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Brownian dynamics simulations of the self- and collective rotational diffusion coefficients of rigid long thin rods

Yu-Guo Tao, W. K. den Otter, and J. T. Padding

Computational Dispersion Rheology, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

J. K. G. Dhont

Forschungszentrum Jülich, Institut für Festkörperforschung (IFF)/Weiche Materie, D-52425 Jülich, Germany

W. J. Briels^{a)}

Computational Dispersion Rheology, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

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Recently a microscopic theory for the dynamics of suspensions of long thin rigid rods was presented, confirming and expanding the well-known theory by Doi and Edwards [*The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986)] and Kuzuu [J. Phys. Soc. Jpn. **52**, 3486 (1983)]. Here this theory is put to the test by comparing it against computer simulations. A Brownian dynamics simulation program was developed to follow the dynamics of the rods, with a length over a diameter ratio of 60, on the Smoluchowski time scale. The model accounts for excluded volume interactions between rods, but neglects hydrodynamic interactions. The self-rotational diffusion coefficients $D_r(\varphi)$ of the rods were calculated by standard methods and by a new, more efficient method based on calculating average restoring torques. Collective decay of orientational order was calculated by means of equilibrium and nonequilibrium simulations. Our results show that, for the currently accessible volume fractions, the decay times in both cases are virtually identical. Moreover, the observed decay of diffusion coefficients with volume fraction is much quicker than predicted by the theory, which is attributed to an oversimplification of dynamic correlations in the theory. © 2005 American Institute of Physics. [DOI: 10.1063/1.1940031]

I. INTRODUCTION

Suspensions of rigid rodlike colloids dissolved in Newtonian liquids are of great importance both in biological and in industrial applications. Already in the first half of the previous century, Onsager¹⁻³ understood that very long and thin rods will display interesting thermodynamic phase behavior at very low volume fractions. The complete phase diagram for varying aspect ratios and volume fractions was determined a decade ago by Bolhuis and co-workers^{4,5} by means of Monte Carlo simulation. In dilute solutions, the basic equation describing the dynamics of rigid long thin rods is well established⁶⁻⁸ and the dynamical properties have been calculated by various authors.⁹⁻¹³ The self-orientational diffusion of rods in semidilute or concentrated solution, however, is difficult to understand quantitatively due to the complexity of the restoring torque exerted by surrounding rods. A theoretical analysis is very complicated because in principle both excluded volume interactions and hydrodynamic interactions have to be taken into account. Fortunately, it may be argued¹⁴ that the latter are negligible for very large aspect ratios L/D , where L is the length of the rods and D

their diameter. Even then, the problem remains to be very tough and results are only obtained on the basis of severe approximations.

In this paper we present the results of Brownian dynamics simulations of a system of interacting rods without hydrodynamic interactions. A justification for the neglect of the latter has been presented in Ref. 14. Besides this justification, the main reason to neglect hydrodynamic interactions in this work is that we intend to provide results with which to compare the theoretical predictions. Any possible deviation between theoretical prediction and corresponding simulation results must then be due to one or more of the remaining approximations in the theory. In Sec. II we briefly discuss these approximations.

In Sec. III we describe our simulation model, which we prove in Appendix B to be equivalent to the Smoluchowski equation on which the theory is based. Excluded volume interactions are modeled with a pairwise interaction potential whose terms are proportional to the overlap volume of the corresponding pair of rods. It will be shown that this potential is accurate enough to simulate collections of hard rods. In Sec. IV we present the results of our simulations and compare them to the corresponding theoretical prediction. Finally, in Sec. V we summarize our findings.

^{a)}Electronic mail: w.j.briels@utwente.nl

II. THEORY

For long and thin rigid rodlike colloids suspended in Newtonian liquids, the fundamental equation of motion, in the overdamped limit, is the N -particle Smoluchowski equation, describing the time evolution of the probability density function (pdf) of the phase-space coordinates of the rods. When hydrodynamic interactions between rods are neglected, integration of the N -particle Smoluchowski equation for a very large aspect ratio leads to (see Appendix A)

$$\frac{\partial}{\partial t} P(\hat{\mathbf{u}}, t) = D_r \hat{\mathcal{R}} \cdot \{ \hat{\mathcal{R}} P(\hat{\mathbf{u}}, t) - \beta P(\hat{\mathbf{u}}, t) \bar{\mathbf{T}}(\hat{\mathbf{u}}, t) \}. \quad (1)$$

Here, $P(\hat{\mathbf{u}}, t)$ is the one-particle pdf of the orientation $\hat{\mathbf{u}}$ of some rod, with $\hat{\mathbf{u}}$ being the unit vector along the long axis of the rod at time t . The rotational operator $\hat{\mathcal{R}} \equiv \hat{\mathbf{u}} \times \partial / \partial \hat{\mathbf{u}}$ plays a role analogous to that of the gradient operator ∇_r in translational diffusion. β is defined as $1/k_B T$ with Boltzmann's constant k_B and temperature T , and D_r is the rotational diffusion coefficient of a single rod

$$D_r = \frac{k_B T}{\gamma_r} = \frac{3k_B T \ln(L/D)}{\pi \eta_s L^3}, \quad (2)$$

where γ_r is the rotational friction coefficient and η_s the viscosity of the solvent. The average torque acting on the central rod $\bar{\mathbf{T}}(\hat{\mathbf{u}}, t)$ in Eq. (1) is expressed as

$$\begin{aligned} \bar{\mathbf{T}}(\hat{\mathbf{u}}, t) = & -\bar{\rho} \int d\mathbf{r}' \oint d\hat{\mathbf{u}}' \bar{P}(\hat{\mathbf{u}}', t) g(\mathbf{r} - \mathbf{r}', \hat{\mathbf{u}}, \hat{\mathbf{u}}', t) \\ & \times \hat{\mathcal{R}} V(\mathbf{r} - \mathbf{r}', \hat{\mathbf{u}}, \hat{\mathbf{u}}'), \end{aligned} \quad (3)$$

where $\bar{\rho}$ is the number density of rods and $V(\mathbf{r} - \mathbf{r}', \hat{\mathbf{u}}, \hat{\mathbf{u}}')$ is the pair-interaction potential for two rods with orientations $\hat{\mathbf{u}}$ and $\hat{\mathbf{u}}'$ and center-center separation $\mathbf{r} - \mathbf{r}'$; because of translational invariance the pair-correlation function $g(\mathbf{r} - \mathbf{r}', \hat{\mathbf{u}}, \hat{\mathbf{u}}', t)$ depends on $\mathbf{r} - \mathbf{r}'$ instead of $\mathbf{r}$ and $\mathbf{r}'$ separately and consequently $\bar{\mathbf{T}}(\hat{\mathbf{u}}, t)$ does not depend on $\mathbf{r}$. $\bar{P}(\hat{\mathbf{u}}', t)$ is the one-particle pdf of the surrounding rods.

A few remarks about the average torque $\bar{\mathbf{T}}(\hat{\mathbf{u}}, t)$ and its use in Eq. (1) should be made at this point. First, we note that the most basic equation of motion describing the dynamics of our system, the N -particle Smoluchowski equation, is a first-order differential equation of time. Therefore, it requires for its solution a precise description of the initial N -particle pdf, the initial state for short, which obviously depends on the specific experiment that we want to describe. The ensuing N -particle pdf at later times, and consequently the corresponding reduced pdf's such as $P(\hat{\mathbf{u}}, t)$, $\bar{P}(\hat{\mathbf{u}}', t)$, and $g(\mathbf{r} - \mathbf{r}', \hat{\mathbf{u}}, \hat{\mathbf{u}}', t)$, will depend on this initial state as well. Now suppose that during our experiment we only monitor the one-particle pdf $P(\hat{\mathbf{u}}, t)$. Equation (1) then in principle suffices to describe our results. In order to solve this equation, however, we need to specify the average torque $\bar{\mathbf{T}}(\hat{\mathbf{u}}, t)$, which according to Eq. (3) and the remarks just made depends on the initial state. In Eq. (3), depending on the specific experiment under investigation, $\bar{P}(\hat{\mathbf{u}}', t)$ may be equal to $P(\hat{\mathbf{u}}, t)$ or not. To describe the decay of a single rod initially aligned along $\hat{\mathbf{u}}_0$

in an isotropic environment, $\bar{P}(\hat{\mathbf{u}}, t) = 1/4\pi$ while $P(\hat{\mathbf{u}}, t)$ decays from $P(\hat{\mathbf{u}}, 0) = \delta(\hat{\mathbf{u}} - \hat{\mathbf{u}}_0)$ to $P(\hat{\mathbf{u}}, \infty) = 1/4\pi$. To study the decay of rods which are all initially aligned along $\hat{\mathbf{u}}_0$, $\bar{P}(\hat{\mathbf{u}}, t) = P(\hat{\mathbf{u}}, t)$ at all times.

In Ref. 14 only the case with $\bar{P}(\hat{\mathbf{u}}, t) = P(\hat{\mathbf{u}}, t)$ has been investigated. Moreover, for analytical purposes, Dhont and Briels¹⁴ neglect all dynamical correlations and put $g(\mathbf{r} - \mathbf{r}', \hat{\mathbf{u}}, \hat{\mathbf{u}}', t)$ equal to its equilibrium value $g(\mathbf{r} - \mathbf{r}', \hat{\mathbf{u}}, \hat{\mathbf{u}}')$. Next, following Onsager,^{2,3} for long and thin rods they write

$$g(\mathbf{r} - \mathbf{r}', \hat{\mathbf{u}}, \hat{\mathbf{u}}') = \exp\{-\beta V(\mathbf{r} - \mathbf{r}', \hat{\mathbf{u}}, \hat{\mathbf{u}}')\}. \quad (4)$$

With this approximation, the torque is given by¹⁴

$$\bar{\mathbf{T}}(\hat{\mathbf{u}}, t) = -2\beta^{-1} D L^2 \bar{\rho} \hat{\mathcal{R}} \oint d\hat{\mathbf{u}}' P(\hat{\mathbf{u}}', t) |\hat{\mathbf{u}} \times \hat{\mathbf{u}}'|. \quad (5)$$

In a final step, they use a Ginzburg–Landau-type expansion of $|\hat{\mathbf{u}} \times \hat{\mathbf{u}}'|$ in the above equation:

$$|\hat{\mathbf{u}} \times \hat{\mathbf{u}}'| \approx \frac{5\pi}{16} \left(1 - \frac{3}{5} \hat{\mathbf{u}} \hat{\mathbf{u}} : \hat{\mathbf{u}}' \hat{\mathbf{u}}' \right). \quad (6)$$

Note that in this expansion a factor of $\sqrt{2/3}$ has been replaced by $\pi/4$ for cosmetic reasons (with 3.8% deviation). Evaluation of the average torque $\bar{\mathbf{T}}(\hat{\mathbf{u}}, t)$ then leads to¹⁴

$$\bar{\mathbf{T}}(\hat{\mathbf{u}}, t) = -\frac{5}{2} \beta^{-1} \left(\frac{L}{D} \varphi \right) \hat{\mathcal{R}} \left\{ 1 - \oint d\hat{\mathbf{u}}' \hat{\mathbf{u}}' \hat{\mathbf{u}}' P(\hat{\mathbf{u}}', t) : \hat{\mathbf{u}} \hat{\mathbf{u}} \right\}, \quad (7)$$

where φ is the volume fraction of rods.

We now introduce a quantity of central importance for homogeneous suspensions of long thin rods: the orientational order tensor

$$\mathbf{S}(t) = \oint d\hat{\mathbf{u}} \hat{\mathbf{u}} \hat{\mathbf{u}} P(\hat{\mathbf{u}}, t), \quad (8)$$

which measures the orientational order. The largest eigenvalue of this tensor $\mathbf{S}$ is a measure of the degree of nematic order, while the corresponding eigenvector is “the director” of an aligned state and points in the preferred direction of the orientation of the rods.

Multiplying both sides of Eq. (1) by $\hat{\mathbf{u}} \hat{\mathbf{u}}$, applying Eq. (7) for the torque, and integrating with respect to $\hat{\mathbf{u}}$, we obtain the equation of motion of the orientational order-parameter tensor $\mathbf{S}$ as

$$\frac{d}{dt} \mathbf{S} = -6D_r \left\{ \mathbf{S} - \frac{1}{3} \hat{\mathbf{I}} + \frac{L}{D} \varphi (\mathbf{S}^{(4)} : \mathbf{S} - \mathbf{S} \cdot \mathbf{S}) \right\}, \quad (9)$$

where $\hat{\mathbf{I}}$ is the unit tensor, $\mathbf{S}^{(4)} = \langle \hat{\mathbf{u}} \hat{\mathbf{u}} \hat{\mathbf{u}} \hat{\mathbf{u}} \rangle$ is a fourth-order tensor, and the brackets $\langle \cdots \rangle$ denote ensemble averaging. In order to make further progress we approximate¹⁴

$$\mathbf{S}^{(4)} : \mathbf{S} = \frac{1}{5} \{ 2\mathbf{S} \cdot \mathbf{S} + 3\mathbf{S}\mathbf{S} : \mathbf{S} \}. \quad (10)$$

Equation (9) is called the DEK equation after Doi and Edwards and Kuzuu and Doi.^{6,15} Note that in order to arrive at the DEK equation, $\bar{P}(\hat{\mathbf{u}}', t)$ in Eq. (7) has been put equal to the pdf $P(\hat{\mathbf{u}}', t)$ of the central rod. This means that the DEK

equation applies to the dynamics of $\mathbf{S}$ of a rod floating among other rods, all having the same initial pdf as the central rod. Consequently, the DEK equation applies to the order tensor of one rod monitored during a collective decay of some collective perturbation. We therefore apply a small perturbation $\delta\mathbf{S}(t)$ to our system and write $\mathbf{S}(t)$ as

$$\mathbf{S}(t) = \mathbf{S}_0 + \delta\mathbf{S}(t), \quad (11)$$

where $\mathbf{S}_0$ is the stationary solution of the equation of motion in Eq. (9). Linearizing Eq. (9) with respect to $\delta\mathbf{S}(t)$, we obtain

$$\frac{d}{dt}\delta\mathbf{S} = -6D_r^{\text{coll}}(\varphi)\delta\mathbf{S}. \quad (12)$$

The collective rotational diffusion coefficient $D_r^{\text{coll}}(\varphi)$ is given by

$$D_r^{\text{coll}}(\varphi) = D_r \left\{ 1 - \frac{1}{5} \frac{L}{D} \varphi \right\}. \quad (13)$$

As has been stressed above, $D_r^{\text{coll}}(\varphi)$ is a collective diffusion coefficient, which describes the decay of a very small perturbation of an initially isotropic state. The spinodal concentration can be found at the point where $D_r^{\text{coll}}(\varphi)$ is equal to zero.

III. SIMULATION METHOD

A. Dynamics

In this section we will briefly sketch a motivation for the equations of motion on the diffusive time scale used in this paper, starting from the more fundamental Langevin equation on the Fokker–Planck time scale. In Appendix B, we will prove that the resulting equations, Eqs. (27), (28), (30), and (31), indeed give rise to a probability distribution function evolving according to the Smoluchowski equation Eq. (A1).

Brownian dynamics is basically the solution of a set of Langevin equations on the Smoluchowski time scale. For very long and thin rods,¹⁶ the rotational motion around the cylindrical axis does not couple to the remaining degrees of freedom and may be neglected. Assuming that for large aspect ratios L/D and low volume fractions $L/D\varphi$ the flow field around the rods is equal to the externally applied field, the Langevin equations of motion for translation and rotation can be written as

$$\frac{d\mathbf{p}}{dt} = -\mathbf{\Xi} \cdot \mathbf{v} + \mathbf{F}_R + \mathbf{F}_S, \quad (14)$$

$$\mathbf{v} = \frac{d\mathbf{r}}{dt}, \quad (15)$$

$$\frac{d\mathbf{J}}{dt} = -\gamma_r \mathbf{\Omega} + \mathbf{T}_R + \mathbf{T}_S, \quad (16)$$

$$\mathbf{\Omega} = \hat{\mathbf{u}} \times \frac{d\hat{\mathbf{u}}}{dt}. \quad (17)$$

Here $\mathbf{p}$ and $\mathbf{J}$ denote the momentum and angular momentum of some rod, $\mathbf{v}$ and $\mathbf{\Omega}$ the linear and angular velocity, and $\mathbf{F}$

and $\mathbf{T}$ denote the force and torque, respectively. The subscripts R and S refer to random (caused by thermal collisions with solvent molecules) and systematic (due to the interactions between rods). In Eq. (14), the translational friction tensor $\mathbf{\Xi}$ is orientation dependent:

$$\mathbf{\Xi} = \gamma_{\parallel} \hat{\mathbf{u}} \hat{\mathbf{u}} + \gamma_{\perp} (\hat{\mathbf{I}} - \hat{\mathbf{u}} \hat{\mathbf{u}}), \quad (18)$$

where $\gamma_{\parallel}$ and $\gamma_{\perp}$ are the translational friction coefficients for motions parallel and perpendicular to the axis of the rod, respectively, while in Eq. (16) γ_r denotes the orientational friction coefficient.^{6,17} From hydrodynamics, the following expressions can be derived for long thin rods:

$$\gamma_r = \frac{\pi \eta_s L^3}{3 \ln(L/D)}, \quad (19)$$

$$\gamma_{\parallel} = \frac{2\pi \eta_s L}{\ln(L/D)}, \quad (20)$$

$$\gamma_{\perp} = 2\gamma_{\parallel}. \quad (21)$$

In Eqs. (19) and (20), η_s denotes the viscosity of the solvent. Finally, the random force and torque are related to the corresponding friction tensors by fluctuation-dissipation theorems,

$$\langle \mathbf{F}_R(t) \mathbf{F}_R(0) \rangle = 2k_B T \mathbf{\Xi} \delta(t), \quad (22)$$

$$\langle \mathbf{T}_R(t) \mathbf{T}_R(0) \rangle = 2k_B T \gamma_r (\hat{\mathbf{I}} - \hat{\mathbf{u}} \hat{\mathbf{u}}) \delta(t), \quad (23)$$

where $\delta(t)$ is the Dirac delta function.

In the highly damped systems that we will study, momenta lose their memory and relax to thermal equilibrium well within a time interval Δt , which is still too short for the configuration to change appreciably. We therefore average Eq. (14) over time Δt while keeping $\mathbf{\Xi}$ fixed at its value at the beginning of the interval. Doing so, we arrive at

$$0 = -\mathbf{\Xi} \cdot \langle \mathbf{v} \rangle + \langle \mathbf{F}_R \rangle + \mathbf{F}_S, \quad (24)$$

which is the equation of motion on the Smoluchowski, i.e., diffusive, time scale. The left-hand side is equal to zero because the average acceleration is very small compared to the individual terms on the right-hand side. $\langle \mathbf{v} \rangle$ is the average velocity, which is equal to $d\langle \mathbf{r} \rangle / dt$. Being a sum of Gaussian variables, the average random force $\langle \mathbf{F}_R \rangle$ is itself a Gaussian variable, with autocorrelation function

$$\langle \langle \mathbf{F}_R(\tau \Delta t) \rangle \langle \mathbf{F}_R(0) \rangle \rangle = 2k_B T \mathbf{\Xi} \frac{\delta_{\tau,0}}{\Delta t}, \quad (25)$$

for integer τ and with δ the Kronecker delta. On the Smoluchowski time scale $\delta_{\tau,0}/\Delta t$ acts as a Dirac delta function.

Since from now on we are only interested in the dynamics at the Smoluchowski time scale, we omit the bracket indicating the time average, and simply write $\mathbf{r}$, $\mathbf{v}$, and $\mathbf{F}_R$ instead of $\langle \mathbf{r} \rangle$, $\langle \mathbf{v} \rangle$, and $\langle \mathbf{F}_R \rangle$. Equation (24) then reads

$$\frac{d\mathbf{r}}{dt} = \Xi^{-1} \cdot (\mathbf{F}_R + \mathbf{F}_S). \quad (26)$$

Assuming that the friction tensor Ξ and the systematic force $\mathbf{F}_S$ are constant over the integration time step δt , we integrate Eq. (26), obtaining

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \Xi^{-1}(t) \cdot \mathbf{F}_S(t) \delta t + \delta \mathbf{r}(t), \quad (27)$$

$$\langle \delta \mathbf{r}(t) \delta \mathbf{r}(t) \rangle = 2k_B T \Xi^{-1}(t) \delta t. \quad (28)$$

The random displacement $\delta \mathbf{r}(t)$, which is contributed by the random force, is defined as

$$\begin{aligned} \delta \mathbf{r}(t) &= \int_0^{\delta t} d\tau \Xi^{-1}(t + \tau) \cdot \mathbf{F}_R(t + \tau) \\ &\approx \Xi^{-1}(t) \cdot \int_0^{\delta t} d\tau \mathbf{F}_R(t + \tau). \end{aligned} \quad (29)$$

Since $\Xi^{-1} = \gamma_{\parallel}^{-1} \hat{\mathbf{u}} \hat{\mathbf{u}} + \gamma_{\perp}^{-1} (\hat{\mathbf{I}} - \hat{\mathbf{u}} \hat{\mathbf{u}})$ depends on the fluctuating variable $\hat{\mathbf{u}}$, the first integral in Eq. (29) is ambiguous and a choice has to be made to its interpretation. Since reorientations are generally much slower than displacements we have chosen to put $\Xi^{-1}(t + \tau)$ equal to $\Xi^{-1}(t)$, which in the mathematical literature is known as the Itô interpretation. Given this interpretation, the moments in Eq. (28) follow from the autocorrelations in Eq. (25). In the simulation program, the random displacements $\delta \mathbf{r}(t)$ are calculated as follows: a random displacement with standard deviation $\sqrt{2k_B T \delta t / \gamma_{\parallel}}$ is applied along the cylindrical axis direction $\hat{\mathbf{u}}$, and two random displacements, each with standard deviation $\sqrt{2k_B T \delta t / \gamma_{\perp}}$, are applied in two mutually perpendicular directions, both perpendicular to $\hat{\mathbf{u}}$.

A similar treatment of the reorientations in the strongly damped limit leads to

$$\hat{\mathbf{u}}(t + \delta t) = \hat{\mathbf{u}}(t) + \frac{1}{\gamma_r} \mathbf{T}_S(t) \times \hat{\mathbf{u}}(t) \delta t + \delta \hat{\mathbf{u}}(t), \quad (30)$$

$$\langle \delta \hat{\mathbf{u}}(t) \delta \hat{\mathbf{u}}(t) \rangle = 2k_B T \frac{1}{\gamma_r} (\hat{\mathbf{I}} - \hat{\mathbf{u}} \hat{\mathbf{u}}) \delta t. \quad (31)$$

Again we have used the Itô interpretation to calculate the moments in Eq. (31). The random reorientations $\delta \hat{\mathbf{u}}(t)$ are treated in the same way as $\delta \mathbf{r}(t)$ above: two Gaussian reorientations, with standard deviation $\sqrt{2k_B T \delta t / \gamma_r}$, are applied in two mutually orthogonal directions, both perpendicular to $\hat{\mathbf{u}}$. Since this procedure will slightly change the length of $\hat{\mathbf{u}}(t)$, the latter is normalized to unity after the integration step has been applied.

Equations (27), (28), (30), and (31) constitute the equations of motion used in this paper. In Appendix B we prove that they indeed give rise to the Smoluchowski equation Eq. (A1). This proof should be considered to be the decisive motivation for choosing the above equations of motion.

The simulation system in the present work was based on the experimental data of fd virus.¹⁶ All simulations were run using a time step δt of 0.05 μ s. The simulation box was cubic, and contained $N = 1000L/D\varphi$ rods of diameter

$D = 14.8$ nm and length $L = 0.88$ μ m, hence $L/D = 60$. Water was used as the solvent, with viscosity $\eta = 10^{-3}$ Pa s. The temperature was 300 K.

B. Potential

In this section, the implementation of the excluded volume interactions between rods will briefly be discussed. Excluded volume interactions are described by means of the potential

$$\Phi = k \sum_{i \neq j} V_{\text{ov}}(\mathbf{r}_i, \mathbf{r}_j, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j), \quad (32)$$

where the sum runs over all pairs of rods. The “hardness” k of the potential is independent of the position $\mathbf{r}$ and orientation $\hat{\mathbf{u}}$ of the rod. In our simulations, the value of this parameter k is chosen such that the pair potential equals the thermal energy $k_B T$ when the distance between two perpendicular rods equals 0.8 times their diameter. The overlap volume between rods i and j , $V_{\text{ov}}(\mathbf{r}_i, \mathbf{r}_j, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j)$, is calculated from

$$V_{\text{ov}}(\mathbf{r}_i, \mathbf{r}_j, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = V_{\text{ov}}(d(\mathbf{r}_i, \mathbf{r}_j, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j), \theta(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j)), \quad (33)$$

$$\begin{aligned} V_{\text{ov}}(d, \theta) &= \frac{4}{\sin \theta} \int_{-(D+d)/2}^{(D-d)/2} dp \sqrt{\left(\frac{D}{2}\right)^2 - \left(\frac{d}{2} + p\right)^2} \\ &\quad \times \sqrt{\left(\frac{D}{2}\right)^2 - \left(\frac{d}{2} - p\right)^2}, \end{aligned} \quad (34)$$

where d is the shortest distance between the two rods, i.e., d is the projection of the center to center separation onto the direction of $\hat{\mathbf{u}}_i \times \hat{\mathbf{u}}_j$,

$$d(\mathbf{r}_i, \mathbf{r}_j, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = \frac{|(\mathbf{r}_i - \mathbf{r}_j) \cdot (\hat{\mathbf{u}}_i \times \hat{\mathbf{u}}_j)|}{|\hat{\mathbf{u}}_i \times \hat{\mathbf{u}}_j|}, \quad (35)$$

and θ is the angle between the long axes of the two rods. Details can be found in Ref. 18.

Equation (33) is valid only for infinitely long rods. For long thin rods of finite length, the overlap volume must be calculated in a different way in cases when two rods are almost parallel, or, to be more precise, when $\sin \theta < D/L$. In this work we have set the overlap volume in these cases equal to

$$\begin{aligned} V_{\text{ov}}(\mathbf{r}_i, \mathbf{r}_j, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) &= A_{\text{ov}} L_{\text{ov}} \\ &= 2 \left(\frac{1}{4} D^2 \arccos \frac{d}{D} - \frac{d}{4} \sqrt{D^2 - d^2} \right) \\ &\quad \times \left(L - \frac{1}{2} (|(\mathbf{r}_i - \mathbf{r}_j) \cdot \hat{\mathbf{u}}_i| + |(\mathbf{r}_i - \mathbf{r}_j) \cdot \hat{\mathbf{u}}_j|) \right). \end{aligned} \quad (36)$$

Here, A_{ov} and L_{ov} denote the overlap area and the overlap length, respectively.

A consequence of using a continuous potential to describe the repulsive or excluded volume interaction between two rods is that the rods can partly overlap. The parameter D is no longer a legitimate measure of the rod's diameter. We therefore propose to use the average shortest distance, calculated according to Eq. (35), of two interacting, i.e., overlap-

FIG. 1. The probability distribution $P_d(x)$ of the dimensionless closest distance x , defined as d/D , between two interacting rods at various volume fractions. There is no overlap between rods when the dimensionless closest distance x becomes larger than one.

ping, rods as an effective diameter D^{eff} . The measured probability densities $P_d(x)$ of shortest dimensionless distances x , defined as d/D , between interacting rod pairs are plotted in Fig. 1 for various volume fractions $L/D\phi$. The effective diameter of the rods can be calculated according to

$$D^{\text{eff}} = D \frac{\int_0^1 dx P_d(x) x}{\int_0^1 dx P_d(x)} = 0.88D, \quad (37)$$

and is independent of the density, which illustrates the hardness of the potential. The small root-mean-square deviation

$$\sigma = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \approx 0.1 \quad (38)$$

confirms the impenetrability of the rods. By introducing the effective diameter, the rods become “thinner,” which changes the aspect ratio L/D^{eff} from 60 to 68. Henceforth we will use D as a shorthand for D^{eff} , except of course in the calculation of V_{ov} . The volume fraction of the rod material will be calculated as if all rods have a fixed diameter equal to D^{eff} .

Given the potential Φ , the forces and torques that are needed to propagate the system are calculated according to

$$\mathbf{F}_i = -\nabla_i \Phi = -k \frac{\partial}{\partial \mathbf{r}_i} V_{\text{ov}}(\mathbf{r}_i, \mathbf{r}_j, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j), \quad (39)$$

$$\mathbf{T}_i = -\hat{\mathcal{R}}_i \Phi = -\hat{\mathbf{u}}_i \times \frac{\partial}{\partial \hat{\mathbf{u}}_i} \Phi = -k \hat{\mathbf{u}}_i \times \frac{\partial}{\partial \hat{\mathbf{u}}_i} V_{\text{ov}}(\mathbf{r}_i, \mathbf{r}_j, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j). \quad (40)$$

Occasionally two rods may come very close to each other, mainly as a result of the random parts in the equations of motion; the forces and torques become extremely large in these cases. In order to keep the maximum displacements and reorientations per time step within reasonable limits, one-tenth of a diameter and $2D/(10L)$ radians, respectively, we have restricted forces and torques to be smaller than

$$F^{\text{max}} = \frac{1}{10} \frac{D\gamma_{\perp}}{\delta t}, \quad (41)$$

FIG. 2. Rotational self-diffusion coefficients $D_r(\phi)$, calculated by three different kinds of simulations at various volume fractions of rods. The curves are normalized by D_r , the rotational diffusion coefficient of a single noninteracting rod. Method I is based on the Debye theory, Eq. (44), method II on the drag torque on a forceably rotated rod, Eq. (46), and method III on the restoring torque, Eq. (52).

$$T^{\text{max}} = \frac{1}{10} \frac{2D\gamma_r}{L\delta t}, \quad (42)$$

respectively. The probability densities in Fig. 1 used to calculate D^{eff} were sampled from runs based on the forces and torques just described.

IV. RESULTS

We first performed Brownian dynamics simulations on long and thin noninteracting rods, i.e., without considering excluded volume interactions between the rods. By calculating the mean-square displacement¹⁹ of the centers of mass of the rods, we confirmed that the translational diffusion coefficient obeys

$$D_t = \frac{D_{\parallel} + 2D_{\perp}}{3}, \quad (43)$$

with $D_{\parallel} = k_B T / \gamma_{\parallel}$ and $D_{\perp} = k_B T / \gamma_{\perp}$. We measured the rotational diffusion coefficient by calculating

$$\langle P_n(\hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0)) \rangle = \exp(-n(n+1)D_r t), \quad (44)$$

where $P_n(x)$ is the Legendre polynomial of n th order,

$$P_n(x) = \frac{1}{2^n n!} \frac{d^n}{dx^n} (x^2 - 1)^n, \quad (45)$$

and found that it agreed well with its input value [see Eqs. (2) and (19)].

A. Measurements of the rotational diffusion coefficient $D_r(\phi)$

In semidilute and concentrated solutions the rotational motion of a typical rod is very much restricted by the rods in its direct neighborhood. This is the more true, the higher the concentration is, and as a consequence the rotational self-diffusion coefficient depends on the volume fraction ϕ . It may still be calculated according to Eq. (44), but with D_r replaced by $D_r(\phi)$. The results of these calculations are presented in Fig. 2, together with those of two alternative methods. The second method consists of applying a constant ex-

ternal torque $\mathbf{T}_{\text{ex}}$ on a chosen rod and measuring the resulting average angular velocity $\langle \mathbf{\Omega} \rangle$. A small extra potential was applied to restrict the motion of the rod to a plane perpendicular to $\mathbf{T}_{\text{ex}}$. The rotational diffusion coefficient $D_r(\varphi)$ is then obtained from the measured rotational friction coefficient according to the Einstein equation:

$$\mathbf{T}_{\text{ex}} = \gamma_r(\varphi) \langle \mathbf{\Omega} \rangle = \frac{k_B T}{D_r(\varphi)} \langle \mathbf{\Omega} \rangle. \quad (46)$$

As can be seen from Fig. 2, the results of the two methods are in good agreement with each other, and depend strongly on the volume fraction φ .

In order to obtain reasonable estimates of the rotational diffusion coefficients for the higher volume fractions, the correlation function $\langle P_1(\hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0)) \rangle = \langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle$ had to be calculated for correlation times up to $t=0.5$ s. In this subsection we present a method to obtain the same information in a much shorter time. First, take the time derivative of the correlation function $\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle$:

$$\frac{d}{dt} \langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle = \oint d\hat{\mathbf{u}} \hat{\mathbf{u}} \cdot \hat{\mathbf{u}}(0) \frac{\partial}{\partial t} P(\hat{\mathbf{u}}, t), \quad (47)$$

where $P(\hat{\mathbf{u}}, t)$ is the probability distribution function of a rod with initial distribution $P(\hat{\mathbf{u}}, 0) = \delta(\hat{\mathbf{u}} - \hat{\mathbf{u}}(0))$. Introducing Eq. (1) for the time derivative of the pdf we obtain

$$\begin{aligned} \frac{d}{dt} \langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle &= D_r \oint d\hat{\mathbf{u}} \hat{\mathbf{u}} \cdot \hat{\mathbf{u}}(0) \hat{\mathcal{R}} \cdot \hat{\mathcal{R}} P(\hat{\mathbf{u}}, t) \\ &\quad - \beta D_r \oint d\hat{\mathbf{u}} \hat{\mathbf{u}} \cdot \hat{\mathbf{u}}(0) \hat{\mathcal{R}} \cdot P(\hat{\mathbf{u}}, t) \bar{\mathbf{T}}(\hat{\mathbf{u}}, t). \end{aligned} \quad (48)$$

Performing two integrations by parts in the first term and one in the second term according to⁶

$$\oint d\hat{\mathbf{u}} \hat{\mathbf{u}} \mathbf{A}(\hat{\mathbf{u}}) \hat{\mathcal{R}} \mathbf{B}(\hat{\mathbf{u}}) = - \oint d\hat{\mathbf{u}} [\hat{\mathcal{R}} \mathbf{A}(\hat{\mathbf{u}})] \mathbf{B}(\hat{\mathbf{u}}), \quad (49)$$

we obtain

$$\begin{aligned} \frac{d}{dt} \langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle &= -2D_r \langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle \\ &\quad + \beta D_r T_r(\hat{\mathbf{u}}, t) \langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle. \end{aligned} \quad (50)$$

The second term, with

$$T_r(\hat{\mathbf{u}}, t) = \frac{\langle (\hat{\mathbf{u}}(t) \times \hat{\mathbf{u}}(0)) \cdot \bar{\mathbf{T}}(\hat{\mathbf{u}}, t) \rangle}{\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle}, \quad (51)$$

represents the contribution of the restoring torque exerted by the surrounding rods to the time evolution of $\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle$.

For long time $T_r(\hat{\mathbf{u}}, t)$ becomes constant and $\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle$ diffusive. Inserting Eq. (44), with $n=1$, into the left-hand side of Eq. (50) and performing the time derivative, we obtain

FIG. 3. The “restoring torques” T_r shown as functions of time, see Eq. (51). From bottom to top, the lines correspond to $L/D\varphi=0.09$, 0.22, 0.44, 0.88, and 1.76. In each case, a plateau value is reached in a short time.

$$D_r(\varphi) = \lim_{t \rightarrow \infty} D_r(\varphi, t) = \lim_{t \rightarrow \infty} D_r \left\{ 1 - \frac{1}{2} \beta T_r(\hat{\mathbf{u}}, t) \right\}. \quad (52)$$

Repeating the same procedure, starting at Eq. (47), with higher values of n yields

$$\begin{aligned} D_r(\varphi) &= \lim_{t \rightarrow \infty} D_r \left\{ 1 - \frac{\beta}{n(n+1)} \right. \\ &\quad \times \frac{\langle P'_n(\hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0)) [(\hat{\mathbf{u}}(t) \times \hat{\mathbf{u}}(0)) \cdot \bar{\mathbf{T}}(\hat{\mathbf{u}}, t)] \rangle}{\langle P_n(\hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0)) \rangle} \left. \right\}, \end{aligned} \quad (53)$$

where $P'_n(x)$ is the derivative of $P_n(x)$.

The results of our calculations of $\beta T_r(\hat{\mathbf{u}}, t)$ are plotted in Fig. 3. The total time of these simulations is around 0.1–0.2 s, which is considerably shorter than the traditional methods. The corresponding rotational diffusion coefficients are plotted in Fig. 2, referred to as method III. It is seen that all these methods give the same results within statistical errors.

Figure 3 reveals clearly that for all volume fractions $\beta T_r(\hat{\mathbf{u}}, t)$ becomes constant within about 0.005 s. As a result, only rather short simulations are needed to calculate the rotational diffusion coefficients. Contrary to this, for the higher volume fractions $\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle$ becomes diffusive only after 0.05 s. In order to understand why this correlation takes much longer to become diffusive than the time needed for the restoring torque to become constant, we formally solve Eq. (50), obtaining

$$\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle = \exp \left\{ -2t \left[\frac{1}{t} \int_0^t d\tau D_r(\varphi, \tau) \right] \right\}. \quad (54)$$

Although $T_r(\hat{\mathbf{u}}, t)$, and therefore $D_r(\varphi, t)$, becomes constant very quickly, it takes some extra time before the corresponding transient effects in $1/t \int_0^t d\tau D_r(\varphi, \tau)$ have converged. In Fig. 4 the results of $\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle$ calculated according to Eq. (54) are plotted, together with those obtained directly from the simulations. Both agree well within statistical errors.

B. Collective orientational decay

In this subsection we will study the collective orientational decay of initially aligned, but transitionally disordered,

FIG. 4. The autocorrelation of $\hat{\mathbf{u}}$ in isotropic systems at various volume fractions, calculated directly (symbols) and from the restoring torque (lines), see Eq. (54).

rodlike colloids. Since we are only interested in exponential decay close to the equilibrium state, see Eq. (12), all runs had to be extended up to the point where the order tensor elements started to fluctuate. The collective rotational diffusion coefficient defined in Eq. (12) was calculated for various volume fractions and is plotted in Fig. 5, referred to as method A. Obviously, this is not a very efficient method to obtain the quantities aimed for. For this reason, and also to have an independent check of the results, we have resorted to Onsager's regression hypothesis^{20,21} to write

$$\langle \delta \mathbf{S}(t) \delta \mathbf{S}(0) \rangle = \langle \delta \mathbf{S}(0) \delta \mathbf{S}(0) \rangle \exp\{-6D_r^{\text{coll}}(\varphi)t\}, \quad (55)$$

where the brackets indicate averages in the equilibrium state. The results of these calculations are also plotted in Fig. 5, referred to as method B. The results of both methods agree very well with each other but deviate considerably from the theoretical prediction of Dhont and Briels given in Eq. (13). Moreover, they are almost equal to the corresponding self-rotational diffusion coefficients $D_r(\varphi)$ discussed in Sec. IV.

In order to test if our potential $\Phi = V_{\text{ov}}$ given in Eq. (32) is sufficiently hard, we have performed additional simula-

FIG. 5. The collective rotational diffusion coefficient $D_r^{\text{coll}}(\varphi)$ at various volume fractions. In method A, an initially fully aligned system is decaying to the isotropic state, while method B uses Onsager's regression hypothesis to analyze equilibrium fluctuations. The dashed and dotted lines are fits to these methods. The value of the potential parameter k for the "harder" and "softer" simulations (both using method A) are twice and half the standard value, respectively. The straight line is the prediction by the theory of Dhont and Briels, and D_r is the rotational diffusion coefficient of a single noninteracting rod.

FIG. 6. Validation of the approximation made in the doubly contracted form of $\mathbf{S}^{(4)}:\mathbf{S}$, see Eq. (10). For the xx (a) and yy (b) component of this contraction, the approximate right-hand side is plotted against the exact left-hand side. The analyzed configurations are extracted from nonequilibrium simulations, decaying from fully aligned to isotropic, with arrows indicating the evolution in time. The approximations are seen to hold very well for the isotropic system.

tions with somewhat different potentials. The results of runs with double and half the original hardness parameter k are included in Fig. 5, denoted as "harder" and "softer," respectively. It turns out that the harder potential yields the same results as our original potential, indicating that the latter is most probably hard enough to represent hard colloids.

As already mentioned above, the simulation results of the collective rotational diffusion coefficients differ markedly from the theoretical predictions of Dhont and Briels based on DEK theory. As was shown by these authors, several approximations are used to arrive at the DEK equations. First, the time dependence of $g(\mathbf{r}-\mathbf{r}', \hat{\mathbf{u}}, \hat{\mathbf{u}}', t)$ is neglected by putting it equal to its equilibrium value, which to a very good approximation is given by the Onsager formula Eq. (4). Next, $|\hat{\mathbf{u}} \times \hat{\mathbf{u}}'|$ occurring in the torque is approximated by a Landau-Ginzburg expansion. Finally, contractions of the fourth-order tensor $\mathbf{S}^{(4)}$ are calculated by means of closure relations like the one in Eq. (10). Let us start our discussion with the last of these possible shortcomings of the theory. In order to check the quality of Eq. (10), we have calculated both sides directly from the simulations during four typical runs and plotted them in Fig. 6. It is seen that the closure approximation performs very well for all values of the order parameter. Next we turn our attention to the Landau-Ginzburg expansion. From Eq. (5), i.e., right after the neglect of dynamic correlations, it is obvious that the average torque and, therefore, the equation of motion of the order tensor $\mathbf{S}$ are linear in $L/D\varphi$, although they may be highly nonlinear in $\mathbf{S}$. Since, in order to calculate the decay of $\delta \mathbf{S}$ close to equilibrium, we linearize the equation of motion of $\mathbf{S}$ in any case, we obtain a linear dependence of $D_r^{\text{coll}}(\varphi)$ on $L/D\varphi$ irrespective of how exactly the average torque is approximated. This leaves us with the neglect of dynamic correlations as the only possible cause of the difference between theory and

simulations. Notice that both in the theory and in the simulations hydrodynamic interactions were neglected, and that these therefore cannot be the cause of the large deviations between theory and simulations.

Finally, let us return to the fact that the collective rotational diffusion coefficients are virtually equal to the rotational self-diffusion coefficients. Obviously this tells us that the average decay of different rods is hardly correlated, if at all. In Appendix C we prove that under this condition,

$$\langle \delta S_{ii}(t) \delta S_{ii}(0) \rangle = \langle \delta S_{ii}(0) \delta S_{ii}(0) \rangle \langle P_2(\hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0)) \rangle. \quad (56)$$

Together with $\langle P_2(\hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0)) \rangle = \exp\{-6D_r(\varphi)t\}$, this proves that under these assumptions $D_r^{\text{coll}}(\varphi) = D_r(\varphi)$.

V. CONCLUSION

A Brownian dynamics simulation program has been written to investigate the diffusion properties of rigid long thin rodlike colloids. This program is based on the solution of the Langevin equations of motion on the Smoluchowski time scale. Hard-core interactions are taken into account by means of a pairwise additive potential, with each pair contributing proportional to the overlap of the corresponding rods. Hydrodynamic interactions between different rods are neglected. Self- and collective rotational diffusion coefficients were calculated from isotropic equilibrium simulations as well as from nonequilibrium simulations of initially fully aligned systems. The results of the present paper can be summarized as follows:

- (i) A new method for calculating the self-rotational diffusion coefficient $D_r(\varphi)$ is proposed by exploiting the restoring torque on a rod by its surrounding rods. The simulation results based on this much quicker technique agree very well with those calculated from two traditional time-consuming approaches, at various volume fractions $L/D\varphi$.
- (ii) The measured collective rotational diffusion coefficients $D_r^{\text{coll}}(\varphi)$ show large deviations from the theoretical prediction of Dhont and Briels, for both equilibrium and nonequilibrium Brownian dynamics simulations. This is attributed to the neglect of dynamical correlations in the theory.
- (iii) The simulations indicate that the self-rotational diffusion coefficients $D_r(\varphi)$ and the collective rotational diffusion coefficients $D_r^{\text{coll}}(\varphi)$ are virtually identical for the systems studied here. A theoretical investigation corroborates this observation and the conditions for which it is expected to hold true.

The insights gained from the simulations in the importance of the dynamical correlation between rods are a valuable asset to guide future improvements of the theory on the dynamics of long thin rigid rods. Further algorithmic improvements are needed to extend the current simulations to higher volume fractions, in order to study the dynamics of liquid crystal-like phase transitions, which are computationally too demanding for the current program.

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APPENDIX A: DERIVATION OF EQ. (1) FROM THE N -PARTICLE SMOLUCHOWSKI EQUATION

The N -particle Smoluchowski equation is the equation of motion for the probability density function P of the positions $\{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ and orientations $\{\hat{\mathbf{u}}_1, \dots, \hat{\mathbf{u}}_N\}$ of the N rigid rods in the system under consideration. This equation reads,^{17,22–24}

$$\begin{aligned} \frac{\partial P}{\partial t} = \sum_{j=1}^N \left\{ \frac{3}{4} D_i \nabla_j \cdot (\hat{\mathbf{I}} + \hat{\mathbf{u}}_j \hat{\mathbf{u}}_j) \cdot [\nabla_j P + \beta P \nabla_j \Phi] \right. \\ \left. + D_r \hat{\mathcal{R}}_j \cdot [\hat{\mathcal{R}}_j P + \beta P \hat{\mathcal{R}}_j \Phi] \right\}, \quad (A1) \end{aligned}$$

where D_i and D_r are the translational and rotational diffusion coefficients of a free, noninteracting rod, and Φ is the total interaction energy of the assembly of N rods. Hydrodynamic interactions between the rods are neglected in the above equation.

Analytical progress can be made by assuming a pairwise additive total potential, that is,

$$\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N, \hat{\mathbf{u}}_1, \dots, \hat{\mathbf{u}}_N) = \sum_{i < j} V(\mathbf{r}_i - \mathbf{r}_j, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j), \quad (A2)$$

with V the pair-interaction potential. This is exact for the rods with hard-core interactions considered here. According to the integral theorems of Gauss and Stokes, we have, respectively,

$$\int d\mathbf{r}_j \nabla_j \cdot (\dots) = 0 \quad \text{and} \quad \oint d\hat{\mathbf{u}}_j \hat{\mathcal{R}}_j \cdot (\dots) = 0. \quad (A3)$$

Using these relations, and noting that

$$\begin{aligned} P(\hat{\mathbf{u}}_1, t) = \int d\mathbf{r}_1 \dots \int d\mathbf{r}_N \oint d\hat{\mathbf{u}}_2 \dots \oint d\hat{\mathbf{u}}_N \\ \times P(\mathbf{r}_1, \dots, \mathbf{r}_N, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \dots, \hat{\mathbf{u}}_N, t), \quad (A4) \end{aligned}$$

the integration of both sides of the Smoluchowski equation with respect to $\mathbf{r}_1, \dots, \mathbf{r}_N$ and $\hat{\mathbf{u}}_2, \dots, \hat{\mathbf{u}}_N$ leads to Eqs. (1) and (3) (with $\hat{\mathbf{u}} = \hat{\mathbf{u}}_1$, $\hat{\mathbf{u}}' = \hat{\mathbf{u}}_2$, $\mathbf{r} = \mathbf{r}_1$, and $\mathbf{r}' = \mathbf{r}_2$), where the pair-correlation function g is defined as

$$\begin{aligned} P(\mathbf{r}, \mathbf{r}', \hat{\mathbf{u}}, \hat{\mathbf{u}}', t) &\equiv \int d\mathbf{r}_3 \dots \int d\mathbf{r}_N \oint d\hat{\mathbf{u}}_3 \dots \oint d\hat{\mathbf{u}}_N \\ &\times P(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \dots, \mathbf{r}_N, \hat{\mathbf{u}}, \hat{\mathbf{u}}', \hat{\mathbf{u}}_3, \dots, \hat{\mathbf{u}}_N, t) \\ &\equiv \frac{1}{V^2} P(\hat{\mathbf{u}}, t) \bar{P}(\hat{\mathbf{u}}', t) g(\mathbf{r} - \mathbf{r}', \hat{\mathbf{u}}, \hat{\mathbf{u}}', t), \quad (A5) \end{aligned}$$

with $P(\mathbf{r}, \mathbf{r}', \hat{\mathbf{u}}, \hat{\mathbf{u}}', t)$ the pdf for the positions and orientations of two rods and V the volume. The two one-particle pdf's have been assumed to possibly differ. This point is further discussed in Sec. II.

APPENDIX B: EQUIVALENCE OF BROWNIAN DYNAMICS EQUATIONS OF MOTION AND THE SMOLUCHOWSKI EQUATION

In this Appendix we will briefly sketch the proof of the equivalence of the equations of motion used in this paper, Eqs. (27), (28), (30), and (31), and the Smoluchowski equation Eq. (A1). Although the general approach in this Appendix is fairly standard,^{25–27} some of the technical details are a bit intricate. We will closely follow Appendix IV C in Ref. 27.

From the equations of motion it is obvious that our system is Markovian. Therefore, the pdf $P=P(z, z_0; t)$ with $z=\{z_1, \dots, z_N\}$ and $z_i=\{\mathbf{r}_i, \hat{\mathbf{u}}_i\}$ satisfies the Chapman–Kolmogorov equation

$$P(z', z_0; t + \delta t) = \int dz P(z', z; \delta t) P(z, z_0; t). \quad (\text{B1})$$

We explicitly mention the initial value z_0 of z to clarify the meaning of the Chapman–Kolmogorov equation. Since we are interested in the limit of $\delta t \rightarrow 0$, in which case $P(z', z; \delta t)$ approaches a Dirac delta distribution, and we prefer not to make a Taylor expansion of the latter, we multiply the Chapman–Kolmogorov equation by $F(z')$ and integrate, obtaining

$$\begin{aligned} \int dz P(z, z_0; t + \delta t) F(z) \\ = \int dz \left[\int dz' P(z', z; \delta t) F(z') \right] P(z, z_0; t). \end{aligned} \quad (\text{B2})$$

In the integral between the square brackets on the right-hand side we may now safely expand $F(z')$ around $z'=z$, writing

$$\begin{aligned} F(z') &= F(z) + (z' - z) \cdot \nabla_z F(z) \\ &+ \frac{1}{2} (z' - z)(z' - z) : \nabla_z \nabla_z F(z) + \dots \end{aligned} \quad (\text{B3})$$

It will turn out that all terms of order higher than two do not contribute to the final result. Performing the integral we find

$$\begin{aligned} \int dz' P(z, z'; \delta t) F(z') &= F(z) + \langle \Delta z; \delta t \rangle \cdot \nabla_z F(z) \\ &+ \frac{1}{2} \langle \Delta z \Delta z; \delta t \rangle : \nabla_z \nabla_z F(z), \end{aligned} \quad (\text{B4})$$

with moments defined by

$$\langle \Delta z; \delta t \rangle = \int dz' (z' - z) P(z', z; \delta t), \quad (\text{B5})$$

$$\langle \Delta z \Delta z; \delta t \rangle = \int dz' (z' - z)(z' - z) P(z', z; \delta t). \quad (\text{B6})$$

Although the second-order moments contribute a $5N \times 5N$ matrix, only those elements which are of first order in δt contribute to the final result. Since elements corresponding to two different particles are of order $(\delta t)^2$, we may restrict our attention to just one particle and write in more detail

$$\begin{aligned} \langle \delta z; \delta t \rangle \cdot \nabla_z F(z) &+ \frac{1}{2} \langle \Delta z \Delta z; \delta t \rangle : \nabla_z \nabla_z F(z) \\ &= \langle \Delta \mathbf{r}; \delta t \rangle \cdot \nabla F(z) + \langle \Delta \hat{\mathbf{u}}; \delta t \rangle \cdot (\hat{\mathbf{I}} - \hat{\mathbf{u}}\hat{\mathbf{u}}) \cdot \nabla_{\hat{\mathbf{u}}} F(z) \\ &+ \frac{1}{2} \langle \Delta \mathbf{r} \Delta \mathbf{r}; \delta t \rangle : \nabla \nabla F(z) \\ &+ \frac{1}{2} \langle \Delta \hat{\mathbf{u}} \Delta \hat{\mathbf{u}}; \delta t \rangle : (\hat{\mathbf{I}} - \hat{\mathbf{u}}\hat{\mathbf{u}}) \cdot \nabla_{\hat{\mathbf{u}}} (\hat{\mathbf{I}} - \hat{\mathbf{u}}\hat{\mathbf{u}}) \cdot \nabla_{\hat{\mathbf{u}}} F(z), \end{aligned} \quad (\text{B7})$$

where ∇ is the gradient with respect to $\mathbf{r}$ and $\nabla_{\hat{\mathbf{u}}}$ the derivative with respect to $\hat{\mathbf{u}}$. In the Itô interpretation of the stochastic integrals Eqs. (28) and (31), mixed second-order moments of translational and rotational displacements are uncorrelated and therefore of second order in δt . The remaining moments are

$$\langle \Delta \mathbf{r}; \delta t \rangle = -\Xi^{-1}(t) \cdot \nabla \Phi(t) \delta t,$$

$$\langle \Delta \hat{\mathbf{u}}; \delta t \rangle = \frac{1}{\gamma_r} \hat{\mathbf{u}}(t) \times \hat{\mathcal{R}} \Phi(t) \delta t,$$

$$\langle \Delta \mathbf{r} \Delta \mathbf{r}; \delta t \rangle = 2k_B T \Xi^{-1}(t) \delta t,$$

$$\langle \Delta \hat{\mathbf{u}} \Delta \hat{\mathbf{u}}; \delta t \rangle = 2k_B T \frac{1}{\gamma_r} (\hat{\mathbf{I}} - \hat{\mathbf{u}}(t)\hat{\mathbf{u}}(t)) \delta t, \quad (\text{B8})$$

where we have used Eqs. (27), (28), (30), (31), (39), and (40). Introducing these moments into Eq. (B7), using $(\hat{\mathbf{I}} - \hat{\mathbf{u}}\hat{\mathbf{u}}) \cdot \nabla_{\hat{\mathbf{u}}} = -\hat{\mathbf{u}} \times \hat{\mathcal{R}}$, $(\hat{\mathbf{u}} \times (\hat{\mathcal{R}}\Phi)) \cdot (\hat{\mathbf{u}} \times \hat{\mathcal{R}}) = (\hat{\mathcal{R}}\Phi) \cdot \hat{\mathcal{R}}$ and $(\hat{\mathbf{I}} - \hat{\mathbf{u}}\hat{\mathbf{u}}) : (\hat{\mathbf{u}} \times \hat{\mathcal{R}})(\hat{\mathbf{u}} \times \hat{\mathcal{R}}) = (\hat{\mathbf{u}} \times \hat{\mathcal{R}}) \cdot (\hat{\mathbf{u}} \times \hat{\mathcal{R}}) = \hat{\mathcal{R}} \cdot \hat{\mathcal{R}}$, we obtain

$$\begin{aligned} \langle \Delta z; \delta t \rangle \cdot \nabla_z F(z) &+ \frac{1}{2} \langle \Delta z \Delta z; \delta t \rangle : \nabla_z \nabla_z F(z) \\ &= -(\Xi^{-1} \cdot \nabla \Phi) \cdot \nabla F(z) \delta t - \gamma_r^{-1} (\hat{\mathcal{R}}\Phi) \cdot \hat{\mathcal{R}} F(z) \delta t \\ &+ k_B T \Xi^{-1} : \nabla \nabla F(z) \delta t + k_B T \gamma_r^{-1} \hat{\mathcal{R}} \cdot \hat{\mathcal{R}} F(z) \delta t. \end{aligned} \quad (\text{B9})$$

We finally combine Eqs. (B2), (B4), and (B9) and perform some partial integrations according to¹⁴

$$\begin{aligned} \int d^3 \mathbf{r} \mathbf{A}(\mathbf{r}) \cdot \nabla F(z) &= - \int d^3 \mathbf{r} (\nabla \cdot \mathbf{A}(\mathbf{r})) F(z), \\ \oint d\hat{\mathbf{u}} \mathbf{A}(\hat{\mathbf{u}}) \cdot \hat{\mathcal{R}} F(z) &= - \oint d\hat{\mathbf{u}} (\hat{\mathcal{R}} \cdot \mathbf{A}(\hat{\mathbf{u}})) F(z), \end{aligned} \quad (\text{B10})$$

obtaining in the limit of $\delta t \rightarrow 0$:

$$\begin{aligned} \int dz \frac{\partial}{\partial t} P(z, z_0; t) F(z) &= \int dz \{ \nabla \cdot \Xi^{-1} \cdot (\nabla \Phi) P(z, z_0; t) \\ &+ \gamma_r^{-1} \hat{\mathcal{R}} \cdot (\hat{\mathcal{R}}\Phi) P(z, z_0; t) \\ &+ k_B T \nabla \nabla : \Xi^{-1} P(z, z_0; t) \\ &+ k_B T \gamma_r^{-1} \hat{\mathcal{R}} \cdot \hat{\mathcal{R}} P(z, z_0; t) \} F(z). \end{aligned} \quad (\text{B11})$$

Since $F(z)$ is completely general, $\partial/\partial t P(z, z_0; t)$ must be equal to the sum between curly brackets on the right-hand side. Summing over all particles on the right-hand side and using $\nabla \nabla : \Xi^{-1} P = \nabla \cdot \Xi^{-1} \cdot \nabla P$, we obtain the Smoluchowski

equation Eq. (A1). The reader will have no difficulties to justify the unproven claims made in the course of the derivation.

APPENDIX C: DERIVATION OF EQ. (56) WITH APPROXIMATIONS OF TIME CORRELATION FUNCTION

For a homogeneous isotropic equilibrium system the time correlation functions of the spontaneous fluctuations of the orientational order-parameter tensor $\langle \delta \mathbf{S}(t) \delta \mathbf{S}(0) \rangle$ are given by

$$\langle \delta S_{yy}(t) \delta S_{yy}(0) \rangle = \frac{1}{N^2} \sum_n \sum_m \left\langle \left(u_{yn}(t) u_{yn}(0) - \frac{1}{3} \right) \times \left(u_{ym}(0) u_{ym}(0) - \frac{1}{3} \right) \right\rangle, \quad (\text{C1})$$

where we have chosen the yy component for convenience. Rewriting Eq. (C1) leads to

$$\begin{aligned} \langle \delta S_{yy}(t) \delta S_{yy}(0) \rangle &= -\frac{1}{9} + \frac{1}{N^2} \sum_n \langle u_{yn}(t) u_{yn}(t) u_{yn}(0) u_{yn}(0) \rangle \\ &+ \frac{1}{N^2} \sum_n \sum_{n \neq m} \langle u_{yn}(t) u_{yn}(t) u_{ym}(0) u_{ym}(0) \rangle. \end{aligned} \quad (\text{C2})$$

Assuming that correlations of $u_y(t)$ for different rods can be neglected, i.e.,

$$\begin{aligned} \sum_n \sum_{n \neq m} \langle u_{yn}(t) u_{yn}(t) u_{ym}(0) u_{ym}(0) \rangle \\ = \sum_n \sum_{n \neq m} \langle u_{yn}(t) u_{yn}(t) \rangle \langle u_{ym}(0) u_{ym}(0) \rangle, \end{aligned} \quad (\text{C3})$$

the right-hand side of Eq. (C2) results in

$$\begin{aligned} -\frac{1}{9} + \frac{1}{N^2} \sum_n \sum_m \langle u_{yn}(t) u_{yn}(t) \rangle \langle u_{ym}(0) u_{ym}(0) \rangle \\ + \frac{1}{N^2} \sum_n \{ \langle u_{yn}(t) u_{yn}(t) u_{yn}(0) u_{yn}(0) \rangle \\ - \langle u_{yn}(t) u_{yn}(t) \rangle \langle u_{yn}(0) u_{yn}(0) \rangle \}. \end{aligned} \quad (\text{C4})$$

Thus,

$$\langle \delta S_{yy}(t) \delta S_{yy}(0) \rangle = \frac{1}{N^2} \sum_n \left\{ \langle (u_{yn}(t) u_{yn}(0))^2 \rangle - \frac{1}{9} \right\}. \quad (\text{C5})$$

In the isotropic state, the time correlation functions for x , y , and z components are identical,

$$\begin{aligned} \sum_n \langle (u_{yn}(t) u_{yn}(0))^2 \rangle &= \frac{1}{3} \sum_n [\langle (u_{xn}(t) u_{xn}(0))^2 \rangle \\ &+ \langle (u_{yn}(t) u_{yn}(0))^2 \rangle \\ &+ \langle (u_{zn}(t) u_{zn}(0))^2 \rangle]. \end{aligned} \quad (\text{C6})$$

Assuming that the off-diagonal correlations of the one-

particle orientational order-parameter tensor decay extremely fast, i.e., $\langle S_{ii}(t) S_{jj}(0) \rangle \sim 0$, we obtain

$$\begin{aligned} \sum_n \langle (u_{yn}(t) u_{yn}(0))^2 \rangle &\approx \frac{1}{3} \sum_n \langle (u_{xn}(t) u_{xn}(0) + u_{yn}(t) u_{yn}(0) \\ &+ u_{zn}(t) u_{zn}(0))^2 \rangle. \end{aligned} \quad (\text{C7})$$

Finally, Eq. (C1) results in

$$\langle \delta S_{yy}(t) \delta S_{yy}(0) \rangle \approx \frac{2}{9} \frac{1}{N^2} \sum_n \left\langle \frac{3}{2} (\hat{\mathbf{u}}_n(t) \cdot \hat{\mathbf{u}}_n(0))^2 - \frac{1}{2} \right\rangle. \quad (\text{C8})$$

Apart from a constant factor, this is nothing but $\langle P_2(\hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0)) \rangle$.

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²⁴The general form for the diffusion tensor of uniaxial rods is $k_B T \Xi^{-1} = D_{\parallel} \hat{\mathbf{I}} + \Delta D (\hat{\mathbf{u}} \hat{\mathbf{u}} - \hat{\mathbf{I}})$, where $\Delta D = D_{\parallel} - D_{\perp}$, with $D_{\parallel}$ and $D_{\perp}$ the inverse friction coefficients for motion parallel and perpendicular to the long axis, respectively. For very long and thin rods, $D_{\parallel} = 2D_{\perp}$, in which case the above general expression reduces to $\frac{3}{4} D_{\parallel} [\hat{\mathbf{I}} + \hat{\mathbf{u}} \hat{\mathbf{u}}]$, with $D_{\parallel} = \frac{1}{3} (D_{\parallel} + 2D_{\perp})$. This expression for the translational diffusion tensor has been used in the first term in (A1).

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