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Melting of Crystalline Suspensions of Polystyrene Spheres

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We have measured the melting temperatures of crystallized suspensions of polystyrene spheres as a function of concentration. By analyzing the data on the basis of a simple model we can estimate the heat of melting and the entropy change.

Charged spherical polymer particles in aqueous suspension[1] can form an ordered crystalline array.[2-5] The particle size is nearly uniform and typically around 0.1 μm. In the crystallized suspension the interparticle separation is typically around 0.5 μm. Iridescence, due to strong Bragg scattering of visible light by the crystal lattice, gives visual evidence of long-range order. Well-defined individual crystallites, up to several millimeters in size, are visible. The crystal structure is bcc with some admixture of fcc at high particle concentrations.[6] A remarkable feature of this system is that, by crystallizing suspensions of different concentrations, it is possible to vary the lattice constant systematically, by a factor of 3, without changing the crystal structure. This, together with the long range of the forces involved, has led us to propose[6] that the crystal-ordering forces must be electrostatic, similar to those in the electron Wigner crystal. A similar crystalline order among large particles has been reported for some virus suspensions.[7] In this Letter we report the first observation of the melting point in such a system as a function of the particle concentration. The melting temperature increases with increasing particle concentration. We interpret the data with an elementary model that gives an estimate of the heat of fusion and the corresponding entropy change.

Recently, Schaefer and Ackerson[8] reported a melting transition in a crystalline suspension of polystyrene particles. We have investigated this transition further and find that the melting temperature can be strongly influenced by ionic impurities. By proper treatment with an ion-exchange resin, these can be removed, to give reproducible melting temperatures. The melting temperature then depends in a regular way on the concentration of polymer particles. For the concentration range over which we have worked, when care is taken to minimize ionic impurities, the crystals always grow to fill the entire volume of water. The phase separation reported by others[3] does not appear under these conditions.

The behavior of the system indicates that the melting is a first-order transition. The crystallites have sharp boundaries and the melting of an individual crystallite takes place over a narrow temperature range of no more than 1 K. Thus, to analyze the concentration dependence of the melting point we will use a model with a finite energy and entropy of transition.

We used a suspension of uniform latex particles of polystyrene supplied by the Dow Chemical Co. The original suspension contained 1.4×10^{14} particles per cubic centimeter and the mean particle diameter was 0.109 μm. It was a nearly monodisperse suspension. The standard deviation of the

particle diameter was 2% of the mean diameter.[9] Each polystyrene particle has a negative charge, Q, of several thousand electron charges. This is due to sulfate groups that are bonded to the particle. There is an equivalent countercharge on ions, probably protons, that are distributed in the surrounding solution. The supplier of the particles[9] gave us an estimate of Q, based on electrophoresis measurements, of 4900 electron charges. We measured the electrical conductivity of suspensions for the concentration range used. The conductivity is proportional to the particle concentration, showing that the ions present are mainly the counter ions belonging to the particles, with no significant contribution due to desorption of ions from the container walls or other spurious sources. If we assume that the counter ions are protons we obtain a value for Q of 1900 electron charges.

To grow crystals, the suspension was diluted to the desired concentration and allowed to stand in a covered beaker together with a mixed-bed ion-exchange resin (Rexyn I-300, Fisher Scientific Co.). Crystals begin to form in about a day and after several days the crystallization is completed. The function of the resin is to remove all ions except the counter ions belonging to the particles and those intrinsic to the water. At this stage the crystallites are several millimeters in size. In measuring the melting temperature, the main difficulties arise from possible ionic impurities and from the extreme sensitivity of the crystals to deformation. Small amounts of ionic impurities lower the melting point to below room temperature. For example, a few percent of CO_2, introduced into the air over the sample, destroys the crystals within minutes, leaving simply a disordered suspension. Slight convection of the water deforms the crystals, fuzzing out the highly directional Bragg scattering. It is then difficult to determine whether crystals are present or not, and the melting temperature cannot be accurately specified. If the melting temperature is not too high, convection can be reduced to a satisfactory level by heating the crystallized suspension, in its original beaker, with the radiation from an infrared lamp, incident from above. This gave satisfactory, reversible melting temperatures for the suspensions of lower concentrations that melted at 55°C and below. For the more concentrated suspensions, melting at higher temperatures, this method of heating gave too much convection to observe a sharp melting point. The method that gave re-

producible results for concentrated suspensions was to grow the crystals first in a beaker, as before, then they were stirred, agitated with an ultrasonic bath, and allowed to stand for several days. This gave very small crystallites. At this stage the liquid could be drawn by capillary action into a glass melting-point tube of rectangular cross section. The tubes were 10 cm long, with inside cross-sectional dimensions of 1 mm×0.2 mm. The partially filled tube was then sealed off by fusing the ends in a burner. To determine the melting points, the tubes were then attached to a thermometer and immersed in a temperature bath filled with either water or oil. When samples enclosed in this way were heated, convection was almost absent. With proper illumination, the crystalline phase was brilliantly iridescent, and a melting transition could be easily seen. The melting temperature, as a function of concentration, is shown in Fig. 1.

We can construct a simple model of the melting transition, assuming that the significant interaction stabilizing the crystalline arrangement is the screened Coulomb repulsion between the charged polystyrene spheres. Analysis of the electron Wigner lattice[10] shows that the repulsive energy among electrons is lower in an ordered lattice than in a disordered structure. The model accounts for the concentration dependence of the observed melting temperatures. Analysis of the data, using the model, then gives us heats of melting and entropies of transition.

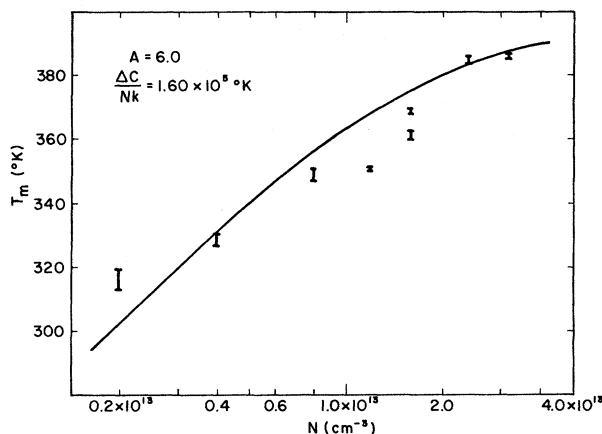The temperature at which a first-order phase change takes place is determined by the condition

FIG. 1. Melting temperature, T_m, as a function of the particle concentration. The vertical error bars indicate the temperature range over which melting took place.

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$\Delta F = 0$, i.e., by the vanishing of the free-energy difference between the two phases. For the present melting transition, the condition becomes $T_M = \Delta H / \Delta S$, where T_M is the melting temperature, ΔH is the heat of melting and ΔS is the entropy change. The concentration dependence of ΔH and ΔS can now be determined from the following model.

The entropy of the ordered crystalline arrangement of the spheres is very small and we assume it to be zero. The entropy of the disordered suspension can be estimated by considering the distribution of the N spheres (of volume v) among a number, V/v, of discrete cells (also of volume v):

$$S_{\text{disord}} = k \ln[(V/v)! / N!(V/v - N)!], \qquad (1)$$

where V is the volume of the suspension and k is Boltzmann's constant. Using Stirling's approximation, the entropy change can be expressed as

$$\Delta S = Nk[f^{-1}\ln f^{-1} - (f^{-1} - 1)\ln(f^{-1} - 1)], \qquad (2)$$

where $f = Nv/V$ is the volume fraction occupied by the N spheres.

The important energies of interaction in these suspensions are the electrostatic energies of the charged species. Van der Waals forces between the spheres and interactions between the charges and the water are not considered to be important to the stabilization of the ordered lattice. The electrostatic energy can be divided into three parts: (a) the repulsive interactions among the charged polystyrene spheres, (b) the repulsive interactions among the counter ions in solution; and (c) the attractive interactions between the spheres and counter ions. We assume that both energies (b) and (c) are nearly the same in both the ordered and disordered suspensions, and do not contribute significantly to the phase transition. Energy (a), on the other hand, is considered to be lower in the ordered structure by analogy with the electron Wigner lattice.

Since the Debye screening length is comparable to the separation between charged spheres, the energy of the repulsive interaction between spheres can be conveniently estimated by taking only the interactions among nearest neighbors. The energy (a) of the ordered phase can then be approximated by

$$H_{\text{ord}} = (K/R) \exp(-R/R_D), \qquad (3)$$

where R is the nearest-neighbor distance in the lattice, R_D is the Debye length, and K a constant. We will now assume that the energy (a) of the disordered phase can be approximated in a similar way:

$$H_{\text{disord}} = (K'/R_m) \exp(-R_m/R_D), \qquad (4)$$

where R_m is some mean nearest-neighbor distance and K' is a different constant (reflecting the possible different number of neighbors in the disordered suspension). Both of these energies can be expressed in terms of the concentration of spheres by noting that $R \propto f^{-1/3}$, $R_m \propto f^{-1/3}$, and $R_D \propto f^{-1/2}$:

$$H_{\text{ord}} = Cf^{1/3} \exp(-Af^{1/6}),$$
$$H_{\text{disord}} = C'f^{1/3} \exp(-A'f^{1/6}), \qquad (5)$$

where C, C', A, and A' are constants, and the temperature dependence of R_D has been neglected. If we now permit the screening constants, A and A', to be equal we obtain the heat of melting as

$$\Delta H = \Delta C f^{1/3} \exp(-Af^{1/6}), \qquad (6)$$

where $\Delta C = C' - C$ is assumed positive. Combining Eqs. (2) and (6) gives the volume fraction dependence of the melting temperature:

$$T_M = \frac{\Delta C}{Nk} \frac{f^{1/3} \exp(-Af^{1/6})}{f^{-1}\ln f^{-1} - (f^{-1} - 1)\ln(f^{-1} - 1)}. \qquad (7)$$

Equation (7) was fitted to the data by adjusting the values of $\Delta C/Nk$ and A. The solid line in Fig. 1 is a representation of Eq. (7) with $\Delta C/Nk = 1.60 \times 10^5$ K and $A = 6.0$. Possibly a better fit could be obtained by a least-squares procedure and by allowing for the temperature dependence of R_D (and hence A); the elementary nature of the model, however, precludes such embellishments. For $A = 6.0$, the Debye length is about one half to one third of the interparticle distance, R.

The heats of melting can be calculated from Eq. (6) using the values of the constants quoted above. ΔH varies smoothly from about 4.8 to 4.0 kcal/mole for values of N/V ranging from 0.2×10^{13} to 3.2×10^{13} cm^{-3}, respectively. The entropy changes can likewise be calculated; ΔS varies from about 16 to 10 cal/mole K over the same concentration range.

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Compton Profile Due to Magnetic Electrons in Ferromagnetic Iron Measured with Circularly Polarized γ Rays

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The Compton scattering of circularly polarized γ rays was used for studying the linear momentum distribution of electrons with unpaired spins in ferromagnetic iron metal. The observed Compton profile shows a broad minimum around zero momentum. The results are discussed in comparison with those calculated by Wakoh, Kubo, and Yamashita using the augmented-plane-wave method.

The Compton scattering of circularly polarized γ rays can be used for studying the spin density in momentum space in ferromagnetic materials,[1] because the relativistic Compton scattering cross section does depend on the spin of the electron.[2] The present paper reports the first measurement of this type on a ferromagnetic metal.

The Compton scattering cross section for γ rays circularly polarized parallel (antiparallel) to the spin of a single electron at rest is given by[1]

$$(d\sigma/d\Omega)^{\pm} = \tfrac{1}{2}(e^2/mc^2)^2\{(1 + \cos^2\theta)[1 - (2h\nu/mc^2)(1 - \cos\theta)] \pm (2h\nu/mc^2)\cos\theta(\cos\theta - 1)\}, \qquad (1)$$

where the upper (lower) sign corresponds to the γ-ray polarization parallel (antiparallel) to the electron spin, θ is the scattering angle, and other notations have conventional meanings. The first term in the equation gives the ordinary Compton scattering cross section and the second gives the spin-dependent one. This equation can be easily generalized for many electrons in motion in a magnetic solid and the difference between the cross sections, $(d\sigma/d\Omega)^{+} - (d\sigma/d\Omega)^{-}$, can give information on the magnetic electrons.[1]

The experimental arrangement is shown in Fig. 1. 10 mCi of ^{57}Co diffused in an iron foil was used as a source. The decay scheme of ^{57}Co is shown in Fig. 2. The source was cooled down to about 40 mK by adiabatic demagnetization of Cr-K alum. The temperature of the source rose to 60 mK in about 4 h. A superconducting magnet
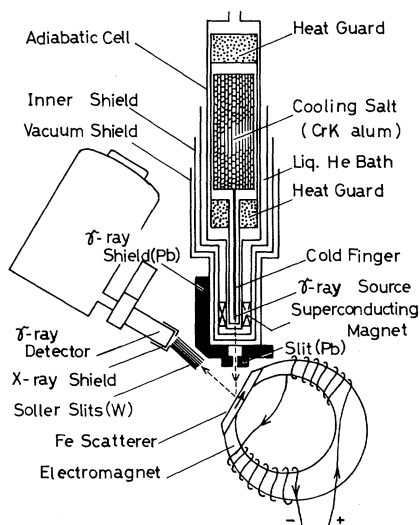

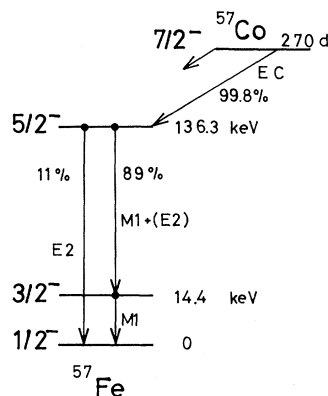FIG. 1. Apparatus for measuring the Compton profiles by circularly polarized γ rays.

FIG. 2. Decay scheme of ^{57}Co.