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Kinetic-Theory Derivation of the Stokes-Einstein Law*

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We employed repeated-ring kinetic theory incorporating the equilibrium correlations in a dense fluid to study Brownian motion. It is demonstrated that the theory predicts the Stokes-Einstein law relating the diffusion coefficient of a Brownian particle to its radius and the fluid shear viscosity. In addition, the correct long-time behavior ($t^{-3/2}$) of the velocity autocorrelation function is obtained.

The diffusion coefficient D of a large spherical Brownian particle of radius $R_B = \frac{1}{2}\sigma_B$ immersed in a fluid with coefficient of shear viscosity η and temperature T obeys the Stokes-Einstein law[1]

$$D = kT/6\pi\eta R_B, \tag{1}$$

where k is Boltzmann's constant. In the derivation of Eq. (1), the Brownian particle is assumed to be sufficiently large that the host fluid (the bath) can be treated as a continuous medium and can thus be described by the linearized Navier-Stokes equation of hydrodynamics. The solution of this equation with the boundary condition that the fluid sticks to the sphere's surface leads to Eq. (1). However, recent investigations[2] demonstrate that the Brownian particle need not have macroscopic dimensions for the functional form of Eq. (1) to hold.

The purpose of this Letter is to present a kinetic theory that leads to the Stokes-Einstein law for a Brownian particle which is larger than the bath particles but still of microscopic size. It has been shown that a kinetic theory including contributions from two successive correlated binary collisions (the "ring" terms) in addition to uncorrelated (Enskog) collisions provides a good description of the dynamics of the one-component, hard-sphere fluid.[3,4] However, to describe the motion of a Brownian particle of diameter σ_B and mass m_B in a fluid of bath particles with effective hard-core diameter σ_b and mass m_b when $\sigma_B > \sigma_b$, contributions from three or more successive correlated binary collisions (i.e., repeated "ring" terms[5]) must also be included. Simple arguments dictate that this be the case. At liquid densities, the bath-particle mean free path l_b is such that $l_b \lesssim \sigma_b$, so that one can have $l_b \ll \sigma_B$. Consequently, a typical bath particle may experience a large number of correlated collisions with the larger Brownian particle. We propose a repeated-ring kinetic theory which incorporates successive correlated binary collisions and also includes the exact equilibrium (static) correlations in the fluid (essential at liquid densities). This kinetic theory is shown to predict the Stokes-Einstein form for the Brownian-particle diffusion coefficient as well as the accepted long-time behavior of the Brownian-particle velocity autocorrelation function.

Of central interest to the theory are the Brownian-particle phase-space density $f^B(1) = \sqrt{N}\delta(1 - q_B)$ and the bath-particle phase-space density

$$f^b(\bar{1}) = \sum_{j=2}^{N} \delta(\bar{1} - q_j).$$

Here, 1 and $\bar{1}$ represent the field points $(\vec{r}_1, \vec{p}_1)$ and $(\vec{r}_{\bar{1}}, \vec{p}_{\bar{1}})$, respectively, q_j the phase-space co-

ordinates $(\vec{r}_j, \vec{p}_j)$ of the jth particle, and N the total number of particles. The time-dependent Brownian-particle and bath density correlation functions are defined, respectively, as

$$C^B(12,t) = \langle \delta f^B(2) e^{iLt} \delta f^B(1) \rangle_0,$$

and

$$C^b(\bar{1}\bar{2},t) = \langle \delta f^b(\bar{2}) e^{iLt} \delta f^b(\bar{1}) \rangle_0, \quad (2)$$

where L is the Liouville operator of the system, $\langle \ldots \rangle_0$ represents the equilibrium average, and $\delta A = A - \langle A \rangle_0$. The Laplace transform of $C^B(12,t)$ is $C^B(12) = -i\int_0^\infty dt \exp(ist) C^B(12,t)$, with $\mathrm{Im}s > 0$.

Guided by the manner[3] in which the equilibrium correlations in a dense fluid are systematically incorporated into ring kinetic theories[3,4] we assume that the Brownian-particle correlation function satisfies the analogously generalized repeated-ring kinetic equation of Ernst and Dorfman.[5] Thus, our kinetic equation has the form

$$[s - L_0^B(1)]C^B(12) - \int d3\,[\Lambda^B(13) + R^B(13)]C^B(32) = C^B(12, t=0), \quad (3)$$

where $L_0^B(1) = -i\vec{p}_1 m_B \cdot \nabla_{r_1}$, and Λ^B and R^B are, respectively, the Enskog and "generalized repeated-ring" memory functions:

$$\Lambda^B(13)\varphi_0^B(p_3) = n_b \int d4\,d\bar{4}\,\varphi_0^B(p_4)\varphi_0^b(p_{\bar{4}})\delta(14)T_E^{Bb}(4\bar{4})\delta(34), \quad (4)$$

and

$$R^B(13)\varphi_0^B(p_3) = n_B^{-1}\int d4\,d\bar{4}\,d5\,d\bar{5}\,d6\,d\bar{6}\,\delta(15)[T_E^{Bb}(5\bar{5})]^t \times \{[s - L_0^{Bb}(5\bar{5}) - T_E^{Bb}(5\bar{5})]\delta(56)\delta(\bar{5}\bar{6}) - \Lambda^B(56)\delta(\bar{5}\bar{6}) - \Lambda^b(\bar{5}\bar{6})\delta(56)\}^{-1} \times C^B(64, t=0)C^b(\bar{6}\bar{4}, t=0)T_E^{Bb}(4\bar{4})\delta(34). \quad (5)$$

In Eqs. (4) and (5) the Brownian- and bath-particle number densities are $n_B = 1/V$ and $n_b = (N-1)/V$, with V the volume of the system, and $\varphi_0^B(p_3)$ is the Maxwellian momentum distribution function. $T_E^{Bb}(4\bar{4})$ is the Enskog collision operator. Henceforth we will assume that the bath particles are also hard spheres so that $T_E^{Bb}(4\bar{4})$ is the low-density hard-sphere collision operator multiplied by the species-dependent radial distribution function evaluated at contact, $g^{Bb}(\sigma^{Bb})$, where $\sigma^{Bb} = \frac{1}{2}(\sigma_B + \sigma_b)$. Finally, the bath-particle memory function Λ^b is the sum of the mean-field memory function (involving the direct correlation function) and the bath-particle Enskog memory function (a simple generalization of Λ^B).

The interpretation of this kinetic equation is as follows. Λ^B represents contributions from uncorrelated binary collisions. Expanding the repeated-ring term about $T_E^{Bb}(5\bar{5})$ we have

$$R^B(13)\varphi_0^B(p_3) = n_B^{-1}\int d4\,d\bar{4}\,d5\,d\bar{5}\,\delta(15)[T_E^{Bb}(5\bar{5})]^t \times \{G_E^{BbBb}(5\bar{5};4\bar{4}) + \int d6\,d\bar{6}\,d7\,d\bar{7}\,G_E^{BbBb}(5\bar{5};6\bar{6})[G_E^{BbBb}(6\bar{6};7\bar{7}, t=0)]^{-1} \times T_E^{Bb}(7\bar{7})G_E^{BbBb}(7\bar{7};4\bar{4}) + \ldots\}T_E^{Bb}(4\bar{4})\delta(34), \quad (6)$$

with

$$G_E^{BbBb}(5\bar{5};4\bar{4}) = -i\int_0^\infty dt\, e^{ist} C_E^B(54,t)C_E^b(\bar{5}\bar{4},t). \quad (7)$$

C_E^B and C_E^b are the correlation functions calculated in the Enskog approximation, and t represents the transpose operation. Clearly, R^B includes the contributions from two or more correlated collisions. Consider the term in Eq. (6) with n T_E^{Bb} operators. It describes processes in which first the Brownian particle and another particle j undergo an "Enskog" collision (T_E^{Bb}). They then travel independently of one another (G_E) interacting with the rest of the bath via Enskog collisions. After some time, the Brownian particle again collides with particle j (T_E^{Bb}) or with some particle i which has collided with particle j since the Brownian-particle–j-particle collision. This process continues until there have been n such correlated binary collisions.

The Brownian particle's diffusion coefficient is the $s \to i0+$ limit of its velocity autocorrelation function $\psi_v^B(s)$. For the generalized repeated-ring kinetic theory

$$\psi_v^B(s) = (kT/m_B)[s - \Lambda(s) - R(s)]^{-1}. \quad (8)$$

Here we have assumed that Λ^B and R^B are "diagonal" on p_{1z} such that $R(s)$ is the following momentum

matrix element of R^B:

$$R(s) = (m_B/kTV)\int d1\,d3\; p_{1z} R^B(13)\varphi_0{}^B(p_3)p_{3z}\,. \tag{9}$$

A similar expression holds for $\Lambda(s)$. For the hard-sphere model, $\Lambda(s)$ is independent of s and given as $\Lambda(s) = -i\lambda$, where

$$\lambda = \tfrac{8}{3} n_b (\sigma^{Bb})^2 g^{Bb}(\sigma^{Bb})[2\pi m_b kT/m_B(m_b+m_B)]^{1/2}\,. \tag{10}$$

We have carried out an analysis for the *generalized repeated-ring term* $R(s)$ analogous to procedures recently[3,4] used for the ring term [the first term in the expansion of Eq. (6) for R^B]. One proceeds term by term in (6) as follows. First one introduces the spatial Fourier representations of the correlation functions in Eq. (6); this introduces intermediate wave vectors, $q, q', \ldots$. The laboratory z components of $\vec{p}_1$ and $\vec{p}_3$ in Eq. (9) are then expressed in the appropriate wave-vector reference frame. One then uses kinetic modeling procedures to express $C_E{}^B(\vec{q},\vec{p}_5,\vec{p}_4;t)$ and $C_E{}^b(-\vec{q},\vec{p}_{\bar{5}},\vec{p}_{\bar{4}};t)$ in terms of correlation functions of conserved variables (those which persist for long times).

For a large, but still microscopic, Brownian particle, the analysis of the generalized repeated-ring kinetic equation is much easier than for a one-component system. We find that if $\sigma_B > \sigma_b$, the coupling of the Brownian-particle momentum to the conserved variable modes via $C_E{}^b$ is dominated by the transverse current correlation function $V_\perp{}^b(-\vec{q},t)$. The analogous coupling $C_E{}^B$ is through the self-part of the dynamic structure factor $S_s{}^B(\vec{q},t)$. This simplifies the memory function such that, for $|s| \ll \lambda$,

$$\Lambda(s)+R(s) = -i\lambda + R_1(s) + R_1(s)(-i\lambda)^{-1}R_1(s) + \ldots = -i\lambda[1+R_1(s)/i\lambda]^{-1}, \tag{11}$$

where $R_1(s)$ is the ring contribution

$$R_1(s) = i(n_b/3\pi)\int_0^\infty dt\, e^{ist}\int_0^\infty dq\, q^2 |B^{Bb}(q)|^2 S_s{}^B(q,t)\mathcal{V}_\perp{}^b(-q,t). \tag{12}$$

In Eq. (12), $B^{Bb}(q)$ is a momentum matrix element of the collision operator $T_E{}^{Bb}$. In terms of the spherical Bessel function j_1,

$$B^{Bb}(q) = i3\lambda/n_b(m_B/m_b)^{1/2} j_1(q\sigma^{Bb})/q\sigma^{Bb}\,. \tag{13}$$

The calculation of $R_1(s)$ is also simplified by the size of the Brownian particle. The factor $q^2|B^{Bb}(q)|^2$ in Eq. (12) effectively cuts off the q integration when $q\sigma^B{}_b{}^b \sim 4$. Thus, for $l_b \ll \sigma_B$ the significant contributions to the q integration come from the range $0 \leq q l_b \ll 1$. Consequently, the product $S_s{}^B\mathcal{V}_\perp{}^b$ can, for the long times, be replaced by its hydrodynamic form with frequency- and wave-vector-independent transport coefficients. Also, at short times, the restriction $0 \leq q l_b \ll 1$ implies $S_s{}^B\mathcal{V}_\perp{}^b \sim 1$ over the q integration. This condition is satisfied by the hydrodynamic form of $S_s{}^B\mathcal{V}_\perp{}^b$. To summarize, the large size of the Brownian particle introduces a wave-vector cutoff in $R_1(s)$ such that only the long-time, small-wave-vector (hydrodynamic) forms of the intermediate propagations $S_s{}^B$ and $\mathcal{V}_\perp{}^b$ are required. Therefore, we make the approximation

$$S_s{}^B(q,t)\mathcal{V}_\perp{}^b(-q,t) \approx \exp[-q^2(D_E+\nu_E)t] \approx \exp(-q^2\nu_E t)\,, \tag{14}$$

where $D_E = kT/m_B\lambda$ and ν_E are, respectively, the Brownian-particle diffusion coefficient and the bath-particle kinematic viscosity in the hard-sphere Enskog approximation. In the second step of Eq. (14) we have noted that $\nu_E \gg D_E$ if $\sigma_B > \sigma_b$. Substituting Eq. (14) into Eq. (12), we are able to evaluate $R_1(s)$ analytically.

The analytic expression for $R_1(s)$ is substituted in Eq. (11) and the resultant momentum matrix element of the memory function is used in Eq. (8) to determine $\psi_v(s)$. We find that the velocity autocorrelation function has the accepted long-time asymptotic form[6]

$$\lim_{t\to\infty} \psi_v{}^B(t) \sim \tfrac{2}{3}(kT/m_b n_b)(4\pi\nu_E t)^{-3/2}, \tag{15}$$

and that the diffusion coefficient is given as

$$D = i\psi_v{}^B(s=i0+) = D_E + kT/5\pi\eta_E R_B\,. \tag{16}$$

In Eq. (16) the Enskog shear viscosity is $\eta_E = m_b n_b \nu_E$ and $R_B = \frac{1}{2}\sigma_B$. If $\sigma_B > \sigma_b$, it is readily demonstrated that the second term in Eq. (16) dominates the Enskog diffusion coefficient D_E. Thus, our generalized repeated-ring kinetic theory predicts the correct functional form of the Stokes-Einstein law, $D \propto kT/\eta_E R_B$.

It should be noted that in the long-time form of $\psi_v(t)$, Eq. (15), and in the Stokes-Einstein relation, Eq. (16), it is the Enskog value of the bath shear viscosity which appears in our theory, rather than its full hydrodynamic value.

Our kinetic theory predicts a factor $\frac{1}{5}$ in the

Stokes-Einstein law. Keyes and Oppenheim[7] have presented a hydrodynamic bilinear mode-coupling derivation based on the Mori formalism which also leads to a factor of $\frac{1}{5}$. A hydrodynamic calculation using the Navier-Stokes equation with "stick" boundary condition ("slip" boundary condition) for the fluid velocity at the surface of the Brownian particle predicts $\frac{1}{6}$ ($\frac{1}{4}$). It is intriguing that kinetic theory, which requires no boundary condition, yields a factor intermediate between these hydrodynamic extremes.

The generalized repeated-ring kinetic theory yields the same asymptotic behavior as the ring kinetic theory since the latter already includes the most divergent contribution. However, D, which requires the full time behavior of $\psi_v^B(t)$, satisfies the Stokes-Einstein relation only for the generalized repeated-ring theory. This suggests that the theory used here should be investigated as a theory of equilibrium time correlation functions in dense fluids.

Finally, we emphasize that the kinetic equation used here, while physically plausible, has not been derived for a dense fluid. We are currently investigating its derivation.

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Hamiltonian Expectation Values for Time-Dependent Foldy-Wouthuysen Transformations: Implications for Electrodynamics and Resolution of the External-Field πN Ambiguity

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Although the time-dependent Foldy-Wouthuysen (FW) transformation of the "Schrödinger" equation $i\partial\psi/\partial t = H\psi$ yields the transformed equation $i\partial\psi'/\partial t = H'\psi'$, where $\psi' = U\psi$ and $H' = UHU^{-1} - iU\partial(U^{-1})/\partial t$, the expectation values $(\psi_1, H\psi_j)$ of H are not equal to $(\psi_i', H'\psi_j')$, but rather, to $(\psi_i', UHU^{-1}\psi_j')$. But one still has $(\psi_i', \psi_j') = (\psi_i, \psi_j)$. I discuss implications for perturbation calculations, scattering amplitudes, electrodynamics, and the external-field πN ambiguity, and look at exact special cases.

In their classic paper,[1] Foldy and Wouthuysen (FW) showed that a relativistic time-dependent "Schrödinger" equation

$$i(\partial/\partial t)\psi = H\psi, \tag{1}$$

after undergoing a time-dependent unitary transformation U, is given by the Schrödinger equation (dot signifies $\partial/\partial t$)

$$i(\partial/\partial t)\psi' = H'\psi', \quad \psi' = U\psi, \tag{2}$$

$$H' = UHU^{-1} - iU\dot{U}^{-1}. \tag{3}$$

More specifically, Foldy and Wouthuysen were interested in starting with the external-field Dirac electromagnetic Hamiltonian

$$H = \gamma_0\vec{\gamma}\cdot(\vec{p} - e\vec{A}) + \gamma_0 m + eV, \tag{4}$$

and then using successive transformations to diagonalize H order by order in $1/m$ (in the sense of decoupling the positive-energy components from the negative-energy components). FW found that by using Eq. (3) they could transform the Dirac Hamiltonian to order $1/m^2$ into the generalized Pauli time-dependent Hamiltonian[1]

$$H_P = \gamma_0\left(m + \frac{(\vec{p} - e\vec{A})^2}{2m}\right) + eV - \frac{e}{2m}\gamma_0\vec{\sigma}\cdot\vec{B} - \frac{ie}{8m^2}\vec{\sigma}\cdot(\nabla\times\vec{E}) - \frac{e}{4m^2}\vec{\sigma}\cdot(\vec{E}\times\vec{p}) - \frac{e}{8m^2}\nabla\cdot\vec{E}, \tag{5}$$