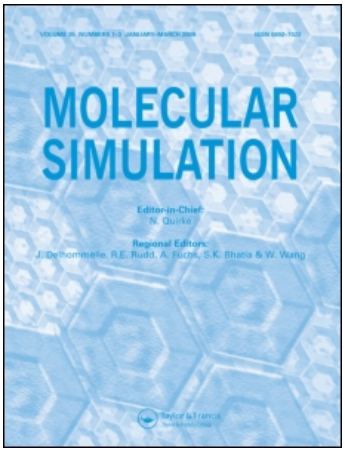

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Computer Simulation of Vapor-Liquid Phase Separation

Ryoichi Yamamoto[a]; Koichiro Nakanishi[b]
[a] Division of Science of Materials, Graduate School of Science and Technology, Kobe University, Kobe, Japan [b] Division of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan

To cite this Article Yamamoto, Ryoichi and Nakanishi, Koichiro(1996) 'Computer Simulation of Vapor-Liquid Phase Separation', Molecular Simulation, 16: 1, 119 — 126
To link to this Article: DOI: 10.1080/08927029608024066
URL: http://dx.doi.org/10.1080/08927029608024066

Molecular Simulation, 1996, Vol. 16, pp. 119–126
Reprints available directly from the publisher
Photocopying permitted by license only

COMPUTER SIMULATION OF VAPOR-LIQUID PHASE SEPARATION

RYOICHI YAMAMOTO

Division of Science of Materials, Graduate School of Science and Technology, Kobe University, Kobe 657, Japan

KOICHIRO NAKANISHI

Division of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-01, Japan

(Received February 1995, accepted May 1995)

A late-time growth law of domains undergoing vapor-liquid phase separation is studied for two- and three-dimensional Lennard-Jones fluids by molecular dynamics simulations. The characteristic domain size shows a power law growth in a late stage with the growth exponent of 1/2 for both two- and three-dimensional fluids. This study concerns also the relationship between statistical properties of domain patterns and temperatures. The asymptotic form factor of each system is obtained using scaling and the asymptotic tail of the form factor is analyzed. This tail is related to the domain-wall structure. At low system temperatures, the form factor satisfies Porod's law; the asymptotic tail decreases as $S(k) \sim k^{-(D+1)}$ where D is the system dimensionality. However, it is found that the decay of the asymptotic tail becomes slower than that of the Porod tail at higher temperatures in both two- and three-dimensional systems. This indicates that the dimension of the domain wall is fractal and increases with increasing system temperature.

KEY WORDS: Domain growth, domain structure, fractal surface, vapor-liquid phase separation.

1 INTRODUCTION

Phase separations exhibit many complicated pattern formations far from equilibrium. It is of interest to study statistical properties of domain patterns and its growth dynamics [1]. The growth law of the domain size has been extensively investigated by means of computer simulation. Phase separations can generally be put into two categories: those of a conserved order parameter and those of a nonconserved order parameter. In vapor-liquid phase separation, the order parameter is the local density of fluids. Since the total density of the system is conserved, this process is believed to belong to the case of a conserved order parameter. The following two models have been widely employed in numerical studies of conserved systems [1]. One is the Kawasaki model which is a conserved-order-parameter version of the kinetic Ising model; the other one is given by the Cahn-Hilliard-Cook (CHC) equation based on a phenomenological theory. The CHC

equation corresponds to a conserved-order-parameter version of the time-dependent Ginzburg-Landau equation and have been applied to many complex fluid systems such as surfactant solutions [2] with some modifications. Computer simulations using these models provide evolutions of domain patterns during phase separation, showing that there exists an apparent scaling property in the course of evolution [1,3,4]. In a late-time stage of the phase separation, it has been found that the temporal patterns are statistically equivalent to each other if they are scaled by the proper time-dependent characteristic length which exhibits a power law growth. Molecular dynamics (MD) simulation enables us to study phase separations in more realistic fluids such as Lennard-Jones (LJ) fluids [5–8]. An advantage of MD simulation is that static and dynamic correlations as well as hydrodynamic effects are taken into consideration. In this study, we investigate accurately the dynamics of vapor-liquid phase separation in two- and three-dimensional fluids via MD simulations with a 50000-particle system for two dimensions and with a 78732-particle system for three dimensions.

Another important finding from MD simulation is a fractal nature observed in domain patterns undergoing phase separation. Schöbinger *et al.* [9] have performed a constant temperature Langevin dynamics simulation for the two-dimensional LJ fluid at a reduced temperature $T^* = 0.45$ [10]. They found that the capacity dimension of the domain (liquid cluster) is 1.8, being significantly smaller than the Euclidean dimension of two. Desai and Denton [11] have performed a constant-NVE MD simulation for the two-dimensional LJ fluid at a reduced temperature $T^* \approx 0.5$ and found that the domain has a capacity dimension of 1.7. In the present study, we investigate the relationship between statistical properties of domain patterns and temperatures by means of MD simulation. The asymptotic form factor of the domain pattern is determined for various temperatures using scaling and its temperature dependence is studied. In particular, we analyze the asymptotic behavior of the form factor in the large-wavenumber limit to determine the domain-wall structure.

2 SIMULATION METHODOLOGY

We used a 50000-particle system for a two-dimensional fluid and a 78732-particle system for a three-dimensional fluid. In both two- and three-dimensional fluids, each particle interacts through the LJ potential with a cutoff length r_{cut} of 2.7σ. The leapfrog algorithm was used with an integration time step of 0.01τ, where $\tau = \sqrt{m\sigma^2/4\varepsilon}$ is the unit time of the LJ fluid. In the present MD simulations we carried out instantaneous quenching of homogeneous systems which are initially equilibrated at the supercritical (one phase) region, into an unstable (two phase) region. After the quenching, the system was annealed at a constant temperature by the constraint isotherm method [2].

We performed three simulation runs (A–C) for the two-dimensional LJ fluid (critical temperature $T_c^* \approx 0.56$), and another three runs (D–F) for the three-dimensional LJ fluid (critical temperature $T_c^* \approx 1.35$). The simulation conditions are summarized in Table 1. The raw structure factors $S(k,t)$ was calculated directly from particle configurations. $S(k,t)$ can be divided into two parts: a macroscopic part which determines the domain pattern, and a microscopic part which represents a

Table 1 Simulation conditions.

Run	*Dimension*	*N*	*Before quenching*		*After quenching*		*Time* (τ)
			ρ^*	T^*	ρ^*	T^*	
Sim. A	2	50000	0.325	0.80	0.325	0.35	220
Sim. B	2	50000	0.325	0.80	0.325	0.41	300
Sim. C	2	50000	0.325	0.80	0.325	0.45	300
Sim. D	3	78732	0.350	1.80	0.350	0.70	50
Sim. E	3	78732	0.350	1.80	0.350	0.80	70
Sim. F	3	78732	0.350	1.80	0.350	0.90	100

short-ranged particle-particle correlation. In this study we are only interested in the macroscopic part, that is, the form factor of the domain pattern. To eliminate the microscopic part of the raw structure factor, we define $\tilde{S}(k,t)$:

$$\tilde{S}(k,t) \equiv S(k,t) - S^{eq}(k,T^*), \tag{1}$$

where $S^{eq}(k,T^*)$ denotes the equilibrium structure factor for a fully segregated macroscopic two-phase system at a temperature T^*. We have determined $S^{eq}(k,T^*)$ by quenching a smaller simulation system to the temperature T^* on the coexistence curve and waiting for the system to reach an equilibrium. Thus, $\tilde{S}(k,t)$ stands for the form factor of the pattern. The first moment of the wavenumber $k_1(t)$ was determined by

$$k_1(t) = \frac{\int_0^{k_{cut}} k\tilde{S}(k,t)\,dk}{\int_0^{k_{cut}} \tilde{S}(k,t)\,dk}, \tag{2}$$

which measures a characteristic domain size of the system. Here k_{cut} is an appropriate cutoff wavenumber, and $k_{cut} = \pi/\sigma$ is adopted in this work.

To determine the asymptotic form factor of the domain patterns, scaling was used;

$$F(x) = (k_1)^D \tilde{S}(k,t), \tag{3}$$

where $F(x)$ is a time-independent master form factor, D is the dimensionality of the system, and x is the reduced wavenumber defined as k/k_1.

3 RESULTS AND DISCUSSIONS

3.1 Growth Law

Temporal particle configurations from simulation B are shown in Figure 1 as an example. One can see that the phase separation begins immediately after the quench and the domain size increase with time. Time evolutions of the first moment of the wavenumber $k_1(t)$ for two-and three-dimensional fluids were shown in Figures 2 and 3, respectively. One can find that a power law growth clearly exists in the late-time region. The growth exponent is given by the negative of the slope; these are

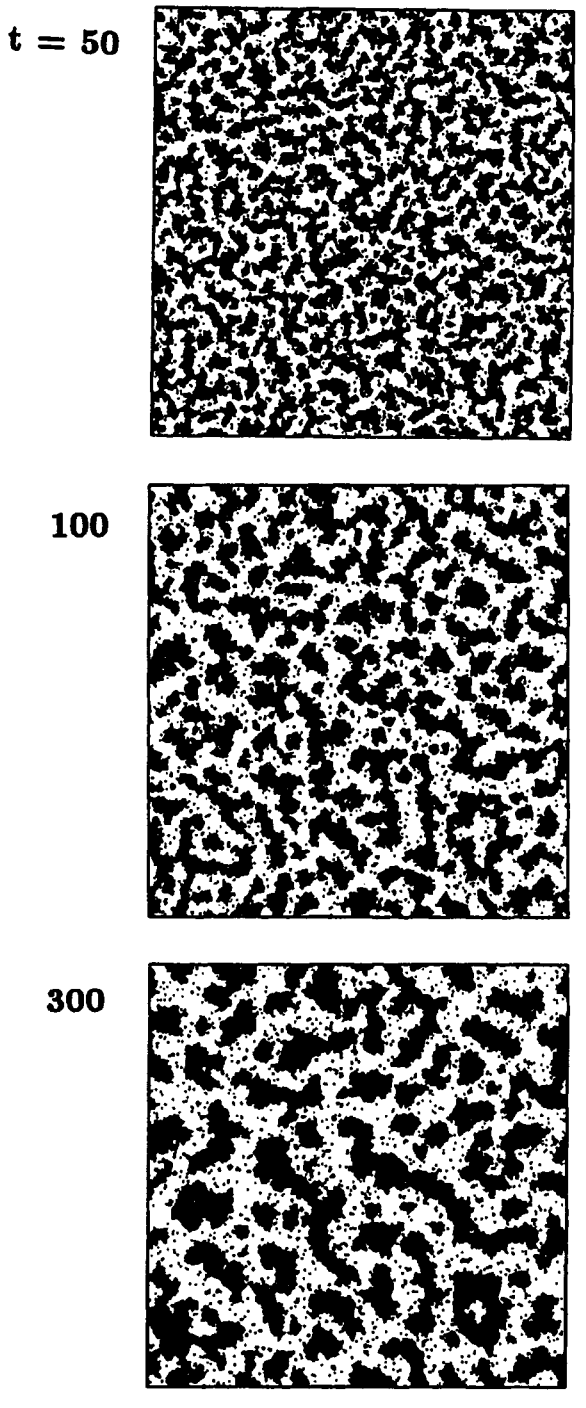

Figure 1 *Snapshots from* Simulation B ($T^* = 0.41$). The labels refer to simulation time in the reduced unit.

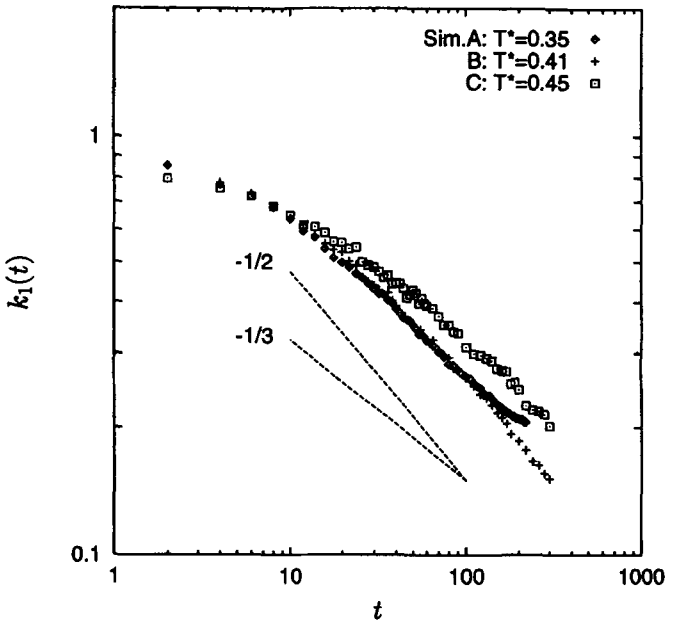

Figure 2 The first moment of the wavenumber $k_1(t)$ versus simulation time for the two-dimensional system. The dashed lines show slopes of $-1/2$ and $-1/3$ for a comparison. The growth exponent converges to $-1/2$ at late stages.

summarized in Table 2. Volume fractions ϕ of the liquid phase is simply estimated from phase diagrams of the fluids [13] because the domain growth in the presence of hydrodynamic effects is known to be sensitive to the morphology of the domain pattern. These are also listed in Table 2. The asymptotic growth exponent seems to converge to 1/2 in both two and three dimensions; it is clearly larger than 1/3 which were obtained for systems neglecting hydrodynamic effects. The growth exponent is apparently smaller than 1/2 only for simulation A. This is attributed to either (or both) of the following reasons: 1) since the triple point temperature of the two-dimensional LJ fluid is about 0.41, simulation A corresponds to a vapor-solid separation rather than vapor-liquid one, 2) liquid domains are no more bicontinuous in the late stage because of the small volume fraction ($\phi = 0.38$). It is also found that thermal noise has no effect on the asymptotic exponent, but gives rise to a substantial delay of the transition time till the asymptotic regime is reached.

The present MD results strongly suggest that the growth exponent is 1/2 for vapor-liquid phase separations and independent of the system dimensionality. This is consistent with the theoretical analysis [5] of Koch *et al.* However, there is another theoretical prediction for the growth exponent for binary-fluid-mixtures including hydrodynamic effects. It is generally believed that the vapor-liquid system belongs to the same universality class as the binary-fluid-mixture (liquid-liquid) system. The theory predicts that the growth exponent is 1/2 for two-dimensional [14] and unity for three dimensional [15] liquid-liquid systems in late stages. Our two-dimensional results agree with the theory, but three-dimensional results

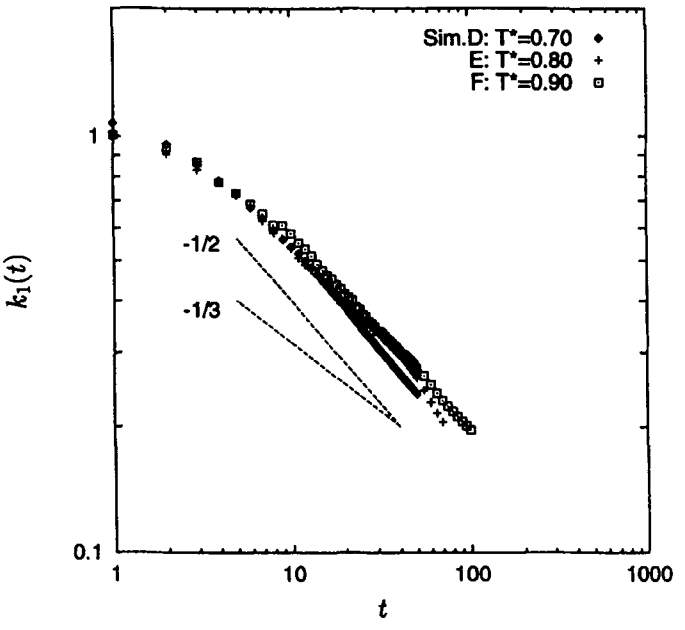

Figure 3 The first moment of the wavenumber $k_1(t)$ versus simulation time for the three-dimensional system. The dashed lines show slopes of $-1/2$ and $-1/3$ for a comparison. The growth exponent converges to $-1/2$ at late stages.

Table 2 Simulation results for the growth exponent.

Run	T^*	*Exponent*[a]	σ_s^b	ϕ
Sim. A	0.35	0.34[c]	0.006	0.38
Sim. B	0.41	0.50	0.008	0.42
Sim. C	0.45	0.47	0.030	0.42
Sim. D	0.70	0.53	0.002	0.41
Sim. E	0.80	0.51	0.012	0.44
Sim. F	0.90	0.48	0.004	0.47

[a] Evaluated by least-squares fitting of the present data.
[b] Standard deviation according to the present data fitting.
[c] Since the triple point temperature of this fluid is about 0.41, simulation A corresponds to vapor-solid separation rather than vapor-liquid. This is why the exponent is 1/3, which is apparently smaller than 1/2.

contradict with it. We think that it is difficult to reach final conclusion only from simulation results; a strong theoretical explanations are needed for the three-dimensional vapor-liquid system.

3.2 *Domain Structures*

The asymptotic tail of the form factor is related to the domain-wall structure [16]. It is widely known that the master form factor follows Porod's law in the large

Table 3 Simulation results for the domain-wall dimension.

Run	T^*	*Slope*[a]	σ_s^b	F_s
Sim. A	0.35	−2.7	0.064	1.3
Sim. B	0.41	−2.4	0.080	1.6
Sim. C	0.45	−2.2	0.080	1.8
Sim. D	0.70	−4.0	0.072	2.0
Sim. E	0.80	−3.6	0.082	2.4
Sim. F	0.90	−3.0	0.109	3.0

[a] Evaluated by least-squares fitting of the present data.
[b] Standard deviation according to the present data fitting.

wavenumber limit;

$$F(x) \sim x^{-(D+1)}. \tag{4}$$

Porod's law has been extended to the case of a rough interface as follows,

$$F(x) \sim x^{-(2D-F_s)}, \tag{5}$$

where F_s is the fractal dimension of the domain wall. Equation (5) indicates that the decay of the asymptotic tail of the master form factor for a fractal domain wall is slower than that of the Porod tail. If the domain has a smooth interface, that is, if $F_s = D - 1$, then Equation (5) reduces to Porod's law. According to Equation (5), the asymptotic tail in the large-wavenumber limit follows a straight line with a slope equals to $-(2D - F_s)$. We analyzed the form factor obtained from the present MD simulations. It turns out that the asymptotic tail satisfies Porod's law at low temperatures, whereas significant discrepancies are observed at higher temperatures. The fractal dimensions of the domain wall is determined from the slope of the tail. The domain-wall dimension F_S obtained is listed in Table 3. It is clear that the fractal dimension of the domain wall increases with increasing temperature.

4 CONCLUSION

We have carried out large scale MD simulations for two- and three-dimensional LJ fluids in order to investigate accurately the growth law of the domain. The characteristic domain size $l(t)$ was found to grow as $l(t) \sim t^a$ in the late-time regime. It was also found that the asymptotic growth exponent is 1/2 in both two and three dimensions. This strongly suggest that the growth exponent is independent of the system dimensionality according to the vapor-liquid phase separation. Thermal noise was found to have no effect on the asymptotic exponent, but to give rise to a substantial delay of the transition time to the asymptotic regime.

Statistical properties of the domain pattern were also investigated in terms of system temperatures. We analyzed the asymptotic behavior of the master form factor of the domain pattern. If the domain wall is smooth, the tail should follow Porod's law. Indeed, we found that the form factor satisfies Porod's law only at low temperatures. The slope of the asymptotic tail in a log-log plot becomes less than that of Porod's law at higher temperatures. This shows that the domain wall is not

smooth but has a fractal nature at higher temperatures. We have observed that the fractal dimension of the domain wall increases with increasing temperature.

Acknowledgments

R.Y. would like to thank Professors H. Tomita and Y. Hiwatari for helpful discussions. He acknowledges also Professor Y. Kawamoto for continuous encouragements. Calculations were carried out at the Supercomputer Laboratory of the Institute for Chemical Research, Kyoto University and the Computer Center of the Institute for Molecular Science, Okazaki, Japan.

References

[1] J. D. Gunton, M. San Miguel, and P. S. Sahni, "The dynamics of first-order phase transitions" in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz, (Academic, New York, 1983), Vol. 8.

[2] T. Kawakatsu, "Computer simulations of phase separations in surfactant solutions" in *Proceedings of the International Symposium on Molecular Simulation*, edited by A. Ueda (Fukui, 1994); T. Kawakatsu, K. Kawasaki, M. Furusaka, H. Okabayashi, and T. Kanaya, " Theories and computer simulations of self-assembling surfactant solutions"*J. Phys.: Condens. Matt.*, **6**, 6385 (1994).

[3] A. Sadiq and K. Binder, "Dynamics of the formation of two-dimensional ordered structures" *J. Stat. Phys.*, **35**, 517 (1984).

[4] Y. Oono and S. Puri, "Study of phase-separation dynamics by use of cell dynamical systems. I. Modeling" *Phys. Rev.*, **A38**, 434 (1988); "Study of phase-separation dynamics by cell dynamical systems. II. Two dimensional demonstrations" **38**, 1542 (1988).

[5] S. W. Koch, R. C. Desai, and F. F. Abraham, "Dynamics of phase separation in two-dimensional fluids: Spinodal decomposition" *Phys. Rev.*, **A27**, 2152 (1983).

[6] W-J. Ma, A. Maritan, J. R. Banavar, and J. Koplik, "Dynamics of phase separation of binary fluids" *Phys. Rev.*, **A45**, R5347 (1992).

[7] E. Velasco and S. Toxvaerd, "Computer simulation of phase separation in a two-dimensional binary fluid mixture" *Phys. Rev. Lett.*, **71**, 388 (1993); P. Ossadnik, M. F. Gyure, and H. E. Stanley, Comment on "Computer simulation of phase separation in a two-dimensional binary fluid mixture" *ibid.* **72**, 2498 (1994).

[8] R. Yamamoto and K. Nakanishi, "Computer simulation of vapor-liquid phase separation in two- and three-dimensional fluids: Growth law of domain size" *Phys. Rev.*, **B49**, 14958 (1994): "Computer simulation of vapor-liquid phase separation in two- and three-dimensional fluids. II. Domain structure" *Phys. Rev.*, **B51**, 2715 (1995).

[9] M. Schöbinger, S. W. Koch, and F. F. Abraham, "Langevin dynamics simulation of phase separation in a one-component system" *J. Stat. Phys.*, **42**, 1071 (1986).

[10] The asterisk denotes the reduced quantities according to the LJ parameters σ and ε, *i.e.*, $T^* = Tk_B/\varepsilon$ and $\rho^* = \rho\sigma^3$. These reduced quantities are used throughout this paper.

[11] R. C. Desai and A. R. Denton, "Fractal properties of clusters during spinodal decomposition" in *On Growth and Form*, edited by H. E. Stanley, and N. Ostrowsky (Martinus Nijhoff, The Hague, 1986).

[12] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).

[13] J. M. Phillips, L. W. Bruch, and R. D. Murphy, "The two-dimensional Lennard-Jones system: Sublimation, Vaporization, and Melting" *J. Chem. Phys.*, **75**, 5097 (1981); J. J. Nicolas, K. E. Gubbins, W. B. Streett, and D. J. Tildesley, "Equation of state for the Lennard-Jones fluid" *Molec. Phys.*, **37**, 1429 (1979).

[14] M. San Miguel, M. Grant, and J. D. Gunton, "Phase separation in two-dimensional binary fluids" *Phys. Rev.*, **A31**, 1001 (1985).

[15] E. D. Siggia, "Late stages of spinodal decomposition in binary mixtures" *Phys. Rev.*, **A20**, 595 (1979).

[16] H. Tomita, "Statistics and geometry of random interface systems" in *Formation, Dynamics and Statistics of Patterns*, edited by K. Kawasaki, M. Suzuki, and A. Onuki (World Scientific, Singapore, 1990), Vol. 1.