

NON-HYDRODYNAMIC CONTRIBUTION TO THE CONCENTRATION DEPENDENCE OF THE SELF DIFFUSION OF INTERACTING BROWNIAN MACROPARTICLES

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The generalized Langevin equation and the stationary requirement for an equilibrium system are used to calculate the modification of the self (tracer) diffusion coefficient by direct interactions. In the absence of hydrodynamics, this modification of D_s is equal to the previously predicted modification of the mutual-diffusion coefficient D_m by the same effect, though D_m is also modified by direct interactions in another way. The effect treated here may be viewed as being a change in the generalized Smoluchowski equation in which the free-particle diffusion coefficient D_0 is replaced by a dressed diffusion coefficient, and not as being a memory-function effect in the conventional generalized Smoluchowski equation.

1. Introduction

In a suspension of interacting brownian molecules, there are two operationally distinct, numerically unequal, diffusion coefficients. One of these, the mutual-diffusion coefficient, D_m , describes the relaxation of a concentration gradient. The other, the self-diffusion coefficient D_s , characterizes the motion of individual particles through a uniform solution. These coefficients have been argued [e.g., ref. [1]] to be related via the generalized Stokes–Einstein equation

$$D_m = D_s (\partial\pi/\partial c)_{\mu_0} \tau (1 - \phi) / K_B T, \quad (1)$$

where $(\partial\pi/\partial c)_{\mu_0} \tau$ is the osmotic compressibility, ϕ is the solute volume fraction, and K_B is Boltzmann's constant. For solutions of macromolecules in which D_m , D_s and τ may be obtained from quasi-elastic light scattering, tracer diffusion and equilibrium centrifugation studies respectively, eq. (1) agrees with experiment to better than 5% [2,3].

Recently, several theoretical studies have argued [4–6] that eq. (1) ought not be correct, in that there are physical effects which modify the self-diffusion coefficient but not the mutual-diffusion coefficient. One writes

$$D_s = K_B T / f_s, \quad D_m = (\partial\pi/\partial c)_{\mu_0} \tau (1 - \phi) / f_m. \quad (2)$$

For this discussion, it is convenient to divide all intermacromolecular forces into two types: the direct interactions (e.g. the hard-sphere potential) and the solvent-mediated, velocity-dependent, hydrodynamic interactions. In a model system with no hydrodynamic forces, it was predicted by Ackerson [4], Dieterich and Peschel [5], and Marqusee [6] that the friction factor f_s of the self-diffusion coefficient is modified by direct interactions. However, these workers found that direct interactions do not modify the friction factor f_m of the mutual-diffusion coefficient unless hydrodynamic interactions are present. In contrast, with a different approach this author has argued that direct interactions do modify f_m even if hydrodynamic

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interactions are absent [7]. If different effects contributed to f_c and to f_m , one would expect that f_c and f_m could not in general be equal, as is implied by eq. (1)

This recent work on the friction factors f should be contrasted with classical studies on the diffusion of brownian molecules [8], in which direct interactions were assumed to contribute the thermodynamic factor to D_m and provide the statistical weighting factor for the (distance-dependent) hydrodynamic interactions, but were assumed not to make a contribution separate from the hydrodynamic one to the friction factor f . (A historic exception is provided by the work of Mazo [9], who used the Kirkwood fluctuation-dissipation formula for f to compute the effect of a screened electrostatic interaction on f_c . Perhaps because this work was applied to the diffusion of micelles rather than covalently bonded polymers, it has largely been overlooked. More recently, Deulin [10] and this author [11] have treated the non-hydrodynamic contribution of direct interactions to the viscosity and the Stokes' law drag coefficient.)

The purposes of this paper are: first, to show that the previously obtained non-hydrodynamic contribution to f_m also appears in f_c and, second, to show that the results of refs [4-7,11] are in fact consistent with each other. Section 2 of this paper presents our general calculation, the results are discussed in section 3.

2. Method and calculation

Our approach is based on the generalized Langevin equation

$$Mdv_i(t)/dt = -fv_i(t) - \nabla_i W^N + F_i(t), \quad (3)$$

v_i being the velocity of particle i , f being its drag coefficient, W^N being the total potential energy of the macroparticles, and $F_i(t)$ being the fluctuating force on macroparticle i due to its interactions with the adjoining solvent molecules. F_i has some very short correlation time τ_H , which corresponds to the shortest times over which the drag force is described by the $-fv_i(t)$ term. τ_H should not be confused with the much longer time $\tau_B = m/f$ which is the relaxation time for the particle velocity. The distinction between τ_H and τ_B is treated in more detail by Rice and Gray [12]

Conventional experimental techniques, such as diaphragm diffusion and light-scattering spectroscopy, are limited to times $t \gg 10$ ns. Over these relatively long periods, the inertia of a brownian particle is negligible, so that eq. (3) may be rewritten

$$v_i(t) = v_{B,i}(t) + v_{I,i}(t), \quad (4)$$

where by definition $v_{I,i}(t) = -\nabla_i W^N / f$ and $v_{B,i}(t) = \overline{F_i(t)} / f$, the overstroke "—" denoting the effect of the fluctuating force F_i over a period sufficiently long that the frequency dependence of the drag coefficient f is unimportant. For an equilibrium system, stationarity appears to require that eq. (4) be equally valid at all times, including $t = 0$. It is sometimes [13] asserted that eq. (4) is not valid at $t = 0$, since the brownian particles require some initial time to achieve their drift velocity $v_{I,i}$. It is here preferred to assume that the system was created at some time $t \ll 0$, so the particles' drift velocities at $t = 0$ were attained during the moments before $t = 0$. This assumption requires that the interparticle forces change appreciably only over times much longer than τ_B , a condition which almost always obtains

The use of the form $-\nabla_i W^N$ to represent the intermacroparticle force implies that the interparticle potential is differentiable everywhere. This requirement is satisfied by any physical system, but not by a model hard-sphere suspension. However, if one views a hard sphere as a limiting case of a differentiable potential, and if f is large enough that the conditions of the previous paragraph are still satisfied, the results of this paper would still be relevant.

The work presented here rests on a careful analysis of the correlations between the brownian and

interactive velocities v_B and v_I at the same and different times. One often encounters the assertion that these velocities are always uncorrelated, because the interparticle force depends on the relative positions of the particles, while in the absence of hydrodynamic interactions the fluctuating solvent-solute force $F_I(t)$ is independent of the particle positions, so that

$$\langle v_{B_i}(t) v_{I_i}(\tau) \rangle = 0 \quad (5)$$

One does clearly have

$$\langle v_i(t) \rangle = \langle v_{B_i}(t) \rangle = \langle v_{I_i}(t) \rangle = 0 \quad (6)$$

(the brackets " $\langle \rangle$ " denoting an ensemble average) because the fluid as a whole has rotational isotropy. For the calculations below, one is interested in averages taken with a given initial configuration of the macroparticles, since v_{I_i} is only non-vanishing if one specifies the macroparticle configuration. An average over the positions and momenta of the solvent molecules for a fixed macroparticle configuration is a sub-ensemble average (hereinafter denoted " $\overline{\quad}$ ") over a part of the system's canonical ensemble

From time reversal invariance,

$$\overline{v_i(t)} = 0, \quad \overline{v_{I_i}(t)} = -\nabla_i W^\lambda. \quad (7)$$

On combining eqs. (7) and (4), there follows the surprising result

$$\overline{v_{B_i}(t)} = \overline{v_{I_i}(t)} = \nabla_i W^\lambda / f. \quad (8)$$

Eq (8) at first sight seems inconsistent with the statistical independence of the particle positions and the random force $F_I(t)$. A proper interpretation of a result equivalent to eq (8) was first presented by Batchelor [14]. As the explanation is somewhat involved, we first show in general how a non-uniform particle density leads at later times to correlations between particle positions and particle brownian velocities. The discussion will then be specialized to the case of a solution of interacting brownian particles. Consider the set of particles which at time t lie in some surface S . Since their velocity-velocity correlation time has the non-zero value τ_B , at a time $t - \epsilon$, $\epsilon \ll \tau_B$, the particles must have been located away from S by distances of order $-\epsilon v$. Thus, particles in S at time t , which are moving to the left, must at $t - \epsilon$ have been found to the right of S , and vice versa. If at $t - \epsilon$ each particle had an equal likelihood of having a leftwards or rightwards velocity, and if at $t - \epsilon$ the densities of particles on the left and right sides of S were equal, then at time t one would expect an isotropic distribution of velocities for the particles lying within S . Contrarywise, if at time $t - \epsilon$ each particle had an equal likelihood of having a leftwards or rightwards velocity, but if at $t - \epsilon$ there were more particles on one side of S than on the other, then at time t one would find a net flux of particles within S : particles would be found moving from the region of higher concentration to the region of lower concentration more often than in the other direction. A non-uniform position distribution at $t - \epsilon$, even when coupled to an isotropic velocity distribution at $t - \epsilon$, results in a non-isotropic velocity distribution at a later time t .

In a suspension of interacting brownian particles, the N -particle spatial-distribution function is not a constant; rather, the likelihood of finding a pair of particles some distance apart is determined by the Boltzmann factor $\exp(-\beta W^\lambda)$. If the particle density around some point is non-uniform, then at later times τ , $t < \tau < \tau_B$, the brownian velocities v_B will become correlated with the initial non-uniformities in the particle density. The points where the particle density gradients are non-zero, and hence where the particle positions and brownian velocities are correlated, are precisely the points where W^λ is non-vanishing. From the second equation of (7), these are also precisely the points where the interactive velocity v_I is non-zero. A quantitative relation between the interactive velocity and the sub-ensemble average brownian velocity then follows either from a detailed calculation or from stationarity. If the Boltzmann statistical weight is to be independent of time, the rate at which the interactive velocity creates concentration gradients must exactly

cancel the rate at which the sub-ensemble average brownian velocity relaxes those same concentration gradients, as will occur if eq. (8) is correct.

In applying this argument to a solution of interacting particles, one must require that the surface S moves with the local drift velocity v_1 . In the argument of the preceding paragraph, one might be tempted to say that one has a "non-equilibrium" distribution for the brownian velocity because one first had a "non-equilibrium" density distribution for the particles. However, this paper is concerned only with equilibrium systems. Properly speaking, eq. (8) gives an equilibrium correlation between macroparticle positions and the brownian component of the macroparticle velocity

Several other properties of the brownian velocity are worth noting. As has been emphasized by Pusey [15] in a dilute system $v_1(t)$ [and therefore, from our arguments, also $\overline{v_B(t)}$] is much less than $v_B(t)$, so if one writes

$$v_B(t) = \overline{v_B(t)} + \delta v_B(t), \quad (9)$$

in general $v_B(t) \approx \delta v_B(t)$. For non-interacting particles in the absence of an external potential, $\overline{v_B(t)} = 0$ and $v_B(t) = \delta v_B(t)$. Furthermore, from eq. (4) v_B is defined to be the difference between the total velocity of the particle (which is odd under time reversal) and the interactive velocity of the particle (which is defined in terms of the particle positions, and hence is even under time reversal), so $v_B(t)$ is a variable without definite time reversal parity.

Having exhibited the correlation between the brownian and interactive velocities, the self-diffusion coefficient of a suspension of interacting brownian particles is now calculated. The self (tracer) diffusion coefficient D_s describes the motion of labelled solute molecules through a background of unlabelled but otherwise identical solute molecules, the experiment being so arranged that the total concentration of solute molecules is everywhere the same. D_s may be related to the ensemble average displacement r of a typical labelled solute molecule during the time interval Δt

$$6D_s\Delta t = \langle |r|^2 \rangle. \quad (10)$$

If Δt is too small, or so large that the increase in $|r|^2$ is obstructed by the walls of the container, D_s is no longer a simple constant. Since r is the integral of the particle velocity $v(t)$, one has

$$6D_s t = \left\langle \int_0^t ds_1 \int_0^{s_1} ds_2 v(s_2) \right\rangle. \quad (11)$$

The velocity correlation function in (11) depends only on the time interval $t = s_2 - s_1$. Substitution of eq. (4) into eq. (11) gives

$$D_s = \frac{1}{6} \left\langle \int_{-t}^t d\tau [v_1(0) \cdot v_1(\tau) + v_1(0) \cdot v_B(\tau) + v_B(0) \cdot v_1(\tau) + v_B(0) \cdot v_B(\tau)] (1 - |\tau|/t) \right\rangle. \quad (12)$$

Here the low-frequency ($t \rightarrow \infty$) limit is considered. Substitution of eqs. (4), (8) and (9) into (12) leads to

$$D_s = \frac{1}{6} \left\langle \int_{-\infty}^{\infty} d\tau v_1(0) \cdot v_1(\tau) + \int_{-\infty}^0 d\tau v_1(0) \cdot v_B(\tau) - \int_0^{\infty} d\tau v_B(0) \cdot v_B(\tau) + \int_{-\infty}^{\infty} d\tau [-v_1(0) \cdot v_1(\tau) + \delta v_B(0) \cdot v_1(\tau) + v_B(0) \cdot v_B(\tau)] \right\rangle. \quad (13)$$

In eq. (13), the first and fourth terms of the right-hand-side cancel. The third term has a correlation time τ_B ; since $\overline{v_B}$ is typically much less than v_B , the third term is negligible by comparison with the sixth. In interpreting the fifth term, the induced flow of the solute does not result in stress fluctuations in the solvent, so this term must vanish for $\tau < 0$. The inverse does occur; brownian motion can move particles into configurations in which $v_1 \neq 0$. The fifth term therefore does not vanish for $\tau > 0$, time translation

invariance permits a merger of the second and fifth terms. Invoking the definition (2) of f_s in terms of D_s , one finds

$$D_s \equiv \frac{k_B T}{f_s} = \frac{1}{6} \left\langle \int_{-\infty}^{\infty} \mathbf{v}_B(0) \cdot \mathbf{v}_B(t) dt + 2 \int_{-\infty}^0 dt \mathbf{v}_B(t) \cdot \mathbf{v}_1(0) \right\rangle. \quad (14)$$

From the usual theory of brownian motion for particles without hydrodynamic interactions,

$$6D_0 = \left\langle \int_{-\infty}^{\infty} \mathbf{v}_B(0) \cdot \mathbf{v}_B(t) dt \right\rangle, \quad (15)$$

so

$$D_s = D_0 \left[1 + \frac{2}{D_0} \int_{-\infty}^0 dt \langle \mathbf{v}_B(t) \cdot \mathbf{v}_1(0) \rangle \right]. \quad (16)$$

The final integral in eq (16) represents the modification of the self-diffusion coefficient by direct interactions. This integral is identical to the one previously obtained in ref. [7] for the modification of the friction factor of the mutual-diffusion coefficient by direct interactions. For the specific case of particles with a weak gaussian interaction such that their radial distribution function $g(r)$ is

$$g(r) = 1 + B_0 \exp(-r^2/r_0^2)/8\pi^{3/2}, \quad (17)$$

it was found that

$$\left\langle 2 \int_{-\infty}^0 dt \mathbf{v}_B(t) \cdot \mathbf{v}_1(0) \right\rangle = -0.3917 D_0 \phi_T [g(0) - 1/8\sqrt{2}]. \quad (18)$$

where $\phi = cV$, c is the macroparticle number concentration, $V = 4|B_0|r_0^3$ is the effective volume of a particle. B_0 is an interaction strength parameter, and r_0 is an effective range for the interaction. [The dispute between ref. [7] and refs. [4–6] over the modification of f_m by direct interactions could be said to involve a disagreement as to whether that modification is given by the final integral in eq (16) or by the similar form

$$\sum_{i,j=1}^N \int_{-\infty}^0 dt \mathbf{v}_{B_i}(t) \cdot \mathbf{v}_{1_j}(0), \quad (19)$$

the double sum being over all N particles in the system. This double sum may be argued to vanish identically. If (19) were the correct form, it would appear that direct interactions would not modify f_m . It is not presently disputed that eqs. (16) and (17) lead to eq. (18).]

3. Discussion

In the above, a Langevin-type approach has been used to calculate the contribution of direct interactions to the self-diffusion coefficient D_s . It was found that direct interactions lead to a concentration dependence of D_s even if there are no hydrodynamic forces present. This result is in qualitative agreement with the results of Mazo [9] and Marqusee and Deutch [16], who found from fluctuation–dissipation and Mori theory arguments that direct interactions lead to a concentration dependence of D_s even if hydrodynamic forces are not considered. Our results differ from those presented previously in that this paper used a Langevin-type approach, similar to that used by Pusey and Tough [13], rather than the generalized Smoluchowski equation

$$\partial P(\mathbf{r}^N, t) / \partial t = \sum_i \left[D_0 \nabla_i^2 - \nabla_i \cdot \mathbf{F}_i / f \right] P(\mathbf{r}^N, t). \quad (20)$$

A qualitative image of the mechanism whereby direct interactions reduce the self-diffusion coefficient may be of some interest. In the absence of direct interactions, the Langevin model indicates that each particle is acted on by a drag force $-fv$ and a fluctuating force $F_i(t)$. If one adds direct interactions between neighboring brownian macroparticles, a brownian particle i which attempts to move a substantial distance suffers encounters with its neighbors. Through these encounters, the fluctuating force F_i on the moving particle is effectively dispersed over some number n of neighbors, so that the particle motion is opposed by a drag coefficient $\approx nf$, reducing the displacement of the particle from the displacement which it would have experienced if direct interactions had not been present. This resistance to the motion of a particle is rather like the "cage model" of Pusey [15]. By symmetry, particle i , while dispersing the force F_i of itself over n neighbors, will also on the average receive a fraction $1/n$ of the random forces $F_1 \dots F_n$ on each of its neighbors. Since the random forces $F_1 \dots F_n, F_i$ are uncorrelated, the total force on particle i grows only as $n^{1/2}$, in contrast to the total drag coefficient, which is proportional to n^1 . The self-diffusion coefficient D_i depends on the mean-square ratio of the force to the drag coefficient, so one qualitatively predicts $D \approx n^{-1}$. For the special case in which the "interparticle" interaction is a covalent bond, this prediction is exact. In the absence of hydrodynamic interactions, the diffusion coefficient of an n -mer is expected to be precisely $1/n$ of the diffusion coefficient of the corresponding monomer.

An alternative explanation for part of the failure of refs. [4-6] to identify any contribution of direct interactions to f_m may lie in the calculational basis used in some of that work. Refs [4-6] are in part based on the generalized Smoluchowski equation (20). The generalized Smoluchowski equation was originally used to calculate the diffusion of macroparticles in the presence of rigid walls and constant external potentials, as encountered, e.g. in the sedimentation problem [17]. In these original papers, the movement of a given brownian particle has no effect on the position of walls or the spatial dependence of the external potential, so the walls and potentials were fixed and determinate. In a solution of interacting brownian particles, the motion of each particle can affect the motions of the other particles, so that the potential encountered by a diffusing particle is not a determinate function of that particle's path in space. The consequences of this difference may be seen by calculating the initial slope of the dynamic structure factor $S(k, t)$ measured by light-scattering spectroscopy, either by using the generalized Smoluchowski equation

$$\left. \frac{dS(k, t)}{dt} \right|_{t \rightarrow 0} = \left\langle \frac{1}{N} \sum_{i,j=1}^N \exp\{ik \cdot [r_i(0) - r_j(0)]\} (-D_0 k^2 - ik \cdot \nabla_i W \setminus / f) \right\rangle, \quad (21)$$

or by using the Langevin equation

$$\left. \frac{dS(k, t)}{dt} \right|_{t \rightarrow 0} = \left\langle \frac{1}{N} \sum_{i,j=1}^N \exp\{ik \cdot [r_i(0) - r_j(0)]\} \times \left[-k^2: \int_0^t [v_{B_i}(s) v_{B_i}(t) + v_{B_i}(s) v_{i_i}(t)] ds + ik \cdot v_{i_i}(t) \right] \right\rangle. \quad (22)$$

Eq. (22) is the same as eq. (20) or ref. [7]. These equations would agree with each other if one had

$$D_0 k^2 = \int_0^t ds [k \cdot v_{B_i}(s) k \cdot v_{B_i}(t) + k \cdot v_{B_i}(s) k \cdot v_{i_i}(t)]. \quad (23)$$

However, in eq (21) D_0 has consistently been interpreted as the bare diffusion coefficient of eq. (15), while from (23) one concludes that the D_0 of the generalized Smoluchowski equation is properly a "dressed" diffusion coefficient, in which the direct interactions have perturbed the diffusion rate. Calculations based on the generalized Smoluchowski equation and the identification of D_0 as the free-particle diffusion coefficient should therefore predict that the effect treated here does not contribute to f_m .

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