Molecular dynamics simulation of hard sphere mixtures

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Abstract

From molecular dynamics simulations for binary hard sphere mixtures, the self- and mutual diffusion coefficients were calculated based on both velocity correlation functions and the mean square displacements of atoms or Einstein relation. Satisfactory behavior of the back scattering factor was obtained in the latter case. The obtained back scattering factor is similar to the case of one component hard spheres. The mutual diffusion coefficient was, within 10%, in agreement with the linear relation of particle number ratio between respective self-diffusion coefficients. Some discussions were given for the role of mass difference on the mechanism of diffusion.

1. Introduction

In our previous study, the validity of the hard sphere model for simple liquid metals(Li) was shown based on the comparison between the theoretical calculations and the results of microgravity experiment. However, the multi-component hard sphere model is needed in more complex liquids, i.e. liquid Ge and Si, and liquid complex mixtures. In this study, we performed the molecular dynamics simulation of hard sphere mixtures to present a tool for the discussion and the clarification of the diffusion in complex liquids.

2. Analytical Methods

Two component hard sphere mixtures were considered. Component α(1 or 2) has the hard sphere diameter, σ_α and the mass of particle, m_α. The velocity v_α of component α, position r and time t were written in the non-dimensional form. (k: the Boltzman's constant)

$$V_\alpha = v_\alpha / \sqrt{kT/m_2} . \tag{1a}$$

$$R_\alpha = r_\alpha / \sigma_2 . \tag{1b}$$

$$\tau = t / \sqrt{m_2 \sigma_2^2 / kT} . \tag{1c}$$

The order parameters of this system are σ (ratio of hard sphere diameter), m(ratio of mass of particle), n (particle number fraction of component 1)and y (packing fraction) defined below.

$$\sigma \equiv \frac{\sigma_1}{\sigma_2}, \quad m \equiv \frac{m_1}{m_2}, \quad n \equiv \frac{N_1}{N_1 + N_2}, \quad y \equiv \frac{4\pi}{3L^3}\left\{ N_1 \left(\frac{\sigma_1}{2}\right)^3 + N_2 \left(\frac{\sigma_2}{2}\right)^3 \right\}. \tag{2}$$

In these definitions, N_α is the particle number of component α in a unit cell with the length L of simulation. Non-dimensional diffusion coefficient, $\delta_{\alpha\beta}$, is expressed as below,

$$\delta_{\alpha\beta} = \sqrt{\frac{m_2}{kT\sigma_2^2}} D_{\alpha\beta} . \qquad (3)$$

If β equals to α, $\delta_{\alpha\alpha}$ means the self- diffusion constant for component α, and if $\alpha \neq \beta$, $\delta_{\alpha\beta}$ is mutual diffusion constant.

At first, applications of the present results were expected for the analysis of the diffusion experiment for liquid Ag-Cu alloys by TR-IA No.7 rocket. For this reason, δ = 0.96 and m = 0.59 are adopted as initial conditions. The particle number fraction, n, and packing fraction, y, are set to be varying parameters. The velocity auto-correlation function (VAF) and the mean square displacement (MSD) were calculated. From these the self- and mutual diffusion coefficients and the back scattering factor were evaluated.

3. Results and Discussions

Though the phase diagram of hard sphere mixtures has not been obtained completely, the Mansoori's equation is known for the equation of state of hard sphere mixtures in the fluid state.

$$Z_M = \left[1 + y + y^2 - \frac{3y_1 y_2}{(y_1 + \sigma^3 y_2)} (1-\sigma)^2 \{\sigma(y_2+1) + (y_1+1)\} - \frac{y}{(y_1+\sigma^3 y_2)} (y_1 + \sigma y_2)^3 \right] \Big/ (1-y)^3 , \qquad (4)$$

In this equation, Z and y_i are the compressibility factor and the packing fraction of components i respectively. The compressibility factors Z's at σ = 0.96 is shown in Fig.1. There is no relation between Z and particle number fraction, n.

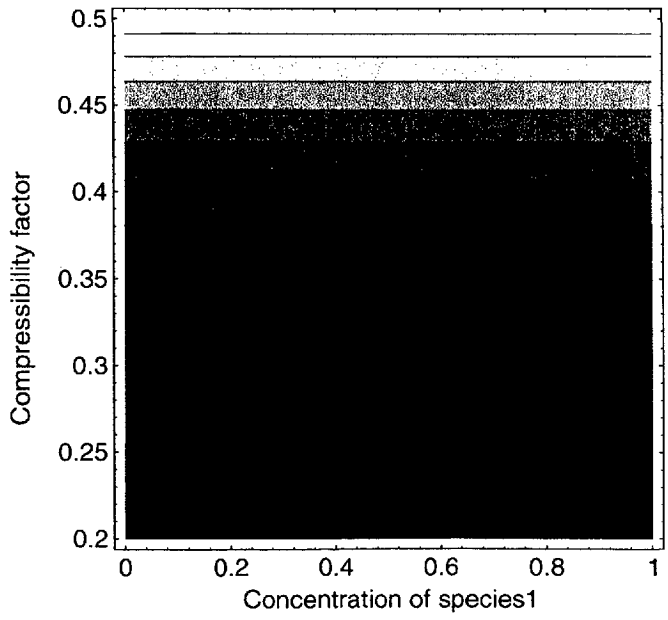


Fig.1 Compressibility factors of 2 component hard-sphere mixtures

In Tab. 1 a summary is given for the compressibility factors Z's obtained by the present simulation and Z_M based on Eqn. (4).

Table1 Compressibility factors

n	y	Z	Z / Z_M
0.25	0.3	3.98	1.00
	0.4	6.96	1.01
	0.45	9.41	1.00
0.5	0.05	1.23	1.00
	0.1	1.52	1.00
	0.2	2.40	1.00
	0.3	3.98	1.00
	0.4	6.95	1.00
	0.45	9.40	1.00
0.75	0.3	3.99	1.01
	0.4	6.95	1.00
	0.45	9.41	1.00

Tab.1 shows that the results of the present simulation agree with the Mansoori's equation. This fact indicates the validity of the present simulations.

Next, we performed the analysis of the diffusion process in binary hard sphere mixtures. As in the case of one component case, the Enskog's equation for binary mixtures was written as follows:

$$\delta_E = \delta_{12} / g_{12} , \tag{5a}$$

$$\delta_{12} = \frac{\sqrt{\pi}}{4} \frac{1-\left(1-\sigma^3\right)n}{y(1+\sigma)^2} \sqrt{\frac{1}{2}\left(1+\frac{1}{m}\right)}, \tag{5b}$$

$$g_{12} = \frac{2-y}{(s+y)(1-Y)^3}\left[1+\frac{y}{2}\left\{1+3\frac{\sigma-1}{\sigma+1}\frac{1-\left(1+\sigma^3\right)n}{1-\left(1-\sigma^3\right)n}\right\}\right] . \tag{5c}$$

Fig.2 shows the mutual diffusion coefficient obtained by the Enskog's formula at $\sigma = 0.96$ and $m = 0.59$.

In the present analysis, the self-diffusions, δ_{11} and δ_{22}, are calculated in terms of the velocity auto-correlation function(VAF), $< V_1(t) \bullet V_1(0) >$ and $< V_2(t) \bullet V_2(0) >$.

$$\delta_{11} = \frac{1}{3m}\int_0^\infty \langle V_1(\tau) \cdot V_1(0) \rangle d\tau . \tag{6a}$$

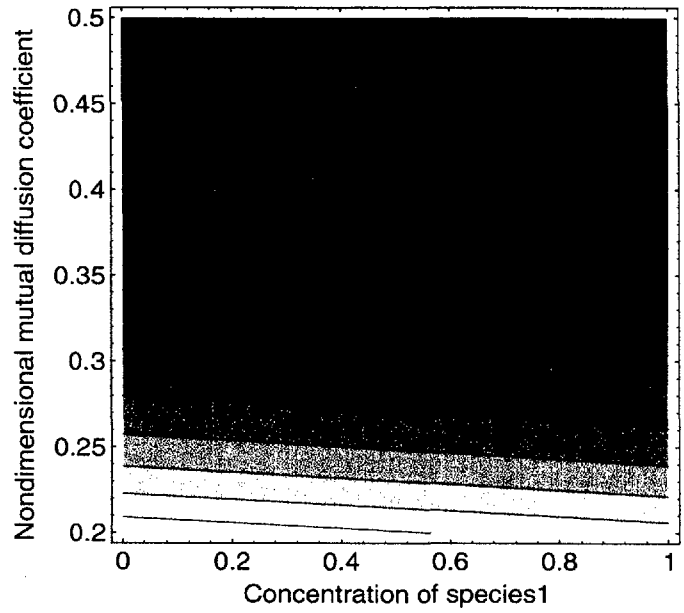
$$\delta_{22} = \frac{1}{3}\int_0^\infty \langle V_2(\tau) \cdot V_2(0) \rangle d\tau . \tag{6b}$$

The mutual diffusion coefficient, δ_{12}, was evaluated using Eqn.(7a-7c),

$$\delta_{12} = \left(\frac{1-n}{m} + n\right)\int_0^\infty Z_{12}(\tau)d\tau . \tag{7a}$$

$$Z_{12} = \langle J(\tau)\cdot J(0)\rangle \Big/ \langle J^2 \rangle \tag{7b}$$

$$J(\tau) = (1-n)\sum_i V_{1i} - n\sum_j V_{2j} \tag{7c}$$



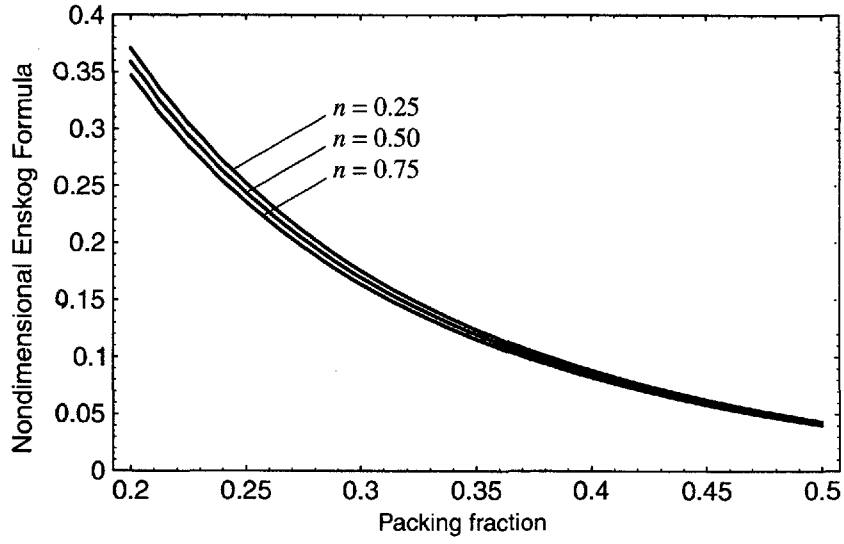


Fig.2 Mutual diffusion coefficient obtained by Enskog's theory

The velocity auto-correlation function and the example of $Z_{12}(r)$ is shown in Fig.3 and Fig.4. Fig.3 is the packing fraction dependence in the case of n = 0.5.

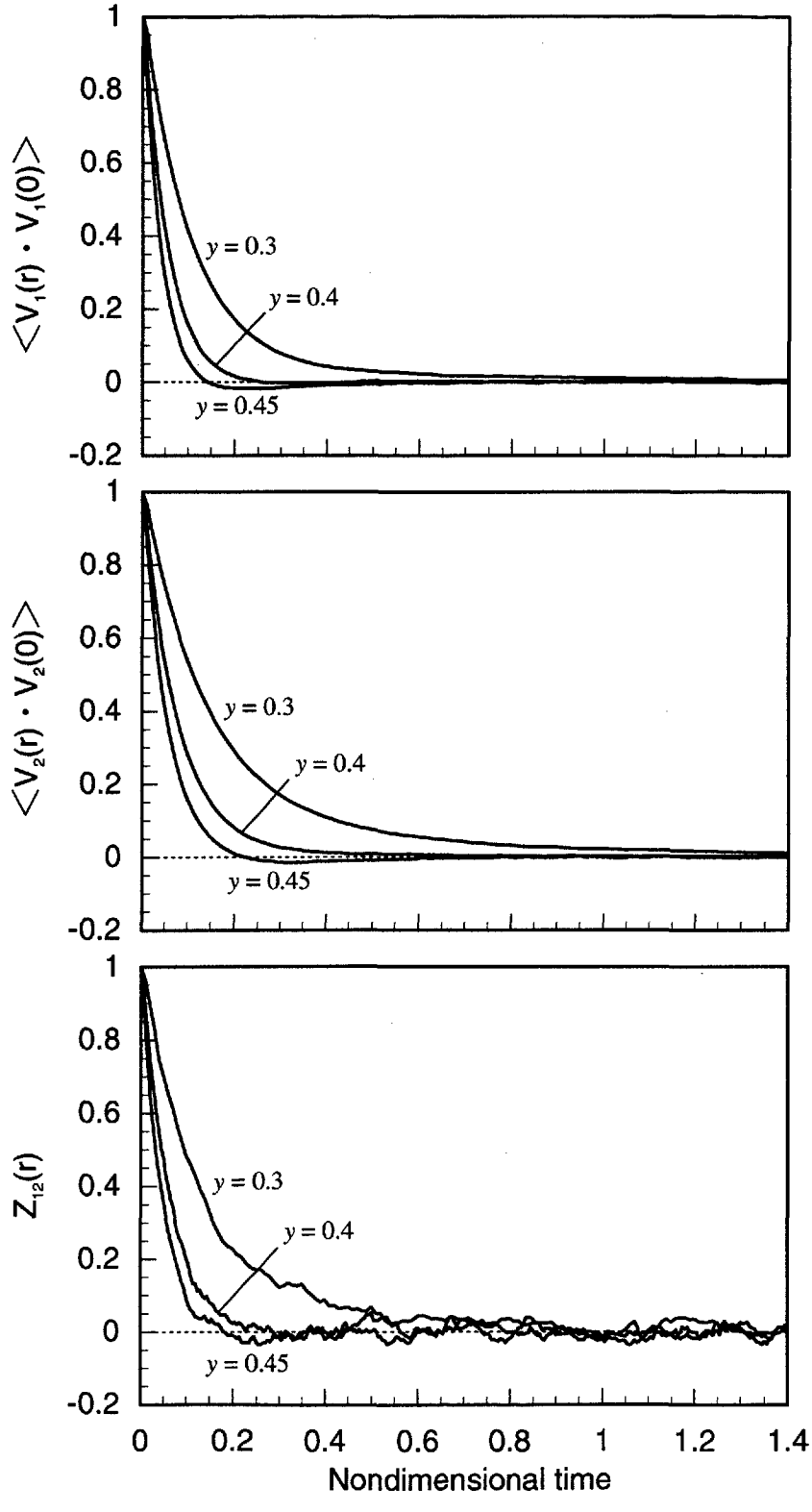


Fig.3 The velocity correlation functions at n = 0.5

(a) VAF of component1, (b) VAF of Component2, (c) Z(τ) between component 1 and 2(Eqn.7b)

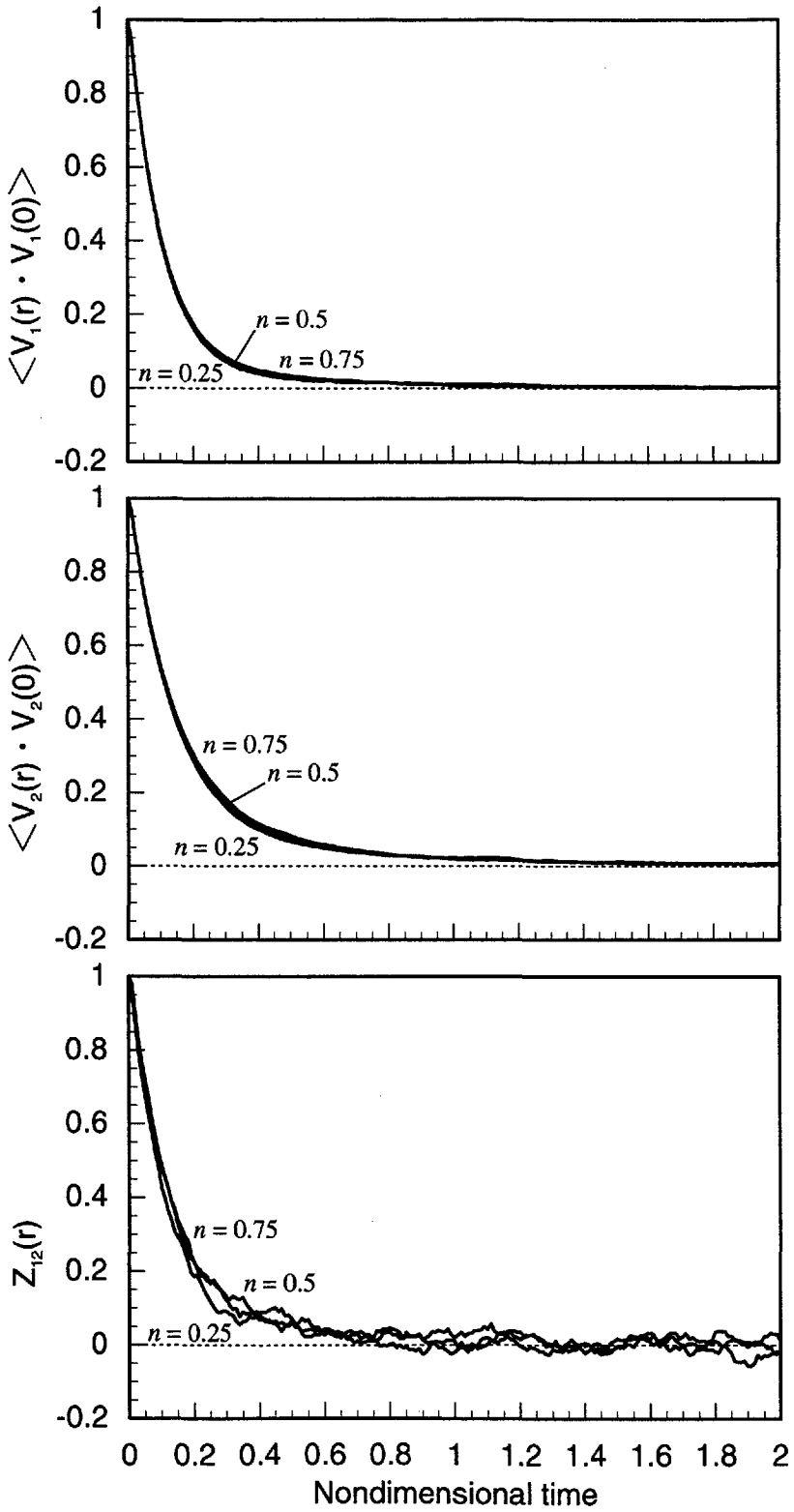


Fig.4 The velocity correlation functions for the case of n = 0.3

(a) VAF of component 1, (b) VAF of component2, (c) Z(τ) between component 1 and 2(Eqn.7b)

As shown in Fig.4, only monotonous decrease to zero value (no correlation) was observed for VAFs of component 1 and component 2 in the case of n= 0.3. VAF' of n=0.5 differs from VAF' of n=0.3. With the increase of packing fraction, VAF decreases more rapidly in the case of n=0.5. In the extreme case of y=0.45, they showed a negative value before particles lose the memory of collision. This strongly suggests the existence of the cage effect of surrounding atoms on the motion of centered particle. Therefore, Z_{12} also has a negative value. In the intermediate case of y = 0.4, a slight negative region for VAF' is not observed only among heavier (component 2) particles. This fact indicates that the correlation of velocity among lighter particles is different from that among heavier particles. The heavier particles can only ran away from the cage and the lighter particles may be captured in that cage. This may be derived from the reason that the cage derived from the cooperative motion of surrounding atoms may be more easily broken by the motion of heavier particles with larger momentum. This effect of particle velocity may explain the rather monotonous behavior of VAF for n=0.3. Correlation among lighter particles is bot strong because of the dilute concentration of lighter particles. As for the VAF among heavier particles the velocity is sufficient for the escape from the cage.composed of heavier particles.

In Tab.2 is shown the diffusion coefficients obtained from velocity-correlation functions together with the back scattering factor C_{BS} ($\equiv \delta_{12}/\delta_E$) for various n and y($\delta_E$:Eqn.(5a)). In Fig.5, C_{BS} obtained in the present study is shown together with C_{BS} of single component hard spheres.

Table2 Self- and Inter- diffusion constant of 2 components hard sphere

n	y	δ_{11}	δ_{22}	δ_{12}	δ_{12}/δ_E
0.25	0.3	2.27×10^{-1}	1.95×10^{-1}	2.27×10^{-1}	1.29
	0.4	9.82×10^{-2}	8.60×10^{-2}	1.05×10^{-1}	1.18
	0.45	6.00×10^{-2}	5.03×10^{-2}	5.89×10^{-2}	0.94
0.5	0.05	2.55	2.15	2.58	1.16
	0.1	1.16	9.71×10^{-1}	9.46×10^{-1}	0.98
	0.2	4.78×10^{-1}	4.06×10^{-1}	4.73×10^{-1}	1.32
	0.3	2.32×10^{-1}	2.02×10^{-1}	2.16×10^{-1}	1.27
	0.4	9.93×10^{-2}	8.76×10^{-2}	9.18×10^{-2}	1.08
	0.45	6.09×10^{-2}	5.24×10^{-2}	5.73×10^{-2}	0.95
0.75	0.3	2.40×10^{-1}	2.07×10^{-1}	2.03×10^{-1}	1.24
	0.4	1.04×10^{-1}	9.21×10^{-2}	8.02×10^{-2}	0.98
	0.45	6.19×10^{-2}	5.41×10^{-2}	4.45×10^{-2}	0.77

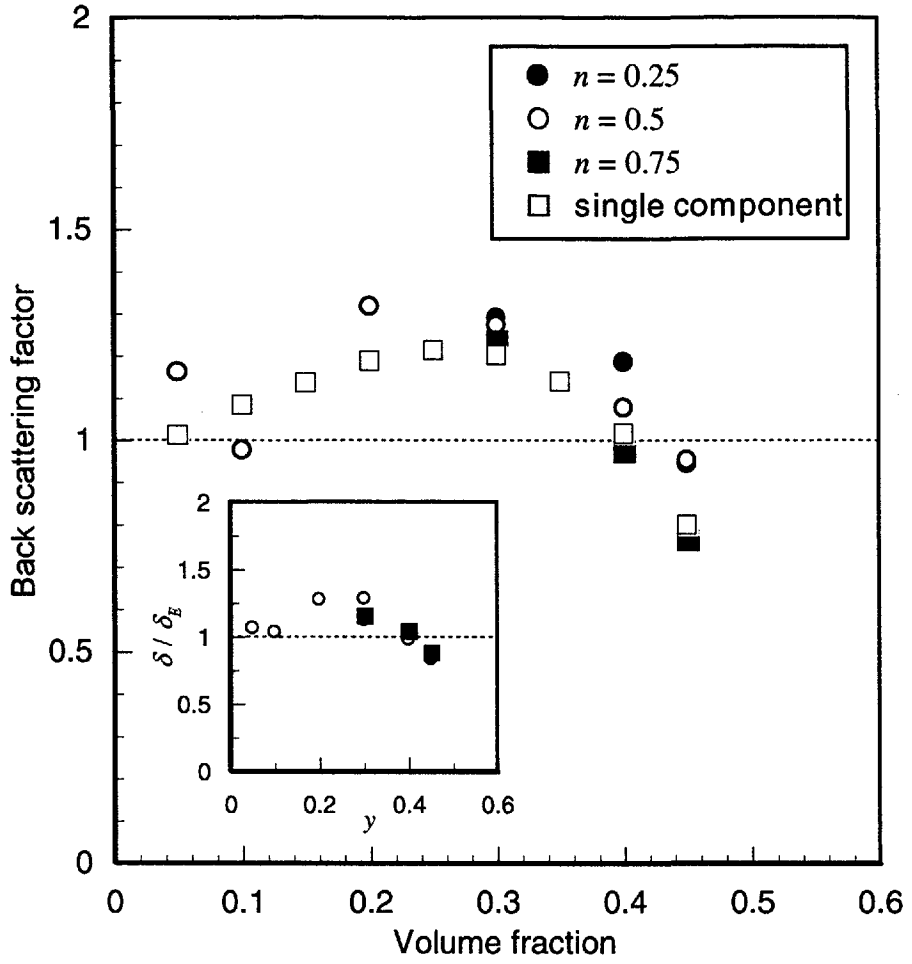


Fig.5 Back scattering factor of hard sphere mixtures together with that of single component

As can be seen in the Fig.5, the behavior of back scattering factor is similar to that of single component hard spheres. The back scattering factor is a decreasing function of y in the range y>0.3, which is the important region for the study of liquids. The considerable enhancement of diffusion is obtained at y=0.45. However, the present back scattering factor is not satisfactory from the view point that it should be 1 in the low packing limit. As can be seen in Fig.5, the large discrepancy from 1 was observed for y=0.05. It should be noted that the mutual diffusion coefficient adopted for the evaluation of back scattering factor is derived from the velocity correlation functions. As can be seen in Figs.3 and 4 Z_{12} shows unstable behavior.Therefore, the diffusion coefficients were calculated from the mean square displacement of particles. The back scattering factors obtained from these mutual diffusion coefficients are shown in the inset of Fig.5. Obtained results seem to be sound; the back scattering factor is 1 in the low packing limit and the decreasing function of y in the range y>0.3..

Next, we discussed the relation between self- and mutual diffusion coefficients. Z_{12} in Equation (4) could be divided into self- and inter- correlation terms between component 1 and component 2.

$$\delta_{12} = (1-n)\delta_{11} + n\delta_{22} + \left(\frac{1-n}{m} + n\right)\int_0^\infty Q(\tau)d\tau \qquad (8)$$

In this equation, the third term is the integral of inter-correlation terms between component 1 and component 2. It could be neglected if there is only a small difference among particles. In the present simulation, σ = 0.96 and m = 0.59. There was no large difference as for the diameter of particles. Therefore, we evaluated $\Delta\delta$ defined below in order to check the adaptability of linear relation δ_L between self-diffusion of component 1 and that of component 2.

$$\Delta\delta \equiv (\delta_L - \delta_{12})/\delta_L \qquad (9)$$

The δ_L is the linear relation(particle fraction average) between self-diffusion coefficient of component 1 and that of 2. The result is shown in Fig.6. In the analysis, the difference between mutual-diffusion coefficient and the linear law is under 20%. If the diffusion coefficient is calculated from the Einstein relation, the agreement is improved to be less than 20%, as shown in the inset of Fig.6.

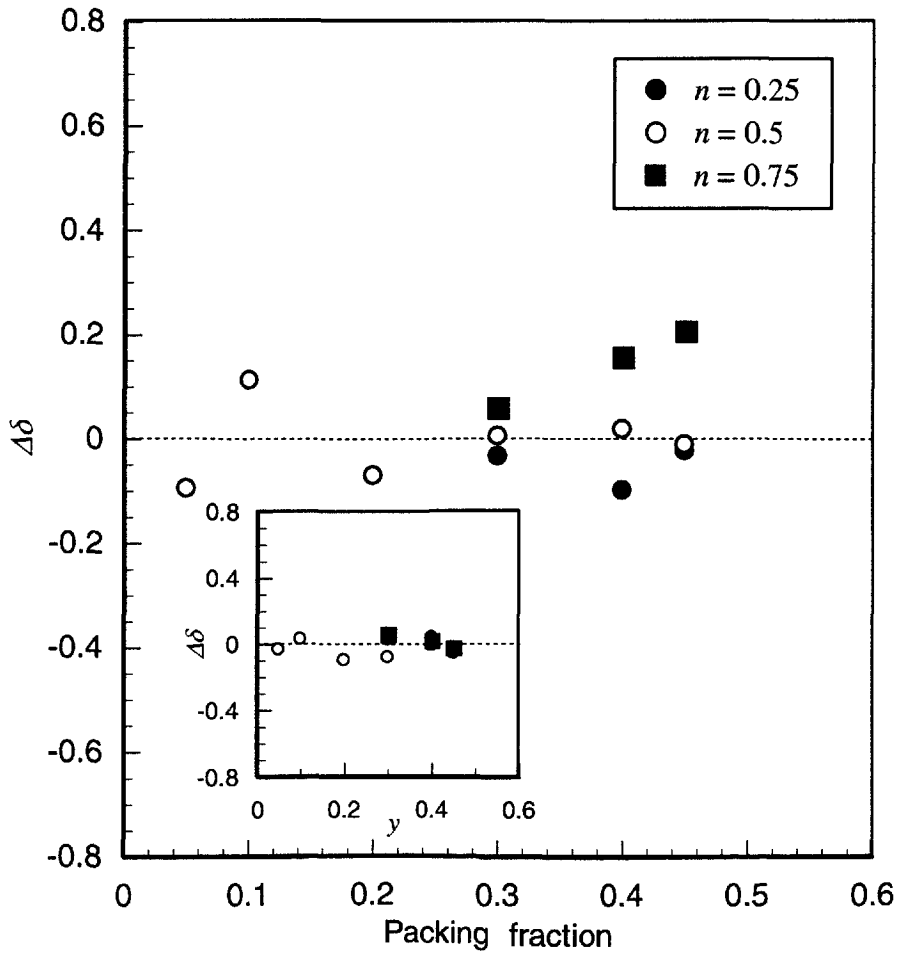


Fig.6 The deviation of the mutual diffusion coefficient from the linear relation between self-diffusion coefficients linear- relation.

4. Conclusions

The analysis of diffusion process of binary component sphere mixtures was performed by molecular dynamics simulation. Self- and mutual diffusion coefficient and their relation were evaluated, in which the ratio of diameters was set to be 0.96 and that of mass was to be 0.59, by which the condition of liquid Ag-Cu was simulated. The packing fraction dependence of back scattering factor is similar to that of single component hard spheres. It is found that, in the hard sphere system, the mutual diffusion coefficient can be evaluated with a deviation less than 10 % from the linear relation between the self-diffusion coefficient of component 1 and that of component 2. The correlation of velocity is more stronger among lighter particles.

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