

Molecular dynamics simulations of phase separation in chemically reactive binary mixtures

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A molecular dynamics system of a two dimensional immiscible binary mixture with a first order chemical reaction that changes a particle from one of the species to the other, is set up, in close analogy to the Monte Carlo investigation of a similar system on a square lattice by S. Glotzer *et al.* [Phys. Rev. Lett. **72**, 4110 (1994)]. In contrast to their investigation we do not find any labyrinthlike domain formation at the steady states and no direct equality between the way in that the system scales with respect to reaction rate and growth exponent in the absence of a chemical reaction. The differences are explained by the fact that a stochastic model misses the hydrodynamic modes that are mainly responsible for the phase separation in this system and that the discrete lattice imposes an external field on the domains that order the steady-state domains in a labyrinthlike structure.

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I. INTRODUCTION

The domain structures of immiscible multi-component systems may be affected by chemical reactions between the components. The theoretical treatments of such systems are typically based on analysis of the time development of the appropriate order parameter and using the Ginsburg-Landau-Wilson equation for the local free energy functional [1]. Recently, however, Glotzer, Stauffer, and Jan [2] simulated a two dimensional (2D) binary system of particles A, B where a homogeneous mixture of equal numbers of the two species was quenched to decomposition. At the same time a competing first order "chemical" reaction



exchanged the identity of the two components in a first order reaction, i.e., independently of the dynamics of the order parameter, which in this case is the local particle fraction of one of the components in the subdomains. The two competing processes, a slow domain ordering and a fast first order reaction that destroys the domain structure, created a steady-state pattern formation of domains. The simulations were performed for particles on square lattices by the Monte Carlo technique (MC) extended with a temperature independent probability p_c of converting A to B and vice versa. The main findings of the investigation were that the systems ended in a steady-state labyrinthlike domain formation with a mean domain size that scales with the reaction rate to a power s , which equals the domain growth exponent α in the absence of chemical reactions.

The growth exponent for decompositions in 2D has been the subject of heavy theoretical as well as computer experimental investigations. In the classification scheme, set up by Hohenberg and Halperin [3] the stochastic 2D system without a chemical reaction corresponds to the model B (conserved order parameter and without hydrodynamics). In this case one often observes a growth exponent $\alpha \approx 1/4$ [4]. Other stochastic dynamics simulations, of the Ising model [5], as well as stochastic dynamics based on the Ginsburg-Landau free energy functional, however, suggest an asymptotic

growth exponent of $1/3$ [6,7] in accordance with theoretical predictions [8,9]; but with a persistent transient of $1/4$. This transient may be caused by stochastic surface diffusion in the absence of the asymptotic Lifshitz-Slyoslov mechanism [9].

The present work is in close analogy to [2], except that it is performed in continuous space and by a molecular dynamics technique (MD). The motivation for the change in method is based on several facts. First it is noticed that the steady-state domain formation is affected by the discreteness of the space. For the square lattice the labyrinthlike domain structure was obtained with the interfaces oriented along the diagonals of the squares, which ensures minimum excess interfacial energy [10]. But for a continuous space no such "external" anisotropic field can compete with the domain formation. A second reason for investigating a nonequilibrium system with chemical reaction is that the stochastic Monte Carlo technique gives results that differ from the corresponding results obtained by the deterministic molecular dynamics technique [11]. This fact is generally ignored in the literature, which is not surprising since when it comes to establishing equilibrium properties both methods scan the phase space correctly. However, non-equilibrium dynamics might often be dominated by hydrodynamic modes and these cooperative modes are not simulated in a typical MC simulation, which consists of single particle moves. For this reason the MC trajectories do not represent the dynamical evolution in systems with hydrodynamics. A simple critical quench of a binary mixture to spinodal decomposition demonstrates this fact by giving a different growth exponent α by using MC and MD, respectively [11]. Whereas the stochastic MC decomposes slowly and asymptotically with an exponent $\alpha = 1/3$, [12] the MD decomposition is much faster with an exponent that starts by $1/2$, but crosses over to $2/3$ [11,12], in accordance with a recent free energy functional investigation [13,14]. Extending the deterministic MD system by a chemical reaction still allows for hydrodynamic modes, which, however, now are coupled with the chemical reaction in a nondeterministic way.

This paper is structured in the following way. In Sec. II the nontrivial procedure of setting up a chemical reaction in a MD system of interacting (simple) particles is presented.

Section III gives the result for a system of two dimensional particles with competing phase separation and chemical reaction, and the controversies between MC and MD are discussed in Sec. IV.

II. MOLECULAR DYNAMICS WITH CHEMICAL REACTIONS

The dynamics of N classical particles will in general be chaotic and thus it has little meaning to concentrate the numerical effort on an accurate calculation of the analytic trajectories of the individual particles. The trajectories numerically obtained will deviate exponentially from the exact analytic solution. Instead of trying to determine the trajectories one has to concentrate on maintaining the right global behavior of the dynamic operator in the phase space. Both quantum dynamics as well as classical dynamics are time reversible and the propagation in the phase space is symplectic, i.e., area preserving of the phase space. An example of such a dynamical operator is the so-called Verlet algorithm or leap-frog algorithm, that is the simplest example of a *discrete* classical mechanical time operator in the phase space that ensures both time reversibility and symplectic mapping [15].

Discrete dynamics imply that the particles are exposed to discrete forces. This fact is generally ignored in the debate about MD and many authors have been concerned about the discontinuity of the force field by truncating the potential of the forces at a certain range of interaction. However, under the total time simulation all the particles are in each step exposed to discontinuities of the force field due to the finite order of the algorithm [16]. A MD system of particles will typically exhibit the biggest force gradients at (high energy) particle collisions. By introducing first order reactions (i.e., proportional to the overall concentration of the species and independent of the local environment where the reaction takes place) we introduce force gradients on the particles at the place of reaction. Thus we need guidance for the stability of MD when we introduce chemical reactions in the system, and as a guide for the choice of possible chemical reactions one should not introduce bigger force gradients than those to which the particles are already exposed, from time to time, during high energy particle collisions.

The qualitative feature of the system we want to set up is a competition between a fast first order chemical reaction, which destroys the phase separation, and a slow phase separation, ensured by slow hydrodynamic modes. For this reason we chose a kinetics with a low energy barrier between A and B , in close analogy with [2]. The first order kinetics will be given by (1). With a rate of reaction that is proportional to exchange probability p_r , an A particle is *spontaneously* changed to a B particle. If we apply the rule of thumb that this change should not impose new force gradients that are bigger than those to which the particles already can be exposed in their next discrete step, we must, for systems with spontaneous exchanges, necessarily choose A and B particles with the same strong repulsive short range potential that determines the (high energy) particle collisions. A simple candidate of such a system is a mixture of labeled (A and B) Lennard-Jones particles where particles exchange labels spontaneously and where there is a net loss of poten-

tial energy between particles in the fluid at the exchange. And since we want to maintain the same excluded volumes of the particles at the exchange this net loss of potential energy must come from the long range attractions between different particles with different labels. In order to obtain a phase separation in such a system we must ensure that a positive excess potential energy of mixing is larger than the gain in entropy of mixing. In statistical mechanical models of simple mixtures one obtains the excess energy of mixing by using the fluid structure given by the radial distribution function $g(r)$ of pairs of particles and the resulting excess potential energy is obtained at the density ρ and temperature T as

$$\beta U_{\text{excess}}(\rho, T) = \rho \int_V d\mathbf{r} g(r) \delta u(r) \quad (2)$$

from the local excess potential energy of mixing $\delta u(r)$ at particle distance r

$$\delta u(r) \equiv u_{AB}(r) - \frac{1}{2}[u_{AA}(r) + u_{BB}(r)] \quad (3)$$

and in order to ensure a phase separation, the integrated effect of $\delta u(r)$ must dominate above the entropy gain by mixing [17].

With all these facts in mind a critical quench of an immiscible binary mixture with a fast chemical reaction can be set up by choosing labeled Lennard-Jones particles, but with only short range repulsive Lennard-Jones forces between particles with different labels. The corresponding potential is the Weeks-Chandler-Andersen (WCA) potential [18]. Due to the symmetry of the system an upper consolute temperature (critical temperature) $T_c(x)$ must be for the critical particle fraction $x=0.5$ (critical quench means only that the system is quenched at this particle fraction). The kinetics is set up by randomly choosing n A and n B particles at every time interval δt and exchanging the labels, thereby ensuring first order kinetics by the random choice and strict microscopic (kinetic) reversibility so that the system cannot spontaneously break the symmetry and drive away from the critical concentration. This system fulfills the MD requirements for numerical stability; without the kinetics it will perform a spinodal decomposition, and it must be the proper continuous space analog to the discrete MC system investigated in [2].

The main findings of the MC investigation [2] were that the systems ended in a steady-state labyrinthlike domain formation with domain sizes that scaled with the reaction rate or exchange probability p_r , to a power s equal to the domain growth exponent α in the absence of a chemical reaction. Thus we need a measure of the degree of the decomposition suitable for the present MD system. The ramified domains shown in the next section can both be described by their mean size, by the first peak in the structure factor, and by the mean behavior of the radial distribution function for the individual components of the mixture. We find, however, the mean potential energy per particle, $u(t)$, at time t to be not only the easiest but also the most accurate quantity to monitor the scaling behavior and steady-state limit of the systems, and in fact it is also the measure used in [2].

As the system is quenched with or without kinetics, $u(t)$ decreases first exponentially and later algebraically. There is, however, one obstacle to overcome using $u(t)$ as a measure:

we need to know the energy of coexisting phases at equilibrium, $u(\infty)$. [It is the total excess potential energy, (2) and (3), and not a fraction, like u_{AB} , which sets up the interfaces, drives the decomposition, and enters into the nonlinear algebraic relations.] In terms of $u(t)$, the main findings of [2] were

$$|u(t) - u(\infty)| \approx k_0 t^{-\alpha} \quad (4)$$

for spinodal decomposition without competing kinetics and

$$|u_{\text{eq}} - u(\infty)| \approx k_{\text{eq}} \rho^s, \quad (5)$$

where u_{eq} is the steady-state mean potential energy per particle, and the MC result then suggests that

$$s = \alpha \approx 1/4 \quad (6)$$

for a critical decomposition in a two dimensional space. (In [2] the authors did not obtain the exponent $\alpha = 1/3$ for stochastic dynamics, but the persistent transient $\alpha \approx 1/4$.)

For the corresponding MD system and in 2D, α equals $2/3$ at late times [11,12] in accordance with a theoretical investigation [13,14], so the questions that remain is whether there is a steady state domain structure with a relation or equality between s and α , and whether these domains perform a “self-organizing” labyrinthlike domain structure.

III. RESULTS FOR A TWO DIMENSIONAL BINARY MIXTURE

The system consisted of $N = 40\,000$ Lennard-Jones (LJ) particles with periodical boundaries and at the particle density $\rho\sigma^2 = 0.8$ and temperature $T^* = k_B T / \epsilon = 1.0$ (σ and ϵ are length and energy parameters in the LJ potential, k_B is Boltzmann’s constant). This corresponds to a dense fluid state, and the system was instantaneously quenched by randomly selecting $N_A = 20\,000$ particles and the particles were labeled by choosing the potential between the N_A and the $N_B = N - N_A$ particles to be purely repulsive (WCA potential) by instantaneously cutting away the attraction of the u_{AB} potentials. The corresponding binary mixture is immiscible below temperature $T_c^* \approx 1.7$, [17] and the solubility of solute particles at $T^* = 1$ is very low. For a critical quench with $N_A = N_B$ the system separates and performs a spinodal decomposition. The time development at constant temperature was followed using the symplectic and time reversible algorithm given in [19] with a time increment $h = 0.005$ ($\approx 10^{-14}$ sec). Figure 1 shows some examples of particle distributions for different quench times for the MD system without a chemical reaction. Subphases of A and B are created rather rapidly and after 100 000 time steps (500 time units) the system is already divided into percolating subphases [Fig. 1(a)]. The phase separation takes place by decreasing the length of the interfaces whereby also the mean energy $u(t)$ decreases. The slow spinodal decomposition was followed 10 000 time units (2×10^6 time steps). At that time the system still contained an island of A -rich drop in the B -rich phase [Fig Fig1(c)] and the evolution in the system was extremely slow.

According to (4) we need to know $u(\infty)$ in order to determine the algebraic relaxation at late times. So the mini-

um energy at equilibrium $u(\infty)$ was obtained in another way by starting with a configuration of the system with planar subphases [20] and the configuration given in Fig. 1(d) is the particle distribution after 5×10^6 time steps. The system was found to equilibrate very slowly, but showed no drift in the energy after 4×10^6 steps and the mean energy obtained in the succeeding 1×10^6 time steps gave $u(\infty)/\epsilon = -1.931 \pm 0.001$. We can now determine α in (4) for a system without a competing chemical reaction and as found in [11] we obtain at late times $t > 500$, an exponent $\alpha = 2/3$ in accordance with [13] and [14].

The system with both phase separation and a first order reaction was then set up by quenching the system but at the same time randomly selecting n A particles and n B particles and exchanging their label every δt time steps. The steady state was identified as the state where the energy per particle $u(t)$ no longer exhibited any drift but remained constant for averages over long subsequent time intervals. The mean energy per particle, u_{eq} , in the steady state was then obtained from these subsequent time intervals. For an exchange of 20 of the 20 000 A particles with 20 B particles per time steps the steady state was reached within a few thousand time steps whereas the system is much more sluggish for smaller exchange rates. Figure 2 shows different particle configurations by the end of the simulations for different exchange rates n . As can be seen from Fig. 2(a) the system for $n = 20$ consists of very small clusters; but as the exchange rate is decreased a domain separation takes place.

The subdomains in the steady states, however, are not compact, but infected by smaller domains of the other species as can be seen in Fig. 2(d). Inspection of subsequent distributions of particles shows that the steady-state clusters grow but at the same time are affected by the kinetics so that at a certain point they separate into smaller and more compact subclusters: These events are associated with a rapid increase in $u(t)$. The upper part of Fig. 3 in large scale shows this behavior. It gives the energy $u(t)$ in the last 500 time units of the simulation for the system with the smallest exchange rate $n = 0.1$, corresponding to only two particles out of 40 000 exchanging labels every 10 time steps. Two (main) frequencies in the energy variations can be identified. One fast frequency is due to a sum of contributions from exchange between potential and kinetic energy, from the coupling with the thermostat, and from the direct (local) impact of the chemical reaction. The other long time change in $u(t)$ is due to the infection of the large clusters by the (bulk) chemical reaction by which they finally fall apart into more compact subclusters corresponding to a less separated state with a higher potential energy.

The lower part of in Fig. 3 compares the same steady-state energy evolution as shown above, with the corresponding evolution in the system without a chemical reaction and for the time interval where its mean domain size is of the same order of magnitude as the steady states with $n = 0.1$ [Fig 2(d)]. This happens for times in the interval [500,1000] and the lower curve shows this energy evolution together with the dashed curve (4): $f(t) = k_0(t)^{-2/3} + u(\infty) + a$, shifted by a for illustrative reasons. Inspection of this curve and a log-log plot [12] shows that the system without a chemical reaction reaches the asymptotic regime with a growth exponent equal to $2/3$ within this time interval. The

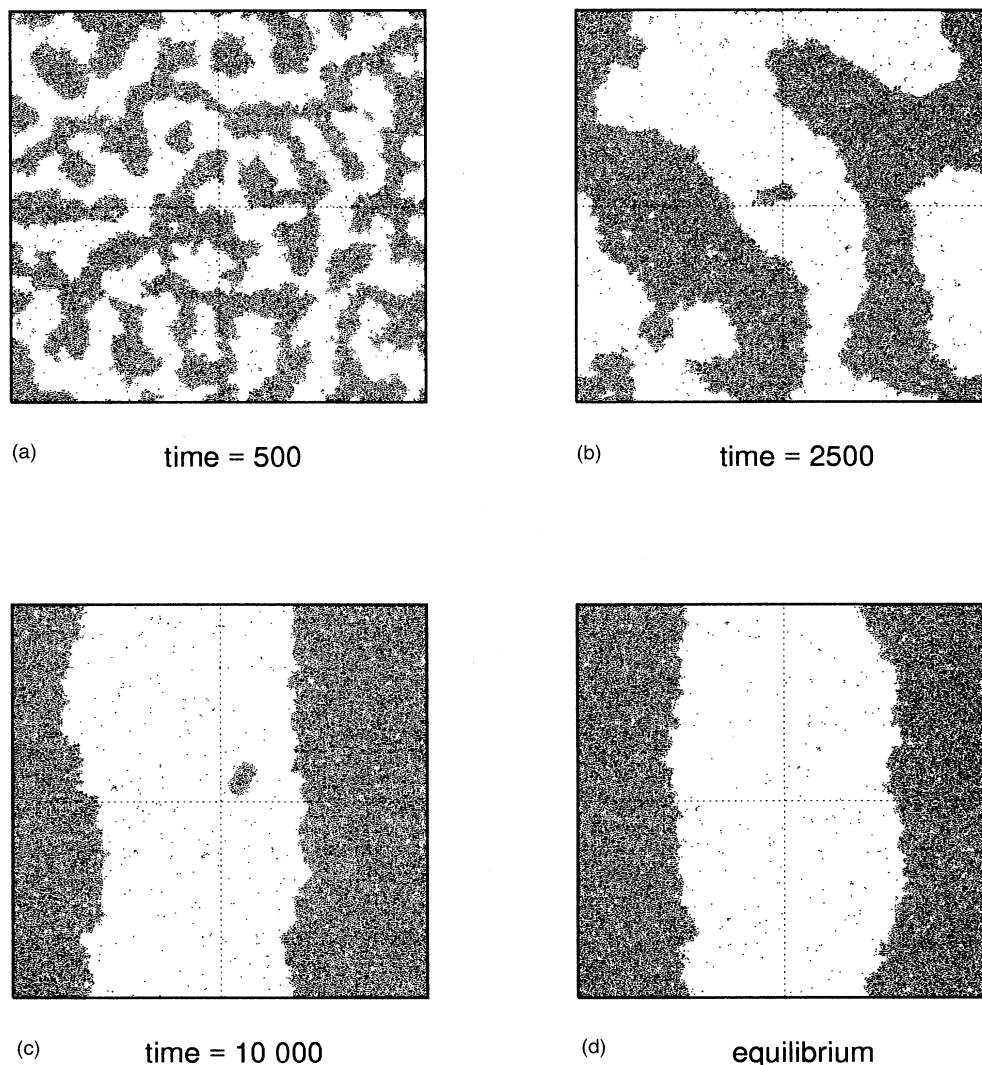
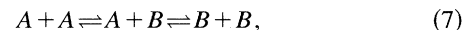


FIG. 1. Domain evolution in the system without a chemical reaction. For clarity the figures only show the distribution of A particles.

potential energy is not constant due to the exchange between kinetic and potential energy. In addition to this we have introduced a fast chemical reaction that causes new force and energy gradients. But as can be estimated from the width of the two curves in the lower part of Fig. 3, which are equal, the gradients due to the chemical reaction are smaller or of the same order as already present in the MD system due to the way the system was deliberately set up. For smaller exchange rates than $n=0.1$ the system of 40 000 particles shows a final size effect, which, among other things, is described by the mean domain size being bigger or of the order of half the system size. Returning to Figs. 2(a)–2(d) one can see that the systems show no sign of a labyrinthlike domain structure, which in the case of the MC simulation must be caused by the extra force field coming from the discrete space, which favors interfaces in the direction of the diagonals [10].

The MD chemical reaction technique introduced in the present paper can be used to simulate more complex chemical reactions than given by the unimolecular elementary re-

action (1). We have investigated a series of different chemical reactions. Also for a bimolecular reaction, where the color shift is performed at a molecular collision,



we obtained a steady state with the same kind of ramified domain structures as shown in Fig. 2, and in no case did we observe laminarlike domain structures. (The collision introduced color shift was performed by changing the color of one of the components in the pair at collision.)

The main finding in [2] was the equality between α and s obtained from (4) and (5). We have obtained $\ln|u_{\text{eq}}(n) - u(\infty)|$ for n in the interval $[0.1, 20]$, corresponding to two decades on a logarithmic scale. The steady-state mean energy was obtained as described above and the points shown in Fig. 4 are for averages over time intervals of 200 000 except for $n=0.1$ and 0.2 where we needed longer

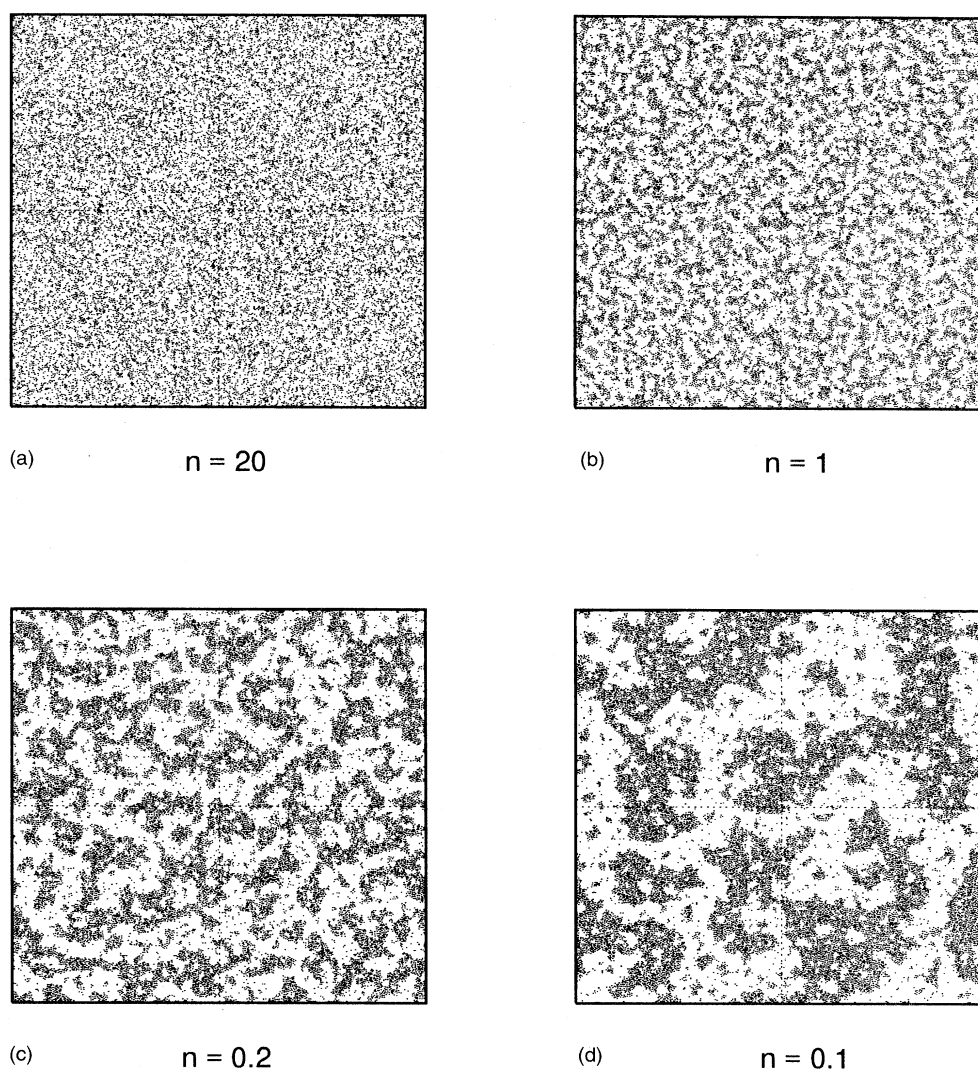


FIG. 2. The same system as shown in Fig. 1 and started from the same fluid state, but now with the fast chemical reaction included. The A -rich “domains” for $n=20$ exchanges of A particles to B particles and vice versa per time step (a) are very small and the phase separation is suppressed. Both reactions are present only for a significantly smaller exchange rate (b)–(d).

runs. The uncertainties (logarithmic scale) are estimated to be smaller or of the same size as the marks for the points in the figure. As can be seen there is no simple dependence of $\ln|u_{\text{eq}}(n) - u(\infty)|$ on the rate constant of the competing reaction. Also shown in the figure is a straight line with the slope of $s = 2/3$, which is the slope for which s equals the growth exponent α in the MD system without a chemical reaction [11,12].

IV. DISCUSSION

The differences between the MC result and the present MD result for phase separation dynamics with chemical reactions demand an explanation. Although it is not simple to compare the sizes of a MC discrete lattice system of 316^2 particles with nearest neighbor interaction and a MD system of 40 000 particles, inspection of the domain sizes in the two

systems reveals that the present simulations cover steady-state domain sizes over at least the same reaction rate intervals as in [2]. So we believe that both results are not affected by finite size effects and are correct and describe the dynamics, but within different models. In the classification scheme in [3] the MC system corresponds to model B and the MD system corresponds to model H for systems with hydrodynamics and conserved order parameter.

The qualitative and important difference between the two models is, as mentioned, that pure MD, in contrast to MC, contains the hydrodynamic modes. However, with a chemical interaction of the kind introduced here we suppress these modes—not completely if the reaction rate is small, but the modes must be suppressed for high reaction rates and we shall expect a growth exponent of $\alpha = 1/4 - 1/3$ [11,12]. We notice that s in fact takes the value 0.23 for $n=1$ in accordance with the MC result [2]. First for this exchange rate the

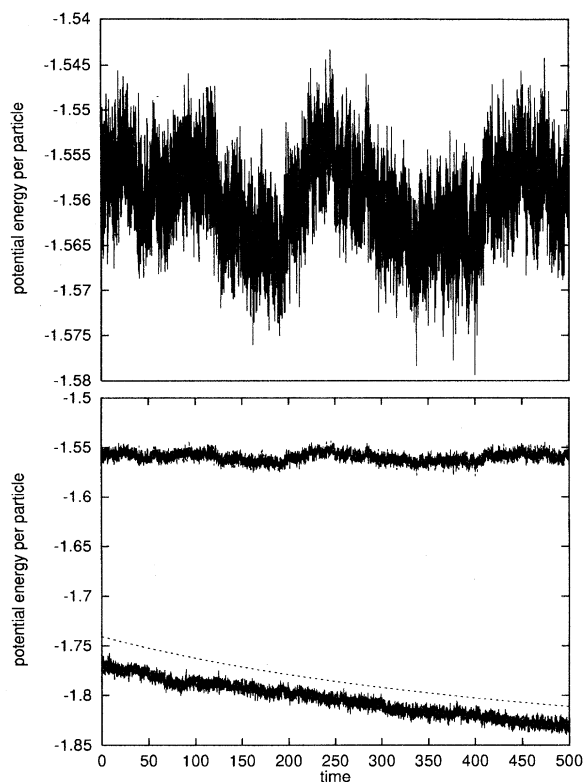


FIG. 3. The upper figure shows the potential energy evolution $u(t)$ in units of ϵ , during the last 10^5 time steps for the most steady-state phase separated system with $n=0.1$ shown in Fig. 2(d). In the lower figure the same energy evolution is compared with the corresponding evolution in the system without a chemical reaction, and the dashed line gives its asymptotic algebraic behavior with an exponent equal to $2/3$ (shifted by a small amount for illustrative reasons).

domains contain many particles, as can be seen from Fig. 2(b), so the state can qualitatively be characterized as a state where both processes take place: the fast chemical reaction and the slow phase separation. As the reaction rate is lowered, the hydrodynamic modes can persist (locally) until an exchange of labels destroys the velocity field. This may be understood from the following simple fact: The hydrodynamic modes show up in the velocity autocorrelation function $\Psi(\tau)$ of velocities at time t and $t + \tau$ [21]:

$$\Psi(\tau) = \frac{\langle \mathbf{v}_i(t+\tau) \mathbf{v}_i(t) \rangle}{\langle \mathbf{v}_i(t)^2 \rangle}, \quad (8)$$

where the angular brackets denote the average over the velocities \mathbf{v}_i of the particles in the system. In real fluids, as in MD fluids, the hydrodynamic modes cause a long time correlation of the velocities, which results in a slow algebraic decaying autocorrelation function $\Psi(\tau)$ [22]. On the other hand stochastic dynamics, like Langevin dynamics and MC, miss these modes and as a result of that their autocorrelation functions decay rapidly and exponentially to zero. When a reaction takes place we have carefully ensured that we do not introduce bigger force gradients than are already present within the pure MD system; *but* we have not ensured that

the force has a certain direction. In fact it is random and thus in a random way instantaneously changes the direction of the velocity of the reacting particle and thereby its velocity autocorrelation function accordingly to (8). So if there exists an equality in the growth exponents s and α we should in fact expect this continuous crossover in the MD system from a value of s from about $1/4-1/3$ to $2/3$ as the exchange rate is lowered. The fact that we only see part of this crossover is explained by the fact that we need even smaller exchange rates to recover $2/3$. This is, however, not possible at the moment, since it also requires a significantly bigger system and longer runs. In [12] we have tested this hypothesis in a simple way by quenching the binary mixture, without a chemical reaction, but by adding a random force field from time to time to the MD force field. As the time interval of this disturbance was increased we observed, as expected, a continuous crossover from a growth exponent $\alpha \approx 0.33$ to 0.66 .

How a real system would behave remains speculative. We believe, however, that the present model describes qualitatively the dynamics of a system with phase separation and a first order reversible chemical reaction. The argument is that a chemical reaction is associated with breaking and reestablishing covalent bonds. These bonds have a short ranged and random orientation, given by the local and strong anisotropic force field, and thus have exactly the same qualitative impact on the direction of the velocities of the reacting species and their nearest neighbors as changing the color in the MD system.

The purpose of this investigation was to set up an *open* MD system with a fast chemical reaction in order to determine its steady-state behavior. For this reason we chose a system with a spontaneous exchange of particles between the two chemical states. This corresponds to a small transition energy barrier between the two states. On the other hand this instantaneous change is only a technical detail and it would be easy to simulate a first order, unimolecular chemical reaction in a more smooth way by charging up the differences between the intermolecular force field before, at, and after the reaction during many time steps. This should be the case

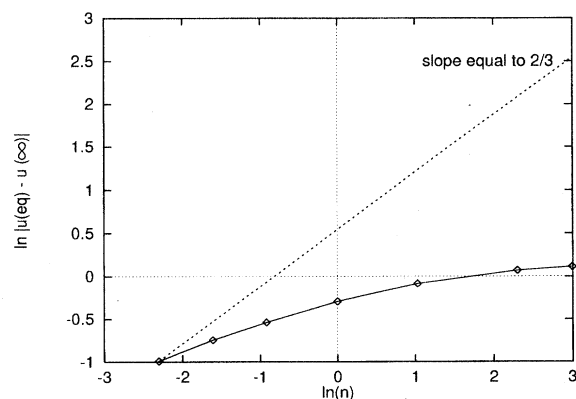


FIG. 4. Log-log plot of the steady-state excess energy, $u_{\text{eq}} - u(\infty)$, in units of ϵ against the exchange rate n . The change in excess energy between the two smallest exchange rates (the two first points in the figure) is 0.33 , and far from a slope of $2/3$ given by the dashed line.

if one wants to explain quantitatively a specific experiment with a given transition state energy barrier.

The fast chemical reaction was taken to be unimolecular in order to compare with the investigation [2]. This is probably unrealistic for many real experiments where the elementary chemical reactions are of higher order. It is, however, straightforward to extend the present MD model to simulate, e.g., a bimolecular reaction by changing the labels with a conditional probability for pairs of nearest neighbors. Doing

so we obtained the same qualitative behavior of the steady state with ramified domain structures as by the unimolecular first order reaction (1).

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