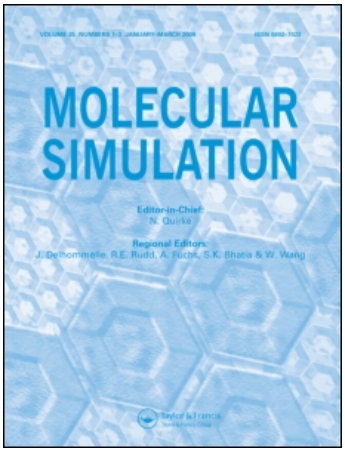

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THE ROLE OF MOLECULAR DYNAMICS SIMULATIONS FOR THE STUDY OF SLOW DYNAMICS

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A two step strategy is proposed to study dynamical properties of a physical system much slower than the time scales accessible by molecular dynamics simulations. The strategy is applied to investigate the slow dynamics of supercooled liquids.

KEY WORDS: Slow dynamics, Molecular dynamics, two step strategy, trapping diffusion model

1 INTRODUCTION

Computer simulations at the molecular level have successfully been utilized to investigate macroscopic properties of complex condensed systems. A system consisting of up to $\sim 10^4$ atoms is simulated for a time period limited by an available computer time and the time average of physical quantities is evaluated to estimate the ensemble average of the quantities. In these computations, it is assumed that most of the representative points in the phase space are sampled within such simulations. In some systems, however, the available computational time may not be long enough for the system to travel around the entire phase space during the simulation. Supercooled liquids and high polymers are typical among these examples which exhibit slow dynamics [1]. To be more specific, there are several different modes in significantly different time scales, where the slower dynamics is derived by the faster dynamics. Therefore, it requires a simulation for prohibitingly long time to obtain a sufficient statistics for the slowest dynamics, and properties defined through the long time limit such as the diffusion constant cannot be obtained correctly. This phenomenon is analogous to the "stiff problem" in numerical analysis [2] and we may call it a stiff phenomenon. Since the computer time will not increase drastically in the foreseeable future, the important role of molecular simulation at present is to provide informations which can be used (1)

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to identify specific modes in each time scale and (2) to construct a theoretical model from which we can obtain macroscopic properties.

In this paper, we propose a two step strategy for the slow dynamics of a supercooled liquid beyond the limit (time scale) of simulation imposed by the computer. In this approach, a model system, the trapping diffusion model (TDM), at the mesoscopic level is constructed from the information obtained by the molecular dynamics simulation, and the macroscopic properties are obtained from the mesoscopic model. We show that the non-Gaussian parameter is a promising quantity which contains useful informations about the slow dynamics and can be analyzed with the available computational times. In §2, we discuss the limit of the size and time scale of systems which can be simulated with currently available computers. We introduce a notion of the "horizon of simulation world". In §3, we explain a mesoscopic model for the dynamics of atoms in supercooled liquids, in which stochastic dynamics of atoms is focused upon. We investigate the non-Gaussian parameter in §4, where the analysis of the mesoscopic model is compared with molecular dynamics simulation for a binary soft-sphere fluid. Conluding remarks are given in §5.

2 THE HORIZON OF SIMULATION WORLD

When we carry out a computer simulation, the number of floating-point-number operations is limited by the speed of the central processing unit(CPU) of the computer. For each time step in simulation of an N atom system, N^m floating-point-number operations are required, where m defines the algorithm employed ($m \geq 1$). Thus, for a simulation of N atoms for T time steps using an m-th order algorithm, the following condition must be satisfied

$$TN^m \leq tP \equiv M, \tag{1}$$

where t is the available CPU time and P is the power of the CPU measured in floating-point-number operations per unit time (FLOPS). In the practical simulations, $t \leqslant 10^7$ sec and $P \leqslant 10^9$ FLOPS, and thus $M \leqslant 10^{16}$. Equation (1) determines a region in $T - N$ domain accessible by conventional computer simulation, which is shown in Figure 1. While we may access the lower left side below the thick line corresponding to $m = 1$, the upper right side of the line cannot be reached by any simulation. Thus, we can call the line *the horizon of simulation world.*

It should be mentioned here that the time mesh, h, used in ordinary molecular simulations is of the order of 10^{-15} sec which is used in Figure 1. If one treats electrons in simulation, one should take much shorter time as a step and the horizon becomes much shorter in the real time scale. Therefore, to avoid the difficulty of the different time scales, one has to mimic the real simulation of the electronic part of the simulation. The Car-Parinello method recently proposed [3] is considered to be one of these methods.

3 MESOSCOPIC MODEL

Since we cannot expect rapid advancement of the horizon of simulation world, we must take a strategy to maximize the efficiency of simulation. As already stated in

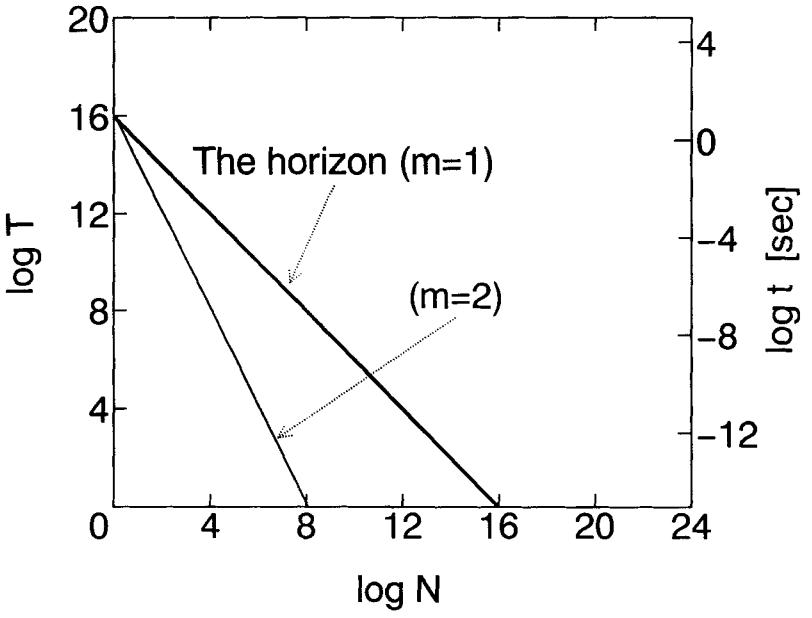

Figure 1 The accessible region in the T (computational time) $-N$ (the number of system size) plane by molecular simulation which is defined by Equation (1) with $M \sim 10^{16}$. The thick line corresponds to $m = 1$ and the thin line corresponds to $m = 2$. The upper right side of the line cannot be accessed by conventional molecular simulations. The line may be called the horizon of simulation world. The time scale on the right-hand axis corresponds to the case h (time mesh) $=10^{-15}$ sec.

the Introduction, informations obtained through the accessible region can be utilized to construct a model system at the mesoscopic level and the macroscopic properties are obtained by analyzing the mesoscopic model by some analytic methods or by computer simulation. We call this approach a *two step strategy*.

To illustrate the two step strategy, we consider below the slow dynamics in supercooled liquids. Recent computer simulation of upto 4000 atoms for 10^6 time steps has revealed that there are three specific modes of atomic motions [4] corresponding to significantly different time scales: (1) Atomic vibration with time scale $t_\gamma \sim 10^{-13}$ sec, (2) large fluctuation of position with time scale $t_\beta \sim 10^{-11}$ sec, and (3) a jump motion with time scale $t_\alpha \sim 10^{-9}$ sec. The latter two of three motions are apparently driven by the first one. Since the long time behaviors of the system are determined by the slowest mode, we have to carry out simulation over a much longer time interval than t_α in order to obtain correct long time behaviors. However, as we can see in Figure 1, it is almost impossible to carry out the simulation for t much longer than t_α with a system of $\sim 10^4$ atoms.

We employ the two step strategy focussing on the slowest dynamics. If we trace the trajectory of a particular atom by coarse-graining rapid motions, then the atom appears to be staying on a site for a while and occasionally making a quick jump to adjacent places. In other words, by coarse graining motions of other atoms the dynamics of the tagged atom will be of stochastic nature. Therefore, we assume that the atom obeys a stochastic dynamics described by the master equation:

$$\frac{\partial}{\partial t} P(\mathrm{s}, t|\mathrm{s}_0, 0) = \sum_{\mathrm{s}'} \{ w_{\mathrm{s}'} P(\mathrm{s}', t|\mathrm{s}_0, 0) - w_{\mathrm{s}} P(\mathrm{s}, t|\mathrm{s}_0, 0) \}, \tag{2}$$

where $P(\mathrm{s}, t|\mathrm{s}_0, 0)$ is the conditional probability that the tagged atom is occupied at site s at time t when it was at s_0 at time $t = 0$. The summation in Equation (2) is taken over the adjacent nearest neighbor sites. The jump rate w_{s} from s to an adjacent place is assumed to depend on s but not on the destination of the jump. This model is known as the trapping diffusion model [5, 6] (TDM), in which the jump rate w_{s}, depending on s, is a random quantity. In our two step strategy, the distribution of w_{s} is estimated from the computer simulation. By comparing the waiting time distribution, it has been shown [7] that the power law distribution

$$P(w_{\mathrm{s}}) = \frac{\rho + 1}{w_0^{\rho+1}} w_{\mathrm{s}}^{\rho} \tag{3}$$

gives rise to a good coincidence with the results of the molecular dynamics simulation, in which the parameter ρ is related to the effective coupling constant of the binary soft sphere Γ via

$$\rho = 398.1(\Gamma_g - \Gamma)^3, \tag{4}$$

with Γ_g ($\sim$1.58), the glass transition point for the soft sphere.

As the second stage we solve Equation (2) by an analytical method or even by a computer simulation. We can calculate all of the one-particle properties determined by the slowest mode from the ensemble average of $P(\mathrm{s}, t|\mathrm{s}_0, 0)$. As an illustration, we employ the coherent medium approximation [8] to evaluate the non-Gaussian parameter in §4.

4 NON-GAUSSIAN PARAMETER

As we have discussed already, it is virtually impossible to extrapolate the behavior of physical quantities obtained through a finite time window to $t = \infty$ when slow dynamics is involved. For example, the diffusion constant cannot be determined by the simulation, since it is defined as the asymptotic behavior at $t = \infty$. However, some dynamical quantities of interest can be investigated in the restricted time window of the simulation. The non-Gaussian parameter is a good example:

$$A(t) = \frac{5\langle \mathrm{r}(t)^4 \rangle}{3\langle \mathrm{r}(t)^2 \rangle^2} - 1, \tag{5}$$

where r is the displacement of an atom for time t. As we have explained in §2, the displacement essentially results from three contributions; the two contributions due to faster motions reach a constant ($\langle \mathrm{r}(t)^2 \rangle \equiv l^2$) before $t = t_\alpha$. Thus, the non-Gaussian parameter is shown to have a maximum at the time when the mean square diaplacement due to the jump motion becomes comparable to l^2. In fact, the computer simulation shows such a maximum and the "quasi"-divergent behavior of the position of the maximum was used to estimate the glass transition point [9]. The decay of $A(t)$ beyond the maximum is determined by the slowest dynamics. According to the trapping diffusion model, it is obtained that $A(t)$ behaves as $A(t) \sim t^{-\delta}$ for $t \to \infty$ and the exponent δ is shown to be

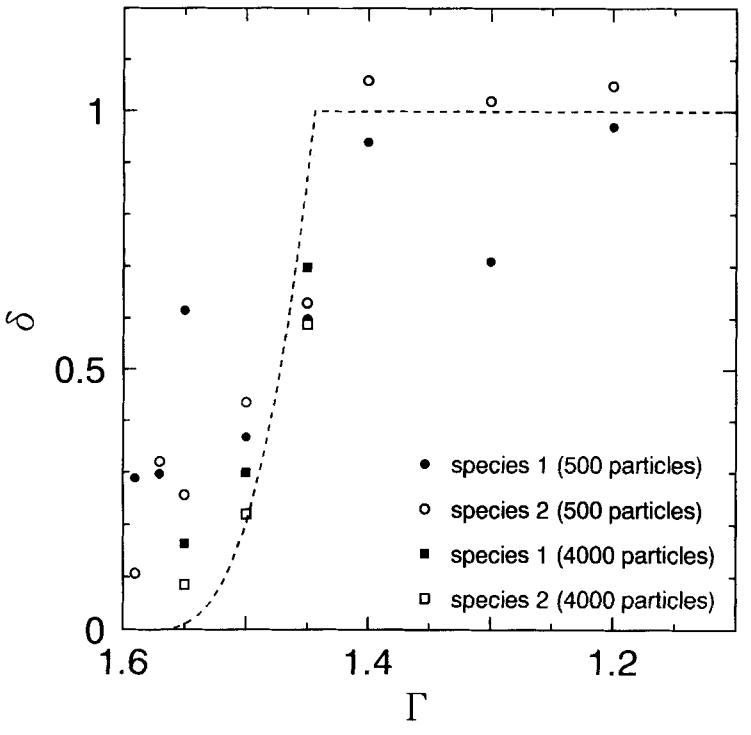

Figure 2 The dependence of decay exponent δ of the non-Gaussian parameter on the coupling parameter Γ of the binary soft sphere systems. The dashed line is the prediction of the trapping diffusion model, and circles and squares are the result obtained by the molecular dynamics simulation.

$$\delta = \begin{cases} \rho & \text{for } 0 < \rho < 1 \\ 1 & \text{for } \rho > 1 \end{cases} . \tag{6}$$

Using Equation (4), we obtain the dependence of exponent δ on the coupling constant Γ for soft sphere fluids, which is shown by the dashed line in Figure 2. A careful analysis of the data obtained by molecular dynamics simulation for the binary soft sphere system shows in good agreement with the theoretical prediction (see the circles and squares in Figure 2).

As this example shows, the non-Gaussian parameter observed for a relatively short time period gives us useful informations since the cross-over in the mean square displacement occurs at a relatively short time accessible by the simulation.

5 CONCLUSION

In this paper, we have discussed a two step strategy: Namely, for the first step, the computer simulation in microscopic time scales is performed and the result is used to construct a model at mesoscales. For the second step, the model is analyzed either by simulation or by an analytical method to obtain macroscopic properties. This

strategy is extremely useful in systems for which dynamics in widely different time scales exists. When many time scales exist, we can consider multi-step strategy as well [10]. By using these strategies, it is possible to overcome the difficulties of the horizon of simulation world. Even for an ordinary system, this strategy may also be useful to construct a phenomenological macroscopic model.

We have applied this strategy to the slow dynamics in supercooled liquids and showed that the slowest dynamics resulted from the jump motion is responsible for the α-relaxation. We have also investigated the non-Gaussian parameter which gives us useful informations from simulation carried out in a limited time scale. In particular, the exponent of the decay of the non-Gaussian parameter is predicted to be determined by the jump motion and its dependence on the thermodynamic parameter predicted by the trapping diffusion model is in good agreement with the simulation.

Although the rapid advancement of hardware technologies, computer architeture and softwares in recent years is pushing the horizon of simulation world up, it is still far from the macroscopic region and the two step or multi-step strategy as discussed in the present paper will provide an efficient way in studying macroscopic properties with molecular simulation.

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