Dynamics of semiflexible and rigid particles. I. The velocity distribution and the Smoluchowski equation

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In this paper we present a derivation of Langevin equations of motion for long semiflexible particles and the Smoluchowski equation together with the velocity distribution for suspended rigid polymers in the long-time limit. The starting point is the induced force method of Mazur and Bedeaux [Physica A **76**, 235 (1976)] and Landau-Lifshitz [*Fluid Mechanics* (Pergamon, Oxford, 1987)] fluctuating hydrodynamics. Such a procedure permits us to introduce in the description all the properties of the dynamics of the solvent in a rather straightforward way, which leads us to a precise derivation of friction coefficients, without assumptions taken out of the theory itself, and to a description in terms of Langevin equations. The link between the mesoscopic hydrodynamic description and a more coarse-grained one in terms of the Smoluchowski equation is thus established by means of a singular perturbation method. The long-time limit in the dynamics of the suspended particles permits us to also obtain the velocity distribution, which is not Maxwellian as postulated in classical treatments of Brownian motion. The velocity distribution obtained in this way relates the dynamics of suspensions to the dynamics of simple liquids. In addition, buoyancy and centrifugal forces are also obtained. [S1063-651X(96)02810-3]

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I. INTRODUCTION

In the analysis of the dynamics of suspensions, it is of great importance to develop models that, on one hand, reproduce the important features of the system and, on the other, disregard all unimportant details, in a difficult balance between accuracy and feasibiliy. Suspensions are characterized by a large difference in size and mass between the suspended particles and the solvent molecules. Such a difference is the basis of most of the simplifications that can be made to propose tractable models. We can mention two relevant ones: first, the detailed molecular structure of the suspended particle is commonly ignored when the interest is in overall motions and, second, the solvent can be regarded as a continuum interacting with the suspended particles via frictional forces.

For instance, the classical theory of polymer solutions as formulated by Kirkwood [1–4] is based on the classical theory of Brownian motion [5] almost always in the diffusion limit, which suppresses the explicit consideration of the inertial forces. Thus the segments of the chain are considered as moving with a mean drift velocity determined by the balance between the systematic frictional force, potential forces, and the Brownian force. The latter is introduced as a thermodynamic force according to

$$\vec{F}_i^B(\{\vec{r}_k\},t) \equiv -k_B T \frac{\partial}{\partial \vec{r}_i} \ln \psi(\{\vec{r}_k\},t), \tag{1.1}$$

where $\vec{r}_i$ stands for the position of the ith particle, $\{\vec{r}_k\}$ denotes the ensemble of positions of the $k=1,\ldots,N$ particles, and $\psi(\{\vec{r}_k\},t)$ is the probability density in configurational space. $\psi(\{\vec{r}_k\},t)$ then follows the so-called Kirkwood diffusion equation or Smoluchowski equation, which reads

$$\frac{\partial}{\partial t}\psi = -\sum_i \frac{\partial}{\partial \vec{r}_i}\cdot \vec{v}_i^{\,0}\psi + \sum_{i,j} \frac{\partial}{\partial \vec{r}_i}\cdot \vec{\vec{D}}_{ij}\cdot\left(\frac{\partial}{\partial \vec{r}_j}\psi + \frac{\psi}{k_B T}\frac{\partial}{\partial \vec{r}_j}U\right), \tag{1.2}$$

where $\vec{v}_i^{\,0}$ is the imposed velocity field at the position $\vec{r}_i$ of the ith particle. $\vec{\vec{D}}_{ij}$ is the diffusion matrix obtained from hydrodynamic calculations and U is a given potential energy.

Kirkwood's diffusion equation can be derived in the framework of a complete phase space theory where the positions and velocities of polymer segments and solvent molecules are taken into account [6]. In Ref. [6], for instance, the starting point is the Liouville equation for the composite system of solvent and polymers. The information about the relevant dynamic quantity is thus extracted by means of a projector operator formalism. This procedure gives the functional form of the equation for the probability density in configuration space, as well as formal expressions for the coefficients (friction or mobility tensors, for example) appearing in this equation. The complexity of these formal expressions is such that no explicit calculation can be carried out without further assumptions [6]. A common one is due to the fact that the solvent must satisfy the macroscopic equations of motion in the range of wavelengths and frequencies concerned with the overall motions of the macromolecule, and then the formal expressions for the friction coefficients are replaced by those obtained from hydrodynamic calculations. In the context of the transport processes [7] and Brownian motion, there are similar procedures to obtain either Fokker-Planck equations for the probability density in the complete phase space of the particles (velocities and positions) or Smoluchowski equations for the probability density in the configuration space. Again, such procedures start with the Liouville equations for the complete systems [8–10] in which hydrodynamics is invoked to obtain the desired

expressions for the friction or mobility tensors. When establishing the diffusion equation to describe the dynamics of a given system it is not always obvious which friction coefficient is appropriate. This can lead to errors in the choice [11].

Kirkwood's diffusion equation or the Smoluchowski equation describes only the evolution of the system in the configuration space and no reference is made to the distribution function in velocity space that is needed to perform averages on those quatities depending on the velocity. It is then assumed that the distribution function in velocity space follows a local Maxwellian of the form

$$\prod_i \exp\left\{ \frac{[\vec{u}_i - \vec{v}^{\,0}(\vec{r}_i)]^2}{2k_B T} \right\}, \tag{1.3}$$

where $\vec{u}_i$ is the velocity of the ith particle and $k_B T$ has the usual meaning.

In this paper our aim is twofold. First, from a *mesoscopic* description based on both the induced forces method [12] and fluctuating hydrodynamics [14] we will obtain Langevin equations for the motion of semiflexible particles modeled as wormlike chains. The presence of rigid constraints is explicitly considered. Second, we derive the long-time behavior of a suspension of rigid rods by using the fact that the velocity of the particles reaches its steady-state distribution much faster than the time in which configurational changes take place. We then obtain the probability distribution in the complete phase space, in which the dependence in the velocity is explicitly given, as well as its relation with the Smoluchowski equation.

In our procedure, we start by describing the macromolecule as an object of a given instantaneous shape with a well-defined surface, under the action of some internal or external potentials that contribute to its configuration and dynamics. The solvent, constituted by much smaller molecules, is assumed as being a continuum whose dynamics is well described by hydrodynamic equations for the density, velocity field, pressure, and temperature. In addition, due to the thermal motion of the solvent molecules there can exist local variations of the hydrodynamic fields in space and time. We will introduce random fluxes accounting for the cause of these fluctuations [14]. With only these initial hypotheses, it is possible to derive Langevin equations for the motion of the macromolecule. These Langevin equations contain friction coefficients given in terms of integrals over the fluid velocity field propagator that can be explicitly carried out for some particular cases [15–18]. The stochastic properties of the random forces follow from those of the spontaneous fluctuations in the velocity field. From these Langevin equations we will derive the equation of motion in the phase space or Kramers equation. Such an equation will be studied in the particular case of rigid rods in the long-time limit with the aim of deriving the velocity distribution as well as the Smoluchowski equation. It is found that the velocity distribution can be explicitly given in this long-time limit if the friction dominates over the inertia, showing a non-Maxwellian behavior. This behavior is very important from the formal point of view, since it allows the easy derivation of transport equations.

Although, in this paper, we restrict our study to semiflexible long particles, the analysis can straightforwardly be extended to interacting particles, both hydrodynamically and via electromagnetic fields, for instance, and to objects of different shapes in colloidal dispersions. We believe that the formalism developed here can be a poweful tool in the study of suspension dynamics due to the analogy established between these Brownian systems and simple liquids. Although this analogy has already been treated in the literature [19], the long-time limit discussed here constitutes a great simplification, although it retains the relevant information and, at the same time, makes the theory useful for systems of interest.

The paper is organized as follows. In Sec. II we will discuss the concept of induced force and derive the formal solution of the velocity field in terms of the induced force density and the random pressure tensor. In Sec. III we introduce the mobility and friction kernels for semiflexible wormlike chains and derive the equation of motion for the particles as well as an expansion of the surface fields in terms of a complete orthogonal set of functions when constraints are present. In Sec. IV, after arriving at the Kramers equation from the equations of motion for the semiflexible wormlike chain, we obtain the Smoluchowski equation and the probability distribution function for the particular case of a rigid rod. Sections II and III are mainly devoted to details of the use of the induced forces method to the system under consideration. The reader interested only in the derivation of the long-time limit of the Kramers equation can skip these two sections and go directly to Sec. IV. Finally, Sec. V is devoted to the conclusions drawn in this paper.

II. FORMAL SOLUTION OF THE VELOCITY FIELD

The system under consideration here will be an incompressible Newtonian fluid of density ρ_s and shear viscosity η_s at constant temperature T with particles in suspension. Under these conditions of constant temperature and density, the dynamic state of the solvent is thus described by the Navier-Stokes equation for the velocity field $\vec{v}(\vec{r},t)$ [14]

$$\rho_s \left(\frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \vec{\nabla} \vec{v} \right) = -\vec{\nabla} \cdot \vec{\vec{P}}(\vec{r},t) + \vec{\mathcal{F}} \tag{2.1}$$

together with the incompressibility condition

$$\vec{\nabla} \cdot \vec{v} = 0, \tag{2.2}$$

valid outside the particles. In Eq. (2.1) $\vec{\mathcal{F}}(\vec{r},t)$ is a volume force density acting on every fluid element as, for instance, a gravitational field. $\vec{\vec{P}}(\vec{r},t)$ is the pressure tensor given by

$$P_{\alpha\beta} = p\,\delta_{\alpha\beta} - \eta_s \left(\frac{\partial v_\beta}{\partial r_\alpha} + \frac{\partial v_\alpha}{\partial r_\beta} \right) + \Pi^R_{\alpha\beta} = P^s_{\alpha\beta} + \Pi^R_{\alpha\beta}, \tag{2.3}$$

where p is the hydrostatic pressure, $P^S_{\alpha\beta}$ is the systematic part of the pressure tensor, and the random pressure tensor is denoted by $\Pi^R_{\alpha\beta}$ According to fluctuating hydrodynamics [14], the random pressure tensor introduces a Gaussian white-noise stochastic process with

$$\langle \vec{\vec{\Pi}}^R(\vec{r},t)\rangle = 0, \tag{2.4}$$

$$\langle \Pi^R_{\alpha\beta}(\vec{r},t)\Pi^R_{\gamma\mu}(\vec{r}',t')\rangle = 2k_BT\eta\Delta_{\alpha\beta\gamma\mu}\delta(\vec{r}-\vec{r}')\,\delta(t-t'), \tag{2.5}$$

where use has been made of the definition

$$\Delta_{\alpha\beta\gamma\mu} \equiv \delta_{\alpha\gamma}\delta_{\beta\mu} + \delta_{\alpha\mu}\delta_{\beta\gamma} - \tfrac{2}{3}\delta_{\alpha\beta}\delta_{\gamma\mu}. \tag{2.6}$$

The hydrodynamic problem is completly specified by giving the boundary conditions on the surface of the particles and on external boundaries. If the suspended particles are of size much larger than the solvent molecules, the fluid velocity field is found to satisfy stick boundary conditions on the surface of the particles. Thus the fluid in contact with a given element at the surface of a particle moves with the same velocity as the surface element. Stick boundary conditions will be assumed throughout the paper.

Since we want to describe the interaction between the suspended particles and the solvent, we separate the complete velocity field into an unperturbed velocity field $\vec{v}_0$ and a perturbation $\vec{v}_1$. The former is caused by the external boundaries and by the external fields acting on the bulk, while the latter is due to the presence of the particles and to the random pressure tensor. Throughout the paper we will focus our attention on externally imposed steady homogeneous flows of the form $\vec{v}_0(\vec{r}) = \vec{r}\cdot\vec{\vec{\beta}}$, where $\vec{\vec{\beta}}$ is a constant tensor. The unperturbed velocity field is a solution of Eq. (2.1) without perturbations and in the absence of particles

$$\rho_s\left(\frac{\partial \vec{v}_0}{\partial t} + \vec{v}_0\cdot\vec{\nabla}\vec{v}_0\right) = -\vec{\nabla}\cdot\vec{\vec{P}}^S_0(\vec{r},t) + \vec{\mathcal{F}}, \tag{2.7}$$

where we have also made use of the fact that the pressure tensor also admits a decomposition of the form $\vec{\vec{P}}^S = \vec{\vec{P}}^S_0 + \vec{\vec{P}}^S_1$. For steady homogeneous flows Eq. (2.7) reads

$$\rho_s\vec{v}_0(\vec{r})\cdot\vec{\nabla}\vec{v}_0(\vec{r}) = -\vec{\nabla}p_0(\vec{r}) + \vec{\mathcal{F}}(\vec{r}) \tag{2.8}$$

since $\nabla^2\vec{v}_0(\vec{r}) = 0$. The incompressibility condition implies that $\vec{\nabla}\cdot\vec{v}_0 = 0$, which, in our case, turns into $\vec{\vec{1}}:\vec{\vec{\beta}} \equiv \mathrm{tr}\vec{\vec{\beta}} = 0$, where the symbol tr stands for the trace. In Eq. (2.8) $p_0(\vec{r})$ is the unperturbed pressure field. This last equation is in fact an equation for the unperturbed pressure field whose role will be discussed later on.

Since the particles as well as the fluctuations are very small, the evolution of these perturbations satisfy the fully linearized Navier-Stokes equation [14]

$$\rho_s\frac{\partial \vec{v}_1(\vec{r},t)}{\partial t} = -\vec{\nabla}\cdot\vec{\vec{P}}^S_1(\vec{r},t) - \vec{\nabla}\cdot\vec{\vec{\Pi}}^R(\vec{r},t). \tag{2.9}$$

Note that we have neglected the terms proportional to $\vec{v}_0\cdot\vec{\nabla}\vec{v}_1$ and $\vec{v}_1\cdot\vec{\nabla}\vec{v}_0$, which introduce dependences of the friction coefficients in the externally imposed velocity gradients. These corrections, although important, scale, however, with the Reynolds number of the particles, which is extremely small for Brownian particles and usual velocity gradients [20]. These corrections will be discussed elsewhere.

The solution of Eq. (2.9) satisfying the boundary conditions at the surface of the particles gives the perturbed velocity field from which the forces that the solvent exerts on the particles can be calculated. However, the problem can be reformulated by introducing induced forces, whose main advantage is to permit the evaluation of the hydrodynamic forces without explicit determination of the velocity field. One then reformulates the problem by assuming that the fluid field is also defined inside the particles, so that Eq. (2.9) is now valid in all the space, and the perturbations caused by their motion are introduced through induced force densities [12] $\vec{F}(\vec{r},t)$. These are nonzero only inside and at the surface of the particles. These induced force densities are chosen such that the pressure is constant inside the particle and that the velocity field is continuous through the surface, which in fact stands for the stick boundary conditions. Thus, taking all of this into consideration, we arrive at

$$\rho_s\frac{\partial \vec{v}_1(\vec{r},t)}{\partial t} = -\vec{\nabla}p_1(\vec{r},t) + \eta_s\vec{\nabla}^2\vec{v}_1(\vec{r},t) + \vec{F}(\vec{r},t) - \vec{\nabla}\cdot\vec{\vec{\Pi}}^R(\vec{r},t). \tag{2.10}$$

For convenience, we introduce here the Green's function of the perturbed field, which satisfies

$$\rho_s\frac{\partial \vec{\vec{G}}(\vec{r},t)}{\partial t} - \eta_s\vec{\nabla}^2\vec{\vec{G}}(\vec{r},t) = \vec{\vec{1}}\,\delta(\vec{r})\,\delta(t), \tag{2.11}$$

with

$$\vec{\nabla}\cdot\vec{\vec{G}}(\vec{r},t) = 0 \tag{2.12}$$

due to the incompressibility of the fluid. To obtain an expression for $\vec{\vec{G}}$ we introduce here the Fourier transform in space of an arbitrary field $A(\vec{r},t)$ as

$$A(\vec{r},t) = \int \frac{d\vec{k}}{(2\pi)^3}e^{i\vec{k}\cdot\vec{r}}A(\vec{k},t), \tag{2.13}$$

with

$$A(\vec{k},t) = \int d\vec{r}\,e^{-i\vec{k}\cdot\vec{r}}A(\vec{r},t). \tag{2.14}$$

Fourier transforming Eq. (2.11), solving for $\vec{\vec{G}}(\vec{k},t)$, and using Eq. (2.13), one can then obtain

$$\vec{\vec{G}}(\vec{r},t) = \int \frac{d\vec{k}}{(2\pi)^3}\,e^{i\vec{k}\cdot\vec{r}}e^{-\nu k^2 t}\frac{\vec{\vec{1}} - \hat{\vec{k}}\hat{\vec{k}}}{\rho_s}, \tag{2.15}$$

where the incompressibility condition has been used, $\hat{\vec{k}} = \vec{k}/k$, and $\nu \equiv \eta_s/\rho_s$ is the kinematic viscosity. An explicit expression for this integral can be found in Eq. (2.26) of Ref. [15]. Then the formal solution for the total velocity field reads

$$\vec{v}(\vec{r},t)=\vec{v}_0+\vec{v}_1$$
$$=\vec{r}\cdot\vec{\vec{\beta}}+\int_{-\infty}^{t}dt'\int d\vec{r}'\,\vec{\vec{G}}(\vec{r}-\vec{r}',t-t')\cdot\vec{F}(\vec{r}',t')$$
$$+\vec{v}^R(\vec{r},t). \tag{2.16}$$

The random velocity field is defined by

$$\vec{v}^R(\vec{r},t)\equiv\int_{-\infty}^{t}dt'\int d\vec{r}'\,\vec{\vec{G}}(\vec{r}-\vec{r}',t-t')\cdot[-\vec{\nabla}\cdot\vec{\vec{\Pi}}^R(\vec{r}',t')]. \tag{2.17}$$

Equations (2.16) and (2.17) show that the response of the velocity field to the perturbations is neither instantaneous nor local in space. This fact will be important in the derivation of the transport equations. Here we will be concerned, however, with the analysis of the long-time evolution equation for the system. With this aim we then disregard the explicit time dependence of the relaxation of the velocity field, referred to as quasistatic approximation, which is valid for times larger than l^2/ν, l being some characteristic length of the particle. In this case, Eq. (2.16) reduces to

$$\vec{v}(\vec{r},t)=\vec{v}_0(\vec{r},t)+\int d\vec{r}'\,\vec{\vec{T}}(\vec{r}-\vec{r}')\cdot\vec{F}(\vec{r}',t)+\vec{v}^R(\vec{r},t), \tag{2.18}$$

where $\vec{\vec{T}}(\vec{r})$ is the Oseen tensor, which is given by

$$\vec{\vec{T}}(\vec{r})\equiv\int_0^\infty dt\,\vec{\vec{G}}(\vec{r},t)=\int\frac{d\vec{k}}{(2\pi)^3}\frac{\vec{\vec{1}}-\hat{\hat{k}}\hat{\hat{k}}}{\eta_s k^2}e^{i\vec{k}\cdot\vec{r}}$$
$$=\frac{1}{8\pi\eta_s|\vec{r}|}(\vec{\vec{1}}+\hat{\hat{r}}\hat{\hat{r}}). \tag{2.19}$$

Correspondingly, in Eq. (2.18) the random velocity field is

$$\vec{v}^R(\vec{r},t)\equiv\int d\vec{r}'\,\vec{\vec{T}}(\vec{r}-\vec{r})\cdot[-\vec{\nabla}\cdot\vec{\vec{\Pi}}^R(\vec{r}',t)]. \tag{2.20}$$

Further physical insight on the nature of the induced forces can be obtained by analyzing the quasistatic approximation. Effectively, in this approximation the explicit time dependence of the fluid field is disregarded. In this case, the induced force density has only a surface component accounting for the discontinuity in the velocity gradient through the surface (the velocity itself is continuous). With such a force field, the fluid inside moves as a rigid body in steady motion, while the fluid motion outside caused by the induced force field is the same as that caused by the presence of the real particle [12,21].

In this section we have obtained the formal solution for the velocity field in terms of the induced forces and the random stress tensor. In the next section we will use these results to derive the effect of the fluid on the motion of the particle.

III. THE LANGEVIN EQUATION

Let us consider a single wormlike chain in suspension [13]. The chain is of length L and circular section of radius a. The circular shape of the section is assumed not to change during the motion of the particle. Since we want to analyze the long-time properties of the suspension, the formal solution of the velocity field will be given by Eq. (2.18).

We introduce here a set of intrinsic coordinates for the surface of the chain and the volume infinitesimally close to it. We will define the central line as the curve joining the centers of mass of the cross sections of the particle. The position of the points of the central line at a given time t expressed by the one-parameter vector field $\vec{c}(s,t)$, where s is the contour length satisfying $|s|\leqslant L/2$. It is convenient to define the unit vectors [22]

$$\hat{\vec{\tau}}(s,t)\equiv\frac{d\vec{c}(s,t)}{ds}, \tag{3.1}$$

$$\hat{\vec{n}}(s,t)\equiv R(s,t)\frac{d\hat{\vec{\tau}}(s,t)}{ds}=R(s,t)\frac{d^2\vec{c}(s,t)}{ds^2}, \tag{3.2}$$

$$\hat{\vec{b}}(s,t)\equiv\hat{\vec{\tau}}(s,t)\times\hat{\vec{n}}(s,t), \tag{3.3}$$

where $R(s,t)\equiv|d^2\vec{c}(s,t)/ds^2|^{-1}$ is the radius of curvature at s at the time t. The use of the contour length s as a parameter, on one hand, ensures that the tangent vector satisfies $|\hat{\vec{\tau}}|=1$ while, on the other, the normal vector $\hat{\vec{n}}$ is orthogonal to $\hat{\vec{\tau}}$. The third vector is often referred to as *binormal* and $\kappa(s,t)\equiv|d\hat{\vec{b}}(s,t)/ds|$ is the geometrical torsion of the curve [22].

If $\vec{c}(s,t)$ is specified, a given point $\vec{r}$ very close to the surface of the particle can be univocally expressed as

$$\vec{r}=\vec{c}(s,t)+\vec{r}_\perp(s,t), \tag{3.4}$$

where $\vec{r}_\perp(s,t)$ is a vector lying on the plane defined by the vectors $\hat{\vec{n}}(s,t)$ and $\hat{\vec{b}}(s,t)$, i.e., perpendicular, by construction, to the tangent vector $\hat{\vec{\tau}}$. Then, denoting by φ the angle between $\vec{r}_\perp(s,t)$ and $\hat{\vec{n}}(s,t)$ and $r_\perp\equiv|\vec{r}_\perp|$, the point $\vec{r}$ can be given by specifying the set of quantities $(s,r_\perp,\varphi)$, which will be used to parametrize the space inside and very close to the particle.

In the quasistatic case under consideration, the induced force density introduced in Sec. II is only nonzero at the surface of the particle, which can be written as [21]

$$\vec{F}(\vec{r},t)d\vec{r}=\vec{F}^{(s)}(s,\varphi,t)\,\delta^{(s)}(\vec{r},t)r_\perp dr_\perp d\varphi ds, \tag{3.5}$$

where we have introduced the surface δ function $\delta^{(s)}(\vec{r},t)$ (cf. Appendix A). In this paper we will consider that $R(s,t)\gg a$ for every s, which allows us to write

$$\delta^{(s)}(\vec{r},t)=\delta(r_\perp-a), \tag{3.6}$$

which is a function of the instantaneous configuration. In Eq. (3.5), $\vec{F}^{(s)}$ is the induced force per unit area. Up to this point our treatment has been exact. However, for a particle whose aspect ratio a/L is smaller than 1 and for properties whose characteristic length scale is larger than a, one can introduce the following approximation: the induced force density is a function only of the contour length s. One then disregards the explicit induced force distribution around the central line and substitutes it by a uniform force distribution independent of φ

$$\vec{F}^{(s)}(s,\varphi,t) \simeq \frac{\vec{f}(s,t)}{2\pi a}, \tag{3.7}$$

where the new quantity $\vec{f}(s,t)$ is an induced force per unit of length, which will be used in what follows.

To obtain the equation of motion for the chain we will multiply Eq. (2.18) by the surface δ function. In view of the stick boundary condition and the properties of the surface δ function given in Eqs. (A3) and (A4), we can substitute the complete velocity field $\vec{v}(\vec{r},t)$ by $\vec{u}(\varphi,s,t)$, where this last quantity is the velocity of a given point of the surface of the particle. Thus

$$\vec{u}(s,\varphi,t)\,\delta(r_\perp - a) = \vec{v}_0(\vec{r})\,\delta(r_\perp - a) + \delta(r_\perp - a) \times \int d\vec{r}\,' \vec{\vec{T}}(\vec{r}-\vec{r}\,')\cdot[\vec{F}(\vec{r}\,',t) - \vec{\nabla} \cdot \vec{\vec{\Pi}}^R(\vec{r}\,',t)]. \tag{3.8}$$

One can also disregard the φ dependence of the velocity at the surface since rotations around the central line cause a very small perturbation in the fluid field. This is in agreement with the approximation given by Eq. (3.7). These two approximations are not valid for the rotation of a rodlike particle around its axis of symmetry [17], which requires specific treatment of the force and velocity distributions around its symmetry axis. According to this approximation, we can integrate both members of Eq. (3.8) with respect to $r_\perp dr_\perp d\varphi \equiv d\vec{r}_\perp$ and divide by $2\pi a$ to obtain

$$\vec{u}(s,t) \equiv \vec{c}(s,t)\cdot\vec{\beta} + \int ds'\,\vec{\vec{\mu}}(s,s')\cdot\vec{f}(s',t) + \vec{u}^R(s,t), \tag{3.9}$$

where we have introduced the random velocity

$$\vec{u}^R(s,t) \equiv \int \frac{d\vec{r}_\perp}{2\pi a}\delta(r_\perp - a)\int d\vec{r}\,' \vec{\vec{T}}(\vec{r}-\vec{r}\,')\cdot[-\vec{\nabla}\cdot\vec{\vec{\Pi}}^R(\vec{r}\,',t)] \tag{3.10}$$

and the spatial mobility kernel

$$\vec{\vec{\mu}}(s,s') \equiv \int \frac{d\vec{r}_\perp}{2\pi a}\int \frac{d\vec{r}_\perp\,'}{2\pi a}\delta(r_\perp - a)\vec{\vec{T}}(\vec{r}-\vec{r}\,')\,\delta(r_\perp' - a). \tag{3.11}$$

Using Eq. (2.19) and changing the order of integration, the mobility kernel can be rewritten as

$$\vec{\vec{\mu}}(s,s') = \int \frac{d\vec{k}}{(2\pi)^3}\frac{\vec{\vec{1}} - \hat{\vec{k}}\hat{\vec{k}}}{\eta_s k^2}\phi(\vec{k},s,t)\,\phi^*(\vec{k},s',t), \tag{3.12}$$

where the asterisk stands for the complex conjugate. The mobility kernel is a 3×3 symmetric tensor. This property arises from the symmetry of the Oseen tensor. The form factor $\phi(\vec{k},s,t)$ depends on the actual configuration of the system. Using Eq. (3.4), the form factor reads

$$\phi(\vec{k},s,t) = \int \frac{d\vec{r}_\perp}{2\pi a} e^{i\vec{k}\cdot\vec{r}}\delta(r_\perp - a) = e^{i\vec{k}\cdot\vec{c}(s,t)}J_0(k_\perp a), \tag{3.13}$$

where $k_\perp \equiv |\vec{k}\cdot(\vec{\vec{1}} - \hat{\vec{\tau}}\hat{\vec{\tau}})|$, which depends on s, and $J_0(x)$ is the Bessel function of first kind and zeroth order. $J_0(x)$ is the form factor taking into account the finite size of the cross section of the particle and in fact ensures that the integration in Eq. (3.12) is perfectly convergent. Moreover, from Eqs. (3.12) and (3.13) it follows that the mobility kernel, $\vec{\vec{\mu}}(s,s')$ is invariant under the exchange $s \to s'$.

Introducing the friction kernel $\vec{\vec{\xi}}(s,s')$ as the generalized inverse of the mobility kernel $\vec{\vec{\mu}}(s,s')$ [23] (the symmetry properties of the friction kernel are the same as those of the mobility kernel, as it follows from its definition), according to

$$\int_{-L/2}^{L/2} ds''\,\vec{\vec{\xi}}(s,s'')\cdot\vec{\vec{\mu}}(s'',s') = \int_{-L/2}^{L/2} ds''\,\vec{\vec{\mu}}(s,s'')\cdot\vec{\vec{\xi}}(s'',s') = \delta(s-s')\vec{\vec{1}}, \tag{3.14}$$

we can invert Eq. (3.9) to obtain $\vec{f}(s,t)$ in terms of $\vec{u}(s,t) - \vec{c}(s,t)\cdot\vec{\vec{\beta}}$ and $\vec{u}^R(s,t)$, yielding

$$\vec{f}(s,t) = \int_{-L/2}^{L/2} ds'\,\vec{\vec{\xi}}(s,s')\cdot[\vec{u}(s',t) - \vec{c}(s',t)\cdot\vec{\vec{\beta}}] + \vec{f}^R(s,t), \tag{3.15}$$

where the random force is given by

$$\vec{f}^R(s,t) \equiv \int_{-L/2}^{L/2} ds'\,\vec{\vec{\xi}}(s,s')\cdot\vec{u}^R(s',t). \tag{3.16}$$

From the properties of the random pressure tensor given in Eqs. (2.4) and (2.5) and the definition of the random velocity Eq. (3.10), it can be proved that the random force satisfies the properties

$$\langle \vec{f}^R(s,t)\rangle = 0, \tag{3.17}$$

$$\langle \vec{f}^R(s,t)\vec{f}^R(s',t')\rangle = 2k_B T\vec{\vec{\xi}}(s,s')\,\delta(t-t'), \tag{3.18}$$

where the configuration is kept frozen while the average over all the realizations of $\vec{\vec{\Pi}}^R$ is performed. Equation (3.18) is the fluctuation-dissipation theorem.

The motion of a given segment of the chain is given by the system of equations

$$\dot{\vec{c}}(s,t)=\vec{u}(s,t), \tag{3.19}$$

$$\tilde{\mu}\dot{\vec{u}}(s,t)=\vec{f}^{H}(s,t)+\vec{f}^{\text{int}}(s,t)+\vec{f}^{\text{ext}}(s,t)+\vec{g}(s,t), \tag{3.20}$$

where $\tilde{\mu}$ is the mass of the particle per unit of length and $\vec{f}^{H}$ is the hydrodynamic force that accounts for the interaction between the segment and the surrounding solvent. This hydrodynamic force has two contributions. The first one $\vec{f}^{Ha}$ is related to the induced force density and will account for the frictional and Brownian forces. The second contribution $\vec{f}^{Hb}$ is a buoyancy force that appears due to the existence of an unperturbed pressure gradient, according to Eq. (2.8). Effectively, the buoyancy force per unit of length experienced by a segment located at the space point $\vec{c}(s,t)$ simply follows from the integration of the pressure gradient over the volume dV of the segment

$$\begin{aligned}\vec{f}^{Hb}(s,t)ds&=-\int_{dV}\vec{\nabla}p_0\\&=ds\int_0^a dr_\perp r_\perp\int_0^{2\pi}d\varphi[\rho_s\vec{v}_0(\vec{r})\cdot\vec{\nabla}\vec{v}_0(\vec{r})-\vec{\mathcal{F}}(\vec{r})]\\&\equiv[\tilde{\mu}_s\vec{c}(s,t)\cdot\vec{\vec{\beta}}\cdot\vec{\vec{\beta}}+\vec{f}^{b}(s,t)]ds,\end{aligned} \tag{3.21}$$

where we have defined the displaced solvent mass per unit of length $\tilde{\mu}_s\equiv\rho_s\pi a^2$ and

$$\vec{f}^{b}(s,t)\equiv-\int_0^{2\pi}d\varphi\int_0^a dr_\perp r_\perp\vec{\mathcal{F}}(\vec{r}). \tag{3.22}$$

The homogeneous nature of the unperturbed velocity field has also been used. In Eq. (3.20), $\vec{f}^{\text{int}}$ stands for the segment-segment interaction force in which we have included the forces due stretching, bending, and torsion potentials [4], as well as the excluded-volume interactions [24]. We assume that the constraints can be specified by a set of scalar equations of the form

$$\Lambda(\vec{c}(s,t))=0, \tag{3.23}$$

so that the system would be *holonomic* [25] if friction and Brownian forces were not present [24]. The constraints responding to this equation are *rigid* (or *scleronomic* since they do not explicitly depend on the time). This would physically correspond to some hindrance in the configuration of the real polymer that we want to reflect in the model used to describe it. For instance, polymers whose chemical structure imposes very large potential energies for the bending of the backbone can be thought of as rigid polymers or piecewise rigid polymers if the rigidity is not global [26]. Such constraints can be formulated by introducing equations of the type of Eq. (3.23). Another example is the less familiar model of a continuous chain whose local radius of curvature is constant, which would be reminiscent of the fact that locally the bond angles are fixed, although rotation is not hindered. Note that such a chain does not correspond to the so-called Kratky-Porod chain [13]. The constraint equation for the case described is given by $[\partial\vec{\tau}(s,t)/\partial s]^2=1/R^2$. In general, the reader should decide whether or not a particular physical polymer under study can be modeled by a chain responding to some kind of rigid constraint described by an equation of the form of Eq. (3.23). Mechanical constraints that involve the velocity in a way that does not reduce to a time differentiation of Eq. (3.23) are excluded from our description since the associated forces involve energy dissipation [25]. Another important class of systems that are beyond the scope of this work are those responding to constraints formulated as inequalities. An example is a system whose local radius of curvature is forced to be larger than a minimum value.

The existence of constraints gives rise to a force that we have called $\vec{g}(s,t)$. In the term $\vec{f}^{\text{ext}}$ we have gathered the forces due to interactions with external fields such as gravitational, electric, or magnetic. Except for the constraint forces, which will be discussed later on, we demand only that $\vec{f}^{\text{int}}$ as well as $\vec{f}^{\text{ext}}$ are functions of $\vec{c}(s,t)$, of external parameters, and of time. No explicit functional form for these forces, however, has to be assumed in our derivation.

Equations (3.19) and (3.20) do not constitute a closed system of differential equations for $\vec{c}(s,t)$ and $\vec{u}(s,t)$ until $\vec{f}^{Ha}(s,t)$ is specified in terms of these two fields. The relationship between the hydrodynamic force and $\vec{c}(s,t)$ and $\vec{u}(s,t)$ for the polymer can be obtained by realizing that the induced force density $\vec{f}(s,t)$ in Eq. (3.9) is the force that the segment placed at s exerts on the fluid due to its motion. Consequently, the hydrodynamic force that this segment experiences is directly related to the induced force density simply by

$$\vec{f}^{Ha}(s,t)=-\vec{f}(s,t) \tag{3.24}$$

due to the action-reaction principle. Then, using this relation between the induced force and the hydrodynamic force $\vec{f}^{Ha}$ together with Eqs. (3.15) and (3.21), Eqs. (3.19) and (3.20) become

$$\dot{\vec{c}}(s,t)=\vec{u}(s,t), \tag{3.25}$$

$$\begin{aligned}\tilde{\mu}\dot{\vec{u}}(s,t)=&-\int_{-L/2}^{L/2}ds'\vec{\vec{\xi}}(s,s')\cdot[\vec{u}(s',t)-\vec{c}(s',t)\cdot\vec{\vec{\beta}}]\\&+\vec{f}^{\text{int}}(s,t)+\vec{f}^{\text{ext}}(s,t)+\tilde{\mu}_s\vec{c}(s,t)\cdot\vec{\vec{\beta}}\cdot\vec{\vec{\beta}}+\vec{f}^{b}(s,t)\\&+\vec{g}(s,t)+\vec{f}^{R}(s,t).\end{aligned} \tag{3.26}$$

The first term on the right-hand side of Eq. (3.26) describes a nonlocal interaction in space, reflecting the hydrodynamic interactions between differents segments of the particle.

The main difference of the induced force (IF) method and the so-called Oseen-Burgers (OB) procedure employed by Broersma [27–29] and by Yamakawa and co-workers [30–33] is the following: the location of the force in the IF method is at the surface of the particle, accounting for the discontinuities of the velocity gradient through the boundary, while the OB method locates the force on the central line. Another difference lies in the fact that in the IF method, the velocity field at a given surface element is imposed to be the same as the velocity of the particle at the same surface element, which is clearly a statement of stick boundary conditions, while the OB procedure imposes that the average of

the velocity field on a section orthogonal to the central line equals the velocity of the particle at the same central line point. This last condition resembles the stick boundary condition, but does not have a sound physical justification. Both methods, however, lead to the same results when the thickness of the semiflexible chain is very small compared to the global size as, for instance, for infinitely long cylinders [16,32], but it gives significantly different results for particles whose aspect ratio a/L is not infinitely small [16,27–29]. The IF method gives notably better agreement with respect to experiments and numerical calculations [34–37] than the OB procedure.

Representation in a complete and orthonormal set of functions

We will now express Eqs. (3.25) and (3.26) in terms of an orthogonal set of functions, explicitly taking into account the constraint forces. This procedure permits us to pass from a continuum description of the chain, where the variables are positions and velocities of the segments, to a discrete picture, where the variables are the components of $\vec{c}(s,t)$ and $\vec{u}(s,t)$ in the chosen basis. These components of the fields describe global motions of the chain and, furthermore, permit us to establish an analogy between the motion of a single semiflexible continuous chain and that of a set of particles whose coordinates are precisely the components of the fields.

Let us consider a complete and orthonormal set of functions $\varphi_i(x)$, defined in some interval $x\in[a,b]$, i.e.,

$$\int_a^b dx\,\varphi_i(x)\varphi_j(x)=\delta_{ij}, \tag{3.27}$$

$$\sum_i \varphi_i(x)\varphi_i(x')=\delta(x-x'). \tag{3.28}$$

For simplicity, we will take $-1\leqslant x\leqslant 1$. Choosing $x\equiv 2s/L$, a given function of s, $\chi(s,t)=\chi(x,t)$ can be expressed as

$$\chi(x,t)=\sum_i \chi_i(t)\varphi_i(x), \tag{3.29}$$

where the sum is extended over all the values of i and

$$\chi_i(t)=\int_{-1}^{1} dx\,\chi(x,t)\varphi_i(x). \tag{3.30}$$

In this way we can expand $\vec{c}(s,t)$, $\vec{u}(s,t)$, and all the forces in terms of the basis functions. Introducing these expansions in Eqs. (3.25) and (3.26) and using Eq. (3.27), we obtain the equation of motion for the components, referred to as moments from now on,

$$\dot{\vec{c}}_i(t)=\vec{u}_i(t), \tag{3.31}$$

$$\begin{aligned}\tilde{\mu}\dot{\vec{u}}_i(t)=&-\frac{L}{2}\sum_j \vec{\vec{\xi}}_{ij}\cdot[\vec{u}_j(t)-\vec{c}_j(t)\cdot\vec{\vec{\beta}}]+\vec{f}_i^{\,\mathrm{int}}(t)+\vec{f}_i^{\,\mathrm{ext}}(t)\\&+\tilde{\mu}_s\vec{c}_i(t)\cdot\vec{\vec{\beta}}\cdot\vec{\vec{\beta}}+\vec{f}_i^{\,b}(t)+\vec{g}_i(t)+\vec{f}_i^{\,R}(t),\end{aligned} \tag{3.32}$$

where the components of the friction kernel, or friction moments, are defined as

$$\vec{\vec{\xi}}_{ij}\equiv\int_{-1}^{1} dx\,dx'\,\varphi_i(x)\vec{\vec{\xi}}(x,x')\varphi_j(x'), \tag{3.33}$$

which are 3×3 symmetric matrices. In addition, due to the invariance of the friction kernel under the change $s\to s'$ we have that $\vec{\vec{\xi}}_{ij}=\vec{\vec{\xi}}_{ji}$. On the other hand, $\vec{f}_i^{\,R}(t)$ satisfies

$$\langle\vec{f}_i^{\,R}(t)\rangle=0, \tag{3.34}$$

$$\langle\vec{f}_i^{\,R}(t)\vec{f}_j^{\,R}(t')\rangle=2k_BT\vec{\vec{\xi}}_{ij}\delta(t-t'), \tag{3.35}$$

as follows from Eqs. (3.17), (3.18), and (3.33). Again, the averages are performed over all the realizations of the random stress tensor introduced in Eq. (2.3), keeping the configuration of the system frozen. Furthermore, Eq. (3.14) becomes

$$\sum_j \vec{\vec{\xi}}_{ij}\cdot\vec{\vec{\mu}}_{jk}=\sum_j \vec{\vec{\mu}}_{ij}\cdot\vec{\vec{\xi}}_{jk}=\vec{\vec{1}}\left(\frac{2}{L}\right)^2\delta_{ik}, \tag{3.36}$$

where the mobility moments $\vec{\vec{\mu}}_{ij}$ are defined as the friction moments in Eq. (3.33).

Equation (3.23) is equivalent to a set of constraint equations for the moments of the configuration. A possible scheme, although it is not unique, to obtain these constraint equations is to multiply both sides of Eq. (3.23) by $\varphi_i(x)$ and integrate with respect to x. One then gets the system of n equations

$$\Lambda_\alpha(\{\vec{c}_i\})=0 \quad \text{for} \quad \alpha=1,\ldots,n. \tag{3.37}$$

To account for the constraint forces, we introduce a set of n Lagrange multiplyers $\{\lambda_\alpha\}$ [24]. Thus the moments of the constraint forces can be written as

$$\vec{g}_i=\sum_\alpha^n \lambda_\alpha\frac{\partial\Lambda_\alpha}{\partial\vec{c}_i}. \tag{3.38}$$

In order to determine the Lagrange multipliers, let us differentiate Eq. (3.37) twice with respect to time. We obtain

$$\sum_i \frac{\partial\Lambda_\alpha}{\partial\vec{c}_i}\cdot\dot{\vec{u}}_i=-\sum_{i,j}\frac{\partial^2\Lambda_\alpha}{\partial\vec{c}_i\partial\vec{c}_j}:\vec{u}_j\vec{u}_i. \tag{3.39}$$

Multiplying both sides of Eq. (3.32) by $\partial\Lambda_\alpha/\partial\vec{c}_i$, summing over α, and then using Eqs. (3.38) and (3.39), we can arrive at

$$\begin{aligned}\lambda_\alpha=\sum_\beta H^{-1}_{\alpha\beta}\Bigg\{&-\tilde{\mu}\sum_{i,j}\frac{\partial^2\Lambda_\beta}{\partial\vec{c}_i\partial\vec{c}_j}:\vec{u}_j\vec{u}_i+\sum_i\frac{\partial\Lambda_\beta}{\partial\vec{c}_i}\cdot\frac{L}{2}\\&\times\sum_j[\vec{\vec{\xi}}_{ij}\cdot(\vec{u}_j-\vec{c}_j\cdot\vec{\vec{\beta}})-\vec{f}_i-\vec{f}_i^{\,R}]\Bigg\},\end{aligned} \tag{3.40}$$

where here $\vec{f}_i\equiv\vec{f}_i^{\,\mathrm{int}}+\vec{f}_i^{\,\mathrm{ext}}+\tilde{\mu}_s\vec{c}_i\cdot\vec{\vec{\beta}}\cdot\vec{\vec{\beta}}+\vec{f}_i^{\,b}$ and we have defined the $n\times n$ matrix

$$H_{\alpha\beta} \equiv \sum_i \frac{\partial \Lambda_\alpha}{\partial \vec{c}_i} \cdot \frac{\partial \Lambda_\beta}{\partial \vec{c}_i}. \tag{3.41}$$

Using the expressions for the constraint force and the Lagrange multipliers, Eqs. (3.31) and (3.32) take the form

$$\dot{\vec{c}}_i = \vec{u}_i, \tag{3.42}$$

$$\begin{aligned}\tilde{\mu}\left[\dot{\vec{u}}_i + \sum_{\alpha,\beta} \frac{\partial \Lambda_\alpha}{\partial \vec{c}_i} H^{-1}_{\alpha\beta} \sum_{j,k} \frac{\partial^2 \Lambda_\beta}{\partial \vec{c}_j \partial \vec{c}_k} : \vec{u}_k \vec{u}_j\right] \\ = \sum_j \left[\vec{\vec{1}}\delta_{ij} - \sum_{\alpha,\beta} \frac{\partial \Lambda_\alpha}{\partial \vec{c}_i} H^{-1}_{\alpha\beta} \frac{\partial \Lambda_\beta}{\partial \vec{c}_j}\right] \cdot \left[-\frac{L}{2} \sum_k \vec{\vec{\xi}}_{jk} \cdot (\vec{u}_k \right. \\ \left. - \vec{c}_k \cdot \vec{\vec{\beta}}) + \vec{f}_j + \vec{f}^R_j\right].\end{aligned} \tag{3.43}$$

Finally, for ease of notation, let us introduce the tensors

$$\vec{\vec{\vec{R}}}_{ijk} \equiv \sum_{\alpha,\beta} \frac{\partial \Lambda_\alpha}{\partial \vec{c}_i} H^{-1}_{\alpha\beta} \frac{\partial^2 \Lambda_\beta}{\partial \vec{c}_j \partial \vec{c}_k}, \tag{3.44}$$

$$\vec{\vec{Q}}_{ij} \equiv \sum_{\alpha,\beta} \frac{\partial \Lambda_\alpha}{\partial \vec{c}_i} H^{-1}_{\alpha\beta} \frac{\partial \Lambda_\beta}{\partial \vec{c}_j}, \tag{3.45}$$

with the properties

$$\sum_j \vec{\vec{Q}}_{ij} \cdot \vec{\vec{Q}}_{jk} = \vec{\vec{Q}}_{ik}, \tag{3.46}$$

as follows from Eqs. (3.41) and (3.45),

$$\frac{\partial \Lambda_\alpha}{\partial \vec{c}_i} \cdot \vec{u}_i = 0 \Rightarrow \vec{u}_i = \sum_j (\vec{\vec{1}}\delta_{ij} - \vec{\vec{Q}}_{ij}) \cdot \vec{u}_j, \tag{3.47}$$

which is obtained by differentiating Eq. (3.37) once with respect to the time, and

$$\sum_j \vec{\vec{Q}}_{ij} \cdot \vec{\vec{\vec{R}}}_{jkl} = \vec{\vec{\vec{R}}}_{ikl}, \tag{3.48}$$

making use again of Eqs. (3.41), (3.44), and (3.45).

Here we have derived these Langevin equations for the moments, that is, for global motions of the particle. Langevin equations are suitable to perform Brownian dynamics simulations. Equations (3.42) and (3.43) describe the motion of these global motions of the particle in the complete phase space when rigid constraints are present [38,39].

IV. THE VELOCITY DISTRIBUTION AND THE SMOLUCHOWSKI EQUATION

In this section we will use the set of stochastic equations (3.42) and (3.43) to derive the equation for the evolution of the probability density in configuration and velocity spaces when inertial effects are negligible. Directly neglecting the acceleration terms from the stochastic system of equations (3.42) and (3.43) leads to a nonlinear Langevin equation with δ-correlated noise. It is well known that there are uncertainities in the interpretation of that kind of equation [40] when the noise is due to thermal fluctuations, in the literature referred to as the Itô-Stratonovich dilemma. Here we overcome this difficulty by writing the evolution equation for the probability distribution in the complete phase space, referred to as Kramers equation. Then, we will assume that to the time scales under consideration, the inertial effects are negligible compared to the frictional effects. Although this derivation in principle could be done for the general situation, we will concentrate on the particular case of rodlike particles to make more transparent the main points of this paper. Due to the analogy between the Kramers equation and the Boltzmann equation, the procedure to be developed here has many points in common with the derivation of the so-called *normal solution* of the Boltzmann equation [41] and has the remarkable property of yielding the Smoluchowski equation for the probability distribution in configuration space as well as the velocity distribution compatible with it. This velocity distribution is non-Maxwellian and is planned to be used in a forthcoming paper in the derivation of transport equations, proving that its non-Maxwellian nature is conceptually very important.

A. The Kramers equation

Since the state of the chain is completely given by the set of moments $\{\vec{c}_i(t)\}$ of the configuration and $\{\vec{u}_i(t)\}$ of the velocity, let us consider that we have a phase space whose coordinates are these moments. The actual state of the system will be represented by a single point in this space. Let us then consider the density of state points in phase space, i.e.,

$$W(\{\vec{c}_i\},\{\vec{u}_i\},t) \equiv \prod_i \delta(\vec{c}_i - \vec{c}_i(t))\delta(\vec{u}_i - \vec{u}_i(t)). \tag{4.1}$$

According to Ref. [40], the probability density in phase space is given by

$$\Psi(\{\vec{c}_i\},\{\vec{u}_i\},t) = \langle W(\{\vec{c}_i\},\{\vec{u}_i\},t)\rangle, \tag{4.2}$$

where the average is done over all the realizations of the random force. Since the number of phase space points is conserved, we can write a continuity equation for W, which reads

$$\frac{\partial W}{\partial t} = -\sum_i \left[\frac{\partial}{\partial \vec{c}_i} \cdot \dot{\vec{c}}_i W + \frac{\partial}{\partial \vec{u}_i} \cdot \dot{\vec{u}}_i W\right]. \tag{4.3}$$

We then use Eqs. (3.31) and (3.32) to eliminate $\dot{\vec{c}}_i$ and $\dot{\vec{u}}_i$ from Eq. (4.3) and then average this equation to get

$$\frac{\partial\langle W\rangle}{\partial t}=-\sum_i \frac{\partial}{\partial \vec{c}_i}\cdot\vec{u}_i\langle W\rangle-\sum_i \frac{\partial}{\partial \vec{u}_i}\cdot\frac{1}{\tilde{\mu}}\sum_j \left\{ -\sum_k \vec{\vec{R}}_{ijk}:\vec{u}_k\vec{u}_j \right.$$

$$\left. +(\vec{\vec{1}}\delta_{ij}-\vec{\vec{Q}}_{ij})\cdot\left[-\frac{L}{2}\sum_k \vec{\vec{\xi}}_{jk}\cdot(\vec{u}_k-\vec{c}_k\cdot\vec{\vec{\beta}})+\vec{f}_j \right]\right\}\langle W\rangle-\sum_i \frac{\partial}{\partial \vec{u}_i}\cdot\frac{1}{\tilde{\mu}}\sum_j (\vec{\vec{1}}\delta_{ij}-\vec{\vec{Q}}_{ij})\langle \vec{f}_j^R W\rangle. \tag{4.4}$$

The last term gives

$$\langle \vec{f}_i^R W\rangle=-k_BT\frac{1}{\tilde{\mu}}\sum_{j,k}\vec{\vec{\xi}}_{ij}\cdot(\vec{\vec{1}}\delta_{jk}-\vec{\vec{Q}}_{jk})\cdot\frac{\partial}{\partial \vec{u}_k}\langle W\rangle \tag{4.5}$$

according to Appendix B. Making use of this result in Eq. (4.4), one arrives at the Kramers equation

$$\frac{\partial\Psi}{\partial t}=-\sum_i \frac{\partial}{\partial \vec{c}_i}\cdot\vec{u}_i\Psi-\sum_{i,j}\frac{1}{\tilde{\mu}}\frac{\partial}{\partial \vec{u}_i}\cdot(\vec{\vec{1}}\delta_{ij}-\vec{\vec{Q}}_{ij})\cdot\left[-\frac{L}{2}\sum_k \vec{\vec{\xi}}_{jk}\cdot(\vec{u}_k-\vec{c}_k\cdot\vec{\vec{\beta}})+\vec{f}_j \right]\Psi$$

$$+\sum_i \frac{\partial}{\partial \vec{u}_i}\cdot\frac{1}{\tilde{\mu}}\sum_{j,k}\vec{\vec{R}}_{ijk}:\vec{u}_k\vec{u}_j\Psi+\sum_{i,j}\frac{k_BT}{\tilde{\mu}^2}\frac{\partial}{\partial \vec{u}_i}\cdot\sum_{k,l}(\vec{\vec{1}}\delta_{ik}-\vec{\vec{Q}}_{ik})\cdot\vec{\vec{\xi}}_{kl}\cdot(\vec{\vec{1}}\delta_{lj}-\vec{\vec{Q}}_{lj})\cdot\frac{\partial}{\partial \vec{u}_j}\Psi. \tag{4.6}$$

It is important to note from Eq. (4.6) that the relevant quantities bearing the information concerning the dynamics of the solvent are the friction tensors $\vec{\vec{\xi}}_{ij}$ instead of the mobility tensors $\vec{\vec{\mu}}_{ij}$. These friction tensors are functions of the configuration of the system but not of the velocities, in view of Eqs. (3.11) and (3.36).

B. Normal solution of the Kramers equation for rodlike particles

For the sake of clarity, we will restrict our derivation to the case of rodlike particles. The configuration field for a rigid rod of length L is given by

$$\vec{c}(s,t)=\vec{R}(t)+s\hat{\vec{s}}(t),\quad s\in[-L/2,L/2], \tag{4.7}$$

where $\vec{R}$ is the position of the center of mass and $\hat{\vec{s}}$ is the unit vector in the direction of the axis. Equation (4.7) expresses in fact the constraint. For this particular case it is convenient to use Legendre polynomials as the basis set

$$P_l(x)=\left(\frac{2l+1}{2}\right)^{1/2}\frac{1}{2^l l!}\frac{d}{dx^l}(x^2-1)^l. \tag{4.8}$$

Note the normalization factor $\sqrt{(2l+1)/2}$ included in the above expression. This choice is especially useful since the moments of the configuration field given in Eq. (4.7) simply read

$$\vec{c}_0(t)=\sqrt{2}\vec{R}(t), \tag{4.9}$$

$$\vec{c}_1(t)=\frac{L}{\sqrt{6}}\hat{\vec{s}}(t), \tag{4.10}$$

$$\vec{c}_l(t)=0\quad \text{for } l\geqslant 2. \tag{4.11}$$

Differentiating Eq. (4.7) with respect to time and calculating the moments of the velocity field, we get

$$\vec{u}_0(t)=\sqrt{2}\dot{\vec{R}}(t), \tag{4.12}$$

$$\vec{u}_1(t)=\frac{L}{\sqrt{6}}\dot{\hat{\vec{s}}}(t)=\frac{L}{\sqrt{6}}\vec{\omega}(t)\times\hat{\vec{s}}(t), \tag{4.13}$$

$$\vec{u}_l=0\quad \text{for } l\geqslant 2, \tag{4.14}$$

where $\vec{\omega}(t)$ is the angular velocity. Since we have neglected rotations around the axis, this vector lies in the plane orthogonal to $\hat{\vec{s}}$. In this case, the equations for the constraints can be directly obtained from Eqs. (4.10) and (4.11). That is,

$$\Lambda_1(\{\vec{c}_i\})=c_1^2-\frac{L^2}{6}=0, \tag{4.15}$$

$$\Lambda_l(\{\vec{c}_i\})=c_l^2=0\quad \text{for } l\geqslant 2. \tag{4.16}$$

Equations (4.9)–(4.16) indicate that the moments for $l\geqslant 2$ are irrelevant coordinates, which will be ignored from now on. From Eq. (4.6), after some algebra, we arrive at the Kramers equation for the rod written in the most convenient way

$$\frac{\partial}{\partial t}\Psi = -\frac{\partial}{\partial \vec{R}}\cdot\vec{u}\Psi - \frac{\vec{K}}{M}\cdot\frac{\partial}{\partial \vec{u}}\Psi - \vec{\mathcal{R}}\cdot\vec{\omega}\Psi - \frac{\vec{T}}{I}\cdot\frac{\partial}{\partial\vec{\omega}}\Psi + \frac{\partial}{\partial\vec{u}}\cdot\frac{\overset{\rightrightarrows}{\zeta}_t}{M}\cdot\left[(\vec{u}-\vec{R}\cdot\overset{\rightrightarrows}{\beta}) + \frac{k_BT}{M}\frac{\partial}{\partial\vec{u}}\right]\Psi + \frac{\zeta_r}{I}\frac{\partial}{\partial\vec{\omega}}\cdot\left[(\vec{\omega}-\vec{\Omega}) + \frac{k_BT}{I}\frac{\partial}{\partial\vec{\omega}}\right]\Psi, \tag{4.17}$$

where we have defined the velocity of the center of mass $\vec{u}(t)\equiv\dot{\vec{R}}(t)$. Furthermore, the total effective force $\vec{K}$ acting on the particle is

$$\begin{aligned}\vec{K}(t) &= \int_{-L/2}^{L/2} ds[\vec{f}^{\,\mathrm{int}}(s,t)+\vec{f}^{\,\mathrm{ext}}(s,t)+\widetilde{\mu}_s\vec{c}(s,t)\cdot\overset{\rightrightarrows}{\beta}\cdot\overset{\rightrightarrows}{\beta} \\ &\quad +\vec{f}^{\,b}(s,t)] \\ &= \frac{L}{\sqrt{2}}[\vec{f}_0^{\,\mathrm{ext}}(t)+\vec{f}_0^{\,b}(t)]+M_s\vec{R}\cdot\overset{\rightrightarrows}{\beta}\cdot\overset{\rightrightarrows}{\beta}\equiv\vec{K}^{\mathrm{ext}}(t)+\vec{K}^{b}(t) \\ &\quad +M_s\vec{R}\cdot\overset{\rightrightarrows}{\beta}\cdot\overset{\rightrightarrows}{\beta}\end{aligned} \tag{4.18}$$

and the total effective torque $\vec{T}$

$$\begin{aligned}\vec{T}(t) &= \int_{-L/2}^{L/2} dss\hat{\vec{s}}(t)\times[\vec{f}^{\,\mathrm{int}}(s,t)+\vec{f}^{\,\mathrm{ext}}(s,t) \\ &\quad +\widetilde{\mu}_s\vec{c}(s,t)\cdot\overset{\rightrightarrows}{\beta}\cdot\overset{\rightrightarrows}{\beta}+\vec{f}^{\,b}(s,t)] \\ &= \frac{L^2}{2\sqrt{6}}\,\hat{\vec{s}}(t)\times[\vec{f}_1^{\,\mathrm{ext}}(t)+\vec{f}_1^{\,b}(t)]+I_s\hat{\vec{s}}\times(\hat{\vec{s}}\cdot\overset{\rightrightarrows}{\beta}\cdot\overset{\rightrightarrows}{\beta}) \\ &\equiv\vec{T}^{\mathrm{ext}}(t)+\vec{T}^{b}(t)+I_s\vec{\Omega}\cdot(\vec{\mathcal{R}}\vec{\Omega}),\end{aligned} \tag{4.19}$$

where the contributions due to internal forces identically cancel. We have also defined the total mass and the moment of inertia

$$M\equiv\widetilde{\mu}L, \tag{4.20}$$

$$I\equiv\tfrac{1}{12}\widetilde{\mu}L^3. \tag{4.21}$$

In Eqs. (4.18) and (4.19) M_s and I_s are also given by Eqs. (4.20) and (4.21), respectively, by replacing $\widetilde{\mu}$ by the displaced solvent mass per unit of length $\widetilde{\mu}_s$ defined after Eq. (3.21). The translational friction tensor is given by

$$\overset{\rightrightarrows}{\zeta}_t\equiv\frac{L^2}{2}\overset{\rightrightarrows}{\xi}_{00}, \tag{4.22}$$

whereas the rotational friction coefficient reads

$$\zeta_r\equiv\frac{L^4}{24}\xi_{11}^{\perp}, \tag{4.23}$$

where we have used the property

$$\overset{\rightrightarrows}{\xi}_{11}=\xi_{11}^{\perp}(\overset{\rightrightarrows}{1}-\hat{\vec{s}}\hat{\vec{s}})+\xi_{11}^{\parallel}\hat{\vec{s}}\hat{\vec{s}} \tag{4.24}$$

due to the rotational symmetry of the rod around its axis and the inversion symmetry with respect to its center. In Refs. [16,18] explicit expressions for the friction coefficient and the rotational friction coefficient as functions of the aspect ratio a/L have been obtained, in good agreement with numerical calculations [34–36] and experiments [37]. Finally, we have also introduced the rotational operator [24]

$$\vec{\mathcal{R}}\equiv\hat{\vec{s}}\times\frac{\partial}{\partial\hat{\vec{s}}} \tag{4.25}$$

and defined

$$\vec{\Omega}\equiv\hat{\vec{s}}\times(\hat{\vec{s}}\cdot\overset{\rightrightarrows}{\beta}). \tag{4.26}$$

The Kramers equation contains more information than needed to deal with long-time properties of polymer solutions. In normal situations the characteristic time scales for the relaxation of the velocity are much shorter than those for configurational changes due to the fact that the inertial effects are much smaller than the frictional effects. Let us introduce the deviations with respect to the velocities imposed by the external flux

$$\Delta\vec{u}\equiv\vec{u}-\vec{R}\cdot\overset{\rightrightarrows}{\beta}, \tag{4.27}$$

$$\Delta\vec{\omega}\equiv\vec{\omega}-\vec{\Omega}. \tag{4.28}$$

With this change, the differentiation with respect to the velocity is transformed as

$$\frac{\partial}{\partial\vec{u}}\rightarrow\frac{\partial}{\partial\Delta\vec{u}}, \tag{4.29}$$

$$\frac{\partial}{\partial\vec{\omega}}\rightarrow\frac{\partial}{\partial\Delta\vec{\omega}}. \tag{4.30}$$

Differentiation with respect to the position and the rotational operator results in

$$\frac{\partial}{\partial\vec{R}}\rightarrow\frac{\partial}{\partial\vec{R}}-\overset{\rightrightarrows}{\beta}\cdot\frac{\partial}{\partial\Delta\vec{u}}, \tag{4.31}$$

$$\vec{\mathcal{R}}\rightarrow\vec{\mathcal{R}}-\vec{\mathcal{R}}\vec{\Omega}\cdot\frac{\partial}{\partial\Delta\vec{\omega}}. \tag{4.32}$$

Under such transformations, Eq. (4.17) becomes

$$\frac{\partial}{\partial t}\Psi=-(\Delta\vec{u}+\vec{R}\cdot\vec{\vec{\beta}})\cdot\left[\frac{\partial}{\partial\vec{R}}-\vec{\vec{\beta}}\cdot\frac{\partial}{\partial\Delta\vec{u}}\right]\Psi-\frac{\vec{K}}{M}\cdot\frac{\partial}{\partial\Delta\vec{u}}\Psi$$
$$-(\Delta\vec{\omega}+\vec{\Omega})\cdot\left[\vec{\mathcal{R}}-(\vec{\mathcal{R}}\vec{\Omega})\cdot\frac{\partial}{\partial\Delta\vec{\omega}}\right]\Psi-\frac{\vec{T}}{I}\cdot\frac{\partial}{\partial\Delta\vec{\omega}}\Psi$$
$$+\frac{\partial}{\partial\Delta\vec{u}}\cdot\frac{\vec{\vec{\zeta}}_t}{M}\cdot\left[\Delta\vec{u}+\frac{k_BT}{M}\frac{\partial}{\partial\Delta\vec{u}}\right]\Psi+\frac{\zeta_r}{I}\frac{\partial}{\partial\Delta\vec{\omega}}\cdot\left[\Delta\vec{\omega}+\frac{k_BT}{I}\frac{\partial}{\partial\Delta\vec{\omega}}\right]\Psi. \tag{4.33}$$

This equation can be written in a more compact form by introducing the *convective* operator

$$\Gamma^{(c)}=-(\Delta\vec{u}+\vec{R}\cdot\vec{\vec{\beta}})\cdot\left[\frac{\partial}{\partial\vec{R}}-\vec{\vec{\beta}}\cdot\frac{\partial}{\partial\Delta\vec{u}}\right]-\frac{\vec{K}}{M}\cdot\frac{\partial}{\partial\Delta\vec{u}}-(\Delta\vec{\omega}+\vec{\Omega})\cdot\left[\vec{\mathcal{R}}-(\vec{\mathcal{R}}\vec{\Omega})\cdot\frac{\partial}{\partial\Delta\vec{\omega}}\right]-\frac{\vec{T}}{I}\cdot\frac{\partial}{\partial\Delta\vec{\omega}} \tag{4.34}$$

and the *diffusive* operator

$$\Gamma^{(d)}=\frac{\partial}{\partial\Delta\vec{u}}\cdot\frac{\vec{\vec{\zeta}}_t}{M\gamma}\cdot\left[\Delta\vec{u}+\frac{k_BT}{M}\frac{\partial}{\partial\Delta\vec{u}}\right]+\frac{\partial}{\partial\Delta\vec{\omega}}\cdot\left[\Delta\vec{\omega}+\frac{k_BT}{I}\frac{\partial}{\partial\Delta\vec{\omega}}\right], \tag{4.35}$$

which will be useful in what follows. We then obtain

$$\frac{\partial}{\partial t}\Psi=\Gamma^{(c)}\Psi+\gamma\Gamma^{(d)}\Psi. \tag{4.36}$$

In Eq. (4.35) we have introduced the coefficient

$$\gamma\equiv\frac{\zeta_r}{I}, \tag{4.37}$$

which corresponds to the reciprocal of the relaxation time related to the rotational inertial effects of a Brownian particle.

The large friction limit of Eq. (4.36) will lead us to the Smoluchowski equation. We will follow the line of reasoning as described in Refs. [40,42,43]. Then one expands the probability distribution function in the form

$$\Psi=\Psi^{(0)}+\frac{1}{\gamma}\Psi^{(1)}+\cdots. \tag{4.38}$$

Note that in our expansion we will regard γ as being very large or, in other words, that the inertial effects relax very fast compared to configurational changes. The Smoluchowski equation will then be valid for times larger than γ^{-1}. Furthermore, the components of the tensor

$$\frac{1}{M\gamma}\vec{\vec{\zeta}}_t \tag{4.39}$$

are of the order of unity since these components simply compare relaxation times for inertial effects for lengthwise and sidewise motion with γ^{-1} that are of the same order of magnitude.

Our next step is to replace Ψ in Eq. (4.36) by the expansion given in Eq. (4.38) and equate terms of the same order in γ. Thus the zeroth-order solution is obtained from the equation

$$\Gamma^{(d)}\Psi^{(0)}=0 \tag{4.40}$$

and is found to be

$$\Psi^{(0)}(\Delta\vec{u},\Delta\vec{\omega},\vec{R},\hat{\vec{s}},t)=\frac{1}{N}e^{-M\Delta u^2/2k_BT}e^{-I\Delta\omega^2/2k_BT}\phi^{(0)}(\vec{R},\hat{\vec{s}},t) \tag{4.41}$$

due to the fact that the differential operator $\Gamma^{(d)}$ acts only on the velocities. In this equation, N is the normalization constant, which has been computed in Appendix C. The unknown function $\phi^{(0)}(\vec{R},\hat{\vec{s}},t)$ is only configuration dependent. One can also see that the zeroth-order solution leads us to a distribution function in the velocities space corresponding to the local equilibrium. This is often referred to as ''equilibration in momentum space'' [6]. Furthermore, the integrability condition for the next order, obtained by integrating both sides of the equation for the next order [Eq. (4.45)] with respect to the velocities, imposes

$$\int d\Delta\vec{u}d\Delta\vec{\omega}\left[\frac{\partial}{\partial t}\Psi^{(0)}-\Gamma^{(c)}\Psi^{(0)}\right]=0, \tag{4.42}$$

that is, $\phi^{(0)}(\vec{R},\hat{\vec{s}},t)$ has to satisfy

$$\frac{\partial}{\partial t}\phi^{(0)}+\frac{\partial}{\partial\vec{R}}\cdot(\vec{R}\cdot\vec{\vec{\beta}})\phi^{(0)}+\vec{\mathcal{R}}\cdot\vec{\Omega}\phi^{(0)}=0, \tag{4.43}$$

which is precisely a continuity equation for $\phi^{(0)}(\vec{R},\hat{\vec{s}},t)$. Integrating Eq. (4.41) with respect to the velocities (see Appendix C), we get that, up to this order of approximation, $\phi^{(0)}(\vec{R},\hat{\vec{s}},t)$ is the probability distribution function in the configuration space

$$\psi(\vec{R},\hat{\vec{s}},t)\equiv\frac{1}{N}\int d\Delta\vec{u}d\Delta\vec{\omega}e^{-M\Delta u^2/2k_BT}e^{-I\Delta\omega^2/2k_BT}\phi^{(0)}\times(\vec{R},\hat{\vec{s}},t)$$
$$=\phi^{(0)}(\vec{R},\hat{\vec{s}},t). \tag{4.44}$$

To summarize, from the zeroth order in the γ^{-1} we have obtained, on one hand, the above mentioned equilibration in momentum space and, on the other hand, the evolution equation for the probability distribution function in the configuration space, which is a continuity equation describing the motion of an ''ideal fluid'' [14] without dissipation.

The first-order solution satisfies the equation

$$\frac{\partial}{\partial t}\Psi^{(0)}-\Gamma^{(c)}\Psi^{(0)}=\Gamma^{(d)}\Psi^{(1)}, \tag{4.45}$$

which leads us to

$$\Psi^{(1)}=\frac{1}{N}e^{-M\Delta u^2/2k_BT}e^{-I\Delta\omega^2/2k_BT}\Bigg[\phi^{(1)}+\Bigg(\Delta\vec{u}\cdot\vec{A}_t^*+\Delta\vec{\omega}\cdot\vec{A}_r-\frac{M}{2k_BT}\Delta\vec{u}\cdot\vec{\vec{\beta}}^*\cdot\Delta\vec{u}-\frac{I}{2k_BT}\Delta\vec{\omega}\cdot(\vec{\mathcal{R}}\vec{\Omega})\cdot\Delta\vec{\omega}\Bigg)\phi^{(0)}\Bigg], \tag{4.46}$$

where use has been made of the definitions

$$\vec{A}_t^*\equiv\gamma M\vec{\vec{\zeta}}_t^{-1}\cdot\vec{A}_t, \tag{4.47}$$

$$\vec{\vec{\beta}}^*\equiv\gamma M\vec{\vec{\zeta}}_t^{-1}\cdot\vec{\vec{\beta}}. \tag{4.48}$$

In these expressions, the operators $\vec{A}_t$ and $\vec{A}_r$, acting only on $\vec{R}$ and $\hat{\vec{s}}$, respectively, are given by

$$\vec{A}_t\equiv\frac{\vec{K}}{k_BT}-\frac{\partial}{\partial\vec{R}}-\frac{M}{k_BT}(\vec{R}\cdot\vec{\vec{\beta}}\cdot\vec{\vec{\beta}}), \tag{4.49}$$

$$\vec{A}_r\equiv\frac{\vec{T}}{k_BT}-\vec{\mathcal{R}}-\frac{I}{k_BT}\vec{\Omega}\cdot(\vec{\mathcal{R}}\vec{\Omega}). \tag{4.50}$$

Again, the unknown function $\phi^{(1)}(\vec{R},\hat{\vec{s}},t)$ has to satisfy

$$\begin{aligned}&\frac{\partial}{\partial t}\phi^{(1)}+\frac{1}{2}(\mathrm{tr}\vec{\vec{\beta}}^*+\vec{\mathcal{R}}\cdot\vec{\Omega})\Bigg(\vec{R}\cdot\vec{\vec{\beta}}\cdot\frac{\partial}{\partial\vec{R}}\phi^{(0)}+\vec{\mathcal{R}}\cdot(\vec{\Omega}\phi^{(0)})\Bigg)+\frac{k_BT}{M}\frac{\partial}{\partial\vec{R}}\cdot(\vec{A}_t^*\phi^{(0)})\\&+\frac{k_BT}{I}\vec{\mathcal{R}}\cdot(\vec{A}_r\phi^{(0)})+\Bigg(\vec{R}\cdot\vec{\vec{\beta}}\cdot\frac{\partial}{\partial\vec{R}}+(\vec{\mathcal{R}}\cdot\vec{\Omega})+\vec{\Omega}\cdot\vec{\mathcal{R}}\Bigg)\\&\times\Bigg(\phi^{(1)}-\frac{1}{2}\mathrm{tr}\vec{\vec{\beta}}^*\phi^{(0)}-\frac{1}{2}(\vec{\mathcal{R}}\cdot\vec{\Omega})\phi^{(0)}\Bigg)\\&=0\end{aligned} \tag{4.51}$$

which follows from the corresponding integrability condition similar to Eq. (4.42), now considering the second order.

One can construct the probability distribution function $\Psi(\Delta\vec{u},\Delta\vec{\omega},\vec{R},\hat{\vec{s}},t)$ up to first order in γ^{-1}, yielding

$$\Psi=\frac{1}{N}e^{-M\Delta u^2/2k_BT}e^{-I\Delta\omega^2/2k_BT}\Bigg\{\phi^{(0)}+\frac{1}{\gamma}\Bigg[\phi^{(1)}+\Bigg(\Delta\vec{u}\cdot\vec{A}_t^*+\Delta\vec{\omega}\cdot\vec{A}_r-\frac{M}{2k_BT}\Delta\vec{u}\cdot\vec{\vec{\beta}}^*\cdot\Delta\vec{u}-\frac{I}{2k_BT}\Delta\vec{\omega}\cdot(\vec{\mathcal{R}}\vec{\Omega})\cdot\Delta\vec{\omega}\Bigg)\phi^{(0)}\Bigg]\Bigg\}. \tag{4.52}$$

The form of the probability distribution function reflects its non-Gaussian nature due to the appearance of linear and quadratic terms in $\Delta\vec{u}$ and $\Delta\vec{\omega}$.

The probability distribution function in the configuration space is obtained, as in Eq. (4.44), after integration of Eq. (4.52) with respect to the relative velocities

$$\psi(\vec{R},\hat{\vec{s}},t)=\phi^{(0)}+\frac{1}{\gamma}\Bigg[\phi^{(1)}-\Bigg(\frac{1}{2}\mathrm{tr}\vec{\vec{\beta}}^*+\frac{1}{2}(\vec{\mathcal{R}}\cdot\vec{\Omega})\Bigg)\phi^{(0)}\Bigg]. \tag{4.53}$$

Then, Eq. (4.52) can be rewritten by using $\psi(\vec{R},\hat{\vec{s}},t)$, that is,

$$\begin{aligned}\Psi=\frac{1}{N}e^{-M\Delta u^2/2k_BT}e^{-I\Delta\omega^2/2k_BT}\Bigg\{&\psi+\frac{1}{\gamma}(\Delta\vec{u}\cdot\vec{A}_t^*+\Delta\vec{\omega}\cdot\vec{A}_r)\psi\\&+\frac{1}{2\gamma}\Bigg[\Bigg(\vec{\vec{1}}-\frac{M}{k_BT}\Delta\vec{u}\Delta\vec{u}\Bigg):\vec{\vec{\beta}}^*\\&+\Bigg(\vec{\vec{1}}-\frac{I}{k_BT}\Delta\vec{\omega}\Delta\vec{\omega}\Bigg):(\vec{\mathcal{R}}\vec{\Omega})\Bigg]\psi\Bigg\}.\end{aligned} \tag{4.54}$$

The error made when replacing $\phi^{(0)}$ by ψ in this equation is of the order γ^{-2} and is therefore negligible in our approximation. After time differentiation of both members of Eq. (4.53), using the integrability conditions given in Eqs. (4.43), and (4.51), and employing again Eq. (4.53) to eliminate $\phi^{(0)}$ and $\phi^{(1)}$, we arrive at the Smoluchowski equation

$$\begin{aligned}\frac{\partial}{\partial t}\psi=&-\vec{R}\cdot\vec{\vec{\beta}}\cdot\frac{\partial}{\partial\vec{R}}\psi-\vec{\mathcal{R}}\cdot(\vec{\Omega}\psi)\\&+k_BT\frac{\partial}{\partial\vec{R}}\cdot\vec{\vec{\zeta}}_t^{-1}\cdot\Bigg(-\frac{\vec{K}^{\mathrm{ext}}+\vec{K}^b}{k_BT}+\frac{\partial}{\partial\vec{R}}\\&+\frac{M-M_s}{k_BT}\vec{R}\cdot\vec{\vec{\beta}}\cdot\vec{\vec{\beta}}\Bigg)\psi+\frac{k_BT}{\zeta_r}\vec{\mathcal{R}}\cdot\Bigg(-\frac{\vec{T}^{\mathrm{ext}}+\vec{T}^b}{k_BT}\\&+\vec{\mathcal{R}}+\frac{I-I_s}{k_BT}\vec{\Omega}\cdot(\vec{\mathcal{R}}\vec{\Omega})\Bigg)\psi,\end{aligned} \tag{4.55}$$

where use has been made of the definition of $\vec{K}$ and $\vec{T}$ given in Eqs. (4.18) and (4.19). Equations (4.54) and (4.55) are the main results of this paper.

V. CONCLUSIONS

In this paper we have developed a general *mesoscopic* formalism to deal with the dynamics of suspensions. Although we have analyzed a particular case, it is not restricted to semiflexible or rigid polymers in dilute solution, but it can be applied to semidilute and concentrated suspensions either of flexible, semiflexible, or rigid polymers, spheres, micelles, bubbles, and surfaces immersed in solvents. The main hypothesis underlying the theory is that the suspended objects need to be much larger than the size of the solvent molecules so that the dynamics of the solvent could be described by means of a continuum theory. In a first step, we have derived Langevin equations where the friction tensors are explicitly given and the statistical properties of the random forces follow from those of the fluctuating velocity field. The formalism differs from the Oseen-Burgers procedure and it has been proved that it leads to more accurate results. The evolution of the system in phase space is governed by these Langevin equations and it is found to satisfy the Kramers equation, where positions and velocities are independent variables.

The long-time motion of the suspension has been obtained from the Kramers equation. The procedure employed here is analogous to that leading to the normal solution of the Boltzmann equation, in which it is assumed that the processes related to the relaxation of the velocity are much faster than changes in the configuration of the system. This separation in time scales is ensured in our case if the frictional effects are much more important than inertial effects. It is worth pointing out that the Kramers equation cannot correctly describe the short-time dynamics of our system, $10^{-8}-10^{-6}$ s, since the explicit time dependence of fluid motion has been neglected. This point has not been sufficiently emphasized in the literature [19]. In the case of flexible polymers in dilute solution, for instance, the mass of the solvent dragged with the coil is much more important than the mass of the polymer itself and therefore it is crucial in the analysis of its short-time behavior [15]. These inertial effects associated with fluid motion lead, furthermore, to the long-time tail behavior of the velocity autocorrelation function of a Brownian particle [12,44]. The use of the quasistatic approximation for the fluid dynamics, as it has been done here, introduces an enormous simplification in the calculation that, in addition, leads to the correct behavior at long times. In this way, our Kramers equation must be considered as a minimal model containing the relevant information to derive the long-time behavior when frictional effects are dominant in front of inertial effects.

Equation (4.54) gives the probability distribution in the complete phase space Ψ in our approximation. The procedure developed permits us to obtain the explicit dependence of Ψ in the velocity, while the dependence in the configuration appears through ψ, which is precisely the solution of the Smoluchowski equation, Eq. (4.55). One of the more interesting aspects of the velocity dependence of Ψ is that it does not correspond to a local Maxwellian distribution, but additional terms appear. In the analysis of the dynamics of suspensions, it has been customary to supplement the solution of the Smoluchowski equation with a local Maxwellian distribution function [6]. However, our derivation points out that, to the lowest order in $1/\gamma$, we get a continuity equation for ψ and a local Maxwellian, while, up to first order, one obtains correction terms with respect to the local Maxwellian behavior in the velocity distribution and the Smoluchowski equation for ψ. By means of Eq. (4.54), the macroscopic behavior of a given physical magnitude associated with the dynamics of the Brownian particles can be obtained in the same way as done in the theory of simple liquids [45]. To clarify, let us take the simplest case of a system with neither an externally applied velocity field nor external forces acting on the particles. Let us then calculate the macroscopic particle flow by averaging the mesoscopic particle density. Under certain conditions of decoupling between translational and rotational motion, we have (the particles are noninteracting and the index i labels the particles)

$$\vec{J}(\vec{r},t)\equiv\left\langle \sum_{i}^{N} \vec{u}_i \delta(\vec{r}-\vec{R}_i)\right\rangle = -k_B T\langle \vec{\vec{\zeta}}_t^{-1}\rangle\cdot\frac{\partial}{\partial\vec{r}}\rho(\vec{r},t), \tag{5.1}$$

where $\rho(\vec{r},t)\equiv\langle\Sigma_i\delta(\vec{r}-\vec{R}_i)\rangle$ is the particle's number density. Clearly, this expression is nothing but Fick's law, where, in addition, we can identify the diffusion coefficient in terms of geometrical aspects of the particle and the dynamics of the solvent through $\vec{\vec{\zeta}}_t$. The use of a Maxwellian distribution in the average would have led us to $\vec{J}(\vec{r},t)=0$. To recover Fick's law it would have been necesssary to relate the velocity of the particles to the Brownian thermodynamic force given in Eq. (1.1) and then write

$$\vec{u}_i=\vec{\vec{\zeta}}_t^{-1}\cdot\vec{F}_i^B \tag{5.2}$$

as a result of a force balance (the inertia is neglected) between the frictional force and the Brownian thermodynamic force. Such a procedure is not always obvious, as in the case of the stress tensor of a suspension of rigid rods, for instance. Some time ago, there were still some doubts about whether or not the Brownian thermodynamic force played the same role as the external and internal forces in the expression of the stress tensor [46–50]. The derivation of the expression for the stress tensor from the mesoscopic theory presented here is planned to be developed in a forthcoming paper.

Another important result of this paper is shown in Eq. (4.55), which is the Smoluchowski equation that describes the evolution of the probability density in configuration space. First, we want to mention that the mesoscopic theory presented here led us to the knowledge of the friction tensors since the hydrodynamic nature of the evolution of the solvent is a basic ingredient of the theory itself [15]. This permits us to deal with different situations such as, for instance, viscoelastic solvents, provided that the equation of motion for the velocity field is known.

Second, we have obtained several additional contributions acting as if they were effective forces and torques together with the total external force and torque. Let us first analyze the role of $\vec{K}^b$ by considering that there is a gravitational field acting on the system that is in thermodynamic equilibrium. Thus

$$\vec{K}^{\rm ext}+\vec{K}^b=-(M-M_s)g\hat{\vec{z}}, \tag{5.3}$$

where $-g\hat{\vec{z}}$ is the gravitational field, parallel to the z axis of the laboratory reference frame, and use has been made of Eqs. (4.18) and (3.22). This is obviously the balance between the weight of the particle and the hydrostatic force. Clearly, solving the Smoluchowski equation for these equilibrium conditions gives a number density distribution

$$\psi\sim e^{-(M-M_s)gz/2k_BT}. \tag{5.4}$$

Thus, to have a thermodynamically stable suspension of macroscopic size $z\sim 10$ cm at room temperature, it is necessary that $(M-M_s)\sim k_BT/gz\sim 10^{-18}$ g. This implies that in the situations of interest for Brownian systems of particles of size $\sim 10^{-4}-10^{-6}$ cm, the masses of the particles and of the displaced fluid must be rather close or practically identical. This reinforces our statement about the important role that fluid inertia plays in the short-time dynamics.

The analysis of the force due to the term $(M-M_s)\vec{R}\cdot\vec{\vec{\beta}}\cdot\vec{\vec{\beta}}$ is also very simple. Take, for instance, a system in pure rotation around the z axis. This force is then directed in the radial direction, towards the external wall if

$M>M_s$ or towards the axis of rotation if $M<M_s$. Thus this stands for a centrifuge force due to the curvature of the flow lines of the carrier fluid. For the rotational motion, the analogous term proportional to $\vec{\Omega}\cdot(\hat{\hat{R}}\vec{\Omega})$ tries to make the cylinders lie in a plane orthogonal to the axis of rotation if $I>I_s$ and align the particles with the axis of rotation if $I<I_s$. This effect is, however, very small for Brownian particles and, in fact, of higher order than other shear-dependent contributions neglected in linearizing the Navier-Stokes equation [20]. These neglected contributions lead to friction tensors depending on the velocity gradient, which are responsible for the appearance of lift forces on the particles, and will be discussed elsewhere.

In summary, this paper has been devoted to the development of a theory for suspension dynamics based on a mesoscopic starting point, which allows for a precise description of the solvent dynamics and its influence on the particle's motion. In this way we have related the friction coefficients to integrals involving the Oseen tensor and geometrical factors. From a statistical point of view, we arrived at the nonequilibrium velocity distribution compatible with the Smoluchowski equation. Finally, the *ab initio* treatment of the properties of the solvent permitted us to obtain in a natural way buoyancy and centrifugal forces in the Smoluchowski equation that are currently added without justification.

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APPENDIX A: THE SURFACE δ FUNCTION

In this appendix we will discuss the meaning of the surface δ function used in Sec. II.

For simplicity's sake, we will consider only that the shape of the sections is circular and independent of the actual configuration of the system. The surface of the particle is given by the points satisfying $r_\perp=a$. Very close to the surface, according to Eq. (3.4), the volume element $d\vec{r}$ and the area element at the surface dA read

$$d\vec{r}=\left(1-\frac{r_\perp}{R(s,t)}\cos\varphi\right)r_\perp dr_\perp d\varphi ds, \tag{A1}$$

$$dA=\left(1-\frac{a}{R(s,t)}\cos\varphi\right)a\,d\varphi ds. \tag{A2}$$

We define here $\delta^{(s)}(\vec{r},t)$, referred to as the surface delta function, as the generalized function that satisfies the properties

$$\int \delta^{(s)}(\vec{r})r_\perp dr_\perp d\varphi ds=A, \tag{A3}$$

$$\int \delta^{(s)}(\vec{r})g(\vec{r})r_\perp dr_\perp d\varphi ds=\int g(r_\perp=a,\varphi,s)dA, \tag{A4}$$

where A is the total area of the particle and $g(\vec{r})$ is some function defined in the bulk. One can easily see from Eqs. (A1) and (A2) that the surface δ function is given by

$$\delta^{(s)}(\vec{r},t)=\delta(r_\perp-a)\left(1-\frac{a}{R(s,t)}\cos\varphi\right). \tag{A5}$$

In the case in which the radius of curvature is much larger than the radius of the section, the surface δ function reduces to $\delta(r_\perp-a)$.

APPENDIX B: CALCULATION OF $\langle\vec{f}_j^R W\rangle$

Employing the Furutsu-Novikov formula [51], the last term in Eq. (4.4) can be written as

$$\begin{aligned}\langle\vec{f}_j^R(t)W[\vec{f}_k^R]\rangle&=\langle\vec{f}_j^R\rangle\langle W\rangle\\&\quad+\int_{-\infty}^{t}dt'\sum_k\langle\vec{f}_j^R(t)\vec{f}_k^R(t')\rangle\cdot\left\langle\frac{\delta W}{\delta\vec{f}_k^R(t')}\right\rangle\\&=\lim_{t'\to t^-}k_BT\sum_k\hat{\hat{\xi}}_{jk}\cdot\left\langle\frac{\delta W}{\delta\vec{f}_k^R(t')}\right\rangle,\end{aligned} \tag{B1}$$

where Eqs. (3.17) and (3.18) have been used. Note that the factor 2 has been dropped and $t'\to t^-$ due to causality. The argument of W simply indicates that this density is functionally dependent of the random force through $\{\vec{u}_i(t)\}$ and $\{\vec{c}_i(t)\}$. The averages are again with the configuration frozen. The functional derivative is defined as

$$\frac{\delta W[f_{i,\alpha}^R(t)]}{\delta f_{j,\beta}^R(t')}\equiv\left(\frac{d}{d\sigma}W[f_{i,\alpha}^R(t)+\sigma\delta_{\alpha\beta}\delta_{ij}\delta(t-t')]\right)_{\sigma=0}. \tag{B2}$$

Here greek indices stand for Cartesian coordinates of the vectors. The functional derivative contained in Eq. (B1) can be reduced to

$$\frac{\delta W}{\delta\vec{f}_k^R(t')}=-\sum_l\frac{\partial}{\partial\vec{u}_l}\left(W\frac{\delta\vec{u}_l(t)}{\delta\vec{f}_k^R(t')}\right). \tag{B3}$$

The properties of the δ functions contained in W have been used. Finally, formally integrating Eq. (3.43) in terms of the forces and applying the functional derivative to this formal solution, we arrive at

$$\frac{\delta\vec{u}_l(t)}{\delta\vec{f}_k^R(t')}=\frac{1}{\tilde{\mu}}\int_\infty^t dt''\sum_m[\hat{\hat{1}}\delta_{lm}-\hat{\hat{Q}}_{lm}]\cdot\{\hat{\hat{1}}\delta_{mk}\delta(t'-t'')\}, \tag{B4}$$

where the only contribution when $t'\to t$ comes from the term proportional to the random force. The factor in curly brackets is precisely $\delta\vec{f}_m^R(t'')/\delta\vec{f}_k^R(t')$. Gathering all these results, we arrive at Eq. (4.5).

APPENDIX C: VELOCITY AVERAGES

In this appendix we compute the different integrals involved in the velocity averages. For the center of mass motion we have

$$\int d\Delta\vec{u}e^{-M\Delta u^2/2k_BT}=\left(\frac{2\pi k_BT}{M}\right)^{3/2}, \tag{C1}$$

which is the normalization constant N_u. The second integral, corresponding to the exponential together with the second rank tensor $\Delta\vec{u}\Delta\vec{u}$, is given by

$$\frac{1}{N_u}\int d\Delta\vec{u}(\Delta\vec{u}\Delta\vec{u})e^{-M\Delta u^2/2k_BT}=\frac{k_BT}{M}\vec{\vec{1}}. \tag{C2}$$

Integrals of the same kind but with tensors of $\Delta\vec{u}$ of odd rank are clearly zero. Finally, the integral of the four-rank tensor $\Delta\vec{u}\Delta\vec{u}\Delta\vec{u}\Delta\vec{u}$ and the exponential yields

$$\frac{1}{N_u}\int d\Delta\vec{u}(\Delta u_\alpha\Delta u_\beta\Delta u_\gamma\Delta u_\nu)e^{-M\Delta u^2/2k_BT}$$
$$=\left(\frac{k_BT}{M}\right)^2[\delta_{\alpha\beta}\delta_{\gamma\nu}+\delta_{\alpha\gamma}\delta_{\beta\nu}+\delta_{\alpha\nu}\delta_{\beta\gamma}]. \tag{C3}$$

The integrals for the rotational velocity follow lines similar to these for the center of mass velocity. One has to take into account, however, that for a fixed vector $\hat{\vec{s}}$ the domain of integration is bidimensional and lies in the plane orthogonal to $\hat{\vec{s}}$. According to this we have

$$\int d\Delta\vec{\omega}e^{-I\Delta\omega^2/2k_BT}=\left(\frac{2\pi k_BT}{I}\right), \tag{C4}$$

which is the normalization constant N_ω. The integral analogous to Eq. (C2) in this case gives

$$\frac{1}{N_\omega}\int d\Delta\vec{\omega}(\Delta\vec{\omega}\Delta\vec{\omega})e^{-I\Delta\omega^2/2k_BT}=\frac{k_BT}{I}(\vec{\vec{1}}-\hat{\vec{s}}\hat{\vec{s}}). \tag{C5}$$

The last integral leads us to

$$\frac{1}{N_\omega}\int d\Delta\vec{\omega}(\Delta\omega_\alpha\Delta\omega_\beta\Delta\omega_\gamma\Delta\omega_\nu)e^{-I\Delta\omega^2/2k_BT}$$
$$=\left(\frac{k_BT}{I}\right)^2[\mathcal{T}^{(1)}_{\alpha\beta\gamma\nu}-\mathcal{T}^{(2)}_{\alpha\beta\gamma\nu}+3\mathcal{T}^{(3)}_{\alpha\beta\gamma\nu}], \tag{C6}$$

where the tensors $\mathcal{T}^{(i)}_{\alpha\beta\gamma\nu}$ read

$$\mathcal{T}^{(1)}_{\alpha\beta\gamma\nu}\equiv\delta_{\alpha\beta}\delta_{\gamma\nu}+\delta_{\alpha\gamma}\delta_{\beta\nu}+\delta_{\alpha\nu}\delta_{\beta\gamma}, \tag{C7}$$

$$\mathcal{T}^{(2)}_{\alpha\beta\gamma\nu}\equiv\delta_{\alpha\beta}\hat{\vec{s}}_\gamma\hat{\vec{s}}_\nu+\delta_{\alpha\gamma}\hat{\vec{s}}_\beta\hat{\vec{s}}_\nu+\delta_{\alpha\nu}\hat{\vec{s}}_\beta\hat{\vec{s}}_\gamma+\delta_{\beta\gamma}\hat{\vec{s}}_\alpha\hat{\vec{s}}_\nu+\delta_{\beta\nu}\hat{\vec{s}}_\alpha\hat{\vec{s}}_\gamma$$
$$+\delta_{\gamma\nu}\hat{\vec{s}}_\alpha\hat{\vec{s}}_\beta, \tag{C8}$$

$$\mathcal{T}^{(3)}_{\alpha\beta\gamma\nu}\equiv\hat{\vec{s}}_\alpha\hat{\vec{s}}_\beta\hat{\vec{s}}_\gamma\hat{\vec{s}}_\nu. \tag{C9}$$

The normalization constant N is defined as

$$N\equiv N_uN_\omega. \tag{C10}$$

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