

Universal Aspects of Coulomb-Frustrated Phase Separation

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(Received 28 July 2004; published 10 February 2005)

We study the consequences of Coulomb interactions on a system undergoing a putative first order phase transition. In two dimensions (2D), near the critical density, the system is universally unstable to the formation of new intermediate phases, which we call “electronic microemulsion phases,” which consist of an intermediate scale mixture of regions of the two competing phases. A corollary is that there can be no direct transition as a function of density from a 2D Wigner crystal to a uniform electron liquid. In 3D, if the strength of the Coulomb interactions exceeds a critical value, no phase separation occurs, while for the weaker Coulomb strength electronic microemulsions are inevitable. This tendency is considerably more pronounced in anisotropic (quasi-2D or quasi-1D) systems, where a devil’s staircase of transitions is possible.

DOI: 10.1103/PhysRevLett.94.056805

PACS numbers: 73.20.Qt, 73.43.-f

We consider the effect of long-range Coulomb interactions on a system undergoing a first order phase transition between two compressible states. In the absence of Coulomb interactions, a first order transition implies an interval of mean density in which the equilibrium state is macroscopically phase separated into regions of higher and lower than average density. A Coulomb interaction precludes macroscopic phase separation; consequently, the system can either undergo a direct, first order phase transition between the two competing uniform states or can form intermediate phases, “electronic microemulsions,” which can be thought of as a mesoscale mixture of the two competing phases. It has been suggested that such states resulting from Coulomb-frustrated electronic phase separation are relevant to the physics of various highly correlated materials, including the cuprate high temperature superconductors and the colossal magnetoresistance manganates [1,2], as well as to [3,4] the pure two dimensional electron liquid at large r_s (low density).

In the present Letter, we consider several universal (i.e., independent of microscopic details) aspects of Coulomb-frustrated phase separation. In two dimensions (2D), we show that a direct first order phase transition as a function of density between two distinct thermodynamic phases is forbidden. More precisely, since macroscopic phase separation is excluded, a finite discontinuity, $\bar{\mu} > 0$, in the first derivative of the free energy density f with respect to a fixed background charge density $\bar{\rho}$

$$\bar{\mu} \equiv \lim_{\delta \rightarrow 0} \{ \partial f / \partial \bar{\rho} |_{\bar{\rho} = \bar{\rho}_c - \delta} - \partial f / \partial \bar{\rho} |_{\bar{\rho} = \bar{\rho}_c + \delta} \} \quad (1)$$

is generically [5] expected at a first order transition where the free energy curves of two distinct phases cross at a critical density, $\bar{\rho}_c$. However, we here prove that such a discontinuity is forbidden in 2D. Rather, we find that in the neighborhood of the putative critical density, there is an instability of the uniform state to some form of mesoscale phase coexistence, leading to new intermediate phases [6].

In particular, this theorem applies to the 2D Wigner crystal to electron fluid transition [7].

In 3D, a direct first order transition (with no region of phase coexistence) occurs if the strength of the Coulomb interaction, Q , exceeds a critical [8] strength, $Q > Q_c$, while if $Q < Q_c$, one or more microemulsion phases occur. Under many circumstances, at least at mean-field level, the transition from homogeneous to microemulsion phases as a function of decreasing Q is a Lifshitz transition [9], in which the characteristic period of the mixture diverges as $Q \rightarrow Q_c$ from below, and there can be a devil’s staircase consisting of a complex mixture of commensurate and incommensurate density waves. For $Q \ll Q_c$, the characteristic size of the regions of each phase is small, and more detailed, microscopic considerations become important. In anisotropic (quasi-2D or quasi-1D) systems, Q_c becomes increasingly large with increasing anisotropy, making some form of Coulomb-frustrated mesoscopic phase separation nearly inevitable.

An explicit model.—The analysis described in the present Letter is quite general, as we will show later, but it is nevertheless convenient first to present it in the context of a simple model described by the following Hamiltonian density

$$\mathcal{H} = \sum_{\alpha=1}^D \frac{\kappa_{\alpha}}{2} [\partial_{\alpha} \phi]^2 + U(\phi) - \gamma(\rho - \rho_c)\phi + \dots + \frac{1}{2}[\rho - \bar{\rho}]V[\rho - \bar{\rho}], \quad (2)$$

where U is a potential, which to be concrete we take to be $U = \lambda[\phi^2 - 1]^2/4$, ρ is the charge density, $\bar{\rho}$ is the (nondynamical) uniform background charge density, and we have expressed the Coulomb interaction, in an operator form, such that $Vf \equiv \int d^D r' V(\vec{r} - \vec{r}') f(\vec{r}')$ with $V(r) = Q/r$. In this model, the two uniform phases have $\phi = \pm 1 + \gamma(\bar{\rho} - \rho_c)/2\lambda + \dots$ which we label as $\phi \approx \pm 1$, assuming λ to be large. The term in \mathcal{H} proportional

to γ expresses the fact that the $\phi \approx 1$ phase is favored at higher densities, and the $\phi \approx -1$ phase is favored at low. For an isotropic 3D system, $\kappa_\alpha = \kappa$, while we will call a system quasi 2D if there exists one direction in which κ_α is very small, and quasi 1D if there are two such directions. (We will label spatial directions in such a way that $\kappa_1 \geq \kappa_2 \geq \kappa_3$.) We use a uniform continuum notation, but where discreteness is important (such as in a layered system, in which position in the perpendicular direction is labeled by a layer index), it is to be understood that $\partial_\alpha \phi \equiv [\phi(n+1) - \phi(n)]/b_\alpha$ where b_α is the lattice constant. The terms \dots represent higher derivative terms, and terms proportional to higher powers of $\rho - \bar{\rho}$. κ_α and λ determine the local (i.e., the $Q \rightarrow 0$ limit) structure of an interface running perpendicular to the α direction: Specifically, the surface tension is $\sigma_\alpha = (\pi/2)\sqrt{\lambda\kappa_\alpha/2}$ and the width of the interface is $a_\alpha = \sqrt{\kappa_\alpha/2\lambda}$.

Because the Hamiltonian density is a quadratic function of ρ , density fluctuations can be integrated out to yield an effective Hamiltonian for ϕ , alone. The result can be expressed formally as

$$\mathcal{H}^{\text{eff}} = \sum_{\alpha=1}^D \frac{\kappa_\alpha}{2} [\partial_\alpha \phi]^2 + U(\phi) - \gamma(\bar{\rho} - \rho_c)\phi + \dots - \frac{1}{2} \sum_{\alpha=1}^D \partial_\alpha \phi \tilde{V} \partial_\alpha \phi, \quad (3)$$

where the renormalized interaction, \tilde{V} , is defined in terms of the inverse of V according to $-\nabla^2 \tilde{V} = \gamma^2 V^{-1}$, or taking the Fourier transform: $\tilde{V}_{\vec{k}} = \gamma^2 [k^2 V_{\vec{k}}]^{-1}$.

The 2D case.—In 2D, the Fourier transform of \tilde{V} is $\tilde{V}_{\vec{k}} = \gamma^2 [\pi Q |k|]^{-1}$. Transforming back to real space, the final term in Eq. (3) is

$$E_{\text{Coulomb}} = -\frac{\gamma^2}{4\pi^2 Q} \int d^2 r d^2 r' \frac{\vec{\nabla} \phi(\vec{r}) \cdot \vec{\nabla} \phi(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (4)$$

In the limit in which the interfaces between phases are narrow compared to the size of domains, $|\phi(r)| \approx 1$ in the bulk of the phases, so the expression for the total energy can be simplified to read

$$E = \gamma[\bar{\rho} - \rho_c][A_+ - A_-] + \int d\vec{l} \sigma(\theta) - \frac{\gamma^2}{\pi^2 Q} \times \int \frac{d\vec{l} \cdot d\vec{l}'}{|\vec{l} - \vec{l}'|}, \quad (5)$$

where the integrals run along the interface in the direction such that the $\phi \approx +1$ phase is to the left, A_\pm are the areas of the two phases, $\sigma(\theta)$ is the microscopic contribution to the surface tension, which can depend on the direction of the interface, and any short-distance singularities in the final integral are cut off at the scale of the interface width, a .

Eqs. (4) and (5) are the principle results of our Letter; the classical low temperature thermodynamics is obtained by

integrating over all domain patterns with Boltzman weight determined by this effective Hamiltonian. The key feature of this sum is that the third term in Eq. (5) is negative and logarithmically divergent whenever the domain size is large. [See, e.g., Eq. (6).] Thus, close enough to $\bar{\rho} = \bar{\rho}_c$, microemulsion phases which are phase separated on a mesoscopic scale always have lower energy than the uniform phases. It has previously been shown [10] on quite general grounds that if there is a direct transition from a crystal to a uniform fluid, it must be first order [9]. Combined with the present result, this implies that there can be no direct transition. Rather, there must exist one or more intermediate phase, and a sequence two or more continuous transitions [11]. Moreover, in the case of the 2DEG, the first of these transitions must occur at strictly higher density (smaller r_s) than the putative Wigner crystal to uniform liquid transition [12].

To find the mean-field phase diagram one should minimize Eq. (5) with respect to the geometry of the interfaces. Remarkably, the same expression for the interfacial energies [the third term in Eq. (5)] arises [3,4,13,14] in a 2D problem where phase separation is frustrated by long-range dipolar interactions (although in this case the first, bulk contribution to the energy is different). Thus what is known about that problem can be applied to the present case.

On the mean-field level the shape of the micro-emulsion depends on the degree of anisotropy of the surface tension. The simplest situation arises if σ is highly anisotropic—in this case, the domain walls always lie preferentially along the easy direction and thus, at least at mean-field level, the lowest energy micro-emulsion phases are striped [4].

The energy per unit area, relative to the uniform phase, of an alternating array of stripes of $\phi \approx +1$ of width W and $\phi \approx -1$ of width $L - W$ is computable from Eq. (5):

$$\varepsilon = 2L^{-1} \{ \gamma \delta \bar{\rho} W + \sigma [1 - g \log(W/a) - g f(W/L)] \} \quad (6)$$

where $\delta \bar{\rho} = \bar{\rho} - \rho_c$, $g \equiv \gamma^2 / (\pi^2 \sigma Q)$, and $f(x) = \log[\sin(\pi x) / \pi x]$. For $\bar{\rho} = \rho_c$, this energy is minimized by alternating stripes of equal width, $L = 2W$, with $W = (2/\pi)W_0$ and

$$W_0 = a \exp[1 + 1/g] \quad (7)$$

is a characteristic emergent length scale. For $\bar{\rho} > \rho_c$, the ratio of W/L decreases monotonically, until as $\delta \bar{\rho} \rightarrow \Delta \rho \equiv (\sigma g / \gamma) W_0^{-1}$, the period of the stripes diverges as

$$L \sim W_0 \sqrt{\frac{3\zeta(2)\Delta\rho}{\Delta\rho - \delta\bar{\rho}}} \quad (8)$$

and the width of the stripes, $W \rightarrow W_0$, where $\zeta(2) = \pi^2/6$ is the zeta function.

Thus, as a function of decreasing $\bar{\rho}$, there is a “Lifshitz” transition [9] from the uniform phase to the stripe phase at $\bar{\rho} = \rho_c + \Delta \rho$, then a continuous evolution of the stripe phase with the identity of the minority and majority phases interchanging at $\bar{\rho} = \rho_c$, and finally a second Lifshitz

transition at $\bar{\rho} = \rho_c - \Delta\rho$. The mean-field phase diagram is qualitatively identical to the phase diagram in the case with dipolar interactions—see Fig. 2c of Ref. [4]. However, in the dipole case, the density differences between the two phases is roughly determined by a Maxwell construction, and the characteristic stripe width is determined by the size of the dipole, d , which is an independent physical parameter, which in some physical realizations can be large compared to the spacing between particles. In the present case, the density contrast and the characteristic width of the stripes, W_0 , is determined by microscopic physics.

When the surface tension is more nearly isotropic, the mean-field phase diagram is more complicated. Although for $\bar{\rho}$ near ρ_c , stripe phases continue to have the lowest energy, near the transition to the uniform phase, bubble phases, consisting of isolated bubbles of the minority phase, have lower energy than the stripe phase. The Lifshitz points at $\bar{\rho} = \rho_c \pm \Delta\rho$ now mark the transition between a uniform and a long-period bubble phase [3,4]. In the case of the triangular Wigner crystal to Fermi liquid transition the anisotropy of the surface tension is such as to produce stable bubble phases. Although the optimal bubble is faceted, one can establish the stability of the bubble phase by using as a variational ansatz hexagonal bubbles. On approach to the Lifshitz point, the size of the bubbles is of order W_0 while the distance between them diverges as

$$L_B \sim W_0[\Delta\rho/(\Delta\rho - \delta\bar{\rho})]^{-1/3}. \quad (9)$$

This is not quite the end of the story; since the transition between the bubble and stripe phases is expected to be first order, a second level of frustrated phase separation occurs producing a new set of intermediate phases. These states consist of alternating stripes of stripes and stripes of bubbles. The resulting phase diagram is qualitative identical to that shown in Fig. 2d of Ref. [4] for the 2D dipolar case.

The 2D case generalized.—Because of the importance of the 2D case, it is worth deriving Eq. (5) in a second way. For simplicity, consider the situation in which the background charge density is tuned to the critical value $\bar{\rho} = \rho_c$. We compute the difference in energy between the uniform density state and that in which there is an interface such that (other than in a narrow interface region of width $2a$), there is phase $\phi \approx -1$ for $x < -a$ and phase $\phi \approx +1$ for $x > a$. So as to minimize the Coulomb cost of this interface, while at the same time gaining maximal energy from phase separation, we allow the charge density to assume the profile $\rho(\vec{r}) = \bar{\rho} + \phi(x)\Delta(a|x|)^{-1}$. With this profile, we see that the Coulomb cost of the interface is $E_c = \Delta^2 QL \log(W/a)$, where L is the length of interface and W is the transverse width of the two regions separated by it. Similarly, the energy of phase separation gained within each region by the density redistribution is $E_{PS} = -2\bar{\mu}\Delta(L/a)\log(W/a)$, with $\bar{\mu}$ defined in Eq. (1). Because the major contributions to the logarithms comes from regions far from the interface, where deviations from uni-

form density are small and slowly varying, the result is insensitive to microscopic details. The energy of the interface is minimized by $\Delta = \bar{\mu}/aQ$, for which

$$E_{\text{interface}} = [\sigma_0 - (\bar{\mu}^2/aQ)\log(W/a)]L \quad (10)$$

which is manifestly negative for large enough W .

Taking, as an example, a striped state, where W is the width of the stripes, the logarithm in Eq. (10) can be seen to be precisely the same one that comes from integrating the expression in Eq. (5) over the interface, Eq. (6). Equation (10), by itself, constitutes a proof that a first order phase transition is forbidden—it implies an absolute instability of any uniform (or macroscopically phase separated) state at the point of the putative transition. Although the analysis that leads to this conclusion is classical, because it is a long-wavelength instability, it is unaffected by quantum fluctuations, and so applies at zero temperature, $T = 0$, as well as nonzero T .

The characteristic size of bubbles and stripes depends exponentially on the ratio of microscopic energies, g : If g is roughly 1 or more, then the size of the domains is microscopic. Moreover, in this case, there is no reason to expect quantum or thermal fluctuations to be small. Consequently, although the instability of the uniform phases is a robust long-distance phenomenon, the mean-field phases we have found may or may not survive these fluctuations. However, because of the exponential dependence, it can happen that g is small compared to 1, in which case W_0 can be very large compared to a . In this case, the mean-field analysis presented here should be reliable, and W_0 is a nontrivial emergent length. The significance of the classical and quantum fluctuations has been discussed in [3,4].

The 3D case.—In 3D, it follows simply from the fact that the Fourier transform of the Coulomb interaction is $V(\vec{k}) = 4\pi Q/k^2$, that \mathcal{H}^{eff} is local

$$\begin{aligned} \mathcal{H}^{\text{eff}} = & \sum_{\alpha=1}^3 \frac{[\kappa_{\alpha} - \gamma^2/4\pi Q]}{2} [\partial_{\alpha}\phi]^2 + U(\phi) \\ & - \gamma\bar{\rho}\phi + \dots \end{aligned} \quad (11)$$

Thus, if the Coulomb interactions are sufficiently strong that $Q > Q_c \equiv \gamma^2/4\pi\kappa_3$, then as a function of $\bar{\rho}$, the system undergoes a direct first order transition from a uniform $\phi \approx 1$ phase for $\bar{\rho} > \rho_c$, to a uniform $\phi \approx -1$ phase for $\bar{\rho} < \rho_c$. In contrast to 2D, there is no absolute proscription against first order transitions in 3D.

However, for weaker Coulomb interactions, for $\bar{\rho}$ in the neighborhood of ρ_c , there is an intermediate modulated phase whose precise structure is determined by the higher derivative terms which are not explicitly exhibited. (In part, this case has been previously considered in [15].) For illustration, consider the phase diagram at the critical density, $\bar{\rho} = \rho_c$. At the critical value, $Q = Q_c$, the coefficient of the leading stiffness term changes sign, the uniform state must be unstable, and higher order elastic

constants (more derivatives) must be included in the effective Hamiltonian. Most simply, we can include the next order terms in Eq. (11), $\dots = \sum_{\alpha} \kappa'_{\alpha} (\partial_{\alpha}^2 \phi)^2 + \dots$. So long as these higher order elastic constants remain positive, the transition to the modulated phase as a function of Q is the classic Lifshitz transition. Specifically, as Q approaches the critical value Q_c from below, the period of the modulated phase diverges as $L \sim a\sqrt{Q_c/(Q_c - Q)}$. Alternatively, if $\kappa'_3 < 0$, this Lifshitz transition is preempted by a first order transition (at a larger critical Q) to a modulated phase with a short period.

Layered systems.—A natural realization of a quasi 2D system is in a layered material. This is still a 3D system, and so subject to the analysis of the previous paragraphs, but now there can be significant effects of the discrete, lattice structure. In particular, so long as the spacing between layers, a_3 , is not too large, this discreteness introduces the only important modification of the above discussion. Where the continuum theory predicts a discontinuous transition to the modulated phases, lattice discreteness generally locks the period of the resulting modulation to a specific, low-order commensurate structure. Alternatively, near the Lifshitz transition, the competition between the period favored by the elastic constants and the underlying lattice typically results in a devil's staircase of modulated phases, and moreover can lead to intrinsically glassy behavior associated with the pinning of domain walls.

The easiest way to get a flavor of the resulting possibilities is by simply discretizing the spatial derivatives in Eq. (11): in the case in which $\kappa_1 = \kappa_2 > \kappa_3$, and $\kappa'_{\alpha} > 0$, the resulting model is the soft-spin version of the much studied [8] antiferromagnetic next-nearest-neighbor Ising model, in which the antiferromagnetic coupling between second neighbor planes is proportional to κ'_3 , the couplings between nearest-neighbor planes has a strength (and sign) which varies as a function of $\kappa_3 - \gamma^2/4\pi Q$, and the in plane nearest-neighbor ferromagnetic couplings are proportional to κ_1 . This model has a remarkably subtle and beautiful phase diagram consisting of uniform (ferromagnetic) phases, short period commensurate phases, of which the most prominent are the period 2 (alternating up and down planes) and period 4 (2 up 2 down) phases, and then a “devil's flower” consisting of high order commensurate and incommensurate phases.

In the limit of larger a_3 , the phase diagram is still more complex. So long as a_3 is less than the characteristic size, W_0 , which characterizes the domain size in an isolated layer, interlayer phase separation is energetically preferred over intralayer phase separation. However, for $a_3 \gg W_0$, 2D patterns of phase separation dominate the physics at shorter length scales, while intralayer considerations become important only at much longer distances.

Quenched disorder produces its own form of locally pinned mixtures of the two competing phases. Distinguishing the two effects in experiment requires studying the properties of progressively cleaner systems. With this ca-

veat, we believe the present results are significant for a host of phenomena in layered and quasi-1D crystalline materials [16], as well as for [3,4] the 2DEG in high mobility semiconductor devices at large r_s .

We acknowledge useful discussions with S. Chakravarty, M. E. Fisher, and D. Fisher. This work was supported in part by the National Science Foundation under Contract Nos. DMR-01-10329 (R.J. and S.A.K.) and DMR-0228014 (B.S.).

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