Wavelength Selection in Slowly Quenched Systems

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In systems rapidly quenched into the unstable regime, the wavelength of the fastest growing unstable mode depends on the quench depth. In systems which are gradually driven unstable, there is no quench depth, hence a different mechanism must be responsible for the wavelength selection. We propose a selection mechanism in this case, obtain scaling relations, and discuss the criterion to determine whether a quench is rapid or slow.

Keywords: Slowly quenched systems; polymerization induced phase separation

I. INTRODUCTION

Spatio-temporal patterns frequently arise in systems which are driven out of equilibrium. Examples are phase separation, dendritic growth, interfacial instabilities, etc. The spatial length scale of the emerging patterns is determined at early times by the wavelength of the fastest growing unstable mode. In rapidly quenched systems, the quench depth determines this length scale. Typically, the wavelength of the emerging mode is a 'bare' length in the system, divided by the dimensionless quench depth raised to some power. In many physical situations, systems are naturally 'slowly quenched'; that is, they are slowly driven out of equilibrium. Since in this case there is no quench depth, the selection mechanism must be fundamentally different from that in rapidly quenched systems. We examine the selection mechanism in this case by considering a slowly cooled binary mixture as an example. We argue that this type of selection is ubiquitous, and plays

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a key role in polymerization induced phase separation in polymer-liquid crystal systems. We discuss the crossover in the selection mechanism from the rapidly quenched to the slowly quenched behavior.

II. SLOWLY COOLED BINARY MIXTURE

We consider a simple binary fluid mixture, with free energy

$$F = \int \{ F(\phi) + \frac{1}{2} \kappa \, (\nabla \phi)^2 \} \, d^3 r \tag{1}$$

where

$$F(\phi)v = \frac{1}{2} A \, \phi \, (1 - \phi) + kT \phi \ln \phi + kT(1 - \phi) \ln (1 - \phi) \tag{2}$$

and $\phi(r)$ is the volume fraction and v is a molecular volume. Away from equilibrium, the diffusion current is driven by the gradient of the chemical potential. The volume current is

$$J \sim \nabla \left\{ \frac{\partial F}{\partial \phi} - \kappa \nabla^2 \phi \right\} \tag{3}$$

and the equation of continuity gives

$$\frac{\partial \phi}{\partial t} = \nabla \cdot M \nabla \left\{ \frac{\partial F}{\partial \phi} - \kappa \nabla^2 \phi \right\} \tag{4}$$

as in the usual Kahn-Hilliard theory [1]. If ϕ has the form $\phi = \phi_o e^{iq \cdot r + \Gamma t}$, where Γ is the growth rate of the mode with wavevector q, gives

$$\Gamma = M \left\{ -\frac{\partial^2 F}{\partial \phi^2} q^2 - \kappa q^4 \right\} \tag{5}$$

The wavenumber of the fastest growing mode which maximizes Γ is $q_{max} = (-\frac{1}{2\kappa} \frac{\partial^2 F}{\partial \phi^2})^{1/2}$. From Eq. 2, $-\frac{\partial^2 F}{\partial \phi^2} = A(1 - \frac{T}{T_c})$, where $T_c = Av\phi_o(1 - \phi_o)/k$.

Since $A/2\kappa \approx l_o^{-2}$, where l_o is a molecular length, we find that in a rapidly quenched system, where the dimensionless quench depth $(1 - \frac{T}{T_c})$ is a constant,

$$q_{max}^{-1} \simeq \frac{l_o}{\left(1 - \frac{T}{T_c}\right)^{1/2}} \qquad (6)$$

and the corresponding growth rate

$$\Gamma_{max} = M \kappa q_{max}^4. \qquad (7)$$

Thus in a rapidly quenched system, the wavelength of the fastest growing mode and its growth rate are determined by the quench depth.

We now consider a slowly cooled system, where T decreases slowly in time. Here

$$-\frac{\partial^2 F}{\partial \phi^2} = A\left(1 - \frac{T}{T_c}\right) = A\alpha t \qquad (8)$$

where α is the cooling rate. The fastest growing mode at time t is given by

$$q_{max} l_o = (\alpha t)^{1/2} \qquad (9)$$

$$\Gamma_{max} = M \kappa q_{max}^4 = \frac{M\kappa}{l_o^4} \alpha^2 t^2 \qquad (10)$$

When the system first goes unstable, at $t = 0$, the fastest growing mode has infinite wavelength and zero growth rate. As t increases, the wavelength decreases, and the growth rate increases. We conjecture that the first observable instability, emerging at the onset time t_{on}, will be one for which $\Gamma_{max} t_{on} \approx 1$. Then, from , the onset time is

$$t_{on} = \left(\frac{l_o^4}{M\kappa}\right)^{1/3} \alpha^{-2/3} \qquad (11)$$

and from Eq. 9, the wavenumber of the emerging instability at onset, is

$$q_{on} = \left(\frac{1}{M \kappa l_o^2}\right)^{1/6} \alpha^{1/6} \tag{12}$$

Eqs. 11 and 12 are our key results. As expected, both the onset time t_{on} and the wavelength of the emerging pattern q_{on}^{-1} increase as the quench rate α decreases. It is interesting to note that the mobility M appers in the expressions for t_{on} and q_{on}; unlike in the rapid quench case, the selection mechanism here involves the transport coefficients. Eliminating α, we obtain the scaling relation [2], $q_{on} = (M \kappa)^{-1/4} t_{on}^{-1/4}$, or

$$q_{on} \sim t_{on}^{-1/4} \tag{13}$$

III. DISCUSSION

Although the above expressions for the onset time of the instability and the emerging wavelength have been obtained for a slowly cooled binary mixture, we expect the results to hold in general for systems where the quench rate is nearly constant in the interval $0 < t < t_{on}$. Such behaviour might be observed in Hele-Shaw experiments, where the liquid-air interface becomes unstable as the air bubble expands [3], laser induced instabilities in nematics, where the instability occurs as a consequence of the optical Freedericksz transition [4], buckling instabilities in smectic filaments which become unstable as they elongate [5], and perhaps most importantly, in polymerization induced phase separation [6]. Here the instability arises gradually as a result of polymerization. The quench rate α is the rate of polymerization; in condensation reactions occuring in epoxy systems α is the reaction rate, while in UV cured polymers α is proportional to the UV intensity. The scaling behavior proposed above may be studied therefore in both polymer dispersed and polymer stabilized liquid crystal systems, and could provide valuable insight into the physical mechanisms responsible for the emerging complex structures.

In real physical systems, instantaneous quenches are not possible. A good approximation is a rapid quench with large α for some quench time t_q, and no quench thereafter. In such a case, we expect the wavelength selection mechanism for a rapidly quenched system to dominate if $t_{on} > t_q$, and for a

slowly quenched one if $t_{on} < t_q$. The crossover occurs when the quench time $t_q = (\frac{l_0^4}{M\kappa})^{1/3} \alpha^{-2/3}$.

Acknowledgements

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