Minimal Model for Phase Separation under Slow Cooling

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Inducing phase separation by a sustained change of temperature often induces repeated waves of nucleation. As demonstrated in an accompanying movie, these oscillations can easily be demonstrated in the classroom by slowly cooling raw spirit (i.e., ethanol) and vegetable oil. In the present communication we suggest a minimal theoretical model predicting that they are of thermodynamic origin. Their frequency depends on the diffusion constant and ramp rate, and is not affected by the overall composition and sample geometry. Our experimental data support this model.

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Phase separation arises when an isotropic multicomponent mixture is subjected to a change of temperature after which its isotropic state is no longer thermodynamically stable. Nucleation or spinodal decomposition induce then local phase separation on very small length scales. It is followed by diffusive transport processes leading to coarsening of the domain structure [1–7]. During this process the composition $\phi(\mathbf{x}, t)$ of the mixture evolves according to a diffusion equation [4–7]

$$\frac{d\phi(\mathbf{x}, t)}{dt} = \nabla[D(\phi(\mathbf{x}, t))\nabla\phi(\mathbf{x}, t)], \tag{1}$$

with a composition-dependent diffusion coefficient $D(\phi)$ [8]. Close to equilibrium the diffusion coefficient takes on values in the order of $D_{\mathrm{eq}} = 10^{-5}\ \mathrm{cm}^2/\mathrm{s}$ for low molecular weight mixtures and orders of magnitude smaller values in more viscous liquids like polymer solutions. $D(\phi)$ decreases when $\phi(\mathbf{x}, t)$ deviates from the equilibrium composition $\phi_{\mathrm{eq}}(T)$, until it approaches zero at the so-called spinodal composition $\phi_s(T)$.

On macroscopic length scales $L \sim 1$ cm the composition relaxes with a rate $D_{\mathrm{eq}}/L^2 \sim 10^{-5}$–$10^{-8}\ \mathrm{s}^{-1}$. This is much slower than the change of the equilibrium composition during a moderate temperature ramp of $v_s \sim 0.1$ K/s, which changes the equilibrium composition with a rate $v_s\Delta\phi_{\mathrm{eq}}/\Delta T \sim 10^{-2}$–$10^{-5}\ \mathrm{s}^{-1}$ [9]. When temperature is ramped diffusion is therefore not fast enough to keep the system close to equilibrium. In the absence of catalyzers of phase separation [5] there will eventually be a massive wave of nucleation producing a large number of tiny droplets in the bulk. Immediately after this nucleation the diffusion can act on length scales of typical droplet distances of (less than) $L \sim 100$ nm, such that it relaxes supersaturation by orders of magnitude faster than it is generated by the temperature ramping. However, due to coagulation of droplets the rates of the two processes become comparable. Consequently, a theoretical treatment of systems subjected to a temperature ramp must explicitly deal with the change of the equilibrium composition due to the temperature ramp, with nucleation and with coagulation of droplets.

A common approach in studies on liquid-liquid phase separation avoids this complication by addressing the situation after a rapid quench of the control parameter (temperature or pressure), which is subsequently carefully kept constant in order not to perturb the phase separation. They concentrate on the coarsening of the domain structure, during which the length scale L grows like a power law [1,3,4,6].

In contrast, an oscillatory evolution of L is observed when samples are taken through a temperature ramp [10–13], where the temperature is slowly varying in time but kept spatially uniform. Up to now attempts to model these oscillations addressed specific materials such as microemulsions [14,15] or liquid Ga-Pb mixtures [12]. In contrast, in the present study we discuss the arising of oscillations in the ϕ^4 model for phase separation in binary mixtures. This allows us to identify general criteria for the appearance of oscillations. The predictions are subsequently compared to recent experimental findings.

Denoting the width of the two-phase region as $2\phi_0(T)$ and its center as $\bar{\phi}(T)$, the supersaturation can be characterized by $\sigma(\mathbf{x}, t) = [\phi(\mathbf{x}, t) - \bar{\phi}]/\phi_0$. It takes the values ± 1 in equilibrium, and its modulus is smaller for a supersaturated sample. Inserting this linear transformation into (1), and observing that $\bar{\phi}(T)$ and $\phi_0(T)$ acquire a time dependence due to the time evolution of temperature, one finds a nonlinear diffusion equation for $\sigma(\mathbf{x}, t)$,

$$\frac{d\sigma(\mathbf{x}, t)}{dt} = \nabla[\tilde{D}(\sigma(\mathbf{x}, t))\nabla\sigma(\mathbf{x}, t)] - [\zeta + \xi\sigma(\mathbf{x}, t)]. \tag{2}$$

It involves the diffusion coefficient $\tilde{D}(\sigma) = D(\phi(\sigma))$. The temporal change of the equilibrium composition of the coexisting phases, enters this equation as a source of supersaturation $\zeta + \xi\sigma$, where

$$\zeta \equiv \phi_0(T)^{-1}\frac{\partial\bar{\phi}(T(t))}{\partial t}, \tag{3a}$$

$$\xi \equiv \phi_0(T)^{-1}\frac{\partial\phi_0(T(t))}{\partial t}. \tag{3b}$$

The source term $\zeta + \xi\sigma$ enforces a sustained flux of matter across the meniscus. This flux picks up an oscillatory modulation, when there are repeated waves of nucleation.

To gain insight into the origin of oscillations we explore the situation where, after a first wave of nucleation, supersaturation is diffusively collected by droplets. The droplet number density changes due to coalescence and is assumed to be spatially uniform on large scales. We take the phase with $\sigma > 0$ as a reference state, and adopt the σ dependence of the diffusion coefficient from the ϕ^4 model, $\tilde{D}(\sigma) = D_{\mathrm{eq}}(3\sigma^2 - 1)/2$.

For typical droplet distances Λ the supersaturation relaxes at a rate $D(\Sigma)/\Lambda^2$, where Σ is an estimate of the supersaturation far off the droplets. To estimate Σ we concentrate on large voids in between the droplets. The surrounding droplets efficiently collect supersaturation, and hence keep the concentration at the surface of the void close to the equilibrium value [Fig. 1(a)]. Let x be a variable, which vanishes in the center of the void and takes on the value 1 at its surface. Consequently, $\sigma(x = 1, t) \simeq 1$, while in the center $x = 0$ of the void $\sigma(x = 0, t) \equiv \Sigma(t)$ most strongly deviates from unity.

As long as σ varies slowly in time the terms on the right-hand side of Eq. (2) have to balance. When $1 - \Sigma$ is small $\tilde{D}$ hardly deviates from its equilibrium values, and $\sigma(x, t)$ takes on a close to parabolic shape. On the other hand, when Σ approaches the spinodal value $3^{-1/2}$ the diffusion coefficient $\tilde{D}(\sigma)$ vanishes, and $d\tilde{D}/d\sigma(d\sigma/dx)^2$ has to balance the source term. Since $\zeta \ll \xi$ for the systems to be considered the profile $\sigma(x)$ is then approximately linear with slope $n^{-1/3} \equiv (\xi\Lambda^2/3D_{\mathrm{eq}})^{1/2}$. The Padé approximant

$$\sigma(x, t) = \Sigma(t) + \frac{n^{-1/3}(t)[1 - \Sigma(t)]x^2}{n^{-1/3}(t) - [1 - \Sigma(t)](1 - x)} \quad (4)$$

fulfills the boundary conditions, and reflects this crossover. It reduces to $\Sigma(t) + (1 - \Sigma(t))x^2$ when supersaturation is small $1 - \Sigma(t) \ll n^{-1/3}(t)$. It reduces to $\Sigma(t) + (1 - \Sigma(t))x$ when $1 - \Sigma(t)$ approaches $n^{-1/3}(t)$. In a (close to) steady state this only happens for Σ closely above the spinodal. A sequence of profiles, which illustrates this crossover is shown in Fig. 1(b).

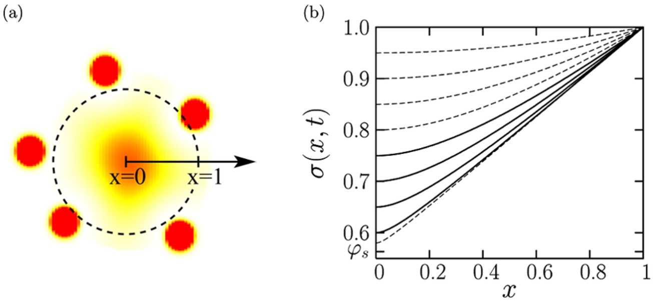

FIG. 1 (color online). Diffusion in voids between droplets. (a) Choice of coordinates. The solid circles represent droplets at the boundary of the void, and the shades of gray indicate the distribution of supersaturation $\sigma(x, t)$. (b) Profiles (4) for $\sigma(x, t)$ at a fixed $n = 12$ and different values of $\Sigma \equiv \sigma(x = 0)$. Values of Σ that are realized in the limit cycle Fig. 2(c) are shown by solid lines.

Inserting the ansatz (4) into Eq. (2) and keeping only the leading-order contribution in x yields an ordinary differential equation for the evolution of the typical supersaturation Σ far off the droplets,

$$\frac{d\Sigma}{dt} = \frac{1}{3}\frac{(3\Sigma^2 - 1)(1 - \Sigma)}{1 - (1 - \Sigma)n^{-2/3}} - (\zeta/\xi + \Sigma). \quad (5a)$$

Droplets disappear due to merging with rate γn. They are created at a rate involving a dimensionless function $\mathcal{N}(\Sigma)$ and a constant ν subsuming the system-specific time dependence of nucleation. Consequently,

$$\frac{dn}{dt} = \nu\mathcal{N}(\Sigma) - \gamma n^2. \quad (5b)$$

Because of the use of dimensionless units ν and γ pick up a dependence on ξ and D_{eq}.

Figure 2 shows the numerical solution of Eqs. (5) for the functional form of the nucleation $\mathcal{N}(\Sigma) = (1 - \Sigma^2)^2/(3\Sigma^2 - 1)^2$, which respects the symmetry between the phases in the ϕ^4 model [16]. For a noticeable range of the control parameters the model predicts the arising of stable oscillations in the form of a limit cycle [Fig. 2(a)]. Outside that range relaxation oscillation are observed which decay only slowly. Details of initial conditions cannot be followed beyond the first wave of nucleation, and the relaxation time of the subsequent exponential approach towards the asymptotic state strongly depends on the (reduced) system parameters.

Typical oscillations of the supersaturation and of the droplet density are shown in Figs. 2(b) and 2(c). The number density n increases by nucleation, and it decreases due to coagulation of droplets. The model identifies three characteristic processes [cf. Fig. 2(c)], whose interplay leads to the oscillations: (i) driving of the system by slowly ramping the temperature; (ii) rapid nucleation of droplets once Σ approaches a critical value; (iii) coarsening of the droplet distribution which is initially fast, but eventually becomes much slower than the driving.

To compare these findings with experiments we consider two vastly different mixtures: methanol in hexane (Meth/Hex) and polystyrene in cyclohexane (PS/cHex). The mixtures considerably differ in the density contrast between the two components, in the diffusion coefficients and in the viscosity of the coexisting phases. Varying these parameters allows us to tune ξ, and factors characterizing the hydrodynamic stability (cf., below). For the considered systems ζ is much smaller than $\xi\sigma$ such that it is justified to fix ξ in the experiments and set $\zeta \simeq 0$.

We monitored the phase separation for a wide range of ξ values, continuously adjusting the cooling rate according to Eq. (3b) to keep ξ constant (cf. [13] for details on the experimental technique). There are well-defined periodic

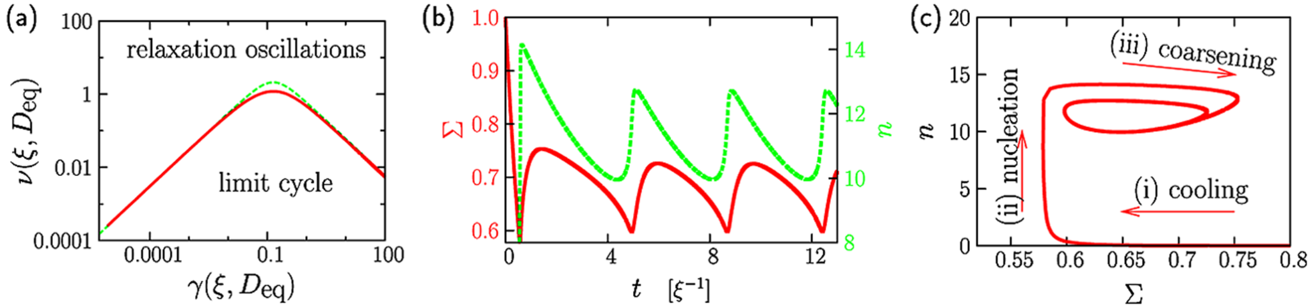

FIG. 2 (color online). Numerical solution of Eqs. (5) for $\zeta = 0$. (a) Phase diagram (solid, red) as function of γ and ν. The curve $\nu = 30\gamma/(1 + 50\gamma^2)$ (dashed, green) provides a remarkably good fit of the tails of the phase boundary. (b) Temporal evolution of the supersaturation Σ (solid, red) and droplet density n (dashed, green) for $\nu = 0.2$ and $\gamma = 0.01$ [initial condition: $\Sigma(t = 0) = 1$ and $n(t = 0) = 0$]. (c) Relaxation to the limit cycle in phase-space representation. The arrows indicate the contribution of elementary processes (i)–(iii) described in the main text.

oscillations of the turbidity in a range of $7 \times 10^{-5} \leq \xi \leq 3 \times 10^{-4}\ \mathrm{s}^{-1}$ for Meth/Hex, and $2 \times 10^{-6} \leq \xi \leq 2 \times 10^{-5}\ \mathrm{s}^{-1}$ for PS/cHex. This corresponds to cooling rates between $v_s = 5.6 \times 10^{-6}$ K/s and 1.4×10^{-2} K/s.

Cooling initially leads to complete clouding of the sample, which we let relax at constant temperature. During the subsequently temperature ramp at constant ξ, phase separation results in a large number of oscillations of the turbidity (cf. [13], and see [17] for the accompanying movie). Oscillations are observed in both phases. However, coupling of the phases and a higher viscosity tend to significantly reduce their amplitude in one of the phases.

The theory disregards spatial degrees of freedom. If this is justified, i.e., if the oscillations are not caused by oscillatory hydrodynamic instabilities, the characteristics of the oscillations must not depend on the shape and size of the sample. To corroborate this assumption, we used a "three-storied" modified hourglass configuration. The frequency of oscillations is indeed identical in all three compartments [Fig. 3(a)], and is the same as the one observed in rectangular cuvettes. Since convection strongly differs in (the compartments of) the cells, this result also rules out convection and interfacial effects as factors determining the oscillation frequency.

The theory focuses on the evolution in one of the phases (we chose $\sigma > 0$). The overall composition, which determines the relative volume of the macroscopic coexisting phases, has no impact on the oscillations. Figure 3(b) demonstrates that this is in line with the experiments for a broad range of compositions. The slight decrease in oscillation frequency is expected since all material parameters are a function of temperature.

In contrast, changes of the cooling rate can have a drastic impact on the frequency. In the theory this has its counterpart in the dependence of the frequency on the coalescence rate $\gamma(\xi, D_{eq})$ and on the nucleation rate $\nu(\xi, D_{eq})$.

Altogether, the comparison of the predictions of the model with the experiments admits a number of conclusions of general nature: (i) Oscillations are observed in a multitude of common binary mixtures. They appear in a substantial range of experimentally accessible settings. Often they are relaxation oscillations towards a process, where the compositions monotonously follows the change

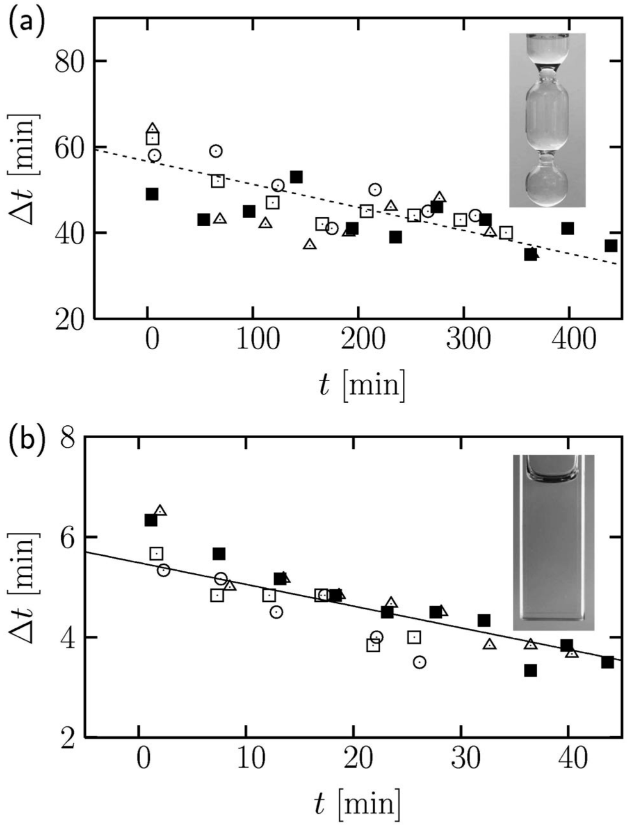

FIG. 3. Time dependence of period Δt. (a) Dependence on choice of container for PS/cHex at $\xi = 2.8 \times 10^{-6}\ \mathrm{s}^{-1}$ and $\phi_{\mathrm{PS}} = 4$ wt %. ⊙: lower, □: middle, △: upper part of a three-storied hour glass shown in the inset (waist diameter: 1 cm, height 4 cm); ■: rectangular cuvette also used in (b). (b) composition dependence (in wt %) for Meth/Hex at $\xi = 2.1 \times 10^{-4}\ \mathrm{s}^{-1}$. △: $\phi_{\mathrm{Meth}} = 0.22$; ■: $\phi_{\mathrm{Meth}} = 0.24$; ⊙: $\phi_{\mathrm{Meth}} = 0.27$; ⊡: $\phi_{\mathrm{Meth}} = 0.30$ in a rectangular cuvette (Hellma, $1 \times 1 \times 4$ cm) shown in the inset.

of temperature. In addition, the present, very basic model predicts the arising of a stable limit cycle [Fig. 2(a)]. (ii) From the perspective of the time scales discussed in the introduction, the oscillations arise due to the repeated periodic crossing of the time scale of diffusive relaxation and the one characterizing the temperature ramp [Fig. 2(c)]: Nucleation arises only when there are very few droplets, such that diffusion cannot keep pace with temperature ramping, and supersaturation grows large. Diffusive relaxation and coarsening are most efficient when there is a high density of (tiny) droplets immediately after a wave of nucleation. In this situation the supersaturation is small. (iii) Convection induced by concentration effects is typically so vigorous that its main role is an efficient stirring inside the macroscopic coexisting phases. As a result the periodicity of oscillations in a bulk system barely depends on the shape of the container (Fig. 3).

Taking into account the speeding up of coarsening due to hydrodynamic flow and sedimentation in a gravitational field leads to a faster crossover of the rates of diffusive relaxation and the temperature ramp. We expect that these effects enhance the chance to find oscillatory demixing and stable limit cycles. It will be interesting to see whether an extension of the minimal model, which explicitly includes sedimentation and flow, can provide a quantitative description of the dynamics.

Another worthwhile extension is to study the phase separation of a binary mixture flowing through a pipe with a fixed in time spatial temperature gradient chosen such that initially the fluid is in a single-phase region while it is in the phase-separated regime at the other end of the pipe. Based on the formal similarity of the equations to those suggested to describe Liesegang patterns [18] one might expect in that case the repeated arising of precipitation waves.

Our main finding is that slowly driving binary mixtures into the metastable region leads to long-lasting oscillations for a vast range of mixtures of academic and practical interest. The suggested mechanism is generic: It arises from thermodynamics and is not of hydrodynamic nature.

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[8] The Cahn-Hilliard model typically adopted at this point involves the additional term $D_{\mathrm{eq}}\lambda^2\nabla^4\phi(\mathbf{x},t)$, where D_{eq} and λ are the diffusion coefficient and the correlation length, respectively. Rather than dealing with this term, we request that $\phi(\mathbf{x},t)$ takes on its equilibrium value $\phi_{\mathrm{eq}}(T)$ at each position on an interface between coexisting phases. This simplification of the structure of the diffusion equation is admissible when one considers droplets large in comparison to the correlation length λ.

[9] When induced by a temperature ramp, phase separation has to be followed in each of the coexisting phases. Hence, $\Delta\phi_{\mathrm{eq}}/\Delta T$ refers to some average slope of the phase boundary far off the critical point. The composition of these phases is very asymmetric. Consequently, there will always be droplet nucleation rather than phase separation into bicontinuous domains.

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[16] The idea behind this choice is that $\mathcal{N}(\Sigma)$ is arguably the simplest symmetric function of Σ that vanishes for $\Sigma = \pm 1$ and diverges at the spinodal value $\Sigma = 1/\sqrt{3}$.

[17] See EPAPS Document No. E-PRLTAO-98-001713 for the accompanying movie. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

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