

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

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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 static 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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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

$$\begin{aligned} \frac{\partial \rho_N(\mathbf{\Gamma}; \mathbf{t})}{\partial t} + \sum_{a=1}^N \frac{\mathbf{P}_a}{M} \frac{\partial \rho_N(\mathbf{\Gamma}; \mathbf{t})}{\partial \mathbf{R}_a} - \sum_{a,b=1}^N \frac{\partial U_{ab}}{\partial \mathbf{R}_a} \frac{\partial \rho_N(\mathbf{\Gamma}; \mathbf{t})}{\partial \mathbf{P}_a} \\ = \sum_{a,b=1}^N \frac{\partial}{\partial \mathbf{P}_a} \xi^{(ab)} \left(\frac{\partial}{\partial \mathbf{P}_b} + \frac{1}{k_B T M} \mathbf{P}_b \right) \rho_N(\mathbf{\Gamma}; \mathbf{t}) \end{aligned} \quad (1)$$

as recently derived for the time evolution of the phase-space

distribution function $\rho_N(\mathbf{\Gamma}; \mathbf{t})$ 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 , $a=1, \dots, N$ denote the positions or, respectively, the momenta of the individual beads, while we will use $\mathbf{\Gamma} \equiv \{\mathbf{R}_1, \dots, \mathbf{R}_N; \mathbf{P}_1, \dots, \mathbf{P}_N\}$ below in order to abbreviate the phase-space coordinates altogether. 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 $\rho_N(\mathbf{\Gamma}; \mathbf{t})$ 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,

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

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 $\rho_N(\mathbf{\Gamma}; \mathbf{t})$ of a macromolecule, the time average $\langle \rangle$ of *any* function $A \equiv A(\{\mathbf{\Gamma}\})$ can be easily derived from the integral

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

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

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

where \mathbf{P}_b / 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]

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

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 $W(\mathbf{k}) = \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} W(\mathbf{r})$ 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 $\xi^{(ab)}$ 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 $e^{i\mathbf{k} \cdot \mathbf{R}_a(0)} e^{-i\mathbf{k} \cdot \mathbf{R}_b(\tau)} = e^{i\mathbf{k} \cdot \mathbf{R}_a(0)} e^{-i\mathbf{k} \cdot \mathbf{R}_b(0)} e^{-i\mathbf{k} \cdot \mathbf{P}_b(0) \tau / M}$]. 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 averaged*) friction tensor $\hat{\xi}^{(ab)}$ 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 (val-

ues) 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

$$\rho_N(\mathbf{\Gamma}; t) = \varrho_N(\{\mathbf{R}_a\}; t) \cdot p_N(\{\mathbf{P}_a\}; t) \quad (6)$$

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

$$\langle \dots \rangle_{\mathbf{P}} \equiv \frac{\int d\{\mathbf{P}_b\} \dots p_N(\{\mathbf{P}_b\}; t)}{\left[\int d\{\mathbf{P}_b\} p_N(\{\mathbf{P}_b\}; t) \right]} \quad (7)$$

over the momenta with respect to the momentum-space distribution function $p_N(\{\mathbf{P}_a\}; t)$. Let us note that the momentum-space distribution function may be assumed both equilibrium as well as not equilibrium. In fact, in order to 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 quantitatively 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

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

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]

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

As seen from expression (8), the friction tensors $\hat{\xi}_{\alpha\beta}^{(ab)}$ 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]

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

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

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

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

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

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 then 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

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

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

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

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

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

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]

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

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

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

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

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

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)

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

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

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

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)

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

to describe the properties of a solvent with the local density $\rho(\mathbf{r}) = \sum_{s=1}^n \delta(\mathbf{r}_s - \mathbf{r})$. In practice, of course, either the PCF or

the statical structure factor can be used alternatively due to the well-known relation [11]

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

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

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

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 $k_B T_{cp} \approx 1.2\epsilon_B$, 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 $k_B T \approx 1.2\epsilon_B$, 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 $k \geq 20\sigma$ (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

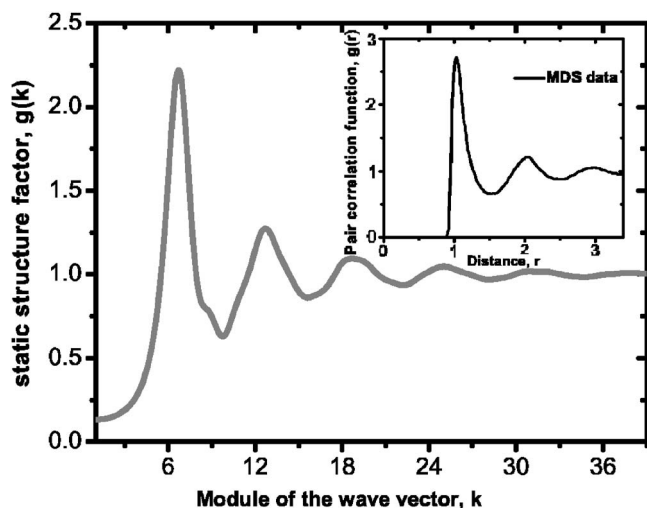


FIG. 1. Wave-vector dependence of the static (equilibrium) structure factor $g(k)$ of the solvent. The static (equilibrium) structure factor was obtained from expression (23) by using the MDS data from Ref. [4] for the pair correlation function. See text for further discussion.

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

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

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

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

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. Let 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 $k \leq 20\sigma$ 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))].

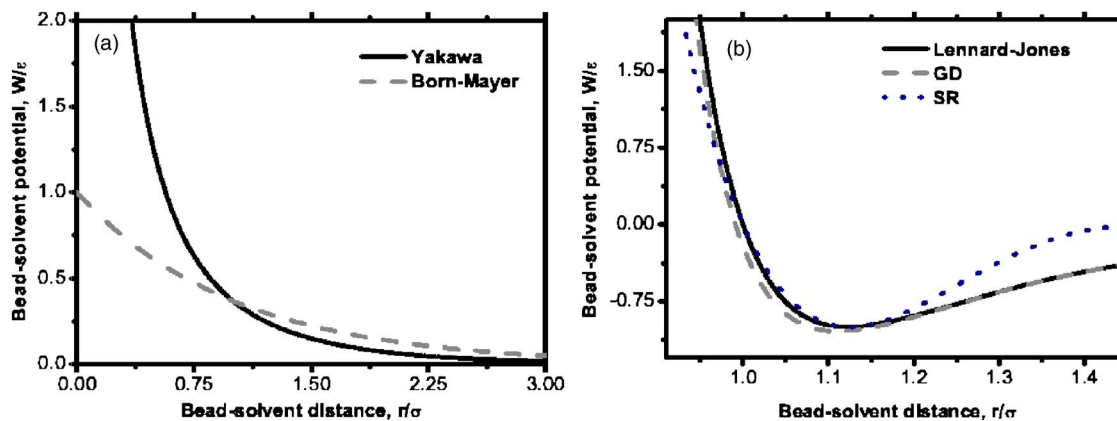


FIG. 2. (Color online) Different bead-solvent potentials to describe the influence of the solvent particles on the dynamics of the macromolecules. (a) Yukawa (25) and Born-Mayer potential (26) and (b) three commonly applied bead-solvent potentials (27)–(29) to model the *long-range* Van der Waals interaction;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

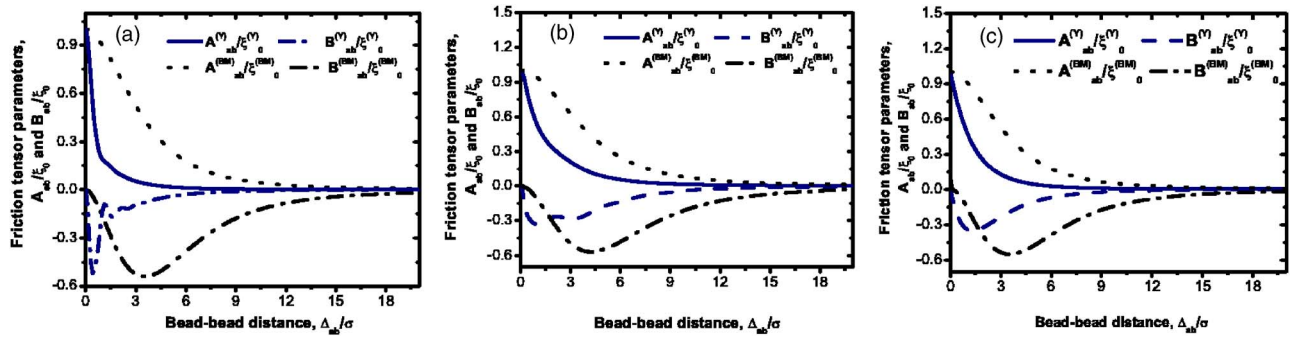


FIG. 3. (Color online) Normalized friction tensor parameters A/ξ_0 and B/ξ_0 as function of the bead-bead distance Δ_{ab} ; [cf. Eqs. (11) and (12)]. They are shown for a Y and BM bead-solvent potential. These friction parameters are shown for three cases: (a) the long-wave part ($k \rightarrow 0$) of the static 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 ($k \geq 0$) of the static 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]

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

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

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

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

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

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 static 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

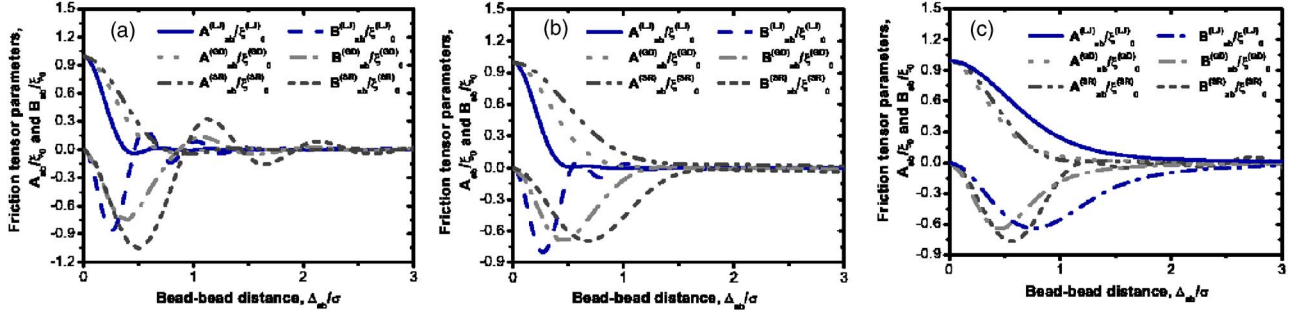


FIG. 4. (Color online) The same as in Fig. 2 but here displayed for the Lennard-Jones (LJ), the short-range approach (SR), and for a Gaussian decomposition (GD) of the bead-solvent potential. See text for further discussion.

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}_a , \mathbf{P}_a , $a=1, \dots, N$ 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

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

while we will use

$$\mathbf{Q}_a = \mathbf{R}_a - \mathbf{R}_{a+1}, \quad \mathbf{P}_{Q_a} = \mathbf{P}_a - \mathbf{P}_{a+1}, \quad (31)$$

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 $\rho_N(\Gamma; \mathbf{t})$ of the N -bead macromolecule factorizes (once more) into

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

where $\phi(\mathbf{R}_{\text{cm}}, \mathbf{P}_{\text{cm}}; \mathbf{t})$ is the distribution function of the center-of-mass coordinate and $\psi(\{\mathbf{Q}_a, \mathbf{P}_{Q_a}\}; \mathbf{t})$ the phase-space distribution of the internal motion, sometimes briefly referred 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

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

and

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

respectively.

With the separation (32) for $\rho_N(\Gamma; \mathbf{t})$ at hand, it can be shown that the center-of-mass distribution function $\phi(\mathbf{R}_{\text{cm}}, \mathbf{P}_{\text{cm}}; \mathbf{t})$ 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 $\phi \equiv \phi(\mathbf{R}_{\text{cm}}, \mathbf{P}_{\text{cm}}; \mathbf{t})$ fulfills the equation

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

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,

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

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

$$\langle \dots \rangle \equiv \frac{\int d\{\mathbf{P}_{Q_a}, \mathbf{Q}_a\} \dots \psi(\{\mathbf{P}_{Q_a}, \mathbf{Q}_a\}; \mathbf{t})}{\int d\{\mathbf{P}_{Q_a}, \mathbf{Q}_a\} \psi(\{\mathbf{P}_{Q_a}, \mathbf{Q}_a\}; \mathbf{t})} \quad (37)$$

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

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

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

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

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

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

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

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

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 static 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

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

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]

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

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 $\xi_N^{(cm)}$ 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

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

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 the Debye’s form of the static structure factor

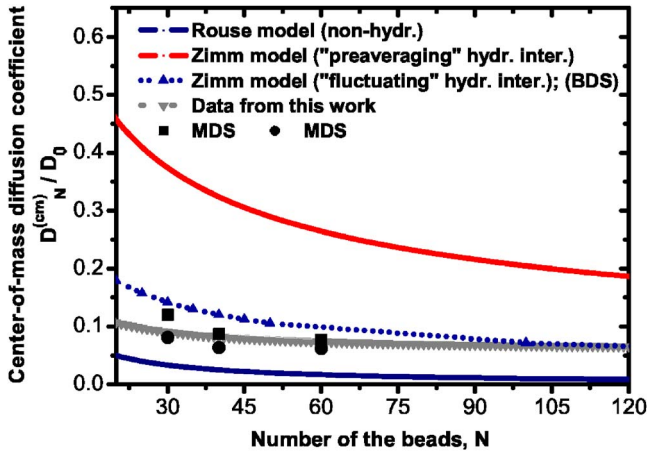


FIG. 5. (Color online) Center-of-mass diffusion coefficient $D_N^{(cm)}$ as function of N , the number of beads in the macromolecule. The results from this work for “truncated” Lennard-Jones potential (42) (triangles) are compared with the MDS data from Ref. [4] (squares) and Ref. [5] (circles) as well 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.

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

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., $R_N^G = \sum_{a,b=1}^N \langle (\mathbf{R}_a - \mathbf{R}_b)^2 \rangle / (2N^2)$. From previous numerical MDS investigations,[4] a fit formula for the radius of the gyration of the N -bead macromolecule immersed in the solvent

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

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 $D_N^{(cm)}/D_0$ 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 ≥ 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 static 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

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

for $a, b=1, \dots, N$. 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

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

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 $\hat{\xi}_{\alpha\beta}^{(ab)}$ from Eq. (A1)

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

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

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

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

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

and

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

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

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

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

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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