

Short time dynamics of glass-forming liquids

C. M. Roland and K. L. Ngai

Naval Research Laboratory, Washington, D.C. 20375-5320

(Received 27 January 1995; accepted 14 April 1995)

Calculations have been presented for the intermediate scattering function, dynamic structure factor, and dynamic susceptibility of a complex correlated system undergoing relaxation with independent vibrations. The vibrational contribution was approximated by a Debye spectrum, smoothed at high frequency, while the coupling model was used to describe the relaxation. This model asserts for nonpolymeric glass-forming liquids a crossover at a microscopic time from intermolecularly uncorrelated relaxation at a constant rate to intermolecularly coupled relaxation with a time-dependent, slowed-down rate. Although the model has previously been employed to successfully predict and otherwise account for a number of macroscopic relaxation phenomena, critical phenomena are not included in, and cannot be addressed by, the coupling model. Notwithstanding an absence of any change in transport mechanism for the supercooled liquid at a critical temperature, the coupling model data, when analyzed in the manner used for mode coupling theory, shows various features interpreted by MCT as critical dynamic singularities. These include an apparent fast “ β ” relaxation giving rise to a cusp in the temperature dependence of the Debye–Waller factor, a power-law divergence in the temperature dependence of the relaxation time for the α process, and critical exponents for the relaxation having a defined relationship to one another. Additionally, other experimental features of the short-time dynamics, such as the anomalous Debye–Waller factor and the von Schweidler law, are also observed in results derived from the coupling model. Whatever similarities underlie the coupling model and MCT, a crucial difference is that only the latter predicts the existence of critical phenomena. Yet these and other distinct features are exhibited by the coupling model data. Evidently, any interpretation of short-time behavior in terms of MCT is ambiguous, if not necessarily incorrect. This indicates the importance of the many macroscopic-time relaxation properties found over the years in glass forming liquids (including polymers, small molecule van der Waal liquids, and inorganic materials), and the necessity that they be addressed by any theory, including MCT, purporting to offer a fundamental description of relaxation phenomena. © 1995 American Institute of Physics.

INTRODUCTION

The transition of glass-forming liquids from the lower temperature glassy state to the higher temperature viscous melt has long been a subject of considerable scientific interest, but the phenomenon is still not adequately understood. The most relevant problem regarding the glass transition is the nature of the relaxational dynamics of the molecular or ionic constituents, which ultimately determine the physical properties of the glass transition. Resolution of this issue will not come easily, because we are dealing with a many-body problem involving densely packed moieties interacting in a nontrivial fashion. In such a situation, the dynamics of the relaxation process cannot be described in terms of one-body language, even when some effective mean field approximation is used.

Traditionally, experimental investigations of the dynamics are carried out by spectroscopies (such as mechanical, dielectric, and photon correlation) that probe the relaxation in the “macroscopic” time domain, typically much longer than 10^{-10} s.^{1–3} Experimental data on glass-forming materials collected over the years have enabled a number of interesting phenomenologies to be established. It was found early on that transport coefficients, such as the zero shear viscosity, diffusion constant and dc conductivity, usually do not have an Arrhenius temperature dependence, but are well ap-

proximated by the Vogel–Fulcher empirical function, at least over some restricted temperature range. Other phenomenologies include (i) the time-dependence of the relaxation process conforming to the Kohlrausch fractional exponential correlation function,

$$C_K = \exp\left(-\left(\frac{t}{\tau^*}\right)^\beta\right); \quad (1)$$

(ii) a strong correlation between the Kohlrausch fractional exponent, β , and the normalized temperature, T_g/T , dependence of the Kohlrausch relaxation time, τ^* ;^{4–8} (iii) within a family of chemically similar materials, a trend of decrease in β with increasing severity of the dynamical constraints between the relaxing moieties (i.e., stronger intermolecular cooperativity);^{9,10} (iv) the shear viscosity and orientational relaxation time have a similar temperature dependence, which however differs from that of the diffusion coefficient.¹¹ These are just a few among many examples, particularly when polymers are included.¹²

These phenomenologies and experimental facts involve macroscopic times and have been the main concern of past theoretical efforts. However, with the advent of mode coupling theory (MCT),^{1,13} which addresses the microscopic time regime ($\sim 10^{-14}$ – 10^{-9} s), much attention has shifted to testing the predictions of MCT for neutron and light scattering experimental data and for molecular dynamics simula-

tions performed on glass-forming systems.^{14–24} These types of measurements provide relaxation data in the microscopic time regime and beyond, and thus should confirm certain quantitative MCT predictions, such as the “fast β process,” the “von Schweidler law,” a critical slowing down of the density correlation function at some temperature T_c , certain scaling laws, and the anomalous Debye–Waller factor.^{13–23} The “success” of some of the comparisons between MCT and experimental data remains controversial,^{25–27} and possibly there are alternative ways to interpret the data; nevertheless, the current emphasis of research on the glass transition has shifted from the macroscopic time properties to microscopic time ones. This shift is not undesirable, since the properties at microscopic times are more fundamental. Although MCT enjoys an almost unique position among theoretical models in being able to address short-time behavior, it has not yet been developed to the extent of a demonstrated consistency with all the *macroscopic* time properties mentioned above.

The coupling model¹² is a general theoretical framework to treat relaxation in densely packed systems. The theoretical basis for the model is chaos in classical mechanics, arising from the nonlinear nature of the intermolecular interaction potential, such as the often employed Lennard-Jones potential.^{12,28,29} The coupling model at present lacks the mathematical rigor of MCT and much work remains before a completely fundamental theory is in hand. However, it is believed that the model captures the important physics of cooperativity dynamics, and, moreover, leads to various qualitative and quantitative predictions.^{4–10,12} Indeed, the phenomenologies in the macroscopic time regime mentioned above were either anticipated by or consistent with the coupling model.

Although the coupling model is based on microscopic time considerations, previously no attempt was made to compare its predictions for microscopic time properties with neutron and light scattering experimental data and molecular dynamics simulation results. Recently, Colmenero and co-workers^{30,31} used the model in analyzing their quasielastic neutron scattering measurements, and found good correspondence between theory and experiment. In this work we examine the results of the coupling model for the microscopic time regime by carrying out an analysis in the manner employed by for MCT.^{13–23} Our interest is to determine if the coupling model can reproduce results having the same or similar features as predicted by MCT. Such comparisons are made more difficult by the existence of two—the idealized and the extended—MCT variants, which are employed sometimes simultaneously in applying the theory to experimental data.^{25–27} Nevertheless, as described below, results obtained from the coupling model capture many of the features predicted by MCT, including the presence of a “fast process,” the manifestation of apparent critical behavior at some temperature T_c , the anomalous Debye–Waller factor, the observation of the von Schweidler law and its scaling behavior. These findings call into question the uniqueness of theoretical interpretations of experimental observations in the microscopic time regime.

COUPLING MODEL RESULTS

The coupling model of relaxation in densely packed interacting systems¹² proposes the existence of a temperature independent crossover time, t_c , separating two time regimes in which the relaxation dynamics differ. At short times, $t < t_c$, the basic units relax independently of each other with a constant rate $\Omega_0 \equiv \tau_0^{-1}$, as if the intermolecular interaction has no effect other than providing a time independent mean field which determines Ω_0 . The correlation function of the relaxation process then has the Debye form

$$C_D(t) = \exp\left(-\frac{t}{\tau_0}\right). \quad (2)$$

This description of the relaxation is only appropriate for simple molecular units without intramolecular interaction. The motion of polymers is intramolecularly correlated because of bonded interactions along the polymer chain; this causes the independent relaxation rate to be time dependent, even before intermolecular interaction is taken into consideration.³²

For times $t > t_c$, neighboring molecules impose constraints on the relaxation of each unit. The coupling model describes the ensuing many-body (or cooperative) relaxation dynamics by an effective relaxation rate, obtained by averaging over all units. Each has the time dependent, retarded relaxation rate

$$\Omega(t) = \Omega_0(\omega_c t)^{-n}, \quad (3)$$

where n is the coupling parameter, whose magnitude ($0 < n < 1$) determines the degree of intermolecular cooperativity. This cooperativity gives rise to random variations in the success rate for reorientations, conformational transitions, etc., by the segments. At any given time on the molecular level the individual motions are not identical nor do they proceed homogeneously; however, the averaging over all units appropriate for a description of macroscopic variables results in an effective description which ostensibly implies homogeneous relaxation.³³

The relation between ω_c and t_c is

$$\omega_c = [(1-n)^{1/n} t_c]^{-1}. \quad (4)$$

The correlation function that has the time dependent relaxation rate of Eq. (3) is the Kohlrausch stretched exponential function [Eq. (1)] with $\beta = 1 - n$. However, this correlation function is only valid for $t > t_c$, and moreover must satisfy the condition,

$$\exp\left(-\frac{t_c}{\tau_0}\right) = \exp\left(-\frac{t_c}{\tau^*}\right)^{1-n} \quad (5)$$

or equivalently,

$$\tau^* = (t_c^{-n} \tau_0)^{1/1-n} \quad (6)$$

in order that the function $C(t)$, which is comprised of two parts [Eqs. (1) and (2)], be continuous everywhere. Of course, the crossover at time t_c is only an approximation. The actual crossover occurs over a range of times in the

neighborhood of t_c . In this neighborhood, the correlation function, as well as its derivatives, must be continuous at all times.

For comparison with microscopic time experiments we are interested in the density–density self-correlation function, or the incoherent intermediate scattering function

$$F_s(t; \mathbf{Q}, T) = \langle \exp\{-i\mathbf{Q} \cdot [\mathbf{r}_i(t) - \mathbf{r}_i(0)]\} \rangle, \quad (7)$$

where $\mathbf{r}_i(t)$ is the position of the i th molecule at time t , Q is the wave vector, and T the temperature. Both vibration (phonon) and relaxation (diffusion) of the molecules contribute to $F_s(t; \mathbf{Q}, T)$. The phonon contribution $F_{\text{phonon}}(t; \mathbf{Q}, T)$ is determined by the density of states of the phonon modes, $g(\omega)$, according to the formula³⁴

$$F_{\text{phonon}}(t; \mathbf{Q}, T) = \exp[-Q^2 W(t, T)], \quad (8)$$

where, if the phonons are harmonic throughout the temperature region of interest,

$$W(t, T) = KT^2 \int g(\omega) [1 - \cos(\omega t)] \omega^{-1} \times \left[\frac{2}{\exp(\hbar\omega/kT)} + 1 \right] d\omega, \quad (9)$$

with K representing a collection of constants. $W(t, T)$ decreases with time, leveling off to a constant value $W(T) = \lim_{t \rightarrow \infty} W(t, T)$. Correspondingly, $F_{\text{phonon}}(t \rightarrow \infty; \mathbf{Q}, T)$ has the value $\exp[-Q^2 W(T)]$, which is the well-known Debye–Waller (or Lamb–Mössbauer) factor.³⁴ The objective of the present work is the demonstration of general features. Hence, we eschew consideration of specific experimental data, and instead can choose any reasonable phonon spectrum. The Debye spectrum³⁴ has a density of normal modes, $g_D(\omega)$, of the form

$$g_D(\omega) = \left(\frac{3}{2\pi^2 c^2} \right) \omega^2 \quad (10)$$

for $\omega < \omega_D$ and $g_D(\omega) = 0$ for $\omega > \omega_D$. The abrupt cutoff of $g_D(\omega)$ at $\omega = \omega_D$ leads to oscillations in $F_{\text{phonon}}(t; \mathbf{Q}, t)$. In this work these oscillations are eliminated by smoothing the obtained correlation function with a low pass Blackman filter.³⁵ Taking $\omega_D = 1.5 \times 10^{13}$, the $F_{\text{phonon}}(t; \mathbf{Q}, T)$ calculated for a constant $Q = Q_0$ is shown in Fig. 1. The corresponding Debye–Waller factors, shown as open circles in a semilogarithmic plot in Fig. 2, lie on a straight line, as expected for harmonic phonons.

Intuitively, the vibrational phonon spectrum contributing to $F_s(t; \mathbf{Q}, T)$ is expected to be associated with the same molecular degrees of freedom involved in the relaxation process transpiring at the same time. Relaxation will damp the oscillation, introducing anharmonicity into the phonon response. Since relaxation is thermally activated, the degree of anharmonicity should increase with temperature. These considerations are beyond the scope of the present paper, but will be the subject of a future investigation.³⁶

We make the assumption^{18,30,31} that vibration and relaxation contribute independently to the density–density correlation function; thus, $F_s(t; \mathbf{Q}, T)$ is equal to the product $F_{\text{phonon}}(t; \mathbf{Q}, T) \times F_{\text{relax}}(t; \mathbf{Q}, T)$. While not exact, this as-

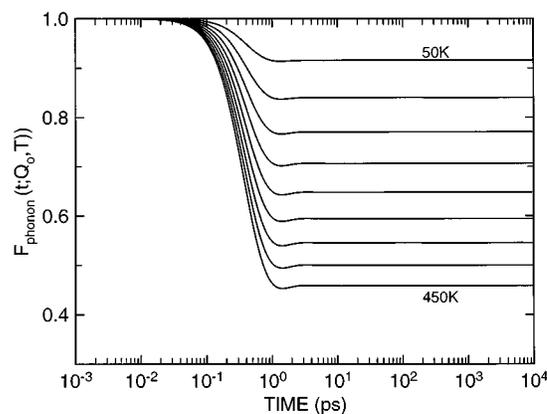


FIG. 1. Intermediate scattering function with phonon contribution only, F_{phonon} , calculated from the Debye spectrum for different temperatures using Eqs. (8)–(10). From top to bottom, $T = 50, 100, 150, 200, 250, 300, 350, 400,$ and 450 K.

sumption is adequate for the purposes of this paper. According to the coupling model form for $F_{\text{relax}}(t; \mathbf{Q}, T)$ given above, the following result is obtained:

$$F_s(t; \mathbf{Q}, T) = F_{\text{phonon}} \begin{cases} \exp[-t/\tau_0(Q, T)] & \text{for } t < t_c \\ \exp[-t/\tau^*(Q, T)]^{1-n} & \text{for } t > t_c \end{cases} \quad (11)$$

In the spirit of the coupling model, $\tau_0(Q, T)$, the relaxation time for independent motion of a molecular unit, is written as

$$\tau_0(Q, T) = \left(\frac{Q}{Q_0} \right)^{-2} \tau_{\infty}(Q_0) \exp\left(\frac{E_a}{kT} \right) \quad (12)$$

which explicitly displays the Q^{-2} -dependence and Arrhenius temperature dependence of independent (Fickian) diffusion. We calculate $F_{\text{relax}}(t; \mathbf{Q}, T)$ for $Q = Q_0$ by letting the crossover time assume the value $t_c = 2$ ps, and taking $E_a = 3.0$ kcal/mol and $\tau_{\infty}(Q_0) = 0.1$ ps. The value of t_c is suggested by the experimental data of Colmenero *et al.*³⁰ and by preliminary comparisons with molecular dynamics simulations.³⁷ The choice of E_a is guided by the fact that the conforma-

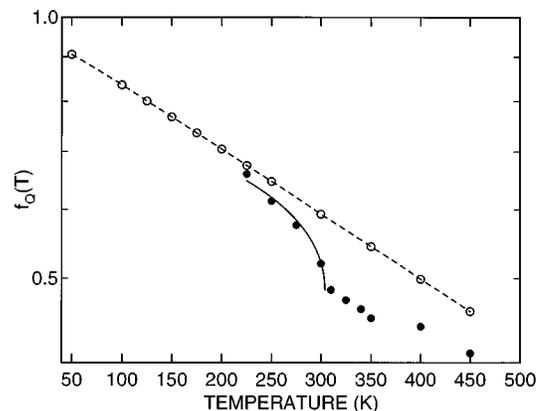


FIG. 2. Debye–Waller factor (with phonon contribution only) calculated for different temperatures using Eq. (9) in the long time limit (open circles). Filled circles denote the values of the “nonergodicity parameter,” $f_Q(T)$, obtained by fitting the slow α -process of $F_s(t; \mathbf{Q}, T)$ by Eq. (23) as shown in Fig. 3.

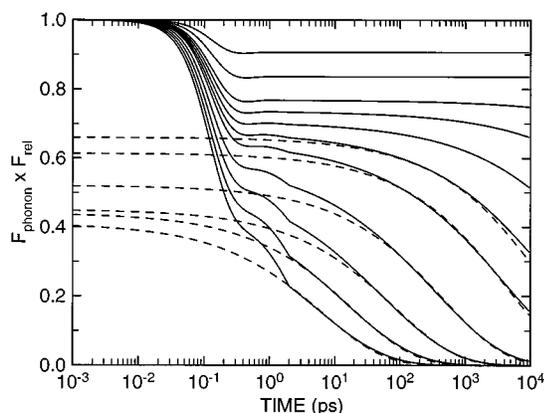


FIG. 3. Density-density correlation function calculated at different temperatures according to Eq. (11) for $n=0.60$ ($\beta=1-n=0.40$), shown as solid curves. Temperatures from top to bottom are 50, 100, 150, 175, 200, 225, 250, 300, 350, 400, and 450 K. The dashed curves represent the fits of Eq. (23), obtained using the procedure of Refs. 21 and 22, to the slow α -process with a constant $\beta_{\text{MCT}}=0.46$. The anomalous Debye-Waller factors $f_Q(T)$ determined by this process are displayed as full circles in Fig. 2. The singularity in $f_Q(T)$ in Fig. 2 derives from the data for $250 \leq T \leq 350$, for which the fit of Eq. (23) deviates for each temperature over the same range of times. For clarity, not all data and fits at each temperature are shown.

tional energy barrier of van der Waals liquids such as OTP (Ref. 38) and polyethylene³⁹ are of this order of magnitude.

Results for $F_s(t; Q_0, T)$ at various temperatures for $\beta=0.40$ (or $n=1-\beta=0.60$) are displayed in Fig. 3 by solid curves. From $F_s(t; Q_0, T)$ the dynamic structure factor, $S(\omega; Q_0, T)$, and the loss part of the dynamic susceptibility, $\chi''(\omega; Q_0, T)$, are calculated according to the formulas,

$$S(\omega; Q_0, T) = \frac{1}{2\pi} \int_0^\infty F_s(t; Q_0, T) \exp(i\omega t) dt \quad (13)$$

and

$$\chi''(\omega; Q_0, T) = \omega S(\omega; Q_0, T). \quad (14)$$

These quantities are shown in Figs. 4 and 5 for $n=0.6$; simi-

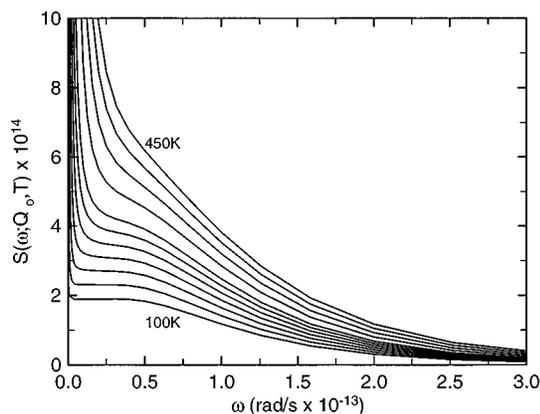


FIG. 4. Dynamic structure factor $S(\omega; Q_0, T)$ calculated by Eq. (13) with the $F_s(t; Q_0, T)$ given in Fig. 3. Temperatures from top to bottom are 450, 400, 350, 300, 250, 225, 200, 175, 150, 125, and 100 K.

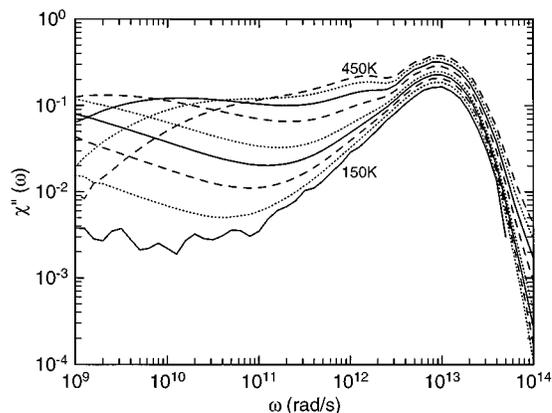


FIG. 5. Dynamic susceptibility $\chi''(\omega; Q_0, T)$ calculated from Eq. (14) and the $S(\omega; Q_0, T)$ given in Fig. 4. Temperatures from top to bottom are 450, 400, 350, 300, 250, 225, 200, 175, and 150 K.

lar calculations were performed for other values of the coupling parameter, including 0.2 and 0.4, but are not shown here.

MODE COUPLING THEORY

The coupling model results given in the previous section at least qualitatively resemble those obtained experimentally by quasielastic neutron scattering¹⁴⁻¹⁸ and light scattering,^{19,20} as well as by molecular dynamics simulations.²¹⁻²⁴ Most though not all investigators have chosen to analyze their data in a manner allowing for detailed comparisons with the predictions of mode coupling theory (MCT). In the sections to follow we shall subject the data generated from the coupling model to a similar treatment. The MCT has been extensively reviewed and discussed in the literature,^{13-20,27} here we summarize the essential results.

MCT predicts the existence of dynamic singularities at some temperature T_c above the calorimetric glass transition temperature T_g . Above T_c the density correlation function exhibits a two step decay—a fast local process (called the β relaxation) followed in time by the primary α relaxation responsible for the glass transition. In MCT much attention has been given to the fast β relaxation, which determines the density correlation function $\Phi_Q(t)$ for temperatures close to T_c and in a time region centered at a time defined by

$$t_\epsilon = t_0 / |\epsilon|^{1/2a}, \quad (15)$$

where $0 < a < 1/2$ and

$$\epsilon = |(T - T_c) / T_c|. \quad (16)$$

This t_ϵ is intermediate between the short microscopic time, t_0 , and the longer time associated with the α relaxation. For times $t_0 \ll t \ll t_\epsilon$ and $T < T_c$ or $T > T_c$, $\Phi_Q(t)$ decays according to a power law to a finite plateau value f_Q^c ,

$$\Phi_Q(t) = f_Q^c + h_Q(t_0/t)^a \quad (17)$$

with a temperature independent amplitude h_Q . For times $t \gg t_\epsilon$ the behavior of $\Phi_Q(t)$ depends on whether $T < T_c$ or $T > T_c$. For $T < T_c$,

$$\Phi_Q(t \gg t_\epsilon) = f_Q(T), \quad (18)$$

where

$$f_Q(T) = f_Q^c + h_Q[(T_c - T)/T_c]^{1/2}. \quad (19)$$

Thus, the long time limit $f_Q(T)$ of the β -process, which is often referred to as the “nonergodicity parameter” and may be viewed as an anomalous Debye–Waller factor, shows a critical behavior as T approaches T_c from below.

For $T > T_c$, $\Phi_Q(t)$ undergoes another decay in the time regime $t_\epsilon \ll t \ll t_\alpha$ according to another power law (referred to as the von Schweidler law)

$$\Phi_Q(t) = f_Q^c - h_Q[t/\tau_\alpha(T)]^b \quad (20)$$

which joins smoothly with the α -relaxation. This new time scale τ_α is given by

$$\tau_\alpha(T) = t_0 |\epsilon|^{-(1/2a + 1/2b)} = t_0 |\epsilon|^{-\gamma}, \quad (21)$$

where $0 < b < 1$ is another critical exponent. The two critical exponents a and b are related to each other by an equation that involve the Γ -function,

$$\Gamma^2(1-a)/\Gamma(1-2a) = \Gamma^2(1+b)/\Gamma(1+2b) = \lambda. \quad (22)$$

APPARENT EXISTENCE OF T_c AND THE $(T_c - T)^{1/2}$ ANOMALY

When the first power law decay [Eq. (16)] and the second von Schweidler law are well separated in time, the long time limit $f_Q(T)$ of the β -process for $T > T_c$ is given by f_Q^c together with the normal Debye–Waller factor contributed by the phonons. Combining this result of a long time limit for the β -process for $T > T_c$ with that for $T < T_c$ [see Eq. (19)], the MCT predicts a cusp in the temperature dependence of the anomalous Debye–Waller factor. The presence of such a cusp^{15,22,27} in experimental data has been used to support the existence of a critical temperature T_c and hence mode coupling theory.

We can analyze our coupling model derived data in the manner of others^{15,21,22} to deduce the anomalous Debye–Waller factor. The slow α -process, identified by MCT and evident in intermediate scattering function data (for example, see Fig. 4 of Ref. 15, Fig. 5 of Ref. 22, and Fig. 8 of Ref. 21), can be fitted by

$$F_s(t; Q, T) = f_Q(T) \exp[-t/\tau(Q, T)]^{\beta_{\text{MCT}}} \quad (23)$$

with the amplitudes $f_Q(T)$ identified with the anomalous Debye–Waller factors introduced in Eqs. (18) and (19). In carrying out this fitting of the synthetic data, the actual β used to construct the latter is ignored; instead the fitted KWW curve is chosen to deviate from the data at times similar to those found in MCT analyses (see, for example, Fig. 5 of Ref. 22).

Using this procedure in treating our density–density correlation function (Fig. 3 for $n=0.60$ or $\beta=0.40$), the resulting fits to the slow α process with a temperature independent $\beta_{\text{MCT}}=0.46$ are shown as dashed lines in Fig. 3. A temperature independent β_{MCT} according to Eq. (23) from MCT has constrained the fits in Fig. 3 to the forms shown there. The difference between $\beta_{\text{MCT}}=0.46$ and the $\beta=0.40$ used to generate the coupling model data via Eq. (11) is due to the absence of the nonergodicity parameter in the latter model.

At low temperatures, where there is no decay of the correlation function due to the α -process, the Debye–Waller factors are determined entirely by the harmonic phonons. The results for $f_Q(T)$ are plotted (as filled circles) in Fig. 2. At low temperatures, $f_Q(T)$ conforms to the well-known expression for a harmonic Debye phonon spectrum, viz., $\ln f_Q(T) = -WQ^2T$, as indicated by the dashed line in Fig. 2. However, for $T > 250$ K, $f_Q(T)$ begins to exhibit an anomalous decrease. This departure from linearity was fitted to the form given by Eq. (19) with a square root singularity. A good fit to our coupling model data for $T < T_c$ is obtained using Eq. (19) with $T_c=310$ K, $f_Q^c=0.47$, and $h_Q=0.32$ (solid curve in Fig. 2). In accord with MCT, the fit suggests the existence of a critical temperature T_c , both by the $(T_c - T)^{1/2}$ behavior and the cusp found in the temperature dependence of the Debye–Waller factor $f_Q(T)$.

Such behavior ostensibly implies the existence of the fast β -process of MCT; however, this cannot be the case. There is no critical behavior in the data, since it was generated from the coupling model. Rather than the fast β -process of MCT, there is instead a “fast” Debye relaxation operative at short times $t < t_c$. The anomalous behavior of the Debye–Waller factor is caused by this fast Debye process. The $(T_c - T)^{1/2}$ behavior, suggestive of an apparent critical temperature, is merely the consequence of the rapid increase in the decay of the short-time relaxation with temperature due to the Arrhenius temperature dependence of the relaxation time τ_0 [Eq. (12)]. The magnitude of activation enthalpy E_a of τ_0 depends on the chemical structure of the glass-forming liquid. For example, within a given class of materials, an increase in steric constraint usually raises the activation enthalpy barrier.^{9,10} The presence of E_a in the correlation function of the fast Debye process indicates the connection between relaxation dynamics and chemical structure.

A similar situation prevails for the slow α -process. In the coupling model, the coupling parameter n increases (Kohlrausch exponent, $\beta=1-n$, decreases) when the chemical structure is altered in a manner which enhances intermolecular constraints. This effect, property number (iii) in the Introduction, has been observed experimentally.^{9,10} A similar result is expected for microscopic relaxation via $F_s(t; Q, T)$. On the other hand, the relation between the Kohlrausch exponent β and chemical structure is not obvious from MCT.

APPARENT VON SCHWEIDLER LAW

One of the most important predictions of MCT is the existence of a von Schweidler law [Eq. (20)] for the beginning of the primary α -relaxation process. Both light scattering^{19,20,27} and neutron scattering^{15,18} experiments reveal evidence of the von Schweidler law in several glass-forming liquids. The exponents a , b , and γ were found to satisfy the relationship predicted by MCT. The idealized MCT also predicts that the relaxation time $\tau_\alpha(T)$ shows a power-law divergence at $T=T_c$ [see Eq. (21)], with the exponent γ related to the value of b [see Eqs. (21) and (22)]. This divergence is eliminated in the extended version of MCT.¹³ Recently, a molecular dynamics simulation of a su-

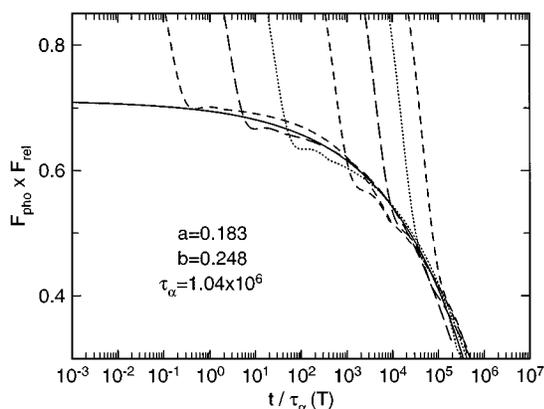


FIG. 6. Semilog plot of $F_s(t; Q_0, T)$ from Fig. 3 vs the scaled time $t/\tau_\alpha(T_{\text{ref}})$ to test for the presence of a von Schweidler law and any relation between the exponents, a and b .

percooled atomic liquid²³ also exhibited the von Schweidler law, with the correct time and temperature exponents' relationships.

We can examine our coupling model data for the presence of a von Schweidler law, and determine whether the exponents satisfy the exponent relations. To do this we adopt the procedure of Ref. 23. The variable is the scaled time $t/\tau_\alpha(T)$, and in order to test the scaling behavior we choose a reference temperature T_{ref} to be 200 K. In a semilog plot of $F_s(t; Q, T)$ against $\log t$, we shift the data for each temperature $T > 200$ K horizontally by the amount $\log A(T)$. This should produce a master curve, having the von Schweidler form given by Eq. (20). Furthermore, the temperature dependence of the relaxation time $\tau_\alpha(T)$, now given by

$$\tau_\alpha(T) = A(T) \tau_\alpha(T_{\text{ref}}) \quad (24)$$

should show a power-law divergence at some critical temperature T_c [Eq. (21)]. Finally, the exponents b and γ must satisfy the exponent relationship

$$\gamma = \frac{1}{2a} + \frac{1}{2b}. \quad (25)$$

The results of this procedure are shown in Fig. 6. The shifted curves superpose well to form a master curve only over a limited region as shown. For values of the ordinate below 0.3 (not shown), wherein contributions from the α -relaxation of MCT are present, the individual curves fan out, away from the master curve. This property is consistent with MCT in that the von Schweidler decay and the α -relaxation scale differently. The master curve is well fit by the functional form

$$\Phi(t) = 0.71 - 0.54 \left(\frac{t}{1.04 \times 10^6} \right)^{0.248} \quad (26)$$

and therefore $b = 0.248$. Using this value for b we obtain from Eqs. (22) and (25), $a = 0.183$ and $\gamma = 4.75$.

In Fig. 7 we have plotted $-\log A(T)$ against $\log(T - T_c)$, with T_c chosen to be T_{ref} . The data were fitted to a power law:

$$A(T) \propto (T - T_c)^{-4.3}. \quad (27)$$

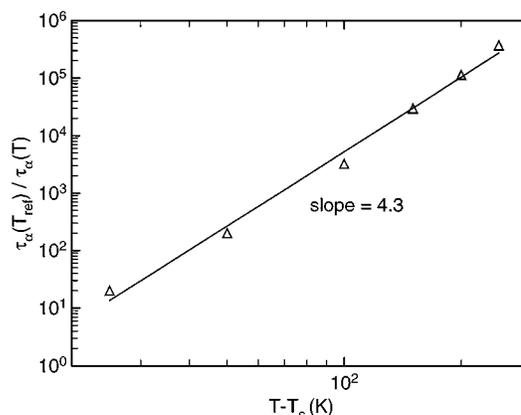


FIG. 7. Double logarithmic plot of the shift factor vs $(T - T_c)$; the straight line is the power law given by Eq. (27).

From the definition of the shift factor $A(T)$, the temperature dependence of $-\log A(T)$ is the same as that of $\log[\tau_\alpha^{-1}(T)]$, whereby $\tau_\alpha \propto (T - T_c)^{-4.3}$, with the exponent having a value close to that predicted by the relationship between the exponents b and γ . Thus, the predictions of MCT concerning the von Schweidler law are fulfilled in our data (synthesized using the coupling model) to comparable accuracy as found for a supercooled Lennard-Jones binary mixture of classical particles.²³

DEPARTURE FROM MCT (GLYCEROL)

Good agreement of the predictions of MCT with experimental observations^{14,19,20,27} has been found in a number of fragile glass formers, including calcium potassium nitrate (CKN), salol and o-terphenyl. However, a recent combined neutron and light scattering study of supercooled glycerol [$C_3H_5(OH)_3$] indicated deviations of the exponents of the β -process from their MCT-predicted values.⁴⁰ From these experiments the dynamic susceptibility, $\chi''(\omega; Q, T)$, which has a minimum at ω_{min} , was deduced. Above T_c , MCT predicts that

$$\chi''(\omega) = \chi_{\text{min}} [b(\omega/\omega_{\text{min}})^a + a(\omega_{\text{min}}/\omega)^b] / (a + b), \quad (28)$$

where a and b are related by Eq. (22), subject to the constraints $a < b$ and (if $b < 1$), $a < 0.395$. However, experimentally the susceptibility minimum occurs between ω^{-b} and ω^{+1} .⁴⁰ For frequencies above the minimum, $\chi''(\omega)$ increases much more steeply than the ω^a law with $a < 0.395$ expected from MCT. The experimental data yield values of a close to unity, while a fit using the above MCT Eq. (28) gave $b = 0.61$ and $a = 0.32$.

The macroscopic relaxation time of glycerol has a normalized (T_g/T) temperature dependence which is intermediate between the rapid variation seen in fragile glass formers and the mild variation in the so-called strong glass formers.^{9,41,42} As stated in the Introduction, the Kohlrausch exponent β anticorrelates with the normalized temperature dependence. Relaxation measurements performed in the macroscopic time regime have indeed found that the value of β for glycerol is larger than that of other fragile glass formers.⁴¹⁻⁴⁴ Susceptibility spectra from light scattering ex-

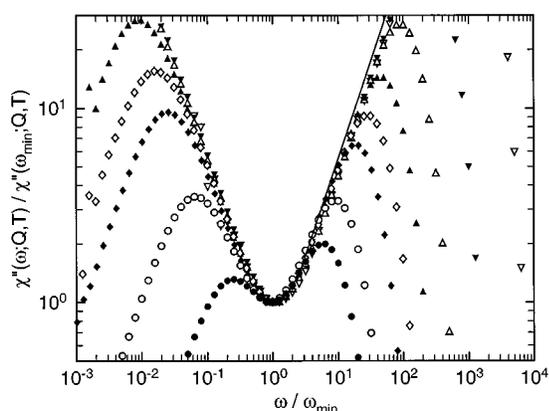


FIG. 8. The MCT scaling plot of the scaled dynamic susceptibility vs scaled frequency. The χ'' data are calculated for $n=0.20$ ($\beta=0.80$). The straight line with slope = +1 is drawn to illustrate the correspondence to experimental results (Ref. 40) for glycerol.

periments on glycerol at high temperatures⁴⁰ exhibit a low frequency peak which originates from the α -relaxation. The narrow width of this peak also indicates a relatively large β value for glycerol. Thus, it is appropriate to compare the behavior of glycerol with coupling model data employing a larger β value (e.g., $\beta=0.80$).

From the $F_s(t; Q, T)$ calculated for $\beta=0.80$, we obtain $\chi''(\omega; Q, T)$ via Eqs. (13) and (14). These data are used to construct a scaling plot of $\chi''(\omega; Q, T) / \chi''(\omega_{\min}; Q, T)$ against ω / ω_{\min} (see Fig. 8). The solid straight line, with slope = +1, illustrates the good agreement between the glycerol results and the coupling model data. Glycerol provides an example of a supercooled liquid whose behavior deviates from expectations drawn from MCT; however, the experimental results are in accord with the coupling model. It would be valuable to have neutron and light scattering data for other intermediate glass formers like glycerol, but having different chemical structures, as well as for strong glass formers. If the dynamic susceptibility of such materials behaves similarly to glycerol, the results will have significant implications for theoretical models.

CONCLUSIONS

The coupling model with additive phonon contribution was used to calculate the short (\sim ps) time dynamic properties of a dense system. Two simplifying assumptions were adopted—the transition from noncooperative to intermolecularly coupled relaxation occurs instantaneously at t_c , and the contribution from lattice vibrations is independent of the relaxation process—leading to Eq. (11). The intermediate scattering function, $F_s(t; Q, T)$, and, from its transform, the dynamic structure factor, $S(\omega; Q_0, T)$, and susceptibility, $\chi''(\omega; Q_0, T)$, were obtained at a series of temperatures, and analyzed in the manner suggested by mode coupling theory. The important result of this work is our finding that features of experimental data often taken as signifying the presence of critical phenomena, and hence serving to corroborate MCT, are present in data generated from the coupling model. We do not claim that the synthetic data generated from the

coupling model are consistent simultaneously in every respect with MCT. Nevertheless, since the coupling model asserts no critical temperature, evidently short-time relaxation results are ambiguous and perhaps misleading when interpreted according to the prescriptions of MCT.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research, in part under Contract No. N0001495WX20203. We would like to thank H. Z. Cummins, F. Fujara, W. Götze, W. Kob, W. Petry, R. Richert, J. Wuttke, and R. Zorn for helpful comments and suggestions.

- ¹ See papers published in *Proceedings of the 1st International Discussion Meeting on Relaxations in Complex Systems, Heraklion, Crete, Greece 1990*, published in *J. Non-Cryst. Solids*, 131 (1991); and *Proceedings of the 2nd International Discussion Meeting on Relaxations in Complex Systems, Alicante, Spain, 1993*, published in *J. Non-Cryst. Solid*, 172 (1994).
- ² J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980).
- ³ E. W. Fischer, *Physica A* **201**, 183 (1993).
- ⁴ D. J. Plazek and K. L. Ngai, *Macromolecules* **24**, 1222 (1991).
- ⁵ C. A. Angell, L. Monnerie, and L. Torell, *Symp. Mater. Res. Soc.* **215**, 3 (1992).
- ⁶ R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, *J. Chem. Phys.* **99**, 4201 (1993).
- ⁷ C. M. Roland and K. L. Ngai, *Macromolecules* **25**, 5765 (1992).
- ⁸ C. M. Roland, *Macromolecules* **27**, 4242 (1994).
- ⁹ K. L. Ngai and C. M. Roland, *Macromolecules* **26**, 6824 (1993).
- ¹⁰ C. M. Roland and K. L. Ngai, *Macromolecules* **24**, 5315 (1991); **25**, 1844 (1992).
- ¹¹ F. Fujara, B. Geil, H. Sillescu, and G. Fleischer, *Z. Phys. B* **88**, 195 (1992).
- ¹² For recent reviews, see, K. L. Ngai, in *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer, Berlin, 1994), pp. 89–152; K. L. Ngai and D. J. Plazek, *Rubber Chem. Technol.* (in press).
- ¹³ W. Götze and L. Sjögren, *Rep. Prog. Phys.* **55**, 241 (1992).
- ¹⁴ W. Knaak, F. Mezei, and B. Farago, *Europhys. Lett.* **7**, 529 (1988).
- ¹⁵ W. Petry, E. Bartsch, F. Fujara, M. Kiebel, H. Sillescu, and B. Farago, *Z. Phys. B* **83**, 175 (1991).
- ¹⁶ F. Fujara and W. Petry, *Europhys. Lett.* **4**, 921 (1987).
- ¹⁷ B. Frick, B. Farago, and D. Richter, *Phys. Rev. Lett.* **64**, 2921 (1990).
- ¹⁸ M. Kiebel, E. Bartsch, O. Debus, F. Fujara, W. Petry, and H. Sillescu, *Phys. Rev. B* **45**, 10 301 (1992).
- ¹⁹ G. Li, W. M. Du, A. Sakai, and H. Z. Cummins, *Phys. Rev. A* **46**, 3343 (1992).
- ²⁰ G. Li, W. M. Du, X. K. Chen, H. Z. Cummins, and N. J. Tao, *Phys. Rev. A* **45**, 3867 (1992).
- ²¹ R.-J. Roe, *J. Chem. Phys.* **100**, 1610 (1994).
- ²² L. J. Lewis and G. Wahnström, *Phys. Rev. E* **50**, 3865 (1994).
- ²³ W. Kob and H. C. Andersen, *Phys. Rev. Lett.* **73**, 1376 (1994).
- ²⁴ E.-G. Kim and W. L. Mattice, *J. Chem. Phys.* **101**, 6242 (1994).
- ²⁵ X. C. Zeng, D. Kivelson, and G. Tarjus, *Phys. Rev. E* **50**, 1711 (1994).
- ²⁶ P. K. Dixon, N. Menon, and S. R. Nagel, *Phys. Rev. E* **50**, 1717 (1994).
- ²⁷ H. Z. Cummins and G. Li, *Phys. Rev. E* **50**, 1720 (1994).
- ²⁸ K. L. Ngai, S. L. Peng, and K. Y. Tsang, *Physica A* **191**, 523 (1992).
- ²⁹ K. L. Ngai and K. Y. Tsang, *Macromolecular Chem. Phys.* (in press).
- ³⁰ J. Colmenero, A. Arbe, and A. Alegria, *Phys. Rev. Lett.* **71**, 2603 (1993).
- ³¹ J. Colmenero, in *Proceedings of the IV International Workshop on Non-Crystalline Solids* (World Scientific, Singapore, 1995).
- ³² K. L. Ngai and R. W. Rendell, *J. Non-Cryst. Solids* **131**, 942 (1991).
- ³³ K. Schmidt-Rohr and H. W. Spiess, *Phys. Rev. Lett.* **66**, 3020 (1991).
- ³⁴ C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963).
- ³⁵ R. B. Blackman and J. W. Tukey, *The Measurement of Power Spectra* (Dover, New York, 1958).
- ³⁶ W. Dieterich and K. L. Ngai (unpublished).
- ³⁷ K. L. Ngai, C. M. Roland, and G. N. Greaves, *J. Non-Cryst. Solids* **182**, 172 (1995).
- ³⁸ K. L. Ngai, C. H. Wang, G. Fytas, D. L. Plazek, and D. J. Plazek, *J. Chem. Phys.* **86**, 4768 (1987).

- ³⁹P. J. Flory, *Statistical Mechanics of Chain Molecules* (Hanser, New York, 1988).
- ⁴⁰J. Wuttke, J. Hernandez, G. Li, G. Coddens, H. Z. Cummins, F. Fujara, W. Petry, and H. Sillescu, *Phys. Rev. Lett.* **72**, 3052 (1994).
- ⁴¹K. L. Ngai, R. W. Rendell, and D. J. Plazek, *J. Chem. Phys.* **94**, 4 (1990).
- ⁴²C. A. Angell, in *Relaxations in Complex Systems*, edited by K. L. Ngai and G. B. Wright (U.S. GPO, Washington, D.C., 1984), p. 5.
- ⁴³N. O. Birge and S. R. Nagel, *Phys. Rev. Lett.* **54**, 2674 (1985).
- ⁴⁴S. R. Nagel, B. D. Williams, and J. P. Carini, *Phys. Rev. Lett.* **61**, 341 (1988).