Coulomb-Frustrated Phase Separation Phase Diagram in Systems with Short-Range Negative Compressibility

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Using numerical techniques and asymptotic expansions we obtain the phase diagram of a paradigmatic model of Coulomb-frustrated phase separation in systems with negative short-range compressibility. The transition from the homogeneous phase to the inhomogeneous phase is generically first order in isotropic three-dimensional systems except for a critical point. Close to the critical point, inhomogeneities are predicted to form a bcc lattice with subsequent transitions to a triangular lattice of rods and a layered structure. Inclusion of a strong anisotropy allows for second- and first-order transition lines joined by a tricritical point.

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The appearance of spatial inhomogeneities is a general phenomenon occurring in a wide variety of systems with competing interactions on different length scales [1–15]. In many-body systems correlations often drive the electronic compressibility negative as in the Hubbard [16] and Falicov-Kimball [17] models, the electron gas [18], cuprates [3,10,19,20] and manganites [6,8] models, heterostructures [4], and nuclear matter [5]. This signals a tendency to phase separation at macroscopic lengths which is frustrated by the long-range Coulomb interaction. Although there is agreement that the system can become inhomogeneous at a mesoscopic scale if the Coulomb frustration is not too large, the nature of the transition has not yet been settled. This is an important question in general but particularly so in metallic systems where the existence of a second-order quantum critical point separating an homogeneous phase from an inhomogeneous one can disrupt the Fermi liquid behavior [3].

In this work we study a ϕ^4 model augmented with long-range interactions as a generic model of Coulomb-frustrated phase separation in systems with negative short-range compressibility. The model (or closely related variants) has been used to describe inhomogeneities in a variety of systems [9–14] including mixtures of block copolymers [9], charged colloids in polymeric solutions [13], and electronic systems [10,11]. We determine the transition line from the homogeneous to the inhomogeneous state using numerical and analytical techniques and show that generically the transition is first order in three dimensions (3D) except for a critical point (CP) (Fig. 1). This outcome changes if a strong anisotropy is taken into account. Then both first- and second-order transitions are allowed separated by a tricritical point (Fig. 3). In addition, we study the crossover from harmonic to unharmonic inhomogeneities and the different topological transitions of the 3D isotropic system. Close to the CP the inhomogeneities are shown to form a bcc lattice.

The model is defined by the following Hamiltonian

$$\mathcal{H} = \int d\mathbf{x}[\phi(\mathbf{x})^2 - 1]^2 + |\nabla\phi(\mathbf{x})|^2 + \frac{Q^2}{2} \times \int d\mathbf{x} \int d\mathbf{x}' \frac{[\phi(\mathbf{x}) - \bar{\phi}][\phi(\mathbf{x}') - \bar{\phi}]}{|\mathbf{x} - \mathbf{x}'|}, \quad (1)$$

with the scalar classical field ϕ representing the local charge density, $\bar{\phi}$ the average density. A rigid background ensures charge neutrality. In the case of electronic systems with a negative compressibility the model describes phenomena at large length scales compared to the underlying lattice constant. It can be derived by expanding the coarse grained energy of the system around a reference density

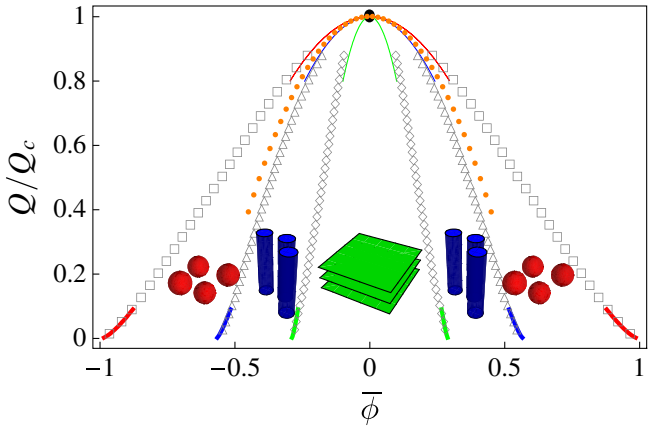

FIG. 1 (color online). Phase diagram in three-dimensional isotropic systems. The small dots indicate the Gaussian instability line Q_g. The thin (thick) lines represent first-order transitions in the strong (weak) coupling approximation. In the two limits they overlap with the corresponding numerically determined transition lines from homogeneous to dropletlike inhomogeneities (□), from droplets to rods (△), and from rods to layers (◇).

belonging to the negative compressibility density region. The reference density can be fine-tuned so as to eliminate a small cubic term. Constant and linear terms are inessential; thus, one obtains a double well energy which can be taken to the dimensionless form of Eq. (1) by measuring energies in terms of the barrier height, distances in terms of the bare correlation length ξ, and density ϕ in units such that the double well minima are at $\phi = \pm 1$. This leads to a renormalized Coulomb coupling in 3D, $Q^2 \equiv 4e^2\xi^2/(\epsilon_0|a|)$. Here e is the electron charge, ϵ_0 is a dielectric constant due to external degrees of freedom, and $a < 0$ is proportional to the inverse short-range compressibility. More precisely, it is the second derivative of the short-range part of the energy per unit volume with respect to the density at the reference density.

In general a and ξ will depend on external parameters like pressure. They can even be taken as temperature dependent, as in Landau theory, in which case $\mathcal{H}$ has to be interpreted as a free energy and the model becomes a mean-field description of a temperature driven transition to an inhomogeneous state. This can be useful, for example, to model inhomogeneities appearing below some temperature in manganites [21].

By computing the static response to an external field in momentum space, we get the charge susceptibility at finite momentum $\mathbf{k}$ which depends only on the modulus of the momentum k measured in units of ξ^{-1}:

$$\chi(\mathbf{k}) = \left[k^2 + \frac{2\pi Q^2}{k^2} - 2 + 6\bar{\phi}^2\right]^{-1} \qquad (\mathbf{k} \neq 0). \quad (2)$$

The susceptibility has a maximum at $k_0 = [2\pi Q^2]^{1/4}$ which diverges as Q approaches the Gaussian instability line Q_g (the dotted line in Fig. 1) from above, where $Q_g = Q_c[1 - 3\bar{\phi}^2]$ and $Q_c = 1/\sqrt{2\pi}$. This indicates an instability of the homogeneous phase toward a sinusoidal charge density wave (SCDW) of periodicity $2R_c = 2\pi/k_0$ with vanishing wave amplitude at the transition and direction chosen by spontaneous symmetry breaking.

The Gaussian transition cannot survive at low Q. Indeed as $Q \to 0$ the Gaussian theory predicts inhomogeneities in the range $|\bar{\phi}| < 1/\sqrt{3}$ as opposed to Maxwell construction at $Q = 0$ which predicts a globally inhomogeneous state in the range $|\bar{\phi}| < 1$. We now show that the system never reaches the Gaussian instability except for a CP in the phase diagram: the Gaussian line is preempted by a first-order transition. Restricting to periodic textures, the free energy density difference with respect to the uniform state can be written in Fourier space as

$$\frac{\delta F}{V} = \sum_{\mathbf{G}\neq 0} \phi_{\mathbf{G}}\chi^{-1}(\mathbf{G})\phi_{-\mathbf{G}} + 4\bar{\phi} \sum_{\mathbf{G}_1,\mathbf{G}_2,\mathbf{G}_3\neq 0} \phi_{\mathbf{G}_1}\phi_{\mathbf{G}_2}\phi_{\mathbf{G}_3}\delta_{\mathbf{G}_1+\mathbf{G}_2+\mathbf{G}_3,0} + \sum_{\mathbf{G}_1,\mathbf{G}_2,\mathbf{G}_3,\mathbf{G}_4\neq 0} \phi_{\mathbf{G}_1}\phi_{\mathbf{G}_2}\phi_{\mathbf{G}_3}\phi_{\mathbf{G}_4}\delta_{\mathbf{G}_1+\mathbf{G}_2+\mathbf{G}_3+\mathbf{G}_4,0}, \quad (3)$$

where the $\mathbf{G}$'s are the reciprocal lattice vectors and V is the volume.

The appearance of a self-generated cubic term in Eq. (3) calls for the possibility of a first-order transition which can be treated analogously to the liquid-solid transition [22,23]. Assuming that the instability is weakly first order, which can be checked *a posteriori*, we restrict the sum to wave vectors with magnitude G close to k_0. To have an energetic advantage from the cubic term of Eq. (3) we need to find reciprocal lattices with triads of wave vectors forming equilateral triangles so that they add to zero. By requiring symmetric structures with inversion only three sets of vectors L_G are allowed that correspond to fcc, planar hexagonal, and icosahedral reciprocal lattices [23]. The free energy density reads

$$\frac{\delta F}{V} = \chi^{-1}(G)m\phi_G^2 + 8\bar{\phi}pm\phi_G^3 + \phi_G^4[3m(m-1) + 6qm], \quad (4)$$

where the Fourier component amplitudes ϕ_G depend only on the modulus of $\mathbf{G}$, m is the number of vectors in L_G, and p (q) is the number of triangles (nonplanar diamonds) to which each vector belongs when the triangles are accommodated in regular geometrical objects [24]. Upon minimizing Eq. (4) with respect to the wave amplitude ϕ_G and G one finds $G \equiv k_0$. Equating the energies for the different structures one finds three first-order transition lines between phases X and Y:

$$Q_{X,Y} = Q_c(1 - \alpha_{X,Y}\bar{\phi}^2). \quad (5)$$

where $X, Y = U, B, T, L$ stand for uniform, bcc, triangular, and layered structures, respectively (see below). The three first-order transition lines [thin lines in Fig. 1] join at the CP $(\bar{\phi}, Q) = (0, Q_c)$ shown with a solid circle. At the CP one recovers a SCDW second-order phase transition with a charge susceptibility divergence since the cubic term of Eq. (3) vanishes. Away from the CP the Gaussian line is the limit of metastability of the homogeneous phase (dotted line). For all the phases, which we describe next, the order parameter at the transition goes linearly to zero as $\bar{\phi} \to 0$ confirming that the transition is weakly first order close to the CP.

Approaching the first-order lines from above the first structure to become stable corresponds to the fcc reciprocal lattice defined by the $m = 12$ wave vectors $\mathbf{G}\sqrt{2}/G = (\pm 1, \pm 1, 0), (\pm 1, 0, \pm 1), (0, \pm 1, \pm 1)$ for which $p = q = 2$. This corresponds to a bcc crystal of inhomogeneities in real space with $\alpha_{U,B} = 103/45 \approx 2.29$.

Decreasing Q at finite $\bar{\phi}$ the planar hexagonal lattice, with $m = 6$, $p = 1$, $q = 0$, and $\alpha_{BT} \approx 3.44$, becomes

stable corresponding to rodlike inhomogeneities forming a triangular lattice similar to an Abrikosov lattice in a type II superconductor (middle thin line in Fig. 1). For weaker Coulomb coupling and close to $\bar{\phi} = 0$ we find a subsequent morphological transition (lower thin line) that restores the translational symmetry in an additional direction and leads to a layered structure ($m = 2$, $p = q = 0$) with $\alpha_{T,L} = 87/(19 - 6\sqrt{6}) \approx 20.22$. We also find that the icosahedral reciprocal lattice which corresponds to an icosahedral quasicrystal never becomes favorable.

The transitions of Eq. (5) are asymptotically exact close to the CP. Instead for $Q \to 0$ they are clearly inaccurate since, still, the range of stability of the inhomogeneous state is smaller than Maxwell construction. In this limit the weak first-order character of the transition is lost and more harmonics should be taken into account.

A good approximation for small Q consists in assuming domains of uniform density of one or the other phase separated by sharp interfaces [2,7,12,14]. This is a reasonable approximation for $Q \to 0$ since there is a strong separation ($l_S \gg l_d \gg \xi$) between the typical interface scale length ξ, the typical size of the domains $l_d \equiv \xi/Q^{2/3}$, and the screening length $l_S \equiv \xi/(\pi^{1/2}Q)$ which controls the relaxation of the charge inside a domain. The transition lines in this approximation are shown with the thick lines at the bottom of Fig. 1. Again one finds the same topological transitions as in strong coupling but now the inhomogeneities form sharply defined spherical drops, cylinders, and layers. The lattice is treated in the Wigner-Seitz approximation (WSA) [6,18].

The crossover from weak to strong coupling has been studied numerically minimizing a discretized version of the energy in the WSA. For rodlike and dropletlike inhomogeneities we assume, respectively, cylindrical and spherical symmetry in order to reduce the minimization to a one-dimensional effective problem. The numerically located first-order transition points are shown with the squares, triangles, and diamonds in Fig. 1. We find that, as the coupling is decreased, the size of the domains becomes much smaller than their distance which should make the approximation particularly accurate at weak coupling. Nevertheless the numerical result converges to the asymptotic expansions both at weak and strong coupling indicating a range of applicability of the WSA wider than expected.

If one relaxes the WSA, the bcc lattice, found at strong coupling, is expected to evolve into a bcc Wigner crystal of drops at small Q which is the lowest energy Wigner crystal lattice [18]. Other lattices however (fcc, hcp) are very close in energy which suggests that amorphous configurations will be very competitive as well.

It is interesting to see how unharmonicity is built in as the coupling is decreased. Figure 2(a) shows the charge profile for $\bar{\phi} = 0$ and different couplings. The SCDW smoothly evolves into the domain morphology that has, as a limiting case, the macroscopically phase separated

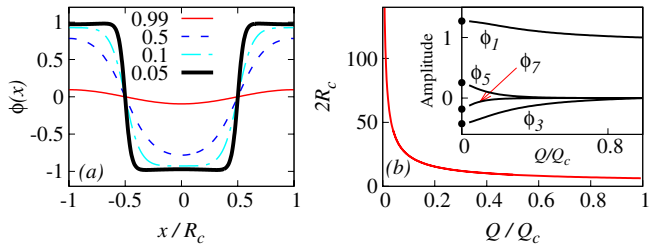

FIG. 2 (color online). (a) Behavior of the charge density modulation for $\bar{\phi} = 0$ and different couplings (labeled by the value of Q/Q_c). Near the Gaussian instability the modulation is close to a SCDW (thin full line). As Q decreases, unharmonicity is built in and the charge modulation tends to a square wave which has, as limiting case, Maxwell construction at $Q = 0$. (b) Evolution of the periodicity of the charge density wave measured in units of ξ. Inset: Evolution of the harmonic amplitudes $\phi_n/\sum_{n'>0}\phi_{n'}$ as a function of Q. The dots indicate the amplitudes for a layered structure of $\phi = \pm 1$ as ruled by Maxwell construction at $Q = 0$. Amplitudes for even n vanish by symmetry.

state at $Q = 0$. Notice that the horizontal axis is normalized by the cell periodicity $2R_c$, which becomes of the order of the linear size of the system as $Q \to 0$ [Fig. 2(b)].

The inset of Fig. 2(b) shows the behavior of the Fourier components. Close to the second-order phase transition the order n harmonics, $\phi_n \equiv \phi_{G_n}$ with $G_n = n\pi/R_c$, behave as $\phi_n \propto (Q_g - Q)^{|n/2|}$. This follows from the fact that the modulation ϕ_n couples with $(\phi_1)^{|n|}$ in the quartic term of Eq. (3). Higher harmonics proliferate as Q is decreased and converge to a rectangular profile corresponding to macroscopic phase separation at $Q = 0$ (shown by solid circles in the inset).

The phase diagram changes dramatically if the gradient term is made anisotropic, i.e., $\xi_\parallel/\xi_\perp > 1$ where $\xi_\parallel$ ($\xi_\perp$) is the bare correlation length in the "hard" ("soft") direction. This can originate from an underlying crystal which favors certain orientations of the interfaces. In Fig. 3 we show the 3D phase diagram with two hard directions and one soft direction for $\xi_\parallel/\xi_\perp \to \infty$ so that only one-dimensional modulations are allowed. The units are fixed as before with $\xi_\perp$ replacing ξ.

In this case the cubic term in Eq. (3) has no effect and one recovers the Gaussian instability where SCDW appears at a second-order transition in an extended range of coupling. Thus, for a metallic system, Landau damping becomes relevant and one should take the coupling to the fermions explicitly into account [3].

As before the Gaussian line cannot persist up to $Q = 0$. We find, in fact a tricritical point at $(\bar{\phi}, Q) = (\pm\sqrt{3}/5, 16/25Q_c)$ where the transition becomes first-order (solid circles in Fig. 3). The position of the tricritical points and the behavior of the charge density modulation around it can be studied retaining only two harmonics in the order parameter with collinear wave vectors:

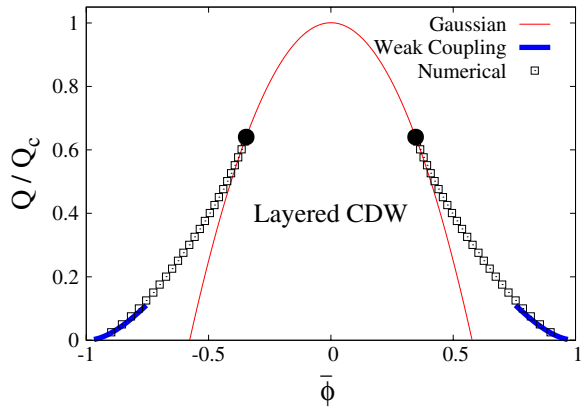

FIG. 3 (color online). The phase diagram for anisotropic 3D systems. The thin line corresponding to the Gaussian instability determines the second-order transition line above the tricritical point (●). Below the tricritical point the transition is first order and is determined numerically (□) and in the weak coupling limit assuming sharp interfaces [2] (thick line). Below the tricritical point the Gaussian line becomes the limit of metastability of the uniform phase.

$$\phi(x) = \bar{\phi} + 2[\phi_1 \cos(G_1 x) + \phi_2 \cos(G_2 x)]$$

and assuming $\phi_2 \ll \phi_1$.

By expanding the energy around the tricritical point and minimizing with respect to the second-harmonic amplitude ϕ_2 one obtains an effective Landau free energy expansion for the modulated phase in terms of ϕ_1 only,

$$\frac{\delta F_{II}}{V} = r\phi_1^2 + u_4\phi_1^4 + u_6\phi_1^6, \qquad (6)$$

with $r \equiv 4(Q - Q_g)/Q_c$, $u_4 \equiv 6 - 32\bar{\phi}^2 Q_c/Q > 0$, and u_6 is a positive constant. This free energy has the canonical form for a tricritical point which is determined by the vanishing of the quartic term on the Gaussian line [23].

In the first-order transition region ($u_4 < 0$), the appearance of the inhomogeneities is determined by the coefficient u_6 in the free energy expansion, Eq. (6), whose precise value depends upon higher-order harmonic contributions. As before we have determined the first-order transition line by numerical minimization (open square in Fig. 3) and from the weak coupling expansion assuming sharp interfaces [2] (thick line).

In conclusion, we have obtained the phase diagram and characterized the crossover of inhomogeneities from strong to weak coupling in a model of Coulomb-frustrated phase separation for systems with a negative short-range compressibility. For isotropic systems we find that the transition from the uniform phase to the inhomogeneous phase is always first order except for a CP. Close to the CP inhomogeneities are predicted to form a bcc lattice with a subsequent transition to a triangular lattice of rods and finally to a layered structure. The transition lines continuously evolve into the weak coupling limit. In the case of anisotropic systems the transition to the inhomogeneous state can become second order with a tricritical point separating the second-order line at strong coupling from the first-order line at weak coupling. Inclusion of an explicit cubic term in Eq. (1), not considered here, will make the phase diagram asymmetric maintaining the topology. Thus we expect our results to be qualitative valid for a wide range of systems with Coulomb-frustrated phase separation.

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[24] For details see Ref. [23] which we follow closely. We caution that Eq. (4) differs from the one reported in Ref. [23]. We are indebted to T. C. Lubensky for confirming to us that the result in the book has to be modified.