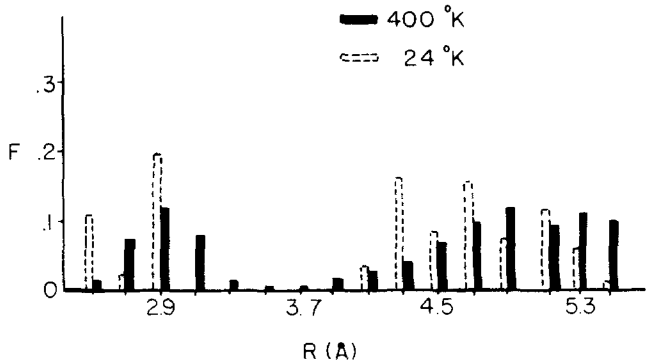

FIG. 3. The fraction (F) of bonds whose length is between r and $r+0.2$ Å.

was not obtained by Abraham[5] in his Monte Carlo simulations on octomers at 263.2° or 298 °K which proceeded from an initial ice configuration.

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Concentration dependence of the self-diffusion coefficient[a]

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We present a calculation of the first order concentration dependence of the self-diffusion coefficient for macroparticles in solution. This problem has been addressed by many authors as has the concentration dependence of the mutual diffusion coefficient.[1–10] The mutual diffusion coefficient D_m consists of two terms; thermodynamic and kinetic, i.e., the friction coefficient, while the self-diffusion coefficient D_s contains only a kinetic term.

Previous work on the concentration dependence of D_s has taken one of three approaches:[11] (1) Relating the two diffusion coefficients by considering a ternary mixture where two of the species differ in a trivial way.[1,4] The conclusion of these arguments which are based on irreversible thermodynamics is that D_s and D_m differ only by a thermodynamic factor. This is incorrect because it employs an argument that assumes a concentration independent friction coefficient.[12] This reasoning leads to the following conclusions; direct interactions alone produce no concentration dependence and the hydrodynamic interaction (in the Oseen approximation) coupled with the hard sphere interaction yields[13] $D_s = D_0\,(1-6\phi)$ where ϕ is the volume fraction of macroparticles and D_0 is the infinite dilution diffusion coefficient.

(2) Combined use of irreversible thermodynamics and a density expansion of the diffusion coefficient from the N-particle Smoluchowski equation[10] or its two-body hydrodynamic equivalent.[5] These arguments predict that neither direct interactions nor the Oseen tensor contribute to D_s. This is a consequence of the assumption that the configuration of macroparticles is effectively constant over the time that characterizes diffusion.

(3) Construction of an equation for the time evolution of the autocorrelation function by use of Mori's[14] projection operator technique on the N-particle Smoluchowski equation.[7,9] This approach yields a D_s which has a contribution from direct interactions and the Oseen tensor in the low frequency limit. These vanish at high frequency.[15]

Employing the techniques of the third approach we report explicit results for two simple models that are frequently used to describe macroparticles; hard spheres with and without the hydrodynamic interaction and screened Coulombic interactions.

First, we consider the role of direct interactions. They contribute an additional source of friction and thus lower D_s. The relative motion of the tagged particle and the surrounding macromolecules introduces a new fluctuating force which is not included in the second approach

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because of the assumption of essentially fixed particle configuration. This fluctuating force is driven by the diffusion process itself and thus decays on a time scale long compared to that of the solvent. By explicit calculation we determine the entire frequency dependence of the first order concentration dependence.

For a charged macroparticle the interaction can be approximated by

$$u(r)=u_0\frac{\exp(-\kappa r)}{r} \tag{1}$$

where κ is the Debye screening aonstant. Using a weak interaction approximation[7,9] that approximates the time evolution of the fluctuating force by the free diffusion propagator, we obtain[16]

$$D_s(\omega)=D_0\left\{1-\frac{(\beta u_0)^2\pi\rho}{3\kappa}\left[\frac{1+2\omega^{3/2}-3\omega}{(1-\omega)^2}\right]\right\} \tag{2}$$

where ρ is the density of macroions and $\omega=z/2D_0\kappa^2$. For hard spheres of diameter σ, we obtain,

$$D_s(\nu)=D_0\{1-\tfrac{4}{3}\,\phi[3I_{3/2}(\nu^{1/2})K_{3/2}(\nu^{1/2})]\} \tag{3}$$

where $I(K)$ is a modified bessel function and $\nu=z\sigma^2/2D_0$. In both expressions z is the frequency; the frequency dependent term in the square brackets approaches unity in the zero frequency limit.

Two points should be noted about the zero frequency results. First, the sign of the concentration correction is negative which is the opposite of the contribution these direct interactions make to D_m through the thermodynamic term.[3] Second, the correction for screened Coulombic interactions can be quite large even at low densities due to the large variation in κ that is possible. Thus, one can have a small enough volume fraction of macroions to justify ignoring the hydrodynamic interaction and still have a large concentration dependence due to direct interactions.

The frequency dependence for screened Coulombic and hard sphere interactions is determined by the dimensionless parameters ω and ν, respectively. Typical values[17] for the infinite dilution diffusion coefficient for macroparticles range from $D_0\simeq 10^{-6}$–10^{-8} cm^2 s^{-1}. The hard sphere diameter typically has values $\sigma\simeq 10^{-7}$–10^{-8} cm while the screening constant takes on a much wider range $\kappa\simeq 10^4$–10^8 cm^{-1}. For a hard sphere system the low frequency limit is reached for $z\ll 10^8$ s^{-1} but for screened Coulombic interactions depending on the size of κ, the low frequency region may range from $z\ll 1$ to 10^8 s^{-1}. Therefore, for hard sphere systems the frequency dependence is unimportant but for macroions it may be of considerable importance.

The Oseen tensor also contributes to the concentration dependence of D_s. Employing a weak interaction approximation, we have, to first order in the density the following contribution,[16]

$$\Delta D_H(k,z)=-\frac{\beta^2\rho}{(2\pi)^9k^2}\int\frac{d\mathbf{q}\,d\mathbf{q}'\,d\mathbf{q}''\,\mathbf{k}\cdot\hat{\mathbf{D}}(\mathbf{q}+\mathbf{q}')\cdot\mathbf{q}\hat{u}(q')\mathbf{k}}{z+D_0[q'^2+(\mathbf{k}-\mathbf{q}')^2]}\cdot[2D_0\mathbf{I}\,\delta(\mathbf{q}'-\mathbf{q}'')(2\pi)^3+\hat{\mathbf{D}}(\mathbf{q}''+\mathbf{q}')]\cdot\mathbf{q}''\hat{u}(q'') \tag{4}$$

where $\hat{\mathbf{D}}(\mathbf{q})$ and $\hat{u}(q)$ are the Fourier transform of the Oseen tensor and two body potential. In the low $\mathbf{k}$ and z limit, these integrals may be analytically reduced to a one-dimensional integral that must be numerically evaluated. Using Stokes' law for D_0, we obtain for hard spheres that $\Delta D_H=D_0\,1.26\,\phi$. The effect of the Oseen tensor is to reduce the concentration dependence of D_s. Combining the hydrodynamic result with the direct [Eq. (3)] we have

$$D_s=D_0(1-0.07\phi)\,. \tag{5}$$

Thus, in the Oseen approximation the self-diffusion coefficient has a very small concentration dependence due to the cancelling of direct and hydrodynamic contributions.

We see from these calculations that the assumptions behind either approach (1) or approach (2) are unjustified. Approach (2) ignores the fluctuating force due to the relative motion of the macroparticles, which may lead to a significant contribution for the case of macroions. Approach (1) has been commonly used in the analysis of experimental data.[18,19] However, there is no justification for equating the concentration dependence of the two friction coefficients and for the cases we have explicitly considered, they are not approximately equal.

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