A new universal dynamics preceding the early stage of spinodal decomposition

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The theory of spinodal decomposition has been developed in the '60s through '70s. The concept of spinodal was then reexamined for an Ising system [1]. However, no explicit discussion has been given to a fluid system, which is believed to belong to the same universality class. Ushcats has suggested [2], extending the equation of state beyond the thermodynamically stable region, that the spinodal line of the modified Lennard-Jones (mLJ) system [3] approaches the liquid–gas coexistence (binodal) line. Our prediction based on the coarse-graining limit for the coarse-grained free energy, estimated using the block spin coarsening technique, supports Ushcats' conjecture [4]. This finding suggests that a system's dynamics can also depend on a coarsening level. We conducted isothermal–isobaric molecular dynamics simulations for an mLJ system consisting of 4×10^6 particles to examine the dynamical liquid–gas phase separation process. Length, time, and temperature are expressed in units of mLJ parameters. The critical temperature, pressure, and density of the mLJ system are $T_c = 1.0762(2)$, $p_c = 0.09394(17)$, and $\rho_c = 0.331(3)$, respectively [5]. We treated two systems with different densities: 0.02 and ρ_c. The fluid system well-equilibrated at $20T_c$ was instantaneously brought to $0.7T_c$ for phase separation. The lower- and critical-density systems were expected to be quenched in the metastable and unstable regions, respectively, judging from the shape of the coarse-grained free energy. The term "local density" has often been used in mesoscopic descriptions. However, it has been far unclear what is meant by "local." In this case, we can define the local density unambiguously using the length L, the coarse-graining scale based on which the coarse-grained free energy was described [4]. Based on this well-defined "local" density and its fluctuations around the average density, we defined the structure factor S and examined its time evolution after the quench. On the short-time side ($t < 2$), L predominantly determines the peak position of S, whereas the peak position approaches the value determined by the average density on the long-time side ($t > 2$). To examine in detail the L-dependence of the wavelength at which structural destabilization occurs, S was scaled by its peak position and height. The dynamical process in another state, obtained by quenching the critical-density system to $0.97T_c$, was also examined. We could identify in the short-time region the new universal process, in which phase separation proceeds in a statistically self-similar fashion irrespective of the average density, quenching temperature, and coarsening length. We speculate that such a "super-early" stage precedes the early stage covered by the linear theories.

References

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