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On the Brownian Motion of a Massive Sphere Suspended in a Hard-Sphere Fluid. I. Multiple-Time-Scale Analysis and Microscopic Expression for the Friction Coefficient

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The Fokker–Planck equation governing the evolution of the distribution function of a massive Brownian hard sphere suspended in a fluid of much lighter spheres is derived from the exact hierarchy of kinetic equations for the total system via a multiple-time-scale analysis akin to a uniform expansion in powers of the square root of the mass ratio. The derivation leads to an exact expression for the friction coefficient which naturally splits into an Enskog contribution and a dynamical correction. The latter, which accounts for correlated collisions events, reduces to the integral of a time-displaced correlation function of dynamical variables linked to the collisional transfer of momentum between the infinitively heavy (i.e., immobile) Brownian sphere and the fluid particles.

KEY WORDS: Brownian motion; hard-sphere fluid; friction coefficient; kinetic theory; Enskog theory.

1. INTRODUCTION

Since the pioneering work of Einstein, Langevin, Planck, and Smoluchowski, the dynamics of mesoscopic particles suspended in a fluid has been the object of continuous experimental and theoretical investigations by many authors. As long as the Péclet number Pe, i.e., the ratio of characteristic times associated with diffusive and convective motion of the particles, is much larger than one, the motion is entirely governed by macroscopic hydrodynamics. In particular, the drag exerted by the fluid on a single

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suspended particle is given by Stokes' law, while the much more difficult problem of the hydrodynamic interactions between particles, induced by interfering backflow patterns of the fluid in concentrated suspensions, has been the object of intense investigation over the last two decades (see, e.g., ref. 1). In the opposite regime where $Pe < 1$, the thermal fluctuations of the host fluid can no longer be neglected, i.e., the discrete molecular nature of the fluid gives rise to "erratic" Brownian motion of the suspended particles. This regime typically holds for particles having diameters of the order of 1 μm or less. The interest in the Brownian motion of dilute and concentrated suspensions of submicrometer spherical particles has seen a strong recent revival, due to the availability of synthetic colloidal particles of well-controlled composition, size, and charge, and of powerful dynamic light scattering techniques (photon correlation spectroscopy), which provide a convenient and accurate probe of collective dynamics in such stable colloidal suspensions (see, e.g., ref. 2).

The statistical description of systems as asymmetric as these suspensions, which involve very disparate size and time scales, presents a formidable theoretical challenge. The traditional approach is a stochastic one, whereby the thermal motion of the fluid molecules gives rise to a random force acting on the individual colloidal particles. For the description of the motion of a single Brownian particle, this approach culminates in the Fokker–Planck equation, which governs the time evolution of the distribution function associated with this particle.[3] The Fokker–Planck description may be extended to concentrated suspensions of interacting Brownian particles,[4] but this approach is limited by the complexity and lack of understanding of indirect, hydrodynamic interactions between the particles.

Despite the aforementioned disparity in length and time scales, some attempts at a fully microscopic (or "first principles") description of the dynamics of suspended particles have been made. In particular, it has been possible to derive the Fokker–Planck equation for a single Brownian particle from the complete dynamical equations (i.e., the Liouville equation and the resulting BBGKY hierarchy) for the system made up of one massive particle and N fluid (bath) particles via a systematic expansion in powers of the square root of the mass ratio $\varepsilon = (m/M)^{1/2}$ (where M and m are the masses of the Brownian and bath particles).[5-7] Such derivations lead, in particular, to a microscopic formula for the friction coefficient ζ, which results from the action of the fluid on the Brownian particle, in terms of the autocorrelation function of the instantaneous microscopic force experienced by that particle. The reduction of the full Liouville equation to a Fokker–Planck equation has been generalized to the case of n interacting Brownian particles, and an Einstein relation between diffusion and friction tensors has been obtained.[8]

Approximate kinetic equations have been used to calculate the frictional drag exerted by the host fluid on a massive Brownian particle. If the latter is much larger than the bath molecules, the friction coefficient is expected to be given by the macroscopic Stokes law:

$$\zeta = \frac{4\pi\eta R}{M} \tag{1}$$

where M and R are the mass and radius of the spherical Brownian particle, while η is the shear viscosity of the bath. In their seminal paper, which dealt with the dilute gas limit for the host fluid, Dorfman *et al.*[9] already pointed out the crucial importance of recollision events in deriving the correct expression for ζ in the limit where the mean free path of the bath particles is much less than the radius of the Brownian particle. In order to account, at least approximately, for dynamical correlations, subsequent kinetic calculations[10] used the repeated-ring collision operator for hard-sphere fluids[11] or the closely related mode coupling approach in the case of continuous interactions between particles.[12]

In the present paper, the first of a series devoted to the kinetic theory of colloid dynamics in a hard-sphere fluid, we derive the Fokker–Planck equation for a single massive hard sphere, by adapting Cukier and Deutch's[6] multiple-time-scale analysis to a system of hard spheres. Due to the instantaneous nature of the collisions, the expansion scheme for hard spheres differs in many aspects from that obtained by Cukier and Deutch for the continuous case. The main result is an explicit, exact expression for the friction coefficient ζ, valid in the Brownian limit $\varepsilon \ll 1$, for arbitrary fixed size ratio. ζ turns out to split naturally into the sum of an Enskog contribution and a correction arising from dynamical correlations, which is the integral over time of a momentum transfer correlation function, to be evaluated for an infinitely massive Brownian particle. The so-called Enskog contribution could be obtained directly from the low-mass-ratio limit of the Enskog equation.[13] Practical procedures to evaluate the dynamical corrections by molecular dynamics simulations will be described and implemented in the second paper of the series.

2. HARD-SPHERE HIERARCHY OF KINETIC EQUATIONS

We consider here a hard sphere of mass M and diameter Σ immersed in a hard-sphere fluid composed of particles of mass m and diameter σ. Our object is to study the dynamics of the system in the limit

$$\varepsilon = \left(\frac{m}{M}\right)^{1/2} \ll 1 \tag{2}$$

at fixed particle diameters Σ and σ. The sphere (M, Σ) will be called the Brownian particle. Its position and velocity will be denoted by $\mathbf{R}$ and $\mathbf{V}$, respectively. We shall use the notation $\mathbf{r}_j$, $\mathbf{v}_j$ for the position and velocity of particle j of the suspending fluid. The short-hand notation

$$B \equiv (\mathbf{R}, \mathbf{V}); \qquad j \equiv (\mathbf{r}_j, \mathbf{v}_j), \qquad j = 1, 2,... \tag{3}$$

will be convenient.

We wish to determine the evolution of the probability density

$$f_1(\mathbf{R}, \mathbf{V}; t) \equiv f_1(B; t) \tag{4}$$

for finding the Brownian particle at point $\mathbf{R}$ with velocity $\mathbf{V}$ at time t. To this end we introduce the reduced distributions

$$f_{1s}(B, 1, 2,..., s; t), \qquad s = 1, 2,... \tag{5}$$

representing at time t the number density of s-tuples of fluid particles occupying the states

$$(1, 2,..., s) \equiv (\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2,..., \mathbf{r}_s, \mathbf{v}_s) \tag{6}$$

when at the same time the state of the Brownian particle is $B = (\mathbf{R}, \mathbf{V})$. The densities (4) and (5) are coupled by an infinite hierarchy of equations:

$$\left(\frac{\partial}{\partial t} + \mathbf{V} \cdot \frac{\partial}{\partial \mathbf{R}}\right) f_1(B; t) = \int d\mathbf{1}\, \bar{T}_-(B, 1)\, f_{11}(B, 1; t) \tag{7}$$

$$\begin{aligned} &\left\{\frac{\partial}{\partial t} + \mathbf{V} \cdot \frac{\partial}{\partial \mathbf{R}} + \sum_{i=1}^{s} \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} - \sum_{j=1}^{s} \bar{T}_-(B, j) - \sum_{i<j}^{s} \sum^{s} \bar{T}_-(i, j)\right\} \\ &\quad \times f_{1s}(B, 1,..., s; t) \\ &\quad = \int d(\mathbf{s}+\mathbf{1}) \left\{\bar{T}_-(B, s+1) + \sum_{j=1}^{s} \bar{T}_-(j, s+1)\right\} \\ &\quad \times f_{1(s+1)}(B, 1,..., (s+1); t) \end{aligned} \tag{8}$$

with $s = 1, 2,...$. The first of these, Eq. (7), expresses the fact that the state of the Brownian particle is changing in the course of time owing to free motion and to binary collisions with the fluid particles. The notation $d\mathbf{1} \equiv d\mathbf{r}_1\, d\mathbf{v}_1$ has been used. $\bar{T}_-(B, 1)$ is the hard-sphere binary collision operator, which can be written as

$$\bar{T}_-(B,1)=\left(\frac{\sigma+\Sigma}{2}\right)^2\int d\hat{\sigma}\,[(\mathbf{V}-\mathbf{v}_1)\cdot\hat{\sigma}]\,\theta[(\mathbf{V}-\mathbf{v}_1)\cdot\hat{\sigma}]$$
$$\times\left\{\delta\left(\mathbf{R}-\left(\frac{\sigma+\Sigma}{2}\right)\hat{\sigma}-\mathbf{r}_1\right)b_{\hat{\sigma}}(B,1)\right.$$
$$\left.-\,\delta\left(\mathbf{R}+\left(\frac{\sigma+\Sigma}{2}\right)\hat{\sigma}-\mathbf{r}_1\right)\right\}\tag{9}$$

In Eq. (9), the integration $\int d\hat{\sigma}$ spreads over the surface of a unit sphere $|\hat{\sigma}|=1$. The operator $b_{\hat{\sigma}}(B,1)$, when applied to a function $\chi(\mathbf{V},\mathbf{v}_1)$, replaces the velocities $\mathbf{V}$, $\mathbf{v}_1$ by their postcollisional values

$$[b_{\hat{\sigma}}(B,1)\chi](\mathbf{V},\mathbf{v}_1)=\chi\left(\mathbf{V}-\frac{2\varepsilon^2}{1+\varepsilon^2}[(\mathbf{V}-\mathbf{v}_1)\cdot\hat{\sigma}]\,\hat{\sigma},\right.$$
$$\left.\mathbf{v}_1+\frac{2}{1+\varepsilon^2}[(\mathbf{V}-\mathbf{v}_1)\cdot\hat{\sigma}]\,\hat{\sigma}\right)\tag{10}$$

θ is the Heaviside unit step function. The explicit form of Eq. (7) is thus

$$\left(\frac{\partial}{\partial t}+\mathbf{V}\cdot\frac{\partial}{\partial\mathbf{R}}\right)f_1(B;t)$$
$$=\left(\frac{\sigma+\Sigma}{2}\right)^2\int d\mathbf{v}_1\int d\hat{\sigma}\,[(\mathbf{V}-\mathbf{v}_1)\cdot\hat{\sigma}]\,\theta[(\mathbf{V}-\mathbf{v}_1)\cdot\hat{\sigma}]$$
$$\times\left\{f_{11}\left(\mathbf{R},\mathbf{V}-\frac{2\varepsilon^2}{1+\varepsilon^2}[(\mathbf{V}-\mathbf{v}_1)\cdot\hat{\sigma}]\,\hat{\sigma},\mathbf{R}-\left(\frac{\sigma+\Sigma}{2}\right)\hat{\sigma},\right.\right.$$
$$\left.\mathbf{v}_1+\frac{2}{1+\varepsilon^2}[(\mathbf{V}-\mathbf{v}_1)\cdot\hat{\sigma}]\,\hat{\sigma};t\right)$$
$$\left.-f_{11}\left(\mathbf{R},\mathbf{V},\mathbf{R}+\left(\frac{\sigma+\Sigma}{2}\right)\hat{\sigma},\mathbf{v}_1;t\right)\right\}\tag{11}$$

In Eq. (8), in addition to the operator $\bar{T}_-(B,j)$ describing collisions between the Brownian particle and the fluid particles, there appear the binary collision operators $\bar{T}_-(i,j)$ representing the effect of elastic encounters between identical spheres of diameter σ and mass m (fluid particles). Using the notation

$$\begin{aligned}\mathbf{v}_{ij}&=\mathbf{v}_i-\mathbf{v}_j\\ \mathbf{r}_{ij}&=\mathbf{r}_i-\mathbf{r}_j\end{aligned}\tag{12}$$

we can cast $\bar{T}_-$ in the form

$$\bar{T}_-(i, j) = \sigma^2 \int d\hat{\sigma} \, (\mathbf{v}_{ij} \cdot \hat{\sigma}) \, \theta(\mathbf{v}_{ij} \cdot \hat{\sigma}) \times \{\delta(\mathbf{r}_{ij} - \sigma\hat{\sigma}) \, b_{\hat{\sigma}}(i, j) - \delta(\mathbf{r}_{ij} + \sigma\hat{\sigma})\} \tag{13}$$

where the operator $b_{\hat{\sigma}}(i, j)$ acts according to the binary collision law

$$[b_{\hat{\sigma}}(i, j)\chi](\mathbf{v}_i, \mathbf{v}_j) = \chi(\mathbf{v}_i - (\mathbf{v}_{ij} \cdot \hat{\sigma})\hat{\sigma}, \mathbf{v}_j + (\mathbf{v}_{ij} \cdot \hat{\sigma})\hat{\sigma}) \tag{14}$$

where χ is any function of the variables $\mathbf{v}_i$, $\mathbf{v}_j$.

The hierarchy (7), (8) follows from the so-called pseudo-Liouville equation (ref. 14; see also ref. 3, pp. 241–247)

$$\left\{\frac{\partial}{\partial t} + \mathbf{V} \cdot \frac{\partial}{\partial \mathbf{R}} + \sum_{i=1}^{N} \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} - \sum_{j=1}^{N} \bar{T}_-(B, j) - \sum_{i<j}^{N} \sum^{N} \bar{T}_-(i, j)\right\} \rho(B, 1, 2,..., N; t) = 0 \tag{15}$$

which describes the evolution of the state $\rho(B, 1, 2,..., N; t)$ of the total (Brownian particle $+N$ fluid particles) system.

We are interested in the Brownian motion under thermal equilibrium conditions when the characteristic velocities of the Brownian and the fluid particles are $(k_B T/M)^{1/2}$ and $(k_B T/m)^{1/2}$, respectively (T is the temperature). When $\varepsilon = (m/M)^{1/2} \to 0$, separation of time scales is to be expected. A convenient way of describing this situation is to use a set of dimensionless variables defined by

$$\begin{aligned} \mathbf{V} &= \left(\frac{k_B T}{M}\right)^{1/2} \mathbf{U}, & \mathbf{v}_j &= \left(\frac{k_B T}{m}\right)^{1/2} \mathbf{u}_j \\ \mathbf{R} &= \sigma \mathbf{X}, & \mathbf{r}_j &= \sigma \mathbf{x}_j \\ t &= \sigma \left(\frac{m}{k_B T}\right)^{1/2} \tau \end{aligned} \tag{16}$$

The velocities $\mathbf{U}, \mathbf{u}_i$ are essentially of order 1. The distances are measured in units of σ, and the unit of time was chosen to be the time needed to cover the distance σ with the fluid thermal velocity $(k_B T/m)^{1/2}$. Consequently, the distributions $f_1(B; t)$, $f_{11}(B, 1; t)$ are replaced by dimensionless distributions $F_1(B, \tau)$, $F_{11}(B, 1; \tau)$ defined through the conditions

$$\begin{aligned} F_1(B, \tau) \, d\mathbf{X} \, d\mathbf{U} &= f_1(B; t) \, d\mathbf{R} \, d\mathbf{V} \\ F_{11}(B, 1; \tau) \, d\mathbf{X} \, d\mathbf{U} \, d\mathbf{x}_1 \, d\mathbf{u}_1 &= f_{11}(B, 1; t) \, d\mathbf{R} \, d\mathbf{V} \, d\mathbf{r}_1 \, d\mathbf{v}_1 \end{aligned} \tag{17}$$

Equations (16) and (17) imply the relations

$$
\begin{aligned}
F_1(B, \tau) &= \sigma^3 (k_B T/M)^{3/2} f_1(B; t) \\
F_{11}(B, 1; \tau) &= \sigma^6 (k_B T/M)^{3/2} (k_B T/m)^{3/2} f_{11}(B, 1; t)
\end{aligned}
\tag{18}
$$

With the new, reduced variables, the first hierarchy equation (7) takes the form

$$
\left(\frac{\partial}{\partial \tau} + \varepsilon \mathbf{U} \cdot \frac{\partial}{\partial \mathbf{X}}\right) F_1(B; \tau) = \int d\mathbf{1}\, \bar{T}^{\varepsilon}_{-}(B, 1)\, F_{11}(B, \mathbf{1}; \tau) \tag{19}
$$

where

$$
\begin{aligned}
\bar{T}^{\varepsilon}_{-}(B, 1) = \left(\frac{1+\kappa}{2\kappa}\right)^2 \int d\hat{\sigma}\, [(\varepsilon \mathbf{U} - \mathbf{u}_1)\cdot \hat{\sigma}]\, \theta[(\varepsilon \mathbf{U} - \mathbf{u}_1)\cdot \hat{\sigma}] \\
\times \left\{ \delta\left(\mathbf{X} - \left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma} - \mathbf{x}_1\right) b^{\varepsilon}_{\hat{\sigma}}(B, 1) \right. \\
\left. - \delta\left(\mathbf{X} + \left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma} - \mathbf{x}_1\right) \right\}
\end{aligned}
\tag{20}
$$

In Eq. (20), $\kappa = \sigma/\Sigma$, and the operator $b^{\varepsilon}_{\hat{\sigma}}(B, 1)$ acts on functions of velocities $\mathbf{U}$, $\mathbf{u}_1$ according to the formula

$$
\begin{aligned}
&[b^{\varepsilon}_{\hat{\sigma}}(B, 1)\chi](\mathbf{U}, \mathbf{u}_1) \\
&\quad = \chi\left(\mathbf{U} - \frac{2\varepsilon}{1+\varepsilon^2}[(\varepsilon \mathbf{U} - \mathbf{u}_1)\cdot \hat{\sigma}]\hat{\sigma},\ \mathbf{u}_1 + \frac{2}{1+\varepsilon^2}[(\varepsilon \mathbf{U} - \mathbf{u}_1)\cdot \hat{\sigma}]\hat{\sigma}\right)
\end{aligned}
\tag{21}
$$

The subsequent analysis will be based on an expansion of the collision term in Eq. (19) in powers of ε. This is achieved by formally expanding the binary collision operator $\bar{T}^{\varepsilon}_{-}(B, 1)$ in powers of ε, such that the right-hand side (r.h.s.) of Eq. (19) becomes

$$
\begin{aligned}
\int d\mathbf{1}\, \bar{T}^{\varepsilon}_{-}(B, 1)\, F_{11}(B, 1; \tau) &= \int d\mathbf{1}\, \bar{T}^{(0)}_{-}(B, 1)\, F_{11}(B, 1; \tau) \\
&\quad + \int d\mathbf{1}\, \bar{T}^{(1)}_{-}(B, 1)\, F_{11}(B, 1; \tau) \\
&\quad + \int d\mathbf{1}\, \bar{T}^{(2)}_{-}(B, 1)\, F_{11}(B, 1; \tau) \\
&\quad + \cdots
\end{aligned}
\tag{22}
$$

Explicit expressions for $\bar{T}_{-}^{(0)}$ and $\bar{T}_{-}^{(1)}$ are given in the Appendix, and will be used later. An alternative, simpler way of obtaining the ε-expansion of the collision term follows from direct substitution of Eqs. (20) and (21) into the r.h.s. of Eq. (19). This leads, after a straightforward integration over $\mathbf{x}_1$, to the following form of the hierarchy equation:

$$\begin{aligned}
&\left(\frac{\partial}{\partial\tau}+\varepsilon\mathbf{U}\cdot\frac{\partial}{\partial\mathbf{X}}\right)F_1(\mathbf{X},\mathbf{U};\tau)\\
&\quad=\left(\frac{1+\kappa}{2\kappa}\right)^2\int d\mathbf{u}_1\int d\hat{\sigma}\,[(\varepsilon\mathbf{U}-\mathbf{u}_1)\cdot\hat{\sigma}]\,\theta[(\varepsilon\mathbf{U}-\mathbf{u}_1)\cdot\hat{\sigma}]\\
&\quad\quad\times\left\{F_{11}\left(\mathbf{X},\mathbf{U}-\frac{2\varepsilon}{1+\varepsilon^2}[(\varepsilon\mathbf{U}-\mathbf{u}_1)\cdot\hat{\sigma}]\hat{\sigma},\mathbf{X}-\left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma},\right.\right.\\
&\quad\quad\quad\left.\mathbf{u}_1+\frac{2}{1+\varepsilon^2}[(\varepsilon\mathbf{U}-\mathbf{u}_1)\cdot\hat{\sigma}]\hat{\sigma};\tau\right)\\
&\quad\quad\left.-F_{11}\left(\mathbf{X},\mathbf{U},\mathbf{X}+\left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma},\mathbf{u}_1;\tau\right)\right\}
\end{aligned}\tag{23}$$

In view of the desired ε-expansion, it is convenient to transform the gain term on the r.h.s. of Eq. (23) by introducing a new integration variable

$$\mathbf{w}=\mathbf{u}_1-\varepsilon\mathbf{U}+2[(\varepsilon\mathbf{U}-\mathbf{u}_1)\cdot\hat{\sigma}]\,\hat{\sigma}\tag{24}$$

The gain term then takes the form

$$\begin{aligned}
&\left(\frac{1+\kappa}{2\kappa}\right)^2\int d\mathbf{w}\int d\hat{\sigma}\,(\mathbf{w}\cdot\hat{\sigma})\,\theta(\mathbf{w}\cdot\hat{\sigma})\\
&\quad\times F_{11}\left(\mathbf{X},\mathbf{U}-\frac{2\varepsilon}{1+\varepsilon^2}(\mathbf{w}\cdot\hat{\sigma})\,\hat{\sigma},\mathbf{X}-\left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma},\right.\\
&\quad\quad\left.\mathbf{w}+\varepsilon\mathbf{U}-\frac{2\varepsilon^2}{1+\varepsilon^2}(\mathbf{w}\cdot\hat{\sigma})\,\hat{\sigma};\tau\right)
\end{aligned}\tag{25}$$

Similarly the loss term is transformed by performing the following change of integration variables:

$$\mathbf{u}_1\to\mathbf{w}=\mathbf{u}_1-\varepsilon\mathbf{U};\qquad\hat{\sigma}\to-\hat{\sigma}\tag{26}$$

which leads to

$$\begin{aligned}
&-\left(\frac{1+\kappa}{2\kappa}\right)^2\int d\mathbf{w}\int d\hat{\sigma}\,(\mathbf{w}\cdot\hat{\sigma})\,\theta(\mathbf{w}\cdot\hat{\sigma})\\
&\quad\times F_{11}\left(\mathbf{X},\mathbf{U},\mathbf{X}-\left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma},\mathbf{w}+\varepsilon\mathbf{U};\tau\right)
\end{aligned}\tag{27}$$

Using Eqs. (25) and (27), we can cast the first hierarchy equation (23) in the final form

$$\left(\frac{\partial}{\partial \tau}+\varepsilon \mathbf{U}\cdot\frac{\partial}{\partial \mathbf{X}}\right) F_1(\mathbf{X}, \mathbf{U}; \tau)$$

$$=\left(\frac{1+\kappa}{2\kappa}\right)^2 \int d\mathbf{w} \int d\hat{\sigma}\, (\mathbf{w}\cdot\hat{\sigma})\, \theta(\mathbf{w}\cdot\hat{\sigma})$$

$$\times\left\{F_{11}\left(\mathbf{X}, \mathbf{U}-\frac{2\varepsilon}{1+\varepsilon^2}(\mathbf{w}\cdot\hat{\sigma})\,\hat{\sigma}, \mathbf{X}-\left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma},\right.\right.$$

$$\left.\mathbf{w}+\varepsilon\mathbf{U}-\frac{2\varepsilon^2}{1+\varepsilon^2}(\mathbf{w}\cdot\hat{\sigma})\,\hat{\sigma}; \tau\right)$$

$$\left.-F_{11}\left(\mathbf{X}, \mathbf{U}, \mathbf{X}-\left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma}, \mathbf{w}+\varepsilon\mathbf{U}; \tau\right)\right\} \tag{28}$$

The zeroth-order term vanishes,

$$\int d\mathbf{1}\, \bar{T}_{-}^{(0)}(B, 1)\, F_{11}(B, 1; \tau)=0 \tag{29}$$

The first-order term is given by

$$\int d\mathbf{1}\, \bar{T}_{-}^{(1)}(B, 1)\, F_{11}(B, 1; \tau)$$

$$=\left(\frac{1+\kappa}{2\kappa}\right)^2 \int d\mathbf{w} \int d\hat{\sigma}\, [-2(\mathbf{w}\cdot\hat{\sigma})^2\, \theta(\mathbf{w}\cdot\hat{\sigma})]$$

$$\times\left(\hat{\sigma}\cdot\frac{\partial}{\partial \mathbf{U}}\right) F_{11}\left(\mathbf{X}, \mathbf{U}, \mathbf{X}-\left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma}, \mathbf{w}; \tau\right) \tag{30}$$

while the second-order term reads

$$\int d\mathbf{1}\, \bar{T}_{-}^{(2)}(B, 1)\, F_{11}(B, 1; \tau)$$

$$=\left(\frac{1+\kappa}{2\kappa}\right)^2 \int d\mathbf{w} \int d\hat{\sigma}\, 2(\mathbf{w}\cdot\hat{\sigma})^2\, \theta(\mathbf{w}\cdot\hat{\sigma})$$

$$\times\left\{(\mathbf{w}\cdot\hat{\sigma})\left(\hat{\sigma}\cdot\frac{\partial}{\partial \mathbf{U}}\right)\left(\hat{\sigma}\cdot\frac{\partial}{\partial \mathbf{U}}\right)\right.$$

$$\left.-\left(\mathbf{U}\cdot\frac{\partial}{\partial \mathbf{w}}\right)\left(\hat{\sigma}\cdot\frac{\partial}{\partial \mathbf{U}}\right)-\hat{\sigma}\cdot\frac{\partial}{\partial \mathbf{w}}\right\}$$

$$\times F_{11}\left(\mathbf{X}, \mathbf{U}, \mathbf{X}-\left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma}, \mathbf{w}; \tau\right) \tag{31}$$

Having established these results, we now turn to the remaining hierarchy equations. Their general form (8) reflects the coupling between distributions f_{1s} and $f_{1(s+1)}$. When $s=1$ we find

$$\left\{\frac{\partial}{\partial t}+\mathbf{V}\cdot\frac{\partial}{\partial \mathbf{R}}+\mathbf{v}_1\cdot\frac{\partial}{\partial \mathbf{r}_1}-\bar{T}_-(B,1)\right\} f_{11}(B,1;t)$$
$$=\int d\mathbf{2}\,\{\bar{T}_-(B,2)+\bar{T}_-(1,2)\}\, f_{12}(B,1,2;t) \tag{32}$$

We now perform the same dimensional analysis as in the case of the first hierarchy equation and define the dimensionless three-particle density $F_{12}(B,1,2;\tau)$ according to

$$F_{12}(B,1,2;\tau)=\sigma^9(k_B T/M)^{3/2}\,(k_B T/m)^{6/2}\, f_{12}(B,1,2;t) \tag{33}$$

so that, in view of Eqs. (16),

$$F_{12}(B,1,2;\tau)\, d\mathbf{X}\, d\mathbf{U}\, d\mathbf{x}_1\, d\mathbf{u}_1\, d\mathbf{x}_2\, d\mathbf{u}_2$$
$$=f_{12}(B,1,2;t)\, d\mathbf{R}\, d\mathbf{V}\, d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{r}_2\, d\mathbf{v}_2 \tag{34}$$

The second hierarchy equation now takes the form

$$\left\{\frac{\partial}{\partial \tau}+\varepsilon\mathbf{U}\cdot\frac{\partial}{\partial \mathbf{X}}+\mathbf{u}_1\cdot\frac{\partial}{\partial \mathbf{x}_1}-\bar{T}^{\varepsilon}_-(B,1)\right\} F_{11}(B,1;\tau)$$
$$=\int d\mathbf{2}\,\{\bar{T}^{\varepsilon}_-(B,2)+\bar{T}^{d}_-(1,2)\}\, F_{12}(B,1,2;\tau) \tag{35}$$

where the operators $\bar{T}^{\varepsilon}_-(B,j)$, $j=1,2,\ldots$, have been defined in Eq. (20). In Eq. (35), $\bar{T}^{d}_-$ denotes the binary collision operator of the fluid particles, expressed in terms of the dimensionless variables

$$\bar{T}^{d}_-(1,2)=\int d\hat{\sigma}\,(\mathbf{u}_{12}\cdot\hat{\sigma})\,\theta(\mathbf{u}_{12}\cdot\hat{\sigma})\{\delta(\mathbf{x}_{12}-\hat{\sigma})\, b_{\hat{\sigma}}(12)-\delta(\mathbf{x}_{12}+\hat{\sigma})\} \tag{36}$$

Similarly, the general hierarchy equation relating dimensionless distributions $F_{1s}(B,1,\ldots,s;\tau)$ and $F_{1(s+1)}(B,1,\ldots,s,(s+1);\tau)$ reads

$$\left\{\frac{\partial}{\partial \tau}+\varepsilon\mathbf{U}\cdot\frac{\partial}{\partial \mathbf{X}}-\sum_{j=1}^{s}\bar{T}^{\varepsilon}_-(B,j)+\sum_{j=1}^{s}\mathbf{u}_j\cdot\frac{\partial}{\partial \mathbf{x}_j}-\sum_{i<j}^{s}\sum^{s}\bar{T}^{d}_-(i,j)\right\}$$
$$\times F_{1s}(B,1,\ldots,s;\tau)$$
$$=\int d(\mathbf{s}+\mathbf{1})\left\{\bar{T}^{\varepsilon}_-(B,(s+1))+\sum_{j=1}^{s}\bar{T}^{d}_-(j,(s+1))\right\}$$
$$\times F_{1(s+1)}(B,1,\ldots,s,(s+1);\tau) \tag{37}$$

3. MULTIPLE-TIME-SCALE ANALYSIS

At this point we are in a position to turn to our main object, i.e., the equation governing the evolution of the distribution $F_1(B; \tau)$ in the case where $\varepsilon \ll 1$. The separation of time scales in the limit $\varepsilon \to 0$ suggests the application of the multiple-time-scale analysis similar in spirit to that used in ref. 6 in the case of continuous interactions between particles. Limiting the analysis to three time scales, we thus replace the distributions F_1, F_{1s} by auxiliary functions $F_1^\varepsilon(B; \tau_0, \tau_1, \tau_2)$, $F_{1s}^\varepsilon(B, 1,..., s; \tau_0, \tau_1, \tau_2)$, depending on three time arguments. Accordingly, the time derivative $\partial/\partial\tau$ is replaced by the operator

$$\frac{\partial}{\partial \tau_0} + \varepsilon \frac{\partial}{\partial \tau_1} + \varepsilon^2 \frac{\partial}{\partial \tau_2} \tag{38}$$

since we have in mind the perturbation expansion up to terms of order ε^2. The auxiliary functions are next expanded in powers of ε,

$$F_1^\varepsilon = F_1^{(0)} + \varepsilon F_1^{(1)} + \varepsilon^2 F_1^{(2)} + \cdots \tag{39}$$

$$F_{1s}^\varepsilon = F_{1s}^{(0)} + \varepsilon F_{1s}^{(1)} + \varepsilon^2 F_{1s}^{(2)} + \cdots \tag{40}$$

and substituted into the hierarchy equations, where terms of the same order in ε will eventually be identified. The determination of successive corrections $F_1^{(k)}$, $F_{1s}^{(k)}$, $k = 0, 1, 2,...$, will be achieved by combining the chosen initial condition with the requirement that the expansions be uniform in ε, which amounts to eliminating secular divergences. The physically relevant distributions, i.e., the perturbative solution of the hierarchy (28), (37), are then obtained by restricting the multiple time variables τ_0, τ_1, τ_2 to the physical line

$$\tau_0 = \tau, \qquad \tau_1 = \varepsilon\tau, \qquad \tau_2 = \varepsilon^2\tau \tag{41}$$

In particular, up to terms of order ε^2,

$$F_1(B; \tau) = F_1^\varepsilon(B; \tau, \varepsilon\tau, \varepsilon^2\tau) \tag{42}$$

Equation (41) shows that the dependence of the reduced distributions on the variable τ_j essentially defines the dynamical evolution on the time scale $\tau \sim \varepsilon^{-j}$, $j = 0, 1, 2,...$.

4. ZEROTH-ORDER AND INITIAL CONDITION

We begin by analyzing the zeroth-order terms in the hierarchy equations. Equation (19) together with Eq. (29) yields

$$\frac{\partial}{\partial \tau_0} F_1^{(0)} = 0 \tag{43}$$

Hence, $F_1^{(0)}$ does not depend on the variable τ_0. The corresponding general hierarchy equation (37) reads to zeroth order

$$\left\{\frac{\partial}{\partial\tau_0}-\sum_{j=1}^{s}\bar{T}_-^{(0)}(B,j)+\sum_{j=1}^{s}\mathbf{u}_j\cdot\frac{\partial}{\partial\mathbf{x}_j}-\sum_{i<j}^{s}\sum^{s}\bar{T}_-^d(i,j)\right\}F_{1s}^{(0)}$$
$$=\int d(\mathbf{s}+\mathbf{1})\sum_{j=1}^{s}\bar{T}_-^d(j,(s+1))\,F_{1(s+1)}^{(0)} \tag{44}$$

In Eq. (44) the Brownian particle appears as the source of an external field, corresponding to the presence of an infinite spherical mass at point $\mathbf{X}$ from which the fluid particles are specularly reflected [see Eq. (A.2)]. In view of this we choose the solution of the hierarchy (44) in the factorized form

$$F_{1s}^{(0)}(B,1,...,s;\tau_0,\tau_1,\tau_2)=F_1^{(0)}(B,\tau_1,\tau_2)\,F_s^{\mathrm{eq}}(1,...,s\,|\,\mathbf{X}) \tag{45}$$

where $F_s^{\mathrm{eq}}(1,..., s\,|\,\mathbf{X})$ is the s-particle equilibrium distribution of the fluid in the presence of the Brownian particle fixed at point $\mathbf{X}$ (external field). In particular,

$$F_1^{\mathrm{eq}}(1\,|\,\mathbf{X})=h_1^{\mathrm{eq}}(|\mathbf{x}_1-\mathbf{X}|)\,\phi(\mathbf{u}_1) \tag{46}$$

where

$$\phi(\mathbf{u})=(2\pi)^{-3/2}\exp(-u^2/2) \tag{47}$$

is the Maxwell distribution and $h_1^{\mathrm{eq}}(|\mathbf{x}_1-\mathbf{X}|)$ is the dimensionless equilibrium fluid density at point $\mathbf{x}_1$ in the field of the Brownian particle fixed at $\mathbf{X}$. Clearly this density depends only on the distance $|\mathbf{x}_1-\mathbf{X}|$. In principle, the distributions $F_s^{\mathrm{eq}}(1,..., s\,|\,\mathbf{X})$, $s=1, 2,...,$ can be determined from the equilibrium hierarchy:

$$\left\{\sum_{j=1}^{s}\mathbf{u}_j\cdot\frac{\partial}{\partial\mathbf{x}_j}-\sum_{i<j}^{s}\sum^{s}\bar{T}_-^d(i,j)-\sum_{j=1}^{s}\bar{T}_-^{(0)}(B,j)\right\}F_s^{\mathrm{eq}}$$
$$=\int d(\mathbf{s}+\mathbf{1})\sum_{j=1}^{s}\bar{T}_-^d(j,(s+1))\,F_{(s+1)}^{\mathrm{eq}} \tag{48}$$

When multiplied by $F_1^{(0)}(B,\tau_1,\tau_2)$, Eqs. (48) take the form (44); they do not impose any condition on the distribution of the Brownian particle.

The choice (45) makes all distributions of order zero independent of the time variable τ_0. Moreover, we shall assume that the conditional equilibrium of the fluid described above is the initial state of the system, so that

$$F_{1s}^{\varepsilon}(B,1,...,s;\tau_0=0,\tau_1=0,\tau_2=0)=F_1^{(0)}(B;\tau_1=0,\tau_2=0)\,F_s^{\mathrm{eq}}(1,...,s\,|\,\mathbf{X})$$
$$F_1^{\varepsilon}(B;\tau_1=0,\tau_2=0)=F_1^{(0)}(B;\tau_1=0,\tau_2=0) \tag{49}$$

Outside the "physical line" (41), one has the freedom of imposing convenient boundary conditions. We use this freedom here by setting [in accordance with Eq. (49)]

$$\begin{aligned} F_1^{(k)}(B; \tau_0 = 0, \tau_1, \tau_2) &= 0 \\ F_{1s}^{(k)}(B, 1,..., s; \tau_0 = 0, \tau_1, \tau_2) &= 0 \end{aligned} \tag{50}$$

for $k = 1, 2,...$ and arbitrary τ_1, τ_2.

Equations (43), (45), (49), and (50) specify entirely the starting point of the perturbative expansion. We can now turn to the analysis of the first-order terms in the dynamical hierarchy.

5. FIRST-ORDER AND FREE MOTION

To first order in ε, the first hierarchy equation (19) yields together with Eq. (30)

$$\begin{aligned} &\frac{\partial}{\partial \tau_0} F_1^{(1)} + \left(\frac{\partial}{\partial \tau_1} + \mathbf{U} \cdot \frac{\partial}{\partial \mathbf{X}}\right) F_1^{(0)} \\ &\quad = \left(\frac{1+\kappa}{2\kappa}\right)^2 \int d\mathbf{w} \int d\hat{\sigma} \, [-2(\mathbf{w} \cdot \hat{\sigma})^2 \, \theta(\mathbf{w} \cdot \hat{\sigma})] \\ &\quad \times \left(\hat{\sigma} \cdot \frac{\partial}{\partial \mathbf{U}}\right) F_{11}^{(0)} \left(\mathbf{X}, \mathbf{U}, \mathbf{X} - \left(\frac{1+\kappa}{2\kappa}\right) \hat{\sigma}, \mathbf{w}; \tau_1, \tau_2\right) \end{aligned} \tag{51}$$

Since $F_1^{(0)}$ and the r.h.s. of (51) are independent of τ_0, secular divergence is eliminated provided we set

$$\frac{\partial}{\partial \tau_0} F_1^{(1)} = 0 \tag{52}$$

Since $F_1^{(1)}|_{\tau_0 = 0} = 0$ according to Eq. (50), we find that

$$F_1^{(1)} \equiv 0 \tag{53}$$

With our choice of initial condition there is thus no first-order correction to the Brownian particle distribution function. Remembering (45) and (46), we now insert the relation

$$\begin{aligned} &F_{11}^{(0)} \left(\mathbf{X}, \mathbf{U}, \mathbf{X} - \left(\frac{1+\kappa}{2\kappa}\right) \hat{\sigma}, \mathbf{w}; \tau_1, \tau_2\right) \\ &\quad = F_1^{(0)}(\mathbf{X}, \mathbf{U}; \tau_1, \tau_2) \, h_1^{\text{eq}} \left(\frac{1+\kappa}{2\kappa}\right) \phi(\mathbf{w}) \end{aligned} \tag{54}$$

into the r.h.s. of Eq. (51) and find that the collision term vanishes as a result of the isotropy of the fluid density around the Brownian particle. Hence

$$\left(\frac{\partial}{\partial \tau_1} + \mathbf{U} \cdot \frac{\partial}{\partial \mathbf{X}}\right) F_1^{(0)} = 0 \tag{55}$$

Equation (55) determines the dependence of the distribution $F_1^{(0)}$ on the time variable τ_1,

$$F_1^{(0)}(\mathbf{X}, \mathbf{U}; \tau_1, \tau_2) = F_1^{(0)}(\mathbf{X} - \tau_1 \mathbf{U}, \mathbf{U}; \tau_1 = 0, \tau_2) \tag{56}$$

We conclude that on the corresponding time scale, $\tau \sim \varepsilon^{-1}$, the Brownian particle "does not see" the fluid. Its distribution evolves in time due to free particle motion.

6. SECOND ORDER AND DISSIPATION

To determine the dissipative effect of the interaction with the fluid we have to study the evolution of $F_1^{(0)}$ on a longer time scale, corresponding to the variable τ_2. To this end the second-order term resulting from the hierarchy equation (19) has to be considered. Taking Eqs. (29), (45), and (53) into account, we find

$$\begin{aligned} &\frac{\partial}{\partial \tau_2} F_1^{(0)}(B; \tau_1, \tau_2) + \frac{\partial}{\partial \tau_0} F_1^{(2)}(B; \tau_0, \tau_1, \tau_2) \\ &\quad = \int d\mathbf{1} \, \{\bar{T}_-^{(1)}(B, 1) \, F_{11}^{(1)}(B, 1; \tau_0, \tau_1, \tau_2) + \bar{T}_-^{(2)}(B, 1) \, F_{11}^{(0)}(B, 1; \tau_1, \tau_2)\} \end{aligned} \tag{57}$$

Secular divergence is eliminated (and hence a uniform expansion achieved) provided the condition

$$\lim_{\tau_0 \to \infty} \frac{\partial}{\partial \tau_0} F_1^{(2)}(B; \tau_0, \tau_1, \tau_2) = 0 \tag{58}$$

is fulfilled, which is equivalent to

$$\begin{aligned} \frac{\partial}{\partial \tau_2} F_1^{(0)}(B; \tau_1, \tau_2) = &\lim_{\tau_0 \to \infty} \int d\mathbf{1} \, \bar{T}_-^{(1)}(B, 1) \, F_{11}^{(1)}(B, 1; \tau_0, \tau_1, \tau_2) \\ &+ \int d\mathbf{1} \, \bar{T}_-^{(2)}(B, 1) \, F_{11}^{(0)}(B, 1; \tau_1, \tau_2) \end{aligned} \tag{59}$$

Equation (59) determines the τ_2 dependence of the Brownian particle distribution $F_1^{(0)}$. The second term on the r.h.s. can be evaluated in a straightforward way using Eqs. (31) and (45)–(47) with the result

$$\int d1\, \bar{T}_-^{(2)}(B,1)\, F_1^{(0)}(B;\tau_1,\tau_2)\, F_1^{\mathrm{eq}}(1\,|\,\mathbf{X})$$
$$=\left(\frac{1+\kappa}{2\kappa}\right)^2 h_1^{\mathrm{eq}}\left(\frac{1+\kappa}{2\kappa}\right)\frac{8}{3}(2\pi)^{1/2}\frac{\partial}{\partial\mathbf{U}}\cdot\left(\frac{\partial}{\partial\mathbf{U}}+\mathbf{U}\right)F_1^{(0)}(B;\tau_1,\tau_2) \tag{60}$$

A more subtle analysis is required to evaluate the term in Eq. (59) involving the $\tau_0\to\infty$ limit. One has to consider the terms of order ε in the hierarchy (37) which determine the evolution of the first-order corrections $F_{11}^{(1)}, F_{12}^{(1)},\ldots$. In general, the hierarchy equations determining the τ_0 dependence of the first-order corrections $F_{1s}^{(1)}$, $s=1,2,\ldots$, follow from the inhomogeneous pseudo-Liouville equation, derived by a straightforward expansion in powers of ε from the homogeneous equation (15),

$$\left\{\frac{\partial}{\partial\tau_0}+\sum_j\left(\mathbf{u}_j\cdot\frac{\partial}{\partial\mathbf{x}_j}-\bar{T}_-^{(0)}(B,j)\right)-\sum_{i<j}^{N}\sum^{N}\bar{T}_-^{d}(i,j)\right\}$$
$$\times\,\rho^{(1)}(B,1,2,\ldots;\tau_0,\tau_1,\tau_2)$$
$$=\left\{-\left(\frac{\partial}{\partial\tau_1}+\mathbf{U}\cdot\frac{\partial}{\partial\mathbf{X}}\right)+\sum_j\bar{T}_-^{(1)}(B,j)\right\}\rho^{(0)}(B,1,2,\ldots;\tau_1,\tau_2) \tag{61}$$

where $\rho^{(0)}$ and $\rho^{(1)}$ are the zeroth- and first-order terms in the multiple scale expansion of the nonequilibrium ensemble describing the state of the whole system. The structure of $\rho^{(0)}$ is uniquely determined by Eqs. (45)–(47) whereby

$$\rho^{(0)}(B,1,2,\ldots;\tau_1,\tau_2)=F_1^{(0)}(B;\tau_1,\tau_2)\,\rho^{\mathrm{equ}}(1,2,\ldots\,|\,\mathbf{X}) \tag{62}$$

where $\rho^{\mathrm{equ}}(1,2,\ldots\,|\,\mathbf{X})$ is the equilibrium state of the fluid in the presence of the Brownian particle fixed at point **X**. Equations (55) and (62) lead to the relation

$$-\left(\frac{\partial}{\partial\tau_1}+\mathbf{U}\cdot\frac{\partial}{\partial\mathbf{X}}\right)\rho^{(0)}(B,1,2,\ldots;\tau_1,\tau_2)$$
$$=-F_1^{(0)}(B;\tau_1,\tau_2)\,\mathbf{U}\cdot\frac{\partial}{\partial\mathbf{X}}\rho^{\mathrm{equ}}(1,2,\ldots\,|\,\mathbf{X}) \tag{63}$$

The **X** dependence of ρ^{eq} comes from the excluded volume factor

$$\prod_j\theta\left(|\mathbf{X}-\mathbf{x}_j|-\left(\frac{1+\kappa}{2\kappa}\right)\right) \tag{64}$$

Using the identity

$$\delta\left(|\mathbf{X}-\mathbf{x}_j|-\left(\frac{1+\kappa}{2\kappa}\right)\right)=\left(\frac{1+\kappa}{2\kappa}\right)^2\int d\hat{\sigma}\,\delta\left(\mathbf{X}-\mathbf{x}_j-\left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma}\right) \tag{65}$$

we find

$$\frac{\partial}{\partial\mathbf{X}}\rho^{eq}(1,2,...\,|\,\mathbf{X})=\left[\sum_j\left(\frac{1+\kappa}{2\kappa}\right)^2\int d\hat{\sigma}\,\delta\left(\mathbf{X}-\mathbf{x}_j-\left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma}\right)\hat{\sigma}\right]\times\rho^{eq}(1,2,...\,|\,\mathbf{X}) \tag{66}$$

which allows the r.h.s. of Eq. (63) to be reexpressed as

$$-\sum_j\left(\frac{1+\kappa}{2\kappa}\right)^2\int d\hat{\sigma}\,(\mathbf{U}\cdot\hat{\sigma})\,\delta\left(\mathbf{X}-\mathbf{x}_j-\left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma}\right)\times\rho^{eq}(1,2,...\,|\,\mathbf{X})\,F_1^{(0)}(B;\tau_1,\tau_2) \tag{67}$$

Now, taking into account the structure (62) of $\rho^{(0)}$ and using Eq. (A.5), we find

$$\begin{aligned}\left[\sum_j\bar{T}_-^{(1)}(B,j)\right]&\rho^{(0)}(B,1,2,...;\tau_1,\tau_2)\\&=\sum_j\left\{\left(\frac{1+\kappa}{2\kappa}\right)^2\int d\hat{\sigma}\,(\mathbf{U}\cdot\hat{\sigma})\,\delta\left(\mathbf{X}-\mathbf{x}_j-\left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma}\right)\right.\\&\qquad\left.-\mathscr{F}_-^d(j)\cdot\left(\frac{\partial}{\partial\mathbf{U}}+\mathbf{U}\right)\right\}\rho^{(0)}(B,1,2,...;\tau_1,\tau_2)\end{aligned} \tag{68}$$

where the notation $\mathscr{F}_\mp^d(j)$ has been introduced to denote the dimensionless "force"

$$\mathscr{F}_\mp^d(j)=\left(\frac{1+\kappa}{2\kappa}\right)^2\int d\hat{\sigma}\,[2(\mathbf{u}_j\cdot\hat{\sigma})^2\,\theta(\mp\mathbf{u}_j\cdot\hat{\sigma})]\,\hat{\sigma}\,\delta\left(\mathbf{X}-\mathbf{x}_j-\left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma}\right) \tag{69}$$

Adding up (67) and (68), we see that the first term on the r.h.s. of (68) is exactly canceled by the term (67). Hence, the inhomogeneity in Eq. (61) (i.e., its r.h.s.) has the form

$$-\mathscr{F}_-^d(0)\cdot\left(\frac{\partial}{\partial\mathbf{U}}+\mathbf{U}\right)\rho^{(0)}(B,1,2,...;\tau_1,\tau_2) \tag{70}$$

where

$$\mathscr{F}^d_{\mp}(0)=\sum_j \mathscr{F}^d_{\mp}(j) \tag{71}$$

is the total (dimensionless) "force" resulting from collisions of the fluid particles with particle B. Equation (61) has thus been cast in the form

$$\begin{aligned}\left\{\frac{\partial}{\partial\tau_0}+\sum_j\left(\mathbf{u}_j\cdot\frac{\partial}{\partial\mathbf{x}_j}-\bar{T}^{(0)}_{-}(B,j)\right)-\sum_{i<j}^{N}\sum^{N}\bar{T}^d_{-}(i,j)\right\}\\ \times\rho^{(1)}(B,1,2,...;\tau_0,\tau_1,\tau_2)\\ =-\mathscr{F}^d_{-}(0)\cdot\left(\frac{\partial}{\partial\mathbf{U}}+\mathbf{U}\right)\rho^{(0)}(B,1,2,...;\tau_1,\tau_2)\end{aligned} \tag{72}$$

In view of the initial condition (50), we are interested in finding the solution of Eq. (61) which vanishes at $\tau_0=0$. The equilibrium state $\rho^{eq}(1,2,...\,|\,\mathbf{X})$ is invariant under the dynamical evolution of the fluid in the external field exerted by the Brownian particle fixed at $\mathbf{X}$. Hence, the relevant solution of the first-order equation (61) reads

$$\begin{aligned}&\rho^{(1)}(B,1,2,...;\tau_0,\tau_1,\tau_2)\\ &\quad=-\int_0^{\tau_0}d\tau\,\mathscr{F}^d_{-}(-\tau)\cdot\left(\frac{\partial}{\partial\mathbf{U}}+\mathbf{U}\right)\rho^{eq}(1,2,...\,|\,\mathbf{X})\,F_1^{(0)}(B;\tau_1,\tau_2)\end{aligned} \tag{73}$$

In Eq. (73), $\mathscr{F}^d_{-}(-\tau)$ is the "force" $\mathscr{F}^d_{-}(0)$ on particle B propagated by the intrinsic fluid dynamics in the presence of the Brownian particle, fixed at point $\mathbf{X}$, backward in time to the instant $(-\tau)$. The reduced distribution $F_{11}^{(1)}(B,1;\tau_0,\tau_1,\tau_2)$, which we need to evaluate the derivative $\partial F_1^{(0)}/\partial\tau_2$ [see Eq. (59)], can be calculated from Eq. (73) in a straightforward way. It will be convenient to use the notation $\langle\cdots\rangle_{(eq\,|\,\mathbf{X})}$ to denote the average value over the equilibrium ensemble $\rho^{eq}(1,2,...\,|\,\mathbf{X})$. Then

$$\begin{aligned}&F_{11}^{(1)}(B,1;\tau_0,\tau_1,\tau_2)\\ &\quad=-\int_0^{\tau_0}d\tau\,\langle N(1)\,\mathscr{F}^d_{-}(-\tau)\rangle_{(eq\,|\,\mathbf{X})}\cdot\left(\frac{\partial}{\partial\mathbf{U}}+\mathbf{U}\right)F_1^{(0)}(B;\tau_1,\tau_2)\end{aligned} \tag{74}$$

where $N(1)$ is the microscopic fluid number density at the phase point $1=(\mathbf{x}_1,\mathbf{u}_1)$,

$$\begin{aligned}N(1)&=\sum_{j'}\delta(1-j')\\ &=\sum_{j'}\delta(\mathbf{x}_1-\mathbf{x}_{j'})\,\delta(\mathbf{u}_1-\mathbf{u}_{j'})\end{aligned} \tag{75}$$

Inserting Eq. (74) into Eq. (59) and using the result (60), we eventually find

$$\begin{aligned}
&\frac{\partial}{\partial \tau_2} F_1^{(0)}(B; \tau_1, \tau_2) \\
&\quad = \left\{ \int_0^\infty d\tau \, \langle \mathscr{F}_+^d(0)\, \mathscr{F}_-^d(-\tau) \rangle_{(\mathrm{eq}\,|\,\mathbf{X})} : \frac{\partial}{\partial \mathbf{U}} \left(\frac{\partial}{\partial \mathbf{U}} + \mathbf{U} \right) \right. \\
&\quad\quad \left. + \left(\frac{1+\kappa}{2\kappa} \right)^2 h_1^{\mathrm{eq}} \left(\frac{1+\kappa}{2\kappa} \right) \frac{8}{3} (2\pi)^{1/2} \frac{\partial}{\partial \mathbf{U}} \cdot \left(\frac{\partial}{\partial \mathbf{U}} + \mathbf{U} \right) \right\} \\
&\quad\quad \times F_1^{(0)}(B; \tau_1, \tau_2)
\end{aligned} \tag{76}$$

where the "forces" $\mathscr{F}_+^d$, $\mathscr{F}_-^d$ have been defined in Eqs. (69), (71).

7. REDUCTION TO THE FOKKER–PLANCK FORM

The isotropy of the equilibrium state allows to rewrite the first term on the r.h.s. of Eq. (76) as

$$\zeta_1^d \frac{\partial}{\partial \mathbf{U}} \cdot \left(\frac{\partial}{\partial \mathbf{U}} + \mathbf{U} \right) F_1^{(0)}(B; \tau_1, \tau_2) \tag{77}$$

where

$$\zeta_1^d = \tfrac{1}{3} \int_0^\infty \langle \mathscr{F}_+^d(0) \cdot \mathscr{F}_-^d(-\tau) \rangle_{(\mathrm{eq}\,|\,\mathbf{X})} \tag{78}$$

We shall also use the notation

$$\zeta_2^d = \left(\frac{1+\kappa}{2\kappa} \right)^2 \frac{8}{3} (2\pi)^{1/2} h_1^{\mathrm{eq}} \left(\frac{1+\kappa}{2\kappa} \right) \tag{79}$$

Then, combining Eqs. (37), (55), and (76)–(79) and considering the "physical line" (41), we obtain the evolution equation

$$\begin{aligned}
\frac{\partial}{\partial \tau} F_1^{(0)}(B; \varepsilon\tau, \varepsilon^2\tau) = &\left\{ -\varepsilon \mathbf{U} \cdot \frac{\partial}{\partial \mathbf{X}} + \varepsilon^2 \zeta^d \frac{\partial}{\partial \mathbf{U}} \cdot \left(\frac{\partial}{\partial \mathbf{U}} + \mathbf{U} \right) \right\} \\
&\times F_1^{(0)}(B; \varepsilon\tau, \varepsilon^2\tau)
\end{aligned} \tag{80}$$

where the dimensionless friction coefficient is

$$\zeta^d = \zeta_1^d + \zeta_2^d \tag{81}$$

Finally, returning to the original variables **R** and **V** [see Eq. (16)], we arrive at the Fokker–Planck equation

$$\left(\frac{\partial}{\partial t}+\mathbf{V}\cdot\frac{\partial}{\partial \mathbf{R}}\right)f_1(B;t)=\zeta\frac{\partial}{\partial \mathbf{V}}\cdot\left(\mathbf{V}+\frac{k_BT}{M}\frac{\partial}{\partial \mathbf{V}}\right)f_1(B;t) \tag{82}$$

In accordance with (81), the friction coefficient ζ appearing in Eq. (82) is the sum of two terms

$$\zeta_1=\frac{1}{M}\left(\frac{\sigma+\Sigma}{2}\right)^2\frac{8}{3}(2\pi mk_BT)^{1/2}\rho^{\mathrm{eq}}\left(\frac{\sigma+\Sigma}{2}\right) \tag{83}$$

and

$$\zeta_2=\frac{1}{3Mk_BT}\int_0^\infty d\tau\,\langle\mathscr{F}_+(0)\cdot\mathscr{F}_-(-\tau)\rangle_{(\mathrm{eq}\,|\,\mathbf{X})} \tag{84}$$

where

$$\rho^{\mathrm{eq}}\left(\frac{\sigma+\Sigma}{2}\right)=\sigma^{-3}h_1^{\mathrm{eq}}\left(\frac{\sigma+\Sigma}{2}\right)$$

The final form of the microscopic "forces" appearing in (84) is

$$\mathscr{F}_\mp=\sum_i\left(\frac{\sigma+\Sigma}{2}\right)^2\int d\hat{\sigma}\,2m(\mathbf{v}_i\cdot\hat{\sigma})^2\,\theta(\mp\mathbf{v}_i\cdot\hat{\sigma})\hat{\sigma}\,\delta\left(\mathbf{R}-\left(\frac{\sigma+\Sigma}{2}\right)\hat{\sigma}-\mathbf{r}_i\right) \tag{85}$$

8. DISCUSSION

The main result of this paper is the derivation of the Fokker–Planck equation governing the evolution of the distribution function of a single heavy particle in a hard-sphere fluid from the exact hard-sphere hierarchy of kinetic equations for the total system (Brownian particle and bath particles). The derivation is based on a multiple-time-scale analysis, already used by Cukier and Deutch[6] for the case of continuous interactions between all particles of the system. Although similar in spirit, the present derivation is technically more involved, due to the singular nature of the hard-sphere dynamics. A byproduct of our calculation is an exact expression for the friction coefficient ζ, which, within our perturbative analysis, naturally splits into two contributions

$$\zeta=\zeta_1+\zeta_2 \tag{86}$$

which are of quite different nature. The term ζ_1, which, according to Eq. (83), is proportional to the equilibrium fluid density at contact with the Brownian particle, $\rho^{eq}((\sigma+\Sigma)/2)$, corresponds to the prediction of Enskog's kinetic theory.[13] The term ζ_2, given by (84), involves dynamical correlations between time-displaced momentum transfers absorbed by the Brownian particle from the equilibrium fluctuations of the suspending fluid. Both terms are seen to be proportional to Σ^2, while, according to Stokes' law, valid for large Σ, the sum should be proportional to Σ, indicating a large degree of cancellation between both contributions; this will be explicitly apparent in the second paper of this series. The formulas are valid for any size ratio Σ/σ, provided the Brownian particle is much heavier than the bath particles, since the derivation is valid in the limit $(m/M)^{1/2} \to 0$. The evaluation of the Enskog contribution ζ_1 requires the knowledge of the equilibrium fluid density at contact ρ^{eq}, i.e., of the contact value of the distinct pair distribution function in a binary mixture of σ and Σ spheres, in the infinite-dilution (tracer) limit of the large spheres. This is readily available, e.g., from scaled particle theory.[15] An evauation of the dynamical contribution, which accounts for correlated collision events not included at the Enskog level of approximation, requires a calculation of the equilibrium time correlation function appearing in the Kubo integral of equation (84). An "exact" calculation of this function can only be achieved by molecular dynamics simulations, provided finite-size effects are handled correctly. Such a calculation will be the object of the second paper of this series.

APPENDIX

The expansion of the collision operator $\bar{T}^{\varepsilon}_{-}$, defined in Eq. (20), in powers of ε requires a similar expansion of the operator $b^{\varepsilon}_{\hat{\sigma}}$, defined via Eq. (21). In the subsequent analysis, we shall make use of the expansion of this operator in powers of ε,

$$b^{\varepsilon}_{\hat{\sigma}}(B, 1) = b^{(0)}_{\hat{\sigma}}(B, 1) + \varepsilon b^{(1)}_{\hat{\sigma}}(B, 1) + \cdots \tag{A.1}$$

To zeroth order in ε

$$[b^{(0)}_{\hat{\sigma}}(B, 1)\chi](\mathbf{U}, \mathbf{u}_1) = \chi(\mathbf{U}, \mathbf{u}_1 - 2(\hat{\sigma}\cdot\mathbf{u}_1)\hat{\sigma}) \tag{A.2}$$

where χ is any function of the reduced velocities $\mathbf{U}$ and $\mathbf{u}_1$. The operator $b^{(0)}_{\hat{\sigma}}$ thus describes the effect of collisions of the fluid particles with the Brownian particle of infinite mass (particle B acts here as a fixed external field).

The first-order correction $b_{\hat{\sigma}}^{(1)}(B, 1)$ acts according to the formula

$$[b_{\hat{\sigma}}^{(1)}(B, 1)\chi](\mathbf{U}, \mathbf{u}_1) = 2\left\{(\hat{\sigma}\cdot\mathbf{u}_1)\hat{\sigma}\cdot\frac{\partial}{\partial\mathbf{U}} - (\hat{\sigma}\cdot\mathbf{U})\hat{\sigma}\cdot\frac{\partial}{\partial\mathbf{u}_1}\right\}$$
$$\times\chi(\mathbf{U}, \mathbf{u}_1 - 2(\hat{\sigma}\cdot\mathbf{u}_1)\hat{\sigma}) \tag{A.3}$$

Combination of Eqs. (A.2) and (A.3) with Eq. (20) leads to the first two terms of the ε-expansion of the binary collision operator $\bar{T}_{-}^{\varepsilon}(B, 1)$,

$$\bar{T}_{-}^{\varepsilon}(B, 1) = \bar{T}_{-}^{(0)}(B, 1) + \varepsilon\bar{T}_{-}^{(1)}(B, 1) + \cdots \tag{A.4}$$

One finds

$$\bar{T}_{-}^{(0)}(B, 1) = \left(\frac{1+\kappa}{2\kappa}\right)^2 \int d\hat{\sigma}\,(-\mathbf{u}_1\cdot\hat{\sigma})\,\theta(-\mathbf{u}_1\cdot\hat{\sigma})$$
$$\times\left\{\delta\left(\mathbf{X} - \left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma} - \mathbf{x}_1\right) b_{\hat{\sigma}}^{(0)}(B, 1)\right.$$
$$\left. - \delta\left(\mathbf{X} + \left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma} - \mathbf{x}_1\right)\right\} \tag{A.5}$$

$$\bar{T}_{-}^{(1)}(B, 1) = \left(\frac{1+\kappa}{2\kappa}\right)^2 \int d\hat{\sigma}\,(\mathbf{U}\cdot\hat{\sigma})\,\theta(-\mathbf{u}_1\cdot\hat{\sigma})$$
$$\times\left\{\delta\left(\mathbf{X} - \left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma} - \mathbf{x}_1\right) b_{\hat{\sigma}}^{(0)}(B, 1)\right.$$
$$\left. - \delta\left(\mathbf{X} + \left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma} - \mathbf{x}_1\right)\right\}$$
$$+\left(\frac{1+\kappa}{2\kappa}\right)^2 \int d\hat{\sigma}\,2(-\mathbf{u}_1\cdot\hat{\sigma})\,\theta(-\mathbf{u}_1\cdot\hat{\sigma})$$
$$\times\delta\left(\mathbf{X} - \left(\frac{1+\kappa}{2\kappa}\right)\hat{\sigma} - \mathbf{x}_1\right)$$
$$\times\left\{(\hat{\sigma}\cdot\mathbf{u}_1)\,\hat{\sigma}\cdot\frac{\partial}{\partial\mathbf{U}} - (\hat{\sigma}\cdot\mathbf{U})\,\hat{\sigma}\cdot\frac{\partial}{\partial\mathbf{u}_1}\right\} b_{\hat{\sigma}}^{(0)}(B, 1) \tag{A.6}$$

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