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Domain Growth of First-Order Phase Transitions: An Exactly Solvable Model

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We consider a simple exactly solvable model of an order–disorder transition: noninteracting interfaces moving with constant speed in one dimension. We obtain a linear increase with time of the average domain size and a weak oscillatory behavior of the scattering structure function.

KEY WORDS: Metastability; domain growth; structure function.

1. INTRODUCTION

Since the pioneering work of Lifshitz and Slyozov,[1] the dynamics of the transitional processes governing phase separation has been investigated theoretically[2] and by using computer simulation.[3] The order–disorder phase transition of systems quenched into the two phase regions has also been investigated by means of several experimental techniques especially in binary alloys[4] and critical fluid mixtures.[5–7] One of the most challenging problems is how the growth rate and the distribution function of the sizes of the ordered domains change with time.[8] Many theoretical investigations are concerned with a decay from thermodynamically unstable states, where the equilibrium state can be obtained by successive transitions through a continuous series of intermediate states without any need of nucleation centers.[4] On the contrary, for initial metastable states the ordering is initially due to the production and finally to the growth of nuclei of the new phase.

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[4] See Ref. 9, which contains an extensive review of both the theoretical and experimental aspects of phase separation dynamics.

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In this paper the growth rate of the ordered domains, for initially metastable states, will be investigated using a simplified model similar to the one recently proposed by Sekimoto[10] but which can be solved exactly.

2. THE MODEL

We consider a one-dimensional system with two possible equilibrium phases. At time $t=0$ there are N nucleation centers $x_1^0, x_2^0, \ldots, x_N^0$ randomly distributed between the two phases. To be definite we assume the following Poissonian probability distribution function for the nucleation centers

$$P_N^0(x_1^0, x_2^0, \ldots, x_N^0) = \frac{1}{V_N} W_N \tag{1}$$

V_N represents the volume in the restricted configurational space given by $0 = x_1^0 < x_2^0 < \cdots < x_N^0 = L$ with periodic boundary conditions $x_{N+1}^0 = x_1^0$ and L is the system size:

$$V_N = \int dx_1^0 \int dx_2^0 \cdots \int_{(x_1^0 < x_2^0 < \cdots < x_N^0)} dx_N^0 = \frac{L^N}{N!} \tag{2}$$

Furthermore,

$$W_N = \frac{1}{N!} (Ln_0)^N e^{-Ln_0} \tag{3}$$

where

$$n_0 = \frac{N}{L} \tag{4}$$

is the average number of nucleation centers. The critical size of nucleation centers is assumed to be zero. We thus neglect the early stage of the formation of these nuclei.[5] As time goes on the size of each nucleation center grows with constant velocity.

The physical picture corresponding to the model corresponds to considering a system in the disordered phase with the Landau free energy having three minima at a given temperature: one central stable minimum and two symmetric metastable ones.

Then by a rapid quench, we allow the system to reach the ordered phase where the two metastable minima become stable and the previous stable one

[5] The choice of zero critical size is only a matter of convenience. The following considerations will not be modified by critical size different from zero.

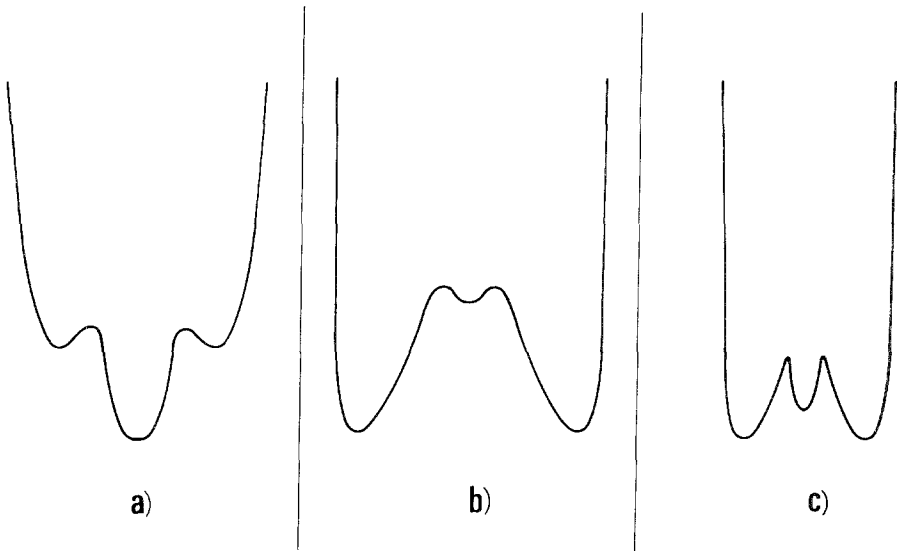

Fig. 1. The free energy of the system. (a) Disordered phase. (b) System quenched into the order phase. (c) Initial configuration for the present model.

becomes metastable. In this situation there will be the possibility of having nucleation centers of both phases characterized by the two stable minima. Then the temperature is suddenly changed so that the activation energy of the metastable state becomes much greater than the thermal energy, as it is shown in Fig. 1. However, the energy difference between stable and metastable minima provides a driving force for maintaining finite speed of domain wall motions.

The initial configuration of the system at $t=0$ will be a given distribution of domains of zero size (i.e., nucleation centers) whose spatial extension grows in time.

In order to simplify the model, we assume noninteracting interfaces in a one-dimensional system. Thus, the profile of each interface can be approximated by a step function moving in the forward or backward direction with constant velocity v. Owing to the possibility of having two stable minima in the free energy, there will be two types of domains. Let us call then "up" and "down." At a generic time t the one-dimensional ring of length L will be decomposed in switched up, switched down, and unswitched domains. When two interfaces belonging to switched domains collide there will be the possibility of forming a "stationary" wall or a "virtual" wall. The former for collision between interfaces belonging to opposite switched domains, and the latter for the equally switched ones. Since we neglect domain interaction, the

growth will stop once the ring will be completely decomposed in up or down domains separated by stationary walls.

In order to identify the domains we assign a topological charge ε_j to them, where $\varepsilon_j = -1, 0, 1$ for the switched up, unswitched, and switched down jth domains, respectively. Let us call $x_j(t)$ ($\bar{x}_j(t)$) the position at time t of the forward (backward) moving interface belonging to the jth switched domain. We immediately write down their evolution equations

$$x_j(t) = \begin{cases} x_j^0 + vt, & t < t_j \\ \frac{1}{2}(x_j^0 + x_{j+1}^0), & t \geqslant t_j \end{cases} \tag{5}$$

$$\bar{x}_j(t) = \begin{cases} x_j^0 - vt, & t < t_{j-1} \\ \frac{1}{2}(x_{j-1}^0 + x_j^0), & t \geqslant t_{j-1} \end{cases} \tag{6}$$

where

$$t_j = \frac{x_{j+1}^0 - x_j^0}{2v} \tag{7}$$

and $x_j(0) = \bar{x}_j(0) = x_j^0$ represents the initial position of the jth nucleation center (switched domain of zero size). One may also note that $x_j(t_j) = \bar{x}_{j+1}(t_j) = \frac{1}{2}(x_j^0 + x_{j+1}^0)$.

3. THE STRUCTURE FUNCTION

A physical quantity of experimental and theoretical importance is the spatial correlation function of the order parameter defined by

$$S(x, x', t) = \langle u(x, t)\, u(x', t) \rangle \tag{8}$$

Its Fourier transform defines the structure function $S(k, t)$ which is directly proportional to the scattered intensity in any scattering experiment; thus, as a consequence of the invariance by translation, we obtain

$$k^2 S(k, t) = \frac{1}{L} \iint dx\, dx' \left\langle \frac{\partial u(x, t)}{\partial x} \frac{\partial u(x', t)}{\partial x'} \right\rangle e^{ik(x - x')} \tag{9}$$

In the above expressions $u(x, t)$ represents the order parameter profile and the expectation value is taken with respect to the initial probability distribution function of the N nucleation centers (1).

Since

$$\frac{\partial u(x, t)}{\partial x} = \sum_1^N{}_j \varepsilon_j [\delta(x - x_j(t)) - \delta(x - \bar{x}_j(t))] \tag{10}$$

using (8) and (9) we find

$$S(k,t)=\frac{1}{k^2L}\left\langle\left|\sum_j^N \varepsilon_j(e^{ikx_j(t)}-e^{ik\bar{x}_j(t)})\right|^2\right\rangle \tag{11}$$

Thus, because of our choice of the initial random ε_j sign distribution and as a consequence of the spatial homogeneity on the average, we can reduce (11) by using

$$\varepsilon_j\varepsilon_l\to\delta_{jl} \tag{12}$$

obtaining

$$\begin{aligned}S(k,t)&=\frac{1}{k^2L}\left\langle\sum_j|e^{ikx_j(t)}-e^{ik\bar{x}_j(t)}|^2\right\rangle\\&=\frac{2}{k^2L}\left\langle\sum_j[1-\cos k(x_j(t)-\bar{x}_j(t))]\right\rangle\end{aligned} \tag{13}$$

Equation (13) is easily evaluated using (5), (6), and (1). As a consequence of the spatial homogeneity on the average, equation (13) can be rewritten as

$$S(k,t)=\frac{2n_0}{k^2}\{1-\langle\cos k(x_j(t)-\bar{x}_j(t))\rangle\} \tag{14}$$

(independent of j). We define the unswitched domain size at $t=0$ by

$$y_j^0=x_{j+1}^0-x_j^0 \tag{15}$$

thus from (5), (6), and (7) we find

(a) for $y_j\geqslant y_{j-1}$

$$x_j(t)-\bar{x}_j(t)=\begin{cases}2vt, & t<t_{j-1}\\ vt+\frac{1}{2}y_{j-1}, & t_{j-1}<t<t_j\\ \frac{1}{2}(y_{j-1}+y_j), & t\geqslant t_j\end{cases} \tag{16a}$$

(b) for $y_j\leqslant y_{j-1}$

$$x_j(t)-\bar{x}_j(t)=\begin{cases}2vt, & t<t_j\\ vt+\frac{1}{2}y_j, & t_j<t<t_{j-1}\\ \frac{1}{2}(y_{j-1}+y_j), & t\geqslant t_{j-1}\end{cases} \tag{16b}$$

As we can see (16a, b) involve only two variables, y_{j-1} and y_j; thus in order to calculate (14), we only need the joint probability distribution

function $P_2^0(y_{j-1}, y_j)$ for two consecutive unswitched domains at time $t=0$. In the thermodynamic limit we introduce the following function:

$$\mathscr{F}(k, t) = \langle \cos k(x_j(t) - \bar{x}_j(t)) \rangle = \int_0^\infty dy \int_0^\infty dy' P_2^0(y, y') \cos[kX(y, y', t)] \tag{17}$$

where

$$X(y_{j-1}, y_j, t) = x_j(t) - \bar{x}_j(t) \tag{18}$$

represents the size of the jth switched domain in terms of y_{j-1} and y_j. Our assumption for the Poisson distribution (1) implies

$$P_2^0(y, y') = P_1^0(y) P_1^0(y') \tag{19}$$

where

$$P_1^0(y) = n_0 e^{-n_0 y} \tag{20}$$

Thus

$$\mathscr{F}(x, t) = 2 \int_0^\infty dy \int_y^\infty dy' P_1^0(y) P_1^0(y') \cos[kX(y, y', t)] \tag{21}$$

can be evaluated using (16a, b). After lengthy but straightforward algebra we obtain

$$\begin{aligned} \mathscr{F}(k, t) = {} & \frac{1-q^2}{(1+q^2)^2} + \frac{2q^2 e^{-\tau}}{(1+q^2)^2} \left\{ 2 \cos \tau q + \frac{1-q^2}{q} \sin \tau q \right\} \\ & + \frac{q^2 e^{-2\tau}}{(1+q^2)^2} \{ 2q \sin 2\tau q - (1-q^2) \cos 2\tau q \} \end{aligned} \tag{22}$$

with the dimensionless quantities

$$q = \frac{k}{2n_0}, \qquad \tau = 2n_0 vt \tag{23}$$

Finally (13) becomes

$$\begin{aligned} S(k, t) = {} & \frac{2n_0}{k^2} [1 - \mathscr{F}(k, t)] \\ = {} & \frac{1}{2n_0(1+q^2)^2} \left\{ 3 + q^2 - 2e^{-\tau} \left(2 \cos \tau q + \frac{1-q^2}{q} \sin \tau q \right) \right. \\ & \left. - e^{-2\tau} [2q \sin 2\tau q - (1-q^2) \cos 2\tau q] \right\} \end{aligned} \tag{24}$$

We immediately verify

$$S(k, 0) = 0 \tag{25}$$

$$S(k, \infty) = \frac{1}{2n_0} \frac{3 + q^2}{(1 + q^2)^2} \tag{26}$$

4. THE AVERAGE DOMAIN SIZE

Given the order parameter correlation function $S(x, x', t)$ the average square domain size can be defined as

$$z^2(t) = \frac{\int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dx' (x - x')^2 S(x, x', t)}{\int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dx' S(x, x', t)} \tag{27}$$

Because of the space translational invariance we can rewrite (27) by

$$z^2(t) = \frac{-(\partial^2/\partial k^2) S(k, t)}{S(k, t)} \bigg|_{k=0} \tag{28}$$

with $S(k, t)$ given by (24). It is more useful to introduce the dimensionless average domain size defined by

$$l(t) = \left[\frac{z^2(t)}{z^2(\infty)} \right]^{1/2} \tag{29}$$

which is a universal quantity. By using (28) and (24) we easily obtain

$$l(t) = \left\{ \frac{3}{5} \left[2 - \frac{S_2(\tau)}{S_0(\tau)} \right] \right\}^{1/2} \tag{30}$$

Where

$$S_0(\tau) = 3 - 2e^{-\tau}(2 + \tau) + e^{-2\tau} \tag{31}$$

$$S_2(\tau) = 1 + \tau e^{-\tau}(2 + 2\tau + \tfrac{1}{3}\tau^2) - e^{-2\tau}(1 + 4\tau + 2\tau^2) \tag{32}$$

In Fig. 2 is shown the log–log plot of the universal quantity $l(t)$ given by Eq. (30) as function of the dimensionless "time" $\tau = 2n_0 vt$. From this figure we see that the average domain size grows to reach the steady state value with a power law linear in τ. Since we are neglecting the interaction among stationary walls (i.e., kinks and antikinks) we should expect that for the latter times the domain growth quickly stops. Actually, however, weak attractive interactions among nearest-neighbor kinks and antikinks lead to very slow domain growth afterwards, as shown in Ref. 11.

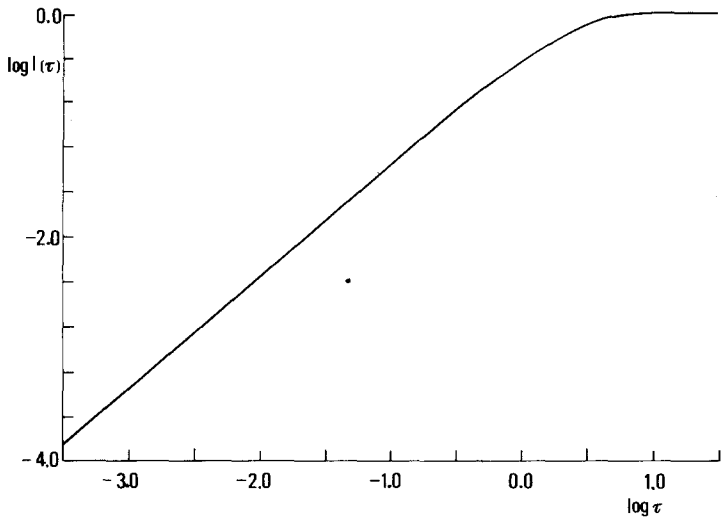

Fig. 2. The log–log plot of the dimensionless average domain size $l(\tau)$ clearly shows that it grows linearly in $\tau = 2n_0 vt$.

5. DISCUSSION

Here we have considered a simple one-dimensional model of domain growth which can be solved exactly. A possibly interesting feature is the oscillatory behavior of $S(k, t)$ arising from the appearance of a finite number of domains with the same size at the early times. A numerical study indicates, however, that such an oscillation occurs only in τ at large q values [$S(k, t)$ increases once and then decreases again at large q]. Such an oscillation has also been seen in spinodal decomposition[4] but presumably for different reasons. We believe that this exactly solvable model is useful as a first step toward the understanding of the notoriously difficult problem of the kinetics of first order phase transitions.

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