A unified theory for the glass transition singularities

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A unified view for the glass transition singularities is given on the basis of a heuristic argument for the elementary relaxtion process. Three predictions are made: (i) the Kauzmann temperature T_K is eqaul to the Vogel-Fulcher temperature T_{VF}, and the glass transition temerature T_g satisfies (ii) $T_g s_C(T_g) \sim$ constant and (iii) $T_x s_C(T_x)/T_g s_C(T_g) = 2$, where T_x is the crossover temperature and $s_C(T)$ is the excess entropy per molecule.

1   Introduction

When a liquid is cooled down, there are two routes to solidify; one is the crystallization at the melting point and the other is the vitrification. In the crytallization process, molecules (or atoms), which move around without trapping in the liquid state, become completely localized around local potential minima. On the other hand, the dynamics of molecules in the vitrification process takes a significantly different path: In the vicinity of the melting point molecules perform diffusive motion without retardation. When they are further cooled down, some molecules may be trapped and begin to do a trapped-diffusive motion for a while and sometime later they moves out the trapped region by making a long non-trapped (jump) motion. At much lower temperatures, the fraction of trapped molecules increases, and below a certain temperature all molecules become localized.

In the vitrification process, several characteristic temperatures have been observed or defined: the Vogel-Fulcher point T_{VF} is a temperature obtained by extrapolating the viscosity η in the supercooled state above the glass transition point by $\eta \propto \exp[DT_{VF}/(T - T_{VF})]$ ($D > 0$) to lower temeratures[1]. The glass transition temperature T_g is usually defined as the temperature where calorimetric quantities show an anomaly[2]. Recently, T_g is believed to be the temperature at which dynamical properties instead of thermodynamic properties change their nature. Kauzmann[3] 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. There are some evidences that there exists a characteristic temperature T_x between the glass transition and melting temperatures where the dynamical trait begins to change [4, 5].

In this paper, I present a clear and unified view for the characteristic temperatures T_{VF}, T_K, T_g and T_x on the basis of the stochastic model for the elementary relaxation process. These points are shown to be essential in the vitrification process and to be related to the divergence of various moments of the waiting time distribution. Furthermore, I predict that (i) $T_K = T_{VF}$, (ii) $T_g s_C(T_g) \sim$ constant and (iii) $T_x s_C(T_x)/T_g s_C(T_g) = 2$, where $s_C(T)$ is the excess entropy per molecule. These predictions are appeared to be consistent with experimental observations.

2 Waiting time distribution

As explained in the Introduction, the non-trapped motion occuring among localized molecules plays important role in the vitrification process. The change in the characteristics of the non-trapped motion can be understood by the waiting time distribution (WTD) $\psi(t)$ for the non-trapped motion, which is defined as the probability density that a molecule makes a jump motion at time t with no jumps betwee time $t = 0$ and t. The WTD acquires a long tail as the temperature is reduced. Figure 1 shows typical behavior of the WTD.

The elementary relaxation process is possible only 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 Boltzman constant, as proposed first by Adam and Gibbs[6]. I denote the excess entropy per molecule by $s_C(T)$. Then, the number of molecules in the area is given by $n = S_0^*/s_C(T)$.

The non-trapped dynamics can be considered as an activation process. Exploiting the argument of the absolute rate process by Eyring[7], one can write the jump rate w as

$$w = w_0 \exp[-n\Delta\mu/kT], \tag{1}$$

where w_0 is a constant determined by the attempt frequency comparable to the jump rate for the trapped motion and the efficiency of moving out from the excited state, $\Delta\mu$ is the excitation chemical potential per molecule. Note that $w \le w_0$ in general.

Let the distribution of excited energy (chemical potential) levels of the region to be $\sigma(\epsilon)$. Then, the distribution $p(\Delta\mu)$ of the excitation chemical potential is determined 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. I assume the existence of the mean value of $\sigma(\epsilon)$: $\bar{\sigma} = \frac{1}{\Delta\mu}\int_0^{\Delta\mu} \sigma(\epsilon)d\epsilon$. Using the mean value theorem for integration, one can write $p(\Delta\mu)$ as

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

From Eqs. (1) and (3), we find the distribution function $P(w)$ for the jump rate w

$$P(w) = \begin{cases} \dfrac{(\rho+1)w^\rho}{w_0^{\rho+1}} & \text{when } w \le w_0 \\ 0 & \text{when } w > w_0 \end{cases}. \tag{4}$$

with $\rho = k\bar{\sigma}Ts_C(T)/S_0^* - 1$. Here, we have neglected the dependence of $\bar{\sigma}$ on $\Delta\mu$ and approximated $\sigma[\Delta\mu(w)]$ by $\bar{\sigma}$ since $\sigma[\Delta\mu(w)]$ depends only weakly on w through $\ln w$.

It has been shown [8] that when the jump rate distribution is given by Eq. (4), the WTD $\psi(t)$ behaves as

$$\psi(t) \sim t^{-(\rho+2)} = t^{-[k\bar{\sigma}Ts_C(T)/S_0^*+1]} \qquad (\text{as } t \to \infty). \tag{5}$$

It is straightforward to show that the n-th moment of the WTD $\tau_n \equiv \int_0^\infty t^n\psi(t)dt$ diverges when $\rho \le n - 1$, namely when $k\bar{\sigma}Ts_C(T)/S_0^* \le n$.
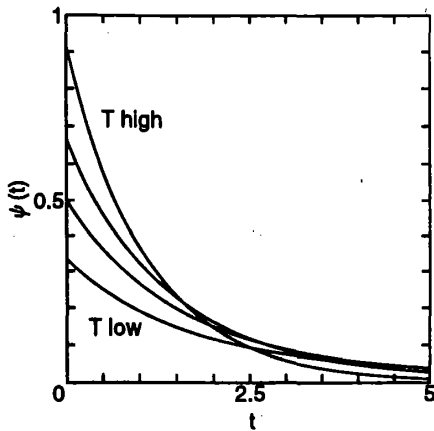
Fig. 1. A schematic plot of the waiting time distribution (WTD) for various temperature. While the WTD decays rapidly for higher temperatures, it acquires a long tail for lower temperatures.
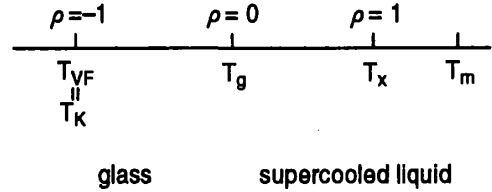

Fig. 2. A schematic figure for the glass transition singularities.

3 Glass transition singularities

The trapping diffusion model(TDM) of the glass transition introduced by Odagaki and Hiwatari treats the stochastic dynamics governed by the jump rate distribution (4) on a lattice.[9] Solving a trapping-type master equation with the jump rate distribution (4) using the coherent medium approximation, they showed that $\rho = -1$, 0 and 1 can be considered as the Vogel-Fulcher, glass transition and crossover temeratures, respectively.[9,10]

Combining the relation between rho and $s_C(T)$ and results described above, I arrive at the following conclusions.[11] (1) At the Vogel-Fulcher temperature $(\rho = -1)$, the excess entropy must vanish, $s_C = 0$, and thus we expect $T_{VF} = T_K$. For experiments where $\bar{\sigma}$ is kept constant, (2) $T_g s_C(T_g)$ =constant and (3) the crossover temperature satisfies $T_x s_C(T_x)/T_g s_C(T_g) = 2$.

We can compare these predictions with experiments. Although some experiments suggest the opposite,[12] the relation $T_K = T_{VF}$ has long been expected. Direct comparison of them is rather ambiguous because both T_K and T_{VF} are defined by extrapolation. It is significant, however, that $T_K = T_{VF}$ is predicted by a simple theory.

The second prediction that the relevant parameter for glass transition is $T s_C(T)$ instead of $s_C(T)$ is identical to the conclusion given by Adam and Gibbs[6]. This statement has recently been confirmed by Takahara et al for 1-propanol and 3-methyl-pentane.[13]

The third prediction $T_x s_C(T_x)/T_g s_C(T_g) = 2$ can also be tested by experiments. The definition of T_x so far reported is ambiguous and it is not clear if it is identical to that defined above. Angell[5] suggested $T_x/T_g \sim 1.3$ for various glass forming materials. Assuming that T_x is more or less same as that defined by Angell and using the data in Fig. 2(b) of Ref. [5], I found for polypylene carbonate, tri α-naphtyl benzene, 3 methyl pentane and ethanol that the ratio is indeed in 2.0 - 2.2. Thus the experimental data seem to be in line with the present prediction.

4 Summary

I have presented a unified view for the dynamical singularities in supercooled liquids on the basis of a stochastic dynamics of molecules. The dynamical singularities are related to the divergence of various moments of the WTD. Figure 2 shows the relative position of the singular points and their relation to the parameter ρ.

I have made three predictions for the dynamical singularities which seem to be in rough agreement with experiments.

The present model can also explain the slow relaxations in supercooled liquids[9]: α-relaxation is produced by the non-trapped diffusive motion and the trapped motion gives rise to the β-relaxation. 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. One may think singularities due to higher moments. It should be, however, emphasized that the present argument is valid only when the WTD is well defined, namely the trapped motion can be distinguished from the non-trapped motion. Therefore, it is irrelevant to discuss the divergence of every higher moments.

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 be applied to glass transitions in general.

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