which has the solution

$$w \approx 0.6\times 10^{-3}.$$

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Phase Separation in Fluid Systems by Spinodal Decomposition: A Molecular-Dynamics Simulation

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Using the molecular-dynamics technique, we describe the dynamical evolution of phase separation by spinodal decomposition for a Lennard-Jones fluid quenched to the unstable region. This is the first direct observation of the initial stages of spinodal decomposition.

We describe a numerical molecular-dynamics simulation of phase separation of a single-component Lennard-Jones fluid within the unstable (spinodal) region of the phase diagram. This computer "experiment" yields the first direct observation on an atomic scale of the spatial density variations during the early stages of spinodal decomposition. Until now, spinodal decomposition has been experimentally studied in real physical systems, such as glasses and metallic alloys,[1-3] and binary fluids near the critical point,[4] but experimental limitations have prevented microscopic observations of the early-time morphologies. As a result, x-ray and light-scattering experiments and micrographs of the later stages of phase separation have been used to surmise the features of the initial decomposition process. Our experiment eliminates this bottleneck. The practicality of this experiment was indicated by recent advances in spinodal-decomposition theory which elevated it from a phenomenological theory[5,6] to a first-principles (microscopic) theory.[7-9] However, the computer experiment itself is, of course, quite independent of any theory. We observe a highly connected morphology in the spatial density variations during the early stages of spinodal decomposition, corroborating the prediction of Cahn's linear theory.[6]

Our computer experiment consists in solving the equations of motion for a classical fluid of 1372 Lennard-Jones (LJ) atoms by numerical integration using an IBM 360/195 digital computer. We adopt the numerical procedures first developed by Verlet[10] for his molecular-dynamics experiments on the equilibrium properties of classical LJ fluids. The thermodynamic quantities are measured in the usual "reduced" units.[11] Our system of atoms is enclosed in a cube of length $L = 15.8\sigma$ and reduced density $\rho^* = 0.35$, with the standard periodic boundary conditions being imposed in order to simulate an infinite fluid system.[10] We make special note of the fact that the periodic boundary prevents the occurrence of inhomogeneities of a size larger than the side of the box, L. The LJ potential is truncated at 2.25σ. The time unit is chosen so that $m=\epsilon\sigma^{-2}$, and the time increment Δt taken for the numerical integration is 0.004 636; for argon $\Delta t=10^{-14}$ sec. The fluid is quenched from an equilibrium state $T^*=2.0$, $\rho^*=0.35$ above the critical temperature $T_c^*=1.36$ to an unstable state $T^*\simeq 0.8$, $\rho^*=0.35$ in the vicinity of the center of the miscibility gap (see Fig. 9 of Ref. 7) over a time interval of $\sim 600\Delta t=6\times 10^{-12}$ sec. Two separate algorithms are employed to reduce rapidly the fluid temperature. (1) The first procedure involves scaling at equal intervals of time (2×10^{-14} sec) all velocities by the same factor so that the total kinetic energy of the system corresponds to the desired temperature, and this is continued until the average temperature becomes approximately constant. (2) The second procedure scales all the velocities at the beginning of the quench so that the total internal energy (kinetic plus potential) is equal to the value at $T^*=0.8$. Both procedures give comparable results. The motivation for carefully choosing this final-state quench is described succinctly by a quote from de Fontaine[3] (pp. 159–160): "... it is apparent that nucleation versus spinodal decomposition is not an either/or situation. Nevertheless, there is such a thing as 'typical' spinodal decomposition. It occurs for compositions well inside the spinodal, i.e., at large supersaturations or undercoolings, and owes its popularity to the fact that for these cases the nonlinear terms (of the generalized diffusion equation of Cahn[5,6]) can be neglected for the initial stages of the (spinodal-decomposition) process. . . ." The measured mobility B of our fluid at $T^*=0.8$ is $6.25\times 10^{-2}\sigma/\sqrt{\epsilon m}$.

A generalized diffusion equation for spinodal decomposition has recently been derived[9] using liquid-state perturbation theory for nonuniform fluids.[7,8] Unlike Cahn's phenomenological theory,[5,6] there are no unknown or adjustable quantities in the theory. We will outline those aspects of the theory which are relevant to our computer experiment. Perturbation theories of the uniform liquid state[12] are based on the basic idea that the structure of a liquid is determined by the strong repulsive part of the atomic potential (which defines a "reference" fluid), with the relatively weak attractive part of the atomic potential (the perturbation potential) providing the internal pressure which holds the liquid together. The Helmholtz free energy per unit volume, $f(z)$, for a nonuniform fluid with density inhomogeneity $\rho(z)$ in the z direction is given by the expression[7]

$$f(z)=f^{\dagger}(\rho(z))+\pi\rho(z)\int_{-\infty}^{+\infty}[\rho(z+w)-\rho(z)]\,\Omega(|w|,\rho(z))\,dw, \tag{1}$$

where

$$\Omega(|w|,\rho(z))=\int_{|w|}^{\infty}\varphi_1(\xi)g_0(\xi,\rho(z))\xi\,d\xi. \tag{2}$$

If $f(\rho)$ denotes the Helmholtz free-energy density as a function of ρ in the one-phase region, $f^{\dagger}(\rho)$ is the free-energy density of a single-phase fluid of uniform density ρ in the two-phase region. $\varphi_1(\xi)$ is the attractive perturbation potential energy between a pair of atoms separated by a distance ξ, and $g_0(\xi,\rho(z))$ is the radial distribution function of the *uniform* reference fluid with a density equal to the local density $\rho(z)$. $f^{\dagger}(\rho)$, φ_1, and g_0 are specified by liquid-state theory for uniform fluids.[12] The generalized diffusion equation is (e.g., see Ref. 5)

$$\frac{\partial\rho(z)}{\partial t}=\frac{\partial}{\partial z}\left\{\rho B\frac{\partial}{\partial z}\mu(\rho(z))\right\}, \tag{3}$$

where the generalized chemical potential $\mu(\rho(z))$ is defined by

$$\delta\mathfrak{F}=\int\mu(\rho(z))\delta\rho(z)\,dV. \tag{4}$$

$\delta\mathfrak{F}$ is the functional variation of the total free energy $\mathfrak{F}$ with respect to the infinitesimal variations $\delta\rho(z)$. In our case, $\mathfrak{F}$ is the integral of $f(z)$, Eq. (1), over the volume V of the fluid. Assuming small-amplitude density variations from ρ_0 and expressing $f^{\dagger}(\rho)$ in a truncated Taylor expansion to second

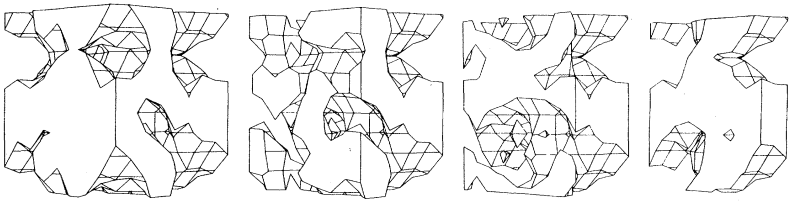

FIG. 1. Perspective renderings of the isodensity surface $\rho^* = 0.35$ for the LJ fluid undergoing spinodal decomposition, the time (in reduced units) being 4800 after the quench.

order,[5] we find that the general solution to the linearized approximation to Eq. (3) is[9]

$$\rho - \rho_0 = A(k, t)\cos(kz), \tag{5}$$

$$A(k, t) = A(k, 0)\exp[\mathcal{R}(k)t], \tag{6}$$

$$\mathcal{R}(k) = -\rho B k^2\{(\partial^2 f^\dagger/\partial\rho^2)_0 + 4\pi\int_0^\infty[\cos(kw) - 1]\,\Omega(w, \rho_0)\,dw\}. \tag{7}$$

$\mathcal{R}(k_c) = 0$ gives the critical wavelength $\lambda_c = 2\pi/k_c$ for the onset of exponential growth. Using Eq. (7), we find that $\lambda_c = 4.8\sigma$ for our experiment, well within the cutoff bound of $L = 15.8\sigma$ imposed by the periodic boundary conditions in the molecular-dynamics simulation. The wavelength λ_m having the maximum amplification factor $\mathcal{R}_m$ is 8.2σ with an e-fold time of $t_m = 1/\mathcal{R}_m = 3\times10^{-11}$ sec, the time for 3000 iterations. Hence, these theoretical estimates suggest that we would observe significant phase separation by performing the dynamical simulation of 1372 LJ atoms at $T^* = 0.8$, $\rho^* = 0.35$ for a time period of 5×10^{-11} sec from time of quench.

For the density-distribution analysis, we divide the simulated fluid cube into 343 smaller cubes with an edge length equal to $L/7$; a cube containing four atoms would be assigned a density of $\rho^* = 0.35$. In Fig. 1, a set of perspective renderings showing the morphological features of the isodensity surface $\rho^* = 0.35$ is presented for the simulated fluid at $t = 4.8\times10^{-11}$ sec. This graphical representation was produced by computing isodensity points lying on the mesh links connecting the simulation data points. These points were then organized into triangular faces of a polyhedron which were computationally rendered with hidden lines eliminated. Each successively smaller rendering contains two less planes of density points, the result of this technique being to display the interior structure of the simulated fluid. Figure 1 exhibits a highly connected morphology of high densities ($\rho^* > 0.35$ represented by the solid region) and low densities ($\rho^* < 0.35$ represented by the open region) and, hence, the "signature" of classical spinodal decomposition in an isotropic system as first expounded by Cahn.[6] Earlier-time renderings show an essential similarity to the general features of this surface.

A two-dimensional histogram of the average density $\langle\rho(x, y)\rangle$ of a column of cubes with common (x, y) positions was calculated at different simulation times. These histograms are presented in Fig. 2, where the height of a column depicts the magnitude of the average density. While Fig. 2 gives an (x, y) projection of superimposed density waves ($\lambda_c < \lambda < L$) with various wave vectors $\vec{k}$, we note that the amplitudes of the projected density fluctuations are growing continuously as suggested in Eqs. (5)–(7), a property of true spinodal decomposition.[5,6]

We are presently extending the study to include the calculation of the far-field light-scattering

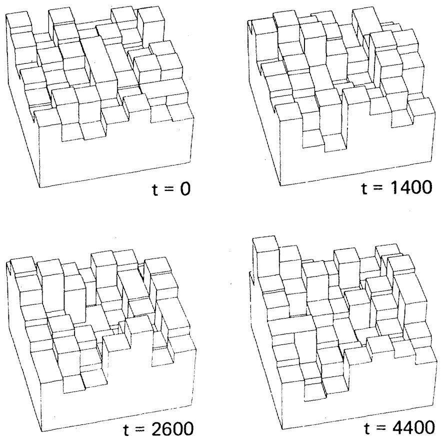

FIG. 2. Two-dimensional histograms of $\langle\rho(x,y)\rangle$ for different simulation times t.

pattern,[4] computationally a very time-consuming calculation, and the simulation of spinodal decomposition in binary fluids.

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Dispersion of Collective Excitations in a Nematic Liquid Crystal

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Coherent inelastic neutron scattering in fully deuterated nematic p-azoxyanisole indicates, for momentum transfers $\vec{Q}$ perpendicular to the director $\vec{n}$, phononlike collective excitations having a dispersion with two maxima and one minimum within $0.9 \leq Q \leq 3.2$ Å^{-1}.

Nematic crystals are disordered with respect to the positions of the molecular centers of gravity but ordered with respect to the orientations of the long axes of the molecules. The experiment described here is a study of the extent to which there are excitations in the system involving collective motions in the disordered degrees of freedom. This question is most interesting, of course, for wave numbers Q which are so large that the excitations cannot be considered as mere hydrodynamic density fluctuations present in all condensed systems. For this reason the study was done with neutron scattering.

Quite a number of neutron-scattering experiments have been performed to study the motions of the individual molecule in nematic systems, especially in p-azoxyanisole (PAA).[1] As information on these motions is obtained with incoherent scattering, hydrogeneous compounds can be used conveniently, because of the large incoherent neutron-scattering cross section of protons. For studies on collective motions via inelastic interferences in the scattered radiation, the sample must be deuterated. For deuterons the coherent cross section is 5.76 b and the incoherent cross section 2.0 b.[2] To our knowledge such studies on collective motions have been carried out so far only for the most solidlike of all liquid crystalline phases, namely for smectic B. For the most liquidlike, the nematic phase, studies on coherent scattering[4,5] were not concerned with the dynamics.

In the following we report first results of an energy analysis of neutrons scattered in fully deuterated nematic PAA. We discuss here only the inelastic part of the spectra. The quasielastic lines shall be considered in a forthcoming publication.

The measurements were done with the time-of-flight spectrometer SV 5-C at the FRJ-2 reactor in Jülich.[6] The incident energy of the neutrons was 3.55 meV; the Gaussian resolution function of the instrument had a full width at half-maximum corresponding to four adjacent points of the data presented in Fig. 2. The fully deuterated PAA sample was held in a flat aluminum container with dimensions 5× 25× 30 mm^3. The specimen was heated from top and bottom with two resistance wires independently controlled, thus keeping the temperature gradient and tempera-