PHYSICAL REVIEW A VOLUME 29, NUMBER 5 MAY 1984

# Dynamical model of the liquid-glass transition

E. Leutheusser
*Physik-Department der Technischen Universität München, D-8046 Garching, Federal Republic of Germany*

(Received 5 December 1983)

Based on a microscopic theory developed recently, a dynamical model of density fluctuations in simple fluids and glasses is proposed and analyzed analytically and numerically. The model exhibits a liquid-glass transition, where the glassy phase is characterized by a zero-frequency pole of the longitudinal and transverse viscosities indicating the systems' stability against stress. This also implies an elastic peak in the density-fluctuation spectrum. Approaching the glass transition the slowing down of density fluctuations is controlled by the increasing longitudinal viscosity, which in turn is coupled via a nonlinear feedback mechanism to the slowly decaying density fluctuations. This causes a divergence of the structural relaxation time at a certain critical coupling constant $\lambda_c$. At the glass transition density fluctuations decay with a long-time power law $\Phi(t) \sim t^{-\alpha}$ with $\alpha = 0.395$ and approaching the transition the viscosity diverges proportional to $\epsilon^{-\mu}$ and $\epsilon^{-\mu'}$, where $\epsilon = |1-\lambda/\lambda_c|$ and $\mu = (1+\alpha)/2\alpha$, $\mu' = \mu - 1$ below and above the transition, respectively. The long-time tail "paradox" in dense fluids is briefly discussed.

## I. INTRODUCTION

When liquids are cooled down sufficiently the relaxation time for structural rearrangements increases drastically. If crystallization can be avoided by large cooling rates most supercooled liquids will enter a metastable glassy state.[1] The glass transition is characterized experimentally by relaxation times of the order of minutes or hours and associated large viscosities of typically $10^{13}$ poise. At this transition temperature $T_g$ one also observes a gradual drop in various thermodynamic quantities like compressibility, specific heat, and thermal expansion due to the freezing in of the translational degrees of freedom. In this so-called glass transformation range the various measured quantities also depend on the duration of the experiments. By reducing the time scale of the measurements, e.g., in ultrasound experiments,[2] one can observe a glasslike transition at temperatures well above $T_g$, namely, when the system's relaxation time is of the order of the inverse sound frequency. Thus the glass transition is not well defined experimentally. Theoretically, however, the ideal glass transition can be defined to occur at that temperature $T_0$ or corresponding density where the structural relaxation time becomes infinite assuming that on cooling the liquid remains in equilibrium and crystallization does not occur.

The glass transition can be studied by molecular-dynamic experiments for systems of particles interacting with various types of pair potentials; for reviews see Ref. 3. Although these simulations are limited by the small system size and the short time intervals, they can provide detailed information on the dynamical processes. Transport coefficients, thermodynamic quantities, time-dependent correlation functions, and dispersion relations in the amorphous state[4] were examined. Neutron scattering is also a valuable tool to investigate the dynamical structure factor of supercooled liquids and glasses and to obtain various kinds of information like dispersion relations and line widths.

Theoretically, to describe the behavior of the diffusion constant and thermodynamic quantities near the glass transition the phenomenological free volume theory was developed by Cohen and Turnbull,[5] where the decrease of the diffusion constant is attributed to the decreasing free volume available to a particle by the rearrangement of its neighborhood upon approaching the transition. Concepts of percolation theory were introduced later by Cohen and Grest.[6] In mean-field theories[7] it is argued that the narrowing of the quasielastic peak of the dynamical structure factor of a supercooled liquid observed in neutron scattering experiments[8] is due to a soft mode instability caused by the divergence of the static structure factor at the wave number corresponding to its main peak. These theories were critically discussed by Sjölander and Turski.[9] The authors argued that the narrowing may be caused by the decreasing diffusion constant. The important role of the increasing shear viscosity in the previtrification regime was also noted recently.[10]

An interesting question is what the dynamical behavior of a liquid would be if it could be cooled down so slowly that it always remains in equilibrium and if crystallization would not occur. It is this question that will be addressed in this work using a simple model which, however, is supposed to represent some essential features of the liquid-glass transition.

The microscopic theory[11,12] on which the model to be discussed here is based and the resulting picture of the liquid-glass transition shall be summarized briefly. The basic quantity of the theory is the dynamical structure factor describing the dynamical properties of density fluctuations. Their decay is controlled mainly by the longitudinal viscosity.[13] Among the various contributions to the dynamical transport coefficients the most important one at high density is that representing configurational relaxation or, in microscopic terms, dynamically correlated collisions. This part was expressed in terms of bilinear products of fluctuations of the slowly decaying conserved variables of the fluid. Among those the density fluctuations were found to yield the main contribution in a dense fluid. The relaxation time of density fluctuations is by this nonlinear feedback coupled and increased by the slow decay of density fluctuations itself. The theory was evaluated numerically at a density near the freezing point. The results[12] showed an enhancement of the longitudinal and shear viscosity compared to the known kinetic theory values in qualitative agreement with molecular-dynamic results.[14,15] Also in agreement with the molecular-dynamic experiments a slowly decaying component in the density correlation function and propagating shear waves in the transverse current correlation function were found at intermediate wave numbers. These phenomena can be interpreted as indications of the nearby transition to the solid state.

With increasing density the structural rearrangement becomes more difficult and at a certain density the particles will be arrested in their cages formed by neighboring particles. At this density the relaxation time diverges and bulk and shear viscosity are infinite, as signaled mathematically by a zero-frequency pole. This entails that the system becomes stable against shear stress which is the main characteristic of a solid body. In the glass phase the particles execute vibrational motion around their arrested positions. The configurational contributions to the various thermodynamic quantities such as the compressibility are frozen in. Transverse sound waves of arbitrary small wave number can propagate in the glass where the sound velocity is determined by the modulus of rigidity of the glass which is the residue of the zero-frequency pole of the shear viscosity.

The simplifications of the microscopic theory leading to the model presented below are based on the observation that the glass transition is neither accompanied by an essential change in the short-range order compared to a dense fluid nor by the divergence of the static structure factor. Therefore, the static correlations will be ignored in a first approximation in order to isolate and discuss the essential dynamical mechanism of the slowing down of density fluctuations in its purest form.

The paper is organized as follows. In Sec. II the basic equation of motion for the density fluctuations will be presented and motivated. In Sec. III it is shown that this equation exhibits a phase transition at a critical value of the coupling constant and perturbation theory in the weak- and strong-coupling regimes is discussed. The critical regime is investigated in Sec. IV and the nature of the phase transition, the divergence of the relaxation time, and the viscosity is examined. In Sec. V the dynamical shear viscosity is discussed and the results are summarized in Sec. VI.

## II. THE MODEL

Let us consider the following nonlinear equation of motion for a damped oscillator:

$$\ddot{\Phi}(t)+\gamma\dot{\Phi}(t)+\Omega_0^2\Phi(t)+4\lambda\Omega_0^2\int_0^t d\tau\,\Phi^2(\tau)\dot{\Phi}(t-\tau)=0 \qquad (1)$$

with the initial condition $\Phi(t=0)=1$, $\dot{\Phi}(t=0)=0$, where the dot denotes the time derivative. Here $\Omega_0$ is the frequency of the free oscillator and $\gamma$ is a damping constant. The nonlinear term has the form of a memory kernel depending on the past motion of the oscillator and its strength is controlled by the dimensionless coupling constant $\lambda$ which is assumed to vary between zero and infinity. The important question concerns the time evolution of the oscillator, in particular its long-time behavior depending on the coupling constant. Equation (1) is of interest also for mathematical reasons as an example of a nonlinear equation of motion with memory effects. Physically the oscillatory coordinate $\Phi(t)$ is thought to represent the density correlation function of a classical fluid at a certain wave number. This interpretation becomes clearer by introducing Laplace transforms

$$\Phi(z)=\mathscr{L}\{\Phi(t)\}=i\int_0^\infty dt\,e^{izt}\Phi(t),\quad \operatorname{Im}z>0 \qquad (2)$$

and rewriting (1) in the form

$$\Phi(z)=-\cfrac{1}{z-\cfrac{\Omega_0^2}{z+D(z)}}\ , \qquad (3a)$$

$$D(z)=i\gamma+4\lambda\Omega_0^2\mathscr{L}\{\Phi^2(t)\}\ . \qquad (3b)$$

Equation (3a) is the well-known representation of the density correlation function in terms of its second frequency moment $\Omega_0^2$ and the dynamical longitudinal viscosity $D(z)$ assuming that energy fluctuations can be ignored.[13] Energy density fluctuations are not included in our model since the microscopic theory[11] showed that bilinear products of density fluctuations do not contribute to the thermal conductivity. As one expects, this quantity is therefore not singular at the glass transition. Also, computer simulations[14] show no significant enhancement of the thermal conductivity near the freezing point.

The wave-number dependence of all quantities in Eqs. (3) is not indicated explicitly. For small frequency, assuming that the zero-frequency limit of $D(z)$ is finite,

$$\lim_{q,z\to 0} D(z)=iD\ , \qquad (4)$$

the spectrum $\Phi''(\omega)$ of $\Phi(\omega+i0)=\Phi'(\omega)+i\Phi''(\omega)$,

$$\Phi''(\omega)=\frac{\Omega_0^2 D}{(\omega^2-\Omega_0^2)^2+(\omega D)^2}\ , \qquad (5)$$

exhibits peaks at the frequencies $\omega=\pm(\Omega_0^2-D^2/2)^{1/2}$, if $\Omega_0^2>D^2/2$. This case is realized in fluids for sufficiently small wave numbers $q$, since $\Omega_0\cong cq$, and $D=q^2D_1$, where $c$ is the sound velocity and $D_1=(\zeta+\frac{4}{3}\eta)/\rho$ is the longitudinal viscosity, $\zeta$ and $\eta$ are bulk and shear viscosity, and $\rho$ is the mass density. Thus in this small-wave-number hydrodynamic regime the spectrum consists of two sharp sound peaks. The quasielastic heat diffusion peak present in real liquids is not included in our model for reasons discussed above and to make the model as simple as possible. One observes that for increasing $D_1$, i.e., approaching the glass transition, the above mentioned wave-number regime shrinks to zero. Instead, for $q>q_0$, where $q_0=\sqrt{2}c/D_1$, there appears a quasielastic peak in $\Phi''(\omega)$ with a wave-number-independent width

$1/\tau=\Omega_0^2/D=c^2/D_1$ decreasing for increasing $D_1$. Also, the wave-number-independent zero-frequency value $\Phi''(0)=D_1/c^2$ increases indefinitely. Approaching the glass transition the frequency range where $D(z)$ can be assumed to be constant is also expected to shrink. Thus the dynamical viscosity $D(z)$ is the fundamental quantity to be calculated.

In the microscopic theory[11] $D(z)$ was written as a sum of various contributions of different physical origin. One part results from the transport of momentum by dynamically uncorrelated collisions of particles as described by Enskog's equation. This part behaves regularly near the glass transition and is approximated in (3b) by the constant $i\gamma$, vanishing $\sim q^2$ for small wave number. The other part describing dynamically correlated processes was approximately evaluated in terms of bilinear products of correlation functions of conserved variables of the system. It was found[12] that the product of two density modes is the important contribution and this is expressed by the second term on the right-hand side (rhs) of (3b) in our model.

A further simplification in establishing the model equation (3b) was achieved by replacing the density correlation function in the wave-number integral of the microscopic theory[11] by that at a typical intermediate wave number assuming that the detailed wave-number dependence is not essential for the liquid-glass transition. The wave-number integral can then be included in the coupling constant $\lambda$, which is an increasing function of the density. An argument in favor of this approximation is that, as discussed above, the wave-number-independent quasielastic peak of $\Phi''(\omega)$ is the dominating feature of $\Phi$. Also one expects that the glass transition is not caused by a small wave-number infrared singularity, i.e., by long-range phenomena, but that it is rather a phenomenon where intermediate wave numbers are important. The approximation leading to (3b) is, however, not allowed in two dimensions because of hydrodynamic singularities.

Equations (3) or, equivalently, (1) is probably the simplest conceivable model for a glasslike transition. Although it is based on a microscopic theory for the dynamical correlation functions of a hard-core fluid, the model is valid and useful for fluids in general. In (3b) the dynamical longitudinal viscosity $D(z)$ is expressed by the bilinear product of the density correlation $\Phi(t)$, which in turn is controlled by $D(z)$ in (3a). The equations will be analyzed in subsequent sections. In the following, frequency and time will be measured in units of $\Omega_0$ or $\Omega_0^{-1}$, respectively, or equivalently $\Omega_0=1$ unless stated otherwise in order to simplify the notation.

## III. THE PHASE TRANSITION

For small coupling constant $\lambda$ a weak-coupling expansion of (3) is straightforward. In zeroth order in $\lambda$

$$D(z)=i\gamma \tag{6}$$

and the density correlation function $\Phi(z)$ has two simple poles in the lower complex half-plane:

$$\Phi(z)=-\cfrac{1}{z-\cfrac{1}{z+i\gamma}}=-\frac{a_1}{z+i\nu_1}-\frac{a_2}{z+i\nu_2}\,, \tag{7}$$

where $\nu_{1/2}=[\gamma\mp(\gamma^2-4)^{1/2}]/2$ and $a_{1/2}=[1\pm\gamma/(\gamma^2-4)^{1/2}]/2$. Inserting this in (3b) the longitudinal viscosity in first order is

$$D(z)=i\gamma-\cfrac{4\lambda}{z-\cfrac{2}{z+i\gamma-\cfrac{2}{z+2i\gamma}}}\,. \tag{8a}$$

The zero-frequency value is enhanced compared to zeroth order

$$D=\gamma+2\lambda(\gamma+1/\gamma)\,, \tag{8b}$$

which suggests that there may be a divergence characterized by an infinite $D(z)$ and $\Phi(z)$ for zero frequency.

To examine this possibility we try the following ansatz:

$$\Phi(z)=-f/z+(1-f)\Phi_v(z)\,, \tag{9}$$

where $\Phi(z)$ is written as a zero-frequency pole contribution with weight $f$ to be determined and a remainder $\Phi_v(z)$ with weight $(1-f)$, so that $\Phi_v(t=0)=1$. Then (3b) shows that $D(z)$ has a similar structure:

$$D(z)=-4\lambda f^2/z+D_v(z)\,, \tag{10a}$$

$$D_v(z)=i\gamma+8\lambda f(1-f)\Phi_v(z)+4\lambda(1-f)^2\mathscr{L}\{\Phi_v^2(t)\}\,. \tag{10b}$$

Inserting (10a) into (3) and comparing with the ansatz (9) the strength $f$ is given by

$$f=(1+\sqrt{1-1/\lambda})/2\,. \tag{11}$$

Also, the remaining part $\Phi_v(z)$ can be expressed by $D_v(z)$ in a simple way:

$$\Phi_v(z)=-\cfrac{1}{z-\cfrac{\Omega^2}{z+D_v(z)}}\,, \tag{12a}$$

where

$$\Omega^2=1+4\lambda f^2\,. \tag{12b}$$

Equation (11) shows that when the coupling constant is larger than the critical value $\lambda_c=1$ the ansatz (9) leads to an acceptable solution. This means that for $\lambda\geq 1$ density fluctuations do not decay to zero for long times as for $\lambda<1$ but they decay to the finite value $f$ which increases from $f=\frac{1}{2}$ at the transition to $f=1$ for $\lambda\rightarrow\infty$. This is shown in Fig. 1 where the density correlation function $\Phi(t)$ obtained by numerical solution of (1) is plotted for various coupling constants. Thus the spectrum of density fluctuations exhibits a $\delta(\omega)$ peak with strength $f$ which is characteristic for the glass phase. The nonzero infinite-time limit of $\Phi(t)$ is analogous to the Edwards-Anderson[16] order parameter in spin-glasses. In the glass phase the translational motion is frozen in. The vibrational motion around the arrested positions is described by $\Phi_v(z)$ where $\Omega$ in (12b) is the oscillator frequency, increas-

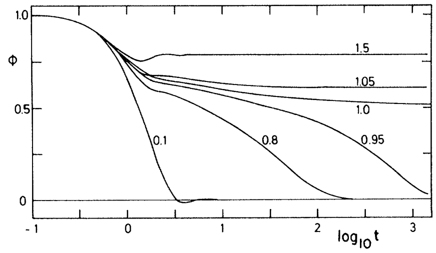

FIG. 1. Time dependence of the density correlation function $\Phi(t)$ for various coupling constants $\lambda$ indicated. Parameters are $\Omega_0=1$ and $\gamma=1$. Transition point is at $\lambda_c=1$.

ing from $\Omega=\sqrt{2}\Omega_0$ at $\lambda=1$ with increasing coupling constant. $D_v(z)$ will be called the longitudinal viscosity of the glass phase since it describes the damping of the vibrational motion. The residue of the zero-frequency pole in (10a) is related to the bulk and shear moduli of the glass phase, $B$ and $G$, respectively, by $(B+\frac{4}{3}G)/\rho=4\lambda\Omega_0^2 f^2/q^2$.

It is convenient for the following discussion to rewrite (10b) with the use of (12a) as

$$\frac{z[z+D_v(z)]D_v(z)+2z-D_v(z)(\Omega^2-2)}{z[z+D_v(z)]-\Omega^2}=\mathscr{C}(z)\ , \tag{13a}$$

where

$$\mathscr{C}(z)=i\gamma+4\lambda(1-f)^2\mathscr{L}\{\Phi_v^2(t)\}\ . \tag{13b}$$

In this way the theory in the glass phase is formulated entirely in terms of the vibrational component $\Phi_v(z)$ of $\Phi(z)$ alone. For a given $\Phi_v(t)$ the memory kernel $\mathscr{C}(z)$ is determined by (13b), which in turn determines $D_v(z)$ via (13a) and finally $\Phi_v(z)$ by (12a). The main advantage of this reformulation is that a perturbation expansion in the glass phase for $\lambda\rightarrow 1$ becomes obvious. For example, (13a) simplifies for $z\rightarrow 0$ to

$$D_v(z=0)=\mathscr{C}(z=0)/\sqrt{1-1/\lambda}\ . \tag{14}$$

Thus, if $\mathscr{C}(z=0)$ were regular for $\lambda\rightarrow 1$ the longitudinal viscosity would diverge with exponent $\frac{1}{2}$ approaching the transition. However, as will be discussed in Sec. IV, the feedback mechanism, expressed by the second term in (13b), leads to a somewhat stronger divergence. A similar reformulation of the theory allowing a perturbation expansion in the fluid phase $\lambda<1$ near the glass transition will be presented in Sec. IV.

The special value $\lambda_c=1$ as the glass transition point was of course achieved in this model by appropriate definition of the parameters in (1) or equivalently (3). In the microscopic theory, however, $\lambda_c$ is determined by a certain wave-number integral over static two- and three-particle correlations.

In the limit $\lambda\rightarrow\infty$ the weight $(1-f)$ of the vibrational spectrum which is proportional to the compressibility of the glass tends to zero according to (11) and (9), thus also the vibrations are frozen in. This limit can be interpreted as the random close-packing density of the glass. Perturbation theory can be performed also in this strong-coupling regime. According to (13b) one has in zeroth order in $1/\lambda$

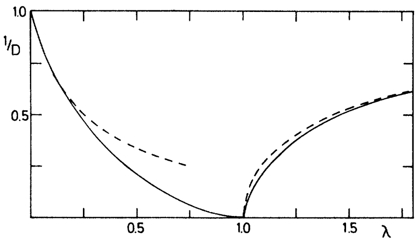

FIG. 2. Inverse longitudinal viscosity vs coupling constant $\lambda$ in the fluid and amorphous phase. Parameters are $\Omega_0=1$ and $\gamma=1$. Solid line represents the numerical solution of the model and the dashed lines represent the weak- and strong-coupling expansions.

$$\mathscr{C}(z)=i\gamma \tag{15a}$$

and the vibrational part of the density correlation function reads

$$\Phi_v(z)=-\cfrac{1}{z-\cfrac{\Omega^2}{z+i\gamma}}\ . \tag{15b}$$

In first order (13b) leads to

$$\mathscr{C}(z)=i\gamma-\cfrac{4\lambda(1-f)^2}{z-\cfrac{2\Omega^2}{z+i\gamma-\cfrac{2\Omega^2}{z+2i\gamma}}}\ . \tag{16a}$$

Thus with decreasing $\lambda$ the zero-frequency value $\mathscr{C}(z=0)$ increases leading with (14) to an increasing viscosity

$$D_v=\frac{\gamma}{\sqrt{1-1/\lambda}}\left[1+\frac{1}{8\gamma\lambda}+O(1/\lambda^2)\right]\ . \tag{16b}$$

The asymptotic expansion (16b) for $D_v$ is compared in Fig. 2 with the numerical solution obtained by integrating the differential equation (1). The good agreement down to values near $\lambda\gtrsim 1$ is remarkable. Also shown is the numerical solution and the weak-coupling expansion (8b) in the fluid phase. The nature of the singularity near $\lambda=1$ will be discussed in Sec. IV.

## IV. CRITICAL REGIME

In the following the small-frequency behavior near the phase transition will be investigated where the inequality

$$|z/D_v(z)|\ll 1 \tag{17}$$

is fulfilled. The point $\lambda=1$ and the regimes $\lambda>1$ and $\lambda<1$ are considered separately.

*1. $\lambda=1$.* At the glass transition point (13) simplifies with the assumption (17) to

$$D_v(z)=\{\mathscr{C}(z)+[\mathscr{C}^2(z)-8\mathscr{C}(z)/z]^{1/2}\}/2\ , \tag{18a}$$

$$\mathscr{C}(z)=i\gamma+\mathscr{L}\{\Phi_v^2(t)\}\ . \tag{18b}$$

Assuming for the moment that $\mathscr{C}(z)$ is constant for small frequency, (18a) would imply that $D_v(z)$ and also $\Phi_v(z)$ exhibit a square root singularity for small frequency. This would imply a long-time power-law decay propor-

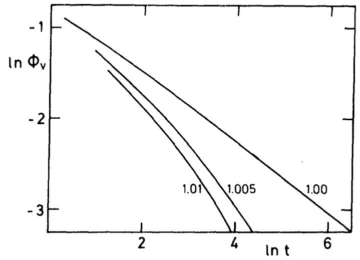

FIG. 3. Time dependence of the vibrational part $\Phi_v(t)$ of the density correlation function at the transition $\lambda_c=1$ and in the amorphous phase for two coupling constants $\lambda$. Parameters are $\Omega_0=1$ and $\gamma=1$.

tional $t^{-1/2}$. The singularity of $\Phi_v(z)$, however, also implies a singularity of $\mathscr{C}(z)$ by the feedback mechanism manifested in (18b) and so the assumption of a constant $\mathscr{C}(z)$ is not justified. It is easy to show that a self-consistent solution of (18) and (12a) for $z \to 0$ is

$$D_v(z) \sim z^{\alpha-1} , \tag{19a}$$

$$\mathscr{C}(z) \sim z^{2\alpha-1} , \tag{19b}$$

where $\alpha=0.395$ is a solution of $\Gamma(1-2\alpha)=2\Gamma^2(1-\alpha)$, implying a power-law decay $\Phi_v(t) \sim t^{-\alpha}$, thus a singularity somewhat stronger than a square root. So the density correlation function $\Phi(t)$ decays very slowly with the exponent $\alpha$ to the time persistent value $\frac{1}{2}$ for $t \to \infty$. This is shown in Figs. 1 and 3. The spectrum $\Phi''(\omega)$ exhibits a $\delta(\omega)$ peak of strength $\frac{1}{2}$ and a $\omega^{-(1-\alpha)}$ singularity for small frequency.

*2.* $\lambda > 1$. Defining $\epsilon=\lambda-1$ the Eq. (13a) for $D_v(z)$ for small frequency can be rewritten as

$$z^2 D_v^2(z) - 2\sqrt{\epsilon} D_v(z) + 2\mathscr{C}(z) = 0 . \tag{20}$$

In view of (19) for $\epsilon=0$ the scaling ansatz

$$D_v(z) = z^{\alpha-1} d(z/s) , \tag{21a}$$

$$\mathscr{C}(z) = z^{2\alpha-1} c(z/s) , \tag{21b}$$

with the critical frequency $s=\epsilon^{\nu}$ and $\nu=1/2\alpha$ leads to the equation for the scaling functions

$$d^2(x) - 2x^{-\alpha} d(x) + 2c(x) = 0 . \tag{21c}$$

This implies that the zero-frequency limit of the viscosity scales like

$$D_v \sim s^{\alpha-1} \sim \epsilon^{-\mu'} , \tag{22}$$

where $\mu'=(1-\alpha)/2\alpha=0.765$. This is in agreement with the numerical solution for $D$ shown in Fig. 2. The density-fluctuation spectrum for $\lambda \gtrsim 1$ consists of a $\delta(\omega)$ peak of strength $f \gtrsim \frac{1}{2}$ and a vibrational part of strength $1-f \lesssim \frac{1}{2}$ with a quasielastic peak of width $1/D_v$ vanishing proportional $(\lambda-1)^{\mu'}$ when approaching the transition point. Correspondingly, the time-dependent correlation function $\Phi(t)$, after an initial short-time decay, shows a crossover from the critical power law proportional to $t^{-\alpha}$ to an exponential decay with a relaxation time $\tau \sim D_v$. In Fig. 3 the numerical solution $\Phi_v(t)$ near the transition point is plotted indicating that the critical region where the crossover can be observed is quite small.

*3.* $\lambda < 1$. In this section it will be shown, starting from (3), that the viscosity is also diverging when one approaches the transition point $\lambda_c=1$ from below. At first sight it is not obvious how an expansion of (3) in terms of $\epsilon=1-\lambda$ can be achieved, but it can be accomplished as follows. We assume that $\Phi(z)$ can be written as the sum of a pole contribution and a remaining part $\Phi_v(z)$. The pole contribution is expected to evolve continuously into the elastic component of $\Phi(z)$ for $\lambda \geq 1$. Then equations for the pole position, the residue of the pole, and for $\Phi_v(z)$ can be derived. Thus the ansatz is

$$\Phi(z) = -\frac{a}{z+i\delta} + b\Phi_v(z) , \tag{23}$$

where $a+b=1$, so that $\Phi_v(t=0)=1$. Then according to (3b) the viscosity can also be divided into a pole part and a remaining part

$$D(z) = -(4\lambda a^2)/(z+2i\delta) + D_v(z) , \tag{24a}$$

$$D_v(z) = i\gamma + 8\lambda ab\Phi_v(z+i\delta) + 4\lambda b^2 \mathscr{L}\{\Phi_v^2(t)\} . \tag{24b}$$

The pole part in (24a) can be considered as a viscoelastic component with a Maxwell relaxation[17] time $\tau=1/2\delta$. For the density correlation function $\Phi(z)$ instead of (3a) the simpler representation

$$\Phi(z) = -\cfrac{1}{z - \cfrac{1}{D(z)}} \tag{25}$$

which is valid for $|z/D(z)| \ll 1$ will be used in order to simplify the formulas. The method is applicable, however, also to (3a). Inserting (24a) and (24b) into (25) one finds for the pole position and pole residue two equations

$$i\delta D_v(-i\delta) = 4a^2\lambda - 1 , \tag{26a}$$

$$a = [2 + i\delta D_v(-i\delta) - \delta^2 D_v'(-i\delta)]^{-1} , \tag{26b}$$

expressing $\delta$ and $a$ in terms of $D_v(z)$, where in (26b) $D_v'(z)=dD_v(z)/dz$. The equation which determines $D_v(z)$ reads

$$D_v(z) - 8ab\lambda\Phi_v(z+i\delta) = \mathscr{C}(z) , \tag{27a}$$

$$b\Phi_v(z) = -\frac{D_v(z)(z+2i\delta) - 4a^2\lambda}{zD_v(z)(z+2i\delta) - 4a^2\lambda z - z - 2i\delta} + \frac{a}{z+i\delta} , \tag{27b}$$

$$\mathscr{C}(z) = i\gamma + 4\lambda b^2 \mathscr{L}\{\Phi_v^2(t)\} . \tag{27c}$$

In this way the theory is formulated entirely in terms of $D_v(z)$. Equation (27) is analogous to (13) for $\lambda \geq 1$. Once $D_v(z)$ is known, $\delta$ and $a$ can be evaluated using (26). The viscosity is determined by (24a), yielding

$$D = 2\lambda a^2/\delta + D_v . \tag{28}$$

Equations (26) and (27) are a reformulation of the original problem admitting an expansion for small $\epsilon=1-\lambda$. In the small-frequency regime $|z| \ll \epsilon$ one finds, after some calculation, in leading order

$$a=\tfrac{1}{2}+\epsilon/8\ , \tag{29a}$$

$$D_v(z)=i\epsilon/2\delta,\quad |z| \ll \epsilon \tag{29b}$$

assuming that $\delta$ vanishes faster than $\epsilon$ for $\epsilon \rightarrow 0$. The variation of the pole position $\delta$ with $\epsilon$ can be determined in the following way. In the frequency regime $\delta \ll |z| \ll \dot{\epsilon}^{\mu'}$ the set of equations (27) simplifies to

$$2zi\delta D_v'(z)+z^2D_v^2(z)+4i\delta D_v(z)+2\epsilon+2z\mathscr{C}(z)=0\ . \tag{30}$$

If one could replace $\mathscr{C}(z)$ by $i\gamma$ then the choice $\delta \sim \epsilon^{3/2}$ would lead to the scaling form $D_v(z)=\epsilon^{-1/2}d(z/\epsilon)$, implying that $D \sim \epsilon^{-3/2}$ according to (28). However, $\mathscr{C}(z=0)$ is singular for $\lambda \rightarrow 1$ because of the nonlinear term in (27c). The scaling ansatz

$$D_v(z)=s^{\alpha-1}d(z/s)\ , \tag{31a}$$

$$\mathscr{C}(z)=s^{2\alpha-1}c(z/s)\ , \tag{31b}$$

where $s=\epsilon^{1/2\alpha}$ is a critical frequency, $\alpha=0.395$, and $\delta=s^{1+\alpha}$ leads to a Riccati equation for the scaling functions

$$2ixd^2(x)+x^2d^2(x)+4id(x)+2+2xc(x)=0\ . \tag{32}$$

Thus for zero frequency, according to (31a), $D_v$ diverges proportional to $s^{\alpha-1}=\epsilon^{-(1-\alpha)/2\alpha}$, with the same exponent as for $\lambda \geq 1$. The relaxation rate $\delta$ vanishes as $\delta \sim s^{1+\alpha} \sim \epsilon^{(1+\alpha)/2\alpha}$. So one finds with (28) that in leading order the longitudinal viscosity diverges as

$$D \sim \epsilon^{-\mu},\quad \mu=(\alpha+1)/2\alpha=1.765 \tag{33}$$

where the exponent $\mu$ is related to the exponent $\mu'$ of $D_v$ by $\mu=\mu'+1$.

Qualitatively, the behavior of the solution for $\lambda \lesssim 1$ near the transition can be characterized as follows. The spectrum $\Phi''(\omega)$ consists of two contributions. One part is a very sharp quasielastic Lorentzian peak of strength $a \approx \frac{1}{2}$ and width $\delta \sim \epsilon^{\mu}$ shrinking to zero for $\lambda \rightarrow 1$. This part evolves continuously into the $\delta(\omega)$ peak in the glass phase. The other part of weight $b \approx \frac{1}{2}$ also exhibits a quasielastic peak, but its width is proportional $1/D_v \sim \epsilon^{\mu-1}$ similar to above the transition. This part diverges at the transition as $\omega^{-(1-\alpha)}$ for small frequency. So the main difference between the two phases near the transition as it shows up in the density-fluctuation spectrum is that there is a very sharp quasielastic peak in the fluid phase while it is elastic in the glass phase. In both phases an additional broader quasielastic peak is superposed, whose width shrinks to zero upon approaching the transition. In Fig. 1 the numerical solution for the time-dependent density correlation function is shown. For $\lambda < 1$ near the transition the slow exponential decay stemming from the quasielastic Lorentzian dominates the behavior at long times. This is also clearly shown in Fig. 4 where the straight line corresponds to $\frac{1}{2}\exp(-t/2D)$ as discussed above. This part evolves into the time persistent component $f$ [see (11)] for $\lambda \geq 1$. An exponential decay near the fluid-solid transition was recently observed in molecular-dynamic experiments for supercooled liquid rubidium.[18] The other component of $\Phi(t)$ behaves akin to $\lambda \gtrsim 1$. It has a crossover from power-law decay $\sim t^{-\alpha}$ for intermediate times to an exponential decay with relaxation time increasing proportional to $D_v$ for long time. The typical time separating power-law decay from exponential decay tends to infinity when the transition point is approached. At the transition $\Phi(t)$ decays according to the power law $\Phi(t) \sim t^{-\alpha}$ with $\alpha=0.395$ to the value $\frac{1}{2}$ for $t \rightarrow \infty$.

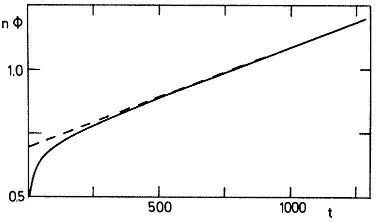

FIG. 4. Time dependence of the density correlation function $\Phi(t)$ in the fluid phase near the transition at $\lambda=0.98$. Parameters are $\Omega_0=1$ and $\gamma=1$. Solid line represents the numerical solution of the model and the dashed line represents the viscoelastic exponentially decaying component.

## V. THE SHEAR VISCOSITY

In this section the implications of the liquid-glass transition for the transverse current correlation function and the shear viscosity shall be discussed. The transverse current correlation function[13] can be represented in terms of the generalized dynamical kinematic shear viscosity $D_t(z)$ by

$$\Phi_t(z)=-\frac{1}{z+D_t(z)}\ , \tag{34a}$$

where in the limit of small wave number $q$ and frequency $z$ for fluids the shear viscosity $\eta$ is given by

$$\lim_{z\rightarrow 0}\lim_{q\rightarrow 0} D_t(z)=iq^2\eta/\rho\ . \tag{34b}$$

In the framework of the microscopic theory[11] the dynamical shear viscosity, similar to the longitudinal viscosity in (3b), has two contributions of different physical origin,

$$D_t(z)=i\gamma_t+\beta\lambda\Omega_0^2\mathscr{L}\{\Phi^2(t)\}\ . \tag{35}$$

The first part stems from the usual two-particle collision processes described by kinetic theory. It has the form of a Lorentzian with a width given by the collision frequency, but for simplicity it is approximated in (35) by the constant $i\gamma_t \sim q^2$ for $q \rightarrow 0$. The second part in (35) arises from the structural rearrangements in a dense fluid. In the microscopic theory[11] it is represented by bilinear products of correlation functions of conserved variables and it was found[12] that, as in the longitudinal case, the product of two density modes is the dominant contribution at high density. Only this contribution is considered in the model equation (35) where $\beta$ is a numerical constant arising from a wave-number integral over static two-particle correlations. Note that this structural rearrangement contribution to $D_t(z)$ is proportional to the corresponding one for the longitudinal viscosity $D(z)$ in (3b) so that the dynamical behavior of $D_t(z)$ is governed by that of $D(z)$ which we have already discussed.

In particular, the shear viscosity diverges at the same critical point $\lambda_c = 1$ and with the same exponent as the longitudinal viscosity in both phases. Furthermore, in the fluid phase near the phase transition, the time-dependent transverse stress correlation function which is essentially the inverse Laplace transform of $D_t(z)$ has a very slowly exponentially decaying component, stemming from the pole contribution of

$$D_t(z) = -\beta\lambda\Omega_0^2 a^2/(z+2i\delta) + D_{tv}(z) \ . \tag{36}$$

In (36) $D_{tv}(z)$ is the remaining part of $D_t(z)$, which is proportional to $D_v(z)$ in (24a). The relaxation time $\tau = 1/2\delta$ of the exponential in the transverse stress correlation function is the same as the corresponding one of the longitudinal stress correlation function in (24a). At the phase transition the transverse stress correlation function decays according to a power law with the same critical exponent as the longitudinal stress correlation function.

In the amorphous phase $D_t(z)$ has a zero-frequency pole

$$D_t(z) = -\beta\lambda f^2\Omega_0^2/z + D_{tv}(z) \ , \tag{37}$$

where the residue is related to the modulus of rigidity $G$ of the glass phase by $G/\rho = \beta\lambda f^2\Omega_0^2/q^2$. Thus the system has the property of a solid being stable against shear stress. Inserting (37) into (34a), the resulting form of the transverse current correlation function

$$\Phi_t(z) = -\frac{z}{z^2 - q^2 c_t^2 + z D_{tv}(z)} \tag{38}$$

shows that transverse waves can propagate with the transverse sound velocity $c_t = \sqrt{G/\rho}$ at arbitrarily small wave numbers. Their damping is described by $D_{tv}(z=0) \sim q^2$ for small wave number.

It is interesting to note that the residue of the viscoelastic pole is continuous at the glass transition since $f = a = \frac{1}{2}$ at $\lambda = 1$. Thus one can observe solidlike behavior already in the fluid phase below $\lambda_c$ for $\omega \gtrsim 2\delta$ and can determine the bulk and shear moduli of the amorphous phase. It should, however, be emphasized that these bulk and shear moduli are not the high-frequency moduli of the liquid as is often assumed in viscoelastic models of fluids.[13] For example, in the model presented here as well as in fluids with hard-core interaction, the high frequency elastic moduli, defined in terms of the second frequency moments of the longitudinal and transverse currents, are infinite. In this model it becomes apparent, that the viscoelastic component of the stress correlation functions in (24a) and (30) which determines their long-time properties is not related to the short-time behavior of the system. One may conclude that the liquid-glass transition is universal in the sense that short-time properties are irrelevant.

## VI. SUMMARY AND CONCLUSIONS

In this work the liquid-glass transition was studied using a model derived from a microscopic theory[11] of density fluctuations in a dense hard-core liquid. It was shown that a system described by (1) or (3) evolves from the fluid to the amorphous state when the coupling constant $\lambda$ related to the density is increased beyond a critical value $\lambda_c$. An ergodic-nonergodic phase transition similar to the liquid-glass transition occurs also in the Anderson localization problem[19,20] and the diffusion-localization problem of a classical tagged particle in a static random potential.[21] In these theories,[20,21] however, the relation between the current relaxation kernel and the tagged-particle density correlation function, which corresponds to (3b) in this model, is a linear one entailing enormous simplifications since the frequency is simply a parameter. The physical reason is that the tagged particle is scattered elastically by the fixed scatterers. In the case of a fluid, however, scattering is inelastic, and momentum and energy are transferred via interaction processes into at least two other modes. It was the main purpose of this paper to study the pure effect of this nonlinearity in (3b) by neglecting the wave-number dependences in a first approximation. Qualitatively, however, no change is expected when this is incorporated.

For small coupling constant $\lambda$ the dynamical viscosity $D(z)$ in (3a) is a constant $i\gamma$. For increasing $\lambda$ it becomes frequency dependent, $D(z=0)$ increases, the system slows down and becomes more and more rigid and a viscoelastic part develops, as described by (24a). The irreversible structural rearrangement, as described by the product of two density modes in (3b), leads to an enhancement of the longitudinal viscosity, resulting in turn in a slower relaxation of density fluctuations via (3a). This process may be called self-induced slowing down. For increasing $\lambda$ this finally leads to the freezing in of the translational motion at the transition point $\lambda_c = 1$ where the relaxation time $\tau = 1/2\delta$ and the longitudinal and shear viscosities diverge proportional to $|1-\lambda/\lambda_c|^{-\mu}$, $\mu = 1.765$. This result is intermediate between the Batchinski-Hildebrand[22,23] law $\sim(\lambda_c - \lambda)^{-1}$ and Fulcher[24] law $\sim \exp[1/(\lambda_c - \lambda)]$.

At this density the viscosities and the density correlation function acquire a zero-frequency pole, characteristic of the glass phase, signaling an ergodic-nonergodic transition.[25] The particles can only sample a restricted phase space since they are arrested by their neighboring particles in a cage. At the transition the compressibility drops to $(1-f) \cong \frac{1}{2}$, e.g., one-half of its fluid value, but in any experiment involving nonzero frequencies or finite observation times a gradual decrease of the compressibility will be observed. At $\lambda = \lambda_c$ the density correlation function decays to $\frac{1}{2}$ for long times with a power law $\Phi(t) \sim t^{-\alpha}$ with $\alpha = 0.395$, related to $\mu$ by $\mu = (1+\alpha)/2\alpha$.

For increasing $\lambda$ the viscoelastic component of the density fluctuations in the fluid evolves continuously into the elastic peak $\sim \pi f \delta(\omega)$ in the glass phase. In addition, there is a vibrational part whose spectral weight $(1-f)$ approaches 1 for $\lambda \rightarrow \infty$. Near the transition the vibrational motion of the particles around their arrested positions is overdamped since the viscosity diverges proportional to $(\lambda - 1)^{-\mu'}$ where $\mu' = (1-\alpha)/2\alpha = 0.765$.

The time dependence of the longitudinal and transverse stress correlation function is particularly interesting. As was already discussed in connection with (36), the viscoelastic part in (24a) and (36) manifests itself near the transition in a very slow exponential decay where the relaxation times of the longitudinal and transverse stress correlations are both $\tau = 1/2\delta$, approaching infinity for $\lambda \rightarrow 1$.

This may provide an explanation for the slowly exponentially decaying component observed in molecular-dynamic experiments for liquid argon at the triple point performed by Levesque *et al.*[26] They found that the longitudinal as well as the transverse stress correlation functions could be fitted by two exponentials with relaxation times $\tau_<$ and $\tau_>$ where $\tau_> \gg \tau_<$. The slower relaxation process corresponds to the cooperative process of structural rearrangements in the fluid and $\tau_>$ can be viewed as the Maxwell relaxation time $\tau = 1/2\delta$. As in the model presented here, $\tau_>$ was found to be the same in the longitudinal and transverse case. The faster initial exponential decay with relaxation time $\tau_<$ probably is due to binary collisions, characterized by the collision frequency. This part is also present in the microscopic theory[11] but was replaced in the model equations (3b) and (35) by an instantaneous term $\gamma\delta(t)$ or $\gamma_t\delta(t)$, respectively, for simplicity.

The long-time tail of the stress correlation function is, at present, not well understood. The stress correlation function can be divided into a kinetic part, a potential part, and a cross term. Kinetic theory[27] predicts that, of these contributions, only the kinetic part has a long-time power-law decay, with exponent $d/2$ and well-known amplitude, where $d$ is the space dimension. Molecular-dynamic experiments[14,26,28,29] show, however, that the cross term and to a greater extent the potential contribution are very slowly decaying in dense liquids in the time regime observable in these experiments. If the slow decay observed in liquid argon[26] is interpreted as the power-law decay $\sim t^{-3/2}$ one finds[28] an amplitude which is 2 orders of magnitude larger than predicted for the kinetic part. Similarly, computer simulations for the hard-sphere system[14,29] near the liquid-solid transition clearly demonstrated that both the cross and the potential part of the transverse stress correlation function have a slowly decaying component. If the slow decay of the potential part is interpreted[29] as a power law $\sim t^{-3/2}$, its amplitude is 372 times larger than the one of the kinetic part, while the kinetic-theory prediction is zero.

The theory of the liquid-glass transition may provide an explanation to this phenomenon. As explained above, the stress correlation function has a very slowly, exponentially decaying component, which is a precursor of the nearby liquid-solid transition. Therefore, it is understandable that to explain this effect, the theory must be able to describe the liquid-solid transition.

It is also remarkable that the slowly decaying component of the stress correlation function found by Erpenbeck and Wood[29] in the hard-sphere system can be fitted equally as well by an exponential as by a $t^{-3/2}$ power law.

Note that the time integral of the stress correlation function is the viscosity which diverges at the liquid-glass transition. In the present theory this divergency is not related to the hydrodynamic long-time power-law decay $\sim t^{-d/2}$. In fact, this power-law decay due to hydrodynamic singularities is not contained in the present model because of the approximations leading to the model equations (3) and (35), as discussed in Sec. II. The inclusion of the hydrodynamic singularities is expected to affect the stress correlation functions only at very long times. Moreover, approaching the transition the decay $\sim t^{-d/2}$ disappears and is replaced by the critical power-law behavior.

The tagged-particle motion and the self-diffusion coefficient do not play a direct role in the formulation of the liquid-glass transition presented here. This is physically reasonable, since the motion of a tagged particle is not expected to have any influence on the glass transition which is rather a cooperative phenomenon where all particles are involved and thus is expressed in terms of the density correlation function and the longitudinal viscosity. On the other hand, the tagged particle is strongly influenced by its surroundings and thus the self-motion is strongly coupled to the density fluctuations of the system.[20,21,30] The effect of the liquid-glass transition on the incoherent dynamical structure factor and the extension of the present model to include the wave-number dependence will be discussed elsewhere.[31]

## ACKNOWLEDGMENTS

It is a pleasure to thank Professor Sidney Yip for the hospitality offered by him at the Massachusetts Institute of Technology (MIT) and for interesting discussions. Financial support by the Alexander von Humboldt-Stiftung as a Feodor Lynen Fellow and by MIT is gratefully acknowledged.

---

[1] W. Kauzmann, Chem. Rev. 43, 219 (1948).

[2] T. A. Litovitz and C. M. Davies, in *Physical Acoustics,* edited by W. P. Mason (Academic, New York, 1965), Vol. II, Pt. A, p. 281.

[3] D. Frenkel and J. P. McTague, Annu. Rev. Phys. Chem. 31, 491 (1980); C. A. Angell, J. H. R. Clarke, and L. V. Woodcock, Adv. Chem. Phys. 48, 398 (1981).

[4] A. Rahman, M. J. Mandell, and J. P. McTague, J. Chem. Phys. 64, 1564 (1976); S. R. Nagel, A. Rahman, and G. S. Grest, Phys. Rev. Lett. 47, 1665 (1981); G. S. Grest, S. R. Nagel, and A. Rahman, *ibid.* 49, 1271 (1982).

[5] M. H. Cohen and D. Turnbull, J. Chem. Phys. 31, 1164 (1959); D. Turnbull and M. H. Cohen, *ibid.* 52, 3038 (1970).

[6] M. H. Cohen and G. S. Grest, Phys. Rev. B 20, 1077 (1979); G. S. Grest and M. H. Cohen, *ibid.* 21, 4113 (1980).

[7] T. Schneider, R. Brout, H. Thomas, and J. Feder, Phys. Rev. Lett. 25, 1423 (1970); T. Schneider, Phys. Rev. A 3, 2145 (1971).

[8] L. Bosio and C. G. Windsor, Phys. Rev. Lett. 35, 1652 (1975).

[9] A. Sjölander and L. A. Turski, J. Phys. C 11, 1973 (1978).

[10] T. Geszti, J. Phys. C 16, 5805 (1983).

[11] E. Leutheusser, J. Phys. C 15, 2801 (1982).

[12] E. Leutheusser, J. Phys. C 15, 2827 (1982).

[13] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1976); J.-P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).

[14] B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. 53, 3813 (1970).

[15] W. E. Alley and B. J. Alder, Phys. Rev. A 27, 3158 (1983); W. E. Alley, B. J. Alder, and S. Yip, *ibid* 27, 3174 (1983).

[16] S. F. Edwards and P. W. Anderson, J. Phys. F 12, 965 (1975).

[17] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, London, 1959); J. Frenkel, *Kinetic Theory of Liquids* (Oxford University, London, 1946).

[18] R. D. Mountain, Phys. Rev. A 26, 2859 (1982); R. D. Mountain and P. K. Basu, *ibid.* 28, 370 (1983).

[19] P. W. Anderson, Phys. Rev. 109, 1492 (1958).

[20] W. Götze, Solid State Commun. 27, 1393 (1978); J. Phys. C 12, 1279 (1979).

[21] W. Götze, E. Leutheusser, and S. Yip, Phys. Rev. A 23, 2634 (1981); 24, 1008 (1981); 25, 533 (1982).

[22] A. J. Batchinski, Z. Phys. Chem. 84, 643 (1913).

[23] J. H. Hildebrand, *Viscosity and Diffusion* (Wiley, New York, 1977).

[24] G. S. Fulcher, J. Am. Ceram. Soc. 8, 339 (1925).

[25] R. Kubo, J. Phys. Soc. Jpn. 12, 570 (1957).

[26] D. Levesque, L. Verlet, and J. Kürkijarvi, Phys. Rev. A 7, 1690 (1973).

[27] Y. Pomeau and P. Résibois, Phys. Rep. 19C, 63 (1975).

[28] D. J. Evans, J. Stat. Phys. 22, 81 (1980).

[29] J. J. Erpenbeck and W. W. Wood, J. Stat. Phys. 24, 455 (1981).

[30] E. Leutheusser, Phys. Rev. A 28, 2510 (1983).

[31] E. Leutheusser and S. Yip (unpublished).