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Stochastic model for the glass transition of simple classical liquids

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Dynamics of atoms near the glass transition of simple classical liquids is studied on the basis of the mesoscopic stochastic-trapping diffusion model recently developed by Odagaki [J. Phys. A **20**, 6455 (1987); Phys. Rev. B. **38**, 9044 (1988)]. The jump rate of an atom (tracer) is assumed to have a distribution following a power-law function with exponent ρ, where ρ is a phenomenological parameter. A sharp transition is predicted at $\rho=0$, that is, the self-diffusion vanishes when $\rho<0$ and takes a nonzero finite value when $\rho>0$. This transition is identified as the glass transition. With use of the coherent-medium approximation, the mean-square displacement is shown to exhibit a power-law dependence on time with exponent less than unity, and hence the incoherent scattering function for small wave vectors shows stretched exponential decay when $\rho<0$. The non-Gaussian parameter at time $t=\infty$ is shown to be nonzero in the glassy state ($\rho<0$) and vanishes in the fluid state ($\rho>0$), indicating that this quantity may be used as an order parameter of the glass transition. The mean-square displacement and the non-Gaussian parameter are obtained in the intermediate time scale as well from the frequency-dependent diffusion constant. The apparent diffusion constant determined by the derivative of the mean-square displacement at an imtermediate time shows a smooth transition instead of the sharp one, which coincides with observations in molecular dynamics studies. The incoherent scattering function in the intermediate time scale agrees qualitatively with experiments and the exponent of its stretched exponential decay deviates from unity before the glass transition takes place, in agreement with observations made via computer experiments.

I. INTRODUCTION

Recent experimental studies[1] and computer simulations[2-5] on glassy systems have revealed various characteristics of the dynamic properties near the glass transition: (i) The diffusion constant observed in molecular dynamics studies shows a sharp drop near the transition point, but it does not become as small as that extrapolated from the behavior at higher temperatures to the glass transition region. (ii) The density-density correlation function shows the William-Watts-type stretched-exponential decay. (iii) The time dependence of the mean-square displacement observed for an intermediate time window in molecular dynamics simulations shows a power law with an exponent less than unity. (iv) The so-called non-Gaussian parameter tends to slow down its decrement for a long time as the glass transition is approached.

Several theories have been proposed to understand these characteristic behaviors of the glass transition. The most frequently utilized analysis is based on the mode-coupling theory. In this approach, a feedback mechanism due to a nonlinear coupling between different modes is considered to be responsible for the glass transition. Various kinds of the coupling have been investigated.[6-8] The main conclusion drawn from these studies is that a structural arrest, i.e., a transition from ergodic to nonergodic behavior, takes place at a critical strength of the coupling. As a result, the diffusion constant vanishes in the glassy state, and hence the density-density correlation function stays nonzero in the glassy state in the long-time limit. Since this function decays (simple) exponentially in the fluid state, the value of the density-density correlation function at time $t=\infty$ is considered to be used as an order parameter of the glass transition. Krieger and Bosse[8] showed that when the density and charge-density fluctuations mutually couple, then the density-density correlation function exhibits a stretched-exponential dependence on time, which is in good agreement with experiments.[1] However, a sharp glass transition predicted in this theory is not seen in computer simulations for the soft-sphere or Lennard-Jones glasses.

The origin of the mode coupling has been studied on the basis of fluctuating nonlinear hydrodynamics.[9,10] Although a simple approximation[9] led to the mode coupling exploited by Leutheusser[7] and hence to the prediction of a sharp glass transition, a more detailed study revealed that nonlinear density fluctuations cut off the instability and no sharp transition is expected.[10] The diffusion constant predicted in the improved theory does not vanish at any density. The result seems to be consistent with the molecular dynamics calculations as mentioned above. However, the density-density correlation function is expected to show a simple exponential decay in time, which does not agree with observations. (The decay constant shows a sharp decrement near a critical point, though it does not vanish at any strength of the coupling constant.)

Prior to these theoretical approaches, Chudley and Elliott considered a jump diffusion model for the dynamics in liquids.[11] In their theory, jump motions as well as the rapid vibrational motion were taken into consideration. The jump motion was characterized by a single jump rate and a jump distance. The rapid vibrational motion gives rise to the Debye-Waller factor while the jump motion produces a simple exponential decay in time in the self-part of the density-density correlation function. No glass transition is expected in this model.

In this paper, we propose a stochastic model for the dynamics of a simple classical liquid near its glass transition point. We investigate how the characteristic properties (i)–(iv) mentioned above can be explained in a unified theory. The present model is based on the observation by Miyagawa *et al.*[4] that atoms in the glass transition region perform a jump motion induced by the surrounding atoms as well as vibrational motion around local potential minima and that the jump motion will determine the long-time behaviors of the system. We focus on the motion of a "tracer" atom and obtain the properties of the system through a statistical average of the properties of this tracer. We assume that the tracer atom performs stochastic motion governed by a random-walk equation, in which the jump rate is a random quantity reflecting the random environment. We further assume that the motion of the tracer is restricted on an underlying lattice. This assumption will be justified since near the glass transition point atoms are densly packed and their elementary motion responsible to the diffusion process will be restricted within nearest-neighbor distance even though the motion occurs stochastically. We also assume that the jump rate between two sites is determined only by the nature of the origin of the jump, and independent of the nature of the destination of the jump. This model is sometimes referred to as the trapping model which can be viewed as a mesoscopic or quasimicroscopic description of the dynamics of atoms. We introduce a power-law distribution for the jump rate w with a sharp cutoff at large w. The power is related to thermodynamic parameters of the system which drive the glass transition; for example, the coupling constant (the reduced density) in the soft-sphere glass. We study the self-diffusion constant, the mean-square displacement, the incoherent scattering function, and the non-Gaussian parameter. It is known that the diffusion constant of the trapping model is exactly given by the first inverse moment of the jump rate if it exists.[12] When this is the case, we can calculate without difficulty the mean-square displacement and hence the intermediate scattering function for small wave vectors. When the inverse moments of the random jump rates do not exist, we need a careful analysis. We employ the coherent medium approximation[13,14] to obtain the various physical quantities. As has generally been discussed,[15] behaviors of these quantities depend on the distribution, thus on the thermodynamic parameters. In our theory, no assumption will be made about the constituents of the system. Therefore the present model may be applied to any type of glass transitions. We feel, however, that atoms in the network glasses may obey dynamics more complicated than we study here and that it will be safe to apply the present results only to the glassy state of simple liquids.

It should be remarked here that when the atoms are initially distributed in equilibrium positions, the frequency dependence of the ac diffusion constant in the trapping model disappears and the mean-square displacement is always linear in time.[12] We note that the glass transition is not a true thermodynamic phase transition but a kind of a slow relaxation phenomenon. The relaxation time of the structure becomes as long as, or longer than, the order of observation time. Thus the system cannot reach equilibrium within observation time. Namely, the phase space accessible in a glassy state for a certain time period is restricted to a subspace which is separated from other subspaces by very narrow channels. Therefore it takes a very long time for a representative point in the phase space to travel through the entire space under restrictions imposed by conservation laws (for example, constant energy). Thus properties observed in this time period will be a statistical average within the subspace to which the system is placed initially and depend on the initial conditions. Thus we assume in this paper that the initial position of the tracer atom is completely random and that the properties of the system are determined by an ensemble average over different samples. We will see that results obtained on the basis of these assumptions agree with observations.

It should also be mentioned that there has been considerable confusion about the definition of the glass transition. Most experimental works on the glass transition discuss thermodynamic properties such as specific heat, enthalpy, and specific volume. In the mode coupling theory, the transition is supposed to occur between the ergodic and nonergodic regimes at the critical strength of a coupling constant. As stated above, we consider the glass transition a dynamical transition in which the diffusion constant becomes vanishingly small at a critical value of some parameters such as the density or the temperature. In fact, we will show that such a transition occurs in the stochastic model and study various dynamical properties near the glass transition point.

We organize this paper as follows. In Sec. II, we explain the stochastic model for the dynamics of atoms near the glass transition and give a brief summary of the coherent medium approximation. In Sec. III, we present results for the self-diffusion constant near the static limit and the mean-square displacement, the incoherent scattering function for small wave vectors, and the non-Gaussian parameter in the asymptotic region near time $t=\infty$. We discuss, in Sec. IV, behaviors of these quantities in an intermediate time scale which will directly be compared with results obtained by molecular dynamics studies. In the concluding section, Sec. V, we include a brief qualitative comparison of the present results with molecular dynamics calculations. More detailed analysis will be given elsewhere of the results of molecular dynamics studies for soft-sphere glasses along the present theory.

II. STOCHASTIC MODEL

Atomic motion near the glass transition can be observed microscopically by a molecular dynamics study. According to recent molecular dynamics studies on soft-sphere glasses,[4] atoms perform stochastic motion as the system approaches the glass transition: Most of the time, they stay around local potential minima, performing rather small vibrational motion. They make occasionally a concerted motion to change their positions. The latter motion is considered to be responsible for determining the long-time behaviors of atomic motion such as the diffusion constant. The concerted motion of atoms consists of simultaneous motion of several atoms and occurs randomly since it becomes possible only when the surrounding atoms induce such motion cooperatively.[4] Thus, if one focuses on the motion of a particular atom (tracer), it changes its position randomly, typically by the order of the interatomic distance in each jump, and moves around in the system as the time goes on. The jump rate of an atom depends on the location (i.e., the environment) of the atom and hence should be considered to be widely distributed in its magnitude. Therefore one can take the amorphous nature of the system into consideration by introducing distribution of the jump rates. The distribution of jump distance is considered, however, to be less important, for the actual displacement of the atom due to the concerted motion is more or less limited to the adjacent neighbor distance.[4] Consequently, in order to describe the stochastic motions of atoms, we take a lattice model (for convenience, a simple-cubic lattice is employed), in which the dynamics of the tracer atom is governed by the random-walk master equation

$$\frac{\partial P(\mathbf{s},t|\mathbf{s}_0,0)}{\partial t}=\sum_{\substack{\mathbf{s}'\\ \in \mathrm{NN of }\mathbf{s}}}[w_{\mathbf{s}'}P(\mathbf{s}',t|\mathbf{s}_0,0)-w_{\mathbf{s}}P(\mathbf{s},t|\mathbf{s}_0,0)] \ . \tag{1}$$

Here, $P(\mathbf{s},t|\mathbf{s}_0,0)$ is the conditional probability that the tracer is at site $\mathbf{s}$ at time t when it was at site $\mathbf{s}_0$ at time $t=0$, and the summation is taken over the nearest neighbors (NN) of site $\mathbf{s}$. We assume that the jump rate $w_{\mathbf{s}}$ from site $\mathbf{s}$ to its nearest neighbors does not depend on the nature of the destination of the jump and is distributed according to a power-law function

$$P(w_{\mathbf{s}})=\begin{cases}\dfrac{\rho+1}{w_0^{\rho+1}}w_{\mathbf{s}}^{\rho}, & 0\le w_{\mathbf{s}}\le w_0 \ ,\\ 0, & \text{otherwise} \ .\end{cases} \tag{2}$$

The exponent ρ represents the nature of the distribution: When $\rho>0$, larger jump rates appear with higher probability and when $\rho<0$, smaller jump rates appear with higher probability. $\rho=0$ corresponds to the critical value. The parameter ρ is expected to decrease as the density is increased or the temperature is reduced because smaller jump rates appear more often for smaller ρ. The explicit relation between the parameter ρ and thermodynamic parameters should be determined from a microscopic theory and will be a subject of future studies. In this paper, we treat ρ as a phenomenological parameter. As we will show later, $\rho>0$ ($\rho<0$) corresponds to the states before (after) the glass transition. The cutoff w_0 is considered to be[4] of the order of $10^{10}-10^{12}\ \mathrm{sec}^{-1}$.

We note that the nth inverse moment of $w_{\mathbf{s}}$ does not exist when $\rho\le n-1$. It is known that when the first inverse moment of $w_{\mathbf{s}}$ exists, the static self-diffusion constant $D(0)$ is given exactly by[12,13]

$$D(0)=a^2\left\langle\frac{1}{w_{\mathbf{s}}}\right\rangle^{-1} . \tag{3}$$

Here, a is the lattice constant which is of the order of the interatomic distance of the system and the angular brackets $\langle\ \rangle$ denote an ensemble average. When the first inverse moment does not exist, the static diffusion constant vanishes.

We calculate the time dependence of various physical quantities mentioned in the introduction from the frequency-dependent (ac) diffusion constant. The ac diffusion constant $D(u)$ is defined by the Laplace transform of the mean-square displacement $\tilde{R}_2(u)$

$$D(u)=\tfrac{1}{6}u^2\tilde{R}_2(u) \ , \tag{4}$$

where

$$\begin{aligned}\tilde{R}_2(u)&=\int_0^\infty\langle\langle[\mathbf{r}(t)-\mathbf{r}(0)]^2\rangle\rangle e^{-ut}dt\\ &\equiv\int_0^\infty R_2(t)e^{-ut}dt \ .\end{aligned} \tag{5}$$

Here, $\langle\langle\ \rangle\rangle$ denotes an ensemble average as well as an average over all atoms, and u is the "frequency." (To get the real frequency dependence, one has to set $u=i\omega$.) In the stochastic model, $R_2(t)$ is given by

$$R_2(t)=\sum_{\mathbf{s}}\sum_{\mathbf{s}_0}(\mathbf{s}-\mathbf{s}_0)^2\langle P(\mathbf{s},t|\mathbf{s}_0,0)f(\mathbf{s}_0)\rangle \ , \tag{6}$$

where $f(\mathbf{s}_0)$ is the distribution of the initial site $\mathbf{s}_0$. As we explained in the Introduction, we assume the uniform distribution for $f(\mathbf{s}_0)$ and we can drop the average over $f(\mathbf{s}_0)$ from Eq. (6) since the ensemble-averaged quantity does not depend on $\mathbf{s}_0$. It is apparent from Eq. (4) that we have

$$D(u)=\tfrac{1}{6}u^2\sum_{\mathbf{s}}(\mathbf{s}-\mathbf{s}_0)^2\langle\tilde{P}(\mathbf{s},u|\mathbf{s}_0)\rangle \ , \tag{7}$$

where $\tilde{P}(s,u|\mathbf{s}_0)$ is the Laplace transform of the conditional probability $P(\mathbf{s},t|\mathbf{s}_0,0)$

$$\tilde{P}(\mathbf{s},u|\mathbf{s}_0)=\int_0^\infty P(\mathbf{s},t|\mathbf{s}_0,0)e^{-ut}dt \ . \tag{8}$$

We obtain the ensemble average of $\tilde{P}(\mathbf{s},u|\mathbf{s}_0)$ by the coherent-medium approximation.[13,14] In this approach, $\langle\tilde{P}(\mathbf{s},u|\mathbf{s}_0)\rangle$ is approximated by the corresponding quantity of the coherent system in which every jump rate is a coherent one $w_c(u)$. The coherent jump rate $w_c(u)$ is determined by the condition[13]

$$\frac{1}{\Omega+w_c(u)}=\left\langle\frac{1}{\Omega+w_{\mathbf{s}}}\right\rangle , \tag{9}$$

where $\Omega=w_c(u)/(1-u\bar{P}_{00})-w_c(u)$ and

$$\bar{P}_{00}=\int\frac{n(x)}{u+zw_c(u)(1-x)}dx \ . \tag{10}$$

Here, z ($=6$) is the coordination number of the lattice and $n(x)$ is the density of states of the simple-cubic lattice

$$n(x)=\frac{1}{N}\sum_{\mathbf{k}}\delta(x-v(\mathbf{k}))=\frac{1}{2\pi}\int_{-\infty}^{\infty}[J_0(y)]^3e^{ixy}dy\ , \tag{11}$$

with

$$v(\mathbf{k})=\tfrac{1}{3}(\cos k_xa+\cos k_ya+\cos k_za)\ , \tag{12}$$

where N is the total number of the lattice sites and $J_0(y)$ is the zeroth-order Bessel function. It is straightforward to show that the ac diffusion constant is related to the coherent jump rate through

$$D(u)=a^2w_c(u)\ . \tag{13}$$

Another quantity of interest is the incoherent scattering function or the self-part of the density-density correlation function $F_s(\mathbf{k},t)$, which is defined by

$$F_s(\mathbf{k},t)=\langle\langle\exp\{i\mathbf{k}\cdot[\mathbf{r}(t)-\mathbf{r}(0)]\}\rangle\rangle\ . \tag{14}$$

In the stochastic model, $F_s(\mathbf{k},t)$ is reducible to

$$F_s(\mathbf{k},t)=\sum_{\mathbf{s}}\exp[i\mathbf{k}\cdot(\mathbf{s}-\mathbf{s}_0)]\langle P(\mathbf{s},t|\mathbf{s}_0,0)\rangle\ . \tag{15}$$

Replacing $\langle P(\mathbf{s},t|\mathbf{s}_0,0)\rangle$ in Eq. (15) by that of the coherent system, we find

$$F_s(\mathbf{k},t)=\frac{1}{2\pi i}\int_{0^+-i\infty}^{0^++i\infty}\frac{1}{u+zw_c(u)[1-v(\mathbf{k})]}e^{ut}du\ . \tag{16}$$

III. ASYMPTOTIC BEHAVIORS NEAR $t=\infty$

A. Self-diffusion constant

The dc diffusion constant is determined by the long-time behavior of the atomic motion and given by the first inverse moment of w_s in the trapping model as mentioned in Sec. II. Therefore we find for our distribution (2)

$$\frac{D(0)}{a^2w_0}=\begin{cases}\rho/(\rho+1), & \text{when } \rho\geq 0\ ,\\ 0, & \text{when } -1<\rho\leq 0\ .\end{cases} \tag{17}$$

Note that this is the exact result.[13] The dc diffusion constant is plotted against ρ by the solid curve in Fig. 1. The diffusion constant shows a sharp transition at $\rho=0$ which may be identified as the glass transition. The critical exponent μ defined by $D(0)\sim\rho^{\mu}$ $(\rho\sim 0^+)$ is unity. We also summarize the behavior of the ac diffusion constant near the static limit $u\sim 0$ in Table I, which is obtained by careful analysis of Eqs. (9) and (10). (For details, see Ref. 15.)

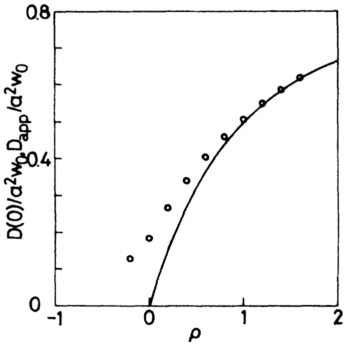

FIG. 1. Self-diffusion constant as a function of the parameter ρ. The solid curve is the exact result for the static diffusion constant. The critical exponent $\mu[D(0)\sim\rho^{\mu}]$ at $\rho=0$ is unity. The open circles are the apparent diffusion constant D_{app} determined by the derivative of the mean-square displacement at $w_0t=20$.

TABLE I. The ac parts of the frequency-dependent diffusion constant. The leading terms near $u=0$ are shown. $D(0)/a^2w_0=\rho/(\rho+1)$ when $\rho\geq 0$ and $D(0)=0$ when $\rho\leq 0$. $S(x)=\sin(\pi x)/\pi x$ and $\bar{u}=m_1u/zw_0$, $m_1=1.516\,28\ldots$ is the Watson integral of the simple-cubic lattice.

ρ	$[D(u)-D(0)]/a^2w_0$
$-1<\rho<0$	$S(\rho+1)(\bar{u}^{-\rho}-\bar{u}^{-2\rho})$ $+[27S(\rho+1)/2m_1^3]^{1/2}\bar{u}^{(1-\rho)/2}$
$\rho=0$	$-1/\ln(\bar{u})$
$0<\rho<1$	$[\rho/(\rho+1)S(\rho)]\bar{u}^{\rho}$
$\rho=1$	$-\frac{1}{2}\bar{u}\ln\bar{u}$
$1<\rho$	$\bar{u}/(\rho^2-1)$

B. Mean-square displacement

The asymptotic properties of the mean-square displacement can be analyzed from the behavior of the ac diffusion constant $D(u)$ near $u=0$ via the inverse Laplace transformation

$$R_2(t)=\frac{1}{2\pi i}\int_{0^+-i\infty}^{0^++i\infty}\frac{6D(u)}{u^2}e^{ut}du\ . \tag{18}$$

TABLE II. Mean-square displacement in the asymptotic region. The leading terms near $t=\infty$ are shown. $S(x)=\sin(\pi x)/\pi x$, $\tilde{t}=w_0t$, $m_1=1.516\,28\ldots$ is the Watson integral of the simple-cubic lattice and $\bar{\gamma}=0.577\,21\ldots$ is the Euler constant.

ρ	$R_2(t)/6a^2$
$-1<\rho<0$	$S(\rho+1)\left[\frac{(z/m_1)^{\rho}}{\Gamma(2+\rho)}\tilde{t}^{1+\rho}-\frac{(z/m_1)^{2\rho}}{\Gamma(2+2\rho)}\tilde{t}^{1+2\rho}\right]$ $+\frac{[27S(\rho+1)/2m_1^3]^{1/2}(z/m_1)^{(\rho-1)/2}}{\Gamma[(3+\rho)/2]}\tilde{t}^{(1+\rho)/2}$
$\rho=0$	$-\frac{\tilde{t}}{\ln(m_1/z\tilde{t})}\left[1-\frac{1-\bar{\gamma}}{\ln(m_1/z\tilde{t})}\right]$
$0<\rho<1$	$\frac{\rho}{\rho+1}\left[\tilde{t}+\frac{(m_1/z)^{\rho}}{S(\rho)\Gamma(2-\rho)}\tilde{t}^{1-\rho}\right]$
$\rho=1$	$\frac{1}{2}\{\tilde{t}+(m_1/z)[\ln(z\tilde{t}/m_1)+\bar{\gamma}]\}$
$1<\rho$	$[\rho/(\rho+1)]\tilde{t}+[1/(\rho^2-1)](m_1/z)$

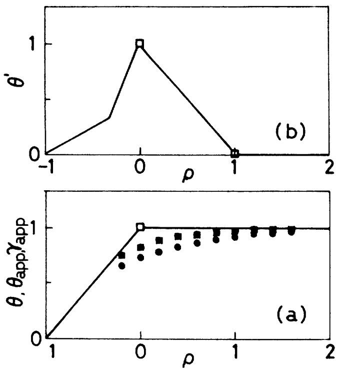

FIG. 2. (a) The exponent θ of the mean-square displacement and (b) the exponent θ' of its correction term. The solid lines are determined from the asymptotic behavior of the mean-square displacement and correspond to an idealistic observation. The open circles (almost overlapped with crosses) in (a) are the apparent exponent θ_{app} determined at $w_0 t = 20$. The squares denote existence of logarithmic corrections. Crosses ($|\mathbf{k}|a = 0.1$) and closed circles ($|\mathbf{k}|a = 0.5$) in (a) are the William-Watts exponent γ_{app} determined from the incoherent scattering function at $w_0 t = 20$. For small $|\mathbf{k}|$'s, the William-Watts exponent (γ_{app}, the crosses) and the exponent of the mean-square displacement (θ_{app}, open circles) are virtually identical.

The leading terms of $R_2(t)$ in the asymptotic region $t \sim \infty$ are listed in Table II. We define an exponent θ by $R_2(t) \sim t^{\theta}$ $(t \sim \infty)$ when the mean-square displacement obeys a power law. The exponent θ is found to be

$$\theta = \begin{cases} \rho + 1, & -1 < \rho < 0 \\ 1, & 0 < \rho \,. \end{cases} \tag{19}$$

The logarithmic dependence $R_2(t) \sim t / \ln t$ is expected when $\rho = 0$. The correction to the leading term in $R_2(t)$ can be written as $\sim t^{\theta'}$ for most ρ's: $\theta' = (\rho + 1)/2$ when $-1 < \rho \leq -\frac{1}{3}$, $\theta' = 2\rho + 1$ when $\frac{1}{3} \leq \rho < 0$, $\theta' = 1 - \rho$ when $0 < \rho < 1$, and $\theta' = 0$ when $\rho > 1$. When $\rho = 0$ and 1, the correction to the leading term in $R_2(t)$ is in proportion to $t / [\ln(m_1 / z\tilde{t})]^2$ and $\ln(z\tilde{t}/m_1)$, respectively. Here, $\tilde{t} = w_0 t$ and m_1 is the Watson integral of the simple-cubic lattice. Figures 2(a) and 2(b) show the dependence of θ and θ' on the parameter ρ, respectively. Notice that when the static diffusion constant does not vanish ($\rho > 0$), the leading term is always in proportion to t. When $\rho \leq 0$, anomalous diffusion is observed, that is, the self-diffusion constant vanishes while the mean-square displacement diverges with an exponent less than unity as the time approaches the infinity. When $0 < \rho \leq 1$, subanomalous diffusion is seen,[15] namely, the first correction to the leading term of the asymptotic expansion of $R_2(t)$ is nonanalytic.

C. Incoherent scattering function

Determination of the asymptotic behavior of $F_s(\mathbf{k},t)$ requires the knowledge of all of the singularities of $\langle \tilde{P}(\mathbf{s},u|\mathbf{s}_0) \rangle$. In the present study, $\langle \tilde{P}(\mathbf{s},u|\mathbf{s}_0) \rangle$ can be obtained only through numerical calculation, and hence we are not able to determine the asymptotic behavior of $F_s(\mathbf{k},t)$ for general wave vectors. For small wave vectors, however, we can write the incoherent scattering function as[16]

$$F_s(\mathbf{k},t) = \exp[-\tfrac{1}{6}k^2 R_2(t) + \tfrac{1}{72}k^4 R_2(t)^2 A(t) + O(k^6)] \,, \tag{20}$$

where

$$A(t) = \frac{3}{5} \frac{\langle [\mathbf{r}(t) - \mathbf{r}(0)]^4 \rangle}{[R_2(t)]^2} - 1 \,. \tag{21}$$

Therefore, for small $|\mathbf{k}|$, $F_s(\mathbf{k},t)$ is mainly determined by the mean-square displacement. The incoherent scattering function is often written as[17]

$$F_s(\mathbf{k},t) = \exp[-(t/t_0)^{\gamma}] \tag{22}$$

when it is possible, where the exponent γ may be called as the William-Watts exponent. Apparently, the William-Watts exponent for small wave vectors is identical to the exponent θ defined in Sec. III B. Thus $F_s(\mathbf{k},t)$ is expected to be a stretched exponential function when $-1 < \rho < 0$ and a simple exponential function when $0 < \rho$. When $\rho = 0$, $F_s(\mathbf{k},t)$ carries a logarithmic correction in the exponent instead of a simple power-law function.

D. Non-Gaussian parameter

In the Gaussian approximation,[18] the incoherent scattering function is given by the first term of the exponent in Eq. (20). Thus $A(t)$ defined by Eq. (21) is referred to as the non-Gaussian parameter. In order to obtain the non-Gaussian parameter, we calculate the mean-quartic displacement $R_4(t) \equiv \langle [\mathbf{r}(t) - \mathbf{r}(0)]^4 \rangle$ in the coherent-medium approximation. It is easy to show that the Laplace transform of the mean-quartic displacement in the coherent system is given by

$$\begin{aligned} \tilde{R}_4(u) &\equiv \int_0^{\infty} R_4(t) e^{-ut} du \\ &= 6a^4 \left[\frac{w_c(u)}{u^2} + \frac{20 w_c(u)^2}{u^3} \right] . \end{aligned} \tag{23}$$

We obtain $R_4(t)$ through the inverse Laplace transformation of this relation using $w_c(u)$ determined by the

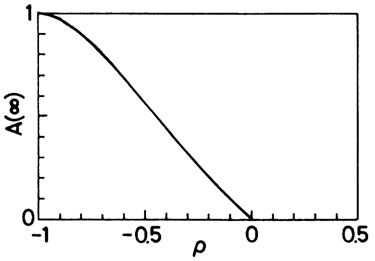

FIG. 3. The $t = \infty$ limit $A(\infty)$ of the non-Gaussian parameter as a function of the parameter ρ. The critical exponent $\beta[A(\infty) \sim (-\rho)^{\beta}]$ at $\rho = -0^{+}$ is unity.

TABLE III. Leading terms near $t=\infty$ in the non-Gaussian parameter $A(t)-A(\infty)$. $A(\infty)=0$ when $\rho\geq 0$ and $A(\infty)=2[\Gamma(2+\rho)]^2/\Gamma(3+2\rho)-1$ when $\rho\leq 0$. $\tilde{t}=w_0t$, $C=S(\rho+1)(z/m_1)^{\rho}$, $d_1=-S(\rho+1)(z/m_1)^{2\rho}$, $d_2=[27S(\rho+1)/2m_1^3]^{1/2}(z/m_1)^{(\rho-1)/2}$, $\alpha_1=2\rho$, $\alpha_2=(\rho-1)/2$, where $S(x)=\sin(\pi x)/\pi x$ and $m_1=1.516\,28\ldots$ is the Watson integral of the simple-cubic lattice. For $\rho<0$, the leading term is given by $i=1$ when $-\frac{1}{3}<\rho$ and by $i=2$ when $\rho<-\frac{1}{3}$. Both terms contribute when $\rho=-\frac{1}{3}$.

ρ	$A(t)-A(\infty)$
$-1<\rho<0$	$\displaystyle\sum_{i=1,2}\frac{4d_i[\Gamma(2+\rho)]^2}{C\Gamma(3+2\rho)}\times\left[\frac{\Gamma(3+2\rho)}{\Gamma(3+\alpha_i+\rho)}-\frac{\Gamma(2+\rho)}{\Gamma(2+\alpha_i)}\right]\tilde{t}^{\rho-\alpha_i}$
$\rho=0$	$\dfrac{1}{\ln(z\tilde{t}/m_1)}$
$0<\rho<1$	$\dfrac{2\rho}{(2-\rho)S(\rho)\Gamma(2-\rho)}\left[\dfrac{z\tilde{t}}{m_1}\right]^{-\rho}$
$\rho=1$	$\dfrac{2m_1\ln\tilde{t}}{z\tilde{t}}$
$1<\rho$	$\dfrac{1}{\rho}\left[\dfrac{2m_1}{z(\rho-1)}+\dfrac{\rho+1}{10}\right]\tilde{t}^{-1}$

coherent-medium approximation. Inserting the expressions of $R_2(t)$ and $R_4(t)$ into Eq. (21), we find the asymptotic behavior of the non-Gaussian parameter $A(t)$. At $t=\infty$, $A(t)$ is given by

$$A(\infty)=\begin{cases}\dfrac{2[\Gamma(2+\rho)]^2}{\Gamma(3+2\rho)}-1, & \text{when } -1<\rho\leq 0\\ 0, \text{ when } 0\leq\rho\ . & \end{cases} \tag{24}$$

Figure 3 shows the dependence of $A(\infty)$ on ρ. This quantity $A(\infty)$ vanishes when the self-diffusion constant is nonzero ($\rho>0$), and takes a finite nonzero value when the diffusion vanishes ($\rho<0$). Thus $A(\infty)$ can be regarded as an order parameter of the transition. The quantity $A(\infty)$ near $\rho\sim-0^+$ can be written as $A(\infty)\sim(-\rho)^{\beta}$ with $\beta=1$.

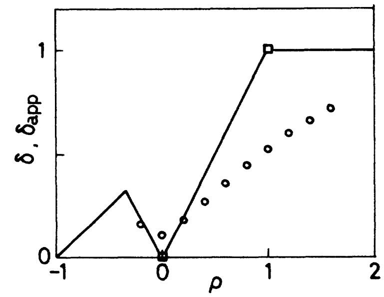

FIG. 4. The exponent δ of the non-Gaussian parameter as a function of the parameter ρ. The solid line is determined from the asymptotic behavior of the mean-square and quartic displacements and the open circles are the apparent exponent δ_{app} determined at $w_0t=20$. The squares represent existence of logarithmic corrections.

The leading term of $A(t)-A(\infty)$ near $t=\infty$ is listed in Table III. We define an exponent δ by $A(t)-A(\infty)\sim t^{-\delta}$ when the power law is obeyed. The dependence of δ on ρ is depicted by the solid line in Fig. 4. When $\rho=0$ and 1, logarithmic corrections appear.

IV. BEHAVIORS IN THE INTERMEDIATE TIME SCALE

As we stated in Sec. III, the mean-square displacement and the non-Gaussian parameter can be evaluated from the ac diffusion constant through the inverse Laplace transformation. We first obtain the ac diffusion constant by solving numerically the set of equations (9) and (10). To simplify the numerical task, we approximate the density of states of the simple-cubic lattice by a semiellipse

$$n(x)=2(1-x^2)^{1/2}/\pi\ , \tag{25}$$

for which the function $\bar{P}_{00}$ is given by

$$\bar{P}_{00}=2[u+zw_c+\sqrt{u(u+2zw_c)}]^{-1}\ . \tag{26}$$

The density of state (25) has the correct singularity of a three-dimensional lattice at the upper band edge which determines the low-frequency or long-time behaviors. Using the numerical solution for the coherent jump rate $w_c(u)$, we performed the inverse Laplace transformation of $\tilde{R}_2(u)$, $\tilde{R}_4(u)$, and $\bar{P}_{00}$ numerically[19] to obtain the mean-square displacement, the mean-quartic displacement, and the incoherent scattering function. The time dependence of these quantities in the intermdiate time scale can directly be compared with computer simulations.

A. Mean-square displacement and apparent diffusion constant

Figure 5 shows the mean-square displacement in the intermediate time scale for $\rho=-0.2$ to 1.6. Correspond-

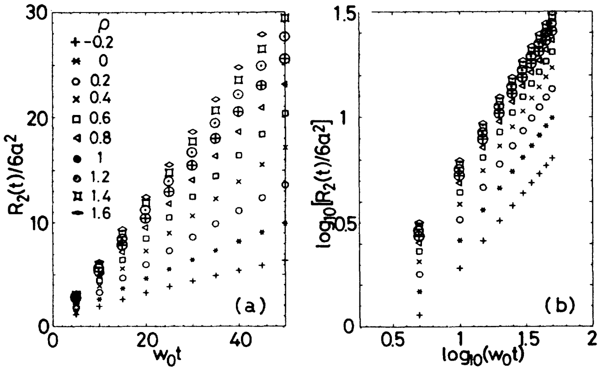

FIG. 5. Mean-square displacement in the intermediate time window; (a) a regular plot and (b) a log-log plot. Different symbols represent data for different ρ's between -0.2 and 1.6 for every 0.2, the lowest one corresponding to $\rho=-0.2$ and the highest one to $\rho=1.6$.

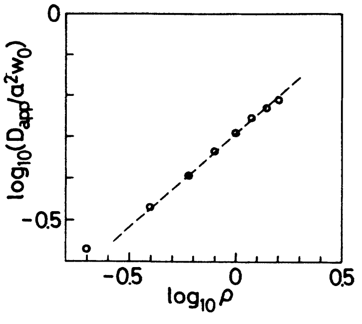

FIG. 6. The apparent diffusion constant $D_{\rm app}$ determined at $w_0t=20$ for $\rho>0$ is plotted against ρ in a log-log scale. In a certain range of ρ, $D_{\rm app}$ is appeared to be in proportion to $\rho^{\mu_{\rm app}}$ as shown by the dashed line. The apparent exponent $\mu_{\rm app}$ is read as 0.45.

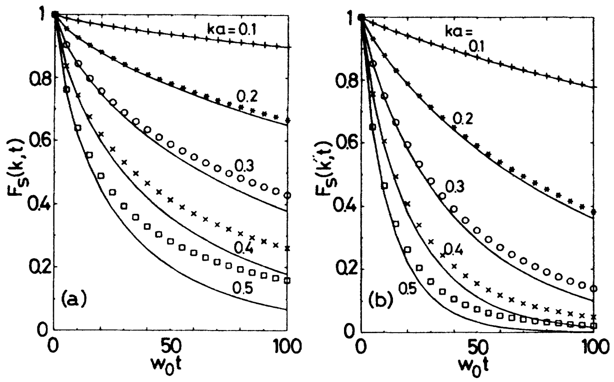

FIG. 8. The incoherent scattering function is shown as a function of time for various values of $|\mathbf{k}|a$ and fixed ρ; (a) $\rho=-0.2$ and (b) $\rho=0.2$. The solid lines are the contribution of the Gaussian term to $F_s(\mathbf{k},t)$.

ing to the exponent θ defined in Sec. III B, we define an apparent exponent $\theta_{\rm app}$ by

$$\theta_{\rm app}=\frac{d\log_{10}R_2(t)}{d\log_{10}t}\ . \tag{27}$$

The open circles in Fig. 2(a) show the apparent exponent $\theta_{\rm app}$ determined at $w_0t=20$ as a function of ρ. When the parameter ρ is decreased from above, the apparent exponent $\theta_{\rm app}$ becomes smaller than unity before the transition takes place at $\rho=0$. Namely, in the intermediate time scale, the mean-square displacement appears to be different from the Einstein limit $R_2(t)\sim t$ even though the dc diffusion exists. This tendency is enhanced when the observation is made at a shorter time and when the glass transition point is approached.

We also define the apparent (or differential) diffusion constant by

$$D_{\rm app}=\frac{1}{6}\frac{dR_2(t)}{dt}\ . \tag{28}$$

The apparent diffusion constant evaluated at $w_0t=20$ is shown by the open circles in Fig. 1. Apparently, the sharp transition is smeared out and we do not observe clear transition in the apparent diffusion constant. When the apparent diffusion constant is evaluated at a longer time, the transition becomes sharper. The apparent diffusion constant for $\rho<0$ vanishes only when the observation is made at $t=\infty$.

An apparent critical exponent $\mu_{\rm app}$ can be estimated by plotting $\log_{10}D_{\rm app}$ against $\log_{10}\rho$ for $\rho>0$ (see Fig. 6). We observe that for some range of ρ, $D_{\rm app}$ behaves as $D_{\rm app}\sim\rho^{\mu_{\rm app}}$ and $\mu_{\rm app}\simeq 0.45$.

B. Non-Gaussian parameter

From the mean-square and quartic displacements, we calculated the non-Gaussian parameter $A(t)$ which is shown in Fig. 7 for $\rho=-0.2$ to 1.6. We also determine an apparent exponent $\delta_{\rm app}$ from the logarithmic derivative of $A(t)$ with respect to $\log_{10}t$. The open circles in Fig. 4 show the apparent exponent $\delta_{\rm app}$. We see that the dependence of the exponent $\delta_{\rm app}$ on ρ is smoother than that of exponent δ determined in the asymptotic region.

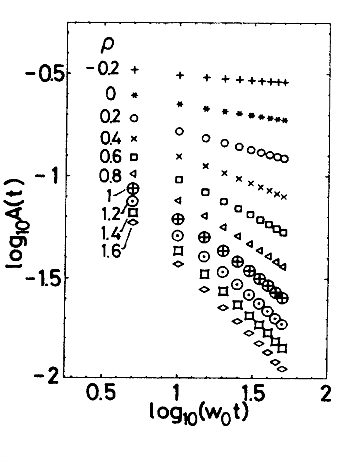

FIG. 7. The non-Gaussian parameter in the intermediate time window. Different symbols represent data for ρ between -0.2 and 1.6 for every 0.2. (The same symbols as in Fig. 5 are used.)

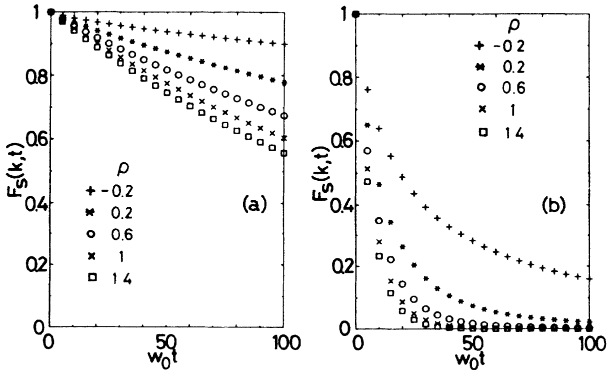

FIG. 9. The incoherent scattering function is shown as a function of time for various values of ρ and fixed $|\mathbf{k}|a$; (a) $|\mathbf{k}|a=0.1$ and (b) $|\mathbf{k}|a=0.5$.

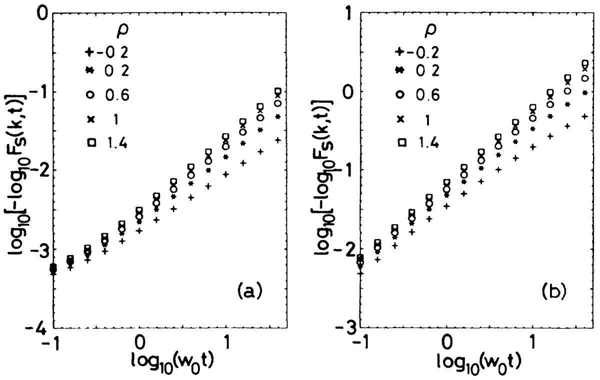

FIG. 10. The incoherent scattering function is plotted as $\log_{10}[-\log_{10}F_s(\mathbf{k},t)]$ vs $\log_{10}(w_0t)$ for various values of ρ and fixed $|\mathbf{k}|a$; (a) $|\mathbf{k}|a=0.1$ and (b) $|\mathbf{k}|a=0.5$. The apparent William-Watts exponent γ_{app} is given by the slope.

C. Incoherent scattering function

The incoherent scattering function was obtained from Eq. (16). Figure 8 shows the time-dependent behavior of $F_s(\mathbf{k},t)$ for (a) $\rho=-0.2$ and (b) $\rho=0.2$ at various wave numbers and Fig. 9 shows $F_s(\mathbf{k},t)$ for (a) $|\mathbf{k}|a=0.1$ and (b) $|\mathbf{k}|a=0.5$ at various ρ's. Solid lines in Fig. 8(a) represent the Gaussian approximation $F_s(\mathbf{k},t)=\exp[-k^2R_2(t)/6]$. The incoherent scattering functions are replotted in Fig. 10 as $\log_{10}[-\log_{10}F_s(\mathbf{k},t)]$ versus $\log_{10}(tw_0)$. We define an apparent William-Watts exponent γ_{app}, of the incoherent scattering function by

$$\gamma_{\text{app}}=\frac{d\log_{10}[-\log_{10}F_s(\mathbf{k},t)]}{d\log_{10}t}\ , \tag{29}$$

where the differential coefficient is evaluated at the observation time. The solid circles and crosses in Fig. 2(a) show the apparent William-Watts exponent determined at $w_0t=20$ for $|\mathbf{k}|a=0.1$ (crosses) and 0.5 (solid circles). We find that the dependence of γ_{app} on the parameter ρ is smoothed out and that the stretched-exponential dependence of the incoherent scattering function may be observed before the glass transition takes place at $\rho=0$. The difference between θ_{app} and γ_{app} is very small for smaller wave vectors.

Note that γ_{app} depends on the wave vector $|\mathbf{k}|$. The apparent William-Watts exponent γ_{app} is smaller for larger wave vectors. This may be the reason why the molecular dynamics calculations for the soft sphere model by Kambayashi and Hiwatari (Ref. 3) yielded the William-Watts exponent in the supercooled liquid near the glass transition point which appeared to be significantly smaller than those of Fig. 2(a).

V. CONCLUSION

We presented a stochastic model for the glass transition and obtained various dynamical properties near the glass transition. The model is not based on the usual dynamics of atoms in the microscopic scale nor on the dynamics of macroscopic variables like in the mode-coupling theory. Instead, it is constructed on the basis of the stochastic motion of atoms recently found in molecular dynamics simulations by Miyagawa *et al.*[4] Thus the present model can be viewed as a quasimicroscopic or a mesoscopic model. In the present model, the microscopic motion like vibration around the local potential minimum is not taken into consideration since it is irrelevant to the transport properties. Such motions contribute to the incoherent scattering function as a Debye-Waller factor in a much shorter time scale ($\ll w_0^{-1}$).[11] This explains the offset of $F_s(\mathbf{k},t)$ in the short-time behavior observed in experiments.[1]

Our model predicts that $F_s(\mathbf{k},t)$ vanishes at $t=\infty$ since the mean-square displacement diverges even in the glass region due to the anomalous diffusion. Therefore it cannot be used as an order parameter of the transition. This is a clear contrast to the prediction by the mode-coupling theory, where $F_s(\mathbf{k},\infty)$ is regarded as an order parameter of the transition. We proposed the non-Gaussian parameter at $t=\infty$ to be a candidate of an order parameter of the glass transition. We found the critical exponent β of the order parameter $A(\infty)$ is unity. The self-diffusion constant is also critical at the transition point and the critical exponent of the diffusion constant μ as a function of the parameter ρ is also unity.

We predicted anomalous and subanomalous diffusion will be observed near the glass transition point. In fact, the stretched exponential dependence of the incoherent scattering function is the sign of the anomalous diffusion. Mezei, Knaak, and Farago[1] proposed the time dependence of the density-density correlation function may be scaled by the static diffusion constant. In our model, the leading term of the Gaussian approximation for the self-part of the density-density correlation function shows this scaling property. However, this property does not hold for general wave numbers.

We also studied effects of the observation carried out in the intermediate time window on the nature of the glass transition. When dynamical quantities are estimated at an intermediate time, they show smeared-out dependence on the parameter ρ. Thus the apparent diffusion constant D_{app} does not show a sharp transition and the apparent critical exponent μ_{app} is reduced to 0.45 instead of unity as expected in the ideal observation. The apparent William-Watts exponent γ_{app} deviates from unity before the glass transition takes place. These behaviors of the dynamical properties coincide qualitatively with results observed by molecular dynamics studies.[3-5] Therefore the actual observation time affects significantly the apparent dynamical properties of the system near the glass transition point.

In this paper we employed the coherent-medium approximation to determine the time dependence of various physical quantities. As has already been shown,[15] the critical exponent θ of the mean-square displacement obtained in the present approximation agrees with the result calculated by a renormalization group method.[20] Furthermore, the result for the static diffusion constant and hence the critical exponent μ is rigorous.[12,13] When the first few inverse moments of the jump rate w_s exist, present results for the low-frequency ac diffusion constant agree with the exact result[21] apart from a minor numerical factor. We note from Fig. 10(b) that the incoherent scattering function $F_s(\mathbf{k},t)$ for large $|\mathbf{k}|a$ and small ρ does not appear to be linear in this plot and thus may not obey the William-Watts law. This may be due to the lattice model employed here. More refined work is necessary to get a conclusive result. We will report more quantitative comparison of the present theory with results obtained by molecular dynamics studies for soft-sphere glasses elsewhere.[22]

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