# Dynamics of semiflexible and rigid particles. II. Derivation of the stress tensor and transport equations

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In this paper we derive transport equations for a suspension of semiflexible and rigid particles for several cases of interest. The analysis is based on a mesoscopic description introduced in the preceding paper [Phys. Rev. E **54**, 3955 (1996)]. The non-Maxwellian contributions to the phase-space probability distribution obtained in the preceding paper give rise to the dissipative fluxes arising in the transport equations for the mass density and the magnetization as particular cases. In addition, a derivation of the contribution of the particles to the stress tensor, where the momentum density of the suspended particles as well as that of the carrier fluid are taken into account, has been developed. An expression for the stress tensor for continuous semiflexible particles with rigid constraints has been found. [S1063-651X(96)02910-8]

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## I. INTRODUCTION

The study of the macroscopic dynamic properties of suspensions is of great fundamental and applied interest. The macroscopic state of a system can be specified by giving the values that a set of relevant fields (such as, for instance, the mass density, the velocity field, the temperature, or the pressure) take at each point of space and each instant of time. These macroscopic fields satisfy a set of coupled differential equations, here referred to as *transport equations*, which are in the basis of any analysis of irreversible phenomena occurring in many fields of physics, chemistry, biology, and engineering.

The transport equations can be phenomenologically determined and incorporate the so-called transport coefficients. The transport coefficients occur as proportionality coefficients relating the irreversible fluxes to spatial gradients of the macroscopic variables used to specify the state of the system [2]. A theory aiming to derive the macroscopic behavior from more microscopic grounds starts from the dynamics of the constituents of the system, either from the molecules, as in the theory of simple liquids [3,4], or from the dynamics of the suspended particles, as in the theory of Brownian motion. Magnitudes borne by the particles, as mass or momentum, are responsible for macroscopic phenomena such as mass diffusion or fluid flow. By means of averaging and performing the hydrodynamic limit, the long-wavelength and long-time behavior of the system can be extracted from the microscopic dynamics. Then the resulting transport equation, when compared with the phenomenological description of the system, permits us to relate the phenomenological transport coefficients with expressions involving details of the underlying microscopic nature of the system.

In obtaining the transport equations for suspensions from either microscopic or mesoscopic views, a great difficulty lies in the treatment of the dynamics of the solvent. If the *ab initio* calculation from the Liouville equation for the entire system is chosen [5,6], the degrees of freedom of the solvent are projected out in favor of mesoscopic equations describing the dynamics of the degrees of freedom of the suspended particles alone. However, the cumbersome expressions for the friction coefficients as found by this method cannot be further carried out and are usually substituted by expressions taken directly from hydrodynamics [7,8]. Other treatments propose equations of motion for the ensemble of suspended particles at the mesoscopic level, in which these friction coefficients play the role of phenomenological coefficients by themselves since they are not determined by the theory.

In Ref. [1], referred to hereinafter as paper I, we have developed an approach to the dynamics of suspensions of semiflexible and rigid particles from a *mesoscopic* point of view based on both Landau-Lifshitz fluctuating hydrodynamics [9] and the induced force method of Mazur and Bedeaux [11,12]. The system studied in paper I and also in the present work consists of an ensemble of noninteracting wormlike particles of length $L$ and cross section $a$ embedded in a Newtonian solvent of viscosity $\eta_s$ at constant temperature $T$. The configuration of the particle can change with time and is given by the vector field $\vec{c}(s,t)$, where $|s|\leq L/2$. The treatment of the solvent as a continuum undergoing fluctuations enables us to study the coupling between the dynamics of the solvent and that of the particles. On one hand, our mesoscopic approach is simpler than the microscopic one based on the Lioville equation for the whole system [5,6] in that it retains only the hydrodynamic behavior of the solvent but ignores its short-time, short-wavelength motion, related to details of the molecule-molecule interactions. On the other hand, our description still retains information about how the perturbations caused by the particles propagate in the solvent, information ignored in other mesoscopic points of view [13], but that is crucial in deriving the proper friction coefficients.

Thus, in this paper we apply the main ideas and results developed in paper I to derive several macroscopic transport equations for suspensions of semiflexible and rigid long particles. The treatment permits us to obtain explicit expressions for the transport coefficients occurring in the transport equations, in terms of the friction matrices introduced in paper I, which are ultimately related to geometrical aspects of the suspended particles as well as to the dynamics of the solvent at the hydrodynamic level. In particular, we will derive transport equations for mass, magnetization, and momentum densities in the same spirit as in the theory of simple fluids [3]. We will first identify a mesoscopic variable (referred to as a dynamic variable) and study its mean behavior for long wavelengths and small frequencies, i.e., in the so-called hydrodynamic limit. To perform the averages, we will use the non-Maxwellian phase-space probability distribution for nonequilibrium situations given in Eq. (I.4.54) (references to formulas of paper I will be made by adding ''I.'' in front of the label of the equation). We will see that the deviations from the Maxwellian behavior are related to irreversible fluxes as that given by Fick's law, for instance, in analogy with the so-called *normal* solution of the Boltzman equation [14,15]. Special emphasis will be put on the analysis of the momentum transport, mainly on a derivation of the stress tensor, since for this quantity the solvent does not play a passive role but carries itself momentum that has to be accounted for. We obtain an expression of the stress tensor for a semiflexible chain in which the rigid constraints are taken into consideration. In addition, an extra term relevant at finite wavelengths accounts for the effect of the momentum carried by the solvent due to the perturbations caused by the motion of the particles. Such a contribution is currently ignored in those treatments in which the momentum carried by the suspended particles is taken as a dynamic variable.

The paper is organized as follows. Section II is devoted to the derivation of the transport equations for mass and magnetization for a suspension of wormlike particles. These examples will serve as simple and, at the same time, nontrivial cases to illustrate the procedure and the relevance of the non-Maxwellian nature of the velocity dependence of the probability distribution. Explicit results will be obtained only for the case of a rigid rod, for which the phase-space probability distribution given in Eq. (I.4.54), as well as the Smoluchowski equation Eq. (I.4.55), appies. In this paper we have further introduced some simplifications in these two equations. First, we have neglected terms quadratic in the velocity gradient, assumed small, as well as buoyancy forces. The external force and torque acting on the particle, however, are considered to be position and orientation dependent, although the external fields causing this force and torque do not explicitly depend on time. It is the case, for instance, when an inhomogeneous and stationary magnetic field $\vec{H}(\vec{r})$ is applied to the sample. If the particles carry magnetic moment $m_0\hat{\vec{s}}$, then the force $\vec{K}^{\text{ext}}$ and torque $\vec{T}^{\text{ext}}$ experienced are given by the expressions [16]

$$\vec{K}^{\text{ext}}(\vec{r},\hat{\vec{s}})=m_0\hat{\vec{s}}\cdot\vec{\nabla}\vec{H}(\vec{r}), \tag{1.1}$$

$$\vec{T}^{\text{ext}}(\vec{r},\hat{\vec{s}})=m_0\hat{\vec{s}}\times\vec{H}(\vec{r}), \tag{1.2}$$

which is a case of practical interest, although our results are not restrictied only to the magnetic case. Section III is exclusively devoted to the derivation of the mesoscopic expression for the stress tensor for semiflexible wormlike chains and the discussion of the coupling between the dynamics of the particles and the solvent. An explicit form for the stress tensor for a chain including rigid constraints is derived. As a particular case we will consider again the rigid rod for which explicit results for the linear viscosity are obtained. Finally, Sec. IV is devoted to a brief discussion of the main points developed and the conclusions that can be drawn from the present work.

## II. MASS AND MAGNETIZATION TRANSPORT FOR RIGID RODS

In this section we derive equations for mass transport and for properties related to the orientation of the particle, denoted by magnetization in a wide sense, for a suspension of wormlike chains in dilute solution. With these two examples we want to illustrate the use of the phase-space probability distribution given in Eq. (I.4.54) and the consistency of the whole scheme.

Let us consider a system of volume $V$ with $\mathcal{N}$ noninteracting identical particles in suspension. Since the system is assumed to be diluted, the motion of each particle is statistically independent. Thus the phase-space probability distribution for the system is given by

$$\Psi(\{\vec{X}^{(i)}\},t)=\prod_{i=1}^{\mathcal{N}}\Psi(\vec{X}^{(i)},t), \tag{2.1}$$

where $\vec{X}^{(i)}$ denotes configuration and the velocities of the $i$th particle, $\{\vec{X}^{(i)}\}$ being the ensemble of coordinates of all the particles.

The mesoscopic dynamic quantity associated with the mass density of suspended particles is given by

$$\rho(\vec{r},t)\equiv\tilde{\mu}\sum_i\int_{-L/2}^{L/2}ds\,\delta(\vec{r}-\vec{c}^{(i)}(s,t)), \tag{2.2}$$

which is functionally dependent on the position and configuration of the particles through $\vec{c}^{(i)}(s,t)$. $\tilde{\mu}$ is the mass of the particle per unit of length. Note that we have implicitly assumed that the particles have no thickness since we are interested in wavelengths much larger than any characteristic particle dimension. To perform the hydrodynamic limit, let us explicitly show the position of the center of mass $\vec{R}^{(i)}(t)$, writing the configuration of a wormlike chain as

$$\vec{c}^{(i)}(s,t)\equiv\vec{R}^{(i)}(t)+\Delta\vec{c}^{(i)}(s,t), \tag{2.3}$$

where $|\Delta\vec{c}^{(i)}(s,t)|\equiv|\vec{c}^{(i)}(s,t)-\vec{R}^{(i)}(t)|\sim L$.

The Fourier transform of the mass density reads

$$\rho(\vec{k},t)\equiv\tilde{\mu}\sum_i\int_{-L/2}^{L/2}ds\,e^{-i\vec{k}\cdot\vec{c}^{(i)}(s,t)}$$

$$=\tilde{\mu}\sum_i\int_{-L/2}^{L/2}ds\,e^{-i\vec{k}\cdot[\vec{R}^{(i)}(t)+\Delta\vec{c}^{(i)}(s,t)]}, \tag{2.4}$$

where use has been made of the definition of the Fourier transform given in Eq. (I.2.13). The hydrodynamic limit implies that one is interested in length scales much larger than the size of the suspended particles, so that we can expand the right-hand side of Eq. (2.4) in powers of $kL$ and retain the lowest order. We then have

$$\rho(\vec{k},t)\to M\sum_i e^{-i\vec{k}\cdot\vec{R}^{(i)}(t)}, \tag{2.5}$$

where $M\equiv\tilde{\mu}L$ is the total mass of the particle. This limiting procedure permits us to extract the part of the dynamic variable that survives at the macroscopic limit [3]. Equation (2.5) indicates that in the hydrodynamic limit the particles are regarded as points where all the mass is located. The balance equation for the mesoscopic mass density is obtained by time differentiating both sides of Eq. (2.5), giving

$$\frac{\partial}{\partial t}\rho(\vec{k},t)=-i\vec{k}\cdot\sum_i M\vec{u}^{(i)}(t)e^{-i\vec{k}\cdot\vec{R}^{(i)}(t)}, \tag{2.6}$$

where $\vec{u}^{(i)}(t)$ is the velocity of the center of mass. Equivalently, in real space we have that Eq. (2.5) corresponds to

$$\rho(\vec{r},t)=M\sum_i \delta(\vec{r}-\vec{R}^{(i)}(t)), \tag{2.7}$$

while the balance equation (2.6) in real space reads

$$\frac{\partial}{\partial t}\rho(\vec{r},t)=-\vec{\nabla}\cdot M\sum_i \vec{u}^{(i)}(t)\,\delta(\vec{r}-\vec{R}^{(i)}(t)). \tag{2.8}$$

In this last equation we have used the symbol $\vec{\nabla}$ to denote $\partial/\partial\vec{r}$. The macroscopic mass density $\overline{\rho(\vec{r},t)}$ is then obtained after averaging Eq. (2.7). That is

$$\overline{\rho(\vec{r},t)}\equiv M\sum_i \langle\delta(\vec{r}-\vec{R}^{(i)}(t))\rangle_0=M\sum_i \langle\delta(\vec{r}-\vec{R}^{(i)})\rangle, \tag{2.9}$$

where the average $\langle\rangle_0$ corresponds to an average with respect to all the realizations of the random force and of the initial conditions, while $\langle\rangle$ stands for an average of the corresponding phase-space function with respect to the phase-space probability distribution (see Appendix A). In the first equality the time dependence of the average is charged on the evolution of the dynamic variable. In the second equality the evolution in time of the average is related to the time dependence of the phase-space probability distribution. We will focus on the second interpretation of the averages with the aim of using the phase-space probability distribution Eq. (I.4.54). Note that the hydrodynamic limit also involves a limiting procedure in time similar to that already performed in space. Effectively, the relevant time scales at the macroscopic level of description are much larger than those related to characteristic motions of the particle. Equation (I.4.54) corresponds to the form of the phase-space probability density for times larger than the decay time for velocity perturbations [$\gamma^{-1}\equiv I/\zeta_r$ for the case of rigid particles, where $I$ is the moment of inertia of the rod and $\zeta_r$ is the rotational friction coefficient, according to Eqs. (I.4.21) and (I.4.23), respectively]. Therefore, the average with respect to Eq. (I.4.54) smoothes out the short-time dynamics but still retains the long-time behavior of the system. Since the suspension is diluted, in addition we have

$$\overline{\rho(\vec{r},t)}=M\mathcal{N}\langle\delta(\vec{r}-\vec{R})\rangle \tag{2.10}$$

due to the fact that all terms in the sum in Eq. (2.9) are identical.

With the aim of obtaining explicit results, let us consider the particular case of rod-like particles for which the probability distribution (I.4.54) applies. Let us recall that the configurational field for a rigid rod takes the form

$$\vec{c}(s,t)=\vec{R}(t)+s\hat{\vec{s}}(t),\quad |s|\leqslant L/2, \tag{2.11}$$

as given in Eq. (I.4.7). Thus, averaging Eq. (2.8) with respect to the mentioned probability distribution, the equation

$$\begin{aligned}\frac{\partial}{\partial t}\overline{\rho(\vec{r},t)}&=-\vec{\nabla}\cdot M\sum_i \langle\vec{u}^{(i)}(t)\,\delta(\vec{r}-\vec{R}^{(i)}(t))\rangle_0\\&=-\vec{\nabla}\cdot M\mathcal{N}\langle\vec{u}\,\delta(\vec{r}-\vec{R})\rangle\end{aligned} \tag{2.12}$$

yields the long-time, long-wavelength equation for the evolution of the mass density for rigid rods, i.e.,

$$\begin{aligned}\frac{\partial}{\partial t}\overline{\rho(\vec{r},t)}&=-\vec{\nabla}\cdot(\vec{r}\cdot\vec{\vec{\beta}})\overline{\rho(\vec{r},t)}\\&\quad-\vec{\nabla}\cdot\left\langle\left[k_BT\vec{\vec{\zeta}}_t^{-1}(\hat{\vec{s}})\cdot\left(\frac{\vec{K}^{\rm ext}(\vec{r},\hat{\vec{s}})}{k_BT}-\vec{\nabla}\right)\rho(\vec{r},t)\right]\right\rangle\\&=-\vec{\nabla}\cdot(\vec{r}\cdot\vec{\vec{\beta}})\overline{\rho(\vec{r},t)}-\vec{\nabla}\cdot\int d\hat{\vec{s}}\Bigg[M\mathcal{N}k_BT\\&\quad\vec{\vec{\zeta}}_t^{-1}(\hat{\vec{s}})\cdot\left(\frac{\vec{K}^{\rm ext}(\vec{r},\hat{\vec{s}})}{k_BT}-\vec{\nabla}\right)\psi(\vec{r},\hat{\vec{s}},t)\Bigg],\end{aligned} \tag{2.13}$$

where $\psi(\vec{r},\hat{\vec{s}},t)$ is the probability distribution in configuration space, a solution of the Smoluchowski equation, Eq. (I.4.55).

Since we will use them later in the analysis, let us write more explicitly the friction tensors for the particular case of rigid rods that will appear in the transport equations studied in this paper. First of all, the translational friction tensor is given by the expression

$$\begin{aligned}\vec{\vec{\zeta}}_t^{-1}(\hat{\vec{s}})=\frac{1}{4\pi\eta_sL}\Bigg\{&\left[\ln\frac{1}{2\epsilon}+\gamma_t^{\perp}(\epsilon)\right](\vec{\vec{1}}-\hat{\vec{s}}\hat{\vec{s}})\\&+2\left[\ln\frac{1}{2\epsilon}+\gamma_t^{\parallel}(\epsilon)\right]\hat{\vec{s}}\hat{\vec{s}}\Bigg\},\end{aligned} \tag{2.14}$$

where $\epsilon\equiv a/L$ is the aspect ratio. Equation (2.14) follows from the existent relation between the translational friction tensor and the friction moments given in Eq. (I.4.20). Equation (2.14) is explicitly obtained in Ref. [17], where the functions $\gamma_t^{\parallel,\perp}(\epsilon)$ are furnished. The rotational friction coefficient is related to the $\xi_{11}^{\perp}$ component of the corresponding friction moment. In view of Eq. (I.4.23), it takes the form

$$\zeta_r^{-1}=\frac{3}{\pi\eta_sL^3}\left[\ln\frac{1}{2\epsilon}+\gamma_r^{\perp}(\epsilon)\right], \tag{2.15}$$

where the unspecified function $\gamma_r^{\perp}(\epsilon)$ is also given in [17].

On the right-hand side of Eq. (2.15) we can identify first the flux of mass advected by the externally imposed flow. The second term, however, contains the flux due to the external forces as well as the dissipative contribution to the flux of mass. In the case of spherical particles such a term is precisely Fick's law. Here, however, the coupling between the translation and the rotation [18], which is reflected in the functional form of the friction tensor as seen in Eq. (2.14), shows up in that the last term in Eq. (2.13) cannot be written in terms of the macroscopic mass density $\overline{\rho(\vec{r},t)}$. Therfore, the diffusion of rodlike particles is in general non-Fickian. It is worth noting that this second term is entirely due to the non-Maxwellian corrections in the velocity probability distribution (I.4.54). The circumstances under which diffusion of rodlike particles is Fickian are discussed later on in this section.

The second example to be treated here is the transport of properties related to the orientation. This case is particularly interesting in situations in which the segments of the chain bear magnetic or electric dipole moments, and one is interested in the evolution of the magnetization (or, equivalently, the polarization) of a dilute suspension of such objects. Although the treatment is general, we will focus on the magnetization problem. In this case we define the mesoscopic dynamic variable as

$$\vec{m}(\vec{r},t) \equiv \mu_0 \sum_i \int_{-L/2}^{L/2} ds \left( \frac{d}{ds} \vec{c}^{(i)}(s,t) \right) \delta(\vec{r} - \vec{c}^{(i)}(s,t)), \tag{2.16}$$

where $\mu_0$ is the magnetic dipole moment per unit of length. As before, we Fourier transform $\vec{m}$ in space and apply the hydrodynamic limit

$$\begin{aligned} \vec{m}(\vec{k},t) &= \mu_0 \sum_i \int_{-L/2}^{L/2} ds \frac{d}{ds} \vec{c}^{(i)}(s,t) e^{-i\vec{k}\cdot[\vec{R}^{(i)}(t) + \Delta\vec{c}^{(i)}(s,t)]} \\ &\simeq \mu_0 \sum_i [\vec{c}^{(i)}(L/2,t) - \vec{c}^{(i)}(-L/2,t)] e^{-i\vec{k}\cdot\vec{R}^{(i)}(t)} \\ &= m_0 \sum_i \hat{\vec{s}}^{(i)}(t) e^{-i\vec{k}\cdot\vec{R}^{(i)}(t)} \quad \text{as} \quad kL \to 0, \end{aligned} \tag{2.17}$$

where the second equality applies only for rigid rods, in which case $m_0 \equiv \mu_0 L$ is the total magnetic dipole moment per particle and $d\vec{c}^{(i)}(s,t)/ds = \hat{\vec{s}}$, in view of eqs. (I.3.1) and (I.4.7). Differentiating both sides of Eq. (2.17) with respect to time we get

$$\begin{aligned} \frac{\partial}{\partial t} \vec{m}(\vec{k},t) = &- i\vec{k} \cdot \sum_i m_0 \vec{u}^{(i)}(t) [\hat{\vec{s}}^{(i)} e^{-i\vec{k}\cdot\vec{R}^{(i)}(t)}] \\ &+ \sum_i m_0 \vec{\omega}^{(i)}(t) \times [\hat{\vec{s}}^{(i)}(t) e^{-i\vec{k}\cdot\vec{R}^{(i)}(t)}]. \end{aligned} \tag{2.18}$$

On the right-hand side of this equation, we identify two terms corresponding to the two modes of relaxation of the magnetization. The first mode is the change in the magnetization due to the motion of the center of mass of the particles, while the second mode accounts for the change in the magnetization due to its rotational motion. In real space, Eqs. (2.17) and (2.18) correspond to

$$\vec{m}(\vec{r},t) = m_0 \sum_i \hat{\vec{s}}^{(i)}(t) \delta(\vec{r} - \vec{R}^{(i)}(t)) \tag{2.19}$$

and

$$\begin{aligned} \frac{\partial}{\partial t} \vec{m}(\vec{r},t) = &- \vec{\nabla} \cdot \sum_i \vec{u}^{(i)}(t) m_0 \hat{\vec{s}}^{(i)}(t) \delta(\vec{r} - \vec{R}^{(i)}(t)) \\ &+ \sum_i \vec{\omega}^{(i)}(t) \times \hat{\vec{s}}^{(i)}(t) m_0 \delta(\vec{r} - \vec{R}^{(i)}(t)), \end{aligned} \tag{2.20}$$

respectively. Finally, after averaging both members of Eq. (2.20) with respect to the probability distribution Eq. (I.4.54), we arrive at the desired transport equation

$$\begin{aligned} \frac{\partial}{\partial t} \overline{\vec{m}(\vec{r},t)} = &- \vec{\nabla} \cdot (\vec{r} \cdot \vec{\vec{\beta}}) \overline{\vec{m}(\vec{r},t)} \\ &- \vec{\nabla} \cdot \left\langle \left[ k_B T \vec{\vec{\zeta}}_t^{-1} \cdot \left( \frac{\vec{K}^{\text{ext}}(\vec{r},\hat{\vec{s}})}{k_B T} - \vec{\nabla} \right) \vec{m}(\vec{r},t) \right] \right\rangle \\ &+ \langle \vec{\Omega}(\hat{\vec{s}}) \times \vec{m}(\vec{r},t) \rangle + \frac{1}{\zeta_r} \langle \vec{T}^{\text{ext}}(\vec{r},\hat{\vec{s}}) \\ &\times \vec{m}(\vec{r},t) \rangle - 2 D_r \overline{\vec{m}(\vec{r},t)}, \end{aligned} \tag{2.21}$$

where we have defined the rotational diffusion coefficient as $D_r \equiv k_B t/\zeta_r$. The macroscopic magnetization field is in turn given by

$$\overline{\vec{m}(\vec{r},t)} \equiv \langle \vec{m}(\vec{r},t) \rangle = \int d\hat{\vec{s}} m_0 \hat{\vec{s}} \psi(\vec{r},\hat{\vec{s}},t). \tag{2.22}$$

Again, due to the remaining averages we cannot find a closed equation for the macroscopic magnetization $\overline{\vec{m}(\vec{r},t)}$. On one hand, the translational friction coefficient depends on the orientation of the particle so that it is coupled with $\vec{m}(\vec{r},t)$ in view of Eqs. (I.4.22) and (2.19). The coupling between translation and rotation can be eliminated by taking a homogeneous system so that the spatial dependence of the magnetization is no longer relevant. Thus the resulting equation contains only terms related to the rotation as a mode of relaxation. Assuming that the external torque is due to the action of a magnetic field, one has

$$\frac{\partial}{\partial t} \overline{\vec{m}(t)} = \langle \vec{\Omega}(\hat{\vec{s}}) \times \vec{m}(t) \rangle + \frac{1}{\zeta_r} \langle (\hat{\vec{s}} \times \vec{H}) \times \vec{m}(t) \rangle - 2 D_r \overline{\vec{m}(t)}, \tag{2.23}$$

where Eq. (1.2) has been used. The three terms on the right-hand side of Eq. (2.23) can easily be analyzed. The first one is the effect of the external flow in the magnetization and represents an advective flux in the orientational space. The second term gives the flux due to the interaction with an externally applied torque on the system. The last term stands for the diffusive flux in orientational space. Again, the third term is entirely due to the non-Maxwellian contributions in Eq. (I.4.54). The remaining averages in Eq. (2.23) couple the dynamics of the macroscopic magnetization with that of moments of the orientation of higher order. For a complete analysis, it is necessary to introduce transport equations for a set of dynamic variables of the form

$$\vec{\vec{m}}^{p}(\vec{r},t)\equiv\hat{\vec{s}}(t)\cdots{}^{(p}\cdots\hat{\vec{s}}(t)\,\delta(\vec{r}-\vec{R}(t)), \qquad (2.24)$$

which are dynamically coupled to each other. However, such a procedure is beyond the scope of the present work. Different schemes of decoupling for the term involving the magnetic field in Eq. (2.23) can be used to express this contribution in terms of the macroscopic magnetization $\overline{\vec{m}}$ [19,20]. The analysis of the relaxation of the magnetization of rodlike particles in homogeneous systems has been performed by using Eq. (2.23) in [19,20] and will not be further analyzed here.

To end this section, let us discuss under which conditions diffusion of rodlike particles can be considered as Fickian. First of all we consider the dynamics of the orientation of the particles in the simplest case, i.e., when external torques and velocity fields are absent and the system is spatially homogeneous. Thus, from Eq. (2.23) we get that the average (macroscopic) magnetization satisfies the closed equation

$$\frac{\partial}{\partial t}\overline{\vec{m}(\vec{r},t)}=-2D_r\overline{\vec{m}(\vec{r},t)}. \qquad (2.25)$$

This equation can be readily integrated to give $\overline{\vec{m}(\vec{r},t)}=\overline{\vec{m}(\vec{r},0)}\exp(-2D_rt)$. This result illustrates that the magnetization fades away in a characteristic time $1/2D_r\sim\eta_sL^3/k_BT$ in view of Eq. (2.15). In general, due to rotational Brownian motion, magnitudes related to the orientation show a characteristic time that is proportional to $1/D_r$ [18]. In a purely diffusive system, however, the relaxation of a density perturbation of wave number $k$ is proportional to $\exp(-Dk^2t)$, $D$ being the translational diffusion coefficient [3]. This suggests that for the relaxation of density perturbations of sufficiently small wave number, the orientation of the particles can be regarded as being in its steady state compatible with the externally applied fields. This statement can be put in more mathematical terms following the same procedure applied in paper I to derive the phase-space probability density from the Kramers equation. Let us consider that the fields of force and torque vary in space in a characteristic length $l$ much larger than the size $L$ of the particles. Using this length to reduce the spatial coordinates to a dimensionless form, the Smoluchowski equation (I.4.55) can be rewritten as

$$\frac{\partial}{\partial t}\psi=-\vec{R}^{*}\cdot\vec{\vec{\beta}}\cdot\frac{\partial}{\partial\vec{R}^{*}}\psi+\frac{k_BT}{\eta Ll^2}\frac{\partial}{\partial\vec{R}^{*}}\cdot\vec{\vec{\zeta}}_t^{*-1}\cdot\left(-\frac{\vec{K}^{\rm ext}l}{k_BT}+\frac{\partial}{\partial\vec{R}^{*}}\right)\psi-\vec{\mathcal{R}}\cdot(\vec{\Omega}\psi)+\frac{k_BT}{\eta L^3\zeta_r^{*}}\vec{\mathcal{R}}\cdot\left(-\frac{\vec{T}^{\rm ext}}{k_BT}+\vec{\mathcal{R}}\right)\psi, \qquad (2.26)$$

where $\vec{R}^{*}\equiv\vec{R}/l$, $\vec{\vec{\zeta}}_t^{*}\equiv\vec{\vec{\zeta}}_t/\eta L$, $\zeta_r^{*}\equiv\zeta_r/\eta L^3$, and the rotational operator $\vec{\mathcal{R}}$ is defined in Eq. (I.4.25) and has no dimensions. In Eq. (2.26) we can identify one operator acting on the $\vec{R}^{*}$ dependence of the probability distribution and another acting on the orientational part. Assuming that flow effects are always small, comparing the coefficients of the space operator and the orientation operator is equivalent to comparing the inverse relaxation time, of a density inhomogenity of size $l$, $\tau_t^{-1}\sim k_BT/\eta Ll^2$, with the inverse relaxation time of the orientation $\tau_r^{-1}\sim k_BT/\eta L^3$. One can then see that if $L/l\to0$ the orientational term dominates the relaxation of the probability distribution. Thus, as in paper I, we can expand $\psi$ in powers of $(L/l)^2\ll1$ and solve Eq. (2.26) order by order. The lowest order reads

$$\vec{\mathcal{R}}\cdot\left(-\frac{\vec{T}^{\rm ext}(\vec{r},\hat{\vec{s}})}{k_BT}+\vec{\mathcal{R}}\right)\psi^{(0)}=0, \qquad (2.27)$$

where we have implicitly assumed that the time scales of interest are larger than $\tau_r$. Rewriting $\psi(\vec{r},\hat{\vec{s}};t)$ in terms of the conditional probability $\chi(\hat{\vec{s}}|\vec{r},t)$ as

$$\psi(\vec{r},\hat{\vec{s}};t)=\chi(\hat{\vec{s}}|\vec{r},t)\,\phi(\vec{r},t), \qquad (2.28)$$

Eq. (2.27) turns into a time-independent equation for $\chi^{(0)}(\hat{\vec{s}}|\vec{r})$, $\phi(\vec{r},t)$ simply being $\overline{\rho(\vec{r},t)}/M\mathcal{N}$ or the probability density in position space. Therefore, inserting this result into Eq. (2.13), one arrives at

$$\frac{\partial}{\partial t}\overline{\rho(\vec{r},t)}=-\vec{\nabla}\cdot(\vec{r}\cdot\vec{\vec{\beta}})\overline{\rho(\vec{r},t)}+\vec{\nabla}\cdot\vec{\vec{D}}_t(\vec{r})\cdot\vec{\nabla}\overline{\rho(\vec{r},t)}-\vec{\nabla}\cdot\vec{J}^{\rm ext}(\vec{r},t), \qquad (2.29)$$

where we have defined the position-dependent diffusion coefficient according to

$$\vec{\vec{D}}_t(\vec{r})\equiv k_BT\int d\hat{\vec{s}}\,\vec{\vec{\zeta}}_t^{-1}(\hat{\vec{s}})\chi^{(0)}(\hat{\vec{s}}|\vec{r}) \qquad (2.30)$$

and the flux due to the external forces

$$\vec{J}^{\rm ext}(\vec{r},t)\equiv\overline{\rho(\vec{r},t)}\int d\hat{\vec{s}}\,\vec{\vec{\zeta}}_t^{-1}(\hat{\vec{s}})\cdot\vec{K}^{\rm ext}(\vec{r},\hat{\vec{s}})\chi^{(0)}(\hat{\vec{s}}|\vec{r}). \qquad (2.31)$$

Only in the case in which the externally applied forces are independent of the orientation does one have the so-called Einstein relation, that is,

$$\vec{J}^{\rm ext}(\vec{r},t)=\overline{\rho(\vec{r},t)}\frac{D_t(\vec{r})}{k_BT}\vec{K}^{\rm ext}(\vec{r}). \qquad (2.32)$$

Note that the diffusion coefficient defined in Eq. (2.30) depends on the dynamics of the orientation of the rods and therefore on the external torques acting on the particles. The simplest situation takes place when there are neither external torque and force applied on the system nor velocity field imposed. It is then straightforward to see that under the conditions discussed above, the system satisfies Fick's law, the diffusion coefficient given by [17]

$$D_t = \frac{1}{3}\left(\frac{1}{\zeta_t^{\parallel}} + \frac{2}{\zeta_t^{\perp}}\right) = \frac{1}{3\pi\eta_s L}\left(\ln\frac{1}{2\epsilon} + \frac{\gamma_t^{\parallel}(\epsilon)+\gamma_t^{\perp}(\epsilon)}{2}\right), \tag{2.33}$$

where use has been made of Eq. (2.14) and the fact that $\chi(\hat{\vec{s}}|\vec{r}) = 1/4\pi$ if external fields are absent.

Hence, in this section we have found that transport equations can be obtained from the phase-space probability distribution Eq. (I.4.54). The macroscopic irreversible fluxes are thus derived from the non-Maxwellian contribution of this probability density without making use of the Brownian thermodynamic force, Eq. (I.1.1). This is one of the main results of this paper. In addition, under the restrictive conditions giving rise to a decoupling of the translational motion from the rotational motion, transport coefficients are obtained in terms of geometrical aspects of the particles and the dynamics of the solvent at its hydrodynamic level.

## III. MOMENTUM TRANSPORT

Our main concern in this section is the derivation of the transport equation for the total momentum of the suspension. By comparing the resulting equation with the phenomenological equation, we find an expression for the contribution of the suspended particles to the pressure tensor $\Pi_{\alpha\beta}^{(p)}$ (or, equivalently, to the stress tensor $\sigma_{\alpha\beta}^{(p)}$ with $\sigma_{\alpha\beta}^{(p)} = -\Pi_{\alpha\beta}^{(p)}$), from which the effective viscosity of the suspension can be obtained.

The analysis of the effective viscosity of suspensions was initiated by Einstein [21], who studied suspensions of spherical particles. The increase of the stress in the system is due, in this case, to the rigid constraint that the spheres offer to the incoming flow externally imposed. Preliminary works on viscosity of polymer solutions were due to Burgers [22], Kuhn and Kuhn [23], and Kramers [24]. Wormlike particles can model polymers with a certain degree of rigidity. Thus the stress in a suspension of such a kind of particles is not only due to its rigidity to the imposed flow, but also configurational changes play an important role.

There are several ways to arrive at an expression for the contribution of suspended long particles to the stress tensor [25]. One can find in Ref. [26], for instance, a derivation based on the classical work of Kirkwood [27]. Kirkwood considered a given volume of the system as divided by a hypothetical plane arbitrarily taken as perpendicular to the $z$ axis. The stress tensor $\sigma_{\alpha z}$ is thus given by the force per unit of area $F_\alpha^{(s)}$, which the upper part of the volume exerts on the lower part through the plane. Such a force consists of two contributions: the first one is the force through the plane between solvent molecules, which accounts for the stress of the pure solvent, and the second corresponds to the force between portions of the suspended particle placed at different sides of the plane. The excess stress in the suspension is thus due to this second contribution. Assuming, for example, that the particles are polymers, each modeled as a linear sequence of beads, and that the suspension is homogeneous, the expression found for the contribution of the suspended particles to the pressure tensor [cf. Eq. (3.134) of Ref. [18]] reads

$$\Pi_{\alpha\beta}^{(p)} = -\sigma_{\alpha\beta}^{(p)} = \frac{\mathcal{N}}{V}\sum_m \langle F_{m\alpha} R_{m\beta}\rangle, \tag{3.1}$$

where $F_{m\alpha}$ is the $\alpha$ component of the force acting on the $m$th bead placed at $\vec{R}_m$ and the sum is extended to all the beads of a polymer. The force $\vec{F}_m$ in Eq. (3.1) must be given by

$$\vec{F}_m = -\frac{\partial}{\partial \vec{R}_m}\{k_B T \ \ln\psi(\{\vec{R}_m\}) + U(\{\vec{R}_m\})\}. \tag{3.2}$$

Note that this force contains two terms. The second is due to the possible existence of interaction potentials (electrostatic, elastic effective potentials, etc.) between the beads placed on different sides of the dividing plane. The first one, however, is the Brownian thermodynamic force defined in Eq. (I.1.1). The Brownian thermodynamic force here plays the role of an externally applied force that particles transmit to the fluid causing an additional stress. It ensures, for instance, that the pressure tensor is isotropic in equilibrium and significantly contributes to the elastic part of the stress. Its presence in the expression of the pressure tensor, however, is not evident [28–32,17] since in a completely microscopic view of the momentum transport only particle-particle interaction potentials play a role [3], as in the case of simple liquids. Therefore, its presence in a mesoscopic description of a system must reflect the averaged effect of smoothed out degrees of freedom in the stress. In Refs. [29] and [30], for instance, the complete phase space of the whole system (polymer plus solvent molecules) is considered, aiming the derivation of the expression for the contribution of polymers at the pressure tensor. A projector operator formalism permits us to eliminate the dynamics of the solvent, leading to an expression of the pressure tensor involving only polymer coordinates, where a contribution of the form of the Brownian thermodynamic force was found. Again, although the formal expressions have the appropriate functional form, the expressions for the various coefficients are far too complex to be of any practical use.

With the aim of analyzing the transport of momentum in a dilute suspension of worm-like particles, in this section we will develop a methodology that conceptually parallels that used to derive the expression of the stress tensor in simple liquids [3], here, however, starting from the mesoscopic point of view described in paper I. We will find an expression for the contribution of the suspended particles to the pressure tensor, in which the corresponding friction coefficients can be explicitly found in the framework of the theory itself.

With respect to the dynamics of magnitudes analyzed in Sec. II, momentum transport in a suspension is more involved than those examples already treated. In the case of mass and magnetization transport, the solvent plays a passive role, but in the case of momentum transport, frictional forces produce a momentum exchange between the solvent and the subsystem constituted by the suspended particles. Effectively, if we define the mesoscopic momentum density of the suspended particles [7] according to

$$\vec{j}\,'(\vec{r},t) \equiv \int_{-L/2}^{L/2} \tilde{\mu}\vec{u}(s,t)\,\delta(\vec{r}-\vec{c}(s,t)), \tag{3.3}$$

it is obviously found that $\vec{j}'$ is not a conserved quantity precisely due to the momentum loss arising from the frictional forces accounting for the momentum transferred from the particles to the solvent. Then the macroscopic transport equation for $\vec{j}'$ does not correspond to the phenomenological Navier-Stokes equation [33] and therefore the identification of the expression of the stress tensor from the evolution equation of $\vec{j}'$ is not legitimate.

The right mesoscopic (conserved) variable is thus the total momentum density, involving both the momentum carried by the particles as well as that propagated through the solvent by the perturbations caused in the velocity field [34]. Effectively, let us define the dynamic variable corresponding to the instantaneous momentum density as given by

$$\vec{j}(\vec{r},t) \equiv \rho_t(\vec{r},t)\vec{v}(\vec{r},t). \tag{3.4}$$

In this equation, $\rho_t(\vec{r},t)$ is the instantaneous density of the whole system fluid plus particles, which is given by

$$\rho_t(\vec{r},t) = \rho_s + \tilde{\mu}\int_{-L/2}^{L/2} ds\, \delta(\vec{r}-\vec{c}(s,t)), \tag{3.5}$$

$\vec{v}(\vec{r},t)$ being the actual velocity field. Here and in the following we will take a single suspended particle to simplify the notation. To generalize the results to an ensemble of noninteracting particles, we will simply multiply the final results by the number of particles $\mathcal{N}$.

Before proceeding, some remarks need to be made about the nature of the hydrodynamic limit. In the case discussed in this section, where perturbations carrying momentum, as sound waves or shear disturbances in the velocity field, can propagate in the system, it is crucial to take the limit $k \to 0$ before the long-time limit is performed [3] because these limits do not commute. An intuitive picture of the underlying physical reason for this can be obtained as follows. Let us consider a volume of lateral size $l \sim 1/k$, $k$ being a given wave vector, embedded in an infinite liquid at rest. At $t=0$, we transfer an amount of momentum to a point inside the volume and study how this momentum propagates. At a certain time $t$, the perturbations in the velocity field, carrying a part of the initial momentum transferred, occupy a region of size [9] $\sqrt{\nu t}$, where $\nu \equiv \eta_s/\rho_s$ is the kinematic viscosity. However, sound waves, propagating at the speed of sound $c$ and transporting another portion of the initial momentum, have traveled a distance $ct$. Therefore, in making $l \to \infty$ much faster than $ct$ (or, equivalently, $k \to 0$ much faster than $\omega/c$, $\omega$ being the frequency), we ensure that the total initially transferred momentum is contained in the volume and the proper balance can be established. Thus we can perform the same analysis as in Sec. II (also as in Ref. [3]) with the dynamic variable given in Eq. (3.4) by taking the fluid as compressible.

In taking the solvent as incompressible *ab initio*, we are implicitly assuming that the speed of sound is formally infinite. Thus, if we take the same volume of size $l$ as before but now for an incompressible fluid and transfer a given amount of momentum at a point inside, the momentum carried by the sound waves is instantaneously lost through the boundaries of the volume. In other words, the boundaries of our volume exert a force on the surroundings. Hence the amount of momentum contained in the velocity disturbances propagating still inside the volume is less than the initially transferred momentum. Thus, for an incompressible fluid the proper balance is established by accounting for both the momentum carried by the disturbances in the velocity field and the momentum transferred through the boundaries by means of surface forces. In addition, if $l \gg \sqrt{\nu t}$, these surface forces are only due to the pressure.

Let us consider again the dynamic variable given in Eq. (3.4) with $\vec{v}$ being the velocity field for an incompressible fluid, hence a solution of Eq. (I.2.1). The dynamic variable Eq. (3.4) now describes only a part of the momentum transport phenomenon, according to our previous discussion. Identifying the excess of the dynamic variable as $\Delta\vec{j}(\vec{r},t) \equiv \vec{j}(\vec{r},t) - \vec{j}_s(\vec{r},t)$, where $\vec{j}_s(\vec{r},t)$ is the momentum density in the absence of the particles, i.e., $\rho_s[\vec{v}_0(\vec{r},t) + \vec{v}^R(\vec{r},t)]$, we have

$$\Delta\vec{j}(\vec{r},t) = \rho_s\vec{v}_1(\vec{r},t) + \tilde{\mu}\int_{-L/2}^{L/2} ds\, \delta(\vec{r}-\vec{c}(s,t))\vec{u}(s,t), \tag{3.6}$$

where $\vec{v}_1(\vec{r},t)$ is the solution of Eq. (I.2.10) without the random pressure tensor $\vec{\vec{\Pi}}^R$. Moreover, we have made use of the fact that the velocity field at the postion of the particle is the velocity of the particle itself, in view of stick boundary conditions. As in paper I, $\vec{v}_0(\vec{r},t)$ is the velocity field in the absence of perturbations and $\vec{v}_R(\vec{r},t)$ is the random velocity field due to the thermal fluctuations, which already contains the effect of the random pressure tensor. Fourier transforming Eq. (3.6), we get

$$\Delta\vec{j}(\vec{k},t) = \rho_s\vec{v}_1(\vec{k},t) + \tilde{\mu}\int_{-L/2}^{L/2} ds\, e^{-i\vec{k}\cdot\vec{c}(s,t)}\vec{u}(s,t). \tag{3.7}$$

Finally, to obtain the desired equation for the transport of momentum, we proceed as in Sec. II by time differentiating the dynamic variable. Here, however, according to the preceding discussion, to account for the variation of the total momentum, together with the time derivative of the dynamic variable Eq. (3.4) we explicitly add the portion of the momentum instantaneously transmitted by pressure forces $-i\vec{k}p_1(\vec{k},t)$ since the fluid is taken as incompressible. Therefore, we have

$$\begin{aligned}\frac{\partial}{\partial t}\Delta\vec{j}(\vec{k},t) + i\vec{k}p_1(\vec{k},t) = {}& \rho_s\frac{\partial}{\partial t}\vec{v}_1(\vec{k},t) \\ & + \tilde{\mu}\int_{-L/2}^{L/2} ds\, \frac{\partial}{\partial t}[e^{-i\vec{k}\cdot\vec{c}(s,t)}\vec{u}(s,t)] \\ & + i\vec{k}p_1(\vec{k},t).\end{aligned} \tag{3.8}$$

Here $p_1(\vec{k},t)$ is the excess pressure due to the presence of the particles in suspension. Making use of the Fourier transform of Eq. (I.2.10) to eliminate $\partial\vec{v}_1(\vec{k},t)/\partial t$, we arrive at

$$\frac{\partial}{\partial t}\Delta\vec{j}(\vec{k},t)=-\eta_s k^2\vec{v}_1(\vec{k},t)+\int_{-L/2}^{L/2}ds\{\vec{f}^{\text{ind}}(s,t)+\tilde{\mu}[-i\vec{k}\cdot\vec{u}(s,t)\vec{u}(s,t)+\dot{\vec{u}}(s,t)]\}e^{-i\vec{k}\cdot\vec{c}(s,t)}. \tag{3.9}$$

The reader can verify that this result is recovered by time differentiating $\Delta\vec{j}(\vec{k},t)$ as in Eq. (3.7), but with $\vec{v}_1(\vec{k},t)$ beging the perturbation in a velocity field for a compressible solvent and then taking the limit $c\rightarrow\infty$. However, sound waves cause fluctuations in the density and also in the temperature, thus making necessary the explicit consideration of the balance equations for the density and internal energy for the solvent, coupled with the evolution of the perturbation $\vec{v}_1(\vec{k},t)$ [10].

To proceed further, we rewrite the expressions in Eq. (3.9) by developing $\exp[-i\vec{k}\cdot\vec{c}(s,t)]$ in powers of $\vec{k}\cdot\Delta\vec{c}(s,t)$, according to Eq. (2.3), and retain terms only up to first order. We get

$$\frac{\partial}{\partial t}\Delta\vec{j}(\vec{k},t)=-\eta_s k^2\vec{v}_1(\vec{k},t)+\int_{-L/2}^{L/2}ds[\vec{f}^{\text{ind}}(s,t)+\tilde{\mu}\dot{\vec{u}}(s,t)]e^{-i\vec{k}\cdot\vec{R}(t)}-i\vec{k}\cdot\int_{-L/2}^{L/2}ds\{\tilde{\mu}\vec{u}(s,t)\vec{u}(s,t)+\Delta\vec{c}(s,t)[\vec{f}^{\text{ind}}(s,t)+\tilde{\mu}\dot{\vec{u}}(s,t)]e^{-i\vec{k}\cdot\vec{R}(t)}. \tag{3.10}$$

The first term on the right-hand side stands for the momentum transported by the solvent due to the perturbations caused by the particles. In appearance, this term contains no characteristic length scale. However, in Appendix B we show that it is in fact of order $(kL)^2$ and can be neglected. In the analysis of the second term on the right-hand side of Eq. (3.10), we can use the relationship between the induced force density $\vec{f}^{\text{ind}}$ and the hydrodynamic force $\vec{f}^{Ha}$ as given in Eq. (I.3.24) and the equation of motion for the particle, Eq. (I.3.20). We thus have

$$\int_{-L/2}^{L/2}ds[\vec{f}^{\text{ind}}(s,t)+\tilde{\mu}\dot{\vec{u}}(s,t)]=\int_{-L/2}^{L/2}ds[\vec{f}^{\text{int}}(s,t)+\vec{f}^{\text{ext}}(s,t)+\vec{g}(s,t)], \tag{3.11}$$

where $\vec{g}$ is the constraint force. The right-hand side of this equation stands for a total external force acting on the fluid since we have neglected the buoyancy forces. Integrating with respect to $s$ and making use of the fact that $\vec{f}^{\text{int}}$ and the constraint forces give no contribution to the total force, we arrive at

$$e^{i\vec{k}\cdot\vec{R}(t)}\int_{-L/2}^{L/2}ds[\vec{f}^{\text{ind}}(s,t)+\tilde{\mu}\dot{\vec{u}}(s,t)]=e^{i\vec{k}\cdot\vec{R}(t)}\vec{K}^{\text{ext}}(t)\equiv\vec{K}^{\text{ext}}(\vec{k},t). \tag{3.12}$$

The third term on the right-hand side of Eq. (3.10) can also be worked out by using the expansion of the functions of $s$ in terms of the basis set describing the fields defined along the chain contour, according to Eqs. (I.3.29) and (I.3.30). Due to the orthonormality of the basis set and using Eq. (I.3.24) together with Eq. (I.3.32) to eliminate the induced force, we obtain

$$\int_{-L/2}^{L/2}ds\{\tilde{\mu}\vec{u}(s,t)\vec{u}(s,t)+\Delta\vec{c}(s,t)[\vec{f}^{\text{ind}}(s,t)+\tilde{\mu}\dot{\vec{u}}(s,t)]\}=\frac{L}{2}\sum_i(\tilde{\mu}\vec{u}_i\vec{u}_i+\Delta\vec{c}_i[\vec{f}_i^{\text{int}}+\vec{f}_i^{\text{ext}}+\vec{g}_i]), \tag{3.13}$$

where here the subindex $i$ labels the corresponding moment of the configuration and velocity fields of the same particle. From the first contribution on the right-hand side of this equation, one should extract the part that stands for the advection of momentum by the externally applied flow, to separate it from the part that contributes to the stress tensor, which is related to the Brownian motion of the particle. Note that if one uses Legendre polynomials as a basis set, the zeroth-order moment of the position is proportional to the position of the center of mass $\vec{R}$ according to

$$\vec{R}=\frac{\int_{-L/2}^{L/2}ds\tilde{\mu}\vec{c}(s,t)}{\int_{-L/2}^{L/2}ds\tilde{\mu}}=\frac{1}{\sqrt{2}}\int_{-1}^{1}dx\vec{c}(x,t)\frac{1}{\sqrt{2}}=\frac{1}{\sqrt{2}}\vec{c}_0. \tag{3.14}$$

In the same way, the velocity of the center of mass is given by $\vec{u}=\vec{u}_0/\sqrt{2}$. Thus the first term on the right-hand side of Eq. (3.13) can be written as

$$\frac{L}{2}\sum_i\tilde{\mu}\vec{u}_i\vec{u}_i=M(\vec{R}\cdot\vec{\vec{\beta}})(\vec{R}\cdot\vec{\vec{\beta}})+\left[M\Delta\vec{u}\Delta\vec{u}+\frac{L}{2}\sum_{i>0}(\tilde{\mu}\vec{u}_i\vec{u}_i)\right]. \tag{3.15}$$

To find a final expression of the stress tensor as a function only of velocity and configuration averages, we proceed to eliminate the constraint force in Eq. (3.15) by using Eqs. (I.3.38) and (I.3.40), yielding

$$\Delta\vec{c}_i[\vec{f}_i^{\text{int}}+\vec{f}_i^{\text{ext}}+\vec{g}_i]=\Delta\vec{c}_i\left[-\tilde{\mu}\sum_{j,k}\vec{\vec{\vec{R}}}_{ijk}:\vec{u}_k\vec{u}_j+\sum_j(\vec{\vec{1}}\delta_{ij}-\vec{\vec{Q}}_{ij})\cdot\vec{f}_i+\frac{L}{2}\sum_{j,k}\vec{\vec{Q}}_{ij}\cdot\vec{\vec{\xi}}_{jk}\cdot(\vec{u}_k-\vec{c}_k\cdot\vec{\vec{\beta}})+\sum_j\vec{\vec{Q}}_{ij}\cdot\vec{f}_j^{B}\right], \tag{3.16}$$

where we have used again $\vec{f}_i=\vec{f}_i^{\text{int}}+\vec{f}_i^{\text{ext}}$ to shorten the notation. In this equation $\vec{\vec{R}}_{ijk}$ and $\vec{\vec{Q}}_{ij}$ are the geometrical tensors defined in Eqs. (I.3.44) and (I.3.45), respectively. The Brownian force $\vec{f}_i^B$ should be not confused with the thermodynamic Brownian force defined in Eq. (I.1.1). The last term on the right-hand side of Eq. (3.16) is a contribution of the particle to the total random stress tensor, which is extremely fast compared to the characteristic time scales of the velocity or the configurational changes. This term vanishes after averaging, in view of Eq. (I.3.35), keeping the configuration frozen.

We will further assume that the macroscopic velocity field is the same as the unperturbed velocity field [18]. We then arrive at the balance equation for the momentum excess, which takes the form

$$\frac{\partial}{\partial t}\Delta\vec{j}(\vec{k},t)+i\vec{k}\cdot\{[(\vec{R}\cdot\vec{\vec{\beta}})(\vec{R}\cdot\vec{\vec{\beta}})]\rho(\vec{k},t)\}=-i\vec{k}\cdot\vec{\vec{\Pi}}^{(p)}(\vec{k},t)+\vec{K}^{\text{ext}}(\vec{k},t)-i\vec{k}\cdot\vec{\vec{\pi}}^R(\vec{k},t), \tag{3.17}$$

where we have written $\rho(\vec{k},t)=M\exp(-i\vec{k}\cdot\vec{R})$ [as in Eq. (2.5), but for a single particle] to introduce the particle's mass density. On the right-hand side of this expression, together with the total external force we have defined the contribution of the particles to the pressure tensor, which can be split into a rapidly varying term $\vec{\vec{\pi}}^R$, which is associated with the random force and a slower one related to variables of the particles only $\vec{\vec{\Pi}}^{(p)}$, from which one can obtain the viscosity of the suspension. The first one is given by

$$\vec{\vec{\pi}}^R(\vec{k},t)\equiv e^{-i\vec{k}\cdot\vec{R}(t)}\frac{L}{2}\sum_{i,j}\Delta\vec{c}_i\vec{\vec{Q}}_{ij}\cdot\vec{f}_j^B, \tag{3.18}$$

while the second reads

$$\vec{\vec{\Pi}}^{(p)}(\vec{k},t)=e^{-i\vec{k}\cdot\vec{R}(t)}\Bigg\{M\Delta\vec{u}\Delta\vec{u}+\frac{L}{2}\Bigg[\sum_{i>0}\tilde{\mu}\vec{u}_i(t)\vec{u}_i(t)+\Delta\vec{c}_i\Bigg(-\tilde{\mu}\sum_{j,k}\vec{\vec{R}}_{ijk}:\vec{u}_k\vec{u}_j+\sum_j(\vec{\vec{1}}\delta_{ij}-\vec{\vec{Q}}_{ij})\cdot\vec{f}_j+\frac{L}{2}\sum_{j,k}\vec{\vec{Q}}_{ij}\cdot\vec{\vec{\xi}}_{jk}\cdot(\vec{u}_k-\vec{c}_k\cdot\vec{\vec{\beta}})\Bigg)\Bigg]\Bigg\}. \tag{3.19}$$

This last expression is one important result of this paper, which deserves some comments. First, we have obtained an expression for the stress tensor of a continuous chain with constraints, in terms of the moments of the functions dependent of the contour length $s$. We see that there are contributions linked to the velocity and others to the configuration. If the chain is under the action of rigid constraints, the constraint forces introduce additional velocity-dependent terms whose effect on the viscosity depend on the geometrical aspects of these constraints. In expression (3.19) the friction moments defined in paper I explicitly appear, we can thus immediately relate them to the mobility moments, according to Eq. (I.3.36), which can be calculated. Precisely these terms involve contributions linear in the velocity gradients, responsible for the so-called viscous contributions to the stress tensor. Terms related to the velocity can depend on the velocity gradients through the probability distribution giving rise to the elastic contributions to the stress tensor [18]. Moreover, we have found that the momentum transported by the fluid, given by the first term on the right-hand side of Eq. (3.10), does not contribute to the pressure tensor to the lowest order in $kL$. It contributes, however, when higher orders in $kL$ are considered [34]; thus it will play an important role in the calculation of the $k$-dependent viscosity.

Let us study the rigid rod case for a homogeneous suspension of particles with the purpose of explicitly deriving the intrinsic viscosity of the suspension in the simplest situation and compare with other results. We recall that the configuration of a rigid rod is given in Eq. (I.4.7), showing that the thin cylinder has only five degrees of freedom: three associated with the motion of the center of mass and two due to the rotation around an axis orthogonal to the cylinder's axis. Using the expressions for the geometric tensors $\vec{\vec{R}}_{ijk}$ and $\vec{\vec{Q}}_{ij}$, obtained from Eqs. (I.3.44), and (I.3.45), together with Eqs. (I.4.10), (I.4.13), and (I.4.15), in Eq. (3.19), we arrive at the expression for particle's contribution to the pressure tensor for a suspension of rigid rods

$$\vec{\vec{\Pi}}^{(p)}(\vec{k},t)=e^{-i\vec{k}\cdot\vec{R}}\Bigg\{M\Delta\vec{u}\Delta\vec{u}+I(\vec{\omega}\times\hat{\vec{s}})(\vec{\omega}\times\hat{\vec{s}})-I\omega^2\hat{\vec{s}}\hat{\vec{s}}+\frac{L^2}{2\sqrt{6}}\hat{\vec{s}}(\vec{\vec{1}}-\hat{\vec{s}}\hat{\vec{s}})\cdot\vec{f}_1+\left(\frac{L^4}{24}\right)\xi_{11}^{\parallel}\hat{\vec{s}}\hat{\vec{s}}\hat{\vec{s}}\hat{\vec{s}}:\vec{\vec{\beta}}\Bigg\}. \tag{3.20}$$

Note that the term bearing the velocity gradient is proportional to the parallel component of the friction moment $\vec{\vec{\xi}}_{11}$, in view of the general form of the friction moments for a rigid rod given in Eq. (I.4.24). As in Eq. (2.15), we can define a new friction coefficient associated with the viscous stress $\zeta_s\equiv\xi_{11}^{\parallel}L^4/24$, which has also been explicitly calculated in Ref. [17] as a function of the cylinder's aspect ratio. It takes the form

$$\zeta_s^{-1}=\frac{6}{\pi\eta_s L^3}\left[\ln\frac{1}{2\epsilon}+\gamma_r^{\parallel}(\epsilon)\right]. \tag{3.21}$$

This friction coefficient has the same order of magnitude as $\zeta_r$, but different numerical value since it corresponds to different components of the same friction moment $\vec{\vec{\xi}}_{11}$. Finally, we get

$$\vec{\vec{\Pi}}^{(p)}(\vec{k},t)=e^{-i\vec{k}\cdot\vec{R}}\{M\Delta\vec{u}\Delta\vec{u}-I[(\hat{\vec{s}}\times\Delta\vec{\omega}\Delta\vec{\omega}\times\hat{\vec{s}})+\omega^2\hat{\vec{s}}\hat{\vec{s}}]-\hat{\vec{s}}(\hat{\vec{s}}\times\vec{T})+\zeta_s\hat{\vec{s}}\hat{\vec{s}}\hat{\vec{s}}\hat{\vec{s}}:\vec{\vec{\beta}}\}-e^{-i\vec{k}\cdot\vec{R}}\{\hat{\vec{s}}\times\vec{\Omega}\Delta\vec{\omega}\times\hat{\vec{s}}+\hat{\vec{s}}\times\Delta\vec{\omega}\vec{\Omega}\times\hat{\vec{s}}\}, \tag{3.22}$$

where we have neglected the term $\hat{\vec{s}}\times\vec{\Omega}\vec{\Omega}\times\hat{\vec{s}}$ being quadratic in the velocity gradient.

Let us analyze the linear viscosity with the aim of deriving explicit and simple results. With this pourpose, some points have to be taken into consideration.

First of all, we will assume that the unperturbed flow is a Couette (simple shear) flow given by

$$\vec{v}_0(\vec{r})=\vec{r}\cdot\beta\begin{pmatrix}0&0&0\\1&0&0\\0&0&0\end{pmatrix}, \tag{3.23}$$

where $\beta$ is the shear rate. Second, as we have already mentioned, we will assume that the macroscopic flow is equal to the unperturbed flow, so that it is also given by the expression (3.23). The linear viscosity then follows by retaining only linear terms in the shear rate in Eq. (3.22).

To perform the averaging procedure, we will use Eq. (I.4.54). In this expression, the dependence on the velocity is explicitly given, but the spatial dependence of the probability distribution function is, however, a solution of the Smoluchowski equation, Eq. (I.4.55). To simplify the present derivation of the effective viscosity, we will consider, third, that the system is homogeneous and that no external net forces are acting on the particles, although they can experience externally applied torques, homogeneous in space. Under these circumstances, configurational averages will only concern the orientation variables. Using these hypothesis together with Eq. (2.28), we get

$$\psi(\vec{R},\hat{\vec{s}})=\chi(\hat{\vec{s}})\frac{\mathcal{N}}{V}, \tag{3.24}$$

where $V$ is the volume of the whole system and use has been made of the fact that $\chi$ is independent of the position in a homogeneous system. The factor $\mathcal{N}$ stands for the fact that at this point we consider the ensemble of $\mathcal{N}$ independent particles, as commented at the beginning of this section. Substitution of Eq. (3.24) into Eq. (I.4.55) leads to

$$-\vec{\mathcal{R}}\cdot\vec{\Omega}\chi(\hat{\vec{s}})+D_r\vec{\mathcal{R}}\cdot\left(-\frac{\vec{T}^{\mathrm{ext}}(\hat{\vec{s}})}{k_BT}+\vec{\mathcal{R}}\right)\chi(\hat{\vec{s}})=0. \tag{3.25}$$

Finally, note that, unlike the case of the mass and magnetization transport, in which all macroscopic mass and magnetization fluxes were given by the corrective non-Maxwellian terms in the probability distribution (I.4.54), the expression of the pressure tensor does not vanish when averaged with respect to the dominant term, i.e., with the local Maxwellian. The non-Maxwellian terms give corrections to the pressure tensor proportional to the mass and the moment of inertia of the particles. Compared to the dominant terms, the corrections scale as $I\beta/\zeta_r\ll 1$, negligibly small if frictional effects dominate over inertial effects. Therefore, the probability distribution giving the leading contribution of the pressure tensor for a suspension of rodlike particles under the circumstances described above reads

$$\Psi(\Delta\vec{u},\Delta\vec{\omega},\vec{R},\hat{\vec{s}},t)=\frac{1}{N}e^{-M\Delta u^2/2k_BT}e^{-I\Delta\omega^2/2k_BT}\frac{\mathcal{N}}{V}\chi(\hat{\vec{s}}), \tag{3.26}$$

where use has been made of Eq. (3.24).

Thus, averaging Eq. (3.20) with respect to Eq. (3.26) one arrives at [18]

$$\langle\vec{\vec{\Pi}}^{(p)}\rangle=nk_BT\vec{\vec{1}}-3nk_BT\langle\hat{\vec{s}}\hat{\vec{s}}-\tfrac{1}{3}\vec{\vec{1}}\rangle_\chi-n\zeta_s\langle\hat{\vec{s}}\hat{\vec{s}}\hat{\vec{s}}\hat{\vec{s}}\rangle_\chi:\vec{\vec{\beta}}$$
$$-n\langle\hat{\vec{s}}(\hat{\vec{s}}\times\vec{T}^{\mathrm{ext}})\rangle_\chi, \tag{3.27}$$

where $n\equiv\mathcal{N}/V$ is the number of particles per unit of volume. The subscript $\chi$ indicates that the remaining average concerns the orientational probability distribution only. In this expression we can identify four different contributions. The first one gives the osmotic pressure of the suspension. The second term is the so-called elastic contribution to the pressure tensor, associated with the change in the orientational probability distribution $\chi$ when an external flow is acting on the system. It is well known [18] that this term can be cast in the form of a thermodynamic Brownian force, according to

$$\langle\hat{\vec{s}}_\beta\varepsilon_{\alpha\mu\nu}\hat{\vec{s}}_\nu\mathcal{R}_\mu\ln\chi(\hat{\vec{s}})\rangle_\chi=3\langle\hat{\vec{s}}_\alpha\hat{\vec{s}}_\beta-\delta_{\alpha\beta}/3\rangle_\chi, \tag{3.28}$$

where $\varepsilon_{\alpha\beta\gamma}$ is the $\alpha\beta\gamma$ component of the Levi-Civita tensor. It is then clear that the thermodynamic rotational Brownian force appears after elimination of the rotational velocity of the rod. Hence we have recovered the same result as in Refs. [29,30], here from a completely mesoscopic theory.

The third term in Eq. (3.27) is the viscous contribution to the stress tensor. The elastic and viscous terms constitute two different relaxation mechanisms of the stress in the system when a preexisting velocity gradient is switched off. The elastic contribution relaxes due to rotational Brownian motion, with a characteristic time related to the time that the probability distribution takes to recover the equilibrium form ($6k_BT/\zeta_r$ in dilute solution). The viscous contribution, however, relaxes instantaneously since it is related to the tension that the velocity gradient exerts on the rod, instantaneously compensated by constraint forces. The last contribution is due to the effect of external torques on the particle. It is very important for cases where the particles bear magnetic or electric dipole moments, as it is the case of ferrofluids, since they are responsible for the dependence of the effective viscosity in the externally applied fields.

The effective shear viscosity $\eta$ is obtained from the expression of the pressure tensor by demanding that

$$\langle\vec{\vec{\Pi}}^{(p)}\rangle=-(\eta-\eta_s)(\vec{\vec{\beta}}+\vec{\vec{\beta}}^T). \tag{3.29}$$

The reduced viscosity is defined as [18]

$$[\eta]\equiv\lim_{\overline{\rho}\to 0}\frac{1}{\overline{\rho}\,\eta_s}(\eta-\eta_s). \tag{3.30}$$

The mass density $\overline{\rho}$ in the case discussed in this section is obtained from Eq. (2.9) by averaging with respect to the probability distribution function, Eq. (3.26), giving

$$\overline{\rho}=\frac{M\mathcal{N}}{V}=\frac{M_w\mathcal{N}}{N_AV}, \tag{3.31}$$

where $M_w$ is the molecular weight of the polymer and $N_A$ is Avogadro's number. Thus, for the shear reduced viscosity we get

$$[\eta]=-\frac{N_A V}{\eta_s M_w \beta}\langle \Pi_{xy}^{(p)}\rangle, \tag{3.32}$$

where use has been made of Eq. (3.23).

The stationary zero shear viscosity in the absence of externally applied torques on the particles can be readily obtained by solving Eq. (3.25) for $\chi(\hat{s})$ up to first order in the velocity gradient [35]. One finally arrives at

$$[\eta]=\frac{N_A}{M_w \eta_s}\left(\frac{\zeta_r}{10}+\frac{\zeta_s}{15}\right)$$
$$=\frac{N_A \pi L^3}{90 M_w}\left(\frac{3}{\ln 1/2\epsilon+\gamma_r^{\perp}(\epsilon)}+\frac{1}{\ln 1/2\epsilon+\gamma_r^{\parallel}(\epsilon)}\right). \tag{3.33}$$

In Ref. [17] explicit evaluation of $[\eta]$ has been performed as a function of the aspect ratio of the rod $a/L$, which are the only results for this quantity for finite aspect ratio existing, to the best of our knowledge.

The analysis can be also performed, for instance, for the components of the viscosity tensor of a ferrofluid [36], using the friction coefficients that arise from our treatment. In the same way, the rotational viscosity [2] can also be evaluated from the transport equation obtained by considering the angular momentum density of the suspension as the dynamic variable and proceeding along the lines developed in this paper.

## IV. CONCLUSIONS

The analysis developed in this paper shows that the study of the dynamics of suspensions from a mesoscopic point of view based on the induced forces method and the fluctuating hydrodynamics permits a precise analysis of the coupling between the dynamics of the solvent and the dynamics of the suspended particles. While in paper I we put the emphasis on the derivation of the probability distribution at long times and to the (formal) calculation of the friction moments, here we have derived transport equations for different macroscopic quantities and identify some transport coefficients in terms of these friction moments. In particular, we have analyzed the dynamics of the mass density and the magnetization, as well as the momentum density. The paper stresses the analogy between simple liquids and suspensions, showing that the same lines of reasoning can be used in both domains if one takes into account that for suspensions the governing equations are not conservative. In Ref. [13], for instance, the formal analogy is also developed. There the basic equation is the Kramers equation (or the Fokker-Planck equation for configurations and velocities) and the main liquidlike features of the suspension are due to the direct interaction between the Brownian particles, the solvent playing a passive role. In paper I we started also from the Kramers equation considered as the minimal model incorporating all the long-time features of the suspension, but we derived the long-time behavior of the probability distribution function [Eq. (I.4.54)], where the velocity probability distribution explicitly appeared. This permits us to deal with the time dependence of the equations at a time scale much larger than that characteristic for the relaxation of velocity perturbations, allowing for a simpler treatment.

Another point worth mentioning is that the hydrodynamic nature of the dynamics of the solvent is considered from the beginning, which allows for a determination of the friction coefficients. Thus the transport coefficients appearing in the transport equations are directly related to those friction coefficients without ambiguity. From our point of view, one of the major inconveniences of theories starting from the Liouville equation for the system suspended particles plus solvent molecules [7,8] is that in a given stage of the derivation, the formal expressions for the transport coefficients have to be replaced by those obtained from hydrodynamic calculations, this not always being obvious. A good example is the derivation of the pressure tensor for the suspension from the mesoscopic theory developed here. We have reasoned along the lines of the derivation of the stress tensor in the theory of simple liquids by introducing the total momentum density as the dynamic variable. An important result is the expression [Eq. (3.19)] of the stress tensor for a continuous wormlike chain with rigid constraints. Since the momentum carried by the solvent has been explicitly taken into consideration, the analysis performed here can be used as a good starting point to study the $k$ and the $\omega$ dependence of the effective viscosity of a suspension, in the spirit of the generalized hydrodynamics [3,13,4,34].

Finally, another important aspect of the developments of this article together with paper I is that the friction tensors can be explicitly calculated in the framework of the mesoscopic theory developed. In this paper, we have restricted ourselves only to the derivation of the formal expressions without making a detailed analysis. As it has been already commented, explicit calculations have been done in Refs. [17,37] for rigid rods with finite aspect ratio. The details of the calculations can be found in these references.

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## APPENDIX A: PHASE-SPACE AVERAGES

Let us briefly discuss the averages performed in Secs. III and IV. For simplicity, let us denote by $X$ any of the variables $\{\vec{c}_i\}$ and $\{\vec{u}_i\}$ that characterize the dynamic state of our system and by $w$ any of the random forces $\vec{f}_i^R$. Given a particular realization $w(t)$ of the random forces and an initial condition $X_0$ at $t=0$, the solution of Eqs. (I.3.42) and (I.3.43) gives us $X(t)$, which we denote by $X[w(t),X_0]$ to emphasize the fact that this solution is functionally dependent on the particular realization of the random force and on the initial conditions. Moreover, let us introduce the probability distribution of a given realization of the random force as $\mathcal{P}[w(t)]$. The phase-space probability distribution given a initial condition is simply given by [38]

$$\mathcal{W}(X,t|X_0)=\int \delta w(t)\mathcal{P}[w(t)]\delta(X-X[w(t),X_0]), \tag{A1}$$

where $\int \delta w(t)\cdots$ denotes a sum over all the realizations of the random force $w(t)$. Obviously, if the probability distribution of the initial conditions is given, one can write

$$\Psi(X,t)=\int dX_0\mathcal{W}(X,t|X_0)\Psi(X_0). \tag{A2}$$

Let $A(X(t))$ be a given function of the $X(t)$, again the latter a solution of Eqs. (I.3.42) and (I.3.43) for a given realization of the random force and for some initial conditions. The average of $A$ must be interpreted as

$$\langle A(X(t))\rangle_0 \equiv \int dX_0\Psi(X_0)\int \delta w(t)\mathcal{P}[w(t)]A(X[w(t),X_0]), \tag{A3}$$

where $\langle\rangle_0$ denotes the average with respect to the realizations of the random force and over initial conditions. Introducing $1=\int dX\,\delta(X-X[w(t),X_0])$ on the right-hand side and changing the order of integration, Eq. (A3) can be written as

$$\langle A(X(t))\rangle_0=\int dX_0\Psi(X_0)\int dX\left\{\int \delta w(t)\mathcal{P}[w(t)]\delta(X-X[w(t),X_0])\right\}A(X), \tag{A4}$$

where we have replaced $A[w(t),X_0]$ by $A(X)$ in view of the $\delta$ function. Now, using Eq. (A1), we end up having

$$\langle A(X(t))\rangle_0=\int dX\Psi(X,t)A(X)=\langle A(X)\rangle. \tag{A5}$$

Therefore, we can replace $A(X(t))$, which should be averaged over all the realizations of the random forces, by $A(X)$, a function of the phase-space variable $X$, and perform the averages with respect to the phase-space probability distribution.

## APPENDIX B: MOMENTUM CARRIED BY THE SOLVENT

The momentum carried by the perturbations caused by the particles in the velocity field of the solvent are described by the first term on the right-hand side of Eq. (3.10). In this appendix we show that this term is in fact of order $(kL)^2$, thus negligible in the hydrodynamic limit. The formal solution for $\vec{v}_1(\vec{k},t)$ can be obtained by solving Eq. (I.2.10), which gives

$$\vec{v}_1(\vec{k},t)=\int_{-\infty}^{t}dt'\,e^{-\nu k^2(t-t')}\frac{\vec{\vec{1}}-\hat{k}\hat{k}}{\rho_s}\cdot\vec{F}(\vec{k},t'), \tag{B1}$$

where use has been made of the Fourier transform of the propagator of the velocity field given in Eq. (I.2.15). $\vec{F}(\vec{k},t)$ is the Fourier transform of the induced force density, as it appears in Eq. (I.2.10). The induced force density for $k\to 0$ must be of the form

$$\vec{F}(\vec{k},t)\sim e^{-i\vec{k}\cdot\vec{R}(t)}\int ds\vec{f}(s,t). \tag{B2}$$

The integral stands for the total induced force density, which, due to the action reaction principle, is also the total frictional force acting on the particle [see the discussion preceding Eq. (I.3.24)]. The total induced force density thus being a frictional force scales as a friction coefficient times a characteristic velocity. Since in the absence of externally applied forces the particle is dragged by the flow, the only characteristic velocity is the rotational velocity imposed by the velocity gradient, thus being proportional to $\beta L$. The friction coefficient, on the other hand, must scale as the solvent viscosity times a length. We thus get

$$|\vec{F}(\vec{k}=0,t)|\sim \eta_s L^2\beta e^{-i\vec{k}\cdot\vec{R}(t)}. \tag{B3}$$

By using these-dimensional arguments, we arrive at the scaling of the first term on the right-hand side of Eq. (3.10)

$$k^2\vec{v}_1(\vec{k},t)\sim \nu(kL)^2\beta\int_{-\infty}^{t}dt'\,e^{-\nu k^2(t-t')}e^{-i\vec{k}\cdot\vec{R}(t')}, \tag{B4}$$

showing, therefore, that this term is of second order in $kL$. Note that here it is crucial to consider $kL\to 0$ before the quasistatic $(\omega\to 0)$ limit is performed, in agreement with the prescribed ordering of these limits.

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