

Aggregation Kinetics for a One-Dimensional Zero-Degree Kelvin Model of Spinodal Decomposition

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We study analytically the approach to equilibrium in a simple zero-temperature model for phase separation in a binary alloy, in which nearest neighbor interchange can occur only if the portion of AB bonds is thereby decreased. The approach to equilibrium is found analytically. Because of the existence of infinitely many possible stationary states, the asymptotic distribution of AB pairs depends on the details of the initial state and must be obtained by a recursion method.

KEY WORDS: Phase separation; aggregation; nonergodic processes.

1. INTRODUCTION

In this paper we study the time-dependent kinetics of a one-dimensional model for spinodal decomposition at $0\text{ K}^{(1-4)}$ on a lattice whose atoms exchange in nearest neighbor pairs independently, with an exponential waiting time distribution. The asymptotic long-time behavior of such models was studied by a numerical Monte Carlo method by Reich and co-workers^(1,2) mainly for cubic lattices in $d=1-5$, and by Palmer and Frisch⁽³⁾ analytically in $d=1$ and numerically for an infinite-dimensional limit of this model. The model is formulated as a computer game whose evolution to its final stationary state is strongly dependent on its initial state; its dynamics is described by the following Monte Carlo procedures:

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1. Generate a sequence of atoms of species A and B (on a ring of length N or on the infinite line).
2. Select a nearest neighbor pair of atoms at random and exchange them if the exchange results in enrichment of "good" (AA or BB) nearest neighbor pairs.
3. Repeat step 2 until no pair allows for possible enrichment.

This model may be considered to mimic spinodal decomposition in $d \leq 3$ and to correspond to a special case of a kinetic aggregation process ("coagulation") in $d = 1$. In Ref. 4, the approach to equilibrium was studied numerically and compared to a mean-field theory, in dimension $d = 2$ and on a fractal lattice.

In Section 2, we describe the evolution of this one-dimensional game to its stationary state; we briefly comment on some generalizations in our concluding remarks (Section 3).

2. EVOLUTION AND THE STATIONARY STATE

Let us denote by X_n a sequence of n atoms of the same species (n A's or n B's), and by Y_n a sequence of n atoms of alternating species. Any sequence of A's and B's is then uniquely (up to substituting all A's and B's) described by a sequence of the form $(X_{n_i} Y_{m_i})$, $i \in \mathbb{Z}$, with $n_i \geq 2$ and $m_i \geq 0$ to avoid ambiguities. For instance,

$$\dots \text{AABABBBAAA} \dots = \dots X_2 Y_2 X_3 Y_0 X_3 \dots$$

The fundamental observation is that no atom in a sequence X_n can be exchanged with its neighbor: X_m thus acts as a barrier to the migration of atoms, and the only evolution occurs inside sequences Y_n . Moreover:

1. Y_0 is only a notation for the separation between two "pure phases" ($X_m Y_0 X_q = X_m X_q$).
2. $X_m Y_1 X_q$ cannot evolve further.
3. $X_m Y_2 X_q$ can only produce $X_{m+1} Y_0 X_{q+1}$.
4. $X_m Y_n X_q$ can evolve in $n - 1$ equally likely ways:

$$X_m Y_n X_q \rightarrow \begin{cases} X_{m+1} Y_0 X_2 Y_{n-3} X_q \\ X_m Y_p X_2 Y_0 X_2 Y_{n-4-p} X_q \\ X_m Y_{n-3} X_2 Y_0 X_{q+1} \end{cases} \quad (0 \leq p \leq n-4) \quad (1)$$

The stationary state is thus a sequence of X_n 's, Y_0 's, and Y_1 's; Y_m ultimately generates only Y_0 's, Y_1 's, and X_2 's and may add one atom to its left and right neighboring X -sequences.

The degree of phase separation in our model may be measured by the fraction $\rho(t)$ of “bad” bonds (A–B). Let us denote by $x_n(t)$ [resp. $y_n(t)$] the number of bad bonds at time t associated to a sequence of atoms initially in the state X_n (resp. Y_n); to be definite, we consider that a bond between two distinct sequences (X – Y) belongs to the Y -sequence:

$$\begin{aligned} y_n(t) &\leq y_n(0) = n + 1 \\ x_n(t) &= x_n(0) = 0 \end{aligned} \tag{2}$$

The total fraction of bad bonds in a chain of N atoms is then

$$\rho(t) = \frac{1}{N-1} \sum_{n=0}^{\infty} y_n(t) f_n(0) \tag{3}$$

where $f_n(0)$ is the initial number of sequences of type Y_n .

The actual expression for $y_n(t)$ depends on the dynamics of the atom exchange process. For a large ring of atoms (and for the infinite line), the continuous-time version amounts to letting each bond wait a time Δt before choosing it to try performing the exchange; the time Δt has an exponential distribution with expectation τ (which we set to unity for simplicity). This implies the following relation between the average values $\bar{y}_n(t)$ of $y_n(t)$:

$$\begin{aligned} \bar{y}_n(t) &= y_n(0) e^{-(n-1)t} \\ &+ \int_0^t e^{-(n-1)\theta} \frac{1}{n-1} \sum_{p=-1}^{n-3} [\bar{y}_p(t-\theta) + 1 + \bar{y}_{n-p-4}(t-\theta)](n-1) d\theta \\ &= 1 + ne^{-(n-1)t} + \int_0^t 2 \sum_{p=-1}^{n-3} \bar{y}_p(t-\theta) e^{-(n-1)\theta} d\theta \end{aligned} \tag{4}$$

where we introduce the notation $\bar{y}_{-1}(t) = y_{-1}(t) = 0$, corresponding to the addition of an atom to a sequence X_n . The Laplace transform of $\bar{y}_n(t)$ is the sum $\hat{y}_n(k) = \sum_{k=0}^{n-1} \hat{y}_n(k) e^{-kt}$; the coefficients satisfy

$$\begin{aligned} \hat{y}_n(n-1) &= n + 1 - \sum_{k=0}^{n-2} \hat{y}_n(k) \\ \hat{y}_n(n-2) &= \hat{y}_n(n-3) = 0 \\ \hat{y}_n(k) &= \frac{2}{n-k-1} \sum_{p=0}^{n-3} \hat{y}_p(k) \\ \hat{y}_n(0) &= 1 + \frac{2}{n-1} \sum_{p=0}^{n-3} \hat{y}_p(0) \end{aligned} \tag{5}$$

These recursion relations are easily solved; they all reduce to the third-order difference equation⁽³⁾ $nu_n = (n-1)u_{n-1} + 2u_{n-3}$ through an adequate change of variables [$u_n = \hat{y}_{n+k+1}(k)$ for $k > 0$; $u_n = \hat{y}_{n+1}(0) - 1$ for $k = 0$].

The stationary state values $y_n(\infty) = \hat{y}_n(0)$ are [see Ref. 3, where $r_n = 1 + y_n(\infty)$]

$$y_{-1}(\infty) = 0, \quad y_0(\infty) = 1, \quad y_1(\infty) = 2, \quad y_2(\infty) = 1, \dots, \quad (6)$$

$$\lim_{n \rightarrow \infty} \frac{1}{n} y_n(\infty) = 0.4509\dots$$

The coefficients $\hat{y}_n(k)$ characterize the decay of $y_n(t)$ to its asymptotic value; for the main term ($\sim e^{-t}$)

$$\hat{y}_2(1) = 2, \quad \hat{y}_3(1) = \hat{y}_4(1) = 0, \quad \hat{y}_5(1) = 4/3, \dots, \quad (7)$$

$$\lim_{n \rightarrow \infty} \frac{1}{n} \hat{y}_n(1) = 0.0996\dots$$

For higher terms, it is easily seen that

$$\hat{y}_{n+k}(k)/\hat{y}_{k+1}(k) = \hat{y}_{n+1}(1)/2 \quad (8)$$

The evolution of the sequences Y_n determines the evolution of all initial states. For the alternating initial sequences Y_∞ considered in Ref. 3, Eq. (3) reduces to

$$\rho(t) = \lim_{n \rightarrow \infty} \frac{1}{n} y_n(t) \quad (9)$$

and the average fraction of bad bonds is

$$\bar{\rho}(t) = \sum_{k=0}^{\infty} \hat{\rho}(k) e^{-kt} \quad (10)$$

where

$$\hat{\rho}(k) = \lim_{n \rightarrow \infty} \frac{1}{n} y_{n+k}(k)$$

As indicated above, $\hat{\rho}(0) = 45\%$, $\hat{\rho}(1) = 10\%$,...

A random mixture of pure-phase clusters can be described by an initial state where each atom is followed with probability λ by an atom of the same species. The fraction of bad bonds then evolves like

$$\begin{aligned} \rho(0) &= 1 - \lambda \\ \bar{\rho}(t) &= \lambda^2 \sum_{n=0}^{\infty} (1 - \lambda)^{n+1} \bar{y}_n(t) \\ \hat{\rho}(k) &= \lambda^2 \sum_{n=0}^{\infty} (1 - \lambda)^{n+1} \hat{y}_n(k) \end{aligned} \tag{11}$$

as follows from the law of large numbers. For the purely random case $\lambda = 1/2$, this gives

$$\rho(t) = 0.3630 + 0.0716e^{-t} + 0.0358e^{-2t} + \dots$$

3. CONCLUDING REMARKS

More complicated initial conditions can also be considered: according to (3), one only needs to know the initial distribution of alternating sequences Y_n ($0 \leq n \leq \infty$) in the sample's initial state. In particular, one need not restrict oneself to initial states with equal proportions of A's and B's: provided that the initial state contains sequences Y_n , $n \geq 2$, the approach to the stationary state will always be in the form (9), with appropriate coefficients $\hat{\rho}(k)$.

The Markovian nature of the decay process (1) of sequences Y_n of course suggests an alternative description of the kinetics: if we denote by $f_n(t)$ the number of sequences Y_n at time t , Eq. (2) also implies

$$\rho(t) = \frac{1}{N-1} \sum_{n=0}^{\infty} (n+1) f_n(t) \tag{12}$$

The decay process (1) is a birth-and-death process, and its kinetics is described by the rate equations

$$\begin{aligned} \frac{d}{dt} \bar{f}_n &= -(n-1) \bar{f}_n + 2 \sum_{p=-1}^{\infty} \bar{f}_{n+p+4} \quad (n \geq 2) \\ \frac{d}{dt} \bar{f}_n &= 2 \sum_{p=-1}^{\infty} \bar{f}_{n+p+4} \quad (-1 \leq n \leq 1) \end{aligned} \tag{13}$$

where f_{-1} indicates [cf. Eq. (5)] the number of single atoms added to a neighboring sequence X_m . Equations (13) refer to the averages $\bar{f}_n(t)$, since the evolution of the actual numbers $f_n(t)$ is a stochastic process.

Given an initial distribution (f_n), these equations lead to the asymptotic distribution ($\bar{f}_n(\infty)$), $-1 \leq n \leq 1$, and to $f_n(\infty) = 0$ for any $n \geq 2$. But this asymptotic distribution cannot be computed from the single

requirement of stationarity in (13): there are infinitely many stationary states (the kinetic model is not ergodic).⁽³⁾

We would therefore not be able to determine the average fraction of bad bonds $\bar{\rho}(\infty)$ without solving explicitly the evolution equations (13). It is then easier to deduce $\bar{\rho}(t)$ and $\bar{\rho}(\infty)$ by (3) from the evolution of $\bar{y}_n(t)$, where the convolutions (5) make an explicit use of the hierarchical structure (1) associated with the dynamics. Thus it appears that the nonergodic nature of the final state—as implied by the dynamics (1)—requires a constructive approach to the problem.

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