Glass Transition Singularities

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A unified understanding is given for the Vogel-Fulcher (T_{VF}), Kauzmann (T_K), glass transition (T_g), and crossover (T_x) temperatures in supercooled liquids on the basis of a heuristic ansatz for trapped and nontrapped diffusive motions, where these characteristic temperatures are related to the divergence of various moments of the waiting time distribution for the nontrapped diffusive motion. Three predictions (i) $T_K = T_{\mathrm{VF}}$, (ii) $T_g s_c(T_g) \sim$ const, and (iii) $T_x s_c(T_x)/T_g s_c(T_g) = 2$, where $s_c(T)$ is the excess entropy per atom, are made, which are consistent with experimental observations.

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Since the early 1920s, several characteristic temperatures in supercooled liquids, which I call the glass transition singularities, have been defined or determined through the analysis of dynamic and thermodynamic properties: the Vogel-Fulcher (VF) point T_{VF} is a temperature obtained by extrapolating the viscosity η in the supercooled state above the glass transition point by $\eta \propto \exp[DT_{\mathrm{VF}}/(T - T_{\mathrm{VF}})]$ $(D > 0)$ to lower temperatures [1]. The glass transition temperature T_g is usually defined as the temperature where calorimetric quantities show an anomaly [2]. Recently, T_g is understood as the temperature at which dynamical properties instead of thermodynamic properties change their nature. For example, it is considered to be related to the ergodic to nonergodic transition in the density fluctuation in the mode-coupling theory [3]. In the trapping diffusion model [4], it is considered to be a transition from the Gaussian to non-Gaussian dynamics. Kauzmann [5] argued that there would be a temperature T_K below which the entropy of a liquid in the supercooled state becomes smaller than that in the crystalline state and that this is possible only if the system were kept in metastable equilibrium. From dielectric measurements, Johari and Goldstein [6] distinguished two relaxation modes (α and β relaxations) below a certain temperature T_{JG}. A crossover temperature T_x between liquid-type and solid-type dynamics has also been argued by Angell [7]. According to the present consensus, the relation $T_{\mathrm{VF}} \sim T_K < T_g < T_x \sim T_{\mathrm{JG}} < T_M$ (T_m is the melting temperature) is believed to hold. The ergodic-to-nonergodic transition point T_c predicted by the mode-coupling theory [3] is supposed to be between T_g and T_m, in particular, between T_x and T_m for a soft-sphere system.

In this Letter, I give a clear and unified view of the characteristic temperatures T_{VF}, T_K, T_g, and T_x which are clearly defined in the present model. I base my argument on the following observations of the dynamics in supercooled liquids: Near the freezing point atoms perform diffusive motion all the time as in the liquid state. When they are further cooled, some atoms begin a trapped-diffusive (or stray) motion for a while, and some time later a long nontrapped motion occurs, which can be viewed as a jump motion. At much lower temperatures, the fraction of atoms with trapped-diffusive motion increases, and below a certain temperature all atoms become trapped and nontrapped motion cannot occur again. The structural relaxation is mainly caused by the nontrapped motion.

The characteristic feature of these changes can be well described by the waiting time distribution (WTD) $\psi(t)$ for the nontrapped diffusive motion, which is defined as the probability density that an atom makes a jump motion at time t with no jumps between time $t = 0$ and time t. Note that one can define the WTD only when the trapped and nontrapped motions can be distinguished. The WTD acquires a long tail as the temperature is lowered. One can identify three characteristic temperatures by various moments of the WTD [8]. When the tail gets longer, the second moment begins to diverge at some point (T_2), while the first moment is finite. At a lower temperature (T_1), the first moment begins to diverge. Finally, at much lower temperatures below some point (T_0), the WTD cannot be normalized because of the long tail, namely, the zeroth moment diverges. I argue that T_0, T_1, and T_2 can be considered to be the VF temperature ($T_{\mathrm{VF}} = T_0$), the glass transition temperature ($T_g = T_1$), and the crossover temperature ($T_x = T_2$), respectively. I further show that (1) the VF temperature must be identical to the Kauzmann temperature ($T_{\mathrm{VF}} = T_K$), (2) the glass transition point is determined by $Ts_c(T)$ as Adam and Gibbs [9] suggested, and (3) $T_x s_c(T_x)/T_g s_c(T_g) = 2$ would hold. Here $s_c(T)$ is the excess entropy per atom of the supercooled liquid. Although predictions (2) and (3) are derived under a certain ansatz, experiments currently available appear to support these predictions.

The elementary relaxation process can occur in an area which can provide the critical excess entropy S_0^* required for the process. The critical excess entropy S_0^* is supposed to be close to $k\ln 2$, where k is the Boltzmann constant, as proposed first by Adam and Gibbs [9]. Now suppose the excess entropy per atom for a given system to be $s_c(T)$. Then the number of atoms in the area is given by

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$n = S_0^*/s_c(T)$. The existence of these kinds of regions has been proposed by many authors [10] as cooperatively rearranging domains (or regions). In these regions, atoms perform two types of diffusive motion: trapped diffusion (or stray motion) and jump (nontrapped) motion. The latter is mainly responsible for the structural relaxation. To determine the jump rate of the nontrapped motion, I follow the argument of the absolute rate process by Eyring [11]. If one focuses on one particular atom in the domain, its jump rate w leading to the structural relaxation at a given temperature T and pressure would be written as

$$w = \nu w_b \exp[-n\Delta\mu/kT], \tag{1}$$

where w_b is the attempt frequency which is comparable to the jump rate producing the trapped diffusive motion, $\Delta\mu$ is the excitation chemical potential per atom, and ν denotes the efficiency of moving out from the excited state [11]. I denote $\nu\omega_b$ as w_0, which serves as the time scale of the jump motion, and note that $w \leq w_0$ holds in general since $\Delta\mu \geq 0$.

The distribution $p(\Delta\mu)$ of the excitation chemical potential $\Delta\mu$ is determined by the distribution of excited energy (chemical potential) levels of the region. Suppose $\sigma(\epsilon)$ is the density of possible excited levels at ϵ through which a transition might be possible. The probability distribution for the excited energy is determined by the probability that the system goes through the channel at $\Delta\mu$, namely, it is given by the product of the probability of a level being at $\Delta\mu$ and the probability that the other possible levels below $\Delta\mu$ are not used [12]. Therefore, $p(\Delta\mu)$ is given by

$$p(\Delta\mu) = C\sigma(\Delta\mu)\exp\left[-\int_0^{\Delta\mu} \sigma(\epsilon)\, d\epsilon\right], \tag{2}$$

where C is a normalizing constant. Using the mean value theorem for integration, $p(\Delta\mu)$ can be written as

$$p(\Delta\mu) = C\sigma(\Delta\mu)\exp(-\overline{\sigma}\Delta\mu), \tag{3}$$

where $\overline{\sigma} = \int_0^{\Delta\mu} \sigma(\epsilon)\, d\epsilon/\Delta\mu$ is the mean value of $\sigma(\epsilon)$. Since the distribution function $P(w)$ for the jump rate w is related to $p(\Delta\mu)$ by

$$P(w) = p[\Delta\mu(w)] \left| \frac{d\Delta\mu}{dw} \right|, \tag{4}$$

it is straightforward to show that $P(w)$ is given by

$$P(w) = \begin{cases} \frac{(\rho+1)w^\rho}{w_0^{\rho+1}} & \text{when } w \leq w_0, \\ 0 & \text{when } w > w_0, \end{cases} \tag{5}$$

with

$$\rho = \frac{kT\overline{\sigma}s_c(T)}{S_0^*} - 1. \tag{6}$$

Here, I have neglected the dependence of $\overline{\sigma}$ on $\Delta\mu$ and approximated $\sigma[\Delta\mu(w)]$ by $\overline{\sigma}$, since $\sigma[\Delta\mu(w)]$ depends on w through $\ln w$. It should be noted that the cutoff in Eq. (5) appears due to Eq. (1) with $\Delta\mu \geq 0$. It should also be emphasized that the jump rate distribution (5) coincides exactly with that found from the molecular dynamics simulation of soft spheres in the supercooled state and employed in the trapping diffusion model (TDM) of the glass transition [4] and with the lifetime distribution of hydrogen bonds in a water model [13]. In the TDM, $w_b/w_0 \sim 20$ was found by assigning the β peak of the generalized susceptibility to the trapped dynamics with a constant jump rate w_b.

It has been shown [14] that the WTD corresponding to the jump rate distribution (5) is given by

$$\psi(t) = (\rho + 1)w_0\Gamma(\rho + 2)\gamma^*(\rho + 2, w_0 t), \tag{7}$$

where $\Gamma(x)$ and $\gamma^*(a,x)$ are the gamma function and the Tricomi incomplete gamma function, respectively. Thus it is easy to show that the mth moment $\tau_m \equiv \int_0^\infty t^m \psi(t)\, dt$ of the WTD is given by

$$\tau_m = \begin{cases} \frac{\rho+1}{\rho-m+1} w_0^{-m} & \text{when } \rho > m - 1, \\ \infty & \text{when } \rho \leq m - 1, \end{cases} \tag{8}$$

namely, when ρ is reduced, the mth moment begins to diverge at $\rho = m - 1$. In particular, the second and first moments begin to diverge at $\rho = 1$ and $\rho = 0$. For $\rho \leq -1$, the zeroth moment diverges, which indicates that the WTD cannot be normalized.

One can expect significant changes in the dynamical aspects of the structural relaxation at these points. In fact, in the TDM of glass transition the stochastic dynamics of a tagged particle which is determined by the jump rate distribution (5) was studied on a lattice, and the following conclusions were obtained: (1) The main relaxation time diverges exponentially at $\rho = -1$, indicating that $\rho = -1$ is the VF temperature [4,15]. (2) A transition between Gaussian and non-Gaussian dynamics is expected at $\rho = 0$, which is considered to be the glass transition point T_g [4]. (3) A kinetic transition is expected at $\rho = 1$, where some of the dynamic characteristics change [4]. The typical behavior of this transition is seen in the exponent representing the decay of the non-Gaussian parameter, which is unity for $\rho \geq 1$ and becomes less than unity for $\rho < 1$. The self-part of the dynamic structure factor $S_s(\mathbf{q}, \omega)$ is also expected to show a change; for $0 < \rho < 1$, the first derivative of $S_s(\mathbf{q}, \omega)$ at $\omega = 0$ must be singular and for $\rho > 1$ $dS_s(\mathbf{q}, \omega)/d\omega$ is not singular at $\omega = 0$ [4]. I define the crossover temperature T_x by these behaviors.

Comparing Eq. (6) and these results of the TDM, I predict that (1) $T_K = T_{\mathrm{VF}} = T_0$, since $\rho = -1$ indicates $s_c = 0$; (2) $T_g = T_1$ ($\rho = 0$) satisfies $kT_g s_c(T_g) = S_0^*/\overline{\sigma}$; and (3) $T_x = T_2$ ($\rho = 1$) satisfies $kT_x s_c(T_x) = 2S_0^*/\overline{\sigma}$. Therefore, for a given material, $Ts_c(T)$ is the relevant parameter for glass transition and $T_g s_c(T_g) \sim$ const and $T_x s_c(T_x)/T_g s_c(T_g) = 2$ for experiments in which $S_0^*/\overline{\sigma}$ can be kept constant.

These predictions can be tested by experiments. The first prediction $T_K = T_{\rm VF}$ has long been expected, though some experiments show differences in these two temperatures [16]. Although this ambiguity is inevitable since T_K and $T_{\rm VF}$ are defined by extrapolation, the present model predicts that T_K and $T_{\rm VF}$ must coincide if they are defined properly.

The second prediction that the glass transition point is determined by $Ts_c(T)$ and not by $s_c(T)$ was first given by Adam and Gibbs [9]. This statement has recently been tested by Takahara, Yamamuro, and Suga [17], in which they studied the pressure dependence of T_g up to 198 MPa of pressure of 1-propanol and 3-methyl-pentane and found little dependence of $T_g s_c(T_g)$ on pressure. According to their analysis, the activation chemical potential changes only 10% even for the highest pressure they studied. Thus we expect that $\overline{\sigma}$ did not change much in their experiment, and the present prediction can be applied to their experiment. The third prediction $T_x s_c(T_x)/T_g s_c(T_g) = 2$ can also be tested by experimental data. It is not clear at this moment that T_x defined above is identical to those observed and/or defined previously. Angell [7] suggested $T_x/T_g \sim 1.3$ for various glass forming materials. Assuming that T_x is more or less the same as that defined by Angell and using the data in Fig. 2(b) of Ref. [7], I found for polypylene carbonate, tri-α-naphtyl benzene, 3-methyl pentane, $H_2SO_4 \cdot 3H_2O$, and ethanol that the ratio is in the range 2.0–2.2. Here $T_x/T_g = 1.3$ is assumed except for $H_2SO_4 \cdot 3H_2O$ for which $T_x/T_g = 1.2$ is used. For $Ca(NO_3)_2 \cdot 4H_2O$ and $KCl \cdot 2BiCl$ ($T_x/T_g = 1.2$ is used), the ratio is 2.4–2.5. In view of the ambiguity in determining the crossover temperature, no firm conclusion can be drawn at this stage, but the data do seem to be in rough agreement with the present prediction.

In conclusion, I have presented a unified understanding of the glass transition singularities on the basis of an heuristic argument and have given three predictions which seem to be in rough agreement with experiments. It should also be noted that the slow relaxations in supercooled liquids have been well explained by the TDM; the α relaxation is due to the nontrapped diffusive motion, and the trapped diffusive motion gives rise to the β relaxation [4]. Although there is no abrupt change in the microscopic dynamics nor in the form of the WTD, the nature of dynamics can show transitions when the various moments of the WTD begin to diverge.

It is important to note that this view of the glass transition singularities based on the singularities of the WTD does not depend on the details of the mechanism of the structural relaxation, and is considered to be fairly universal and can be applied to glass transitions in general.

Prediction (3) can be tested directly by experiments, since the non-Gaussian parameter can be measured by the small angle neutron scattering and thus T_x can be determined without ambiguity. The transition at T_x can also be observed through the behavior of $S_s(\mathbf{q}, \omega)$ near $\omega = 0$. I strongly urge that these experiments be performed.

Finally, I would like to mention the cooling rate dependence of the glass transition point. In the present approach, this dependence can be understood from the cooling rate dependence of the density of excited levels $\sigma(\epsilon)$ and the excess entropy $s_c(T)$. It will be plausible to assume that the dependence of $\sigma(\epsilon)$ is much weaker than that of $s_c(T)$. For slow cooling $s_c(T)$ stays at a rather higher value till the temperature gets closer to T_0 and decreases rapidly near T_0, and $s_c(T)$ for fast cooling decreases more gradually. This accounts for the fact that the glass transition point for fast cooling is higher than that for slow cooling. I also expect that T_0, T_1, and T_2 come closer for slow cooling.

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