

tem at the same density. That term is absent for bosons. In addition, the energies have been extrapolated to zero time step by empirically establishing the validity of linear extrapolation. This correction is quite small, on the order of the statistical error for the time steps used. However, this correction can be completely avoided by using an integral formulation of Eq. (1).⁵

The results for the energy of the plasma in four different phases is given in Table I and plotted in Fig. 2. The boson system undergoes Wigner⁶ crystallization at $r_s = 160 \pm 10$. The fermion system has two phase transitions, crystallization at $r_s = 100 \pm 20$ and depolarization at $r_s = 75 \pm 5$. We have found that the difference in energy between a boson crystal and a fermion crystal is less than $1.0 \times 10^{-6}R$ at $r_s = 100$. The energies of the three Fermion states are sufficiently close in the low-density regime that still more accurate calculations on larger systems would be desirable to confirm these results. Although the Bijl-Jastrow-Slater results are quite accurate,⁴ the error is different for the different phases, changing their relative stability. This demonstrates how essential it is to perform exact simu-

lations to calculate reliably phase-transition densities.

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Two-Dimensional Interfacial Colloidal Crystals

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Polystyrene spheres (2450 Å in diameter) are trapped in a surface energy well at water/air interface. Because of asymmetry of charge distribution, electrical dipoles are associated with each interfacial particle. The dipole-dipole repulsive interactions organize the polystyrene spheres into a two-dimensional triangular lattice. The direct microscopic observations of such an interfacial colloidal crystal are reported for the first time.

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Theoretical progress in phase transitions in two dimensions¹ stimulated research of adequate physical systems; the formation of the two-dimensional crystals was demonstrated both experimentally²⁻⁴ and by computer simulations.⁵⁻⁹ The experiments on an electron layer floating on a surface of liquid helium³ are very attractive because of simplicity of the interactions which are long range and purely repulsive. However, the detection of the crystalline ordering from the existence of plasmon-rippion modes is only indirect. Direct optical observations of the triangular two-dimensional lattice were reported in

computer experiments⁵⁻⁹ and in the model of hard spheres (few millimeters in diameter) forming a layer on a vibrating solid surface.²

In this Letter, I investigate the system of monolayer of polystyrene spheres trapped at water/air interface. I will show that the interactions are long range and purely repulsive as in the electron layer³ and that because of these interactions the polymer particles order in a two-dimensional lattice. This is the first report of the microscopic observation of such interfacial colloidal crystals.

The experiments were made with the colloidal crystal of polystyrene spheres of radius $R = 1225$

Å at concentration $N = 20 \times 10^{12}$ particles/cm³. A drop of the latex was introduced in the cylindrical test tube with the bottom made of microscopic glass slide (Fig. 1). Because of the action of capillary forces, a meniscus formed at the circular edge of the bottom and in its central part the latex layer became very thin after a few minutes. The observations were made with use of an inverted microscopic operating in reflected light mode. It was possible to observe the water/air interface across the bottom layer when its thickness was less than $\sim 3 \mu\text{m}$.

Even if the finite field depth of the microscope objective did not allow determination of the position of particles with respect to interface, the distinction between the particles trapped at interface and those inside the water layer was easy to make; the spheres at interface appeared in the microscope as very distinct black dots (Fig. 2) while those in bulk offered very poor contrast and were difficult to perceive separately. This large difference in the optical contrast is due to different interfacial indices; $n_{p/A} = 1.60$ for particles trapped at the interface and $n_{p/W} = 1.20$ for those in bulk.

In spite of vigorous Brownian motion it is possible to follow the position of one interfacial particle; I have never seen it penetrate into the bulk. This behavior suggests that the polystyrene spheres are trapped at interface in a surface energy well deeper than $k_B T$. On the contrary, the transfer of the bulk particles into the interface was possible and I observed it in the following situation: The local thickness of the bottom layer was continuously decreased from a few microns to zero. This thickness variation was evident from the optical interference pattern and also from emission of edge dislocation loops¹⁰ in the colloidal crystal layer. For the latex thickness approximately equal to 3000 Å only one layer of bulk particles remained. Further evolution depended on the rate of decrease of thickness. When

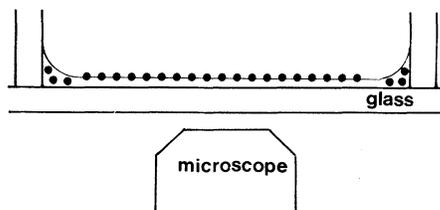


FIG. 1. Conditions of the microscopic observations of the latex/air interface.

the thickness was decreased very slowly, the bulk particles were expelled into the thicker regions of the sample. On the other hand, when the thickness of the water layer was decreased very rapidly, the particles were transferred from bulk onto the interface.

In Fig. 2, I show the photographs of the surface monolayer obtained by this method. They show both the crystalline and disordered structure.

From the fact that the interparticle distance ($d \geq 1 \mu\text{m}$) is larger than the spheres' diameter ($2R = 2450 \text{ \AA}$) it is evident that the interaction must have a range longer than $2R$. The observations were also made with samples in which the distance was as large as $10 \mu\text{m}$. In these samples crystallization did not occur. However, the uniform distribution of particles over all the available area of the interface clearly indicates that the interactions are repulsive and extend over a range longer than $10 \mu\text{m}$.

The essential feature of the polystyrene spheres at water/air interface is that they seem to be trapped in a surface energy well. The stability of spheres at the interface, crucial for the definition of the system as a two-dimensional one, is determined by the depth of the well.

For the sphere shown in Fig. 3, there are three contributions to the surface energy:

(i) energy of polystyrene/air interface

$$E_{p/A} = \sigma_{p/A} \cdot 2\pi R^2(1 + \bar{z}),$$

(ii) energy of polystyrene/water interface

$$E_{p/W} = \sigma_{p/W} \cdot 2\pi R^2(1 - \bar{z}),$$

(iii) negative energy of the missing water/air interface

$$E_{W/A} = -\sigma_{W/A} \cdot \pi R^2(1 - \bar{z}^2),$$

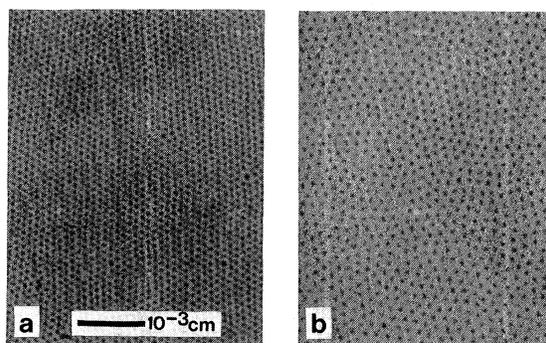


FIG. 2. Photographs of polystyrene spheres (black dots) trapped at water/air interface. (a) Crystalline structure; (b) disordered structure.

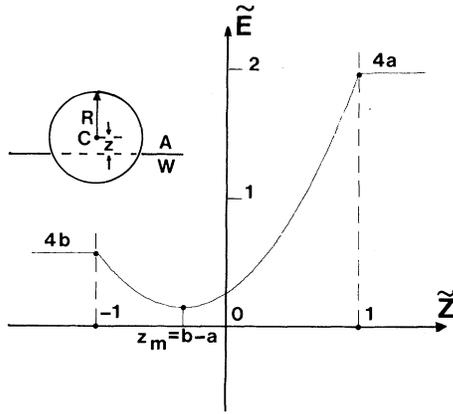


FIG. 3. Estimate of surface energy well.

where σ 's are the corresponding surface tensions and $\tilde{z} = z/R$ is the vertical coordinate of the center C with respect to the water level (Fig. 3).

The total energy which can be written as

$$\tilde{E} = E/\pi R^2 \sigma_{W/A} = \tilde{z}^2 + 2(a-b)\tilde{z} + 2a + 2b - 1, \quad (1)$$

with $a = \sigma_{p/A}/\sigma_{W/A} = 0.49$ ¹¹ and $b = \sigma_{p/W}/\sigma_{W/A} = 0.14$,¹¹ has a minimum $\tilde{E}_{\min} = 2a + 2b - 1 - (a-b)^2 = 0.14$ for $\tilde{z} = b - a = 0.35$. From the energies of the well edges, $E_A = 4a = 1.96$ (sphere in air) and $E_W = 4b = 0.64$ (sphere in water), one calculates the heights of the corresponding energy barriers:

$$\Delta E_A = E_A - E_{\min} = 1.82;$$

$$\Delta E_W = E_W - E_{\min} = 0.50.$$

The absolute values of these energies are determined by the quantity $E_{\text{unit}}^s = \pi R^2 \sigma_{W/A}$ which was chosen in Eq. (1) to scale the surface energies. For polystyrene spheres of radius $R = 1.2 \times 10^{-5}$ cm, and $\sigma_{W/A} = 72$ erg/cm² one gets $E_{\text{unit}}^s = 3.4 \times 10^{-8}$ erg. This energy is larger than the thermal energy $k_B T$ by a factor of 10^6 . The position of the spheres at the interface is practically unperturbed by gravity; the energy involved, given by $E^g = \frac{4}{3}\pi R^4 \rho g \approx 10^{-16}$ erg for $\rho = 1$ g/cm³ and $R = 1.2 \times 10^{-5}$ cm, is negligible when compared with E_{unit}^s .

In the experimental section I have concluded that the interactions, other than simple steric repulsions (hard-spheres model), were responsible for the formation of the two-dimensional crystal. The usual model of interactions in three-dimensional colloidal crystals is that of screened electrostatic forces. In the present case only a part of the surface of the polystyrene spheres is immersed in water. Therefore the distribution of

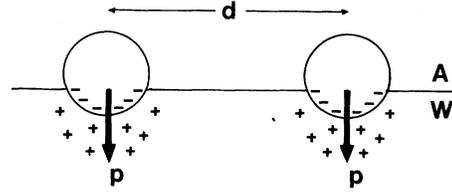


FIG. 4. Schematic of the model of interactions.

charges, resulting from the dissociation of the sulfonic acid groups, must be asymmetric with respect to the reflection in the plane of the interface (Fig. 4). The dipoles associated with such axially symmetric distribution of charges must be vertical. The magnitude of each dipole p is of the order of $Q_{2D} \lambda_D$ where Q_{2D} is the charge of the dissociated sulfonic ions and λ_D the Debye length. From the total charge Q_{3D} of the sulfonic acid groups,¹² the fraction Q_{2D} , available in two dimensions, may be estimated to be approximately $1000 e$.

The Debye length λ_D in our samples was larger than the lattice spacing of the three-dimensional colloidal crystals ($d \approx N^{-1/3} \approx 0.3 \times 10^{-4}$ cm). From these estimates one gets the energy of dipole-dipole interaction,

$$E^{d-d} = \frac{2(Q_{2D} \lambda_D)^2}{\epsilon d^3} = 2 \frac{Q_{2D}^2}{\epsilon d} \left(\frac{\lambda_D}{d} \right)^2 \approx \frac{50}{80} 10^{-11} \text{ erg}, \quad (2)$$

for $d = 10^{-4}$ and $\epsilon = 80$. The ratio $\Gamma^{d-d} = E^{d-d}/k_B T$ plays in the two-dimensional colloidal crystal the same role as $\Gamma^{e-e} = E^{e-e}/k_B T$ in the electron-layer experiments.³ In this last case the computer calculations provided the value $\Gamma \sim 130$ as a condition necessary for crystallization. In the present case the interaction potential varies as d^{-3} so that the critical value of parameter Γ^{d-d} can be somewhat different.

The possibility of realization of two-dimensional colloidal crystals under different conditions was proposed previously in Ref. 10. Instead of being trapped at an interface, spheres were proposed to form a monolayer in a film of water between two solid (glass) plane boundaries. The two systems are very different from the point of view of interactions. In the case of spheres completely immersed in water, the interaction would be only of short range with $\exp(-d/\lambda_D)$ factor [instead of $(\lambda_D/d)^2$ in the present case—Eq. (2)] and the ionic purity conditions would be crucial for maintaining interactions strong enough. The interactions between polymer spheres in an interfacial layer are, on the other hand, very sensi-

tive to the presence of surface impurities.

From the preliminary observations (which I will report in detail in another article) I have concluded that the interaction can have an attractive term due to the presence of a monolayer of impurities. A condensation into small two-dimensional "molecules" (dimers, trimers, ...) and larger crystalline "droplets" was observed. An interesting feature of the interfacial colloidal crystal is that the dipoles associated with each polymer sphere interact with an inhomogeneous electric field. Observations of these phenomena will be reported elsewhere.

The interfacial colloidal crystals combine the exclusive features of other two-dimensional systems. I have shown that the polymer spheres are trapped at water-air interface as efficiently as the electrons at free surface of liquid helium. The dipole-dipole interactions between polymeric spheres were shown to be repulsive and long range as are electrostatic forces between electrons. In contradistinction with elementary particles, the size of the polystyrene spheres can be chosen; in the present experiment, they were large enough to be observed directly by microscope. At the same time they were small enough to be subjected to a vigorous Brownian motion, which means that the temperature of the system is well defined. I believe that this possibility of the direct microscopic observation may be very useful for the comprehension of the phenomena of two-dimensional melting.

I would like to thank Professor R. Meyer for his invitation to Brandeis University and for the use of his microscopic equipment. I benefitted great-

ly from discussions with him and with Professor D. Schneider and Professor C. Young. The polystyrene spheres were synthesized by Dr. L. Strzelocki, and their size determined by Mr. P. Norton. I thank Miss D. MacKnight for preparing the manuscript and critically reviewing it. Last but not least, I would like to thank Dr. Piotr Pieranski for introducing me to physics in two dimensions; the present work owes much to his modeling² of two-dimensional crystals.

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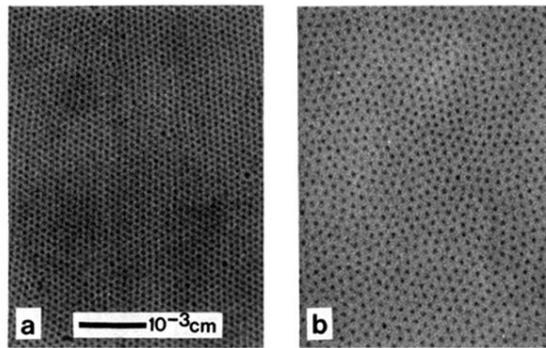


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