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Commensurate-Incommensurate Transitions with Quenched Random Impurities

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Commensurate-incommensurate transitions in uniaxial two-dimensional systems are examined in the presence of impurities that interact with domain walls. Exact Bethe-*Ansatz* calculations, tested by numerical studies, indicate that randomness is relevant and leads to new critical behavior—a discontinuity in the specific heat and divergence of domain size with an exponent of 1. The results are interpreted in terms of the behavior of a single interface. Global phase diagrams are presented and experimental implications are discussed.

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Close to the commensurate-incommensurate transition (CIT), the incommensurate phase (IC) is composed of large commensurate domains separated by domain walls.[1-7] The critical behavior at the transition at finite temperatures is determined entirely by the statistical mechanics of these domain walls. In two-dimensional uniaxial systems the interfaces are primarily aligned to a single lattice direction, and energy considerations prevent neighboring domain walls from crossing.[1-7] The transition to the IC phase occurs when the free energy f_1 of a single interface vanishes. In the IC phase the average domain size l is determined by a repulsive interaction between interfaces due to a loss in entropy.[6] Each interface in the pure system undergoes a random walk between collisions with its neighbors. If the domain size is l, the average distance between collisions will scale as l^2. Balancing the gain in energy f_1 for each interface with the entropy loss $\sim 1/l^2$ due to collisions leads to a divergence of domain size l, with an exponent of $\frac{1}{2}$ as the CIT is approached (the specific heat also diverges with a similar exponent).

The predicted exponent of $\frac{1}{2}$ has indeed been observed experimentally for bromine intercalated in graphite.[8] There are several experimental and theoretical realizations of systems of noncrossing interfaces. Steps on the surfaces of three-dimensional crystals do not cross, leading to a singular signature in equilibrium crystal shapes.[9] The characteristic exponent of $\frac{1}{2}$ also describes the ferroelectric transition in the six-vertex model,[10] and appears in certain dimer problems[11] and in models of two-dimensional polymer crystalization.[12]

In this paper we examine the effects of quenched random impurities on this transition. The defects considered here couple locally to the domain walls (i.e., they attract or repel the interface), but have no coupling to the domains. (Defects that couple to the order parameter have the effect of random fields, and have been examined by Villain.[13]) In adsorbed layers this type of randomness is caused by impurities that are sources of local dilations and compressions, but are free to move with the film on the substrate without interchanging positions with their neighbors. Such impurities lead to reentrant melting at sufficiently low temperatures on a smooth substrate.[14,15] On a smooth substrate there is a long-range strain field ($u_{ij} \sim 1/r^2$) associated with an impurity. Close to a CIT on the incommensurate side, however, the large regions of registered adsorbate lead to a strain field which falls off exponentially. Consequently, we shall assume short-range interactions between the domain walls and these impurities. Similar approximations apply to the steps on a crystal surface. The defects in this case are either impurities or dislocations terminating on the surface. Bond randomness in the six-vertex model of ferroelectric leads to similar effects.

In this note we point out that the Harris criterion[16] implies that this type of randomness is relevant at the

CIT. When the domain size exceeds a characteristic length l_d, new critical behavior is expected. An exact Bethe-*Ansatz* calculation in conjunction with the replica method predicts that there is now a divergence of domain size with an exponent of 1, and a discontinuous specific heat. These predictions have also been confirmed numerically, and can be explained in terms of the loss of energy for an impurity-roughened interface due to confinement by its neighbors. A global phase diagram with reentrant CIT and melting transitions leading to a glasslike phase at low temperatures is suggested.

The following simple model will be used for describing the CIT. The domain walls are placed on the bonds of a rectangular lattice. At zero temperature, and in the absence of impurities, the interfaces are straight lines along the y direction. At finite temperatures (or as a result of randomness) the interface becomes rough and fluctuates away from its equilibrium position. There is an energy μ_{ij} associated with crossing a bond in the y direction, and energy E_0 for bonds in the x direction. For technical reasons spatial variations in E_0 are not allowed, although we do not expect this limitation to effect our results near the CIT. The CIT takes place in the limit $\mu \sim e^{-E_0/kT} \equiv \gamma$, and in this limit it is sufficient to consider configurations in which the interfaces jump only one step (to right or left along the x direction) at a time, and overhangs do not occur (the familiar solid-on-solid assumptions). The partition function Z is obtained by summing over all possible wall configurations with appropriate Boltzmann weights. This sum is evaluated by use of a transfer matrix along the y direction. As originally pointed out by Pokrovski and Talapov,[2] and extended by several other authors,[3-7] the noncrossing condition for interfaces is naturally incorporated in the transfer matrix $\mathscr{T}$ by regarding the configurations of domain walls as fermion world lines. The Pauli exclusion principle automatically prevents crossings. In the limit $\gamma \ll 1$, a continuum approximation leads to $\mathscr{T} = e^{-\mathscr{H}}$, with a Hamiltonian[5,7]

$$\mathscr{H}(t) = \int dx \{[\mu(x,t) - 2\gamma] c(x)^\dagger c(x) - \gamma c(x)^\dagger \partial^2 c(x)/\partial x^2\}, \tag{1}$$

where c and $c^\dagger$ are fermion fields. The free energy (the largest eigenvalue of the transfer matrix) corresponds to the ground-state energy of this Hamiltonian. For a uniform μ, the free energy with a density $r = 1/l$ of domain walls is

$$f(l) = (\mu - 2\gamma) r + \gamma \pi^2 r^3/3. \tag{2}$$

For $\mu > \mu_c = 2\gamma$, the density r is zero; while in the IC phase it vanishes as $r \simeq [(\mu_c - \mu)/\gamma]^{1/2}/\pi$, i.e., with the previously mentioned exponent of $\frac{1}{2}$.

Now consider the case where the μ_{ij} are quenched random variables, with independent Gaussian distributions of mean $\bar{\mu}$ and variance σ^2. Harris's criterion[16] states that randomness becomes relevant when the shift in μ_c due to randomness in a coherence volume Ω_c is comparable to $\mu - \mu_c$. Because of the anisotropy of the system some care is necessary in identifying the coherence volume Ω_c. At finite temperatures in the pure system, the fluctuations of a single wall after y steps obey $\langle \delta x^2 \rangle = 2\gamma y$. If the domain size is l (in the IC phase), the distance between collisions is $y_c \sim l^2/\gamma$. We identify the coherence volume to be the area over which a single collision occurs, i.e., $\Omega_c \simeq l^3/\gamma$. The variance of μ due to randomness in a volume Ω_c is

$$\langle \delta\mu^2 \rangle = \langle [\int dx\, dy\, \mu(x,y)/\Omega_c]^2 \rangle \simeq \sigma^2/\Omega_c \simeq \gamma\sigma^2/l^3. \tag{3}$$

For randomness to be irrelevant, we require $\langle \delta\mu^2 \rangle \ll (\mu - \mu_c)^2$; i.e., $(\gamma\sigma^2/l^3)(l^4/\gamma^2) \sim l/l_d \ll 1$, where $l_d \equiv 2\gamma/\sigma^2$ is a characteristic length associated with disorder. As the CIT is approached l diverges, eventually exceeding l_d, and a crossover to new critical behavior takes place.

The quenched average free energy corresponds to the ground state energy of Hamiltonian (1) in a potential that is random in *both* space and time. (A potential that is random in space *only* is familiar in the context of localization. It corresponds to strips of correlated randomness in two dimensions, which if the distribution is Gaussian destroys the CIT.) The replica method is used to calculate the quenched average free energy $[\langle \ln Z \rangle = \lim_{n\to\infty}(\langle Z^n \rangle - 1)/n]$. The partition sum $Z(\{\mu\})$ corresponds to all noncrossing wall configurations with random energies. The walls are replicated n times in $Z(\{\mu\})^n$. Although walls of the same replica do not cross, walls of different replicas can cross. The averaging process $\langle Z(\{\mu\})^n \rangle$ results in an attractive interaction between walls of different replicas when they do cross. {If m walls cross at a bond μ_{ij}, the average

$$\langle e^{-m\mu_{ij}} \rangle = \exp[-m(\bar{\mu} - \sigma^2/2) + m(m-1)\sigma^2/2]$$

leads to a renormalized single-wall energy $\bar{\mu} - \sigma^2/2$, and a pairwise attraction of order σ^2.} Again the transfer matrix formalism can be used, and in the continuum limit (when *both* $\gamma \ll 1$, and $l_d \gg 1$), the Hamiltonian is

$$\mathscr{H}_n = \int dx \left\{ \sum_{\alpha=1}^{n} \left[(\bar{\mu} - 2\gamma - \tfrac{1}{2}\sigma^2) c_\alpha^\dagger c_\alpha - \gamma c_\alpha^\dagger \frac{\partial^2 c_\alpha}{\partial x^2} \right] - \tfrac{1}{2}\sigma^2 \sum_{\alpha\neq\beta} c_\alpha^\dagger c_\alpha c_\beta^\dagger c_\beta \right\}, \tag{4}$$

which describes n species of fermions interacting by an attractive contact potential. For repulsive potentials such Hamiltonians have been studied by Yang,[17] and Sutherland.[18] Their results can be extended to (4), and a brief summary is given here, with the details to appear elsewhere.

The ground-state wave function for nN fermions has the form

$$\psi(x_1, \ldots, x_{nN}) \sum_P [Q,P] \exp[i(k_{P1}x_{Q1} + \ldots + k_{PnN}x_{QnN})],$$

where P and Q are permutations of nN particles and $[Q,P]$ are $(nN)!^2$ coefficients. We make the *Ansatz* that the momenta are in n bands as $ik_{\alpha,t} = ik_t + (n+1-2\alpha)/2l_d$, with $\alpha = 1, \ldots, n$ and $t = 1, \ldots, N$. In the $N \to \infty$ limit, the density $\rho(k)$ of momenta obeys

$$\int_{-k_F}^{k_F} dk'\, l_d G_n(l_d(k-k'))\rho(k') = 1,$$

with

$$G_n(x) = \left[2\pi\delta(x) + \sum_{\alpha=1}^{n-1} \frac{2\alpha}{x^2+\alpha^2}\right] n^{-1}. \quad (5)$$

The energy and density are calculated in terms of $\rho(k)$ as

$$E_n(N) = nL\left\{[\bar{\mu} - 2\gamma - \sigma^2/2 - (n^2-1)\sigma^4/48\gamma]r + \gamma\int_{-k_F}^{k_F} dk\, \rho(k)k^2\right\}, \quad \int_{-k_F}^{k_F} dk\, \rho(k) = N/L = r. \quad (6)$$

The $n \to 0$ limit of the kernel in (5) exists, and gives the following results for the quenched average free energy:

$$\langle f(r)\rangle = [\bar{\mu} - 2\gamma - \sigma^2/2 + \sigma^4/48\gamma]r + \gamma\int_{-k_F}^{k_F} dk\, \rho(k)k^2, \quad (7)$$

where

$$P\int_{-k_F}^{k_F} dk'\{1/l_d(k-k') + \pi\coth[\pi l_d(k-k')]\}\rho(k') = k.$$

In the limit $k_F l_d \gg 1$ ($l \ll l_d$), $\rho(k) \simeq 1/2\pi$, and the nonrandom [Eq. (2)] results are recovered. For $k_F l_d \gg 1$, where random effects dominate, $\rho(k) = l_d(k_F^2 - k^2)^{1/2}/2\pi$; and from (7)

$$\langle f(l)\rangle = (\bar{\mu} - 2\gamma - \sigma^2/2 + \sigma^4/48\gamma)/l + \pi\sigma^2/2l^2 + \ldots,$$

i.e., the second leading term is order of $1/l^2$ rather than $1/l^3$. This leads to random criticality characterized by a domain-size divergence $l \simeq \pi\sigma^2/(\bar{\mu} - \mu_c)$, and a discontinuous specific heat as indicated in Fig. 1.

There are usually many difficulties associated with calculating quenched average free energies by the replica method. Although no such problems were encountered in the present calculations, we decided to check the analytical results numerically. Since each wall is confined by its neighbors to a distance of order l, Eq. (7) implies that the free energy of a single interface confined to l will behave as $\langle f_1(l)\rangle \simeq (\bar{\mu} - \mu_c) + \pi\sigma^2/2l + \ldots$. This free energy was calculated numerically for various l's up to $l = 200$, and is plotted in Fig. 2. The results are indeed consistent with a $1/l$ dependence, as compared to $1/l^2$ for the nonrandom case.

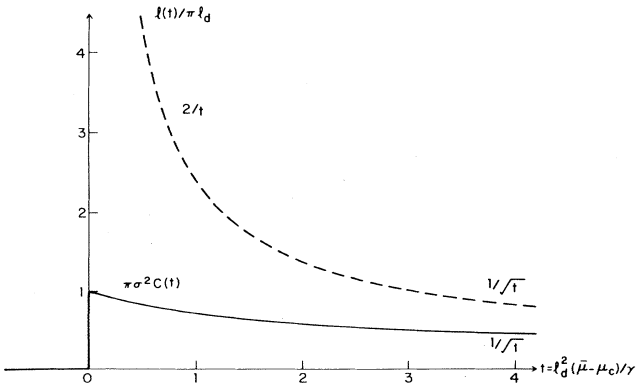

FIG. 1. Critical behavior close to a CIT with impurities: specific heat (solid line), and domain size (dashed line).

For the CIT in nonrandom systems it was possible to give a simple explanation for the exponent of $\frac{1}{2}$ (entropy loss due to collisions of interfaces undergoing random walks). It would be desirable to have such an explanation for the exponent 1 in random systems in terms of the behavior of a single interface. It turns out that the most important effect in random systems is not the loss of entropy, but the loss of energy due to the blocking of favorable paths by neighboring walls. Recent numerical simulations by Huse and Henley[19] in a similar interface model indicate that in the presence of randomness the interface is rough at zero temperature. The fluctuations of a wall scale as $|\delta x| \sim y^{\alpha}$, while the energy gain from randomness scales as y^{β} with $\alpha \simeq \frac{2}{3}$ and $\beta \simeq \frac{1}{3}$ (the exponents α and β are related by $\beta = 2\alpha - 1$). We have checked numerically that these exponents still apply to interfaces at finite temperatures. When the domain size is l, the distance between collisions scales as $y_c \sim l^{1/\alpha}$. The energy loss due to collisions for a single wall scales as

$$E(l) \sim y_c^{\beta}(1/y_c) \sim l^{(\beta-1)/\alpha} \sim l^{2(\alpha-1)/\alpha}.$$

With the numerical estimate $\alpha \simeq \frac{2}{3}$, the predicted scaling $E(l) \sim 1/l$ is regained. Alternatively, the above

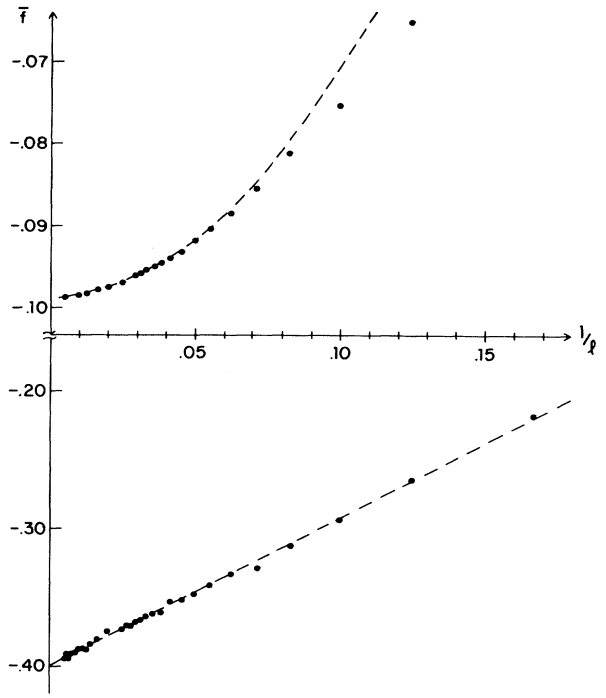

FIG. 2. Free energies for interfaces confined to a strip of width l, with (lower) and without (upper) randomness. Results are obtained numerically by summing over all configurations in a long strip ($\gamma = 1$, for $\sigma^2 = \frac{5}{6}$ and 0).

explanation, in conjunction with the exact results of Eq. (7), provides an indirect proof that the exponent determining the roughening of interfaces due to randomness is *exactly* $\alpha = \frac{2}{3}$. It would, of course, be desirable to have a direct evaluation of this exponent.

It is interesting to use the above results to conjecture the form of the global phase diagram of adsorbed layers undergoing CIT with quenched randomness. A possible phase diagram is given in Fig. 3 and is compared to the nonrandom phase diagram. With randomness present, it is easier to form domain walls, and the commensurate phase occupies a smaller portion of the phase diagram. Also as in nonrandom systems the stability of the IC phase against dislocations has to be checked.[4-7] We have not determined the limits of stability although, in general, disorder makes the IC phase less stable.[14] The criticality condition $\bar{\mu}_c = \sigma^2/2 + 2\gamma - \sigma^4/48\gamma$ indicates a reentrant IC phase, although the continuum limit ($l_d >> 1$) breaks down at very low temperatures. The IC phase itself becomes unstable at low temperatures as a result of the unbinding of dislocations by random strains.[14,15] Kinetic constraints probably lead to a glassy disordered phase at low temperatures in this case.

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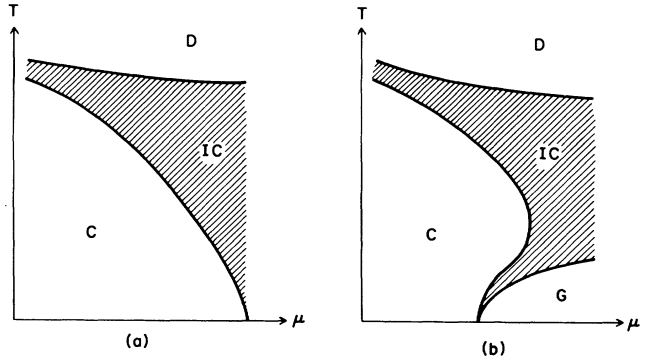

FIG. 3. Possible phase diagrams in temperature–chemical-potential space, in (a) nonrandom and (b) random cases. In addition to the commensurate (C), incommensurate (IC), and disordered (D) phases, there can be a glass (G) phase in the random system.

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