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On the Derivation of Smoluchowski Equations with Corrections in the Classical Theory of Brownian Motion

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Differential equations governing the time evolution of distribution functions for Brownian motion in the full phase space were first derived independently by Klein and Kramers. From these so-called Fokker–Planck equations one may derive the reduced differential equations in coordinate space known as Smoluchowski equations. Many such derivations have previously been reported, but these either involved unnecessary assumptions or approximations, or were performed incompletely. We employ an iterative reduction scheme, free of assumptions, and calculate formally exact corrections to the Smoluchowski equations for many-particle systems with and without hydrodynamic interaction, and for a single particle in an external field. In the absence of hydrodynamic interaction, the lowest order corrections have been expressed explicitly in terms of the coordinate space distribution function. An additional application of the method is made to the reduction of the stress tensor used in evaluating the intrinsic viscosity of particles in solution. Most of the present work is based on classical Brownian motion theory, but brief consideration is given in an appendix to some recent developments regarding non-Markovian equations for Brownian motion.

KEY WORDS: Brownian motion; Fokker–Planck equation; Smoluchowski equation; diffusion; hydrodynamic interaction; intrinsic viscosity.

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1. INTRODUCTION

By 1917 the theory of Brownian motion pioneered by Einstein,[1] Smoluchowski,[2] and Langevin[3] had been generalized in two significant ways. Fokker[4] and, more generally, Planck[5] had considered Brownian motion in velocity space, while Smoluchowski[6] extended the coordinate-space description to account for the influence of an external force on the Brownian particle. Both of these generalizations consisted in finding a differential equation whose solution was the distribution function for the process being considered. To complete this picture, there remained the task of finding the appropriate differential equation in the full phase space of the Brownian particle.

Kramers[7] is often credited with first presenting this generalization. Actually this had already been accomplished much earlier by Klein,[8] who treated a many-particle system in which interparticle forces were present, but hydrodynamic interactions among the particles were absent. Basing his analysis on the Langevin equations for the velocities of the particles, he obtained a differential equation in phase space of the type commonly described by the names Fokker–Planck or Kramers. Klein further provided an approximate reduction of this equation to a many-particle diffusion equation, thus generalizing Smoluchowski's[6] earlier work and providing a link between the two levels of description.

Not too long after Kramers, Chandrasekhar[9],[2] presented a somewhat different derivation of the single-particle equation in phase space, but still followed Kramers'[7] argument in order to extract Smoluchowski's equation. The relationship of these two levels of description has continued to be the subject of further investigation, and the present article deigns to proceed in that spirit.

The Smoluchowski equation is conventionally described as the long-time limit of the velocity-averaged Fokker–Planck–Klein–Kramers (FPKK) equation. Yet, in 1954 Mark Kac is reported[10] to have remarked that a satisfactory demonstration of this reduction had still not been presented. As we shall see, subsequent work seems still not to have fully remedied this deficiency. More recently, Nelson[11] has expressed a similar concern. He considers the problem in terms of the Langevin equations employed in the Ornstein–Uhlenbeck[12,13] theory. Then he shows that "...the Smoluchowski approximation in the case of a general external force...is in a very strong sense the limiting case of the Ornstein–Uhlenbeck theory for large friction" (Ref. 11, p. 70). He has also suggested how to obtain a similar result using the language of partial differential equations. This is the result we desire. How-

[2] This article contains an extensive bibliography concerning the early development of classical Brownian motion theory.

ever, we shall not embark upon his program, but choose instead to follow a conceptually simpler route (at least to a nonmathematician) which leads to the desired end and, in addition, gives rise to some interesting and physically satisfactory fringe benefits.

We begin by imitating Maxwell[(14)] in calculating coordinate-space equations for successively higher moments of the velocity. Maxwell's interest, of course, lay in the determination of transport coefficients from the kinetic theory of gases, whereas the present equations are derived from the FPKK equation. Though the hierarchy thus generated is not closed, it nonetheless affords, at any level, a formally exact coordinate-space description of the Brownian process. The moment equations may be solved and combined in a manner which permits a systematic expansion in inverse powers of the friction constant ζ. The Smoluchowski diffusion operator then appears straightforwardly as the leading term of this asymptotic expansion. Consideration of the first five equations of the hierarchy is sufficient and necessary to effect the explicit determination of the lowest order correction term.

The method can more generally be applied to reduce a many-particle FPKK equation which includes both interparticle forces and full hydrodynamic interaction to the corresponding many-particle diffusion equation. For this system, however, it has so far been possible to obtain an explicit correction term only when hydrodynamic interactions are absent.

Before attending to the single-particle equation, let us briefly discuss the limitations of some of the other known methods for handling this problem. All of these proposals succeed in obtaining Smoluchowski's equation; but all, it would seem, have failed to ground the result in a fully consistent development.

The desirability of having an asymptotic expansion of the coordinate-space operator in powers of ζ^{-1} has previously been recognized,[(15–20)] and in several cases[(16,17,19)] lowest order correction terms have also been presented. These terms, although derived from the same hierarchy of moment equations to be considered here, are incorrect, most probably because of incomplete analysis of the hierarchy.[3]

Brinkman's[(21)] method also resembles the present one. This method is blemished by the superfluous choice of an initial Maxwellian velocity distribution, but it suffers more seriously from an uneconomical choice of moments. These higher moments (Hermite polynomials in the velocity) are actually linear combinations of the physically more important moments. This mixing prevents the straightforward collection of all terms of a given order, and may lead to errors. For example, Brinkman obtains his lowest

[3] We feel sure of this with regard to Ref. 19. Our knowledge of Ref. 16, however, is based solely on results and descriptions provided in Refs. 17, 18, and 20.

order equation by ignoring the second and all higher moments, but in the process he neglects a contribution of the same order as terms retained.

Brinkman's lowest order equation is actually the Laplace transform of the so-called telegraph equation.[4] This equation has been proposed several other times as a generalization of Smoluchowski's equation. Two methods[22,23] are related to Brinkman's scheme. In the others,[10,24,25] there is a failure to appreciate that the second moment (the kinetic contribution to the momentum transport in the present scheme) relaxes only slightly faster than the first moment, the current. It is thus inconsistent to use the asymptotic form of the second moment in an exact equation for the current and attribute significance to the result for other than long times. Now, it may be that for some fundamental reason the telegraph equation does afford a better description of Brownian motion than the Smoluchowski equation. In this regard we make only the following observation. It is not difficult to compare (numerically) the solutions of the telegraph equation[10] and the diffusion equation for a free particle with an initial Maxwellian velocity distribution. What we have found, in agreement with Hemmer,[26] is that particularly for short times it is the solution of the diffusion equation rather than the telegraph equation that is in much better agreement with the "exact" distribution obtained from the Langevin equation. Furthermore, only for times greater than about $10(m/\zeta)$, where m is the mass of the particle, does the solution of the telegraph equation come into good agreement with the other two. An additional quirk is that the telegraph equation is a hyperbolic equation for the density because of the presence of a second-order time derivative. This would ordinarily imply freedom in choosing initial values for the density and its first time derivative. Yet, from the moment equations [Eqs. (2)–(6)] it can be seen that once the initial density and velocity distribution have been chosen, the initial values of *all* the remaining moments and their time derivatives are determined.

Other reduction schemes[27–30] have been based on a Chapman–Enskog approximation in which the entire time dependence is assumed to reside entirely in the coordinate-space distribution function. A physically equivalent assumption is made by de Groot and Mazur,[31] who factor the full distribution function into a coordinate-space distribution function and a locally Maxwellian velocity distribution. Though these assumptions are physically reasonable, they are unnecessary for the attainment of the desired result. A more rigorous alternative has been presented by Resibois,[27] but even here a linearized FPKK equation has been used.

In closing this (possibly incomplete) survey we first note two recent developments in polymer theory. In one, Kramers' procedure has been employed[32] in reducing a many-particle FPKK equation with hydrodynamic

[4] Strictly, the telegraph equation has the form of Eq. (12) with **K** absent, but we will use the term in a looser sense, applying it even when **K** does not vanish.

interaction to the diffusion equation governing the motion of the polymer chain. In the other,[33] a formally exact coordinate-space equation, formulated in terms of generalized coordinates, was derived for a many-particle system without hydrodynamic interaction. The Smoluchowski equation in generalized coordinates (or Kirkwood equation[34]) is obtained after several approximations, including the assumption of locally Maxwellian velocity distributions and the neglect of inertial terms in the moment equations. In these latter aspects, the method is similar to the original derivations[34,35] of this equation.

Finally, we observe that the existence of FPKK equations is sufficient, but apparently not necessary, to permit the derivation of Smoluchowski equations. Illustrative of this point are several derivations[36] of many-particle diffusion equations which begin with the Liouville equation and avoid recourse to an intermediate FPKK equation. The calculation of correction terms using this alternate approach is certainly a desirable goal for future work, but for now we restrict our attention to a development based on FPKK equations.

2. SINGLE PARTICLE IN AN EXTERNAL FIELD

The distribution function $f(\mathbf{r}, \mathbf{u}, t)$ satisfies the FPKK equation[7,9]

$$\partial f/\partial t + \mathbf{u}\cdot\nabla f + m^{-1}\mathbf{K}\cdot\nabla_u f = (\zeta/m)\nabla_u\cdot[\mathbf{u}f + (kT/m)\,\nabla_u f] \tag{1}$$

where $\mathbf{r}$ and $\mathbf{u}$ are the position and velocity vectors, $\mathbf{K}$ is the external force, and ζ and m are the friction constant and mass of the particle. The coordinate space density is defined as

$$w(\mathbf{r}, t) = \int f\,d\mathbf{u} \tag{2}$$

The following equations define successively the current,

$$\mathbf{j} = \int \mathbf{u}f\,d\mathbf{u} \tag{3}$$

the kinetic contribution to the momentum flux tensor,

$$\mathbf{P} = m\int \mathbf{uu}f\,d\mathbf{u} \tag{4}$$

a tensor proportional to the kinetic energy flux tensor,

$$\mathbf{Q} = m^2\int \mathbf{uuu}f\,d\mathbf{u} \tag{5}$$

and finally

$$\mathbf{R} = m^3\int \mathbf{uuuu}f\,d\mathbf{u} \tag{6}$$

Exact coordinate-space equations involving these moments may be obtained by multiplying Eq. (1) by the appropriate product of **u**'s and performing the necessary integrations. The first three of these equations are

$$\partial w/\partial t + \nabla\cdot\mathbf{j} = 0 \tag{7}$$

$$m\,\partial\mathbf{j}/\partial t + \nabla\cdot\mathbf{P} - \mathbf{K}w + \zeta\mathbf{j} = 0 \tag{8}$$

$$m\,\partial\mathbf{P}/\partial t + \nabla\cdot\mathbf{Q} - m(\mathbf{Kj} + \mathbf{jK}) - 2\zeta kT\mathbf{I}w + 2\zeta\mathbf{P} = 0 \tag{9}$$

The Laplace transforms of these three equations may be combined to give

$$\begin{aligned} s\hat{w} = {} & w(0) - \frac{\nabla\cdot\mathbf{j}(0)}{s+\beta} + \frac{\nabla\cdot[\nabla\cdot\mathbf{P}(0)]}{m(s+\beta)(s+2\beta)} \\ & + \frac{1}{s+\beta}\nabla\cdot\left[\frac{2\beta kT\nabla\hat{w}}{s+2\beta} - (\widehat{\mathbf{K}w})\right] \\ & - \frac{\nabla\cdot(\nabla\cdot\{\nabla\cdot\hat{\mathbf{Q}} - m[(\widehat{\mathbf{Kj}}) + (\widehat{\mathbf{jK}})]\})}{m(s+\beta)(s+2\beta)} \end{aligned} \tag{10}$$

where

$$\beta = \zeta/m \tag{11}$$

and $w(0)$, $\mathbf{j}(0)$, and $\mathbf{P}(0)$ are initial values. Note that $\mathbf{K}$ may be time dependent.

Equation (10) can readily be inverted to give an exact differointegral equation for w that is valid on the same time scale as is the FPKK equation. Although the practical utility of this equation is limited by the presence of the additional unknown function $\mathbf{Q}$, it can be systematically expanded and converted into the desired asymptotic expansion of the coordinate-space operator. Care must be taken, however, to properly account for the lowest order contributions arising from the term involving $\mathbf{Q}$. With Eq. (10) at hand this is a convenient place to interrupt our development of the asymptotic expansion and, instead, to complete our discussion of the telegraph equation.

This equation

$$\beta^{-1}\,\partial^2 w/\partial t^2 + \partial w/\partial t = (kT/\zeta)\nabla\cdot[\nabla w - (kT)^{-1}\mathbf{K}w] \tag{12}$$

has the following Laplace transform:

$$s\hat{w} = w(0) + (s+\beta)^{-1}(\partial w/\partial t)_{t=0} + (s+\beta)^{-1}(kT/m)\nabla\cdot[\nabla\hat{w} - (kT)^{-1}(\widehat{\mathbf{K}w})] \tag{13}$$

Upon realizing that

$$(\partial w/\partial t)_{t=0} = -\nabla\cdot\mathbf{j}(0) \tag{14}$$

we see from simple inspection of Eq. (10) which terms must be inconsistently neglected in order to obtain Eq. (13).

It is also interesting to note[22,24,26] that for a free particle with an initial Maxwellian velocity distribution, Eq. (12) gives[5] the exact Ornstein–Uhlenbeck[12] result for the average square of the particle displacement $\langle(\mathbf{r}-\mathbf{r}_0)^2\rangle$, where $\mathbf{r}_0$ is the initial position. In fact this result is purely accidental. From the exact Eq. (10) we see that the last term rigorously vanishes in the averaging and for the Maxwellian distribution the contributions from the $\mathbf{P}(0)$ and $\nabla\cdot\nabla w$ terms combine to give just the result of the telegraph equation. The average displacement may also be calculated correctly from the telegraph equation, even for an arbitrary initial velocity distribution, but as noted previously,[24] no higher moments will be correctly determined by this equation. Furthermore, if external forces are present or the initial velocity distribution is not Maxwellian, not even $\langle(\mathbf{r} - \mathbf{r}_0)^2\rangle$ will be given correctly. Of course, exact results may always be obtained from Eq. (10), using when necessary the exact equations for $\mathbf{Q}$, $\mathbf{R}$, etc.

Resuming pursuit of the desired goal, an expansion in which only spatial derivatives of w are present, we proceed by solving Eqs. (8) and (9). For example, the solution to Eq. (8) is

$$\mathbf{j}(t) = \mathbf{j}(0)e^{-\beta t} - m^{-1}\int_0^t d\tau\, e^{-\beta(t-\tau)}[\nabla\cdot\mathbf{P}(\tau) - \mathbf{K}(\tau)w(\tau)] \tag{15}$$

Successive integration by parts generates the asymptotic expansion

$$\begin{aligned}\mathbf{j}(t) = (\text{i.v.})e^{-\beta t} - m^{-1}[&\beta^{-1}(\nabla\cdot\mathbf{P} - \mathbf{K}w)\\ &- \beta^{-2}(\nabla\cdot\partial\mathbf{P}/\partial t - \partial(\mathbf{K}w)/\partial t) + \cdots]\end{aligned} \tag{16}$$

The designation (i.v.) indicates the collection of all initial value terms. These always decay at least as fast as $\exp(-\beta t)$. Equation (9) may be similarly solved and expanded. We find

$$\begin{aligned}\mathbf{P}(t) = (\text{i.v.})e^{-\beta t} &+ kT\mathbf{I}[w - (2\beta)^{-1}\,\partial w/\partial t + \cdots]\\ &+ (2\beta)^{-1}(\mathbf{K}\mathbf{j} + \mathbf{j}\mathbf{K} - m^{-1}\nabla\cdot\mathbf{Q}) + \cdots\end{aligned} \tag{17}$$

To be consistent, the time derivatives of the moments must themselves be replaced by their asymptotic expansions. These may be calculated either by directly differentiating Eqs. (16) and (17) or by iterating these expressions in Eqs. (7)–(9). In similar fashion, expansions for the higher time derivatives may be calculated. This iterative process generates the desired expansion in inverse powers of the friction constant. A shortcut in the early going would be provided by expanding the inverted form of Eq. (10). In any event, no matter

[5] The telegraph equation has no explicit velocity dependence, but a particular value of $(\partial w/\partial t)_{t=0}$ is required in order either to perform averages with or to solve Eq. (12). Equations (3) and (14) should be used to infer this value. This will maintain a consistent basis for comparison with averages calculated from Langevin or FPKK equations with a specific initial velocity distribution. In the above example, the initial Maxwellian distribution implies that $(\partial w/\partial t)_{t=0} = 0$.

which particular route is taken, the final result is always the same. One finds

$$\partial w/\partial t = -\nabla\cdot\mathbf{j} \tag{18}$$

where

$$\mathbf{j} = (\text{i.v.})e^{-\beta t} + \mathbf{j}^s - m^{-1}\beta^{-2}\{\partial(\mathbf{K}w)/\partial t - (3kT/2)\nabla\,\partial w/\partial t + (1/2)\nabla\cdot[(\mathbf{K}\mathbf{j}^s + \mathbf{j}^s\mathbf{K}) - m^{-1}\nabla\cdot\mathbf{Q}]\} + m^{-1}\beta^{-3}\,\partial^2(\mathbf{K}w)/\partial t^2 + \cdots \tag{19}$$

and $\mathbf{j}^s$ is the single-particle Smoluchowski current

$$\mathbf{j}^s = -(kT/\zeta)[\nabla w - (kT)^{-1}\mathbf{K}w] \tag{20}$$

Only terms that give rise to the lowest order corrections have been displayed.

In order to calculate the corrections explicitly in terms of w, the exact equations for $\mathbf{Q}$ and $\mathbf{R}$ must be available. These are

$$m\,\partial\mathbf{Q}/\partial t + \nabla\cdot\mathbf{R} - m\mathbf{K}\cdot\mathbf{P}^{(1)} - m\zeta kT\mathbf{J} + 3\zeta\mathbf{Q} = 0 \tag{21}$$

and, with only the display of terms that contribute to lowest order,

$$m\,\partial\mathbf{R}/\partial t + \cdots + 4\zeta\mathbf{R} = m\zeta kT\mathbf{P}^{(2)} \tag{22}$$

Here, $\mathbf{J}$, $\mathbf{P}^{(1)}$, and $\mathbf{P}^{(2)}$ are defined by

$$\mathbf{J} = \int f\nabla_u^2(\mathbf{uuu})\,d\mathbf{u} \tag{23}$$

$$\mathbf{K}\cdot\mathbf{P}^{(1)} = m\int f\mathbf{K}\cdot\nabla_u(\mathbf{uuu})\,d\mathbf{u} \tag{24}$$

$$\mathbf{P}^{(2)} = m\int f\nabla_u^2(\mathbf{uuuu})\,d\mathbf{u} \tag{25}$$

After performing the required operations, we find that in lowest order the terms contributed by $\mathbf{Q}$ and $(3/2)\nabla\,\partial w/\partial t$ cancel, leaving

$$\begin{aligned}\partial w/\partial t = {} & -\nabla\cdot\mathbf{j}^s + m^{-1}\beta^{-2}\nabla\cdot[\tfrac{1}{2}\nabla\cdot(\mathbf{K}\mathbf{j}^s + \mathbf{j}^s\mathbf{K}) - \mathbf{K}\nabla\cdot\mathbf{j}^s] \\ & + m^{-1}\beta^{-2}\,\nabla\cdot[w\,\partial\mathbf{K}/\partial t - \beta^{-1}w\,\partial^2\mathbf{K}/\partial t^2] + \cdots \\ & + (\text{i.v.})e^{-\beta t}\end{aligned} \tag{26}$$

which is Smoluchowski's equation plus the desired correction terms. Notice that these lowest order correction terms vanish if there are no external forces present, leaving us with the diffusion equation, initial-value terms, and possibly only much higher order corrections. This seems consistent with the role of the friction constant in damping out accelerations. The absence of external forces implies the absence of accelerations other than those arising from the stochastic force on the particle, and the solution to the diffusion equation is a very good approximation to the Langevin distribution function for this case. Inspect, for example, Eqs. (171) and (172) of Chandrasekhar.[9]

Note, however, that the Brownian particle never forgets its initial velocity in a finite time (unless $\beta \to \infty$, but $D = kT/\zeta$ is finite). This is in contrast to the solution of the diffusion equation.

The initial-value terms in Eq. (26) will decay to less than 0.01% of their original values in times on the order of $10\beta^{-1}$. This suggests that the Smoluchowski equation may be valid on much shorter time scales than were previously recognized. In the aforementioned calculation, for example, at $t = 10\beta^{-1}$ reasonable agreement was obtained between the solution of the diffusion equation and the exact Langevin distribution function.

Of perhaps greater importance is the size of the correction term in Eq. (26). In this regard it may be instructive to examine Eq. (26) for several special cases. For three-dimensional problems with spherical symmetry and time-independent **K**, Eq. (26) reduces to

$$\partial w/\partial t = -r^{-2}(\partial/\partial r)\{r^2 j^s[1 - (m\beta^2)^{-1}\, \partial K/\partial r]\} \tag{27}$$

where

$$j^s = -(kT/\zeta)(\partial w/\partial r - Kw) \tag{28}$$

Similarly, in one dimension we have

$$\partial w/\partial t = -(\partial/\partial x)\{j^s[1 - (m\beta^{-2})^{-1}\, \partial K/\partial x]\} \tag{29}$$

For the Smoluchowski equation to be a good approximation, the inequality

$$\left| \frac{1}{m\beta^2} \frac{\partial \mathbf{K}}{\partial x} \right| \ll 1 \tag{30}$$

must be satisfied. If **K** is derivable from a potential, this inequality becomes a condition on the curvature of the potential. In both of the above cases, although not in general, the lowest order correction vanishes if **K** is constant, as, e.g., is approximately true for the gravitational force near the earth's surface.

A desirable check of the validity of our results can be made for the case of a harmonically bound particle. Equations (27) and (29) may now be solved exactly, since they have the form of the uncorrected Smoluchowski equation with a modified diffusion constant. It is easy to verify from the exact Langevin distribution function for this problem, Eq. (213) of Chandrasekhar,[9] that the modified diffusion constant is correct to the order presented.

3. MANY INTERACTING PARTICLES

We now turn our attention to a system of N interacting particles in which the effects of hydrodynamic interaction are included through the presence of a position-dependent interparticle friction tensor $\boldsymbol{\zeta}_{ij}$. The

N-particle distribution function $F(\{\mathbf{r}\}, \{\mathbf{p}\}, t)$ satisfies the FPKK equation

$$\partial F/\partial t + \sum_i (m_i^{-1}\mathbf{p}_i \cdot \nabla_i F + \mathbf{K}_i \cdot \nabla_i{}^p F) = \sum_i \sum_j \nabla_i{}^p \cdot \boldsymbol{\zeta}_{ij} \cdot (m_j^{-1}\mathbf{p}_j F + kT\,\nabla_j{}^p F) \tag{31}$$

where $\mathbf{K}_i$ is the force on particle i derivable from the usual potential of mean force, and m_i, $\mathbf{r}_i$, and $\mathbf{p}_i$ are the mass, position vector, and momentum of particle i. Equations of this form have recently been derived from microscopic considerations for systems of massive simple particles[30,37,39] and for polymeric systems.[32] Reduction of the FPKK equation with hydrodynamic interaction was apparently first considered by Aguirre and Murphy,[29] who used a Chapman–Enskog scheme to obtain the Smoluchowski equation. Our reduction to a many-particle diffusion equation proceeds in the same spirit as in Section 2, but varies in detail because of the added complexity of Eq. (31).

The use of supermatrix notation facilitates the presentation. Unsubscripted boldface symbols represent column or $N \times N$ matrices whose elements are vectors or tensors, respectively. First, define a diagonal supermatrix $\mathbf{W}$ whose elements are

$$\mathbf{W}_{ii} = m_i^{-1}\mathbf{I} \tag{32}$$

where $\mathbf{I}$ is the unit dyadic. Then, let

$$\mathscr{K} = \mathbf{W}\cdot\mathbf{K} \tag{33}$$

$$\boldsymbol{\lambda} = \mathbf{W}\cdot\boldsymbol{\zeta} \tag{34}$$

and

$$\boldsymbol{\rho} = \boldsymbol{\zeta}\cdot\mathbf{W} \tag{35}$$

and define the coordinate-space distribution function

$$\psi(\{\mathbf{r}\}, t) = \int F\, d\{\mathbf{p}\} \tag{36}$$

and the higher moments

$$\mathbf{j}_i = m_i^{-1} \int \mathbf{p}_i F\, d\{\mathbf{p}\} \tag{37}$$

$$\mathbf{U}_{ij}^{(2)} = (m_i m_j)^{-1} \int \mathbf{p}_i \mathbf{p}_j F\, d\{\mathbf{p}\} \tag{38}$$

$$\mathbf{U}_{ijk}^{(3)} = (m_i m_j m_k)^{-1} \int \mathbf{p}_i \mathbf{p}_j \mathbf{p}_k F\, d\{\mathbf{p}\} \tag{39}$$

Equation (31) may now be rewritten as

$$\partial F/\partial t + \mathbf{p}^T\cdot\mathbf{W}\cdot\nabla F + \mathbf{K}^T\cdot\nabla^p F = (\nabla^p)^T\cdot\boldsymbol{\zeta}\cdot(\mathbf{W}\cdot\mathbf{p}F + kT\,\nabla^p F) \tag{40}$$

where superscript T designates the transpose, and the following exact moment equations may be obtained:

$$\partial\psi/\partial t + \nabla^T \cdot \mathbf{j} = 0 \tag{41}$$

$$\partial \mathbf{j}/\partial t + (\nabla^T \cdot \mathbf{U}^{(2)})^T - \mathscr{K}\psi + \boldsymbol{\lambda}\cdot\mathbf{j} = 0 \tag{42}$$

$$\partial \mathbf{U}^{(2)}/\partial t + \nabla^T \cdot \mathbf{U}^{(3)} - (\mathscr{K}\mathbf{j}^T + \mathbf{j}\mathscr{K}^T) - 2kT\mathbf{W}\cdot\boldsymbol{\zeta}\cdot\mathbf{W}\psi + \boldsymbol{\lambda}\cdot\mathbf{U}^{(2)} + \mathbf{U}^{(2)}\cdot\boldsymbol{\rho} = 0 \tag{43}$$

where

$$(\nabla^T \cdot \mathbf{U}^{(3)})_{jk} \equiv \sum_i \nabla_i \cdot \mathbf{U}^{(3)}_{ijk} \tag{44}$$

The formal solutions of Eqs. (42) and (43) are

$$\mathbf{j}(t) = [\exp(-\boldsymbol{\lambda}t)]\cdot\mathbf{j}(0) - \int_0^t d\tau\,\{\exp[-\boldsymbol{\lambda}(t-\tau)]\}\cdot[(\nabla^T\cdot\mathbf{U}^{(2)})^T - \mathscr{K}\psi] \tag{45}$$

and

$$\begin{aligned}\mathbf{U}^{(2)}(t) = {}& [\exp(-\boldsymbol{\lambda}t)]\cdot\mathbf{U}^{(2)}(0)\cdot[\exp(-\boldsymbol{\rho}t)] \\ & + 2kT\int_0^t d\tau\,\{\exp[-\boldsymbol{\lambda}(t-\tau)]\}\cdot\mathbf{W}\cdot\boldsymbol{\zeta}\cdot\mathbf{W}\cdot\{\exp[-\boldsymbol{\rho}(t-\tau)]\}\psi(\tau) \\ & - \int_0^t d\tau\,\{\exp[-\boldsymbol{\lambda}(t-\tau)]\}\cdot[\nabla^T\cdot\mathbf{U}^{(3)}(\tau) \\ & - (\mathscr{K}\mathbf{j}^T + \mathbf{j}\mathscr{K}^T)]\cdot\exp[-\boldsymbol{\rho}(t-\tau)]\end{aligned} \tag{46}$$

where the exponentials are defined by their series expansion. Since

$$\mathbf{W}\cdot\exp(-\boldsymbol{\rho}t) = [\exp(-\boldsymbol{\lambda}t)]\cdot\mathbf{W} \tag{47}$$

then

$$[\exp(-\boldsymbol{\lambda}t)]\cdot\mathbf{W}\cdot\boldsymbol{\zeta}\cdot\mathbf{W}\cdot\exp(-\boldsymbol{\rho}t) = [\exp(-2\boldsymbol{\lambda}t)]\cdot\boldsymbol{\lambda}\cdot\mathbf{W} \tag{48}$$

and a single integration by parts produces

$$\begin{aligned}2\int_0^t d\tau\,\{\exp[-\boldsymbol{\lambda}(t-\tau)]\}\cdot\mathbf{W}\cdot\boldsymbol{\zeta}\cdot\mathbf{W}\cdot\{\exp[-\boldsymbol{\rho}(t-\tau)]\}\psi(\tau) \\ = -[\exp(-2\boldsymbol{\lambda}t)]\cdot\mathbf{W}\psi(0) + \mathbf{W}\psi(t) \\ - \int_0^t d\tau\,\{\exp[-2\boldsymbol{\lambda}(t-\tau)]\}\cdot\mathbf{W}\,\partial\psi/\partial\tau\end{aligned} \tag{49}$$

Assuming the existence of $\boldsymbol{\lambda}^{-1}$, Eq. (45) may also be integrated by parts, and after the insertion of Eqs. (46) and (49), one obtains the formally exact expression

$$\begin{aligned}\mathbf{j}(t) = \mathbf{j}^s &+ [\exp(-\boldsymbol{\lambda} t)](\text{i.v.}) \\ &+ \int_0^t d\tau\, \boldsymbol{\lambda}^{-1}\cdot\{[\nabla^T\cdot(\exp[-2\boldsymbol{\lambda}(t-\tau)]\cdot\mathbf{W}(\partial\psi/\partial\tau))]^T kT \\ &+ \exp[-\boldsymbol{\lambda}(t-\tau)]\cdot(\partial/\partial\tau)[(\nabla^T\cdot\mathbf{U}^{(2)})^T - \mathscr{K}\psi] \\ &+ [\nabla^T\cdot(\exp[-\boldsymbol{\lambda}(t-\tau)]\cdot[\nabla^T\cdot\mathbf{U}^{(3)} \\ &- (\mathscr{K}\mathbf{j}^T + \mathbf{j}\mathscr{K}^T)]\cdot\exp[-\boldsymbol{\rho}(t-\tau)])]^T\}\end{aligned} \tag{50}$$

where the generalized Smoluchowski current is found to be

$$\mathbf{j}^s = -\boldsymbol{\lambda}^{-1}\cdot(kT\mathbf{W}\cdot\nabla\psi - \mathscr{K}\psi) \tag{51}$$

Since

$$\boldsymbol{\lambda}^{-1} = \boldsymbol{\zeta}^{-1}\cdot\mathbf{M} \tag{52}$$

where, obviously,

$$\mathbf{M} = \mathbf{W}^{-1} \tag{53}$$

the usual[30,40] form for $\mathbf{j}^s$ is obtained

$$\mathbf{j}^s = -\boldsymbol{\zeta}^{-1}\cdot(kT\,\nabla\psi - \mathscr{K}\psi) \tag{54}$$

Further explicit progress in calculating a first correction term has so far been made only when hydrodynamic interactions are absent. If the remaining diagonal elements are isotropic and constant

$$\boldsymbol{\zeta}_{ij} = \delta_{ij}\zeta_i\mathbf{I} \tag{55}$$

and the moment equations simplify greatly, allowing us to proceed exactly as in Section 2. As before, the exact equations for $\mathbf{U}^{(3)}_{ijk}$ and the next higher moment must be calculated, solved, and systematically expanded. The operations are simple, but tedious, to perform, and it is uninstructive to display them. The result of the analysis is the following expression:

$$\begin{aligned}\partial\psi/\partial t = &-\sum_i \nabla_i\cdot\mathbf{j}_i^0 + [\exp(-\boldsymbol{\beta} t)](\text{i.v.}) \\ &+ \sum_i\sum_j ((\beta_i^2 m_i)^{-1}\,\nabla_i\cdot(\mathbf{K}_i\,\nabla_j\cdot\mathbf{j}_j^0) \\ &- [\beta_j(\beta_i+\beta_j)]^{-1}\,\nabla_i\cdot[\nabla_j\cdot(m_j^{-1}\mathbf{K}_j\mathbf{j}_i^0 + \mathbf{j}_j^0\mathbf{K}_i m_i^{-1})] \\ &+ kT(\beta_j-\beta_i)(m_i m_j \beta_i^2\beta_j^2)^{-1}\,\nabla_j^2[\nabla_i\cdot(\mathbf{K}_i\psi)]) \\ &- \sum_i (\beta_i^2 m_i)^{-1}\,\nabla_i\cdot[\psi(\partial\mathbf{K}_i/\partial t - \beta_i^{-1}\,\partial^2\mathbf{K}_i/\partial t^2)] + \cdots\end{aligned} \tag{56}$$

where $\mathbf{j}_i^0$ is the free draining Smoluchowski current

$$\mathbf{j}_i^0 = -\zeta_i^{-1}(kT\,\nabla_i\psi - \mathbf{K}_i\psi) \tag{57}$$

The last term in Eq. (56) accounts for the possiblity that a time-dependent external force might also be present.

Despite its added complexity, this result greatly resembles the earlier one for a single particle. The expression simplifies somewhat if all the friction constants are identical, and, of course, it reduces properly to the earlier case if $N = 1$. Note again that all purely diffusionlike corrections are absent, so if all forces vanish, Eq. (56) reduces, as far as the order presented, to the diffusion equation for N independent particles, a result which happily does not conflict with our knowledge of the exact solution of the FPKK equation for this case.

Regarding the applicability of the Smoluchowski equation, remarks similar to those ending Section 2 could be made. It would be gratifying if the correction terms derived here could prove to be more than qualitatively useful in this respect.[17,25,41]

4. MOMENTUM FLUX TENSOR IN POLYMER VISCOSITY

A simple application of the preceding method can be made to a problem of current interest.[32,42,43] It is now known[42,43] that an expression for the intrinsic viscosity $[\eta]$ of a polymer solution can be written in terms of the autocorrelation function of an off-diagonal element J^{xy} of the momentum flux tensor

$$\mathbf{J} = \sum_{i=1}^{N} \mathbf{r}_i \mathbf{K}_i \tag{58}$$

The required average of $\mathbf{J}$ is calculated with the aid of the Green's function $\psi(\{\mathbf{r}\}, \{\mathbf{r}^0\}, t)$ of the many-particle diffusion (Smoluchowski) equation,

$$\langle \mathbf{J} \rangle = \int \psi \mathbf{J} \, d\{\mathbf{r}\} \tag{59}$$

The corresponding problem in the full polymer phase space has not yet been completely treated.[32,43] However, it is believed[43] that the stress tensor in this case is given by

$$\mathbf{J}_p = \sum_i (m_i^{-1} \mathbf{p}_i \mathbf{p}_i + \mathbf{r}_i \mathbf{K}_i) \tag{60}$$

and the appropriate average here is

$$\langle \mathbf{J}_p \rangle = \int \mathbf{J}_p F(\{\mathbf{r}\}, \{\mathbf{p}\}; \{\mathbf{r}^0\}, \{\mathbf{p}^0\}; t) \, d\{\mathbf{p}\} \, d\{\mathbf{r}\} \tag{61}$$

where F is the Green's function of the FPKK equation of the polymer.

The momentum average may be performed in the previous manner, and to lowest order in the inverse friction constant, with the neglect of initial-value terms,

$$\langle \mathbf{J}_p \rangle = \sum_i \int (kT\mathbf{I} + \mathbf{r}_i\mathbf{K}_i)\psi \, d\{\mathbf{r}\} \tag{62}$$

An integration by parts reveals that the following expression for $\mathbf{J}_p$ is identical to the preceding one:

$$\langle \mathbf{J}_p \rangle = \sum_i \int (\mathbf{r}_i\mathbf{K}_i - kT\mathbf{r}_i \nabla_i \ln \psi)\psi \, d\{\mathbf{r}\} \tag{63}$$

Interestingly, the diffusion force term, previously suggested on intuitive grounds,[44] appears in this latter form. As known,[42,43] however, this term makes no contribution to J_p^{xy} when the average is performed using a full, i.e., unconstrained, set of coordinates.

5. CONCLUSION

The Fokker–Planck–Klein–Kramers equations for a single particle in an external field and for many interacting particles have been rigorously reduced to the corresponding Smoluchowski equations. An iterative method was used which involved the asymptotic expansions of the solutions of the exact equations for the position-dependent moments of the velocity. The method does not involve the assumption of any special initial conditions nor of local equilibrium in the velocity distribution (or physically equivalent assumptions).

The principal result is an asymptotic expansion of the coordinate-space diffusion operator in powers of the inverse friction tensor (or constant) in which the Smoluchowski current appears as the leading term. In addition, lowest order correction terms have been explicitly calculated in terms of the coordinate-space distribution function for both a single-particle system and a many-particle system free of hydrodynamic interaction.

In closing, it is important to mention that, so far, these results are firmly established only within the framework of classical Brownian motion theory and depend on the validity of the FPKK equations, Eqs. (1) and (31). It will be interesting to reexamine this problem taking into consideration recent developments[45] in the theory of the long-time dependence of time correlation functions. Some initial work in this direction is presented in the appendix.

APPENDIX. REDUCTION OF A NON-MARKOVIAN FPKK EQUATION

Very recently Hwang and Freed[46] have used the Chapman–Enskog approach to derive a non-Markovian many-particle diffusion equation from a non-Markovian FPKK equation. We take the opportunity here to present an alternate derivation based on the use of moment equations. The non-Markovian FPKK equation[30,32,37–39,47] involves a time-dependent memory kernel $G(t)$ which is independent of the Brownian particles' momentum at our level of consideration. For simplicity we let all of the Brownian particles be of equal mass m; then the FPKK equation reads

$$\partial F/\partial t + m^{-1}\mathbf{p}^T\cdot\nabla F + \mathbf{K}^T\cdot\nabla^p F$$
$$= (\nabla^p)^T\cdot\int_0^t d\tau\, \mathbf{G}(t-\tau)\cdot[(mkT)^{-1}\mathbf{p} + \nabla^p]F(\tau) \tag{A.1}$$

where we have again employed supermatrix notation.

From this equation we readily calculate the following two Laplace-transformed moment equations:

$$s\hat{\mathbf{j}} - \mathbf{j}(0) = -(\nabla^T\cdot\hat{\mathbf{U}}^{(2)})^T + m^{-1}\mathbf{K}\hat{\psi} - (mkT)^{-1}\hat{\mathbf{G}}\cdot\hat{\mathbf{j}} \tag{A.2}$$

and

$$s\hat{\mathbf{U}}^{(2)} - \mathbf{U}^{(2)}(0) = \hat{\mathbf{H}} - (mkT)^{-1}[\hat{\mathbf{G}}\cdot\hat{\mathbf{U}}^{(2)} + \hat{\mathbf{U}}^{(2)}\cdot\hat{\mathbf{G}}] \tag{A.3}$$

where

$$\hat{\mathbf{H}} = 2m^{-2}\hat{\mathbf{G}}\hat{\psi} - [\nabla^T\cdot\hat{\mathbf{U}}^{(3)} - m^{-1}(\mathbf{K}\hat{\mathbf{j}}^T + \hat{\mathbf{j}}\mathbf{K}^T)] \tag{A.4}$$

We need to consider only the small-s behavior to account for the long-time dependence. Hence, Eq. (A.2) yields

$$\hat{\mathbf{j}} \sim -[\boldsymbol{\zeta}(s)]^{-1}\cdot[m(\nabla^T\cdot\hat{\mathbf{U}}^{(2)})^T - \mathbf{K}\hat{\psi}] \tag{A.5}$$

where

$$\boldsymbol{\zeta}(s) = (kT)^{-1}\hat{\mathbf{G}} \tag{A.6}$$

defines the s-dependent friction tensor.

If we further define

$$\boldsymbol{\beta}(s) = m^{-1}\boldsymbol{\zeta} \tag{A.7}$$

and rearrange Eq. (A.3) to read

$$\hat{\mathbf{U}}^{(2)} = [\hat{\mathbf{H}} + \mathbf{U}^{(2)}(0)]\cdot\boldsymbol{\beta}^{-1} - (s\mathbf{I} + \boldsymbol{\beta})\cdot\hat{\mathbf{U}}^{(2)}\cdot\boldsymbol{\beta}^{-1} \tag{A.8}$$

we may iterate to obtain the formal solution

$$\hat{\mathbf{U}}^{(2)} = \sum_{n=0}^{\infty}(-1)^n(s\mathbf{I} + \boldsymbol{\beta})^n\cdot[\hat{\mathbf{H}} + \mathbf{U}^{(2)}(0)]\cdot(\boldsymbol{\beta}^{-1})^{n+1} \tag{A.9}$$

Now, since

$$\sum_{n=0}^{\infty}(-1)^n(s\mathbf{I} + \boldsymbol{\beta})^n\cdot\hat{\mathbf{G}}\cdot(\boldsymbol{\beta}^{-1})^{n+1} = mkT\sum_{n=0}^{\infty}(-1)^n(s\boldsymbol{\beta}^{-1} + \mathbf{I})^n \tag{A.10}$$

$$= (mkT/2)(\mathbf{I} + \tfrac{1}{2}s\boldsymbol{\beta}^{-1})^{-1}\cdot\mathbf{I} \tag{A.11}$$

we find in lowest order

$$\hat{\mathbf{U}}^{(2)} \sim (kT/m)\hat{\psi}\mathbf{I} \tag{A.12}$$

After Eqs. (A.12) and (A.5) are combined, inverted, and substituted in the equation of continuity, we obtain

$$\partial\psi/\partial t = \int_0^t d\tau\, \nabla^T \cdot \tilde{\mathbf{D}}(t-\tau)\cdot[\nabla - (kT)^{-1}\mathbf{K}]\psi(\tau) \tag{A.13}$$

where $\tilde{\mathbf{D}}(t)$ is the Laplace inverse of the supermatrix of s-dependent diffusion tensors,

$$\mathbf{D}(s) = kT\boldsymbol{\zeta}^{-1} \tag{A.14}$$

Equation (A.13) is the desired non-Markovian many-particle diffusion equation.

Two additional comments are worth making. First, because $G(t)$ has been approximated to be momentum independent and because of the asymptotic nature of the result, Eq. (A.13) is less general than the earlier results[36] of Falkenhagen, Ebling, and Gray. Second, the propriety of using the approximate, momentum-independent form for $G(t)$ in non-Markovian FPKK equations is not yet completely decided.[47]

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