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ABSTRACT

Melting of a two-dimensional electron lattice and a two-dimensional dipolar solid are studied using molecular-dynamics techniques. The existence of hysteresis and latent heat of melting are observed, and the melting transitions in the two cases are found to be first order. For an electron lattice the melting occurs between  $\Gamma=129\pm 3$  whereas in the dipolar solid it is between  $\Gamma=62\pm 3$ , with a transition entropy of 0.3  $k_B$  per particle for both the systems.

INTRODUCTION

Two dimensional solids are known to lack long range translational order at finite temperatures,<sup>1-3</sup> but they have long range orientational order. Kosterlitz and Thouless<sup>4</sup> in 1973 proposed a theory of melting for the 2D solids; the solids in their theory have bound pairs of dislocations and the dissociation of the dislocation pairs is taken to be the cause of melting. Halperin and Nelson<sup>5</sup> in 1978 proposed a two-step melting process for 2D solids; in the first stage a 2D solid melts at a temperature  $T_M$  by dissociation of dislocation pairs into a liquid crystal like phase called a "hexatic" phase, which has bound disclination pairs; on further increase in temperature the hexatic phase transforms into an isotropic liquid at a certain temperature  $T_I$ , where the disclination pairs become unbound. The two transitions at temperatures  $T_M$  and  $T_I$  are supposed to be continuous, and according to Halperin and Nelson<sup>5</sup> the melting of 2D solids by a pair of continuous transition is possible provided that it is not preempted by a first order transition.

In this paper we shall describe the nature of the melting transitions in two systems, one where the particles interact via Coulomb interaction  $1/r$ , and the other is where the pair-wise interaction is the dipole-dipole interaction,  $1/r^3$ , where  $\vec{r}$  is a two dimensional vector. Experimentally, electrons on the surface of liquid helium represent a 2D Coulomb system. The nature of the melting transition in this system has been studied both experimentally<sup>6</sup> and by computer simulation methods.<sup>7-11</sup> Recently, Pieranski<sup>12</sup> has argued that polystyrene spheres ( $\sim 3000 \text{ \AA}$  in diameter) on the water-air interface act as electric dipoles aligned parallel to each other; the interaction in a plane perpendicular to the dipoles is  $1/r^3$ . The investigation of melting in a 2D dipolar system was recently made through the molecular dynamics method.<sup>13</sup>

In systems where the interaction energy is of the form  $V(\vec{r}) = \epsilon(\sigma/|\vec{r}|)^n$ , all the properties are fully characterized by a single, dimensionless variable,

$$\Gamma = \beta \epsilon (\sigma/r_0)^n, \tag{1}$$

where  $\beta = 1/k_B T$ ,  $\pi r_0^2 = \rho^{-1}$ ,  $\rho$  being the number density. For the Coulomb system  $n = 1$  and  $\epsilon \sigma = e^2$ , where  $e$  is the electronic charge.

MOLECULAR DYNAMICS (MD)

The calculations are performed on 100, 256 and 576 particles for the Coulomb system and on 256 particles for the dipolar system. In both cases the particles are confined in a rectangular cell of area  $A$  whose sides have a ratio of  $\sqrt{3}/2$  so that the cell can accommodate  $4M^2$  particles on a triangular lattice. Because of the long range nature of  $1/r$  and  $1/r^3$  potentials, special care is needed in the calculation of forces and potential energy; they should include not only the interaction of a given particle with all particles in the cell, but also its interaction with all the images in the periodically repeated replicas of the central cell. The forces and the potential energy are calculated by the Ewald method.<sup>14</sup> The Newton's equations of motion were integrated using a predictor-corrector method which involves up to fifth time derivatives of the positions.<sup>15</sup> The time step in the calculations was chosen so that the energy was conserved to at least 1 part in 50,000 even after 15,000 time steps. At each temperature, the system was first thermalized for several thousand time steps; results reported in this paper are based on long MD runs after thermalization. The results are independent of the starting configurations. Near the melting transition calculations extending up to 40,000 time steps were carried out.

## RESULTS

In what follows we shall discuss the structural and dynamical properties of the 2D Coulomb and dipolar systems.

### a) Coulomb System

MD results for the internal energy  $E$  are shown in Fig. 1. The squares correspond to an electron liquid which has been monotonically cooled from a temperature of 1 K ( $\Gamma = 36$ ), and the solid circles represent the results for the electron solid which has been monotonically heated from a low temperature triangular lattice. The presence of hysteresis is evident in the figure, and the hysteresis region is marked by vertical dotted lines. In the temperature range shown in Fig. 1,  $E$  seems to vary almost linearly with temperature. The point marked  $L_2$  on the upper line corresponds to the

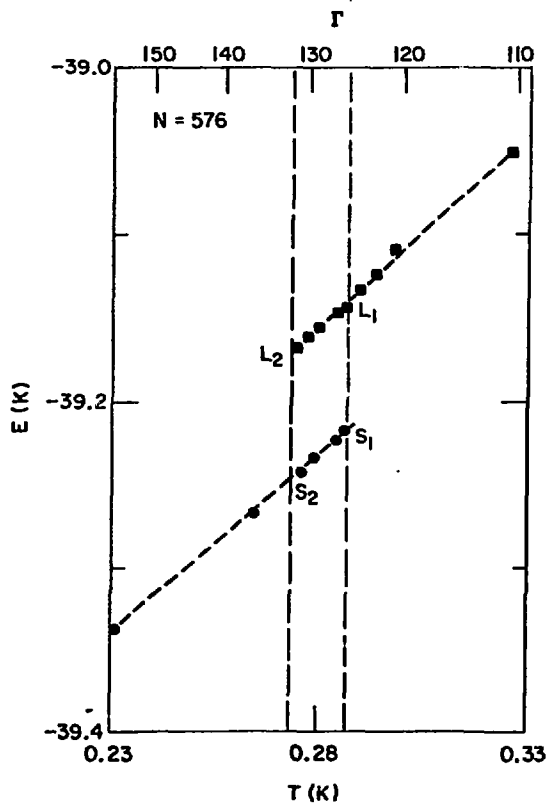


Figure 1. Temperature variation of internal energy for an electron system.

last supercooled liquid state. That the system at  $L_2$  is a liquid is evident from the fact that it has a finite value of self-diffusion constant  $D = 0.5 \text{ cm}^2/\text{sec}$ . To further confirm the diffusivity of the supercooled liquid at  $L_2$  we show in Fig. 2 the behavior of mean square displacement  $\langle R^2(t) \rangle$ , which increases linearly with time  $t$ . The point marked  $S_1$  on the lower line in Fig. 1 represents the last superheated solid. It has no diffusion, and its solid-like behavior is evident also from Fig. 2 where the variation of  $\langle R^2(t) \rangle$  does not increase with time. The results for the self-diffusion constant show that in the hysteresis region  $D$  has two values at each temperature; zero in the solid phase and around  $0.6 \text{ cm}^2/\text{sec}$  in the liquid phase.

The hysteresis in Fig. 1 extends from the superheated solid system at  $S_1$  to the supercooled liquid system at  $L_2$ . The hysteresis was found in all three sizes of the system, ( $N = 100, 256$  and  $576$ ). In all three cases when the last superheated solid system is heated, it melts abruptly and goes into the liquid phase marked  $L_1$ . While at  $S_1$  the diffusion is zero, it acquires a value of  $\approx 0.7 \text{ cm}^2/\text{sec}$  after the system becomes a liquid at  $L_1$ . The hysteresis decreases slightly with increase in the size of the system and the transition moves slightly toward a higher value of  $\Gamma = 126-132$ , in good agreement with the experimental value of

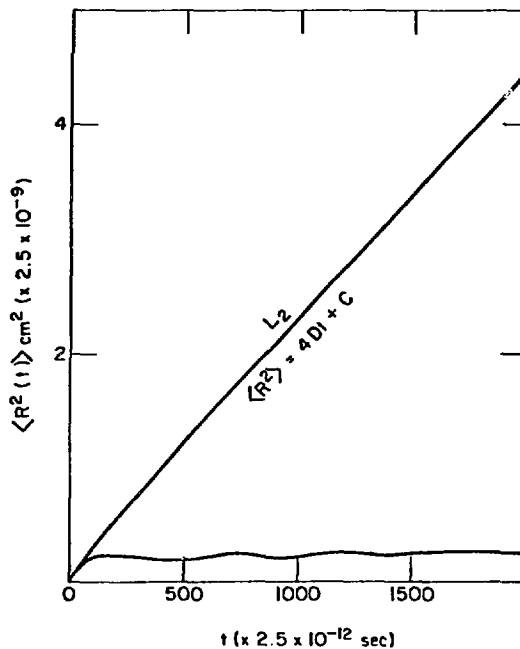


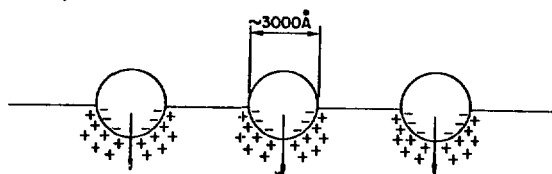
Figure 2. Mean square displacement vs. time.

$\Gamma = 137 \pm 15$ . It should be emphasized that the latent heat of melting,  $E(L_1) - E(S_1)$ , is the same for all three sizes of the system. Taking the middle point in the hysteresis region to be the melting temperature  $T_M$ , we find that the change in entropy on melting is  $\Delta s \approx 0.3 k_B$  per particle.

The observed hysteresis in the temperature dependence of  $E$  and  $D$ , and the attendant latent heat of melting indicate that melting transition in the 2D electron system is first order. To further confirm the nature of the phase transition we have investigated the homogeneous nucleation of an electron solid from a supercooled liquid in a 576 particle system. At time  $t = 0$ , the system is cooled by lowering the energy by an amount slightly greater than the latent heat. It is then allowed to run for 20,000 time steps. The time dependence of the instantaneous temperature,  $T(t)$ , shows that for the first several thousand time steps it fluctuates around a mean value and the system in the  $E$  vs  $T$  graph lies above the lower line for the solid, but then in a small time interval ( $\sim 1000$  time steps),  $T(t)$  increases and settles to a value where the  $(E, T)$  point for the system lies on the lower line for the solid, and the self-diffusion constant becomes zero. Afterwards the mean temperature of the system stayed constant for as long as we investigated it, which was several thousand more time steps. The above mentioned variation of  $T(t)$  in homogeneous nucleation is unique to systems which undergo first order phase transition.<sup>16,17</sup>

#### b) Dipolar System

A schematic diagram of an interfacial colloidal crystal system—polystyrene spheres on water-air interface interacting via dipole-dipole interaction—is shown in Fig. 3. In Fig. 4 we show the temperature dependence of total energy  $E^* = E/\epsilon$  for 256-particle system at a reduced density  $\rho^* = \rho\sigma^2 = \pi^{-1}$ . The solid circles represent the MD results for the dipolar liquid which has been monotonically cooled from a reduced temperature  $T^* = T/\epsilon = 28.3 \times 10^{-3}$ . The solid squares correspond to the dipolar solid phase, and they are obtained by monotonically heating a low temperature triangular lattice. As in the electron system, the points  $L_2$  and  $S_1$  represent the last supercooled liquid and superheated solid systems, respectively. When the system at  $S_1$  is heated, it melts abruptly and goes into a state marked  $L_1$  where it has a finite mobility. The melting takes place in only about 1000 time steps and after that the system reaches equilibrium and settles into the state  $L_1$ .



POLYSTYRENE SPHERES ON WATER SURFACE

Figure 3

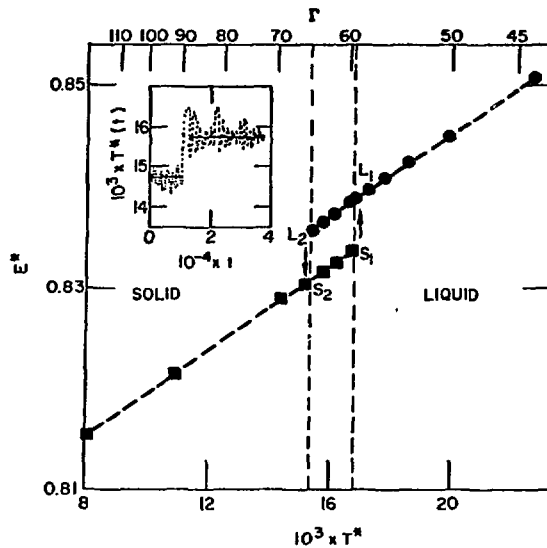


Figure 4. Reduced energy  $E^*$  as a function of reduced temperature  $T^*$  for a dipolar system in two dimensions. The inset shows the homogeneous nucleation of a dipolar solid from a supercooled liquid state.

The homogeneous nucleation of a solid from a supercooled liquid was also investigated along the lines we discussed in the last section. The behavior of  $T^*(t)$  is shown in the inset in Fig. 4. During the first 10,000 time steps,  $T^*(t)$  fluctuates around a mean value of  $14.7 \times 10^{-3}$  and then in the next 500 time steps,  $T^*(t)$  increases and fluctuates around a mean value of  $15.8 \times 10^{-3}$ . The energy  $E^*$  and the corresponding mean temperature of  $15.8 \times 10^{-3}$  constitute the point marked  $S_2$  in Fig. 4; at  $S_2$  the system has zero mobility.

The hysteresis in  $E^*$  vs  $T^*$  for the dipolar system, the presence of latent heat, and the homogeneous nucleation of the dipolar solid from the supercooled liquid, clearly show that the melting transition is first order. The melting transition occurs between  $\Gamma = 59-65$  and the entropy change on melting is again found to be  $\approx 0.3 k_B$  per particle, which is the same as the transition entropy for the electron system.

A remark on the nature of interparticle interaction in interfacial colloidal crystals is in order here. According to Pieranski<sup>12</sup> the experiment shows a long range interaction between the colloidal particles. Since the polystyrene spheres are only partly immersed in water, Pieranski claims that the interaction will vary as  $1/r^3$ .

If the interaction is indeed  $1/r^3$ , then the properties of the system, as we showed earlier, depend on a single variable  $\Gamma = \beta \epsilon (\sigma^2 \pi \rho)^{3/2}$  and not on  $\rho$  and  $T$  separately. A plot of the melting temperature  $T_M$  and density  $\rho^{3/2}$  will be a straight line in case the interaction is  $1/r^3$ . Experiments should therefore be carried out to verify if  $T_M$  vs  $\rho^{3/2}$  is a straight line. It is hoped that the MD results on the melting transition of a dipolar system will stimulate further experimental investigations.

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