

Molecular Dynamics Study of a Supercooled Binary Soft-Sphere System: Calculation of the Generalized Susceptibility in Supercooled and Glassy States

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To study how the motion of atoms changes through a glass forming process, we have carried out the molecular dynamics simulation for a binary soft-sphere system and calculated the self-part of the generalized susceptibility $\chi_s(q, \omega)$ at various temperatures above/below T_g . At higher temperature, only one peak appears in the imaginary part of χ_s , which corresponds to random motion of atoms in the liquid state. When the temperature is reduced, the α -peak tends to separate out from the main peak and to move to lower frequencies. At the lowest temperature, the peak disappears from our frequency window. We show that the temperature dependence of the peak frequency is well described by the Vogel-Fulcher law.

We also test the mode coupling theory. The two exponents do not agree with the universality of the mode coupling theory, $\lambda = \Gamma(1-a)^2/\Gamma(1+2b) = \text{const.}$

§1. Introduction

Computer glasses simulated in computers by molecular dynamics methods are very good glasses for studies, because it is possible not only to trail the motion of atoms directly but also to calculate the spectrum corresponding to the scattering experiment results without any approximation. In many systems, such as Lennard-Jones system and soft sphere system, the characteristic motions of atoms have been detected which cannot be observed in normal liquid states.¹⁾ In highly supercooled states, the most of atoms stray around their stable points and sometimes several atoms jump cooperatively toward to the neighbor stable points, that is the diffusion process in highly supercooled states. The time scale of jump motions becomes larger and larger than the one of stray motions when the temperature is reduced. It provides a microscopic aspect of the glass transition.

On the other hand, the calculation of the dynamic structure factor and the generalized susceptibility is very tough, because it takes so long computational time to integrate over long time scale motion of atoms.^{2),3)} We have tried to do it for a binary soft sphere system at various temperatures from liquid states to glassy states below the glass transition temperature. We focus on the temperature dependence of the peaks appearing on $\chi_s''(q, \omega)$ and test the mode coupling theory⁴⁾ as many experimentalists do.⁵⁾

§2. Model for simulation

The model we use is a binary soft-sphere system: the total number of particles $N(= N_1 + N_2) = 500$, the ratio of mixture $N_1/N_2 = 1$, radius $r_1/r_2 = 1.2$ and mass

$m_1/m_2 = 2.0$. The inter-particle potential is soft-sphere type:

$$\phi_{\alpha\beta}(r) = \epsilon \left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12}; \quad \alpha, \beta = 1, 2, \quad (2.1)$$

where $\sigma_{\alpha\beta} = r_\alpha + r_\beta$. All parameters can be reduced to one parameter,

$$\Gamma_{\text{eff}} = (N/V) \sigma_{\text{eff}}^3 (\epsilon/k_B T)^{\frac{1}{4}}, \quad (2.2)$$

where $\sigma_{\text{eff}}^3 = (\sigma_{11}^3 + \sigma_{12}^3 + \sigma_{21}^3 + \sigma_{22}^3)/4$.

The simulation starts from a liquid state at $\Gamma_{\text{eff}} = 0.8$ by using the constant temperature simulation. Next, the system is quenched to each temperature for measurement and annealed. Then we start the calculation of the generalized susceptibility by using the micro canonical simulation.

Molecular dynamics simulations compute the position and the velocity of each particle at each time step. To calculate the self part of the generalized susceptibility $\chi(q, \omega)$, we use the following equation,³⁾

$$\chi_s(\mathbf{q}, \omega) = 1 + \frac{i\omega}{T_{\text{total}}} \left\langle \sum_j \int_0^{T_{\text{total}}} dt_0 e^{i\mathbf{q} \cdot \mathbf{r}_i(t_0)} e^{-i\omega t_0} \int_0^{t_0} dt e^{-i\mathbf{q} \cdot \mathbf{r}_j(t)} e^{i\omega t} \right\rangle_i, \quad (2.3)$$

where $\mathbf{r}_i(t)$ is the position of the i th atom at time t . T_{total} is the total time steps of the computation, which has to be sufficiently large. In our calculation we have integrated up to 1,000,000 time steps, which corresponds to the order of 10 nano second.

§3. The temperature dependence of the imaginary part of the generalized susceptibility

In Fig. 1 we show the frequency dependence of $\chi_s''(q, \omega)$ at various temperatures. At high temperature (low Γ_{eff}) only one peak appears on $\chi_s''(q, \omega)$, which is corresponding to the random motion of atoms in liquid states. When the temperature is reduced, so-called α -peak tends to separate out and to move to lower frequencies. It means that the stray motion of atoms becomes distinguishable from the diffusive jump motion which corresponds to the α -peak. In Fig. 2 we plot the peak frequencies of both α - and β - peaks against inverse temperature. For α -peak, it is well fitted by the Vogel-Fulcher law $\sim \exp[-DT_0/(T - T_0)]$ as represented by solid line in Fig. 2. T_0 is called the Vogel-Fulcher temperature where the viscosity and the relaxation time asymptotically diverge, and D implies the fragility. From the fitting, we estimate these values, $T_0 = 11.8\epsilon/k_B$, $\Gamma_0 = 1.89$ and $D = 13.1$. α -peak is related to diffusive jump motion of atoms which is the slowest microscopic motion. Thus, the peak frequencies of α -peak can be supposed to be the inverse relaxation time. On the other hand, for the second peak called β -peak appearing at higher frequencies, the peak position does not move so much.

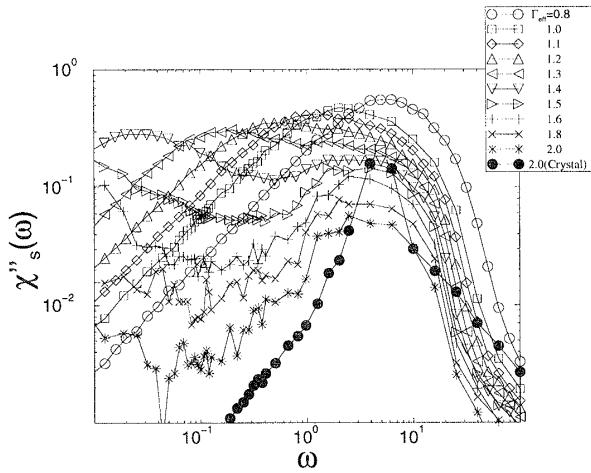


Fig. 1. The frequency dependence of $\chi''_s(q, \omega)$ in liquid states, supercooled states and glassy states at $q = 2\pi/\sigma_{11}$ which corresponds to the inverse inter-particle distance. The glass transition point is $\Gamma_{\text{eff}} = 1.58$. $\chi''_s(q, \omega)$ in crystalline state is plotted by closed circles.

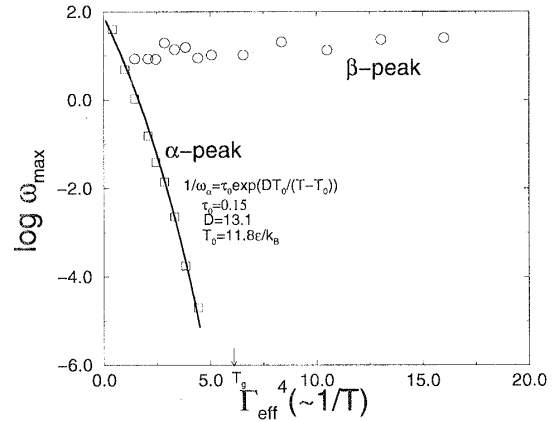


Fig. 2. The temperature dependence of peak frequency. Squares and circles represent for the α - and β -peaks respectively. The fitted curve for α -peak is drawn by solid curve, which is well described by Vogel-Fulcher law: $\tau = \tau_0 \exp[DT_0/(T - T_0)]$. The fitted values are $\tau_0 = 0.15$, $D = 13.1$, $T_0 = 11.8\epsilon/k_B$ and $\Gamma_0 = 1.89$.

§4. Tests of the mode coupling theory

The mode coupling theory (MCT) for the liquid-glass transition predicts that (1) α -peak disappears below the critical temperature T_C which is higher than the glass transition temperature T_g ; $T_C > T_g$. (2) Near the minimum of $\chi''_s(q, \omega)$, the curves can be reduced an temperature-independent function: $(a\omega^{-b} + b\omega^a)(a + b)^{-1}$, where the both exponents a and b are decided by so-called exponent parameter $\lambda = \Gamma(1 - a)^2/\Gamma(1 + 2b) = \text{const.}$ ⁴⁾ As we have seen in Fig. 1, it is quite clear that the α -peak still exists even below the glass transition point ($\Gamma_g = 1.58$), which is inconsistent with MCT. In Fig. 3, we plot the reduced $\chi''(q, \omega)$ which are scaled by their minimum values. It looks to be well suited by a unified function as predicted in MCT. We have obtained the exponent values by fitting data, $a = 0.98 \pm 0.15$ and $b = 0.48 \pm 0.15$. The exponent $-b$ takes the value around -0.48 , we paint it by the gray zone in Fig. 4. Then the exponent a should take the value around 0.3, which does not coincide with our results. Besides, the value of a is out of the range which cannot be explained in MCT. These two values make broken down the second prediction $\lambda = \Gamma(1 - a)^2/\Gamma(1 + 2b) = \text{const.}$ Thus, our results do not agree with both of their predictions.

§5. Summary

We have discussed the temperature dependence of the generalized susceptibility of a *computer glass*. The peak position of α -peak is well described by the Vogel-Fulcher law, as same as many *real glasses*. We have also tested the mode coupling

theory. The results do not agree with their predictions, although the model we using is very simple.

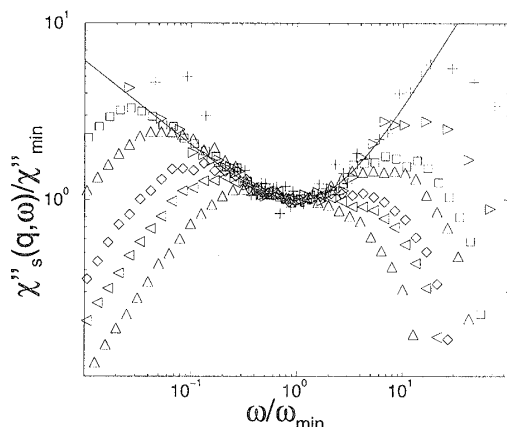


Fig. 3. Reduced $\chi''(q, \omega)$ at $\Gamma_{\text{eff}} = 1.2$ to 1.8 . Solid curve shows the fitted curve, $(a\omega^{-b} + b\omega^a)(a+b)^{-1}$, $a = 0.98 \pm 0.15$ and $b = 0.48 \pm 0.15$.

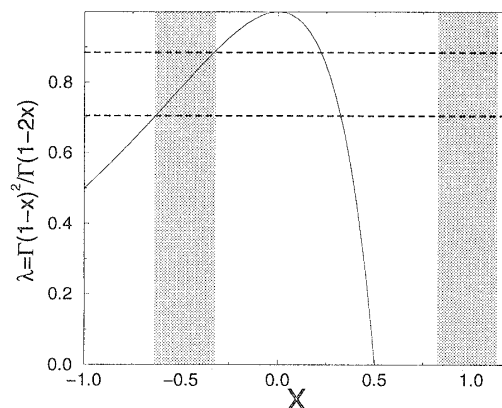


Fig. 4. Test of the two exponents a and b . According to MCT, a and b are related to a constant parameter $\lambda = \Gamma(1-a)^2/\Gamma(1+2b)$. The value of λ is plotted as the function of a and b . If b is known, λ is decided by $\lambda(-b)$. Then, a takes the value which satisfies $\lambda = \lambda(a)$. Our results $a = 0.98 \pm 0.15$, $b = 0.48 \pm 0.15$, marked in gray, do not agree with this relation.

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