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Article *in* The Journal of Chemical Physics · December 1988

DOI: 10.1063/1.455323

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The effects of bead inertia on the Rouse model

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(Received 10 February 1988; accepted 19 August 1988)

The Rouse model for dilute polymer solutions undergoing homogeneous flows has been generalized to include the inertia of the beads in the equations of motion. To obtain the correct "diffusion equation" for the probability density distribution function in phase space, we generalize the diffusion equation derived by Murphy and Aguirre [J. Chem. Phys. **57**, 2098 (1972)] from Hamilton's equations of motion for an arbitrary number of interacting Brownian particles at equilibrium. Material functions are found, and the noninertial case is seen to be obtained as the zero mass limit in all steps of the development. In particular, the steady-state shear results are unaffected by the inclusion of inertia. It is also shown how two assumptions, "equilibration in momentum space," and the neglect of acceleration, made independently by Curtiss, Bird, and Hassager in their phase-space kinetic theory, are actually the result of assuming zero mass.

I. INTRODUCTION

Most models of polymers in solution are of two types: beads connected by elastic springs, and beads connected by rigid rods. A model of the first type which has Hookean springs and neglects hydrodynamic interaction between the beads is the Rouse model.[1] Models which have nonlinear springs are the inverse Langevin spring model,[2] finitely extensible nonlinear elastic (FENE) spring model,[3,4] and the consistently averaged FENE spring or FENE-P model.[5,6] Zimm[7] has developed a model of Hookean springs with preaveraged hydrodynamic interaction, and Oettinger and coworkers[8-11] have studied Hookean spring models and FENE-P models with consistently averaged hydrodynamic interaction. Examples of bead-rod chains without hydrodynamic interaction are those proposed by Kuhn and Kuhn,[12] Debye,[13] and Kramers.[14] Kirkwood and Riseman[15] considered a freely rotating bead-rod chain with preaveraged hydrodynamic interaction. A compilation of many of these papers may be found in a book edited by Hermans [16] and much of the work is summarized in a book by Bird, Curtiss, Armstrong, and Hassager.[17]

All of these works have two points in common: They begin from a phenomenological approach in the chain configuration space instead of Hamilton's equations of motion, and they neglect the mass or inertia of the beads in the equations of motion describing the dynamics of the polymer chain. The most explicit argument for the neglect of bead masses was given by Fixman[18] who made order-of-magnitude estimates for the prefactors of the important terms in the equations of motion for the beads. Using dimensional arguments, he concluded that bead inertia was unimportant for measurements involving frequencies much less than 10^{13} s^{-1}. However, we suggest below that this argument is quantitatively and qualitatively incorrect.

Although all of the workers mentioned above began from a phenomenological approach, it was not until 1976, that Curtiss, Bird, and Hassager[19] illustrated how these various models could be derived from Hamilton's equations of motion using a kinetic theory approach[38] by making various assumptions. This is accomplished by closing two sets of hierarchical equations. The truncation of the first hierarchy eliminates the degrees of freedom of the solvent particles, and the truncation of the second eliminates the momenta of the chain particles.

Curtiss *et al.*[19] begin by writing the Liouville equation for both the solvent particles and the particles of a single chain (N total), and then express this in the form of the BBGKY hierarchy of equations (named for Bogulyubov,[20] Born and Green,[21] Kirkwood,[22] and Yvon[23]) obtained by taking appropriate integrations over the phases of the particles. In general, the first equation of this hierarchy involves both the single and two-particle distribution functions, the second equation involves the two- and three-particle distribution functions, and so on until the final equation which involves the N - 1 and N-particle distribution functions. Taken together, these contain all of the information of the original Liouville equation.

If there are l particles in the chain, Curtiss *et al.*[19] consider the equation in the hierarchy involving the l- and l + 1particle distribution functions and make an important assumption about the interaction between the l chain particles and the N - l solvent particles called "the modified Stokes law empiricism." This assumes that the hydrodynamic interaction between the "solvent" and the chain can be approximated by a linear, possibly anisotropic, drag law. The resulting equation contains $6l$ degrees of freedom rather than $6N$, where l is usually many orders of magnitude smaller than N.

From this equation, Curtiss *et al.*[19] create the second hierarchy of equations involving the zeroth, first, second, etc., moments of the generalized momenta of the chain particles by taking appropriate integrations of this equation over the bead momenta. Analogously to the first hierarchy, the first equation involves the zeroth and first moment of the

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particle momenta and is called "the equation of continuity" for the l-particle configuration distribution function. The second equation involves the first and second moments of the bead momenta and is called "the equation of motion." Two important assumptions are then made to close these two equations: (i) an explicit form is assumed for the second moments of the particle momenta; for the dumbbell, this form is given by the equipartition of energy, and (ii) the acceleration of the chain particles is assumed to be negligible. These assumptions are taken to be independent by Curtiss et al., but it is shown below how they may be interpreted more consistently as the result of a single assumption.

In this way, the general diffusion equation for the configuration probability distribution function for the chain particles, which may then be specialized for many types of models, is obtained, and the dynamical equations are no longer deterministic, but stochastic and irreversible in time. We note here that there exist many different names in the literature for these diffusion equations; therefore, we will use the convention that diffusion equations for probability distribution functions in configuration space will be referred to as Smoluchowski equations and those in the full phase space will be referred to as Fokker-Planck equations, or FPEs.

It is our goal to parallel the work done in the past for the noninertial Rouse model with the inertial one. In order to accomplish this, we must begin with the correct equations of motion derived from Hamilton's equations of motion for a dumbbell. These are obtained from the equations of motion derived at equilibrium which are generalized to account for flows and the corresponding Fokker-Planck equation is found. From this FPE, the constitutive equation for the inertial model is found by solving the four coupled ordinary differential equations involving the ensemble average of the second moments of the phase space coordinates. These moment equations are seen to reduce to the usual moment equation for the noninertial dumbbell in the limit of zero mass. The usual Smoluchowski equation for the noninertial case is also obtained from the FPE in the zero mass case when appropriate manipulations are made.

From the rheological equation of state, we are able to calculate several material functions. These are compared to the usual results for the noninertial Hookean dumbbell which are found as a limiting case of the inertial model. We then generalize our results for a Rouse chain.

II. DEVELOPMENT OF THE MODEL

Because of the two assumptions made by Curtiss, Bird, and Hassager" about the first and second moments of the bead momenta, namely the neglect of the acceleration terms and equilibration in momentum space, their work may not be taken over here. Instead, we begin by considering the work of Murphy and Aguirre," who derived a FPE for interacting Brownian particles at equilibrium. We point out that this equation was originally derived by Klein" in 1921 from a phenomenological approach; however, we are interested here in the connection to Hamilton's equations of motion.

In a method similar to Curtiss, Bird, and Hassager,[19] Murphy and Aguirre[24] also begin with the Liouville equation for both the Brownian particles and solvent particles and use a kinetic theory approach; however, they require only one hierarchical set of equations. They follow a methodology pioneered by Kirkwood (e.g., see Ref. 38) and illustrated in a textbook by Resibois and DeLeener.[26] The same methodology was used by Lebowitz and Rubin[27] to derive the FPE for a single Brownian particle in phase space.

Murphy and Aguirre also begin with the equation in the BBGKY hierarchical set involving the l- and l+1-particle distribution functions. However, they derive the linear Stokes law drag from approximations based on a few physical ideas similar to Kirkwood's derivation of the friction coefficient.[28] More importantly, in order to close this equation, they assume that the mass of the Brownian particles is much greater than that of the solvent particles. For such an assumption, the solvent particles are always at equilibrium and depend parametrically upon the positions of the Brownian particles. At this pont, they arrive at a FPE for interacting Brownian particles:

$$\frac{\partial f_l}{\partial t} + \sum_{i=1}^{l} \left(\mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} + \mathbf{F}_i^{(c)} \cdot \frac{1}{m} \frac{\partial}{\partial \mathbf{v}_i} \right) f_l = kT \sum_{i,j=1}^{l} \frac{1}{m} \frac{\partial}{\partial \mathbf{v}_i} \cdot \boldsymbol{\zeta}_{ij} \cdot \left(\frac{1}{m} \frac{\partial}{\partial \mathbf{v}_j} + \frac{1}{kT} \mathbf{v}_j \right) f_l, \tag{1}$$

where f_l is the l-particle probability density distribution function for the l interacting Brownian particles, $\mathbf{v}_i$ is the velocity and $\mathbf{r}_i$ is the position of the ith particle relative to a fixed frame of reference, and $\mathbf{F}_i^{(c)}$ is the force on particle i due to the presence of all the other Brownian particles. T is the absolute temperature, k is Boltzmann's constant, and m is the mass of a particle. The tensors $\boldsymbol{\zeta}_{ij}$ are l^2 hydrodynamic friction tensors.

For the sake of clarity, we consider first only the Hookean dumbbell. For this model, we are able to find a Fokker–Planck equation, and then a constitutive equation; from the constitutive equation we are able to calculate several material functions. Finally, we show how the results may be generalized to describe a Rouse chain of arbitrary length. Thus, we take the above diffusion equation for the case of $l = 2$. We also neglect hydrodynamic interaction so that

$$\boldsymbol{\zeta}_{ij} = \zeta \boldsymbol{\delta} \delta_{ij}, \tag{2}$$

where ζ is a scalar friction coefficient, $\boldsymbol{\delta}$ is the unit tensor, and δ_{ij} is the Kronecker delta. We introduce the internal coordinate $\mathbf{Q} = \mathbf{r}_2 - \mathbf{r}_1$ and note that the interaction forces for a Hookean dumbbell are

$$\mathbf{F}_1^{(c)} = -\mathbf{F}_2^{(c)} = H\mathbf{Q}. \tag{3}$$

The FPE is then

$$\begin{aligned} \frac{\partial f_2}{\partial t} = & -\left[\mathbf{v}_1 \cdot \frac{\partial'}{\partial \mathbf{r}_1} + \frac{H}{m} \mathbf{Q} \cdot \frac{\partial}{\partial \mathbf{v}_1} \right] f_2 \\ & - \left[\mathbf{v}_2 \cdot \frac{\partial}{\partial \mathbf{r}_2} - \frac{H}{m} \mathbf{Q} \cdot \frac{\partial}{\partial \mathbf{v}_2} \right] f_2 \\ & + \frac{kT\zeta}{m} \left\{ \frac{\partial}{\partial \mathbf{v}_1} \cdot \left(\frac{1}{m} \frac{\partial}{\partial \mathbf{v}_i} + \frac{1}{kT} \mathbf{v}_1 \right) \right. \\ & \left. + \frac{\partial}{\partial \mathbf{v}_2} \cdot \left(\frac{1}{m} \frac{\partial}{\partial \mathbf{v}_2} + \frac{1}{kT} \mathbf{v}_2 \right) \right\} f_2. \end{aligned} \tag{4}$$

According to a method begun by Lord Rayleigh and developed separately by Fokker, Planck, and Ornstein[29] a complete equivalence between Fokker-Planck equations or Smoluchowski equations and stochastic differential equations (or SDEs, sometimes referred to as Langevin equations) is known.[30-32] Using this method (and Ito calculus), the following SDEs for each bead are found:

$$m\,d\mathbf{v}_i = \mathbf{F}_i^{(c)}\,dt - \zeta\mathbf{v}_i\,dt + (2kT\zeta)^{1/2}\,d\mathbf{W}_i(t) \quad (i=1,2), \tag{5}$$

$$d\mathbf{r}_i = \mathbf{v}_i\,dt, \tag{6}$$

where the three components of $dW_i(t)$ represent three independent Wiener processes which are completely described by their first and second moment ensemble

$$\langle d\mathbf{W}_i\rangle = 0,$$

$$\langle d\mathbf{W}_i(t)d\mathbf{W}_j(t')\rangle = \delta_{ij}\delta(t-t')\boldsymbol{\delta}\,dt\,dt', \tag{7}$$

where <...> denotes an ensemble average. These stochastic differential equations contain all of the information contained in the Fokker-Planck equation and no additional assumptions are necessary to obtain these. We also point out that other workers have obtained similar SDEs for Brownian particles from Hamilton's equations of motion by using Mori-Zwanzig projection operators.[37]

We now wish to generalize these equations to account for systems undergoing flow. This is accomplished by replacing $\boldsymbol{v}_i$ on both sides of Eq. (5) with $\boldsymbol{v}'_i$ where

$$\mathbf{v}'_i = \mathbf{v}_i - \boldsymbol{\kappa}\cdot\mathbf{r}_i. \tag{8}$$

The tensor $\boldsymbol{\kappa}(t)$ describes the imposed, incompressible, homogeneous solution flow field by $\mathbf{v}_f(\mathbf{r},t) = \boldsymbol{\kappa}(t)\cdot\mathbf{r}$ and is not a function of position. This method of generalization is justified by the assumption that we expect the fluid to appear to be in equilibrium locally in the frame of reference of the macroscopic motion of the fluid at the center of the bead. Also, in the limit of $H = 0$, the two beads then reduce to noninteracting Brownian particles.

Before considering these generalizations, we note that Szu and Hermans" attempted to find the viscosity for a Hookean dumbbell with inertia and wrote an equation of the type

$$m\,d\mathbf{v}_i = \mathbf{F}_i^{(c)}\,dt - \zeta(\mathbf{v}_i - \boldsymbol{\kappa}\cdot\mathbf{r}_i)dt + (2kT\zeta)^{1/2}\,d\mathbf{W}_i. \tag{9}$$

They did not find a constitutive equation, but found the viscosity from energy dissipation arguments. However, the equation suggested by Szu and Hermans, Eq. (9), leads to very nonphysical results for the center-of-mass motion. For example, in steady shear flow of the type $v_{f,x} = \dot\gamma y,\ v_{f,y} = v_{f,z} = 0$, one obtains

$$m\langle(v_{c,x} - [\boldsymbol{\kappa}\cdot\mathbf{r}_c]_x)^2\rangle = (kT/2) + (mkT\dot\gamma^2/2\zeta^2)[\zeta\dot\gamma t^2 - m\dot\gamma t - \zeta t - (5m^2\dot\gamma/\zeta) - (m/24)].$$

That is, the x-component of the velocity of the center of mass relative to the velocity of the fluid at the center of mass grows unbounded with time. However, the same SDEs that govern the internal-configuration motion may be obtained by making the following generalization of Eq. (5):

$$m\,d(\mathbf{v}_i - \boldsymbol{\kappa}\cdot\mathbf{r}_c) = \mathbf{F}_i^{(c)}\,dt - \zeta(\mathbf{v}_i - \boldsymbol{\kappa}\cdot\mathbf{r}_i)dt + (2kT\zeta)^{1/2}\,d\mathbf{W}_i. \tag{10}$$

Using Eq. (10), we can reinterpret the results obtained by Szu and Hermans as the results of a model with dumbbellcentered isotropic Brownian forces. We note in passing that one obtains no correction to the steady-state shear viscosity and first normal stress coefficient for this unphysical model.

Booij[39] also wrote an equation of motion similar to Eq. (10), but did not obtain any results. He estimated what the relative magnitude of various terms in the equation were in an instantaneous jump strain only.

We note that the question of bead-centered vs dumbbell centered isotropic Brownian forces was first raised by Bird, Fan, and Curtiss.[34] They did not work in the full phase space of the chain, but compared results for two different assumptions in their closure of the second hierarchical set of equations mentioned above: A Maxwell-Boltzmann distributed velocity field of the beads around (i) the center of mass of the dumbbell, and (ii) the center of mass of the beads. For the second case, they obtained an additional mass-dependent term in the constitutive equation that was not present for dumbbell-centered Brownian forces. As shown below, however, the presence of the mass-dependent term is not compatible with neglecting bead inertia.

The stochastic differential equations of motion for the beads are thus obtained from Eqs. (5) and (6) by the introduction of $\boldsymbol{v}'_i$ defined in Eq. (8):

$$m\,d\mathbf{v}'_i = \mathbf{F}_i^{(c)}\,dt - \zeta\mathbf{v}'_i\,dt + (2kT\zeta)^{1/2}\,d\mathbf{W}_i, \quad i=1,2, \tag{11}$$

$$d\mathbf{r}_i = \mathbf{v}'_i\,dt + \boldsymbol{\kappa}\cdot\mathbf{r}_i\,dt. \tag{12}$$

We now define the generalized coordinates and corresponding velocities

$$\mathbf{Q} = \mathbf{r}_2 - \mathbf{r}_1, \quad \mathbf{V}' = \mathbf{v}'_2 - \mathbf{v}'_1,$$

$$\mathbf{r}_c = (\mathbf{r}_1 + \mathbf{r}_2)/2, \quad \mathbf{v}'_c = (\mathbf{v}'_1 + \mathbf{v}'_2)/2. \tag{13}$$

It is the evolution of these quantities in time in which we are interested.

A. Center-of-mass motion

The SDE describing the motion of the center-of-mass coordinates may be obtained from Eqs. (11) and (12) by adding the $i = 1$ and $i = 2$ equations and using Eqs. (3) and (13):

$$m\,d\mathbf{v}'_c = -\zeta\mathbf{v}'_c\,dt + (kT\zeta)^{1/2}\,d\mathbf{W}_c, \tag{14}$$

$$d\mathbf{r}_c = \mathbf{v}'_c\,dt + \boldsymbol{\kappa}\cdot\mathbf{r}_c\,dt, \tag{15}$$

where $d\mathbf{W}_c = (d\mathbf{W}_1 + d\mathbf{W}_2)/\sqrt{2}$ whose three components represent three independent Wiener processes, which can be verified by the definition, Eq. (7). Using the rules of Ito calculus found elsewhere,[27,28] we obtain the following second moment equation for $\boldsymbol{v}'_c$ from Eq. (14) (alternatively, one could write down the corresponding FPE for $\boldsymbol{r}_c$ and

$\mathbf{v}_c'$, multiply by $\mathbf{v}_c'\mathbf{v}_c'$, and integrate both sides of the resulting equation over $\mathbf{r}_c$ and $\mathbf{v}_c'$):

$$\frac{d}{dt}\langle \mathbf{v}_c'\mathbf{v}_c'\rangle = -\frac{2\zeta}{m}\langle \mathbf{v}_c'\mathbf{v}_c'\rangle + \frac{kT\zeta}{m^2}\boldsymbol{\delta}. \tag{16}$$

This has the solution

$$\langle \mathbf{v}_c'\mathbf{v}_c'\rangle = \frac{kT}{2m}(1-e^{-2t\zeta/m})\boldsymbol{\delta} + \langle \mathbf{v}_c'\mathbf{v}_c'\rangle_0 e^{-2t\zeta/m}$$

or, for the experimentally accessible times of interest, $t \gg m/2\zeta$,

$$\langle \mathbf{v}_c'\mathbf{v}_c'\rangle = \frac{kT}{2m}\boldsymbol{\delta} \tag{17}$$

for all imposed, homogeneous flow fields. Thus, physically reasonable results are obtained for the center-of-mass motion in contrast to the results obtained using the equations of motion posited by Szu and Hermans.[33]

B. Internal configuration motion

The equations of motion for the internal configuration phase space coordinates are found from Eqs. (11) and (12) by taking the difference between the $i = 2$ and $i = 1$ equations and using Eqs. (3) and (13) to obtain

$$m\,d\mathbf{V}' = -2H\mathbf{Q}\,dt - \zeta\mathbf{V}'\,dt + 2(kT\zeta)^{1/2}\,d\mathbf{W}, \tag{18}$$

$$d\mathbf{Q} = \mathbf{V}'\,dt + \boldsymbol{\kappa}\cdot\mathbf{Q}\,dt, \tag{19}$$

where $d\mathbf{W} = (d\mathbf{W}_2 - d\mathbf{W}_1)/\sqrt{2}$ can also be verified by Eq. (7) as three independent Wiener processes independent of $\boldsymbol{W}_c(t)$. The SDEs for the well-known Hookean dumbbell without inertia may be obtained by setting $m = 0$ in Eq. (18), multiplying Eq. (18) by $1/\zeta$, and adding Eq. (19) . In this way, one obtains

$$d\mathbf{Q} = \boldsymbol{\kappa}\cdot\mathbf{Q}\,dt - (2H/\zeta)\mathbf{Q}\,dt + 2(kT/\zeta)^{1/2}\,d\mathbf{W}. \tag{20}$$

This has an equivalent Smoluchowski equation of the form

$$\frac{\partial\psi}{\partial t} = -\frac{\partial}{\partial\mathbf{Q}}\cdot\{[\boldsymbol{\kappa}\cdot\mathbf{Q}] - \frac{2H}{\zeta}\mathbf{Q} - \frac{2kT}{\zeta}\frac{\partial}{\partial\mathbf{Q}}\}\psi, \tag{21}$$

where $\psi(\mathbf{Q};t)$ is the configuration distribution function. This is equivalent to Eq. (13.2--13) of Ref. 35 for no external forces, and is the well-known Smoluchowski equation for a noninertial Hookean dumbbell.

We now continue toward our goal of finding the corresponding material functions. Equations (18) and (19) have an equivalent FPE of the form

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial\mathbf{Q}}\cdot\{\mathbf{V}' + [\boldsymbol{\kappa}\cdot\mathbf{Q}]\}f + \frac{\partial}{\partial\mathbf{V}'}\cdot\left\{\frac{2H}{m}\mathbf{Q} + \frac{\zeta}{m}\mathbf{V}' + \frac{2kT\zeta}{m^2}\frac{\partial}{\partial\mathbf{V}'}\right\}f, \tag{22}$$

where $f(\mathbf{Q},\mathbf{V}';t)$ is the probability distribution function for the internal motion. This is a so-called "linear" FPE since it has linear drift terms and constant diffusion terms. Therefore, it has a solution which is Gaussian in $\boldsymbol{Q}$ and $\boldsymbol{V}$ and is completely characterized by its first and second moments. Rather than solve the partial differential equation for f and integrate over $\boldsymbol{Q}$ and $\boldsymbol{V}$ to find the desired second moments $\langle\boldsymbol{QQ}\rangle$, $\langle\boldsymbol{V'V'}\rangle$, $\langle\boldsymbol{QV'}\rangle$, and $\langle\boldsymbol{V'Q}\rangle$, we find the coupled ordinary differential equations describing their time evolution. This may be done in two ways: (i) multiplying the FPE, Eq. (22), by the desired moment, say $\boldsymbol{QQ}$, and integrating over $\boldsymbol{Q}$ and $\boldsymbol{V}'$, or (ii) by using Ito calculus and Eqs. (18) and (19) . Either method yields

$$\langle\mathbf{QQ}\rangle_{(1)} = \langle\mathbf{V'Q}\rangle + \langle\mathbf{QV'}\rangle, \tag{23}$$

$$\frac{d}{dt}\langle\mathbf{QV'}\rangle + \frac{\zeta}{m}\langle\mathbf{QV'}\rangle - \boldsymbol{\kappa}\cdot\langle\mathbf{QV'}\rangle = \langle\mathbf{V'V'}\rangle - \frac{2H}{m}\langle\mathbf{QQ}\rangle, \tag{24}$$

$$\frac{d}{dt}\langle\mathbf{V'Q}\rangle + \frac{\zeta}{m}\langle\mathbf{V'Q}\rangle - \langle\mathbf{V'Q}\rangle\cdot\boldsymbol{\kappa}^\dagger = \langle\mathbf{V'V'}\rangle - \frac{2H}{m}\langle\mathbf{QQ}\rangle, \tag{25}$$

$$\frac{d}{dt}\langle\mathbf{V'V'}\rangle + \frac{2\zeta}{m}\langle\mathbf{V'V'}\rangle = \frac{4kT\zeta}{m^2}\boldsymbol{\delta} - \frac{2H}{m}\langle\mathbf{QQ}\rangle_{(1)}. \tag{26}$$

The subscript (1) indicates a convected derivative defined by

$$\mathbf{A}_{(1)} \equiv \frac{\delta}{\delta t}\mathbf{A} = \frac{d}{dt}\mathbf{A} - \boldsymbol{\kappa}\cdot\mathbf{A} - \mathbf{A}\cdot\boldsymbol{\kappa}^\dagger. \tag{27}$$

$$\langle\mathbf{V'Q}\rangle = \tfrac{1}{2}\langle\mathbf{QQ}\rangle_{(1)} - \mathbf{I}(t), \tag{28}$$

$$\langle\mathbf{QV'}\rangle = \tfrac{1}{2}\langle\mathbf{QQ}\rangle_{(1)} + \mathbf{I}(t). \tag{29}$$

By taking the operation $[(d/dt)\boldsymbol{\delta} + (\zeta/m)\boldsymbol{\delta} - \boldsymbol{\kappa}]\cdot$ on Eq. (29) and subtracting from Eq. (24), one obtains

$$\frac{1}{2}\left(\frac{d}{dt} + \frac{\zeta}{m}\right)\langle\mathbf{QQ}\rangle_{(1)} - \tfrac{1}{2}\boldsymbol{\kappa}\cdot\langle\mathbf{QQ}\rangle_{(1)} + \frac{2H}{m}\langle\mathbf{QQ}\rangle - \left(\frac{d}{dt} + \frac{\zeta}{m}\right)\mathbf{I}(t) + \boldsymbol{\kappa}\cdot\mathbf{I}(t) = \langle\mathbf{V'V'}\rangle.$$

By performing a similar operation on Eq. (28) (replacing the left-hand dot product with $\boldsymbol{\kappa}\cdot$ by a right-hand dot product $\cdot\boldsymbol{\kappa}^\dagger$) and subtracting from Eq. (23), one obtains

$$\frac{1}{2}\left(\frac{d}{dt} + \frac{\zeta}{m}\right)\langle\mathbf{QQ}\rangle_{(1)} - \tfrac{1}{2}\langle\mathbf{QQ}\rangle_{(1)}\cdot\boldsymbol{\kappa}^\dagger + 2Hm\langle\mathbf{QQ}\rangle + \left(\frac{d}{dt} + \frac{\zeta}{m}\right)\mathbf{I}(t) - \mathbf{I}(t)\cdot\boldsymbol{\kappa}^\dagger = \langle\mathbf{V'V'}\rangle. \tag{31}$$

Subtracting Eq. (31) from Eq. (30) yields

$$\frac{d}{dt}\mathbf{I}(t) + \frac{\zeta}{m}\mathbf{I}(t) - \tfrac{1}{2}[\boldsymbol{\kappa}\cdot\mathbf{I}(t) + \mathbf{I}(t)\cdot\boldsymbol{\kappa}^\dagger] = \tfrac{1}{4}\langle\mathbf{QQ}\rangle_{(1)}\cdot\boldsymbol{\kappa}^\dagger - \tfrac{1}{4}\boldsymbol{\kappa}\cdot\langle\mathbf{QQ}\rangle_{(1)}.$$

If equilibrium at $t = -\infty$ is used as the initial condition, this has the solution

$$\mathbf{I}(t) = \frac{1}{4}\int_{-\infty}^{t} e^{-\zeta(t-t')/m}\boldsymbol{\Lambda}(t,t')\cdot[\langle\mathbf{QQ}\rangle_{(1)}\cdot\boldsymbol{\kappa}^\dagger - \boldsymbol{\kappa}\cdot\langle\mathbf{QQ}\rangle_{(1)}]\cdot[\boldsymbol{\Lambda}(t,t')]^\dagger\,dt', \tag{32}$$

where $\boldsymbol{\Lambda}(t,t') = T\{\exp[(1/2)\int_{t'}^{t}\boldsymbol{\kappa}(s)ds]\}$ and $T(\quad)$ is a time ordering operator [see Appendix D of Ref. 35 for a more detailed explanation of a similar function, $\mathbf{E}(t,t')$ which is equivalent to $\boldsymbol{\Lambda}$ when $\boldsymbol{\kappa}$ is replaced by $(1/2)\boldsymbol{\kappa}$].

Equation (26) may be solved for $\langle \mathbf{V'V'} \rangle$ as a function of $\langle \mathbf{QQ} \rangle$ and time by an integrating factor and has the solution

$$\langle \mathbf{V'V'} \rangle = \int_{-\infty}^{t} e^{-2\zeta(t-t')/m}\left\{ \frac{4kT\zeta}{m^2}\boldsymbol{\delta} - \frac{2H}{m}\langle \mathbf{QQ} \rangle_{(1)} \right\} dt'. \tag{33}$$

By adding Eqs. (30) and (31) one

$$\left(\frac{d}{dt} + \frac{\zeta}{m}\right)\langle \mathbf{QQ} \rangle_{(1)} - \tfrac{1}{2}(\boldsymbol{\kappa}\cdot\langle \mathbf{QQ} \rangle_{(1)} + \langle \mathbf{QQ} \rangle_{(1)}\cdot\boldsymbol{\kappa}^\dagger) + \frac{4H}{m}\langle \mathbf{QQ} \rangle = 2\langle \mathbf{V'V'} \rangle - \boldsymbol{\kappa}\cdot\mathbf{I}(t) + \mathbf{I}(t)\cdot\boldsymbol{\kappa}^\dagger. \tag{34}$$

Thus, insertion of Eqs. (32) and (33) into Eq. (34) gives a closed integrodifferential equation involving only $\langle \mathbf{QQ} \rangle$, $\boldsymbol{\kappa}$, and time. As shown below, these equations contain all of the information necessary in order to find the stress tensor as a function of any imposed, incompressible, homogeneous flow field for this model.

We note that for steady, potential flows, $\boldsymbol{\kappa} = \boldsymbol{\kappa}^\dagger$, so that $\langle \mathbf{QQ} \rangle$ can be written as an expansion involving only $\boldsymbol{\delta}$ and $\boldsymbol{\kappa}$. If we then transform to some coordinate system where the matrix representation of $\boldsymbol{\kappa}$ is diagonal, the representation of $\langle \mathbf{QQ} \rangle$ also becomes diagonal. Then, the quantity inside of the square brackets in the integral expression for $\mathbf{I}(t)$ in Eq. (32) becomes zero and $\mathbf{I}(t) = \mathbf{0}$. Thus, for steady, potential flows, the governing equation simplifies greatly:

$$\langle \mathbf{QQ} \rangle - \left(\frac{\zeta}{2H} + \frac{m}{\zeta}\right)\boldsymbol{\kappa}\cdot\langle \mathbf{QQ} \rangle + \frac{m}{2H}\boldsymbol{\kappa}^2\cdot\langle \mathbf{QQ} \rangle = \frac{kT}{H}\boldsymbol{\delta}. \tag{35}$$

For the SDEs, we have already studied the limit $m \to 0$. Thus, before calculating material functions, we consider the limit of zero mass for the moment equations, and then the FPE. If Eq. (26), is multiplied by m^2 and m is allowed to approach zero, we find

$$(m\langle \mathbf{V'V'} \rangle)_{m=0} = 2kT\boldsymbol{\delta} \tag{36}$$

which is the assumption made by Curtiss, Bird, and Hassager19 called "equilibration in momentum space." Multiplying Eqs. (24) and (25) by m, letting m approach zero, and using Eq. (36) we obtain

$$\langle \mathbf{QV'} \rangle = \frac{2kT}{\zeta}\boldsymbol{\delta} - \frac{2H}{\zeta}\langle \mathbf{QQ} \rangle, \tag{37}$$

$$\langle \mathbf{V'Q'} \rangle = \frac{2kT}{\zeta}\boldsymbol{\delta} - \frac{2H}{\zeta}\langle \mathbf{QQ} \rangle. \tag{38}$$

Adding Eqs. (23), (37), and (38)

$$\langle \mathbf{QQ} \rangle_{(1)} = \frac{4kT}{\zeta}\boldsymbol{\delta} - \frac{4H}{\zeta}\langle \mathbf{QQ} \rangle. \tag{39}$$

This is exactly the result found for Hookean dumbbells without inertia [see Eq. (13.2-17), Ref. 35]. Note that Eq. (36) is simply a consequence of assuming zero mass, and is not introduced as an assumption.

We now consider what happens to the FPE for the dumbbell, Eq. (22) in the limit that m = 0. We use a method which is analogous to that used by Curtiss, Bird,and Hassager to close the second hierarchical set of equations. First, we define the contracted configuration distribution function $\tilde{\psi}$:

$$\tilde{\psi}(\mathbf{Q};t) = \int f(\mathbf{Q}',\mathbf{V}';t)\,d\mathbf{V}' \tag{40}$$

and also the notation

$$[[\cdots]] = \tilde{\psi}^{-1}\int (\cdots) f(\mathbf{Q}',\mathbf{V}';t)\,d\mathbf{V}'. \tag{41}$$

We begin by integrating Eq. (22) over the velocity V' to obtain "the equation of continuity":

$$\frac{\partial\tilde{\psi}}{\partial t} = -\frac{\partial}{\partial \mathbf{Q}}\cdot([[\mathbf{V}']] + \boldsymbol{\kappa}\cdot\mathbf{Q})\tilde{\psi}. \tag{42}$$

Then, we multiply Eq. (22) by V' and integrate over V' to obtain "the equation of motion":

$$\frac{d}{dt}([[V']]\tilde{\psi}) = -\frac{\partial}{\partial \mathbf{Q}}\cdot([[\mathbf{V'V'}]] + \boldsymbol{\kappa}\cdot\mathbf{Q}[[\mathbf{V}']])\tilde{\psi} - \frac{2H}{m}\mathbf{Q}\tilde{\psi} - \frac{\zeta}{m}[[\mathbf{V}']]\tilde{\psi}.$$

By multiplying by m/ζ and letting $m = 0$, keeping only those terms involving $m^0\mathbf{Q}$ and $(m)^{1/2}\mathbf{V}'$, we get

$$-[[\mathbf{V}']]\tilde{\psi} = \frac{2H}{\zeta}\mathbf{Q}\tilde{\psi} + \frac{\partial}{\partial \mathbf{Q}}\cdot\left(\frac{m}{\zeta}[[\mathbf{V'V'}]]\right)\tilde{\psi}. \tag{43}$$

Next, we multiply the FPE by $V'V'$, and integrate over V' to obtain

$$\frac{d}{dt}[[\mathbf{V'V'}]]\tilde{\psi} = -\frac{\partial}{\partial \mathbf{Q}}\cdot[[\mathbf{V'V'V'}]]\tilde{\psi} - \frac{2H}{m}(\mathbf{Q}[[\mathbf{V}']] + [[\mathbf{V}']]\mathbf{Q})\tilde{\psi} - \frac{2\zeta}{m}[[\mathbf{V'V'}]]\tilde{\psi} + \frac{4kT\zeta}{m^2}\tilde{\psi}\boldsymbol{\delta},$$

where we have used the property tr($\boldsymbol{\kappa}$) = 0. If we multiply both sides of this equation by m^2 and let m→0, we see that

$$m[[\mathbf{V'V'}]]_{m=0} = 2kT\boldsymbol{\delta}$$

which is what Curtiss et al. call "equilibration in momentum space" (see p. 71 of Ref. 19). Inserting this result into Eq. (43) yields

$$-[[\mathbf{V}']]\tilde{\psi} = \frac{2H}{\zeta}\mathbf{Q}\tilde{\psi} + \frac{2kT}{\zeta}\frac{\partial}{\partial \mathbf{Q}}\tilde{\psi}. \tag{44}$$

Inserting Eq. (44) into Eq. (42) yields

$$\frac{\partial\tilde{\psi}}{\partial t} = -\frac{\partial}{\partial \mathbf{Q}}\cdot\{\boldsymbol{\kappa}\cdot\mathbf{Q} - \frac{2H}{\zeta}\mathbf{Q} - \frac{2kT}{\zeta}\frac{\partial}{\partial \mathbf{Q}}\}\tilde{\psi} \tag{45}$$

which is just Eq. (21) with $\tilde{\psi} = \psi$. Thus, we see from the above development that equilibration in momentum space and the neglect of the acceleration term $(d/dt)([[\mathbf{V}']]\tilde{\psi})$ are both consequences of allowing the mass to approach zero and are not independent assumptions, as incorrectly assumed in Refs. 17 and 19. This process of eliminating the mass of the Brownian particles corresponds to the limit of zero dimensionless mass defined by $(m/\zeta)/\lambda_H$. This is a formal way of accounting for a large separation of characteristic time scales. The very small time constant m/ζ is a characteristic time scale for the velocity fluctuations due to the

Brownian forces, and the large time constant, $\lambda_H = \zeta/4H$ is a characteristic time scale for the vibrational motions of the dumbbell.

We also point out that this method of obtaining the Smoluchowski equation from a FPE can be generalized to an arbitrary number of interacting Brownian particles in the presence of time-independent external forces and seems to be more straightforward than the method used by Murphy and Aguirre,24 or Wilemski."

C. The stress tensor

From Eq. (13.3-14) of Ref. 35, we know the dependence of the extra stress due to the presence of the polymer, π_p to be for a Hookean dumbbell:

$$\boldsymbol{\pi}_p = nm \sum_\nu \langle \mathbf{v}'_\nu \mathbf{v}'_\nu \rangle - nH \langle \mathbf{QQ} \rangle, \tag{46}$$

where n is the number density of dumbbells. The summation in the first term on the right-hand side of Eq. (46) can be written

$$\sum_\nu \langle \mathbf{v}'_\nu \mathbf{v}'_\nu \rangle = 2\langle \mathbf{v}'_c \mathbf{v}'_c \rangle + \tfrac{1}{2}\langle \mathbf{V}'\mathbf{V}' \rangle = \frac{2kT}{m}\boldsymbol{\delta} - \frac{H}{m}\int_{-\infty}^{t} \exp\left[-\frac{2\zeta}{m}(t-t')\right] \times \frac{\delta}{\delta t'}\langle \mathbf{QQ} \rangle_{t'}\, dt', \tag{47}$$

where Eqs. (17) and (33) have been used and $\delta/\delta t$ represents the convected derivative defined in Eq. (27). As is customarily done, we substract off the isotropic contribution to the stress tensor at equilibrium in the definition of τ_p Thus, using Eqs. (46) and (47) we obtain

$$\boldsymbol{\tau}_p = nkT\boldsymbol{\delta} - nH\langle \mathbf{QQ} \rangle - nH \times \int_{-\infty}^{t} \exp\left[-\frac{2\zeta}{m}(t-t')\right] \frac{\delta}{\delta t'}\langle \mathbf{QQ} \rangle_{t'}\, dt'. \tag{48}$$

The first two terms on the right-hand side are the usual non-inertial contribution to the stress tensor in the Kramers expression. The third term is a contribution from the inertia of the internal motion of the dumbbells.

D. Time-dependent shear flows

We now continue on our goal of finding the material functions. We wish to find $\langle \boldsymbol{QQ} \rangle$ for flows where $\boldsymbol{\kappa}$ has the matrix representation in a laboratory fixed Cartesian coordinate system: ,

$$\boldsymbol{\kappa} \equiv \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \dot{\gamma}(t). \tag{49}$$

We try a solution of the form

$$\langle \mathbf{QQ} \rangle \equiv \frac{kT}{H}\begin{pmatrix} 1+f & g & 0 \\ g & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{50}$$

where f and g are functions of time. For this form of $\langle \boldsymbol{QQ} \rangle$, $\boldsymbol{I}(t) = \boldsymbol{0}$, and Eqs. (33) and (34) yield the following integrodifferential equations for f and g:

$$\left(\frac{d}{dt} + \frac{\zeta}{m}\right)(\dot{g} - \dot{\gamma}) + \frac{4H}{m}g + \frac{4H}{m} \times \int_{-\infty}^{t} \exp\left[-\frac{2\zeta}{m}(t-t')\right](\dot{g} - \dot{\gamma})\, dt' = 0, \tag{51}$$

$$\left(\frac{d}{dt} + \frac{\zeta}{m}\right)(\dot{f} - 2\dot{\gamma}g) + \frac{4H}{m}f + \frac{4H}{m} \times \int_{-\infty}^{t} \exp\left[-\frac{2\zeta}{m}(t-t')\right] \times (\dot{f} - 2\dot{\gamma}g)\, dt' = (\dot{g} - \dot{\gamma})\,\dot{\gamma}, \tag{52}$$

where the dot over the variables f and g indicates a derivative with respect to time. Equivalent ordinary differential equations may be obtained by performing the operation $(d/dt) + (2\zeta/m)$ on Eqs. (51) and (52) to yield

$$\left[\left(\frac{d}{dt} + \frac{2\zeta}{m}\right)\left(\frac{d}{dt} + \frac{\zeta}{m}\right) + \frac{4H}{m}\right](\dot{g} - \dot{\gamma}) + \frac{4H}{m}\left(\frac{d}{dt} + \frac{2\zeta}{m}\right)g = 0, \tag{53}$$

$$\left[\left(\frac{d}{dt} + \frac{2\zeta}{m}\right)\left(\frac{d}{dt} + \frac{\zeta}{m}\right) + \frac{4H}{m}\right](\dot{f} - 2\dot{\gamma}g) + \frac{4H}{m}\left(\frac{d}{dt} + \frac{2\zeta}{m}\right)f = \left(\frac{d}{dt} + \frac{2\zeta}{m}\right)(\dot{g} - \dot{\gamma})\,\dot{\gamma}. \tag{54}$$

If we introduce the time constant λ_H and dimensionless mass μ: $\lambda_H = \zeta/4H$ and $\mu = 4Hm/\zeta^2$, then Eqs. (53) and (54) can be written

$$[(D'+2)(D'+1)D' + 2\mu(D'+1)]g = [(D'+2)(D'+1) + \mu]\lambda_H \mu \dot{\gamma}, \tag{55}$$

$$[(D'+2)(D'+1)D' + 2\mu(D'+1)]f = [(D'+2)(D'+1) + \mu]\,\lambda_H \mu 2\dot{\gamma}g + \lambda_H^2 \mu^2 (D'+2)[(\dot{g} - \dot{\gamma})\dot{\gamma}], \tag{56}$$

where

$$D' = \lambda_H \mu \frac{d}{dt}.$$

1. Oscillatory shear flow

A solution to Eq. (55) may be found for shear flows of the form

$$\dot{\gamma}(t) = \dot{\gamma}^0\,\mathrm{Re}\{e^{i\omega t}\}, \tag{57}$$

where Re{ } represents taking the real part of the enclosed quantity and co is the frequency of oscillation. It is possible to generalize the ordinary differential equations into a complex form if we postulate a solution of the form

$$g = \mathrm{Re}\{g^* e^{i\omega t}\}\lambda_H \dot{\gamma}^0, \tag{58}$$

where $g^* = g^*(\lambda_H\omega, \mu)$. Then Eq. (55) yields

$$g^* = \frac{1 + \frac{1}{2}\lambda_H\omega\mu i + (\mu/2)/(1 + \lambda_H\omega\mu i)}{1 + \lambda_H\omega i(1 + \lambda_H\omega\mu i/2)}. \tag{59}$$

The polymer contribution to the complex shear viscosity, $\eta^* = \eta' - i\eta''$ is defined by the relation (see p. 116, Ref. 35)

$$\tau^0_{yx} = -\eta^* \dot{\gamma}^0, \tag{60}$$

where we have used the relation

$$\boldsymbol{\tau}_p = \mathrm{Re}\{\boldsymbol{\tau}^0 e^{i\omega t}\}. \tag{61}$$

Then, from Eqs. (48), (50), (60), and (61) we find

$$\frac{\eta^*}{nkT\lambda_H} = g^* \frac{(1+\frac{1}{2}\lambda_H\omega\mu i)}{(1+\lambda_H\omega\mu i)} - \frac{\mu/2}{(1+\lambda_H\omega\mu i)}. \tag{62}$$ 1/2

Likewise, once g is known, a solution for f may be found by postulating a solution of the form

$$f = [f^d + \mathrm{Re}\{f^* e^{2i\omega t}\}] \cdot (\lambda_H \dot{\gamma}^0)^2, \tag{63}$$

where f^d and f^* are functions of $\lambda_H\omega$ and μ. From Eq. (56) we obtain

$$f^d = \mathrm{Re}\{(1+\mu/2+\tfrac{1}{2}\lambda_H\omega\mu i)g^* - \mu/2\}, \tag{64}$$

$$f^* = \frac{g^*[1+\lambda_H\,\mu\omega i + (\mu/2)/(1+2\lambda_H\,\mu\omega i)] + \frac{1}{2}\mu(1+\lambda_H\,\mu\omega i)(\lambda_H\omega g^* i - 1)/(1+2\lambda_H\,\mu\omega i)}{1+2\lambda_H\omega i(1+\lambda_H\,\mu\omega i)}. \tag{65}$$

From these relations, we can find the polymer contribution to the complex first normal stress coefficients defined by

$$\tau^0_{yy} - \tau^0_{xx} = (\Psi_1^* e^{2i\omega t} + \Psi_1^d)(\dot{\gamma}^0)^2. \tag{66}$$

Then, from Eqs. (48), (50), (61), (63), (64), and (66), the expression for Ψ_1^d is

$$(\Psi_1^d / nkT\lambda_H^2) = \mathrm{Re}\{f^d - g^*\mu/2\}. \tag{67}$$

The expression for Ψ_1^* is found from Eqs. (48), (50), (61), (63), (65), and (66):

$$\frac{\Psi_1^*}{nkT\lambda_H^2} = \frac{(1+\frac{1}{2}\lambda_H\omega\mu i)}{(1+\lambda_H\omega\mu i)} f^* - \frac{\mu/2}{(1+\lambda_H\omega\mu i)} g^*. \tag{68}$$

Note that the expressions for η^*, Ψ_1^d, and Ψ_1^* reduce to the usual noninertial dumbbell results in the limit that $\mu = 0$:

$$g^* \to \frac{1}{1+\lambda_H\omega i}, \quad \mu \to 0,$$

$$f^d \to \mathrm{Re}\{g^*\}, \quad \mu \to 0,$$

$$f^* \to g^*/(1+2\lambda_H\omega i), \quad \mu \to 0.$$

Thus, the material functions for oscillatory shear flow reduce in the zero mass limit to

$$\frac{\eta^*}{nkT\lambda_H} = \frac{1}{1+\lambda_H\omega i}, \quad \mu \to 0,$$

$$\Psi_1^d = \lambda_H \eta', \quad \mu \to 0,$$

$$\frac{\Psi_1^*}{nkT\lambda_H} = \frac{\lambda_H \eta^*}{1+2\lambda_H\omega i}, \quad \mu \to 0.$$

We note from the expressions for η^* and Ψ_1^* for Hookean dumbbells with inertia and bead-centered isotropic Brownian forces, Eqs. (59), (62), (64), (65), (67), and (68) that there occur corrections involving terms of the order $\lambda_H\omega\mu^{1/2}$, in contradiction with Fixman's argument as to when the mass should become important. Fixman[18] implicitly assumed the importance of only a single time constant m/ζ and based his dimensional arguments on that. However, another governing time constant exists, namely λ_H which allows the existence of a dimensionless mass that is independent of any characteristic dimensionless time. Thus, terms like the one above, where the characteristic dimensionless frequency $\lambda_H\omega$ is scaled by the square root of the dimensionless mass $\mu^{1/2}$ can occur.

For example, Fixman estimates that $\zeta/m[=1/\mu\lambda_H] \cong 10^{-13}\ \mathrm{s}^{-1}$. For systems with a characteristic hydrodynamic time constant $\lambda_H \cong 1$ s, the inertia would be important when $\lambda_H\omega\mu^{1/2}$ is of order unity, or when $\omega \cong 10^{-6}\ \mathrm{s}^{-1}$—instead of $10^{-13}\ \mathrm{s}^{-1}$ as Fixman expected. However, these frequencies are still not experimentally accessible for any data that we have seen.

2. Steady shear and startup of shear flows

For a final calculation of a material function, we look at startup and steady shear flows. For startup of shear flow, $\dot{\gamma}$ of Eq. (49) has the form

$$\dot{\gamma}(t) = \begin{cases} 0, & t<0 \\ \dot{\gamma}_0, & t>0 \end{cases} \tag{69}$$

or $\dot{\gamma}(t) = \dot{\gamma}_0 H(t)$, where $H(t)$ is the Heaviside step function. In order to solve Eq. (55) for this case, we introduce the variable

$$y = g - \lambda_H \dot{\gamma}_0 \mu R(\tau), \tag{70}$$

where $\tau = t/\lambda_H\,\mu$, and

$$R(\tau) = \int_{-\infty}^{\tau} H(\tau')\,d\tau' = \begin{cases} \tau & \text{for } \tau>0 \\ 0 & \text{for } \tau<0 \end{cases}. \tag{71}$$

Using these definitions, Eq. (55) can be written

$$[(D'+2)(D'+1)D' + 2\mu(D'+1)]y = -\lambda_H\dot{\gamma}_0\mu^2(D'+2)R(\tau).$$

The initial conditions are $y(0) = y'(0) = y''(0) = 0$. This is a linear ordinary differential equation which may be solved by standard means such as Laplace transform. The solution is

$$\frac{y}{\lambda_H\dot{\gamma}_0} = \left(1+\frac{1}{2}\mu\right) + \frac{\mu^2}{(1-2\mu)}\left\{e^{-\tau} - \left(\frac{\lambda_+}{2\lambda_-^2}\right)e^{-\lambda_-\tau} - \left(\frac{\lambda_-}{2\lambda_+^2}\right)e^{-\lambda_+\tau}\right\} - \mu\tau, \tag{72}$$

where $\lambda_\pm = 1 \pm (1-2\mu)^{1/2}$. From Eqs. (48) and (50), and the definition of the viscosity growth function

$$\tau_{yx}(\tau) = -\eta^+(\tau)\dot{\gamma}_0$$

we have

$$\frac{\eta^+(\tau)}{nkT\lambda_H} = 2\left(\frac{g}{\lambda_H\dot\gamma_0}\right) - 2\int_{-\infty}^{\tau} e^{-2(\tau-\tau')} \times\left(\frac{g(\tau')}{\lambda_H\dot\gamma_0}\right)d\tau' - \tfrac{1}{2}\mu(1-e^{-2\tau}). \tag{73}$$

From Eqs. (70), (71), (72), and (73) we get

$$\frac{\eta^+(\tau)}{nkT\lambda_H} = 1 + \frac{1}{2}\mu e^{-2\tau} + \frac{\mu^2}{(1-2\mu)^{1/2}} \times\left\{\left(\frac{1}{\lambda_+^2}\right)e^{-\lambda_+\tau} - \left(\frac{1}{\lambda_-^2}\right)e^{-\lambda_-\tau}\right\}. \tag{74}$$

We note that in the limit $\mu = 0$:

$$\frac{\eta^+(t)}{nkT\lambda_H\dot\gamma_0} = 1 - \exp(-t/\lambda_H), \quad \mu = 0$$

which is the usual noninertial Hookean dumbbell result. We may also obtain the steady-state shear viscosity from Eqs. (59) and (62) in the limit $\omega = 0$ or from Eq. (74) in the limit $\tau \to \infty$ to find: $\eta = nkT\lambda_H$. Likewise, from Equations (59), (65), and (68) we get the usual steady-state first normal stress coefficient defined in Ref. 35: $\Psi_1 = 2nkT\lambda_H^2$.

Thus, the steady state shear results are unaffected by inertia. We have shown above how the other material functions for the inertial Hookean dumbbell reduce to the results for the usual noninertial Hookean dumbbell in the limit of zero mass.

III. GENERALIZATIONS TO THE ROUSE MODEL

All of the results found so far may be generalized to a Rouse chain of N structureless beads linearly attached by N-1 identical Hookean springs of spring constant H with bead-centered isotropic Brownian forces. The equations of motion for the beads in this model are

$$m\,d\mathbf{v}'_\nu = \mathbf{F}_\nu^{(c)}\,dt - \zeta\mathbf{v}'_\nu\,dt + (2kT\zeta)^{1/2}\,d\mathbf{W}_\nu, \tag{75}$$

$$d\mathbf{r}_\nu = \mathbf{v}'_\nu\,dt + \boldsymbol{\kappa}\cdot\mathbf{r}_\nu\,dt, \quad \nu = 1,2,\ldots,N, \tag{76}$$

where $\mathbf{F}_\nu^{(c)}$ is now the sum of connector forces on bead ν. We introduce the generalized coordinates

$$\mathbf{r}_c = \frac{1}{N}\sum_\nu \mathbf{r}_\nu, \tag{77}$$

$$\mathbf{Q}_k = \mathbf{r}_{k+1} - \mathbf{r}_k, \tag{78}$$

and the corresponding velocities

$$\mathbf{v}'_c = \frac{1}{N}\sum_\nu \mathbf{v}'_\nu, \tag{79}$$

$$\mathbf{V}'_k = \mathbf{v}'_{k+1} - \mathbf{v}'_k. \tag{80}$$

By subtracting the $\nu = k+1$ case of Eqs. (75) and (76) from the $\nu = k$ case, and using the definitions given by Eqs. (77)–(80), the appropriate SDEs for the internal configuration are obtained:

$$m\,d\mathbf{V}'_k = \sum_\nu \overline{B}_{k\nu}\,\mathbf{F}_\nu^{(c)}\,dt - \zeta\,\mathbf{V}'_k\,dt + (2kT\zeta)^{1/2}\sum_\nu \overline{B}_{k\nu}\,d\mathbf{W}_\nu, \tag{81}$$

$$d\mathbf{Q}_k = \mathbf{V}'_k\,dt + \boldsymbol{\kappa}\cdot\mathbf{Q}_k\,dt, \quad k = 1,2,\ldots,N-1, \tag{82}$$

where the $N\times(N-1)$ matrix $\overline{B}_{k\nu}$ has been introduced. It is defined as

$$\overline{B}_{k\nu} = \delta_{k+1,\nu} - \delta_{k,\nu}. \tag{83}$$

The term containing the connector forces on bead ν, $\mathbf{F}_\nu^{(c)}$ may be rewritten

$$\sum_j \overline{B}_{\nu j}\,\mathbf{F}_\nu^{(c)} = -H\sum_j A_{jk}\,\mathbf{Q}_j, \tag{84}$$

where we have used the $(N-1)\times(N-1)$ Rouse matrix, A_{ij} defined by

$$A_{ij} = \sum_\nu \overline{B}_{i\nu}\,\overline{B}_{j\nu}. \tag{85}$$

It has eigenvalues $a_i = 4\sin^2(i\pi/2N)$, $i = 1,2,\ldots,N-1$ and may be diagonalized by an orthogonal matrix Ω_{ij} such that

$$\sum_{jk}\Omega_{ji}\,A_{jk}\Omega_{kl} = a_i\delta_{il}. \tag{86}$$

This same matrix can then be used to transform the original internal coordinates into normal mode coordinates, $\tilde{\mathbf{Q}}_i$ and $\tilde{\mathbf{V}}'_i$:

$$\tilde{\mathbf{Q}}_k = \sum_l \Omega_{kl}\mathbf{Q}_l, \quad \tilde{\mathbf{V}}'_k = \sum_l \Omega_{kl}\mathbf{V}'_l. \tag{87}$$

Using these relations, we multiply Eqs. (87) and (82) by Ω_{ki} and sum over k to obtain

$$m\,d\tilde{\mathbf{V}}'_i = -a_iH\tilde{\mathbf{Q}}_i\,dt - \zeta\tilde{\mathbf{V}}'_i\,dt + (2kT\zeta)^{1/2} \times\sum_k\sum_\nu \overline{B}_{k\nu}\Omega_{ki}\,d\mathbf{W}_\nu, \tag{88}$$

$$d\tilde{\mathbf{Q}}_i = \tilde{\mathbf{V}}'_i\,dt + \boldsymbol{\kappa}\cdot\tilde{\mathbf{Q}}_i\,dt.$$

This has the corresponding FPE:

$$\frac{\partial\tilde f}{\partial t} = -\sum_i\left(\frac{\partial}{\partial\tilde{\mathbf{Q}}_i}\cdot\{\tilde{\mathbf{V}}'_i + [\boldsymbol{\kappa}\cdot\tilde{\mathbf{Q}}_i]\}\tilde f + \frac{\partial}{\partial\tilde{\mathbf{V}}'_i}\cdot\left\{\frac{a_iH}{m}\tilde{\mathbf{Q}}_i + \frac{\zeta}{m}\tilde{\mathbf{V}}'_i + \frac{a_ikT\zeta}{m^2}\frac{\partial}{\partial\tilde{\mathbf{V}}'_i}\right\}\tilde f\right), \tag{89}$$

where Eqs. (84), (85), and (86) have been used. If we postulate a solution of the form

$$\tilde f(\tilde{\mathbf{Q}}_1,\ldots,\tilde{\mathbf{Q}}_{N-1},\tilde{\mathbf{V}}'_1,\ldots,\tilde{\mathbf{V}}'_{N-1};t) = \prod_i f_i(\tilde{\mathbf{Q}}_i,\tilde{\mathbf{V}}'_i;t) \tag{90}$$

then Eq. (89) can be written as $(N-1)$ separate, uncoupled FPEs:

$$\frac{\partial f_i}{\partial t} = -\frac{\partial}{\partial\tilde{\mathbf{Q}}_i}\cdot\{\tilde{\mathbf{V}}'_i + [\boldsymbol{\kappa}\cdot\tilde{\mathbf{Q}}_i]\}f_i + \frac{\partial}{\partial\mathbf{V}'_i}\cdot\left\{\frac{a_iH}{m}\tilde{\mathbf{Q}}_i + \frac{\zeta}{m}\tilde{\mathbf{V}}'_i + \frac{a_ikT\zeta}{m^2}\frac{\partial}{\partial\tilde{\mathbf{V}}'_i}\right\}f_i \tag{91}$$

provided that the initial conditions may also be uncoupled. This is satisfied if we choose our initial conditions to be equilibrium at t = - ∞. Now we note that Eq. (91) has exactly the same form as the FPE derived for the single dumbbell, Eq. (22) when the following substitutions are made:

$$H \to a_i H/2, \quad kT \to a_i kT/2.$$

The previously defined constants must be replaced by new ones;

$$\lambda_H \to \lambda_i = \zeta/2a_i H, \quad \mu \to \mu_i = 2ma_i H/\zeta^2. \tag{92}$$

Then, the solutions for each of the normal mode coordinates, $\langle \tilde{\mathbf{Q}}_i \tilde{\mathbf{Q}}_i \rangle$ may be obtained from the dumbbell results in a manner exactly analogous to the noninertial case. The polymer contribution to the stress tensor is

$$\boldsymbol{\tau}_p = nkT\boldsymbol{\delta} - nH \sum_i \langle \tilde{\mathbf{Q}}_i \tilde{\mathbf{Q}}_i \rangle - nH \int_{-\infty}^{t} \exp\left[-\frac{2\zeta}{m} (t-t') \right] \times \sum_i \frac{\delta}{\delta t'} \langle \tilde{\mathbf{Q}}_i \tilde{\mathbf{Q}}_i \rangle_{t'} \, dt'. \tag{93}$$

In other words, the chain provides a contribution to the stress as if there were a spectrum of N - 1 dumbbells with time constants given by Eq. (92).

IV. CONCLUSIONS

We began with the diffusion equation of Murphy and Aguirre derived for an arbitrary number of interacting Brownian particles at equilibrium from Hamilton's equations of motion and generalized these to account for flow fields. The resulting stochastic differential equations of motion may be solved analytically without omitting inertial effects. When this is done, Fixman's argument for the omission of the acceleration terms in the equations of motion for the beads are seen to be qualitatively incorrect. However, the finite-mass corrections to the material functions studied are still seen to be negligible for small-amplitude oscillatory shear flow. For samples in solvents of extremely low viscosity, e.g., "supercritical solvents," we may expect the inertia of the chains to become more important since the dimensionless mass ,u depends inversely upon the solvent viscosity squared.

It was also shown how the equations of motion used by Szu and Hermans for inertial dumbbells in flow fields are incorrect. However, their results may be correctly reinterpreted as dumbbell-centered isotropic Brownian forces. The same viscosity results were found here. That is, inertial effects give no additional contribution to the viscosity for dumbbell-centered isotropic Brownian forces.

In every step of the development, it was demonstrated how the usual results for the noninertial Hookean dumbbell may be obtained as a limiting case of zero mass from the inertial case. In particular, a simple and straightforward method was illustrated to obtain a Smoluchowski equation as a limiting case of a Fokker-Planck equation that is as general as, but more straightforward than methods used elsewhere.[24,36]

Finally, the development provides an example of the connection between work done independently by Murphy and Aguirre" and Curtiss, Bird, and Hassager.[19] Also, two important assumptions concerning acceleration and Brownian forces made by the latter can be interpreted as the consequences of a single assumption of vanishing mass of the chain particles.

Perhaps the weakest point of our development is the generalization of the work by Murphy and Aguirre to account for flows. While the field of nonequilibrium thermodynamics has recently been extensively investigated, most work has been done either in situations which are only slightly perturbed from equilibrium (linear response theory) or by methods which study locally defined thermodynamic properties and do not make considerations about the microscopic mechanics. This suggests that much work remains to be done to account for flows in more than just the phenomenological approach done here.

We also point out that it should be possible to generalize this work to include both hydrodynamic interaction and fluid inertia. A large effect is not expected in the presence of hydrodynamic interaction. On the other hand, the effect of fluid inertia may be quite important but is outside the scope of this paper.

ACKNOWLEDGMENTS

J.D.S. wishes to acknowledge the support of the National Science Foundation (Grant No. CPE-8104705), the MacArthur Foundation, the Vilas Trust Fund, and Dow Chemical, USA all provided through grants to Professor R. Byron Bird. H.C.O. wishes to acknowledge the support of the Max Kade Foundation.

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