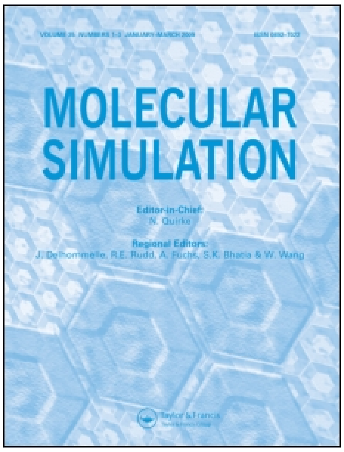

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Molecular Dynamics Study of High Temperature Phase-Separation in a H_2O/N_2 Mixture with Exp-6 Interactions

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MOLECULAR DYNAMICS STUDY OF HIGH TEMPERATURE PHASE-SEPARATION IN A H_2O/N_2 MIXTURE WITH EXP-6 INTERACTIONS

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Equimolar H_2O/N_2 fluid mixture was studied by molecular dynamics simulations for NVT ensemble. Calculations were performed with the modified Buckingham (exp-6) potentials at T = 2000 K. Particular attention was given to the phase separation at very high pressures relevant to a detonation environment. Calculations of pair correlation functions and local mole fractions clearly indicated the occurrence of the fluid separation into N_2-rich and H_2O-rich phase. The density at the phase boundary between homogeneous and inhomogeneous phase-separated state was determined to be $\rho = 1.35\ g/cm^3$ on the basis of the static cross correlation factor which is defined by the sum of the local mole fractions. The ratio of the self-diffusion coefficients of N_2 and H_2O at $\rho < 1.35\ g/cm^3$ was found to be approximately equal to the value predicted by the kinetic theory of the ideal gas, whereas the ratio was close to unity at the phase-separated state ($\rho > 1.35\ g/cm^3$). In addition, two distinctive behaviors of the system could be observed for the relaxation from the initial uniform mixture to the phase-separated fluid: at lower densities ($1.35 < \rho < 2.0\ g/cm^3$) the fluid mixture began to relax into the phase-separated system without obvious incubation time, while clear incubation period was associated for the separation at higher densities. During this incubation period, discontinuous jumps in the mean square displacements were found.

KEY WORDS: high temperature phase separation, H_2O/N_2 mixture

INTRODUCTION

The detonation of typical explosives containing C, H, N, and O atoms produces a mixture of N_2, H_2O, CO_2 and other minor chemical species at high temperatures (T = 1000–5000 K) and pressures (p = 1–100 GPa). Since it is very difficult to attain such high temperatures and pressures relevant to the detonation environment by static experiments on mixtures, there still remains interesting question of whether a supercritical fluid phase separation among detonation products may occur or not. Among major products of detonation, Ree [1] predicted that the N_2-H_2O system might exhibit a fluid phase separation behind detonation waves. The phase boundary was determined by the solubility isotherms derived from the free energy, that was calculated by using the van der Waals one fluid theory with exp-6 interactions. He also showed that the detonation properties were largely affected by the fluid separation at some pressures and temperatures. The occurrence of such phase separation is of great interest since not only the thermodynamic properties but also the rate of chemical reactions can be largely affected. However, thermodynamic determination of the boundary for the phase separation can not give any information on the magnitude of the separation, that is, the local concentrations of the phase-separated mixtures. The local concentrations may have large influence on the reaction rates. The dynamic nature of the relaxation processes from uniform to the phase-separated mixtures, such as relaxation rates, is also important for understanding the effects of phase separation behind the detonation waves. The present paper addresses these problems.

The fluid-fluid phase separation has been the target of several Monte Carlo [2-4] and molecular dynamics [5-10] studies. The fluid mixtures interacting with Lennard-Jones (L-J) potential were particularly well studied. For the Lennard-Jones mixtures of molecules *a* and *b*, Hoheisel and coworkers [5-7] showed that the phase separation could occur in the mixtures consisting of molecules of equal size if the energy parameter for the unlike L-J interaction, ε_{ab}, is much less than the arithmetic mean of the energy parameters for the like interactions (i.e., $\varepsilon_{ab} < 0.81\,[(\varepsilon_{aa} + \varepsilon_{bb})/2]$). They also found the phase separation in the mixtures having equal energy parameters of $\varepsilon_{aa} = \varepsilon_{bb} = \varepsilon_{ab}$ and different size parameters of $\sigma_{ab} > (\sigma_{aa} + \sigma_{bb})/2$. These results clearly indicated that the weaker unlike interaction than the like interactions is responsible to the fluid phase separation.

Similar result for the hard-sphere mixtures was obtained by the molecular dynamics simulation made by Melnyk and Sawford [11]: phase separation could occur even in the hard-sphere mixtures if $\sigma_{ab} > (\sigma_{aa} + \sigma_{bb})/2$. Although the value of σ_{ab} is equal to $(\sigma_{aa} + \sigma_{bb})/2$ for the usual hard-sphere mixtures by definition, there is no compelling reason that the collision diameter for the (a, b) molecular pair should be equal to the arithmetic mean of the diameters of molecules *a* and *b* at very high pressure [12]. Since the repulsive intermolecular interaction is more important than the attractive interaction at high temperatures, a study with more realistic repulsive potential functions is required for the phase separation in the detonation waves. Recently, Kerley performed the Monte Carlo calculations of the equations of state for mixtures having repulsive intermolecular potentials proportional to r^{-n} with $n = 6$ or 12. For equimolar mixtures with additive diameters ($\sigma_{ab} = (\sigma_{aa} + \sigma_{bb})/2$) having ratio of $\sigma_{aa}/\sigma_{bb} = 3$, he found that the fluid phase separation could occur with the r^{-6} repulsive interactions at a pressure below the freezing point of the larger component. Such fluid phase separation was not found for mixtures interacting with potentials proportional to r^{-12}. This result strongly suggested that the phase separation at high temperatures could occur in the mixtures of molecules with very large differences in size. However r^{-6} repulsion may be too soft for the real fluid, whereas r^{-12} repulsion in the L-J potential is too steep. Moreover, both quantum mechanical *ab initio* calculations and analyses of experimental data on simple molecular systems have shown that the intermolecular repulsion must be of an exponential character [13].

Since no simulation has been made for mixtures with exponential repulsions at high temperatures and pressures, we performed molecular dynamics simulations for the equimolar binary mixtures interacting with the modified Buckingham (exp-6) potentials. The mixture of H_2O/N_2 is considered because these species are the major detonation products and the fluid phase separation is expected from large difference in molecular sizes.

POTENTIALS AND MOLECULAR DYNAMICS SIMULATIONS

The fluid mixture of N_2/H_2O at equimolar composition was studied by molecular dynamics simulations. The exp-6 potential

$$\phi(r) = \frac{\varepsilon}{\alpha - 6}\left\{6\exp\left[\alpha\left(1 - \frac{r}{\sigma}\right)\right] - \alpha\left(\frac{r}{\sigma}\right)^{-6}\right\} \tag{1}$$

was used for the intermolecular potentials between N_2-N_2, N_2-H_2O, and H_2O-H_2O molecular pairs. The parameter α in Equation (1) gives a measure of the stiffness of the exponential repulsion. The use of a spherical potential is valid only for nonpolar molecules, but it is probably good for polar molecules as well at the conditions relevant to detonation environments, as discussed by Ree [1]. High temperatures of detonation will enhance molecular rotation, which diminishes nonsphericity. Tight compression with sufficient internal energies such as realized in detonation will break up the orientational effect of the electrostatic interaction. The potential parameters for N_2 and H_2O are taken from Ref. [1]: $\varepsilon_{aa}/k = 101.9\,\text{K}$, $\sigma_{aa} = 4.09\,\text{A}$ and $\alpha_{aa} = 13$ for N_2, and $\varepsilon_{bb}/k = 356\ (1 + 996.8/\text{T}) = 533\,\text{K}$ at 2000 K, $\sigma_{bb} = 3.06\,\text{A}$, and $\alpha_{bb} = 13$ for H_2O. The parameters of unlike-pair, N_2-H_2O, are computed from the combination rules: $\sigma_{ab} = (\sigma_{aa} + \sigma_{bb})/2$, $\varepsilon_{ab} = (\varepsilon_{aa}\varepsilon_{bb})^{1/2}$, and $\alpha_{ab} = (\alpha_{aa}\alpha_{bb})^{1/2}$.

Molecular dynamics (MD) calculations were carried out in NVT ensemble. The equations of motion for 256 particles are integrated by using a leapfrog algorithm. Temperature of the system is controlled by a velocity scaling method proposed by Woodcock [14]. All the MD calculations presented in this paper were performed at T = 2000 K. The periodic boundary condition is assumed on a cubic cell. Several calibration runs were performed in microcanonical (NVE) ensemble to determined the time step and the cut-off radius for the calculation of force. The relative errors in total Hamiltonian are within 10^{-4} with a cut-off radius of 10 A and a time step of 1×10^{-15} sec. Typically, the equations of motion are integrated over 5×10^4 time steps but the total run length depends on the relaxation time of the system from an initial fcc-lattice-like configuration to the final equilibrium configuration. Initial positions of molecules a ($=N_2$) and b ($=H_2O$) are determined by using random numbers on the fcc-lattice positions, and small random displacements in the range of $0 \sim d/10$ (d = fcc-lattice constant) from the initial lattice position are imposed before the integration. It was found that the pressure and the internal energy of the NVT ensemble were stabilized within the first 500 integration steps, i.e., the "annealing" of the system was completed within the 500 time steps. The structure change of the system is observed by evaluating the three correlation functions (g_{aa}, g_{ab}, and g_{bb}). Pressure and the internal energy of the system are also monitored.

RESULTS AND DISCUSSION

Fluid Phase Separation in Binary Exp-6 Mixtures

Figure 1 shows the pair correlation functions at three different densities: $\rho = 0.918$, 1.32, and $1.99\,\text{g/cm}^3$. The corresponding pressures at the equilibrium states are

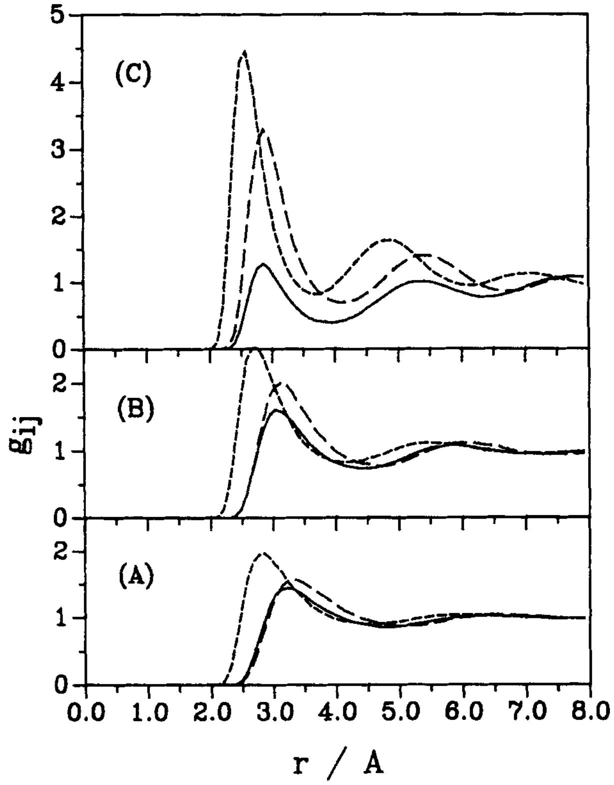

Figure 1 Pair correlation functions of equimolar H_2O/N_2 mixture at T = 2000 K: long-dash curve; g_{aa}, solid curve; g_{ab}, short-dash curve; g_{bb} (a = N_2 and b = H_2O), (A) $\rho = 0.918$, (B) $\rho = 1.318$, (C) = 1.991 g/cm^3.

2.1, 5.82, and 22.6 GPa, respectively. The pair correlation functions and quoted pressures were obtained by averaging over the time steps from 4×10^5 to 5×10^5 (40 to 50 psec). It was confirmed that the calculated pressures, excess internal energies, and running coordination numbers were in steady state in these time periods for the density range of $\rho < 2.0\,\text{g/cm}^3$. By comparing the height of correlation functions of like-pairs with that of unlike-pair, clearly the fluid separation occurs at $\rho = 1.99\,\text{g/cm}^3$ (Figure 1(C)). However, its occurrence is not clear at $\rho = 1.32$ and $0.918\,\text{g/cm}^3$. For more clear definition of the phase separation, Hoheisel and coworkers [5–7] showed that the sum of the local mole fractions could be used as a reliable distinction between homogeneous and inhomogeneous states in a mixture. The local mole fraction of a binary mixture, $x_{aa}(R)$, is defined by [3]

$$\chi_{aa}(R) = \frac{n_{aa}(R)}{n_{aa}(R) + n_{ab}(R)} \tag{2}$$

where $n_{ab}(R)$ denotes the running coordination number of particles of species b

within the distant of R from a particle of kind a, and is defined by the integral over the pair correlation function, $g_{ab}(r)$,

$$n_{ab}(R) = 4\pi\rho_N x_b \int_0^R r^2 g_{ab}(r)dr \tag{3}$$

with the total number density, ρ_N, and the overall mole fraction of species b, x_b. It has been shown [6] that the sum of the local mole fractions,

$$x_s(R) = x_{aa}(R) + x_{bb}(R) \tag{4}$$

represents deviations of the mean number of particles of the two kinds corresponding to specific cross interactions between unlike molecules. The function is normalized to unity at $R \rightarrow \infty$ and its values are also unity for all R if the mixture is uniform. For the inhomogeneous mixtures, particles of the same kind predominate the distribution, and values of $x_s(R)$ for infinite R are larger than unity. The choice of R for $x_s(R)$ is not critical as far as all the three pair correlation functions have already passed their first peak at R but have not lost their structure [6]. In the present study, a value of $R = \sigma_{ab} = 3.68$ A was used for the calculation of $x_s(R)$. Figure 2 shows a plot of $(x_s - 1)$ as a function of density. The pronounced increase of the slope of $x_s - 1$ at higher density region indicates the phase transition to the inhomogeneous mixture. The phase boundary for the transition from homogeneous to inhomogeneous mixture can be defined as the cross point of two straight lines in Figure 2. The transition density at $T = 2000$ K for the equimolar H_2O/N_2 mixture is determined to be $\rho = 1.35$ g/cm^3.

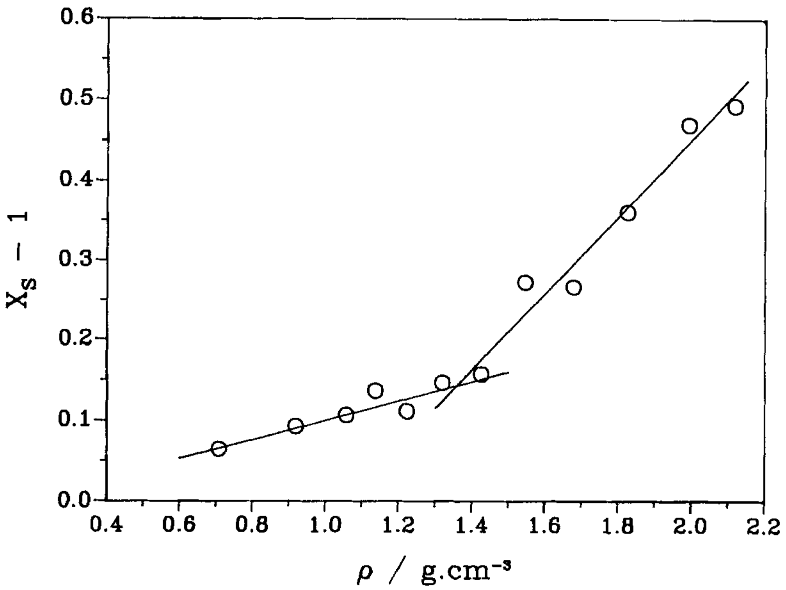

Figure 2 Static cross correlation factor $x_s - 1$ as a function of density at T = 2000 K in equimolar H_2O/N_2 mixture. Definition of x_s is given in Equation (4) in the text.

Rates of Demixing and Diffusion Coefficients

It is confirmed that the fluid phase separation in the binary mixture interacting with exp-6 potential can occur even at T = 2000 K. For the applications to the detonation or the shock compression of fluid mixtures, it is important to understand the relaxation process from homogeneous to inhomogeneous state in the high pressure fluid. The time variations of the quantities $x_s - 1$ are shown in Figure 3 for three different densities at $\rho > 1.35\,\mathrm{g/cm^3}$. Since the value of x_s represents the magnitude of the fluid phase separation, the rate of relaxation may be defined by dx_s/dt. As can be seen in Figure 3, the system relaxes to the equilibrium (phase separated) state without any incubation time at the density range of $1.35 < \rho < 2.0\,\mathrm{g/cm^3}$, and the initial rates of relaxation at $t < 2$ psec are independent on the density. After rapid increase in the value of x_s, it then reaches gradually to the equilibrium value. The rate of this slow approach to the equilibrium is largely dependent on the density. Because the relaxation curve of x_s is not expressed as a single exponential function, and because of relatively large scatter of the data, it is difficult to obtain precise relaxation rates. Nevertheless, the relaxation times are longer at higher densities. To get rough estimation of the relative relaxation rate, we evaluated time constant τ defined by the time required to reach $(1 - 1/e)$ of its equilibrium value. Results are given in Table 1. The absolute value of the time constant in this table may not have significant meaning: it can depend on the number of molecules used in the simulation and different initial configuration can give different relaxation rate. The purpose of the present calculation of these time constants is to investigate the dependence of these values on physical quantities,

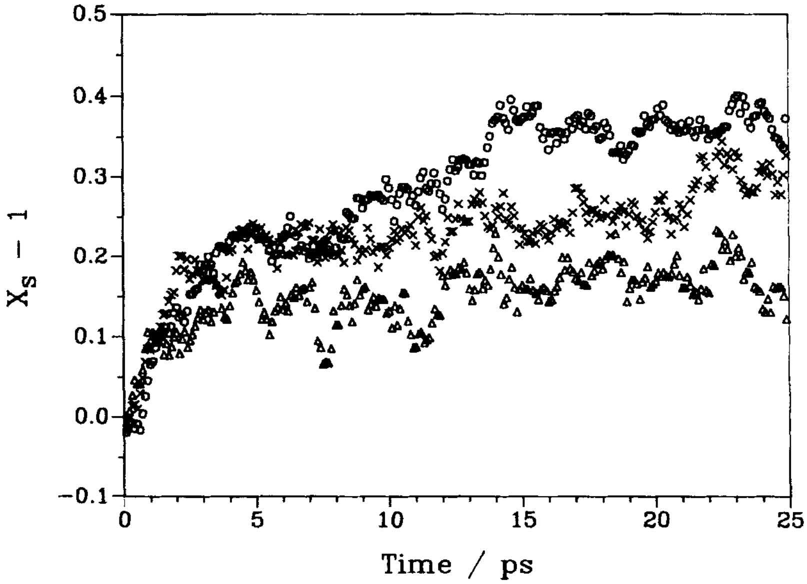

Figure 3 Static cross correlation factor $x_s - 1$ as a function of time at T = 2000 K in equimator H_2O/N_2 mixture: circles; $\rho = 1.824$, crosses; $\rho = 1.676$, triangles; $\rho = 1.425\,\mathrm{g/cm^3}$.

Table 1. Summary of molecular dynamics simulations for the equimolar H_2O/N_2 mixture at T = 2000 K.

ρ g/cm^3	p GPa	U/NkT^a	$D(N_2)^b$	$D(H_2O)^b$	τ^c psec
			10^{-5} cm^2/sec		
0.707	1.155	−0.152	76.2	102.8	—
0.918	2.099	−0.097	58.0	73.3	—
1.056	3.018	−0.011	40.9	57.9	—
1.222	4.634	0.177	29.9	38.0	—
1.318	5.824	0.317	26.0	32.7	—
1.425	7.466	0.525	24.7	25.5	2.2
1.544	9.571	0.771	17.4	19.4	2.8
1.676	12.634	1.156	15.8	16.2	5.7
1.824	16.915	1.701	9.64	10.0	11.5
1.991	22.623	2.380	7.39	7.76	13.2
2.117	31.356	3.466	4.65	4.18	—
2.387	45.691	5.282	—	—	—

a) Internal energy
b) Self-diffusion coefficient
c) Relaxation time for the phase separation

such as densities or self-diffusion coefficients. The calculations of the time constants were performed with similar initial configurations, that is, the initial configurations for different densities were determined with the same set of random numbers and relative magnitudes of the time constants were examined. The same initial slpoe of $x_s - 1$ at $t < 2$ psec observed in Figure 3 is caused by this similar initial configuration.

The self-diffusion coefficients of H_2O and N_2 were calculated to investigate the relationship between the diffusion rates and the relaxation rates. Molecules in the initial positions have to diffuse to their new position to form the phase separated inhomogeneous configurations. Therefore, the relaxation time is expected to correlate with the diffusion rate. The self-diffusion rates during the relaxation processes, D_{aa} for N_2 and D_{bb} for H_2O, can be calculated from the slope of the mean square displacement $\langle(\Delta r)^2\rangle$:

$$\langle(\Delta r)^2\rangle = 6Dt + const. \tag{5}$$

Results are plotted in Figure 4 as a function of density. Although diffusion coefficients in this figure were for the relaxation processes, the diffusion coefficients in the equilibrium states were also very close to the values in this figure (see Figure 5). At lower density region ($\rho < 1.35$ g/cm^3) where the phase separation does not occur, the diffusion coefficient of H_2O is always larger than that of N_2 and the ratio is D_{bb}/D_{aa} is approximately equal to the value expected from the kinetic theory for the ideal gas ($D_{bb}/D_{aa} = (28/18)^{1/2} = 1.25$). On the other hand, the diffusion coefficients become identical at higher densities, and the dependence of the diffusion coefficients on density is less than that in lower densities. As can be seen in Figure 4, the ratio of the self-diffusion coefficients suddenly changes at the point where the transition occurs from inhomogeneous to inhomogeneous state. This sudden change in the ratio was also used to define the phase boundary for the transition. The transition density thus determined in Figure 4 agrees well with that

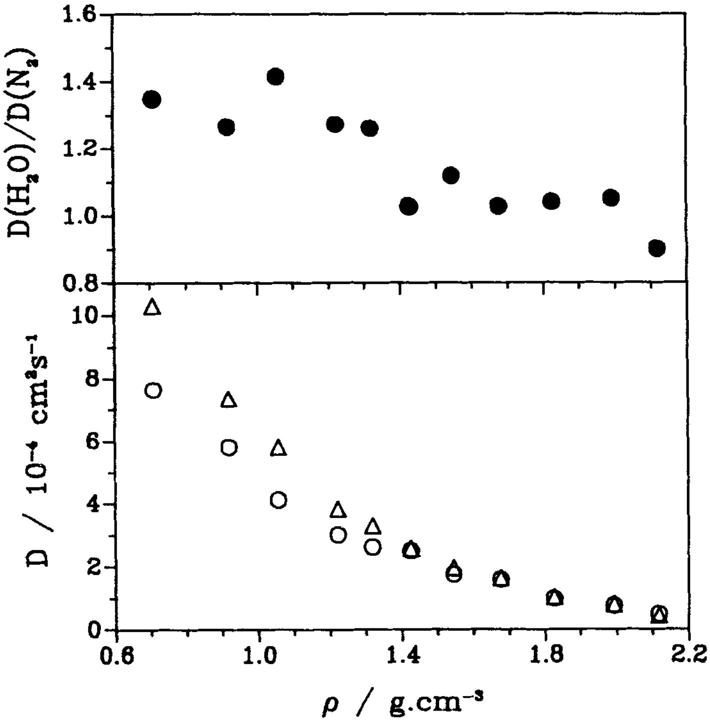

Figure 4 Self-diffusion coefficients of N_2 (circle) and H_2O (triangle) in the equimolar mixture at T = 2000 K.

determined by the static cross correlation factor x_s in Figure 2. Although Hoheisel and coworkers [5, 6] claimed that the ratio of self-diffusion coefficients was an indirect indication of the dynamical cross correlation in the binary fluid mixtures, such sudden change in the ratio and the identical self-diffusion coefficients in the phase-separated mixtures have not been reported in the previous works.

The self-diffusion rates and the time constants for the relaxation are summarized in Table 1. Pressures and internal energies at the equilibrium states are also shown in this table. The relaxation rate (which is the inverse of the time constant) is faster at lower density and it seems to correlate with the self-diffusion rates. Although large uncertainties in the time constants prevent the precise investigation of the relationship between the diffusion rates and the relaxation rates, the observed correlation indicates that the phase separation at the density region of $1.35 < \rho < 2.0\,g/cm^3$ is controlled by the diffusion processes.

Fluid Phase Separation at $\rho = 2.12\,g/cm^3$

It is found that the dynamic features of the relaxation at about $\rho \geq 2.0\,g/cm^3$ are very different from that at $\rho < 2.0\,g/cm^3$. Figure 5(a) shows the time variation of $x_s - 1$ at $\rho = 2.12\,g/cm^3$. It is noted that there is a long incubation period that

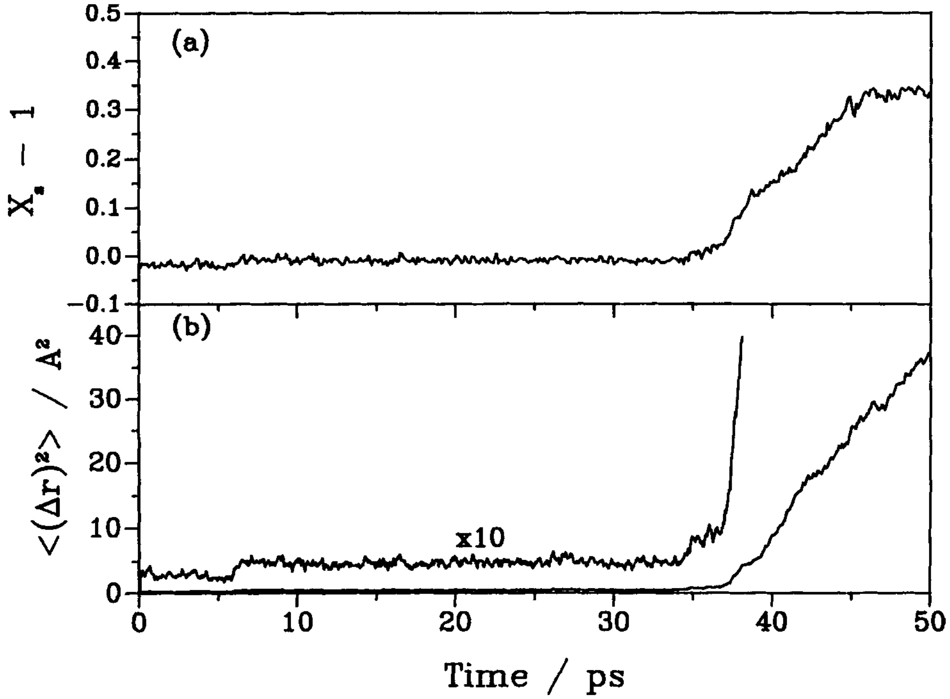

Figure 5 Static cross correlation factor $x_S - 1$ (panel *a*) and mean square displacement of N_2 (panel *b*) in equimolar H_2O/N_2 mixture at T = 2000 K and $\rho = 2.117\,g/cm^2$.

is never found at $\rho < 2.0\,g/cm^3$. The fluid phase separation suddenly starts at around $t = 35$ psec. The mean square displacement $\langle(\Delta r)^2\rangle = \langle[r(t) - r(t_0)]^2\rangle$ of N_2 at the same density is also displayed in Figure 5(b) as a function of time. The mean square displacement (MSD) was obtained by averaging over all like-molecules, but the averaging over the initial time t_0 was not performed, since we are interested in the time evolution of the MSD. The time profile of the MSD for H_2O is similar to that of N_2, except that its value is slightly larger than that of N_2. Although there is a small jump in MSD at abut $t = 6$ psec, the value of MSD is almost constant during the incubation period, that is, the diffusion rates in the fluid is almost zero. This seems to indicate that the fluid mixture in the incubation period has the amorphous-like rigid structure. The pair correlation functions in the incubation period (at $t = 20$ psec) and in the phase separated state (at $t = 62$ psec) are compared in Figure 6. Although the split in the second peak, which is often quoted as the indication of the amorphous state, is not observed in the figure, there are small and broad peaks in-between main peaks. These small peaks disappear in more flexible phase-separated state, as shown in Figure 6(B). It is also noted that the peak positions and their heights for three pair correlation functions (g_{aa}, g_{ab}, and g_{bb}) are almost identical except for the first peaks. These features of the pair correlation functions also indicate somewhat rigid amorphous-like structure. To illustrate such structure in the incubation period, the perspectives of the configura-

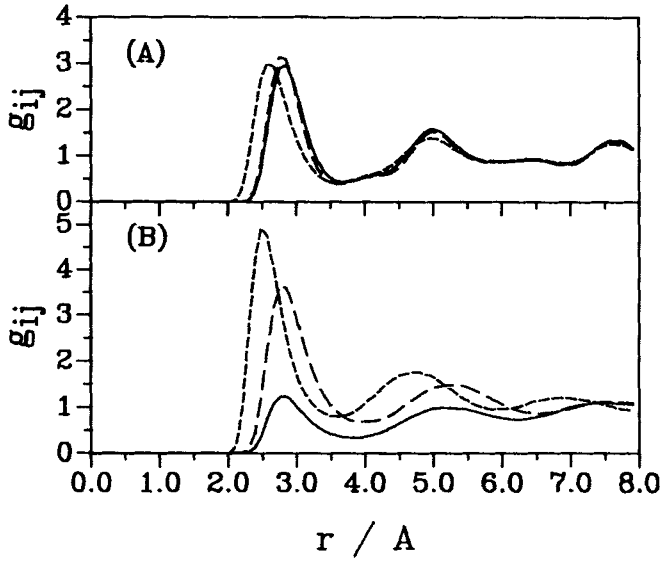

Figure 6 Pair correlation functions of equimolar H_2O/N_2 mixture at T = 2000 K and $\rho = 2.117$ g/cm^3: long-dash curve; g_{aa}, solid curve; g_{ab}, short-dash curve; g_{bb} ($a = N_2$ and $b = H_2O$), panel (A); $t = 20$ psec, panel (B); $t = 62$ psec.

tions at $t = 20$ and 62 psec are displayed in Figure 7. In the incubation period, the distributions of H_2O and N_2 in the box are uniform and the fluid phase separation is not yet started as expected from the value of x_s, but some regularity in configuration can be seen. On the other hand, after the fluid phase separation is completed (at $t = 62$ psec), such regularity disappears and formation of N_2 cluster can be seen in Figure 7(B). It should be noted that the H_2O cluster is also formed at the same time, even though its formation is rather hard to see in Figure 7(B). An example of more direct evidence of the formation of H_2O cluster is shown in Figure 7(C).

Since the amorphous-like structure shown in Figure 7(A) is not found in the lower density region, the existence of the long incubation time at $\rho = 2.12$ g/cm^3 may be due to such rigid configuration. Recently, in molecular dynamics simulations of binary soft-sphere mixtures, Miyagawa *et al.* [15] found that the jump motions of atoms in the glassy state were responsible to the very small self-diffusion coefficient near the glass-transition point. In dense amorphous states, two types of atomic motion may be possible: vibrational motions centered at their local equilibrium positions (defined as local potential minima) and the jump motions to neighboring local equilibrium positions. Since vibrational motions do not induce any structural changes, molecular jump motions may be responsible to the sudden beginning of the relaxation from the amorphous-like state to the phase-separated state. Although only few molecules in the dense rigid fluid state can take place such jump motion and its occurrence is stochastic, it has been demonstrated [15] that the correlated jump motions could be induced in many molecules successively within very short times. Such a dynamically correlated jump motion can cause the sudden stochastic change in the MSD found in Figure 5, and can start the relaxation toward the

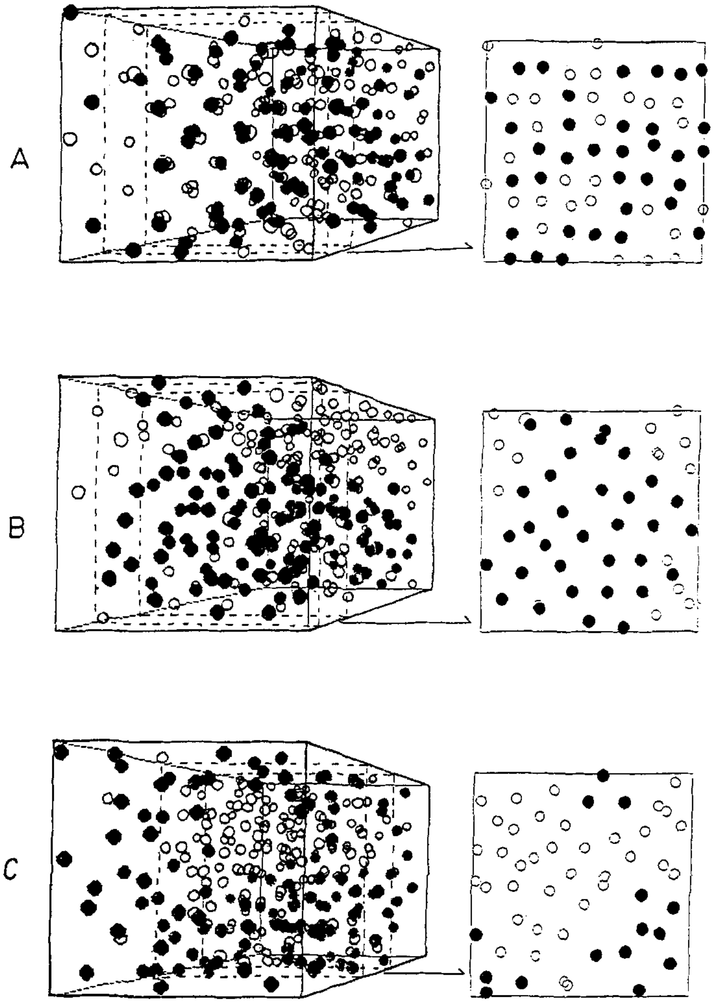

Figure 7 Perspectives of particle configurations of the equimolar H_2O/N_2 mixture at T = 2000 K; closed circles; N_2, open circles; H_2O, (A); $\rho = 2.117\,g/cm^3$ and $t = 20$ psec, (B); $\rho = 2.117\,g/cm^3$ and $t = 62$ psec, (C); $\rho = 1.991\,g/cm^3$ and t = 50 psec. The radius of circles is reduced to $\sigma/8$ in order to avoid the overlap of the drawing.

phase-separated state. Once the relaxation starts, properties of the system such as the time dependence of the MSD and pair correlation functions are not different from those at the lower density region. The self-diffusion coefficients at this density determined from the slope of MSD agree well with the extrapolation of the lower density values, as shown in Figure 4.

If the phase transition is initiated by such jump motions at $\rho > 2.0\,g/cm^3$, it is very difficult to predict the length of the induction period because of the stochastic nature of the jump motion. At $\rho = 2.38\,g/cm^3$, no transition to the phase-separated state could be found even the calculation was continued to 600 psec in our simulation. It was shown that very long integration time was required to detect the jump motion in the molecular dynamics simulations near the glass transition point [15].

CONCLUDING REMARKS

The main conclusions obtained in the present molecular dynamics simulations for the equimolar H_2O/N_2 mixture at $T = 2000\,K$ in the NVT ensemble are summarized as follows.

(1) It is directly shown that the fluid phase separation in equimolar H_2O/N_2 mixture can occur at the condition relevant to the detonation environments.
(2) The density at the phase boundary could be determined on the basis of the static cross correlation factor defined as the sum of local mole fractions.
(3) The self-diffusion coefficients of H_2O and N_2 were found to be almost the same at the density region where the fluid phase separation occurred in the constant volume.
(4) Two different mechanisms for the relaxation from uniform to phase-separated state could be distinguished. At the lower density region ($1.35 < \rho < 2.0$ g/cm^3), the relaxation process is controlled by molecular diffusion. On the other hand, the relaxation at higher density region is initiated by the stochastic jump motions.

We observed the formation of clusters caused by phase separation in high pressure fluid. The size of these clusters is important information for understanding physical and chemical properties of phase-separated high pressure fluid. The cluster size in the present simulations seems to be limited by the size of the box, as can be seen in Figure 7(B) and 7(C). For liquid mixtures at low temperature not far from the critical solution point, the growth of the cluster of about 1000 A size within the order of $10^2\,\mu$sec was observed in the pressure-jump experiment with spectroscopic detection of the droplet formed by the phase separation [16]. For the understanding of the physical and chemical effects of the fluid phase separation at high temperatures, it is important to investigate the mechanisms of large scale cluster formation behind detonation (or shock) waves. Work on this subject is now in progress.

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