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SELF DIFFUSION IN INTERACTING COLLOIDAL LIQUIDS

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Résumé - Nous avons mesuré le coefficient de diffusion $D_s$ propre de sphères monodisperses de polystyrène ionisées dans l'eau en utilisant la diffusion Rayleigh forcée. Nous avons observé une décroissance marquée de $D_s$, de la valeur caractéristique d'une seule particule, quand les interactions entre les particules augmentent. Nous avons également observé un saut d'au moins quatre ordres de grandeur de $D_s$ à la fusion (transition de l'1er ordre). Les valeurs obtenues sont en bon accord avec des relations phénoménologiques connues dans les liquides simples, la diffusion propre variant en sens inverse de la viscosité.

Abstract - We have measured the self diffusion coefficient ($D_s$) of monodisperse charged polystyrene spheres in water by forced Rayleigh scattering. We observed a marked decrease in $D_s$ from the free particle value as the interparticle interactions increase. We also observed a jump of at least four orders of magnitude in $D_s$ at the first order melting transition. The data is found to agree with phenomenological relationships seen in simple liquids with the self diffusion varying inversely with the viscosity.

I. Introduction and Background

Monodisperse charged polystyrene spheres present a convenient model system to study liquids and solids. The interaction can be well characterized by a screened Coulomb potential with an effective charge per sphere. This interaction is also easily controlled by varying the density of the spheres themselves or the density of screening counterions. By varying these two parameters, one can see interactions strong enough to form crystals with long-range order or weak enough for the Coulomb repulsion to be completely screened so that the hydrophobic polystyrene spheres flocculate. This paper will be concerned with an intermediate regime, where the "polyballs" form an interacting colloidal liquid. Measurements of the self-diffusion coefficient will be presented and shown to have a dependence upon viscosity like that of simple liquids.

The mutual (concentration, collective) diffusion coefficient has been measured in polystyrenes spheres by a number of authors by quasielastic light scattering (QELS). This measures the dynamic structure factor $S(k,t)$ which is related to $D_m$:

$$D_m = D_0/S(k,0).$$  (1)
$D_m$ is a measure of how quickly a concentration fluctuation of wave-vector $k$ relaxes. This is described by Fick's law,

$$-D_m \nabla^2 \rho = \frac{\partial \rho}{\partial t} \tag{2}$$

Self (tracer, particle, mass) diffusion, on the other hand, is a single particle phenomena. $D_s$ describes the root-mean-square distance a particle travels on a random walk:

$$D_s t = \langle x^2 \rangle \tag{3}$$

For example, consider a compression fluctuation in a "Wigner" liquid with strong electrostatic repulsions between particles. One can imagine this fluctuation relaxing in two ways. The particles can, by collective motion return to the equilibrium density by lowering the density without spheres interchanging their relative position. Or they can wander to less dense regions by Brownian motion with a great deal of positional interchange. The former process is primarily mutual diffusion, the latter primarily self diffusion.

So one can readily see that $D_s$ and $D_m$ describe two very different physical properties. The manner with which they vary in relation to the strength of the interactions between particles can also be expected to be very different. Again consider the "Wigner" liquid. If the interactions are very strong, mutual diffusion is enhanced, because the particle can more effectively push on each other to relax the fluctuation. Mutual diffusion at $k = 0$ is thus a measure of osmotic compressibility. For the special case that $k$ corresponds to a peak in $S(k)$, the fluctuation is a preferred configuration and increasing the interactions will decrease $D_m$. On the other hand, self diffusion is hindered, because the particle is trapped in a "cage" of its neighbors which gets harder to escape as the interaction increases. So one expects $D_m$ to increase and $D_s$ to decrease as the interparticle interactions increase.

Now suppose we turn the interactions off. There is now only Brownian motion, as the particles have no way of moving collectively (neglecting hydrodynamic interactions). So as the interparticle interaction vanishes, one expects $D_m$ and $D_s$ to approach the free particle self diffusion coefficient, $D_0$ given by the Stokes-Einstein relation.

$$D_0 = \frac{k_B T}{\xi_0} \tag{4}$$

For spheres $\xi_0 = 6 \pi \eta a$, where $a = \text{radius of sphere}$ and $\eta = \text{viscosity of surrounding medium}$. 
II. Experimental Method

Self diffusion is usually measured in normal liquids and solids by radioactive or fluorescent tracers. The technique we employ, "Forced Rayleigh Scattering", is reminiscent of those methods.

A periodic pattern of tagged polyballs is set up in the sample. The concentration of tagged particles $\rho_T$ is then:

$$\rho_T(x,t=0) = \rho_T^0 \cos^2 qx$$  

(5)

$q = 2 \pi / d$, $d$ = period of pattern. These initial conditions are put into equation (2) to get

$$\rho_T(x,t) = \rho_T(x,t=0) e^{-Dq^2 t}$$  

(6)

The point here is that the tagged polyballs interact with each other in the same way they interact with untagged polyballs. That is, they can't tell the pattern is there. A jar of black and white marbles of equal weight and shape will mix when shaken by self diffusion. The marbles interact via hard sphere repulsion. But the interaction is not sensitive to color, so only self diffusion is seen. In a similar fashion, the pattern in our experiments relaxes by self diffusion.

We produced this pattern by introducing a photochromic dye molecule of the spiropyran family into the spheres. To ensure that the spheres were unchanged, we checked their effective charge (by shear modulus measurement) and diameter (by QELS) and found both to be essentially unchanged. This dye molecule, in its initial state, is optically absorbing in the near UV. Upon absorbing a UV photon, however, it becomes strongly absorbing in the red, and looks dark blue. It will relax thermally back to the initial state over a period of several minutes.

The optical set-up is shown in Reference 6. A UV laser beam is split and recombined in the sample. The resulting interference pattern will excite only dye molecules that are in polyballs found on the maxima of the fringes. A He-Ne laser beam will then see a thick diffraction grating, from which it can then Bragg scatter. We monitor the decay of the Bragg reflection as the periodic pattern loses resolution. The UV beam is pulsed for ~1-100 ms, and the resulting signal is stored in a digital oscilloscope. Usually a homodyne signal is seen which can be fit to

$$I(t) = (Ae^{-Dq^2 t} + B)^2 + c^2$$  

(7)
to obtain the self-diffusion coefficient. We only present data where the $q^2$ dependence has been verified.

The minimum fringe spacing we can obtain is about 1 micron. This, along with the intrinsic lifetime of the excited state of the dye sets a lower bound on the $D_s$ we can measure of about $10^{-12}$ cm$^2$/sec.

III. Experimental Results

The self diffusion coefficient vs. added electrolyte concentration for 0.109 micron diameter polyballs ($Z_{eff} = 300$) is shown in Figure 1. Note the sudden jump at $[\text{HCl}] \approx 4 \times 10^{-6}$ M. This is also the point at which the opalescence disappears and agrees with the melting point found in shear modulus measurements. In the solid phase ($< 4 \times 10^{-6}$ M HCl), we observe only the intrinsic relaxation of the dye. Thus we can only set an upper bound of $D_s < 10^{-12}$ cm$^2$/sec for the colloidal crystal. Upon melting, $D_s$ jumps immediately to almost $10^{-8}$ cm$^2$/sec, or at least 4 orders of magnitude. In all solid samples, we observed only the dye lifetime and not diffusion. Upon melting $D_s$ was always on the order of $10^{-8}$ cm$^2$/sec. Notice also that $D_s$ begins about a factor of 4 below $D_o$ and relaxes toward $D_o$ as the interactions are screened by adding electrolyte.

This is seen also in Figures 2-4, where $D_s$ is shown for of 0.038 micron diameter polyballs. The 0.038 micron spheres are never found to crystallize in our experiments. Note the initial large reduction from $D_o$ and the relaxation of $D_s$ toward $D_o$ as HCl is added in Figure 3. Notice also that $D_s$ decreases as the density of polyballs increases. Figure 4 shows a tenfold decrease in $D_s$ from $D_o$ at a volume fraction of 7.8%. It is instructive to note here that this reduction in $D_s$ is due almost entirely to the Coulomb interactions.
Reciprocal diffusion vs viscosity

Figure 2 - Measured reciprocal self diffusion coefficient for .038 micron 5% volume fraction spheres vs. measured total viscosity. Electrolyte concentration is being varied.

Figure 3 - Self diffusion coefficient normalized by the Stokes-Einstein value vs. electrolyte concentration in moles for .038 micron spheres, 5% volume fraction. □'s are experimental, +'s are calculated from equations 10-14 using measured viscosity.
Figure 4 - Normalized self-diffusion coefficient vs. volume fraction for .038 micron spheres. □'s are experimental, +'s are calculated from equations 10-14 from the measured viscosity.

of the polyballs and not due to hydrodynamic interactions. The latter are generally found to vary as:

\[ D_s = D_0 (1-A\phi) \]  

where A is a constant (approximately 28^9). So at most we should see a decrease of 28-30% in \( D_s \) for the most concentrated of our samples.

IV. Discussion

Since we are interested in the polyballs as a model system for interacting liquids, we should test to see if they behave as simple liquids are seen to behave. To do this, we must separate the contributions of the solvent and the polyballs. Suppose we treat them as two interpenetrating liquids interacting only by Stokes drag upon the polyballs (we will neglect hydrodynamic interactions between the polyballs). We can write the Navier-Stokes equation for the two fluids:

\[ \rho_1 \frac{dv_1}{dt} + \rho_1 (v_1 \cdot \nabla)v_1 = -\nabla P + \eta_1 \nabla^2 v_1 + cf(v_2 - v_1) \]
with \( v_1, \rho_1, \eta_1 \), the velocity field, mass density and viscosity of the solvent and \( v_2, \rho_2, \eta_2 \) of the polyball fluid, respectively. For plane couette flow, \( v_1 = v_2 \) throughout and therefore,

\[
\eta_T = \eta_1 + \eta_2 + O(\phi)
\]

where the last term represents corrections from hydrogen interactions. We see that the viscosities approximately add. The self diffusion coefficients should add reciprocally:

\[
\frac{1}{D_s} = \frac{1}{D_1} + \frac{1}{D_2} + O(\phi)
\]

where \( D_1 = D_0 \), the free particle value. \( D_2 \) and \( \eta_2 \) will describe the polyball-polyball interactions with the solvent separated out. Klein and Hess\(^{10} \) have found that

\[
D_s = \frac{K_B T}{\xi_0 + \Delta \xi(0,0)}
\]

which can be rewritten to look like equation 11 to get

\[
D_2 = \frac{K_B T}{\Delta \xi(0,0)}
\]

\( \xi_0 \) is the friction function from Stokes-Einstein, while \( \Delta \xi(0,0) \) is the friction function from interparticle interactions. It is a well known phenomenological result for simple liquids that

\[
D_s = \frac{K_B T}{A \eta r}
\]

where \( A \) is a constant between \( 2\pi \) and \( 4\pi \) (it is always experimentally found between \( 3\pi - 4\pi \)), and \( r \) is half the mean interparticle distance, \( a \phi^{-1/3} \). In Figure 2 we show the measured reciprocal self diffusion vs. the measured viscosity for a 5% sample of 0.038 micron spheres where the quantity varied is electrolyte concentration. From equations 10-14 we should find

\[
D_s^{-1} = D_0^{-1} - A \eta r/kT + A \eta_T r/kT.
\]

Thus the measured \( D_s^{-1} \) should vary linearly with measured total viscosity \( \eta_T \) and the slope gives a value for \( A \).
find $A = 3.3\pi$ for this sample.

In Figures 3 and 4, $A$ is obtained by simultaneous measurements of $D_s$ and $\eta$. We find $A = 3.7\pi$ and $A = 3.3\pi$ respectively for these data. Viscosity measurements on the .109 micron spheres, 1%, also yield $A = 3.3\pi$. Again the agreement with the data is good, and the values for $A$ agree with what is seen in other simple liquids.

V. Conclusions

We have performed the first direct measurements of the self diffusion coefficient in colloidal liquids using the forced Rayleigh scattering technique. We see in $D_s$ evidence of the first order melting transition. While we cannot as yet measure $D_s$ in the solid, we can set an upper bound of $\approx 10^{-12}$ cm$^2$/sec. $D_s$ is seen to reduce from an asymptotic value of $D_0$ for vanishing interparticle interactions to a value as much as an order of magnitude below $D_0$ when the interactions are strong. Also, we have presented evidence that the polyball fluid behaves phenomenologically like a simple liquid, in that the self diffusion coefficient is inversely proportional to the viscosity.

References