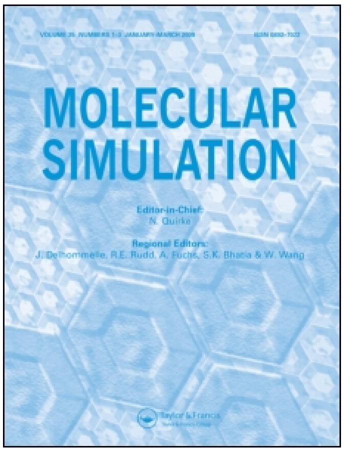

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Study on the β Peak of χ'' for a Two-Dimensional Supercooled Fluid State Via Molecular Dynamics Simulation

Tadashi Muranaka[a]; Yasuaki Hiwatari[b]
[a] General Education, Aichi Institute of Technology, Toyota, Japan [b] Department Of Physics, Kanazawa University, Kanazawa, Japan

To cite this Article Muranaka, Tadashi and Hiwatari, Yasuaki(1996) 'Study on the β Peak of χ'' for a Two-Dimensional Supercooled Fluid State Via Molecular Dynamics Simulation', Molecular Simulation, 16: 4, 387 — 397
To link to this Article: DOI: 10.1080/08927029608024087
URL: http://dx.doi.org/10.1080/08927029608024087

Molecular Simulation, 1996, Vol. 16, pp. 387–397
Reprints available directly from the publisher
Photocopying permitted by license only

STUDY ON THE β PEAK OF χ'' FOR A TWO-DIMENSIONAL SUPERCOOLED FLUID STATE VIA MOLECULAR DYNAMICS SIMULATION

TADASHI MURANAKA and YASUAKI HIWATARI*

General Education, Aichi Institute of Technology, Toyota 470-03, Japan
**Department of Physics, Kanazawa University, Kanazawa 920- 11, Japan*

(Received May 1995, accepted June 1995)

We have computed the generalized susceptibility (imaginary part of χ) of two-dimensional supercooled fluid states through molecular dynamics simulations with different system sizes. It is found that when the temperature of the system is higher than T_c (critical temperature) there is no significant difference between the large (10,000-particle) and small (100-particle) systems in the χ'' obtained, but for much lower temperatures the spectra of the χ'' obtained reveal a remarkable system-size dependent behavior such as the β peak becomes much broader for the large system. This phenomenon is physically understood in terms of the strongly correlated motion of atoms extending over a wide range of space of the system. We will discuss in this work about the relaxations on two-dimensional supercooled fluids and their microscopic origins as well as their system-size dependence.

KEY WORDS: Generalized susceptibility, supercooled fluid, β-relaxation.

1 INTRODUCTION

Freezing of liquid into a glass is still a poorly understood subject in condensed-matter physics, though many researchers have recently been involved in this field. In the 1960's ~ 70's, the dielectric loss and absorption spectrum of glass-forming organic matters and polymers above the liquid-glass transition temperature have extensively been studied [1, 2, 3]. Their results have presented similar features for both α and β peaks, which are sometimes called main peak and Johari-Goldstein peak, respectively.

Neutron spin-echo measurements on $F(k, t)$ [4] revealed two types of distinct relaxations in the ionic system $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ (CKN). Cummins *et al.* [5] have measured the dynamical properties of the same material with light-scattering method and analyzed both α and β relaxations in detail. They concluded that their experiments are consistent witht he mode-coupling theory [6]. On the other hand molecular dynamics (MD) simulations [8] [12] have found that the jump motion of atoms is an essential nature of the α relaxation in supercooled fluids. Theoretical works have been proposed, which take into consideration such jump motions phenomenologically [9, 10, 11].

Recently, D. Richter *et al.* [13] have reported the neutron spin-echo spectra observed for various temperatures on polybutadiene. They have also presented that the decoupled low-temperature relaxation is distinctly different from the high-frequency β process which is sometimes called fast process.

In this paper we study slow dynamics for a highly supercooled fluid via MD simulation, especially β peak (J-G peak) of the imaginary part of generalized susceptibility.

Experimental findings about the characteristics of the β peak in the imaginary part of susceptibility are summarized as follows [14] :

1. The strength of β peak is much weaker than that of α peak [1] [2].
2. The position ω_β of the β peak varies quite smoothly with temperature, which follows Arrhenius plots showing activated processes being involved [2].
3. The β peak intensity increases upon heating and it's resonance seems to disappear below the conventional glass transition temperature [1].
4. The β peak, as opposed to the α-peak, is rather symmetric when it is depicted using a logarithmic frequency abscissa [3].
5. The width of the resonance is more pronounced for the β-peaks than for the α resonances [3].

In this paper we will discuss these properties using the results obtained from MD simulation for our model system. In Sec. 2 presented the model system and the molecular dynamics simulation. The imaginary part of the self part of the generalized susceptibility $\chi_s''(\mathbf{k}, \omega)$ was calculated by MD simulation, which is given in Sec. 3. In Sec. 4 presented results for the β peak. In Sec. 5 summarized the result of atomic-level analyses for the peak in $\chi_s''(\mathbf{k}, \omega)$.

2 MODEL SYSTEM AND MD SIMULATION

The present model is composed of equal numbers of two different species of 5,000 atoms each ($N_1 = 5{,}000, N_2 = 5{,}000$). The smaller (lighter) species has a diameter $\sigma_1 = 1.0$ and a mass $m_1 = 1.0$ and the larger (heavier) species has a diameter $\sigma_2 = 1.4$ and a mass $m_2 = 2.0$. The periodic boundary conditions were adopted as usual. Numerical time integrations were carried out with the velocity form of the Verlet algorithm [15], and the temperature of the system was controlled with the Nosé algorithm [16].

Atoms interact through the purely repulsive soft-core potentials :

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

where

$$\sigma_{\alpha\beta} = \frac{\sigma_\alpha + \sigma_\beta}{2}, \quad r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|, \tag{2}$$

where α and β indicate species (1 or 2).

The cut off radius of the interaction was chosen to be 4.5 σ_1, and the cut off radius of the bookkeeping table was chosen to be $5.0\sigma_1$. We used the Linked Cell method and made renewal of the table, whenever any atom travels over the distance $(5.0-4.5)/2\ \sigma_1$ after the last registration.

Hereafter we use the following units : σ_1 (the unit of length), m_1 (the unit of mass) and ε (the unit of energy). Then we chose the reduced unit of time $\tau=\sqrt{m_1\sigma_1^2/\varepsilon}$. This is 2.45×10^{-12} sec for an argon liquid. And we chose one step time 0.001 τ in liquid state and 0.002 τ in supercooled fluid state.

The density and temperature of the system which we have studied are listed in Table 1. We used the reduced temperature $T^* = k_BT/\varepsilon$ and the reduced number density $\rho^* = N/S$, where N is the total number of atoms and S is the total area of the system in unit of σ_1^2. The reduced number density is fixed at $\rho^* = 0.8$ in all present molecular dynamics simulations.

We have simulated the system with NVE ensemble (constant number of atoms, volume and energy.) It is convenient to use the following effective coupling constant for binary mixtures (effective one-component approximation [17]) as in the case of three dimensional soft-core system :

$$\Gamma_{\text{eff}} = \rho^* T^{*-1/6}\left(\frac{\sigma_{\text{eff}}}{\sigma_1}\right)^2, \tag{3}$$

where

$$\sigma_{\text{eff}}^2 = \sum_\alpha\sum_\beta \chi_\alpha \chi_\beta \sigma_{\alpha\beta}^2 \tag{4}$$

In the present work we studied for $\Gamma_{\text{eff}} = 0.8$, 1.0, 1.1, 1.16, 1.2, 1.24, 1.3 and 1.4. The state of system is liquid for $\Gamma_{\text{eff}} = 0.8$, supercooled state from $\Gamma_{\text{eff}} = 1.0$ to 1.24 and glass state for $\Gamma_{\text{eff}} = 1.3$ and 1.4 [18].

The simulation was started with a liquid state equilibrated at $\Gamma_{\text{eff}} = 0.8$. Then the temperature of the system was rapidly cooled down to $\Gamma_{\text{eff}} = 1.4$ in 8,000 steps (8τ). In this cooling process, configurations for the respective temperatures have been stored, which is used in later annealing MD simulations. The NVE MD simulation at each temperature was carried out for 500,000 steps ($1{,}000\tau$) after annealing MD simulation for 20,000 steps (40τ). $\chi_s''(\mathbf{k},\omega)$ was calculated using a method proposed by Matsui *et al.* [19]. Outline of this method is described below. The imaginary part of the self part of the generalized susceptibility is calculated as follows:

$$\chi_s''(\mathbf{k},\omega) = \omega Re[G_s(\mathbf{k},\omega)] = \omega\pi S_s(\mathbf{k},\omega), \tag{5}$$

$$G_s(\mathbf{k},\omega) = \frac{1}{T}\left\langle \int_0^T dt_0 e^{i\mathbf{k}\mathbf{r}_i(t_0)} e^{-i\omega t_0} \int_0^{t_0} dt e^{i\mathbf{k}\mathbf{r}_i(t)} e^{-i\omega t} \right\rangle_i . \tag{6}$$

Table 1 Thermodynamic states Γ_{eff} and T^* for which our MD simulation has been carried out.

Γ_{eff}	0.8	1.0	1.1	1.16	1.2	1.24	1.3	1.4
T^*	9.685	2.539	1.433	1.042	0.8509	0.6984	0.5260	0.3372

Here, Re[...] means real part, G_s; the self part of the generalized susceptibility and S_s; the self part of the dynamical structure factor. $\langle\cdots\rangle$ means averages over configurations of atoms $\{\mathbf{r}_i\}$, and T is the total time step of the simulation. We have calculated Eq. 6 up to 500,000 steps (1,000 τ) in a glass state and 200, 000 steps (200 τ) in a liquid state.

3 RESULTS

The temperature dependence of $\chi_s''(\mathbf{k}, \omega)$ for the large (10,000-particle) system is shown in Figure 1. The parts of curves at right (higher frequency) side, shown as an increasing function of ω, are due to numerical errors.

In liquid states the curve of $\chi_s''(\mathbf{k}, \omega)$ has one peak. The position of the peaks shifts to lower frequency as the temperature becomes lower. The peak splits into four in the glass states at $\Gamma_{\text{eff}} = 1.3$ and 1.4. The lowest-frequency peak is not shown ($\omega \leqslant 0.1\tau^{-1}$), the second peak is found around $\omega = 0.1 \sim 0.5\tau^{-1}$, the third peak around $\omega = 0.5 \sim 20.0\ \tau^{-1}$ and the fourth peak around $\omega = 20.0 \sim 30.0\ \tau^{-1}$.

The lowest-frequency peak corresponds to α peak (main peak). The second peak shares the characteristics of boson peak. This appears below glass transition temperature and the peak frequency becomes higher as the temperature decreases, but it does not change with the wave number [20]. However, it is shown that this peak has a notable system size dependency (see Figs. 3 and 4), may be caused by the periodic boundary conditions adopted in the MD simulation and thus regarded as spurious one. This is still yet open to discussion. The third peak corresponds to β peak (Johari-Goldstein peak). This appears near the glass transition temperature and the peak position becomes lower as the temperature decreases. The fourth peak corresponds to fast process. The peak frequency does not change as the temperature decreases, found in the highest frequency (fastest time) region.

In liquid and supercooled fluid states $\chi_s''(\mathbf{k}, \omega)$ has only one peak, of which the temperature dependence is shown in Figure 2. This figure, Arrhenius plots, suggests an activated type of processes for the most relevant dynamics.

In liquid states there is no difference of $\chi_s''(\mathbf{k}, \omega)$ obtained between the 10,000-particle system and the 100-particle system. But in glass states $\chi_s''(\mathbf{k}, \omega)$ curve obtained for the 100 particles system may involve much larger errors than for the larger system, as shown in Figure 3. The data seems unstable (largely fluctuated) around $\omega \sim 2\pi/30\tau$ for the large system, and around $\omega \sim 2\pi/3\tau$ for the small system.

Figure 4 shows the density autocorrelation function. The curves show interesting behaviors: The first peak for the large system appears at about 30τ, whereas for the small system the first peak appears at about 4τ. Thus the peak positions depend remarkably on the system size. A similar result was also found for a three dimentional system.

Similar problems of the system-size dependence has been discussed in ref. [7]. The simulation work in 2D with systems of $\sim$ 1,000 particles or less is not highly accurate. They have carried out the simulation for 2D melting with the hard disk or LJ solids, however similar behaviors has been obtained which are shown in Figure 3 and 4.

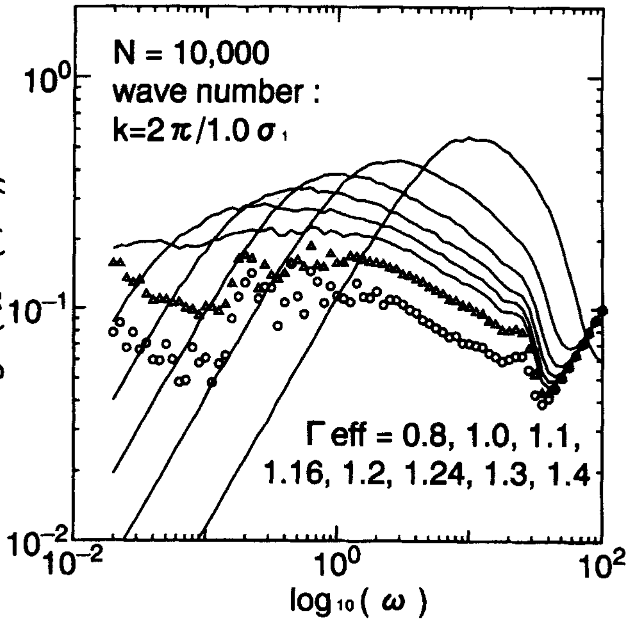

Figure 1 Temperature dependence of the imaginary part of the generalized susceptibility (self-part) for species 1 at $\Gamma_{\rm eff} = 0.8, 1.0, 1.1, 1.16, 1.2, 1.24, 1.3$ and 1.4 from top to bottom. The wave number is $k = 2\pi/1.0\sigma_1$. The abscissa is a logarithmic frequency in unit of τ^{-1}. One time step of simulation is $\Delta t = 0.001\tau$ at $\Gamma_{\rm eff} = 0.8$, but for other temperatures one time step of simulations is $\Delta t = 0.002\tau$. The total time steps of the simulations are 100τ for $\Gamma_{\rm eff} = 0.8$, 200τ for $\Gamma_{\rm eff} = 1.0$, 400τ for $\Gamma_{\rm eff} = 1.1$, 600τ for $\Gamma_{\rm eff} = 1.16$ and $1{,}000\tau$ for $\Gamma_{\rm eff} = 1.2, 1.24, 1.3$ and 1.4.

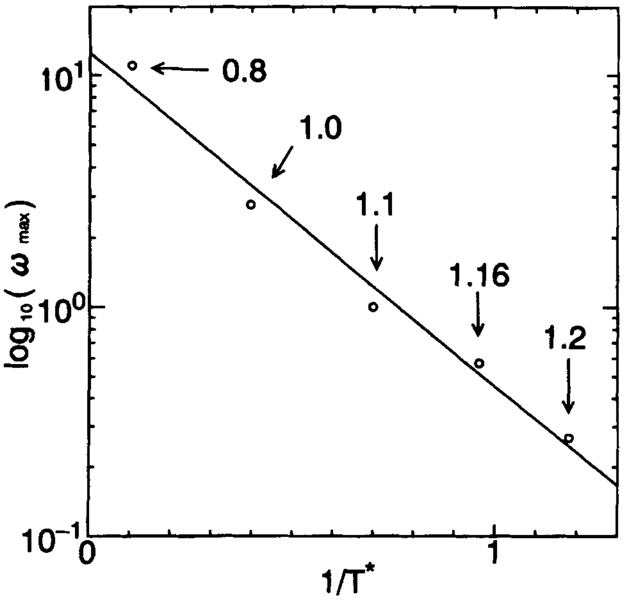

Figure 2 Arrhenius plots of the peak frequencies in Figure 1 for supercooled fluid states. The number shows the value of $\Gamma_{\rm eff}$. The solid line indicates the exponential fitting of the data.

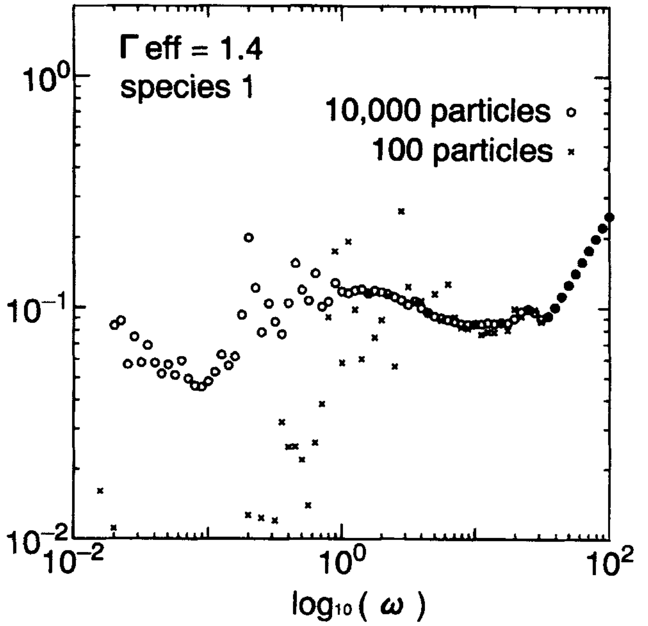

Figure 3 The system-size dependence of the imaginary part of the generalized susceptibility (self-part) for species 1 at $\Gamma_{\mathrm{eff}} = 1.4$ and $k = 2\pi/1.0\sigma_1$. The abscissa is a logrithmic frequency in unit of τ^{-1}. One time step of simulation is $\Delta t = 0.005\tau$ and the total time steps of the simulations are $1{,}000\tau$.

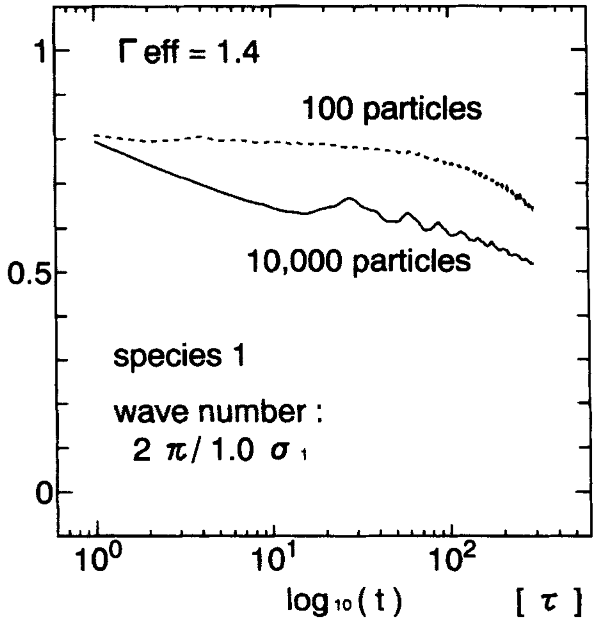

Figure 4 Self part of the density autocorrelation function $F_s^{(1)}(k, t)$ at $\Gamma_{\mathrm{eff}} = 1.4$ for species 1 and $k = 2\pi/1.0\sigma_1$. The abscissa is a logarithmic time in unit of τ.

4 ANALYSES OF ATOMIC MOTIONS

It has previously been shown that the α peak originates 'jump motion' [8, 9, 10]. This type of atomic motion is sparsely observed near the glass transition temperature.

The second peak can be related to 'sway motion', in which a group of many atoms moves at the same time to the same direction and return to the initial positions after some time. This type of motion increase the density autocorelation, but it may be caused by the periodic boundary conditions adopted in the MD simulation. In fact the location of this peak depends strongly on the system size, and it turns out that this is inversely proportional to the length of the simulation cell size (see Figs. 3 and 4). Therefore, we consider this peak to be rather spurious (unphysical) one, though it still remains an open question.

Fast process takes place at the shortest time regime of our model system that is the small peak in the highest frequency region. This peak originates from 'thermal vibrations', shown by the most right side peak of $\chi_s''(\mathbf{k}, \omega)$. It is confirmed that this peak coincides with the time scale (period) of the oscillations of the velocity autocorrelation function. Relevant motions of atoms as local ones and do not need to rearrange the list of the neighboring atoms.

The β peak (process) is due to 'correlated motion' of atoms, which is the mostnoticeable type of atomic motion in the dense supercooled fluids and glasses. Figure 5 shows an example of such correlated motion. To measure the degree

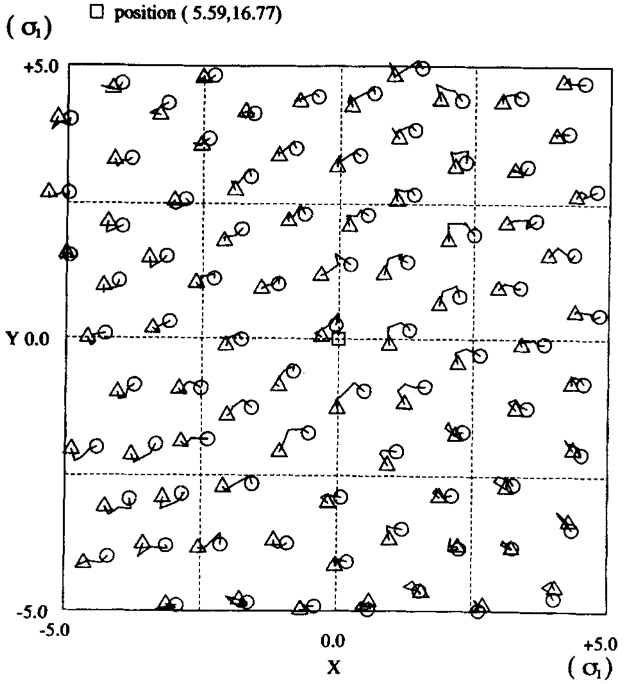

Figure 5 Movement of atoms near the position (5.59, 16.77) [the center of this Figure] of the present simulation cell with a side length $= 111.80\sigma_1$ for the period from τ to 5τ. The initial positions (at $t = \tau$) of atoms are marked by the circles and the final positions (at $t = 5\tau$) of atoms are marked by the triangles.

(strength and range) of the correlation between i-th atom and the surrounding near atoms within the cut-off distance r_c, we define "the correlated motion coefficient" $CM_i(r_c, t)$ for each atom:

$$CM_i(r_c, t) = \sum_{r_{ij} \leqslant r_c}^{N_i} \Delta\mathbf{r}_i(t) \cdot \Delta\mathbf{r}_j(t) \sqrt{\overline{\Delta r^2(t)} N_i}, \tag{7}$$

where $\Delta\mathbf{r}_i(t)$ is the displacement vector of the i-th atom for an elapsed time t, $\overline{\Delta r^2(t)}$ is the mean square displacement for an elapsed time t, and N_i is the number of atoms within the distance r_c centered at the i-th atom for $t = 0$. Analysing this coefficient for the large system, it turns out that the average value increases for increasing t up

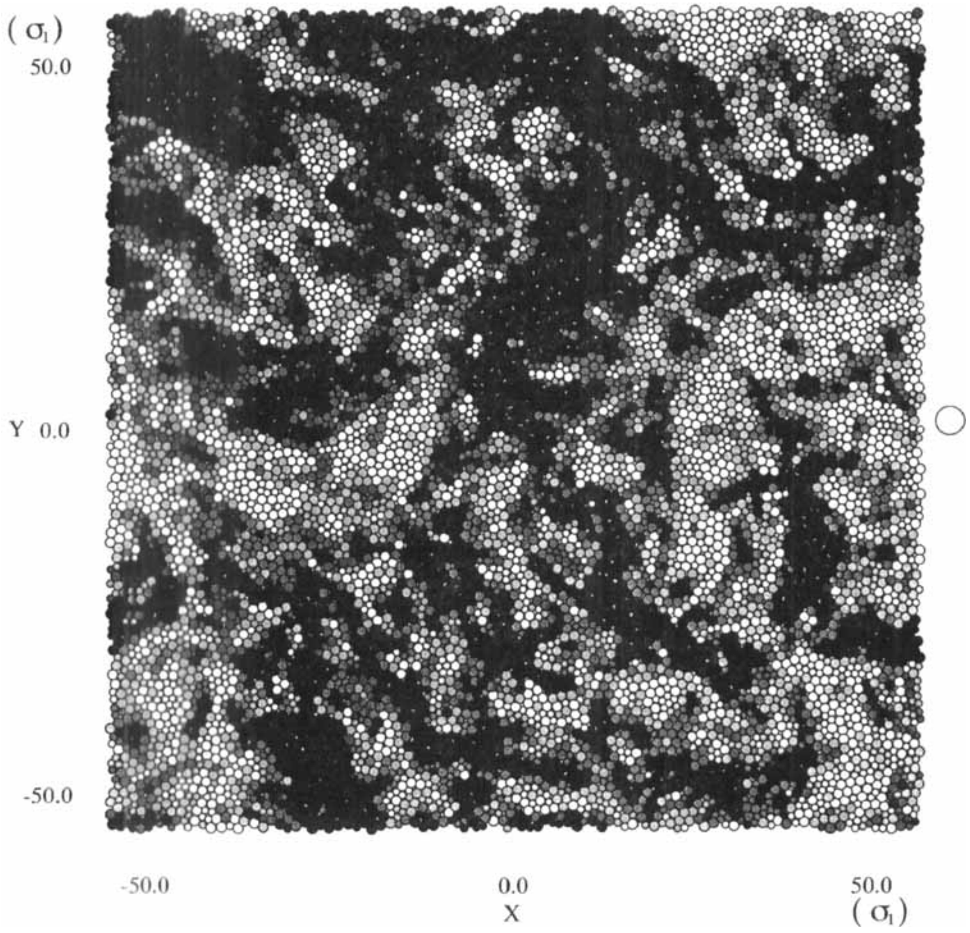

Figure 6 The correlated motion coefficient $CM_i(2.0, 5.0)$ is calculated for all atoms ($N = 10{,}000$) at $\Gamma_{\text{eff}} = 1.4$. A circle on the right side of this Figure denotes the size of the cut-off radius ($r_c = 2.0\sigma_1$). All circles indicate the initial positions of atoms with the respective size of each species. The gradation is made according to the (five classed) values of the CM_i; the darker the gradation is, the higher the value of the CM_i. The axes X,Y are absolute distance from central position (0.0, 0.0) in unit of σ_1.

to about 5τ [20], and the high-value range of this coefficient becomes wider in space for decreasing temperature.

The space distribution of $CM_i(2.0, 5.0)$ at $\Gamma_{\mathrm{eff}} = 1.4$ is shown in Figure 6. It seems that there are large clusters of the dark points marked by the highest gradation in the Figure. The cut-off distance $r_c = 2.0\ \sigma_1$ was used for simplicity. However, even if r_c is made twice larger, *i.e.* $4.0\ \sigma_1$, the space distribution of CM_i is little changed. On the contrary, the space distribution of $CM_i(2.0,\ 1.0)$ for $\Gamma_{\mathrm{eff}} = 1.4$ is shown in Figure 7. The elapsed time of the displacement is chosen to be 1.0τ. The space distribution of CM_i seems that the dark and white points are almost randomly distributed. In this case the time scale corresponds to that of the thermal oscillations. Thus, the present analysis indicates that atoms move correlatedly for the time scales of several times τ. The pattern of the CM_i map (range of the highly correlated areas) is significantly changed with t. Also the correlation domains change in place and time.

The space distribution of $CM_i(2.0, 5.0)$ at $\Gamma_{\mathrm{eff}} = 1.0$ is shown in Figure 8. This is similar to the space distribution of $CM_i(2.0, 1.0)$ at $\Gamma_{\mathrm{eff}} = 1.4$ in Figure 7. The β peak is not clearly shown in Figure 1. For this temperature it seems that the individual atomic motion (like jump motion and thermal vibration) and cooperative atomic motion (correlated motion) are coupled all together, as the highly correlated area is small, less than

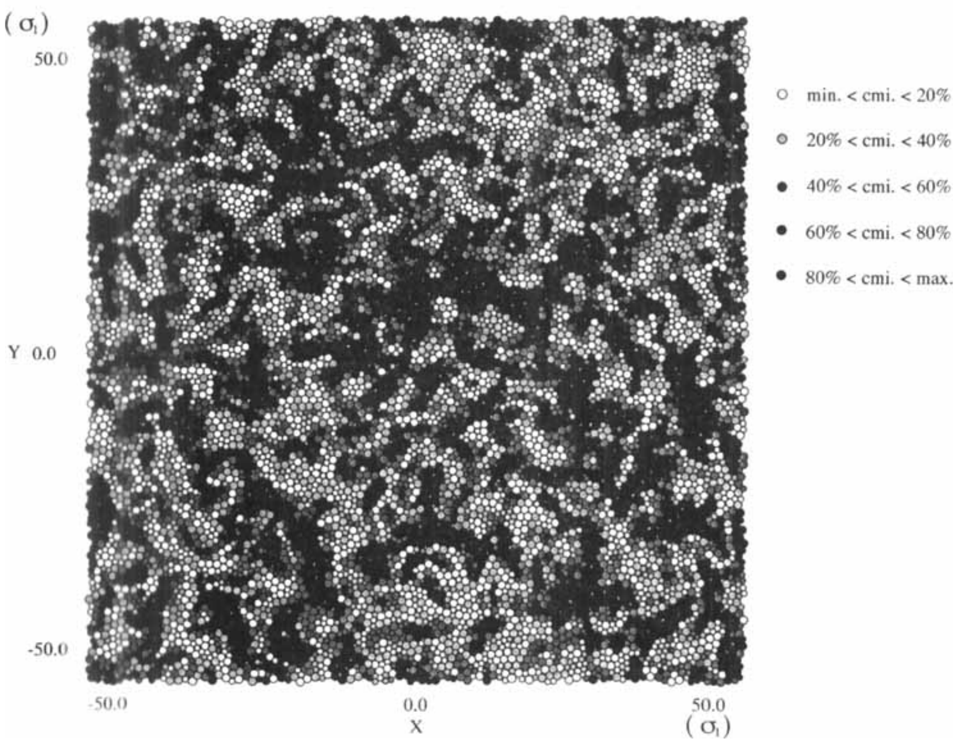

Figure 7 The correlated motion coeficient $CM_i(2.0, 1.0)$ is calculated for all atoms ($N = 10{,}000$) at $\Gamma_{\mathrm{eff}} = 1.4$. The only difference from Figure 6 is the elapsed time of displacement.

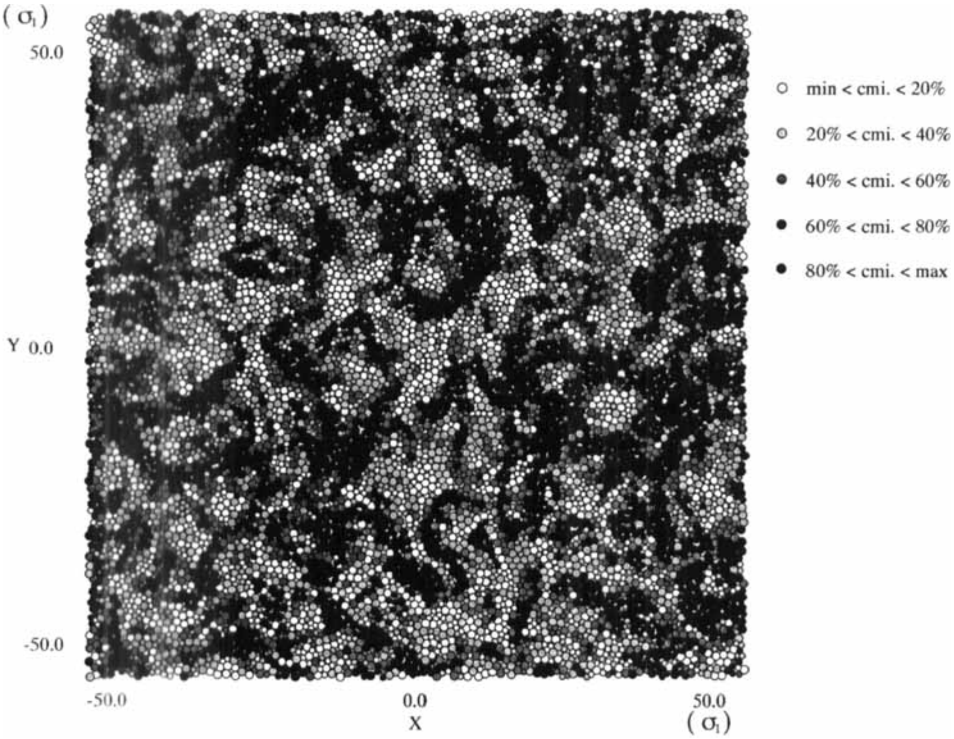

Figure 8 The correlated motion coefficient $CM_i(2.0, 5.0)$ is calculated for all atoms ($N = 10{,}000$) at $\Gamma_{\rm eff} = 1.0$ (normal liquid state). The only difference from Figure 6 is the temperature.

dozens of atoms. As seen in Figure 3, $\chi_s''(\mathbf{k}, \omega)$ for the smaller (100-particle) system begins to decrease around $\omega \sim 1.0\tau^{-1}$, but for the larger (10,000-particle) system begins to decrease around $\omega \sim 0.2\tau^{-1}$ for decreasing ω. If the β peak results from the correlated motion of atoms mentioned above, this result can be reasonably understood.

5 CONCLUSION

Atomic-level nature for the peas of the imaginary self-part of the generalized susceptibility at $\Gamma_{\rm eff} = 1.4$ are obtained: The first peak (α peak or main peak) in the lowest frequency region originates from the jump motion, the second peak originates from the sway motion, the third peak (β peak or J-G peak) originates from the correlated motion and the fourth peak (fast process) originates from the thermal vibration. It is speculated that the correlated motion of atoms is relevant dynamics to the β relaxation.

References

[1] M. Matsuo, Y. Ishida, K. Yamafuji, M. Takayanagi and F.Irie, "Dielectric Behavior of Polychloroprene", *Koll. Z. Z.Polym.*, **201**, 89 (1965).

[2] G. P. Johari, "Intrinsic mobility of molecular glasses", *J. Chem. Phys.*, **58**, 1766 (1973).

[3] Y. Ishida, K. Yamafuji and K. Shimada, "Note on Symmetry of Dielectric β-Absorption Curve of Polyester", *Koll. Z. Z. Polym.*, **200**, 49 (1964).

[4] F. Mezei, W. Knaak and B. Farago, "Neutron Spin-Echo Study of Dynamic Correlations near the Liquid-Glass Transition", *Phys. Rev. Lett.*, **58**, 571 (1987).

[5] H. Z. Cummins, W. M. Du, M. Fuchs, W. Götze, S. Hildebrand, A. Latz, G. Li and N. J. Tao, "Light-scattering spectroscopy of the liquid-glass transition in $CaKNO_3$ and in the molecular glass Salol: Extended-mode-coupling-theory analysis", *Phys. Rev.*, **E47**, 4223 (1993); G. Li, W. M. Du, X. K. Chen and H. Z. Cummins, "Testing mode-coupling predictions for α and β relaxation in $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ near the liquid-glass transition by light scattering', *Phys. Rev.*, **A45**, 3867 (1992).

[6] W.Götze, *in Liquids, Freezing and Glass Tansition*, edited By J. P. Hansen, D. Levesque and J. Zinn-Justin (North-Holland, Amsterdam, 1991), p287.

[7] M. A. Glaser and N. A. Clark, "MELTING AND LIQUID STRUCTURE IN TWO DIMENSIONS", *Advances in Chemical Physics, Volume LXXXIII*, edited by I. Prigogine and S. A. Rice, (John Wiley & Sons, Inc., 1993), p543.

[8] H. Miyagawa, Y. Hiwatari, B. Bernu and J. P. Hansen, "Molecular dynamics study of binary soft-sphere mixtures: Jump motions of atoms in the glassy state", *J. Chem. Phys.*, **88**, 3879 (1988).

[9] Y. Hiwatari, H. Miyagawa and T. Odagaki, "Dynamical singularities near the liquid-glass transition: Theory and molecular dynamics study", *Solid Sate Ionics*, **47**, 179 (1991).

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

[11] J. Matsui, T. Odagaki and Y. Hiwatari, "Study of the Slow Dynamics in a Highly Supercooled Fluid: Superlong-Time Molecular-Dynamics Calculation of the Generalized Susceptibility", *Phys. Rev. Lett.*, **73**, 2452 (1994).

[12] 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).

[13] D. Richter, R. Zorn, B. Farago, B. Frich and L. J. Fetters, "Decoupling of Time Scales of Motion in Polybutadiene Close to the Glass Transition", *Phys. Rev. Lett.*, **68**, 71 (1992).

[14] W. Götze and L. Sjögren, "Relaxation processes in supercooled liquids", *Rep. Prog. Phys.*, **55**, 241 (1992).

[15] W. C. Swope, H. C. Andersen, P. H. Berens and K. R. Wilson, "A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules : Application to small water clusters", *J. Chem. Phys.*, **76**, 637 (1982).

[16] S. Nosé, "A unified formulation of the constant temperature molecular dynamics methods", *J. Chem. Phys.*, **81**, 511 (1984).

[17] B. Bernu, Y. Hiwatari and J. P. Hansen, "A molecular dynamics study of the glass transition in binary mixtures of soft spheres", *J. Phys.*, **C18**, L371 (1985).

[18] F. H. Stillinger and T. A. Weber, "Computer simulation of local order in condensed phases of silicon", *Phys. Rev.*, **B31**, 5262 (1985); R. Kanada (private communication).

[19] J. Matsui, H. Miyagawa, T. Muranaka, K. Uehara, T. Odagaki and Y. Hiwatari, "CALCULATION OF THE GENERALIZED SUSCEPTIBILITY FOR A HIGHLY SUPERCOOLED FLUID THROUGH MOLECULAR-DYNAMICS SIMULATION", *Molecular Simulation*, **12**, 305 (1994).

[20] T. Muranaka and Y. Hiwatari, "A study of the β relaxation in a highly supercooled state via molecular dynamics simulation", *Phys. Rev.*, E51, 2735 (1995).