# Experiment and Theory of Glass transition

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**Abstract**

Though belong to well-known state of matter, microscopic understanding of glassy state is still challenging for scientists. This article will summarize theoretical and experimental effort have been made to unveil mystery of glass, begin with experimental phenomena like dramatic change of viscosity below glass transition temperature $T_g$ , fragility, aging and dynamical correlation function of glass etc. For theoretical side, we emphasize random first-order transition theory of glass transition studied by Peter Wolynes.

# 1 Introduction

Condensed matter physicists study various structures of materials with fascinating properties. Among them, glass is one of most important and mysterious subjects of interest. From view point of material itself, it is interesting as its ubiquitous role in our daily life and its rich physical phenomena under different temperature. Also it is typical materials that have not attained a state of complete thermal equilibrium due to large viscosity , which give rise to glass's aging phenomena. In academia, abundant theory of glass transition and formation are proposed to explain well-defined set of physical phenomena so it's a quite contentious topic. Some fundamental issues like whether there exist ideal glass-transition at low temperature and whether thermodynamics or purely kinetic mechanism play roles in glass formation and dynamics are still unsettled.

We will first begin by introducing rich experimental phenomena of glass under different condition, with focus on fragility of glass. Then we will briefly introduce various theory proposed by researchers, focusing on Random first order transition theory (RFOT) which beautifully unveil universality of fragility property of different materials and fit experiment data point pretty well. Notice RFOT theory argue there is ideal glass transition and answer this question from thermodynamics, in contrast to some purely kinetic theories where thermodynamics plays no role. Readers should refer to article [1] [2] if interested at RFOT , and refer to [3] for thermodynamics and kinetic viewpoint about glass transition, and [4] for thorough theoretical review of this topics.

# 2 Basic Experimental Phenomena of structure glass transition

Glass exhibit rich phenomena and different phases under different temperatures, in the argument following, readers are encourages to visit fig.1 as we proceed our argument below.
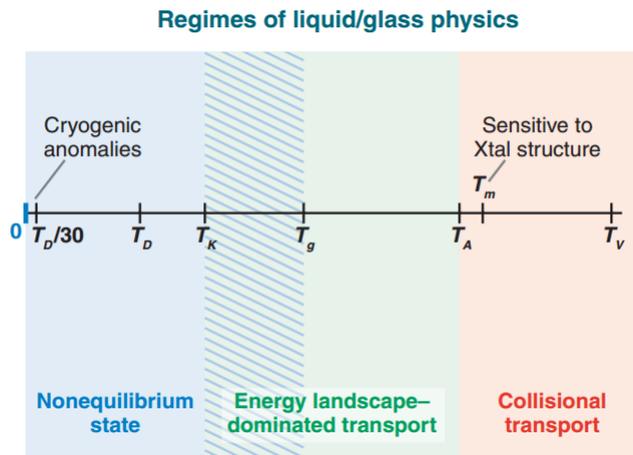


Figure 1: regimes of aperiodic condensed matter phases. Fig.1 from [1]

Starting from gas phase, we may cool glass down and compress it under vapor temperature $T_v$, under which we have liquid phase, which usually above crystallization tem-
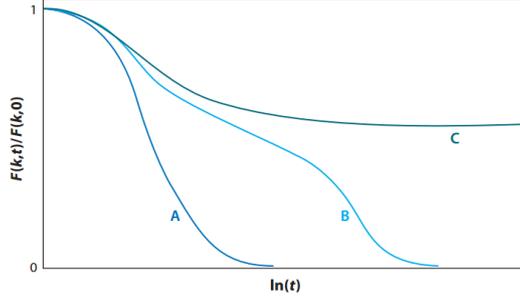
Figure 2: intermediate time structure factor $F(k,t)$ plot against $ln(t)$. **c** is result below $T_A$, **b** is result near $T_A$, **a** is result above $T_A$. Figure from [3]

perature $T_m$. Glass at liquid phase is just very dense gas held together by attractive force between molecules. Interaction between molecules in this phase is collisional, which imply no two molecules will stay close to each other after interaction, which akin to gas phase case. In supercooled regime, glass maintain its neighbor over hundreds thousands times of vibrational and collision time, beginning near temprature $T_A$. These local structural pattern will persist longer as temperature lowered. At low enough temperature, the transition time will exceed our daily life timescale. In this case, structure of glass will slowly evolve with time . We call this phenomena as aging. It is from this sense, we say glass is a form of matter which is not in thermal equilibrium.

Above argument is confirmed by neutron scattering experiment data about intermediate time structure factor $F(k,t)$ which exhibit plateau when temperature is below $T_A$ (fig.2). $F(k,t)$ is defined as :

$$F(\boldsymbol{k},t) = \frac{1}{N} < \rho(\boldsymbol{k},0)\rho(\boldsymbol{k},t) >$$
$$\rho(\boldsymbol{k},t) = \sum_{i=1}^{N} \exp(i\boldsymbol{k} \cdot r_i) \tag{1}$$

In this article , we will focus on fragility of glass, which describes how viscosity of different glass form materials changes as it approaches critical temperature $T_0$, see fig.3. The substances that exihibit Arrhenius-like relationship between temperature T and viscosity $\eta$ is termed as strong glass , whereas those exhibit convex curves is termed as fragile glass. The full dynamics show in figure 3 range from 1 ps on low viscosity side to $10^4$ when approaching glass transition temperature $T_g$. Fitting experimental data, relaxation time $\tau$ (inverse of $\eta$) can be described by Vogel-Fulcher(VF) law:

$$\tau = \tau_0 e^{DT_0/(T-T_0)} \tag{2}$$

There are also different equations for fitting experimental data, since viscosity data below temperature $T_0$ is still unavailable as relaxation time scale exceeds laboratory time scale as T approach $T_0$.

In parallel to dynamical change of supercooling, there is also thermodynamic phase transition at glass transition temperature $T_K$ . See fig.4. The discontinuity of heat capacity $c_p$ implies there is phase transition at $T = T_g$, and it is well approximated
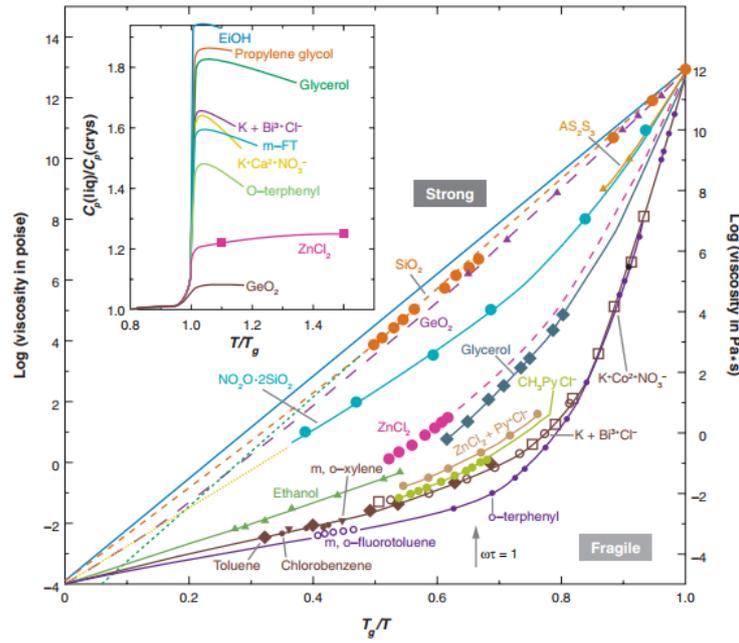
Figure 3: Viscosity of serveral supercooled liquid plot as function of inverse temperature. Substance with Arrhenius-like dependency of temperature is called strong glass wheras those have convex shape curve is called fragile glass. figure from [1]
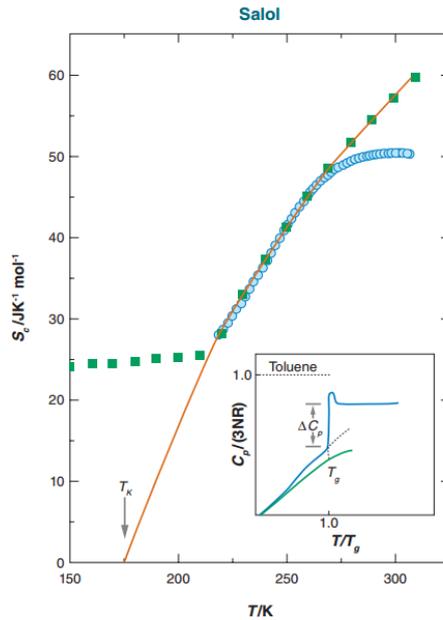


Figure 4: Main figure: extrapolation of experimentally determined configuration entorpy $S_c$ above and below glass transition temperature $T_g$. Here configuration entropy $S_c$ becomes 0 at Kauzmann temperature $T_K$ which equal to $T_0$ in eq.(2) in Vogel-Fulcher law. Inset is heat-capacity jump , which show signature of first order phase transition at $T = T_g$. figure from [5]

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by heat capacity difference between liquid and crystal. An interesting observation is if we extrapolate configurational entropy $s_c$ below $T_g$, there exists finite temperature $T_K$ called Kauzmann temperature where $S_c = 0$, and $T_K = T_0$ in eq.(2) for all glass formers. Using heat capacity jump $\Delta c_p$ at glass transition temperature $T_g$, we have temperature dependence of configuration entropy $S_c$:

$$S_c = \Delta c_p(1 - T_K/T) \tag{3}$$

The beautiful relationship of $T_K$ which is temperature from thermodynamics phase diagram where configuration entropy $s_c$ vanish and $T_0$ which relates to kinetics (viscosity) should not be coincidence. There should be deep connection between thermodynamics and kinetics. Random first order transition theory (RFOT) address this problem beautifully. Below we will give brief introduce RFOT.

# 3    Random First Order Transition Theory

The notion of random first order transition receive its theoretical support from early research of liquid glass transition theory and exactly solvable model of spin glass with quenched disorder including Sherrington Kirkpatrick model [6] , potts model[7] . Early theory about liquid glass transition so-called mode-mode coupling theory [8] suggest features similar to first order transition. It predicts characteristic behavior of correlation function near predicted transition, as indicated in fig.2. Most importantly, it suggests below transition, glass configuration will freeze into random configuration which corresponds to local minimal in state space of density functional $\rho(r)$, i.e. there is broken ergodicity.

Picture here is molecules will vibrate around its local potential minima and interact with its neighbor as in ordinary solid, but instead of having periodic structure, we have aperiodic amorphous structure. Occasionally , when thermal vibrational amplitude exceed roughly one-tenth of interparticle spacing (called Lindemann ratio), molecules will deviate from their fiducial position which corresponds to jumping from one local random configuration to another. Lindamann ratio does not depend on detail of molecular interaction, thus it's universal . We will see this will help explain variation of material's fragility with configurational heat capacity $\Delta c_p$ below.

In RFOT, free energy of system is given by density wave $\rho(r)$:

$$F = \int f(\rho(r))d^3r = k_BT[\int d^3r\rho(r)(ln(\rho(r))-1)+\int d^3rd^3r'(\rho(r)-\rho_0)c(r-r')(\rho(r')-\rho_0)] \tag{4}$$

Here first term is entropy localization penalty , second term is interaction term, where $c(r - r')$ is correlation function. $c(r - r')$ for specific material can be determined by liquid structure factor from experiment. In frozen aperiodic structure, the density wave $\rho(r)$ can be decomposed as sum of localized Gaussian dist around sets $\{r_i\}$ :

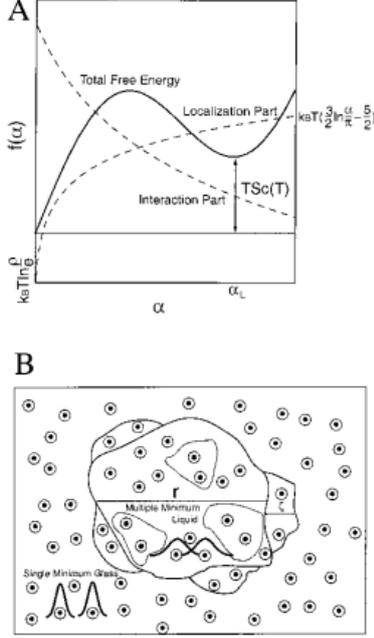$$\rho(r) = \sum_{i=1}^{N}(\pi/a)^{3/2} \exp(-\alpha(r - r_i)^2) \tag{5}$$

Figure 5: **A**. Average free energy as function of localization factor $\alpha$. **B**. illustration of liquid like droplet inside glassy region corresponds to single mean field minimum configuration.

For large $\alpha$, we can say localization site $r_i$ weakly interact with each other. Combining (eq.4) and (eq.5) we have expression for free energy:

$$F/N = k_BT[\frac{3}{2}ln(\frac{\alpha r_0^2}{\pi} - \frac{5}{2}) + 1/N \int \int d^3rd^3r'(\rho(r) - \rho_0)c(r - r')(\rho(r') - \rho_0)] \quad (6)$$

The free energy $F$ of whole system of course vary with location of center $\boldsymbol{r_i}$, but assuming localization factor $\alpha$ in (eq.5) as constant, the average free energy $F(\alpha) =< F(r_i, \alpha) >$ as function of $\alpha$ is shown in fig.5 (A). $\alpha = 0$ corresponds to uniform configuration. We see there is a second local minimum $\alpha = \alpha_L$ which corresponds to localized random configuration. The free energy difference between uniform configuration and localized random configuration is accounted by entropy contribution $TS_c(T)$.

Between metastable state $\alpha = \alpha_L$ and global minimum state $\alpha = 0$ there are point $\alpha \approx 0$ which corresponds to local maxima for averaged free energy $F(\alpha)$. This is saddle point which manifested as spatial structure of large droplet configuration in the midst of localized configuration with $\alpha = \alpha_L$, see fig.5 (B). This saddle point is also transition state for reconfiguring frozen wave density $\rho(r)$. In this droplet, different aperiodic microscopic random configuration can convert to each other.

To compute barrier height for transition state, we note there will be surface tension reflecting deviation of $\alpha$ of layer from bulk configuration $\alpha = \alpha_L$. Also, in droplet region $\alpha \approx 0$ instead of $\alpha = \alpha_L$ so there is also free energy difference proportional to volume of droplet region (per volume $TS_c$). Combining two effect above we have expression for free energy difference:

$$F(r) = -\frac{4}{3}\pi T s_c r^3 + 4\pi\sigma r^2 \tag{7}$$

According to (eq.7), solving maximum of free energy we have reconfiguration energy barrier:

$$\Delta F^\dagger = \frac{16}{3}\pi\sigma^3/(T s_c)^2 \tag{8}$$

The surface tension $\sigma$ can be traced back to interaction between droplet surface with surrounding configurations, it is one half of the difference of interaction energy between $\alpha = 0$ and $\alpha = \alpha_L$. Assuming typical thickness of surface layer is $r_0$ which is average molecular difference, we have:

$$\sigma \times 4\pi r^2 = (-f_{interaction}) \times \frac{1}{2} \times (4\pi r^2) r_0$$
$$\sigma = \frac{r_0}{2}(-f_{interaction}) = \frac{r_0 T}{2}[\frac{3}{2}nk_B \ln(\alpha r_0^2/\pi e) - S_c(T)] \tag{9}$$

As surface tension depend only logarithmically on $\alpha$, we can replace $\alpha$ above by $\alpha_L$, meanwhile near Kauzmann temperature $T_K$, configurational entropy $S_c(T_K) = 0$. For temperature between $T_A$ and $T_K$, above two approximation large cancel and we have:

$$\sigma = \frac{3r_0 nk_B T}{4} \times ln(\alpha_L r_0^2/\pi e) \tag{10}$$

Due to universaility of Lindemann ratio mentioned above, $\alpha_L r_0^{1/2}$ should be universal for all materials, thus for droplet surface tension $\sigma$, $\sigma/nr_0 k_B T$ is universal for all materials.

However, there are still inconsistency between experimental result and theoretical prediction above in (eq.8). Viscosity data show $s_c^{-1}$ scaling for free energy of activation instead of $s_c^{-2}$ there. The right answer comes from complexity of interaction between droplet surface and their environments. To lower interaction energy, surrounding environment will adjust their random configuration, which gives surface tension $\sigma$ depends on droplet size $r$ . This is pretty much like what happened in random field Ising model.

Accounting this , we will have surface tension $\sigma(r)$:

$$\sigma(r) = \sigma_0(\frac{r_0}{r})^{\frac{1}{2}} \tag{11}$$

Using equation above one find expression for $F(r)$:

$$F(r) = -\frac{4}{3}\pi T S_c r^3 + 4\pi\sigma_0 r_0^{\frac{1}{2}} r^{\frac{3}{2}} \tag{12}$$

Its maximum gives right barrier height :

$$\Delta F^\dagger = \frac{3\pi\sigma_0^2 r_0}{T S_c(T)} = \frac{3\pi\sigma_0^2 r_0}{T(\Delta C_p \frac{T-T_K}{T_K})} = Dk_B T \frac{T_K}{T-T_K} \tag{13}$$

We can see from (eq.13) and (eq.2) , it's obvious $T_0$ in VF law equal to $T_K$ which is Kauzmann temperature. We see from point of view of thermodynamics barrier crossing , Random First Order Transition Theory resolve this puzzle beautifully.
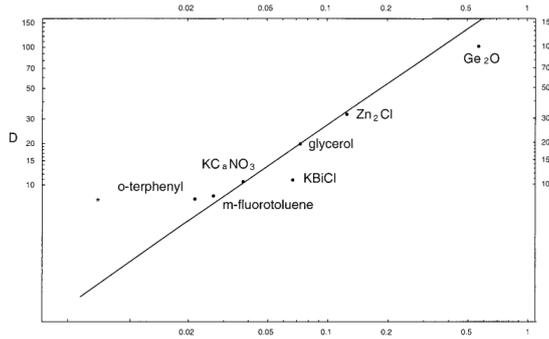
Figure 6: Fragility relationship with configuration entropy jump $\Delta c_p$ for various materials.

Coefficient D is called fragility which using universality of Lindemann ratio takes the form:

$$D = 32R/\Delta c_p \tag{14}$$

Above relationship of fragility agree with experiment beautifully, see fig.6.

Another useful prediction is reconfiguration length scale $\xi$ of droplet. The value $r^\dagger$ corresponds to transition state free energy $F^\dagger$ scale with temperature T as :

$$r^\dagger \propto \frac{1}{(TS_c(T))^{2/3}} = \frac{1}{(T - T_K)^{3/2}} \tag{15}$$

We see cooperative length scale $r^\dagger$ is temperature dependent and RFOT give precise prediction of its scaling.

# 4    Conclusion and Future Outlook

Different glass materials' viscosity show distinct dependence on temperature. Deviation from Arrhenius-like law of viscosity and temperature is characterized by fragility constant $D$. Characterizing microscopic state of glass as random configuration with local free energy minima and transitions between them are local configuration rearrangement in droplet region much like nucleation process, Wolynes and his coworkers successfully relate fragility $D$ with configuration heat capacity jump $\Delta c_p$, thus show there is only quantitative not qualitative difference between strong and fragile glass.

Although with great success of RFOT, we have to bear in mind prediction of RFOT only apply to purely amorphous materials. Many samples exhibit partial crystallization are expected to deviate from prediction of RFOT theory. Another effect worth noting is role of Quantum mechanics in glass transition and fragility. We expect quantitative details of amorphous materials' property like vibrational excitation spectrum and heat capacity $\Delta c_p$ will given by quantum mechanics calculation. But general picture of random configuration and droplet will not be affected by quantum mechanics.

Finally, although RFOT provides insight of relation between viscosity and thermodynamic property, it avoids hardest part of problem: provide quantitative prediction for macroscopic quantity from precise form of molecular interaction potential and structure. Future direction in this field should pay greater attention to liquid-state structure theory and powerful molecular simulation techniques to address problems mentioned above.

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