Modelling phase separation under slow cooling

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Abstract

We propose a new approach to phase separation under slow cooling: we show that binary mixtures subjected to a temperature ramp behave as reactive flows. Exploiting the similarity, we describe the demixing dynamics by an advection–reaction–diffusion model completed with nucleation and coaguation of droplets. This model can contribute to an understanding of the phenomenon beyond the level of mean field theories adopted so far.

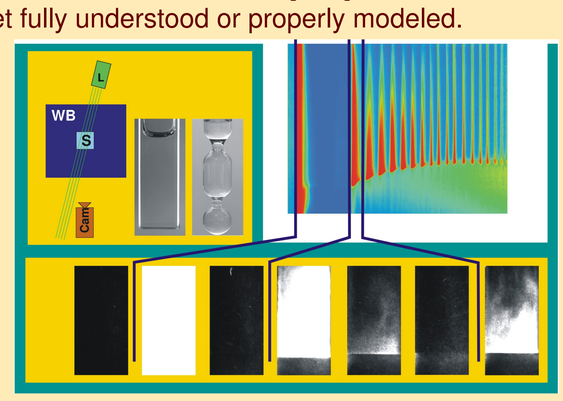
Introduction

Classical approaches to liquid-liquid phase separation considered a rapid quench of the temperature after which the phase separation was left to evolve in constant temperature. Phase separation under slow cooling is different from this approach in the sense that under slow cooling, the phase separation evolves together with the temperature. The normalized composition $\sigma(x,t)$ of the mixture evolves according to the nonlinear diffusion equation [2]:

$$\partial_t \sigma(x,t) = \Gamma(\sigma) - \xi\sigma(x,t) + \nabla[D(\sigma)\nabla\sigma(x,t)]. \qquad (1)$$

where $\Gamma(\sigma)$ describes the nucleation process that resets σ to equilibrium, i.e. to $\sigma_0 \equiv 1$.

Such systems were studied mainly experimentally. The most intriguing observation was that phase separation did not continuously follow the continuous ramp of the temperature. Rather there were oscillating bursts of massive nucleation of droplets, alternating with quiescent periods [1, 2]. Though some theoretical works [2, 3] tried to describe these oscillations, the phenomenon is not yet fully understood or properly modeled.



Oscillations observed in a demixing experiment of a sample of methanol and hexane

Eq. 1 is similar to that of an exponentially decaying passive scalar [5] $c(x,t)$:

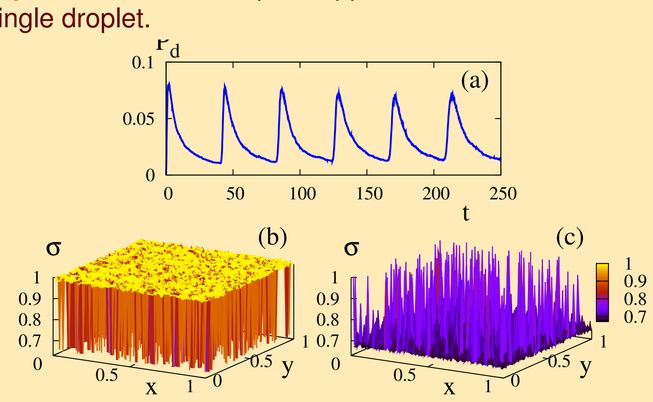
$$\partial_t c(x,t) = S(x) - \beta c(x,t) + D_0\nabla^2 c(x,t), \qquad (2)$$

where β is the decay rate, and $S(x)$ is a source term. The similarity of the equations suggests a treatment of phase separation as an advection – reacton – diffusion system.

The model

We propose a time discrete lattice model of advection – reaction – diffusion as in [4], completed with nucleation and coagulation of droplets:

- **Advection:** we use an alternating shear flow as in [4], a time periodic flow defined in the unit square with periodic boundary conditions that produces chaotic trajectories.
- **Reaction:** describes the exponential decay with rate ξ of the normalized composition $\sigma(x,y)$ in response to the external cooling, i.e. $\sigma_{t+\tau} = (1-\xi\tau)\,\sigma_t$.
- **Diffusion:** as in [4].
- **Nucleation:** In lattice cells where σ is small, droplets are generated with probability $a(\sigma) = 2 - 3\sigma$, if $1/3 \le \sigma < 2/3$. No nucleation occurs close to the equilibrium composition $\sigma_0 \equiv 1$, while nucleation is instantaneous in the spinodal region $\sigma \le 1/3$.
- **Merging of droplets:** When two droplets approach each other to within a distance r_0, they merge into a single droplet.



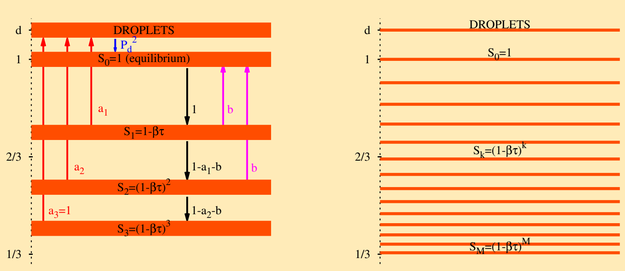
Oscillations of the droplet density observed in the lattice model

Equations

Starting with a uniform spatial distribution of the composition field $\sigma_0 = 1$, and neglecting diffusion, the only possible values of the composition at later times are of form:

$$\sigma_k(x,y) = (1-\xi\tau)^k, \quad k = 0,1,...,M,$$

where $M = \ln(1/3)/\ln(1-\xi\tau)$. Thus, the lattice cells are distributed on M different levels according to their composition (supersaturation). Let us focus on the probabilities $P_k(t)$, $k = 0,1,\ldots,M$ to find lattice cells with composition σ_k at time t, i.e., the population of levels σ_k at time t. The fraction of the cells containing droplets is denoted by P_d.



Supersaturation levels, transitions and transition rates for $\xi\tau = 0.25$ and $\xi\tau = 0.08$.

The following processes can change the state of a cell:

- **black arrows:** the composition in the cell decays from state σ_k to σ_{k+1},
- **red arrows:** a droplet is generated in the cell, i.e. its state is changed from σ_k to d,
- **purple arrows:** resetting the composition from σ_k to the equilibrium value $\sigma_0 = 1$ when a droplet is nucleated in the cell's neighborhood ,
- **blue arrow:** the space left empty after the merging of two droplets will have $\sigma_0 = 1$.

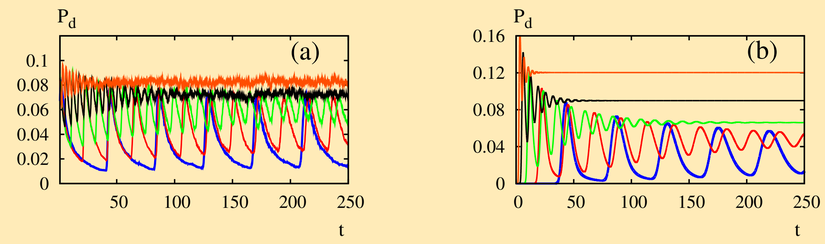
Thus, the dynamics can be described by the system

$$\begin{aligned} \partial_t P_0 &= -P_0 + b\,(P_1 + \ldots + P_{M-1}) + g\,P_d^2. \\ \partial_t P_k &= (1 - a_{k-1} - b)\,P_{k-1} - P_k \\ \partial_t P_d &= b - g\,P_d^2, \end{aligned} \qquad (3)$$

where $b = b(t) = \sum_{n=1}^{M} a_n P_n(t)$ is the fraction of new droplets generated at time t.

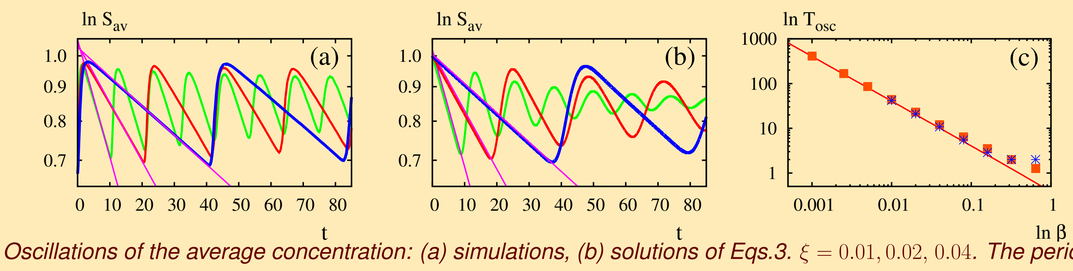
Solutions

- **Time evolution of the droplet density:** In agreement with the experimental findings, the droplet density shows repeated oscillations that disappear rapidly for high cooling rates, but persist for long times under slow cooling.



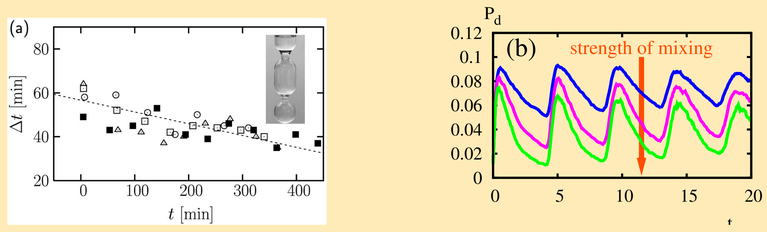
Oscillations of the droplet density: (a) numerical simulations, (b) solutions of Eqs.3.

- **The period of the oscillations:** The average composition σ_{av} shows similar oscillations that consist of a slowly decaying part and a fast jump to the equilibrium value, the latter representing the massive nucleation that takes place in the system. The period of the oscillations seems to be uniquely determined by the cooling rate.



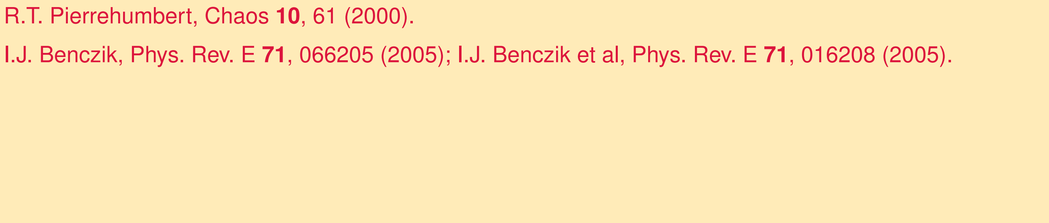
Oscillations of the average concentration: (a) simulations, (b) solutions of Eqs.3. $\xi = 0.01, 0.02, 0.04$. The period of the oscillations (c) shows a $1/\ln(1-\xi\tau)$ dependence on ξ. Stars: simulations, squares: solutions of Eqs.3.

- **Effects of the flow:** Experiments performed in cuvettes of different shape (i.e. producing different types of convection) have shown identical frequencies of oscillations [2]. Our simulations confirm that, indeed, the frequency is independent of the strength of stirring. This rules out oscillatory hydrodynamical instabilities as the origin of the oscillations. The amplitude of the oscillations, however, shows strong sensitivity on the flow rate.



Experimental (a), and numerical (b) studies of different types of convection.

- **Steady states of the system:** The solutions of Eqs.3 – after performing several oscillations – converge to a fixed point which can be obtained with an implicit analytical formula. In numerical simulations, this convergence is much slower. For very slow cooling rates it is yet unclear whether the system approaches a fix point or a limit cycle.



Trajectories in the phase space: (a) simulations, (b) solutions of Eqs.3, and (c) steady states of the system.

Conclusions

- We proposed a simple lattice model for the description of phase separating binary fluids.
- The model was checked to reproduce experimental findings, i.e few oscillations of turbidity for fast cooling, persisting oscillations for slow cooling, or identical frequencies of oscillations for different types of convection.
- The model can predict or explain theoretically some features of the phase separation, such as the steady states of the system, and the β dependence of the oscillation frequencies.
- Beyond the particular results mentioned above, our model can serve as a baseline model for further studies. For instance, gravitational effects, inertial effects, or size distributions of the droplets become numerically accessible within the framework of this lattice model.

References

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