

## Pattern Formation and Glassy Phase in the $\phi^4$ Theory with a Screened Electrostatic Repulsion

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We study analytically the structural properties of a system with a short-range attraction and a competing long-range screened repulsion. This model contains the essential features of the effective interaction potential among charged colloids in polymeric solutions and provides novel insights on the equilibrium phase diagram of these systems. Within the self-consistent Hartree approximation and by using a replica approach, we show that varying the parameters of the repulsive potential and the temperature yields a phase coexistence, a lamellar, and a glassy phase. Our results strongly suggest that the cluster phase observed in charged colloids might be the signature of an underlying equilibrium lamellar phase, hidden on experimental time scales.

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*Introduction.*—In the last few years there has been much interest in the role of the interparticle potential on controlling the structure and the dynamics of colloidal suspensions [1–5] due to the potential application of these systems for designing new materials with a wide range of viscoelastic properties. In charged colloidal systems the effective interaction can be described in terms of a short-range attraction and a long-range screened electrostatic repulsion [well approximated by the Derjaguin-Landau-Verweg-Overbeek interaction potential (DLVO) [6]]. The competition between attractive and repulsive interactions on different length scales stabilizes the formation of aggregates of an optimal size (*cluster phase*) characterized by a peak of the structure factor around a typical wave vector,  $k_m$ , that has been experimentally [1,2] and numerically [3–5] observed. By an appropriate tuning of the control parameters, the system progressively evolves toward an arrested gel-like disordered state (*colloidal gelation*). Although intensely studied both experimentally and numerically, a theoretical understanding of the mechanisms underlying these phenomena is still lacking and many gaps remain in our knowledge of the equilibrium phase diagram of these systems.

In this Letter we study analytically a  $\phi^4$  model with competition between a short-range attraction, described by the Ginzburg-Landau Hamiltonian, and a long-range screened repulsion, described by a Yukawa potential. Albeit schematically, this model contains the essential features of the effective interaction among charged colloids and sheds new light on the structural properties of these systems. Depending on the control parameters, there is a region of the phase diagram where usual phase separation takes place. Conversely, as the screening length and/or the strength of the repulsion exceeds a threshold value, phase separation is prevented. In this case, at moderately high temperature the competition between attraction and repulsion has the effect of producing modulated structures,

which in the terminology of particle systems, correspond to the cluster phase. These modulated structures are the precursors of a first-order transition towards an equilibrium lamellar phase found at lower temperatures. By using a replica approach for systems without quenched disorder [7], and employing the self-consistent screening approximation (SCSA) [8], we also show the presence of a glass transition line in the low-temperature region, once the first-order transition to the lamellar phase is avoided. Note that the mechanism for the glass transition in this case is not due to the presence of hard-core type of potential. Instead, it is due to the formation of the modulated structures which order up to the size of correlation length. The geometric frustration, resulting in arranging such modulated structures in a disordered fashion, leads to a complex free energy landscape and, consequently, to a dynamical slowing down.

Our results suggest that the cluster phase observed in colloidal suspensions should be followed, upon decreasing the temperature (or increasing the volume fraction), by an equilibrium periodic phase (a tubular or a lamellar phase, depending on the volume fraction). If, instead, this ordered phase is avoided, a structural arrest, corresponding to the gel phase observed in the experiments and in numerical simulations, should eventually occur. The existence of ordered phases in colloidal suspension and the fact that the transition to the gel phase could occur in a metastable liquid, are novel predictions, which have never been considered before. Recently, motivated by our work, de Candia *et al.* [9] have unambiguously shown the presence of such ordered phases by using molecular-dynamic (MD) simulations on an atomistic model system of charged colloids, interacting via the DLVO potential.

*Model and phase diagram.*—We consider the standard three dimensional  $\phi^4$  field theory with the addition of a repulsive long-range Yukawa potential:

$$\mathcal{H}[\phi] = \int d^3\mathbf{x} \left[ \frac{r_0}{2} \phi^2(\mathbf{x}) + \frac{g}{4} \phi^4(\mathbf{x}) + \frac{1}{2} (\nabla \phi(\mathbf{x}))^2 \right] + \frac{W}{2} \iint d^3\mathbf{x} d^3\mathbf{x}' \frac{e^{-|\mathbf{x}-\mathbf{x}'|/\lambda} \phi(\mathbf{x}) \phi(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}, \quad (1)$$

where  $\phi(\mathbf{x})$  is the scalar order parameter field. The model has been also studied in [10] in the context of microemulsion. The parameters  $W$  and  $\lambda$  are, respectively, the strength and the range of the repulsive potential. For  $W = 0$  we obtain the canonical short-range ferromagnet. Interestingly, for  $\lambda \rightarrow \infty$  we recover the case of the Coulombic interaction [11–17]. This model has been used to describe the phenomenology of a wide variety of systems, where competing interactions on different length scales stabilize pattern formations and the creation of spatial inhomogeneities (for a review see [18]). These systems include magnetic systems and dipolar fluids characterized by long-range Coulombic interactions [19], mixtures of block copolymers [20], water-oil-surfactant mixtures [21] and doped Mott insulators, including the high  $T_c$  superconductors [22]. As a consequence, our model allows to describe and to interpret in an unified fashion the phenomenology of a wide variety of different systems.

Here we present only the main results, and we refer to a paper in preparation for more details [23]. In Fig. 1 the

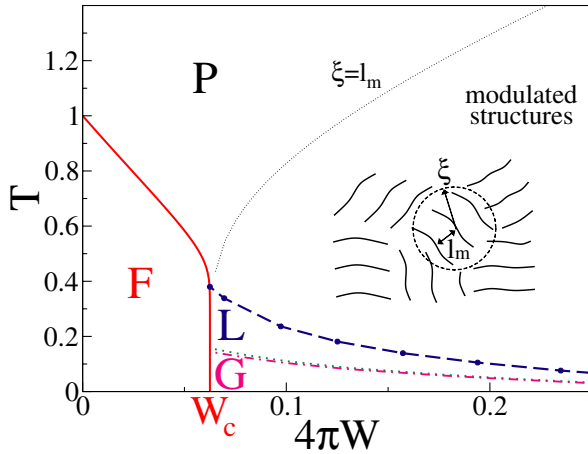


FIG. 1 (color online). Temperature ( $T$ )-repulsion ( $4\pi W$ ) phase diagram of the model for  $\lambda = 2$  (and  $r_0 = -1$ ), showing the relative positions of the paramagnetic (P), ferromagnetic (F), lamellar (L), and glassy (G) phases. The value of  $g$  is such that  $T_c(W = 0) = 1$ . The continuous (black) and the dashed (blue) curves, found within the Hartree approximation, corresponds, respectively, to the second-order phase transition from P to F,  $T_c(W, \lambda)$ , and to the first-order transition from P to L,  $T_L(W, \lambda)$ . The dotted (green) and the dashed-dotted (red) curves, found within the SCSA, identify the dynamical,  $T_d(W, \lambda)$ , and the ideal,  $T_K(W, \lambda)$ , transition temperatures to G. The thin dotted (black) line ( $\xi = l_m$ ) marks a crossover temperature below which the system establishes modulated structures, schematically sketched in the figure.

phase diagram of the model as function of the temperature,  $T$ , and the strength of the repulsion,  $W$ , is presented, for a fixed value of the screening length,  $\lambda = 2$ .

*Ferromagnetic and lamellar phases.*—We first solve the model within the self-consistent Hartree approximation, which consists in replacing the term  $g\phi^4/4$  of Eq. (1) with  $3\langle\phi^2\rangle\phi^2/2$  [24]. This substitution allows us to compute the correlation function  $G(\mathbf{k}) = \langle\phi_{\mathbf{k}}\phi_{-\mathbf{k}}\rangle - \langle\phi_{\mathbf{k}}\rangle \times \langle\phi_{-\mathbf{k}}\rangle$ . In the paramagnetic phase,  $\langle\phi_{\mathbf{k}}\rangle = 0$ , one obtains

$$TG^{-1}(\mathbf{k}) = r + k^2 + 4\pi W/(\lambda^{-2} + k^2), \quad (2)$$

where the renormalized mass term,  $r$ , is defined as  $r \equiv r_0 + 3g\langle\phi^2\rangle$ . Since  $\langle\phi^2\rangle = \int_{|\mathbf{k}| < \Lambda} \frac{d^3\mathbf{k}}{(2\pi)^3} G(\mathbf{k})$ , from Eq. (2) the following self-consistent equation for  $r$  is derived:

$$r = r_0 + 3g \int_{|\mathbf{k}| < \Lambda} \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{T}{r + k^2 + 4\pi W/(\lambda^{-2} + k^2)} \quad (3)$$

( $\Lambda$  is an ultraviolet cutoff). For convenience let us define

$$4\pi W_c \equiv \lambda^{-4}. \quad (4)$$

For  $W \leq W_c$  and a fixed value of  $\lambda$ , we find a line of ordinary second-order critical points,  $T_c(W, \lambda)$  (continuous curve in Fig. 1), separating a high-temperature paramagnetic phase from a low-temperature ferromagnetic one. This transition is characterized by the divergence of the susceptibility, i.e.,  $G^{-1}(\mathbf{k} = \mathbf{0}) = 0$ , with the usual Hartree critical exponents (e.g.,  $\nu = 1$  and  $\gamma = 2$  in three dimensions). Thus, for  $W \leq W_c$  usual phase separation occurs: the effect of the repulsive interaction is to decrease the value of  $T_c$  from the critical temperature of the standard Ginzburg-Landau model (for  $W = 0$ ) to zero temperature (for  $W \rightarrow W_c$ ). Conversely, above  $W_c$  there is no phase separation. This result is quite important for designing new materials as well as in the experimental and numerical study of colloidal systems, where it is crucial to distinguish the slowing down due to colloidal gelation from that due to kinetic of phase separation. Interestingly, the threshold value  $W_c$ , Eq. (4), coincides with that estimated for an atomistic model system of charged colloids interacting via the DLVO potential [5].

In the limit  $\lambda \rightarrow \infty$  we recover the already known results for the Coulombic case: phase separation occurs only for  $W = 0$  [11–17].

For  $W > W_c$ , the model instead exhibits a first-order transition line  $T_L(W, \lambda)$  (dashed curve of Fig. 1), separating the paramagnetic phase from a lamellar phase [17,25], characterized by a spatially modulated order:

$$\langle\phi_{\mathbf{k}}\rangle = A(\delta(\mathbf{k} - \mathbf{k}_m) + \delta(\mathbf{k} + \mathbf{k}_m)), \quad (5)$$

with amplitude  $A$  and wave vector  $k_m$ , given by

$$k_m^2 = \sqrt{4\pi}(W^{1/2} - W_c^{1/2}). \quad (6)$$

For  $W > W_c$  the spinodal line of the “supercooled” para-

magnetic phase is located at  $T = 0$ , where the susceptibility diverges [ $TG^{-1}(\mathbf{k}_m) = 0$ ]. As a result, the first-order transition to the lamellar phase can be kinetically avoided and long-time glassy relaxations can be, instead, observed [14–17,26–28].

*Glass transition.*—In order to analyze the glass transition in our model, we employ a replica approach formulated to deal with systems without quenched disorder [7].

The equilibrium free energy,  $F = -T \ln Z$ , is relevant only if the system is able to explore ergodically the entire phase space. This is not the case, of course, in the glassy phase, where the system is frozen in metastable states. In order to scan the locally stable field configurations, we introduce an appropriate symmetry breaking field  $\psi(\mathbf{x})$ , and compute the following partition function [7]:

$$\tilde{Z}[\psi] = \int \mathcal{D}\phi \exp\left(-\beta \mathcal{H}[\phi] - \frac{u}{2} \int d^3\mathbf{x} [\psi(\mathbf{x}) - \phi(\mathbf{x})]^2\right), \quad (7)$$

where  $u > 0$  denotes the strength of the coupling. The free energy  $\tilde{f}[\psi] = -T \ln \tilde{Z}[\psi]$  will be low if  $\psi(\mathbf{x})$  equals to configurations which locally minimize  $\mathcal{H}[\phi]$ . Thus, in order to scan all metastable states we have to sample all configurations of the field  $\psi$ , weighted with  $\exp(-\beta \tilde{f}[\psi])$

$$\tilde{F} = \lim_{u \rightarrow 0^+} \left[ \int \mathcal{D}\psi \tilde{f}[\psi] e^{-\beta \tilde{f}[\psi]} / \int \mathcal{D}\psi e^{-\beta \tilde{f}[\psi]} \right]. \quad (8)$$

$\tilde{F}$  is a weighted average of the free energy in the various metastable states; if there are only a few local minima, the limit behaves perturbatively and  $\tilde{F}$  equals the true free energy  $F$ . However, in case of the emergence of an exponentially large number of metastable states with large barriers between them, a nontrivial contribution arises from the above integral even in the limit  $u \rightarrow 0^+$  and  $\tilde{F}$  differs from  $F$ . This allows us to identify the complexity  $\Sigma$  via the relation  $F = \tilde{F} - T\Sigma$  [7]. In order to get an explicit expression for  $\Sigma$  we introduce replicas

$$\tilde{F}(m) = - \lim_{u \rightarrow 0^+} \frac{T}{m} \ln \int \mathcal{D}\psi (\tilde{Z}[\psi])^m, \quad (9)$$

from which, we obtain  $\tilde{F} = \partial m \tilde{F}(m) / \partial m|_{m=1}$  and

$$\Sigma = T^{-1} (\partial \tilde{F}(m) / \partial m|_{m=1}). \quad (10)$$

Integrating Eq. (9) over  $\psi$ , we get an action which is formally equivalent to the (replicated) action of a system in a quenched random field. We can thus use the SCSA [8], a technique developed to deal with such systems, which allows to determine the correlators in the replica space. The SCSA amounts to introducing a  $N$ -component version of the model and summing self-consistently all the diagrams of order  $1/N$  [15,16]. Since the attractive coupling between replicas is symmetric with respect to the replica index, one can assume the following structure of the correlators in the replica space:  $G_{ab}(\mathbf{k}) = [G(\mathbf{k}) -$

$F(\mathbf{k})] \delta_{ab} + F(\mathbf{k})$ , i.e., with diagonal elements  $G(\mathbf{k})$  and off-diagonal elements  $F(\mathbf{k})$ . For systems with quenched disorder, this ansatz turns out to be equivalent to the one-step replica symmetry breaking. While the diagonal correlator can be interpreted as the usual one-time equilibrium correlation function,  $TG(\mathbf{k}) = \langle \phi_{\mathbf{k}} \phi_{-\mathbf{k}} \rangle$ , the off-diagonal term can be interpreted as measuring the long-time correlations:  $TF(\mathbf{k}) = \lim_{t \rightarrow \infty} \langle \phi_{\mathbf{k}}(t) \phi_{-\mathbf{k}}(0) \rangle$ . Hence,  $F(\mathbf{k})$  vanishes in the paramagnetic phase while is finite in the glassy one.

The system undergoes a glass transition in the low-temperature region for  $W > W_c$ , with exactly the same nature of that found in mean-field models for glass formers. Lowering the temperature we first find a purely dynamical transition at temperature  $T_d$  (dotted curve in Fig. 1). Here, the complexity, Eq. (10), jumps discontinuously from zero to a finite value, signaling the emergence of an exponentially large number of metastable state. The complexity decreases as the temperature is decreased and vanishes at  $T_K$  (dashed-dotted curve in Fig. 1) where the thermodynamical transition takes place.

*Structural properties.*—The correlation function,  $G(\mathbf{k})$ , is plotted in Fig. 2 at the dynamical transition temperature  $T_d$ , showing a maximum at  $k_m$ , defined in Eq. (6), with width  $\xi^{-1}$ , given by the inverse of the correlation length. The correlation function in the real space reads:  $G(|\mathbf{x}|) \sim e^{-|\mathbf{x}|/\xi} \sin(k_m |\mathbf{x}|) / |\mathbf{x}|$ . This expression implies that, although no periodic order occurs ( $\langle \phi_{\mathbf{k}_m} \rangle = 0$ ), a lamellar structure of wave length  $l_m = 2\pi k_m^{-1}$  over a finite range  $\xi$  is formed (as sketched in Fig. 1). In the glassy phase,  $T \lesssim T_d$ , one has that  $\xi \gtrsim 2l_m$  [16]: thus these modulated structures form over a length larger than their modulation length and become frozen. The glass transition arises from

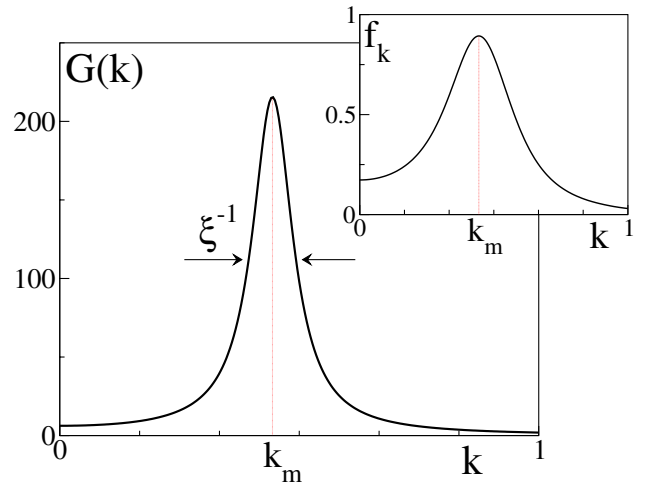


FIG. 2 (color online). Main frame: Momentum dependence of the correlation function,  $G(\mathbf{k})$ , for  $4\pi W = 0.2$  and  $\lambda = 2$  at  $T = T_d$ , showing that it is peaked around the typical modulation wave vector  $k_m$  with broadening  $\xi^{-1}$ , given by the inverse of the correlation length. Inset: Momentum dependence of the non-ergodicity parameter  $f_{\mathbf{k}}$  for the same values of  $W$ ,  $\lambda$ , and  $T$ .

the fact that there are many possible configurations to arrange such modulated structures in a disordered fashion, leading to a great number of metastable states. The presence of this characteristic wave length dominates also the dynamics, as indicated by the momentum dependence of the nonergodicity parameter,  $f_{\mathbf{k}} \equiv \lim_{t \rightarrow \infty} \frac{\langle \phi_{\mathbf{k}}(t) \phi_{-\mathbf{k}}(0) \rangle}{\langle \phi_{\mathbf{k}}(t) \phi_{-\mathbf{k}}(t) \rangle} = \frac{F(\mathbf{k})}{G(\mathbf{k})}$ , plotted in the inset of Fig. 2 at  $T_d$ . The presence of a maximum at  $k_m$  signals the fact that structural arrest is more pronounced over length scales of order  $l_m$ . At higher temperatures,  $T > T_d$ , the nonergodicity parameter  $f_{\mathbf{k}}$  vanishes and the glassy phase disappears; correspondingly,  $G(\mathbf{k})$  broadens and the height of the peak decreases; hence,  $\xi$  decreases until the modulated structures fade continuously, approximately at a crossover temperature where  $\xi \approx l_m$  (dotted curve in Fig. 1).

These results are intimately related to the phenomenology observed in colloidal systems, where the competition between attraction and repulsion leads to the formation of a phase of stable clusters at low temperatures [1–5], which is the analog of the modulated structures here found. Our results suggest that the transition to the disordered gel phase, numerically and experimentally observed in colloidal suspensions, occurs, in fact, in a metastable liquid, due to the presence of an underlying equilibrium lamellar phase (which might be more easily detected by increasing the screening length  $\lambda$ ). This novel prediction has been confirmed by recent MD simulations of a model system of charged colloids in three dimensions [9]; a clear indication of the presence of periodic phases was also numerically found in two dimensions [29].

*Conclusions.*—We have derived analytically the complete phase diagram of a model with competition between short-range attraction and long-range screened repulsion, which contains the essential features of the interaction potential of charged colloids. To our knowledge, this is the first theoretical investigation on these systems. Our predictions have been confirmed by recent numerical simulations and may be also experimentally checked.

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