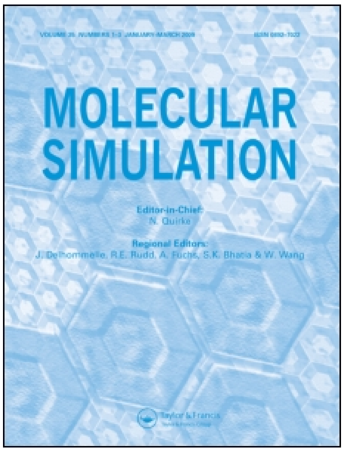
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Calculation of the Generalized Susceptibility for a Highly Supercooled Fluid Through Molecular-Dynamics Simulation

J. Matsui[a]; H. Miyagawa[b]; T. Muranaka[a]; K. Uehara[a]; T. Odagaki[cd]; Y. Hiwatari[a]
[a] Department of Physics, Faculty of Science, Kanazawa University, Kanazawa, Ishikawa, Japan [b] Integral Research Institute, Taisho Seiyaku Co., Ltd, Ohmiya, Saitama, Japan [c] Department of Liberal Arts and Sciences, Kyoto Institute of Technology, Matsugasaki, Kyoto, Japan [d] Department of Physics, Faculty of Science, Kyushu University, Fukuoka, Japan

To cite this Article Matsui, J. , Miyagawa, H. , Muranaka, T. , Uehara, K. , Odagaki, T. and Hiwatari, Y.(1994) 'Calculation of the Generalized Susceptibility for a Highly Supercooled Fluid Through Molecular-Dynamics Simulation', Molecular Simulation, 12: 3, 305 — 316

To link to this Article: DOI: 10.1080/08927029408023039

URL: http://dx.doi.org/10.1080/08927029408023039

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular Simulation, 1994, Vol. 12(3-6), pp. 305-316
Reprints available directly from the publisher
Photocopying permitted by license only

CALCULATION OF THE GENERALIZED SUSCEPTIBILITY FOR A HIGHLY SUPERCOOLED FLUID THROUGH MOLECULAR-DYNAMICS SIMULATION

J. MATSUI, H. MIYAGAWA[†], T. MURANAKA, K. UEHARA,
T. ODAGAKI[‡]* and Y. HIWATARI

Department of Physics, Faculty of Science, Kanazawa University,
Kanazawa, Ishikawa 920-11, Japan
[†]Integral Research Institute, Taisho Seiyaku Co., Ltd, Ohmiya,
Saitama 330, Japan
[‡]Department of Liberal Arts and Sciences, Kyoto Institute of Technology,
Matsugasaki, Kyoto 606, Japan

(Received 22 March 1993, accepted 20 May 1993)

A new method of computation of generalized susceptibility and dynamical structure factor through molecular dynamics (MD) simulation is proposed. This gives rise to a reliable and accurate result more than that calculated from a conventional method with a direct Fourier transformation. Computational results are presented for the imaginary part of the generalized susceptibility, $\chi''(\omega)$, for a binary soft-sphere fluid with a super-long-time molecular dynamics (MD) simulation. Both α- and β-peaks in $\chi''(\omega)$ in a supercooled fluid is shown for the first time through the present MD computation. The MD result obtained is in a good agreement with that obtained by the trapping diffusion model, which we have previously proposed for the glass transition.

KEY WORDS: Generalized susceptibility, dynamical structure factor, α relaxation, β relaxation

1 INTRODUCTION

It is known that the density autocorrelation function in a supercooled fluid phase, $F(k,t)$, can well be described by a stretched exponential decay function of the form $F(k,t) \sim \exp[-(t/t_0)^{\beta}]$ in the long time region with positive constants t_0 and $\beta(<1)$ [1-7] rather than a simple exponential decay form with $\beta = 1$. The former relaxation is therefore of non-Debye type, contrast to the Debye relaxation of the latter. In a stretched exponential decay, it is clear that, a time ratio for which the value of the function becomes $1/e$ times an initial value is not a constant unlike in a simple exponential decay, but becomes longer and longer as the time elapses. This dynamical property in nature is called *slow dynamics*. Slow dynamics is also observed in ω space. It has recently been reported with the neutron scattering experiments [8, 9] and the light scattering experiments [10] that there are two different slow relaxations exhibited in the supercooled fluid states of $K_{0.6}Ca_{0.4}$

---

*Present address: Department of Physics, Faculty of Science, Kyushu University, Fukuoka 812, Japan.

$(NO_3)_{1.4}$. The generalized susceptibility for this substance was measured with the light scattering experiments [10], which exhibits a peak called α peak in the range of 1 to 10 GHz and another peak called β peak in the range of much higher frequency of the order of 10^2 to 10^3 GHz.

The aim of this paper is to study slow relaxations in a supercooled fluid and to distinguish between two peaks exhibited in the imaginary part of the susceptibility, $\chi''(\mathbf{q}, \omega)$, and the dynamical structure factor $S(\mathbf{q}, \omega)$, through a super-long-time molecular dynamics calculation for the model fluid of binary soft-sphere mixtures [11, 12].

In our previous papers, we have shown that various results on dynamical properties obtained by the MD simulation in both normal and supercooled fluid phases for the binary soft-sphere fluid are in good agreement with those predicted by the trapping diffusion model (TDM) [13–17], which include the temperature dependence of the diffusion constant, non-Gaussian parameter, incoherent scattering function and the properties of the jump motions characteristic to highly supercooled fluid states. It is our intention in this work to carry out a super-long-time MD computation to obtain the generalized susceptibility as accurate as possible, which can be compared with theoretical predictions of the TDM [18]. For this purpose, we have carried out MD simulations for the model fluid of soft-sphere mixtures as long as over two-million time steps, which corresponds to 10 nanoseconds for an argon-like fluid.

The α relaxation of the density fluctuations involves the slowest dynamical processes in a supercooled fluid, which is of the same order as a length of time steps in molecular dynamics simulations. Therefore, it is beyond a right problem to extrapolate MD results on non-equilibrium properties to a long-time behaviour. For this, it is inevitable to use a mesoscopic model involving correct slow dynamics resulted from microscopic computations such as MD simulations. This constitutes a two-step strategy [19] for the study of the relaxations of slow dynamics which is of the same order of or sometimes beyond the time scales of molecular dynamics simulations. Such two-step strategy turns out to be especially useful to study slow dynamics in a supercooled liquid, which will be discussed in detail in a separate paper. In this paper, we study slow dynamics of the relaxations of the density fluctuations in a supercooled binary soft-sphere fluid through a million-time-step MD simulation.

2 CALCULATION OF THE GENERALIZED SUSCEPTIBILITY VIA MD SIMULATION

As a simple model for binary alloys, we consider in our MD simulation soft-sphere mixtures composed of N_1 atoms of mass m_1 and diameter σ_1 and N_2 atoms of mass m_2 and diameter σ_2 in a volume V, which interact through the purely repulsive soft-sphere potentials [1–7, 11, 12]:

$$v_{\alpha\beta}(r) = \varepsilon\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12}, \tag{1}$$

where $1 \leq \alpha$, $\beta \leq 2$ are species indices, ε is the energy unit, and we simply assume that $\sigma_{\alpha\beta} = (\sigma_\alpha \sigma_\beta)/2$.

According to the scaling property of the inverse power potentials, it is easily shown that all reduced equilibrium properties of the soft-sphere mixtures, in excess of their ideal gas counterpart, depend only on the coupling constant $\Gamma = n^*(T^*)^{-1/4}$ apart from the concentration x_1 or x_2 and the core size ratio σ_2/σ_1, where $n^* = N\sigma_1^3/V$ denotes the reduced number density with the total number of atoms $N(=N_1+N_2)$. The reduced temperature T^* equals K_BT/ε and $x_1 = N_1/N$ and $x_2 = 1 - x_1$ are concentrations. Using the effective one-component approximation, we introduce the effective coupling constant Γ_{eff} [11, 12]:

$$\Gamma_{\text{eff}} = n^*(T^*)^{-1/4}\left(\frac{\sigma_{\text{eff}}}{\sigma_1}\right)^3, \tag{2}$$

$$\sigma_{\text{eff}}^3 = \sum_\alpha \sum_\beta x_\alpha x_\beta \sigma_{\alpha\beta}^3. \tag{3}$$

The equation of states (compressibility factor PV/NK_BT vs Γ_{eff}) for binary soft-spheres has been found to follow the curve very close to that of the pure soft-sphere model, which implies that the effective one-component approximation works very well [11, 12]. The freezing point of the pure soft-sphere model has been found to occur at $\Gamma_{\text{eff}} = 1.15$.

In the present work, we study binary soft-sphere mixtures with the core-size ratio $\sigma_2/\sigma_1 = 1.2$, mass ratio $m_2/m_1 = 2.0$, and an equimolar system ($x_1 = 0.5$). Using the constant-temperature MD techniques and the seventh-order Gear algorithm together with periodic boundary conditions as usual, we have carried out MD simulations with $N = 500$ particles in a cubic cell. The pair potential, Equation (1), is cut off over the distance $r/\sigma_{\alpha\beta} = 3.5$, and the number density was kept constant ($n^* = 0.8$); the temperature T^* was varied to achieve desired Γ_{eff}'s. The microscopic time scale is chosen to be

$$\tau = \left(\frac{m_1\sigma_1^2}{\varepsilon}\right)^{1/2}, \tag{4}$$

which is nearly the same order of magnitude of the Einstein period τ_E, namely a period of oscillation of atoms in an equivalent solid. This becomes of the order of 10^{-13} sec, if we used the parameter's for an argon liquid in Equation (4). The equation of motions were solved numerically with a time mesh of the order of 100th of τ, which precisely depends on the respective temperature [4].

First, we have simulated an equilibrium fluid of $\Gamma_{\text{eff}} = 0.8$; then, using the configuration at the final step of this run, the fluid was quenched down to $\Gamma_{\text{eff}} = 1.6$ (quenching process). The resulting cooling rate is equivalent to of the order of 10^{13} K/sec for an argon fluid, which is much faster than those achieved by experimental techniques.

Annealing MD simulation has been carried out for various different Γ_{eff}'s, starting with the final configuration of the corresponding Γ_{eff} obtained by the quenching MD simulation mentioned above.

The generalized susceptibility $\chi(\mathbf{q}, \omega)$ has been computed via MD simulations as follows. Let us define the Fourier and Laplace transformations, $S(\mathbf{q}, \omega)$ and $G(\mathbf{q}, \omega)$, of the intermediate scattering function $F(\mathbf{q}, t)$ [20]:

$$S(\mathbf{q}, \omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} F(\mathbf{q}, t)e^{i\omega t}dt, \tag{5}$$

$$G(\mathbf{q},\omega) = \int_0^{\infty} F(\mathbf{q},t)\mathrm{e}^{-i\omega t}\mathrm{d}t, \tag{6}$$

where

$$F(\mathbf{q},t) = \left\langle \sum_j \exp i\mathbf{q}\cdot[\mathbf{r}_i(t+t_0) - \mathbf{r}_j(t_0)] \right\rangle_{i,t_0}. \tag{7}$$

Suffixes i and t_0 denote averages over the configuration of atoms $\{\mathbf{r}_i\}$ and the initial time t_0, respectively. According to the discussions on the generalized susceptibility, the real part of $G(\mathbf{q},\omega)$ is just proportional to the imaginary part of the generalized susceptibility $\chi''(\mathbf{q},\omega)$, which is in turn proportional to dynamical structure factor $S(\mathbf{q},\omega)$. These lead to:

$$\chi''(\mathbf{q},\omega) = \omega\mathrm{Re}[G(\mathbf{q},\omega)] \tag{8}$$

$$= \omega\pi S(\mathbf{q},\omega) \tag{9}$$

Here, Re means real part. In the present MD computations, $G(\mathbf{q},\omega)$ were computed through the equation

$$G(\mathbf{q},\omega) = \frac{1}{T}\left\langle \sum_j \int_0^T \mathrm{d}t_0 \mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}_i(t_0)}\mathrm{e}^{-i\omega t_0}\int_0^{t_0}\mathrm{d}t\mathrm{e}^{-i\mathbf{q}\cdot\mathbf{r}_j(t)}\mathrm{e}^{i\omega t} \right\rangle_i, \tag{10}$$

where $\langle\ldots\rangle$ means an average over the configuration of atoms $\{\mathbf{r}_i\}$, and T is the total time step of the simulation. As we will see below, the above equation turns out to be very useful in computing $G(\mathbf{q},\omega)$ via MD simulations, the proof of which is straight forward, as shown below. Since the average of a function $X(t,t_0)$ over initial times t_0 can generally be written as

$$\langle X(t,t_0)\rangle_{t_0} = \lim_{T\to\infty}\frac{1}{T}\int_0^T \mathrm{d}t_0 X(t,t_0), \tag{11}$$

$S(\mathbf{q},\omega)$ is rewritten into

$$S(\mathbf{q},\omega) = \lim_{T\to\infty}\frac{1}{2\pi}\int_{-T}^{T}\mathrm{d}t_0\langle X(t,t_0)\rangle_{t_0}\exp(i\omega t), \tag{12}$$

$$= \lim_{T\to\infty}\mathrm{Re}\left[\frac{1}{\pi T}\int_0^T \mathrm{d}t\ \langle X(t,t_0)\rangle_{t_0}\exp(i\omega t)\right], \tag{13}$$

$$= \lim_{T\to\infty}\mathrm{Re}\left[\frac{1}{\pi T}\int_0^T \mathrm{d}t_0\int_0^T \mathrm{d}t X(t,t_0)\exp(i\omega t)\right], \tag{14}$$

where

$$X(t,t_0) = \frac{1}{N}\sum_{i,j}\mathrm{d}t\exp[-i\mathbf{q}\cdot(\mathbf{r}_i(t+t_0) - \mathbf{r}_j(t_0))]. \tag{15}$$

Therefore, it can be obtained that

$$G(\mathbf{q},\omega) = \frac{1}{NT}\sum_{i,j}\int_0^T f_j^*(t_0)\mathrm{d}t_0\int_0^T f_i(t+t_0)\mathrm{d}t, \tag{16}$$

where

$$f_i(t) \equiv \exp[i\mathbf{q}\cdot\mathbf{r}_i]\exp[-i\omega t], \tag{17}$$

and f_j^* denotes complex conjugate to f_j. In Equation (16), we have omitted $\lim_{T\to\infty}$, assuming T is sufficiently large. In any molecular dynamics calculation, T is finite, but it should be large enough; otherwise the resultant Fourier components are reliable only to the range of ω such that $\omega > T^{-1}$.

Putting $\tau = t + t_0$.

$$G(\mathbf{q},\omega) = \frac{1}{NT}\sum_{i,j}\int_0^T f_j^*(t_0)\mathrm{d}t_0\int_{t_0}^{T+t_0} f_i(\tau)\mathrm{d}\tau \tag{18}$$

$$= \frac{1}{NT}\sum_{i,j}\int_0^T f_j^*(t_0)\mathrm{d}t_0\left(-\int_0^{t_0}\mathrm{d}\tau + \int_0^T \mathrm{d}\tau + \int_T^{T+t_0}\mathrm{d}\tau\right) f_i(\tau). \tag{19}$$

The right hand side of the Equation (19) can term to term be transformed into the following forms:

$$(\text{1st term}) = -\frac{1}{NT}\sum_{i,j}\int_0^T f_j^*(t_0)\mathrm{d}t_0\int_0^{t_0} f_i(\tau)\mathrm{d}\tau \tag{20}$$

$$= -\frac{1}{NT}\sum_{i,j}\left[\int_0^{t_0} f_j^*(t')\mathrm{d}t'\int_0^{t_0} f_i(\tau)\mathrm{d}\tau\right]_{t_0=0}^{t_0=T}$$

$$+\frac{1}{NT}\sum_{i,j}\int_0^T f_i(t_0)\mathrm{d}t_0\int_0^{t_0} f_j^*(t')\mathrm{d}t' \tag{21}$$

$$= -\frac{1}{NT}\sum_{i,j}\int_0^T f_j^*(t_0)\mathrm{d}t_0\int_0^T f_i(\tau)\mathrm{d}\tau$$

$$+\frac{1}{NT}\sum_{i,j}\int_0^T f_i(t_0)\mathrm{d}t_0\int_0^{t_0} f_j^*(\tau)\mathrm{d}\tau, \tag{22}$$

$$(\text{2nd term}) = \frac{1}{NT}\sum_{i,j}\int_0^T f_j^*(t_0)\mathrm{d}t_0\int_0^T f_i(\tau)\mathrm{d}\tau, \tag{23}$$

$$(\text{3rd term}) = \frac{1}{NT}\sum_{i,j}\int_0^T f_j^*(t_0)\mathrm{d}t_0\int_T^{T+t_0} f_i(\tau)\mathrm{d}\tau. \tag{24}$$

Putting all together into Equation (19), we obtain that

$$G(\mathbf{q},\omega) = \frac{1}{NT}\sum_{i,j}\int_0^T f_i(t_0)\mathrm{d}t_0\int_0^{t_0} f_j^*(\tau)\mathrm{d}\tau + \frac{1}{NT}\sum_{i,j}\int_0^T f_j^*(t_0)\mathrm{d}t_0\int_T^{T+t_0} f_i(\tau)\mathrm{d}\tau. \tag{25}$$

Now, it should be noted that the second term of the right hand side of the above equation is negligibly small compared with the first term when $\omega T \gg 1$ because of the additional factor like $e^{i\omega T}$ in the second term to the first term. Thus, finally we obtain Equation (10) for $\omega T \gg 1$. The self part G_s of $G(\mathbf{q},\omega)$ is similarly obtained by

$$G_s(\mathbf{q},\omega) = \frac{1}{NT}\sum_i \int_0^T f_i(t_0)\mathrm{d}t_0 \int_0^{t_0} f_i^*(\tau)\mathrm{d}\tau + \frac{1}{NT}\sum_i \int_0^T f_i^*(t_0)\mathrm{d}t_0 \int_T^{T+t_0} f_i(\tau)\mathrm{d}\tau. \tag{26}$$

Following the above discussion, the second term of the right hand side of the above equation is negligibly small compared with the first term, when $\omega T \gg 1$. Thus, we obtain for $\omega T \gg 1$

$$G_s(\mathbf{q},\omega) = \frac{1}{NT}\sum_i \int_0^T f_i(t_0)\mathrm{d}t_0 \int_0^{t_0} f_i^*(\tau)\mathrm{d}\tau. \tag{27}$$

The advantage of this method of computation for $G(\mathbf{q},\omega)$ through MD simulation is rather clear from Figure 1, in which numerical results for $S_s(\mathbf{q},\omega)$ are shown. We note that Equation (27), neglecting the second term of Equation (26), effects in turn on reducing high-frequency noises such as $\omega T \gg 1$ in an effective way. This is quite similar to a method of a filter (window) function often used in data analyses. The present form for $G(\mathbf{q},\omega)$ and $G_s(\mathbf{q},\omega)$ provide us a useful calculation formula more than the forms of the direct Fourier-Laplace transforms, Equations (5) and (6).

$\chi''(\mathbf{q},\omega)$ thus obtained from Equation (8) is shown in Figure 2. Here, we have shown only the self parts, $S_s(\mathbf{q},\omega)$ and $\chi_s''(\mathbf{q},\omega)$. Similar results on the full dynamical structure factor and generalized susceptibility are shown in Figure 3, both of which are of less accuracy than the self parts.

Two remarks should be noted here on the numerical integration of Equation (10). First, we note T (the upper limit of the integration) dependence of the α peak in $\chi_s''(\mathbf{q},\omega)$. Since the α relaxations involves the slowest relaxation processes in the density fluctuations in our system, the value of the integration of Equation (10) in low frequencies seems significantly depend on the choice of T values. Fortunately, we can show by careful considerations based on the present MD data that for the longest-time MD simulation of the present work (two million time steps), the α peak in $\chi_s''(\mathbf{q},\omega)$, shown in Figure 2, is reliable. Secondly, we note on another peak, β peak, in $\chi_s''(\mathbf{q},\omega)$, which is much weaker than the α peak. In order to obtain a better evaluation for $\chi''(\mathbf{q},\omega)$ in high frequencies, we have carried out numerical integrations of $G(\mathbf{q},\omega)$ with two different values of $\mathrm{d}t$; one with $\mathrm{d}t = 10\Delta t$ (see Figure 1(a)) and the other with $\mathrm{d}t = \Delta t$ (see Figure 1(b)), where Δt is the time mesh used in the present MD simulation. In the latter case the value of T was used of the order of ten times shorter than that in the former case because of actual difficulties with such time consuming computations. Therefore the integration with the smaller value for $\mathrm{d}t$ ($=\Delta t$) naturally gives us a better estimate for $\chi''(\mathbf{q},\omega)$ in high frequencies. From Figure 2, a clear second peak (β peak) is observed in the high frequency region.

Signorini *et al.* have previously reported on $\chi_s''(\mathbf{q},\omega)$ obtained by their MD simulation for a molten salt [21]. However, their result on $\chi_s''(\mathbf{q},\omega)$ is presented only for the frequency region between α and β peaks (so-called around β minimum), but for neither higher nor lower frequencies. However, for right understandings of the nature of the β relaxation, it is very important to note on the form of the frequency dependence of $\chi_s''(\mathbf{q},\omega)$ in both sides of the β peak, which we will discuss below.

In order to see a frequency dependence in terms of a power-law formula of $S_s(\mathbf{q},\omega)$, we have computed the logarithmic derivative σ:

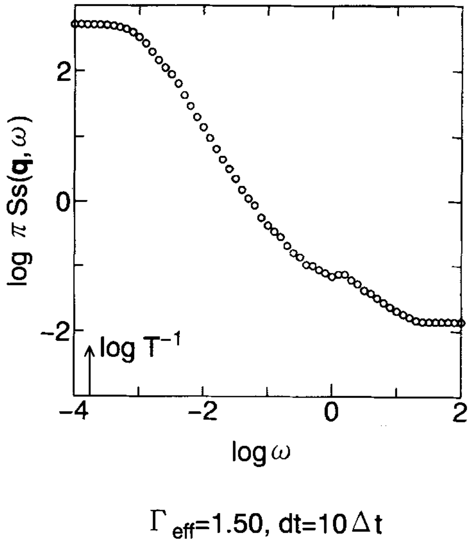


Figure 1 (a) The dynamical structure factor (self part only), $S_s(q, \omega)$, as a function of ω, obtained from the MD simulation with a system size N = 500 for the binary soft-sphere fluid, $\Gamma_{\mathrm{eff}} = 1.50$. The arrow on the ω axis means T^{-1}, the inverse of the upper limit of the integration in Equation (10). Numerical integrations were made with $dt = 10\Delta t$.

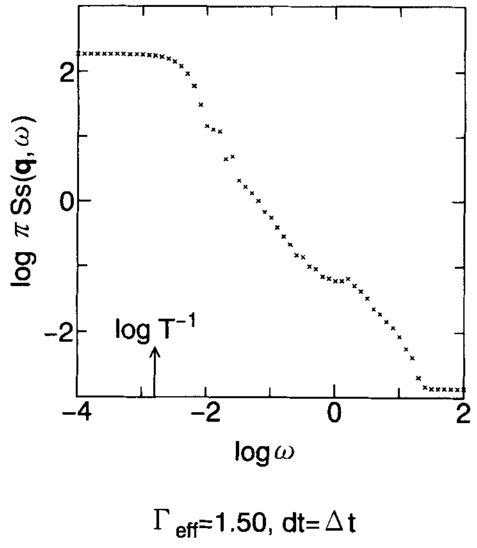


Figure 1(b) The same as Figure 1(a), but with a ten times smaller value of the time increment than in Figure 1(a), $dt = \Delta t$. Compared with the results shown in Figure 1(a), this gives a more accurate result in large frequencies, but less accurate one in small frequecies. The right plateau is nothing but due to the numerical integrations with a finite (non-zero) value of dt.

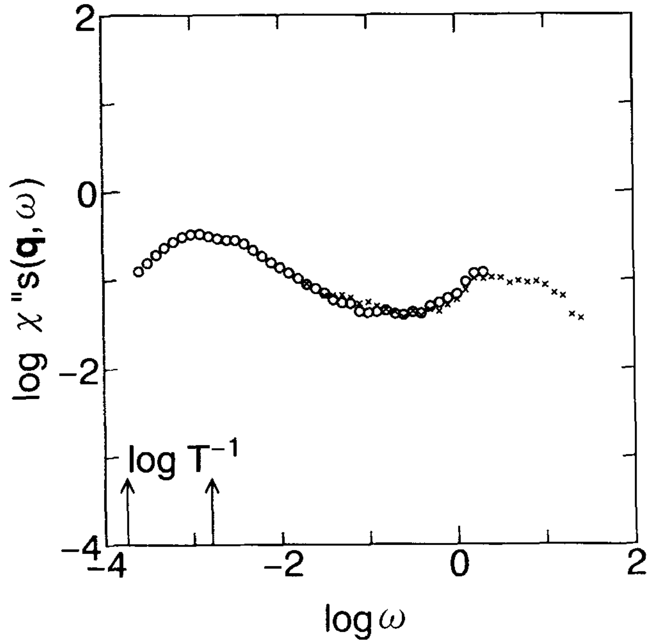


Figure 2 The imaginary part of the generalized susceptibility (self-part) $\chi_s''(\mathbf{q}, \omega)$ vs. ω in logarithmic scales. Results with $dt = 10\Delta t$ are shown as the circles, while the results with $dt = \Delta t$ are shown bv the crosses. According to Figures 1(a) and (b) and the discussions made there, here is shown the result obtained with each accurate parts of the $S_s(\mathbf{q}, \omega)$, that is, the small- and large-frequency parts of the curves in Figures 1(a) and (b), respectively. Two arrows on the ω axis denote the values of T^{-1} used for the integration in Equation (10); the left arrow for the circles, the right arrow for the crosses.

$$\sigma = -\frac{\partial \ln S_s(\mathbf{q}, \omega)}{\partial \ln \omega} \tag{28}$$

The result is shown in Figure 3. Meanings of this result are of interest and given below. The effective exponent σ in the supercooled liquid reveals fairly plateau regions which differ from the usual Debye values, indicating the existence of slow dynamics. These slow dynamics share many characteristic of the α and β relaxations in supercooled fluids [8, 10, 22]. The present result shows that for α relaxation $S_s(\mathbf{q}, \omega) \simeq \omega^{-1.8}$, and that for β relaxation $S_s(\mathbf{q}, \omega) \simeq \omega^{-0.4}$. It is to be noted here that the frequency range in which the latter (β relaxation formula) holds is much narrower than that of the former (α relaxation formula). These power-law formulae around β minimum are qualitatively in agreement with the predictions of the mode coupling theory, but not quantitatively [22]. This disagreement of our MD result with the mode coupling result is of significance. On the other hand, it is possible to show that a good agreement is obtained between the MD result and the prediction from the trapping diffusion model (TDM) [18], which we have previously proposed for the dynamics in supercooled liquids and the liquid-glass transition [1, 13-17]. With the TDM, it can also be shown that the β relaxation is essentially a Debye relaxation [18].

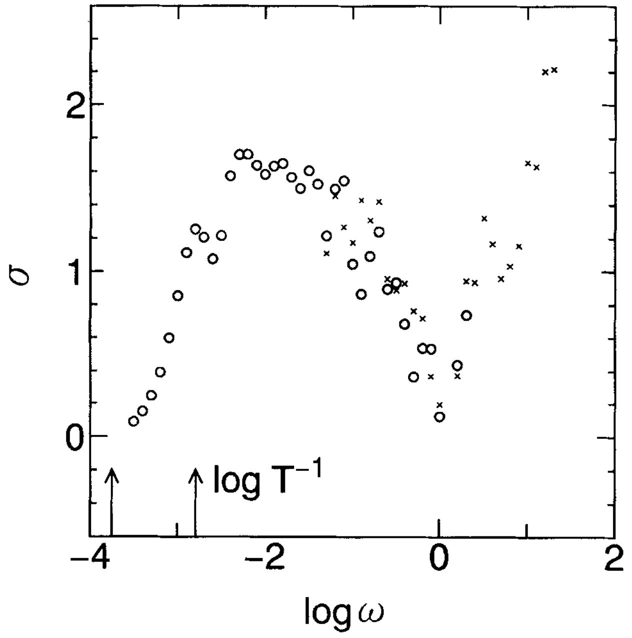


Figure 3 The effective exponent σ (see Equation (28) for the definition) as a function of ω calculated with $S_s(\mathbf{q}, \omega)$. According to Figures 1(a) and (b) and the discussions made there, here is shown the result obtained with each accurate parts of the $S_s(\mathbf{q}, \omega)$, that is, the small- and large-frequency parts of the curves in Figures 1(a) and (b), respectively. Two arrows on the ω axis denote the values of T^{-1} used for the integration in Equation (10); the left arrow for the circles, the right arrow for the crosses.

3 CONCLUSION AND DISCUSSION

The study of the dynamics relevant to the α slow relaxation may be one of the most difficult problems to tackle by a MD simulation with any microscopic model because of the long relaxation time; usually the same order of or even longer than a practical limit of a CPU time available to us even with a modern supercomputer. Such difficulty may be avoided by using other approach such as a mesoscopic trapping diffusion model (TDM) based on the stochastic nature of the system under consideration, which is compatible with the results of MD simulations on the microscopic level, and containing essential modes to such slow dynamics. This constitutes a two-step strategy for the study of slow dynamics such as α- and β-relaxations in a supercooled liquid.

In this paper, we have computed the imaginary part of the generalized susceptibility $\chi''(\mathbf{q}, \omega)$ and dynamical structure factor $S(\mathbf{q}, \omega)$ through a million-time-step MD simulation, focusing our attention on their self parts. Both α- and β-peaks in $\chi''(\mathbf{q}, \omega)$ were observed for the first time by the present MD simulations. From the results of the present work, we conclude that the α relaxation in the supercooled binary soft-sphere fluid obeys $S_s(\mathbf{q}, \omega) \simeq \omega^{-1.8}$ over a few figures of ω in low frequency domain. On the otherhand, the β relaxation is essentially a Debye relaxation, as it is found that the frequency dependence of $S_s(\mathbf{q}, \omega)$ in sufficiently high frequencies above the β peak is the same as the Debye form like $S_s(\mathbf{q}, \omega) \simeq \omega^{-2}$ (see

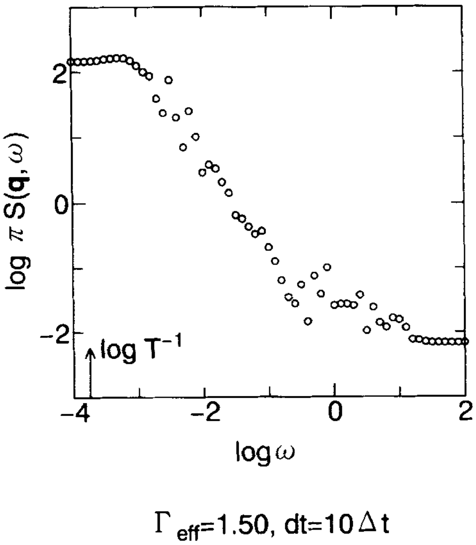


Figure 4(a) The full dynamical structure factor $S(\mathbf{q}, \omega)$ obtained with the MD simulation and $dt = 10\Delta t$. $\Gamma_{eff} = 1.50$.

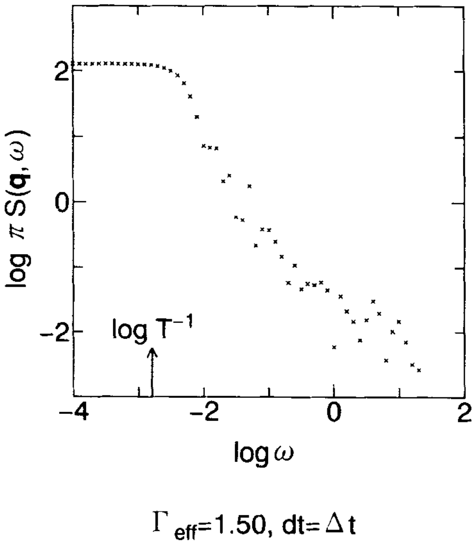


Figure 4(b) The same as Figure 4(a), but with $dt = \Delta t$.

Figure 3). The dynamical significance around the so-called β minimum appears somewhat complicated, because the two dynamics, α and β, which are different in nature, are merged. As a consequence, what we see around the β minimum is nothing but a cross-over phenomenon of these two different dynamics. It is of significance to note that the present MD result differs from the mode coupling predictions [22]. We can show that a direct comparison of the present results with those of the TDM is in a good agreement between both in a wide range of frequencies, which will be discussed in detail in a separate paper.

More careful considerations based on computations with different time steps T lead to following remarks of importance: The present super-long-time molecular dynamics computation on $\chi_s''(\mathbf{q}, \omega)$ provides with reliable α- and β-peaks as well as reliable data in between these two peaks. However, below the α peak and beyond β peak the original data are not reliable. We are currently extending our simulations up to over 10 million time steps, about five times longer than the present longest MD run, in order to confirm the present results and to obtain correct informations on $\chi_s''(\mathbf{q}, \omega)$ at lower frequencies. These will be reported elsewhere.

Finally we remark on the full dynamical structure factor $S(\mathbf{q}, \omega)$. MD results are shown in Figures 4(a) and (b). This function, compared with the self part $S_s(\mathbf{q}, \omega)$, is generally much more difficult to calculate because of less numerical accuracies of the calculations. Our result shown in Figure 4(b) reveals only a faint β peak, much less accurate than that of $S_s(\mathbf{q}, \omega)$. For a quantitative comparison between $S_s(\mathbf{q}, \omega)$ and $S(\mathbf{q}, \omega)$, further careful computations and analyses will be necessary.

Acknowledgements

This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan. Computations were carried out with supercomputers at Kyoto University.

References

[1] For a recent review, see Y. Hiwatari, H. Miyagawa and T. Odagaki, "Dynamical singularities near the liquid-glass transition: Theory and molecular dynamics study", *Solid State Ionics* **47**, 179 (1991).

[2] H. Miyagawa and Y. Hiwatari, "Molecular-dynamics study of binary soft-sphere glasses: Quench-rate effects and aging effects", *Phys. Rev.* **A40**, 6007 (1989).

[3] Y. Hiwatari and H. Miyagawa, "Molecular dynamics study of binary alloys near the glass transition", *J. Non-cryst. Solids* **117/118**, 862 (1990).

[4] H. Miyagawa and Y. Hiwatari, "Molecular-dynamics study of the glass transition in a binary soft-sphere model", *Phys. Rev. A44*, 8278 (1991).

[5] Y. Hiwatari, H. Miyagawa, T. Muranaka and K. Uehara, "Molecular-dynamics study of highly supercooled liquids: Dynamical singularities near the liquid-glass transition", *AIP* **256**, 155 (1992).

[6] G. Pastore, B. Bernu, J.P. Hansen and Y. Hiwatari, "Soft-sphere model for the glass transition in binary alloys. II. Relaxation of the incoherent density-density correlation functions", *Phys. Rev.* **A38**, 454 (1988).

[7] K. Uehara, T. Muranaka, H. Miyagawa, M. Takasu and Y. Hiwatari, "Molecular-dynamics simulations for the density autocorrelation function in a supercooled fluid phase", (to appear in Mol. Simulation).

[8] F. Mezei, W. Knaak and B. Farago, "Neutron spin-echo study of dynamic correlations near the liquid-glass transition", *Phys. Rev. Letters*, **58**, 571 (1987); W. Knaak, F. Mezei and B. Farago, "Observation of scaling behaviour of dynamic correlations near liquid-glass transition", *Europhys. Lett.* **7**, 529 (1988).

[9] F. Mezei, "Dynamic structure factor near the glass transition: Specific features", *AIP* **256**, 53 (1992).

[10] H.Z. Cummins, G. Li, W.M. Du, X.K. Chen, N.J. Tao and A. Sakai, "Brillouin and Raman scattering spectroscopy of the liquid-glass transition", *AIP* **256**, 40 (1992).

[11] B. Bernu, Y. Hiwatari and J.P. Hansen, "A molecular dynamics study of the glass transition in binary mixtures of soft spheres", *J. Phys. C* **18**, L371 (1985).

[12] B. Bernu, J.P. Hansen, Y. Hiwatari and G. Pastore, "Soft-sphere model for the glass transition in binary alloys: Pair structure and self-diffusion", *Phys. Rev.* **A36**, 4891 (1987).

[13] T. Odagaki and Y. Hiwatari, "Stochastic model for the glass transition of simple classical liquids", *Phys. Rev.* **A41**, 929 (1990).

[14] T. Odagaki and Y. Hiwatari, "Gaussian-to-non-Gaussian transition in supercooled fluids", *Phys. Rev.* **A43**, 1103 (1991).

[15] T. Odagaki and Y. Hiwatari, "Residence time distribution of a tracer atom in supercooled fluids", *J. Phys.: Condens. Matter* **3**, 5191 (1991).

[16] T. Odagaki and Y. Hiwatari, "Apparent subdiffusive properties of a supercooled fluid", *Phys. Rev.* **A46**, 1250 (1992).

[17] T. Odagaki and Y. Hiwatari, "Stochastic dynamics in a supercooled fluid", *AIP* **256**, 115 (1992).

[18] T. Odagaki, J. Matsui and Y. Hiwatari, (unpublished).

[19] T. Odagaki, J. Matsui, K. Uehara and Y. Hiwatari, "The role of molecular dynamics simulations for the study of slow dynamics", (to appear in Mol. Simulation).

[20] J.P. Hansen and I.R. McDonald, *Theory of Simple Liquids, 2nd edition*, Academic Press, New York, 1986.

[21] G.F. Signorini, J.L. Barrat and M.L. Klein, "Structural relaxation and dynamical correlations in a molten state near the liquid-glass transition : a molecular dynamics study", *J. Chem. Phys.* **92**, 1294 (1990).

[22] For recent reviews of the mode coupling theories relevant to the glass transition problems, see W. Götze, "Aspects of structural glass transitions", *Les Houches*, Session LI, 1989; W. Götze and L. Sjögren, "Relaxation processes in supercooled liquids", *Rep. Prog. Phys.* **55**, 24 (1992).