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Langevin Dynamics Simulations of Phase Separation in a One-Component System

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Langevin dynamics computer simulations have been performed for a two-dimensional Lennard-Jones fluid quenched into the coexistence region of its liquid–vapor phase diagram. For late stages of the phase-separation process, the average radius of the liquid clusters is found to grow proportional to $(\text{time})^{1/4}$. This growth law is analyzed theoretically and compared to recent molecular dynamics and Monte Carlo results. Details of the different simulation methods are critically discussed.

KEY WORDS: Phase separation; Lennard-Jones system; dynamic scaling; computer simulation techniques; Langevin dynamics.

1. INTRODUCTION

The development of spatial phase coexistence in a physical system undergoing a first-order phase transition is a complex, highly nonlinear phenomenon. Of particular interest is the dynamics of the phase separation process, i.e., the decay of an originally homogeneous system into the spatially inhomogeneous equilibrium state.(1–5) A typical model system studied in this context is a Van der Waals-like liquid, which has been rapidly quenched into the coexistence region of its liquid–vapor phase diagram.(6) Such a homogeneous system breaks up into regions of different densities finally leading to the coexistence of macroscopic gas and liquid phases.

The initial stage of the phase-separation process is usually described as either droplet nucleation or spinodal decomposition, depending on whether

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the respective system is originally quenched to a metastable state or to an unstable state within the coexistence region of its phase diagram. After a short transient period, the separation process reaches in both cases a situation in which small domains are formed whose internal density is already equivalent to that of the equilibrium liquid. With increasing time these domains coarsen in order to reduce the system's excess free energy associated with the "surface" of these spatial inhomogeneities.

Eventually, the average radius $R(t)$ of the little liquid clusters exceeds the microscopic length scale of the system. From that time on, the microscopic details are expected to become less important. The growing cluster radius $R(t)$ is assumed to be the only relevant length scale of the problem. Moreover, dynamic scaling of the system evolution has been proposed(7) in terms of a homogeneity relation for the cluster peak of the time-dependent structure factor $S(k, t)$,

$$S(k, t) = \{R(t)\}^d \tilde{S}(kR(t)) \tag{1a}$$

where d is the dimensionality of the system and $\tilde{S}$ is a scaling function. Theoretical considerations(8,9) and computer-simulation results(6,10,11) indicate that the growth law for the cluster size $R(t)$ and the decay of the excess internal energy $E(t) - E(\infty)$ might have power law form:

$$R(t) \propto t^X \tag{1b}$$

$$E(t) - E(\infty) \propto t^{-Y} \tag{1c}$$

In analogy to the theory of critical phenomena it has been suggested(4,5) to characterize the phase-separation process in the various systems by a small number of "universality classes," each class being determined only by very general properties. These may be, e.g., the degeneracy of the ordered state or the conservation law governing the dynamics. However, in contrast to the expected universal behavior different growth laws have been observed in constant temperature molecular dynamics (MD) and Monte Carlo (MC) studies for basically the same physical system, namely, a two-dimensional one-component system undergoing spinodal decomposition.(6,11) In both cases one has found good scaling of the spinodal peak of the structure factor according to (1a) and growth laws of the form (1b) have been observed for the average cluster size, but with different exponents X for constant temperature MD and MC simulations. Details of the different simulation procedures will be discussed in the following chapters of this paper. Note however, that both MC and constant-temperature MD simulations conserve neither the total energy nor the total momentum of the system. Hence, it is not simply the presence or absence of these conservation laws which explains the different growth behavior. To investigate the origin of these differences, we performed new simulations, again for the same physical system, but using MD simulations with a stochastic heat bath coupling. This technique will be referred to as Langevin simulations.

Details of the investigated model system will be described in Section 2 of this paper. The model may be regarded as a fairly realistic representation of, e.g., a rare-gas monolayer physisorbed on a smooth substrate. The substrate may be assumed to act as a thermal reservoir whose temperature is controlled externally. We are interested mainly in comparing and analyzing the different simulation techniques for this system. The numerical results are presented in Section 3. It is worthwile to stress already at this point that one has to regard the details of the simulation procedure as an integral part of the studied model system. In the case of constant energy conditions a system which has been initialized in a nonequilibrium state and which evolves towards equilibrium in general cannot have a constant temperature. But only under constant energy conditions MD simulations mimic the true physical time evolution of the system, because MD simply involves the solution of Newton's equations of motion. It will be discussed in this paper in what sense the dynamics of a nonequilibrium process under constant mean temperature conditions may be simulated by constant temperature MD or by Langevin dynamics. Generally, there is no *a priori* temporal evolution in MC simulations. However, one often successfully discusses a MC dynamics by taking the random MC steps as a measure of a time unit. This procedure can be justified in many cases through the master-equation description which relates transition probabilities to temporal changes.(12)

In Section 4 we present a Lifshitz–Slyozov type of analysis for the growth mechanism of the liquid clusters. We trace back the origin of the differences between constant-temperature MD simulations and Langevin simulations to the underlying microscopic dynamics of the atoms in the gas phase. In Section 5 we summarize our results. We conclude that the influence of the microscopic dynamics on the scaling properties of the phase-separation process indicates that in contrast to the theory of critical phenomena there might be less "universality" in the domain growth than originally expected. The fractal dimension of the growing clusters is analyzed in the Appendix.

2. NUMERICAL SIMULATIONS OF PHASE SEPARATION

We study a two-dimensional system of 5041 atoms interacting through the Lennard-Jones potential

$$V(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{2}$$

Here, r_{ij} is the interatomic separation and ε, σ are the Lennard-Jones parameters. This potential is known to be a fairly good representation of the interatomic potential for rare-gas atoms. Thus, with appropriate parameters ε, σ our system may be considered as a model for physisorbed rare-gas monolayers on graphite, where a structureless substrate can be assumed.(6)

The molecular dynamics (MD) method(13) invoves the solution of the equations of motion for the particles of our system:

$$\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i \tag{3a}$$

where

$$\mathbf{F}_i = -\nabla_i \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} V(r_{ij}) \tag{3b}$$

During a MD simulation the total energy and the total momentum is conserved, i.e., one employs the microcanonical ensemble. The kinetic energy can be rewritten as

$$\sum_i \frac{\mathbf{p}_i^2}{2m} = \frac{d}{2} N k_B T \tag{4}$$

where d denotes the degrees of freedom per particle. After the system has acquired equilibrium the time average of T is usually referred to as the temperature of the system. However, in a typical experimental situation the substrate temperature determines the temperature of the rare-gas monolayer. Thus the temperature instead of the internal energy is the independent variable. Several numerical procedures have been proposed to fix the mean temperature of the model system.(12) As far as equilibrium properties are concerned these procedures are expected to be equivalent. However, the dynamical phase-separation process is a nonequilibrium phenomenon and the definition of a temperature via Eq. (4) is *a priori* not justified.

The first of the two procedures which we want to discuss in the present paper, has been employed in previous studies of spinodal decomposition in atomic systems. In this simulation technique the atomic velocities are renormalized after each iteration step so that the mean kinetic energy corresponds to the desired temperature. The underlying assumption is that the kinetic energy acquires its equilibrium value in a short period after the quench and that the late stages of the evolution are governed solely by the minimization of the potential energy associated with the liquid–vapor interface. Since only the absolute values of the atomic velocities are changed through the rescaling the particles perform straight flights between subsequent interatomic collisions. Nevertheless, with this procedure, one looses both total energy and total momentum conservation, irrespective of the size of the simulated system. We refer to this method as "velocity renormalization" (VR). To determine the relaxation of the internal excess energy we repeated a run of Ref. 6. In addition, we checked the resulting velocity distribution function, which is an important test since we are dealing with a system of very low initial density and the velocity rescaling provides no mechanism to thermalize the system.

A second procedure to fix the mean temperature is to simulate the system coupled to a heat bath at the desired temperature T. According to Onsager and Machlup(14) this heat bath coupling is described by a friction term $-\Gamma \mathbf{p}_i$ and a random force $\boldsymbol{\eta}_i(t)$. The associated equations of motion are then coupled Langevin equations

$$\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i - \Gamma \mathbf{p}_i + \boldsymbol{\eta}_i(t), \qquad i = 1,..., N \tag{5}$$

The stochastic force $\boldsymbol{\eta}_i(t)$ is assumed to be a Gaussian random vector with the second moment of its components related to the damping Γ and the bath temperature T by the dissipation-fluctuation theorem

$$\langle \eta_i^\alpha(t)\, \eta_j^\alpha(t') \rangle = 2mk_B T \Gamma \delta_{ij}\, \delta(t - t') \tag{6}$$

where k_B denotes the Boltzmann constant.

In contrast to the VR case the propagation direction of the atoms changes randomly due to the noise-source and the particles perform a diffusive type of motion.

In the previous studies(6) the fifth-order Nordsiek–Gear algorithm has been employed to solve the coupled set of deterministic differential equations (3). However, higher-order "predictor-corrector" schemes are not suited to include the effects of stochastic forces consistently.(15) Therefore, it is more appropriate to solve Newton's equations of motion by using the following two-step difference formula(16):

$$\mathbf{v}_i\left(t + \frac{\Delta t}{2}\right) \cong \mathbf{v}_i\left(t - \frac{\Delta t}{2}\right) + \frac{\Delta t}{m} \mathbf{F}_i(\mathbf{r}_1(t),..., \mathbf{r}_N(t)) \tag{7a}$$

$$\mathbf{r}_i(t + \Delta t) \cong \mathbf{r}_i(t) + \Delta t \mathbf{v}_i\left(t + \frac{\Delta t}{2}\right) \tag{7b}$$

which is essentially equivalent to Verlet's centered difference scheme(17)

$$\mathbf{r}_i(t + \Delta t) + \mathbf{r}_i(t - \Delta t) - 2\mathbf{r}_i(t) = \frac{(\Delta t)^2}{m} \mathbf{F}_i(\mathbf{r}_1(t),..., \mathbf{r}_N(t)) \tag{8}$$

In order to integrate the stochastic Langevin equations, formulas (7) have to be modified to include the damping and the random noise source. For a discussion of details of this technique we refer the reader to the work of Schneider and Stoll.(18) Letting $\Gamma \to 0$, Eqs. (5) tend to the Newtonian equations of motion (3) for a microcanonical ensemble. Therefore, Γ must not be chosen too small in order to reach local thermal equilibrium in a reasonable time interval. However, to reduce the modifications of the dynamic properties due to the damping, i.e., to assure that the system is not in the so-called Smoluchovski limit $\Gamma\dot{x} \gg \ddot{x} \simeq \dot{x}/\Delta$, Γ is bounded by the condition

$$\Gamma^{-1} \gg \Delta \tag{9}$$

The results of the Langevin simulations are presented in Section 3.2.

In all numerical procedures we have used a very small integration step of 0.01 ps. This corresponds to $\Delta = 0.005$ in our units of time. For most Langevin simulations we have chosen $\Gamma = 2.5$ which is consistent with condition (9). Some additional runs with $\Gamma = 1.25$, 5.0 were performed in order to check the sensitivity of the results with respect to changes of the damping constant. The remaining parameters which we have to specify are the temperature and the area of the system. The constant area is equivalent to a constant mean density since we are dealing with a fixed number of atoms.

3. SIMULATION RESULTS

3.1. Velocity Renormalization (VR)

For the method of velocity rescaling it has been shown(6) that the memory of the initial configuration is already lost after 3–4 ps. Therefore, it is sufficient to initialize the system by placing the atoms in a triangular lattice at a density $\rho^* = 0.325$ with a Maxwellian velocity distribution corresponding to $T^* = 0.45$ ($\rho^* = \rho\sigma^2$, $T^* = k_B T/\varepsilon$). Hence, the density is the critical density for liquid–vapor coexistence, whereas the temperature is well below the critical temperature $T_c^* = 0.56$.(6)

The detailed analysis of the numerical data has been reported in Ref. 6. For later comparison, we present in Fig. 1 the average size $R(t)$ of the formed liquid clusters as a function of time on a double logarithmic scale. In agreement with previous results we find a crossover for $t \gtrsim 30$ ps to a scaling regime in which $R(t)$ exhibits a simple $t^{1/2}$ power-law behavior.

Let us recall that around 30 ps locally the density extremes have already been achieved, i.e., the density within the clusters reaches that of the equilibrium liquid. The remainder of the phase-separation process is

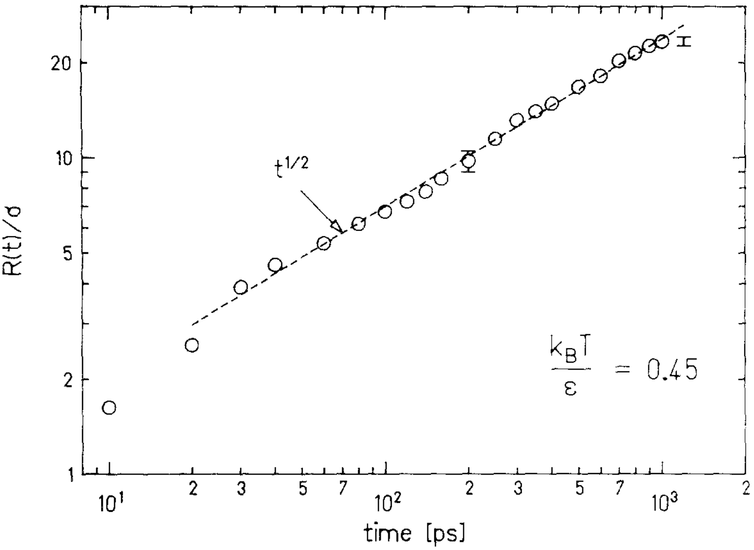

Fig. 1. Cluster size $R(t)$ as a function of time for velocity rescaling (VR).

governed by the growth of isolated clusters. This growth process has been explained in terms of condensation and evaporation of individual atoms (condensation/evaporation mechanism).

To complete the analysis of the VR case we calculated the velocity distribution function for the atoms at various times during the simulation. We did not find any significant deviation from a Maxwellian velocity distribution. Therefore, we conclude that starting with a proper velocity distribution, the velocity rescaling procedure does not lead to artificial features in the distribution function even though we deal with a system of fairly low average density.

3.2. Langevin Simulation

In the Langevin dynamics method, the simulated system is coupled to a heat bath which gives rise to a damping term and to a stochastic force in the equations of motion. We employed this method to simulate spinodal decomposition in the two-dimensional system described above. To investigate the relaxation dynamics of the kinetic energy, we initialized our system at a density $\rho^* = 0.325$ and at a temperature $T^* = 1.0$, i.e., well above the coexistence regime of the liquid-gas phase diagram. Then we quenched the system into this coexistence regime by instantaneously changing the bath temperature to $T^* = 0.45$. We observed a rapid relaxation of the system's kinetic energy superimposed to the spatial phase separation process.

The kinetic energy per particle as a function of time is shown in Fig. 2. It relaxes within 10 ps to its equilibrium value. Because of condition (9) this rapid relaxation is clearly not a consequence of an overdamping of the system. Moreover, the order of magnitude of the relaxation time is independent of the damping constant for our chosen range of values. Again, we have checked the velocity distribution and found good agreement with the exact Maxwell distribution corresponding to $T^* = 0.45$.

We analyzed the temporal evolution of the system's morphology and determined the average cluster size $R(t)$ (Fig. 3). We observe a short transient period for $t \lesssim 40$ ps but in contrast to Fig. 1 the determination of the scaling regime appears to be ambiguous. Even though for late times $\gtrsim 250$ ps $R(t)$ evolves according to the power-law (1a) with $X \simeq 1/4$ we cannot completely rule out the existence of the intermediate interval $50\text{ ps} \lesssim t \lesssim 250$ ps characterized by a power-law behavior with distrinctly smaller exponent $X \simeq 1/5$. Figure 4 shows this feature to be independent of the damping constant Γ.

Several authors$^{(4,19,20)}$ have discussed the situation in which a crossover between various power laws for $R(t)$ occurs, leading to a curvature on a double-logarithmic plot of $R(t)$ versus t. However, in the

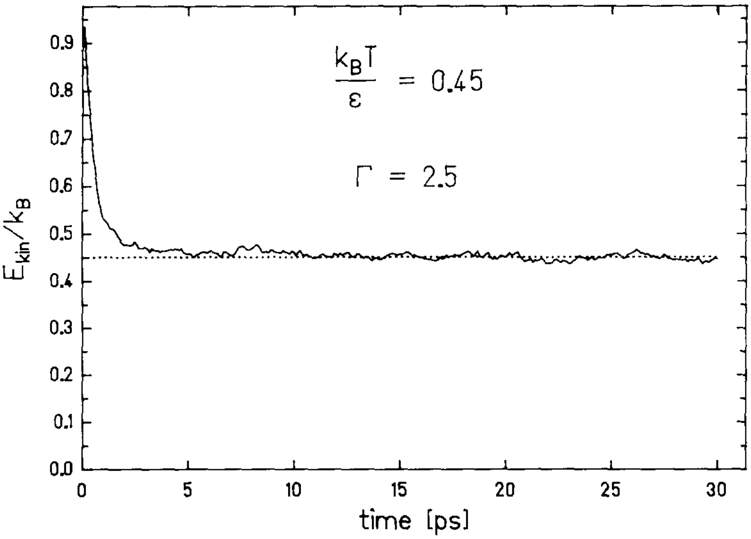

Fig. 2. Time evolution of the kinetic energy vs. time for the Langevin simulation with the damping constant $\Gamma = 2.5$.

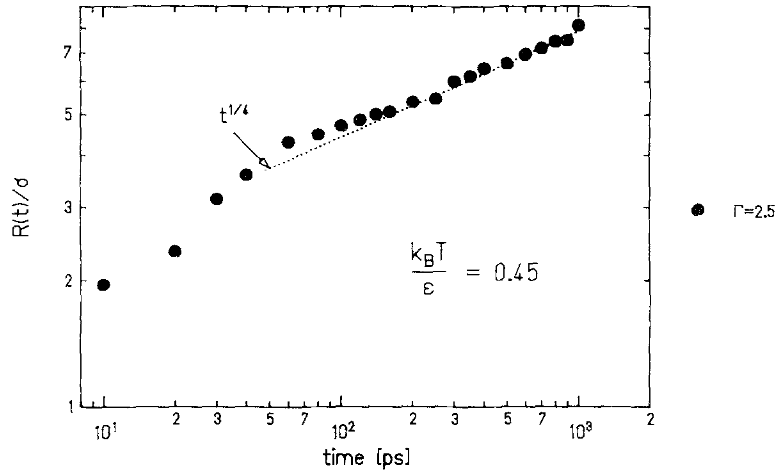

Fig. 3. Cluster size $R(t)$ as a function of time for the Langevin Simulation ($\Gamma = 2.5$).

present study we are not interested in this intermediate regime we only want to determine whether one finds scaling at all. A careful analysis of the temporal evolution of the atomic configurations suggests that the $t^{1/4}$ growth stage may be characterized in the same way as the $t^{1/2}$ regime in Fig. 1. Independent of the simulation method the morphologies corresponding to the same value of $R(t)$ are similar. In Fig. 5, the scaled

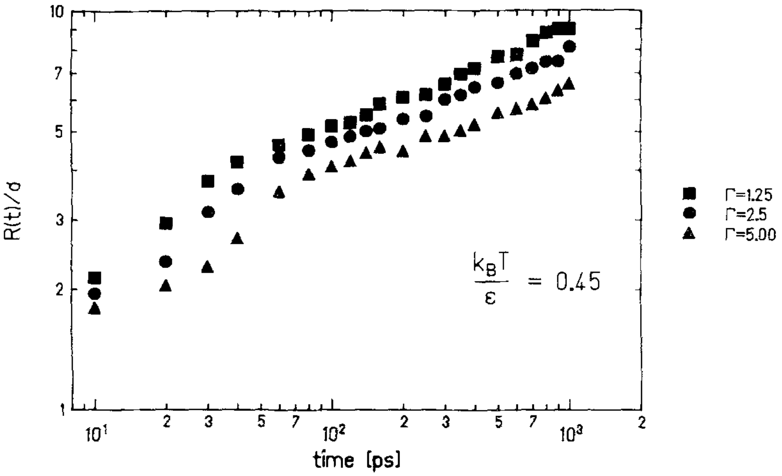

Fig. 4. Comparison of the temporal evolution of the cluster size $R(t)$ for Langevin simulations with different damping constants: $\Gamma = 1.25$ (■), 2.5 (●), 5.0 (▲).

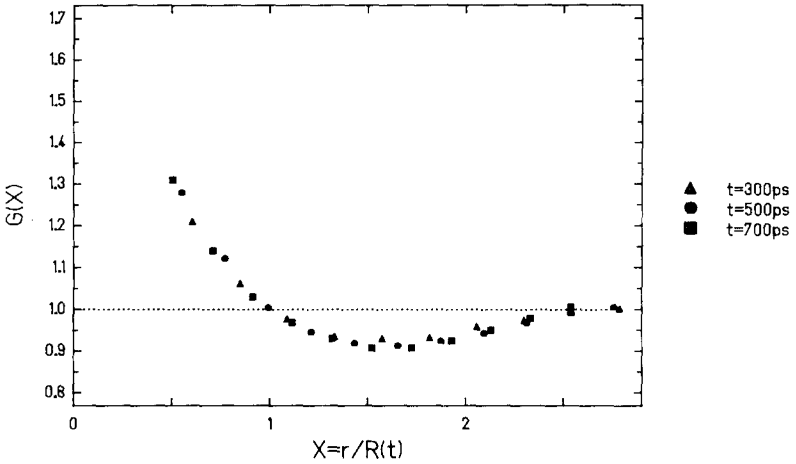

Fig. 5. Scaled radial distribution function $G(x)$, $x = r/R(t)$ for the late time regime of the Langevin simulation ($\Gamma = 2.5$): $t = 300$ psec (▲), 500 psec (●), 700 psec (■).

coarse-grain radial distribution function is presented for various times. From the good scaling invariance we conclude as in Ref. 6 that the density morphology remains approximately topologically invariant, but the actual spatial extension of the density domains expands as $R(t)$. Moreover, we show in Section 4 that the $t^{1/4}$ power-law behavior may be the result of the evaporation–condensation mechanism taking into account that in Langevin simulations the microscopic dynamics of the atoms between two collisions—diffusion instead of straight flight—is different in comparison to VR.

3.3. Time Evolution of the Excess Energy

In general, the exponent X in the power law (1b) for the average cluster size $R(t)$ is different from the exponent Y in the decay law (1c) for the internal excess energy. However, we observe that the late stage of the phase separation process is dominated by the growth of isolated clusters. Therefore, the excess energy $E(t) - E_\infty$ is basically the total surface energy of $N(t)$ liquid clusters of average size $R(t)$ and one expects X and Y to be related.$^{(7)}$

The excess energy is given by

$$E(t) - E_\infty \simeq N(t)\, R(t)^{d-1} \tag{10a}$$

Conservation of the total concentration yields

$$N(t)\, R(t)^d = \text{const} \tag{10b}$$

Thus, $N(t)$ can be eliminated and one finds

$$E(t) - E_\infty \simeq R(t)^{-1} \tag{11}$$

i.e.,

$$X = Y \tag{12}$$

We show in Appendix A that a Lifshitz–Slyozov type of analysis$^{(8)}$ yields the same result.

In order to check this conjecture we analyzed the potential energy data of our various simulations. It turned out to be quite hard to establish the asymptotic decay law because the excess energy $E(t) - E_\infty$ is a small quantity and we did not perform sufficiently many independent runs to average out statistical fluctuations. Moreover, in the simulations, the final equilibrium state is not reached and E_∞ remains unknown. Even if one extends the simulation time, finite size effects eventually prohibit the determination of the proper value for E_∞. However, assuming that the equilibrium energy of the system with two coexistence phases will be given approximately as the sum of the equilibrium energy of the pure phases plus the contribution of the system's interfacial energy, E_∞ could be determined from simulations of the liquid–vapor interface. On the other hand, there is no reason to expect different E_∞ values for VR and Langevin simulations. Hence one may postulate

$$E_L(t) - E_R(t) \simeq C_L t^{-Y_L} - C_R t^{-Y_R} \tag{13}$$

(R and L refer to VR and Langevin dynamics, respectively.) This relation can be tested by plotting $[E_L(t) - E_R(t)]\, t^{Y_R}$ versus $t^{Y_R - Y_L}$. Despite the statistical scattering of the simulation results, we find that a combination $Y_R = 1/2$, $Y_L = 1/4$ is definitely not consistent with the data for $t > 50$ ps. Instead the set of parameters

$$\begin{aligned} E_\infty &\simeq -2.01 \\ Y_R &\simeq 1/2 \\ Y_L &\simeq 1/5 \end{aligned} \tag{14}$$

appears to be more appropriate. The time evolution of the excess energy for these parameters is shown in Figs. 6 and 7. Whereas (14) confirms relation (12) in the case of VR, Fig. 7 provides further evidence for an intermediate time interval of the phase separation process preceding the

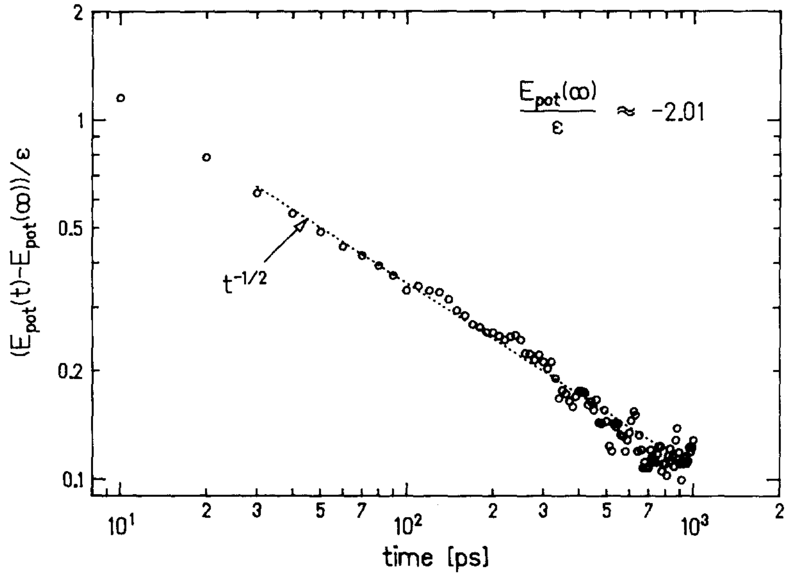

Fig. 6. Excess potential energy $[E_{pot}(t)-E_{pot}(\infty)]/\varepsilon$ for the velocity rescaling simulation (VR).

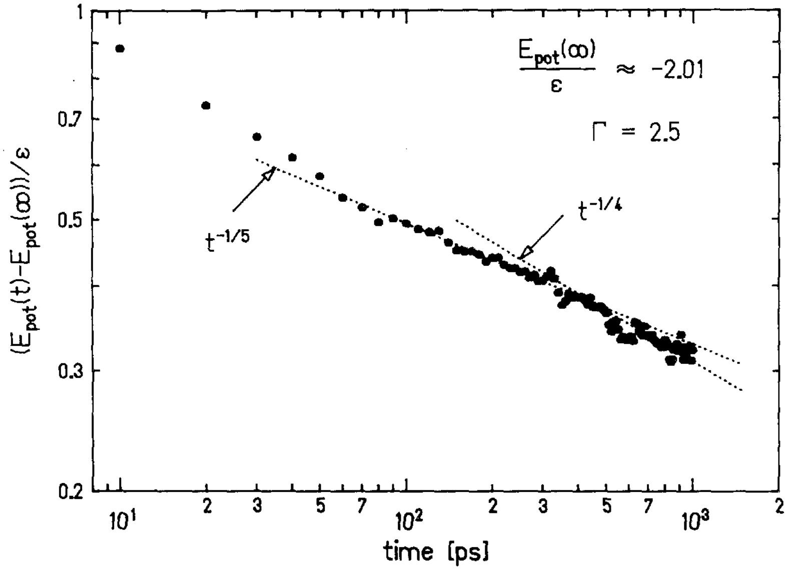

Fig. 7. Excess potential energy $[E_{pot}(t)-E_{pot}(\infty)]/\varepsilon$ for the Langevin simulation ($\Gamma = 2.5$).

asymptotic regime. However, this observation requires further confirmation. In order to ascentain a crossover from $Y=1/5$ to $Y=1/4$ in the scaling regime, additional independent runs are necessary to suppress statistical scattering of the data. Moreover, a determination of E_∞ might be of value.

4. ANALYSIS OF THE SIMULATION RESULTS

An analysis of the fractal dimension D (for details see Appendix B[3]) of the liquid clusters yields $D \sim 1.8$. However, the most important result of the different simulations is that the data (Fig. 9) reveal no significant differen-

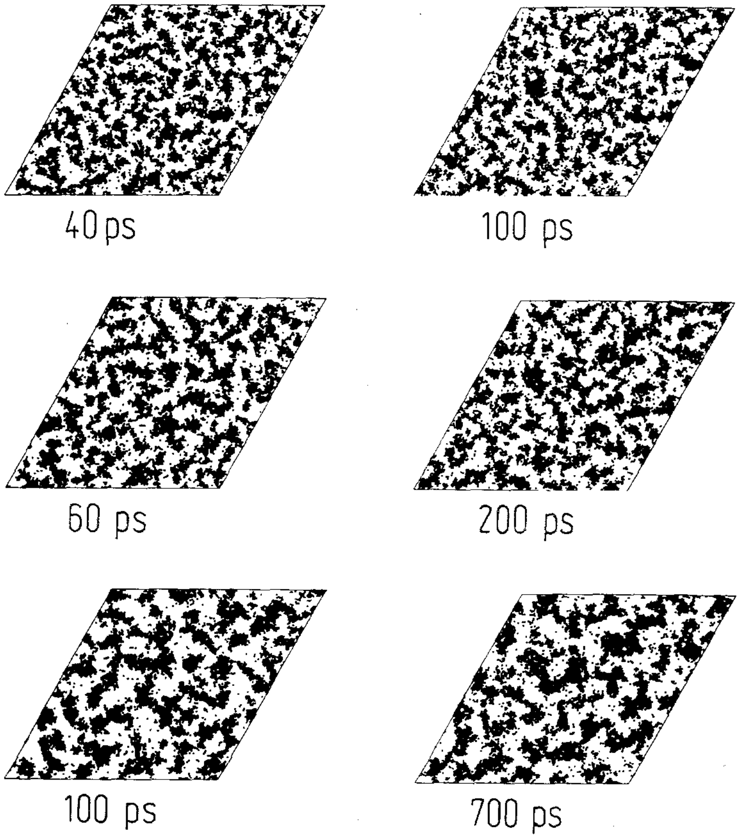

Fig. 8. Snapshots of the cluster growth pattern obtained from velocity rescaling (VR) (left column) and Langevin dynamics (ight column). Each pair of snapshots is chosen to have equal mean cluster radius $R(t) = 4.7, 5.3, 7.1$.

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[3] A similar analysis of the fractal dimension has been performed recently by R. C. Desai *et al.*(22)

ces in the structure of clusters obtained with VR or Langevin dynamics. In addition, atomic configurations are similar if chosen in such a way that the corresponding values of the mean cluster radius $R(t)$ agree (Fig. 8). The major difference between the VR and the Langevin simulation results is the different growth-law exponent X. In this respect the Langevin simulation results are in agreement with the growth law obtained with MC simulations of the kinetic Ising model (cf. MC I in Ref. 11).

In Ref. 6 an asymptotic analysis of a cluster growth equation has been presented, which explains the exponent $X = 1/2$ found for VR. In the following, we want to show how this analysis may be modified to be also consistent with the Langevin simulation results. The original Lifshitz–Slyozov analysis,$^{(8)}$ which yields $X = 1/3$, does not apply here, because it has been performed for a two-component system.

Under the assumption that the number of gas atoms impinging on a liquid cluster is proportional to the thermal velocity of the atoms, the equation

$$\frac{dR}{dt} \sim v_{\text{th}} \left[\frac{1}{R_c(t)} - \frac{1}{R} \right]$$

has been derived for the average cluster radius R.$^{(6,25)}$ Here, $R_c(t)$ is the radius of the critical cluster, which is inversely proportional to the supersaturation of the gas phase. The concept of a critical cluster is appropriate since, as already mentioned in the Introduction, after the initial phase separation period there is no difference in the morphology of systems initially quenched to an unstable or to a metastable state of the phase diagram. With

$$R_c(t) \sim R$$

and the ansatz

$$R \sim t^{X_R}$$

one finds

$$X_R = 1/2$$

in agreement with Section 3.1.

However, for a diffusive type of motion the propagation direction of the atoms changes permanently and the mean atomic displacement Δr is given by

$$\Delta r = (Dt)^{1/2} \tag{16}$$

where D is the diffusion coefficient due to the heat bath coupling. For Langevin dynamics, relation (16) replaces $r = v_{\text{th}} t$ which is valid for VR. Consequently, the number of atoms arriving at a cluster depends on the "mean velocity"

$$v_{\text{av}} \sim \frac{\Delta r}{t} = \left(\frac{D}{t}\right)^{1/2} \tag{17}$$

Therefore, in the gain rate g_n [Eq. (8b) of Ref. 6] of the condensation–evaporation mechanism the thermal velocity v_{th} has to be replaced by v_{av} (17). Concerning the emission of atoms from the cluster one has to take into account detailed balance. For diffusion dynamics the atoms effectively remain longer in the vicinity of the cluster and recapturing of atoms by the cluster is enhanced resulting in a reduction of the loss rate l_n [Eq. (8d) of Ref. 6] by a factor of order $v_{\text{av}}/v_{\text{th}}$. With both identifications one gets

$$\frac{dR}{dt} \sim t^{-\gamma} \left[\frac{1}{R_c(t)} - \frac{1}{R}\right] \tag{18}$$

with $\gamma = 1/2$. The only difference of (18) in comparison to Eq. (14) is the replacement of v_{th} by v_{av}. The ansatz

$$R \sim t^{X_L}$$

leads to

$$X_L = \frac{1-\gamma}{2} = \frac{1}{4} \tag{19}$$

in agreement with the behavior discussed in Section 3.2.

5. SUMMARY AND CONCLUSIONS

We have described, analyzed, and compared data obtained from two different molecular dynamics simulation techniques which both were applied to simulate a system undergoing phase separation by spinodal decomposition under isothermal conditions. In the case of the velocity rescaling procedure, we found a power law growth for the liquid clusters with an exponent $X_R = 1/2$. Also the decay of the excess internal energy was found to exhibit a simple t^{-Y_R} behavior with $Y_R = X_R$. This scenarium is readily understandable for the growth of isolated clusters in the asymptotic time regime.

The atomic velocity distribution for both numerical methods is in good agreement with a Maxwell velocity distribution corresponding to the desired mean temperature $T^* = 0.45$. In contrast to the Langevin simulations this result is not self-evident in the case of VR, since this method provides no mechanism to establish the proper velocity distribution. Another important finding from the Langevin simulations is the fast relaxation of the kinetic energy in response to a change of the bath temperature.

From the comparison between the constant temperature MD, the MC, and the Langevin simulations, one may conclude that there is less universality in cluster growth than originally expected. For example, in MC simulations the choosen computer algorithms for the MC-steps becomes an integral part of the model. In the same way the results of MD simulations are affected by the underlying microscopic dynamics. Note, however, that the agreement of the respective growth laws found in MC (MC I in Ref. 11) and Langevin simulations is a consequence of the fact that the corresponding microscopic dynamics is equivalent in these cases. A similar observation has been reported by Meakin *et al.*⁽²¹⁾ for spinodal decomposition in a two-component system.

APPENDIX A

The power-law behavior

$$R(t) \propto t^X \tag{A1}$$

of the mean cluster radius $R(t)$ can be explained in terms of a condensation-evaporation mechanism (cf. Section 4). In this Appendix we show that a Lifshitz–Slyozov type of analysis⁽⁸⁾ of the same mechanism yields in addition

$$E(t) - E(\infty) \propto t^{-Y} \tag{A2}$$

with

$$Y \equiv X \tag{A3}$$

confirming equations (11) and (12) in Section 3.3.

As already discussed by Binder,⁽⁷⁾ in the asymptotic regime the probability $\rho(n, t)$ to find a cluster with n atoms at time t may be represented by a scaling solution

$$\rho(n, t) = t^z \tilde{\rho}(\xi) \tag{A4}$$

where $\xi = nt^{-dX}$ and $\tilde{\rho}$ is the appropriate scaling function. Conservation of the total number of atoms implies

$$\begin{aligned} 0 &= \frac{d}{dt}\left[\int_0^\infty dn\, n\rho(n, t)\right] \\ &\propto \frac{d}{dt}\left[t^{2dX} t^z \int_0^\infty d\xi\, \xi\tilde{\rho}(\xi)\right] \end{aligned}$$

Since the last integral has to be time-independent, one obtains

$$z = -2\, dX \tag{A5}$$

for the exponent in (A4).

For the surface energy of a cluster with n atoms one has

$$E_n \propto n^{(d-1)/d}$$

Hence, the excess energy is

$$\begin{aligned} E(t) - E(\infty) &= \int_0^\infty dn\, E_n \rho(n, t) \\ &\propto t^{dX + X(d-1) + z} \int_0^\infty d\xi\, \xi^{(d-1)/d} \tilde{\rho}(\xi) \end{aligned}$$

Employing relation (A5) we obtain the result (A2), (A3)

$$E(t) - E(\infty) \propto t^{-X}$$

APPENDIX B

The concept of the fractal dimension D provides a quantitative measure to characterize the structure of the liquid clusters. The number of particles N in a cluster of radius R behaves like$^{(23)}$

$$N \propto R^D \tag{B1}$$

We obtained $N(R)$ from the cluster size distribution using the algorithm outlined in Ref. 24. A least squares fit of the data for $N(R)$ to the form (B1) yields D with an error of order 0.05. In Fig. 9 the results are plotted versus time after the crossover to the scaling regime has occured at the respective time t^*. The data clearly indicate that D is definitely smaller than the Euclidian dimension $d = 2$. Independent of the simulation method we find $D \approx 1.8$.

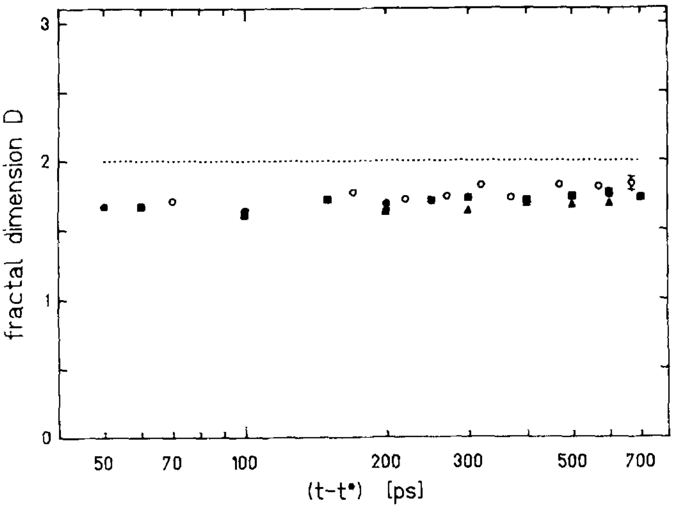

Fig. 9. Fractal dimension D for velocity rescaling (VR) (○) and Langevin dynamics [$\Gamma = 1.25$ (■), 2.5 (●), 5 (▲)] versus time after crossover to the scaling regime at t^*.

This result is consistent with another estimate of D using the coarse-grain radial distribution function $G(r)$. For $1 \ll r \ll R$ it scales like[4]

$$G(r) \propto r^{-A} \tag{B2}$$

with

$$A + D = d$$

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[4] The analysis in Ref. 6 and Appendix A of the present paper is based on the assumption that "surface" and "volume" are determined by the same dimension d. Under this assumption the asymptotic results are found to be independent of d. Possible effects due to the fractal nature of the growing clusters are neglected. They will be investigated in future work. (The authors thank Prof. D. Stauffer for pointing out this problem.)

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