

## Phase separation in two-dimensional binary fluids of different-sized molecules: A molecular-dynamics study

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Phase separation and late-time domain growth in two-dimensional binary fluids of different-sized molecules have been studied by molecular-dynamics simulations. The late-time growth is found to be insensitive to the overall particle fraction of the mixture and with growth exponents approximately equal to 2/3, which corresponds to the inertial growth regime, with interfacial growth for interconnected domains. The result may be explained by the observation that the interfaces for the mixtures are very broad and fuzzy even at low temperatures. [S1063-651X(96)03012-7]

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### I. INTRODUCTION

The dynamics of domain growth in phase-separating systems is an important technological problem and also fundamental as an example of a highly nonlinear process far from equilibrium. The phase separation takes place when a fluid mixture is quenched to the unstable region of its phase diagram and the growth of domains is governed in a scaling regime by a power-law relation of the form  $R(t) \propto t^n$ , where  $t$  is time,  $R(t)$  is the average domain size, and  $n$  is an exponent characterizing the growth. During the past decades many simulations of such phase separations have appeared, mostly for binary mixtures and for separations of lattice systems and by using stochastic dynamics, e.g., Monte Carlo (MC) dynamics. Recently, however, also continuous systems have been simulated by means of the molecular-dynamics (MD) simulation technique. Since many growth dynamics are covered by hydrodynamics [1] this is a nontrivial difference because the stochastic dynamics miss the hydrodynamics modes and thus the growth obtained by MC dynamics must deviate qualitatively from the corresponding growth dynamics obtained by MD simulation for the same system. A simple example of this difference is obtained for the domain growth in a binary fluid mixture in two dimensions [2]. To our knowledge all systems investigated so far have been for particles with equal sizes and interaction energies. This simplification is of course computationally convenient since it is a significant reduction in complexity and implies that systems of many thousands of particles can be followed over sufficiently long times in order to determine their growth. In this work, however, we performed molecular-dynamics simulations of phase separation in a two-dimensional (2D) binary fluid with particles that differ largely in size and energy. As the ratio of molecular sizes or masses takes values significantly different from unity, the systems tend to simulate condensation of (small) particles in random cavities given by the configuration of the big molecules. Such systems might exhibit a complex phase diagram with a wetting transition for sufficient low temperature. However, since our goal is to investigate the influence of particle size on phase growth in a binary fluid mixture we have chosen a ratio of sizes of only 2 and a temperature above the critical (gas-liquid) tempera-

ture of a pure 2D component in order to avoid competing phase changes between the spinodal decomposition, condensation (liquid-gas), and wetting in the system. This paper is organized as follows. The next section sets up the interaction model and gives some details of the simulations. In Sec. III we present the results of our computer experiments. We conclude Sec. IV with a discussion and a summary.

### II. MODELS AND COMPUTATIONAL DETAILS

The system consists of  $N = N_A + N_B$ ,  $A$  and  $B$  particles, respectively, which differs in van der Waals sizes by a factor equal to 2. The present model is taken in close analogy to the model used in [2,3], where all particles were of Lennard-Jones (LJ) type and the immiscibility between the two components in the mixture was ensured in the simplest way possible by choosing different range of attraction between the components. Immiscibility will occur if a positive excess energy of mixing exceeds the gain of mixing entropy. For simplicity and computational accuracy, the range of attraction between unlike species was taken at the minimum of the LJ potential [2,3]. This choice ensures, at the same time, a maximum excess energy of mixing and that no big force gradients occur due to a truncation of the potentials. The corresponding pair potential is the so-called Weeks-Chandler-Andersen potential [4] and simple systems of such particles have the same qualitative equilibrium and transport properties as systems with long-range attractions [5]. The two-dimensional particles are located in a square with area  $A$  and the density  $\rho = N/A$  corresponds to a condensed fluid mixture.

Still there are several properties to be specified for particles with different sizes. Particles that differ largely in size must have "corresponding" differences in masses as well as potential interactions. The relationship between the van der Waals diameters is taken to be  $\sigma_A/\sigma_B = 2$  and the usual Lorentz-Berthelot mixing rules for simple pair potentials

$$\sigma_{\alpha\beta} = \frac{\sigma_\alpha + \sigma_\beta}{2}, \quad (1)$$

$$\epsilon_{\alpha\beta} = (\epsilon_\alpha \epsilon_\beta)^{1/2}, \quad (2)$$

establish some of the necessary relationships; but we still have to specify the relationship between the size and the masses and energies. When these relations were specified we indeed had some real systems in mind, namely, phase separation in colloidal fluid mixtures [6]. Although we are not aware of any spinodal growth experiment for such mixtures, it certainly must be possible. We have chosen the masses proportional to the volume of the particles, i.e., for a 2D system proportional to  $\pi\sigma^2$ , and the energy proportional to the surface of the particles, i.e., proportional to  $2\pi\sigma$ . The reason for this choice is that the van der Waals attraction is proportional to the number of valence electrons and (surface) charges and the qualitative relations thus should be correct for mixture of colloidal. The pair potentials in the simulations are

$$u_{II}(r) = 4\epsilon_I \left[ \left( \frac{\sigma_I}{r} \right)^{12} - \left( \frac{\sigma_I}{r} \right)^6 \right], \quad (3)$$

$$u_{AB}(r) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma_{AB}}{r} \right)^{12} - \left( \frac{\sigma_{AB}}{r} \right)^6 \right] + \epsilon, & r < 2^{1/6}\sigma_{AB} \\ 0, & r \geq 2^{1/6}\sigma_{AB}, \end{cases}$$

where  $I$  represents  $A$  or  $B$  particles,  $\sigma_A = \sigma$ ,  $\sigma_B = \frac{1}{2}\sigma$ ,  $\epsilon_B = (\sigma_B/\sigma_A)\epsilon_A = \frac{1}{2}\epsilon$ ,  $\sigma_{AB} = (\sigma_A + \sigma_B)/2$ , and  $\epsilon_{AB} = (\epsilon_A\epsilon_B)^{1/2} = \sqrt{2}\epsilon$ . In the following the parameters  $\epsilon$  and  $\sigma$  (for the  $A$  particles) set the energy and length scales, respectively, and quantities will be given in reduced units according to these scales. (The LJ potentials between particles of the same species were truncated at  $2.5\sigma$ ).

There are 25 600 particles in our simulations, with  $n_A$   $A$  particles and  $n_B$   $B$  particles. The equations of motion were integrated using the Verlet algorithm and the temperature was controlled by coupling the system to a Nosé-Hoover thermostat [7]. The time interval was  $h = 0.005$  in reduced LJ time units. The system was quenched from a state of perfect mixture to a point of a state with phase separation by equilibrating the mixture with attraction between unlike species and then quenching the system by instantaneously removing the attraction. (With respect to entropy of mixing, this corresponds to a quench from a very high temperature.)

Still there is one more fundamental problem to overcome in the simulation of phase separation in systems of particles that greatly differ in sizes. When such a phase separation takes place it is associated with a relatively big excess of pressure or volume, depending on the constraint on the simulation. At equilibrium the constant-temperature MD simulation corresponds to a canonical  $N$ - $V$ - $T$  ensemble system. A corresponding deep quench at constant volume will be associated with a big change in pressure during the phase separation. Alternatively one could, in principle, perform the quench at constant pressure by which the total volume would relax. In fact, the constant-pressure constraint is more physically relevant since it corresponds closely to usual experimental circumstances. There is, however, a reason for choosing to perform the quench at constant volume instead of constant pressure. Monitoring the pressure is associated with long relaxation times [7] and could interfere with the phase-separation dynamics. It is known that domain structures are very sensitive to the ‘‘external constraint’’ and we were con-

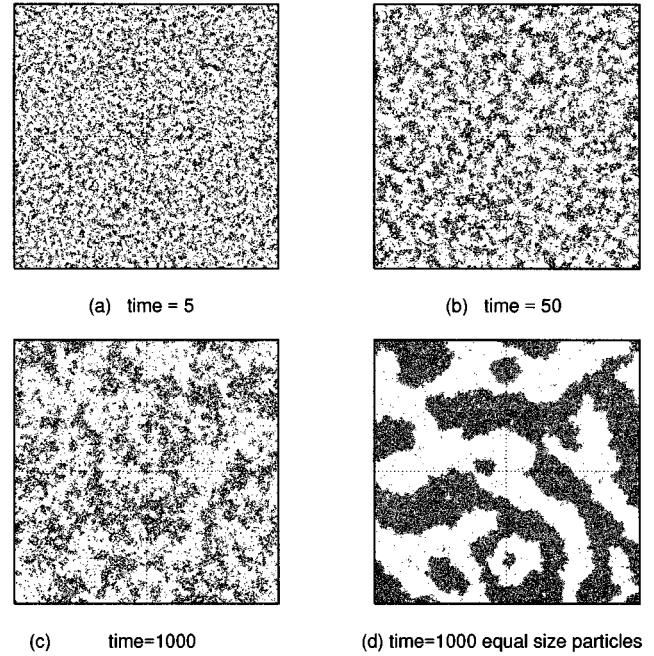


FIG. 1. (a)–(c) Domain formation of the small particles at a critical concentration  $x_A = 0.292$  and temperature  $T^* = 0.75$  of the big particles and as a function of quench time. (d) Corresponding quench for particles of equal sizes and  $T^* = 1$ .

cerned that the phase separation could be driven by the volume scaling at constant pressure. The temperature is kept constant during the phase separation and at a relatively low value of  $T^* = k_B T / \epsilon = 0.75$  in order to enhance the phase separation. On the other hand, it is chosen well above the critical (gas-liquid) point  $(T^*, \rho^*) \approx (0.450, 0.35)$  of a pure two-dimensional Lennard-Jones system [8]. (The critical pressure is approximately zero and all our quenches are performed for condensed mixtures at much higher pressures.)

The quenches for different particle fractions  $x_A = N_A / N$  of the mixture were all performed for the same initial pressure equal to 2.1 in the reduced scale (the average pressure of the first 100 steps, or 0.5 in the reduced time scale) and the temperature is kept at  $T^* = 0.75$  for all the processes. Critical ( $x_A = 0.292$ ) and several off-critical ( $x_A = 0.167, 0.5$ , and  $0.75$ ) quenches were carried out (Figs. 1 and 2). The critical particle fraction  $x_A = 0.292$  was obtained as the relative narrow interval of the particle fraction for which both components percolate the area, whereas the off-critical particle fractions are characterized by one of the components, at late times, in the quenches that are solventlike and percolate the area in both directions and another component that is solute-like with droplets in the solvent. (Percolation and droplet distribution were determined as described in [9].)

The phase-separation dynamics were obtained from several properties of the system during the separation. As in [10], we found that the excess potential energy, which is proportional to the length of the interface, gave the most accurate measurement of the growth. It was obtained in the following way. The internal energy per particle  $u(t)$  was monitored every ten steps from which the scaling regime can be obtained from the excess potential energy as

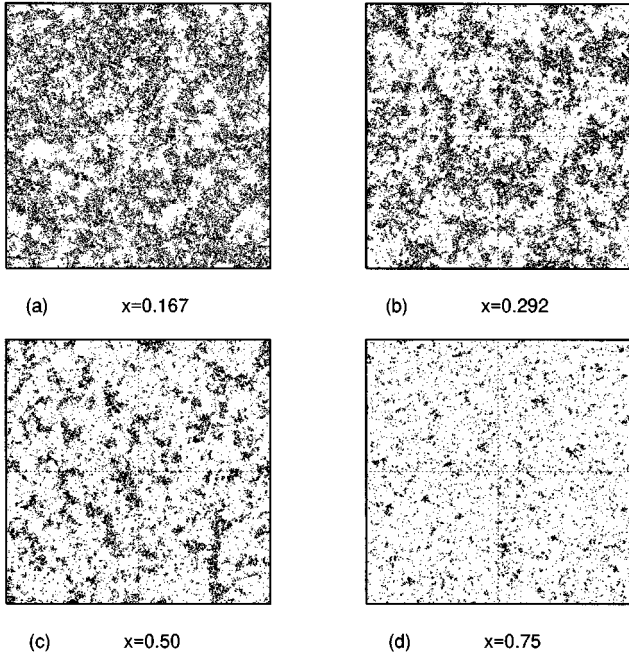


FIG. 2. Distributions of the small particles for mixtures with different particle fractions  $x \equiv x_A$  of big particles. The distributions are obtained after a separation time of 1000, which corresponds to  $2.0 \times 10^5$  time steps.

$$u_{\text{excess}} \equiv u(t) - u_{\infty} \propto t^{-\alpha}, \quad (4)$$

where  $u_{\infty}$  is the potential energy of the system at equilibrium. An accurate determination of the scaling exponent requires, however, a very precise estimate of  $u_{\infty}$ . It was obtained in two different ways: one as the late-state potential energy after more than  $10^6$  time steps and the other by equilibrating a configuration with initially flat interfaces. The equilibrium potential energy was obtained as potential energies in the two systems at times for which they equal each other within the statistical uncertainties [10]. Both systems were found to equilibrate very slowly; but after more than  $10^6$  time steps, the energies were equal within the statistical uncertainties. For example,  $u_{\infty}$  for the critical quench, determined in this way, was  $-0.6752 \pm 0.0040$ . In order to ensure self-averaging and to increase the accuracy of the investigation we have performed ten individual quenches for each particle fraction. The result of this extensive simulation scheme is given in the next section.

### III. RESULTS

The phase separations in the quenched mixtures take place by decreasing the length of the interfaces, whereby the excess energy of mixing and also the mean energy  $u(t)$  decrease. The slow domain decomposition was followed over a time interval of 1000 [in units of  $\sigma(m/\epsilon)^{1/2}$ ], corresponding to  $2.10^5$  time steps. Figures 1(a)–1(c) show the domain formations at various times and for the particle fraction  $x_A = 0.292$  of the big particles where both subphase systems percolate the area at the end of the simulations, as can be seen from Fig. 1(c). For illustrative reasons the figures show only the distribution of the small particles. Also shown, in

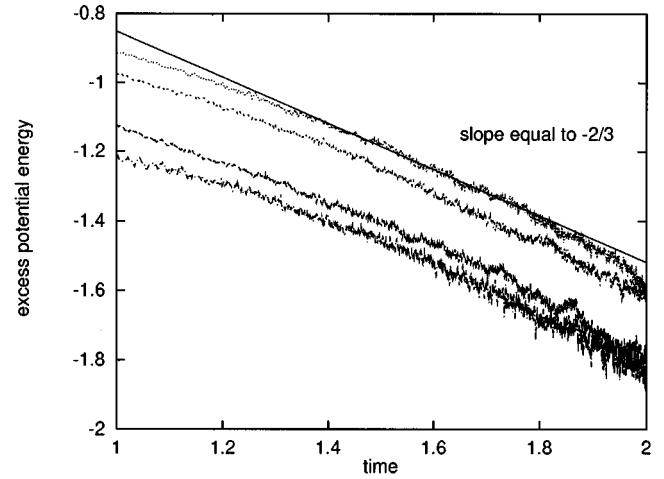


FIG. 3. log-log plot of the late-time excess energy  $u_t - u(\infty)$  for the four different particle fractions of the mixture, as a function of quench time  $t$ . Each curve is the average over ten independent quenches.

Fig. 1(d), is the corresponding domain structure, but for a system of particles with equal sizes [10] and taken at the same separation time 1000, as in Fig. 1(c). The domain structures, in particular the interfaces in the two figures, are significantly different. Whereas the interface between coexisting subphases is sharp and of the order of a few particle diameters for equal size particles [Fig. 1(d)], the interface is very fuzzy in the present case [Fig. 1(c)]. Also the solubility, in particular of small particles in the  $A$ -rich phase, is high, which adds to the fuzzy structure. Both experiments, however, correspond to deep quenches with the creation of big subdomains, as the corresponding structure factors indicate, and we think that it is this qualitative difference of the structure of the interfaces that also shows the qualitative difference in growth between the two systems which will be discussed later. Figure 2 shows the distributions of the small particles at the end of the simulations and for the four different particle fractions. The phase-separation lines for the concentrations in coexisting phases are not symmetrical around  $x_A = 0.5$ , as in the case of equal-size particles, and the critical concentration is, as mentioned, estimated to be  $x_A \approx 0.29$  in the present circumstances. At high concentration of small particles, shown in Fig. 2(a), the small particles percolate in both directions and act as a solvent for the solute of big particles; the opposite is the case for the concentrations shown in Figs. 2(c) and 2(d), respectively. The separations, however, in all four mixtures occur with a growth corresponding to an exponent of the order  $\alpha \approx 2/3$  in (4). This is in fact surprising to us since only one of the quenches is for a concentration where both species occupy an equal amount of the area. In the three other mixtures one of the species, the solvent, dominates and in this case one usually [2] obtains a significantly smaller growth exponent in accordance with the theory for growth [1]. Figure 3 shows the mean excess energy per particle  $u(t) - u_{\infty}$  as a function of time on a log-log plot, where the means are obtained from ten independent quenches. In the time interval  $\tau = 10$ –100, where data still are relatively accurate and the final size of the systems should not affect the growth result, all four sys-

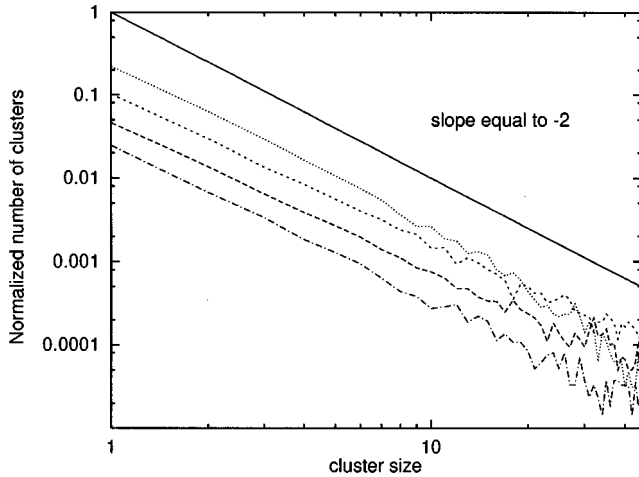


FIG. 4. log-log plot of the cluster density of small particles (number of cluster/ $N_B$ ) as a function of number of particles in the cluster. The values are obtained as the means of ten independent quenches and are for the quench time equal to 250 at  $T^*=0.75$ .

tems have the same growth and with a limit speed consistent with an exponent of the order  $n \approx 2/3$ . The systems also deviate with respect to the distribution of clusters during the growth from the system with particles of the same size. Normally, if a system is quenched in an off-critical concentration, the domains are believed to grow by droplet condensation, i.e., small (of order one) or big, but under all circumstances with a diffusion mechanism that gives a growth exponent  $n \approx 1/3$  [1] and with a distribution of clusters that is exponentially distributed with respect to size [11]. For equal-size particles we do indeed observe a slowing down of growth speed for off-critical quench [2,13], in accordance with theory. With respect to the cluster distribution, the theoretical prediction is not strictly confirmed experimentally. Seul, Morgan, and Sire [12] obtained a Gaussian distribution of domain sizes during the late-stage coarsening in a 2D binary mixture in Langmuir films of dimyristoylphosphatidylcholine and dihydrocholesterol. In the present case, however, the distribution for small clusters is completely different, but universal for all quenches at late-stage times and concentration. Figure 4 gives the (normalized) distributions of clusters of the small particles, at time equal to 250 as a function of the number  $n$  of particles in the clusters. The clusters are determined as described in [9], using the first minimum of the corresponding radial distribution function for the component in the mixture. As can be seen from the log-log plot, the distribution is not exponential but simply algebraic for  $n$  up to order 20–30 and with a universal slope approximately equal to  $-2$ . The growth, however, takes place at larger domains. Figure 5 shows this behavior from the corresponding distribution of clusters as a function of growth time and in system with a critical concentration. The upper curve is the distribution at the start of the quench, where there are only a few clusters that contain more than 20–30 small particles. The dotted curve is the distribution after a short quench time  $t=5$ . The dash-dotted curve gives the late-time behavior, also shown in Fig. 4. The asymptotic equilibrium distribution of small domains for  $n < 20$  is established after very short quench times and is

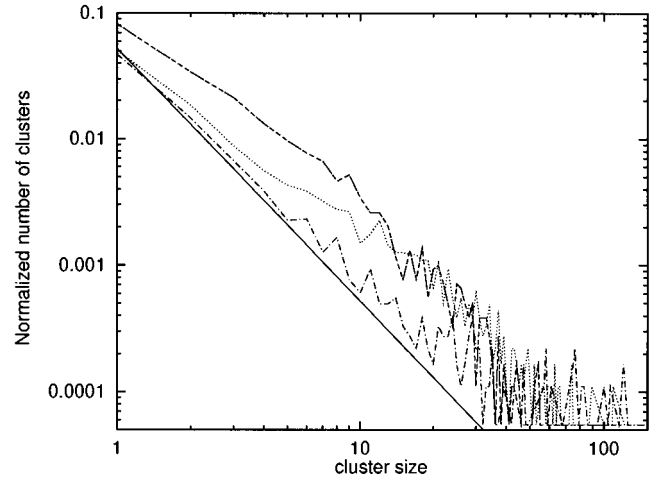


FIG. 5. log-log plot of the cluster density of small particles, as in Fig. 4, but for different quench times and at the temperature  $T^*=0.75$ . The curves (from top to bottom) give the distributions for quench times  $t=0, 5$ , and 250, respectively, and for a system with critical concentration. Also included is a straight line, with slope equal to  $-2$ .

maintained during the phase separation.

#### IV. DISCUSSION AND CONCLUSIONS

The immiscible binary mixtures were deliberately quenched to a low temperature  $T=0.75$  in order to ensure a strong immiscibility and domain separation, and we did indeed observe a separation within the same time interval as for a corresponding mixture of equal-size particles. But there is, however, a significant difference between the two types of mixtures. Whereas the interface for equal-size particles is rather sharp and the mutual solubility in the phases are low, as can be seen in Fig. 1(d), it is the opposite here. In particular, the solubility of small particles in the phases of big particles is high and the distribution in Figs. 4 and 5 demonstrates this. The growth exponent  $\alpha$ , at late times, is of the order  $2/3$ , which corresponds to the so-called inertial (hydrodynamic) late-time regime. This regime should appear for domains larger than  $\eta^2/\gamma\sigma$ , where  $\eta$  is the shear viscosity and  $\gamma$  is the surface tension [1]. Molecular dynamics that includes the hydrodynamics and the particle flow obeys the Navier-Stokes equation, so for concentrations where both components occupy the same volume fraction (critical concentration) this is to be expected, although it has never been observed experimentally (in three dimension) [3]. A series of MD calculations in two dimensions [2] and stochastic 2D-models for phase growth with hydrodynamics, however, exhibit this grow law [14–17], but it is always obtained for interconnected domain structures. In the present case, however, we do not observe any slowing down for concentrations where one of the species dominates the other and acts as a solvent for cluster growth. This is, in fact, surprising to us. The natural explanation is that the interface is very broad and unclear, as can be seen in Fig. 1, so that an instant distribution of the particle does not give an appropriate picture of the domain distribution, which fluctuates largely with the quench time. A broad interface and large fluctuations,

however, are normally a sign that the separation is close to the critical point and it means not only that one should observe a slowing down of the growth, but also that the inertial regime appears for even bigger domains since the surface tension goes to zero and the viscosity is not very temperature dependent. But we do not see any sign of a critical slowing down and the upper consolute temperature is above  $T=1$ , for which we also observe a phase separation. As discussed in Sec. II, a model of particles with different sizes needs additional potential parameters. In the present case we chose realistic circumstances by taking the masses to be proportional to the volume (area) and the energies proportional to the surface; an experimental example of such a binary mix-

ture could be a mixture of colloids with different surface energies to ensure immiscibility. To our knowledge, however, there are no experimental data concerning phase separation in such a mixture. So the present result with phase-separation growth over a wide range of concentrations of mixtures of particles that differ largely in size remains to be seen experimentally.

#### ACKNOWLEDGMENTS

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- [1] A. D. Bray, *Adv. Phys.* **43**, 357 (1994).  
[2] E. Velasco and S. Toxvaerd, *Phys. Rev. Lett.* **71**, 388 (1993); *Phys. Rev. E* **54**, 605 (1996).  
[3] M. Laradji, S. Toxvaerd, and O. G. Mouritsen, *Phys. Rev. Lett.* **77**, 2253 (1996).  
[4] J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.* **54**, 5237 (1971); H. C. Andersen, J. D. Weeks, and D. Chandler, *Phys. Rev. A* **4**, 1597 (1971).  
[5] J. A. Barker and D. Henderson, *Rev. Mod. Phys.* **48**, 578 (1976).  
[6] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions*, 2nd ed. (Cambridge University Press, Cambridge, 1991).  
[7] S. Toxvaerd, *Mol. Phys.* **72**, 159 (1991); *Phys. Rev. E* **47**, 343 (1993).  
[8] B. Smit and D. Frenkel, *J. Chem. Phys.* **94**, 5663 (1991).  
[9] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1989).  
[10] S. Toxvaerd, *Phys. Rev. E* **53**, 3710 (1996).  
[11] T. M. Rogers and R. C. Desai, *Phys. Rev. B* **39**, 11 956 (1989).  
[12] M. Seul, N. Y. Morgan, and C. Sire, *Phys. Rev. Lett.* **73**, 2284 (1994).  
[13] E. Velasco and S. Toxvaerd, *J. Phys. C* **6**, A205 (1994).  
[14] J. E. Farrell and O. T. Valls, *Phys. Rev. B* **40**, 7027 (1989).  
[15] F. J. Alexander, S. Chen, and D. W. Grunau, *Phys. Rev. B* **48**, 634 (1993).  
[16] W. R. Osborn, E. Orlandini, M. R. Swift, J. M. Yeomans, and J. R. Banavar, *Phys. Rev. Lett.* **75**, 4031 (1995).  
[17] S. Bastea and J. L. Lebowitz, *Phys. Rev. E* **52**, 3821 (1995).