Phase-Field Model of Long-Time Glasslike Relaxation in Binary Fluid Mixtures

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We present a new phase-field model for binary fluids, exhibiting typical signatures of soft-glassy behavior, such as long-time relaxation, aging, and long-term dynamical arrest. The present model allows the cost of building an interface to vanish locally within the interface, while preserving positivity of the overall surface tension. A crucial consequence of this property, which we prove analytically, is the emergence of free-energy minimizing density configurations, hereafter named "compactons," to denote their property of being localized to a finite-size region of space and strictly zero elsewhere (no tails). Thanks to compactness, any arbitrary superposition of compactons still is a free-energy minimizer, which provides a direct link between the complexity of the free-energy landscape and the morphological complexity of configurational space.

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The coarsening mechanisms by which a binary fluid mixture attains an ordered state upon a deep quench from a high-temperature disordered phase continue to attract a great deal of attention in the scientific community [1–3]. Apart from their paramount practical interest, these phenomena still set a fascinating challenge to the foundations of nonequilibrium thermodynamics, because of their competition-driven long-time relaxation, often denoted as "glassiness" or "self-glassiness." The literature on glassy systems is huge, covering materials as diverse as colloids, block copolymers, proteins, glass forming liquids, and many others [1,2]. Equally broad is the spectrum of theoretical or computational techniques employed for their study, such as replica methods, mode-coupling theory, mesoscopic kinetic models, as well as molecular dynamics, Monte Carlo and Langevin simulations [3]. More specifically, coarsening phenomena in binary mixtures are typically described by Langevin equations, governing the space-time evolution of the order parameter, i.e., the density deficit between the two-fluid densities [4]. Depending on the specific details, different exponents are then predicted for the power-law growth of the coarsening length, the typical linear size of the coarsening domains. In soft-glassy materials, however, domain growth is observed to undergo long-term slowdown and possibly even dynamical arrest. In this Letter, we present a new phase-field Landau-Ginzburg (LG) model exhibiting most typical signatures of self-glassiness, such as longtime relaxation, aging, and long-term dynamical arrest. The present model can be analytically derived, bottom-up, from a mesoscopic kinetic scheme for complex fluids with competing short-range attraction and long-range repulsion [5]. Similarly to previous phase-field models [6,7], the stiffness coefficient, controlling the cost of building and maintaining an interface between the two fluids, acquires a dependence on the local value of the order parameter. However, unlike any previous work we are aware of, instead of triggering local instabilities by sending the leading interface term to negative values everywhere across the interface, and then stabilizing through higher-order inhomogeneities [8], here the stiffness becomes zero only locally within the interface, thereby preserving the positivity of the overall surface tension. This subtle difference spawns far-reaching consequences. Indeed, the present model is analytically shown to promote the emergence of stable, finite-support, density configurations, which we name "compactons." The dynamics of these compactons is then shown to be ultimately responsible for the self-glassiness of the binary mixture. Here and throughout, at variance with Ref. [9], the term "compacton" is kept within quotes, to imply that it just refers to the property of these density excitations of being localized within a finite-support region of configuration space, and zero everywhere else, throughout the evolution. The emergence of compactons is hereby discussed analytically, both in the continuum and discrete versions of our phase-field models. Typical signatures of self-glassiness, such as ultraslow relaxation, aging, and dynamical arrest, are further demonstrated by direct numerical simulations.

Let us start by considering the following LG-like phase-field equation:

$$\partial_t \phi = -\frac{\delta F[\phi]}{\delta \phi} + \sqrt{\epsilon}\,\eta(\vec{x}, t), \tag{1}$$

$$F[\phi] = \int d\vec{x}\left[V(\phi) + \frac{1}{2}D(\phi)|\nabla\phi|^2 + \frac{\kappa}{4}(\Delta\phi)^2\right], \tag{2}$$

where $\phi(\vec{x}; t)$ is the order parameter, taking values $\phi = \pm 1$ in the bulk, and $\phi = 0$ at the two-fluid interface. In the above, $V(\phi)$ is the bulk free-energy density, which we shall take in the standard double-well form $V(\phi) = -\frac{1}{2}\phi^2 + \frac{1}{4}\phi^4$, supporting jumps between the two bulk phases, $\phi = \pm 1$, where η is a white noise δ correlated in space and time, with variance ϵ. The key ingredient of our model rests with the specific form of the stiffness function $D(\phi)$, describing the lowest order approximation to the energy cost of building an interface between the two fluids. In the standard LG formulation, this is a constant parameter D_0, fixing the value of the surface tension, through the relation $\gamma \sim D_0 \int (\partial_x \phi)^2 dx$, x being the coordinate across the (flat) interface. Positive values of γ promote coarsening, as a result of the surface tension tendency to minimize the surface/volume ratio of the fluid. Negative values of γ, on the other hand, promote an unstable growth of the interface, an instability that is usually tamed at short scale by including higher-order "bending" terms of the form $\sim \kappa (\Delta \phi)^2$ where κ is referred to as bending rigidity. It is readily seen that with $D_0 < 0$ and $\kappa > 0$, the system undergoes instabilities, which are typically responsible for pattern formation [6,8]. Such instabilities are then stabilized at short scales by a positive bending rigidity. Gompper *et al.*, among others [6], studied the case with piecewise constant $D(\phi)$ to describe microemulsions [7]. Our model belongs to the same class as Gompper's, with

$$D(\phi) = D_0 + D_2 \phi^2, \tag{3}$$

yet with a crucial twist: instead of sending D_0 to negative values, in order to trigger local interface instabilities, we just set $D_0 = 0$ and achieve a local zero-cost condition, $D(\phi) = 0$, just at $\phi = 0$, by letting $D_2 > 0$. Thermodynamic stability of the interfaces is still secured, since $\gamma > 0$, and consequently we resolved to set the bending rigidity to $\kappa = 0$ in (2), so as to single out the effect of the modulated stiffness $D(\phi)$ alone. In the following, we shall show that the peculiar feature discussed above holds the key for observing ultimate arrest of the fluid. As anticipated, this is due to the onset of complex density configurations, resulting from arbitrary superpositions of stable, finite-support density configurations, which we name compactons.

Let us then present our analytical analysis by looking at the one-dimensional, stationary solutions of Eqs. (1) and (2) in the limit $D_0 \to 0$ and no noise ($\epsilon = 0$). One quadrature yields

$$\tfrac{1}{2} D_2 \phi^2 (\partial_x \phi)^2 + \tfrac{1}{2}\phi^2 - \tfrac{1}{4}\phi^4 = E, \tag{4}$$

where $E \leq 1/4$ is an arbitrary integration constant. Note that the relation between E and F for a single compacton is $F = \int (D_2 \phi^2 (\partial_x \phi)^2 - E) dx$. The analytical solution is provided by

$$\phi_E(x) = \pm\sqrt{1 - \cosh(\xi) + e \sinh(\xi)}\,\chi(x; x_0, l_e), \tag{5}$$

where $\xi = (x - x_0)/l_d$, $l_d = \sqrt{D_2/2}$, $e = 2\sqrt{E}$. Here x_0 is an arbitrary location and χ is the characteristic function ($\chi = 1$ inside and $\chi = 0$ outside) in the segment $x_0 \leq x \leq x_0 + l_e$, $l_e = l_d \text{arctanh}(2e/(1 + e^2))$ (see Fig. 1). Several comments are now in order. First, this solution

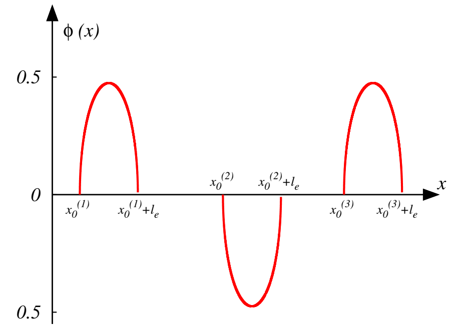

FIG. 1 (color online). An example of a static gas of compactons for the case $D_0 = 0$ and fixed $E < \frac{1}{4}$. The solution is constructed from an arbitrary superposition of stable, finite-support density configurations, each one centered around its $x_0^{(i)}$ and identically zero outside the segment $[x_0^{(i)} < x < x_0^{(i)} + l_e]$. The size l_e is set by E and D_2 as in Eq. (5).

is compact; i.e., it is identically zero outside the segment $[x_0 < x < x_0 + l_e]$. This property is crucially related to the vanishing of the prefactors in front of the differential operators, which allows discontinuity in the slope of $\phi(x)$. The location of the segment x_0 is arbitrary because of translation invariance, whereas its extension l_e is dictated by E. Under the condition that l_d be real, i.e., $D_2 > 0$, a positive $E > 0$ corresponds to the nucleation of a compacton of size $l_e > 0$. The compacton can eventually invade the system, $l_e \to L$, L being the size of the domain, a condition which is met at a value $E_L = 1/4$, since $l_e \to \infty$ as $E \to 1/4$. More interesting, however, is the possibility of a gas of compactons, which can "invade" the system at lower values $E < E_L$, by simply superposing a collection of disjoint compactons centered upon different values of x_0. The possibility of such a linear superposition of elementary solutions of a highly nonlinear field theory, is again a precious consequence of compactness. Since compactons do not overlap, they obey a nonlinear superposition principle $(\sum_i \phi_i)^n = \sum_i \phi_i^n$ for any power n, where $i = 1, N$ labels a series of compactons eventually covering the full interval, $\sum_{i=1}^N l_{e;i} = L$. As a result, an arbitrary superposition of compactons still obeys the generalized LG equation. By using the above nonlinear superposition principle, a standard stability analysis shows that, as long as the overall surface tension is positive, $\gamma > 0$, the gas of compactons is stable against arbitrary (square-integrable) perturbations of the order parameter; hence, it represents a local minimum of the free-energy landscape. This result is crucial to qualify compactons as the relevant effective degrees of freedom responsible for self-glassiness of the complex fluid mixture. Therefore, we arrive at a very elegant and intuitive picture of glassiness, as the nucleation of a "gas of compactons," each of which corresponds to a local minimum of the free energy associated with the LG equations (1) and (2). Most remarkably, these compactons can be added together, each collection of compactons

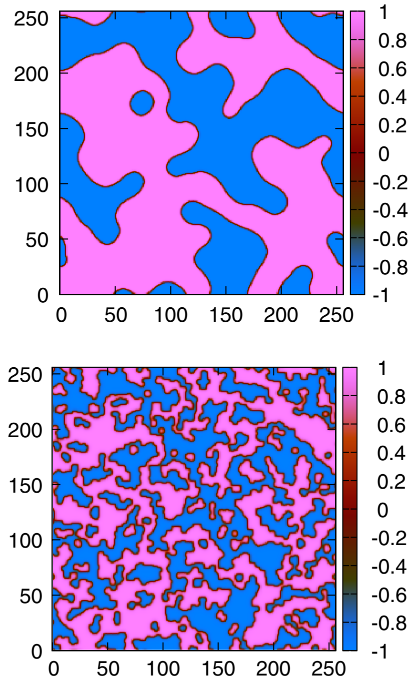

FIG. 2 (color online). Color plates of the order parameter $\phi(x, y; t)$ for the case $D_0 = 0.3$, $D_2 = 0$ (top) and $D_0 = 0.3$, $D_2 = 2$ (bottom), $\epsilon = 0$, at $t = 20\,000$. The much slower coarsening associated with the $D_2 = 2$ case is well visible.

corresponding to a distinct dynamical partition of physical space. This provides a very poignant and direct map between the complexity (coexistence and competition of multiple minima, sometimes referred to as "ruggedness") of the free-energy landscape and the morphological complexity of the fluid density in configuration space.

Since the collective properties of the "gas of compactons" shall be demonstrated via numerical simulations, it is crucial to prove that compactons survive discreteness, as we shall show in the sequel. In particular, we analyze under what condition on D_0 and D_2 one can still find compact solutions on a lattice. To this aim, we considered stationary solutions of the discretized version of (1) which become 0 at $x = 0$ and found a symmetry in the solution; namely, $x \to -x$ implies $\phi \to -\phi$. This symmetry is clearly broken by the solution defined in (5) and the condition for the existence of a nonzero, symmetry-breaking solution of the discrete LG equation, reads $D_0 - \frac{2D_0^2}{\Delta x^2} + 2D_2E > 0$, Δx being the lattice spacing [10]. In the limit of small Δx and large D_2, the latter yields $\frac{D_0^2}{D_2 \Delta x^2} < E$ and can be rephrased in terms of competing scales, as $l_0^2/l_d^2 < 1$, where l_0 is a scale proportional to $D_0/\Delta x$ and l_d has been defined previously. In this way, the limit $D_0 \to 0$, where the system shows self-glassiness, reads as $l_d \gg l_0$. We now proceed to show that such self-glassiness is indeed observed in numerical simulations of the generalized LG equations (1) and (2). To this purpose, we simulated the generalized LG equation, including a noise term, to represent finite-temperature effects. The corresponding Langevin equation is simulated on a square lattice of size 256^2 with periodic boundary conditions. Initial conditions are chosen randomly, $\phi(x, y; t = 0) = r$, where r is a random number uniformly distributed in $[-0.1, 0.1]$. In Fig. 2, we show two color plates of the order parameter $\phi(x, y; t)$ at $t = 20\,000$ for the case $D_0 = 0.3$ and $D_2 = 0$ (top), $D_2 = 2.0$ (bottom), both without noise. It is apparent how the case with $D_2 > 0$ leads to a much retarded coarsening, as a matter of fact to a dynamical arrest.

In Fig. 3, we report the free energy $F(t) + 1/4$ for $D_0 = 0.6$ and three different values $D_2 = 0, 4, 8$ with $\epsilon = 0$. Each point is the result of the averaging on 100 configurations with randomly chosen initial condition. From this figure, it is seen that the asymptotic decay is always a power law $F(t) + 1/4 \sim t^{-a}$, with an exponent a which becomes smaller and smaller as D_2 is increased. Eventually, $a(D_2)$ reaches the zero point (see the inset), formally corresponding to structural arrest, for $D_2 \sim 10.7$. Next, we performed further simulations by including an external forcing, h, constant in space and time, as well as a thermal noise. We monitor the average response to the external drive, $\Phi(t) = M^{-1}L^{-2}\sum_{m=1}^{M}\sum_{x,y}\phi_m(x, y; t)$, where M is the number of realizations corresponding to

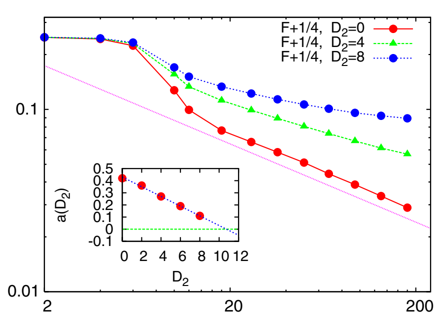

FIG. 3 (color online). Free-energy decay for the case $\epsilon = 0$, $D_0 = 0.6$, and $D_2 = 0, 4, 8$. The inset reports the exponent $a(D_2)$ of the corresponding power-law decay for $D_2 = 0, 2, 4, 6, 8$.

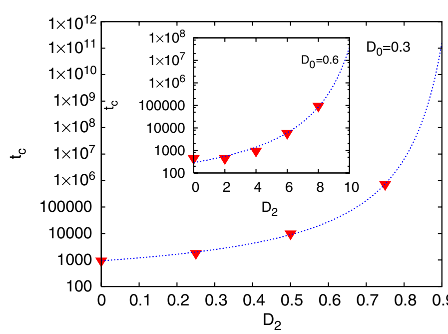

FIG. 4 (color online). Divergence of the relaxation time t_c at increasing values of D_2, for $D_0 = 0.3$ and $D_0 = 0.6$ (inset). The noise amplitude is $\epsilon = 0.01$.

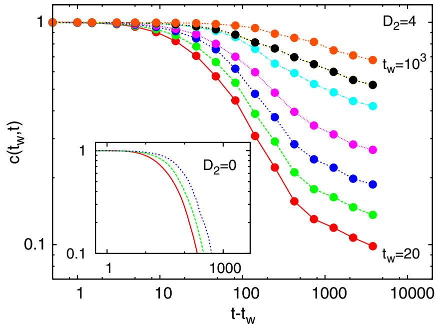

FIG. 5 (color online). Time decay of the density-density correlator for various values of the waiting time t_w and $\epsilon = 3 \times 10^{-4}$. The aging effect, namely, a decreasing loss of memory at increasing t_w, is clearly visible. In the inset we report the case with $D_2 = 0$ for comparison.

different random initial conditions. With $D_2 = 0$ the system reaches its driven steady state, $\phi \approx 1 - O(h)$ in a finite-time t_c. As $D_2 > 0$ is switched on, this relaxation time increases considerably. Structural arrest similar to the one observed in Fig. 3, has been observed also in previous lattice Boltzmann simulations [5], with full hydrodynamic interactions and conserved parameter dynamics. Figure 4 shows the relaxation time as a function of D_2, $t_c(D_2, D_0)$, for $D_0 = 0.3$ and $D_0 = 0.6$ (inset) and $\epsilon = 0.01$. From this figure, it is seen that, as the ratio D_2/D_0^2 is increased, the relaxation time starts to ramp up quite rapidly. This divergence is consistent with a Vogel-Fulcher-Tammann law $t_c(D_2, D_0) = \exp(\frac{C}{D_{2,c} - D_2})$ [11], where $D_{2,c}$ and C both depend on D_0 and D_2 plays the role of a temperature. In particular, we obtain $D_{2,c} \sim 2$, and $D_{2,c} \sim 12$ for $D_0 = 0.3$ and $D_0 = 0.6$, respectively. This ultralow relaxation is in line with the picture of a structural arrest of the mixture, due to the stability of the compactons. Another typical signature of glassy behavior is aging, i.e., the anomalous persistence in time of density-density correlations. A typical aging indicator is the density-density correlator

$$c(t_w, t) = \frac{\langle(\phi(x, y; t_w)\phi(x, y; t)\rangle_c}{\langle\phi(x, y; t_w)\phi(x, y; t_w)\rangle_c},$$

where t_w is the waiting time and brackets denote spatial and ensemble averaging and $\langle \ldots \rangle_c$ stands for connected correlation. In Fig. 5, we show this quantity for the cases $D_0 = 0.6$ and $D_2 = 4$ and $D_2 = 0$ (inset) and $\epsilon = 0.0003$. From this figure, it is apparent that for $D_2 = 0$ the density-density correlator decays to zero, indicating that the system is able to visit all regions of phase space. Such capability, however, is manifestly lost in the case $D_2 = 4$, to an increasing extent as t_w is made larger, which is precisely the aging behavior mentioned above.

Summarizing, we have presented a new phase-field model exhibiting typical signatures of self-glassiness, such as long-time relaxation, aging, and long-term dynamical arrest. The distinctive feature of the present model is to allow the cost of building an interface to become locally zero, while preserving global positivity of the overall surface tension. Analytical solutions are shown to take the form of compact density configurations (compactons), associated with local minima of the corresponding free-energy functional. Direct simulations of the model show that self-glassiness emerges as a collective property of this "gas of compactons." The compacton picture proposed in this work provides a very elegant and conceptually new link between the complexity of the free-energy landscape and the morphological complexity of the fluid density in configuration space.

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