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EXACT SOLUTION OF A PHASE SEPARATION MODEL WITH CONSERVED ORDER PARAMETER DYNAMICS

Vladimir Privman

Department of Physics, Clarkson University, Potsdam, New York 13699–5820, USA

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ABSTRACT

Pairwise particle-exchange model on a linear lattice is solved exactly by a new rate-equation method. Lattice sites are occupied by particles A and B which can exchange irreversibly provided the local energy in reduced. Thus, the model corresponds to a zero-temperature Kawasaki-type phase separation process. Due to local order-parameter conservation, the dynamics reaches a frozen state at large times, the structure of which depends on the initial conditions.

Recently there has been much interest in modeling phase separation and spinodal decomposition [1] by simple irreversible, effectively zero-temperature low-dimensional stochastic dynamical systems [2-4]. Specifically, some variants of nonconserved order parameter dynamical models in $D = 1$, corresponding effectively to $T = 0$ Glauber-type spin systems, have been solved exactly for properties such as the structure factor and average domain size (as functions of time, t); see [4] for details. The underlying mechanism leading to cluster growth in $D = 1$ is pairwise annihilation of interfaces separating ordered domains. The interfacial motion is diffusional and it corresponds also to certain diffusion-limited particle annihilation models [4-12].

The $T \to 0$ limiting model involves interface annihilation which is a process lowering the local energy and therefore has Boltzmann factor $+\infty$ associated with its transition probability at $T = 0$. Interface diffusion does not change the local energy and therefore has Boltzmann factor 1. Finally, interface generation (birth) has Boltzmann factor 0 (due to energy cost) at $T = 0$. The $T = 0$ models referred to earlier, correspond to allowing for both annihilation and diffusion. However, one could also consider processes with interface annihilation only. There has been limited discussion of models of such stationary annihilating particles (interfaces in the phase separation nomenclature) in the literature [13-15]. Specifically, exact $D = 1$ results can be obtained [13].

The phase separation process in the latter, diffusionless case does not continue indefinitely (as it does in the annihilation-with-diffusion models). Indeed, considering $D = 1$ for instance, one can easily visualize that when interfaces initially in "contact" are depleted by annihilation, the resulting configuration still contains some isolated "unreacted" interfaces. Thus the system will actually freeze in a certain partially ordered state which depends on the initial state, — a direct manifestation of the irreversible (nonergodic) nature of the $T = 0$ dynamics.

Let us now turn to conserved order parameter, spin- or particle-exchange Kawasaki-type dynamical models. There are several differences as compared to the nonconserved models just surveyed. Notably, interfacial processes even at $T=0$ are more complicated for the conserved case. Specifically, let us consider the $D=1$ binary AB-mixture model: each site of the $1D$ lattice is occupied by particle A or particle B. The locally conserved order parameter is the difference of the A- and B-particle densities.

Nearest-neighbor particle exchanges can lower local energy (reduce number of interfaces) in the following configurations:

$$\ldots\mathrm{ABAB}\ldots \to \ldots\mathrm{AABB}\ldots\ , \tag{1}$$

$$\ldots\mathrm{BABA}\ldots \to \ldots\mathrm{BBAA}\ldots\ . \tag{2}$$

Note that three interfaces (A–B or B–A bonds) "reacted" to yield one interface. Particle exchanges that do not change energy locally are possible in configurations like

$$\ldots\mathrm{AABA}\ldots \to \ldots\mathrm{ABAA}\ldots\ , \tag{3}$$

and three similar reflected and/or relabeled (A$\leftrightarrow$B) configurations. Here hopping of an interface must be mediated by the presence of another, nearby interface.

Thus interfacial dynamics in the particle-exchange models is more involved than in the nonconserved case, even at $T=0$. Specifically, energy-conserving interfacial motion, (3), is no longer simple free diffusion. Thus, freezing rather than full phase separation occurs asymptotically for large times in models with both energy-lowering and energy-conserving moves allowed, or with only energy-lowering moves allowed. In the former case the $D=1$ frozen state contains single interfaces while in the latter case both single interfaces and pairs of interfaces are "frozen in." Several numerical studies were reported [16-19] of such particle-exchange models for D up to 5. As in the nonconserved case, some of the properties of the $D = 1$ models are different from $D > 1$. However, the general expectation of the "freezing" of the domain structure at large times applies, for conserved dynamics, at all D.

Derivation of exact $D = 1$ results for conserved-dynamics models proved considerably more difficult than for the nonconserved models. Palmer and Frisch [18] developed a method by which the asymptotic ($t = \infty$) density of the residual, frozen in interfaces for the dynamics with energy-lowering moves only, (1)-(2), can be calculated, starting from the initially fully "mixed" alternating-AB state. More recently, Elskens and Frisch [20] extended this approach to allow calculation of the rate of approach to the freezing density, and also obtain results for the initial state randomly populated by the equal-probability mixture of A and B.

In the present work, we present the full time-dependent solution of the $D = 1$ model. We use a new method inspired by techniques developed in studies of $D = 1$ random sequential adsorption [21-23]. The solution is obtained for both alternating and random initial conditions, and it recovers all the asymptotic results of [18,20].

We consider a linear lattice each site of which is occupied by either particle A or particle B. Initially, the particle arrangement is alternating (denoted alt), ...ABABABA..., or random (denoted ran). In the former case we neglect end effects; all our calculations will be for the infinite linear lattice (as opposed to [18,20]). In the random initial case, we assume that each site is either A or B with equal probability, at time $t = 0$, so that the initial densities of A and B species are 50%.

The dynamics consists of particle exchanges which decrease the number of "broken" bonds (interfaces) A–B and B–A. Thus the allowed moves are (1) and (2), i.e., only pairs of particles centered in a fully alternatively-ordered group of 4, can exchange thus reducing the local number of interfaces from 3 to 1. We assume asynchronous, continuous-time dynamics: each allowed-configuration nearest-neighbor pair AB or BA undergoes the exchange process, i.e., the particles switch their lattice sites, at the rate R, independent of other exchange events. As is well known, in the continuum-time limit of asynchronous dynamics one can disregard interference of exchanges of pairs which share a site, such as the two pairs sharing the central A site in ...ABABA.... The rate parameter R will be incorporated in the time variable so that we denote the physical product Rt simply by t (effectively setting $R = 1$).

Our aim is to calculate the density of interfaces, $I(t)$, i.e., the fraction of A–B and B–A bonds, as a function of time. Initially we have

$$I_{alt}(0) = 1 \qquad \text{and} \qquad I_{ran}(0) = \frac{1}{2} \ . \tag{4}$$

Our method of solution involves calculation of probabilities $P(k,t)$ that a randomly selected continuous group of $k \geq 3$ lattice sites is fully alternatively-ordered, i.e., that it is occupied, at time t, by k particles $ABAB\ldots$ or $BABA\ldots$, where the sequence is alternating and k-site long. Note, however, that we do not impose any condition on the configuration outside this group. Thus, the alternatively ordered region need not be exactly k-site long, and in fact it may be part of a longer alternating sequence of sites, at one or both ends. In this respect our definition differs from earlier works and follows instead the ideas developed for random sequential adsorption models [21-23].

The rate of decrease of the interface density is given by

$$-\frac{dI(t)}{dt} = 2P(4,t) \ , \tag{5}$$

where the factor 2 accounts for the reduction by 2 (from 3 to 1) of the local interface number in each exchange event. The factor $P(4,t)$ is the probability that a randomly selected group of 4 sites is one of the allowed-exchange configurations, (1) or (2). As already mentioned, at $t=\infty$ only single isolated interfaces and isolated pairs of nearest-neighbor interfaces survive in a frozen state. The number of interfaces which are paired up is in fact given simply by

$$I^{(paired)}(\infty)=2P(3,\infty)\ , \tag{6}$$

while the number of single interfaces in the final state can be calculated as the difference $I(\infty)-I^{(paired)}(\infty)$. Indeed, only the probability $P(3,t)$ remains finite as $t\to\infty$; all $P(k>3,t)$ vanish in the large-t limit; see explicit results below.

The decrease of the probability $P(k,t)$ with time is governed by the following rate equation,

$$-\frac{dP(k,t)}{dt}=(k-3)P(k,t)+2P(k+1,t)+2P(k+2,t)\ , \qquad (k\geq 3)\ . \tag{7}$$

The first term is the rate at which the alternating order is disrupted by pairwise exchanges of pairs such that their "defining" 4 sites, i.e., the original pair sites and the two neighbor sites on both sides, fall fully within the k-group under consideration. The second term corresponds to exchange events of the pairs which are located at the two ends of the k-group. Indeed, for an end pair to lie within 4-sequences (1) or (2) which correspond to the allowed-exchange configurations, our k-group must in fact be part of a larger ordered group, of length $(k+1)$, including all the four "deciding" sites of a given end-pair. (One of these sites is external to the original k-group.) Finally, the third term corresponds to disruption of alternating order due to exchange of the end sites of the k-group with their nearest neighbors just outside the k-group. For one of these two pairs of sites which are half-external to the k-group to exchange, the four "deciding" sites require consideration of a $(k+2)$-site-long extended group.

The rate equations (7) form a relatively simple hierarchy only in $D=1$. For $D>1$, k-groups are replaced by more complicated clusters and no exact solution is possible by this method. The exact rate equations (7) must be solved with the following initial conditions,

$$P_{alt}(k,0)=1 \qquad \text{and} \qquad P_{ran}(k,0)=2^{1-k} \; . \tag{8}$$

The solution can in principle be obtained by the generation function method. However, a much simpler way is to notice that the hierarchy (7) is solved by the Ansatz

$$P(k,t)=P(k,0)Q(t)e^{-(k-3)t} \; , \tag{9}$$

for both alternating and random initial conditions (but not generally). A straightforward calculation then yields

$$Q_{alt}(t)=\exp\left(2e^{-t}+e^{-2t}-3\right) \qquad \text{and} \qquad Q_{ran}(t)=\exp\left(e^{-t}+\frac{1}{4}e^{-2t}-\frac{5}{4}\right) \; . \tag{10}$$

Collecting all the results and definitions, (4)-(10), and solving for $I(t)$, yields, after some algebra, the results

$$I_{alt}(t)=1-\frac{2}{e^4}\int\limits_{1+e^{-t}}^{2} e^{z^2}\,dz \; , \tag{11}$$

$$I_{alt}(\infty)=1-\frac{2}{e^4}\int\limits_{1}^{2} e^{z^2}\,dz \simeq 0.450898 \; , \tag{12}$$

$$I_{alt}^{(paired)}(\infty) = \frac{2}{e^3} \simeq 0.099574 \ , \tag{13}$$

$$I_{ran}(t) = \frac{1}{2} - \frac{1}{2e^{9/4}} \int\limits_{1+\frac{1}{2}e^{-t}}^{3/2} e^{z^2} dz \ , \tag{14}$$

$$I_{ran}(\infty) = \frac{1}{2} - \frac{1}{2e^{9/4}} \int\limits_{1}^{3/2} e^{z^2} dz \simeq 0.362957 \ , \tag{15}$$

$$I_{ran}^{(paired)}(\infty) = \frac{1}{2e^{5/4}} \simeq 0.143252 \ . \tag{16}$$

The functions (11) and (14) are plotted in Figure 1. To facilitate comparison, their values were normalized by $I(0)$, see (4). The most profound feature of the irreversible dynamics leading to frozen states is of course the dependence of the final state on the initial conditions. Explicit results (11)-(16) are, to author's knowledge, the first exact time dependent expressions available for conserved-dynamics models. It is hoped that the method of solving the $D = 1$ models will be used to obtain additional exact $1D$ results as well as new approximation schemes in $D > 1$.

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Figure 1. Lower curve: density of interfaces, $I(t)$, for alternating initial conditions; see (11). Upper curve: density of interfaces for random initial conditions; see (14). The curves plotted are $I(t)/I(0)$, where the initial densities are given in (4).