essentially constant β_p despite marked changes in MHD intensity. With P_b reduced to 0.6 MW to produce a β_p value out of saturation and a plasma regime in which the independently unstable, high-n, pressure-driven modes are less likely to be important, the amplitude of the instability signals again decreased markedly as B_T was raised (Fig. 4). However, β_p did not increase; neither did the stored energy ($\propto \beta_p I_p^2$) or the gross confinement time ($\propto \beta_p I_p^2/P_{\mathrm{in}}$).

We conclude that the MHD activity observed in ISX-B is well understood in terms of the resistive MHD model and that this observed activity is not responsible for pronounced degradation of confinement. The $n>1$, pressure-driven modes predicted by the model are a possible explanation for the observed degradation, but their presence in this plasma has not been experimentally verified.

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Density-Wave Theory of First-Order Freezing in Two Dimensions

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The spontaneous formation of a finite-amplitude density wave of hcp lattice symmetry is discussed, following the work of Ramakrishnan and Yussouff. The freezing parameters do not depend on the interatomic force law, contain no adjustable parameters, and can be improved perturbatively. The results agree very well with those from computer simulation for a wide range of systems.

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There has been considerable recent interest in the nature of the liquid-solid transition in two dimensions,[1] spurred by the development of a beautiful and detailed dislocation unbinding theory due to Halperin and Nelson[2] (and also Young[2]) based on the ideas of Kosterlitz and Thouless.[3] Many experiments and computer experiments have been carried out[1,4] to test its novel predictions, e.g., that there is a hexatic phase between the solid and the isotropic liquid, and that the transitions are thermodynamically continuous. Most recent computer simulations, e.g., on the Lennard-Jones system at constant pressure,[5] and r^{-n} systems with $n=12$,[6,7] $n=3$,[8,9] and $n=1$,[10] show a first-order transition and no hexatic phase. Freezing parameters such as the entropy change $(\Delta S/k_B)$[6-10] and the structure factor peak near freezing[7,9,11,12] are close to 0.3 and 5.0, respectively, for widely different systems; two-dimensional fluids freeze similarly though suddenly. It is possible that the true long-time phase may not be sampled in simulation studies if defect relaxation times are very long. It is therefore significant that rare-gas monolayers adsorbed on smooth substrates *all* show first-order melting if sufficiently incommensurate and have a triple point T_t to within a few percent of the Lennard-Jones computer simulation value.[13] In this Letter, I present new analytical results and detailed calculations based on a theory due to Ramakrishnan and Yussouff.[14,15] This theory considers the solid near melting as a calculable perturbation on the liquid, and shows that their free-energy difference is determined by short-range correlations and geometrical (structural) factors. The calculated freezing parameters (see also Ref. 14) are close to those obtained in computer experiments. I also make a number of predictions which can be checked.

The mean-field transition is expected to be first order from symmetry arguments; there are cubic terms. The question of whether first-order melting occurs below the dislocation unbinding temperature, or the opposite, is not investigated here. Abraham[16] finds from careful Monte Carlo simulation that the former is true. I briefly comment on this question at the end.

Consider the spontaneous formation of a lattice periodic density wave in the system, so that the density is

$$\rho(\vec{r}) = \rho_0[1 + \eta + \textstyle\sum_G \lambda_G \exp(i\vec{G}\cdot\vec{r})], \tag{1}$$

where the $\vec{G}$'s are reciprocal-lattice vectors (rlv's). This sets up a potential $v(\vec{r})$ which is a functional of the density, i.e.,

$$\beta v(\vec{r}) = \int c(\vec{r}-\vec{r}\,')[\rho(\vec{r}\,') - \rho_0]d^3r' + O(\delta\rho)^2 \tag{2a}$$

$$= c_0\eta + \textstyle\sum_G c_G \lambda_G \exp(i\vec{G}\cdot\vec{r}). \tag{2b}$$

The functional derivative $c(\vec{r}-\vec{r}\,')$ is the fluid direct correlation function. The structure factor $S_{\vec{q}} = (1 - c_{\vec{q}})^{-1}$. The expression (2a) is useful if higher-order terms are relatively small. We discuss their effect later. For this classical system, one has the Boltzmann relation $\rho(\vec{r}) = \rho_0 \exp[-\beta v(\vec{r})]$, i.e., a self-consistency condition for $\{\eta, \lambda_G\}$,

$$[1 + \eta + \textstyle\sum_G \lambda_G \exp(i\vec{G}\cdot\vec{r})] = \exp[c_0\eta + \textstyle\sum_G c_G \lambda_G \exp(i\vec{G}\cdot\vec{r})]. \tag{3}$$

The thermodynamic potential change $\beta(\Omega - \Omega_0) = \omega$ associated with this density change is given by

$$\omega = \beta\int v(\vec{r})\rho(\vec{r})d^3r - \tfrac{1}{2}\int c(\vec{r}-\vec{r}\,')[\rho(r) - \rho_0][\rho(\vec{r}\,') - \rho_0]d^3r\,d^3r' \tag{4a}$$

$$= (-1 + c_0)\eta + \tfrac{1}{2}\textstyle\sum_G c_G|\lambda_G|^2, \tag{4b}$$

where the first term in Eq. (4a) is the internal energy contribution and the second term is from density fluctuations. On integrating Eq. (3) over $\vec{r}$, we see that η is a function of $\{\lambda_G\}$, c_0, and $\{c_G\}$ so that Eq. (4a) for ω depends only on the order parameters $\{\lambda_G\}$. The extremum conditions $\partial\omega/\partial\lambda_G = 0$ are contained in the self-consistency relation Eq. (3).

The structure factor S_q has a single narrow peak for fluids near freezing, in three and even more prominently in two dimensions. Thus $c_{\vec{q}}$ is largest for a wave vector which we identify as the smallest rlv $\vec{G}_1$ of the solid, since condensing into this wave-vector mode is energetically most favorable. To begin with, we therefore ignore all other order-parameter modes. Further, in the regime of interest the fluid phase is virtually incompressible, with $-c_0 \simeq 50 \gg 1$.[6,7] So we consider initially the incompressible limit, i.e., area change $\eta \to 0$, $-c_0 \to \infty$, but $c_0\eta$ finite.

The free-energy balance and extremum equations simplify to

$$\omega = -\ln\{A_{un}{}^{-1}\int d^3r \exp[c_1\lambda_1 \textstyle\sum_{G_1} \exp(i\vec{G}_1\cdot\vec{r})]\} + \tfrac{1}{2}n_1c_1\lambda_1{}^2 \tag{5a}$$

$$= -\ln\varphi(c_1\lambda_1) + \tfrac{1}{2}n_1c_1\lambda_1{}^2 \tag{5b}$$

and

$$n_1\lambda_1 = \varphi'(c_1\lambda_1)/\varphi(c_1\lambda_1), \tag{6}$$

where $c_1 = c_{G_1}$, $\lambda_1 = \lambda_{G_1}$, and the set $\{\vec{G}_1\}$ has n_1 members. The first term in Eq. (5a) (the attractive internal energy) is related to the incompressibility condition, i.e.,

$$\rho(\vec{r}) = \exp[-\ln\varphi(c_1\lambda_1)]\exp[c_1\lambda_1\textstyle\sum_{G_1}\exp(i\vec{G}_1\cdot\vec{r})].$$

The free-energy balance is determined by two-body correlations (c_1) and by geometrical crystal-structure-dependent factors [i.e., $\sum_{G_1}\exp(i\vec{G}_1\cdot\vec{r})$]. The two equations (5) and (6) for the two unknowns c_1 and λ_1 can be solved for a given crystal structure, i.e., a given set of vectors $\{\vec{G}_1\}$. One thus obtains the same freezing condition for *all* fluids, irrespective of their interatomic force law.[14]

In two dimensions there is no freezing into a square lattice. For a hexagonal lattice, there is a solution which we locate numerically. In Fig. 1, ω is exhibited as a function of order parameter λ_1, for various values of c_1. There is always a fluid solution. For $c_1 = 0.85$, the fluid is more stable and at $c_1 = 0.86$, the hexagonal solid is more stable than the fluid. The transition is definitely first order; at the freezing point ($c_{1f} = 0.856$) the order parameter λ_1 jumps from zero to $\lambda_{1f} = 0.51$. The scale of free-energy differences involved is, however, rather small, $\sim 10^{-2} k_B T$ per unit cell. The density distribution in a unit is completely determined:

$$\rho(x,y) = (1.01/3\sqrt{3}a^2)\exp[0.45(2\cos 2v + 4\cos u \cos v)], \tag{7}$$

where $u = 2\pi x/a$ and $v = 2\pi/\sqrt{3}a$, the lattice vectors being $a(\pm 1, 0)$, $(a/2)(\pm 1, \pm\sqrt{3})$. For small compressibility S_0 the fractional area change is

$$\eta = 3c_1\lambda_1^2(1-c_0)^{-1} = 0.7S_0. \tag{8}$$

The corrections to be discussed below increase the constant of proportionality by about 20%. The entropy loss on freezing is given by[17]

$$\Delta S = [\partial(\Omega - \Omega_0)/\partial T]_\mu = 3k_B\lambda_1^2 T(\partial c_1/\partial T)_\mu. \tag{9}$$

The derivative $(\partial c_1/\partial T)_\mu$ is not known. However, in the spirit of this theory it can be estimated from the solid side. In the one-phonon, high-T limit, $S_q \propto (k_B T/M)[\sum_\lambda(\hat{e}_{q\lambda}\cdot\vec{q})^2/\omega_{q\lambda}^2]$. Assuming $\partial\omega_{q\lambda}/\partial T = 0$, we find

$$\Delta S/k_B = (n_1/2)\lambda_1^2(1-c_1). \tag{10}$$

This is equal to 0.12 in two dimensions, a gross underestimate since $S_q \propto \omega_q^{-2}$ and there is considerable phonon softening near T_m.[18] This is not true in three dimensions, and the result Eq. (10) (giving $\Delta S = 0.90k_B$ for *all* bcc crystals, in very good agreement with experiment) resolves the long-standing puzzle of the size and constancy of melting entropy in simple substances.

We now calculate corrections to the above results. This can be done perturbatively, by expanding the free-energy ω around the minimum (c_{1f}, λ_{1f}) and retaining only the leading terms. We find, for example, that

$$\delta c_1 = -\tfrac{3}{2}c_{1f}^2 S_0 - (\lambda_{2f}/\lambda_{1f})^2 c_2 - \tfrac{2}{3}\lambda_{1f}c^{(3)}, \tag{11}$$

where the first term is the correction due to finite small compressibility S_0 and the second arises from the order parameter λ_2 corresponding to a density wave of wave vector $\vec{G}_2 = 2\vec{G}_1$ (c_q has a second smaller peak c_2 at $|\vec{q}| = |\vec{G}_2|$). Other modes n couple less well to the dominant mode λ_1, and have smaller c_n. The third term is from correlations ($c^{(3)}$) between three density fluctuations, which are zero-sum members of the set $\{\vec{G}_1\}$. I have checked by direct numerical computation that Eq. (11) is accurate to within 15% for $S_0 < 0.05$, $c_2 < 0.40$, and $c^{(3)} < 0.15$. Since S_0 is typically 0.02, $(\lambda_{2f}/\lambda_{1f})^2 \simeq 0.075$ [as calculated using Eq. (7)], and $c_2 \sim 0.33$ (Ref. 7) the first two corrections are indeed small. Nothing is known about $c^{(3)}$. We will assume it to be zero. Similar perturbative estimates for the change in η_1, λ_1, and ΔS can be obtained.

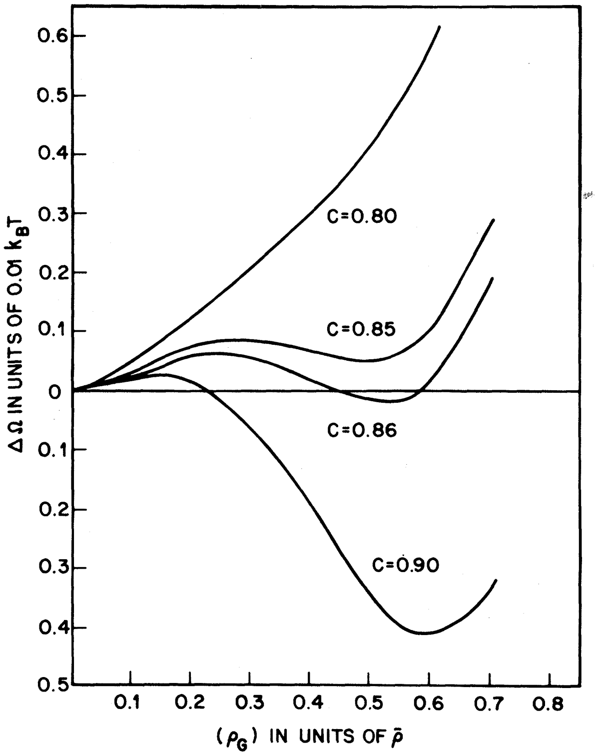

FIG. 1. The free-energy difference between liquid and solid in units of $k_B T$ plotted as a function of the order parameter (lattice periodic component of the density). There is a solidlike minimum for $c_1 = 0.85$, though the liquid has lower free energy. The solid is more stable for $c_1 = 0.86$ and much more so for $c_1 = 0.90$.

TABLE I. Freezing parameters for hcp solid in two dimensions.

	Structure factors c_1	Structure factors S_1	Fractional density change η	Entropy change $(\Delta S/k_B)$	Lattice periodic density λ_1
One–order-parameter theory	0.856	6.94	0.013	0.29	0.51
With perturbative corrections	0.826	5.75	0.015	0.32	0.54
Computer experiment	0.81	5.25	0.020	0.33	

I now compare the present results with those from computer simulation. For concreteness, we compare with the work of Broughton, Gilmer, and Weeks[7] on r^{-12} systems. Their results for c_i, η, and $(\Delta S/k_B)$ are given in the third row of Table I. The calculated values in the one-order-parameter theory are given in the first row. To obtain the fractional density change, we use $S_0 = 0.0185$.[7] For the entropy change, we need $(\partial c_i/\partial T)_\mu$. In Ref. 7 c_i is obtained at $T=1$ for two densities ρ close to freezing. Using this and the fact that μ is a function of ρT^6, we find that $T(\partial c_i/\partial T)_\mu \simeq 0.35$. This estimate could be wrong by 20%, since it involves the difference of two nearly equal quantities. The theoretical numbers are in reasonable agreement with computer experiment, but correspond to a noticeably weaker first-order transition. Perturbative corrections due to the order-parameter mode $\lambda_{G_2}=\lambda_{2G_1}$, with use of Eq. (11) for δc_1 and similar equations for other freezing parameters, and with $S_0=0.0185$ and $c_2 \simeq 0.33$,[7] clearly improve the agreement which is now quite good (as shown in the second row of Table I). We have assumed $c^{(3)}=0$. A positive $c^{(3)}$ and other nonzero Fourier components c_n will stabilize the crystalline solid somewhat more.

I have presented here a mean-field theory. In two dimensions fluctuations (sound waves) lead to a (logarithmically) slow loss of positional correlations in the crystal.[1-3,5] It was assumed that the free-energy balance, determined by short-range correlations and geometrical factors, is not very much affected, so that while a complete theory would have $\langle \rho_q \rangle$ diverging as a power law around $\vec{G}$'s, rather than having a δ-function singularity, the freezing parameters may be nearly the same. In the dislocation melting model, the unbinding of distant dislocation pairs, contributing exponentially little to free energy, leads to sudden vanishing of the shear modulus. Two scenarios are possible. One[16] is that first-order melting preempts the continuous dislocation transition (which is the absolute stability limit of the solid), i.e., $T_f < T_d$. The second is that $T_f > T_d$ so that melting is by dislocation unbinding, but defect relaxation times for $T_d < T < T_f$ are so long that the system is preceived as a solid in computer experiments. One experimental way of distinguishing between these is to examine spatial correlations in systems where T_f is clearly identified, say from pressure isotherms (e.g., near monolayer Xe on graphite). If correlations are exponential for $T > T_f$ but power law for $T < T_f$ the first possibility is indicated, while power-law correlations on either side support the second.

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Observation of Rotational Transitions for H_2, D_2, and HD Adsorbed on Cu(100)

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Energy losses observed when low-energy electrons were scattered from a Cu(100) surface exposed at $T \sim 15$ K to H_2 (and D_2, HD) lie close to rotational and rotational-vibrational transitions (H_2, D_2) of the free molecules. Both o- and p-H_2 and -D_2 physisorb on the surface, with negligible conversion on the time scale of the experiment. The relative populations were different from those characteristic of the adsorbing gas, suggesting a j-dependent sticking coefficient.

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In recent years, electron energy-loss spectroscopy (ELS) has emerged as a powerful probe of the vibrational excitations of adsorbed molecules, thus providing a most important source of new information about them. From measured vibrational frequencies it is relatively straightforward to draw conclusions about, e.g., molecular or dissociative adsorption and possible adsorption geometries. In this Letter we demonstrate that rotational and combined rotational-vibrational transitions of H_2 and D_2 adsorbed weakly on the well-characterized Cu(100) surface can be resolved,[1] and give information about the adsorption state previously inaccessible to any technique.

The system chosen is particularly suited to a study of rotational excitations. There is strong evidence that the ground state of H_2 on Cu(100) corresponds to atomic chemisorption and that the dissociation is activated.[2] The activation barrier might separate physisorption and chemisorption regions. Alternatively, it may cause H_2 to be trapped in a molecular "precursor" of the type recently proposed for the Mg(0001) surface.[3] The two types of adsorption give rise to similar vibration frequencies but completely different rotational spectra. For weak physisorption, one expects transitions of a perturbed three-dimensional rotator, while the molecular precursor would show the spectrum of a strongly hindered, or even confined rotator. Examples of each type have been seen in neutron scattering, for H_2 on Grafoil[4] and on activated alumina,[5] respectively.

In the neutron scattering experiments no attempt was made to adsorb rotationally excited molecules (o-H_2, p-D_2), or to measure relative populations and conversion rates. These quantities are of importance because the mechanism of ortho-para conversion at surfaces is still not understood in detail. They can be estimated directly from the ELS intensities once the relative cross sections for the $j = 0 \rightarrow 2$ and $j = 1 \rightarrow 3$ transi-