in solution

Alexander Uvarov *, Stephan Fritzsche

Institut für Physik, Universität Kassel, Heinrich-Plett-Street 40, D-34132 Kassel, Germany

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Abstract

A recently derived expression [A. Uvarov, S. Fritzsche, Macromol. Theor. Simul. 13 (2004) 241] for the friction coefficient of macromolecules, which are immersed into a solution, is utilized in order to calculate their diffusion and boundary condition coefficients as function of the mass ratio of the molecules, relative to the mass of the solvent particles. The results from this semi-phenomenological theory are found to compare very well with molecular-dynamical simulations over a wide range of mass ratios and at quite different temperatures and viscosities of the solvent. Therefore, the use of this novel approach may help reduce considerably the costs in studying the dynamical behaviour and the transport properties of macromolecules in solution.
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1. Introduction

Accurate dynamical studies on macromolecules in solution are still a challenge for modern DNA and protein research. During the past decade, therefore, a large number of experiments have been carried out in order to understand the translational and rotational motion of macromolecules as well as their (de-) formation processes, if immersed into a solution [1–5]. Theoretically, these investigations have been supplemented by (often large) molecular-dynamical simulations (MDS) [6–14] as well as a few analytical case studies [15–20]. In all these investigations, the dynamical behaviour of the macromolecules is usually characterized by means of the friction ξ or diffusion coefficients D which, in the *phenomenological* Stokes–Einstein (SE) theory [15,16]

$$D = \frac{k_B T}{\xi} \tag{1}$$

are simply related to each other via the temperature T and the Boltzmann constant k_B. This relation, in fact, is a very general result and independent of the microscopic friction mechanism. For a massive spherical macromolecule, in addition, we have Stokes law [15,16]

$$\xi = c\pi\eta R_{\mathrm{hydr}}, \tag{2}$$

which shows the friction coefficient to be proportional to the viscosity η of the solvent and the *effective hydrodynamic* radius R_{hydr} of the macromolecule. In this *macroscopic* relation (2), the numerical constant c is used to specify the boundary conditions (BC) for the velocity of the solvent particles at the surface of the macromolecule with a numerical value within the limits of the (so-called) *stick* and *slip* BC. While, for the stick BC, the first layer of solvent particles is assumed to stick firmly to the surface of the macromolecule, these solvent particles are considered to be free on the surface for the slip BC. In the phenomenological theory, therefore, the BC coefficients is always constant with values ranging from $c = 4$ (slip BC) to $c = 6$ (stick BC), respectively.

Obviously, however, Stokes law (2) only applies for such massive macromolecules for which the *discrete* nature of the solvent is negligible. As known from a series of MDS, this is fulfilled widely if the mass of the macromolecule is $\gtrsim 100$ times larger than the mass of the

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* Corresponding author. Fax: +49561 804 4006.
E-mail address: uvarov@physik.uni-kassel.de (A. Uvarov).

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solvent particles [6,7,14]. For some smaller mass ratio between the macromolecules and the solvent particles, in contrast, the discrete character of the solution and its interaction with the molecules should be taken into account [12,13].

In the present Letter, emphasis is placed on the diffusional motion of macromolecules in solution. Making use of a *semi-phenomenological* expression for the friction coefficient, which has been derived recently by us for a N-bead macromolecule [18,19], detailed computations have been carried out for the diffusion and BC coefficients of a single (spherical) macromolecule in dependence of its mass (ratio), when taken relative to the mass of the solvent particles. For these coefficients, a good agreement with MDS is found over a wide range of the mass ratios and for quite different temperatures and viscosities of the solvent. Apart from new insights into the diffusional motion of macromolecules, therefore, our semi-phenomenological approach allows first of all a very remarkable reduction of the computational costs in studying the transport and diffusion properties of large molecules. It can be used also in the future to explore, for instance, the stick–slip motion of the macromolecules in the solution [12,21–23].

The Letter, is organized as follows. In the following section, we start with a brief recall of the theory and the basic assumptions on the system 'macromolecule + solvent', which were made previously in order to derive a semi-phenomenological expression for the friction coefficient of a general (N-bead) macromolecule in solutions. Beside of the (dynamical) structure factor of the solvent, here we need to specify the interaction between the solvent particles and the macromolecules, assuming an equal mass density in this Letter. The expressions from this section are later applied in Section 3 in order to calculate the diffusion and the BC coefficients of the macromolecule. Comparison of our results is made with other phenomenological theories and with MDS data as available from the literature. In Section 4, finally, a few remarks on the use and further improvement of such a semi-phenomenological treatment is given.

2. Diffusion model and computations

Friction (or diffusion) coefficients provide perhaps the most general form for describing the dynamical behaviour of large molecules in solution. Therefore, in order to analyze the diffusion of macromolecules and how it is influenced by the given BC, let us take a microscopic viewpoint and begin from the expression

$$\xi = \frac{2n_0}{3(2\pi)^2}\int_0^\infty \mathrm{d}k\,k^4 W(k)^2\left[\int_0^\infty \mathrm{d}\tau\, g(\mathbf{k},\tau)\right] \qquad (3)$$

as recently derived for the friction coefficient of a spherical macromolecule which is immersed into a solvent of n particle. In [18,19], this expression was obtained from *first principles*, i.e. by starting from the Hamiltonian of the overall system 'macromolecule + solvent'. To remove the explicit treatment of the solvent (particles), however, a few realistic assumptions need to be made about its dynamical behaviour, including (i) a much faster relaxation of the solvent, when compared to the relaxation time of the macromolecules, and (ii) the assumption that all effects of the solvent onto the dynamics of the macromolecule can be well described by means of a diffusion equation. For the sake of simplicity, moreover, we also assumed a (pairwise) spherical–symmetric potential $W(\mathbf{r})$ between the macromolecules and the solvent particles which only depends on their relative distance $\mathbf{r}$ from each other. In expression (3), n_0 refers to the number density (or concentration) of the solvent, while $W(\mathbf{k}) = \int \mathrm{d}\mathbf{r}\, e^{-\mathbf{kr}} W(\mathbf{r})$ denotes the Fourier transform of the *molecule–solvent* potential with $k = |\mathbf{k}|$ being the modulus of the wave vector. In addition to the interaction between the molecules and the solvent particles, of course, the friction coefficient ξ in Eq. (3) also depends on the dynamical structure factor (or scattering function) of the solvent, $g(\mathbf{k}, \tau)$ which, in fact, contains all the information about the solvent including, for example, its relaxation time back into the equilibrium, temperature, viscosity, and many further properties. Studies on the dynamical structure factor have therefore attracted a lot of interest over then years [24–32]. Using assumption (ii), in particular, it was found that the *time* dependence of the dynamical structure factor can be approximated by a simple analytical expression [24–27]

$$g(\mathbf{k},\tau) = n_0 g(k)\exp[-\mathbf{k}^2 D_0 \tau], \qquad (4)$$

which – via the static structure factor $g(k)$ and the self-diffusion coefficient D_0 – still contains the knowledge about at-least the time-independent properties of the solvent (i.e. density fluctuations, correlation length, temperature, viscosity, etc.). In line with approximation (4), moreover, an explicit expression can be obtained also for the (equilibrium) static structure factor by using the Percus–Yevick theory [26–29]

$$g(k) = 1 - 18\pi n_0 \frac{j_1(k\sigma)}{(k\sigma)}, \qquad (5)$$

where σ refers to the diameter of the solvent particles and $j_1(x) = (\sin x - x\cos x)/x^2$ is the spherical Bessel function of rank 1.

Let us now return to the friction coefficient ξ from Eq. (3). Indeed, the knowledge about this coefficient plays a *key* role in studying the properties of macromolecules in solution. Having the approximations (4) and (5), for instance, Eq. (3) for the friction coefficient can be used in order to analyze how a particular molecule–solvent potential influences the dynamics of a (N-bead) macromolecules if immersed into a solution [18,19]. In the present Letter, we just consider a molecule consisting out of a single bead ($N \equiv 1$), but now ask for the behaviour of the friction coefficient if the mass of the macromolecule M is varied with respect to the mass m of the solvent particles. For this, of course, we need a relation between the mass and the size of the particles. To allow for a later comparison with the MDS by Schmidt and Skinner [6,7], here, we suppose an equal (and constant) mass density of the macromolecule and the solvent particles

$$\frac{M}{R^3} = \frac{m}{(\sigma/2)^3} \tag{6}$$

independent of the radius R of the macromolecule. Similarly, of course, we shall apply the same interaction between the macromolecule and the solvent particles. In [6,7], a so-called Lennard–Jones (LJ) solvent is used for which the interaction among the solvent particles is modeled by a 'truncated' LJ potential

$$V(r) = \begin{cases} 4\epsilon_{\mathrm{S}}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] & \text{if } r \le r_{\mathrm{S}}, \\ 0 & \text{otherwise}, \end{cases} \tag{7}$$

where ϵ_{S} is the interaction strength and r_{S} the cut-off radius beyond which the potential becomes zero. Moreover, the same shape of the interaction has been assumed also for the macromolecule–solvent potential

$$W(r) = \begin{cases} 4\epsilon_{\mathrm{M}}\left[\left(\frac{\sigma}{r-l_{\mathrm{M}}}\right)^{12} - \left(\frac{\sigma}{r-l_{\mathrm{M}}}\right)^{6}\right] & \text{if } l_{\mathrm{M}} \le r \le r_{\mathrm{M}}, \\ 0 & \text{otherwise}, \end{cases} \tag{8}$$

but with independent parameters ϵ_{M}, r_{M} for the strength and the cut-off, and where the (additional) length l_{M} defines a 'hard-sphere like' BC for the macromolecule at small distances: $W(\mathrm{r} \to l_{\mathrm{M}}) \to \infty$. To specify this length l_{M} in terms of the radii of the macromolecule and the solvent particles, we suppose that the *zero* of the potential, $W(\mathbf{r}_0) = 0$ at $r_0 = l_{\mathrm{M}} + \sigma$, occurs if the solvent particles just 'touch' the molecule, i.e. for $r_0 = R + \sigma/2$. This gives rise to $l_{\mathrm{M}} = R - \sigma/2$, and together with the constant mass density (6) of the molecule and the solvent particles, to the 'hard-sphere' length [6,7]

$$l_{\mathrm{M}} = \frac{\sigma}{2}\left[\sqrt[3]{\frac{M}{m}} - 1\right] \tag{9}$$

if expressed in terms of the mass ratio M/m of the particles. Note that expression (9) enables one to vary the radius R of the macromolecule in a physically meaningful way, from a tagged solvent particle (for $M/m = 1$ and $R = \sigma/2$) up to the phenomenological (Brownian) limit where $M/m \to \infty$and $R \to \infty$. Below, we make use of relation (9) in order to calculate the friction coefficient of the macromolecule as function of the mass ratio, M/m, and to compare its behaviour with results from the phenomenological theory [15,16] and from MDS [6,7,14].

3. Results and discussion

Various (large-scale) molecular-dynamic computations have been carried out during the last decade in order to understand the dynamical properties of macromolecules in solution including case studies on the dynamical and statical structure factors [10,11,24,25], the velocity and force autocorrelation functions [8,9], the diffusion coefficients [6,7,12–14], and various other properties. Apart from the interaction parameters, these investigations differ by the size and mass of the macromolecules, as well as by the internal structure of the macromolecule. To facilitate the comparison of the various computations, however, a common 'unit system' is typically applied which is based on the parameters of the LJ potential (7) among the solvent particles. In these (LJ) units ($m = \sigma = \epsilon_{\mathrm{S}} = 1$), all lengths are measured in σ and energies in units of ϵ_{S}. For the other quantities, this leads to the *derived* units: $\tau_{\mathrm{LJ}} = (m\sigma^2/\epsilon_{\mathrm{S}})^{1/2}$ (time); $\xi_{\mathrm{LJ}} = (\epsilon_{\mathrm{S}} m/\sigma^2)$ (friction); $D_{\mathrm{LJ}} = (m/(\epsilon_{\mathrm{S}}\sigma^2))^{-1/2}$ (diffusion coefficients); $\eta_{\mathrm{LJ}} = (m\epsilon_{\mathrm{S}})^{1/2}/\sigma^2$ (viscosity), etc. For the sake of convenience, we will use the same unit system in order to allow for the direct comparison with MDS data.

In this Letter, we focus on the behaviour of the diffusion and the BC coefficients in dependence of the mass ratio, M/m, of the macromolecule and the solvent particles, for which two recent MDS studies are known from the literature [6,11]. Below, we will refer to these computations by Schmidt and Skinner [6] as case A and those by Brey and Ordóñez [11] as case B. In both simulations, a spherical–symmetric macromolecule was assumed which interacts with the solvent particles due to the LJ potential (8) with the interaction strength $\epsilon_{\mathrm{M}} = \epsilon_{\mathrm{S}}$ and with the cut-off parameters $r_{\mathrm{S}} = 2.5\sigma$ for the solvent–solvent potential (7) and $r_{\mathrm{M}} = 2.5\,\sigma + l_{\mathrm{M}}$ for the macromolecule–solvent interaction (8), respectively. These computations differed, however, with respect to their temperatures T, viscosities η, and the number densities n_0 of the solvents, with values $k_{\mathrm{B}}T \approx \epsilon_{\mathrm{S}}$, $\eta \approx 2.83\eta_{\mathrm{LJ}}$, $n_0 \approx 0.85$ in case A [6], and $k_{\mathrm{B}}T \approx 2.95\epsilon_{\mathrm{S}}$, $\eta \approx 7.7\eta_{\mathrm{LJ}}$, $n_0 \approx 0.6$ in case B [11], respectively. For all further details in the initial set-up of the MDS, we refer the reader to the literature.

In our semi-phenomenological approach, the interaction among the solvent particles (cf. Eq. (7)) is described approximately by the statical structure factor $g(k)$ in Eq. (5). For a quick reference on the quality of this approximation, Fig. 1 displays the statical structure factor $g(k)$ in dependence of the modulus of the wave vector k and compares it with those from MDS [6,11]. In both cases

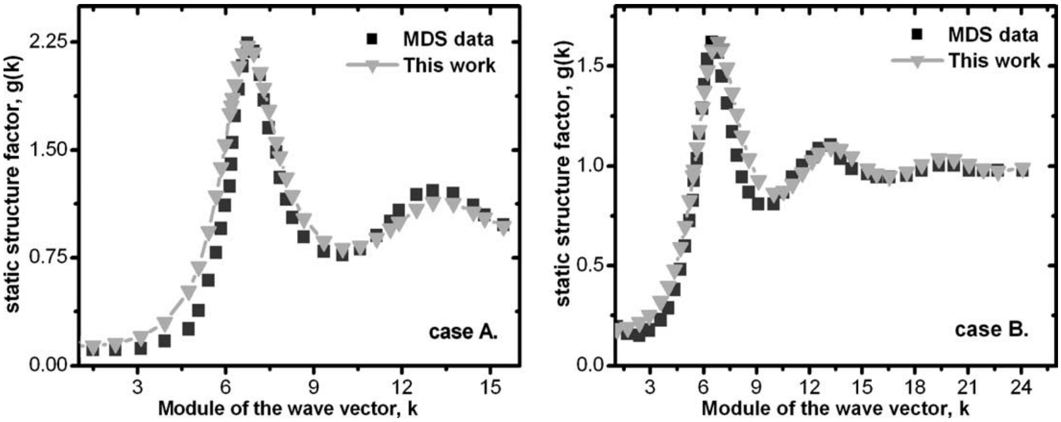

Fig. 1. Wave-vector dependence of the statical (equilibrium) structure factor $g(k)$ of the solvent. The results from the expression (5) are compared with MDS data from [24] for two temperatures T and number densities n_0: (a) case A with $T = 1$, $n_0 = 0.85$; (b) case B with $T = 2.95$, $n_0 = 0.6$. See text for further discussions.

A and B, a good agreement is found for the statical structure factor, supporting the approximation (5). To evaluate the friction (or diffusion) coefficient, however, we also need to perform the Fourier transform $W(k)$ of the macromolecule–solvent potential (8) in order that Eq. (3) can be used. Although, this Fourier transform has (usually) to be calculated numerically, it only has to be determined *once* for each particular choice of the potential and, hence, makes this approach particularly suitable for studying different molecule–solvent interactions.

Having the Fourier transform $W(k)$ of (8) and the statical structure factor $g(k)$ of the solvent, we can – by inserting these functions into Eq. (3) and by using the SE relation (1) – calculate immediately the diffusion coefficient D of the macromolecule for different values M/m of the macromolecule-to-solvent mass ratio, cf. Eq. (9). Fig. 2 displays this mass-ratio dependency from the semi-phenomenological theory and compares it with the purely phenomenological behaviour (for two different choices of the BC, see below) and the MDS data by Schmidt and Skinner [6] and Brey and Ordóñez [11], respectively. As seen from this figure, good agreement with the MDS is obtained for all medium and large mass ratios M/m, and with some deviations only at small mass ratios, independent of the particular choice of the temperatures and viscosities of the solvent (cases A and B). Good agreement is found, in particular, over to a mass ratio M/m ≈45 for which the (asymptotically correct) slip-boundary phenomenological theory already shows a sizeable deviation. The phenomenological theory, in fact, approaches the MDS only for slip-boundary conditions, where the macromolecule–solvent potential W has to be *relative weak* when compared with the solvent–solvent interaction potential V (i.e. when the

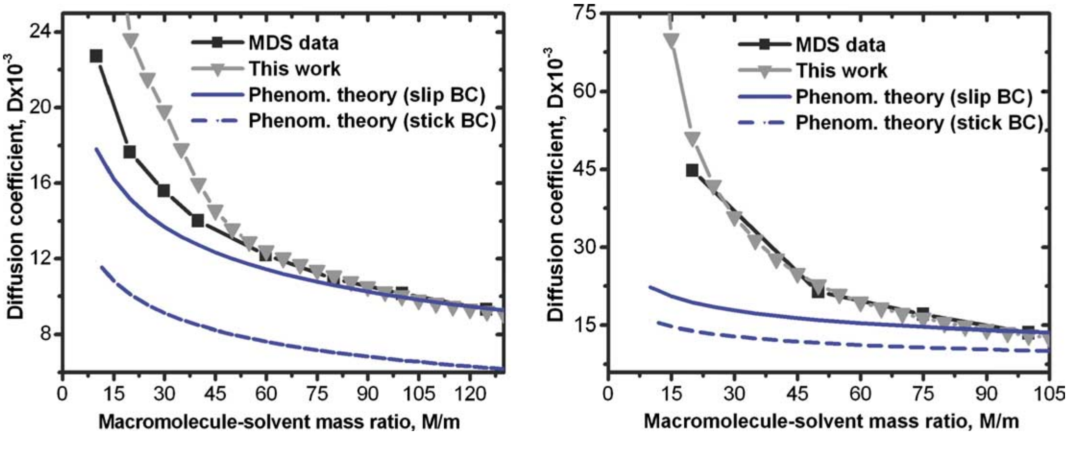

Fig. 2. Diffusion coefficient D of macromolecules in solution as function of the macromolecule-to-solvent mass ratio M/m. The results from our semi-phenomenological theory, calculated for a 'truncated' LJ potential (8) between the macromolecule and the solvent particles, are compared with the MDS data from [6] for the case A (a) and with those from [11] for the case B (b), respectively. See Fig. 1 and the text for further discussion.

macromolecule carries none of the surrounding solvent particles with it and the friction is due to only the solvent which must be displaced to allow macromolecule motion), and for mass ratios $M/m \gtrsim 90$. From the agreement of the semi-phenomenological data with MDS, we can therefore, conclude that the same approach can be used also to compute further statical and dynamical properties of macromolecules as long as their mass does not become too small when compared to the mass of the solvent particles. Let us note, moreover, that when the mass and size of the tagged particle is comparable with the mass and size of the solvent particle, the phenomenological approach can not be used because of that the general postulate of the phenomenological theory about uncorrelated motion of the tagged particle on the larger time interval is not valid in principle [15,16].

Of course, the diffusion coefficient of the macromolecule depends not only on the relative mass M/m of the macromolecule but also on the thermodynamical properties of the solvent. In Table 1, therefore, we list the diffusion coefficient for a fixed mass ratio $M/m = 100$ but at different temperatures and viscosities (or, number densities n_0, respectively) of the solvent. The particular value of the mass ratio $M/m = 100$ has been taken to allow for the comparison with the MDS by Schmidt and Skinner [6] in this table. For all available MDS data, good agreement is found for the diffusion and the BC coefficient (see below).

Table 1
Diffusion coefficients D and BC coefficients c for a fixed macromolecule-to-solvent mass ratio $M/m = 100$

n_0	T	η	D		c	
			This work	MDS [6]	This work	MDS [6]
0.50	1.41	0.571	0.08704	0.0831	3.20130	3.35
0.71	1.41	1.28	0.03232	0.0354	3.84578	3.50
0.85	1.41	2.53	0.01657	0.0162	3.87061	3.89
0.85	1.20	2.67	0.01364	0.0134	3.74208	3.79
0.85	1.00	2.83	0.01009	0.0102	3.89964	3.91
0.85	0.80	3.25	0.00724	0.0072	3.83414	3.81

Coefficients from our semi-phenomenological theory are displayed for different number densities n_0, temperatures T, and viscosities η of the solvent, and are compared with MDS data from [6].

Instead of the diffusion coefficient of the macromolecule, the BC coefficient c is sometimes used in order to describe the properties of macromolecules in solution. Combining the phenomenological expressions for the diffusion (1) and friction coefficients (3) of the macromolecule, this coefficient is given by

$$c = \frac{k_B T}{D \pi \eta R_{\text{hydr}}} \tag{10}$$

and, unlike the diffusion coefficient D, now also depends on the hydrodynamical radius R_{hydr} of the macromolecule. From the literature, several approximations are known to estimate the radius R_{hydr} for a macromolecule. While, for example, the (so-called) *bare-hydrodynamic* radius $R_{\text{hydr}} = l_M + \sigma/2$ is simply taken equal to the radius of the macromolecule, an additional 'layer of solvent particles' is assumed for the *hydrodynamic* radius, $R_{\text{hydr}} = l_M + \sigma$. Following [6,11], both approximations are applied in Fig. 3 to display the BC coefficient c as function of the mass ratio M/m. Again, a good agreement is found for all mass ratios $M/m \gtrsim 60$ when compared with the MDS. For a rather *weak* interaction between the macromolecule and the solvent particles (the left part of Fig. 3 with the interaction strength $\epsilon_M \approx \epsilon_S$), moreover, the BC coefficient approaches the value of 4, if the hydrodynamic radius $R_{\text{hydr}} = l_M + \sigma$ is taken into account for the macromolecules, and a

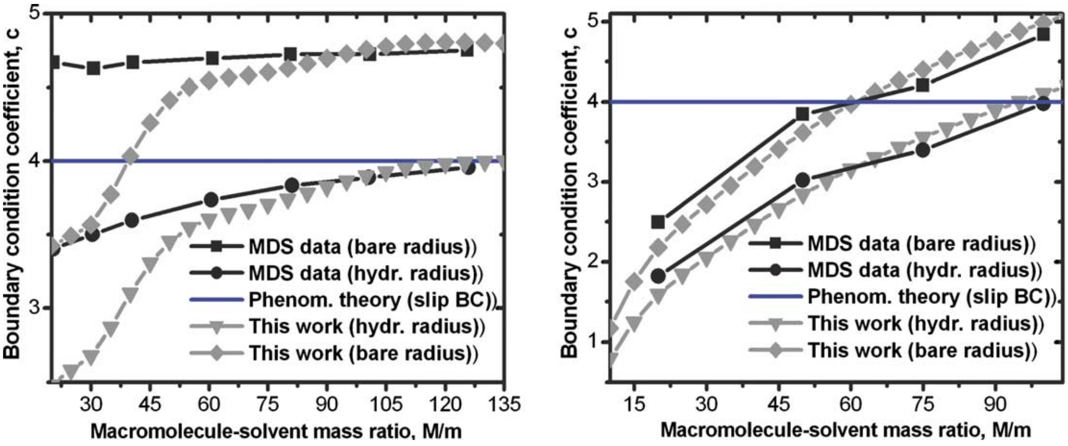

Fig. 3. BC coefficient c of macromolecules in solution as function of the macromolecule-to-solvent mass ratio M/m. The results from this Letter, calculated for the bare and a hydrodynamical radius of the macromolecule, are compared with the MDS data from [6] for the case A (a) and with those from [11] for the case B (b), respectively. See Fig. 1 and the text for further discussion.

value of 4.6 for the case of the bare-hydrodynamic radius from above.

4. Conclusions

The behaviour of the diffusion and BC coefficients of a macromolecule has been studied as function of the mass ratio between the molecule and the solvent particles. Starting from a semi-phenomenological expression for the friction coefficient, which war derived earlier from *first principles* for a (N-bead) macromolecule, good agreement with available MDS has been found all medium and large macromolecule-to-solvent mass ratios. These computations clearly show, that our semi-phenomenological approach [18,19] can be used for studying the dynamical properties of macromolecules in solution and may save (or at least reduce) the need for carrying out expansive MDS. Unlike to the phenomenological theory, in which for instance the diffusion coefficient of macromolecules is properly described only for mass ratios $M/m \approx 100$, the semi-phenomenological allows the correct treatment down to a macromolecule-to-solvent mass ratios of about $M/m \approx 45$.

Based on the Hamiltonian of the overall system 'macromolecule + solvent', a semi-phenomenological approach provides insight into the motion and dynamical properties of macromolecules which can hardly be obtained by the straightforward integration of Newton's law. Apart from a few basic assumptions, namely, concerning (i) the relaxation times of the macromolecules and solvent particles and (ii) a description in terms of a diffusion equation, such insight arises from the approximations which are made in the derivation. In the present theory (cf. Eq. (3)), a minimal coupling (cf. Eqs. (9) and (10) and discussion of its in [18]) between the macromolecule and the solvent was assumed which appears sufficient especially for large macromolecule-to-solvent mass ratios. An extension of our semi-phenomenological approach, including also higher terms in the expansion of the term which describes the coupling between macromolecule and solvent particles [18,19], is currently under work.

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PAPER IV

Friction of N-bead macromolecules in solution: Effects of the bead-solvent interaction.

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Friction of *N*-bead macromolecules in solution: Effects of the bead-solvent interaction

Alexander Uvarov* and Stephan Fritzsche
Fachbereich Physik, Universität Kassel, Heinrich-Plett-Strasse 40, D-34132 Kassel, Germany

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The role of the bead-solvent interaction has been studied for its influence on the dynamics of an *N*-bead macromolecule which is immersed into a solution. Using a Fokker-Planck equation for the phase-space distribution function of the macromolecule, we show that all the effects of the solution can be treated entirely in terms of the friction tensors which are assigned to each pair of interacting beads in the chain. For the high-density as well as for the critical solvent, the properties of these tensors are discussed in detail and are calculated by using several (realistic) choices of the bead-solvent potential. From the friction tensors, moreover, an expression for the center-of-mass friction coefficient of a (*N*-bead) chain macromolecule is derived. Numerical data for this coefficient for "truncated" Lennard-Jones bead-solvent potential are compared with results from molecular dynamic simulations and from the phenomenological theoretical data as found in the literature.

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I. INTRODUCTION

A better understanding of the dynamical behavior of macromolecules in solutions, i.e., of their translational and rotational motion, or of their (de–) formation in the shape, is still one of the central problems in studying proteins and DNA material. During the past few years, therefore, a large number of experiments [1–3] and molecular as well as Brownian dynamics simulations [4–8] have been carried out in order to describe the statical and the dynamical properties of macromolecules. In a first theoretical approach to this problem, the *nonrigid* macromolecules are often treated in terms of—a number of—molecular subsystems which are briefly referred to as the *beads* of the macromolecule. When immersed into a solvent, of course, the shape and the dynamical behavior of such macromolecules will not only depend on the interaction among the beads but will be affected also by the surrounding particles from the solvent. In fact, the solvent can change both the (conformational) static as well as the dynamical properties of the macromolecules dramatically [9]. Therefore, various models have been developed in the past for studying the effects of the solvent on the macromolecular properties. For instance, the most common and simple way to take into account the solvent effects is to replace the bead-solvent interaction by the *Brownian (stochastic) forces* [10,11]. According to this approach, Rouse [12] as well as Kirkwood and Riseman [13] developed the model of the macromolecular behavior which has been widely used for analyzing transport properties of the macromolecule. In the original version of this (Rouse) model, the hydrodynamic interaction is disregarded and the time evolution of the position of the beads obeys the linearized Langevin equation. The Rouse model was later extended by Zimm [14], who explored the various properties of the macromolecular solution in the presence of hydrodynamic interactions (Zimm model). The mathematical foundations of the Rouse as well as Zimm models and their generalizations may be found in the works of Bixon [15], Zwanzig [16], as well as Doi and Edwards [10]. Unfortunately, both Rouse as well as Zimm (phenomenological) methods are based on the assumption that the solvent is a *nondiscrete* and an *incompressible* medium [10,11,17,18]. However, the need for taking the discrete (atomistic) structure of the solvent into account has been recognized mainly due to molecular dynamic simulations (MDS) [4–6,19]. Often, the discrete nature of the solvent leads moreover to rather remarkable deviations from a pure Brownian behavior of the macromolecular beads and hence, may play an important role also in studying the dynamics of macromolecules.

To investigate, therefore, the question of how the solvent particles affect the dynamics of the macromolecules in solutions, Hamiltonian mechanics and master equations for the phase-space distribution functions are commonly used, which totally describe the dynamical behavior of macromolecules [20–22]. Starting from the Hamiltonian of the overall system "macromolecule plus solvent", it is possible to derive a Fokker-Planck equation (FPE) for the time evolution of the phase-space distribution function of the molecule which consists of *N* pairwise interacting beads. In this equation, the dynamics of the macromolecules purely depend on the friction tensors (i.e., the right-hand sides of the FPE) which then incorporate all the information about the interaction of the beads with the particles of the solvent. Under the assumptions of a much *slower* relaxation of the macromolecule to the equilibrium state (when compared to the relaxation time of the solvent), explicit expressions for the ("instantaneous") friction tensors were derived in terms of the bead-solvent potential as well as the dynamic structure factor of the solvent and were discussed, in particular, for the single bead as well as for the (2 bead) *dumbbell* molecule [22,23]. Let us note that the assumption of slow relaxation introduces a physical framework from the beginning of the investigations. So, these approximations generally mean, of course, that we are interested only in the long-time (asymptotic) behavior of the macromolecule.

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*Electronic address: uvarov@physik.uni-kassel.de

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In the present contribution, we now explore the effects of the bead-solvent interaction on the dynamics of N-bead macromolecules which immersed in the high-density as well as in the critical solvent. Making use of the FPE with semiphenomenological friction tensors [20–22], detailed computations are carried out for various bead-solvent potentials including the Yukawa, Born-Mayer, and Lennard-Jones potential. These potentials are all well known from physical chemistry and were used before in molecular dynamic simulations in order to model the behavior of molecules and clusters in different (chemical) environments [24]. In addition to the effects of the bead-solvent interaction potentials, we investigate the contribution of the long-wave as well as the short-wave parts of the static structure factor of the solvent on the dynamical behavior of the macromolecule. Moreover, by using the Einstein relation [10] in order to connect the diffusion and friction of the macromolecule, an expression for the center-of-mass friction coefficient is calculated and compared with (purely numerical) results from molecular dynamic simulations [4,5] as well as with results, which come from the Rouse and Zimm phenomenological theories [7,10,11].

The paper is organized as follows. In the next section, we will start from the Fokker-Planck equation for the time evolution of the phase-space distribution as derived previously [22]. A particular feature of this equation is that the generalized friction tensor is expressed in terms of the bead-solvent interaction as well as the dynamic structure factor of the solvent and, hence, can be analyzed for each choice of bead-solvent interaction independently. Various interaction potentials are considered here including the Yukawa (screened Coulomb), Born-Mayer, and three commonly applied long-ranging (Van der Waals-type) interactions. In addition, we analyze the influence of various thermodynamical regimes of the solvent on the friction of the macromolecule. Later, we also investigate the motion of a N-bead macromolecule as whole. A general expression for the center-of-mass friction coefficient of the N-bead macromolecule is evaluated and discussed. In a further section, the results from this work are compared with available data from molecular dynamic simulation and, finally, a few conclusions about our *semiphenomenological* approach are given.

II. THEORY

A. Basic equations

To analyze the *dynamical* properties of macromolecules in solutions, let us suppose a microscopic view point and start from a FPE

$$\frac{\partial \rho_N(\boldsymbol{\Gamma};\mathbf{t})}{\partial t} + \sum_{a=1}^{N} \frac{\mathbf{P}_a}{M} \frac{\partial \rho_N(\boldsymbol{\Gamma};\mathbf{t})}{\partial \mathbf{R}_a} - \sum_{a,b=1}^{N} \frac{\partial U_{ab}}{\partial \mathbf{R}_a} \frac{\partial \rho_N(\boldsymbol{\Gamma};\mathbf{t})}{\partial \mathbf{P}_a}$$

$$= \sum_{a,b=1}^{N} \frac{\partial}{\partial \mathbf{P}_a} \xi^{(\mathbf{ab})} \left(\frac{\partial}{\partial \mathbf{P}_b} + \frac{1}{k_B T M} \mathbf{P}_b \right) \rho_N(\boldsymbol{\Gamma};\mathbf{t}) \qquad (1)$$

as recently derived for the time evolution of the phase-space distribution function $\rho_N(\boldsymbol{\Gamma};\mathbf{t})$ for the N-bead macromolecule. In Refs. [20,22], Eq. (1) was obtained by starting from the Hamiltonian of the overall system macromolecule plus solvent where, for the sake of simplicity, an equal mass M and pairwise interaction $U_{ab}=U(|\mathbf{R}_a-\mathbf{R}_b|)$ were assumed for all the beads of a macromolecule. In addition, it was supposed the relaxation from a nonequilibrium into the equilibrium state of the macromolecule to be a *slow* process when compared to the relaxation of the solvent particles.

Let us note that an alternative way to study the behavior of the macromolecule in solutions is to use the (so-called) generalized Langevin equation (GLE) with *time-dependent* (dissipative) friction memory kernel and random fluctuating force [17]. Mathematically, both the FPE and GLE methods are equivalent if we take into account the assumption about slow relaxation of the macromolecule. In the frame of this assumption the friction memory kernel reduces to the friction tensors and a δ function in time [10,11,17].

In Equation (1), $\mathbf{R}_a$ and $\mathbf{P}_a$, $a=1,\ldots,N$ denote the positions or, respectively, the momenta of the individual beads, while we will use $\boldsymbol{\Gamma}\equiv\{\mathbf{R}_1,\ldots,\mathbf{R}_N;\mathbf{P}_1,\ldots,\mathbf{P}_N\}$ below in order to abbreviate the phase-space coordinates alltogether. For each pair (a,b) of beads, a friction tensor $\xi^{(ab)}$ is associated also which characterizes the (thermodynamically averaged) interaction of these two beads with the surrounding particles from the solvent. Finally, k_B denotes the Boltzmann constant and T the temperature of the overall system macromolecule plus solvent.

As said before, the FPE (1) describes the time evolution of the phase-space distribution $\rho_N(\boldsymbol{\Gamma};\mathbf{t})$ and, hence, includes all the information about the dynamics of the N-bead macromolecule in solution. From this (probability density) function, in fact, the probability to find the macromolecule at time t within a small volume $d\boldsymbol{\Gamma}$ around the point $\boldsymbol{\Gamma}$ in phase space is simply given by $\rho_N(\boldsymbol{\Gamma};\mathbf{t})d\boldsymbol{\Gamma}$. For this to be right, of course, the distribution function should be normalized,

$$\int d\boldsymbol{\Gamma}\, \rho_N(\boldsymbol{\Gamma};\mathbf{t}) = 1, \qquad (2)$$

by taking the integral over the complete phase-space of the macromolecule. In practice, the knowledge of the phase-space distribution (or, at least, of some of its properties) plays a *key* role in studying the dynamical behavior of molecules in solution. As discussed previously in the literature [10,11,17,25], this distribution function helps calculate, for instance, the *translational* as well as *rotational* properties of macromolecules. Moreover, knowing once the phase-space distribution $\rho_N(\boldsymbol{\Gamma};\mathbf{t})$ of a macromolecule, the time average $\langle\ \rangle$ of *any* function $A\equiv A(\{\boldsymbol{\Gamma}\})$ can be easily derived from the integral

$$\langle A\rangle = \int d\boldsymbol{\Gamma}\, A(\boldsymbol{\Gamma})\rho_N(\boldsymbol{\Gamma};\mathbf{t}). \qquad (3)$$

Equation (1) however merely defines the *framework* for studying the dynamics of large and slow molecules in solution; in order to make use of this frame, we first need to analyze the friction tensors $\xi^{(ab)}$ for the various—neighbored pairs of—beads which incorporate all of the information of how the solvent particles affect their motion. The knowledge of (the properties of) these tensors may then help to understand the dynamical properties of the macromolecules such as the relaxation time from a nonequilibrium into the equilibrium state of the macromolecule or the velocity autocorrelation function [22]. Additionally, the friction tensors $\xi^{(ab)}$ can be used also to calculate the *hydrodynamic* force $\mathbf{F}^{\text{hydr},a}$ on some given bead a owing to the summation over all the beads

$$\mathbf{F}^{\text{hydr},a} = -\sum_{b=1}^{N} \boldsymbol{\xi}^{(\mathbf{ab})}\mathbf{P}_{\mathrm{b}}/M, \tag{4}$$

where $\mathbf{P}_{\mathrm{b}}/\boldsymbol{M}$ is the velocity of the bead b. In the following, we will therefore discuss the friction tensors of the N-bead macromolecule in more detail.

Together with Eq. (1), an explicit expression for the "instantaneous" friction tensor, whose off-diagonal elements describe the hydrodynamic interaction between beads a and b, is also known and can be written in terms of "measurable" parameters of the solvent as Ref. [22,26]

$$\xi^{(\mathbf{ab})} = n_0\left[\int_0^{\infty} d\tau \int \frac{d\mathbf{k}}{(2\pi)^3}\mathbf{k}\otimes\mathbf{k}W(\mathbf{k})^2 e^{i\mathbf{k}\cdot\mathbf{R}_a}e^{-i\mathbf{k}\cdot\mathbf{R}_b}g(\mathbf{k},\tau)\right] \tag{5}$$

if we assume a spherical-symmetric *bead-solvent* potential $W(|\mathbf{R}_a - \mathbf{r}_s|)$, i.e., an interaction term in the Hamiltonian for each pair of bead a and solvent particle s. In this expression, n_0 refers to the number density (or concentration) of the solvent particles, while $W(\mathbf{k}) = \int d\mathbf{r}\, e^{-\mathbf{k}\cdot\mathbf{r}}W(\mathbf{r})$ denotes the Fourier transform of the bead-solvent potential in which $\mathbf{k}$ being the wave vector with the modulus $k=|\mathbf{k}|$ and with the cartesian components k_α $(\alpha=1,2,3)$. In addition, here we use the operation $\otimes$ to denote a tensor (dyadic) product which turns two vectors into a second-rank tensor. Moreover, $g(\mathbf{k},\tau)$ is often better known as the dynamic structure factor (scattering function) of the solvent [10,11]. We shall return later to this factor and discuss its properties in detail. For the moment, we just mention that this dynamic structure factor contains, in fact, all the information about the properties of the solvent including, for example, its relaxation time back into the equilibrium, temperature, viscosity, and many further properties [27–29].

As said above, the generalized friction tensor $\xi^{(\mathbf{ab})}$ contains, in fact, all information about influence of the solvent on the macromolecular behavior. In practice, however, it appears rather infeasible to deal with the coupling between phase-space coordinates of the beads (position and momenta) and dynamic structure factor of the solvent [cf. Eq. (5) and note that $e^{i\mathbf{k}\mathbf{R}_a(0)}e^{-i\mathbf{k}\mathbf{R}_b(\tau)} = e^{i\mathbf{k}\mathbf{R}_a(0)}e^{-i\mathbf{k}\mathbf{R}_b(0)}e^{-i\mathbf{k}\mathbf{P}_b(0)\tau/M}$]. Since the macromolecules as a whole usually have a much larger mass and size than the particles of the solvent, we may use instead a very good approximation for the momentum distribution in order to simplify the generalized friction tensors (5) to the reduced (*momenta everaged*) friction tensor $\hat{\xi}^{(\mathbf{ab})}$ which is averaged over the local momenta and just depends on the coordinates of the beads. For most solutions, namely, we may assume that the relaxation to the equilibrium (values) happens much faster for the momenta of the molecular beads rather than for their positions and, hence, that the phase-space distribution function $\rho_N(\boldsymbol{\Gamma};\mathbf{t})$ can be factorized

$$\rho_N(\boldsymbol{\Gamma};t) = \varrho_N(\{\mathbf{R}_{\mathrm{a}}\};t)\cdot p_N(\{\mathbf{P}_{\mathrm{a}}\};t) \tag{6}$$

into a coordinate-space distribution $\varrho_N(\{\mathbf{R}_{\mathrm{a}}\};t)$ and the momentum-space distribution function $p_N(\{\mathbf{P}_{\mathrm{a}}\};t)$. By making use this factorization (6) we now may obtain the reduced friction tensors $\hat{\xi}^{(\mathbf{ab})}$ by taking the average

$$\langle\cdots\rangle_{\mathbf{P}} \equiv \frac{\displaystyle\int d\{\mathbf{P}_b\}\ldots p_N(\{\mathbf{P}_{\mathrm{b}}\};t)}{\left[\displaystyle\int d\{\mathbf{P}_b\}p_N(\{\mathbf{P}_{\mathrm{b}}\};t)\right]} \tag{7}$$

over the momenta with respect to the momentum-space distribution function $p_N(\{\mathbf{P}_{\mathrm{a}}\};t)$. Let us note that the momentum-space distribution function may be assumed both equilibrium as well as not equilibrium. In fact, in order to the include all nonequilibrium effects, we need to use the nonequilibrium momentum-space distribution function. However, as a first approximation, we restrict ourselves to the Maxwellian equilibrium momentum-space distribution function [10,11] in order to derive the momentum averaged friction tensor of the macromolecule immersed in the solvent. Let us note only, that in order to further understand the behavior of the macromolecule and quantitavely obtain the contribution of the deviation of the momentum-space distribution of the macromolecular beads from the Maxwellian distribution, we can use the nonequilibrium momentum-space distribution function which was derived, for instance, in Ref. [20]. In the late case the calculated friction tensors will describe the behavior of the macromolecule on the short-time or even ballistic time scales [7,10,11] when a macromolecule is far from the equilibrium. Actually, we will perform this work in the next few monthes.

By taking the average (7) to the general friction tensor (5), we derive the reduced (momenta averaged) friction tensors

$$\hat{\xi}^{(\mathbf{ab})} \equiv \langle\xi^{(\mathbf{ab})}\rangle_{\mathbf{P}} = n_0\left[\int_0^{\infty} d\tau \int \frac{d\mathbf{k}}{(2\pi)^3}\mathbf{k} \otimes \mathbf{k}W(\mathbf{k})^2 e^{i\mathbf{k}\cdot\mathbf{R}_a}e^{-i\mathbf{k}\cdot\mathbf{R}_b}C(\mathbf{k},\tau)g(\mathbf{k},\tau)\right] \tag{8}$$

in which the function $C(\mathbf{k},\tau) = \langle e^{-i\mathbf{k}\cdot\mathbf{P}_b\tau/M}\rangle_{\mathbf{P}}$ is nothing else but the *inertial* part of the self-structure factor of the bead. Moreover, in view of the assumption that the momentum-space distribution function is equilibrium one, the self-structure factor $C(\mathbf{k},\tau)$ of the bead can be evaluated analytically: [10,11]

$$C(\mathbf{k},\tau) = \exp\left\{-\frac{k_BT}{2M}\mathbf{k}^2\tau^2\right\}. \tag{9}$$

As seen from expression (8), the friction tensors $\hat{\xi}^{(\mathbf{ab})}_{\alpha\beta}$ are symmetric in the cartesian indices α and β and of rank 2 in the wave vector and, thus, may have just six independent components. Furthermore, since these components only now depend on the positions of the *two* beads, these tensors can always be parametrized in terms of two parameters [10,11,22]

$$\hat{\xi}^{(\mathbf{ab})} = A(\Delta_{ab})\mathbf{I} + B(\Delta_{ab})\mathbf{q}^{(ab)} \otimes \mathbf{q}^{(ab)} \tag{10}$$

with $\mathbf{I}$ being the 3×3 unit tensor. In the expression (10), $\Delta_{ab} = |\mathbf{R}_a - \mathbf{R}_b|$ is the distance between the beads a and b and $\mathbf{q}^{(ab)} = \mathbf{R}_a - \mathbf{R}_b / \Delta_{ab}$ denotes a unit vector which points from bead b to bead a. From a physical view point, of course, this means that the reduced friction tensors merely depend on the *relative orientation* but not on the relative motion of the beads. As shown in the Appendix, the friction parameters can always be recast into the form

$$\begin{aligned} A(\Delta_{ab}) &= \frac{2n_0}{(2\pi)^2}\left[\int_0^\infty d\tau \int_0^\infty dk\, k^4 W(k)^2 C(\mathbf{k},\tau) g(\mathbf{k},\tau) \frac{j_1(k\Delta_{ab})}{k\Delta_{ab}}\right] \\ B(\Delta_{ab}) &= \frac{2n_0}{(2\pi)^2}\left[\int_0^\infty d\tau \int_0^\infty dk\, k^4 W(k)^2 C(\mathbf{k},\tau) g(\mathbf{k},\tau) \right. \\ &\quad \left. \times \left[\left(j_0(k\Delta_{ab}) - \frac{3}{k\Delta_{ab}} j_1(k\Delta_{ab})\right)\right]\right], \end{aligned} \tag{11}$$

where $j_0(x) = \sin x / x$ and $j_1(x) = (\sin x - x \cos x)/x^2$ denote the spherical Bessel functions of zero and first rank [30], respectively. In order to understand that these parameters still contain the information about the solvent, we may consider, for example, the case of a spherical single-bead molecule ($N=1$), for which the influence of the isotropic solvent should not depend on the direction of the motion and, hence, the friction tensor

$$\hat{\xi}^{\mathbf{aa}}_{\alpha\beta} = \xi_0 \mathbf{I}, \tag{12}$$

is expected to be a function of just a single parameter, called the self-friction coefficient of the molecule. Using the expressions (11) and (12) for the case $a=b$, we than find that the contribution of the second term of the friction tensor (5) with $B(\Delta_{aa}=0)$ is always zero. In contrast, the first contribution with $A(\Delta_{aa}=0)$ simply becomes a constant

$$\xi_0 = \frac{2n_0}{3(2\pi)^2}\int_0^\infty dk\, k^4 W(k)^2 \left[\int_0^\infty d\tau\, C(\mathbf{k},\tau) g(\mathbf{k},\tau)\right], \tag{13}$$

and was exploited recently in order to calculate the diffusion and boundary condition coefficients of the single-bead spherical heavy molecule immersed in a solvent [23].

Having the expressions (11) and (12) for the friction parameters of the N-bead macromolecule, we see that the influence of the solvent is entirely determined by the bead-solvent interaction potential W as well as by the dynamic structure factor of the solvent $g(\mathbf{k},\tau)$, which contains all the information about the properties of the solvent (such as temperature, viscosity, etc.). In the past years, therefore, studies of the dynamic structure factor attracted a lot of interest [27–29]. If, in addition, we assume the dynamical behaviour of the solvent to be determined by a diffusion equation, various expressions have been derived for the *time-dependence* of the dynamic structure factor of the solvent. For example, if we neglect the correlation between the solvent particles (i.e., for a noncorrelated solvent), the dynamic structure factor can be approximated by the simple analytical expression

$$g(\mathbf{k},\tau) = g(k)\exp[-\mathbf{k}^2 D_B \tau]. \tag{14}$$

which—via the static structure factor $g(k)$ and the self-diffusion coefficient of the solvent particle D_B—still contains the knowledge about the time-independent properties of the solvent (i.e., density fluctuations, correlation length, temperature, viscosity, etc.). Let us note here that, from a physical viewpoint, the omission of the correlation between the solvent particles is justified only for a low-density solvent. Apart from expression (14), another form of the dynamic structure factor for medium- and high-density solvents

$$g(\mathbf{k},\tau) = g(k)\exp[-\mathbf{k}^2 D_B \tau / g(k)]. \tag{15}$$

was derived from Smoluchowski-Vlasov equation [28] without that the correlation between the solvent particles was neglected. Instead, this Smoluchowski-Vlasov expression (15) was derived from a (so-called) *modified* version of the diffusion equation, in which the static correlation between the solvent particles is incorporated by means of a mean-force potential. As confirmed in molecular dynamics simulations [27,28], the Smoluchowski-Vlasov expression (15) describes the dynamic structure factor $g(\mathbf{k},\tau)$ well as all medium densities while it sometimes fails for high densities. In the latter case, the dynamic structure factor is better described by the Rayleigh-Brillouin expression [26,28,29]

$$g(\mathbf{k},\tau) = g(k)\left[\left(1 - \frac{1}{\gamma}\right)e^{-\mathbf{k}^2 D_T \tau} + \frac{1}{\gamma}\cos(c_s k\tau) e^{-\mathbf{k}^2 \Gamma \tau}\right], \tag{16}$$

where the solvent is treated as a viscoelastic continuum with the shear viscosity η and where, in contrast to the expressions (14) and (15), the (time-independent) properties of the solvent are characterized by the thermal diffusivity D_T, the ratio γ for the specific heat of the solvent, adiabatic sound velocity $c_s = \sqrt{\gamma k_B T / m g(0)}$ as well as by means of the constant Γ for attenuation of sound which in turn is given by $\Gamma = \frac{1}{2}[D_T(\gamma - 1) + 2\eta / n_0 m]$ [26]. Together, the three expressions (14)–(16) for the dynamic structure factor $g(\mathbf{k},\tau)$ describe the properties of the solvent at all density regimes, and, therefore, can be used to analyze the dynamical properties of the macromolecules immersed in the solvent. In our discussion below, however, we restrict ourselves to the Rayleigh–Brillouin expression (16) which, in addition to the high-density solvent, is also often used to describe the solvent properties near the (so-called) critical point (CP) of the solvent [26,29], i.e., when the temperature T and number density n_0 are around the critical values T_{cp} and $n_{0_{cp}}$, respectively. For this critical region, moreover, the time integral over the dynamic structure factor of the solvent and self-structure factor of the bead can be evaluate analytically

$$\begin{aligned}\tau(\mathbf{k}) &= \int_0^\infty d\tau\, g(\mathbf{k},\tau)C(\mathbf{k},\tau)\\ &= \frac{g(k)}{k}\sqrt{\frac{\pi M}{2k_BT}}e^{\mathbf{k}^2D_{\mathrm{T}}^2M/2k_BT}\left[1-\mathrm{erf}\left(\sqrt{\frac{M}{2k_BT}}\mathbf{k}D_{\mathrm{T}}\right)\right]\end{aligned} \tag{17}$$

by using the fact that the specific heat ratio $1/\gamma$ becomes negligible near the critical point. In this expression (17), erf denotes the error function which, for the variable x, is defined by

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x dy\, e^{-y^2}. \tag{18}$$

By using the expression (17) for the time integral, we are able now to bring the two friction tensor parameters $A(\Delta_{ab})$ and $B(\Delta_{ab})$ as well as single-bead friction coefficients into the form (cf. Appendix for details)

$$A(\Delta_{ab}) = \frac{2n_0}{(2\pi)^2}\int_0^\infty dk\, k^2 W(k)^2 \tau(k)\frac{j_1(k\Delta_{ab})}{(k\Delta_{ab})}, \tag{19}$$

$$\begin{aligned}B(\Delta_{ab}) = {}&\frac{2n_0}{(2\pi)^2}\int_0^\infty dk\, k^2 W(k)^2 \tau(k)\\ &\times\left(j_0(k\Delta_{ab}) - \frac{3}{(k\Delta_{ab})}j_1(k\Delta_{ab})\right),\end{aligned} \tag{20}$$

$$\xi_0 = \frac{2n_0}{3(2\pi)^2}\frac{1}{D_T}\int_0^\infty dk\, k^2 W(k)^2 \tau(k). \tag{21}$$

For sufficiently slow relaxation of the beads (when compared to the relaxation of the solvent particles), the tensor parameters (11) and (12) [for critical points (19)–(21), respectively]) still describe all the effects on the dynamics of the macromolecules which are caused by the solvent. In the following subsection, therefore, we make use of this form and of expression (16) in order to analyze the friction tensor parameters of the *N*-bead macromolecules for various common choices of the bead-solvent potential as well as for various choices of the solvent properties.

B. Behavior of the friction tensor parameters of the *N*-bead macromolecule

As seen from the explicit expressions (11) and (12), the friction parameters $A(\Delta_{ab})$ and $B(\Delta_{ab})$ of the macromolecule immersed into a solvent also depend on the static structure factor $g(k)$, in addition to the bead-solvent potentials W. Instead of this static structure factor, that contains the information about the time-independent properties of the solvent, however, one often uses the pair correlation function (PCF)

$$g(\mathbf{r}) = \frac{\langle\rho(\mathbf{r})\rho(0)\rangle}{\langle\rho\rangle^2}, \tag{22}$$

to describe the properties of a solvent with the local density $\rho(\mathbf{r})=\Sigma_{s=1}^{n}\delta(\mathbf{r}_s-\mathbf{r})$. In practice, of course, either the PCF or the statical structure factor can be used alternatively due to the well-known relation [11]

$$g(k) = 1 + 4\pi n_0\int_0^\infty dr[g(r)-1]j_0(kr). \tag{23}$$

To obtain further insight into the behavior of macromolecules in solutions, a Lennard-Jones solvent is often used for which the interaction among the solvent particles is modeled by a truncated Lennard-Jones (LJ) potential

$$V(r) = \begin{cases} 4\epsilon_B\left[\left(\dfrac{\sigma}{r}\right)^{12} - \left(\dfrac{\sigma}{r}\right)^{6} + v_0\right], & \text{if } r \leqslant r_B\\ 0, \quad \text{otherwise} \end{cases}. \tag{24}$$

In this potential, σ is the diameter of the solvent particles, v_0 is a constant, ϵ_B is the interaction strength, and r_B denotes the cut-off radius beyond of which the potential becomes zero. In order to illuminate the role of the various thermodynamical regimes of the solvent on the behavior of the macromolecule we will consider the solvent at the critical point as well as the high-density solvent which is far from criticality. For the critical LJ solvent we will take the constant $v_0=0$ and the cut-off radius $r_B=3.5$. Moreover, we will use the temperature $k_BT_{cp}\approx 1.2\epsilon_B$, the number density $n_{0_{cp}}\approx 0.30/\sigma^3$ [28,36], as well as the static structure factor which was taken from MDS [27]. For the high-density solvent which is far from criticality, in contrast, we will use the same thermodynamic properties as applied recently in the MD simulation by Dünweg and Kremer in Ref. [4] where the number density $n_0\sigma^3\approx 0.86$, the temperature $k_BT\approx 1.2\epsilon_B$, and the constant $v_0=0.25$ as well as the cut-off radius $r_B=\sqrt[6]{2}\sigma$.

These authors also displayed the PCF $g(\mathbf{r})$ of the high-density solvent, which was utilized in order to calculate the statical structure factor $g(k)$ by means of Eq. (23). Both functions are displayed in Fig. 1 and show that the structure factor can be divided into two parts. While for large values of modulus of the wave vector $k \geqslant 20\sigma$ (so-called short-wave part), the static structure factor is almost constant, $g(k)\approx 1$, it has large oscillations for the smaller values of k (long-wave part) due to the fact that dense solvent is a highly correlated system.

Let us now return to the friction parameters $A(\Delta_{ab})$ and $B(\Delta_{ab})$ which, apart from the static structure factor, depend, of course, on the interaction potential W between the solvent particles and the beads of the macromolecule. To understand their influence onto the internal dynamics of the macromolecule, a number of bead-solvent interaction potentials have been selected and utilized below in simulations. In the following, therefore, to model the influence of the solvent on the internal dynamics of macromolecules, a number of bead-solvent interaction potentials W have been suggested and utilized in simulations.

Most of these potentials were applied before in physical chemistry to simulate the various (chemical) environments [24]. For further analysis of how these environments may affect the dynamics of a *N*-bead macromolecule, we consider below the friction tensor parameters (19) and (20) for the

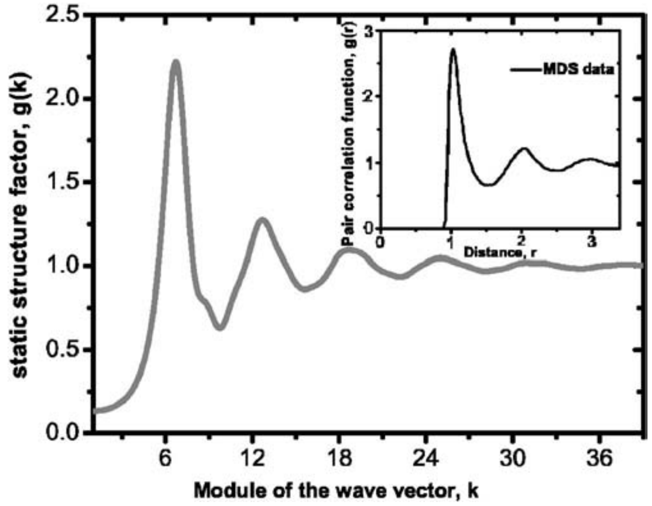

FIG. 1. Wave-vector dependence of the static (equilibrium) structure factor $g(k)$ of the solvent. The static (equilibrium) structure factor was obtained from expression (23) by using the MDS data from Ref. [4] for the pair correlation function. See text for further discussion.

following bead-solvent potentials: (i) Yukawa (screened Coulomb) potential [31], (ii) Born-Mayer potential [32] as well as for the three *Van der Waals–type* interactions as given by (iii) the Lennard-Jones potential [10,11], (iv) a short-range attractive approach to the Van der Waals interaction, [33] and (v) its Gaussian decomposition [34,35]. For these particular choices of the bead-solvent interaction [sf. Fig. 2], we will discuss the corresponding friction tensor parameters and the maximal "effective" distance between the beads up to which the hydrodynamic interaction cannot be neglected. A Yukawa (Y) potential is supposed to be appropriate in order to describe the repulsive interaction between charged particles, i.e., if—owing to the presence of the macromolecule in the solvent. This potential is given by

$$W^{\mathrm{Y}}(r) = \epsilon \frac{e^{-r/\sigma}}{r/\sigma}, \tag{25}$$

where ϵ is called the interaction strength and σ the decay (or Debye) length which characterizes these screening of the Coulomb repulsion. For dilute solutions, in contrast, the Born-Mayer (BM) potential

$$W^{\mathrm{BM}}(r) = \epsilon e^{-r/\sigma} \tag{26}$$

is often taken to be more suitable, which is still repulsive but at a lower rate for $r \rightarrow 0$ [cf. Fig. 2(a)]. Making the Fourier transform of the bead-solvent potentials, we are now able to calculate immediately the friction tensor parameters $A(\Delta_{ab})$ and $B(\Delta_{ab})$ of the macromolecule by using the expressions (11) and (12) as well as the static structure factor $g(k)$ of the high-density solvent as obtained in Fig. 1. Lets us note that, in our calculations, we consider the case when the bead mass is only twice more than the mass of solvent particle, i.e., $M=2m$.

Figure 3 displays the dependence of the (normalized) parameters of the friction tensor $A(\Delta_{ab})/\xi_0$ and $B(\Delta_{ab})/\xi_0$ as a function of (dimensionless) variable Δ_{ab}/σ, measuring the distance between the beads in terms of the characteristic decay length of the potential. A rather different behavior of the friction tensor parameters occurs for the two interaction potentials. While, for a Yukawa potential, the beads do not affect each other anymore for a distance of, say 6σ, they will interact at this or even larger distances in the case of a Born-Mayer potential.

Apart from the dependence on the bead-solvent potential, Fig. 3 also demonstrates that the friction parameters depend rather strongly on the oscillating nature of the static structure for the $k \leqslant 20\sigma$ of the solvent. As seen from Fig. 3, the oscillating of $g(k)$ for small values of k leads to the *qualitative* different behavior [sf. Fig. 3(a)] than obtained in the CP region of the solvent where oscillating of $g(k)$ is not so large [sf. Fig. 3(b)] as well as the high-frequency approximations of the static structure factor where $g(k)=1$ is assumed constant [(Fig. 3(c))].

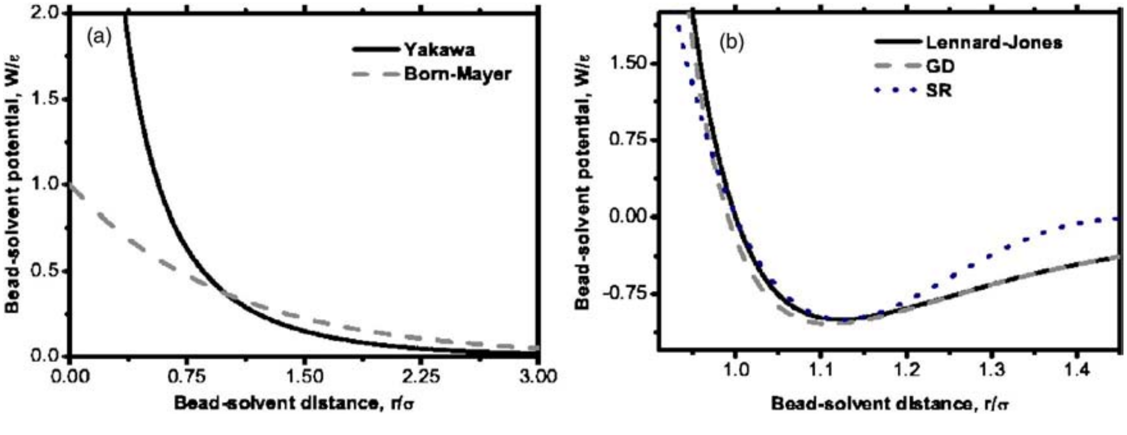

FIG. 2. (Color online) Different bead-solvent potentials to describe the influence of the solvent particles on the dynamics of the macromolecules. (a) Yukawa (25) and Born-Mayer potential (26) and (b) three commonly applied bead-solvent potentials (27)–(29) to model the *long-range* Van der Waals interaction; see text for further discussion.

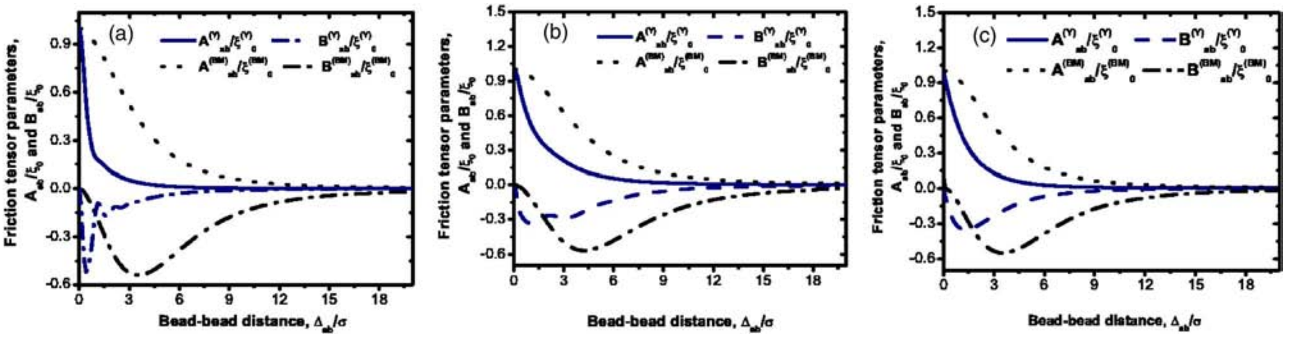

FIG. 3. (Color online) Normalized friction tensor parameters A/ξ_0 and B/ξ_0 as function of the bead-bead distance Δ_{ab}; [cf. Eqs. (11) and (12)]. They are shown for a Y and BM bead-solvent potential. These friction parameters are shown for three cases: (a) the long-wave part ($k \to 0$) of the statical structure factor of the high-density solvent $g(k)$ was taken into account [see Fig. 1]; (b) the same as (a) but for the solvent at the critical point; (c) only short-wave parts ($k \gg 0$) of the statical structure factor of the high-density solvent [$(g(k)=1)$] was taken into account. See text for further discussion.

Apart from a purely repulsive interaction (as discussed above), the interaction between the molecular beads and the particles from the solvent is often modeled also by some long-ranging *Van der Waals* interaction. This interaction usually combines a strong *repulsive* part of the potential at small distances with a (weak) *attractive* part for a large separation of the solvent particles from the beads. Owing in particular to their frequent use in MDS, below we distinguish three cases of such Van der Waals-type interactions including the Lennard-Jones (LJ) potential [10,11]

$$W^{\mathrm{LJ}}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{27}$$

the short-range attractive (SR) or so-called SHRAT potential [33]

$$W^{\mathrm{SR}}(r) = \begin{cases} \dfrac{512}{27}\epsilon\left(1-\dfrac{\sigma}{r}\right)\left(3-2\dfrac{\sigma}{r}\right)^{3}, & \text{if } r \leqslant \dfrac{3}{2}\sigma \\ 0, & \text{if } r > \dfrac{3}{2}\sigma. \end{cases} \tag{28}$$

as well as a Gaussian decomposition (GD) of the Van der Waals interaction [34,35] [see Fig. 1(b)]:

$$W^{\mathrm{GD}}(r) = \epsilon\sum_{i=1}^{4} a_i e^{-b_i/2(r/\sigma)^2}. \tag{29}$$

In all these potentials, the constants ϵ and σ determine again the characteristic strength and decay length of the potential. For the Gaussian decomposition of the Lennard-Jones potential, the parameters a_i and b_i are listed in Table I.

TABLE I. Parameters for the Gaussian decomposition (GD) of the Van der Waals interaction owing to Eq. (29).

$a_1=846706.7$	$b_1=30.92881$
$a_2=2713.651$	$b_2=14.96375$
$a_3=-0.7154420$	$b_3=1.279242$
$a_4=-9.699172$	$b_4=3.700745$

Besides the commonly applied Lennard-Jones potential, the short-range approximation and Gaussian decomposition of the Van der Waals interaction were mainly introduced with the aim to facilitate the numerical computations in the MDS simulations. Figure 4 displays the (normalized) friction tensor parameters $A(\Delta_{ab})/\xi_0$ and $B(\Delta_{ab})/\xi_0$ for the Lennard-Jones, the short-range, and the Gaussian decomposition (bead-solvent) potentials as a function of the separation Δ_{ab} between the beads a and b. They have been determined numerically along a one-dimensional grid for the bead-solvent potentials (27) and (29).

From Fig. 4, we again see that the tensor parameters $A(\Delta_{ab})/\xi_0$ and $B(\Delta_{ab})/\xi_0$ appear very sensitive to the explicit form of the bead-solvent potential as well as to the long-wave part of the static structure factor $g(k)$ of the solvent. When compared with the parameters from the Yukawa and Born-Mayer potentials [cf. Fig. 2], moreover, $A(\Delta_{ab})$ decays rapidly to zero within about 1.5σ for any of the three Van der Waals–type interactions while, for the Yukawa and Born-Mayer potentials, a nonvanishing friction force occurs up to about 5σ or even 10σ. Let us note, moreover, that when we assumed the short-wave approximation for the statical structure factor [$g(k)=1$] only, we can evaluate the expressions (19) and (20) for the friction tensors analytically for the most part of the bead-solvent potential. For the sake of brevity, however, here we omit all the details of this computation. Finally, by comparing Figs. 1(b) and 3, we see that only the *repulsive* part of the interaction is generally responsible for the behavior of the friction tensor parameters.

The friction tensor is one of the *key* ingredients for studying the dynamical properties of macromolecules in solutions. It affects not only the relaxation time (in order to return back from a nonequilibrium into the equilibrium state) or the velocity autocorrelation function of the macromolecule but also its end-to-end vector and radius of gyration.[18,22] In addition to the internal properties of the macromolecular behavior the friction tensors also effects on the dynamical behavior of the macromolecule as a whole are discussed. In the next section, therefore, we make use of the friction tensor in Eq. (5) in order to derive the center-of-mass (cm) friction coefficient of a *N*-bead macromolecule. Information about this coefficient will later help us understand the motion of the

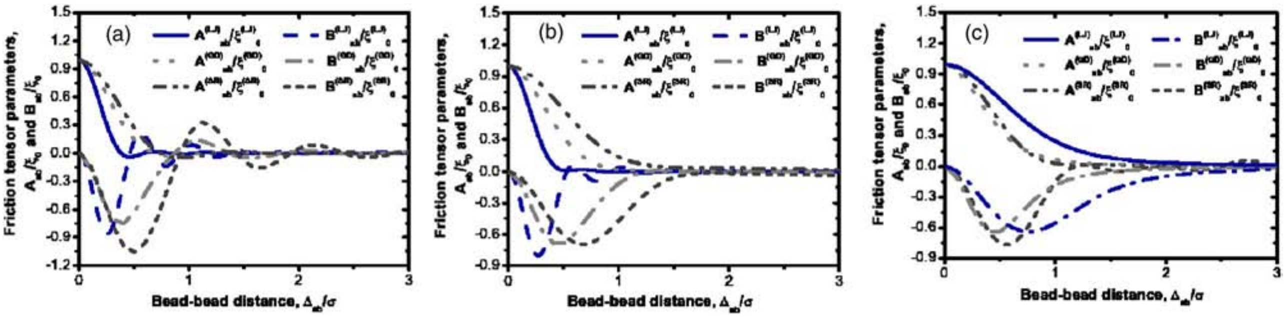

FIG. 4. (Color online) The same as in Fig. 2 but here displayed for the Lennard-Jones (LJ), the short-range approach (SR), and for a Gaussian decomposition (GD) of the bead-solvent potential. See text for further discussion.

macromolecule as a whole within the solvent.

III. CENTER-OF-MASS FRICTION COEFFICIENT OF THE *N*-BEAD MACROMOLECULE

Since, in the following, we are only interested in the dynamics of the macromolecule as a whole, let us return to the Fokker-Planck equation (1) for the phase-space distribution function for the macromolecule and start with separating the cm and the internal (Q) motion of the macromolecule from each other. Instead of the cartesian coordinates $\mathbf{R}_{\rm a}$, $\mathbf{P}_{\rm a}$, $a=1,\ldots,N$ of the individual beads, or course, we then make better use of the center-of-mass and the relative coordinates. For N beads of equal mass, the center-of-mass coordinates are given by

$$\mathbf{R}_{\rm cm} = \frac{1}{N}\sum_{a=1}^{N} \mathbf{R}_a, \quad \mathbf{P}_{\rm cm} = \frac{1}{N}\sum_{a=1}^{N} \mathbf{P}_a \tag{30}$$

while we will use

$$\mathbf{Q}_{\rm a} = \mathbf{R}_{\rm a} - \mathbf{R}_{\rm a+1}, \quad \mathbf{P}_{\mathrm{Q}_{\rm a}} = \mathbf{P}_{\rm a} - \mathbf{P}_{\rm a+1}, \tag{31}$$

for the remaining $2(N-1)$ relative coordinates, assuming the N beads form a chain. In addition, if the internal dynamics of the macromolecule does not depend on its particular position within the solution, we may suppose that the phase-space distribution function $\rho_N(\mathbf{\Gamma};\mathbf{t})$ of the N-bead macromolecule factorizes (once more) into

$$\rho_N(\mathbf{\Gamma};t) = \phi(\mathbf{R}_{\rm cm},\mathbf{P}_{\rm cm};t)\,\psi(\{\mathbf{Q}_a,\mathbf{P}_{Q_a}\};t), \tag{32}$$

where $\phi(\mathbf{R}_{\rm cm},\mathbf{P}_{\rm cm};t)$ is the distribution function of the center-of-mass coordinate and $\psi(\{\mathbf{Q}_a,\mathbf{P}_{Q_a}\};t)$ the phase-space distribution of the internal motion, sometimes briefly refereed to as the configuration-space distribution function (again) of the macromolecule. In line with Eq. (2), both of these distribution functions are taken to be normalized

$$\int d\mathbf{R}_{\rm cm} d\mathbf{P}_{\rm cm}\,\phi(\mathbf{R}_{\rm cm},\mathbf{P}_{\rm cm};t) = 1 \tag{33}$$

and

$$\int d\{\mathbf{Q}_a,\mathbf{P}_{Q_a}\}\,\psi(\{\mathbf{Q}_a,\mathbf{P}_{Q_a}\};t) = 1, \tag{34}$$

respectively.

With the separation (32) for $\rho_N(\mathbf{\Gamma};t)$ at hand, it can be shown that the center-of-mass distribution function $\phi(\mathbf{R}_{\rm cm},\mathbf{P}_{cm};t)$ obeys a Fokker-Planck Equation similar to Eq. (1) above. Inserting (32) into (1) and by making use of the chain rule for a few times, we then find that the cm distribution function $\phi \equiv \phi(\mathbf{R}_{\rm cm},\mathbf{P}_{\rm cm};t)$ fulfills the equation

$$\frac{\partial \phi}{\partial t} + \frac{\mathbf{P}_{\rm cm}}{M}\frac{\partial \phi}{\partial \mathbf{R}_{\rm cm}} = \frac{1}{N}\frac{\partial}{\partial \mathbf{P}_{(\rm cm)}}\xi_N^{\rm cm}\left(\frac{1}{N}\frac{\partial}{\partial \mathbf{P}_{\rm cm}} + \frac{1}{k_B T M}\mathbf{P}_{\rm cm}\right)\phi \tag{35}$$

which we call the Fokker-Planck equation for the center-of-mass motion of the macromolecule below. On the right-hand side of this equation,

$$\xi_N^{(\rm cm)} = \left(\sum_{a,b=1}^{N}\frac{1}{3}\,\mathrm{Tr}\left[\langle \boldsymbol{\xi}^{(ab)}\rangle\right]\right) \tag{36}$$

denotes the center-of-mass friction coefficient for the corresponding (cm) motion of the molecule, including the trace over the friction tensor (5), $\mathrm{Tr}[\hat{\xi}^{(ab)}]$, and by taking the average

$$\langle \ldots \rangle \equiv \frac{\int d\{\mathbf{P}_{Q_a},\mathbf{Q}_a\}\ldots\psi(\{\mathbf{P}_{Q_a},\mathbf{Q}_a\};t)}{\left[\int d\{\mathbf{P}_{Q_a},\mathbf{Q}_a\}\psi(\{\mathbf{P}_{Q_a},\mathbf{Q}_a\};t)\right]} \tag{37}$$

over all the internal coordinates. Of course, we may now combine the general form (36) with the previously derived expressions (5) for the instantaneous friction tensor in order to obtain an expression for the cm friction coefficient of the N-bead macromolecule

$$\xi_N^{(\rm cm)} = \frac{n_0}{3}\left[\int_0^\infty d\tau \int \frac{d\mathbf{k}}{(2\pi)^3}\mathbf{k}^2 W(\mathbf{k})^2 \times \left\langle \sum_{a,b=1}^{N} e^{i\mathbf{k}\cdot\mathbf{R}_a}e^{-i\mathbf{k}\cdot\mathbf{R}_b}\right\rangle g(\mathbf{k},\tau)\right]. \tag{38}$$

As seen from expression (38), the cm friction coefficient fully describes—via the dynamic structure factor $g(\mathbf{k},\tau)$ and the bead-solvent potential W—the influence of the solvent on the center-of-mass motion of the macromolecule. Moreover, the cm friction coefficient implicitly also depends—owing to the average (37) over the internal coordinates of the macromolecule—on the bead-bead potential U and can be used in order to further study the macromolecular properties as a whole.

A further simplification of the cm friction coefficient $\xi_N^{(\mathrm{cm})}$ in expression (38) is obtained, moreover, from the observation that the expression $\langle \Sigma_{a,b=1}^{N} e^{i\mathbf{k}\cdot\mathbf{R}_a} e^{-i\mathbf{k}\cdot\mathbf{R}_b} \rangle$ is nothing else but the *(dynamic) structure factor* of the N-bead macromolecule [4,10,11]

$$S_N(k,\tau) = \frac{1}{N}\left\langle \sum_{a,b=1}^{N} e^{i\mathbf{k}\cdot\mathbf{R}_a} e^{-i\mathbf{k}\cdot\mathbf{R}_b(\tau)} \right\rangle . \tag{39}$$

Therefore, by combining the expressions (38) and (39), we finally obtain the center-of-mass friction coefficient of the larger N-bead macromolecule

$$\xi_N^{(\mathrm{cm})} = \frac{n_0}{3} N \int_0^{\infty} \frac{d\mathbf{k}}{(2\pi)^3} \left[\int_0^{\infty} d\tau\, \mathbf{k}^2 W(\mathbf{k})^2 S_N(\mathbf{k},\tau) g(\mathbf{k},\tau) \right] \tag{40}$$

in terms of the measurable parameters of the system "macromolecule plus solvent." As seen from the expression (40), the center-of-mass friction coefficient depends on both, the structure factor describing both the geometrical configuration as well as dynamical properties of the macromolecule and the dynamic structure factor which contain all the information about the solvent. This is the key result of the present section since the knowledge of the center-of-mass friction coefficient therefore plays quite a central role for understanding the motion of macromolecules in solution. Instead of the cm friction coefficient, however, it is often more convenient to use the center-of-mass diffusion coefficient of the macromolecule which are related to each other by

$$D_N^{(\mathrm{cm})} = k_B T / \xi_N^{(\mathrm{cm})} . \tag{41}$$

In the next section, we will use this relation (41) for calculating the center-of-mass diffusion coefficient of the macromolecule as a function of the number of beads, N, and for comparing its behavior with results as obtained from molecular-dynamics simulations.[4,5]

IV. COMPARISON WITH RESULTS FROM MDS

Recently, a number of dynamic simulations (DS), such as Brownian DS, molecular DS, etc. have been carried out for studying the dynamical properties of macromolecules in solution.[4–8,24] In these case studies, the main emphasis was placed on the translational center-of-mass diffusion coefficient, dynamic and statical structure factors as well as the velocity autocorrelation function of the macromolecule in the solvent. These numerical investigations are, however, useful for comparison as shown in Fig. 4 for the center-of-mass diffusion coefficient of the macromolecule. Results from our semiphenomenological computations are compared with MDS data by Dünweg and Kremer [4] and Ahrichs and Dünweg [5] as well as with calculations from the Rouse phenomenological theory [10,11], respectively. In addition, we also compared our computations with two calculations from the Zimm phenomenological theory as found in the literature. These calculations differed, however, with respect to their description of the hydrodynamic interaction, with "preaveraging" [10,11] and "fluctuating" (nonpre-averaging) [7] hydrodynamic interactions, respectively. In these computations, the molecules were modeled by a N-bead polymer spring with a finitely expandable nonlinear elastic (FENE) potential [18] among the neighboring beads, while a "truncated" Lennard-Jones potential

$$W^{\mathrm{LJ}}(r) = \begin{cases} 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4}\right], & \text{if } r \leqslant 2^{\frac{1}{6}}\sigma \\ 0 \quad \text{otherwise}, \end{cases} \tag{42}$$

was taken for their interaction with the solvent particles (solvent plus macromolecule).

In the MD simulations of Refs. [4,5] the solvent was modeled by hard-sphere particles with a number density $n_0\sigma^3 = 0.86$ and taken from a temperature $k_B T = 1.2\epsilon_S$. This refers to the rather high density and, hence, the (so-called) exclude volume interaction is considered to be screened.[4,5,37] For the same reason, we can assume that the time-independent (static) properties of the macromolecular chain can be described—at least as the first step—by the Gaussian form of the internal phase-space distribution function $\phi(\{\mathbf{P}_{Q_a}, \mathbf{Q}_a\}; t)$ (so-called *Gaussian approximation*).[38] Of course, in such a Gaussian chain the bead-bead potential is simply given by [10,11]

$$U = \frac{3k_B T}{2b^2} \sum_{a=1}^{N-1} \mathbf{Q}_a^2 , \tag{43}$$

where $b^2 = \langle \mathbf{Q}_a^2 \rangle$ denotes the mean square bond length. As expected from previous experience [25,37], moreover, only small differences appear for the properties of the macromolecule if modeled in terms of a FENE or HOOKEAN (43) bead-bead potential. From a physical view point, of course, the Gaussian approximation is of particular interest for the macromolecules behavior near the Θ-point,[11] where the excluded volume interaction is *totally* screened. The same method for calculating the friction tensor, however, can be used to describe macromolecules in those solutions which are fairly away from the Θ-point and for which the macromolecule is either in a collapsed state (bad solvent) or given a dilute chain (good solvent).

The center-of-mass friction coefficient $\hat{\xi}_N^{(cm)}$ from expression (40) still depends on the dynamic structure factor of the macromolecule. For its further simplification, we may therefore use the approximate form of the dynamic structure factor for a macromolecular chain

$$S_N(\mathbf{k},\tau) = S_N(\mathbf{k}) e^{-\mathbf{k}^2 \tau / \xi_0 N} \tag{44}$$

which is expected to provide a fairly sensible description of the dynamic structure factor [10,11]. In this expression (44), $S_N(\mathbf{k})$ is used to denote the *static* structure factor of the N-bead macromolecule. Following [10], we use use the Debye's form of the statical structure factor

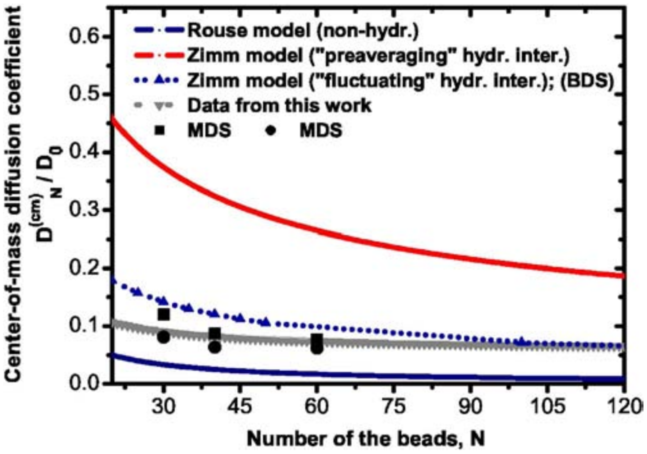

FIG. 5. (Color online) Center-of-mass diffusion coefficient $D_N^{(\mathrm{cm})}$ as function of N, the number of beads in the macromolecule. The results from this work for "truncated" Lennard-Jones potential (42) (triangles) are compared with the MDS data from Ref. [4] (squares) and Ref. [5] (circles) as well as with the theoretical data from the Rouse model (solid line) and from the Zimm model with "preaveraging" (dots line) and "fluctuating" hydrodynamic interactions (BDS data) from Ref. [7] (triangles + dots line). See text for further discussion.

$$S_N(k) = \frac{N}{1 + \frac{1}{2}k^2 R_N^G} \tag{45}$$

which characterizes the quantity of the scattering intensity of the N-bead macromolecules in the regime $k \ll l^{-1}$ (l being a microscopic length of the order of a bondlength). In expression (45), moreover, we use R_N^G in order to denote the radius of gyration on the N-bead macromolecule, i.e., $R_N^G = \Sigma_{a,b=1}^{N} \langle (\mathbf{R}_a - \mathbf{R}_b)^2 \rangle / (2N^2)$. From previous numerical MDS investigations,[4] a fit formula for the radius of the gyration of the N-bead macromolecule immersed in the solvent

$$R_N^G = 0.54(N-1)^{0.53} \tag{46}$$

were determined rather accurately. Inserting the expressions (9) and (16) as well as (40) and (46) into (41) and using the data (cf. Fig. 1) for the static structure factor $g(k)$ of the solvent, we may calculate directly the self-diffusion coefficient D_0 of the bead of macromolecule as well as the center-of-mass diffusion coefficients for a given number $N=30$, 40, or 60 beads. Figure 5 shows the normalized cm diffusion coefficient $D_N^{(\mathrm{cm})}/D_0$ as function of N and in comparison with the available MDS data [4,5] as well as with the phenomenological theory data.[10,11] Good agreement is found, in particular, with the simulations by Dünweg and Kremer [4] for $N=40$ as well as $N=60$ and with some deviation only at $N=30$. In addition, as seen from the Fig. 5, the data, which was calculated from the Rouse phenomenological theory, are always smaller and can give only the *qualitative* information about the behavior of the cm diffusion coefficient for the N-bead macromolecule. While, moreover, the Zimm model with "preaveraging" hydrodynamic interactions predicts the result which is also far from the MDS data, the Zimm model with "fluctuating" hydrodynamic interactions (Brownian DS data) can give the *quantitative* information about the behavior of the cm diffusion coefficient for the N-bead macromolecule but only if the number of the beads $\geqslant 110$. It demonstrates that the semiphenomenological methods help understand and calculate the friction and further properties sometimes without that extensive molecular DS studies become necessary.

V. CONCLUSIONS

The influence of the bead-solvent interaction on the dynamics of macromolecules, that are immersed into a solution, has been investigated in detail by starting from a Fokker-Planck equation for their phase-space distribution function. In this picture, the macromolecules is taken as a *set of beads* which are coupled to each other by some pairwise potential and surrounded by—a large number of—solvent particles. There are two realistic assumptions which were made in our investigations: Since (i) the mass of the molecule as a whole is considered to be much larger than the mass of the solvent particles, we may assume (ii) that the relaxation of the solvent also proceeds much faster in time than when compared to the macromolecules. These two assumptions are made very frequently in studying the behavior of macromolecules in solutions.[10,11,18,22,25]

For the two basic assumptions from above, the dynamics of the macromolecule is determined purely by the "friction tensors" that appear on the right-hand side of the FPE and which can be expressed in terms of the bead-solvent interaction potential as well as the dynamic structure factor of the solvent. Using the explicit expression, as obtained earlier for the friction tensors of the molecule in solution, we then show that the behavior of the friction tensor parameters depend on the distance between the beads as well as on the thermodynamic regime of the solvent. Computation has been carried out for the five cases of (i) a Yukawa, (ii) the Born-Mayer, and (iii)-(v) various types of Van der Waals interaction between the molecular beads and the solvent particles. For each of these interaction potentials, the behavior of the friction tensor parameters has been calculated and discussed in detail for high-density as well as for critical solvent.

To further understand the effect of the bead-solvent potential on the center of mass of macromolecules, we have derived the general expression for the center-of-mass friction coefficient of the larger N-bead macromolecule. This expression is given in terms of the dynamic structure factor of the macromolecule and of the dynamic structure factor of the solvent.

Finally, by using the Einstein relation, we are able to calculate and compare our results for the center-of-mass diffusion coefficient with molecular dynamic simulation works [4,5] as well as with the phenomenological data. Good agreement with MDS data is found for all N and, in particular, for large chains. We therefore believe that this method can be used also to compute other statical and dynamical properties of the macromolecules and the solvents with different properties: neutral chain, charge chain, etc.

APPENDIX: FRICTION TENSOR IN POLAR COORDINATES.

To find a simple parametrization for the friction tensors of the *N*-bead (chain) macromolecule, which is immersed into a solution, let us start from the expression (8) for the momenta averaged friction tensor.

For a spherical-symmetric (bead-solvent) interaction, it was shown that the momenta averaged tensor components of the macromolecule can be expressed in terms of the Fourier transform of the bead-solvent potential $W(\mathbf{k})$, the (so-called) dynamic structure factor $g(\mathbf{k},\tau)$ of the solvent and the correlation function of the momenta of the beads $C(\mathbf{k},\tau)$ as

$$\hat{\boldsymbol{\xi}}^{(ab)} = n_0 \int \frac{d\mathbf{k}}{(2\pi)^3}\left[\int_0^\infty d\tau\, \mathbf{k}\otimes\mathbf{k}\, W(\mathbf{k})^2 e^{i\mathbf{k}\cdot\mathbf{R}_a} e^{-i\mathbf{k}\cdot\mathbf{R}_b} r(\mathbf{k},\tau)\right], \tag{A1}$$

for $a,b=1,\ldots,N$. Here we introduce the function $r(\mathbf{k},\tau) = C(\mathbf{k},\tau)g(\mathbf{k},\tau)$. Apparently, the tensor (A1) is symmetric and of rank 2 and, thus, may have six independent components. Since, in addition, these components only depend on the position of the two beads, they can always be parametrized in terms of just two parameters [10,11,22] and written in the form

$$\hat{\xi}^{(\mathbf{ab})} = A(\Delta_{ab})\mathbf{I} + B(\Delta_{ab})\mathbf{q}^{(\mathbf{ab})} \otimes \mathbf{q}^{(\mathbf{ab})} \tag{A2}$$

where $\Delta_{ab}=|\mathbf{R}_a-\mathbf{R}_b|$ denotes the distance of the two beads and $\mathbf{q}^{(ab)}$ the unit vector which points from bead b to bead a. We can evaluate the functions $A(\Delta_{ab})$ and $B(\Delta_{ab})$ by taking (i) the trace of the tensor $\hat{\xi}^{(ab)}_{\alpha\beta}$ from Eq. (A1)

$$\begin{aligned}\mathrm{Tr}(\hat{\xi}^{(\mathbf{ab})}) &\equiv 3A(\Delta_{ab}) + B(\Delta_{ab}) \\ &= n_0 \int \frac{d\mathbf{k}}{(2\pi)^3}\left[\int_0^\infty d\tau\, \mathbf{k}^2 W(\mathbf{k})^2 e^{i\mathbf{k}\cdot\mathbf{R}_a} e^{-i\mathbf{k}\cdot\mathbf{R}_b} r(\mathbf{k},\tau)\right],\end{aligned} \tag{A3}$$

and (ii) by multiplying both sides of Eqs. (A1) and (A2) with $q^{(ab)}_\alpha q^{(ab)}_\beta$, along with a summation over α and β,

$$\begin{aligned}\sum_{\alpha,\beta=1}^{3} (\hat{\xi}^{(ab)}_{\alpha\beta}) q^{(ab)}_\alpha q^{(ab)}_\beta &\equiv A(\Delta_{ab}) + B(\Delta_{ab}) \\ &= n_0 \int \frac{d\mathbf{k}}{(2\pi)^3}\left[\int_0^\infty d\tau (\mathbf{kq})^2 W(\mathbf{k})^2 e^{i\mathbf{k}\cdot\mathbf{R}_a} e^{-i\mathbf{k}\cdot\mathbf{R}_b} r(\mathbf{k},\tau)\right].\end{aligned} \tag{A4}$$

Using polar coordinates for the representation of the wave vector $\mathbf{k}=(k,\vartheta_{\mathbf{k}},\varphi_{\mathbf{k}})$ and by carrying out the integration over the angles $\vartheta_{\mathbf{k}}$ and $\varphi_{\mathbf{k}}$ explicitly, the two Eqs. (A3) and (A4) then become

$$3A(\Delta_{ab}) + B(\Delta_{ab}) = \frac{2n_0}{(2\pi)^2}\int_0^\infty dk\, k^4 W(k)^2 \times \left[\int_0^\infty d\tau\, r(\mathbf{k},\tau) j_0(k\Delta_{ab})\right] \tag{A5}$$

and

$$A(\Delta_{ab}) + B(\Delta_{ab}) = \frac{2n_0}{(2\pi)^2}\int_0^\infty dk\, k^4 W(k)^2 \left[\int_0^\infty d\tau\, r(\mathbf{k},\tau) \times \left(j_0(k\Delta_{ab}) - \frac{2}{(k\Delta_{ab})} j_1(k\Delta_{ab})\right)\right], \tag{A6}$$

where

$$j_0(x) = \frac{\sin x}{x}, \quad j_1(x) = \frac{\sin x}{x} - \cos x$$

are the two lowest spherical Bessel functions.

We can solve the system of two equations (A5) and (A6) and finally obtain an explicit expression for the friction tensor components $A(\Delta_{ab})$ and $B(\Delta_{ab})$ as function of the distance between the two beads

$$A(\Delta_{ab}) = \frac{2n_0}{(2\pi)^2}\int_0^\infty dk\, k^4 W(k)^2 \left[\int_0^\infty d\tau\, r(\mathbf{k},\tau)\frac{j_1(\mathbf{k}\Delta_{ab})}{(\mathbf{k}\Delta_{ab})}\right] \tag{A7}$$

$$B(\Delta_{ab}) = \frac{2n_0}{(2\pi)^2}\int_0^\infty dk\, k^4 W(k)^2 \left[\int_0^\infty d\tau\, r(\mathbf{k},\tau)\left(j_0(k\Delta_{ab}) - \frac{3}{(k\Delta_{ab})} j_1(k\Delta_{ab})\right)\right] \tag{A8}$$

given as integrals over the modulus k of the wave vector. By using now the explicit for the function $r(\mathbf{k},\tau)$, we can obtain the expressions (11) and (12) for the friction parameters. As mentioned before, it is this representation of the friction tensor which has been used above in Sec. II to analyze the effects of the bead-solvent potential on the internal properties of the macromolecule and to find further insight into the dynamics of macromolecules.

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PAPER V

Restricted rotational diffusion of non–rigid macromolecules on surfaces: Effects of the bead–bead and bead–surface interaction.

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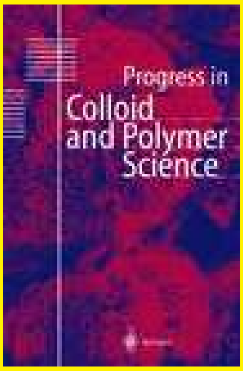

Restricted rotational diffusion of non-rigid dumbbell-type macromolecules on surfaces:

Effects of the Bead - Bead and Bead - Surface interaction.

Alexander Uvarov (✉) and Stephan Fritzsche

Institut für Physik, Universität Kassel, Heinrich – Plett – Str. 40, D – 34132 Kassel, Germany

e-mail: uvarov@physik.uni-kassel.de
Tel.: +49 (0)561 804 4556
Fax.: +49 (0)561 804 4006

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Abstract A recently derived Diffusion equation [Uvarov A, Fritzsche S, (2004) J. Chem. Phys. 121(13):6561] is utilized to analyze the restricted rotational motion of macromolcules in solution if they are immobilized on a surface. Both, the bead-bead and bead-surface interactions are taken into account in order to describe the orientational dynamics of non-rigid macromolecules and its relaxation in time after a perturbation has occured. Using several realistic bead – bead and bead – surface potentials, detailed numerical investigations have been carried out for the rotational diffusion coefficient as well as for the conformational phase - space distribution function of the macromolecules. From this phase-space distribution, the orientational correlation function are derived and compared with phenomenological computations from the literature. Such correlation function can be observed in dielectric relaxation and fluorescence depolarization experiments.

Key words *correlation functions, diffusion equation, immobilized molecule, rotational diffusion, orientational relaxation*

I. Introduction

Accurate dynamical studies on macromolecules in solution are still a challenge for modern DNA and protein research. During the past decade, therefore, a large number of experiments have been carried out in order to understand the translational and rotational motion as well as the shape formation and deformation processes of such molecules. Apart from free macromolecules in solution [1,2], these experiments concerned in particular the restricted mobility of macromolecules which are immobilized on a surface [3-6]. On the theoretical side, moreover, several (often quite large) Molecular and Brownian dynamical simulations [7-11] as well as analytical case studies have been performed [12-15].

In all these investigations, the macromolecules are usually described by means of their molecular subsystems to which we refer below as the beads of the macromolecule. When immersed into a solvent and immobilized onto a surface, of course, the shape and the orientation relaxation dynamics of the macromolecules will be determined not only by the interaction of the beads with the surrounding solvent but also by the interaction among their (neighboring) beads as well as with the surface.

In the present contribution, emphasis is placed on the internal rotational dynamics of macromolecules which are immersed into a solution. In contrast to most previous investigations, in which more often than not a rigid molecule was assumed [16-20], here we consider the rotational dynamics of a non – rigid macromolecule as described recently by us in Ref. [21]. In particular, we explore the question of how the bead – bead as well as bead – surface interactions affect the (restricted) rotational diffusion of such molecules at a surface. In the next section, we start with a brief outline and the basic assumptions which are made for the "non-rigid macromolecule on a surface" in order to derive the diffusion equation for the time evolution of its configuration-space distribution function. These expressions are later utilized in section III to obtain the rotational diffusion coefficient as well as the orientation correlation function for an "extended" dumbbell molecule. Here, the results from our 'semi-phenomenological' theory are compared with computations from Doi and Edwards [12,13] which are based on a rigid-rod model of the macromolecule; finally, a few conclusion are given in section IV.

II Basic Model Equations and Computations

Since we are interested mainly on the internal rotational dynamics of macromolecules and on how the bead-bead and bead-solvent interactions affects their dynamics, let us start from the Diffusion equation (DE)

$$\begin{aligned}\frac{\partial \psi}{\partial t} &= D_{\perp}^{(Q)}\left[\Delta\psi + \beta\psi\,\Delta U + \nabla\psi\cdot\nabla U\right] + \left(D_{\parallel}^{(Q)} - D_{\perp}^{(Q)}\right)\left[\frac{\partial^2 \psi}{\partial Q^2} + \beta\psi\frac{\partial^2 U}{\partial Q^2} + \beta\frac{\partial \psi}{\partial Q}\frac{\partial U}{\partial Q}\right] \\ &+ \left(\frac{\partial D_{\perp}^{(Q)}}{\partial Q} + \frac{2\left(D_{\parallel}^{(Q)} - D_{\perp}^{(Q)}\right)}{Q}\right)\left[\frac{\partial \psi}{\partial Q} + \beta\,\psi\frac{\partial U}{\partial Q}\right]\end{aligned} \tag{1}$$

as derived recently for the time evolution of the configuration – space distribution function $\psi = \psi\left(\vec{Q};t\right)$ of a dumbbell molecule. In this equation, Q denotes the length of the end-to-end vector $\vec{Q}$ of the two beads (with radius σ) of a dumbbell molecule while Δ is the Laplacian in a coordinate-free notation and $\beta = 1/k_B T$ the (inverse) temperature of the overall system. In Ref. [21], this diffusion equation was obtained by starting from a Fokker-Planck equation for the phase – space distribution function of the N - bead macromolecule. However, to remove the explicit dependence of this equation from the momenta of the molecular beads, a number of assumptions had to be made about the dynamical behaviour of macromolecules on a surface. Apart from (i) a fast relaxation of the velocities of the molecular beads (when taken relative to the relaxation of their position), here we assumed (ii) that all the effects of the solvent onto the dynamics of the macromolecule can be well described by means of the parallel $D_{\parallel}^{(Q)}$ and perpendicular $D_{\perp}^{(Q)}$ components of the 'diffusion tensor' of the internal motion of the macromolecule. As seen from Eq. (1), these two components describe the mobility of the dumbbell along and perpendicular to the direction of the end-to-end vector $\vec{Q}$.

A further assumption concerned (iii) the interaction potential $U = U_{BB}(Q) + U_{BS}$ including the bead-bead and bead-solvent interaction of the macromolecule immobilized on a surface [cf. Figure 1].

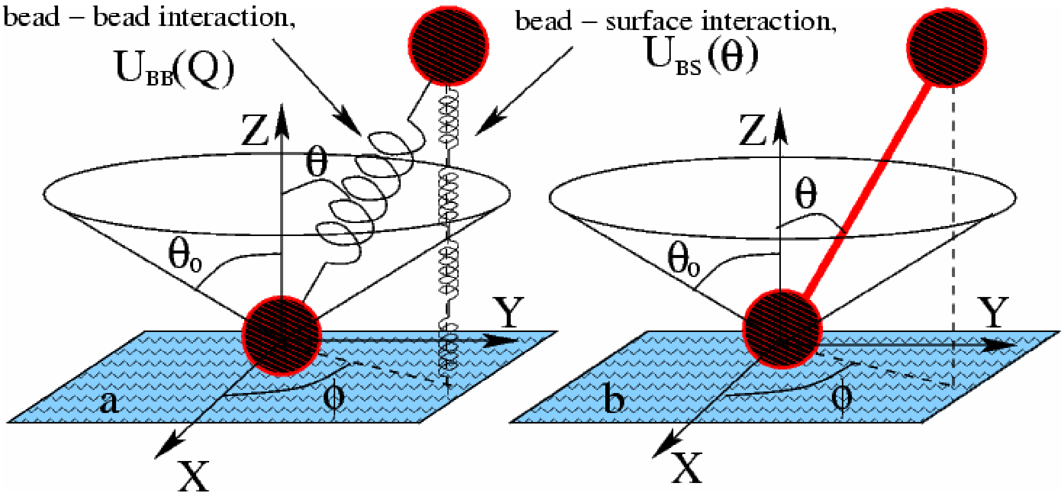

Figure 1. Two models of the dumbbell macromolecule immobilized on a surface: (left) the non – rigid dumbbell and (right) the rigid – rod model.

Here, U_{BS} refers to the interaction of the "upper bead" of the dumbbell molecule with the surface while the bead - bead potential U_{BB} only depends on the distance of the beads. In the following, moreover, we shall restrict ourselves to an `extended' dumbbell molecule with two spherical beads, for which the bead-bead separation is much larger than the radii of the beads. With the assumption (i-iii) in mind, of course, we can use the configuration-space distribution function from Eq. (1) in order to investigate various dynamical properties $A = A(\vec{Q})$ of macromolecules in solution by taking the time average

$$\langle A \rangle = \int d\vec{Q}\, A(\vec{Q})\psi\left(\vec{Q};t\right). \qquad (2)$$

Taking the time average over the configuration-space distribution function $\psi\left(\vec{Q};t\right)$ may in general result in quite lengthy computations as the – parallel and perpendicular – components of the diffusion tensor depend not only on the shape of the beads but also on hydrodynamic interactions [12,13,15,23]. For the case of an extended dumbbell molecule, we may neglect the hydrodynamic interactions and assume an 'isotropic' diffusion tensor $D_{\|}^{(Q)} = D_{\perp}^{(Q)} = D$ with the parameter D being as the self-diffusion constant coefficient of the bead if macromolecule is immersed in the unbounded solvent [21]. However, for the beads in the present of the surface, the parallel $D_{\|}^{(Q)}$ and perpendicular $D_{\perp}^{(Q)}$ components of the diffusion tensor are no longer of constant values but – due to the bead – surface hydrodynamic interaction – have to be described via the scalar mobility functions $\lambda_{\|}(h)$ and $\lambda_{\perp}(h)$ which depend on the bead—surface distance $h = Q\cos\theta$ and described [24, 25] the mobility of the beads along and perpendicular to the bead—surface direction, respectively, i.e. $D_{\|,\perp}^{(Q)} = D\lambda_{\|,\perp}(h)$. While, moreover, the bead - surface hydrodynamic interaction is really inhibit the diffusion of the beads near the surface (especially when the bead - surface distance $h \leq 2\sigma$) [24, 25], in this work we will not take into account the bead - surface hydrodynamic effects by assuming that $\lambda_{\|,\perp}(h) = 1$. Since, we consider only restricted rotational motion of the dumbbell, the simplification about behaviour of the mobility functions $\lambda_{\|,\perp}(h)$, of course, can critically distort our results only when the maximal value of polar angle θ_0 is more than 70^0. This can be seen, for instance, from the fact that averaged bead - bead distance Q of the extended dumbbell is always approximately assumed [21] to be more than 7σ. Therefore, the minimal bead – surface distance is $h_{\min} = Q\cos\theta_0 \geq 2.1\sigma$ and therefore the mobility functions

$\lambda_{\parallel,\perp}(h)$ always close to 1. Nevertheless, an extension of this approach in order to fully include the effects of the bead – surface interaction on the configuration-space distribution function is currently under work and will be published elsewhere.

In the following, we shall not go into the details for deriving the configuration-space distribution function $\psi\left(\vec{Q} \equiv (Q,\theta,\varphi);t\right)$ of a non-rigid dumbbell; using the ansatz $\psi(Q,\theta,\varphi;t) = T(t)\,R(Q)\,\Theta(\theta)\,\Phi(\varphi)$, Eq. (1) can be separated into four ordinary differential equations for the variables Q, θ, φ and the time t which fully describe the dynamical behaviour of the molecule. In order to use these equations, however, we need to specify the proper boundary conditions for $\psi\left(\vec{Q};t\right)$, since the configuration-space distribution function is supposed to be continuous, it must satisfy the reflection (von Neumann) condition for the polar angle and the bead-bead distance as well as the periodic boundary condition for the azimuthal angle:

$$\left.\frac{\partial\psi(Q,\theta,\varphi;t)}{\partial\theta}\right|_{\theta=\theta_0} = 0\ ,\ \left.\frac{\partial\psi(Q,\theta,\varphi;t)}{\partial Q}\right|_{Q=Q_0'} = 0\ , \tag{3}$$

$$\psi(Q,\theta,\varphi=0;t) = \psi(Q,\theta,\varphi=2\pi;t)\,. \tag{4}$$

Making use these boundary conditions, the configuration - space distribution function $\psi(Q,\theta,\varphi;t)$ can be written in the form [21]

$$\psi(Q,\theta,\varphi;t) = \sum_{n=1}^{\infty}\sum_{m=-\infty}^{\infty} e^{-\nu_n^m\left(\nu_n^m+1\right)D_R\,t}\left(A_n^m\ \cos m\varphi + B_n^m\ \sin m\varphi\right)P_{\nu_n^m}^m(\cos\theta)\,\Psi_{\nu_n^m}(Q) \tag{5}$$

where

$$D_R = D\left\langle\frac{1}{Q^2}\right\rangle \tag{6}$$

is the diffusion coefficient for the rotational motion or, shortly, the rotational diffusion coefficient of the dumbbell at the surface. This coefficient still contains all the information about the influence of the solvent as well as the bead-bead and bead-surface interactions owing to the self diffusion coefficient D and the time average of the end-to-end distance [cf. Eq. (2)]. In expression (11), $\Psi_{\nu_n^m}(Q)$ is called the radial distribution function of the end-to-end distance, while $P_{\nu_n^m}^m(\cos\theta)$

denotes an associated Legendre function of degree ν_n^m and order m. For both indices, ν_n^m and m, the allowed values are obtained from the boundary conditions (3, 4). Since the azimuth φ is not restricted and, hence, the configuration-space distribution should have a period 2π, m must be an integer. For the degree ν_n^m (of the Legendre polynomial and radial distribution function), in contrast, the restriction in the polar angle $\theta \le \theta_0 \le \pi/2$ leads to non - integer values in general which, for fixed values of m and n, have to be calculated numerically from the boundary conditions (3). A more detailed discussion about these computations and the properties of the associated Legendre function with a non - integer degree can be found in Refs. [16, 21]. To calculate and understand the behaviour of the configuration space distribution function (5), it is essential to use properties the associated Legendre functions. As known from the literature, the associated Legendre functions obey the symmetry $P^m_{\nu_n^m}(\cos\theta) = P^m_{-\nu_n^m-1}(\cos\theta)$ even in the case if ν_n^m has a non-integer value. In addition, the associated Legendre functions have the well – known orthogonality properties $\int_0^{\theta_0} \sin\theta\, d\theta\, P^m_{\nu_{n_1}^m}(\cos\theta) P^m_{\nu_{n_2}^m}(\cos\theta) = H^m_{n_1}\delta_{n_1 n_2}$ with $\delta_{n_1 n_2} = \begin{cases} 1 \ if \ n_1 = n_2 \\ 0 \ if \ f \ n_1 \ne n_2 \end{cases}$ being the usual Kronecker symbol. In the general form (5) of the configuration – space distribution $\psi(Q,\theta,\varphi;t)$, therefore, the coefficients A_n^m and B_n^m are given by [21]

$$A_n^m = \frac{\cos\varphi(0) P^m_{\nu_n^m}(\cos\theta(0)) Q(0) \Psi_{\nu_n^n}(Q(0))}{\pi H_n^m (1+\delta_{m0})}, \quad B_n^m = \frac{\sin\varphi(0) P^m_{\nu_n^m}(\cos\theta(0)) Q(0) \Psi_{\nu_n^n}(Q(0))}{\pi H_n^m} \tag{7}$$

where $Q(0)$ denote the initial values of the bead – bead distance as well as $\varphi(0)$ and $\theta(0)$ are the initial values of the azimuthal and polar angles, respectively.

As seen from expressions (7), the coefficients A_n^m and B_n^m now depend – via the non-integer degree ν_n^m – on the (maximal allowed) polar angle θ_0 in the restricted motion of the dumbbell molecule. Below, we make use of these coefficients and the orthogonally property of the associated Legendre functions from above in order to calculate the radial distribution function as well as rotational diffusion coefficient of the dumbbell macromolecule.

III. Results and Discussions

From the Diffusion equation (1), we see that the dynamics of the macromolecule depend on the overall potential U, i.e. the interaction $U_{BB}(Q)$ between the beads as well as the interaction U_{BS} of the (upper) bead with the surface. To obtain further insight into the rotational behaviour of a dumbbell molecule at a surface, therefore, let us consider four particular combinations of the bead-bead and bead-surface interactions. Most of these potential have their origin in the field of physical chemistry where they were constructed in order to simulate the chemical bonds in different (chemical) environments. In the following, we will consider (i) a Frenkel potential [22]

$$U_{BB}^{Fr}(Q) = k_{Fr}(Q - Q_0)^2 \tag{8}$$

or (ii) a DNA – type bead – bead potential [23]

$$U_{BB}^{DNA}(Q) = k_{DNA}\left(\frac{1}{4\left(1 - \frac{Q}{Q_0}\right)} - \frac{1}{4}Q + \frac{Q^2}{2Q_0} - \frac{1}{4} \right) \tag{9}$$

while, for the bead-surface interaction, we take (iii) the Cone potential [21]

$$U_{BS}^{Cone}(\theta) = \begin{cases} 0 \;\; if \;\; \theta \le \theta_0 \\ \infty \;\; if \;\; \theta > \theta_0 \end{cases} \tag{10}$$

and (iv) the effective double well (Sin) potential

$$U_{BB}^{Sin} = k_{\sin} \sin^2 \theta\,. \tag{11}$$

In these potentials (8, 9) and (11), the corresponding (interaction) constant $k_{...}$ determines the strength of the interaction. Note, moreover, the different meaning of Q_0 in the bead-bead potentials (8) and (9); while Q_0 is the equilibrium distance in the case of the Frenkel potential, this quantity denotes the maximal length beyond which the beads of the dumbbell cannot be stretched further in the case DNA – type potential.

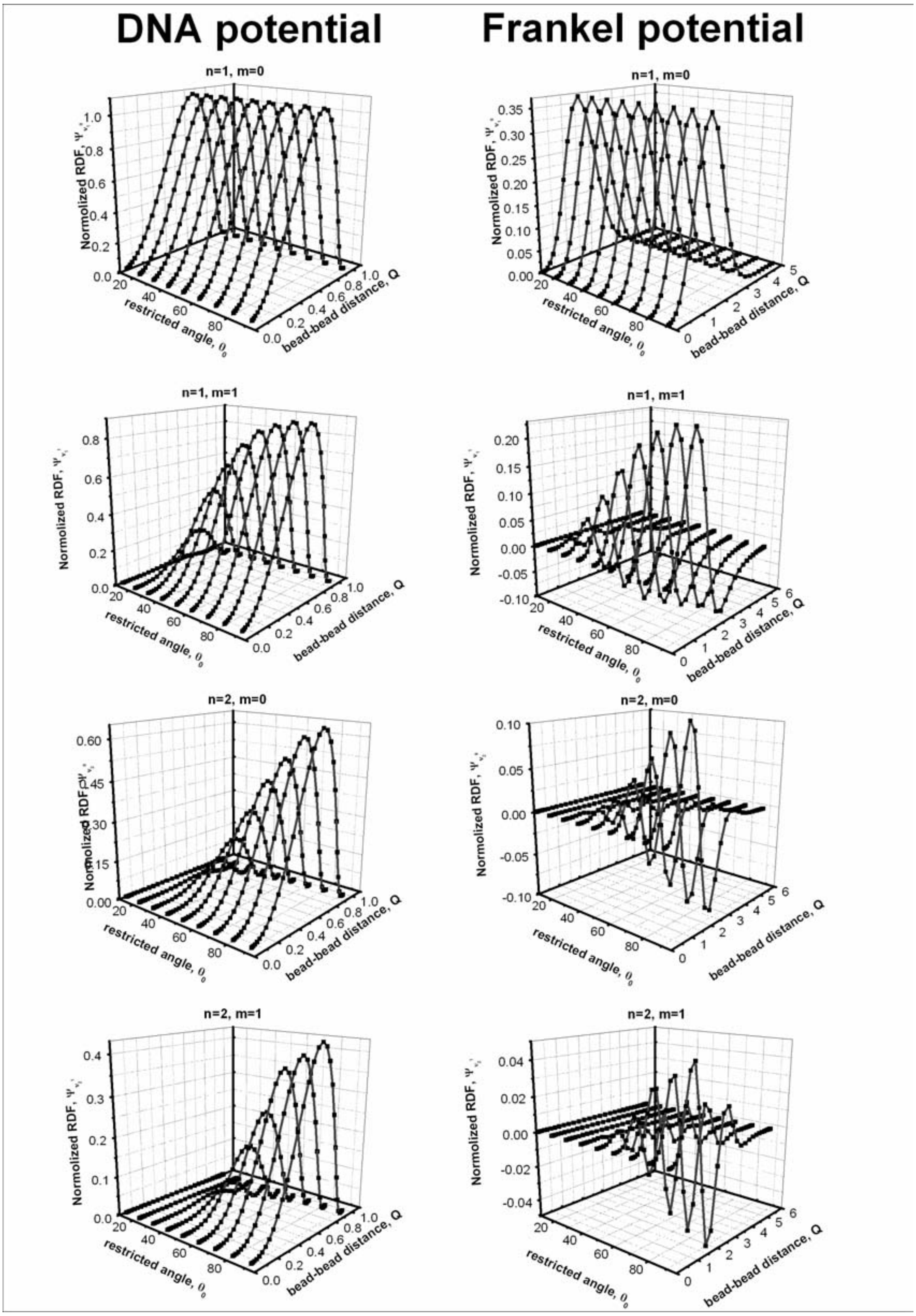

Figure 2. Behaviour of the first three radial distribution functions $Q^2\Psi_{\nu_n^m}(Q)$ of the macromolecule with (left) DNA-type (8) and (right) Fraenkel (9) bead – bead potential as function of the bead – bead distance Q and restricted angle θ_0.

Having selected a bead-bead and bead-surface potential, we can calculate the (set of) radial distribution functions $\Psi_{\nu_n^m}(Q)$. Figure 2 displays the behaviour of the first several normalized functions $\Psi_{\nu_n^m}(Q)$ for a Cone bead – surface potential (10) and by comparing a DNA – type and Frenkel bead-bead potential. Since $\Psi_{\nu_1^0}(Q)$ is just the equilibrium distribution function, it is independent of the maximum polar angle θ_0 in the restricted motion of the dumbbell molecule. As seen from figure 2, however, all other distribution functions with order $m \neq 0$ are rather sensitive to the opening angle of the cone. Moreover, the structure of the radial distribution functions becomes less pronounced for, say, $40^0 \leq \theta_0 \leq 90^0$. Nevertheless, Figure 2 clearly demonstrates that maximal value of the radial distribution functions decreases with increasing of the n and m quite quickly. It was found, in particular, that in order to calculate the time behaviour of the end-to-end correlation function $Q(0)Q(t)$ it is enough to use first 12 radial distribution functions $\Psi_{\nu_n^m}(Q)$ for $n \leq 3$ and $m \leq 3$.

Figure 3 shows the rotational diffusion coefficient D_R and the orientational correlation function $P_1 = \langle \cos\theta \rangle$ for the different bead-bead and bead-surface potentials (14-17). Apparently, the rotational diffusion coefficient behaves quite different for different combinations to the two potentials.

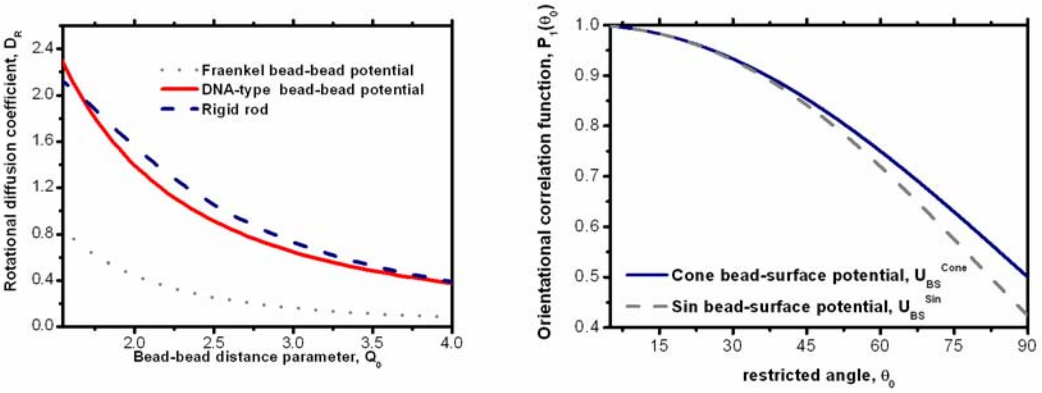

Figure 3. Left: Rotational diffusion coefficient D_R as function of the distance bead – bead separation parameter Q_0 of the dumbbell molecule for the Fraenkel, DNA – type bead – bead potential U_{BB} respectively. Right: Orientational correlation function $P_1 = \langle \cos\theta \rangle$ as function of the maximal restricted angle θ_0 for different bead – surface potentials when the bead – bead potential is assumed as DNA – type (9).

While, for example, the rotational diffusion coefficient D_R goes smoothly to zero at a maximal bead – bead separation of $Q_0 \approx 3$ in the case of a Frenkel potential, we find $D_R \geq 0.5$ at this and even of larger values of Q_0 for a DNA – type potential. For a large maximal separation Q_0, moreover, the diffusion coefficient of the dumbbell with the (strong) DNA – type of the bead – bead potential is approximately the same like for the rigid – rod macromolecule, while it always stays large if compared with the rotational diffusion coefficient of the dumbbell with the (soft) Frenkel potential. In addition to the rotational diffusion coefficient, the Figure 3 also demonstrates the behaviour of the orientational correlation function $P_1 = \langle \cos\theta \rangle$ as function of the (maximal) restricted polar angle θ_0 which is very sensitive to the particular choice of the bead – surface interaction potential. Since the rotational diffusion coefficient as well as the orientational correlation function can be observed directly by means of dielectric relaxation and scattering as well as fluorescence experiments [1-6], the Figure 3 can be – at least in principle – used in order to find the value of the restricted angle θ_0 as well as in order to analyze the properties of both the bead – bead and bead – surface interaction potential.

IV. Conclusion

In this work we have analyzed the influence of the bead – bead and bead – surface interactions on the restricted rotational dynamics of nonrigid macromolecules in solution if they immobilized with one end at a surface. For such (N-bead) macromolecules, we derived earlier a Diffusion equation from first principles [21]. Here, this equation is applied to investigate numerically the behaviour of the conformational phase space distribution function as well as of the rotational diffusion coefficient and the orientational correlation functions. This correlation functions, in particular, can be observed directly by means of dielectric relaxation and fluorescence experiments and can be used to analyze and better understand the internal structure of the macromolecule. As seen from our analysis, both the rotational diffusion coefficient and the radial distribution function clearly depend not only on the bead-bead but also the bead-surface interaction as well as on the maximum polar angle θ_0 for the case of a rotational diffusion in a cone. In the future, we hope that the radial distribution functions from above will help interpret (NMR) experiments from dielectric relaxation and correlation spectroscopy as carried out, for instance, for biological molecules.

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PAPER VI

Restricted rotational diffusion of nonrigid dumbbell macromolecules on a surface: Interplay of the bead–bead and bead–surface interactions.

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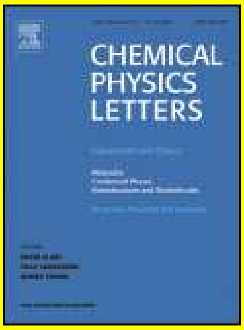

Restricted rotational diffusion of nonrigid dumbbell macromolecules on a surface: Interplay of the bead–bead and bead–surface interactions.

Alexander Uvarov* and Stephan Fritzsche

Institut für Physik, Universität Kassel, Heinrich–Plett–Str. 40, D–34132 Kassel, Germany.

A recently derived Diffusion equation [A. Uvarov and S. Fritzsche, J. Chem. Phys. **121** (2004) 6561] is applied for analyzing the restricted rotational motion of dumbbell macromolcules in solution, if immobilized on a surface. Both, the bead–bead and bead–surface interactions are taken into account in order to describe the relaxation (times), following an external perturbation, as well as the orientational dynamics of such dumbbells. Detailed computations have been performed in particular for the rotational diffusion coefficient D_R and the orientational correlation function P_2 of nonrigid dumbbells, including several realistic bead–bead and bead–surface potentials. The results from our (semi–phenomenological) theory are found to agree very well with expensive Brownian dynamic simulations from the literature over a wide range of parameters. This novel approach may therefore reduce the costs considerably in studying the dynamical behaviour and the transport properties of macromolecules in solution.

1. Introduction

Accurate studies on the dynamical behaviour of macromolecules in solution are still a challenge for modern DNA and protein research. During the past decade, therefore, a large number of experiments [1–5] have been carried out in order to understand the translational and rotational motion of such molecules, together with the (de–) formation of their shapes. Apart from *free* macromolecules in solutions [1–3], attention has been paid by these experiments especially upon the restricted mobility of such macromolecules, if immobilized on a surface [4–6]. On the theoretical side, in addition, several — often quite large — Molecular and Brownian dynamical simulations have been carried out [7–13] together with a number of analytical case studies [14–20]. In all these investigations, the macromolecules are usually described by means of their molecular subsystems to which we shall refer below as the *beads* of the macromolecule. When immersed into a solvent and immobilized onto a surface, of course, both the shape and the orientational relaxation dynamics of the macromolecules are affected not only by the surrounding solvent but also by the interaction among the (neighboured) beads as well as their interaction with the attached surface.

In the present contribution, we focus on the internal rotational dynamics of macromolecules which are immersed into a solution. In contrast to most previous investigations, however, in which more often than not a *rigid* molecule was supposed [21–24], here we consider the rotational dynamics of non–rigid macromolecules as described recently by us in Refs. [19,20]. In particular, we shall explore the question of how the interplay between the bead–bead and bead–surface interactions affect the (restricted) rotational diffusion of such molecules, if they are immobilized on a surface.

The paper is organized as follows. In section 2, our model for (the overall system of) a 'dumbbell on some surface' is presented and discussed briefly in terms of a diffusion equations (DE) for the time evolution of its configuration phase–space distribution function as derived recently by us in Refs. [19,20]. Apart from the basic assumptions, which are made in the present approach, this section shows how this DE can be simplified for the *extended* dumbbell molecule if described in polar coordinates. In section 3, later, the derived expressions are applied in order to calculate the rotational diffusion coefficient D_R as well as

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*Corresponding author. Fax: +49561 804 4006.
E–mail address: uvarov@physik.uni-kassel.de (A. Uvarov).

the orientational correlation function P_2 of the non–rigid dumbbell if immobilized on a surface. The results from our theory are compared with Brownian dynamic simulations available from the literature. Finally, a few conclusion about our *semi–phenomenological* approach are given in section 4.

2. Model and basic equations

In the kinetic theory, the *dynamical* behaviour of macromolecules in solution is often described by means of a Diffusion equation (DE) for the time evolution of its configuration–space distribution function $\psi(\mathbf{t})$, sometimes known also as the Smolukowski equation [14,15]. For any dumbbell–like molecule, such a DE was derived recently by us [19]

$$\begin{aligned} \frac{\partial\psi}{\partial t} \quad &= \quad D_{\perp}^{(Q)} \left(\Delta\,\psi + \frac{1}{k_B T}\,\psi\,\Delta\,U + \frac{1}{k_B T}\nabla\,\psi\cdot\nabla\,U \right) \\ &+ \left(D_{\parallel}^{(Q)} - D_{\perp}^{(Q)} \right) \left[\frac{\partial^2\psi}{\partial Q^2} + \frac{1}{k_B T}\,\frac{\partial^2 U}{\partial Q^2}\,\psi + \frac{1}{k_B T}\,\frac{\partial U}{\partial Q}\,\frac{\partial\psi}{\partial Q} \right] \\ &+ \left(\frac{\partial D_{\parallel}^{(Q)}}{\partial Q} + \frac{2(D_{\parallel}^{(Q)} - D_{\perp}^{(Q)})}{Q} \right) \left(\frac{\partial\psi}{\partial Q} + \frac{1}{k_B T}\,\frac{\partial U}{\partial Q}\,\psi \right), \quad (1) \end{aligned}$$

starting from a general Fokker–Planck–type equation (FPE) of the overall system 'N-bead macromolecule + solvent' and by assuming, for the sake of simplicity, an equal mass M and radius σ for all beads of the macromolecule [19,25]. In order to remove the explicit dependence on the momenta of the beads in the FPE (1) of Ref. [19], however, a number of assumptions had to be made about the dynamical behaviour of the macromolecules. Apart from (i) a rather fast relaxation of the velocities of the beads (when compared to the relaxation times of their positions), here we assumed (ii) that all the effects of the solvent onto the internal dynamics of the macromolecule can be well described in terms of the parallel (longitudinal) $D_{\parallel}^{(Q)}$ and perpendicular (transversal) diffusion parameters $D_{\perp}^{(Q)}$, instead of he six parameters of a most general second–rank diffusion tensor [14]. These two parameters, which describe the mobility of the dumbbell along and perpendicular to the direction of the end–to–end vector $\mathbf{Q}$, then contain all information about the *hydrodynamical* bead–bead and bead–surface interactions. In addition, we assumed (iii) the existence of a total interaction potential U for the dumbbell, which includes both, a (pairwise) spherical–symmetric potential $U_{\mathrm{BB}}(Q)$ between the two beads as well as the (bead–surface) potential U_{BS} between the 'upper' bead and the surface [cf. Fig. 1].

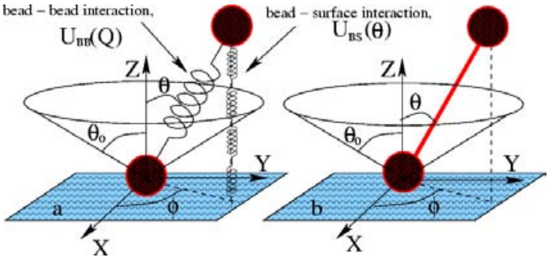

Figure 1. Two models for a dumbbell macromolecule immobilized on a surface: (left) the non–rigid dumbbell and (right) the rigid–rod model. Apart from a (spring–type) interaction $U_{\mathrm{BB}}(Q)$ between the two beads, the 'upper' bead of the dumbbell also interacts with the surface via the potential $U_{\mathrm{BS}}(\theta)$.

Equation (1) describes the time development of the configuration–space distribution function $\psi(\mathbf{t})$ of a non–rigid dumbbell, immobilized on a surface, where Q denotes (as usual) the length of the end–to–endvector $\mathbf{Q}$ and Δ the Laplacian in a coordinate–free notation. Moreover, k_B is the Boltzmann constant and T the temperature of the overall system 'macromolecule + solvent' in this equation. Since the configuration–space distribution function is known to represent the (normalized) probability density, it enables one to describe all the dynamical properties of the dumbbell molecule immersed into a solvent. Once we know this function $\psi(\mathbf{t})$, we could evaluate in particular the time average

$$\langle A \rangle \quad = \quad \int d\,\mathbf{Q}\,A(\{\mathbf{Q}\})\,\psi(\mathbf{Q};\,t) \qquad (2)$$

of *any* given function $A \equiv A(\mathbf{Q}(\mathbf{t}))$ by taking the integral over the allowed values of the end–to–end vector.

Of course, this is a very general equation which is independent of both, the Nature of the macromolecule and its interaction with the surrounding solvent and the surface, respectively. Therefore, the solutions of the DE (1) can be applied to analyze the *translational* and *rotational* dynamics of macromolecules. In practise, however, the explicit solution of this equation may become rather tedious owing to the non–linearity of the diffusion tensor parameters (i.e. of the hydrodynamic interaction) as function of the end–to–end vector **Q** [15]. In our further considerations below, therefore, we shall restrict ourselves to the case of an 'extended' dumbbell in which the bead–bead is much larger than the radii of the beads and, therefore, we may neglect the hydrodynamic interaction among the beads [19]. In fact, the 'extended' dumbbell is probably the simplest model of a non–rigid macromolecule and, hence, has attracted a great deal of interest over the past decades [7,19,20]. For this model, in particular, it was found [19] that the *bead–bead* hydrodynamic interaction can be neglected if the bead–bead distance becomes $Q \geq 8\sigma$. In addition to the properties of the bead–bead hydrodynamic interaction, moreover, the bead–surface hydrodynamic interaction have been also investigated by using both, computer simulations as well as the experiments [26,27]. For the bead near the surface, in particular, it was show [27] that the hydrodynamic bead–surface interaction inhibit the diffusion of the beads near to the surface, i.e. for distances $h = Qcos\theta \leq 3\sigma$. At large distances, in contrast, the effects of the bead–surface interaction were almost negligible. Therefore, taking this prior results from [26,27] into account, we assume below an 'isotropic' diffusion tensor

$$D_{\parallel}^{(Q)} \;=\; D_{\perp}^{(Q)} \;=\; D, \tag{3}$$

for the macromolecule, where D is called the self–diffusion coefficient of the beads [14,19,20]. Although the all hydrodynamic interactions is neglected here, this coefficient contains at least the information about the time–independent properties of the solvent, such as the density fluctuations, correlation length, temperature, viscosity, and several others. Let us note, moreover, that an extension of this approach in order to fully include the effects of the bead - surface hydrodynamic interaction on the rotational diffusion of the immobilized macromolecule is currently under work and will be published elsewhere.

Let us now return to the DE (1) for the time evolution of the configuration–space distribution function $\psi(\mathbf{Q};t)$ of the dumbbell–type molecule. Substituting expression (3) for the parallel and transversal diffusion parameters, this DE can be brought into the operator form

$$\frac{1}{D}\,\frac{\partial\psi}{\partial t} = \left\{ \widehat{R}\,(Q) + \frac{\widehat{O}\,(\theta)}{Q^2} + \frac{\widehat{\Pi}\,(\varphi)}{Q^2\,\sin^2\theta} \right\}\psi \tag{4}$$

if we use polar coordinates $\mathbf{Q} = (Q,\theta,\phi)$ for the end–to–end vector of the dumbbell and if the Laplacian is taken as

$$\Delta \;=\; \frac{1}{Q^2}\,\frac{\partial}{\partial\,Q}\{Q^2\,\frac{\partial}{\partial\,Q}\} + \frac{1}{Q^2\,\sin\theta}\frac{\partial}{\partial\,\theta}\{\sin\theta\,\frac{\partial}{\partial\,\theta}\} + \frac{1}{Q^2\,\sin^2\theta}\frac{\partial^2}{\partial\,\varphi^2}\,. \tag{5}$$

The use of polar coordinates, in fact, enables us to separate the (reduced) DE (4) into four ordinary differential equations as the polar and azimuthal diffusion operators take the form

$$\widehat{O}\,(\theta) \;=\; \frac{1}{\sin\theta}\left[\sin\theta\,\frac{\partial}{\partial\,\theta}\right] + \frac{1}{k_B\,T}\,\frac{\partial\,U}{\partial\,\theta}\,\frac{\partial}{\partial\,\theta} + \frac{1}{k_B\,T}\,\frac{1}{\sin\theta}\left[\sin\theta\,\frac{\partial\,U}{\partial\,\theta}\right] \tag{6}$$

and

$$\widehat{\Pi}(\varphi) \;=\; \frac{\partial^2}{\partial\varphi^2} + \frac{1}{k_B\,T}\,\frac{\partial U}{\partial\varphi}\,\frac{\partial}{\partial\varphi} + \frac{1}{k_B T}\,\frac{\partial^2 U}{\partial\varphi^2}\,, \tag{7}$$

while, respectively, the radial diffusion operator is given by

$$\widehat{R}(Q) \;=\; \frac{1}{Q^2}\,\frac{\partial}{\partial\,Q}\left(Q^2\,\frac{\partial}{\partial\,Q}\right) + \frac{1}{k_B T}\,\frac{\partial\,U_B}{\partial\,Q}\,\frac{\partial}{\partial\,Q} + \frac{1}{k_B T}\,\frac{1}{Q^2}\,\frac{\partial}{\partial\,Q}\left(Q^2\,\frac{\partial\,U_B}{\partial\,Q}\right). \tag{8}$$

If, for example, we try the separation ansatz

$$\psi(Q,\,\theta,\,\varphi;\,t) \;=\; \Psi(Q)\,\Theta(\theta)\,\Phi(\varphi)\,T(t)\,, \tag{9}$$

for the phase–space distribution function, the solution of the reduced equation (4) is 'divided' into (the solution of) the four equations

$$\frac{d\,T(t)}{d\,t} \;=\; -\lambda\,D\,T(t) \qquad (10)$$

$$\widehat{\Pi}(\varphi)\,\Phi(\varphi) \;=\; -m^2\,\Phi(\varphi) \qquad (11)$$

$$\widehat{O}\,(\theta)\,\Theta(\theta) \;=\; -\left[\nu\,(\nu+1) - \frac{m^2}{\sin^2\theta}\right]\Theta(\theta) \quad (12)$$

and

$$\widehat{R}\,(Q)\,\Psi(Q) \;=\; -\left[\lambda - \frac{\nu\,(\nu+1)}{Q^2}\right]\,\Psi(Q), \qquad (13)$$

that is one for each of the four (independent) variables, and where m, ν, and λ are separation constants. We shall return later to these constants in order to discuss their properties in more detail for the rotational motion of a non–rigid macromolecule immobilized at a surface. For the moment, let us mention just that these constants are related closely to the boundary conditions which are associated with the internal motion of the dumbbell–type macromolecule.

In the present work, our main concern is the rotational motion of a non–rigid dumbbell molecule, immobilzed at a surface. For such a molecule, we shall apply Eqs. (10–13) to explore the phase–space distribution as function of the solid angle $\mathbf{\Omega} = (\theta,\,\varphi)$ if the range of polar angles is restricted by some upper bound, $\theta \le \theta_0 \le \frac{\pi}{2}$. In the literature, such a *restricted* rotational motion is sometimes known also as diffusion–in–a–cone. To model this restricted rotation, we assume one bead of the dumbbell to be sticked to the surface as displayed in Figure 1. Owing to the symmetry of the system 'dumbbell + surface', moreover, we may suppose that the bead–surface interaction then only depends on the polar angle θ, i.e. $U_{BS} = U_{BS}(\theta)$. With these assumptions in mind, we are able to write the boundary conditions for the angles θ and φ of the molecular motions as

$$0 \le \theta \le \theta_0 \qquad \text{and} \qquad 0 \le \varphi \le 2\pi\,. \qquad (14)$$

In addition, a similar (boundary) condition is assumed also for the separation of the two beads

$$0 \le Q \le Q_0\,, \qquad (15)$$

where Q_0 denotes the maximum distance beyond which the beads of the dumbbell cannot be stretched. In practise, of course, this maximum is finally determined by the bead–bead interaction potential U_B. Since the configuration–space distribution function $\psi(Q,\theta,\varphi;t)$ is taken as a continuous functions, especially for coordinate values close to the boundaries (14) and (15), this function must satisfy the reflection (or von Neumann) condition

$$\frac{\partial\,\psi(Q,\,\theta,\,\varphi;\,t)}{\partial\,\theta}\Big|_{\theta=\theta_0} \;=\; 0 \qquad (16)$$

for the polar angle θ and the periodicity

$$\psi(Q,\,\theta,\,\varphi=0;\,t) \;=\; \psi(Q,\,\theta,\,\varphi=2\pi;\,t)\,. \quad (17)$$

for the azimuthal angle φ, respectively. For the separation Q of the two beads, moreover, the distribution function $\psi(Q,\theta,\varphi;t)$ has to satisfy the boundary condition

$$\frac{\partial\,\psi(Q,\,\theta,\,\varphi;\,t)}{\partial\,Q}\Big|_{\,Q=Q_0} \;=\; 0\,, \qquad (18)$$

in that not only the distribution itself but also its first derivative becomes zero at the boundary $Q = Q_0$.

The four Eqs. (10–13) from above fully describe the behaviour of the configuration–space distribution function $\psi(Q,\theta,\varphi;t)$ of an 'extended' dumbbell molecule if immobilized at one side to the surface. They enable us therefore to determine (and to analyze) the distribution $\psi(Q,\theta,\varphi;t)$ in the presence of both, the bead–bead interaction U_{BB} and bead–solvent interaction U_{BS}. While the first Eq. (10) refers to the (trivial) time evolution of the distribution function $\psi(Q,\theta,\varphi;t)$, the second and third one (11–12) are the two 'angular equations' which only depend on the *orientation* of the molecule, i.e. the direction of the end–to–end vector $\mathbf{Q}$. In addition to these angular equations, we have to consider also the *radial* Eq. (13) which describe the behaviour of the configuration–space distribution function $\psi(Q,\theta,\varphi;t)$ as function of the distance of the two beads. Here, we shall not discuss the techniques for solving the Eqs. (10–13) with the boundary conditions from above but simply note that, in general, the configuration–

space distribution

$$\begin{aligned}\psi(Q,\theta,\varphi;t) \;=\; & \sum_{n=1}^{\infty}\sum_{m=-\infty}^{\infty} e^{-\nu_n^m(\nu_n^m+1)D_R\, t} \\ & \times (A_n^m \cos m\varphi \; + B_n^m \sin m\varphi) \\ & \times P_{\nu_n^m}^m(\cos\theta)\Psi_{\nu_n^m}(Q), \end{aligned} \qquad (19)$$

can be written in terms of the *rotational* diffusion coefficient of the dumbbell

$$D_R \;=\; D\left\langle \frac{1}{Q^2}\right\rangle, \qquad (20)$$

as well as the radial distribution functions $\Psi_{\nu_n^m}(Q)$. Of course, these distribution functions must obey Eq. (13) for any given set of the separation constants λ and ν. In expression (19), moreover, A_n^m, B_n^m are expansion coefficients and $P_{\nu_n^m}^m(\cos\theta)$ denote the associated Legendre function of degree ν_n^m and order m and are well known as solutions of the angular equation (12).

As mentioned before, the possible values of the separation constants λ, ν, and ν_n^m must be derived from the boundary conditions (16–18). Since the azimuth φ is not restricted in the rotational motion of the dumbbell, the configuration–space distribution should have a period of 2π and, hence, the constant m must be integer. Then, for determining the values of $\nu_1^m < \nu_2^m < \nu_3^m \ldots$ (i.e. the sequence of ν's which satisfy the boundary conditions for a given m) we may utilize a condition on the polar angle,

$$\frac{\partial P_{\nu_n^m}^m(\cos\theta)}{\partial \cos\theta}\Big|_{\cos\theta=\cos\theta_0} \;=\; 0 \qquad (21)$$

similar to Eq. (16).

The condition (21) on the derivative of the associated Legendre functions determines the number and the values of the separation constants ν completely for any given order m. In contrast to a free (that is non–restricted) diffusion of the dumbbell, however, these 'constants' are no integers in general but, for given m and n, functions of the angle θ_0 [cf. Eq. (16)]. Unfortunately, these values cannot be obtained analytically but have to be calculated numerically. A more detailed discussion about the properties of these separation constants as well as of the associated Legendre functions with non–integer degree can be found in Refs. [19,21]. For the sake of brevity, here we shall summarize only those properties as needed in the following discussions. For example, the associated Legendre functions are known to obey the symmetry $P_{\nu_n^m}^m(\cos\theta) = P_{-\nu_n^m-1}^m(\cos\theta)$ even for non-integer values of the degree ν_n^m. In addition, these functions fulfill the orthogonality properties [21,22]

$$\int_{\cos\theta_0}^{1} d\cos\theta\, P_{\nu_{n_1}^m}^m(\cos\theta)\, P_{\nu_{n_2}^m}^m(\cos\theta) \;=\; H_{n_1}^m\,\delta_{n_1 n_2} \qquad (22)$$

where $H_{n_1}^m$ denotes coefficients of the orthogonality and $\delta_{n_1 n_2}$ the Kronecker symbol [19].

In the expansion (19) of the configuration–space distribution $\psi(Q,\,\theta,\,\varphi;\,t)$, the coefficients A_n^m and B_n^m have to be determined from the initial condition $\psi(Q,\,\theta,\,\varphi;\,0) = \delta(Q-Q(0))\,\delta(\phi-\phi(0))\,\delta(\cos\theta-\cos\theta(0))$ as well as from the orthogonality of the associated Legendre functions (22). Leaving apart the details of their derivation, these coefficients are given by [21]

$$A_n^m \;=\; \frac{P_{\nu_n^m}^m(\cos\theta(0))\,\cos m\,\varphi(0)}{\pi\, H_n^m\,(1-\delta_{m\,0})}\,, \qquad (23)$$

and

$$B_n^m \;=\; \frac{P_{\nu_n^m}^m(\cos\theta(0))\,\sin m\,\varphi(0)}{\pi\, H_n^m} \qquad (24)$$

where $\theta(0)$ and $\varphi(0)$ refer to the polar and azimuthal angle at the initial time $t_{in} = 0$, respectively. Below, we make use of these coefficients and the orthogonality (22) of the associated Legendre functions from above in order to calculate the radial distribution function $\Psi_{\nu_n^m}(Q)$. Having these functions, they can be utilized then to evaluate the rotational diffusion coefficient of the dumbbell macromolecule as well as the orientational correlation function (OCF) for different choices of the bead–bead and bead–surface interaction potentials.

3. Result and discussion

During the last two decades, a number of (large-scale) Brownian and molecular dynamical simulations have been carried out in order to understand the dynamical properties of macromolecules in solution, including case studies on the translational as well as rotational diffusion coefficients [7,13], the velocity and force autocorrelation functions [9,10], the time behaviour of the orientational correlation functions [7,8,12,13], and for various others. Apart from different choices of interactions (between the macromolecule and its environment), these investigations mainly differ by the size and mass as well as the internal structure of the macromolecules under consideration. However, in order to allow for a comparison of the various computations, a common '(macromolecular) unit system' has been applied in most investigations, based on the mass and size of the macromolecule: $M = Q_0 = k_B T \equiv 1$. In this unit system, all lengthes are measured in Q_0, energies in units of $k_B T$ while *derived* units are used for all other quantities: $\tau_{\rm Macr} = (Q_0^2/D)$ (time); $D_{\rm Macr} = D/Q_0$ (rotational diffusion coefficient); $F_{\rm Macr} = k_B T/Q_0$ (force), etc. For the sake of convenience, here we shall use the same unit system in order to facilitate the comparison of our semi–phenomenological (rotational) computations with Brownian dynamical simulations from Ref. [7].

From the DE (4) in polar coordinates and the corresponding operators (6–8), we see how the dynamics of the macromolecule depend on the potential $U = U_{\rm BB} + U_{\rm BS}$, i.e. on the interaction $U_{\rm BB}(Q)$ among the beads as well as the interaction $U_{\rm BS}$ of the (free) bead with the surface. To obtain further insight into the rotational behaviour of a dumbbell molecule, immobilized with one bead at a surface, let us consider below four particular combinations of the bead–bead and bead–surface interactions. Most of these potentials are known from the field of physical chemistry where they were constructed originally to simulate the chemical bonds in different (chemical) environments. In the following, we shall consider for the bead–bead interaction (i) a FRENKEL potential [14,15]

$$U_{\rm BB}^{\rm Fr}(Q) \;=\; \frac{1}{2}\, k_{\rm Fr}\,(Q - Q_0)^2, \tag{25}$$

and (ii) a DNA–type potential [28,29]

$$\begin{aligned} U_{\rm BB}^{\rm DNA}(Q) \;&=\; k_{\rm DNA}\left(\frac{1}{4(1-\frac{Q}{Q_0})} - \frac{1}{4}Q \right.\\ &\qquad\left. + \frac{Q^2}{2Q_0} - \frac{1}{4}\right), \end{aligned} \tag{26}$$

while, for the bead–surface interaction, we take (iii) the Cone potential [7,19,20]

$$U_{\rm BS}^{\rm Cone} \;=\; \begin{cases} 0 & \text{if } \theta \le \theta_0 \\ \infty & \text{if } \theta > \theta_0 \end{cases}, \tag{27}$$

and (iv) the effective double well (Sin) potential [7]

$$U_{\rm BS}^{\rm Sin} \;=\; k_{\rm Sin}\, \sin^2\theta\,, \tag{28}$$

and where the (interaction) constants $k_{\rm Fr}$, ... determines the strength of the corresponding interaction. Note the different meaning of the distance Q_0 the the beads in the two potentials (25) and (26); while this 'length' refers to the equilibrium distance in the case of the Frenkel potential, it denotes the maximum length for the DNA–type interaction beyond which the beads of the dumbbell cannot be stretched.

In the following, our emphasis will be placed onto the rotational diffusion of a dumbbell molecule, immobilized on a surface, for which several dynamic simulations are known from the literature [7,13] In particular, we shall refer to the BDS by de la Torre and coworkers [7] in which a FRENKEL–type potential (25) was assumed among the two beads of a dumbbell molecule. In line with Ref. [7], moreover, we make use of the same bead–bead interaction strength $k_{\rm Fr} = 0.4508$ in order to ensure that the equilibrium bead–bead distance is $< Q^2 > \approx Q_0^2$. In contrast to these earlier BDS [7], however, a different bead–surface interaction $U_{\rm BS}$ has been applied in our computations below. For all further details about the initial set–up of the BDS, we refer the reader to the literature.

In our semi–phenomenological approach from above, all information about the rotational properties of the macromolecule is finally contained in

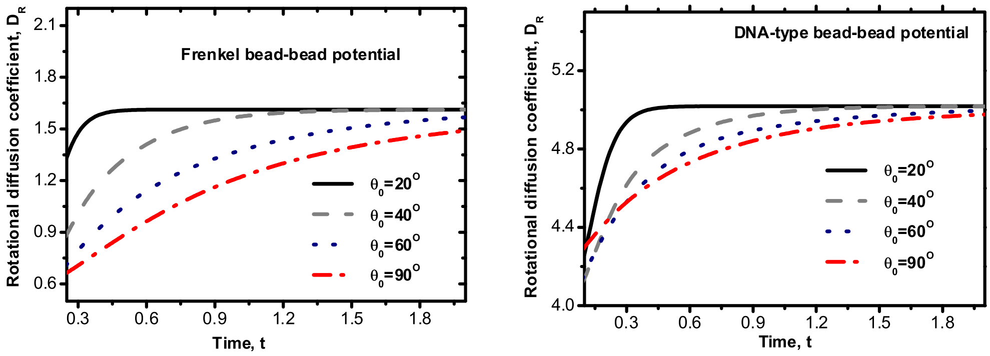

Figure 2. Rotational diffusion coefficient D_R as function of time for different restricted angles θ_0 and for two choices of the bead–bead interaction potential: a) Fraenkel potential 25 and b) DNA–type potential 26. The bead–surface interaction is described by the Cone potential (27).

the (infinite) set $\{\Psi^m_{\nu_n^m}(Q)\}$ of the radial distribution functions. In order to evaluate this functions, of course, we first have to calculate the non–integer degree; however, since these numbers need to be determined only *once* for each (choice of the) restricted angle θ_0, our approach appears very suitable for studying different combinations of bead–bead and bead–surface interactions. For a number of angles θ_0, the possible degrees ν_n^m were calculated in our previous work [cf. Table 1 of the Ref. [19]] and have been utilized below to solve Eq. (13) for the radial functions $\Psi_{\nu_n^m}(Q)$.

Having available the radial distribution functions $\Psi_{\nu_n^m}(Q)$ and the statical structure factor $g(k)$ of the surrounding solvent, we can evaluate the time behaviour of the rotational diffusion coefficient D_R of the macromolecule for different values of the restricted angle θ_0. This is achieved simply by inserting these distribution functions into Eq. (20) and by making use of the average (2). Let us now note that in order to calculate the rotational diffusion coefficient or *any* other measurable function for the macromolecule we — at least in principle — need to calculate the *infinite* set of the radial distribution functions $\Psi_{\nu_n^m}(Q)$. Fortunately, a rather small number of such radial functions is sufficient for the convergence of $\Psi(Q)$ as their contribution decreases rapidly with n and m and because $\Psi_{\nu_n^m}(Q)$ is almost zero for all values θ_0 and Q if $n \leq 3$ *and* $m \leq 3$ [20].

Figure 2 displays the time dependence of the rotational diffusion coefficient D_R for different restricted angles θ_0 and for the two bead–bead interaction potentials (25) and (26) from above. The bead–surface interaction is described by the Cone potential (27). Obviously, a rather different behaviour is found for different angles θ_0 which restrict the polar motion of the molecules. While for small angles θ_0 the diffusion coefficient approaches very rapidly to its equilibrium value, a much longer period is required if the molecule diffuse in big cone. As seen from this figure, moreover, the equilibrium coefficients differ quite sizeable for the two choices of the bead–bead interactions above, i.e in the limit $\lim_{t\to\infty} D_R$.

Apart from studying the time dependence of the rotational diffusion coefficient, we can utilize our semi–phenomenological approach to explore the behaviour of D_R at equilibrium as functions of the allowed bead–bead separation Q_0 [cf. Figure 4]. Owing to the different meaning of this parameter, of course, a qualitative different behaviour is obtained for the Frenkel and DNA–type potential. Even for the (strong) DNA–type inter-

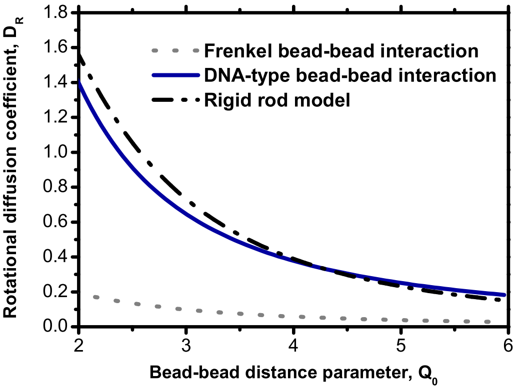

Figure 3. Rotational diffusion coefficient D_R as function of the separation parameter Q_0 for two different choices of the bead–bead interaction potential: a) Fraenkel potential (25) and b) DNA–type potential (26). The bead–surface interaction is described by the Cone potential (27).

action, however, the equilibrium coefficient of a dumbbell molecule becomes similar to those of the rigid–rod model for a rather large separations $Q_0 \geq 5$, while it remains smaller always by a factor of at least 3 for the (soft) Frenkel potential.

Having obtained the dependence of D_R on the restriction angle θ_0 and the separation parameter Q_0 (in the definition of the bead–bead interaction U_{BB}), we shall further investigate also the influence of the bead–surface interaction $U_{\mathrm{BS}}(\theta)$ upon the rotational diffusion coefficient. For a FRENKEL–type dumbbell which, in addition, interacts with the surface via the double well (Sin) potential (28), Table 1 lists the diffusion coefficients D_R for different interaction constants k_{Sin}. As seen from this table, excellent agreement is found with the BDS data by de la Torre[7] if the separation parameter is set to $Q_0 = 7.99\sigma$, i.e when the hydrodynamic interaction may be neglected. Apart from the diffusion coefficient, moreover, the time–dependent orientational correlation function (OCF)

$$P_2(t) \quad = \quad \frac{1}{2}\left(3\,\langle\cos\theta(t)\rangle - 1\right) \qquad (29)$$

is often used in order to characterize the rotational motion of macromolecules in solution, if immobilized on a surface. Studies on the time behaviour of this OCF (29) have attracted indeed a lot of recent interest because it can be observed directly by means of fluorescence depolarization experiments. Again, by making use of the possible non–integer degrees from our recent work [cf. Table 1 in Ref. [19]], Eq. (19) for the radial distribution functions $\Psi_{\nu_n^m}(Q)$ as well as expression (2) for the average, we can compute the orientational CF (29) for any restricted angles. For two of such angles, $\theta_0 = 30^o$ and 66.4^o, Figure 4 shows the normalized orientational CF $< P_2(t)/P_2(0) >$ as function of time t and compares them with those from the Brownian dynamical simulations by Tirado *et al.* [7]. Again, a very good agreement with the BDS data is found in for $\theta_0 = 30^o$ and with some minor deviations also for $\theta_0 = 66.4^o$. As seen from Figure 4, moreover, the OCF from the *triexponential* approximation of Ref. [7] are always larger than our computations, especially for rather large values of θ_0. This demonstrates that our semi–phenomenological approach enables one to understand and calculate the rotational (and further) properties of macromolecules without that extensive dynamical simulations are always necessary.

Table 1
Rotational diffusion coefficients D_R for a 'Frenkel–type' dumbbell which interacts with the surface via the double well (Sin) potential (28). Comparison of our semi–phenomenological theory with data from the BDS [7] for different strength constants k_{Sin} of the bead–bead interaction. See text for further details.

k_{Sin}	D	
	This work	BDS [7]
17.50	0.03191	0.029
8.54	0.06882	0.064
4.49	0.01398	0.013
1.89	0.01816	0.017

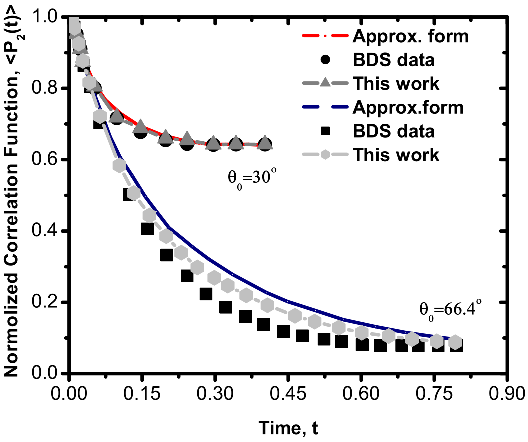

Figure 4. Time behaviour of the orientational CF P_2 of a dumbbell macromolecule which interacts with the surface via the effective double well (Sin) potential (28). OCF from our semi–phenomenological theory are compared with the BDS from Ref. [7].

4. Conclusion

For a non–rigid dumbbell (molecule) immobilized on a surface, the effects of the bead–bead and bead–surface interaction on the rotational motion has been investigated as function of the restricted polar angle θ_0. For this, we started from a diffusion equation for the configuration–space distribution function which was derived recently by us [19] from the Fokker–Planck–type equation for the phase–space distribution function of N–bead macromolecule [19,25]. In this derivation, the (three) assumptions were made that (i) the momenta of the beads relax much faster to their equilibrium values than their spatial coordinates and, hence, that (ii) all the effects of the surrounding solvent onto the internal dynamics of the macromolecule can be well described by two parameters, the parallel and perpendicular diffusion functions. Moreover, (iii) a total interaction potential U has been assumed for the dumbbell, including the spherical–symmetric potential $U_{\rm BB}(Q)$ between the beads of the macromolecule as well as (bead–surface) potential $U_{\rm BS}$ for the interaction between 'upper' bead and the surface. All of these assumptions (i–iii) have been made before frequently in studying the behaviour of macromolecules in solutions [14–18,20]. Using the derived equation (4), then, detailed computations have been carried out for the rotational diffusion coefficient as well as for the orientational correlation function of a non–rigid (2–bead 'extended') dumbbell macromolecule.

To elucidate the influence of the various interactions on the rotational motion of such dumbbell molecules, several potentials have been considered for the bead–bead (FRENKEL, DNA) and bead–surface interaction (CONE, SIN). For these choices of the interaction, our computations clearly reveal that the rotational properties of the macromolecule strongly depend not only on the interaction potentials but also on the maximum value of the polar angle θ_0. The results from this work might useful to interprets dielectric relaxation, the correlation spectroscopy and NMR relaxation experiments which are carried out on the diffusion coefficients and the orrientational correlation functions for biological molecules (such as DNA) [1–6]. Moreover, we are presently also continue this work to better understand the rotational dynamics of N–bead chains or other immobilized macromolecular structures.

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PAPER VII

Higher–order correlation effects on the friction of macromolecules in solution: A semi–phenomenological Fokker–Planck approach.

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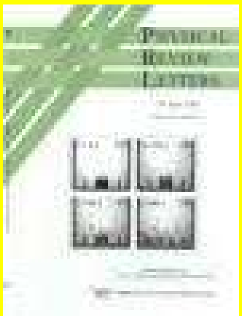

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High–order correlation contributions to the friction of macromolecules in solution: A semi–phenomenological Fokker–Planck approach

Alexander Uvarov and Stephan Fritzsche
Institut für Physik, Universität Kassel, Heinrich–Plett–Str. 40,
D–34132 Kassel, Germany; email uvarov@physik.uni-kassel.de.

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A novel, semi–phenomenological expression is derived for the friction tensor of macromolecules immersed into solution. By making a few realistic assumptions about the interaction of the molecular beads with the particles of the solvent, the friction tensor is expanded into a series of terms which purely depend on the $(j+2)-$point correlation functions of the solvent as defined in the kinetic theory of the liquids. In a first application of this series expansion, the boundary condition coefficient is investigated for a single bead in dependence on the strength of the interaction among the solvent particles and with the macromolecule. When compared with previous molecular–dynamical simulations, excellent agreement is found even for a rather strong coupling between the bead and the solvent. Our new semi–phenomenological approach may therefore help extend the study of transport properties towards complex macromolecules in solution and will reduce the computational *costs* for that by several order of magnitude.

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The idea of *friction* is perhaps the most general concept in order to explore the dynamics of macromolecules in solution. Apart from describing the rotational and translational motion, this concept helps understand the (de–) formation processes of macromolecules which are known to be affected both, by the internal structure of the molecules as well as their interaction with the surrounding solvent. During the past decade, therefore, a number of experiments and molecular dynamic (MD) simulations [1–4] have been carried out in order to investigate the rotational and translational friction of macromolecules. In addition, several ab–initio and semi–empirical models were developed during that time to analyze the static and dynamical properties of macromolecules in solution [6–10].

From the empirically established Stokes relation

$$c \;=\; \xi/\pi\,\eta\,R_{\,\mathrm{hydr}}\,, \tag{1}$$

it is known for instance, that the boundary condition (BC) coefficient c of a mesoscopic particle is proportional to the friction coefficient ξ but *inverse* proportional to the viscosity η of the solvent as well as its *effective hydrodynamic* radius $R_{\,\mathrm{hydr}}$ [6]. In the literature, therefore, this coefficients is often applied to characterize the velocity of the solvent at the surface of the particle. In the phenomenological theory, this coefficient takes a constant value between $c = 4$ (slip BC) and $c = 6$ (stick BC) by assuming a *non–discrete* and *incompressible* medium for the solvent. However, although this Stokes relation is well fulfilled for (heavy) particles with a mass $\gtrsim 100$ times the mass of the solvent particles [2, 3], the discrete character of the solvent and its interaction with the molecular subsystems should be taken into account to understand the dynamical behaviour of most macromolecules [2].

To explore the effects of the solvent onto the dynamics of macromolecules, a Fokker–Planck type equation (FPE) has been derived recently by us for the time evolution of the phase–space distribution function of an (N–bead) macromolecule [9, 11]. In this FPE, all information about the interaction among the beads of the macromolecule as well as the effects from the surrounding solvent is described by means of *semi–phenomenological* friction tensors which are expressed in terms of the bead–solvent interaction and the dynamical structure factor of the solvent [9]. Several typical bead–solvent interaction potentials were explored to analyze the dynamical behaviour in different environments [11]. For a single–bead macromolecule, moreover, we showed that the Stokes relation (1) holds down to a macromolecule–to–solvent mass ratios of $M/m \approx 45$ if slip BC were applied [12].

In all of these previous case studies, a *weak* coupling of the macromolecule with the solvent was assumed throughout. In general, however, the bead–solvent interaction is often not so weak and may become comparable with the interaction among the beads. To improve the treatment of the macromolecular dynamics, therefore, here we generalize the semi–phenomenological expression for the friction tensors of a $N-$bead macromolecule to allow for a realistic coupling of the molecular beads to the solvent. Based on the assumption, that the relaxation time of the macromolecule towards its equilibrium is typically (much) *longer* than those of the solvent, a semi–phenomenological expression is derived for the friction tensors of macromolecules which can be written in terms of the bead–solvent potential as well as the $(k+2)-$point correlation functions of the solvent. In this work, emphasize is placed on the derivation of the friction tensors rather than detailed numerical computations.

Following a brief account on the microscopic theory of friction, we shall start below from the FPE for the phase–space distribution function of a macromolecule in solution to derived a semi–phenomenological expression for its friction tensors. As a first application, this expression is then utilized to calculate the BC coefficient c for a single–bead macromolecule in a solvent in dependence on the interaction strength between the bead and the solvent particles. When compared to previous MD simulations, an excellent agreement is found for the BC coefficient over a wide range of the macromolecule–to–solvent strength of the interaction, in contrast to the phenomenological theory. Apart from new insights into the origin of the macromolecular friction, therefore, our semi–phenomenological approach below allows first of all a very remarkable reduction of the computational costs (by several order of magnitudes at least) in studying the transport properties of large molecules.

In the classical (microscopic) theory, macromolecules in solution are usually described in terms of their (N) molecular subsystems, the so–called beads of the macromolecule, surrounded by n solvent particles of equal mass m and by assuming $n \gg N$. Then, the dynamical properties of the macromolecule can be determined from its phase–space distribution $\rho_N = \rho_N(\mathbf{\Gamma}, t)$ with $\mathbf{\Gamma} = \{\mathbf{R}_1, \mathbf{P}_1, \ldots, \mathbf{R}_N, \mathbf{P}_N\}$ if the integration (averaging) has been carried out over all the position and momenta of the solvent particles, $\{\mathbf{r}_1, \mathbf{p}_1, \ldots, \mathbf{r}_n, \mathbf{p}_n\}$. If, in addition, we suppose equal mass M for all beads and a pairwise interaction $U_{ab} = U\left(|\mathbf{R}_a - \mathbf{R}_b|\right)$ along a given chain, the time evolution of the distribution function $\rho_N(\mathbf{\Gamma}; t)$ of the molecule follows the Fokker–Planck type equation (FPE)

$$\frac{\partial \rho_N}{\partial t} + \sum_{a=1}^{N} \frac{\mathbf{P}_a}{M} \frac{\partial \rho_N}{\partial \mathbf{R}_a} - \sum_{a,b=1}^{N} \frac{\partial U(|\mathbf{R}_a - \mathbf{R}_b|}{\partial \mathbf{R}_a} \frac{\partial \rho_N}{\partial \mathbf{P}_a}$$
$$= \sum_{a,b=1}^{N} \frac{\partial}{\partial \mathbf{P}_a} \, \widehat{\xi}^{(ab)} \left[\frac{\partial}{\partial \mathbf{P}_b} + \frac{\beta}{M} \mathbf{P}_b \right] \rho_N(t) \,, \qquad (2)$$

where $\widehat{\xi}^{(ab)} \equiv \widehat{\xi}^{(ab)}(\mathbf{R}_a, \mathbf{R}_b)$ denotes the friction tensor and $\beta = 1/k_B T$ the (inverse) temperature of the system. This FPE can be derived from the (*exact*) Liouville equation for the phase–space distribution of the overall system 'macromolecule+solvent' by using the techniques of projection operators as well as the two assumptions, that (i) the macromolecule and the solvent particles did not interact *before* some initial time, $t < t_{\text{in}} \equiv 0$, and that (ii) the solvent starts at $t = 0$ from an Boltzmann equilibrium state with the distribution function Φ_{eq} [9].

In Eq. (2), the friction tensors $\widehat{\xi}^{(ab)}$ appear in order to 'characterize' the (thermodynamically averaged) interaction of the beads with the surrounding particles from the solvent and, hences, contain also the hydrodynamic interaction between any pair (a, b) of beads. As shown recently [9], these friction tensors are given by

$$\widehat{\xi}^{(ab)} = -n_0 \int_0^\infty d\tau \int \frac{d\mathbf{k}_1 d\mathbf{k}_2}{(2\pi)^6} \, W(\mathbf{k}_1) W(\mathbf{k}_2) \, \mathbf{k}_1 \, e^{i\mathbf{k}_1 \mathbf{R}_a} e^{\widehat{L}_B \tau} e^{i\mathbf{k}_2 \mathbf{R}_b} \frac{1}{n} \sum\!\!\!\!\!\!\int_{s,t} d\{\mathbf{r}_s, \mathbf{p}_s\} e^{-i\mathbf{k}_1 \mathbf{r}_s} \, e^{\widehat{L}_S \, \tau} \, e^{-i\mathbf{k}_2 \mathbf{r}_t} e^{\widehat{Y} \, \widehat{L}_{BS} \, \tau} \, \Phi_{eq}, \qquad (3)$$

where n_0 is the number density of the solvent, $W(\mathbf{k}) = \int d\mathbf{r} \, e^{-i\,\mathbf{kr}} \, W(\mathbf{r})$ the Fourier transform of the *bead–solvent* interaction, and $\widehat{Y} = 1 - \Phi_{eq}\left(\{\mathbf{r}_s, \mathbf{p}_s\}\right) \int d\{\mathbf{r}_s, \mathbf{p}_s\}$ a linear projection operator satisfying $\widehat{Y}^2 = \widehat{Y}$. Of course, the friction tensors (3) also contains the Liouville operators $\widehat{L}_B$ and $\widehat{L}_S$ for the 'free macromolecule' and the solvent, respectively, as well as the Liouville operator

$$\widehat{L}_{BS} = \sum_{a=1}^{N} \sum_{s=1}^{n} \frac{\partial W(|\mathbf{R}_a - \mathbf{r}_s|)}{\partial \mathbf{R}_a} \left[\frac{\partial}{\partial \mathbf{P}_a} - \frac{\partial}{\partial \mathbf{p}_s} \right] \qquad (4)$$

which is associated to the interaction $W(\mathbf{r})$ of the solvent particles with the beads. With the two assumptions (i–ii) in mind, these friction tensors are *exact* and describe all the effects of the solvent onto the *long–term* dynamical behaviour of the macromolecules. Hence, the expression (3) enables us to describe all dynamical properties of a N–bead macromolecule in solution. In practise, however, it appears rather unfeasible to deal with all the (time–dependent) evolution operators of the macromolecule and solvent as well as with the *interaction operator* $\exp[\tau \widehat{Y} \, \widehat{L}_{BS}]$ simultaneously. Since, owing to the mass and size of the macromolecule, the relaxation of the solvent particles into their equilibrium state occur much faster for most solutions than those of the molecular beads, the interaction operator in Eq. (3) can be replaced by its Taylor expansion

$$e^{\widehat{Y} \; \widehat{L}_{BS} \, \tau} = \sum_{j=0}^{\infty} \frac{\tau^j}{j!} \left(\widehat{Y} \, \widehat{L}_{BS} \right)^j . \qquad (5)$$

Using the operator identity $\widehat{Y} \, \widehat{L}_{BS} = \widehat{L}_{BS}$, then the friction tensor of a $N-$bead macromolecule

$$\widehat{\xi}^{(ab)}(\mathbf{R}_a, \mathbf{R}_b) = \sum_{j=0}^{\infty} \int_0^\infty d\tau \, \frac{\tau^j}{j!} n_0 \int \frac{d\mathbf{k}_1 d\,\mathbf{k}_2}{(2\pi)^6} \, \mathbf{k}_1 \, W(\mathbf{k}_1) W(\mathbf{k}_2) e^{i\mathbf{k}_1 \mathbf{R}_a} e^{\widehat{L}_B \tau} e^{i\mathbf{k}_2 \mathbf{R}_b} \, \mathbf{k}_2$$
$$\times \frac{1}{n} \sum\!\!\!\!\!\!\int_{s,t} d\{\mathbf{r}_s, \mathbf{p}_s\} e^{-i\mathbf{k}_1 \mathbf{r}_s} e^{\widehat{L}_S \tau} e^{-i\mathbf{k}_2 \mathbf{r}_t} \left(\sum_{a',s'} \frac{\partial \, W}{\partial \, \mathbf{R}_{a'}} \left[- \frac{\partial}{\partial \mathbf{p}_{s'}} \right] \right)^j \Phi_{eq} \qquad (6)$$

can be written as an (infinite) series of terms and — at least in principle — be evaluated for *any* strength of the bead–solvent interaction.

Expression (6) for the friction tensor of a macromolecule is still rather general and gives rise to a *series* of approximations owing to the powers in the Fourier transform of the bead–solvent interaction. If we consider only the first term of this series ($j \equiv 0$), the *zero–order* approximation, we obtain again the friction tensor as derived and discussed previously [cf. Eq. (46) in Ref. [9]]. This zero–order approach is appropriate for a *weak* interaction of the macromolecule with the solvent particles. Beside of such a simplified scenario, however, expression (6) enables one also to analyze the first– and higher–order *correlation* contributions to the friction tensors. For instance, by utilizing the well–known property $-\frac{\partial}{\partial \mathbf{p}_t}\Phi_{eq} = \frac{\beta}{m}\mathbf{p}_t\Phi_{eq}$ of the equilibrium distribution of the solvent [9, 13] and by restricting the summation to $j \leq 1$, the friction tensor (6) of a $N-$bead macromolecule read as

$$
\begin{aligned}
\widehat{\xi}^{(ab)} \;=\; & n_0 \int_0^\infty d\tau \left[\int \frac{d\mathbf{k}_1}{(2\pi)^3}\,(\mathbf{k}_1\mathbf{k}_1)W(\mathbf{k}_1)^2\, e^{i\mathbf{k}_1\mathbf{R}_a}\; e^{-i\mathbf{k}_1\mathbf{R}_b} g^{(0)}(\mathbf{k}_1;\tau)\right] \\
& -\beta n_0 \int_0^\infty d\tau \left[\tau \int \frac{d\mathbf{k}_1 d\mathbf{k}_2}{(2\pi)^6}\,(\mathbf{k}_1\mathbf{k}_2)W(\mathbf{k}_1)\,W(\mathbf{k}_2)\, e^{i\mathbf{k}_1\mathbf{R}_a}\; e^{i\mathbf{k}_2\mathbf{R}_b} \sum_{c=1}^{N} e^{-i(\mathbf{k}_1+\mathbf{k}_2)\mathbf{R}_c}\, W(\mathbf{k}_1+\mathbf{k}_2)\, g^{(1)}(\mathbf{k}_1,\mathbf{k}_2;\tau)\right] \qquad (7)
\end{aligned}
$$

where

$$
g^{(0)}(\mathbf{k}_1;\tau) \;=\; \frac{1}{n}\sum\!\!\!\!\!\!\int_{s,t} d\{\mathbf{r},\mathbf{p}\} e^{-i\mathbf{k}_1\mathbf{r}_s}\, e^{\widehat{L}_S\,\tau}\, e^{i\mathbf{k}_1\mathbf{r}_t}\,\Phi_{eq} \qquad (8)
$$

is the two–point correlation function (CF) of the solvent, known also as the the dynamic structure factor [6], and

$$
\begin{aligned}
g^{(1)}(\mathbf{k}_1,\mathbf{k}_2;\tau) \;=\; & \frac{1}{n}\sum\!\!\!\!\!\!\int_{s,t,u} d\{\mathbf{r},\mathbf{p}\} e^{-i\mathbf{k}_1\mathbf{r}_s}\, e^{\tau\widehat{L}_S} \\
& \times\widehat{L}_S\; e^{-i\mathbf{k}_2\mathbf{r}_t} e^{i(\mathbf{k}_1+\mathbf{k}_2)\mathbf{r}_u}\,\Phi_{eq} \qquad (9)
\end{aligned}
$$

the three–point correlation function. Both of these correlation functions, Eqs. (8) and (9), are well–known from the theory of liquids [13, 14, 16] and contain all information about the solvent as, for example, its relaxation time back into the equilibrium, the temperature, viscosity, and many further properties which they could be determined experimentally.

As discussed above, the zero–order term in expression (7) describes the friction properties of the macromolecule for a weak bead–solvent coupling and if the solvent particles return much faster into their equilibrium than the beads of the macromolecule. Apart from calculating the diffusion and boundary condition coefficients for a single–bead spherical macromolecule [12], this zero–order approximation has been applied recently for evaluating the friction tensor components of a N–bead macromolecule for different choices of the bead–bead as well as bead–solvent interaction (Yukawa, Born–Mayer, and Lennard–Jones potential). Including, in addition, at least the first–order term in Eq. (7), we may consider also more realistic bead–solvent interactions as well as the interplay between different measurable correlations functions of the solvent, $(e^{i\mathbf{k}_1\mathbf{R}_a} e^{i\mathbf{k}_2\mathbf{R}_b})$ and $(e^{i\mathbf{k}_1\mathbf{R}_a} e^{i\mathbf{k}_2\mathbf{R}_b} e^{-i(\mathbf{k}_1+\mathbf{k}_2)\mathbf{R}_c})$, which are nothing else than the two– and three–point CF of the macromolecule. Although the incorporation of such higher–order terms will become quite tedious in many cases, especially for a large number of interacting beads, it may provide estimates on the size of these correlations and will be *by far* more efficient than any MD simulation. In a first application of this series expansion for the friction tensors, however, here we shall restrict ourselves to a single–bead molecule ($N = 1$). A more detailed case study for $N > 1$, including macromolecules of different internal shape (chains, stars, ...), is presently under work and will be presented elsewhere.

For the sake of simplicity, let us consider a single bead which interacts isotropically with the surrounding solvent particles. For such a bead, the friction tensor $\widehat{\xi}^{(\mathrm{aa})} = \xi\mathbf{I}$ just depends on a single (friction) coefficient ξ as obtained from expression (7) by setting $a = b$,

$$
\begin{aligned}
\xi \;=\; & \frac{1}{3}\, n_0 \int_0^\infty d\tau \left[\int \frac{d\mathbf{k}_1}{(2\pi)^3}\,\mathbf{k}_1^2 W(\mathbf{k}_1)^2\, g^{(0)}(\mathbf{k}_1;\tau)\right] \\
& - \int_0^\infty d\tau \left[\tau\,\frac{1}{3}\beta n_0 \int \frac{d\mathbf{k}_1 d\mathbf{k}_2}{(2\pi)^6}\,(\mathbf{k}_1\mathbf{k}_2)W(\mathbf{k}_1)\,W(\mathbf{k}_2)\right. \\
& \left.\times\; W(\mathbf{k}_1+\mathbf{k}_2)\, g^{(1)}(\mathbf{k}_1,\mathbf{k}_2;\tau)\right]\,. \qquad (10)
\end{aligned}
$$

Similar to the $N-$bead macromolecule, this friction coefficient now depends on the two– and three–point CF of the solvent, $g^{(0)}$ and $g^{(1)}$, which can be calculated — at least in the limit of $\tau \to \infty$ — by using the (so–called) Mode Coupling Theory (MCT) of liquids [14–17]. In this theory, a ‘truncated’ Lennard–Jones (LJ) potential

$$
V(r) \;=\; \begin{cases} 4\,\epsilon_S\,\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] & \text{if } r \leq r_S \\ 0 \quad \text{otherwise} & \end{cases} \qquad (11)
$$

is usually applied where ϵ_S denotes the interaction strength, σ the diameter of the solvent particles and r_S is taken as a cut–off radius beyond which the potential is set to zero. Here, we shall not discuss how one can calculate these CF but simply note that they can be evaluated numerically by using the MCT formalism as described, for instance, in Ref. [17].

Having access to the two– and three–point CF of the solvent, we can apply expression (10) in order to calculate the friction coefficient for a single–bead macromolecule with mass ratio $M/m = 100$, immersed into a LJ solvent. However, for simplifying the comparison with MD simulations from the literature, below we shall not consider

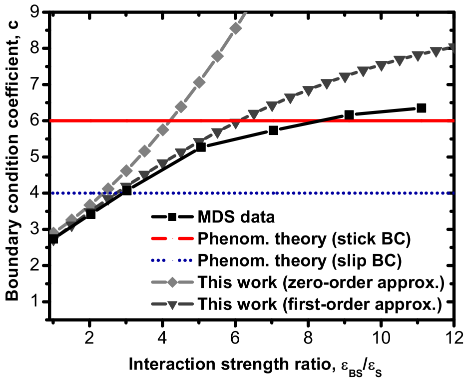

FIG. 1: Boundary condition coefficient c of a single–bead macromolecule in solution with mass $M = 100\,m$ as function of the bead–to–solvent interaction strength ratio ϵ_{BS}/ϵ_S. See text for discussion.

the friction but rather the closely related BC coefficient c of the macromolecule [cf. Eq. (1)]. For similar reasons, moreover, we make use of the same set of parameters for the potential between the bead and solvent particles as Schmidt and Skinner [2, 3] who applied a *Lennard–Jones solvent* (11) with the cut–off radius $r_S = 2.5\,\sigma$ at the temperature $k_B\,T \approx \epsilon_S$, the number density $n_0 \approx 0.85\sigma^3$ as well as the bead–solvent interaction

$$W(r) = 4\,\epsilon_{\rm BS}\left[\left(\frac{\sigma}{r-l_M}\right)^{12} - \left(\frac{\sigma}{r-l_M}\right)^{6}\right] S(r-l_M) \quad (12)$$

with two independent parameters $\epsilon_{\rm BS}$ and r_M, respectively. Moreover, the (additional) length l_M was introduced by these authors to simulate a 'hard–sphere' boundary condition for the macromolecule at the distance $r \to l_M$ between the bead and the solvent particles. For a constant mass density of the macromolecule and the solvent, namely, this length l_M can be written in terms of the bead–to–solvent mass ratio M/m as well as the diameter of the solvent particle σ [2, 3, 12]: $l_M = \frac{\sigma}{2}\left[\sqrt[3]{M/m} - 1\right]$. For all further details on the set–up of the MD simulations, we shall refer the reader to the literature [2, 3].

Figure 1 displays the BC coefficient for a single–bead macromolecule with mass $M = 100\,m$ as function of the relative interaction strength $\epsilon_{\rm BS}/\epsilon_S$ of the underlying LJ potentials. These computations are based on expression (10) for the friction coefficient and the two– and three-point CF as evaluated numerically. The hydrodynamical radius $R_{\rm hydr} = l_M + (1 + \sqrt[6]{2})$ has been used for the macromolecule [3, 12] by applying the criterion that the 'first shell' of solvent particles sits directly at the minimum of the bead–solvent potential (12). Apart from our (semi–empirical) zero– and first–order computations of the BC coefficient, Figure 1 displays also the results of the MD simulations by Schmidt and Skinner [3] as well as the constant coefficients for the stick and slip BC, i.e. for a purely phenomenological treatment of the properties of the solvent. Excellent agreement with the MD data [3] are found for all small and medium ratios of the LJ interaction strengthes in Eqs. (12) and (11). However, while the zero–order approach starts to depart from the numerical values already for ratios $\epsilon_{\rm BS}/\epsilon_S \gtrsim 2$, the first–order approximation (10) remains accurate up to $\epsilon_{\rm BS}/\epsilon_S \approx 6$ and is larger by only 25 % for a ratio of about 8.7 of the bead–solvent to the solvent–solvent interaction. As seens from this figure, the purely phenomenological theory behaves very different and is suitable only for large ratios and if, for the present choice of interactions, stick boundary conditions are applied.

In conclusion, a novel (semi–phenomenological) expression is presented for the friction tensor of macromolecules in solution that can be improved *systemtically.* Starting from a FPE–type equation for the phase–space distribution of the macromolecule [9], we derived a series expansion of the friction tensor which facilitates not only studies on the transport coefficients of macromolecules but also the inclusion of realistic bead–solvent potentials.

In a first application, these expressions for the friction tensor have been utilized to investigate the influence of high–order CF of the solvent upon the friction and BC coefficients of macromolecules. For a moderate bead–solvent interaction, these coefficients agree excellent with MD simulations carried out previously. — We therefore conclude that this semi–phenomenological approach can be applied also for studying other dynamical properties of macromolecules. Compared with often highly expensive MD simulations, a remarkable gain *by several orders of magnitude* is obtained in the efficiency and may thus allow investigations also on complex systems for which other numerical techniques will remain unfeasible.

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