Self-glassiness in binary mixtures: the compacton picture

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We present a new phase-field model for binary fluids exhibiting typical signatures of self-glassiness, such as long-time relaxation, ageing and long-term dynamical arrest. The present model allows the cost of building an interface to become locally zero, while preserving global positivity of the overall surface tension. An important consequence of this property, which we prove analytically, is the emergence of compact configurations of fluid density. Owing to their finite-size support, these "compactons" can be arbitrarily superposed, thereby providing a direct link between the ruggedness of the free-energy landscape and morphological complexity in configurational space. The analytical picture is supported by numerical simulations of the proposed phase-field equation.

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Coarsening phenomena in binary mixtures are typically described by Langevin equations, governing the space-time evolution of the order parameter [1]. 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 slow-down and possibly even dynamical arrest. A thorough understanding of such complex behaviour has been the subject of several decades of intense research [2]. In this Letter, we present a new phase-field Landau-Ginzburg (LG) model exhibiting most typical signatures of self-glassiness, such as long-time relaxation, ageing and long-term dynamical arrest. The present model is inspired by and can be analytically derived from a lattice Boltzmann kinetic scheme for complex fluids with competing short-range attraction and long-range repulsion [3]. Usually, when the coefficients in front of the terms governing the interface dynamics are allowed to become *negative*, they promote large-scale instabilities, which are eventually tamed at short scales by proper compensation via higher-order terms, such as the bending rigidity [5]. Instead of triggering local instabilities by sending the leading interface term to negative values, and then compensating through higher order inhomogeneities, here we allow the coefficients in front of the interface terms to depend on the local value of the order parameter. As a result, the cost of building an interface may become *locally* negative across the interface itself. This difference is subtle but determines non-trivial consequences. Indeed, rather than triggering large-scale instabilities, the present procedure 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 the term "compacton" is kept within quotes, to imply that it just refers to the property of the density field of being localized within a finite-support region of configuration space, throughout the evolution. Such stable and finite-support excitations do not share the properties which characterize the interactions among compactons as "solitons with finite wavelength" [4]. 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 ultra-slow relaxation, ageing and dynamical arrest, are further demonstrated by direct numerical simulations. Let us start by considering the following LG like phase-field equation:

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

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

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 kink/anti-kink bulk phases, $\phi = \pm 1$; ϵ is the variance of the noise and η is a white noise δ-correlated in space and time. The key ingredient of our model lies 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 Ginzburg-Landau 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. Fluid mixtures with positive γ exhibit 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 *rigidity*. It is readily seen that with $D_0 < 0$

and $\kappa > 0$, the system undergoes instabilities, which are typically responsible for pattern formation [5, 6]. Such instabilities are then stabilized at short scales by a positive bending rigidity. Gompper et al., among others [6], studied the case with piece-wise constant $D(\phi)$ to describe microemulsions [7]. Our model belongs to the same class as Gompper's one, 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 modulation factor $D(\phi)$ 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". We wish to emphasize that such gas of "compactons" lies beyond the realm of free-energy models based on quadratic density-density interactions alone, no matter how non-local. Indeed, the present LG field equation, was first inspired by and then analytically derived from a mesoscopic lattice Boltzmann kinetic model, supporting effective mean-field pseudo-potentials of the form: $V_{eff}(\vec{x}) = \psi(\rho(\vec{x})) \int G(\vec{r})\psi(\rho(\vec{x}+\vec{r}))d\vec{r}$, where the displacement $\vec{r}$ runs over suitable regions of a regular lattice [3]. In the above, $G(\vec{r})$ is a suitable lattice Green-function encoding short-range attraction and long-range repulsion and $\psi(\rho)$ is a generalized density which contains powers of the local density $\rho(\vec{x})$ at all orders. It can be analytically shown, that the coefficient D_2 is driven by the second derivative $d^2\psi/d\rho^2$, hence it is identically zero for quadratic density-density interactions [8].

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

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

where $E \leq 1/4$ is an arbitrary constant fixing the energy of the configuration. A further quadrature delivers the analytical solution

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

where $\xi = (x - x_0)/l_d$, $l_d = \sqrt{D_2/2}$, $e = 2\sqrt{E}$. Here x_0 is an arbitrary shift and χ is the characteristic function of the segment centered in x_0 and size $l_e = l_d\,\mathrm{arctanh}\left(2e/(1+e^2)\right)$ (see figure 1). Several comments are now in order. First, this solution is compact,

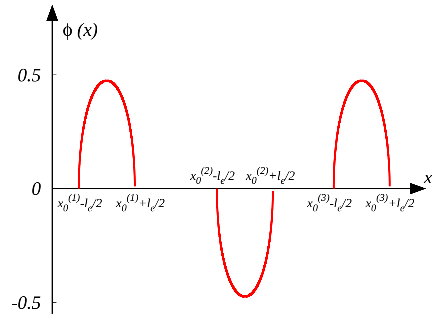

FIG. 1: An example of a static gas of "compactons" for the case $D_0 = 0$ and fixed $E < \frac{1}{4}$. The solution is constructed from an arbitrary superposition of stable, finite-support density configurations, each one centered around its $x_0^{(i)}$ and *identically* zero outside the segment $[x_0^{(i)} - l_e/2 < x < x_0^{(i)} + l_e/2]$. The size l_e is set by E and D_2 as in eq. (5).

i.e., it is *identically* zero outside the segment $[x_0 - l_e/2 < x < x_0 + l_e/2]$. 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 the "energy" E. Under the condition that l_d be real, *i.e.,* $D_2 > 0$, a finite amount of energy $E > 0$ allows 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 an energy 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 non-linear field theory, is again a precious consequence of compactness. Since "compactons" do not overlap, they obey a non-linear 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 non-linear 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 to 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 eqs. (1-2). Most remarkably, these "compactons" can be added together, each collection of "compactons" corresponding to a distinct dynamical partition of physical space. This provides a very poignant and direct map between the complexity (ruggedness) of the free-energy landscape and the morphological complexity of the fluid density in configuration space. This picture is highly reminiscent of the inherent-structures discovered/proposed based on numerical and analytical studies of glass-forming fluids [9]. However, the link between the landscape and configurational complexity emerging from the present compacton-based LG picture, appears to be new, and possibly even more direct. The same considerations extend to higher dimensions, to be described in a future, more detailed publication [8].

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 studied under what condition on D_0 and D_2 we 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 we 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 non-zero, symmetry-breaking solution of the discrete LG equation, reads $D_0 - \frac{2D_0^2}{\Delta x^2} + 2D_2 E > 0$, 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 $\sqrt{D_0/\Delta x}$ and l_d has been defined previously. In this way, the limit $D_0 \to 0$, where the system shows self glassiness, is directly translated into $l_0 \ll l_d$.

Having portrayed the main analytical picture of self-glassiness as an emergent property of the "gas of compactons", we now proceed to show that such self-glassiness is indeed observed in numerical simulations of the generalized LG eqs. (1-2). 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 figure 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. We also wish also to emphasize the visual similarity with density field configurations obtained by lattice Boltzmann simulations of non-ideal fluids with competing interactions [3].

In figure 3, we report the free-energy $F(t) + 1/4$ for

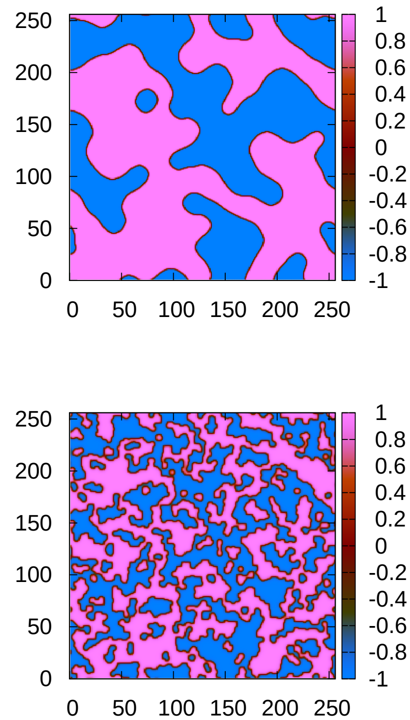

FIG. 2: Color plates of the order parameter $\phi(x, y; t)$ for the case $D_0 = 0.3, D_2 = 0$ (top) and $D_0 = 0.3, D_2 = 2$ (bottom), $\epsilon = 0$, at $t = 20,000$. The much slower coarsening associated with the $D_2 = 2$ case is well visible.

$D_0 = 0.6$ 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 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. 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 de-

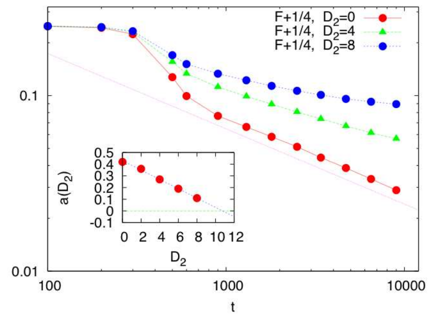

FIG. 3: Free-energy decay for the case $\epsilon = 0$, $D_0 = 0.6$ and $D_2 = 0, 4, 8$. The inset reports the exponent $a(D_2)$ of the corresponding power-law decay for $D_2 = 0, 2, 4, 6, 8$.

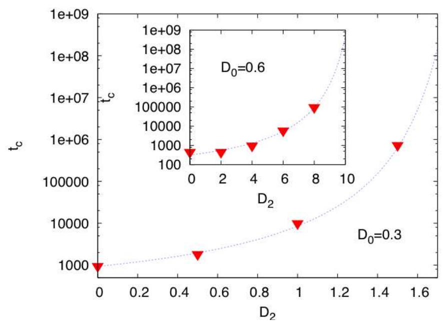

FIG. 4: Divergence of the relaxation time t_c at increasing values of D_2, for $D_0 = 0.3$ and $D_0 = 0.6$ (inset). The noise amplitude is $\epsilon = 0.01$.

pend both 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 ultra-low 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 behaviour is ageing, *i.e.,* the anomalous persistence in time of density-density correlations. A typical ageing indicator is the density-density correlator

$$\langle C(t_w, t_w + t)\rangle = \frac{\langle \phi(x, y; t_w)\phi(x, y; t_w + t)\rangle}{\langle \phi(x, y; t_w)\phi(x, y; t_w)\rangle}$$

where t_w is the waiting time and brackets denote spatial and ensemble averaging. In figure 5, we show this quantity for the case $D_0 = 0.6$ and $D_2 = 4$ and $D_2 = 0$ (inset) and $\epsilon = 0.001$. 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 broken in the case $D_2 = 4$, and to an increasing extent as t_w is made larger, which points precisely to the ageing behaviour mentioned above.

Summarizing, we have presented a new phase-field model exhibiting typical signatures of self-glassiness, such as long-time relaxation, ageing and long-term dynamical

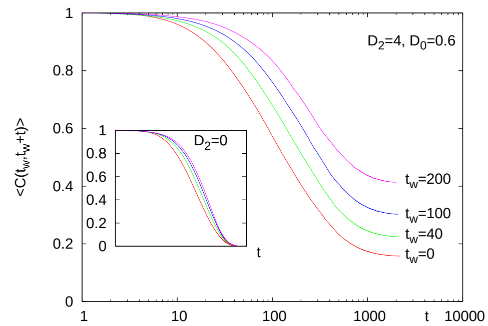

FIG. 5: Time decay of the density-density correlator for various values of the waiting time, $t_w = 0, 40, 100, 200$ and $\epsilon = 10^{-3}$. The ageing effect, namely a decreasing loss of memory at increasing t_w, is clearly visible as compared to the complete loss of memory in the case $D_2 = 0$ (inset).

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 ruggedness of the free-energy landscape and the morphological complexity of the fluid density in configuration space. Valuable discussions with G. Gompper and I. Procaccia are kindly acknowledged.

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