Phase diagram for Coulomb-frustrated phase separation in systems with negative short-range 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. In electronic systems strong electron correlations often drive the electronic compressibility negative as in the Hubbard model in infinite dimension, the Falicov Kimball model, the electron gas, cuprates models, manganite models, semiconductor heterostructures, the electron gas, and from droplets to rods (△), from droplets to rods (△), and from rods to layers (⊗).

In this work we study a \( \phi^4 \) 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 including mixtures of block copolymers, charged colloids in polymeric solutions, and electronic systems. We determine the transition line from the homogeneous state to the inhomogeneous state using numerical and analytical techniques and show that generically the transition is first order in three spatial dimensions (3D) except for a critical point (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. 2). In addition we study the crossover from harmonic to anharmonic inhomogeneities and the different topological transitions of the 3D isotropic system. Close to the critical point the inhomogeneities are shown to form a BCC lattice.

The model is defined by the following Hamiltonian

\[ \mathcal{H} = \int dx \left[ \phi(x)^2 - 1 \right]^2 + |\nabla \phi(x)|^2 \]

\[ + \frac{Q^2}{2} \int dx \int dx' \frac{\phi(x) - \bar{\phi}}{|x - x'|} \left[ \phi(x') - \bar{\phi} \right] \]

with the scalar classical field \( \phi \) 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 belonging to the negative compressibility density region. Fermionic effects like the Pauli exclusion principle are reflected in the coefficients. The reference density
The susceptibility has a maximum at $Q/Q_c$ is close to a SCDW (thin full line). As $Q$ decreases unharmonicity is build 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 $\xi$. 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 monocity is build in and the charge modulation tends to a density wave measured in units of $\xi$ with respect to the density at the reference density.

FIG. 2: (Color online) (a) Behavior of the charge density modulation for $\sigma = 0$ 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 build 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 $\xi$. 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 monocity is build in and the charge modulation tends to a density wave measured in units of $\xi$ with respect to the density at the reference density.

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In general $a$ and $\xi$ 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 [22].

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

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

The susceptibility has a maximum at $k_0 = \left[ 2\pi Q^2 \right]^{1/4}$ which diverges as $Q$ approaches the Gaussian instability line $Q_g$ (the dotted line in Fig. 1) from above, where $Q_g = Q_c \left[ 1 - 3\phi^2 \right]$ 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 can not 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 critical point in the phase diagram: the Gaussian line is preempted by a first order transition. Restricting to periodic textures, the free energy difference respect to the uniform state can be written in Fourier space as:

$$\delta F = \frac{1}{V} \sum_{G \neq 0} \phi_G \chi^{-1}(G) \phi_G + \frac{4V}{\sqrt{3}} \sum_{G_1, G_2, G_3 \neq 0} \phi_{G_1} \phi_{G_2} \phi_{G_3} \delta_{G_1 + G_2 + G_3, 0} + \frac{1}{\sqrt{3}} \sum_{G_1, G_2, G_3, G_4 \neq 0} \phi_{G_1} \phi_{G_2} \phi_{G_3} \phi_{G_4} \delta_{G_1 + G_2 + G_3 + G_4, 0} \tag{3}$$

where the $G$’s are the reciprocal lattice vectors and $V$ is the unit cell volume of the periodic solution.

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 [24]. The free energy reads:

$$\frac{\delta F}{V} = \chi^{-1}(G) m \phi_G^2 + 8\phi p m \phi_G^0 + \phi_G^0 \left[ 3m(m - 1) + 6qm \right] \tag{4}$$

where the Fourier component amplitudes $\phi_G$ depends only on the modulus of $G$, $m$ is the number of vectors in $L_G$ and $p (q)$ is the number of triangles (non-planar 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 $\phi_G$ 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 $Y$ of the form

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

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 critical point \((\bar{\phi}, Q) = (0, Q_c)\) shown with a ♦.

At the critical point one recovers a SCDW second-order phase transition with a charge susceptibility divergence since the cubic term of Eq. (3) vanishes. Away from the critical point 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 \(\phi \to 0\) confirming that the transition is weakly first order close to the critical point.

Approaching the first order lines from above the first inhomogeneous structure to become stable corresponds to the FCC reciprocal lattice defined by the \(m = 12\) wavevectors \(G\sqrt{2}/Q = (\pm 1, \pm 1, 0), (\pm 1, 0, \pm 1), (0, \pm 1, \pm 1)\) for which \(p = q = 2\). This corresponds to a BCC crystal of inhomogeneities in real space with \(\alpha_{U,L} = 103/45 \approx 2.29\).

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 rod-like inhomogeneities forming a triangular lattice similar to an Abrikosov lattice in a type II superconductor (middle thin line in Fig. 1). For weaker Coulomb couplings 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 above transitions [c.f. Eq. (3)] are expected to be asymptotically exact close to the critical point. 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\([\text{2, 22, 16, 25, 26}]\). 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 \(\xi\), 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 layered lattices.

In order to study the crossover from the weak to strong coupling we have numerically minimized a discretized version of the energy, also in the WSA. For rod-like and droplet-like inhomogeneities we assume respectively cylindrical and spherical symmetry in order to reduce the minimization procedure to a one-dimensional effective problem. The first-order transition points numerically located are shown with the □, △, ♦ in Fig. 1. We find that as the coupling is decreased the size of the domains become much smaller than their distance which should make the approximation particularly accurate at weak coupling. Despite of that, 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 weak coupling which is the lowest energy Wigner crystal lattice\([\text{19}]\). 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 build into the system as the coupling is decreased. In Fig. 2(a) we show the charge profile for \(\bar{\phi} = 0\) and different couplings. The SCRW smoothly evolves into the domain morphology that has as a limiting case the macroscopically phase separated 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, \(\phi_n \equiv \phi_n G_n\) 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 \(\phi_n\) 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 ♦ in the inset).

The phase diagram changes dramatically if the gradient term is made anisotropic i.e. \(\xi_\parallel/\xi_\perp > 1\) where \(\xi_\parallel\) and \(\xi_\perp\) are the screening lengths parallel and perpendicular respectively to the charge profile.
\( (\xi \perp) \) 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 \( \xi_0/\xi \perp \to \infty \) so that only one-dimensional modulations are allowed. The units are fixed as before with \( \xi \perp \) replacing \( \xi \).

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.\(^4\)

For the same argument 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 (\( \bullet \) 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:

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

and assuming \( \phi_2 \ll \phi_1 \).

By expanding the energy around the tricritical point and minimizing with respect to the second-harmonic amplitude \( \phi_2 \) one obtains an effective Landau free energy expansion for the modulated phase in terms of \( \phi_1 \) only,

\[
\frac{\delta F_{II}}{V} = r\phi_1^2 + u_4\phi_1^4 + u_6\phi_1^6 \quad (6)
\]

with \( r \equiv 4(Q - Q_c)/Q_c \), \( u_4 \equiv 6 - 32\bar{\phi}^2Q_c/Q > 0 \) and \( u_6 \) a positive constant. This free energy has the canonical form for a tricritical point which as usual is determined by the vanishing of the quartic term on the Gaussian line.\(^8\)

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 (\( \square \) in Fig. 3) and from the weak coupling expansion assuming sharp interfaces \(^2\) (dashed 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 relevant 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 critical point. Close to the critical point 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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