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Heat capacity at the glass transition

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A fundamental problem of glass transition is to provide a quantitative and microscopic explanation of the heat-capacity jump at the glass transition temperature T_g. Similar problems are also common to other disordered systems, including spin glasses. We propose that the jump of heat capacity at T_g takes place as a result of the change of the liquid's elastic, vibrational, and thermal properties. In this theory, we discuss time-dependent effects of glass transition, and identify three distinct regimes of relaxation. Our approach explains a widely observed logarithmic increase of T_g with the quench rate and correlation of the heat-capacity jump with liquid fragility.

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I. INTRODUCTION

When a transition takes place between two distinct phases, the change of heat capacity and other thermodynamic quantities is consistently understood in a theory of phase transitions.[1] Often a disordered system such as a liquid forms a similarly disordered solid glass without a transition into a different phase, yet heat capacity changes with a jump. The jump is considered a hallmark of glass transition, and defines the glass transition temperature T_g. The heat-capacity jump immediately presents a problem that is at the heart of glass transition:[2,3] How can the jump be understood if there is no distinct second phase?

This problem remains unsolved and controversial. One set of theories rationalizes the jump in heat capacity by invoking the thermodynamics of phase transitions. An instructive illustration is the ongoing discussion of a popular theory of glass transition, the Adam-Gibbs theory.[4] The theory connects the change of heat capacity at T_g to the configurational entropy, which becomes zero below T_g where a phase transition between a liquid and a glass takes place.[2,5] The Adam-Gibbs theory has been convincingly criticized for a number of important reasons.[5] The main reason, also present in other similar theories, is that it has not been possible to identify the second low-temperature phase (the glass phase). To circumvent this problem, several theories have subsequently put forward proposals about the nonconventional mechanisms of the phase transition and nontrivial descriptions of the second phase, while retaining the idea of a phase transition of sorts.[2]

Another set of glass transition theories considers that glass transition phenomena at T_g have a purely dynamic origin, and simply correspond to the freezing of atomic jumps in a liquid at the experimental time scale.[2] The absence of a phase transition and thermodynamic effects at T_g are supported by the wide experimental observation that the liquid and the glass at T_g have a nearly identical structure.[2,3] For some of the dynamic theories, such as mode-coupling theories, the challenge is to explain the underlying microscopic physics of the heat-capacity jump and its large magnitude, which for some systems can be of the order of k_B per atom. According to the energy landscape approach to glass transition, the jump in heat capacity is related to the difference in sampling the minima of the potential energy landscape (PEL).[6] As the temperature is decreased, the system becomes trapped in one of the minima of the PEL, corresponding to the glassy state. It has been emphasized that the quantitative development of this idea, and making this idea predictive, is a major challenge.[6]

In addition to glass transition in structural liquids, similar problems exist in other disordered media. For example, spin glasses have seen large developments in ideas based on phase transitions and the existence of the second distinct phase. Similar to the structural glass transition, these theories have been used to explain the cusp in susceptibility at the glass transition temperature. Similar to the structural glass transition, several important problems remain in this field as well, including identifying the nature of a distinct spin-glass phase, dependence of the cusp on field frequency or observation time, slow relaxation effects, etc.[7]

In this paper, we analyze how liquid's elastic, vibrational, and thermal properties change on cooling. This analysis enables us to calculate the jump in heat capacity at T_g. Recall that the glass transition temperature T_g has two experimental definitions that give similar values of T_g. In the calorimetry experiments, T_g is the temperature at which the jump of constant-pressure heat capacity, C_p, is seen. In the experiments that measure τ (e.g., dielectric relaxation experiments), T_g is the temperature at which τ exceeds the time of the experiment t of $\sim 10^2$–10^3 s. We propose that when τ exceeds t, the jump in heat capacity at T_g follows as a necessary consequence, because freezing of local relaxation events alters liquid elastic, vibrational, and thermal properties, including bulk modulus and thermal expansion. In this theory, we discuss time-dependent effects of glass transition, and identify three distinct regimes of relaxation. Our approach explains the widely observed logarithmic increase of T_g with the quench rate and the correlation of the heat-capacity jump with liquid fragility.

II. CHANGE OF HEAT CAPACITY AT T_g

The commonly discussed quantity from the calorimetry experiments is the ratio of constant-pressure liquid heat capacity, C_p^l, to glass heat capacity, C_p^g. We do not consider the overshoot of heat capacity on heating, which is discussed elsewhere.[8,9] Heat capacities are considered at temperatures separated by the interval in which these effects decay to the values of C_p^l and C_p^g attributed to the liquid and the glass.[3,10] For various liquids, $\frac{C_p^l}{C_p^g} = 1.1$–$1.8$.[3] By using the known relationship $C_p - C_v = VT\alpha^2 B$, where C_v is the constant-volume heat capacity, α is the coefficient of thermal expansion, and B is the bulk modulus, we write

$$\frac{C_p^l}{C_p^g} = \frac{C_v^l + V_l T_l \alpha_l^2 B_l}{C_v^g + V_g T_g \alpha_g^2 B_g}, \tag{1}$$

where subscripts l and g refer to the liquid and the glass, respectively.

We start by addressing the origin of the difference between B_l and B_g and between α_l and α_g. Unlike in a solid glass, atoms in a liquid are not fixed, but rearrange in space. This gives liquid flow. Each flow event is a jump of an atom from its surrounding cage, accompanied by large-scale rearrangement of the cage atoms. We call this process a local relaxation event (LRE). A LRE lasts on the order of a Debye vibration period $\tau_0 = 0.1$ ps. Frenkel introduced liquid relaxation time τ as the time between LREs at one point in space in a liquid.[11] Frenkel's main idea was that at short times, $t < \tau$, the liquid response is the same as that of a solid, i.e., is purely elastic. On the other hand, for $t > \tau$, viscous flow takes place, during which each LRE is accompanied by additional viscous displacements. Hence, for $t > \tau$, the liquid response to external perturbation (e.g., pressure) consists of an elastic and a viscous response.[11] This discussion provided the microscopic basis for the earlier phenomenological model by Maxwell,[12] who proposed to separate elastic and viscous response in his viscoelastic approach to liquid flow.

Let us consider that pressure P is applied to a liquid. Pressure induces a certain finite number of LREs, which bring the liquid to the equilibrium state at new external conditions (P,T) after time τ. Following the Maxwell-Frenkel approach, the change of liquid volume, v, is $v = v_{\rm el} + v_r$, where $v_{\rm el}$ and v_r are associated with a solidlike elastic deformation and a viscous relaxation process owing to LREs, respectively. Let us now define T_g as the temperature at which τ exceeds the observation time t. This implies that LREs are not operative at T_g during the time of observation. Therefore, v at T_g is given by a purely elastic response as in the elastic solid. Then, $P = B_l \frac{v_{\rm el}+v_r}{V_l^0}$ and $P = B_g \frac{v_g}{V_g^0}$, where V_l^0 and V_g^0 are initial volumes of the liquid and the glass and v_g is the elastic deformation of the glass. Let ΔT be a small temperature interval that separates the liquid from the glass such that τ in the liquid, τ_l, is $\tau_l = \tau(T_g + \Delta T)$ and $\frac{\Delta T}{T_g} \ll 1$. Then $V_l^0 \approx V_g^0$. Similarly, the difference between the elastic response of the liquid and the glass can be ignored for small ΔT, giving $v_{\rm el} \approx v_g$. By combining the two expressions for B_l and B_g, we find

$$B_l = \frac{B_g}{\epsilon_1 + 1}, \tag{2}$$

where $\epsilon_1 = \frac{v_r}{v_{\rm el}}$ is the ratio of the relaxational and the elastic response to pressure.

α_l can be calculated in a similar way. Let us consider liquid relaxation in response to the increase of temperature by ΔT. We write $\alpha_l = \frac{1}{V_0^l}\frac{v_{\rm el}+v_r}{\Delta T}$ and $\alpha_g = \frac{1}{V_0^g}\frac{v_g}{\Delta T}$, where $v_{\rm el}$ and v_r are temperature-induced volume increases in a liquid that are related to a solidlike elastic and relaxational response, respectively, and v_g is the elastic response of the glass. By combining the two expressions and assuming $V_l^0 = V_g^0$ and $v_{\rm el} = v_g$ as before, we find

$$\alpha_l = (\epsilon_2 + 1)\alpha_g, \tag{3}$$

where $\epsilon_2 = \frac{v_r}{v_{\rm el}}$ is the ratio of relaxational and elastic response to temperature variation.

Equations (2) and (3) describe the relationships between B and α in the liquid and the glass that originate from the presence of LREs in the liquid above T_g and their absence in the glass at T_g, insofar as T_g is the temperature at which $t < \tau$. We note that the relaxational response v_r decays during time τ. Because B_g and α_g correspond to $t < \tau$, B_g and α_g are unrelaxed, or nonequilibrium, values of bulk modulus and thermal expansion, respectively. This point is discussed in Sec. III in detail.

By using Eqs. (2) and (3) in Eq. (1), we write

$$\frac{C_p^l}{C_p^g} = \frac{\frac{C_v^l}{C_v^g} + \gamma\alpha_g T_g \epsilon}{1 + \gamma\alpha_g T_g}, \tag{4}$$

where $\epsilon = \frac{(\epsilon_2+1)^2}{\epsilon_1+1}$, $\gamma = V_g\alpha_g B_g/C_v^g$ is the glass Grüneisen parameter, and C_p^g is the unrelaxed, or nonequilibrium (see Sec. III), heat capacity of the glass. We note that in Eq. (4), as in Eqs. (2) and (3), we set $T_l \approx T_g$ and $V_l \approx V_g$. This underestimates the experimental $\frac{C_p^l}{C_p^g}$, setting its lower limit, because C_p is measured in the finite range of temperature and volume such that $T_l > T_g$ and $V_l > V_g$.

We now calculate $\frac{C_v^l}{C_v^g}$. Generally, vibrational and diffusional motion both contribute C_v^l. However, close to T_g, only vibrational motion contributes to C_v^l, whereas the by contribution to C_v^l from to the diffusional motion is negligible. This is an important assertion that perhaps was not appreciated before, and simplifies the problem greatly. The assertion follows from the explicit calculation of liquid C_v as a function of τ,[13] and is consistent with the experimental results showing that liquid C_v is close to $3N$ close to the melting point.[14,15] It also follows from a more general argument that does not rely on the explicit calculation of C_v^l, as discussed below.

Above T_g, each atom participates in the vibrational motion during time τ and in the diffusional motion when it jumps between two equilibrium positions during a time of approximately τ_0. For $t \gg \tau$, atoms can be separated into two ensembles of $N_{\rm vib}$ vibrating and $N_{\rm dif}$ diffusing atoms. The energy of an atom in each ensemble consists of kinetic and potential energy. Then, the partition sum is $Z = Z_{\rm vib} \cdot Z_{\rm dif}$, where $Z_{\rm vib}$ and $Z_{\rm dif}$ are related to vibrations and diffusion, respectively. The liquid energy is $E = T^2 \frac{d}{dT}[\ln(Z_{\rm vib} \cdot Z_{\rm dif})] = T^2 \frac{d}{dT} \ln Z_{\rm vib} + T^2 \frac{d}{dT} \ln Z_{\rm dif} = E_{\rm vib} + E_{\rm dif}$, where $E_{\rm vib}$ and $E_{\rm dif}$ is the energy of the vibrating and diffusing atoms, respectively. Here and below, temperature derivatives are taken at a constant volume. At any given moment of time, $N_{\rm dif} = N_0 \exp(-U/T)$, where N_0 is the total number of atoms in a system and U is the activation energy barrier for a LRE (U can be temperature dependent). By combining it with $\tau = \tau_0 \exp(U/T)$, where τ_0 is the Debye vibrational period of ~0.1 ps, we write

$$N_{\rm dif} = N_0\frac{\tau_0}{\tau}, \tag{5}$$

which also directly follows by noting that the jump probability is $\frac{\tau_0}{\tau}$.

At T_g, $\frac{\tau_0}{\tau} \approx 10^{-16}$, i.e., the number of diffusing atoms is negligible. Therefore, the ratio of the energy of diffusion to the total energy, $\frac{E_{\rm dif}}{E}$, is negligible. Similarly, $\frac{E_{\rm dif}}{E_{\rm vib}} \ll 1$, giving

$$\frac{\frac{d}{dT}\ln Z_{\rm dif}}{\frac{d}{dT}\ln Z_{\rm vib}} \ll 1. \tag{6}$$

Liquid entropy is

$$\begin{aligned} S &= \frac{d}{dT}[T\ln(Z_{\rm vib}\cdot Z_{\rm dif})] \\ &= \left(T\frac{d}{dT}\ln Z_{\rm vib} + \ln Z_{\rm vib}\right) + \left(T\frac{d}{dT}\ln Z_{\rm dif} + \ln Z_{\rm dif}\right) \\ &= T\frac{d}{dT}\ln Z_{\rm vib} + \ln Z_{\rm vib} + \ln Z_{\rm dif}, \end{aligned}$$

where we have used Eq. (6). Then,

$$\begin{aligned} C_v^l &= T\frac{dS}{dT} \\ &= T\frac{d}{dT}\left(T\frac{d}{dT}\ln Z_{\rm vib}\right) + T\frac{d}{dT}\ln Z_{\rm vib} + T\frac{d}{dT}\ln Z_{\rm dif} \\ &= T\frac{d}{dT}\left(T\frac{d}{dT}\ln Z_{\rm vib}\right) + T\frac{d}{dT}\ln Z_{\rm vib}, \end{aligned}$$

where we have used Eq. (6) once more. Therefore, C_v^l close to T_g (as well as at any temperature T such that $\frac{\tau_0}{\tau(T)} \ll 1$) is essentially given by the vibrational contribution to Z.

We note in passing that if a LRE, as an act of diffusion, separates two distinct liquid configurations, the above result implies the absence of diffusional (or, if appropriate, configurational), contribution to liquid heat capacity at T_g. This is in contrast to previous approaches such as the Adam-Gibbs theory[4] and related models as well as the potential energy landscape approach.[6]

The vibrational states of a liquid are given by one longitudinal mode and two transverse modes with frequency $\omega > 1/\tau$.[11] If $\frac{\tau_0}{\tau} \ll 1$, as is the case close to T_g, transverse modes in a liquid account for essentially all transverse modes that exist in a solid glass. Together with the fact that the phonon density of states increases as $\propto \omega^2$, this means that the energy of the missing transverse waves with frequency $\omega < 1/\tau$ is negligible. Hence, the vibrational energy of a liquid in the regime $\frac{\tau_0}{\tau} \ll 1$ can be calculated as the energy of all $3N$ phonons as in a solid glass.[13] Therefore, in discussing the vibrational C_v of a liquid close to T_g, we can use the results derived for solids.

The partition function of a harmonic solid is $Z = (\frac{T}{\hbar\omega})^{3N}$ ($k_B = 1$), where ω is the geometrically averaged phonon frequency,[1] giving the free energy $F = 3NT\ln\frac{\hbar\omega}{T}$. In the purely harmonic case, ω is constant, giving the entropy $S = -(\frac{\partial F}{\partial T})_v = 3N(1+\ln\frac{T}{\hbar\omega})$ and $C_v = T(\frac{\partial S}{\partial T})_v = 3N$. On the other hand, anharmonicity, particularly large in liquids, results in the decrease of ω with temperature. Importantly, as we show below, this decrease is different below and above T_g because α is different [see Eq. (3)]. If ω is not constant, $S = 3N(1+\ln\frac{T}{\hbar\omega} - \frac{T}{\omega}\frac{d\omega}{dT})$, and

$$C_v = 3N\left[1 - \frac{2T}{\omega}\frac{d\omega}{dT} + \frac{T^2}{\omega^2}\left(\frac{d\omega}{dT}\right)^2 - \frac{T^2}{\omega}\frac{d^2\omega}{dT^2}\right], \tag{7}$$

where the derivatives are taken at constant volume.

The effect of anharmonicity can be discussed in the quasiharmonic approximation by introducing the Grüneisen parameter $\gamma = -\frac{V}{\omega}(\frac{\partial\omega}{\partial V})_T$ to the phonon pressure, $P_{\rm ph} = -(\frac{\partial F}{\partial V})_T = \frac{3NT\gamma}{V}$. Then, the bulk modulus from the (negative) phonon pressure is $B_{\rm ph} = -\frac{3NT\gamma}{V}$ and $(\frac{\partial B_{\rm ph}}{\partial T})_v = -\frac{3N\gamma}{V}$, where we neglected the dependence of γ on V. By using $\gamma = \frac{V\alpha B}{C_v}$ and $B = B_0 + B_{\rm ph}$, where B_0 is the zero-temperature bulk modulus, $(\frac{\partial B_{\rm ph}}{\partial T})_v = -\alpha(B_0 + B_{\rm ph})$, where we set $C_v = 3N$ in this approximation. For small αT, which is often the case in the experimental temperature range, this implies $B \propto -T$, consistent with the experiments.[16] We note that experimentally, B linearly decreases with T at both constant volume and constant pressure.[16] The decrease of B with T at constant volume results from the intrinsic anharmonicity related to the softening of an interatomic potential at large vibrational amplitudes; the decrease of B at constant pressure has an additional contribution from thermal expansion. By assuming $\omega^2 \propto B_0 + B_{\rm ph}$ and combining it with $(\frac{\partial B_{\rm ph}}{\partial T})_v = -\alpha(B_0 + B_{\rm ph})$ from above gives $\frac{1}{\omega}\frac{d\omega}{dT} = -\frac{\alpha}{2}$. Putting this in Eq. (7) gives

$$C_v = 3N(1+\alpha T). \tag{8}$$

We see that the derived expression for C_v is linear with T and depends on α but not on ω, unlike in Eq. (7). This result follows from Eq. (7) as long as $\frac{dB}{dT} \propto B$ or $\frac{d\omega}{dT} \propto \omega$.

From Eq. (8), $\frac{C_v^l}{C_v^g} = \frac{1+\alpha_l T_g}{1+\alpha_g T_g}$ at T_g. By using it in Eq. (4) and retaining only linear terms in αT [we find that the linearization and direct combination of Eqs. (4) and (8) give close values of $\frac{C_p^l}{C_p^g}$ below], we write

$$\frac{C_p^l}{C_p^g} = 1 + \gamma\alpha_g T_g(\epsilon - 1) + T_g(\alpha_l - \alpha_g). \tag{9}$$

Recalling that $\epsilon = \frac{(\epsilon_2+1)^2}{\epsilon_1+1} = \frac{\alpha_l^2}{\alpha_g^2}\frac{B_l}{B_g}$, we see that Eq. (9) relates $\frac{C_p^l}{C_p^g}$ to the changes of α and B that originate from the presence of a relaxational response in the liquid and its absence in the glass.

Interestingly, Eq. (9) predicts that temperature dependence of C_p should follow that of α. This is in agreement with recent simultaneous measurements of C_p and α showing that both quantities closely follow each other across T_g.[17]

Importantly, the jump in heat capacity at T_g in our theory takes place within the same single thermodynamic liquid phase, but below and above T_g the liquid has different values of α and B because LREs freeze at T_g where the liquid falls out of equilibrium. In this sense, our theory is purely dynamic. In contrast to previous glass transition theories,[2] we do not discuss transitions between distinct thermodynamic phases, even though it may be tempting to invoke thermodynamic

TABLE I. Experimental and calculated values of $\frac{C_p^l}{C_p^g}$. When more than one value of α, B, C_p, or γ was available, we have taken the average. PVAC, PS, OTP, OPP, and CKN stand for polyvinylacetate, polystyrene, orthoterphenyl, orthoterphenyl phenol, and $Ca(NO_3)_2$-KNO_3 mixture, respectively. The ratio of the last term in Eq. (9), $T_g(\alpha_l - \alpha_g)$, to the second term, $\gamma\alpha_g T_g(\epsilon - 1)$, varies from 0.1 in glycerol and 0.3 in OTP-OPP to 2 in $NaAlSi_3O_8$ and 4 in GeO_2.

	γ	T_g (K)	$\alpha_l \times 10^4$ (K^{-1})	$\alpha_g \times 10^4$ (K^{-1})	B_l (GPa)	B_g (GPa)	$\frac{C_p^l}{C_p^g}$ Calc.	$\frac{C_p^l}{C_p^g}$ Exp.
Glycerol	2.2[a]	190[b]	5[c]	1[c]	5.5[d]	9.9[d]	1.6	1.8[e]
PVAC	0.6[f]	304[f]	7.1[f]	2.8[f]	2[f]	3.5[f]	1.3	1.4[f]
OTP	1.2[g]	241[b]	7.2[h]	3[h]	2.1[h]	3.7[h]	1.3	1.5[e,i]
OTP-OPP	1.3[g]	235[j]	8.5[j]	2.5[j]	2.9[j]	5[j]	1.6	1.5[j]
PS	0.5[j,k]	355[j]	6[j]	2.5[j]	1.5[j]	2[j]	1.2	1.3[j]
CKN	0.9[f]	340[f]	3.6[f]	1.2[f]	7.6[f]	15.9[f]	1.2	1.6[f]
B_2O_3	0.3[f,l]	550[f]	4[f]	0.5[f]	2.6[f]	10[f]	1.3	1.4[f]
$NaAlSi_3O_8$	0.35[m]	1100[n]	0.54[m]	0.23[m]	20[m]	40[m]	1.05	1.11[m]
GeO_2	0.27[m]	580[m]	0.76[m]	0.27[m]	8.08[m]	23.87[m]	1.04	1.08[e,m]

[a] Reference 18.
[b] Reference 19.
[c] Reference 20.
[d] Reference 21.
[e] Reference 3.
[f] Reference 22.
[g] Reference 23.
[h] Reference 24.
[i] Reference 25.
[j] Reference 26.
[k] Reference 27.
[l] Reference 28.
[m] Reference 29.
[n] Reference 30.

phase transitions, conventional or unconventional, in order to explain the heat-capacity jump.

In Table I, we show $\frac{C_p^l}{C_p^g}$ for several common glass formers with both small and large $\frac{C_p^l}{C_p^g}$ in the range 1.1–1.8.[3] By using the experimental values of γ, T_g, α_g, α_l, B_g, and B_l,[18–30] we calculate $\frac{C_p^l}{C_p^g}$ by using Eq. (9). Given the approximations used, including $T_l = T_g$ and $V_l = V_g$ that underestimate $\frac{C_p^l}{C_p^g}$, Table I shows a reasonable agreement between the calculated and experimental values. The worse agreement for $Ca(NO_3)_2$-KNO_3 (CKN) is probably owing to the fact that it is a solution[3] for which our approximations are expected to be less successful. We further remark that the agreement is subject to uncertainties of γ, α, B, and $\frac{C_p^l}{C_p^g}$,[16,22] which are, moreover, taken from different experiments. For these reasons, we view Table I as an illustration that the differences between the existing values of α_g and α_l and between B_g and B_l are large enough to give the correct magnitude of experimental $\frac{C_p^l}{C_p^g}$.

III. TIME-DEPENDENT EFFECTS

The jump in heat capacity at T_g in Eq. (9) is the result of α and B acquiring different values below and above T_g as LREs freeze at T_g. This reflects the empirical definition of T_g as the temperature at which τ exceeds the observation time t, as in a glass transition experiment. We now remove the empirical constraint $\tau > t$, and consider the general case of the arbitrary relationship between τ and t. This gives time-dependent properties of $\frac{C_p^l}{C_p^g}$.

Lets now consider two liquids at two different temperatures T_1 and T_2 with relaxation times τ_1 and τ_2 such that $T_2 < T_1$ and $\tau_1 < \tau_2$, and calculate the ratio of their heat capacities, $\frac{C_{p,1}}{C_{p,2}}$. The response of both liquids to pressure now includes a viscous relaxational component owing to LREs. Hence, we write $P = B_1\frac{v_{\rm el}+v_{r,1}}{V_0}$ and $P = B_2\frac{v_{\rm el}+v_{r,2}}{V_0}$, where B_1,B_2 are the bulk moduli and $v_{r,1}$,$v_{r,2}$ are the relaxational responses of the two liquids, respectively. Combining the two expressions gives

$$\frac{B_1}{B_2} = \frac{1+\frac{v_{r,2}}{v_{\rm el}}}{1+\frac{v_{r,1}}{v_{\rm el}}}. \tag{10}$$

Similarly, considering temperature-induced response in the two liquids gives

$$\frac{\alpha_1}{\alpha_2} = \frac{1+\frac{v_{r,1}}{v_{\rm el}}}{1+\frac{v_{r,2}}{v_{\rm el}}}, \tag{11}$$

where α_1 and α_2 are thermal expansion coefficients of the two liquids.

When the relaxational response in the low-temperature liquid is absent, $v_{r,2} = 0$, Eqs. (10) and (11) become Eqs. (2) and (3). Note that v_r and $v_{\rm el}$ in Eqs. (10) and (11) are not the same because they are related to different effects of pressure and temperature. This difference will be accounted for below.

We now recall that the time dependence of strain and stress in low-temperature liquids follows a slow stretched-exponential form: $q = q_0[1 - e^{-(t/\tau)^\beta}]$.[2,3,31] Here, q is a relaxing quantity, q_0 is its amplitude, t is the observation time, and β is a stretching exponent that decreases from 1 at high temperature to 0.5–0.8 at T_g.[32] Recently, we proposed that slow relaxation in liquids is a result of elastic interaction between LREs via high-frequency elastic waves that they induce.[33] The stretched-exponential relaxation follows as a result of this interaction.[34]

Hence, $\frac{v_{r,1}}{v_{\mathrm{el}}} = q_0[1 - e^{-(t/\tau_1)^{\beta_1}}]$ and $\frac{v_{r,2}}{v_{\mathrm{el}}} = q_0[1 - e^{-(t/\tau_2)^{\beta_2}}]$, where β_1 and β_2 are stretching exponents in both liquids. Therefore, as follows from Eqs. (9)–(11), the time dependence of $\frac{C_{p,1}}{C_{p,2}}$ is given by the following three equations:

$$\frac{C_{p,1}}{C_{p,2}} = 1 + \gamma\alpha_2 T_2\left(\frac{\alpha_1^2}{\alpha_2^2}\frac{B_1}{B_2} - 1\right) + \alpha_2 T_2\left(\frac{\alpha_1}{\alpha_2} - 1\right), \qquad (12)$$

$$\frac{B_1}{B_2} = \frac{1 + \epsilon_1[1 - e^{-(t/\tau_2)^{\beta_2}}]}{1 + \epsilon_1[1 - e^{-(t/\tau_1)^{\beta_1}}]}, \qquad (13)$$

$$\frac{\alpha_1}{\alpha_2} = \frac{1 + \epsilon_2[1 - e^{-(t/\tau_1)^{\beta_1}}]}{1 + \epsilon_2[1 - e^{-(t/\tau_2)^{\beta_2}}]}, \qquad (14)$$

where we introduced relaxational amplitudes ϵ_1 and ϵ_2 as in Eqs. (2) and (3).

There are three times in Eqs. (12)–(14): t, τ_1, and τ_2. This sets three distinct regimes: (1) the fast regime $t \ll \tau_1 \ll \tau_2$; (2) the intermediate *glass transition* regime $\tau_1 \ll t \ll \tau_2$; and (3) the slow regime $\tau_1 \ll \tau_2 \ll t$. Each regime sets a different mechanism governing the relationship between the heat capacities of the two liquids.

Regimes (1) and (3) both give $\frac{\alpha_1}{\alpha_2} = 1$ and $\frac{B_1}{B_2} = 1$ in Eqs. (13) and (14), and therefore $C_{p,1} = C_{p,2}$ from Eq. (12), albeit for different physical reasons as discussed below.

Regime (1) corresponds to nonequilibrium states of both liquids and to nonequilibrium values of their C_p. In this regime, the terms in brackets in Eqs. (13) and (14) are close to zero because too little time elapses for any relaxation to take place. Physically, zero relaxational response in both liquids follows directly from Frenkel's idea that at short times, the response of a liquid is the same as that of a solid, i.e., purely elastic.[11] In this case, $C_{p,1} = C_{p,2}$ follows from the absence of relaxation in both liquids.

Regime (3) corresponds to equilibrium states of both liquids and to equilibrium values of their C_p. In this regime, the terms in brackets in Eqs. (13) and (14) are close to 1 owing to a relaxational response acquiring its maximal value as both liquids reach their equilibrium state, giving $C_{p,1} = C_{p,2}$. Importantly, our theory predicts no difference between $C_{p,1}$ and $C_{p,2}$ in equilibrium [except for the residual difference owing to $T_1 > T_2$ and $V_1 > V_2$ in Eq. (1) discussed earlier and the difference in C_v in Eq. (8) related to a finite temperature interval where $C_{p,1}$–$C_{p,2}$ is measured].

Regime (2) corresponds to the laboratory glass transition when the first liquid is in equilibrium ($\tau_1 \ll t$) but the second liquid is not ($t \ll \tau_2$). If the second liquid is defined as the glass, the change in heat capacity between the liquid and the glass follows: $1 - e^{-(t/\tau_1)^{\beta_1}}$ is close to 1 but $1 - e^{-(t/\tau_2)^{\beta_2}}$ is close to zero in Eqs. (13) and (14), giving $B_1 = \frac{B_2}{\epsilon_1 + 1}$ and $\alpha_1 = \alpha_2(\epsilon_2 + 1)$ as in Eqs. (2) and (3) and therefore nonzero $C_{p,1}$–$C_{p,2}$ in Eq. (12), as in Eq. (9). This is the important result of our theory.

We note that, by definition, the time range of regimes (1)–(3) is determined by the relationship between τ and the observation time t. In the calorimetry experiments in particular, C_p is measured on the time scale $t = 10^2$–10^3 s. Depending on τ, regimes (1)–(3) can be too fast or too slow for the experiment. For example, if $\tau_1, \tau_2 < 100$ s, regimes (1) and (2) are too fast for the experiment. On the other hand, regime (3) can be too slow for the experiment, and can last for astronomical times and longer. Let us consider SiO$_2$ glass at room temperature $T_r = 300$ K. The activation energy barrier U can be assumed to be temperature independent, because SiO$_2$ is a strong liquid. Then, from $\tau(T_g) = \tau_0 \exp(U/T_g)$ and $\tau(T_r) = \tau_0 \exp(U/T_r)$, $\tau(T_r) = \tau_0[\frac{\tau(T_g)}{\tau_0}]^{T_g/T_r}$. By taking $\tau_0 = 0.1$ ps, $T_g \approx 1500$ K, $\tau(T_g) = 10^3$ s, we find $\tau(T_r) = 10^{67}$ s, approximately the fourth power of the age of the Universe. For $t > \tau(T_r)$, SiO$_2$ at room temperature is an equilibrium liquid, and shows no jump in heat capacity on cooling from high temperature related to the freezing of LREs.

We remark that the above discussion of distinct relaxation regimes does not depend on the specific functional form of the decay of relaxing quantities $q(v_r)$ toward their steady state. We have used a stretched-exponential decay, but the same conclusions are reached for any other functional form of decay of relaxing quantities (e.g., exponential) as long as this decay takes place with a characteristic relaxation time τ.

Our theory explains two widely observed and important effects of glass transition. First, a well-known effect is that T_g, defined as the temperature at which the jump of heat capacity takes place in the calorimetry experiment, logarithmically increases with the quench rate q (see, e.g., Refs. 35 and 36). According to our discussion above, the jump in heat capacity at T_g takes place when the observation time t crosses liquid relaxation time τ. This implies that because $q = \frac{\Delta T}{t}$, τ at which the jump in heat capacity takes place is $\tau(T_g) = \frac{\Delta T}{q}$, where ΔT is the temperature interval of glass transformation range. By combining this with $\tau(T_g) = \tau_0 \exp(U/T_g)$ [here U is approximately constant because τ is nearly Arrhenius close to T_g (Ref. 33)], we find

$$T_g = \frac{U}{\ln\frac{\Delta T}{\tau_0} - \ln q}. \qquad (15)$$

According to Eq. (15), T_g increases with the logarithm of the quench rate q. In particular, this increase is predicted to be faster than linear with $\ln q$. This is consistent with the experimental results.[35] We note that this theory predicts no divergence of T_g because the maximal physically possible quench rate is set by the minimal internal time τ_0, Debye vibration period, so that $\frac{\Delta T}{\tau_0}$ in Eq. (15) is always larger than q.

Second, Eqs. (12)–(14) predict the correlation of $\frac{C_p^l}{C_p^g}$ with liquid fragility.[3,37] Let us apply Eqs. (12)–(14) to the glass transition regime where $t \ll \tau_2$. Then, $1 - e^{-(t/\tau_2)^{\beta_2}} = 0$ in Eqs. (13) and (14), corresponding to the absence of relaxational response in the glass. Next, let us consider that ΔT_g is the temperature interval in which $\frac{C_p^l}{C_p^g}$ is measured so that $\tau_1 = \tau(T_g + \Delta T_g)$ and $\tau_2 \approx \tau(T_g)$. Then, because β is nearly constant near T_g,[32] $f = 1 - e^{-(t/\tau_1)^{\beta_1}}$ in Eqs. (12)–(14) can be expanded close to T_g as $f \approx \frac{df}{d\tau}\frac{d\tau}{dT}\Delta T_g$, where the derivatives are taken close to T_g. From the definition of fragility $m = \frac{d\log\tau}{d\frac{T_g}{T}}|_{T=T_g}$, $\frac{d\tau}{dT}|_{T=T_g} \approx -\frac{\tau(T_g)}{T_g}m$. Next, $\frac{df}{d\tau}|_{\tau=\tau(T_g)} \approx -\frac{1}{\tau(T_g)}$, giving $f = \frac{\Delta T_g}{T_g}m$, and Eq. (12) becomes

$$\frac{C_p^l}{C_p^g} = 1 + \gamma\alpha_g T_g\left[\frac{\left(\epsilon_2\frac{\Delta T_g}{T_g}m + 1\right)^2}{\epsilon_1\frac{\Delta T_g}{T_g}m + 1} - 1\right] + \alpha_g\Delta T_g\epsilon_2 m. \tag{16}$$

If $m\frac{\Delta T}{T_g} \gg 1$, Eq. (16) simplifies to

$$\frac{C_p^l}{C_p^g} \approx 1 + \alpha_g\Delta T_g\epsilon_2\left(\gamma\frac{\epsilon_2}{\epsilon_1} + 1\right)m. \tag{17}$$

Equations (16) and (17) predict that $\frac{C_p^l}{C_p^g}$ increases with liquid fragility, provided other parameters do not change significantly. This is consistent with experimental data from a large set of liquids.[3,37] For a wider range of chemically and structurally different liquids, the correlation holds within distinct families.[38,39]

IV. SUMMARY

In summary, we observe that when a transition takes place between two distinct phases, anomalies in the thermodynamic functions are explained by the phase transition theory, a well-understood topic in physics.[1] If a distinct second phase cannot be identified as in the glass transition, the apparent anomalies can be explained in a picture that does not invoke phase transitions and thermodynamics, but where the system stops relaxing on the experimental time scale. Our approach explains time-dependent effects of glass transition, including a widely observed logarithmic increase of T_g with the quench rate and the correlation of heat-capacity jump with liquid fragility.

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[1] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Nauka, Moscow, 1964).
[2] J. C. Dyre, Rev. Mod. Phys. **78**, 953 (2006).
[3] C. A. Angell, Science **267**, 1924 (1995).
[4] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).
[5] J. C. Dyre, T. Hechsher, and K. Niss, J. Non-Cryst. Solids **355**, 624 (2009).
[6] P. G. Debenedetti and F. H. Stillinger, Nature (London) **410**, 259 (2001).
[7] J. A. Mydosh, *Spin Glasses: An Experimental Introduction* (Taylor & Francis, London, 1993).
[8] C. T. Moynihan, Rev. Mineral. **32**, 1 (1995).
[9] J. P. Sethna, *Entropy, Order Parameters, and Complexity* (Clarendon, Oxford 2009).
[10] L. M. Wang, V. Velikov, and C. A. Angell, J. Chem. Phys. **117**, 10184 (2002).
[11] J. Frenkel, in *Kinetic Theory of Liquids*, edited by R. H. Fowler, P. Kapitza, and N. F. Mott (Oxford University Press, Oxford, UK, 1947), pp. 188–249.
[12] J. C. Maxwell, Philos. Trans. R. Soc. London **157**, 49 (1867).
[13] K. Trachenko, Phys. Rev. B **78**, 104201 (2008).
[14] G. Grimvall, Phys. Scr. **11**, 381 (1975).
[15] D. C. Wallace, Phys. Rev. E **57**, 1717 (1998).
[16] O. L. Anderson, *Equations of State of Solids for Geophysics and Ceramic Science* (Oxford University Press, Oxford, UK, 1995).
[17] K. Takegawa, K. Fukao, and Y. Saruyama, Thermochim. Acta **432**, 212 (2005).
[18] J. Dawidowski, F. J. Bermejo, R. Fayos, R. Fernández Perea, S. M. Bennington, and A. Criado, Phys. Rev. E **53**, 5079 (1996).
[19] R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, J. Chem. Phys. **99**, 4201 (1993).
[20] I. V. Blazhnov, N. P. Malomuzh, and S. V. Lishchuk, J. Chem. Phys. **121**, 6435 (2004).
[21] T. Christensen and N. B. Olsen, Phys. Rev. B **49**, 15396 (1994).
[22] P. K. Gupta and C. T. Moynihan, J. Chem. Phys. **65**, 4136 (1976).
[23] C. M. Roland and R. Casalini, J. Phys. Condens. Matter **19**, 205118 (2007).
[24] M. Naoki and S. Koeda, J. Phys. Chem. **93**, 948 (1989).
[25] S. S. Chang and A. B. Bestul, J. Chem. Phys. **56**, 503 (1972).
[26] S. Takahara, M. Ishikawa, O. Yamamuro, and T. Matsuo, J. Phys. Chem. B **103**, 792 (1999); **103**, 3288 (1999).
[27] C. K. Wu and M. Shen, J. Macromol. Sci., Phys. B **7**, 559 (1973).
[28] G. Carini *et al.*, J. Phys. Condens. Matter **18**, 10915 (2006).
[29] D. B. Dingwell, R. Knoche, and S. L. Webb, Phys. Chem. Miner. **19**, 445 (1993).
[30] A. G. Whittington, M. A. Bouhifd, and P. Richet, Am. Mineral. **94**, 1 (2009).
[31] J. C. Phillips, Phys. Rev. B **73**, 104206 (2006).
[32] R. Casalini, K. L. Ngai, and C. M. Roland, Phys. Rev. B **68**, 014201 (2003).
[33] K. Trachenko and V. V. Brazhkin, J. Phys. Condens. Matter **21**, 425104 (2009).
[34] K. Trachenko, Phys. Rev. B **75**, 212201 (2007).
[35] R. Brüning and K. Samwer, Phys. Rev. B **46**, 11318 (1992).
[36] A. Hunt, J. Non-Cryst. Solids **160**, 183 (1993).
[37] L. M. Wang, C. A. Angell, and R. Richert, J. Chem. Phys. **125**, 074505 (2006).
[38] C. M. Roland, P. G. Santangelo, and K. L. Ngai, J. Chem. Phys. **111**, 5593 (1999).
[39] D. Huang and G. B. McKenna, J. Chem. Phys. **114**, 5621 (2001).