

## Melting of Two-Dimensional Solids

W. F. Brinkman, Daniel S. Fisher, D. E. Moncton

The establishment of order in two-dimensional structures is of considerable interest to condensed matter scientists. Although it is not obvious, nature abounds with two-dimensional formations. Liquid crystals and lipids form

The mechanism of two-dimensional melting that has captured physicists' attention was originally suggested by Kosterlitz and Thouless (1). They showed that a simple defect in the regular lattice structure, called a dislocation, could be

*Summary.* Recent theoretical predictions indicate that melting of a two-dimensional solid may be caused by spontaneous creation of dislocations. The theory predicts that melting occurs by a two-step process involving an intermediate phase, called the hexatic phase, in which there is order in the local crystalline axes but not in the positions of atoms. These ideas are being tested by numerical simulations and by experiments on electrons on liquid helium, liquid crystal films, and rare gas layers adsorbed on graphite. Experiments on liquid crystal films indicate that the three-dimensional analog of the hexatic phase exists, and xenon on graphite exhibits a melting transition close to the form predicted.

films one or two molecules thick. Single layers of atoms can be deposited on crystalline surfaces or other flat substrates. In fact, solid surfaces themselves often undergo structural rearrangements of their outermost atomic layers. Such systems, which have received a great deal of experimental attention recently, are intrinsically two-dimensional.

Perhaps the most fundamental transition that occurs in condensed matter is melting from solids to liquids. Theorists have conjectured that in the two-dimensional world melting may occur by a process in which the order is gradually destroyed, quite unlike the abrupt occurrence of three-dimensional melting. The universal nature of the theoretical predictions near this continuous melting transition provides a challenge for experimentalists. In addition, the results may ultimately affect our understanding of three-dimensional melting phenomena.

the vehicle for the destruction of the regular crystalline periodicity that occurs during melting. Although many years ago Shockley (2) suggested that the melting of three-dimensional solids might be understood in terms of dislocations, the current view is that such a mechanism is more likely to apply directly in two dimensions.

One of the advantages of the Kosterlitz-Thouless dislocation theory of melting is that detailed predictions can be made of both static and dynamic effects near the phase transition, which are universal in the sense that they are independent of the detailed form of microscopic forces. In particular, the theory predicts that, in contrast to the three-dimensional case, the transition is higher order with no latent heat—in fact, only an unobservably weak essential singularity should occur in the specific heat (3). Thus, a two-dimensional solid just below its melting temperature and the fluid just above look very similar on microscopic

length scales, in contrast to the usual behavior in three dimensions, where the transition is first order.

Recently, Halperin and Nelson (4) showed that the two-dimensional melting process may be even more remarkable. They predicted that a new type of anisotropic fluid phase will occur between the solid and the usual isotropic liquid. In their theory two successive phase transitions occur before all vestiges of the solid structure are destroyed. Currently, there is considerable activity both in computer simulations and in experiments on two-dimensional systems designed to test these ideas. Considerable progress has been made and some of the predictions of this theory have been verified, even though we do not yet know under exactly what circumstances the dislocation theory applies.

### Theoretical Concepts

A two-dimensional solid is in many ways similar to its three-dimensional counterpart. It has well-defined crystalline axes, can form grain boundaries, and exhibits resistance to shear forces. The property of resisting shear is probably the best definition of a solid and certainly the one that is most used in practice. There is one important way, however, in which two- and three-dimensional solids differ. Thermal fluctuations in a solid cause displacements of the atoms from their perfect lattice positions. In two dimensions these fluctuations are such that the mean square fluctuation,  $\langle(r - \bar{r})^2\rangle$ , of the distance,  $r$ , between two atoms separated by an average distance  $\bar{r}$  diverges as the logarithm of  $\bar{r}$ . For three-dimensional solids the fluctuations are finite as  $\bar{r} \rightarrow \infty$ , which implies that the position of one atom effectively determines that of all the other atoms in the crystal. This property is known as long-range positional order and has been used frequently to characterize a solid. For two-dimensional solids, however, the divergence of the fluctuations implies that there is no long-range positional

W. F. Brinkman is director of the Physical Research Laboratory and Daniel S. Fisher and D. E. Moncton are members of the technical staff at Bell Laboratories, Murray Hill, New Jersey 07974.

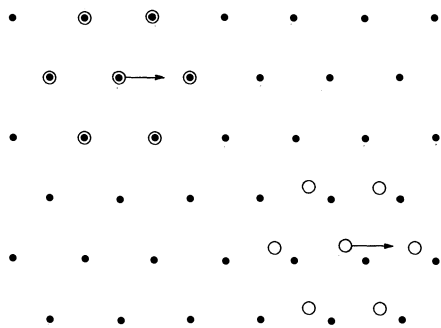


Fig. 1. Schematic representation of a two-dimensional solid. The atoms (open circles) on the left are positioned coincident with the black dots. The atoms in the right-hand region are not in registration with those on the left, as seen by the lack of registry with the dots. The two regions do have the same orientation.

order. This has been known since the 1930's (5) and was used by some to argue that two-dimensional solids do not exist, but ignored by others who pointed out that  $\langle(r - \bar{r})^2\rangle$  is very small unless  $\bar{r}$  is huge.

While a two-dimensional solid does not have true long-range order, the positional correlations do extend to long distances, in contrast to those in a liquid. In a liquid the positional correlations decay exponentially as  $\exp(-r/\xi)$  with a characteristic correlation length  $\xi$  normally only a few angstroms in magnitude. In a two-dimensional solid, as a consequence of its resistance to shear, the correlations decay algebraically as  $1/r^\eta$ , and two-dimensional solids are said to exhibit algebraic long-range order (6). The exponent  $\eta$  is related to the elastic moduli and the temperature,  $T$ , and increases as  $T$  increases. As we shall discuss,  $\eta$  is experimentally measurable.

While a two-dimensional solid does not have long-range positional order, it does have long-range order in the orientation of the crystalline axes—that is, in the direction of the geometric (not chemical) “bond” between adjacent pairs of atoms. A two-dimensional solid therefore looks schematically as shown in Fig. 1. Atoms in each region of the solid will typically be displaced from their positions in a perfect regular lattice by an amount that fluctuates from one region to another. The local crystalline axes in each region will, however, have the same orientation.

In three dimensions, the atoms in every region of a solid fluctuate only slightly about their perfect lattice sites. The periodicity of the atomic arrangement gives rise in three dimensions to a set of sharp delta function peaks in the structure factor,  $S(\mathbf{Q})$ , at the Bragg positions,  $\mathbf{G}$ . These are observed in x-ray Bragg

diffraction experiments, where  $\mathbf{Q}$  is the difference between incident and scattered wave vectors. In a two-dimensional solid, on the other hand, as a consequence of the large, divergent fluctuations of the positions of the atoms, the underlying periodicity yields only power law singularities in  $S(\mathbf{Q})$  of the form  $|\mathbf{Q} - \mathbf{G}|^{-2 + \eta}$ .

With this understanding of the nature of two-dimensional solids the fundamental question is how such solids melt or transform to the liquid phase as temperature increases. This can occur by a first-order transition (as in three dimensions) in which large fluctuations at very short length scales abruptly change the local order of the solid to the disorder of a liquid. As we shall see, this possibility surely does occur. Alternatively, if the two-dimensional solid is relatively stable to short-range disorder, the dominant thermal fluctuations will be of long wavelength and a description in terms of dislocations might apply. The theoretical predictions for this case are quite different from any previous results.

A dislocation in two dimensions is a point defect in an otherwise perfect crystal in which half an extra row of atoms is added. A dislocation in a hexagonal lattice is illustrated in Fig. 2a. Dislocations are described by a Burgers vector  $\mathbf{b}$  (a lattice vector of the crystal) as suggested by the geometric construction shown (7). The additional row of atoms induces a strain field that decreases as the inverse first power of the distance from the dislocation, so that the energy cost,  $U$ , to add the simplest dislocation with  $|\mathbf{b}| = a$  (lattice spacing) to a solid with linear size  $R$  is

$$U = a^2 \frac{K}{8\pi} \ln \left( \frac{R}{a} \right) + E_c \quad (1)$$

where  $K = 4\mu B/(\mu + B)$ , with  $\mu$  and  $B$  the shear and bulk moduli, respectively. Here  $E_c$  is the energy of the core of the dislocation. A simple argument due to Kosterlitz and Thouless yields an estimate of the melting temperature,  $T_M$ , by considering the free energy of a single dislocation. At nonzero temperature the free energy cost to add a dislocation is given by  $U - TS$ , where  $S = k_B \ln(R/a)^2$  is the entropy associated with the number of possible positions of the dislocation ( $k_B$  is the Boltzmann constant). Therefore, neglecting  $E_c$ , the free energy is

$$F = a^2 \frac{K}{8\pi} \ln \left( \frac{R}{a} \right) - k_B T \ln \left( \frac{R}{a} \right)^2 = \left( a^2 \frac{K}{8\pi} - 2k_B T \right) \ln \left( \frac{R}{a} \right) \quad (2)$$

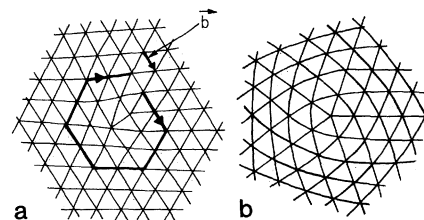


Fig. 2. (a) Schematic representation of a dislocation in a triangular two-dimensional lattice. Such defects are topological defects in the displacement fields of the solid. The atoms are located at the vertices. (b) Disclination in a triangular lattice. The lattice axis rotates by  $60^\circ$  around the central fivefold symmetric site. There are also disclinations in which the rotation is  $-60^\circ$  which have sevenfold symmetry in the central region. In the hexatic phase the large strains in such disclinations are relieved by the free dislocations.

At low temperatures, the free energy for creation of a dislocation is thus very large for a macroscopic system. However, if  $T > T_M$ , the temperature given by  $k_B T_M = a^2 K / 16\pi$ , the free energy becomes negative and hence free dislocations will spontaneously form. Once this occurs, the system will no longer resist shear, since shear stress can be relaxed simply by moving free dislocations. It will hence be a fluid for temperatures above the melting temperature  $T_M$ . The elastic moduli will jump discontinuously to zero at the melting temperature with the combination  $K$  having a universal jump given by

$$K(T_M) = 16\pi k_B T_M / a^2 \quad (3)$$

Remarkably, this prediction (Eq. 3) from the simple free energy argument turns out to agree exactly with detailed calculations of the melting transition, as first pointed out for an analogous case by Nelson and Kosterlitz (8). In order to give a more accurate description of the phase transition it is necessary to consider the effects of interactions between pairs of dislocations. If two dislocations with opposite Burgers vectors are separated by a distance  $r$ , their total energy will be finite but increase as  $\ln r$ . Thus, in the solid phase there will be an equilibrium thermal distribution of dislocation pairs with various separations. In the presence of an applied stress these pairs act very much like electric dipoles in an applied electric field in that they tend to align with the applied stress in such a way as to reduce the stress in the solid just as electric dipoles screen an electric field in a dielectric. This effective screening by the dislocation pairs will thus reduce the elastic constants. A renormalization group theory of the melting transition developed on the basis of these ideas takes into account the effects of

dislocation pairs and also triplets. It yields a higher order phase transition and detailed predictions for the behavior of the elastic moduli and other thermodynamic quantities near  $T_M$ . As mentioned, the jump in the elastic moduli at  $T_M$  still obeys Eq. 3. However, the elastic moduli are found to approach this value in a singular fashion. For example, for a hexagonal crystal

$$\mu(T) = \mu(T_M) + \text{const}(T_M - T)^{\bar{\nu}} \quad (4)$$

where  $\bar{\nu}$  is predicted to be 0.36963 (4, 9). This behavior is represented by the solid line in Fig. 3.

One very peculiar prediction of the dislocation theory is that, in contrast to most higher order phase transitions, at which the specific heat diverges or has a cusp, all the temperature derivatives of the free energy are continuous through the melting temperature. There is only a very difficult to observe essential singularity in the specific heat at  $T_M$ .

Above the melting transition, the positional correlations decay exponentially with a correlation length,  $\xi$ , which is the characteristic separation of the free dislocations. At wavelengths less than  $\xi$ , the fluid can still support shear (and indeed transverse sound can propagate), but at wavelengths greater than  $\xi$  motion of the free dislocations relaxes shear stresses. The correlation length diverges very rapidly as  $T$  approaches  $T_M$  from above, namely

$$\xi(T) \propto \exp[B(T - T_M)^{-\bar{\nu}}] \quad (5)$$

This result is in contrast to the power law divergence of  $\xi(T)$  as  $(T - T_c)^{-\nu}$  at most higher order transitions.

Another interesting prediction of the theory concerns the bond orientational order. In the two-dimensional solid phase the bond orientations exhibit long-range order as illustrated in Fig. 1. Above the transition temperature  $T_M$  the free dislocations destroy the positional order but, as can be crudely seen from Fig. 2a, have a lesser effect on the bond orientational order. In fact, it has been predicted that just above the melting temperature the correlations between the local bond directions at two points in the liquid will decay algebraically with distance (4). This is somewhat analogous to the behavior of a two-dimensional nematic liquid crystal except that a nematic liquid crystal has uniaxial ordering of the orientation of rodlike molecules, whereas this new phase, which has a local hexagonal symmetry, can exist even for spherical molecules with isotropic interactions. For this reason, this fluid phase has been named the hexatic phase. It should exhibit an orientational

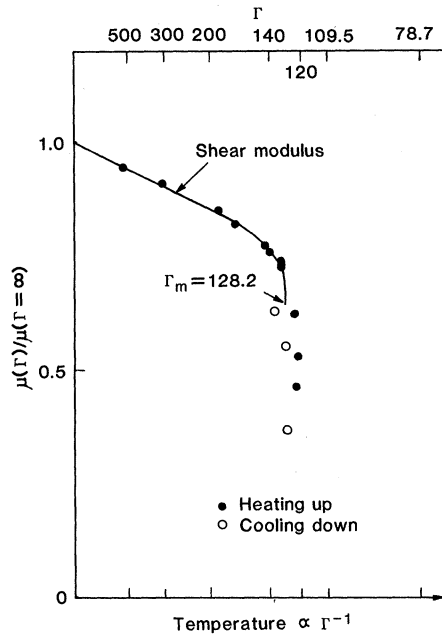


Fig. 3. Shear modulus  $\mu$  plotted against temperature for the two-dimensional electron gas. The solid line is predicted by the dislocation theory (15, 17), while the open and closed circles are the results of Monte Carlo simulations by Morf (15). [Reprinted by permission of the publisher from (15)]

elastic constant  $K_H$  that resists variation of the bond orientations, analogous to the Frank constants of nematic liquid crystals, which likewise describe the resistance to deformation of the local molecular axis.

Since the hexatic phase still has algebraic long-range order in the orientational correlations, there must be a phase transition from this phase to the true isotropic liquid phase. This phase transition, at a temperature  $T_H$ , can again be described in terms of spontaneous creation of defects—in this case disclinations in the hexatic order parameter as illustrated in Fig. 2b. The bond orientation rotates by  $60^\circ$  as one moves around a point disclination. Due to the spontaneous creation of disclinations, the elastic constant  $K_H$  will drop discontinuously to zero at  $T_H$  in a fashion similar to  $K$  at  $T_M$ .

As we have seen, the defect-mediated melting from a solid to an isotropic liquid is predicted to be a two-step process with an intermediate hexatic phase. Although this is an attractive picture, it is based on a long-wavelength renormalization group approach that is strictly valid only in the limit of a low density of thermally activated dislocations. Thus, it is not obviously applicable to any given system of atoms or molecules. The short-wavelength fluctuations, which are ignored, may be important enough to make the transition first order, as in

three dimensions, with no intermediate hexatic phase. Alternatively, the transition could be first order but with a small region of hexatic phase remaining. One recent result that is rather encouraging is the strong confirmation of a similar theory describing two-dimensional superfluids. In a superfluid, the defects analogous to dislocations in the solid are superfluid vortices. Bishop and Reppy (10) performed a series of beautiful experiments on thin helium films which confirm the Kosterlitz-Thouless defect theory of the phase transition from the superfluid to the normal fluid, in particular the universal jump in the superfluid density which is analogous to that in Eq. 3 (8). Additional evidence has accumulated from studies of the analogous transition in thin-film superconductors (11). However, the analogous three-dimensional phase transition in these two cases is second order (in contrast to three-dimensional melting) so that a much stronger case can be made for the dominance of long-wavelength fluctuations near the phase transition of the two-dimensional system. The validity of the dislocation theory for melting is thus much less clear, and indeed there are many cases in which the melting transition is first order (12). The remainder of this article will be devoted to examining the results of computer simulations of two-dimensional solids and a number of experiments on systems in which true two-dimensional behavior can be investigated and which potentially have second-order transitions. These include electrons on the surface of liquid helium, ultrathin free-standing liquid crystal films, and incommensurate rare gas overlayers adsorbed on graphite.

## Numerical Simulations

In order to test the theory of dislocation-mediated melting many numerical simulations with both Monte Carlo and molecular dynamics computations have been carried out (13–16). One of the advantages of these computer simulations, which are strictly two-dimensional, is that many quantities that are difficult to measure in experiments are “measurable” (that is, numerically calculable) in simulations. In addition, computer simulations are possible with a wide variety of interactions between the atoms. The standard Lennard-Jones potential involving a strong repulsive core with an attractive van der Waals tail, a reasonable approximation to the interaction between rare gas atoms, is frequently used, as well as purely repulsive pow-

er law potentials of the form  $V(r) \propto 1/r^\sigma$ . Generally, the properties of the system will depend both on the areal density,  $n_s$ , and the temperature. For power law interactions, however, all the properties are determined by a single dimensionless parameter: the ratio of the characteristic potential energy to the mean kinetic energy  $T$  (the temperature). For example, the case  $\sigma = 1$  describes a two-dimensional layer of electrons (see next section) which interact with a potential  $e^2/r$ , where  $e$  is the electron charge. The dimensionless parameter is then

$$\Gamma = \frac{e^2(\pi n_s)^{1/2}}{k_B T} \quad (6)$$

All the properties of a layer of electrons can thus be determined by varying only the temperature at a fixed density. In the limit where  $\sigma \rightarrow \infty$ , on the other hand, the power law interaction becomes equivalent to that between hard disks. In this case, the order or disorder of the atoms is entirely determined by entropy or free volume. Hard disks form a solid at high densities (near close packing) and melt by a first-order transition below a critical density which is independent of temperature.

Before discussing the results of the computations, we briefly mention the drawbacks of computer simulations. Even with the fastest computers, simulations are limited to a small number of particles, usually less than 1000, so that correlations can be measured only out to rather short distances. Hence, many effects—such as the statistics of dislocations near the Kosterlitz-Thouless transition—may be obscured, especially since the correlation length is expected to grow extremely rapidly just above the melting transition. Another and probably more serious drawback is the relatively short time scale in the simulations. The longest currently affordable runs correspond to only a few hundred picoseconds of real time. Because of the slow motion of defects, the time needed to establish thermal equilibrium will be quite long, and there is considerable controversy over whether the computer simulations are in equilibrium in the region near the melting temperature. With these reservations in mind, we present below a brief summary of the results common to several systems. At low temperatures a nonzero shear modulus is observed, and for most systems the values of the elastic moduli at the apparent melting temperature, obtained both from the dynamic correlation functions and by direct application of stress, are near the Kosterlitz-Thouless prediction (14). In particular, Morf (15) has found (see Fig. 3) quantita-

tive agreement at all  $T < T_M$  between the computed shear modulus for an electron system and analytical calculations (15, 17). In addition, the critical value of  $\Gamma$  obtained agrees well with renormalization group calculations and with experiments with electrons on helium (see below).

In the solid phase, all simulations yield long-range bond orientational and power law positional order. In the fluid phase, on the other hand, the correlations fall off exponentially with a correlation length that grows rapidly as  $T \rightarrow T_M$ . However, the correlation length typically reaches only on the order of five lattice spacings in the liquid phase. This  $\xi$ , though a factor of 3 larger than typical maximum correlation lengths in simple three-dimensional fluids, is considerably less than the system size. In addition, many authors have calculated free energy curves and find hysteresis at the melting transition and an apparent latent heat,  $T\Delta S$ , which they interpret as evidence for a first-order transition. The apparent entropy changes  $\Delta S$  are, however, typically one-third to one-half of the changes at the corresponding three-dimensional melting transition.

Pictures of the dislocation distribution, obtained by a clever method pioneered by McTague *et al.* (16), show only bound pairs below  $T_M$ , as expected. As the temperature increases they tend to show a very rapid rise in the number of dislocations near  $T_M$ , including “free” ones as well as a region of possible two-phase coexistence consistent with a first-order transition. It appears rather unlikely, however, that equilibrium can be reached, even in the longest computer runs, once the correlation length is much more than a few lattice spacings. It is thus not clear whether the results are more consistent with a second-order Kosterlitz-Thouless transition for some interactions or always indicate a first-order transition. The interpretation of the results may well remain a matter of controversy and personal prejudice for some time. As we will see, however, several real experimental systems already yield results that are quite consistent with the Kosterlitz-Thouless-Halperin-Nelson-Young theories.

### Electrons on Helium

One of the simplest two-dimensional systems consists of a single layer of electrons floating 100 angstroms above the surface of superfluid helium-4, repelled by the bulk helium but held to the surface by their image potential interac-

tion and an applied vertical electric field (18). The electrons behave almost completely classically—quantum effects are negligible due to the low densities,  $n_s \approx 10^8$  to  $10^9$  per square centimeter. As mentioned above, due to the simple form of the Coulomb interaction between the electrons, all properties of the system are a function only of the dimensionless ratio  $\Gamma$ , given in Eq. 6. At small  $\Gamma$  the electrons are uncorrelated and form a fluid or two-dimensional plasma. However, when  $\Gamma$  exceeds a critical value  $\Gamma_M$ , the electrons are expected to form a hexagonal Wigner crystal—named for the first physicist to suggest that at low densities electrons should behave classically and crystallize.

A few years ago, in the culmination of a series of experiments on the electron fluid, Grimes and Adams (19) found that if they cooled the electrons on helium in their cylindrical experimental cell to below 0.5 K, several mysterious new resonances appeared in the radio-frequency absorption spectrum. The temperature at which these modes appeared scaled properly with  $\sqrt{n_s}$ , corresponding to a value of  $\Gamma$  at onset of  $\Gamma_M = 137 \pm 15$ , which they interpreted as the melting point of the Wigner crystal.

A detailed analysis of the experiments by Fisher *et al.* (20) led to the interpretation of the new resonances as coupled longitudinal modes of the electron solid and helium surface waves (ripples), with wavelengths determined by the cylindrical sample cell. In the solid phase, the electric field pressing the electrons onto the helium surface causes a very shallow (0.01 to 0.1 Å) dimple to form under each electron (21). In the fluid phase, the electrons move too rapidly for the dimples to form. The coupled modes—which involve relative motion of the electron lattice and dimple lattice—are thus a good indication of the presence of a Wigner crystal.

Experimentally, while the resonances appear rapidly as the system is cooled, there is no jump in frequency or amplitude. In addition, no hysteresis is observed. Both of these observations are consistent with a higher order melting transition.

While it is only possible at present to compare  $\Gamma_M$  with the dislocation theory, as discussed in the previous section, in principle it should be possible to obtain the shear modulus of the electron crystal by exciting long-wavelength shear waves electromagnetically and measuring the transverse sound velocity. Direct comparison with the theoretical prediction for the jump in the elastic moduli should then be possible.

One of the advantages of electrons on helium, in addition to the simple interactions, the lack of impurities, and the possibilities of coupling to the electrons electromagnetically, is that the helium substrate, unlike solid substrates, does not affect any thermodynamic or static properties of the electron layer. In fact, statistical mechanics can immediately "integrate out" the effects of the helium ripplons and henceforth ignore them as far as any static properties are concerned. It is thus rather ironic that the first observation of the long expected Wigner crystal was made possible by the dynamic coupling of the electrons to ripplons.

### Liquid Crystal Films

While electrons on helium form a very low density solid that does not have structure on atomic scales, most two-dimensional solids are formed of atoms or molecules with lattice spacings of a few angstroms. Since two-dimensional melting is basically a structural problem, one expects x-ray scattering, which is sensitive to structure on atomic scales, to be an important experimental probe for studying other two-dimensional systems.

However, two major difficulties generally prevent routine x-ray studies of two-dimensional melting. First, although sur-

faces, interfaces, and thin films literally surround us, it is quite rare to come upon a two-dimensional crystal to use as a sample. Nevertheless, as we will describe below, it has been possible to prepare suitable two-dimensional crystals and study their behavior near melting. Second, the x-ray scattering cross section for a two-dimensional system is generally small, some four to six orders of magnitude weaker than that of three-dimensional crystalline specimens. Fortunately, the recent development of x-ray scattering experiments at high-flux synchrotron radiation sources such as the Stanford Positron Electron Accelerating Ring (SPEAR) has overcome the

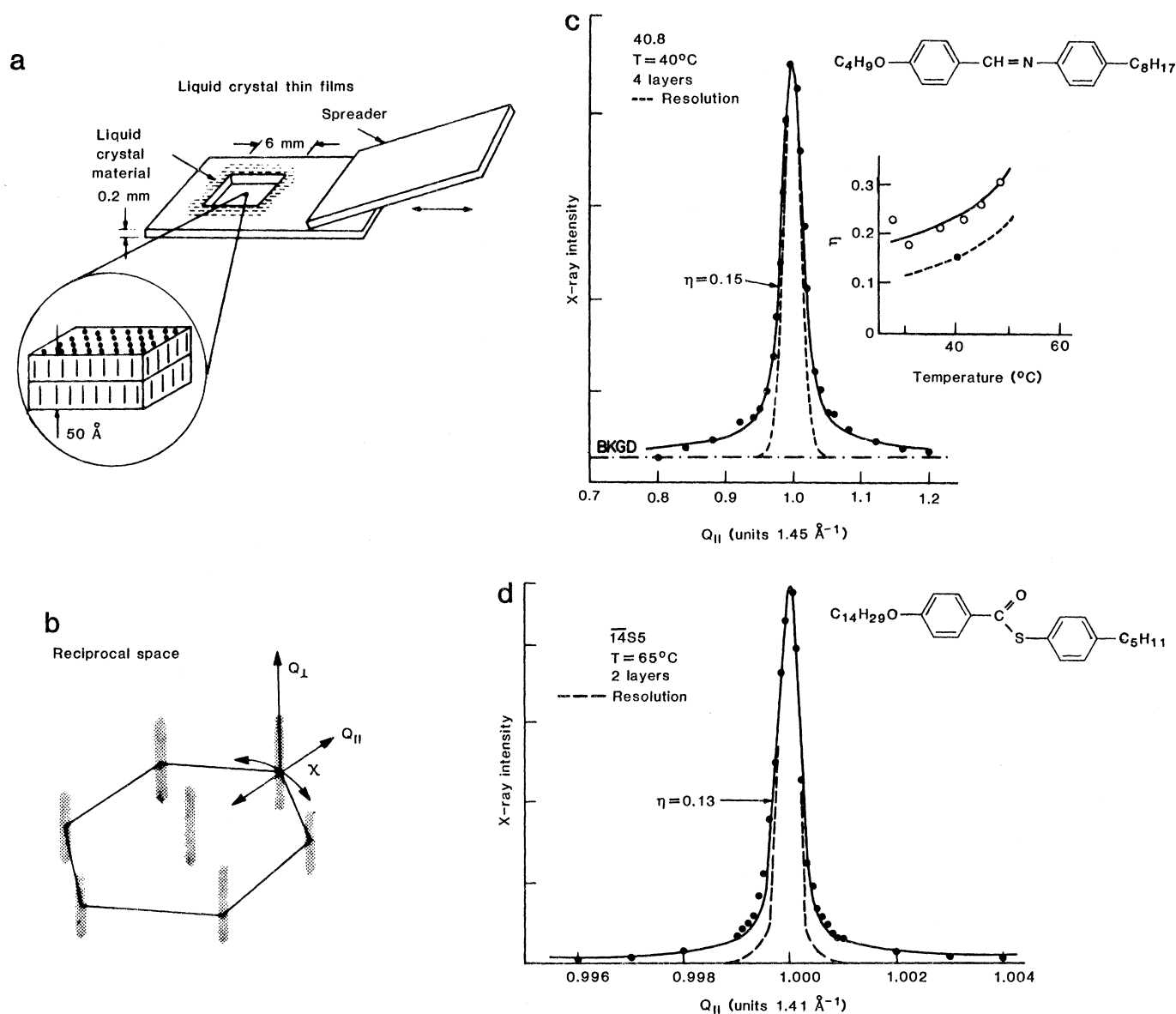


Fig. 4. (a) Schematic representation of the liquid crystal film drawing technique with inset showing an enlarged section of two-layer crystalline film. (b) Reciprocal space appropriate to a simple two-dimensional hexagonal lattice, showing the different directions of the x-ray scans described in the text. (c) X-ray data obtained on a four-layer film by use of a rotating anode x-ray generator with a diffraction apparatus having a resolution shown by the dashed line (width  $\approx 0.04 \text{ \AA}^{-1}$ ). The solid line is a fit of the power law line shape described in the text with exponent  $\eta = 0.15$ . (Inset) Temperature dependence of  $\eta$ ; the two curves represent upper and lower limits of the uncertainty in the fitting procedures. [Reprinted by permission of the publisher from (23)] (d) X-ray data obtained on a two-layer film at the Stanford Synchrotron Radiation Laboratory, using the improved resolution available with synchrotron beams (width  $\approx 6 \times 10^{-4} \text{ \AA}^{-1}$ ). The solid line is a fit to the power law line shape with  $\eta = 0.13$ . [From (25)]

intensity limitations of conventional laboratory x-ray sources.

The first attempts to study the melting of two-dimensional crystals exploited the remarkable ability of some liquid crystals to form freely suspended films (like soap bubble films). These can be made as thin as two molecular layers (50 Å) with an area of 1 cm<sup>2</sup>. This technique was developed at Harvard (22) and has been exploited in x-ray scattering experiments by Moncton and Pindak (23). As shown in Fig. 4a, the film is drawn across an open hole in a glass cover slide. In the crystalline phase, the elongated molecules order with their long axes perpendicular to the plane of the film and form a simple close-packed hexagonal lattice on the plane. Optical reflectivity measurements can easily deter-

mine the thickness of the film—that is, the exact number of layers—which is found to be uniform over the entire sample area. Generally, this thin liquid crystal film technique offers two important advantages. First, it produces single-crystal two-dimensional solids that are not under the influence of any substrate potentials. Second, from the x-ray scattering viewpoint, the lack of any substrate or sample cell walls greatly reduces the background scattering against which the x-ray signal must be visible.

In Fig. 4b we show a schematic view of the reciprocal space representing this two-dimensional hexagonal lattice. In diffraction experiments Bragg rods are observed by scanning the x-ray momentum transfer variable  $Q$  and measuring the scattering intensity. One is generally

interested in the line shape of the rod, scanning out from the origin of reciprocal space; it is this information that is directly related to the Fourier transform of the positional correlation function discussed in the theoretical section. Figure 4c shows data (24) obtained on a material called 4O.8 [*N*-(4-*n*-butyloxybenzylidene)-4'-*n*-octylaniline] by using a conventional (50-kilowatt) rotating anode x-ray generator, and Fig. 4d shows data (25) on another material, 14S5 (4-*n*-pentylbenzenethio-4'-*n*-tetradecyloxybenzoate) taken with synchrotron radiation. In both cases the samples are in the two-dimensional crystalline state, where Bragg singularities should theoretically be of the form  $S(Q) = |Q - G|^{-2+\eta}$ . Indeed, this form does fit the experimental line shapes. The most remarkable aspect

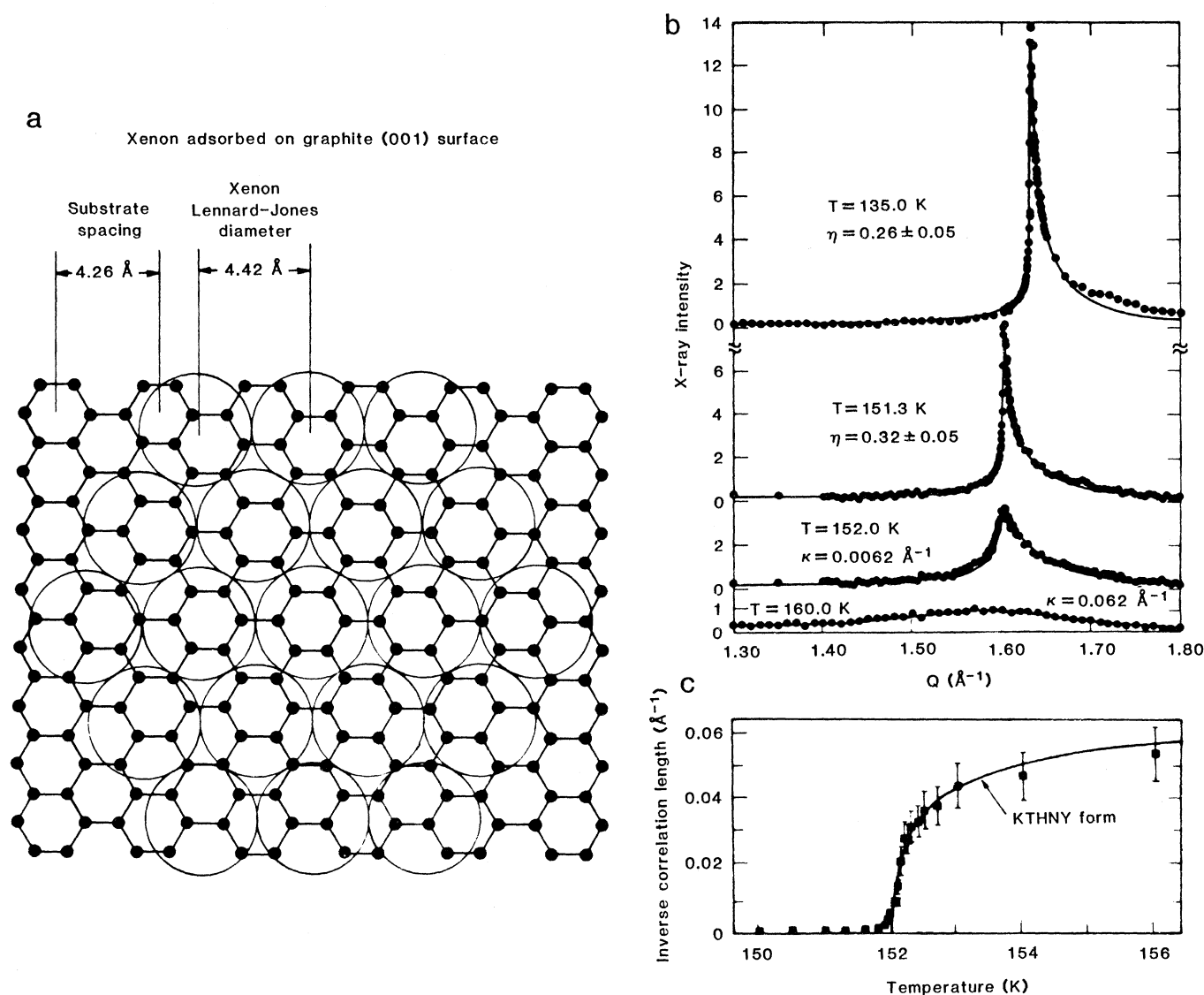


Fig. 5. (a) Illustration of a monolayer of xenon adsorbed on the (001) surface of graphite. The structure at the full monolayer coverage is incommensurate with the substrate because of the large size of the xenon atoms. (b) Typical diffraction profiles from the closed cell solidification runs. Empty cell background, corrected for xenon x-ray absorption, has been subtracted. The solid lines for  $T = 135.0$  and  $151.3$  K are fits to a power law line shape, as discussed in the text. The solid lines for  $T = 152.0$  and  $160.0$  K are fits to a powder and tilt-averaged Lorentzian. [Reprinted by permission of the publisher from (30)] (c) Inverse correlation length  $\kappa$  determined from a Lorentzian line shape analysis. The solid line is a fit of  $\kappa$  versus  $T$  to the theoretical prediction with  $\bar{\nu} = 0.4$  and  $T_M = 152$  K, as discussed in the text. [Reprinted by permission of the publisher from (30)]

of the data is the fact that the line shape scales with the instrumental resolution when the latter is improved by a factor of  $\approx 50$  in going from rotating anode data (Fig. 4c) to synchrotron radiation data (Fig. 4d). The solid lines in Fig. 4, c and d, are fits to the data obtained by convoluting the resolution function (dashed line) with  $S(Q) = |Q - G|^{-2+\eta}$ . Since this form has no length scale, the resulting convoluted function will depend only on the ratio of the momentum transfer to the resolution width. This would clearly not be the case if the system were a liquid, for which the scattering intensity is of the form  $S(Q) \propto (Q^2 + \kappa^2)^{-1}$ , where  $\kappa = 1/\xi$  is the inverse of the liquid correlation length. This resolution scaling is thus strong evidence for the applicability of the two-dimensional crystalline structure factor.

As discussed at the outset of this article, one expects a two-dimensional solid to exhibit a nonzero shear modulus in addition to the characteristic structure factor discussed above. Pindak *et al.* (26) succeeded in measuring the in-plane shear modulus of liquid crystal films by using a very sensitive resonant oscillator technique. From these experiments there is certainly no doubt about the two-dimensional solid nature of these materials, and one is thus encouraged to use x-ray data to extract the temperature dependence of the exponent  $\eta$ . A first attempt to do this is shown in the inset in Fig. 4c. The measurements are subject to some uncertainty and the solid and dashed lines represent upper and lower limits. The results indicate that  $\eta$  at melting ( $T_M = 50^\circ\text{C}$  for 4O.8) is close to the range predicted by theory,  $1/4 \leq \eta \leq 1/3$ . Although there are few data so far above  $T_M$ , experiments on the melting of thin-film liquid crystals are being continued.

Studies of thick films (greater than 100 layers) have produced exciting indirect evidence in support of the existence of the hexatic phase between the solid and fluid phases in a material called 65OBC (27) (*n*-hexyl-4'-*n*-pentylxybiphenyl-4-carboxylate). In this work, a new liquid crystal phase has been discovered which can be thought of as a stack of two-dimensional hexatic layers. The x-ray data show that sixfold bond orientational order develops in the layers upon cooling through a well-defined higher order phase transition. Above the transition, the system is in the smectic A phase, which is a bulk three-dimensional phase that can be thought of as a stack of two-dimensional liquid layers. The x-ray scattering from this phase consists of a cylinder in reciprocal space. The cylin-

der wall has a Lorentzian intensity profile as a function of the radial momentum transfer,  $Q_{\parallel}$  (see Fig. 4b). As the transition takes place, the scattering in the cylinder develops six maxima as a function of  $\chi$ , indicating the development of long-range bond-orientational order; but the Lorentzian shape persists in the  $Q_{\parallel}$  direction. Obviously the system has not developed the positional long-range order characteristic of a three-dimensional crystal. Rather, the observed structure is that expected, and in fact anticipated (28), in extensions of the Halperin-Nelson ideas to a three-dimensional stack of layers, each of which is in the two-dimensional hexatic state. In analogy with the two-dimensional hexatic phase, the three-dimensional stacked hexatic phase is not solid and should not support a shear force. Indeed, measurements of the in-layer shear modulus by Pindak *et al.* (29) reveal that the shear modulus, which is nonzero in the lower temperature three-dimensional crystalline phase, vanishes in the stacked hexatic phase. These experiments strongly suggest that thin liquid crystal films offer the best opportunities for observation of a two-dimensional hexatic phase.

#### Rare Gases Adsorbed on Graphite

Having shown the applicability of the power law structure factor to the Bragg scattering from two-dimensional crystals and mentioned the discovery of a three-dimensional analog to the hexatic phase, we now turn our attention to the details of the two-dimensional melting phase transition. A class of systems consisting of rare gases physisorbed on the (001) basal planes of pyrolytic graphite has provided an enormous array of surface phase transitions that are ideally suited to x-ray scattering studies (30). To date, the most substantial progress on the two-dimensional melting problem has been made with the system consisting of slightly more than one monolayer of xenon atoms, as shown schematically in Fig. 5a. The xenon Lennard-Jones diameter is larger than the separation of the relevant minima in the substrate potential of the graphite, and hence the natural lattice spacing of the adsorbate is incommensurate with the substrate. It has been shown theoretically that the weak graphite potential (37 K) should not qualitatively alter the behavior of the melting phase transition from that on a smooth substrate even though the system differs slightly from the ideal two-dimensional system. In general, substrate potentials and other effects such as promotion to

the second layer can affect the nature of the phase transition. Nevertheless, the data shown in Fig. 5, b and c, demonstrate consistency with the dislocation theory at a remarkably quantitative level (30).

In Fig. 5b, we show a series of scans of x-ray intensity versus the radial momentum transfer through the Bragg rods (see Fig. 4b). The disorder of the graphite substrate causes an azimuthal averaging of the scattering, rendering it effectively cylindrical. In addition, substrate tilt disorder (that is, in the orientations of the graphite planes) leads to an asymmetric line shape with excess high- $Q_{\parallel}$  scattering. However, this disorder is well understood and does not stand in the way of extracting the intrinsic line shapes as the data of Fig. 5b demonstrate. In the experiment, the melting transition occurs at  $T_M = 152$  K. Two scans below  $T_M$  shown in the upper portion of Fig. 5b are well described by line shapes based on convoluting power law singularities with the resolution function and performing the appropriate azimuthal and tilt averages. In contrast to the liquid crystal case, the resolution width here is dominated by the coherence size ( $\approx 2000$  Å) of the substrate domains. At low temperatures (see the  $T = 135$  K scan) a small bump on the high- $Q_{\parallel}$  side can be seen and is understood in terms of weak modulation of the xenon overlayers by the substrate potential. This bump weakens gradually and has vanished before reaching  $T_c$ . Excluding this effect, the data in this two-dimensional crystal phase can be fit within experimental error to the  $\eta$  power law form, with the exponent  $\eta$  increasing with temperature to a value at melting in the range predicted by theory.

Above the higher order transition at  $T_M$ , a free two-dimensional system would presumably be in the hexatic phase with an isotropic liquid phase at higher temperatures. The physisorbed systems are expected to exhibit only one phase above  $T_M$ , which will be orientationally ordered at all temperatures due to the presence of the substrate. Observing even this externally imposed orientational order is not possible, however, in the presence of azimuthal disorder. Nevertheless, one can see the evolution of finite positional correlations above  $T_M$ , which produce a Lorentzian shaped structure factor with a temperature-dependent inverse correlation length  $\kappa$ . Data taken between 152 and 160 K show a continuous evolution of the correlation length over an entire decade limited above by the finite size of the substrate domains. As shown in Fig. 5c, the tem-

perature dependence of the correlation length is marginally better described by the form predicted by the dislocation melting theory,  $\kappa \propto \exp[-B(T - T_M)^{-\nu}]$ , than by the conventional power law singularity of the form  $\kappa \propto (T - T_c)^\nu$ . Of course, the most notable observation is that the correlation length grows increasingly rapidly as  $T_M$  is approached from the fluid side to a length scale far in excess of those seen in any three-dimensional liquid and greater than the size of any two-dimensional computer-simulated system. These data thus provide very convincing evidence for a higher order transition.

While many experiments need to be done to make a conclusive case for dislocation-mediated two-dimensional melting, the results of the experiments described here look extremely encouraging in a number of cases.

#### References and Notes

1. J. M. Kosterlitz and D. J. Thouless, *J. Phys. C* **6**, 1181 (1973); J. M. Kosterlitz, *ibid.* **7**, 1046 (1974).
2. W. Shockley, in *L'Etat Solide*, Proceedings of

the Neuvieme Conseil de Physique, Institut International de Physique Solvay (Stoops, Bruxelles, 1952).

3. Transitions with no latent heat are often called second order, which suggests a jump in the specific heat, or continuous, which suggests no singular behavior. To avoid confusion, we will refer to these phase transitions as higher order.
4. B. I. Halperin and D. R. Nelson, *Phys. Rev. Lett.* **41**, 121 (1978); D. R. Nelson and B. I. Halperin, *Phys. Rev. B* **19**, 2456 (1979).
5. F. Bloch, *Z. Phys.* **61**, 206 (1930); R. E. Peierls, *Ann. Inst. Henri Poincare* **5**, 177 (1935).
6. T. M. Rice, *Phys. Rev. A* **140**, 1889 (1965); N. D. Mermin, *ibid.* **176**, 250 (1968); see also L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, London, ed. 2, 1969), p. 466.
7. See, for example, F. R. N. Nabarro, *Theory of Dislocations* (Clarendon, Oxford, 1967). As may be seen in Fig. 2a, a dislocation in a hexagonal crystal actually consists of two extra half rows of atoms at  $60^\circ$  to each other.
8. D. R. Nelson and J. M. Kosterlitz, *Phys. Rev. Lett.* **39**, 1201 (1977).
9. A. P. Young, *Phys. Rev. B* **19**, 1855 (1979).
10. D. J. Bishop and J. D. Reppy, *Phys. Rev. Lett.* **40**, 1727 (1978).
11. M. R. Beasley, J. E. Mooij, T. P. Orlando, *ibid.* **42**, 1165 (1979); A. F. Hebard and A. T. Fiory, *ibid.* **44**, 291 (1980).
12. R. J. Birgeneau, E. M. Hammons, P. Heiney, P. W. Stephens, P. M. Horn, in *Ordering in Two Dimensions*, S. K. Sinha, Ed. (North-Holland, New York, 1980), p. 29.
13. J. Tobochnik and G. V. Chester, in *ibid.*, p. 339; *Phys. Rev. B*, in press.
14. F. F. Abraham, *Phys. Rev. Lett.* **44**, 463 (1980); in *Ordering in Two Dimensions*, S. K. Sinha, Ed. (North-Holland, New York, 1980), p. 165; J. O. Broughton, G. B. Gilmer, J. D. Weeks, *Phys. Rev. B* **25**, 4651 (1982).

15. R. Morf, *Phys. Rev. Lett.* **43**, 931 (1979).
16. J. P. McTague, D. Frenkel, M. P. Allen, in *Ordering in Two Dimensions*, S. K. Sinha, Ed. (North-Holland, New York, 1980), p. 147.
17. D. S. Fisher, *Phys. Rev. B*, in press.
18. C. C. Grimes, *Surf. Sci.* **73**, 379 (1978).
19. \_\_\_\_\_ and G. Adams, *Phys. Rev. Lett.* **42**, 795 (1979).
20. D. S. Fisher, B. I. Halperin, P. M. Platzman, *ibid.*, p. 798; D. S. Fisher, in *Ordering in Two Dimensions*, S. K. Sinha, Ed. (North-Holland, New York, 1980), p. 189.
21. Yu. P. Monarkha and V. B. Shikin, *Zh. Eksp. Teor. Fiz.* **68**, 1423 (1975) [*Sov. Phys. JETP* **41**, 710 (1976)].
22. C. Y. Young, R. Pindak, N. A. Clark, R. B. Meyer, *Phys. Rev. Lett.* **40**, 773 (1978); C. Rosenblatt, R. Pindak, N. A. Clark, R. B. Meyer, *ibid.* **42**, 1220 (1979).
23. D. E. Moncton and R. Pindak, in *Ordering in Two Dimensions*, S. K. Sinha, Ed. (North-Holland, New York, 1980), p. 83.
24. \_\_\_\_\_, *Phys. Rev. Lett.* **43**, 701 (1979).
25. D. E. Moncton, R. Pindak, S. C. Davey, G. S. Brown, M. E. Neubert, unpublished results.
26. R. Pindak, D. J. Bishop, W. O. Sprenger, *Phys. Rev. Lett.* **44**, 1461 (1980).
27. R. Pindak, D. E. Moncton, S. C. Davey, J. W. Goodby, *ibid.* **46**, 1135 (1981).
28. R. J. Birgeneau and J. D. Litster, *J. Phys. (Paris) Lett.* **39**, 399 (1978).
29. R. Pindak, W. O. Sprenger, D. J. Bishop, D. D. Osheroff, J. W. Goodby, *Phys. Rev. Lett.* **48**, 173 (1982).
30. P. A. Heiney, R. J. Birgeneau, G. S. Brown, P. M. Horn, D. E. Moncton, P. W. Stephens, *ibid.*, p. 104.
31. We wish to acknowledge many suggestions for clarifying the manuscript by J. D. Weeks, P. C. Hohenberg, and M. E. Fisher. In addition, we acknowledge many stimulating discussions with our colleagues and collaborators.

## Critical Care at Tianjin's First Central Hospital and the Fourth Modernization

Renée C. Fox and Judith P. Swazey

The Chinese refer appreciatively to what they call a "window-picture": a dynamic view of a landscape, framed by a window in such a way that it is not only esthetically pleasing but also humanly interesting and intellectually and morally edifying. The Critical Care Unit (CCU) of the Tianjin First Central Hospital constituted such a window-picture for us (1). It provided us with a concrete, focused perspective on the application of China's

current policy of the four modernizations (agriculture, industry, national defense, and science and technology) to the field of medicine. On this unit, the fourth modernization (2)—science and technology—is continuously brought to bear on the cases of critically ill patients who are sent to the hospital from the cities and the countryside of the province in which it is located. The CCU is part of a prominent, urban, "upper middle level hospital" that is known for its leadership in nursing and its competence in medicine and surgery, particularly the treatment of emergency and critical conditions. The hospital is committed to serving the patient by progressively "scaling the heights" of modern medicine through advanced scientific and techno-

logically sophisticated care, scientific research, scientific management and quality control, and the effective teaching and implementation of "medical morality."

In striving to realize these goals, the CCU epitomizes the complex processes of what the Chinese call "walking on two legs" (3). A chain of dualities is involved: an intricate balancing of modern Western and traditional Chinese medicine, community public health and individual patient care, central control and institutional autonomy, preventive and curative medicine, primary and tertiary care, acute and chronic illness, rural and urban needs, mental and manual labor, being "Red" and being "expert," proletarianism and elitism, the old and the new, and the balancing of ideas and resources imported from abroad and "made in China."

A series of dilemmas that ramify beyond the walls of the First Central Hospital and its CCU are contained in these dualities. Societal precepts constantly shift concerning how the dilemmas ideally should be resolved, and what combinations of binary elements and states of equilibrium between them this implies. Proper "two-leggedness" in the medical as in all other spheres of Chinese society is not only defined and monitored but repeatedly altered by the flow of minor and major national policy directives that

Renée C. Fox is Annenberg Professor of the Social Sciences at the University of Pennsylvania, Philadelphia 19104, and was a member of the AAAS Board of Directors from 1978 to 1981. At the time this article was written Judith P. Swazey was Executive Director of Medicine in the Public Interest and Adjunct Professor of Sociomedical Sciences at Boston University Schools of Medicine and Public Health. She is now President of College of the Atlantic, Bar Harbor, Maine 04609.