Slow dynamics in supercooled liquids

T. Odagaki
Department of Physics, Kyushu University, Fukuoka 812, Japan
J. Matsui and Y. Hiwatari
Department of Physics, Kanazawa University, Kanazawa 920-11, Japan
(Received 5 October 1993)

Slow dynamics in supercooled liquids is investigated on the basis of the trapping diffusion model which takes account of two types of diffusive dynamics, jump motion and stray motion. Parameters of the model are determined in such a way that the waiting-time distribution of the model agrees with those found for a binary soft-sphere system through molecular-dynamics simulation. With the use of the coherent-medium approximation, the frequency dependence of the self-part of the dynamical structure factor $S_s(\mathbf{q},\omega)$ and the generalized susceptibility $\chi_s''(\mathbf{q},\omega)$ is obtained. Above the glass-transition point, there exist frequency regions where $S_s(\mathbf{q},\omega)$ shows a power-law decay, corresponding to α relaxation and β relaxation, which are shown to be caused by the subanomalous diffusion due to the jump motion and by the stray motion, respectively. This indicates that above the glass-transition point there exists a certain time window where the intermediate scattering function $F_s(\mathbf{q},t)$ shows a stretched exponential decay. Below the glass-transition point, $F_s(\mathbf{q},t)$ decays in a stretched exponential form in the long-time limit, which is caused by the anomalous diffusion due to the jump motion. Accordingly, $S_s(\mathbf{q},\omega)$ in the static limit is shown to be a cusp between the glass transition and a certain temperature below the freezing point, and to diverge below the glass-transition point. The α-relaxation time determined from the position of the α peak of $\chi_s''(\mathbf{q},\omega)$ is shown to diverge at a certain temperature below the glass-transition point, in line with the Vogel-Fulcher equation. The exponent representing the long-time decay of the non-Gaussian parameter is also obtained, which agrees quantitatively with the result obtained for the soft-sphere system by molecular-dynamics simulation.

PACS number(s): 64.70.Pf, 61.43.Fs, 66.10.−x

I. INTRODUCTION

Slow dynamics in supercooled liquids has been attracting much interest in recent years, since it is believed that the slow structural relaxation is a clue for understanding the mechanism of glass transition in the supercooled state of liquids and in the colloidal suspensions [1]. Many experiments have been performed for $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ (CKN). Mezei and co-workers reported the neutron scattering experiments (time of flight and neutron spin echo) on CKN [2,3]. They showed that the dynamical structure factor $[S(q,\omega)]$ deviates frow the Debye type in the supercooled liquid state. Namely, it shows in a certain frequency region two power-law decay modes with exponent less than the Debye value. These two modes are attributed to α and β dynamics in supercooled liquids predicted by a mode-coupling theory [4–6]. Cummins *et al.* [7,8] performed light-scattering experiments for CKN in which the generalized susceptibility $[\chi''(q,\omega) \equiv \omega\pi S(q,\omega)]$ is measured. The principal peak of $\chi''(q,\omega)$ shows slower decay than the Debye case and the peak position is shifted to the lower-frequency side as the temperature is reduced. The susceptibility also shows the so-called β minimum, indicating a crossover between two different regimes of dynamics. They estimated the Kohlrausch-William-Watt (KWW) exponent β which characterizes the stretching of relaxation in the form $\exp[-(t/t_1)^\beta]$ and found that β is a constant down to a certain temperature far above the glass-transition temperature T_g. The ac conductivity $\sigma(\omega)$ for CKN has also been reported [9]. As the frequency is increased from zero, $\sigma(\omega)$ increases, suggesting that a dispersive transport must be involved as in the impurity conduction [10].

There have been many reports which suggest the existence of at least two kinds of such slow dynamics in supercooled liquids such as orthoterphenyl [11], Salol [12], and poly(propylene glycol) [13] and in colloidal suspensions [14] near the glass transition point.

Extensive molecular-dynamics (MD) simulations have been carried out in recent years to elucidate the microscopic mechanism of glass transition for soft-core systems [15–17], Lenard-Jones systems [18], and ionic melts [19]. Because of the restricted computation time, the total length of simulation and the time step are limited, which puts the boundary to the observation window both in the high- and low-frequency regions. The main results obtained from the MD simulation can be summarized as follows. (i) There is a time region in which the intermediate scattering function shows a stretched exponential decay. (ii) The dynamical trait changes at some temperature T_x above the glass-transition temperature, which can be considered as a kinetic transition. (iii) Two types of diffusive motions exist above and below T_g in the time scale much slower than that of the microscopic motion.

These extensive studies of glass transition were prompted by the predictions made by the mode-coupling theory. The mode coupling theory of glass transition was first proposed by Leutheusser [20] and Bengtzelius *et al.* [21]. They showed that the glass transition could be understood as an ergodic to nonergodic transition due to nonlinear coupling in the density fluctuation mode of a

specified wave vector. The interaction they employed, however, always yields the Debye-type decay of the correlation function which does not agree with experiments. Götze *et al.* [4–6] investigated extensively an improved version of the mode-coupling theory, including interactions to various orders of the density fluctuation itself. Under certain scaling assumptions, they showed the existence of two regimes of relaxation which are called α (long time) and β relaxation (short time). The α relaxation, which is characterized by a power-law decay of the dynamical structure factor, exists down to a certain temperature T_c above T_g and is supposed to disappear below T_c. In the time domain, the α relaxation is seen as a stretched exponential decay of the correlation function. In the β-relaxation regime, the correlation function decays in power law to a certain limiting value and the crossover between α and β relaxations can be seen as a minimum of the generalized susceptibility. These predictions have been shown to be in line with some of experimental observations [7,8] and MD simulations [16]. However, some predictions have been shown to contradict to experiments or MD simulations. For example, the KWW exponent β is shown not to be constant as a function of temperature [11,22], in contrast to the predictions of the mode-coupling theory. Furthermore, data analysis of the light-scattering experiments by Cummins *et al.* [7,8] has strongly been criticized by Zeng *et al.* [23].

These defects of the mode-coupling theory is considered to be due to the fact that the jump motion is neglected in the theory. Götze and co-workers [24,25] introduced an extended mode-coupling theory in which an interaction between the density mode and the current mode is included. They viewed this interaction as producing the relaxation of the density mode due to hopping motion of atoms. The extended mode-coupling theory was applied to analyze the behavior of $\chi''(\mathbf{q},\omega)$ of CKN and Salol obtained by light-scattering experiments [26]. Their extensive analysis revealed that the hopping motion plays a significant role in determining the relaxations. This poses two problems. (i) Since the hopping eliminates the criticality, the analysis based on the scaling assumption around the criticality loses its sense. (ii) The hopping is a stochastic dynamics of localized atoms and one needs many different modes to describe a localized atom, which will invalidate the single mode analysis of the mode coupling theory.

Recently, we proposed a trapping diffusion model of glass transition based on the hopping dynamics of atoms in a mesoscopic scale [27,28]. In this model the glass transition can be understood as a transition from Gaussian to non-Gaussian dynamics. The trapping diffusion model is a phenomenological model, where the stochastic dynamics is extracted by coarse-graining rapid vibrations. We determined the transition-rate distribution for the jump motion from the information obtained by MD simulation [29]. Namely, we employed a power-law distribution for the jump rate in the trapping-diffusion master equation and the exponent of the distribution (ρ) is considered a parameter determined by the thermodynamic state. Using the coherent-medium approximation [30], we showed that the glass transition occurs at $\rho = 0$.

In this paper we study the dynamical properties of supercooled liquids by extending the trapping diffusion model to include an oscillatory-diffusive motion in the theory. We analyze the frequency dependence of the dynamical structure factor and the generalized susceptibility for the entire frequency region. We show that α relaxation can exist above the glass-transition point due to the subanomalous dynamics caused by the fact that the second moment of the waiting-time distribution diverges. The low-frequency limit of the dynamical structure factor is shown to be (i) divergent like $1/f$ noise below the glass-transition point and (ii) a cusp between the glass-transition point and a kinetic transition point. In Sec. II, we first discuss what is meant by "slow dynamics" and introduce the trapping diffusion model, focusing on the necessity of such model. We also summarize the coherent-medium approximation in Sec. II, which is utilized in the following analysis. In Sec. III, we present the dynamical properties of undercooled liquids characterized by the dynamical structure factor. We first analyze the low-frequency behavior and the high-frequency limit of the self-part $S_s(\mathbf{q},\omega)$ of the dynamical structure factor and then we study if there exist frequency regions where the dynamical structure factor decays in a power-law form with exponent less than the Debye relaxation. We also discuss the relaxation time determined from the α peak of $\chi_s''(\mathbf{q},\omega)$. We show that the relaxation time diverges exponentially at $\rho = -1$ below the glass-transition point (the Vogel-Fulcher behavior). In Sec. IV, we investigate the behavior of the non-Gaussian parameter whose long-time decay is determined by the α-relaxation process. We show that the exponent determining the decay deviates from unity at a certain temperature above the glass-transition point. We will make a quantitative comparison of this behavior with MD simulation. We give conclusions in Sec. V.

The main result of the present study is that the jump motion gives rise to the α relaxation whose characteristic time appears to diverge at some point below the glass-transition point, and the oscillatory-diffusive motion produces the β relaxation. Below the glass-transition point, the system is in the anomalous diffusion regime, where the first moment of the waiting-time distribution diverges and one expects to see a superslow dynamics in much longer time window which is signified in the stretched exponential decay of correlation function and the $1/f$-type behavior of $S_s(\mathbf{q},\omega)$ near $\omega = 0$.

The trapping diffusion model is intended to apply to supercooled state of simple liquids, where the structural relaxation is caused by translational motion of individual atoms. It will also apply to some ionic melts [19]. It requires further studies to see if it is applicable to so called strong glass formers.

II. TRAPPING DIFFUSION MODEL

A. Slow dynamics

In regular simple liquids, the structural relaxation is known to be Debye type, or simple exponential

$\exp(-t/\tau)$. This is because frequent random collisions between atoms or molecules make the dynamics diffusive and the system homogeneous. In many complex systems, it has been known that the relaxation function takes a different form such as $\exp[-(t/\tau)^\beta]$ with $\beta < 1$, which is called Kohlrausch-William-Watt relaxation [31]. In fact, any relaxation function of the form $f[(t/\tau)^\beta]$, where $f(x)$ is a monotone decreasing function, represents a slow relaxation when $\beta < 1$, since the time required to relax a certain percentage is longer than that for $\beta = 1$. The slow relaxation manifests itself in the decay of the dynamical structure factor. It is easy to show that the dynamical structure factor decays like $\sim \omega^{-2}$ for the Debye relaxation and $\sim \omega^{-(1+\beta)}$ for the KWW relaxation for large ω. As we mentioned in the Introduction, it is now believed from experimental observations that there exist two slow relaxation regimes, which appear in the frequency regions $\sim 10^9$ Hz and $\sim 10^{11}$ Hz. On the other hand, MD simulation for supercooled liquids [17] revealed two distinct dynamics in these frequency regions: One is the jump motion and the other is an oscillatory motion of diffusive origin. These dynamics are apparently produced by cooperative motion of a few tens to a few hundred atoms [17,32], and it is important to understand dynamical behavior produced by those dynamics. At the present stage, it is virtually impossible to solve the many-body problem analytically. It is also impossible to carry out MD simulation long enough to obtain accurate statistics since the time scale that we are concerned with is just around the time region accessible by conventional computers [33]. Therefore, it is practical and instructive to construct a phenomenological model which represents accurately the effect of the cooperative slow dynamics. The model is necessarily based on a mesoscopic description in time and space. With a good phenomenological model at hand, it will be easier to understand the slow dynamics from the microscopic model which will be pursued in the future.

B. Trapping diffusion model

According to MD simulation [15,17], an atom appears to perform two kinds of diffusive motions if the rapid oscillatory motion is averaged out: One is a motion bound within a local area with a deviation of a few tens of a percent of the mean interatomic distance (we call it the *stray motion*) and the other is a *jump motion* with jump distance in the order of the mean interatomic distance. Furthermore, the stray motion occurs in regions of a few tens of atoms randomly distributed in the system and the jump motion usually occurs at the boundary of the region. The existence of a similar kind of domains has also been suggested by Ngai *et al.* [34], Bendler and Shlesinger [35], and Fischer [36] in somewhat different context. From the data obtained by MD simulation for binary soft spheres [17] we observe that (i) jump distances have a narrow distribution for both diffusive motions and (ii) the waiting-time distribution can be represented well by a simple exponential function for the stray motion and by a power-law function for the jump motion. The second observation indicates that the jump-rate distribution will be sharply peaked for the faster motion and be a power-law function for the slower motion. Noting that the distribution of the number of neighboring atoms is also sharply peaked, we arrive at the following mesoscopic phenomenological model (see Fig. 1). An atom at a given site $\mathbf{s}$ performs a stray motion between $\mathbf{s}$ and neighboring position $\mathbf{u}_\mathbf{s}$ ($|\mathbf{u}_\mathbf{s}|$ is of the order of 30% of the average interatomic distance) with a constant jump rate w_b. Occasionally, it makes a long jump motion to site $\mathbf{s}'$ with jump rate $w_\mathbf{s}$. The jump rate for this motion is assumed to depend only on the origin of the jump and not on the destination of the jump, because a structural relaxation following the jump will eliminate the correlation between forward and backward jumps. We further assume that the distribution of site $\{\mathbf{s}\}$ will not be important and sites $\{\mathbf{s}\}$ form a regular lattice, which can be conveniently assumed to be a simple cubic lattice. Consequently, we describe the motion of a tagged atom by the following trapping master equation [37]:

$$\dot{P}(\mathbf{s},t|\mathbf{s}_0,0) = \sum_{\mathbf{s}'} w_{\mathbf{s}'} P(\mathbf{s}',t|\mathbf{s}_0,0) + \sum_{\mathbf{u}_\mathbf{s}} w_b P(\mathbf{s}+\mathbf{u}_\mathbf{s},t|\mathbf{s}_0,0) - \left\{\sum_{\mathbf{s}'} w_\mathbf{s} + \sum_{\mathbf{u}_\mathbf{s}} w_b\right\} P(\mathbf{s},t|\mathbf{s}_0,0), \quad (1)$$

$$\dot{P}(\mathbf{s}+\mathbf{u}_s,t|\mathbf{s}_0,0) = w_b P(\mathbf{s},t|\mathbf{s}_0,0) - w_b P(\mathbf{s}+\mathbf{u}_s,t|\mathbf{s}_0,0), \quad (2)$$

where $P(\mathbf{x},t|\mathbf{s}_0,0)$ denotes the probability that the tagged atom is at $\mathbf{x}$ at time t when it was at $\mathbf{s}_0$ at time $t = 0$, the summation for $\mathbf{s}'$ is taken over nearest neighbors of site $\mathbf{s}$, and $\{\mathbf{u}_\mathbf{s}\}$ represent neighboring sites to which the atom on $\mathbf{s}$ can stray. Laplace transform $\tilde{P}(\mathbf{x},u|\mathbf{s}_0) = \int_0^\infty e^{-ut} P(\mathbf{x},t|\mathbf{s}_0,0)dt$ then satisfies

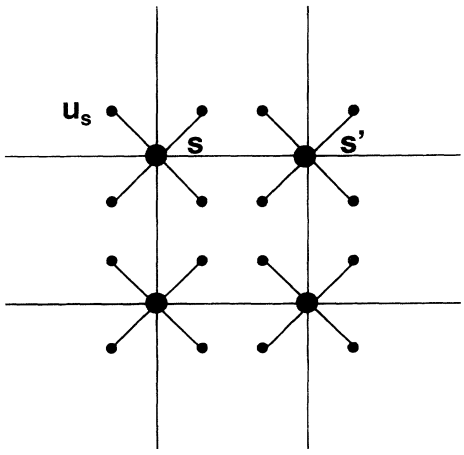

FIG. 1. The trapping diffusion model. A tagged atom makes a jump motion among sites $\{\mathbf{s}\}$ described by the trapping master equation with jump rate distribution (7). It makes a stray motion from $\mathbf{s}$ to $\mathbf{s}+\mathbf{u}_s$ with a constant jump rate w_b.

$$\left[u+\sum_{\mathbf{s}'} w_{\mathbf{s}}+\sum_{\mathbf{u}_s} w_b\right]\tilde{P}(\mathbf{s},u|\mathbf{s}_0)-\sum_{\mathbf{s}'} w_{\mathbf{s}'}\tilde{P}(\mathbf{s}',u|\mathbf{s}_0)$$

$$-\sum_{\mathbf{u}_s} w_b\tilde{P}(\mathbf{s}+\mathbf{u}_{\mathbf{s}},u|\mathbf{s}_0)=\delta_{\mathbf{s},\mathbf{s}_0}\delta_{\mathbf{u}_s,0}, \quad (3)$$

$$[u+w_b]\tilde{P}(\mathbf{s}+\mathbf{u}_s,u|\mathbf{s}_0)-w_b\tilde{P}(\mathbf{s},u|\mathbf{s}_0)=\delta_{\mathbf{s},\mathbf{s}_0}\delta_{\mathbf{u}_s,0}. \quad (4)$$

Decimating $\tilde{P}(\mathbf{s}+\mathbf{u}_s,u|\mathbf{s}_0)$ from these equations, we find

$$\left[u+\sum_{\mathbf{u}_s}\left\{w_b-\frac{w_b^2}{u+w_b}\right\}+\sum_{\mathbf{s}'} w_{\mathbf{s}}\right]\tilde{P}(\mathbf{s},u|\mathbf{s}_0)$$

$$-\sum_{\mathbf{s}'} w_{\mathbf{s}'}\tilde{P}(\mathbf{s}',u|\mathbf{s}_0)=\delta_{\mathbf{s},\mathbf{s}_0}. \quad (5)$$

We denote by z' the number of sites to which the tagged atom can stray and set $u'\equiv u+z'w_bu/(u+w_b)$. Then Eq. (5) reduces to

$$\left[u'+\sum_{\mathbf{s}'} w_{\mathbf{s}}\right]\tilde{P}(\mathbf{s},u|\mathbf{s}_0)-\sum_{\mathbf{s}'} w_{\mathbf{s}'}\tilde{P}(\mathbf{s}',u|\mathbf{s}_0)=\delta_{\mathbf{s},\mathbf{s}_0}, \quad (6)$$

which is nothing but the master equation for the trapping diffusion process [37]. As we discussed above, jump rate $\{w_{\mathbf{s}}\}$ can be assumed to obey the power-law distribution

$$\Phi(w_{\mathbf{s}})=\begin{cases}\frac{\rho+1}{w_0^{\rho+1}}w_{\mathbf{s}}^{\rho} & (0\le w_{\mathbf{s}}\le w_0)\\ 0 & (\text{otherwise})\end{cases} \quad (7)$$

where ρ is a parameter of the model which represents the thermodynamic state of the system. In fact, from a comparison of the waiting-time distribution we found [29]

$$\rho=398[\Gamma_g-\Gamma_{\text{eff}}]^3 \qquad (\Gamma_{\text{eff}}\le\Gamma_g) \quad (8)$$

for binary soft-sphere mixtures, where for N_1 atoms of mass m_1 and diameter σ_1 and N_2 atoms of mass m_2 and diameter σ_2 in volume V

$$\Gamma_{\text{eff}}=n^*(T^*)^{-1/4}\left(\frac{\sigma_{\text{eff}}}{\sigma_1}\right)^3, \quad (9)$$

$$\sigma_{\text{eff}}=\sum_{\alpha}\sum_{\beta} x_\alpha x_\beta\sigma_{\alpha\beta}^3, \quad (10)$$

and

$$v_{\alpha\beta}=\varepsilon\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12}, \quad (11)$$

with the assumption that $\sigma_{\alpha\beta}=(\sigma_\alpha+\sigma_\beta)/2$, $T^*=k_BT/\varepsilon$, $x_\alpha=N_\alpha/(N_1+N_2)$, and $n^*=(N_1+N_2)\sigma_1^3/V$. For this system, the freezing point is at $\Gamma_{\text{eff}}=1.15$ and the glass-transition point is expected to be $\Gamma_{\text{eff}}=1.58$ [17,28].

Equation (6) cannot be solved analytically since $\{w_{\mathbf{s}}\}$ are random. We employ the following coherent medium approximation for the master equation (for details, see Ref. [30]). Namely, we find a u-dependent coherent jump rate $w_c(u)$ by the condition

$$\int_0^\infty \frac{w_{\mathbf{s}}-w_c}{w_c+(w_{\mathbf{s}}-w_c)(1-u'P_{nn})}\Phi(w_s)dw_s=0. \quad (12)$$

Here $P_{nn}=\tilde{P}_c(\mathbf{s}_0,u|\mathbf{s}_0)$ and the coherent Green's function $\tilde{P}_c(\mathbf{s},u|\mathbf{s}_0)$ satisfies Eq. (6) where all $w_{\mathbf{s}}$ are replaced by $w_c(u)$. When we need numerical calculation we approximate P_{nn} by $2\{u'+zw_c+[u'(u'+2zw_c)]^{1/2}\}^{-1}$. As we have shown already [27], there exists a glass transition at $\rho=0$, where the diffusion constant vanishes strictly below $\rho=0$. We also showed that the transition at $\rho=0$ can be understood as a change of dynamics from Gaussian to non-Gaussian [28].

III. DYNAMICAL STRUCTURE FACTOR

The self-part of the dynamical structure factor $S_s(\mathbf{q},\omega)$ is, by definition, given by

$$\mathbf{S}_s(\mathbf{q},\omega)=\frac{1}{\pi}\text{Re}\left[1+\frac{w_b\beta(\mathbf{q})}{w_b+i\omega}\right]$$

$$\times\sum_{\mathbf{s}} e^{i\mathbf{q}(\mathbf{s}-\mathbf{s}_0)}\langle\tilde{P}(\mathbf{s},i\omega|\mathbf{s}_0)\rangle, \quad (13)$$

where the angular brackets $\langle\rangle$ denote an ensemble average and $\beta(\mathbf{q})=\sum_{\mathbf{u}_s} e^{i\mathbf{q}\mathbf{u}_s}$ is assumed to be real and independent of $\mathbf{s}$. In the coherent medium approximation we approximate the ensemble average by

$$\langle\tilde{P}(\mathbf{s},u|\mathbf{s}_0)\rangle=\tilde{P}_c(\mathbf{s},u|\mathbf{s}_0). \quad (14)$$

It may, sometimes, be convenient to look at the generalized susceptibility $\chi_s(\mathbf{q},\omega)$ defined by

$$\chi_s(\mathbf{q},\omega)=1+i\omega\left[1+\frac{w_b\beta(\mathbf{q})}{w_b+i\omega}\right]$$

$$\times\sum_{\mathbf{s}} e^{i\mathbf{q}(\mathbf{s}-\mathbf{s}_0)}\langle\tilde{P}(\mathbf{s},-i\omega|\mathbf{s}_0)\rangle. \quad (15)$$

Thus

$$S_s(\mathbf{q},\omega)=\frac{1}{\pi}\text{Im}\chi_s(\mathbf{q},\omega)/\omega. \quad (16)$$

A. Low-frequency behavior

It is straightforward to derive the low-frequency expansion of $\tilde{P}_c(\mathbf{s},i\omega|\mathbf{s}_0)$, [38] from which we can obtain the low-frequency limit of $S_s(\mathbf{q},\omega)$. In the static limit, we find that for $\rho>0$, $S_s(q,0)$ is in proportion to the inverse of the static diffusion constant

$$S_s(q,0)=\frac{1+\beta(\mathbf{q})}{\pi c(\mathbf{q})}\frac{a^2}{D(0)}, \quad (17)$$

where a is the lattice constant of the underlying lattice which is the scale of the length of the model. Here $c(\mathbf{q})$ is given by

$$c(\mathbf{q})=z-\gamma(\mathbf{q}), \quad (18)$$

with

$$\gamma(\mathbf{q}) = \sum_{\mathbf{s}\in nn \text{ of } \mathbf{s}'} \exp[i\mathbf{q}(\mathbf{s}-\mathbf{s}')]. \tag{19}$$

Table I summarizes the low-frequency expansion of $S_s(\mathbf{q},\omega)$. At $\omega = 0$ $S_s(\mathbf{q},\omega)$ becomes a cusp for $1 > \rho > 0$ and divergent when $0 > \rho > -1$. Note $\rho = 0$ is the glass-transition point for this model. Namely, in the glass state one expects to see $1/f$-noise-type behavior and above T_g one expects to see a new type of singularity of $S_s(\mathbf{q},\omega)$. At the glass transition point, a logarithmic divergence of $S_s(\mathbf{q},\omega)$ at $\omega = 0$ is expected.

B. High-frequency behavior

The high-frequency expansion of $S_s(\mathbf{q},\omega)$ can be obtained exactly since the coherent medium can be determined exactly in the limit $u \to \infty$ [39]. We find after simple manipulation

$$S_s(\mathbf{q},\omega) \sim \frac{1}{\pi}\left[b(\mathbf{q})w_b + c(\mathbf{q})\frac{\rho+1}{\rho+2}w_0\right]\omega^{-2}, \tag{20}$$

where

$$b(\mathbf{q}) = z' - \beta(\mathbf{q}). \tag{21}$$

Therefore, $S_s(\mathbf{q},\omega)$ in the high-frequency limit decays in the same form as a Lorentzian with width $b(\mathbf{q})w_b + c(\mathbf{q})\frac{\rho+1}{\rho+2}w_0$.

TABLE I. The low-frequency expansion of $S_s(\mathbf{q},\omega)$. $S_s(q,0) = (1/\pi)[1+\beta(\mathbf{q})](\rho+1)/c(\mathbf{q})\rho w_0$ for $\rho > 0$ and $S_s(\mathbf{q},0) = \infty$ for $\rho \le 0$. $S(x) = \sin(\pi x)/\pi x$ and $\mu_1 = 1.516\,28\ldots$ is the Watson integral of the simple cubic lattice. For $\rho = 3/2$, a term in proportion to $\omega^{3/2}$ appears whose coefficient is the sum of those in the second and third rows with $\rho = 3/2$.

ρ	$[S_s(\mathbf{q},\omega) - S_s(\mathbf{q},0)]/S_s(\mathbf{q},0)$
$\rho > 3/2$	$-\frac{3\sqrt{3}}{2\rho(\rho-1)}\sqrt{\frac{\rho+1}{\rho}}\left(\frac{1+z'}{zw_0}\right)^{3/2}\omega^{3/2}$
$3/2 > \rho > 1$	$-\frac{\rho\sin\{\frac{\pi}{2}(\rho-1)\}}{(\rho-1)S(\rho-1)}\left[\frac{\mu_1(1+z')}{zw_0}\right]^{\rho}\omega^{\rho}$
$1 \ge \rho > 0$	$-\frac{\cos(\frac{\pi}{2}\rho)}{S(\rho)}\left[\frac{\mu_1(1+z')}{zw_0}\right]^{\rho}\omega^{\rho}$
	$S_s(\mathbf{q},\omega)w_0$
$\rho = 0$	$-\frac{1+\beta(\mathbf{q})}{\pi c(\mathbf{q})}\ln\left[\frac{\mu_1(1+z')}{zw_0}\omega\right]$
$0 > \rho > -1$	$\frac{[1+\beta(\mathbf{q})]\cos(\frac{\pi}{2}\rho)}{\pi c(\mathbf{q})S(1+\rho)}\left[\frac{\mu_1(1+z')}{zw_0}\right]^{\rho}\omega^{\rho}$

C. α and β relaxation

In order to obtain the frequency dependence of $S_s(\mathbf{q},\omega)$ in the entire frequency domain we solved numerically the self-consistent nonlinear equations (7) and (12). Figures 2(a) and (b) show the frequency dependence of $S_s(\mathbf{q},\omega)$ and $\mathrm{Im}\chi_s(\mathbf{q},\omega)$ respectively. To see if $S_s(\mathbf{q},\omega)$ shows a power-law decay, we plot the logarithmic derivative of $S_s(\mathbf{q},\omega)$

$$\sigma = -\frac{\partial \log_{10} S_s(\mathbf{q},\omega)}{\partial \log_{10}\omega}, \tag{22}$$

against $\log_{10}\omega$ in Fig. 3. When σ is a constant in a certain frequency region, $S_s(\mathbf{q},\omega)$ behaves as $S_s(\mathbf{q},\omega) \sim \omega^{-\sigma}$ there. Note $\sigma = 0$ for low frequencies and $\sigma = 2$ for high frequencies for the Debye relaxation. From Fig. 3, we observe that for $1 > \rho > 0$, there is a frequency region where σ is nearly a constant ~ 1.8. In the glass state, the region becomes obscure and we cannot determine the constant accurately. In addition σ takes a minimum at the high-frequency side which corresponds to the crossover between the two dynamics we are considering. This crossover is therefore seen as a slow dynamics corresponding to β relaxation. When $\rho < 0$, i.e., in the glass region, σ at low frequencies takes a finite constant, which behaves similar to α relaxation. We call it the α'

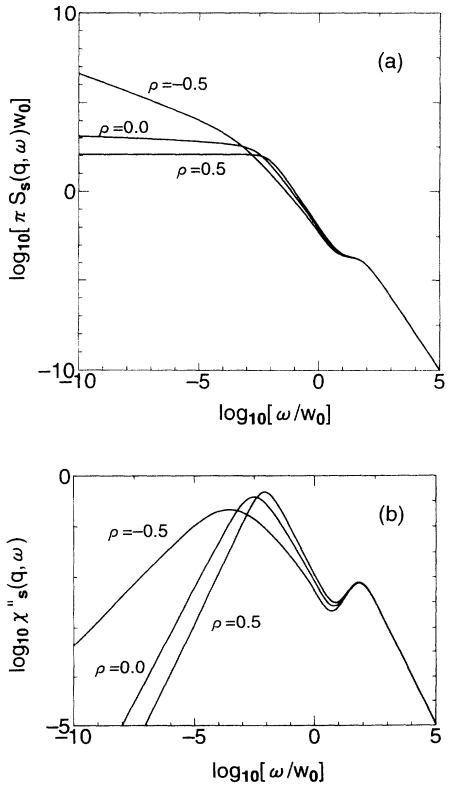

FIG. 2. The frequency dependence of (a) $S_s(\mathbf{q},\omega)$ and (b) $\chi_s''(\mathbf{q},\omega)$ for $\rho = 0.5$, 0, and -0.5. $\mathbf{q} = (1/a)(0.2, 0.2, 0.2)$, $z' = 6$, and $|\mathbf{u}_s| = 0.3a$ are assumed, a being the lattice constant of the underlying simple cubic lattice. $\mathbf{u}_s$'s are put on the bond of the simple cubic lattice.

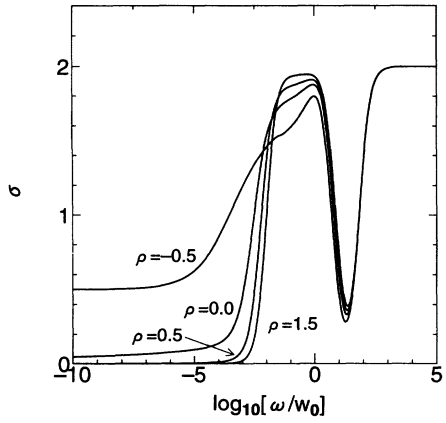

FIG. 3. The logarithmic derivative $\sigma \equiv -\partial \log_{10} S_s(\mathbf{q},\omega)/\partial \log_{10}\omega$ is plotted against $\log_{10}\omega$. For $\rho \geq 0$, σ is nearby constant for $10^{-2} \leq \omega/w_0 \leq 1$, indicating $S_s(\mathbf{q},\omega) \sim \omega^{-\sigma}$ in this region (the α relaxation). For $\rho < 0$, σ is again constant for much smaller frequencies, which corresponds to the α' relaxation. The deep dip around $\omega/w_0 \sim 10$ relates to the β relaxation.

dynamics, which will be observed in much longer time scale in the glass state.

From these figures we can make the following observations. First, when σ is a constant for larger frequencies, we will have the relaxation function of the form $\exp[-(t/\tau)^{\beta}]$ with $\beta \approx \sigma - 1$ in the corresponding time window. We show the dependence of the KWW exponent β on ρ in Fig. 4. The KWW relaxation is thus expected to occurs above T_g in a certain time window. In the α' dynamics, we have the KWW relaxation in the long time limit, whose stretching exponent β' for a small wave vector is also shown in Fig. 4 by the dashed line. These behaviors are consequences of the distribution Eq. (7): When $\rho < 0$, the mean waiting time is divergent and the system is in the anomalous diffusion regime, where the mean square displacement diverges with exponent less than unity, giving rise to vanishing diffusion constant. When $0 < \rho < 1$, the system is in the subanomalous regime where the second moment of the waiting-time distribution is divergent while the first moment exists, namely, the variance of the waiting-time distribution does not exist. The mean square displacement acquires a divergent term with exponent less than unity besides a t-linear term [38]. We thus conclude that α' dynamics is due to the anomalous diffusion, α dynamics is due to the subanomalous diffusion of the jump motion, and β dynamics is caused by the stray motion.

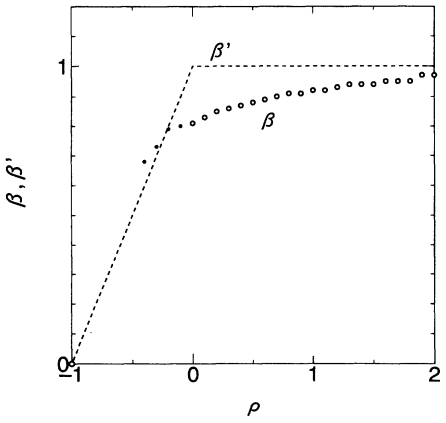

FIG. 4. The KWW stretching exponent β for the α relaxation is shown as a function of parameter ρ. Open circles show β determined from Fig. 3 by $\beta = \sigma - 1$. Solid circles indicate that the determination is less accurate. The dashed line is β', the stretching parameter for the α' relaxation for small $\mathbf{q}$.

D. Relaxation time for the α process

It is known that the relaxation time determined from the α peak of the generalized susceptibility is in proportion to the shear viscosity in normal liquids. Therefore it is tempting to see the dependence of the relaxation time of the α peak on ρ for the present model, although the present treatment provides only the single particle properties. We define the relaxation time τ_α by

$$\tau_\alpha = \frac{2\pi}{\omega_{\max}}, \tag{23}$$

where $\omega_{\max}$ is the frequency at which $\chi_s''(\mathbf{q},\omega)$ takes its maximum. We show by the solid circles in Fig. 5 the ρ dependence of τ_α obtained from Fig. 2(b). It is interesting to note that for $\rho \geq 1$, τ_α is in proportion to the inverse of the diffusion constant $D = \rho/(\rho+1)$ in good approximation. In fact, the dashed curve in Fig. 5 showing $374(\rho+1)/\rho$ is an excellent fit of τ_α for $\rho \geq 1$. The observed relaxation time deviates from this behavior when $\rho \leq 1$. We can numerically fit the entire dependence of τ_α on ρ by

$$\tau_\alpha^{\text{fit}} = 99 \exp\left[1.15\left(\frac{\rho+2}{\rho+1}\right)^{1.4}\right], \tag{24}$$

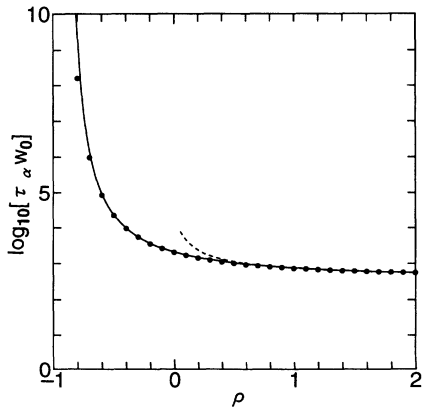

FIG. 5. The α-relaxation time τ_α is shown as a function of ρ. The solid circles are obtained from the trapping diffusion model. The solid curve is a fit to the data by Eq. (24) and the dashed curve is a fit for $\rho \geq 1$ by a curve in proportion to the inverse of the diffusion constant.

which is shown by the solid curve in Fig. 5. Equation (24) indicates that $\rho = -1$ appears as the Vogel-Fulcher point where τ_α diverges. It should be remarked that $(\rho+2)/(\rho+1)$ is the ensemble average of the jump rate itself $\langle w_s \rangle$ and the diffusion constant is given by $1/\langle w_s^{-1} \rangle = \rho/(\rho+1)$ and thus the Stokes-Einstein relation does not hold [40]. It is interesting to note that for $\rho \leq -1$ the jump rate distribution and hence the waiting-time distribution is not normalizable. Equation (24) is simply the numerical fit to the data and the analytical derivation of the form is currently under investigation.

IV. NON-GAUSSIAN PARAMETER

In order to get some quantitative comparison of the present theory with MD simulation, we study the decay of the non-Gaussian parameter $A(t)$ [41] defined by

$$A(t) = \frac{3\langle [\mathbf{r}(t) - \mathbf{r}(0)]^4 \rangle}{5\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle^2} - 1, \tag{25}$$

where $\mathbf{r}(t) = \mathbf{s}(t) + \mathbf{u}_s$. When $\langle \mathbf{s}^2 \rangle \ll \langle \mathbf{u}_s^2 \rangle$, we can show that

$$A(t) \sim \frac{3}{5} b^4 \frac{\rho+1}{\rho+2} z\omega_0 t, \tag{26}$$

where b is the ratio of jump distances due to the jump motion and the stray motion. On the other hand, when $\langle \mathbf{s}^2 \rangle \gg \langle \mathbf{u}_s^2 \rangle$, we find that for $0 < \rho < 1$

$$A(t) \sim \frac{\pi\rho}{\sin(\pi\rho)} \frac{2\rho}{G(3-\rho)} \left(\frac{m_1}{z\omega_0} \right)^\rho t^{-\rho} \tag{27}$$

and for $\rho > 1$

$$A(t) \sim \frac{\rho+1}{\rho} \left[\frac{1}{10} + \frac{2m_1}{z(\rho^2-1)} \right] \frac{1}{\omega_0 t}. \tag{28}$$

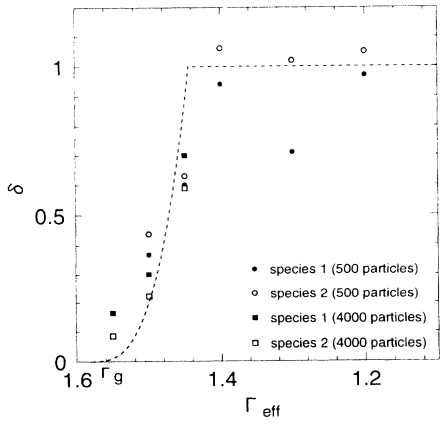

FIG. 6. The dependence of exponent δ representing the long-time decay of the non-Gaussian parameter on the thermodynamic parameter of the binary soft-sphere system. Various symbols show the result obtained from MD simulation and the dashed curve is the behavior predicted by the trapping diffusion model.

$G(x)$ is the Γ function. Therefore, $A(t)$ has a maximum as a function of t, which has been utilized to determine the glass-transition point [28]. We define an exponent δ such that $A(t) \sim t^{-\delta}$ as $t \to \infty$. Using the relation between ρ and Γ in Eq. (8), we expect to see a Γ dependence of the exponent δ for the soft-sphere system as shown by the dashed curve in Fig. 6. This dependence can directly be compared to MD simulation [42], which is shown by various symbols. The quantitative agreement is seen to be excellent. In paticular, the present model predicts a transition around $\Gamma_{\text{eff}} = 1.45$ where δ deviates from unity. This can be identified as the kinetic transition observed in various physical properties of the supercooled soft-sphere liquids [15–17].

V. DISCUSSION

We have presented a detailed discussion of the dynamical properties concerning the dynamical structure factor for the trapping diffusion model and showed the strong evidence which indicates that α relaxation observed in a certain time window is due to the jump motion and β relaxation is due to the stray motion. We also showed that the relaxation time for the α process diverges at $\rho = -1$, not at $\rho = 0$, where the diffusion constant vanishes, and that a superslow relaxation is expected in the glass state. The present trapping diffusion model focuses on localized atoms rather than the collective mode which is utilized in the mode-coupling theory. According to the mode-coupling theory, the system undergoes structural arrest at a certain temperature above the glass-transition point. Therefore the description based on localized atoms will become more appropriate as the temperature is reduced toward the glass-transition point. In the mode-coupling theory, the jump motion is considered to play only minor role which makes the ergodic-nonergodic transition smeared. In the trapping diffusion model, the jump motion plays the essential role. Furthermore, in the mode-coupling theory one particular modes with a special wave vector is focused upon. Therefore the description of atomic dynamics based on the localized picture is essentially different since many different modes are needed to describe the localized atom. The trapping diffusion model is a phenomenological description of the organized motion which gives rise to α (α') and β relaxations. We can thus draw a scenario of the glass transition as follows: As the temperature is reduced below the freezing point, collective dynamics ceases to dominate at some temperature and the system shows large spatial inhomogeneity due to the distribution of excess free energy. In a region where the excess free energy is accumulated, atoms perform a concerted diffusive motion localized in the region which we call the stray motion (so called cage effect: this is not the rattling motion in a fixed cage). This dynamics is considered to be β relaxation. Occasionally, atoms near the boundary of the region make a large deviation involving several atoms which cannot be undone due to the structural relaxation. This is observed as a jump motion which produces α and α' relaxations due to the spacial distribution of jump rates. The

trapping diffusion model thus provides an excellent phenomenological description of these dynamics and gives a unified view of the glass transition and the slow dynamics in supercooled liquids. It should be remarked that α relaxation is observed above the glass-transition point where the second moment of waiting-time distribution diverges and α' relaxation exists temperature below the glass transition where the first moment of waiting time distribution does not exist. Therefore the relaxation discussed in Ref. [35] corresponds to α' relaxation in our model. It is also interesting to note that the divergence of the first moment does not imply the existence of the divergence of the zeroth moment in general, and thus the stretched exponential relaxation is not necessarily coupled to Vogel-Fulcher behavior. We would also like to comment on so called strong glasses such as SiO_2. The present trapping diffusion model applies to simple liquids where rotational modes do not exist or do not play a significant role in structural relaxation. Therefore it can be applied to dipole relaxation or mechanical relaxation when they are determined by translational motion. However, it will not be applicable to dielectric relaxation due to rotational motion. In the highly supercooled state, the rotational motion in strong glasses can be stochastic and thus rotational relaxation in such cases may be analyzed in a similar manner to the present model, which will also be an interesting problem to be studied.

The parameters characterizing the model in the present study were chosen by comparing the waiting-time distribution with MD simulation. It is desirable to derive the distribution function of jump rates from a microscopic model, which will be studied in the future.

ACKNOWLEDGMENT

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Area from the Ministry of Education, Science and Culture.

[1] For example, *Slow Dynamics in Condensed Matter*, AIP Conf. Proc. No. 256, edited by K. Kawasaki, M. Tokuyama, and T. Kawakatsu (AIP, New York, 1992).
[2] F. Mezei, W. Knaak, and B. Farago, Phys. Rev. Lett. **58**, 571 (1987); F. Mezei, J. Non-Cryst. Sol. **131-133**, 317 (1991).
[3] W. Knaak, F. Mezei, and B. Farago, Europhys. Lett. **7**, 529 (1988).
[4] W. Götze, in *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen *et al.* (North-Holland, Amsterdam, 1991), p. 287.
[5] W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).
[6] W. Götze, in *Phase Transitions and Relaxation in Systems with Competing Energy Scales, NATO Advanced Study Institute, Series B: Physics*, edited by T. Riste (Kluwer Academic, Dordrecht, in press).
[7] N. J. Tao, G. Li, and H. Z. Cummins, Phys. Rev. Lett. **66**, 1334 (1991).
[8] G. Li, W. M. Du, X. K. Chen, H. Z. Cummins, and N. J. Tao, Phys. Rev. A **45**, 3867 (1992).
[9] F. S. Howell, R. A. Rose, P. B. Macedo, and C. T. Moynihan, J. Phys. Chem. **78**, 639 (1974); K. Funke, J. Hermeling, and J. Kümpers, Z. Naturforsch. **439**, 1094 (1988).
[10] H. Scher, M. F. Shlesinger, and J. T. Bendler, Phys. Today **44** (1), 26 (1991).
[11] W. Steffen, A. Patkowski, H. Gläser, G. Meier, and E. W. Fischer, J. Non-Cryst. Sol. (to be published).
[12] G. Li, W. M. Du, A. Sakai, and H. Z. Cummins, Phys. Rev. A **46**, 3343 (1992).
[13] D. L. Sidebottom, R. Bergmann, L. Börjesson, and L. M. Torell, Phys. Rev. Lett. **68**, 3587 (1992).
[14] W. van Megen and S. M. Underwood, Phys. Rev. E **47**, 248 (1993).
[15] H. Miyagawa, Y. Hiwatari, B. Bernu, and J. P. Hansen, J. Chem. Phys. **88**, 3879 (1988).
[16] G. F. Signorini, J. L. Barrat, and M. L. Klein, J. Chem. Phys. **92**, 1294 (1990).
[17] H. Miyagawa and H. Hiwatari, Phys. Rev. A **44**, 8278 (1991).
[18] G. Wahnström, Phys. Rev. A **44**, 3752 (1991).
[19] H. Miyagawa, Y. Hiwatari, and S. Itoh, Prog. Theor. Phys. Suppl. **103**, 47 (1991).
[20] E. Leutheusser, Phys. Rev. A **29**, 2765 (1984).
[21] U. Bengtzelius, W. Götze, and A. Sjölander, J. Phys. C **17**, 5915 (1984).
[22] S. Kambayashi and Y. Hiwatari, J. Phys. Soc. Jpn. **56**, 2788 (1987).
[23] X. C. Zeng, D. Kivelson, and G. Tarjus, Phys. Rev. E (to be published).
[24] W. Götze and L. Sjögren, Z. Phys. B **65**, 415 (1987).
[25] M. Fuchs, W. Götze, S. Hildebrand, and A. Latz, J. Phys.: Condens. Matter **4**, 7709 (1992).
[26] H. Z. Cummins, W. M. Du, M. Fuchs, W. Götze, S. Hildebrand, A. Latz, G. Li, and N. J. Tao, Phys. Rev. E **47**, 4223 (1993).
[27] T. Odagaki and Y. Hiwatari, Phys. Rev. A **41**, 929 (1990).
[28] T. Odagaki and Y. Hiwatari, Phys. Rev. A **43**, 1103 (1991).
[29] T. Odagaki and Y. Hiwatari, J. Phys.: Condens. Matter **3**, 5191 (1991).
[30] T. Odagaki, J. Phys. A **20**, 6455 (1987); A. A. Ovchinnikov and K. A. Pronin, J. Phys. C **18**, 5391 (1985); J. W. Haus and K. W. Kehr, Phys. Rev. B **36**, 5639 (1987).
[31] R. Kohlrausch, Pogg. Ann. Phys. **91**, 56 (1854); G. Williams and D. Watts, Trans. Faraday Soc. **66**, 80 (1970).
[32] F. Faupel, P. W. Hüppe, and K. Rätzke, Phys. Rev. Lett. **65**, 1219 (1990).
[33] T. Odagaki, J. Matsui and Y. Hiwatari, Mol. Simul. (to be published).
[34] K. L. Ngai, R. W. Rendell, and D. J. Plazek, J. Chem. Phys. **94**, 3018 (1991); see also G. Adam and J. H. Gibbs, *ibid.* **43**, 139 (1965).
[35] J. T. Bendler and M. F. Shlesinger, J. Phys. Chem. **96**, 3970 (1992).
[36] E. W. Fischer, Physica A (to be published).

[37] J. W. Haus and K. W. Kehr, Phys. Rep. **150**, 141 (1987).
[38] T. Odagaki, Phys. Rev. B **38**, 9044 (1988).
[39] M. Lax and T. Odagaki, in *Macroscopic Properties of Disordered Media*, edited by R. Burridge, S. Childress, and G. Papanicolaou (Springer, New York, 1982), p. 148.
[40] J. A. Hodgdon and F. H. Stillinger, Phys. Rev. E **48**, 207 (1993).
[41] A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. **126**, 986 (1962).
[42] J. Matsui, H. Miyagawa, T. Muranaka, K. Uehara, T. Odagaki, and Y. Hiwatari, Mol. Simul. (to be published).