

Molecular dynamics simulations of atomic transport of hard sphere fluids -a verification of Speedy's equation for the self-diffusion of hard sphere fluids-

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Abstract

The molecular dynamics simulation of hard spheres was performed. The validity was confirmed for the Speedy et al.'s formula of self-diffusion coefficient of hard spheres given as the compilation of many data sources. Some discussions are given for the mechanism of diffusion of hard spheres based on the back scattering factor as a function of packing fraction.

1. Introduction

The precise measurement of diffusion coefficient of melts is one of the most important themes in the field of microgravity utilization. In molten materials, the existence of particular short range order or chemical short range order is presumed. The diffusion behavior seems to be influenced deeply by these particular features of short range order. Recently, much attentions have been focused on the melts of alloys and semiconductors because these melts are regarded as complex liquids with chemical short range order or particular short range order rather than simple liquids with a random assembly of atoms. We have performed the molecular dynamics simulation of simple liquid metals in order to clarify the mechanism of mass transport in liquids. In this paper, we report the molecular dynamics simulations in which the validity is studied for the Speedy et al.'s formula for self-diffusion of hard sphere fluids and the mechanism of diffusion in hard sphere assembly is discussed from the back scattering factor.

2. Numerical modeling and the method of simulations

In this study, the position, r , and velocity, v , of the atom and time, t , are written in the non-dimensional forms, R , V and τ as below:

$$R = r / \sigma, \quad (1)$$

$$V = v / \sqrt{k_B T / m}, \quad (2)$$

$$\tau = t \sqrt{k_B T / (m \sigma^2)}, \quad (3)$$

In these equations σ and m are diameter and mass of a particle, respectively; T is the temperature of the system, and k_B is the Boltzmann's constant. The order parameter of this non-dimensional system is therefore only a packing fraction y , which is defined as below,

$$y = \frac{1}{6} \pi n \sigma^3. \quad (4)$$

In this equation, $n(=N/V$; N : number of particles; V : volume of the system) is the number density of particles.

The diffusion coefficient D is written in the non-dimensional form as follows;

$$\delta = D \sqrt{m/(k_B T \sigma^2)}. \quad (5)$$

Based on Eqn. (5), non-dimensional forms of Enskog's formula and Speedy's formula can be given as the function of only the packing fraction, y , respectively.

$$\delta_{ENS} = \frac{\sqrt{\pi}}{16y g(\sigma)} = \frac{\sqrt{\pi}}{8} \frac{(1-y)^3}{(2y-y^2)}. \quad (6)$$

$$\delta_{Speedy} = \frac{\sqrt{\pi}}{16y} \left(1 - \frac{6y}{1.09\pi}\right) \left[1 + \left(\frac{6y}{\pi}\right)^2 \left\{0.4 - 0.83 \left(\frac{6y}{\pi}\right)^2\right\}\right]. \quad (7)$$

In Eqn.(6), $g(\sigma)$ is the radial distribution function at the hard sphere contact, σ .

In this study, we calculated the back scattering factor based on the diffusion coefficient(Eqn. (5)) and Enskog's formula(Eqn (6)) in the non-dimensional form as a function of packing fraction. In the fcc grid 256 particles were placed. The periodic boundary condition was employed to avoid the surface problem. The calculation was successfully carried out without any numerical instabilities.

3. Results and discussions

Equation of state

The hard sphere system behaves as a liquid(or fluid) or a solid depending on the packing fraction. Previous MD simulation showed that it is a fluid in case of $0 \leq y \leq 0.49$, and it is a solid in $y \geq 0.549$, respectively.

In case of $0.494 \leq y \leq 0.545$, it is transition state and depends not only on y but also on the initial conditions. It is well known that the equation of states for liquid region($0 \leq y \leq 0.49$) follows the Boublik-Nozbeda Equation.

$$Z = \frac{1 + y + y^2 - b_1 y^3 - b_2 y^4 - b_3 y^5}{(1-y)^3}, \quad (8)$$

where Z is compressibility factor, that is $Z = pV/Nk_B T$ (P :pressure). The explicit values of these coefficients in Eqn.(8) are respectively $b_1=0.764314$, $b_2=0.151532$, and $b_3=0.654551$. Fig.1 shows the compressibility factor calculated from the present simulation. The present results well agree with the formula (8), and this agreement shows the validity of the present MD simulation.

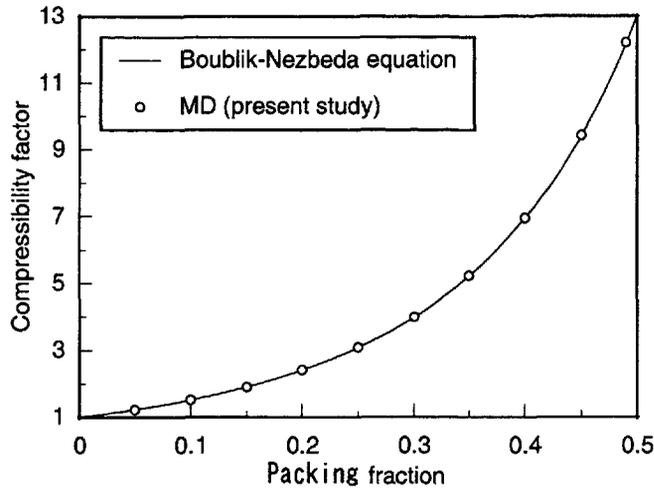


Fig.1 The compressibility factor calculated based on MD simulation

Structure of hard sphere system

The liquid structure of the hard sphere system was evaluated in the form of radial distribution function, $g(r)$, as shown in Fig.2. As expected, the peak height increases with the increase of the packing fraction. For the comparison with the results obtained by X-ray and neutron scattering experiments, the structure factor, which is the Fourier transform of radial distribution function, is

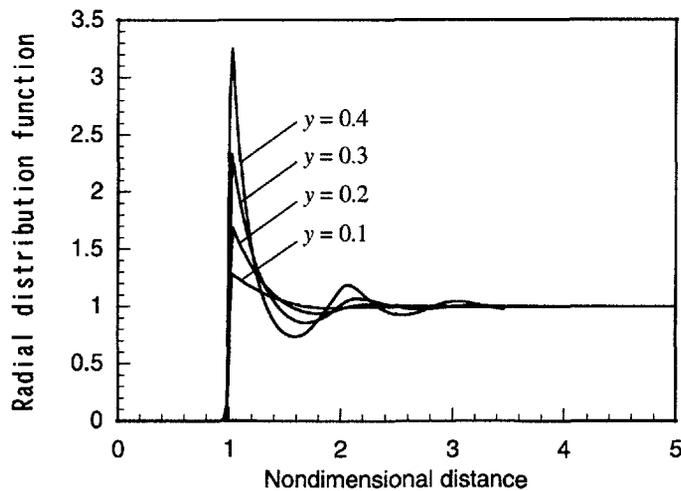


Fig.2 Radial distribution function of hard sphere system

a more appropriate structural information. The structure factor, $S(q)$, was obtained utilizing the well known relation described below.

$$S(q) = 1 + \frac{4\pi n}{q} \int_0^{\infty} r \{g(r) - 1\} \sin(qr) dr \quad (9)$$

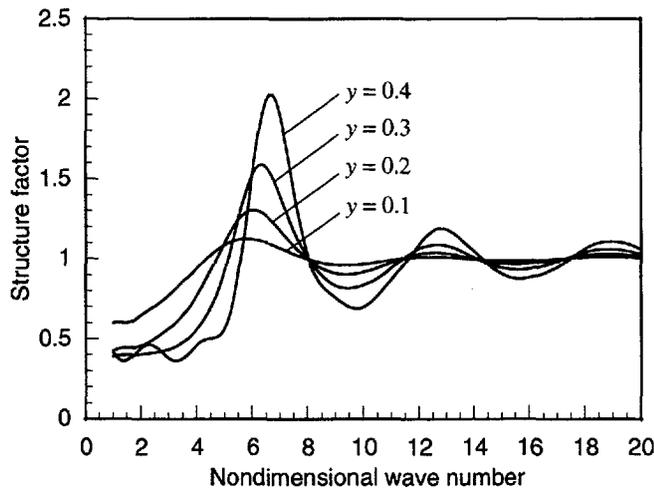


Fig.3 Structure factors of hard-sphere system

In Fig.3 the obtained structure factors are shown. The structure of present hard sphere system seems to be liquid like and there exists a specific oscillation as was often found in the liquid phase. In the region where the packing fraction equals to 0.1, that is the low density condition, the second peak of the structure factor does not appear and it shows a gas like characteristic.

Diffusion process of hand sphere system

Mean square displacements obtained by the present simulation are shown in Fig.4. It can be found that, with the decrease of packing fraction, the longer crossover time is present between the parabolic law(ideal gas behavior) and the linear law(Einstein's relation of diffusive motion). This longer crossover time may be derived from the longer mean free path of particles with the decrease of the packing fraction. Fig.5 shows the velocity auto-correlation functions of hard-sphere system. The rapid decay of the velocity auto-correlation function with the increase of time can be seen with the increase of packing fraction y . This is derived from the frequent collisions of particles with surrounding ones. Moreover, it is to be noted that in this high packing density the negative region can be seen for the velocity auto-correlation function. This indicates the backward motion of particles in the high density of liquids.

Fig.6 shows the dependence of the non-dimensional diffusion coefficient and the back scattering factor on packing fraction calculated by the mean square displacement. The back scattering factor was evaluated as the ratio δ_s/δ_{ENS} . The diffusion agrees with the Speedy's formula over the packing fraction range 0.05 to 0.45. Their deviation was smaller than 4%.

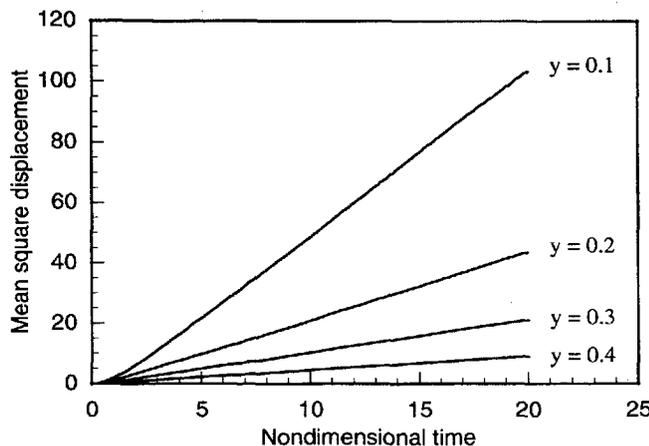


Fig.4 Mean square displacement of hard-sphere

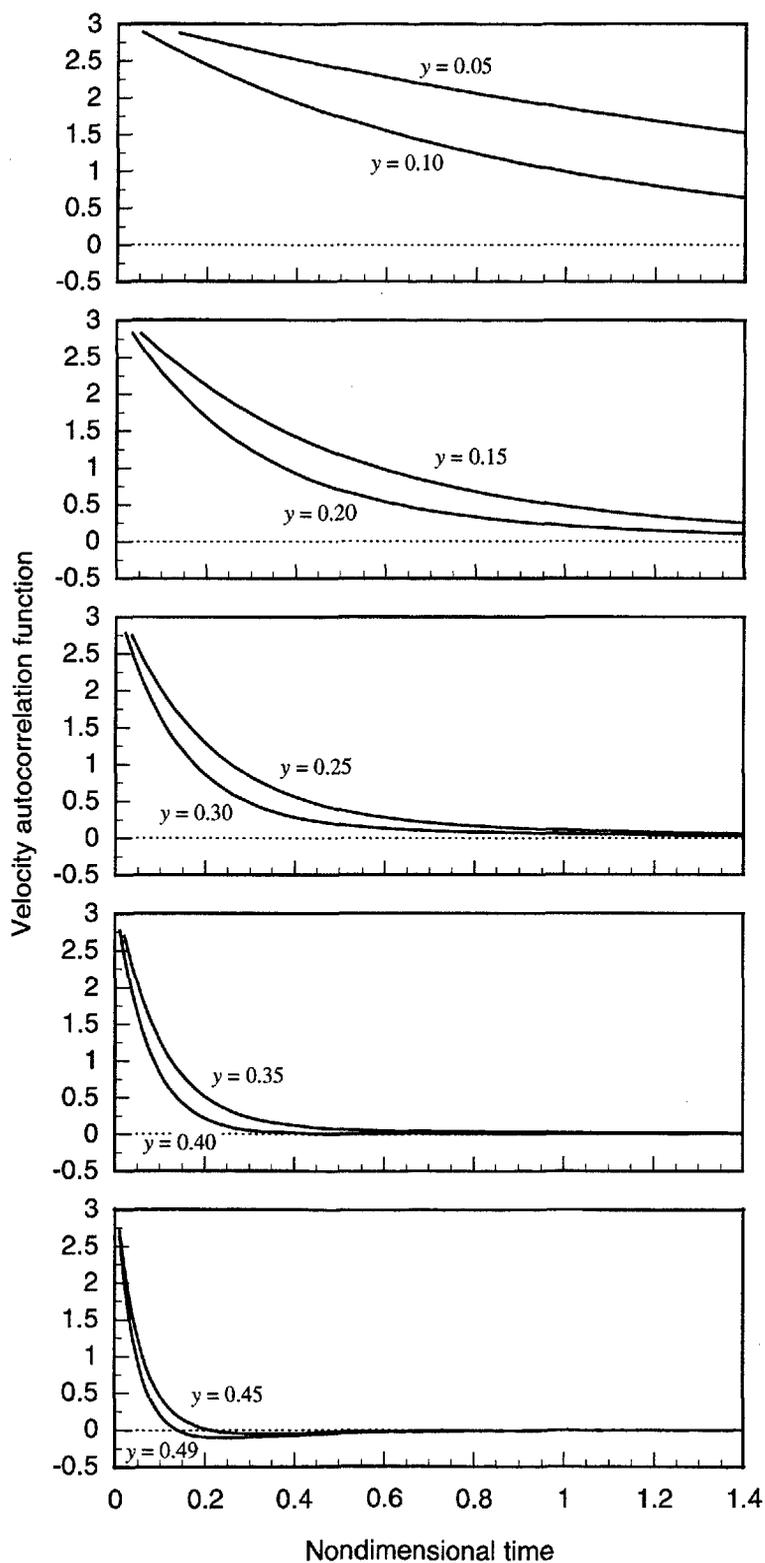


Fig.5 Velocity autocorrelation functions of hard-sphere

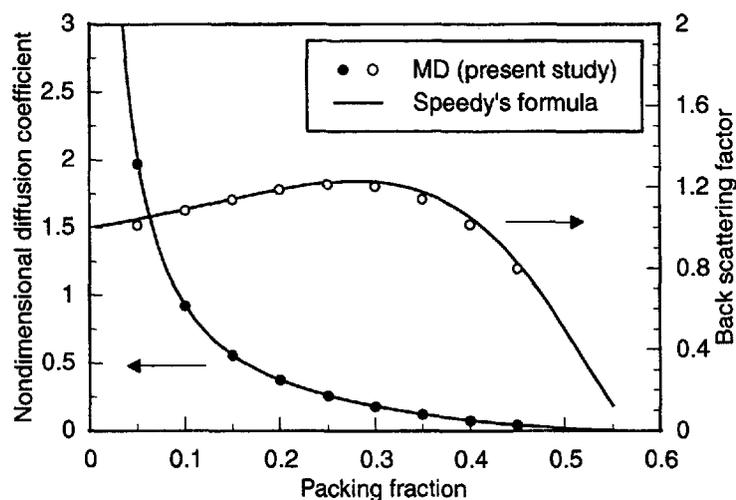


Fig.6 Dependence of non-dimensional diffusion coefficient and back scattering factor on packing fraction

4. Conclusions

In this study, the precise analysis of the structure and the dynamics of hard sphere assembly was performed using MD simulation. The diffusion coefficient was also evaluated. Obtained diffusion coefficients agreed very closely with the Speedy's formula. It is known that the hard sphere model is a good model for liquid alkali metals, that is, simple liquid metals. More complex models are needed in case of complex liquids, for example Ge and Sn. Two(multi) component hard sphere model is one of candidates for the analysis of more complex metals. We present the results of computer simulations of hard sphere mixtures elsewhere.

[References]

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