Molecular Dynamics Simulation of Phase Separation in Lennard-Jones Liquids

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Molecular Dynamics Simulation of Phase Separation in Lennard-Jones Liquids*

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The progress of the liquid-liquid phase separation phenomenon has been investigated by very large scale molecular dynamics simulation for two component three dimensional system. Lennard-Jones potential is used and the concept of Bragg-Williams approximation is introduced to this potential. The phase separation process is traced by monitoring snapshot pictures of the configuration of atoms and the energy change of the system. The phase separation rapidly progresses at lower temperature and the small potential depth between different species. The phase separation does not occur at 300K. The domain growth rate caused by phase separation becomes slow and the interface roughness and the mutual solubility increase with increasing temperature of the system. The non-collective single particle motion is analyzed by the velocity autocorrelation function (VACF) and its power spectra. The self diffusion coefficients are calculated.

KEYWORDS: molecular dynamics (MD), phase separation, liquid, diffusion, interface energy

1. Introduction

The phenomenon of phase separation in multicomponent system is a common occurrence. In engineering applications, one often needs to mix or unmix various substances (metals[1], inorganic glasses[2] and other chemical species). Therefore, it is important to understand the nature of the phase separation from the technological and physical viewpoint. The phase separation is the slow relaxation phenomena from the homogeneous nonequilibrium state to the inhomogeneous equilibrium state.

In the field of the materials science and engineering, the general feature of immiscibility is discussed in terms of a Bragg-Williams approximation[3] in statistical mechanics. In this regular solution model, which is only a crude approximation, the free energy of mixing for two component system may be expressed as

$$\Delta G = \Delta H - T\Delta S = \alpha x(1-x) + RT\left[x\ln x + (1-x)\ln(1-x)\right] \quad (1)$$

where x is the mole fraction of atom 2. Parameter α is given by

$$\alpha = NZ\left[E_{12} - \frac{1}{2}(E_{11} + E_{22})\right] \quad (2)$$

where E_{12} is the bond energy between atom 1 and 2, Z is the number of nearest neighbors surrounding each atom and N is Avogadro's number[2]. If the bond energy between different atomic species is bigger than the average bond energy between the same species, the phase separation occurs. In the case of the negative α, the uniform mixing occurs. The concept of the Bragg-Williams approximation gives only the thermodinamical equilibrium condition, which includes no information on dynamics of the system. Microstrucural level theoretical treatment has been performed by Cahn. He treated phase separation by using thermodynamics and Fick's law of diffusion based on macroscopic continuous model[1].

In the field of physics, the dynamics of aggregation of solutes from supersaturated dilute solutions have been theoretically analyzed by Lifshitz and Slyozov using a scaling concept[4]. They reported that the late-time growth law of the characteristic domain size scaled as power law for the time with exponent 1/3. This relation is known as the Lifshitz-Slyozov rule and agrees with small angle scattering experiments on spinodal decomposition[2].

Computer simulations have also been performed for phase separation phenomenon. Two dimensional system is mainly adopted. Monte Carlo (MC) simulation is applied for the phase separation in two[5] and three[6] dimensional Ising model. The late-time growth law for the domain size is also found to be power law for the Monte Carlo step. However, it is well known that MC is not suitable technique for studying the dynamics. The molecular dynamics (MD) method is the relevant simulation technique to study atomistic structure, energy and dynamics at same time. Gas-liquid phase separation in one component Lennard-Jones systems have been studied by two[7,8] and three[7] dimensional MD simulation. The MD simulations for liquid-liquid phase separation in binary and more component systems have been examined by using Lennard-Jones (LJ) base potential. The interaction between same species is conventional LJ potential. Only the repulsive interaction affects between different species. This treatment is quite artificial. Both the two[9,10,11] and three[12] dimensional simulations are reported. In these MD simulations, the late-time growth law for the average domain size is found to be power law for the time.

In this study, we investigate liquid-liquid phase separation process in three dimensional binary liquid via MD simulation more accurately. We use the Lennard-Jones potential and directly introduced the concept of Bragg-Williams approximation to this potential. We apply MD, which is based on the atomism, to semimicrostrucure level treatment by using very large system. The development of the phase

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separation is followed in three viewpoints. First is the influence of potential and temperature to phase separation rate. Second is the development of the microstructure. Third is the atomistic dynamics under fluctuated structure.

2. Simulation method

In order to investigate the microstructure formation caused by phase separation, we have to use a large system because the characteristic length scale of the microstructure becomes quite larger than the interatomic distance. In present work, we use two components three dimensional system consisting of 78732-atom. This large scale MD simulation requires very long computation time even if we use the most powerful vector processor (Hitachi S3800/380) with optimized program by FORTRAN. Then, we use the smaller size, i.e. 4000-atom system as preliminary simulation.

The Lennard-Jones pair potential,

$$\phi_{12}(r) = 4\varepsilon_{12}\left[\left(\sigma_{12}/r\right)^{12} - \left(\sigma_{12}/r\right)^{6}\right], \quad (3)$$

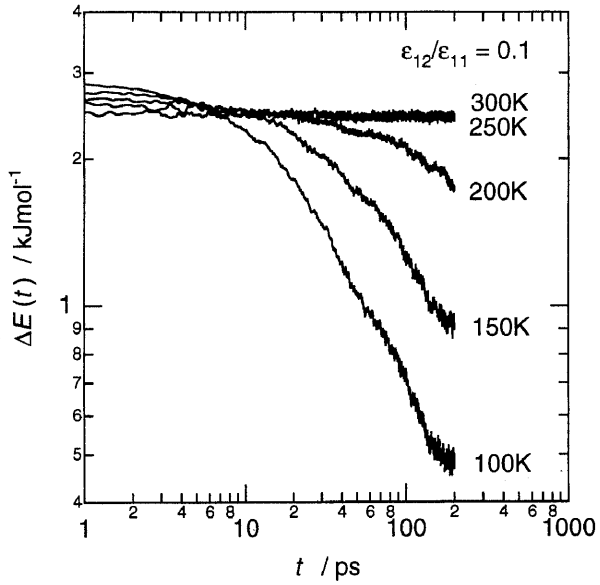


Fig. 1. Progress of the excess interface energy with $\varepsilon_{12}/\varepsilon_{11}$ =0.1.

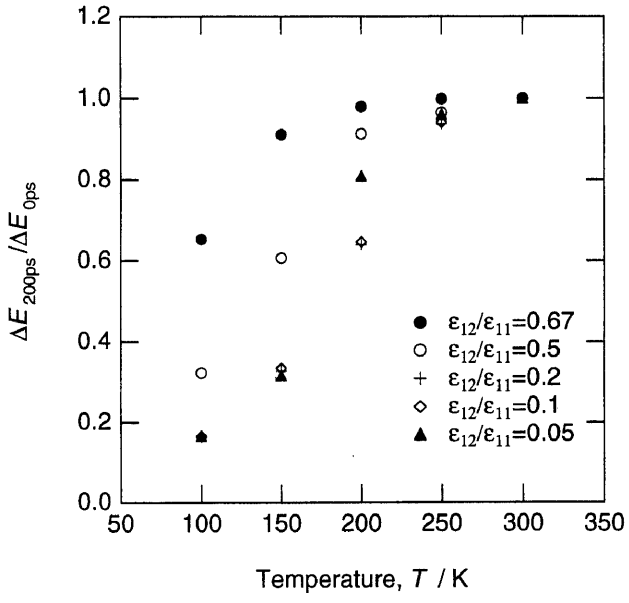
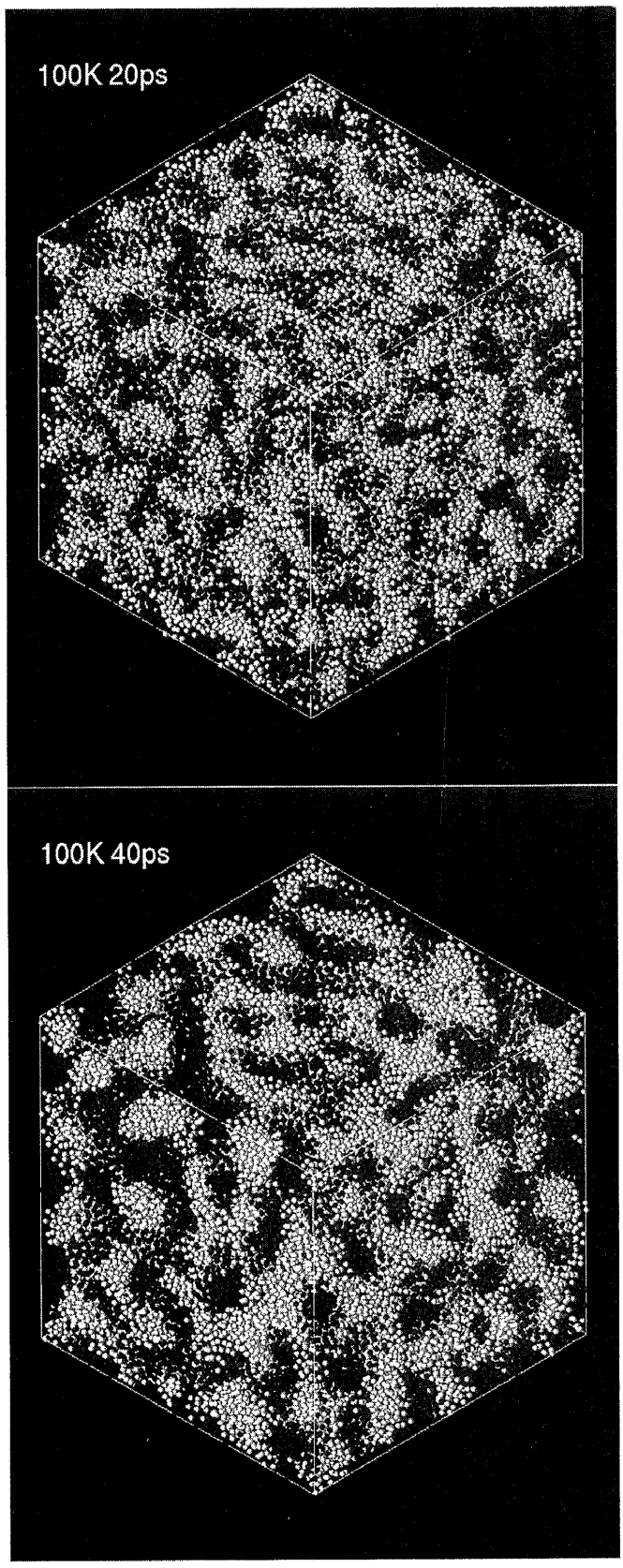


Fig. 2. Ratio of the excess interface energy at 200 ps to that at 0 ps.

is adopted as the interatomic interaction. The parameter σ relates to the diameter of the atom and the parameter ε indicates the potential depth. In the case of the same species interaction, namely 1-1 and 2-2 atom interaction, the potential parameters are same as argon atom. The masses of all atoms equal to the argon atom. Then, the behavior of atom 1 and 2



is symmetric. These treatments simplify analyses of dynamics. In the case of the different atom species interaction, namely 1-2 atom interaction, only the parameter ε_{12} is different from the argon atom. In present work, we vary $\varepsilon_{12} / \varepsilon_{11}$ from 0.05 to 0.67. These values give strong repulsive interaction between the different atomic species. The phase separation occurs rapidly. This is based on the concept of the Bragg-Williams approximation. The potential is truncated at the distance $4\,\sigma_{12}$.

The composition ratio atom 1 to atom 2 is 50 to 50. The normalized density of the system is 0.82 (the cube side is 15.569 nm), which gives 80K as the melting temperature of

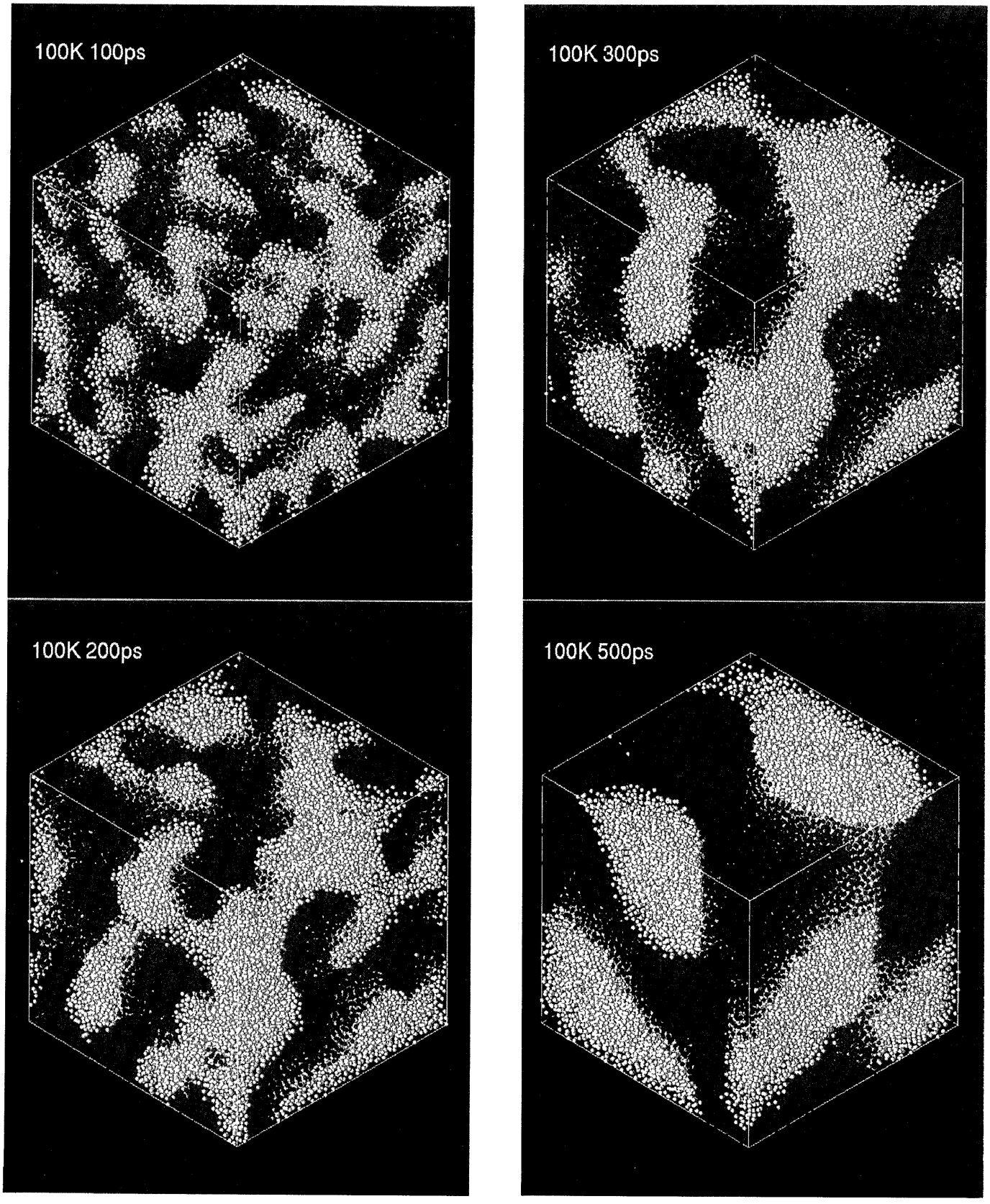


Fig. 3. Snapshots pictures for two component three dimensional 78732-atom system at 100K with $\varepsilon_{12} / \varepsilon_{11}$ =0.1.

the fcc crystal. This density assures that the system is safely inside the liquid phase and the gas phase does not appear[13]. The periodic boundary condition is used. All simulations are performed under constant NVT ensemble by using Nose thermostat[14], which generates the canonical ensemble time series data. Newton's equation of motion is numerically integrated by Gear's 5th order predictor-corrector method with a time step of 2 fs. The neighbor list table is used to save the computation time.

The calculation is begun by constructing a one component (only atom 1) fcc argon crystal. The system is first heated above the melting temperature to obtain a homogeneous

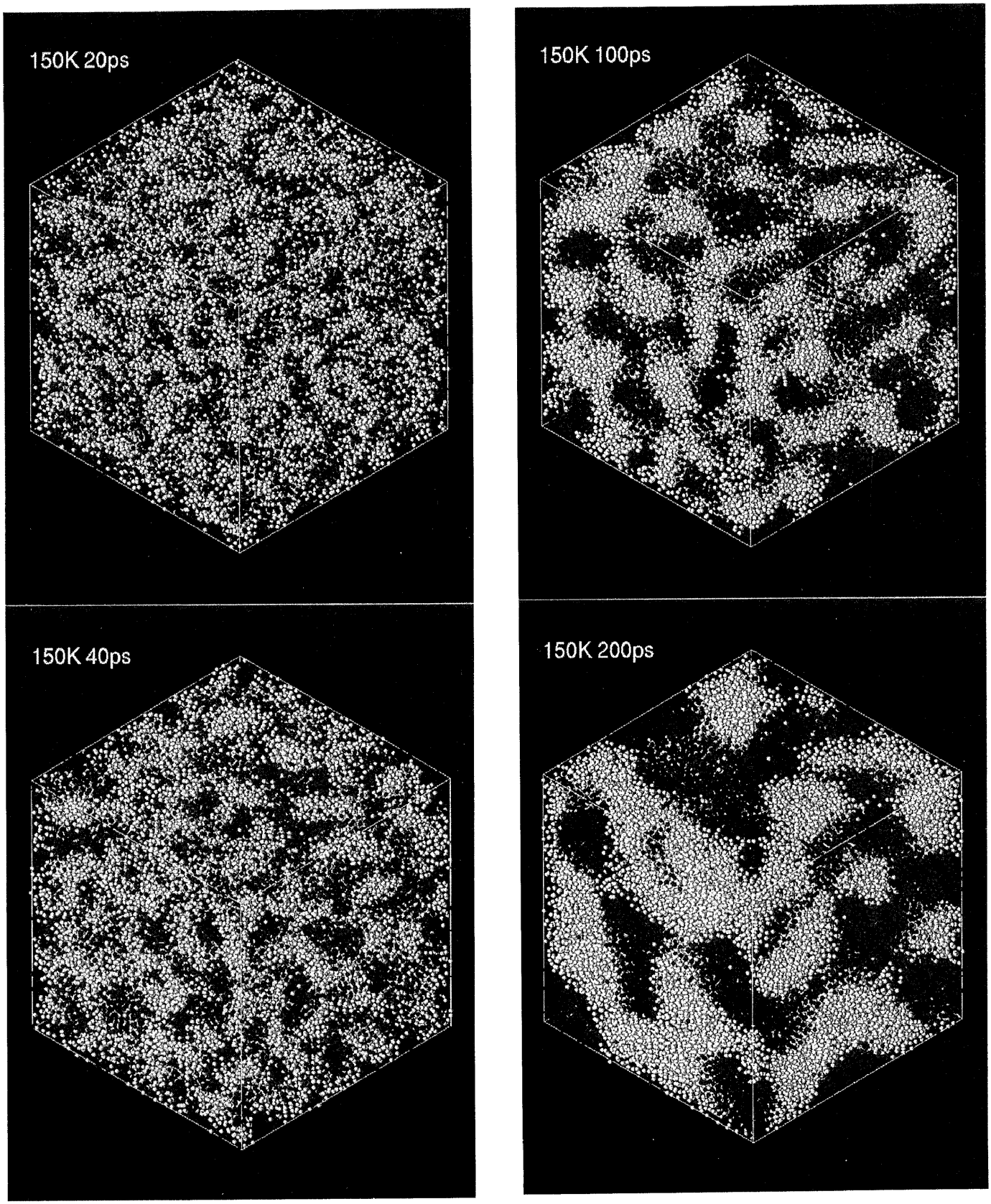


Fig. 4. Snapshots pictures for two component three dimensional 78732-atom system at 150K with $\varepsilon_{12} / \varepsilon_{11} = 0.1$.

equilibrium liquid. After subsequent isothermal annealing at the object temperature, half of atom 1 are randomly selected and replaced by atom 2. Phase separation begins by the effect of the 1-2 atom potential. This potential switching is the origin of the phase separation time. This operation gives the compatible non-equilibrium state obtained by the rapid quenching from the high temperature homogeneous single phase liquid. The phase separation process is traced by monitoring snapshot pictures of the configuration of atoms and the energy change of the system. Properties of phase separated two component system is compared with that of the homogeneous one component system.

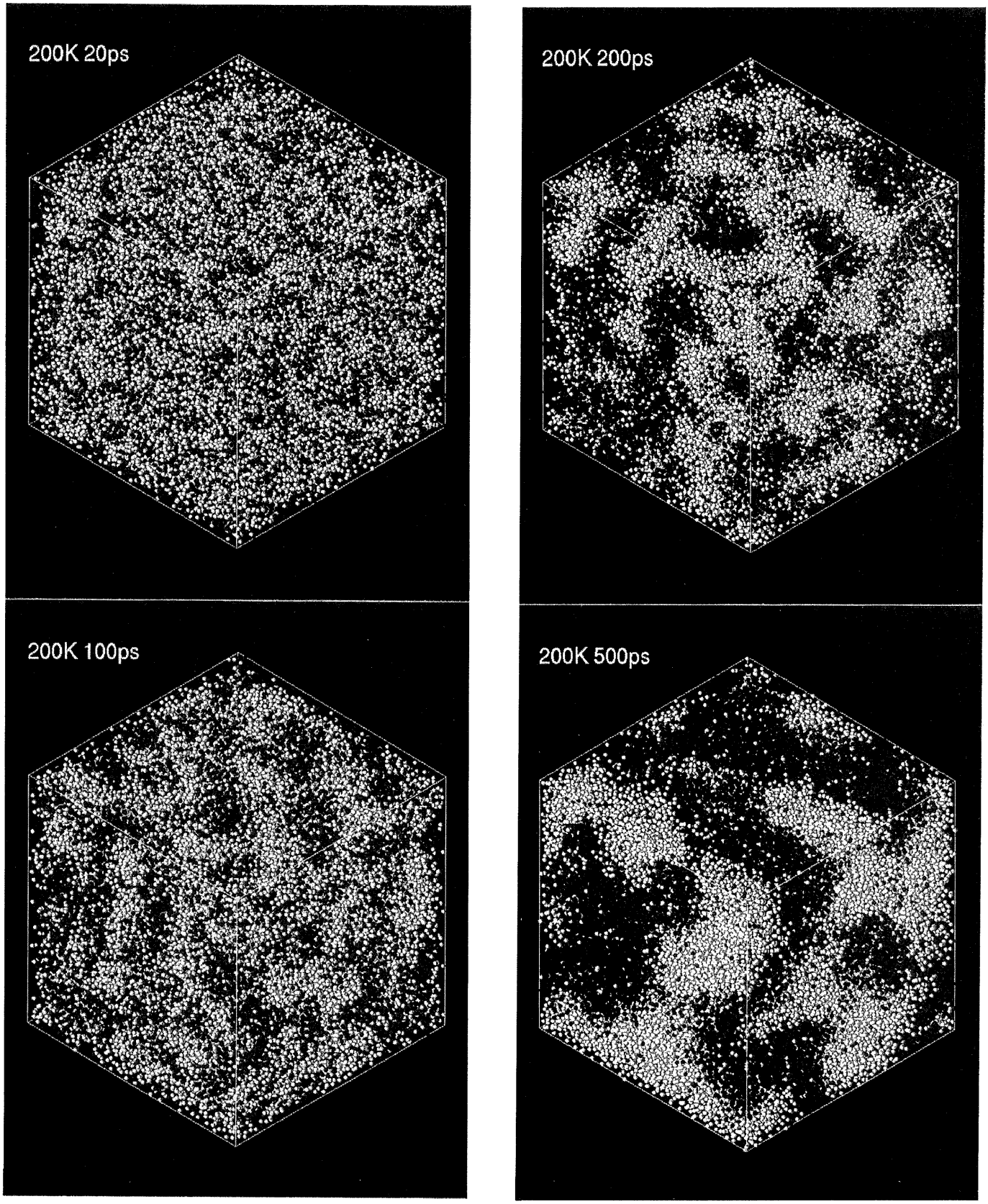


Fig. 5. Snapshots pictures for two component three dimensional 78732-atom system at 200K with $\varepsilon_{12} / \varepsilon_{11} = 0.1$.

3. Results and discussion

The effect of interatomic potential and temperature on the phase separation rate is still unclear. We performed 4000-atom MD simulation as preliminary study to clarify this point. As described in latter of this paper, the microstructure of the phase separated system consists of the phase 1 (atom 1) and phase 2 (atom 2). Because of the repulsive interaction between the different atom species, there is excess interfacial energy between the phase 1 and 2. The progress of the characteristic domain size caused by the phase separation gives the decrease of the total area of the interface. This variation is detected by the decline of the excess interfacial

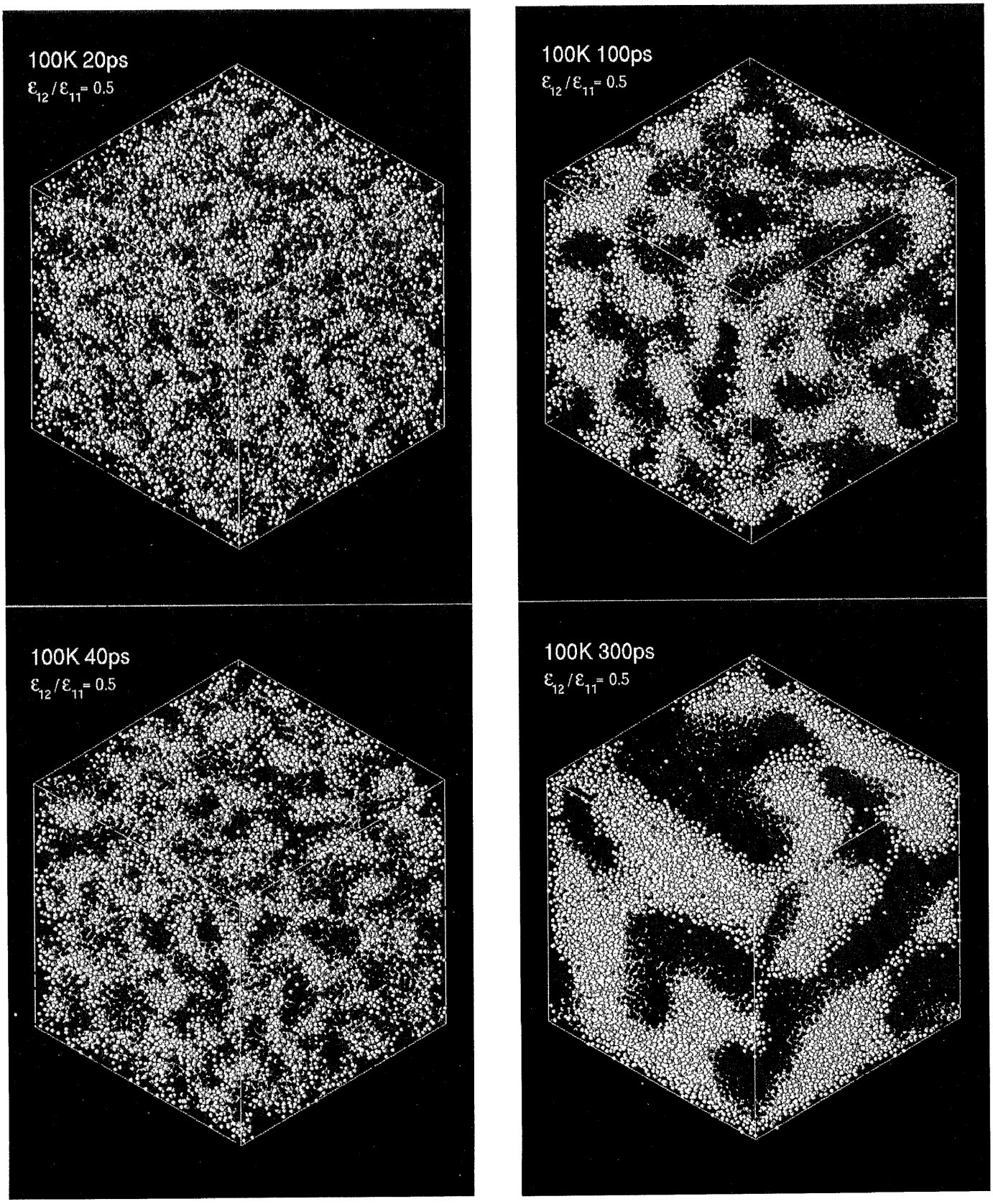


Fig. 6. Snapshots pictures for two component three dimensional 78732-atom system at 100K with $\varepsilon_{12}/\varepsilon_{11}$ =0.5.

energy. In present work, we defined this excess interface energy, ΔE, as the potential energy difference between two component phase separated system and one component homogeneous system at same temperature. Figure 1 shows the progress of the excess interface energy at various temperatures with $\varepsilon_{12}/\varepsilon_{11} = 0.1$. At 100 K the interface energy drastically decreased with time. At lower temperature, the interface energy decreases by power law for the time. At higher temperature, the interface energy decreases slowly. For the quantitative evaluation of the phase separation velocity, the ratio of the excess interface energy at 200 ps to that at 0 ps is plotted as a function of temperature. As shown in Fig. 2, the small $\varepsilon_{12}/\varepsilon_{11}$ gives the rapid phase separation. There is no significant potential dependence in the case of parameter $\varepsilon_{12}/\varepsilon_{11}$ is less than 0.2. At 300K, the phase separation does not occur for all potentials.

To get the picture of the atom configuration in the system helps the intuitive understanding of the static state of the matter. The computer graphics generated from the MD time series data is compatible to the high resolution electron micrograph of the material. Figure 3 through 6 are the bird's eye views of the snapshots pictures for 78732-atom system above the melting temperature. White and dark gray spheres indicate atom 1 and 2. No transparency is introduced. The white line indicates the periodic boundary condition. Figure 3 is the progress of the snapshots pictures at 100 K with $\varepsilon_{12}/\varepsilon_{11} = 0.1$. The phase separation begins immediately after the potential switching. At 20 ps after the switching, small size domain is observed but the interface between phase 1 and 2 is not so clear. At 40 ps, the separated domain develops and the interface becomes clear. After more time progressed, the domain grows and the total area of the interface decreases. The shape of the separated domain is complicated. The microstrucures at 100 and 200 ps consist of the connected and mutually interpenetrated domains, which are very similar to the electron micrograph for spinodal decomposed glass[1]. The interface between phase 1 and 2 is very sharp and mutual solubility is rare. At 500 ps, only very few large domain exist. The domain shape becomes spherical. This shape change is caused by the finite system size and the periodic boundary condition. Structural analyses should be stopped when the characteristic length of the microstructure becomes equivalent value to the quarter of the MD cell length. Figure 4 is the progress of the snapshots pictures at 150 K with $\varepsilon_{12}/\varepsilon_{11} = 0.1$. The interface is somewhat rough and mutual solubility is rather detected. Figure 5 is the progress of the snapshots pictures at 200 K with $\varepsilon_{12}/\varepsilon_{11} = 0.1$. Now, the separated domain is not observed at 20 ps. While the domain structure is observed at 100 ps, the interface is quite rough. As shown in the pictures at 200 and 500 ps, the mutual solubility is very active at 200 K. The domain size increases with time at all temperature. However, the domain growth rate becomes slow and the thermal noise and fluctuation increase with increasing temperature of the system in present simulations. In the previous two and three dimensional MD simulations for the two component phase separation, the very strong repulsive potential is used[9, 10, 11, 12], and the clear mutual solubility is not observed. Figure 6 is the progress of the snapshots pictures at 100 K with $\varepsilon_{12}/\varepsilon_{11} = 0.5$ that gives the rather weak repulsive interaction between atom 1 and 2. The domain growth rate is slow in comparison with the results at same

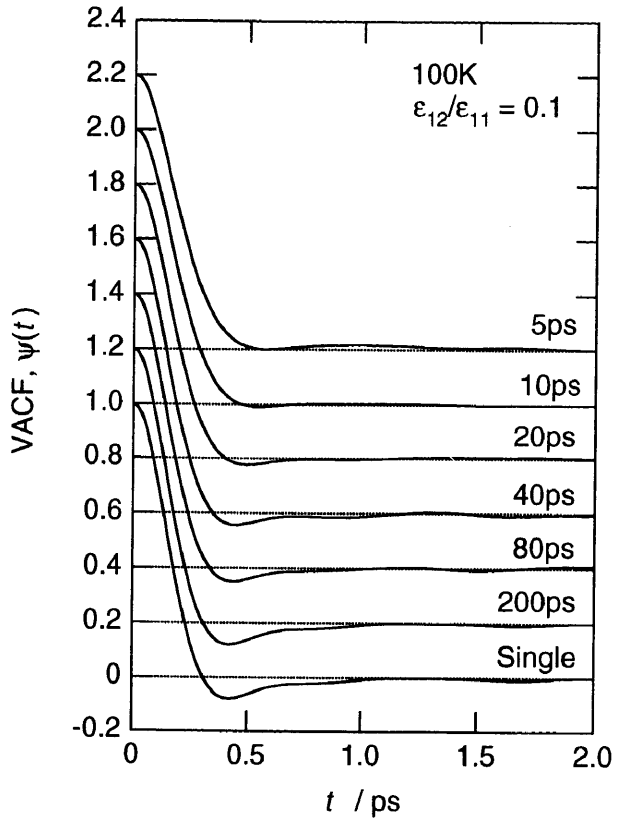


Fig. 7. Time evolution of the velocity autocorrelation function (VACF) of atom 1 at 100K with $\varepsilon_{12}/\varepsilon_{11}$ =0.1 for two component three dimensional 78732-atom system.

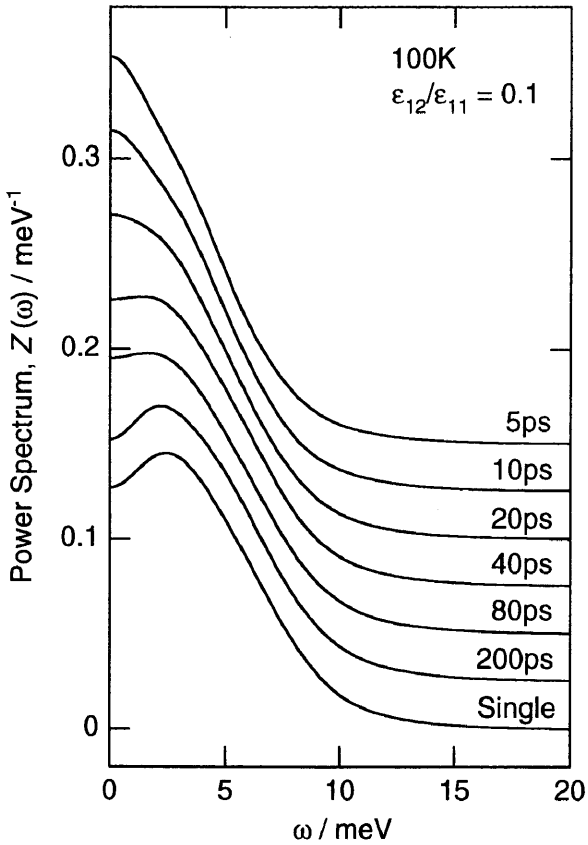


Fig. 8. Time evolution of the power spectra of velocity autocorrelation function of atom 1 at 100K with $\varepsilon_{12}/\varepsilon_{11}$ =0.1 for two component three dimensional 78732-atom system.

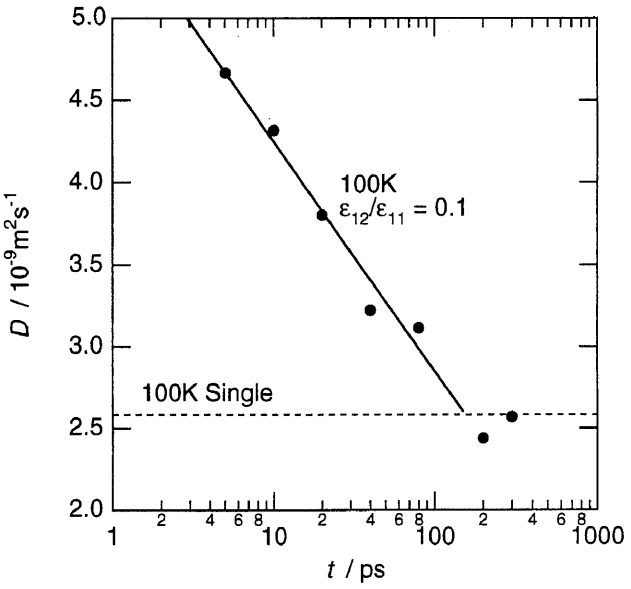


Fig. 9. Self diffusion coefficient of atom 1 at 100K with $\varepsilon_{12}/\varepsilon_{11}$ =0.1 for two component three dimensional 78732-atom system.

temperature with $\varepsilon_{12}/\varepsilon_{11} = 0.1$. However, the roughness of interface is the same level for $\varepsilon_{12}/\varepsilon_{11} = 0.1$ and 0.5.

Atoms in the matter are never at rest at finite temperature[15]. The relation between atomistic dynamics and fluctuated structure introduced by phase separation is still unknown experimentally. In the liquid state, the non-collective single atom motion consists of the thermal vibration and self diffusion of atom. The structure independent dynamics are analyzed by the velocity autocorrelation function (VACF)[16], which is defined by

$$\psi(t) = \frac{\sum_{i=1}^{N} \langle v_i(0) \cdot v_i(t) \rangle}{\sum_{i=1}^{N} \langle v_i(0) \cdot v_i(0) \rangle}, \quad (4)$$

where $v_i(t)$ is the velocity of the i atom at time t. The power spectrum at angular frequency ω is calculated as the Fourier transform of the VACF,

$$Z(\omega) = \frac{2}{\pi} \int_0^\infty \frac{1}{N} \sum_{i=1}^{N} \langle v_i(0) \cdot v_i(t) \rangle \cos(\omega t) dt. \quad (5)$$

Figure 7 shows the VACF of atom 1 at 100 K with $\varepsilon_{12}/\varepsilon_{11}$ = 0.1 for 78732-atom system. At early stage of the phase separation, VACF shows no back scatter at 0.5 ps. With the progress of the time, the shape of the VACF of phase separated system becomes similar to one component homogeneous system indicated as "Single". The power spectra of these VACF's are indicated in Fig. 8. The high energy part of the power spectrum is not so change with time. Great change is observed at the low energy part. The power spectrum at zero frequency indicates the self diffusion. As shown in Fig. 9, the self diffusion coefficient decreases with the logarithm of the time, and saturate to the value for one component homogeneous system at 200 ps.

4. Conclusion

we have performed the large scale molecular dynamics simulation on phase separation phenomena in two component three dimensional Lennard-Jones liquids. The progress of the phase separation is evaluated by the excess interface energy and snapshots pictures of the atom configuration. The phase separation rapidly progresses at lower temperature and the small potential depth between different species. The phase separation does not occur at 300K. The atomistic model generates the domain structure similar to the microstructure of spinodal decomposed glass. The domain size increases with time at all temperature. The domain growth rate becomes slow and the interface roughness and the mutual solubility increase with increasing temperature of the system. The atomistic dynamics changes with time. The self diffusion coefficient decreases with logarithm of the time. More detail structural analyses shall be performed in near future works.

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