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On the Theory of Brownian Motion. III. Two-Body Distribution Function

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The equation of evolution governing the probability density of a pair of heavy particles in a fluid of lighter particles is derived. The derivation starts from the Liouville equation and proceeds by expansion in the ratio of light to heavy masses, using the technique previously applied successfully to the singlet distribution.

KEY WORDS: Brownian motion; two-body distribution function; kinetic equation.

1. INTRODUCTION

In connection with the theory of transport processes in suspensions of heavy particles, it is of interest to have the kinetic equation governing the evolution of the distribution function of pairs of heavy particles. This is especially important if the physical circumstances make it essential to take into consideration the interaction of the heavy particles (or B-particles) with each other, as well as with the light particles of the solvent, or carrier fluid.

In this paper, the equation of evolution for two B-particles in a medium is derived from a molecular basis. The technique used is basically that introduced by Lebowitz and Rubin[(1)] for the one-body distribution function at infinite dilution, and elaborated on by the present author[(2)] for the case of the one-body distribution function at finite concentration. We consider here only the case of two B-particles in the medium, i.e., two B-particles at infinite dilution.

2. FORMALISM

Throughout this paper, we use the notation of ref. 2, and do not repeat definitions of symbols defined there. The notation is, in any case, fairly standard.

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We are considering two B-particles in a solvent, and the Hamiltonian of the system is

$$H = \frac{\mathbf{P}_1^2}{2M} + \frac{\mathbf{P}_2^2}{2M} + \sum_{j=1}^{N} \frac{\mathbf{p}_j^2}{2m} + U \tag{1}$$

The Liouville operator is conveniently broken up into two parts

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

$$L_F = -i \sum_{j=1}^{N} \left(\frac{\mathbf{P}_j}{M} \cdot \nabla_j + \mathbf{f}_j \cdot \frac{\partial}{\partial \mathbf{P}_j}\right) \tag{2b}$$

$$L_B = -i \sum_{k=1}^{2} \left(\frac{\mathbf{P}_j}{M} \cdot \nabla_j + \mathbf{F}_j \cdot \frac{\partial}{\partial \mathbf{P}_j}\right) \tag{2c}$$

We are interested in the reduced distribution function ρ_2, defined in terms of the distribution function of the entire system ρ_{N+2} by

$$\rho_2 = \int \rho_{N+2}\, d\{N\} \tag{3}$$

Let us define a projection operator $\hat{P}_2$ by

$$\hat{P}_2 \phi(\{N+2\}) = \rho_N^{\dagger}\{N\} \int \phi(\{N+2\})\, d\{N\} \tag{4}$$

where $\rho_N^{\dagger}$ is the equilibrium distribution function for the N solvent particles with B-particles 1 and 2 present, *but fixed in position.* The complementary projection operator is then $\hat{Q}_2 = 1 - \hat{P}_2$. Letting $f = \hat{P}_2 \rho_{N+2} = \rho_N^{\dagger} \rho_2$ and $g = \hat{Q}_2 \rho_{N+2}$, the standard projection operator technique[3] yields the following equation for f:

$$i\, \partial f/\partial t = \hat{P}_2 L f + \hat{P}_2 L \exp[-i \hat{Q}_2 L t]\, g(0) - i \hat{P}_2 L \int_0^t \exp[-i \hat{Q}_2 L (t - t')]\, \hat{Q}_2 L f(t - t')\, dt' \tag{5}$$

At this point, we immediately simplify Eq. (5) by assuming $g(0) = 0$. This means that, at $t = 0$, we have chosen the initial state of the system to be that in which the solvent is in equilibrium in the instantaneous field of the B-particles. This is quite analogous to what has been done in the case of the singlet distribution, and we believe it to be a reasonable initial condition for the pair case also.

A further simplification comes from the immediate recognition that $\hat{P}_2 L_F = 0$. The first term on the right-hand-side of (5) is then easy to evaluate:

$$\hat{P}_2 L f = \hat{P}_2 L_B f = -i \rho_N^{\dagger} \left(\frac{\mathbf{P}_1}{M} \cdot \nabla_1 + \frac{\mathbf{P}_2}{M} \cdot \nabla_2\right) \rho_2 - i \rho_N^{\dagger} \left(\mathscr{F}_1 \cdot \frac{\partial}{\partial \mathbf{P}_1} \rho_2 + \mathscr{F}_2 \cdot \frac{\partial}{\partial \mathbf{P}_2} \rho_2\right) \tag{6}$$

where

$$\mathscr{F}_i = \int \mathbf{F}_i \rho_N^\dagger \, d\{N\} \tag{7}$$

That is, $\mathscr{F}_i$ is the equilibrium mean force between two B-particles at infinite dilution, a quantity well known from equilibrium theory. Since $\rho_N^\dagger$ is an equilibrium distribution function, $\mathscr{F}_i$ is momentum-independent.

Now we introduce the hypothesis that the two B-particles have a very large mass with respect to the solvent particles and replace the integral on the right side of (5) by

$$\int_0^t \exp[-iL_F(t-t')] \, \hat{Q}_2 Lf(t-t') \, dt' \tag{8}$$

This is the leading term in an expansion of the exponential operator in powers of $\gamma^2 = (m/M)$, the mass ratio. The argument is exactly the same as in the one-body case, and we do not repeat it.

We analyze $\hat{Q}_2 Lf$ as follows. First note that $L_F f = 0$, since $f = \rho_N^\dagger \rho_2$. The ρ_2 does not depend on the fluid variables and $L_F \rho_N^\dagger = 0$, by construction. Therefore,

$$\begin{aligned}
\hat{Q}_2 Lf &= (1 - \hat{P}_2) L_B f \\
&= \rho_N^\dagger L_B \rho_2 + \rho_2 L_B \rho_N^\dagger - \rho_N^\dagger \int d\{N\} (\rho_N^\dagger L_B \rho_2 + \rho_2 L_B \rho_N^\dagger) \\
&= -i \sum_{j=1}^{2} \left\{ \rho_N^\dagger (\mathbf{F}_j - \mathscr{F}_j) \cdot \frac{\partial}{\partial \mathbf{P}_j} + \frac{\mathbf{P}_j}{M} \cdot \nabla_j \rho_N^\dagger \right\} \rho_2 \\
&= -i \sum_{j=1}^{2} \rho_N^\dagger (\mathbf{F}_j - \mathscr{F}_j) \cdot \left(\frac{\partial}{\partial \mathbf{P}_j} + \frac{\mathbf{P}_j}{MkT} \right) \rho_2
\end{aligned} \tag{9}$$

Thus, putting together Eqs. (5), (6), (8), and (9), one finds

$$\begin{aligned}
&\frac{\partial \rho_2}{\partial t} + \sum_{j=1}^{2} \left(\frac{\mathbf{P}_j}{M} \cdot \nabla_j + \mathscr{F}_j \cdot \frac{\partial}{\partial \mathbf{P}_j} \right) \rho_2 \\
&\quad = \sum_{i=1}^{2} \sum_{j=1}^{2} \int_0^t \frac{\partial}{\partial \mathbf{P}_i} \cdot \langle \mathbf{F}_i(t-t')[\mathbf{F}_j(0) - \mathscr{F}_j] \rangle^\dagger \cdot \left(\frac{\partial}{\partial \mathbf{P}_j} + \frac{\mathbf{P}_j}{MkT} \right) \rho_2(t-t') \, dt'
\end{aligned} \tag{10}$$

where the average is taken with respect to $\rho_N^\dagger$, and in the dynamical calculation of $\mathbf{F}_i(t')$, B-particles 1 and 2 are to be held fixed (similarly to the one-body case). If we assume, as is usually done on intuitive grounds, that the force correlations decay much more rapidly than the distribution function ρ_2 changes, then we may write

$$\mathscr{D}_t \rho_2 = \sum_{j,i=1}^{2} \frac{\partial}{\partial \mathbf{P}_i} \cdot \boldsymbol{\zeta}_{ij}^{(2)} \cdot \left(\frac{\partial}{\partial \mathbf{P}_j} + \frac{\mathbf{P}_j}{MkT} \right) \rho_2 \tag{11}$$

where $\mathscr{D}_t \rho_2$ is short for the left side of Eq. (10) and

$$\boldsymbol{\zeta}_{ij}^{(2)} = \int^{\infty} \langle \mathbf{F}_i(t-t')[\mathbf{F}_j(0) - \mathscr{F}_j] \rangle^\dagger \, dt' \tag{12}$$

We must make two remarks about $\zeta_{ij}^{(2)}$. First of all, by time-reversal invariance and the identity of particles, 1 and 2, $\zeta_{11}^{(2)} = \zeta_{22}^{(2)}$ and $\zeta_{12}^{(2)} = \zeta_{21}^{(2)}$. That is, there are only two friction tensors, not four. Secondly, although not explicit in the notation, the ζ's depend on $\mathbf{R}_1 - \mathbf{R}_2$, because $\mathbf{R}_1$ and $\mathbf{R}_2$ are fixed in their definition. Even in an isotropic system, they are not necessarily isotropic tensors, although the symmetry of the situation requires that they be diagonal in a coordinate system, one of whose axes is in the $\mathbf{R}_1 - \mathbf{R}_2$ direction (if the forces are spherically symmetrical), and the components perpendicular to this direction must be equal. It is also clear intuitively that, as $|\mathbf{R}_1 - \mathbf{R}_2| \to \infty$, $\zeta_{12}^{(2)} \to 0$ and $\zeta_{11}^{(2)} \to \frac{1}{3}\zeta\mathbf{1}$, where ζ is the singlet friction constant.

Equations (11) and (12) are the main results of this paper. They provide the generalization of the Fokker–Planck equation of ordinary Brownian motion theory to pair space.

3. DISCUSSION

Equation (11) is, of course, of exactly the structure one would expect from the theory of random processes (see Ref. 4, for example). We now have, however, a molecular derivation of this equation, with explicit, albeit formal, expressions for the coefficients.

Equations (11) will be very difficult to solve, in general, because the mean forces $\mathscr{F}_i$ and the friction coefficients $\zeta_{ij}^{(2)}$ depend on the relative positions of the B-particles. Although the equation is linear, it has complicated nonconstant coefficients. Furthermore, although we have formulas for the $\zeta_{ij}^{(2)}$, it is, at present, a hopeless task to try to calculate them from first principles. Neither of these problems is really fundamentally discouraging. One could, for example, try various simple models to estimate the $\zeta_{ij}^{(2)}$. Once this is done, the differential equation, though perhaps not amenable to exact solution, could perhaps be handled by one of the available approximate methods. However, these remarks represent suggestions for the direction of future work. The application to the calculation of transport coefficients, which, in fact, was what led us to consider this problem, will have to await the development of methods for handling the equation which has been derived here.

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