Melting of Colloidal Crystals*

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Inelastic light scattering is used to study the dynamics of an ordered suspencion of macromolecules.

There is considerable interest in the dynamics of macromolecular suspensions in which the range of the interparticle interaction is comparable to the interparticle distance.[1-6] Here we study the dynamics of a suspension of particles so highly charged that the repulsive forces between the particles lead to a transition from liquidlike to solidlike structure. This system displays features analogous to melting of atomic crystals, but it is unique in that (a) the structure results from repulsive forces; (b) the system is intrinsically overdamped; and (c) the interparticle spacing is such that the structure can be probed by use of visible sources.

The existence of long-range order in colloidal suspensions has been known for some time. The irridescence of these suspensions in white light has been attributed to Bragg diffraction of visible light.[7] Krieger *et al.*[8] extensively studied diffraction from weakly ordered systems. Finally, Williams and Crandall[9] have observed a sufficient number of Bragg diffraction lines to demonstrate cubic lattice structure. We confirm the cubic lattice and use inelastic light scattering to study particle motion near the transition.

The samples are prepared by deionization of a suspension of 0.1-μm-diam polystyrene particles. These particles are charged as a result of the ionization of acidic end groups.[7] To achieve crystalline ordering the solution is deionized by use of a mixed-bed ion-exchange resin. The resulting solution contains only the macroions and counterions (protons).

We find a "melting" transition near 40°C. Below the melting point (MP) the scattered light intensity shows sharp Bragg peaks due to diffraction from the lattice. In addition to the Bragg peaks (spots or lines depending on the size of the laser beam) we find a diffuse background indicative of the presence of some liquidlike structure. Thus the suspension appears to be a mixed phase just below the transition. Well below the MP the diffuse background becomes very weak with most of the scattered intensity appearing in the Bragg lines. This system is reminiscent of melting of impure atomic crystals, except that here, the "impurity" is due to charge polydispersity. Since the Bragg peaks represent scattering from nearly rigid structures we study only the diffuse background below the MP. At the MP the Bragg peaks disappear and the diffuse scattering reflects short-range order similar to that of simple liquids.[6]

Particles in colloidal arrays are strongly coupled and, therefore, belong to a class of problems for which rigorous theoretical insight is limited. Nevertheless, we develop a one-dimensional model of harmonically coupled Brownian particles. Although this model has obvious limitations because of dimensional restriction and harmonic potential, it is exactly solvable and displays the salient features of the data. Basically we solve the Smoluchowski equation on a cyclic lattice with a harmonic nearest-neighbor potential. This calculation bears some similarity to other theoretical treatments such as the dynamics of flexible macromolecules.[10,11] Here we only outline the calculation.

The Smoluchowski equation[12] for Brownian motion of colloidal particles is

$$\partial P/\partial t = D\left[\sum_i \nabla_i^2 P + \beta\nabla_i(\nabla_i\Phi)P\right], \tag{1}$$

where the distribution $P = P(\vec{x}_1, \vec{x}_2; t)$ is the probability that given a set of particles at $\vec{x}_1$, at time 0, a set of particles will be found at positions $\vec{x}_2$ at time t. $\beta = 1/kT$ where k is the Boltzmann constant and T is temperature. The overdamped nature of the system enters through the diffusion constant D. We presume that D includes the effects of hydrodynamic interaction between macroions[12] as well as macroion-counterion electrostatic interaction.[3-5] The screened Coulomb force between macroions enters through the interaction potential Φ which we assume to be harmonic, nearest-neighbor:

$$\Phi = \sum_{i=1}^{N} \alpha(\delta x_i - \delta x_{i+1})^2, \tag{2}$$

where α is the coupling constant and δx_i is the displacement of the ith particle from its average position (lattice point).

Equation (1) can be solved by normal coordinate techniques and P degenerates into a product of independent-particle solutions. The quantity of interest for light-scattering experiments is the two-particle Fourier transform of P or Van Hove scattering function $G(K,\tau)$. For an infinite lattice we find

$$G(K,\tau) = \exp\left(-\frac{K^2}{4\alpha\beta}\int_0^{4\alpha\beta D\tau} e^{-x} I_0(x)\,dx\right) + \sum_{n=1}^{\infty} 2\cos(Kan)\exp\left(-\frac{K^2}{4\alpha\beta}\left[n + \int_0^{4\alpha\beta D\tau} e^{-x} I_n(x)\,dx\right]\right), \tag{3}$$

where I_n is the modified Bessel function of order n and a is the lattice constant.

The most important limitation of the one-dimensional model is the absence of a phase transition for potentials of finite range.[13] $G(K,\tau)$ reflects this deficiency in that it does not decay to a time-dependent background. Since below the melting point we are concerned only with the diffuse liquidlike background scattering, the phase-transition problem is not severe. Our data, however, do indicate restricted motion at all temperatures. Preliminary results for the three-dimensional case show restricted motion.

Within the framework of the one-dimensional model we may identify the time-dependent part of the photocount correlation function $\langle n(0)n(\tau)\rangle$ with $G^2(K,\tau)$.[14] That is

$$\langle n(0)n(\tau)\rangle / \langle n\rangle^2 = 1 + \gamma(K) G^2(K,\tau)/G^2(K,0), \quad \tau > 0, \tag{4}$$

where $\langle n\rangle \propto G(K,0)$ is the mean counting rate. The constant γ will be less than unity for a detector of finite area. Also, we assume that the restricted motion results only in $\gamma < 1$. This assumption is supported by calculations of the initial decay of $\langle n(0)n(\tau)\rangle$ for independent, restricted Brownian particles.[15]

Since $G(K,\tau)$ is nonexponential the data are analyzed by the method of cumulants.[16] That is, we fit $\ln[\langle n(0)n(\tau)\rangle - \langle n\rangle^2]^{1/2}$ to a polynomial of order M and identify the mth cumulant $K_m^{(M)}$ with the coefficient $(-\tau)^m/m!$. Using Eq. (3) we predict

$$K_1 = DK^2/G(K,0), \tag{5}$$

$$K_2/K_1^2 = G(K,0)\{1 + (4\alpha\beta/K^2)[1 - \cos(Ka)\exp(-K^2/4\alpha\beta)]\} - 1. \tag{6}$$

$G(K,0)$ is the static structure factor familiar in diffraction studies of liquids.[1] From Eq. (3)

$$G(K,0) = \left[\frac{1 - \exp(-K^2/2\alpha\beta)}{1 - 2\cos(Ka)\exp(-K^2/4\alpha\beta) + \exp(-K^2/2\alpha\beta)}\right]. \tag{7}$$

Equation (5) indicates that the mean decay rate K_1 directly mirrors the static structure factor $G(K,0)$. This result is a general result for any Smoluchowski system and has been established experimentally for weakly interacting macromolecules.[2,6]

Figure 1 shows measured photocount correlation functions just above the MP. Data are shown for scattering angles $\theta = 25$, 63, and 119°. $\theta = 63°$ corresponds to scattering from the (111) plane of the face-centered cubic lattice which results when the temperature is dropped a degree. If the sample is shaken it will occasionally adopt a body-centered structure.[9]

Several features of the data in Fig. 1 should be noted. First of all, for $\theta = 63°$ $\langle n(0)n(\tau)\rangle$ decays with two decay rates. We identify the rapidly decaying mode ($\tau_c \sim 1$ msec) with the Brownian motion of the macroions and identify the slowly decaying mode ($\tau_c \sim 1$ sec) with grain boundaries or growth and decay of crystallites. That is, because of the polydisperse nature of the system we envisage domains of different structure and correlation range whose boundaries change slowly. Since domains smaller than the lattice spacing cannot exist, it is reasonable that the slow mode is not observed for $\theta > 63°$.

Figure 2 shows the K dependence of the characteristic time $\tau_c \equiv (K_1^{(3)})^{-1}$ of the rapid mode just above the MP. Data are similar at other temperatures except that the peak is less pro-

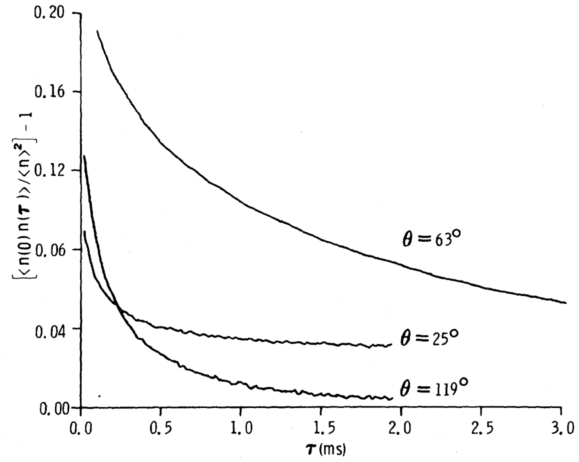

FIG. 1. Photocount correlation function for light scattered from a suspension of 0.1-μm-diam polystyrene particles at 41°C. At the MP (40 ± 0.5°C) sharp Bragg peaks are observed in the scattered intensity at $\theta = 63 \pm 2°$ and $77 \pm 2°$ consistent with the powder pattern of a face-centered cubic lattice. The pH and conductivity are 4.8 ± 0.2 and $(3.0 \pm 0.5) \times 10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. The incident wavelength is 6328 Å.

nounced. For comparison τ_c is also shown for the same sample diluted by a factor of 12. The well-known relationship $\tau_c = (DK^2)^{-1}$ characteristic of independent particles is observed. A peak is also observed in $G(K,0)$ consistent with the peak in $\tau_c(K)$. Since $G(K,0)$ is a measure of the susceptibility of the system to fluctuations of wave vector K, the peak in τ_c indicates that the system responds slowly to those fluctuations which are most easily excited.[2] The data are analyzed by least-squares minimization using Eqs. (5) and (7) with D, α, and a as parameters. The resulting curve is plotted as a solid line in Fig. 2.

The temperature dependence of the coupling constant α and the "hydrodynamic radius" $kT/6\pi\eta D$ are shown in Fig. 3. η is the viscosity of water. We plot $kT/6\pi\eta D$ because this quantity reduces to the radius if the particles are independent. The lattice parameter $a = 0.446 \pm 0.023$ μm is temperature independent.

The hydrodynamic radius is considerably smaller than the physical radius of the macromolecules (0.055 μm). Both the magnitude and the strong temperature dependence of $kT/6\pi\eta D$ are surprising and may indicate a strong influence of counterions on the macromolecular motion.[3,5] No applicable theory of counterion-macroion interaction exists. Nevertheless, Stephen's[3] approximate result indicates that $kT/\pi\eta D$ is expected to be smaller than the radius of the particle. Evidently, the magnitude of D is not an artifact of our $G(K,0)$ since similar values are obtained by use of a Percus-Yevick hard-sphere structure factor.[17]

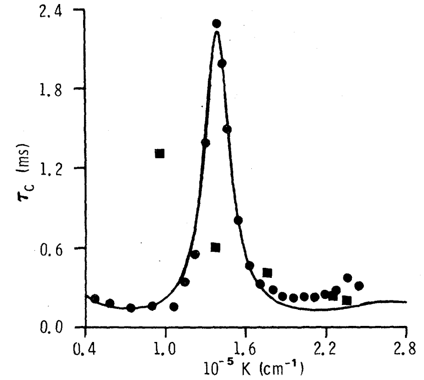

FIG. 2. K dependence of the correlation time at 41°C (circles). Solid line is a least-squares fit using Eqs. (5) and (7). Squares are the independent-particle result at 40°C.

The coupling constant α can be calculated by use of shielded electrostatic potential $U(r)$.[6] We find $\alpha = [2d^2U(r)/dr^2]_{r=a} \cong 0.003$ erg/cm^2 assuming a surface charge density of 0.47 μC cm^{-2} (calculated from the pH of the suspension). We believe that the large discrepancy between the calculated and observed α is due to the fact that $U(r)$ cannot be adequately characterized from the pH of the solution as measured by a glass electrode. That is, because of the strong macroion-counterion interaction, a fraction of the counterions are not detected by the glass electrode although they do shield the macroions. The in-

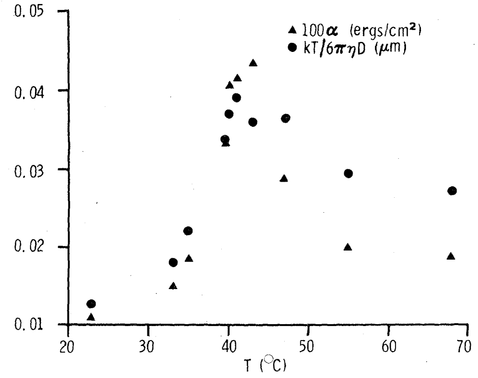

FIG. 3. Temperature dependence of $kT/6\pi\eta D$ and coupling constant α.

crease in α near the transition is probably due to anharmonicity as the fluctuation amplitude becomes large.

Equations (6) and (7) predict maxima in $G(K,0)$ and K_2/K_1^2 consistent with the peaks in τ_c. Such maxima are observed, but in both cases the amplitudes are less than predicted.

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Observation of Coupled Acoustic-Phonon–Reorientation Modes in a Plastic Crystal: Succinonitrile

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Rayleigh-Brillouin measurements of depolarized light scattering in the plastic phase of succinonitrile are reported as a function of crystal orientation. The Rayleigh wing is characterized by two distinct molecular-reorientation modes and strongly angular-dependent shear-wave peaks are seen with typical resonance line shapes. These spectra are understood as arising from coupling between acoustic phonons and reorientation modes. Excellent agreement with a hydrodynamic description of the coupled modes is obtained.

The reorientation of optically anisotropic molecules in plastic crystals produces a depolarized Rayleigh wing[1] similar to that observed in many liquids.[2] Several measurements have already been reported and in some cases shear modes have been seen.[3] The shear-phonon scattering strength in succinonitrile is already known to have a peculiar temperature dependence for which no satisfactory explanation has been given.[4] In view of the present interest in melting, and since the dynamical interaction of reorientation and translation is known to lead to interesting effects in liquids,[5] it seemed of importance to obtain the depolarized-light-scattering spectra in full detail. These are reported here at 45°C, that is, 13°C below melting. The results establish the existence of two reorientational relaxation times. Furthermore, the shear-wave component is not a simple Lorentzian but exhibits a well-developed resonance line shape.[6] To our knowledge, it is the first observation of this type of Brillouin spectra. They are explained by assuming static correlation between the reorientation and displacement of the molecules,[7] and constitute direct evidence for this new coupling. The parameters derived from the spectra are in full agreement with the known low-frequency elastic constants,[8] and with the high-frequency Kerr-effect anisotropy.[9]

The spectra were obtained with a single-mode argon-ion laser source (at 4880 Å and 100 mW power) and a piezoelectrically scanned Fabry-Perot interferometer of adjustable free-spectral range and finesse of ~40.

Succinonitrile single crystals were grown by the Bridgman-Stockbarger technique from highly