Instabilities of micro-phase separated Coulombic systems in constant electric fields.

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Mixtures of near-symmetric oppositely charged components with strong attractive short range interactions exhibit ordered lamellar phases at low temperatures. In the strong segregation limit the state of these systems can be described by the location of the interfaces between the components. It has previously been shown that these systems are stable against small deformations of the interfaces. We examine their stability in the presence of a uniform electric field. When the field is perpendicular to the lamellae, the system is unstable against long wavelength deformations for all non-zero values of the external field. A field parallel to the lamellae produces deformed but persistent interfaces. In a finite thickness system, onset of an external perpendicular field modifies the ground state. Flow between the old and new ground states requires the destruction of the original interfaces; this destruction proceeds through the instabilities identified in the bulk case. We examine the possibility of dynamical stabilization of structures by means of oscillating fields.

In binary mixtures, the competition between repulsive short-range, and attractive long-range interactions leads to micro-phase segregation and pattern formation. A basic example is a mixture of immiscible, oppositely charged particles, where electrostatic interactions frustrate the full phase segregation of the species. This basic scenario has been considered in contexts such as charged polymer blends, polyelectrolytes, multi-component micelles, alloys, and photostimulated semiconductors. These systems can be studied at a more abstract level since concrete models often turn out to be equivalent to those describing other systems such as multiblock copolymers and reaction-diffusion systems, among others.

Control or modification of self-assembled structures is of course of great practical importance. It is natural to consider external electric fields as a mean of morphology control, as these directly couple to the local properties of the system and are directly implementable. Morphology manipulation by electric fields has already proven successful in block copolymer systems in which the microphases are not charged but have different dielectric constants.

We investigate in this article the effects of coupling the charged binary mixture with an external electric field. We describe the ground state of the system in the presence of the field; this turns out to also be a lamellar state with suitably modified thickness at the edges of the system. Our main result is that the original lamellar geometry, at the onset of a perpendicular external field, is an unstable equilibrium state of the system. We use this result and the nature of the perturbation created by external fields parallel to the lamellae to describe some of the main features of the dynamics that bridges the original and final equilibrium state of the system.

The model we discuss operates in the strong segregation limit where concentration fluctuation effects are negligible, and where the electrostatic interaction is weak compared to the segregation tendencies of the mixture. At each point in space there is a well defined majority component and charge. Between these oppositely charged regions there are sharp interfaces and there is a well defined surface tension between them. This approximation is useful when the characteristic thickness of the interface is much smaller than the characteristic size of the segregated domains. The segregated regions are considered large with respect to the particle size and can be treated as continuous media with prescribed charge density \( \rho_0 \).

We can write an effective free energy for the system with contributions from the interfacial surface tension, the electrostatic self-energy, and the interaction with the external field. We consider only the symmetric case where the magnitude of the charge density \( \rho_0 \) is the same for each of the species. Dimensional analysis shows that the system has characteristic length and energy scales given by \( l = (\rho_0^2 / \gamma)^{1/3} \), and \( g = \gamma l^2 \). All physical variables are dimensionalyzed using these scales. We use a charge indicator field \( \rho \) that only takes the values \( \pm 1 \). The electric field and potential generated by the charges in the system are \( \mathbf{E}_i \) and \( \phi_i \), while \( \mathbf{E}_e \) and \( \phi_e \) correspond to the externally imposed field and its associated potential. Using these conventions, the free energy of the system is

\[
F = \int dS + \frac{1}{2} \int_\Lambda dx \int_\Lambda dy \frac{\rho(x) \rho(y)}{|x - y|} + \int_\Lambda d\phi_e \rho - \int_\Lambda d\mathbf{x} \psi(|\rho|^{-1} - 1). \tag{1}
\]

The region occupied by the charges is labelled \( \Lambda \), and the interfaces within the system are labelled by \( \Gamma \). In the last term we introduce a dimensionless pressure field \( \psi \) that
We assign lamellae can be taken to be symmetric with respect to its mode, (c) is the charge symmetric or corrugation mode, and (d) appears at the edge of the Brillouin zone. Panel (b) also shows the surface displacement vector $\Gamma$. White regions are positively charged, shaded regions are negative. The scheme shows our choice of unit cell and coordinate system and the assignment of labels $\Gamma^\pm$, $\Gamma^-$ to the interfaces. Panels (b-d) show different normal deformation modes; (b) is the charge antisymmetric or wiggle mode; (c) is the charge symmetric or corrugation mode, and (d) appears at the edge of the Brillouin zone.

Fig. 2: Ground states of a finite thickness system. On the left, in the absence of an external field, the system is symmetric. The thick lines indicate the boundaries of the system. If the unit cell width $2\lambda_0$ is commensurate with the thickness, the most layers have equal charge and thickness $\lambda_0/2$. As shown in the right frame, in the presence of an external field the ground state is obtained by shifting the location of the interfaces. The new charge distribution at the boundary compensates the external field in the bulk.

$\Gamma^\pm$, are located at $z_\pm = \pm \lambda_0/2$. The collective deformations of the system prescribe a transversal deformation $\Delta u_{n,\pm} = u_{n,\pm} \hat{z}$ for each of the interfaces $\Gamma^\pm_n$, where $n$ is an index for the cell. The normal modes of the system have the form $u_{n,\pm} = A_{\pm} \cos(2\pi n \lambda_0) \cos(q \cdot r)$, where the wave-vector in the transversal direction $q$ is unrestricted while the longitudinal wavevector $p$ takes values within the first Brillouin zone $|p| \leq \pi/(2\lambda_0)$. There are two normal modes for each wave vector $(p, q)$, each with a different ratio between the deformation amplitudes $A_{\pm}$.

A small deformation of the interfaces has the effect of increasing the interfacial area, and producing changes in the charge density localized at the interface. The excess charge density interacts with the background charge and with itself. The excess surface tension energy density associated with a small deformation has the form $(1/2)(\nabla \rho(z))^2$ where $\nabla\rho$ is the gradient along the interface. The excess charge density can be formally written as a series expansion in powers of the deformation amplitude. The terms of these series, $\rho^{(i)}$, and the associated series for the the potential and field are labelled by $i$, the order of the term in the expansion. The first terms of the excess charge density at a given interface have the form $\rho = \rho^{(0)} + 2u(r)\delta(z - z_\pm) - u(r)\delta'(z - z_\pm)$ where $\delta$ and $\delta'$ are the delta function and its derivative. The potential and electric field can be solved order by order in the series. The higher order terms of the potential satisfy the Laplace equation within each homogenous domain and have boundary conditions determined by the excess charge density at the interfaces. The electrostatic excess energy density is $(1/2)\phi^{(1)}\rho^{(1)} + \rho^{(2)}\phi^{(0)}$. Upon integration of the delta functions localized at the interfaces, the excess free energy is the sum, over all interfaces, of the terms

$$
\Delta F_{n,\pm} = \int \frac{1}{2}(\nabla \rho(z))^2 + \phi^{(1)}u \cdot \hat{n} - u^2 E_{i}^{(0)} \cdot \hat{n}.
$$

We choose the orientation of the interface so that its normal vector $n$ points outward from the positive charge regions. The electric field at the interfaces in the ground

![Fig. 1: Panel (a) shows the ground state lamellar structure, with layers of width $\lambda_0$. White regions are positively charged, shaded regions are negative. The scheme shows our choice of unit cell and coordinate system and the assignment of labels $\Gamma^+$. Panels (b-d) show different normal deformation modes; (b) is the charge antisymmetric or wiggle mode; (c) the charge symmetric or corrugation mode, and (d) appears at the edge of the Brillouin zone. Panel (b) also shows the surface displacement vector $u$.](image)
state is \( E^{(0)} = 2\pi \lambda_0 \hat{n} \), so that the last term in the excess energy always has a destabilizing effect.

Carrying out the calculation sketched above, the energies of the normal modes, as well as the relation between the deformation amplitudes of the surfaces in the unit cell can be obtained as a function of the wavevector \((p, q)\). An equivalent calculation has been carried out by Muratov[7], including the case of asymmetric mixtures, and in the presence of screening. The basic result is that all deformations have a non-negative excess energy and therefore the system is stable against small deformations. As shown below, in the presence of constant external fields some of the modes become unstable. The modes that become unstable are deformations of the lowest energy modes at zero field that are located at the center, at \( p = 0 \), and edges \( p = \pm \pi/(2\lambda_0) \) of the first Brillouin zone. The explicit form and energies of these modes at zero field are as follow. For \( p = 0 \), all unit cells have the same displacements, and within each unit cell the normal modes are the charge symmetric \( A_{+} = \pm A_s/\sqrt{2} \), and charge antisymmetric modes \( A_{\pm} = A_a/\sqrt{2} \). The energy per unit volume of each of these modes, for each transverse wavevector \( q \) with magnitude \( q \), are \((1/2)\varepsilon A^2\) with

\[
\varepsilon_a(q) = 2\pi \left[ \frac{\sinh(q\lambda_0/2)}{(q\lambda_0/2) \cosh(q\lambda_0/2)} - 1 + \frac{1}{12}(q\lambda_0)^2 \right],
\]

\[
\varepsilon_s(q) = 2\pi \left[ \frac{\cosh(q\lambda_0/2)}{(q\lambda_0/2) \sinh(q\lambda_0/2)} - 1 + \frac{1}{12}(q\lambda_0)^2 \right]
\]

These results exhibit the softness of the antisymmetric mode, \( \varepsilon_s \sim q^4 \) and the divergent hardness of the symmetric mode \( \varepsilon_a \sim q^{-2} \), for small \( q \). In the edge normal modes with \( p = \pm \pi/(2\lambda_0) \) only one of the unit cell surfaces is deformed. The two modes correspond to the choice of deformed surface and clearly both modes have the same energy density \((1/2)\varepsilon A^2\) with:

\[
\varepsilon(q) = 2\pi \left[ \frac{\cosh(q\lambda_0)}{q\lambda_0 \sinh(q\lambda_0)} - \frac{1}{2} + \frac{1}{12}(q\lambda_0)^2 \right]
\]

The lowest energy modes in this group appear at \( q\lambda_0 = 1.6 \).

Finite size effects and the action of external fields are intimately related in this system. Before addressing the external field, it is useful to consider the properties of the ground state of the finite system. First, we point out that the ground state of a slab of material of width commensurate to \( 2\lambda_0 \) is identical to the bulk solution, with lamellae parallel to the limiting surfaces, terminating at both ends with layers of the same charge of size \( \lambda_0/2 \). Consideration of the surface terms generated by integration by parts during variation of the charge density leads in principle to boundary conditions for the system. In this case, however, these turn out to be equivalent to the bulk equilibrium conditions, and the global minimum must be determined from evaluation of the bulk energy restricted by the incompressibility condition but without extra boundary requirements.

For non-commensurate thicknesses the energy minimum is obtained when the first two layers at both ends are still arranged symmetrically but have thickness different from \( \lambda_0 \). If the end layers do not have equal charge, a net electric field is created within the system. The ground state of the finite system in the presence of a constant perpendicular field is then simply a lamellar structure with unbalanced end layers that create an excess internal field that exactly compensates the external field, as sketched in Fig. 2.

We consider now the effect of the sudden onset of an external uniform electric field on the ground state at zero field. We first note that the original lamellar structure is still an equilibrium state even after the onset of an external field perpendicular to the lamellae. Indeed, due to the incompressibility of the system, rigid translations of the interfaces between components are not possible and all other deformations of the interface lead, to first order, to net zero changes in the energy of the system. In more detail, the equilibrium of the system is achieved again by letting the internal pressure gradient to adjust to compensate the net electric field. This effect can always be achieved when the external field has null curl, as is the case of an uniform field. As we show below, however, this equilibrium state is unstable.

The external field \( E_{e\perp} \) perpendicular to the lamellae couples to the second order term of the charge distribution induced by deformations. The excess energy is given by the same expression as the one obtained for the interaction of the fluctuations with the internally generated field in Eq. (3). For a given surface, this energy is

\[
\Delta F = - \int_{\Gamma} u^2 E_{e\perp} \cdot \hat{n}.
\]

This interaction has a destabilizing effect only in the interfaces whose normal is parallel to the external field. When the deformations are expressed in terms of zero-field normal modes, the field couples to a mixture of the \( p = 0 \) symmetric and antisymmetric modes. The excess energy density is \( \Delta f = E_{e\perp}(A_{s}(q)^2 - A_{a}(q)^2)/(4\lambda_0) = -A_s A_a E_{e\perp}/\lambda_0 \). The new \( p = 0 \) normal modes in the presence of the field are obtained from diagonalization of the new energy quadratic form. These new modes are smooth modifications of the zero-field modes, and will be labelled by the corresponding zero-field labels \( a \) or \( s \). While it is clear that non-zero average excess energies arise for \( p = 0 \) modes, the coupling to the square of the amplitude also gives non-vanishing contributions for the modes at the edge of the Brillouin zone at \( p = \pm \pi/(2\lambda_0) \). The external field shifts the edge modes by \( \Delta f = \pm A_e E_{e\perp}/(2\lambda_0) \).

There are two sets of unstable modes in the system in the presence of an external perpendicular field. The
modes obtained from the deformation of the antisymmetric charge mode, with \( p = 0 \), become unstable for any non-zero value of the external field. These unstable modes appear within a wavevector disk, centered at \( q = 0 \), of radius \( q_c \sim E_c \). The most unstable wavevector has \( q_{\text{max}} \sim E_c \) and the energy coefficient of this mode scales as \( \varepsilon \sim -E_c^2 \). Therefore at very low field strengths the instability is very weak while, at stronger fields, the dynamics are dominated by the exponential growth of finite wavelength modes. A band of edge modes around the softest edge mode, located at \( p = \pi/(2\lambda_0) \), \( q_{\text{sec}} = 1.6 \), also becomes unstable at the finite field value \( E_{\text{sec}} = 0.9 \). Above this threshold value the band of unstable modes has width \( \Delta q \sim (E-E_{\text{sec}})^{1/2} \). The most unstable mode is always \( q_{\text{sec}} \), with energy coefficient \( \varepsilon_c(q_{\text{sec}}) = E/\lambda_0 \). Plots of the energy coefficients for these modes appear in Fig. 3.

We consider now the effect of a field \( E_{\parallel} \) parallel to the lamellae. The ultimate end effect of this field will be to orient the lamellae in a direction perpendicular to the field. There are, however, dynamical steady states with orientations parallel to the field. To show this, we decompose the external potential into its Fourier components \( \hat{\phi}_q \). These components couple linearly to the symmetric deformation modes of same wavevector and their excess energy density in this case is \( \Delta f = (1/2)\varepsilon_s(q)A_s(q)^2 + \sqrt{2}\hat{\phi}_q A_s(q)/\lambda_0 \). Therefore, starting from a parallel orientation, the system flows to a metastable state with symmetric deformations of amplitude \( A_s(q) = \sqrt{2}\hat{\phi}_q/\lambda_0\varepsilon_s(q) \). In a system where the external field is locally constant but periodic, with periodicity \( L \) in the direction of the lamellae (see Fig. 4), the potential has non-vanishing Fourier components of the form \( \hat{\phi}_q \sim E_{\parallel}q^{-2} \). We pointed out above a similar behavior for the self-energy of the long wavelength symmetric fluctuations \( \varepsilon_s \sim q^{-2} \). The deformation amplitudes are then near uniform for small wavevectors, and very small for large ones. The net result for large periodicities \( L \) is an accumulation of charge at the edges of each homogeneous region as in Fig. 4a. These deformations require net charge exchanges between the boundaries of the homogenous field regions. In the limit of infinite size, this charge redistribution emerges as steady exchange currents as sketched in Fig. 4b.

The ground states corresponding to different external fields cannot be connected by charge redistributions that preserve the integrity of the layers since there are no smooth deformations that change the charge of the end layers. Therefore, the flow between ground states always occurs by means of the destruction of the original structure by the growth of instabilities. The flow between the ground states for different external fields requires net transport of charge which, as noted above, occurs naturally in lamellar orientations parallel to the external field. After the destruction of the layers parallel to the boundary, charge transfer might occur through the formation of layers perpendicular to the boundary but parallel to the field, until the charge unbalance necessary to shield the bulk from the external field is achieved. Afterwards, the intermediate layers may become unstable and flow into the final stable conformation with layers parallel to the boundary.

While the presence of instabilities precludes the smooth flow between ground states, i.e. adiabatic control of the system by tuning of external fields, there are interesting possibilities for the creation of structures through slowly varying uniform fields. In particular, we note that smooth deformations of lamellae under parallel fields carry out a similar process as a growing unstable mode in a perpendicular field; namely, both transfer charge along the field direction. That is, from an energetic point of view, the preferred intermediate states
between the ground states of a slab with perpendicular fields are those that connect same-charge regions across the slab. When driven by an oscillating uniform field, the system may oscillate along a set of states of easy charge transfer, as sketched in Fig. 4(c-d), within a suitable range of frequencies determined by the specific dynamics of the system. In other words, oscillating fields may dynamically stabilize lamellar orientations parallel to them.

In conclusion, we have shown how to use the static stability analysis of the system as a guide to describe possible dynamic scenarios for the flow of the system towards equilibrium. The key result is that lamellar structures are unstable equilibrium states in the presence of external perpendicular electric fields, while fields parallel to the lamellae give rise to natural charge transferring currents.

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