

## $\alpha$ Relaxation of a Simple Molten Salt near the Glass Transition

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(Received 13 March 1987)

Predictions of mode-coupling theory for a schematic model of molten salts are shown to be consistent with recent neutron spin-echo experiments on  $\text{K}_{0.6}\text{Ca}_{0.4}(\text{NO}_3)_{1.4}$ . The theory relates the strong increase of viscosity fitted by  $\eta \propto (T - T_0)^{-\gamma}$  to the slow time decay of density fluctuations predicting a scaling function  $f(t/\tau)$  with  $\tau \propto \eta$ . For  $t \gtrsim \tau$ ,  $f(t/\tau)$  is well represented by  $\exp[-(t/\tau)^\beta]$  with  $\beta = 0.56$  in good agreement with experiment.

PACS numbers: 64.70.Pf, 61.25.Ks, 62.20.Hg

The relaxation behavior of liquids in the vicinity of the glass transition (GT) has been studied experimentally for many years. The dynamics of such systems may be characterized by the following observations:

(i) As the temperature is decreased towards the transition temperature  $T_g$ , structural relaxation processes slow down dramatically. This is reflected by certain correlation functions covering more than ten decades of their argument (measured in units typical for liquids at their triple point). Examples are the torsional stress relaxation function, the density relaxation function (see below), etc.

(ii) The shapes of these correlation functions do not change for different temperatures  $T$ , provided  $T$  is sufficiently close to  $T_g$ . They reduce to one master curve<sup>1,2</sup> if plotted versus  $t/\tau$  with a temperature-dependent scaling time  $\tau$ .

(iii) In general, liquids relax nonexponentially near the GT. In many cases the master function may be fitted well by a Kohlrausch-Williams-Watts (KWW) function  $\exp[-(t/\tau)^\beta]$  with  $0 < \beta < 1$ . Measurements of the frequency-dependent susceptibility reflect this phenomenon by showing a broad resonance ( $\alpha$  relaxation) with half-width of about two decades instead of 1.14 decades corresponding to exponential decay.<sup>3</sup>

(iv) Besides the dominant  $\alpha$ -relaxation peak, which disappears in the glass ( $T < T_g$ ), susceptibility measurements reveal a secondary peak ( $\beta$  relaxation) present near  $T_g$  on both sides of the transition.<sup>4</sup>

(v) As temperature is decreased to  $T_g$  the shear viscosity  $\eta$  of the liquid shows a strong increase which is often fitted with a Vogel-Fulcher function.<sup>5</sup> A similar increase is observed for the shear stress scaling time,  $\tau_s \propto \eta$ .

Note that universal exponents valid for large classes of substances are missing in the glass transition problem. Exponents such as  $\beta$  or  $\gamma$  (see below) differ from one system to another.

Theoretically, much effort has been put into deriving models of a liquid which lead to Vogel-Fulcher temperature dependence of the viscosity,<sup>6</sup> or which result in KWW time decay of correlation functions.<sup>7</sup> Only recently, mode-coupling theory (MCA), which had been

used successfully in the dynamics of liquids close to the triple point,<sup>8</sup> was suggested to be applied also to the description of supercooled liquids and the glass transition.<sup>9-13</sup> During the past three years there has been a series of papers<sup>14-24</sup> demonstrating that MCA describes an ergodic to nonergodic phase transition of the supercooled liquid, which seems to have all the features of the liquid-glass transition listed above. Unfortunately, comparison between theory and experiment is complicated by the lack of universality. It has been shown,<sup>16</sup> however, that simple schematic models may well represent certain aspects (e.g.,  $\beta$  relaxation) of actual systems near the glass transition, because various critical exponents all derive from one single system-dependent *exponent parameter*.

In this Letter we compare the predictions<sup>18</sup> of MCA on the behavior of mass-density relaxation functions of a molten salt with recent neutron spin-echo measurements<sup>25</sup> of this correlation function on the highly viscous salt mixture  $\text{K}_{0.6}\text{Ca}_{0.4}(\text{NO}_3)_{1.4}$ . Within our model, mass- and charge-density relaxation functions,  $\Phi_+(t)$  and  $\Phi_-(t)$ , respectively, obey generalized oscillator equations of motion ( $\mu = \pm$ )

$$\ddot{\Phi}_\mu(t) + \Omega_\mu^2 \Phi_\mu(t) + \int_0^t dt' \Omega_\mu^2 k_\mu(t-t') \dot{\Phi}_\mu(t') = 0, \quad (1)$$

with initial conditions  $\Phi_\mu(t=0) = 1$  and  $\dot{\Phi}_\mu(t=0) = 0$ , and they are coupled via the friction kernels

$$\begin{aligned} k_+(t) &= \lambda [\alpha \Phi_+^2(t) + (1-\alpha) \Phi_-^2(t)] + k_+^{\text{rest}}(t), \\ k_-(t) &= \lambda r \Phi_+(t) \Phi_-(t) + k_-^{\text{rest}}(t). \end{aligned} \quad (2)$$

Here  $k_\mu^{\text{rest}}(t)$  denote a regular contribution to the kernels which drops out from the following discussion near the liquid-glass transition. The parameters  $0 \leq \alpha \leq 1$  and  $0 < r < \infty$  are assumed fixed, while  $0 \leq \lambda < \infty$  denotes the interaction parameter driving the transition. It was demonstrated<sup>17</sup> that the models, represented by Eq. (1), for different  $(\alpha, r)$ , show a transition from ergodic to nonergodic behavior of  $\Phi_\mu(t)$  at a critical interaction parameter  $\bar{\lambda}$ . In the following  $\epsilon$  will denote the absolute distance from the transition point,  $\epsilon = |\lambda - \bar{\lambda}|/\bar{\lambda}$ , and  $\bar{f}_\mu$  the nonergodicity parameters at  $\epsilon = 0$ :  $f_\mu = \lim_{t \rightarrow \infty} \Phi_\mu(t)$ . For small  $\epsilon$  numerical solutions of Eq.

(1) for long times (compared to microscopic relaxation times) fall on one master curve, if the time argument is properly scaled. As expected from general considerations,<sup>16</sup> the solutions  $\Phi_\mu(t)$  on the *liquid* side of the GT mark two time regimes:

(1)  $\beta$  relaxation ( $\Omega^{-1} \ll t \ll \tau' \propto \epsilon^{-1/2a}$ ):  $\Phi_\mu(t)$  decrease with time according to a power law,

$$\Phi_\mu(t) \approx \bar{f}_\mu + \text{const}/t^a. \tag{3}$$

(2)  $\alpha$  relaxation ( $t \gg \tau'$ ):  $\Phi_\mu(t)$  decay nonexponentially to zero. This is the “quasielastic” decay with the averaged decay time  $\tau \propto \epsilon^{-\gamma}$  and the initial behavior of the decay

$$\Phi_\mu(t) \approx \bar{f}_\mu - \text{const} \times t^b. \tag{4}$$

Here  $\gamma = (a^{-1} + b^{-1})/2$ , with  $x = b$  ( $0 < b < 1$ ) and  $x = -a < 0$  denoting the two solutions of the equation

$$C(a, r) = \Gamma^2(x+1)/\Gamma(2x+1) \tag{5}$$

for  $\frac{1}{2} \leq C(a, r) \leq 1$ .  $\Gamma(x)$  denotes the  $\Gamma$  function and  $C(a, r)$  is the *exponent parameter*, which determines the dynamical behavior near the GT.

In order to apply the above model to  $\text{K}_{0.6}\text{Ca}_{0.4}(\text{NO}_3)_{1.4}$  we note that MCA of the frequency-dependent shear modulus for  $\alpha$ -relaxation results in (see also Refs. 10 and 16)

$$\eta \approx \sum_\mu V_\mu \int_0^\infty dt \Phi_\mu^2(t) \xrightarrow{\epsilon \rightarrow 0} \tau G_\infty \tag{6}$$

with

$$\Phi_\mu(t) \xrightarrow{\epsilon \rightarrow 0} g_\mu(t/\tau)$$

and

$$G_\infty = \sum_\mu V_\mu \int_0^\infty dt g_\mu^2(t),$$

i.e., the viscosity diverges like  $\tau$  within our approxima-

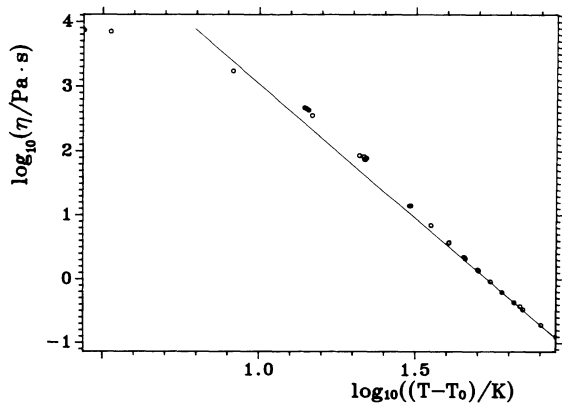


FIG. 1. Shear viscosity of  $\text{K}_{0.6}\text{Ca}_{0.4}(\text{NO}_3)_{1.4}$  ( $T_g \approx 60^\circ\text{C}$ ) circles: measurement (Ref. 5); line:  $\eta \propto (T - T_0)^{-\gamma}$  with fit parameters (Ref. 25)  $\gamma = 4.2$ ,  $T_0 = 90^\circ\text{C}$ .

tion, where  $\tau \propto \epsilon^{-\gamma}$ . The exponent  $\gamma = 4.2$  may be extracted from a fit to the measured viscosity<sup>5</sup> of the salt (see Fig. 1), if  $\epsilon \propto |T - T_0|$  is used. The latter proportionality results from the assumption of  $\lambda$  to be a *regular* function of temperature near the glass transition.<sup>26</sup> Very close to the glass transition  $\eta$  deviates from the power-law behavior as a result of hopping processes *not* included in Eq. (6). Recently, it was demonstrated that taking them into account will suppress the divergence of  $\eta$  and, very close to the transition, Arrhenius behavior of the viscosity will take over.<sup>24</sup> For this reason the temperature  $T_0$  will turn out to be slightly larger than the actual glass temperature  $T_g \approx 60^\circ\text{C}$ .

Now, via Eq. (5),  $\gamma = 4.2$  fixes the exponent parameter  $C(a, r) = 0.907$  and thus  $a = 0.203$  and  $b = 0.289$  (see Fig. 2). For the numerical solution of Eq. (1) we must then choose a pair  $(a, r)$  leading to the given  $C$ . Since  $r$  roughly corresponds to the ratio  $\Omega_+^2/\Omega_-^2$  at the peak positions of the static structure factors,<sup>17</sup> we expect  $r \gtrsim 4$  (a value taken from Fig. 4 in Bosse and Munkata<sup>27</sup> for a simple molten salt at higher temperature). We find that  $r = 6.35$ ,  $\alpha = 0.932$  is that choice leading to  $C = 0.907$  with the smallest possible  $r$  and closest to the above estimate.<sup>28</sup> Instead of finding solutions to Eq. (1) for  $t \gg \tau'$  we chose a different route here and solved on a computer the scaling equations corresponding to Eq. (1), which are given in Ref. 18, Eq. (4). The resulting mass-density master function

$$f(t/\tau) = g_+(t/\tau)/\bar{f}_+ \tag{7}$$

is shown in Fig. 3.

We now use this theoretical prediction to interpret neutron spin-echo experiments on the molten salt  $\text{K}_{0.6}\text{Ca}_{0.4}(\text{NO}_3)_{1.4}$ . For this we use Eq. (6) assuming  $T$ -independent  $G_\infty = 1.2 \times 10^9$  Pa and taking  $\eta(T)$  from Ref. 5 to fix the scaling time  $\tau(T)$ . Then we take the experimental points of Fig. 1 in Ref. 25 for  $T \geq 111^\circ\text{C}$ , normalize them with respect to their value  $A$  at  $t/\tau = 0$ , and insert them into our Fig. 3. The normalization con-

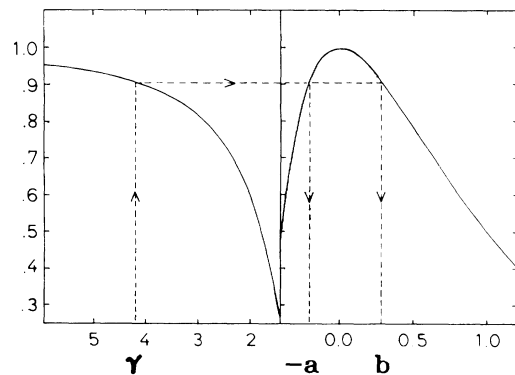


FIG. 2. Graph relating exponents  $\gamma$ ,  $a$ , and  $b$  according to Eq. (5).

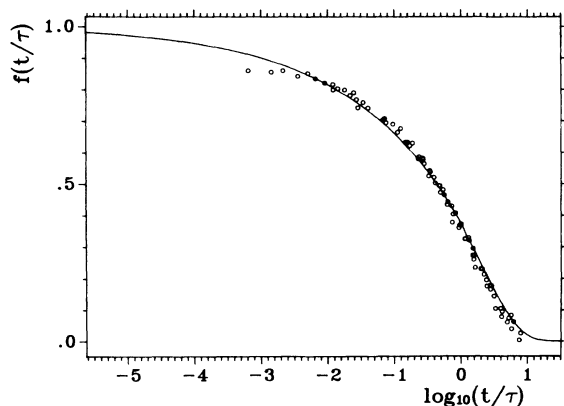


FIG. 3. Master function  $f(t/\tau)$ , Eq. (7), for  $r=6.35$ ,  $\alpha=0.932$  ( $C=0.907$ ) (line). Circles: Measurements from Ref. 25 (see text).

stant  $A$  is determined by a least-squares fit of the data to the theoretical master function to be  $A=0.97$ .

From the result of this procedure (Fig. 3) we note the following:

(i) The fitted normalization constant  $A=0.97$  deviates from the fit value 0.84 used in Ref. 25. This difference is, of course, due to the KWW master function used there. Note that the high value of our  $A$  allows for the inclusion of experimental data points at  $T=73^\circ\text{C}$  into the  $\alpha$ -relaxation regime.

(ii) The functional form of our master curve is not of simple KWW type, but for  $t \gtrsim \tau$  it deviates only negligibly from a KWW function with  $\beta=0.56$ , which is very close to the value 0.58 used in Ref. 25. However, for  $t < \tau$  the KWW function appreciably overestimates the theoretical master curve (up to 11% for  $t \approx 0.02\tau$ ).

(iii) When we consider the simple estimate of  $\tau(T)$  based on MCA, Eq. (6), the small spread of data points in this plot definitely demonstrates scaling behavior of the relaxation function.

(iv) Agreement between the predicted master function and the experimental points is quite reasonable over three decades. However, there seems to be a small systematic deviation between theory and the four shortest-time points of the lowest-temperature ( $T=111^\circ\text{C}$ ) measurement.

Of course, it would be desirable to have more data points in the short-time regime ( $t/\tau \lesssim 10^{-3}$ ) in order to allow for a final decision about the applicability to  $\text{K}_{0.6}\text{Ca}_{0.4}(\text{NO}_3)_{1.4}$  of the simple schematic molten-salt model presented above. We emphasize that earlier schematic models would *not* be applicable to the present salt. While the most simple model<sup>11,12</sup> predicts  $\gamma=1.765$  and exponential long-time decay, the schematic model investigated in Refs. 15 and 21 for given  $\gamma=4.2$  implies a master curve very similar to a KWW function with  $\beta=0.291$  [from Eq. (29) of Ref. 21], which differs only little from  $b=0.289$  of the initial quasielastic decay. Fi-

nally, the one-component Lennard-Jones system studied in Ref. 22 shows a deviation of  $\beta$  from the initial exponent  $b$  which is larger than the aforementioned. However, the fixed exponent parameter  $C=0.714$  of this model clearly prohibits its application to the salt  $\text{K}_{0.6}\text{Ca}_{0.4}(\text{NO}_3)_{1.4}$  (see Fig. 2). From this we conclude that coupling between mass-density and charge-density relaxation functions, which is the prominent feature of the one-wave-number model presented here, seems to be essential in describing the properties of the salt. Our model is the first capable of relating the measured  $T$  dependence of viscosity ( $\gamma=4.2$ ) to the measured nonexponential long-time decay of mass correlations in  $\text{K}_{0.6}\text{Ca}_{0.4}(\text{NO}_3)_{1.4}$ . That is possible because this model predicts a master curve, which interpolates between Eq. (4) for  $t \ll \tau$  with  $b=0.289$  and a KWW-type behavior with  $\beta=0.56$  for  $t \approx \tau$  proceeding to exponential decay for  $t \gg \tau$ .<sup>18,21</sup>

The authors are grateful to F. Mezei and W. Knaak for stimulating discussions on their experimental results prior to publication.

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