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Spinodal-Assisted Crystallization in Polymer Melts

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Recent experiments in some polymer melts quenched below the melting temperature have reported spinodal kinetics in small-angle x-ray scattering before the emergence of a crystalline structure. To explain these observations we propose that the coupling between density and chain conformation induces a liquid-liquid binodal within the equilibrium liquid-crystalline solid coexistence region. A simple phenomenological theory is developed to illustrate this idea, and several experimentally testable consequences are discussed. Shear is shown to enhance the kinetic role of the hidden binodal. [S0031-9007(98)06584-3]

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Upon cooling a crystallizable polymer melt a hierarchy of ordered structures emerges [1]. There are crystalline “lamellae,” comprising regularly packed polymer chains, each of which is ordered into a specific helical conformation. These lamellae interleave with amorphous layers to form “sheaves,” which in turn organize to form superstructures (e.g., spherulites). These structures may be probed by various techniques: e.g., wide-angle x-ray scattering (WAXS) is sensitive to atomic order within lamellae (“Bragg peaks”), while small-angle x-ray scattering (SAXS) probes lamellae and their stacking. Inspired by recent experiments, we propose a model for the earliest stages of ordering in a supercooled polymer melt, and discuss several experimentally testable consequences, including strain and pressure effects.

In a supercooled simple liquid, the following picture [2] is widely accepted. Nuclei of the lower free energy (crystal) phase are constantly formed by thermal fluctuations. But the cost of creating an interface means that only large enough nuclei can grow—the melt is *metastable*. An induction time, τ_i , elapses before the probability of forming such “critical nuclei” becomes significant. This picture is usually deemed appropriate for polymer melts; instead effort is focused on explaining the anisotropic shape and growth rate of crystal nuclei [3].

In the “classical” picture of polymer melt crystallization we expect and observe Bragg peaks in WAXS *after* an induction period τ_i . SAXS accompanies the WAXS, corresponding to interleaved crystal lamellae and amorphous regions [1]. No SAXS is expected during τ_i . However, recent experiments have reported SAXS peaks during the induction period and *before* the emergence of Bragg peaks. Initially the SAXS peak intensity grows exponentially, and it may be accurately fitted to the Cahn-Hilliard (CH) theory for *spinodal decomposition*—the spontaneous growth of fluctuations indicative of thermodynamic *instability* [4]. The peak moves to smaller angles in time, stopping when Bragg peaks emerge. By fitting to CH theory, an extrapolated spinodal temperature (at which the melt first be-

comes unstable towards local density fluctuations) can be obtained. Spinodal kinetics have been reported in different polymer melts: poly(ethylene terephthalate) (PET) [5], poly(ether ketone ketone) [6], polyethylene (PE), and isotactic polypropylene (*i*-PP) [7,8]. Despite these recent results, no coherent model exists for these phenomena.

Such observations can be explained by appealing to the concept of a “metastable phase boundary,” a common strategy in metallurgy [9,10]. Consider an alloy quenched into a region of its phase diagram where we expect coexistence between two phases, say, $\alpha + \beta$. If the two phases are symmetry unrelated there is always an energy barrier for phase separation, and we do *not* expect to see spinodal (unstable) dynamics. Nevertheless, spinodal dynamics and textures have been observed in some such cases. Some time ago, Cahn suggested [9] that this could be due to a metastable phase boundary for coexistence between two symmetry-related phases (say, $\alpha + \alpha'$) *buried within* the equilibrium $\alpha + \beta$ coexistence region. Recently, similar ideas are used to explain slow kinetics in the formation of colloidal crystals in colloid-polymer mixtures [11] and globular protein crystallization [12].

Similarly, a plausible explanation for the observation of spinodal dynamics in polymer melts is the presence of a metastable liquid-liquid (LL) phase coexistence curve (or “binodal”) buried inside the equilibrium liquid-crystal coexistence region (Fig. 1). Quenching sufficiently below the equilibrium melting point T_m , we may cross the spinodal associated with the buried LL binodal at temperature $T_s < T_m$. Below, we give a physical mechanism that can give rise to such a metastable binodal, calculate the phase diagram using a phenomenological free energy, and delineate some consequences of our model.

Our starting point is the unremarkable statement that, in order to crystallize, polymer chains must adopt the correct *conformation*. For example, chains in crystalline PE have the all-*trans* (or “zigzag”) conformation, while in the melt the conformation is randomly *trans* or *gauche*. Generally, the preferred conformation is some form of

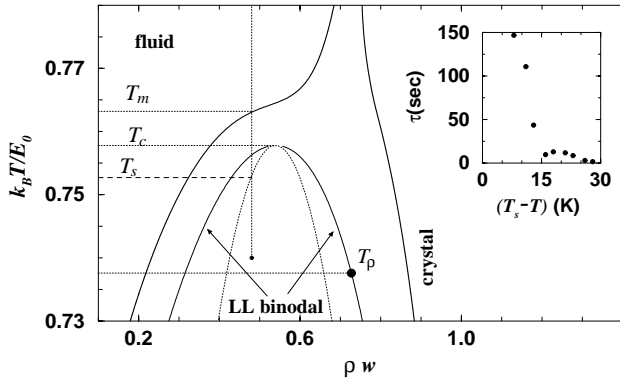


FIG. 1. Proposed generic phase diagram for a polymer melt calculated as described in the text. T_m and T_s are the melting and spinodal temperatures encountered along the (constant density) quench path (dotted line). Parameters used are $RM_b = 0.8$, $k_B T_* = 0.29E_0$, $v = 1.4E_0 w$, $\lambda = 0.1av_0$, $b = -0.4(v_0 a^3 / E_0)^{1/2}$, $c = 0.5a^2 v_0 / E_0$, and $\alpha = 0.8/w$. Inset shows the measured induction time as a function of temperature for isotactic polypropylene [7].

helix. Furthermore, the radius of gyration of a (very long) chain changes little during crystallization, suggesting [13] that neighboring segments adopt the correct conformation and crystallize *in situ*. It is commonly assumed that conformational (intrachain) and crystalline (interchain) ordering occur *simultaneously*. We suggest, in light of recent experiments, that these processes can occur *sequentially*. To motivate this suggestion we examine more closely the physics of conformation changes.

In a melt, it is believed that chain conformation alone cannot drive a phase transition. However, conformation is coupled to density. Chains with the “correct” (helical) conformation typically pack more densely than those with more or less random conformations. Moreover, the energy barriers between different rotational isomeric states (RIS) are density dependent [14]. We now show that *conformation-density coupling can induce a LL phase transition*. A phenomenological free energy which incorporates these effects is a function of the following order parameters: the (average) mass density $\bar{\rho}$; the coefficients $\{\rho_q\}$ in the Fourier expansion of the crystal density in terms of the appropriate stars of reciprocal lattice vectors $\{\mathbf{q}\}$ (essentially the intensities of Bragg peaks) [15]; and the occupancies $\{\eta_i\}$ of various RIS (and thus chain conformation). To illustrate the principles, we assume that a single $\rho_q \equiv \rho_*$ and a single η suffice, corresponding to a fictitious polymer with body-centered cubic crystal structure [16] and two RIS. The free energy per unit volume has three components:

$$f = f_0(\bar{\rho}) + f_*(\bar{\rho}, \rho_*) + f_\eta(\eta, \bar{\rho}, \rho_*). \quad (1)$$

The equation of state $\bar{\rho} \partial f / \partial \bar{\rho} - f = p$ determines the $T - \bar{\rho}$ isobar at pressure p . The first term, f_0 , is the free energy of a melt with random chain conformations. Equation-of-state fits to polymer liquids suggest the following form:

$$f_0(\bar{\rho}) = Rk_B T \bar{\rho} \ln[(1/\bar{\rho}) - w], \quad (2)$$

where R and w are widely tabulated [17]. The (bare) Landau free energy of crystallization is taken to be [15,16]

$$f_*(\bar{\rho}, \rho_*) = \bar{\rho} \left[\frac{1}{2} a(\bar{\rho} T) \rho_*^2 + \frac{1}{3} b \rho_*^3 + \frac{1}{4} c \rho_*^4 \right]. \quad (3)$$

For simplicity we let $a(\bar{\rho}, T) \equiv a_0 k_B [T - T_*(1 + \alpha \bar{\rho})]$, where α and T_* account for the enhancement of crystallization due to increased density. $f_0 + f_*$ has a double well structure and gives a (bare) first-order transition between amorphous ($\rho_* = 0$) and crystalline ($\rho_* \neq 0$) states.

f_η describes how the distribution of chain conformations varies smoothly from random ($\eta = 0$) to totally ordered (helix, $\eta = 1$) as the temperature is lowered to zero [18]. In isolation a polymer thermally populates its RIS with a Boltzmann distribution $P_\alpha \sim \exp\{-\beta E_\alpha\}$, where E_α is the energy of state ϕ_α relative to the ground state ϕ_0 , and $\beta = 1/k_B T$. As the temperature is lowered the mean occupancy η of state ϕ_0 , relative to the $T = \infty$ disordered state ($\eta = 0$), increases. We describe this process, for a two-state model, by

$$f_\eta(\eta, \bar{\rho}, \rho_*) = \frac{k_B T \bar{\rho}}{2M_b} \left[\eta^2 \cosh^2\left(\frac{\beta E}{2}\right) - \eta \sinh(\beta E) \right], \quad (4)$$

where M_b is the mass of a monomer with characteristic volume $v_0 = wM_b$. Minimizing f_η over η yields the correct Boltzmann distribution $\eta(T) = \tanh(\beta E/2)$. We choose [19]

$$E(\bar{\rho}, \rho_*) = E_0 + v\bar{\rho} + \lambda \rho_*^2. \quad (5)$$

As more bond sequences occupy the ground state, monomers can rearrange to pack tighter and reduce the excluded volume interaction (hence, the perturbation $v\bar{\rho}$). A positive v encourages phase separation to take advantage of this density-conformation coupling. Similarly, adjacent ground state sequences enhance crystallization (hence, the term $\lambda \rho_*^2$). The λ term is quadratic in ρ_* by symmetry [16].

To calculate the phase diagram in the temperature-density ($T - \bar{\rho}$) plane we first minimize f with respect to η . Note that minimizing f_η over η and expanding f in $\bar{\rho}$ renormalizes $a(\bar{\rho}, T)$ and c in Eq. (3) and, at sufficiently small T , destabilizes the homogeneous melt. Physically, the system gives up conformational entropy to relieve packing frustration, and separates into a dense, more ordered liquid and a less dense and less ordered liquid. The renormalization of c lowers the barrier to crystallization in the dense, high- η liquid. Next, f is minimized with respect to ρ_* to give a final free energy with two branches, $\hat{f}(\bar{\rho}, \rho_* = 0)$ (liquid) and $\hat{f}(\bar{\rho}, \rho_* \neq 0)$ (solid). The common tangent constructed between these two branches at any temperature gives the densities of coexisting liquid and crystal phases at that temperature (Fig. 2) [20]. At low enough temperatures, the liquid branch gives a spinodal buried entirely within the equilibrium liquid-crystal coexistence region given as usual by the points of inflection, $\partial^2 \hat{f} / \partial \bar{\rho}^2 = 0$. If a melt is quenched inside this spinodal, it will phase separate

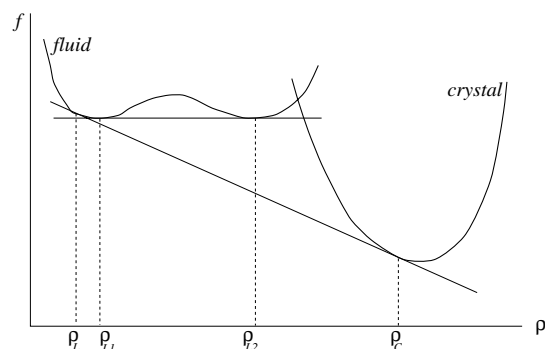


FIG. 2. Schematic free energy density plots at a particular temperature. At this temperature, a melt with density $\rho_L < \rho < \rho_c$ will phase separate into coexisting liquid and crystal phases at densities ρ_L and ρ_c . The common tangent drawn on the liquid branch alone gives the densities, ρ_{L1} and ρ_{L2} , on the metastable LL binodal (see Fig. 1).

into two coexisting liquids, given by the common tangent construction, with a coarsening interconnected domain texture (Fig. 3) in which the regions have (almost) the coexisting LL densities. We expect τ_s to be weakly (at most power-law) dependent on temperature. The exponential term accounts for the barrier to nucleate a crystal from the dense liquid. The strong temperature dependence of τ_i should change over to a much weaker dependence at some $T_\rho < T_s$, where $\Delta(T_\rho, \bar{\rho}) \approx k_B T_\rho$. This has been found in *i*-PP (inset, Fig. 1) [7].

To calculate Fig. 1 we fix the dimensionless parameter $RM_b = 0.8$, appropriate for PE [17], leaving $\nu/(E_0 w)$ as the only adjustable parameter to determine the spinodal temperature T_s . For $\nu = 1.4E_0 w$ we find an LL critical point at $k_B T_c = 0.75E_0$ and $\rho_c w = 0.53$. Experiments on PE, for which $\rho w \approx 0.685$ ($w = 0.875 \text{ cm}^3 \text{ g}^{-1}$ [17] and $\rho = 0.783 \text{ g cm}^{-3}$ [21]), give $k_B T_s \approx 0.86E_0$ [7] (using $E_0 = 930 \text{ cal/mole}$ [14]). The value for ν corresponds to a relative change of E by order +0.58 on going from single chain to melt conditions [Eq. (5)]. This agrees, in sign and magnitude, with the known behavior of common polymers [21]. The agreement over *sign* is particularly significant. We suggest that density and con-

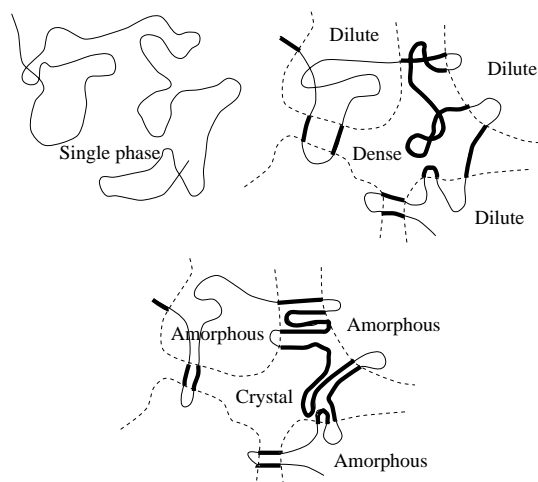


FIG. 3. Schematic representation of the late-stage spinodal texture for coexisting liquid phases with different conformations, showing a single chain; thin line: disordered conformation; thick line: correct (helical) conformation for crystallization. Each chain is a “conformational copolymer.”

formation work cooperatively, i.e., $\nu > 0$; no LL binodal within the required temperature range was obtained for $\nu < 0$. Even a crude Landau theory, therefore, puts constraints on allowable physical mechanisms. Our choice of crystallization coefficients (α, b, c, λ) (caption, Fig. 1) gives a reasonable value for T_m , but the crudeness of Landau theory for first-order transitions renders detailed fitting somewhat meaningless.

One of the coexisting liquids is closer in density and conformation to the crystal phase than the original melt, and has a lower energy barrier, $\Delta(T, \bar{\rho})$, to crystallization, so inducing “spinodal-assisted nucleation.” We expect $\Delta(T, \bar{\rho})$ to decrease with increasing quench depth below T_s (and, hence, widening the LL coexistence gap). Indeed, in our simplified model, we find $\Delta(T, \bar{\rho}) = 0$ at temperature $T_\rho < T_s$. The induction time, τ_i , is then

$$\tau_i \sim \tau_s + \text{const} \times e^{\Delta(T, \bar{\rho})/k_B T}, \quad (6)$$

where τ_s is the time to reach an intermediate spinodal texture (Fig. 3) in which the regions have (almost) the coexisting LL densities. We expect τ_s to be weakly (at most power-law) dependent on temperature. The exponential term accounts for the barrier to nucleate a crystal from the dense liquid. The strong temperature dependence of τ_i should change over to a much weaker dependence at some $T_\rho < T_s$, where $\Delta(T_\rho, \bar{\rho}) \approx k_B T_\rho$. This has been found in *i*-PP (inset, Fig. 1) [7].

The characteristic length scale associated with the developing spinodal texture gives rise to a SAXS peak, which evolves initially according to CH theory [22]. The coarsening of this texture is observed to be arrested at the end of the induction period (typical scale ξ_m), when Bragg peaks appear in WAXS [7]. It is at present unclear how the spinodal texture at the end of the induction period evolves into spherulites. However, the final spinodal texture length scale ξ_m evidently controls the thickness of the first crystal lamellae. Moreover, large stress will develop once one of the two liquids in a bicontinuous texture (Fig. 3) crystallizes. We expect such a texture to fragment into individual crystalline lamellae.

Our arguments so far have been based on conformation-density coupling. Once a polymer segment has adopted the correct (helical) conformation its persistence length should increase, which couples to the *orientational* order of chains. Indeed, depolarized light scattering by Imai and co-workers has suggested the existence of orientational fluctuations during the spinodal phase of a crystallizing PET melt [23]. Provided that orientational ordering is not strong enough to induce a separate transition, then the inclusion of a nematic order parameter in Eq. (1) only renormalizes the coefficients in η -dependent terms. In some cases, the increasing chain stiffness accompanying conformational order may be sufficient to drive an isotropic \rightarrow nematic transition, resulting in a *three-step* process: melt \rightarrow (isotropic) liquid(1) + liquid(2), followed by liquid(2) liquid(2) \rightarrow nematic \rightarrow crystal. This possibility should be investigated. It should also be

possible to model specific polymers, e.g., using density functional theory [21], augmented to include the effects leading to Eq. (5) [14].

Until recently, spinodal scattering was mainly observed in polymer melts crystallizing *under shear* [1,8,24]. This may be understood in a natural way within the present framework. Shear (and extensional) flow couples principally to the orientation of polymer segments, hence, straightening chains and enhancing η , thereby biasing the tendency towards LL separation. A simple way to incorporate this is to renormalize the activation energy E as $E - \nu_0\sigma$, where σ is the stress. It is highly suggestive that, for appropriate values of stress under strong flow (the plateau modulus G_0) and volume (ν_0 above), the LL binodal of Fig. 1 is shifted upward significantly (by $\delta T_s \sim 0.01E_0/k_B$). Flow will shift the liquid-solid coexistence curve much less because the regions with crystalline order will resist deformation.

Our simple theory suggests several interesting experiments. First, and most directly, conformational fluctuations just above T_s could be detected and studied, e.g., by Raman spectroscopy [1], perhaps simultaneously with depolarized light scattering (to monitor orientational fluctuations). Second, on approaching a spinodal line, various properties (e.g., correlation length) should exhibit power-law divergences. The observation of such divergences will lend much weight to the correctness of our model. Third, the point at which the LL spinodal is encountered in a quench can be modified by pressure (Fig. 1). In particular, it may be possible to access the LL critical point, T_c : recent simulations suggest a massive enhancement of the nucleation rate in the vicinity of T_c [25]. More generally, the coupling of density to (molecular) structural order parameters is an emerging generic theme in the study of supercooled liquids (water \rightarrow amorphous ice, [26]; polymer melts near the glass transition [27]). Finally, processes such as surface nucleation could give rise to a SAXS peak, but are unlikely to follow Cahn-Hilliard kinetics. Also, effects other than conformation and orientation (e.g., polydispersity) may induce LL phase separation. Experiments on monodisperse alkanes are under way to address this possibility.

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