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Ergodic-nonergodic glass transition and enthalpy relaxation of a supercooled liquid $[Ca(NO_3)_2]_{0.4}(KNO_3)_{0.6}$

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The nonstationary enthalpy relaxation associated with the ergodicity-breaking glass transition as well as the dynamic specific heat, which characterizes the dynamics of the system in equilibrium, were investigated for a supercooled liquid $[Ca(NO_3)_2]_{0.4}(KNO_3)_{0.6}$. Dynamic specific-heat data show that serial decoupling of various relaxing modes does not occur in the glass transition region. It is demonstrated that the nonstationary enthalpy relaxation in the ergodic-nonergodic glass transition is accountable in terms of the equilibrium relaxation function if the latter is properly extended.

In recent years particular interest has been focused on the nature of the glass transition from a liquid to an amorphous solid.[1] Although liquids under equilibrium conditions are considered as disordered arrangements, lacking a long-range order, of molecules, they still possess structures in the short range. However, these orders are not of static nature and consequently they appear as structural fluctuations. When the temperature of a liquid, for example, is changed, the structure of a liquid changes according to the new equilibrium condition. While this *structural relaxation* occurs on a microscopic time scale in ordinary situations, slow relaxation manifests itself when a liquid is sufficiently cooled below the freezing temperature. Then the glass transition can be considered as a phenomenon of the relaxation time becoming longer, as the temperature is lowered at a certain rate, than the experimental time scale set by the cooling rate. The glass transition, therefore, describes the process in which a system falls out of equilibrium;[2] the transition is from an ergodic state to a nonergodic one.

Since this ergodicity breaking occurs due to the elongation of the time scale of the underlying dynamics, the glass transition phenomenon offers an opportunity to study the relationship between the fluctuations of an observable, enthalpy for instance, in equilibrium and its relaxation under the nonequilibrium condition (falling out of or recovering equilibrium). Since statistical mechanics rests on the ergodic principle, this constitutes a problem of fundamental interest.

In this letter, we report our investigation on this problem. Specifically, we measured the equilibrium isobaric dynamic specific heat $C_p(\omega)$ of supercooled $[Ca(NO_3)_2]_{0.4}(KNO_3)_{0.6}$ (CKN) as a function of temperature and frequency, and also obtained the enthalpy relaxation data of the glass transition at constant cooling and hearing rates using a differential scanning calorimeter (DSC). We will show that the *nonstationary,* instead of nonlinear, enthalpy relaxation of CKN in the process of ergodicity breaking or restoring can be accounted for if the equilibrium response function is properly modified. CKN is a binary mixture which becomes an ionic liquid when melted. Since potassium and calcium ions have spherical charge distributions and nitrate ions are of trigon shape, CKN represents one of simple systems which can stay undercooled for days without crystallization. This good glass-forming ability was essential for time-consuming dynamic specific-heat measurements. The sample preparation was done in the usual way.[3]

We first set up the theoretical framework within which the above two types of measurements can be described. The general equation for the response $\epsilon(t)$ of a system to an external perturbation $\sigma(t)$ can be written as[4]

$$\epsilon(t)=\int_{-\infty}^{t} K_1(t,t')\sigma(t')dt' + \int_{-\infty}^{t}\int_{-\infty}^{t} K_2(t,t',t'')\sigma(t')\sigma(t'')dt'dt'' + \cdots \quad (1)$$

Here ϵ is any strain quantity, σ is an externally applied stress quantity, and K_1 and K_2 represent the response functions. Equation (1) was derived under only two assumptions, causality and analyticity,[5] and therefore is applicable to a variety of linear and nonlinear situations. From the statistical-mechanical point of view, all the equilibrium or near-equilibrium properties of the system are described as a function of $\mathcal{H}_0/k_BT$, where $\mathcal{H}_0$, k_B, and T are the Hamiltonian of the system, the Boltzmann constant, and the temperature, respectively. For the temperature variation δT, the perturbing term in the Hamiltonian can be obtained from

$$\mathcal{H}_0/k_B(T+\delta T)\approx\mathcal{H}_0(1-\delta T/T)/k_BT \ .$$

Thus, the external perturbing field σ in our case is represented by $\delta T/T$ which couples to the Hamiltonian of the system. For the glass temperature of a few hundred degrees, $\delta T/T$ is small and thus only the first term in Eq. (1) is necessary not only for the dynamic specific-heat measurements where we keep δT intentionally small but also for the rate-scanning experiments where the constant cooling or heating can be considered as a succession of small temperature jumps.

For the isobaric thermal responses ϵ is equal to the enthalpy deviation from the equilibrium value, δH, per unit volume and Eq. (1) becomes

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$$\frac{\delta H(t)}{V}=\int_{-\infty}^{t} K_H(t,t')\delta T(t')dt'+C_p^{\infty}\delta T(t) , \tag{2}$$

where V denotes the volume. Here we have taken δT as the perturbation instead of $\delta T/T$ following the usual definition of the specific heat. C_p^{∞} represents the contribution from the fast degrees of freedom such as phonons and K_H is the response function due to the slow relaxation of the system. One can also represent Eq. (2) in terms of the relaxation function $R(t,t')=\int_{-\infty}^{t'} K_H(t,t'')dt''$. It is quite straightforward to show that Eq. (2) becomes

$$\frac{\delta H(t)}{V}=\Delta C_p\int_{-\infty}^{t}[1-\phi(t,t')]\delta\dot{T}(t')dt'+C_p^{\infty}\delta T(t) , \tag{3}$$

where $\Delta C_p \equiv R(t,t)$ and $\phi(t,t')\equiv R(t,t')/R(t,t)$ and the dot stands for the derivative. A couple of remarks on the nature of this equation are in order. First, the derivation is general enough that Eq. (3) may be regarded as a phenomenological equation applicable to general situations including rate-scanning measurements. Second, although Eq. (3) appears to be linear, it can become mathematically nonlinear if the function $\phi(t,t')$ itself changes in time. It is emphasized that this nonlinearity occurs as a result of the loss of stationariness, for example due to the elongation of the system dynamics, even for a small δT and will be called nonstationary relaxation. It is contrasted to the nonlinear response to a large perturbation represented by higher-order terms in Eq. (1). It is the nonstationary relaxation that may be dealt with by modifying the equilibrium relaxation function to account for the nonstationariness.

For the system in equilibrium the relaxation function has the additional property of being stationary, i.e., $R(t,t')=R(t-t')$. From the linear-response theory,[6] $R(t)=\langle \delta H_R(t)\delta H_R(0)\rangle /k_B T^2 V$ where δH_R represents the enthalpy fluctuation associated with the slow relaxation and $\Delta C_p = R(0)$. Then the complex dynamic specific heat may be expressed as

$$C_p(\omega)=C_p^0+i\omega\Delta C_p\int_0^{\infty}\phi(t)e^{i\omega t}dt , \tag{4}$$

where $C_p^0 \equiv C_p^{\infty}+\Delta C_p$ denotes the static specific heat.

For the measurements of the isobaric dynamic specific heat of CKN we used the fully automated dynamic calorimeter developed in this laboratory[7] and the technical details will be reported elsewhere.[8] The calorimeter adopts the 3ω technique which was originally developed by Birge and Nagle.[9,10] The 3ω technique is an ac method that uses a heater, which is in contact with a liquid sample, as a sensor simultaneously. By measuring the temperature oscillation of the heater due to an oscillating ac power in it as a function of frequency, one can measure a certain combination of the specific heat and the thermal conductivity depending on the geometry of the heater. The frequency range covered was from 0.01 Hz to 5 kHz and it means that we had a frequency window of more than five decades. By using line and planar heaters, we were able to obtain the specific heat C_p and the thermal conductivity κ of CKN independently.[8] κ of CKN did not show any appreciable change or any frequency dependence in the whole glass transition region and $\kappa \approx 5.9$ mW/cmK.[10] This suggests that the heat carrying modes, probably high-frequency phonons, are not affected at all by the glass transition.

In Fig. 1 shown are the real (C_p') and imaginary parts (C_p'') of the dynamic specific heat of CKN versus log$f$ (heating frequency $f=\omega/2\pi$). As is easily seen from the data, the dynamics of the system slows down with decreasing temperature (T) and the shape of C_p'' is asymmetrical. These features are typical of many glass formers; since it has been found that the Kohlrausch-Williams-Watts (KWW) function adequately describes the dynamics for them, the data at each temperature were fitted to

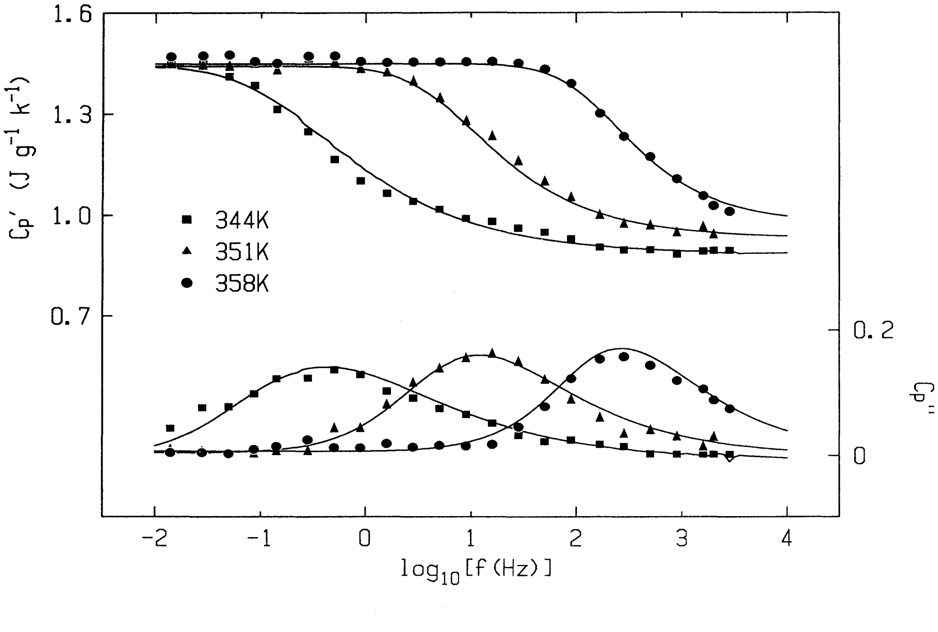

FIG. 1. The real and imaginary parts of $C_p(\omega)$ of CKN as a function of frequency. The solid lines are fits to the data with a Kaulrausch-Williams-Watts function, $\exp[-(t/\tau)^{\beta}]$, with β=0.53 (344 K), 0.57 (351 K), and 0.62 (358 K).

Eq. (4) with $\phi(t)=\exp[-(t/\tau)^{\beta}]$. To enhance the precision we have used the set of real and imaginary data simultaneously in fitting; it is noted that since C_p^0 does not vary with T, the fitting was done with three parameters, i.e., ΔC_p, τ, and β. The best-fit curves drawn through the data indicate that the KWW function is reasonable in describing the enthalpy relaxation of CKN.

In the upper inset of Fig. 2, the relaxation time τ obtained from the fitting is shown against $1/T$. The data illustrate that τ is not behaving in an Arrhenius fashion, but in a Vogel-Fulcher one. The solid line represents the best fit to the data using the Vogel-Fulcher form, $\tau=\tau_0\exp[\Delta/(T-T_0)]$. The fitting procedure yielded the values for parameters: $\tau_0=10^{-14.6}$ sec, $\Delta=1800$ K, $T_0=288\pm8$ K. These are reasonable physical values and T_0 is probably close to the Kauzmann temperature. Although the crossover from a Vogel-Fulcher to an Arrhenius behavior at low temperature was noted from the viscosity data,[11] we were not able to see the crossover in τ from our data alone, which represent the lowest-frequency dynamic characterization of CKN to date. The lower inset of Fig. 2 shows the KWW fitting parameter β versus T. From the figure it is found that β varies linearly in T. The significance of this behavior is that the width of $C_p''(\omega)$ increases as T decreases and thus any analysis based upon the fact that $\beta=$const, for instance time-temperature superposition, is not correct. This will also be of importance in analyzing the nonequilibrium data. It is of value to note that if we attempt the linear fitting of β versus T, we obtain, within experimental error, $\beta=\alpha(T-T_0)$ where α is a constant. With the reservation that the temperature range for the data is very far from T_0, it is worth pointing out that there exists a theory predicting such a behavior.[12] The relaxation strength, ΔC_p, also varies with T. Since C_p^0 remains constant for this particular system, the ΔC_p variation reflects the change in C_p^∞ of the liquid, the significance of which is discussed below.

One important consequence of our equilibrium measurements in CKN is that we can test a very interesting idea of serial decoupling of various relaxing modes in the glass transition region.[13] The idea is that while on short-time scales (or at high temperatures) the shear, volume, and enthalpy relaxation times are all the same, the shear modes decouple from the rest and the shear relaxation occurs at a faster rate as T is reduced toward the glass transition. To check the occurrence of decoupling, we plotted together, in Fig. 2, the enthalpy relaxation time (solid circles) and the shear relaxation time (= shear viscosity/infinity-frequency shear modulus, open circles) taken from Ref. 11. As is clear from the figure, the two kinds of relaxation times coincide reasonably well and no evidence of decoupling is seen within our time window. Thus, if decoupling did indeed occur, it should do so at longer times than ~10 sec.

Now that we have the full characterization of the equilibrium relaxation, we may attempt to explain the rate-scanning results. In the inset of Fig. 3, we show the DSC trace (solid lines) of CKN, as a function of T, taken at cooling and heating rates of 10 K/min with a Perkin-Elmer DSC-7 calorimeter. The DSC data on cooling show a typical transition from the value of the liquid specific heat (C_{pl}) at high temperatures to that of the glass specific heat (C_{pg}) at low temperatures, while the data on heating are the result of the system recovering equilibrium For comparison we have overlayed the dynamic specific heat measured at 100 Hz (open circles). Also plotted as solid circles in the figure is C_p^∞ from the KWW fitting of $C_p(\omega)$. It should be noticed that C_p^∞ varies with T, while C_{pg} does not show any appreciable variation as illustrated by the broken line in the figure. This can be understood if we remember that C_p^∞ is the

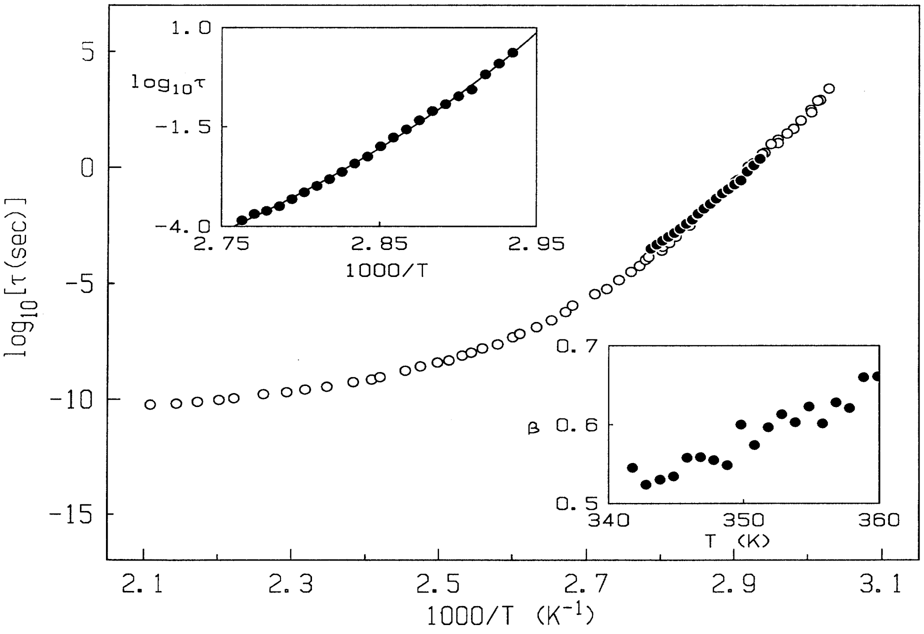

FIG. 2. The relaxation times of CKN on a log scale, vs T^{-1}. The solid circles denote the relaxation time from the dynamic specific-heat data, while the open circles denote the shear relaxation times from Ref. 11. The upper inset displays the Vogel-Fulcher fit of τ from the dynamic specific-heat data and the lower inset shows β as a function of T.

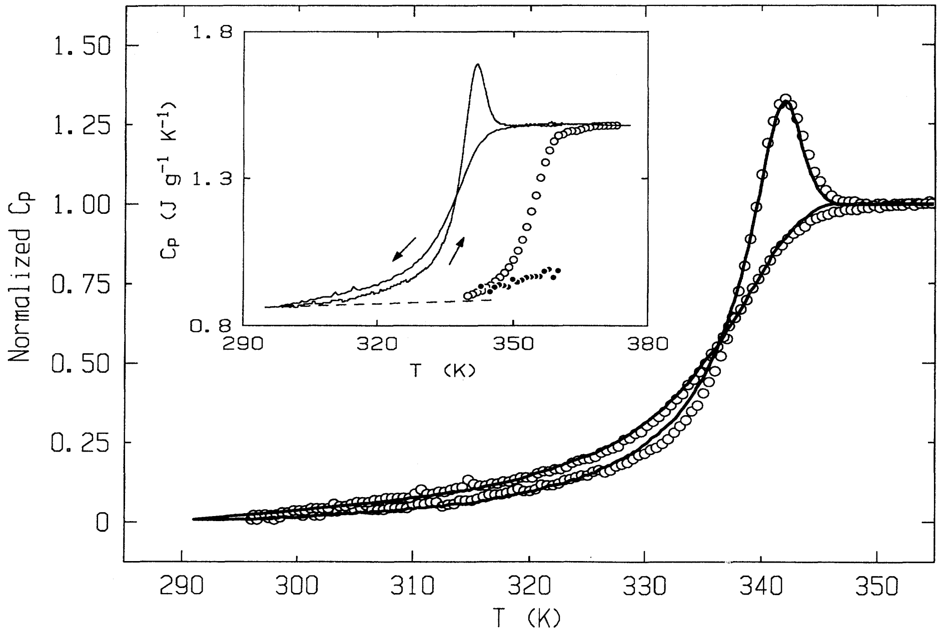

FIG. 3. The open circles represent the normalized specific heat, $[C_p(T)-C_{pg}(T)]/[C_{pl}(T_f)-C_{pg}(T_f)]$, and the solid lines are from the calculation. (See text.) Inset shows the DSC data on cooling and heating at 10 K/min (solid lines) and the dynamic specific-heat data at 100 Hz (circles). The dots in the inset denote C_p^∞ values of the equilibrium liquid, while the broken line denotes C_{pg}.

specific heat of the *equilibrium* liquid probed at high frequency and thus the structure of the liquid, which appears frozen to high-frequency thermal excitation, continues to change with T, while that of the glass does not vary much in T.

To understand the DSC results, we recall that the essence of the data lies in the broken stationariness; as the system is cooled at constant rate, the characteristic time of the relaxing modes gets longer and at some point the relaxing modes split off from other fast degrees of freedom which set the system temperature, T. (The converse is true in the case of heating.) To deal with this situation in a phenomenologically simple way, the configurational (or fictive) temperature T_f, which itself is a function of T, is defined through

$$H(T)=H_l(T_f)-\int_T^{T_f} C_{pg}(T')dT' , \tag{5}$$

where $H(T)$ is the measured enthalpy and $H_l(T)$ is the enthalpy of the equilibrium liquid.[14–16] Since C_{pg} represents the contribution from the fast degrees of freedom, Eq. (5) states that the enthalpy due to the relaxing modes is that at T_f while the temperature of the fast degrees of freedom is T. Thus, T_f signifies the temperature of the structural configuration of the relaxing modes. It is easy to show that dT_f/dT is the normalized specific heat due to the relaxing components, i.e., $dT_f/dT=[C_p(T)-C_{pg}(T)]/[C_{pl}(T_f)-C_{pg}(T_f)]$. Then, noting that the relaxation strength ΔC_p in the nonequilibrium situation is determined by the configuration temperature and C_{pg} is due to the fast degrees of freedom, Eq. (3) is transformed to the one for T_f (Ref. 17)

$$T_f(t)=T_i+\int_0^t[1-\phi(t,t')]\delta\dot{T}(t')dt' , \tag{6}$$

where T_i is the initial temperature.

To evaluate Eq. (6), one need to specify $\phi(t,t')$ which, however, is known only for equilibrium situations, where

$$\phi(t,t')=\phi(t-t')=\exp\{-[(t-t')/\tau]^\beta\} .$$

Moynihan *et al.*[14] developed a theory, building on previous works,[18] to deal with this situation and had great success in interpreting their DSC data of various glass-forming materials. However, one of the key assumptions they made in the absence of the equilibrium data, that is, β is constant, does not seem to be valid and therefore the theory must be improved. Since we do not have a universally accepted theory for the equilibrium KWW function, not to mention the nonstationary case, we resort to the idea of distribution of relaxation times and seek to extend it. The KWW function is expressed as

$$\exp\left[-\left[\frac{t-t'}{\tau}\right]^\beta\right]=\int d\tau_D g(\tau_D)\exp\left[-\frac{t-t'}{\tau_D}\right] ,$$

where $g(\tau_D)$ is the distribution function. Now we assume that the characteristics of the KWW function, β and τ, are determined by T_f, since T_f is the effective temperature of the relaxing modes; $\beta=\alpha(T_f-T_0)$ and

$$\tau=\tau_0\exp\left[\frac{1}{T}\left[\frac{\Delta}{1-T_0/T_f}\right]\right]$$

if T_f deviates from T. The latter assumption can be justified, as shown by Scherer,[19] by remembering the Adam-Gibbs theory:[20] $\tau=\tau_0\exp[\text{const}/TS_c]$, where S_c is the configurational entropy of the system. Thus the temperature-dependent barrier $\Delta/(1-T_0/T)$ of the Vogel-Fulcher law is determined by S_c and if $T\neq T_f$, T_f determines $S_c(T_f)$ which in turn fixes the barrier.

The distribution of the relaxation times can be represented either by the prefactor distribution with the barrier given by $S_c(T_f)$ or by the barrier distribution around $\Delta/(1-T_0/T_f)$. While the physical interpretation of the former representation is not easy compared to the latter, it gives the best results and so we used the former in the present calculation. Now that each τ_D is time dependent via T_f, each Debye relaxation of Eq. (7), $\exp[-(t-t')/\tau_D]$, is replaced by $\exp[-\int_{t'}^{t} dt''/\tau_D(t'')]$. Note that this is equivalent to assuming the exponential decay at each instant with τ_D of that moment. The time-varying nature of β is taken into account by making the distribution function $g(\tau_D)$ time dependent. It is noted that when β is constant, this becomes equivalent to the Moynihan method, i.e., $\phi(t,t')=\exp[-(\int_{t'}^{t} dt''/\tau)^{\beta}]$. With these ingredients, we solve numerically Eq. (6) with the same initial conditions as in actual experiments and calculate dT_f/dT. The results are shown, as thick solid lines, in Fig. 3 along with the properly normalized data points. The coincidence is striking. The main features of the rate-scanning, cooling as well as heating, data are faithfully reproduced. We have also calculated for the cases with different thermal histories with equal success.[8] Therefore, we have shown that the glass transition is basically a phenomenon due to the splitting off of the slow relaxing modes from the rest and the associated nonstationary relaxation can be described in the theoretical framework for the equilibrium relaxation if the latter is properly modified. Currently investigation of the nonlinear relaxation due to a large temperature jump, which would include higher-order effects in addition to nonstationariness, is underway.

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