

Tagged chain diffusion equation and effective friction tensor in dense polymer solutions

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We start from the many-chain Smoluchowski equation that describes dynamics of dense polymer solutions and derive an effective diffusion equation for a tagged (probe) chain distribution function. In the tagged chain diffusion equation the effects of the inter-chain interactions are incorporated through an effective friction tensor. We propose a simple phenomenological formula for the friction tensor in which the friction on a given bead depends only on the positions of its two neighbors along the chain. This formula is used in conjunction with an exact lower bound for the center of mass self-diffusion coefficient. We show that the necessary condition for reproducing N^{-2} scaling of the self-diffusion coefficient is not weaker-than-linear dependence of the anisotropy on the chain length N . To check whether this also a sufficient condition, we perform a set of single chain Brownian dynamics simulations. We show that the linear chain length dependence of the anisotropy leads to $D_s \sim N^{-1.6}$ whereas the N^2 and N^3 scaling of the anisotropy result in the chain length dependence of D that is consistent with the observed N^{-2} behavior. © 1998 American Institute of Physics. [S0021-9606(98)51201-9]

I. INTRODUCTION

The dynamics of polymer melts and concentrated solutions is qualitatively different from that of simple liquids.¹ A unique feature of polymeric liquids is strong dependence of transport coefficients on the degree of polymerization N . Experimentally, for a given kind of a linear polymer, one finds two distinctive regimes. For chains shorter than a critical chain length N_c (we use terms degree of polymerization, chain length, and number of monomers in the chain interchangeably) the self-diffusion coefficient D and the shear viscosity η , scale as $D \sim N^{-1}$ and $\eta \sim N$, respectively. For chains longer than N_c the chain length dependence is much stronger: the self-diffusion coefficient D and the shear viscosity η , scale as $D \sim N^{-2}$ and $\eta \sim N^{3.4}$, respectively. The transition between these two different regimes is attributed to the onset of entanglement effects, loosely interpreted as topological constraints on the motion of polymer molecules that originate from chain uncrossability. It is not well understood why these effects manifest themselves only for relatively long chains whereas both long and short chains cannot cross.

A basis for the present understanding of polymer dynamics has been laid down by de Gennes,² and Doi and Edwards.³ In their elegant phenomenological theory the topological restrictions experienced by a given (probe) chain are replaced by an average constraint, a tube. The probe chain is assumed to move like a snake along the tube (hence the name reptation theory).

The reptation theory predicts $D_s \sim N^{-2}$ and, with some additional assumptions concerning the origin of the stress, $\eta \sim N^3$. The tube constraint, however, is assumed rather than derived and the tube diameter, that enters into prefactors of the scaling laws, cannot be calculated from the reptation theory. The theory, therefore, cannot make *quantitative* pre-

dictions for the transport coefficients and a number of other measurable quantities (such as the critical chain length N_c or the plateau of the relaxation modulus).

An approach that can be viewed as an alternative to the reptation theory has been put forward by Curtiss and Bird.⁴ In a sense, in their theory the tube constraint is replaced by the anisotropic friction tensor that builds in *some* preference for snake-like motions. However, it does not seem to be appreciated⁵ that in the Curtiss-Bird theory the overall magnitude of the friction on the probe chain and differences of the magnitudes of the friction on adjacent beads are treated separately. The overall magnitude is estimated by the requirement that the experimentally observed dependence of the self-diffusion constant on the chain length is reproduced. The anisotropic friction tensor is introduced in the relation concerning the differences of the friction on adjacent beads.

The important argument for the Curtiss-Bird approach is that it should be possible to start from the rigorous many-chain description of a dense polymer system and derive an exact formal expression for the effective single molecule friction tensor (as we will see such a formal expression does treat the center of mass motion and the segmental motions in a unified way). Furthermore, by using a combination of analytical and numerical methods one should be able to calculate the friction tensor approximately.⁶ An analogous procedure seems to be difficult to perform in the case of the reptation theory where it is not obvious how to express the tube constraint in terms of inter-molecular forces.⁸

The aim of this work is twofold. First, starting from the many-chain Smoluchowski equation we derive an effective diffusion equation for the tagged (probe) chain distribution function. In this equation the effects of the inter-chain inter-

actions are incorporated in two different ways. The average (mean-field) effects are accounted for by replacing (renormalizing) the bare intra-chain potential with an effective potential known in the context of small molecule fluids as the potential of the mean force. It should be emphasized that this renormalization does not change the long-time tagged chain dynamics. All the other effects are taken into account by introducing an effective friction tensor. These non-mean-field effects lead to slowing down of the long-time tagged chain motion. The effective diffusion equation derived here is the Fokker-Planck counterpart of the generalized Langevin equation derived in Ref. 9.

The second aim of this work is to establish whether an anisotropic friction tensor can reproduce the observed N^{-2} dependence of the self-diffusion coefficient on the chain length. To this end we use an exact lower bound for the center of mass self-diffusion coefficient (in terms of the effective friction tensor) in conjunction with the simplest phenomenological formula for the friction tensor in which the friction on a given bead depends only on the positions of its two neighbors along the chain. We show that, in this case, the necessary condition for reproducing N^{-2} scaling of the self-diffusion coefficient is not weaker-than-linear dependence of the anisotropy on the chain length N . Finally, to check whether this also a sufficient condition, we perform a set of single chain Brownian dynamics simulations.

The paper is organized as follows: We start with a brief discussion of the tagged chain diffusion equation. Next we analyze the chain length dependence of the self-diffusion coefficient that follows from a simple phenomenological friction tensor. Finally, in the last section we relate the tagged chain diffusion equation to Langevin equations used in other works, and briefly discuss the implications of the conditions on the friction tensor anisotropy for the general theory of polymer dynamics. The derivations of the tagged chain diffusion equation and the bound are presented in the appendices.

II. TAGGED CHAIN DIFFUSION EQUATION

Starting from the many-chain Smoluchowski equation and using well-established projection operator technique¹⁰ we can derive an effective diffusion equation that describes the motion of the tagged chain among other chains. The derivation from the Smoluchowski equation contains an additional non-trivial step^{11,12} compared to the standard projection operator derivation from the Liouville equation. Moreover, here we are interested in the self-diffusion problem rather than in the collective diffusion problem discussed in Ref. 11. This fact introduces another modification in the formalism. For these reasons we present in Appendix A a full detailed derivation of the effective diffusion equation. Here we discuss the physical interpretation of the general form of this equation.

The tagged chain diffusion equation has the following form:

$$\begin{aligned} \frac{\partial}{\partial t} f(\mathbf{R}_1, \dots, \mathbf{R}_N; t) = & D_0 \sum_{\alpha\beta} \int_0^t dt' \int d\mathbf{R}' \frac{\partial}{\partial \mathbf{R}_\alpha} \\ & \cdot [\vec{I} + \vec{M}^{irr}]_{\alpha\beta}^{-1}(\mathbf{R}, \mathbf{R}'; t-t') \\ & \cdot \left[\frac{\partial}{\partial \mathbf{R}'_\beta} - \left(\frac{\partial}{\partial \mathbf{R}'_\beta} \ln \omega(\mathbf{R}') \right) \right] \\ & \times f(\mathbf{R}'_1, \dots, \mathbf{R}'_N; t'). \end{aligned} \quad (1)$$

In Eq. (1) $f(\mathbf{R}_1, \dots, \mathbf{R}_N; t)$ is the joint probability distribution for the beads of the tagged chain to be at points $\mathbf{R}_1, \dots, \mathbf{R}_N$ at time t . The shorthand notation \mathbf{R} is used for the full collection of the bead coordinates, $\mathbf{R} \equiv \mathbf{R}_1, \dots, \mathbf{R}_\alpha, \dots, \mathbf{R}_N$. Also, the shorthand notation \vec{I} is used for the identity tensor $\vec{I} \delta_{\alpha\beta} \delta(t-t') \delta(\mathbf{R}-\mathbf{R}')$. The inverse $[\vec{I} + \vec{M}^{irr}]^{-1}$ denotes the kernel of the inverse integral operator. The tensor $\vec{I} \delta_{\alpha\beta} \delta(t-t') \delta(\mathbf{R}-\mathbf{R}') + \vec{M}_{\alpha\beta}^{irr}(\mathbf{R}, \mathbf{R}'; t-t')$ is the dimensionless effective friction tensor that, in general, is nonlocal in the bead index, and time and space. Finally $-k_B T \ln \omega(\mathbf{R})$ is the N -body potential of the mean force and $\omega(\mathbf{R})$ is the tagged chain equilibrium intra-chain distribution function. Both the effective friction tensor and the potential of the mean force are precisely defined in Appendix A.

Physically, the diffusion Eq. (1) describes motion of the probe chain among other chains of the solution. These other chains do not enter the equation explicitly. They, however, are responsible for two important renormalizations: First, according to Eq. (1) the chain beads interact via the potential of the mean force rather than via the original (bare) intra-chain interactions. This renormalization describes the influence of other chains on the tagged chain intra-chain equilibrium structure. Second, other chains slow down the motion of the tagged chain by contributing to the friction felt by it. Note that this effect is different from the renormalization of the intra-chain interactions. For example, the renormalization of the intra-chain interactions does not influence the diffusion of the center of mass of the tagged chain.

It is worth noticing that the renormalization of the intra-chain structure is in a sense decoupled from the renormalization of its center of mass dynamics; tagged chains can have Gaussian *equilibrium* statistics but its *dynamics* does not have to be Gaussian.

As was anticipated in the Introduction, the friction tensor in Eq. (1) treats the center of mass motion and the segmental motions in a unified fashion. In the language of the Curtiss-Bird approach,¹³ our exact formal derivation suggest that one should look for the following ‘‘empiricisms’’ for the hydrodynamic forces on the polymer beads

$$\mathbf{F}_\alpha^{(h)} \sim - \sum_\beta (\vec{I} \delta_{\alpha\beta} + \vec{M}_{\alpha\beta}^{irr}) \cdot \dot{\mathbf{R}}_\beta \quad (2)$$

rather than using two different sets of ‘‘empiricisms’’ originally proposed by Curtiss and Bird¹³

$$\mathbf{F}_{\alpha+1}^{(h)} - \mathbf{F}_\alpha^{(h)} \sim - \vec{\xi}_\alpha \cdot (\dot{\mathbf{R}}_{\alpha+1} - \dot{\mathbf{R}}_\alpha), \quad (3)$$

$$\sum_{\alpha} \mathbf{F}_{\alpha}^{(h)} \sim -\xi N^{-1} \sum_{\alpha} \dot{\mathbf{R}}_{\alpha}. \quad (4)$$

In Eqs. (3)–(4) tensor $\vec{\xi}$ and coefficient ξ are the anisotropic friction tensor and the center of mass friction coefficient, respectively.

Finally, let us note that in order to get the effective diffusion equation that corresponds to the *linear* generalized Langevin equation of Ref. 9 one should introduce the following approximations: First, a Gaussian form of the equilibrium intra-chain distribution should be taken,

$$\ln \omega(\mathbf{R}) \sim -\sum_{\alpha} (\mathbf{R}_{\alpha} - \mathbf{R}_{\alpha+1})^2. \quad (5)$$

Second, the \mathbf{R} and \mathbf{R}' dependence of the inter-chain interaction induced contribution to the effective friction tensor should be neglected,

$$\vec{M}_{\alpha\beta}^{\text{irr}}(\mathbf{R}, \mathbf{R}'; t-t') \approx \vec{M}_{\alpha\beta}^{\text{irr}}(t-t'). \quad (6)$$

Note that the isotropy of the interaction contribution M is the necessary result of the second approximation.

III. PHENOMENOLOGICAL EFFECTIVE FRICTION TENSOR

The effective tagged chain diffusion Eq. (1) with the potential of the mean force and the friction tensor given by Eqs. (A7) and (A24), respectively, is exact. However, to make it useful we have to abandon these exact expressions and come up with explicit formulas of some sort. Since it is a well established fact that in concentrated solutions and melts the conformations of the chains are Gaussian, the approximation (5) seems quite reasonable. The main problem is what expression to use for the effective friction tensor.

There seem to be two ways to proceed. First, one could try to calculate the friction tensor approximately. Such an approach has been pioneered by Schweizer.⁹ Briefly, he used a decoupling approximation that reduced the effective friction tensor to an isotropic friction coefficient, and then calculated this coefficient using a mode-mode coupling approximation. For linear chains predictions^{14–16} of this approach agree well with available experimental data. The main problem with it seems to be the isotropic character of chain motions. This problem was addressed in a short paper by Kawasaki.⁶ He argued that the friction tensor anisotropy should be retained in the Langevin equations for the bead coordinates. However, it seems to be impossible to do that on the level of the *linear* equations of motion for the bead coordinates.

The second way to proceed is to propose a phenomenological expression for the friction tensor. In spirit, that was the route taken by Curtiss and Bird.⁴ Here we will follow their approach.

In proposing a specific form for the friction tensor we will assume that because of the inter-chain interactions the *effective* friction felt by a particular bead depends on the direction of the bead's motion. In particular, the friction is supposed to be larger for motions that are perpendicular to

the local direction of the backbone and smaller (equal to the solvent friction) for motions that are parallel to it.

From physical point of view such a friction tensor corresponds to the inter-chain interactions that satisfy the principle of curvilinear displacement invariance that was first introduced by Hess.¹⁷ Simply speaking curvilinear displacement invariance means that the chains are “smooth” and hence any inter-chain forces are perpendicular to the local backbone directions. It is obvious that this does not hold literally. However, it seems to be a reasonable starting point.

Explicitly, we assume the following form for the inter-chain interactions induced contribution to the dimensionless friction tensor,

$$\vec{M}_{\alpha\beta}^{\text{irr}}(\mathbf{R}, \mathbf{R}'; t) = (\Lambda - 1) (\vec{I} - \mathbf{u}_{\alpha} \mathbf{u}_{\alpha}) \delta_{\alpha\beta} \delta(\mathbf{R} - \mathbf{R}') \delta(t), \quad (7)$$

where \mathbf{u}_{α} is the local direction of the backbone at the bead α ,

$$\mathbf{u}_{\alpha} = \frac{\mathbf{R}_{\alpha+1} - \mathbf{R}_{\alpha-1}}{|\mathbf{R}_{\alpha+1} - \mathbf{R}_{\alpha-1}|}. \quad (8)$$

In addition to the general spirit of having an anisotropic friction (for a given bead the *total* dimensionless friction equals to 1 for motions along the local backbone direction and Λ for motions perpendicular to it) the specific form (7) assumes that: the friction on a given bead depends only on the positions of the nearest neighbors along the chain; the friction is local along the chain (tensor \vec{M}^{irr} is proportional to the Kroneker delta $\delta_{\alpha\beta}$); the friction is local in space and time (tensor \vec{M}^{irr} is proportional to the Dirac's deltas $\delta(\mathbf{R} - \mathbf{R}')$ and $\delta(t)$). It seems that these additional assumptions can be slightly relaxed. What is really important is, e.g., that the friction on a given bead depends only on the positions of a small finite number of neighboring beads.

The most important parameter in the formula (7) is Λ . It specifies the anisotropy of the friction tensor. The main question that we want to answer here is how strong the anisotropy of the friction tensor (7) has to be in order to reproduce the N^{-2} scaling of the self-diffusion constant. To this end we will first use an exact bound for the center of mass diffusion constant that is briefly motivated in Appendix B.

Substituting the phenomenological formula (7) into the bound (B7) and using the Gaussian form of the intra-chain distribution function we immediately get

$$D \geq \frac{3D_0}{N(1+2\Lambda)}. \quad (9)$$

This result shows that in order to reproduce the observed N^{-2} scaling of the self-diffusion coefficient the anisotropy Λ of the friction tensor has to be chain length dependent (for friction tensors that are *local* along the chain, and in space and time). Moreover, if we assume that the anisotropy scales with N as $\Lambda \sim N^a$, then exponent a has to be equal to or greater than 1. Note that this is only a necessary condition.

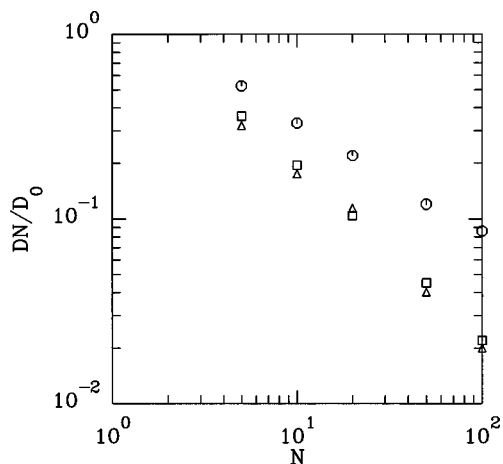


FIG. 1. Center of mass self-diffusion coefficient normalized by its Rouse value, DN/D_0 , as a function of the chain length. Circles: results for anisotropy parameter $\Lambda = N$; squares: $\Lambda = N^2$; triangles: $\Lambda = N^3$.

IV. TAGGED CHAIN BROWNIAN DYNAMICS SIMULATIONS

To check whether linear scaling of the anisotropy with the chain length is sufficient to reproduce N^{-2} scaling of the self-diffusion coefficient we solved the effective diffusion Eq. (1) with the phenomenological friction tensor (7) numerically by performing a set of single chain Brownian Dynamics simulations. We simulated the following set of stochastic differential equations that is equivalent to Eq. (1) with Eq. (7),

$$\frac{d}{dt} \mathbf{R}_\alpha(t) = \frac{D_0}{k_B T} [\mathbf{u}_\alpha \mathbf{u}_\alpha + \Lambda (\vec{I} - \mathbf{u}_\alpha \mathbf{u}_\alpha)]^{-1} [-k(2\mathbf{R}_\alpha(t) - \mathbf{R}_{\alpha+1}(t) - \mathbf{R}_{\alpha-1}(t))] + \Delta \mathbf{R}_\alpha(t), \quad (10)$$

where the Gaussian random displacements $\Delta \mathbf{R}_\alpha(t)$ are characterized by their moments,

$$\langle \Delta \mathbf{R}_\alpha(t) \rangle_G = 0, \quad (11)$$

$$\langle \Delta \mathbf{R}_\alpha(t) \Delta \mathbf{R}_\beta(t') \rangle_G = 2D_0 [\mathbf{u}_\alpha \mathbf{u}_\alpha + \Lambda (\vec{I} - \mathbf{u}_\alpha \mathbf{u}_\alpha)]^{-1} \times \delta_{\alpha\beta} \delta(t-t'). \quad (12)$$

In Eqs. (11)–(12) $\langle \dots \rangle_G$ denotes the averaging over the distribution of Gaussian random displacements. Note that in order to arrive at the set of Eqs. (10) from the effective diffusion equation we have used the fact that the phenomenological mobility tensor is diagonal in the bead indices and that the mobility of a given bead does not depend on its position.¹⁸

We calculated the long-time center of mass self-diffusion coefficients for the anisotropy parameters Λ equal¹⁹ to N , N^2 , and N^3 . To minimize statistical errors we performed multiple long runs monitoring the mean square center of mass displacements over more than 50 radii of gyration. The resulting self-diffusion coefficients are presented in Fig. 1.

It is clear from Fig. 1 that the linear scaling of the anisotropy with the chain length $\Lambda \sim N$ leads to a slower than

observed scaling of the self-diffusion coefficient $D \sim N^{-1.6}$. On the other hand, both quadratic and cubic scaling of the anisotropy lead to the chain length dependence of the self-diffusion coefficient that is compatible with the observed N^{-2} scaling (note that also the *values* of the self-diffusion coefficients are almost identical). Actual least squares fits give in both cases approximate scaling laws $N^{-1.9}$. We conclude that it is the quadratic (rather than the linear) scaling of the anisotropy that is a sufficient condition for reproducing the observed N^{-2} scaling of the self-diffusion coefficient on the chain length.

V. DISCUSSION

The first major result of this work is the derivation of the effective diffusion equation describing the time evolution of the tagged chain distribution function. The effective diffusion equation is a Fokker-Planck counterpart of the generalized Langevin equation derived by Schweizer⁹ (if one allows for an anisotropic friction tensor in the latter) and of the Langevin equation used by Kawasaki.⁷

The advantage of working in the Smoluchowski language rather than in the Langevin language is that it is easier to use standard methods of non-equilibrium statistical mechanics of simple fluids within the former formalism. It should be noted that the method used in this work (projection operator technique) is by far not a unique one. The same effective diffusion equation can be derived from the many-chain Smoluchowski equation using kinetic theory methods. Such methods were used before to analyze dynamics of colloidal suspensions^{20,21} and rod-like polymers.²²

The equations of motion for the bead correlation functions were derived from the Smoluchowski equation in Ref. 23. The disadvantage of the approach of Ref. 23 is that the “vertices” of the memory matrix are no longer associated with the inter-chain interactions but have also intra-chain pieces. In addition, there are technical difficulties associated with the diffusive mode (see Ref. 23, Sec. 3.1).

In the present work we used a phenomenological friction tensor in the tagged diffusion equation. However, it is a straightforward (although quite tedious) exercise to derive an approximate formula for the friction tensor following approach used in Ref. 22 to derive approximate expression for the friction tensor in a system of rod-like polymers. Unfortunately at present it seems impossible to derive any explicit results from such a formula.

The second result of the present work concerns modeling the effects of inter-chain interactions by a phenomenological anisotropic friction tensor.⁴ In order to reproduce the observed scaling of the self-diffusion coefficient with the chain length the anisotropy should be chain length dependent. It seems that the quadratic scaling of the anisotropy with the chain length is sufficient to reproduce the self-diffusion data. It should be recalled that the above result is strictly valid only for phenomenological friction tensors that are *local* along the chain, and in space and time. It is plausible that the result remain valid if a nonlocality is of a short range.

The question arises how to interpret this massive renor-

malization of local friction (note that similar N dependent renormalizations are present in the polymer mode-coupling theory). This is especially important since virtually all the dynamical simulations show that on short time scales long (entangled) and short (unentangled) chains move in the same way. It seems that there are two ways out: first, one could interpret the phenomenological form (7) of the friction tensor as a Markovian approximation to the real one, i.e., one could assume that the real friction tensor is non-local in time and the renormalization applies only to the time-integrated quantity. The second possibility is that the present result suggests that the real friction is strongly non-local along the chain and/or in space. In fact, a similar idea has been proposed by Brereton and Rusli.²⁴ From this perspective it would be of great interest to analyze the structure of non-localities that follow from the formal expression for the friction tensor.

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APPENDIX A: DERIVATION OF THE TAGGED CHAIN DIFFUSION EQUATION

The starting point of the derivation is the many-chain Smoluchowski equation. This equation describes motion of a concentrated polymer solution in a small molecule solvent. It contains the full dynamical information about the system and thus it has to undergo a projection operator type analysis in order to render useful single chain quantities.

Physically, according to the many-chain Smoluchowski equation a given bead moves in a viscous continuum solvent; the forces on the bead consist of intra- and inter-molecular parts; the medium, in addition to exerting a systematic friction force on the bead, applies a fluctuating force; the magnitude of the latter is related to the friction by a fluctuation-dissipation theorem.

As pointed out by Oono²⁵ there is a potential problem with this approach; polymer beads and small molecules comprising the solvent are treated on two different levels. It is not clear whether this objection has important consequences for the *long-time* tagged chain dynamics. In this work we will adopt the Smoluchowski equation as the starting point for further analysis.²⁶

The many-chain Smoluchowski equation has the following form:

$$\frac{\partial}{\partial t} P(\mathbf{r}_1^0, \dots, \mathbf{r}_N^n; t) = \mathcal{O}_S P(\mathbf{r}_1^0, \dots, \mathbf{r}_N^n; t). \quad (\text{A1})$$

Here $P(\mathbf{r}_1^0, \dots, \mathbf{r}_N^n; t)$ is the many-chain probability distribution (note that the superscript 0 denotes the tagged chain variables), \mathbf{r}_α^i denotes the position of bead α of the i th chain, n and N are the number of untagged chains and the number of beads in the chain, respectively, and \mathcal{O}_S is the many-chain Smoluchowski operator,

$$\mathcal{O}_S = D_0 \sum_{i=0}^n \sum_{\alpha=1}^N \frac{\partial}{\partial \mathbf{r}_\alpha^i} \cdot \left(\frac{\partial}{\partial \mathbf{r}_\alpha^i} - \beta \mathbf{F}_\alpha^i \right). \quad (\text{A2})$$

In Eq. (A2) D_0 is the bead diffusion constant that can be expressed in terms of the bead friction coefficient ξ_0 , $D_0 = k_B T / \xi_0$. Furthermore, \mathbf{F}_α^i is the force acting on bead α of the i th chain. It consists of two different parts: the intra-molecular force $\mathbf{F}_\alpha^{i,\text{intra}}$ and the inter-molecular force $\mathbf{F}_\alpha^{i,\text{inter}}$,

$$\mathbf{F}_\alpha^i = \mathbf{F}_\alpha^{i,\text{intra}} + \mathbf{F}_\alpha^{i,\text{inter}}. \quad (\text{A3})$$

The intra-molecular force consists of the bonding force that keeps the chain together, and the intra-molecular excluded volume force that prevents the beads that are separated along the chain from occupying the same location. The inter-molecular force is the excluded volume force that prevents beads from different chains from occupying the same location. Note that we disregard any attractive forces, mainly because transport properties (far from critical points) are only indirectly influenced by them.

We define the tagged chain distribution function as the joint distribution for positions of all the beads of the test chain molecule:

$$f(\mathbf{R}_1, \dots, \mathbf{R}_N; t) = \left\langle \prod_{\alpha} \delta(\mathbf{R}_\alpha - \mathbf{r}_\alpha^0) \right\rangle_P. \quad (\text{A4})$$

Here $\langle \dots \rangle_P$ denotes the averaging over the probability distribution P satisfying the many-chain Smoluchowski equation. Since the Smoluchowski operator is not self-adjoint it is important to remember that the probability distribution always stands to the right of the quantity that is being averaged.

The usual initial condition for the probability distribution is adopted:

$$P(\mathbf{r}_1^0, \dots, \mathbf{r}_N^n; t=0) = \prod_{\alpha} \delta(\mathbf{r}_\alpha^0 - \mathbf{q}_\alpha^0) P_{\text{eq}}(\mathbf{r}_1^0, \dots, \mathbf{r}_N^n). \quad (\text{A5})$$

Here $P_{\text{eq}}(\mathbf{r}_1^0, \dots, \mathbf{r}_N^n)$ is the equilibrium probability distribution for the system. The initial condition (A5) implies the following initial condition for the tagged chain distribution function:

$$f(\mathbf{R}_1, \dots, \mathbf{R}_N; t=0) = \prod_{\alpha} \delta(\mathbf{R}_\alpha - \mathbf{q}_\alpha^0) \omega(\mathbf{R}_1, \dots, \mathbf{R}_N), \quad (\text{A6})$$

where $\omega(\mathbf{R}_1, \dots, \mathbf{R}_N)$ is the equilibrium intra-chain distribution function of the tagged chain,

$$\omega(\mathbf{R}_1, \dots, \mathbf{R}_N) = \left\langle \prod_{\alpha} \delta(\mathbf{R}_\alpha - \mathbf{r}_\alpha^0) \right\rangle_{\text{eq}}. \quad (\text{A7})$$

In the following we will use the identity

$$\langle \dots \rangle_P = \left\langle \dots \exp(\mathcal{O}_S t) \prod_{\alpha} \delta(\mathbf{r}_\alpha^0 - \mathbf{q}_\alpha^0) \right\rangle_{\text{eq}}, \quad (\text{A8})$$

where the evolution operator $\exp(\mathcal{O}_S t)$ acts on everything to its right, and $\langle \dots \rangle_{\text{eq}}$ denotes averaging over the equilibrium many-chain probability distribution.

To derive the effective diffusion equation we use the projection operator method.¹⁰ We start with writing the formal expression for the first time derivative of the tagged chain distribution function,

$$\frac{\partial}{\partial t} f(\mathbf{R}_1, \dots, \mathbf{R}_N; t) = \left\langle \prod_{\alpha} \delta(\mathbf{R}_{\alpha} - \mathbf{r}_{\alpha}^0) \mathcal{O}_S \exp(\mathcal{O}_S t) \times \prod_{\beta} \delta(\mathbf{r}_{\beta}^0 - \mathbf{q}_{\beta}^0) \right\rangle_{\text{eq}}. \quad (\text{A9})$$

To project on the tagged chain subspace we define a projection operator,

$$\begin{aligned} \mathcal{P}G(\mathbf{r}_1^0, \dots, \mathbf{r}_N^0) &= \int d\mathbf{R} d\mathbf{R}' \prod_{\alpha} \delta(\mathbf{R}_{\alpha} - \mathbf{r}_{\alpha}^0) \\ &\times \left\langle \prod_{\alpha} \delta(\mathbf{R}_{\alpha} - \mathbf{r}_{\alpha}^0) \prod_{\beta} \delta(\mathbf{R}'_{\beta} - \mathbf{r}_{\beta}^0) \right\rangle_{\text{eq}}^{-1} \\ &\times \left\langle \prod_{\alpha} \delta(\mathbf{R}'_{\alpha} - \mathbf{r}_{\alpha}^0) G(\mathbf{r}_1^0, \dots, \mathbf{r}_N^0) \right\rangle_{\text{eq}}. \end{aligned} \quad (\text{A10})$$

In Eq. (A10) we introduced the shorthand notation for the full collection of bead coordinates, $\mathbf{R} \equiv \mathbf{R}_1, \dots, \mathbf{R}_N$.

It should be noted that the ‘canonical’ form of the projection operator can be greatly simplified by using the following identity

$$\begin{aligned} &\left\langle \prod_{\alpha} \delta(\mathbf{R}_{\alpha} - \mathbf{r}_{\alpha}^0) \prod_{\beta} \delta(\mathbf{R}'_{\beta} - \mathbf{r}_{\beta}^0) \right\rangle_{\text{eq}}^{-1} \\ &= \prod_{\alpha} \delta(\mathbf{R}_{\alpha} - \mathbf{R}'_{\alpha}) \frac{1}{\omega(\mathbf{R}_1, \dots, \mathbf{R}_N)}. \end{aligned} \quad (\text{A11})$$

Next, we define projection operator \mathcal{Q} that projects on the space orthogonal to the subspace of the tagged chain,

$$\mathcal{Q} = \mathcal{I} - \mathcal{P}, \quad (\text{A12})$$

where \mathcal{I} is the identity operator.

We insert the identity operator into the formal expression (A9) for the time derivative,

$$\begin{aligned} \frac{\partial}{\partial t} f(\mathbf{R}_1, \dots, \mathbf{R}_N; t) &= \left\langle \prod_{\alpha} \delta(\mathbf{R}_{\alpha} - \mathbf{r}_{\alpha}^0) \mathcal{O}_S (\mathcal{P} + \mathcal{Q}) \right. \\ &\times \left. \exp(\mathcal{O}_S t) \prod_{\beta} \delta(\mathbf{r}_{\beta}^0 - \mathbf{q}_{\beta}^0) \right\rangle_{\text{eq}} \end{aligned} \quad (\text{A13})$$

The first term gives the frequency matrix Ω ,

$$\begin{aligned} &\left\langle \prod_{\alpha} \delta(\mathbf{R}_{\alpha} - \mathbf{r}_{\alpha}^0) \mathcal{O}_S \mathcal{P} \exp(\mathcal{O}_S t) \prod_{\beta} \delta(\mathbf{r}_{\beta}^0 - \mathbf{q}_{\beta}^0) \right\rangle_{\text{eq}} \\ &= \int d\mathbf{R}' \Omega(\mathbf{R}, \mathbf{R}') f(\mathbf{R}'_1, \dots, \mathbf{R}'_N; t), \end{aligned} \quad (\text{A14})$$

that with the help of Eq. (A11) can be written as

$$\begin{aligned} \Omega(\mathbf{R}, \mathbf{R}') &= \left\langle \prod_{\alpha} \delta(\mathbf{R}_{\alpha} - \mathbf{r}_{\alpha}^0) \mathcal{O}_S \prod_{\beta} \delta(\mathbf{R}'_{\beta} - \mathbf{r}_{\beta}^0) \right\rangle_{\text{eq}} \\ &\times \frac{1}{\omega(\mathbf{R}'_1, \dots, \mathbf{R}'_N)}. \end{aligned} \quad (\text{A15})$$

Using the explicit form of the Smoluchowski operator (A2) one can rewrite Eq. (A15) in the following simple form

$$\begin{aligned} \Omega(\mathbf{R}, \mathbf{R}') &= D_0 \sum_{\alpha} \frac{\partial}{\partial \mathbf{R}_{\alpha}} \cdot \prod_{\beta} \delta(\mathbf{R}_{\beta} - \mathbf{R}'_{\beta}) \\ &\times \left(\frac{\partial}{\partial \mathbf{R}'_{\alpha}} - \left(\frac{\partial}{\partial \mathbf{R}'_{\alpha}} \ln \omega(\mathbf{R}') \right) \right). \end{aligned} \quad (\text{A16})$$

The second term in Eq. (A13) is rewritten with the help of the standard identity,

$$\begin{aligned} \exp[(A+B)t] &= \exp(At) + \int_0^t dt' \exp[A(t-t')] \\ &\times B \exp[(A+B)t'], \end{aligned} \quad (\text{A17})$$

with $A = \mathcal{O}_S \mathcal{Q}$ and $B = \mathcal{O}_S \mathcal{P}$. As usual, the first term does not contribute, and the second term gives the memory matrix \mathcal{M} ,

$$\begin{aligned} &\int_0^t dt' \left\langle \prod_{\alpha} \delta(\mathbf{R}_{\alpha} - \mathbf{r}_{\alpha}^0) \mathcal{O}_S \mathcal{Q} \exp(\mathcal{O}_S \mathcal{Q}(t-t')) \mathcal{O}_S \mathcal{P} \right. \\ &\times \left. \exp(\mathcal{O}_S t') \prod_{\beta} \delta(\mathbf{r}_{\beta}^0 - \mathbf{q}_{\beta}^0) \right\rangle_{\text{eq}} \\ &= \int_0^t dt' \int d\mathbf{R}' \mathcal{M}(\mathbf{R}, \mathbf{R}'; t-t') f(\mathbf{R}'_1, \dots, \mathbf{R}'_N; t'). \end{aligned} \quad (\text{A18})$$

Explicitly, with the help of the identity (A11), we find

$$\begin{aligned} \mathcal{M}(\mathbf{R}, \mathbf{R}'; t) &= \left\langle \prod_{\alpha} \delta(\mathbf{R}_{\alpha} - \mathbf{r}_{\alpha}^0) \mathcal{O}_S \mathcal{Q} \exp(\mathcal{Q} \mathcal{O}_S \mathcal{Q} t) \mathcal{Q} \mathcal{O}_S \right. \\ &\times \left. \prod_{\beta} \delta(\mathbf{R}'_{\beta} - \mathbf{r}_{\beta}^0) \right\rangle_{\text{eq}} \frac{1}{\omega(\mathbf{R}'_1, \dots, \mathbf{R}'_N)}. \end{aligned} \quad (\text{A19})$$

The memory matrix (A19) is further rewritten in the following form,

$$\mathcal{M}(\mathbf{R}, \mathbf{R}'; t) = -D_0 \sum_{\alpha\beta} \frac{\partial}{\partial \mathbf{R}_\alpha} \cdot \vec{M}_{\alpha\beta}(\mathbf{R}, \mathbf{R}'; t) \times \left(\frac{\partial}{\partial \mathbf{R}'_\beta} - \left(\frac{\partial}{\partial \mathbf{R}'_\beta} \ln \omega(\mathbf{R}') \right) \right). \quad (\text{A20})$$

In Eq. (A20) the tensor \vec{M} is the part of the generalized diffusion tensor that originates from the inter-chain interactions,

$$\vec{M}_{\alpha\beta}(\mathbf{R}, \mathbf{R}'; t) = \frac{D_0}{(k_B T)^2} \left\langle \prod_\gamma \delta(\mathbf{R}_\gamma - \mathbf{r}_\gamma^0) \mathbf{F}_\alpha^{0, \text{inter}} \mathcal{Q} \times \exp(\mathcal{Q} \mathcal{O}_S \mathcal{Q} t) \mathcal{Q} \mathbf{F}_\beta^{0, \text{inter}} \prod_\delta \delta(\mathbf{R}'_\delta - \mathbf{r}_\delta^0) \right\rangle_{\text{eq}} \times \frac{1}{\omega(\mathbf{R}'_1, \dots, \mathbf{R}'_N)}. \quad (\text{A21})$$

It should be noted here that the ‘‘vertices’’ of the tensor \vec{M} involve the inter-chain forces only.

The final step of the derivation is further reduction of the tensor \vec{M} . As was pointed out by Cichocki and Hess¹¹ and by Kawasaki¹² the inter-chain interactions induced contribution to the diffusion tensor is not an irreducible quantity. It is the inter-chain interactions induced contribution to the *friction* tensor that is completely irreducible.

To get the friction tensor we have to introduce an irreducible projected Smoluchowski operator,

$$\mathcal{Q} \mathcal{O}_S^{\text{irr}} \mathcal{Q} = \mathcal{Q} D_0 \left[\sum_\alpha \frac{\partial}{\partial \mathbf{r}_\alpha^0} \cdot \mathcal{Q} \left(\frac{\partial}{\partial \mathbf{r}_\alpha^0} - \beta \mathbf{F}_\alpha^0 \right) + \sum_{\alpha, i \neq 0} \frac{\partial}{\partial \mathbf{r}_\alpha^i} \cdot \left(\frac{\partial}{\partial \mathbf{r}_\alpha^i} - \beta \mathbf{F}_\alpha^i \right) \right] \mathcal{Q}. \quad (\text{A22})$$

It is important to note that the additional projection operator introduced in Eq. (A22) is, first, identical to the projection used in the derivation of the memory function (A18), and, second, inserted only between parts of the Smoluchowski operator pertaining to the tagged chain. This is different from the general scheme outlined in Refs. 11,12. The difference stems from the fact that we are dealing with the tagged chain problem (self-diffusion, *not* collective diffusion).

Next, we rewrite Eq. (A21) with the help of the identity (A17) substituting this time $A = \mathcal{Q} \mathcal{O}_S^{\text{irr}} \mathcal{Q}$ and $B = \mathcal{Q}(\mathcal{O}_S - \mathcal{O}_S^{\text{irr}}) \mathcal{Q}$. We get

$$\vec{M}_{\alpha\beta}(\mathbf{R}, \mathbf{R}'; t) = \vec{M}_{\alpha\beta}^{\text{irr}}(\mathbf{R}, \mathbf{R}'; t) - \sum_\gamma \int_0^t dt' \int d\mathbf{R}'' \times \vec{M}_{\alpha\gamma}^{\text{irr}}(\mathbf{R}, \mathbf{R}''; t-t') \vec{M}_{\gamma\beta}(\mathbf{R}'', \mathbf{R}'; t'), \quad (\text{A23})$$

where the inter-chain interactions induced contribution to the friction is given explicitly by the following formula

$$\vec{M}_{\alpha\beta}^{\text{irr}}(\mathbf{R}, \mathbf{R}'; t) = \frac{D_0}{(k_B T)^2} \left\langle \prod_\gamma \delta(\mathbf{R}_\gamma - \mathbf{r}_\gamma^0) \mathbf{F}_\alpha^{0, \text{inter}} \mathcal{Q} \times \exp(\mathcal{Q} \mathcal{O}_S^{\text{irr}} \mathcal{Q} t) \mathcal{Q} \mathbf{F}_\beta^{0, \text{inter}} \prod_\delta \delta(\mathbf{R}'_\delta - \mathbf{r}_\delta^0) \right\rangle_{\text{eq}} \times \frac{1}{\omega(\mathbf{R}'_1, \dots, \mathbf{R}'_N)}. \quad (\text{A24})$$

As the last step we note that with the help of the tensor \vec{M}^{irr} the memory matrix (A20) can be written as

$$\mathcal{M}(\mathbf{R}, \mathbf{R}'; t) = -D_0 \sum_{\alpha\beta} \frac{\partial}{\partial \mathbf{R}_\alpha} \cdot [\vec{I} + \vec{M}^{\text{irr}}]^{-1} \vec{M}_{\alpha\beta}^{\text{irr}}(\mathbf{R}, \mathbf{R}'; t) \times \left(\frac{\partial}{\partial \mathbf{R}'_\beta} - \left(\frac{\partial}{\partial \mathbf{R}'_\beta} \ln \omega(\mathbf{R}') \right) \right). \quad (\text{A25})$$

Note that here (and in the main text) the inverse $[\vec{I} + \vec{M}^{\text{irr}}]^{-1}$ is understood as the kernel of the inverse integral operator.

Now we combine the formal expression (A9) for the time derivative of the tagged chain distribution function with the expressions (A16) and (A25) for the frequency and memory matrices, respectively, and we arrive at the effective diffusion equation Eq. (1).

APPENDIX B: BOUND FOR THE DIFFUSION CONSTANT

The analysis presented in this section is valid for any friction tensor that leads to a mobility tensor that is symmetric, positive definite, and divergenceless. Note that the phenomenological friction tensor (7) satisfies these conditions.

We start with the lower bound for the self-diffusion constant that was derived by Fixman.²⁷ In terms of the dimensionless friction tensor $(\vec{I} \delta_{\alpha\beta} + \vec{M}_{\alpha\beta})$ this bound can be written in the following way,

$$D \geq D^{(K)} - \frac{D_0}{N^2} \left\langle \sum_{\alpha\beta} (\mathbf{V}_\alpha - \mathbf{V}_\alpha^{(0)}) \cdot (\vec{I} \delta_{\alpha\beta} + \vec{M}_{\alpha\beta}) \cdot (\mathbf{V}_\beta - \mathbf{V}_\beta^{(0)}) \right\rangle_{\text{eq}}^0. \quad (\text{B1})$$

Here $D^{(K)}$ is the Kirkwood approximation for the diffusion constant,

$$D^{(K)} = \frac{D_0}{N^2} \left\langle \sum_{\alpha\beta} \mathbf{e}_z \cdot [\vec{I} \delta_{\alpha\beta} + \vec{M}_{\alpha\beta}]^{-1} \cdot \mathbf{e}_z \right\rangle_{\text{eq}}^0. \quad (\text{B2})$$

Furthermore,

$$\mathbf{V}_\alpha^{(0)} = \sum_\beta [\vec{I} \delta_{\alpha\beta} + \vec{M}_{\alpha\beta}]^{-1} \cdot \mathbf{e}_z, \quad (\text{B3})$$

$\langle \dots \rangle_{\text{eq}}^0$ denotes averaging over the tagged chain equilibrium distribution $\omega(\mathbf{R})$, and \mathbf{e}_z denotes a unit vector in the z -di-

rection. Finally, in Eq. (B1) \mathbf{V}_α are variational parameters that satisfy the following condition (note that \mathbf{V}_α can be functions of the bead positions \mathbf{R}),

$$\sum_{\alpha} \frac{\partial}{\partial \mathbf{R}_{\alpha}} \cdot (\mathbf{V}_{\alpha} \omega(\mathbf{R})) = 0. \quad (\text{B4})$$

For our purposes it is convenient to combine the two terms at the right hand side of Eq. (B1) and to rewrite it in the following way,

$$D \geq 2 \frac{D_0}{N^2} \left\langle \sum_{\alpha} \mathbf{V}_{\alpha} \cdot \mathbf{e}_z \right\rangle_{\text{eq}}^0 - \frac{D_0}{N^2} \left\langle \sum_{\alpha\beta} \mathbf{V}_{\alpha} \cdot (\vec{\Gamma} \delta_{\alpha\beta} + \vec{M}_{\alpha\beta}) \cdot \mathbf{V}_{\beta} \right\rangle_{\text{eq}}^0. \quad (\text{B5})$$

Now let us chose the simplest possible set of trial \mathbf{V}_{α} ,

$$\mathbf{V}_{\alpha} = c \mathbf{e}_z, \quad (\text{B6})$$

where c is a constant that will be determined variationally. Due to the translational invariance of the equilibrium distribution the condition (B4) is satisfied automatically. Substituting Eq. (B6) into the bound (B5), minimizing the result with respect to c , and finally using the optimal c we get the following result

$$D \geq \frac{D_0}{\left\langle \sum_{\alpha\beta} \mathbf{e}_z \cdot (\vec{\Gamma} \delta_{\alpha\beta} + \vec{M}_{\alpha\beta}) \cdot \mathbf{e}_z \right\rangle_{\text{eq}}^0}. \quad (\text{B7})$$

The result (B7) is used in Sec. IV to determine the minimal scaling of the anisotropy that is consistent with the observed scaling of the self-diffusion coefficient.

¹For a recent critical review see, e.g., T. P. Lodge, N. A. Rotstein, and S. Prager, *Adv. Chem. Phys.* **LXXIX**, 1 (1990).

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⁵See, e.g., Ref. 1, p. 30.

⁶For a work along these lines within a mode-coupling approximation see Ref. 7.

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¹⁰See, e.g., J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).

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²⁵Y. Oono, *Adv. Chem. Phys.* **LXI**, 301 (1985).

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