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LETTER TO THE EDITOR

The dynamics of Brownian particles

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Abstract. The recent result of Pusey for the initial decay of the temporal correlation function of the K th spatial Fourier component of particle number density in a dilute solution of Brownian particles is re-examined for the case where the friction coefficient is frequency dependent and given by a hydrodynamical model. For the conditions realized in recent light scattering experiments it is shown that there is a small, but not dramatic, quantitative difference between our results and his.

Pusey (1975) has recently presented a theoretical discussion of a particular facet of the interesting light scattering experiments carried out by Brown *et al* (1975). A key approximation in his analysis is that at properly defined small times the motion of a Brownian solute particle is unaffected by the presence of the other solute particles. This leads to the following result:

$$\frac{d|g^{(1)}(K, \tau)|}{d\tau} = -\frac{K^2 D_0}{S(K)} \quad (1)$$

where $g^{(1)}(K, \tau)$ is the normalized field correlation function, K is the magnitude of the scattering vector, τ is the correlation delay time, $S(K)$ is the static structure factor, and D_0 is the diffusion coefficient at infinite dilution for the solute particles. This result is valid provided that $\tau_B \leq \tau \leq \tau_1$, where the lower bound is the translational Brownian motion relaxation time at infinite dilution and the upper bound is the time for a solute particle to diffuse some appreciable portion of the mean solute particle separation.

Equation (1) is contingent on the replacement of $\int_0^\tau dt' \phi(t')$ in a preceding equation by D_0 ; $\phi(t)$ is the solute particle velocity autocorrelation function at infinite dilution. The purpose of this letter is to suggest that despite the inequality $\tau_B \leq \tau$ this replacement is not strictly valid if the friction coefficient which describes the solute motion is frequency dependent (Hynes 1972). For the case where the solute motion is governed by the classical Langevin equation $\phi(t)$ decays exponentially with relaxation time τ_B , however when this motion is given by the generalized Langevin equation with memory function given by a hydrodynamical model (Hynes 1972) $\phi(t)$ decays much slower, as $t^{-3/2}$, and although for $\tau \rightarrow \infty$ the integral over $\phi(t)$ is equal to D_0 , as for the classical model, for finite τ this is no longer the case. Rather, for this hydrodynamical model a renormalization of D_0 in (1) occurs. An experiment under conditions for which this effect was sizeable could thus serve as a probe of the solute particle motion.

In the experiment of Brown *et al* (1975) $\tau > 10^{-8}$ s is imposed by instrumental considerations. Under the conditions of the experiment $\tau_B \sim 1.5 \times 10^{-10}$ s so that at

the smallest possible τ we have

$$\int_0^\tau dt' \phi(t') = \int_0^\tau dt' \phi(0) \exp(-t'/\tau_B) = \tau_B \phi(0) [1 - \exp(-10^2/1.5)]$$

which is indistinguishable from $\tau_B \phi(0)$. For the hydrodynamical model $\phi(t)$ is most simply defined by its Laplace transform $\tilde{\phi}(s)$ (Hynes 1972):

$$\tilde{\phi}(s) = \tau_B \phi(0) [1 + \alpha s^{1/2} + (\beta + \tau_B)s]^{-1} \quad (2)$$

with $\alpha = Rv^{-1/2}$, R the solute particle radius and v the kinematic viscosity of the solvent, and $\beta = (\alpha^2/9)$. Then we have

$$\int_0^\tau dt' \phi(t') = \mathcal{L}^{-1}(s^{-1}\tilde{\phi}(s)) = \tau_B \phi(0) \left(1 - \operatorname{Re} W(z) - \frac{\epsilon^{1/2}}{(1-\epsilon^2)^{1/2}} \operatorname{Im} W(z) \right) \equiv D_0(\tau) \quad (3)$$

where

$$\epsilon = \frac{\alpha}{2(\beta + \tau_B)^{1/2}}, \quad z = \frac{(1-\epsilon^2)^{1/2} + i\epsilon}{\beta + \tau_B} \tau$$

and $W(z)$ is a standard tabulated function (Abramowitz and Stegun 1964). For the hydrodynamical model D_0 in (1) must be replaced by $D_0(\tau)$; it is particularly in the initial stages of decay which (1) describes that these two quantities may differ appreciably. For the experimental conditions of Brown *et al* we find $D_0(10^{-8}) = 0.98D_0$ so that a dramatic effect does not in fact occur, and the classical Langevin model can be considered as valid. This is unfortunate from the point of view of utilizing the experiment as a probe of the solute particle motion, but from the point of view of extending the results of Pusey to higher-order effects in the concentration it is useful in that it indicates that models which ignore memory effects such as the Brownian model of Friedman (1964) can be used with confidence.

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