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On the Theory of Brownian Motion. I. Interaction Between Brownian Particles

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The molecular theory of the Brownian motion of heavy particles in a homogeneous solvent of light particles is extended to cover the case of interactions between the Brownian particles. This will have physical effects in the concentration dependence of the Brownian particle self-diffusion coefficient. A density expansion for the Brownian particle friction coefficient is derived, and an approximation permitting the first density correction to be calculated is suggested.

KEY WORDS: Brownian motion; Molecular theory; Friction coefficient, density dependence of; Fokker-Planck equation; Homogeneous systems.

1. INTRODUCTION

The motion of small particles suspended in a fluid, the Brownian motion, has been a subject of interest in physics since 1905.[2] Since the pioneering papers of Einstein(2) and Smoluchowski(3) the theory of this motion has been treated as a stochastic theory, and, until recently, no satisfactory *molecular* derivation of the basic equation of the theory, the Fokker–Planck equation, had been given. Within the past few years, however, the molecular theory of the Brownian motion of a single heavy particle in a medium of light particles has been placed on a firm footing by the work of Lebowitz, Résibois, and associates.(4–7) These authors have shown that the Fokker–Planck equation is the equation of evolution for the one-body distribution function of the heavy particle, to lowest order in the mass ratio of light to heavy particles.

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[2] For an interesting history of the early days of the subject, see Reference 1.

The methods used by these authors lend themselves to further generalizations of the theory. One such generalization is the consideration of higher-order terms in in the mass ratio. This has already been treated in References 4–7. Another generalization is Brownian motion in nonuniform systems. Although this has already been considered by several authors,(8–10) it seems to us to be most simply treated by the methods under discussion. However, the generalization which we wish to pursue in this paper is the consideration of interaction between the Brownian particles themselves, which must occur whenever they are present at nonvanishing concentration. These interactions will manifest themselves in a concentration dependence of the friction constant, which in turn manifests itself in a concentration dependence of the self-diffusion coefficient. We have already published some calculations on this effect(11) based on an intuitive extension of the molecular formula for the friction constant. One of the purposes of the present paper is to put these earlier calculations on a firm footing.

The paper is organized as follows: Section 2 derives the appropriate Fokker–Plack equation for a nonvanishing concentration of Brownian particles; Section 3 derives a density expansion for the friction constant; and Section 4 contains a discussion of the results.

2. THE FOKKER–PLANCK EQUATION

The system under consideration consists of $N + 1$ heavy particles, all of mass M, and n light particles, collectively called the solvent. The light particles need not be of the same type; they may differ in mass, charge, and interactions. However, to avoid a plethora of subscripts, we will not distinguish in our notation between the various species of small particles present. To do so would only make the equations appear very complicated, without adding anything to the problem.

Our notation is the following: we use capital letters, $\mathbf{R}_0, \ldots, \mathbf{P}_N$ for the coordinates and momenta of the heavy particles (from now on called B-particles), and lower case letter $\mathbf{r}_1, \ldots, \mathbf{p}_n$ for the coordinates and momenta of the solvent. We use the abbreviations $d\{N\} = d\mathbf{R}_1 \cdots d\mathbf{R}_N \, d\mathbf{P}_1 \cdots d\mathbf{P}_N$ and $d\{n\} = d\mathbf{r}_1 \cdots d\mathbf{r}_n \, d\mathbf{p}_1 \cdots d\mathbf{p}_n$. The Hamiltonian of the system is

$$H = \frac{P_0^2}{2M} + \sum_{j=1}^{N} \frac{P_j^2}{2M} + \sum_k \frac{p_k^2}{2m} + U \tag{1}$$

Here U is the potential energy of interaction of solvent with solvent, of solvent with B-particles, of B-particles with B-particles, and B-particles with external fields. The Liouville operator for the system is then

$$L = L_F + L_B \tag{2}$$

$$L_F = -i \left\{ \sum_{j \neq 0} \left(\frac{\mathbf{P}_j}{M} \cdot \nabla_j + \mathbf{F}_j \cdot \frac{\partial}{\partial \mathbf{P}_j} \right) + \sum_k \left(\frac{\mathbf{p}_k}{m_k} \cdot \nabla_k + \mathbf{f}_k \cdot \frac{\partial}{\partial \mathbf{p}_k} \right) \right\} \tag{3a}$$

$$L_B = -i \left\{ \frac{\mathbf{P}_0}{M} \cdot \nabla_0 + \mathbf{F}_0 \cdot \frac{\partial}{\partial \mathbf{P}_0} \right\} \tag{3b}$$

Here $\mathbf{F}_l$ or $\mathbf{f}_l$ is the force on a B- or solvent particle, respectively. We have denoted the gradient in configuration space by ∇, and the gradient in momentum space by $\partial/\partial\mathbf{P}$. Clearly, the notation treats the B-particle labeled "0" in a very unsymmetrical way from the other B-particles; we do this because we are interested in the singlet distribution function of the B-particles.

The distribution function for the total system, ρ_{n+N+1} satisfies, of course,

$$i\frac{\partial\rho_{n+N+1}}{\partial t} = L\rho_{n+N+1} \tag{4}$$

and we are interested in

$$\rho_1 = \int \rho_{n+N+1}\, d\{n\}\, d\{N\} \tag{5}$$

Let us define a projection operator $\hat{P}$ by

$$\hat{P} = \eta \int d\{n\}\, d\{N\} \tag{6}$$

η being a function which is independent of $\mathbf{P}_0$ and which has the property

$$\int \eta\, d\{n\}\, d\{N\} = 1 \tag{7}$$

for all $\mathbf{R}_0$. We shall specify it more fully below. Furthermore, define the complementary projection operator

$$\hat{Q} = 1 - \hat{P} \tag{8}$$

and set

$$\begin{aligned} \hat{P}\rho_{n+N+1} &= f = \eta\rho_1 \\ \hat{Q}\rho_{n+N+1} &= g \end{aligned} \tag{9}$$

It is now a simple matter to use the projection operator technique of Zwanzig[12] to show that f satisfies the equation

$$i\frac{\partial f}{\partial t} = \hat{P}Lf + \hat{P}L\exp[-i\hat{Q}Lt]\,g(0) - i\hat{P}L\int_0^t \exp[i\hat{Q}L(t-t')]\,\hat{Q}Lf(t')\,dt' \tag{10}$$

Since $g(0) = \rho_{N+n+1}(0) - \eta\rho_1(0)$, we shall follow Lebowitz and Rubin,[4] and choose η to be the equilibrium distribution function of the $n + N$ particles in the field of particle zero, and, furthermore, set $g(0) = 0$. We emphasize that this is not an approximation, in a mathematical sense. Since the problem of solving the Liouville equation is an initial-value problem, we are completely free to choose the initial conditions. Physically, however, one must choose the initial conditions to correspond to the phenomenon under investigation. We feel that this initial condition does correspond, very closely, to the state of a B-particle in a homogeneous medium. In an inhomogeneous medium it would, of course, not be correct. In that case, it would be much better to take η to be the *local* equilibrium distribution function of the $n + N$ particles. We intend to return to this point in a future article.

From this point on, the formal development overlaps considerably the treatment of Lebowitz and Résibois.(6,13) Therefore we shall be brief, and only emphasize the new features connected with the B-particle–B-particle interactions. Let us call $\gamma^2 = m/M$, where m is the largest of the masses of the light particles. Since $\langle P^2 \rangle / \langle p^2 \rangle = O(\gamma^2)$, it follows that L_B is, *on the average* $O(\gamma)$ times smaller than L_F. The fact that there are some B-particle terms in L_F, which are $O(\gamma)$ smaller than the solvent terms, does not, of course, alter this conclusion.

We can therefore expand the exponential operator in Eq. (10) in powers of L_B, retaining only the zeroth-order term:

$$i \frac{\partial f}{\partial t} = \hat{P} L f - i \hat{P} L \int_0^t \exp[-i \hat{Q} L_F (t - t')] \, \hat{Q} L f(t') \, dt' \tag{11}$$

Note that this is not a systematic expansion in powers of γ as was the case in the single B-particle problem; there are some terms of order γ in L_F. There is, however, no requirement that one expand everything available in terms of a small parameter. In fact, cases are known, notably in the theory of nonlinear oscillations, where this is a very bad thing to do; it leads to secular terms which increase in time without limit. That would also have been the case here if we had expanded the exponential operator in powers of γ, rather than L_B.

Since L_F is a divergence-like operator in $n + N$ space, $\hat{P} L_F = 0$ and $\hat{Q} L_F = L_F$. At this point, we can abandon the formal development and go directly to the result. There is considerable algebra between Eq. (11) and the final result, but, from this stage on, it is word for word, step for step, the same as given by Lebowitz and Résibois(6) and Résibois(13). We therefore omit it. The final equation is

$$\frac{\partial \rho_1}{\partial t} + \frac{\mathbf{P}_0}{M} \cdot \nabla_0 \rho_1 = \int_0^t \langle \mathbf{F}_0(t - t') \, \mathbf{F}_0(0) \rangle : \frac{\partial}{\partial \mathbf{P}_0} \left(\frac{\partial}{\partial \mathbf{P}_0} + \frac{\mathbf{P}_0}{MkT} \right) \rho_1(t') \, dt' \tag{12}$$

The brackets $\langle \cdots \rangle$ indicate an equilibrium average and $\mathbf{F}_0$ is the total force on the B-particle zero due to the solvent and the other B-particles. In its computation, particle zero is held fixed during the time evolution, but all the other B-particles are permitted to move according to the dictates of the equations of motion.

Had we done a systematic expansion γ in going from (10) to (11), then Eq. (12) would look formally the same, though the meaning of the average $\langle \cdots \rangle$ would change. The time evolution of $\mathbf{F}_0(t)$ would have to be computed with *all* of the B-particles held fixed, and then averaged over the configurations of the $N + 1$ B-particles. This would lead to a time-independent term in $\langle \mathbf{F}_0(t - t') \, \mathbf{F}_0(0) \rangle$ due to B-particle–B-particle forces. Since $\rho_1(t')$ is a slowly varying function of t', a constant term in the average would lead to secular behavior on the right-hand side of Eq. (12). We have avoided this difficulty in our expansion.

3. THE FORCE CORRELATION

We now want to analyze the force correlation function $\langle \mathbf{F}_0(\tau)\, \mathbf{F}_0(0)\rangle$. In particular, we would like to study its dependence on the concentration of B-particles. When this concentration is small, an analysis is possible in terms of a densitity expansion, analogous to the virial expansion of the properties of a gas.

Let us define

$$M_N = \int \exp(-\beta H_{n+N})\, \mathbf{F}_0(t)\, \mathbf{F}_0(0)\, d\{n\} \tag{13}$$

The B-particles, except for number zero, all move and contribute to $\mathbf{F}_0(t)$, but are not yet averaged over. We have

$$\langle \mathbf{F}_0(t)\, \mathbf{F}_0(0)\rangle = \int S_N\, d\{N\} \tag{14}$$

where

$$\begin{aligned} S_N &= M_N/Z_{N+n} \\ Z_{N+n} &= \int \exp(-\beta H_{N+n})\, d\{n\}\, d\{N\} \end{aligned} \tag{15}$$

Now the conditional average of the force correlation (conditional on the initial phase of the B-particles) is

$$M_N\Big/\!\int \exp(-\beta H_{N+n})\, d\{n\}$$

Let the N B-particles be divided into two groups, say $\{N'\}$ and $\{N''\}$ and let the two groups be separated very far in space at time zero. Then at least one of the groups, say $\{N''\}$, is very far from particle zero, and these particles then cannot affect the force correlation. Hence

$$M_N\Big/\!\int \exp(-\beta H_{N+n})\, d\{n\} \to M_{N'}\Big/\!\int \exp(-\beta H_{N'+n})\, d\{n\} \tag{16}$$

as the sets $\{N'\}$ and $\{N''\}$ get far apart. Since M_N is time dependent, this need not hold for all times, but will hold for longer and longer times, the further $\{N'\}$ and $\{N''\}$ are separated at the initial time.

Equation (16) then implies that, under the same circumstances,

$$S_N \to M_{N'} \frac{\int \exp(-\beta H_{N+n})\, d\{n\}}{\int \exp(-\beta H_{N'+n})\, d\{n\}\, Z_{N+n}} \tag{17}$$

or

$$S_N \to S_{N'}(P_N/P_{N'}) \tag{18}$$

where P_N and $P_{N'}$ are the N (or N') body distribution functions for N (or N') B-particles in the solvent. In the limit under discussion, however,

$$P_N \to P_{N'} P^*_{N''} \tag{19}$$

where $P^*_{N''}$ has none of the effects of particle zero in the Hamiltonian. Finally, then

$$S_N \to S_{N'} P^*_{N''} \tag{20}$$

when the set $\{N\}$ goes into separated sets $\{N'\}$ and $\{N''\}$ .That is, the functions S_N have a generalized product property.

The functions $P_N{}^*$ have the ordinary product property of cluster theory [cf. Eq. (19)]. Hence one may define U functions by the recursive definitions[3]

$$\begin{aligned} P_1{}^* &= U_1 \\ P_2{}^* &= U_2 + U_1 U_1 \\ P_3{}^* &= U_3 + \sum U_2 U_1 + U_1 U_1 U_1 \\ &\cdots\cdots\cdots\cdots\cdots\cdots \end{aligned} \tag{21}$$

In the definition of $P_3{}^*$, for example, the sum is over all permutations of function arguments among the factors in the product $U_2 U_1$. Since the $P_N{}^*$ have the product property, it follows, by standard arguments, that the U_N have the cluster property. They vanish when their arguments are divided into spatially separated groups.

We note that $P_1{}^* = U_1$ is a constant, since particle zero plays no role in its definition. Since $\int P_N{}^* \, d\{N\} = 1$, we must have $U_1 = \Omega^{-1}$, where Ω is the volume of the system. Similarly, recursively from (21), one finds

$$\int U_j \, d\{j\} = 0, \qquad j \neq 1 \tag{22}$$

Now we define new cluster function, V_N , by

$$\begin{aligned} S_0 &= V_0 \\ S_1 &= V_1 + V_0 U_1 \\ S_2 &= V_2 + \sum V_1 U_1 + V_0 U_2 + V_0 U_1 U_1 \qquad (23) \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ S_N &= V_N + \sum V_{N+1} U_1 + \sum V_{N-2} U_2 + \sum V_{N-2} U_1 U_1 + \cdots + V_0 U_1 \cdots U_1 \end{aligned}$$

We have seen above that the S_N have a generalized product property (20). It then follows that the V_N have the cluster property, $V_N \to 0$ as $\{N\}$ separates into spatially divided subsets $\{N'\}$ and $\{N''\}$. The argument is quite akin to the usual one for the U functions. Briefly, in the expansion of $S_{N'} P^*_{N''}$, V_m functions for $m > N'$ cannot occur. They do occur in S_N , however, and so they must vanish in the limit $S_N \to S_{N'} P^*_{N''}$

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[3] See, for example, Reference 14.

Now we are interested in

$$\langle \mathbf{F}_0(t)\,\mathbf{F}_0(0)\rangle = \int S_N\, d\{N\} \tag{14}$$

Using (23), we have

$$\begin{aligned}\int S_N\, d\{N\} = \int V_N\, d\{N\} &+ N \int d\{N-1\}\, V_{N-1} \int d\{1\}\, U_1 \\ &+ \frac{N(N-1)}{2} \int d\{N-2\}\, V_{N-2} \int d\{2\}\, U_2 \\ &+ \frac{N(N-1)}{2} \int d\{N-2\}\, V_{N-2} \left[\int d\{1\}\, U_1\right]^2 \\ &+ \cdots + V_0 \left[\int d\{1\}\, U_1\right]^N \end{aligned} \tag{24}$$

By (22) we therefore have

$$\int S_N\, d\{N\} = \sum_{k=0}^{N} \frac{N!}{k!\,(N-k)!} \int V_k\, d\{k\} \tag{25}$$

Writing

$$\Omega^{-k}\beta_V(k) = \frac{1}{k!} \int V_k\, d\{k\} \tag{26}$$

we finally have

$$\langle \mathbf{F}_0(t)\,\mathbf{F}_0(0)\rangle = V_0 + (N/\Omega)\,\beta_V(1) + (N/\Omega)^2\,\beta_V(2) + \cdots \tag{27}$$

where we have approximated $N(N-1)$ by N^2. It may look at first sight as though the Ω factors in (26) are brought in artificially, so that $\beta_V(k)$ may be volume dependent and (27) not a real density expansion. This is not the case, however. To see this, we consider the functions S_J at $t = 0$. Using the usual trick of integration by parts, it is easy to show that

$$S_J(0) = n \int \rho_{J+1} \nabla_0 \nabla_0 V_{0\alpha}\, d\mathbf{r}_\alpha + J \int P_J \nabla_0 \nabla_0 W_{0j}\, d\mathbf{R}_j \tag{28}$$

Here $V_{0\alpha}$ and W_{0j} are the B-particle, solvent, and B-particle–B-particle potentials

$$\begin{aligned} \rho_{J+1} &= \int \exp(-\beta H_{J+n}\}\, d\{n-1\}/Z_{J+n} \\ P_J &= \int \exp(-\beta H_{J+n})\, d\{n\}/Z_{J+n} \end{aligned} \tag{29}$$

Because of the normalization of ρ_{J+1} and P_J (normalized to unity), both integrals in (28) are $O(\Omega^{-J})$ for J small compared to n and N. Thus, the factors Ω^{-k} in (26) come in naturally, and $\beta_V(k)$ is of the order of a mean square force times a volume (k-dimensional) of the order of the (range of the forces)^{3k}.

The first density correction, $\beta_V(1)$, is especially interesting, and we give it in detail below:

$$\beta_V(1) = \int d\mathbf{R}_1\, d\mathbf{P}_1\, d\{n\} \left[\frac{\exp(-\beta H_{n+1})}{Z_{n+1}}\, \mathbf{F}_0^{(1)}(t)\, \mathbf{F}_0^{(1)}(0) - \frac{\exp(-\beta H_n)}{\Omega\lambda Z_n}\, \mathbf{F}_0^{(0)}(t)\, \mathbf{F}_0^{(0)}(0)\right] \tag{30}$$

$\lambda = (2\pi MkT)^{3/2}$, and is included because of the $\mathbf{P}_1$ integration since $\mathbf{P}_1$ does not occur in H_n. The superscripts on the **F**'s are to remind one of the number of B-particles, in addition to particle zero, which participate in determining $\mathbf{F}_0$. Equations (12), (27), and (30) are the main results of this paper.

4. DISCUSSION

We have developed a density expansion for the force autocorrelation function. How do we know that this series converges, or that the terms even exist (i.e., that the integrals defining them are finite)? As far as the convergence at the series is concerned, we are in the same situation as in most problems of theoretical physics and chemistry; we simply do not know, and hope for the best.

Density expansions for time correlation functions in the theory of moderately dense gases have been plagued by the problem that the individual coefficients in the series are divergent.(15,16) This has been circumvented by rather sophisticated resummation of the most divergent terms of the series. Will such divergences take place in the series derived here? We argue that they will not. In the gas case, the coefficients in the density series depend on the dynamics of quite small numbers of molecules which allow certain repeated collisions involving initial correlations in far separated parts of phase space. In reality, these collisions do not occur; there are always other molecules present to destroy the delicate correlations causing the divergence. The divergences are an artifice of the expansion method, and are not inherent in the phenomena.

In our case, the solvent molecules are always present, and in constant interaction with the B-particles. The expansion is in the B-particle density, the solvent density being held constant. The motion of the B-particles is thus dominated by their interactions with the solvent, and hence the conditions which cause the difficulty in the dense gas case do not appear to be present in the case at hand.

Another question of principle which must be discussed in this connection is that of the range of the force between B-particles. Wo do not expect our density expansion to be valid when the force between B-particles is long-range; one could not, for example, treat self-diffusion in an electrolytic solution by our density expansion. However, there are a large number of interesting case in which short-range forces are operative. Even for charged colloids, or polyelectrolytes, the Coulomb forces are always screened by the small ions inevitably present, so that the forces are effectively short-range. The situation is fundamentally different from that in solutions of small electrolytes, where the particles under study themselves do the screening. In the polymer case the screening is performed by the charged components of the solvent.

We now return to the first density correction, Eq. (30), to suggest an approximation which would remove this equation from the class of purely formal expressions, and permit effective calculation. Let us consider $\langle \mathbf{F}_0^{(1)}(t)\, \mathbf{F}_0^{(1)}(0)\rangle$, where the superscripts have the same meaning as in (30). Initially, this force correlation will decay, due to interaction of the solvent with particle zero, in a manner very similar to the decay of the force correlation in the infinitely dilute case, e.g., $\langle \mathbf{F}_0^{(0)}(t)\, \mathbf{F}_0^{(0)}(0)\rangle$. The decay time will be independent of M but the force correlation will not decay to zero in this time, as it does in the infinitely dilute case, because the mean force on particle zero (averaged over solvent only) does not vanish. One expects

$$\langle \mathbf{F}_0^{(1)}(t)\, \mathbf{F}_0^{(1)}(0)\rangle \xrightarrow[t>\tau]{} \langle \mathcal{F}_0^{(1)}(t)\, \mathbf{F}_0^{(1)}(0)\rangle \tag{31}$$

where $\mathcal{F}_0$ is the *average* force on particle zero, the average being taken over the solvent only. That is, at any time, the force on 0 is the mean force, plus fluctuations due to initial conditions. After a time τ, the fluctuations become uncorrelated with the initial force, but the mean force need not be uncorrelated with the initial force. In the infinitely dilute case, of course, the mean force vanishes.

One can now carry out the average over the solvent phases and obtain

$$\langle \mathbf{F}_0^{(1)}(t)\, \mathbf{F}_0^{(1)}(0)\rangle \xrightarrow[t>\tau]{} \langle \mathcal{F}_0^{(1)}(t)\, \mathcal{F}_0^{(1)}(0)\rangle \tag{32}$$

This last correlation function will, itself, decay to zero, due to the motion of particle 1, but its decay time τ_B will be mass dependent, and rather long. The situation is shown qualitatively in Fig. 1. According to Eq. (30), we have to subtract the dashed curve in Fig. 1 from the solid curve. This leaves, in effect, only the slowly decaying tail of the correlation function, except for very short times of the order of τ.

Now the average force on particle zero depends on time only through the

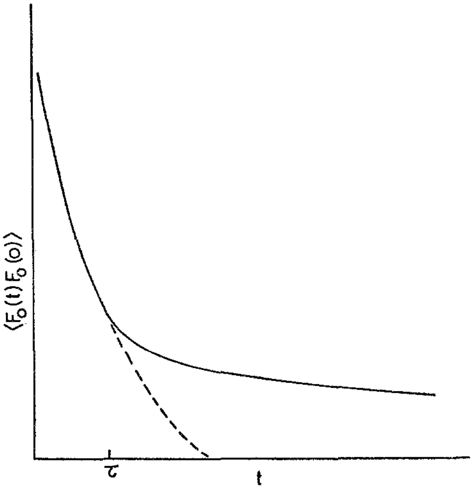

Fig. 1. Schematic representation of the force correlation as a function of time. The solid curve gives the expected behavior when there is more than one Brownian particle present, and the dashed curve is for the case of only a single Brownian particle.

dependence of $\mathbf{R}_1$ on time. The explicit dependence on solvent molecule coordinates has been taken into account in forming the average $\mathscr{F}_0$. But we already have a first-order theory of how $\mathbf{R}_1$ depends on time, namely, Brownian motion theory in the infinitely dilute limit, i.e., Eq. (12) with only the V_0 contribution to the force correlation being taken into account. Therefore, if $\rho_1^{(0)}$ is the appropriate solution of (12), i.e., that which approaches $\delta(\mathbf{R}_1' - \mathbf{R}_1)$ as $t \to 0$, then

$$\beta_V(1) \approx \int d\mathbf{R}_1\, d\mathbf{R}_1' \mathscr{F}_0^{(1)}(\mathbf{R}_1' - \mathbf{R}_0)\, \mathscr{F}_0^{(0)}(\mathbf{R}_1 - \mathbf{R}_0)\, \rho_1^{(0)}(\mathbf{R}_1', t) \tag{33}$$

This formula is relatively easy to use for computation, as has been shown earlier.[11] It is rather remarkable that this approximation renders $\beta_V(1)$ so much easier to calculate than the leading term.

Unfortunately, one would appear to be on very shaky grounds were one to try to extend this "bootstrap" type of calculation to higher-order terms, if only because of the well known nonadditivity of average forces for more than two particles.

We have waited until the end to remark that (12) is, of course, not the usual Fokker–Planck equation. This latter is obtained from (12) by noting that $\rho_1(t')$ is very slowly varying compared to $\langle \mathbf{F}_0(t)\, \mathbf{F}_0(0)\rangle$. Hence one may write

$$\int_0^t \langle \mathbf{F}_0(t - t')\, \mathbf{F}_0(0)\rangle\, \rho_1(t')\, dt' \approx \rho_1(t) \int_0^\infty \langle \mathbf{F}_0(t')\, \mathbf{F}_0(0)\rangle\, dt' \tag{34}$$

The integral on the right-hand side of (13) is the usual friction constant $kT\zeta$. In our case, although the contribution to the force correlation corresponding to V_0 is rapidly decaying, we have just finished arguing that $\beta_V(1)$ is slowly varying, its time variation being due to the Brownian motion of the heavy particles, the very motion described by ρ_1. Hence it is not at all clear that the non-Markoffian equation (12) can be reduced to a Markoffian equation via (34), except for rather long times. Each case must be judged on its own merits, and this can be done rather efficaciously through the estimate given by Eq. (33).

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