MOLECULAR COOPERATIVITY IN THE DYNAMICS OF GLASS-FORMING MATERIALS

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Liang Hong
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ABSTRACT

Although glass has been fabricated for thousands of years, the microscopic mechanism governing the glass transition process remains unclear. The main challenge is to understand the non-Arrhenius temperature dependence of the structural relaxation time of the supercooled liquids upon approaching the glass transition temperature. Most researchers ascribe it to cooperative molecular motions. Various experimental results and simulations show that the structural relaxation of a supercooled liquid is spatially heterogeneous. This dynamic heterogeneity is usually attributed to the cooperative molecular motions in local domains. The cooperativity size is estimated from the spatial heterogeneity to be ~1-4 nanometers. However, many important questions are still unsolved, e.g. what is the role of molecular cooperativity in the temperature dependence of the structural relaxation time?

On the other hand, the collective vibration in the GHz-THz frequency range, the so-called boson peak, is also considered to be a manifestation of a cooperative process with a characteristic length scale of a few nanometers. Some researchers even speculate that the length scale associated with the boson peak is related to the cooperativity length scale of the main structural relaxation.
In this dissertation, we estimated the characteristic length scale from the boson peak spectra measured using light scattering for a large number of glass-forming materials. By comparing it to the dynamic heterogeneity length scale of the main structural relaxation acquired via 4-dimensional NMR, we find that the collective vibrations and the structural relaxation involve a similar length scale of molecular cooperativity.

When a supercooled liquid is cooled down to the glass transition temperature, decreases in free volume and thermal energy both contribute to slowing down the structural relaxation. Our analysis demonstrates that only the volume contribution to the variation of the structural relaxation time has a direct correlation with the cooperativity size among different materials, whereas the thermal energy contribution does not. The latter is more dependent on the chemical structure of the studied materials. These results call for a conceptually new approach to the analysis of the mechanism of the glass transition and to the role of molecular cooperativity.
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CHAPTER I

INTRODUCTION

Once a liquid is cooled down fast enough to prevent crystallization, it will turn to a disordered solid, i.e. glass. This phenomenon is usually named glass transition process. As early as the 3rd millennium BC, Egyptian people were already capable of fabricating glassy beads as decoration through this process. Currently, the glass transition process is widely used to manufacture all kinds of daily used products, such as plastics, window glasses, and eye glasses, etc. Moreover, nature also makes use of it to preserve life, e.g. the hibernation of frogs in winter time\(^1\). However, the mechanism behind the sharp increase of the viscosity ($\eta$) or the structural relaxation time ($\tau_\alpha$) of a supercooled liquid upon approaching the glass transition temperature ($T_g$) still remains a great puzzle\(^2,3,4,5\). An article published in New York Times well described the situation by its title: “The nature of glass remains anything but clear”\(^6\).

The main challenges for understanding the temperature dependence of the structural relaxation in supercooled liquids during the glass transition process are two-fold. First, the steep rise of $\eta$ (or $\tau_\alpha$) indicates a dramatic increase of the apparent activation energy, i.e. $E_A = R \left. \frac{\partial \ln(\tau_\alpha)}{\partial (1/T)} \right|_p$, where $R$ is the gas constant. In many polymeric
systems, \( E_A \) can achieve some unreasonably high value around \( T_g \), which is often far above the energy required to break the chemical bonds, yet the chains remain intact.

Second, the temperature variation of viscosity around \( T_g \), as measured by the so-called fragility parameter\(^2\), is remarkably distinct among various materials. For example, in the case of \( \text{SiO}_2 \), the viscosity only increases 100 times when temperature is decreased from \( 1.1T_g \) to \( T_g \), but an ortho terphenyl (OTP) liquid would become 100 million times more viscous by the same temperature variation. The above two experimental phenomena can hardly be explained by any simple-liquid theory. To understand them, a phenomenological picture in which it is assumed that the glass transition process involves cooperative molecular motions has been invoked. Briefly, molecules move cooperatively in a supercooled liquid, and \( E_A \) is the activation energy for a group of molecules in the cooperative relaxation domain. The cooperativity size increases with decreasing temperature, which drastically raises \( E_A \) and slows down the dynamics of the supercooled liquids. According to this idea, once a material has a larger cooperativity size as \( T_g \) is approached, its structural relaxation time would exhibit a steeper temperature dependence, i.e. higher fragility. Recently, various experimental results and simulations have shown that the structural relaxation in supercooled liquids is heterogeneous, i.e. slow and fast relaxing domains spatially coexist. Most researchers ascribe this dynamic heterogeneity to the cooperative molecular motions at a relevant length scale in the supercooled systems\(^7,8,9,10,11,12\). The cooperativity size is estimated from the spatial heterogeneity to be a few nanometers\(^7-12\). However, many important questions remain unclear, tow of these are what is the relationship between the cooperativity (heterogeneity) size and fragility
and is there any connection between the molecular cooperativity and the chemical structure of the materials?

Moreover, it has been recognized for a long time that both changes in volume and thermal energy contribute to the temperature variations of the structural relaxation time of supercooled liquids at isobaric conditions\textsuperscript{13,14,15,16}. The relative contribution of the two factors is substantially distinct among different materials. For example, the thermal energetic contribution is dominant in the case of hydrogen bonding materials, while the volume contribution is comparable to or even more important than the energetic one for van der Walls small molecule systems\textsuperscript{13}. An intriguing question is “How are the two contributions to the variations of $\tau_\alpha$ connected to the molecular cooperativity among different materials?”

On the other hand, the collective vibrations in the GHz-THz frequency range, responsible for the so-called boson peak, are also considered as a cooperative process with a characteristic length scale ($\xi$) of about a few nanometers\textsuperscript{17,18,19,20,21,22,23}. Moreover, recent studies of glass-forming materials reveal that the fast dynamics and the main structural relaxation are intimately connected\textsuperscript{18,24,25,26}, and some researchers even speculate that the length scale associated with the boson peak is related to the cooperativity length scale of the main structural relaxation\textsuperscript{27,28,29,30}.

In this dissertation research, we performed light scattering on a large number of glass-forming systems, including polymers and van der Walls small molecule systems as well as hydrogen-bonded, covalently bonded and ionic bonded materials. The characteristic length scale ($\xi$) associated with the boson peak was estimated for each of the materials. The study starts from comparing $\xi$ with the dynamic heterogeneity length
scale estimated by 4-D NMR in the same materials to verify whether the collective vibrations and the structural relaxation indeed involve the same length scale for cooperative molecular motions. Then we examine the relationship between $\xi$ and fragility among different materials to investigate the role of molecular cooperativity in determining the dynamics during the glass transition process. This dissertation is organized in the following way.

In Chapter II, the historical background of various theoretical models and experimental investigations on the cooperativity involved in the molecular motions in glass-forming systems is presented. It starts from the structural relaxation, and then goes to the pico-second collective vibrations. At the end of this chapter, a brief introduction to the basic principles of light scattering is presented.

Chapter III provides detailed information on the light-scattering instrumentations, experimental conditions and the data treatment. Particularly, we describe the features of the anvil pressure cell, which is used for pressure study.

The experimental data for $\xi$ estimated from boson peak spectra for all the studied materials measured deep in the glassy state are tabulated in Chapter IV. By comparing values of $\xi$ to the dynamic heterogeneity length scale for the structural relaxation estimated from 4D NMR in the same systems, we find that the boson peak vibrations and the structural relaxation indeed involve a similar length scale for cooperative molecular motions. More importantly, the analysis reveals that, in contrast to expectations from the traditional cooperativity idea, $\xi$ does not have a clear correlation with fragility among various glass-forming materials. However, we discover an intriguing proportional relationship between $\xi^3$ and the activation volume $\Delta V^\#$, i.e. the pressure dependence of $\tau_\alpha$. 

4
This correlation is demonstrated to be valid not only among different chemical species, but also for the same specie with different molecular weight or under densification. At the end of this chapter, a theoretical justification of the observed correlation is provided based on the Random first-order transition theory\textsuperscript{29}.

In Chapter 5, the relationships between $\xi$ and the two contributions (thermal energy and volume) to variations of $\tau_\alpha$ are discussed separately. The analysis shows that only the volume contribution has a direct correlation with the cooperativity size among different materials, while the energetic one does not, because it has a strong dependence on the chemical structure of the studied materials.

In Chapter 6, we explore the temperature dependence of $\xi$ in a few systems. The analysis shows that $\xi$ does not change much within the temperature range studied, which is contradictory to the predictions of most models and also the traditional cooperativity idea. Some preliminary understanding of this result is provided. Finally, a brief summary of this thesis is presented in Chapter 7.
CHAPTER II
HISTORICAL BACKGROUND

2.1. General features of the temperature variation of the structural relaxation in supercooled liquids

Although the glass transition process has been studied for almost a hundred years, the microscopic mechanism governing this process remains unclear$^{2-5}$. Numerous theories were proposed to describe the dynamics of supercooled liquids, and the essential assignment is to find a sound explanation of the non-Arrhenius temperature dependence of viscosity or the structural relaxation time of the supercooled liquids upon approaching $T_g$. This temperature dependence is schematically presented in Figure 2.1$^{31}$. 

As illustrated by the above graph, the temperature dependence of $\tau_\alpha$ in glass-forming materials can be separated into a few regions based on their distinct features. The purple one above $T_A$ exhibits an Arrhenius temperature dependence, i.e.

a constant slope of $\frac{\partial \ln(\tau_\alpha)}{\partial(1/T)}$, where $T_A$ is called Arrhenius Temperature, often $\sim 2T_g$. Once the liquid is cooled below $T_A$, the slope starts to increase with decreasing $T$. To characterize the slowing down of the structural relaxation between $T_A$ and $T_g$, the empirical Vogel-Fulcher-Tamman (VFT) equation\textsuperscript{32,33,34} is traditionally applied

$$\tau_\alpha = \tau_0 \exp\left(\frac{B}{T - T_0}\right).$$

(2.1)
Here $\tau_0$, B and $T_0$ are fitting parameters. $\tau_0$ is $\sim 10^{-14}$ s, B is related to fragility (introduced later) and $T_0$ is a characteristic temperature below $T_g$, called the VFT temperature. To provide a good fit for relaxation data in the whole temperature range between $T_A$ and $T_g$, two VFT equations instead of one are often required\textsuperscript{35,36,37,38}. One fits the blue region and the other one fits the red region at $T > T_g$ (Fig 2.1). The slope of the blue curve usually increases sharper with decreasing temperature than the red one does. A critical temperature used to separate the two regions is named the crossover temperature $T_c$. $\tau_\alpha$ at this characteristic temperature has been shown to be a rather universal value: $10^{-6} \sim 10^{-8}$ s for many glass forming materials regardless of the chemical structures\textsuperscript{36}. $T_c$ is often considered as a crossover between liquid- and solid-like dynamics\textsuperscript{36}. Furthermore, this temperature has been predicted by the idealized mode-coupling theory\textsuperscript{39}, where it marks an ergodic-to-nonergodic transition. The red curve at $T < T_g$ is actually an extrapolation from above $T_g$, and not accessible in regular experiments. Normally, the available relaxation data below $T_g$ (the brown dash line of Figure 2.1) is measured in the non-equilibrium glassy state, where aging effects will be observed.

Enormous research works have been performed in the non-Arrhenius region from $T_A$ to $T_g$, especially at values of $T$ close to $T_g$. In particular, a parameter proposed by Angell and coworkers, so-called fragility, is often used to characterize the steepness of the temperature variations of viscosity or $\tau_\alpha$ around $T_g$ under isobaric conditions\textsuperscript{2}

\[ m = \frac{d \log \tau_\alpha}{\frac{T_g}{T}} \bigg|_{T=T_g,P} \]  

(2.2)
As shown in Figure 2.2, if a material has a temperature dependence of viscosity (or $\tau_\alpha$) deviating significantly from the Arrhenius behavior, such as the case for OTP, it has high fragility and is called a “fragile” system. By contrast, if the material has a temperature dependence of viscosity close to the Arrhenius behavior, such as SiO$_2$ does, it has low fragility and is considered to be “strong”.

Figure 2.2: Temperature dependence of viscosity (Angell’s plot)$^3$. The slope at $T=T_g$ defines fragility. (Figure reprinted with permission from$^3$. Copyright (2010) by Nature publishing group.)

Figure 2.1 exhibits how the structural relaxation time changes with temperature at constant pressure (more often at ambient pressure). In fact, the isobaric cooling results in two consequences: decrease of thermal energy and reduction of free volume in the system. Both will contribute to slowing down the dynamics of the supercooled liquid.

Experimental study on separating the two contributions has been started a half century ago$^{13-15}$. The ratio of the isochoric apparent activation energy $E_N = R \frac{\partial \ln(\tau_\alpha)}{\partial(1/T)}$ |$_v$, to the
isobaric apparent activation energy \( E_A = R \left. \frac{\partial \ln(\tau_\alpha)}{\partial (1/T)} \right|_p \), is usually presented to quantify the relative contribution of thermal energy and volume to the temperature variation of \( \tau_\alpha \). If the value of \( E_V/E_A \) exceeds 0.5, the structural relaxation in the system is mostly thermally activated, otherwise it would be primarily volume activated. In general, hydrogen bonding materials have the highest value of \( E_V/E_A \) (close to 1). Most polymers have a smaller value of \( E_V/E_A \) but still above 0.5, while this ratio is rather low (~0.5 or smaller) in most of the van der Waals small molecule liquids. The common explanation for the high ratio of \( E_V/E_A \) in hydrogen bonding materials is that breaking of hydrogen bonds (purely energetic factor) controls the structural relaxation, and change in volume plays only a secondary role in these systems.

Similar to the activation energy, fragility can also be defined in two ways: isobaric (m) and isochoric (mV). They both characterize the steepness of temperature dependence of \( \tau_\alpha \) around \( T_g \). The former is defined at constant pressure (Eq. (2.2)), while the latter is measured at constant volume

\[
m_V = \left. \frac{d \log \tau_\alpha}{d \frac{T_g}{T}} \right|_{T=T_g,V}.
\]

The quantities \( m, m_V, E_P \) and \( E_V \) satisfies the following relationship

\[
\frac{m_V}{m} \equiv \frac{E_V}{E_A \mid_{T_g}}.
\]

Since experimental work performed at elevated pressure is much more difficult and complicated than that at ambient pressure, the isobaric fragility is more widely studied.
and used than is \(m_\gamma\). For simplicity, we refer to isobaric fragility as fragility in the rest of this thesis.

2.2. Molecular cooperativity in the structural relaxation

As illustrated in Figure 2.1, the slope of the curve increases with decreasing temperature from \(T_A\) to \(T_g\), which indicates the apparent activation energy rises with cooling. The puzzling phenomenon is that \(E_A\) increases very abruptly, and achieves some un-physically high value around \(T_g\). For example, \(E_A(T_g)\) of PS is three times larger than the bond energy of C-C bond, but PS chains never decompose at \(T_g\). To solve this puzzle, the traditional idea is to describe the structural relaxation in supercooled liquids as a cooperative process and specify \(E_A\) as the activation energy for a group of molecules in the cooperatively relaxing domain. According to this idea, the cooperativity size would increase with cooling, which substantially raises \(E_A\) and slows down the dynamics.

Intuitively, a higher slope of \(\frac{\partial \ln(\tau_{\alpha})}{\partial (1/T)}\) around \(T_g\) should correspond to a larger size of molecular cooperativity. Therefore, the value of fragility in different glass-forming materials is connected to their cooperativity size at \(T_g\).

2.2.1. Theories for molecular cooperativity in the structural relaxation

Inspired by the above traditional idea, various theories have been proposed to describe the dynamics in glass formers and have attempted to provide microscopic
pictures for the molecular cooperativity in the structural relaxation. In general, theories can be categorized into three major types\textsuperscript{27}. In the first type of models, the transition between two energy minima is attained through cooperative motions of a group of molecules in the local domains. The energy barrier between the two energy minima is often connected to the apparent activation energy for the structural relaxation. Typical examples are the Adam-Gibbs approach\textsuperscript{40}, the Random first-order transition theory (RFOT)\textsuperscript{29} and the entropic barrier hopping theory\textsuperscript{41}. In particular, the Adam-Gibbs approach has had far-reaching influence on the later works\textsuperscript{42,43,44}. The second type of model ascribes the molecular cooperativity to the environment fluctuations at an intermediate length scale (a few nanometers)\textsuperscript{7,28,45-47,48,49,50,51,52,53,54,55,56,57,58}, including fluctuation of density\textsuperscript{28,45-47}, temperature\textsuperscript{7,48,49}, and entropy\textsuperscript{50,51}. Lastly, the molecular cooperativity has been connected to structural frustration\textsuperscript{59,60,61}. For example, the icosahedra were considered as a possible candidate shape for the cooperative domains\textsuperscript{27}. In the following text, we will introduce several representative models to give a general picture of what molecular cooperativity is.

2.2.1.1. The Adam-Gibbs approach

In this theory\textsuperscript{40}, the structural relaxation is realized through a cooperative rearrangement of a group of molecules in a localized domain, the so-called cooperative rearranging region (CRR). The main assumption of this approach is that the number of the molecules in a CRR must exceed a minimum value $z^*$ for the CRR to have at least
one extra configurational state to perform the rearrangement. Thus, the configuration entropy for this CRR is

\[ s^* = k \ln 2 \]  

(2.5)

where \( k \) is the Boltzmann constant. Adam and Gibbs derived that the average rate for each CRR to transit between two configurational states is

\[ W(T) = A \exp(-z^* \Delta \mu / kT) \]  

(2.6)

Here \( A \) is thought to have negligible dependence on both temperature and \( z^* \). \( \Delta \mu \) is the energy barrier per molecule for the rearrangement of a CRR, which is assumed to be temperature independent. Since the relaxation time of the system can be considered to be inversely proportional to the average transition rate, one obtains

\[ \tau_s(T) \propto 1/W(T) = \frac{1}{A} \exp(z^* \Delta \mu / kT) \]  

(2.7)

Because the configurational entropy of one CRR is \( s^* = k \ln 2 \), and all the CRRs are assumed to be thermodynamically independent, the total configurational entropy per mole of molecules can be estimated as

\[ S_c(T) = \frac{N_A}{z^*(T)} s^* = \frac{N_A}{z^*(T)} k \ln 2 \]  

(2.8)

Here \( N_A \) is the Avogadro’s number.

The configurational entropy is defined as the difference between the total entropy and the vibrational one. It can be approximated as the excess entropy in the liquid state with respect to the crystalline counterpart by integrating the difference of heat capacity between the liquid and crystalline state (\( \Delta C_P \))
\[ S_c(T) = \int_{T_k}^{T} \frac{\Delta C_p}{T} dT. \]  

(2.9)

Here \( T_K \) is the Kauzmann temperature, where the excess entropy disappears\(^{62} \) Taking the approximation of \( \Delta C_p \equiv C/T \)\(^{57,62,63} \), where \( C \) is a constant, into Eq. (2.9), one obtains

\[ S_c(T) = \frac{C}{T_k} \left( \frac{T - T_K}{T} \right). \]  

(2.10)

In this approach as well as in the RFOT, \( T_K \) is considered to be equal to the VFT temperature \( T_0 \), thus Eq. (2.10) can be converted to

\[ S_c(T) = \frac{C}{T_0} \left( \frac{T - T_0}{T} \right). \]  

(2.11)

Combining Eq. (2.8) and Eq. (2.11), the temperature dependence of \( z^* (T) \) can be obtained

\[ z^*(T) = \frac{N_A T_0 k \ln 2}{C} \left( \frac{T}{T - T_0} \right) \propto \frac{T}{T - T_0}. \]  

(2.12)

As indicated by Eq. (2.12), \( z^* \) gradually grows with cooling. The explicit value of \( z^* \) in many materials has been estimated in later works, where \( z^*(T_g) \) is usually smaller than \( 10^{43,64,65} \). For example, the lattice cluster entropy theory (LCET) predicts that the CRR grows from \( z^*=1 \) at \( T_A \), to \( z^*\sim2 \) at \( T_c \), and to \( z^*\sim4-5 \) at \( T_g \) in polymers\(^{43} \).

2.2.1.2. The random first-order transition theory (RFOT)

Within the framework of the RFOT\(^{29} \), the vitrification is described analogous to crystallization with the difference that the system is frozen into a set of aperiodic structures instead of a periodic crystalline structure. The domains for cooperative
molecular motions are named “entropic droplets”. The entropic droplets are formed and stabilized by the competition between a favorable driving force, i.e. increase of the configurational entropy, and an unfavorable surface mismatch penalty. The temperature dependence of the domain size is predicted as

$$\xi(T) \propto \frac{T^{1/3}}{(T - T_K)^{2/3}}. \quad (2.13)$$

Moreover, the number of elementary structural units in the entropic droplet ($\xi/a$) around $T_g$ is predicted to be a rather universal number (4~6) regardless of chemical structures and fragility$^{29,66}$, where $a$ is the size of an elementary structural unit, namely bead$^{67}$. This prediction has been supported by experimental data, where the molecular cooperativity size is estimated via the multipoint dynamic susceptibility function$^{74,68}$. Besides, RFOT also successfully explains many other experimental phenomena, including the decoupling between translation and rotation, the heat capacity jump at $T_g$, non-exponential relaxation and its connection with fragility, etc.

2.2.1.3. Entropic barrier hopping theory

This theory$^{41}$ is designed for supercooled liquids between $T_g$ and $T_c$. Within this temperature range, molecules are packed so densely that the hopping process of each molecule can be attained only via a cooperative manner with many neighbors. According to this theory, the energy barrier for the cooperative hopping process ($F_B$), which is intimately related to $E_A$, has a Gaussian distribution. This leads to dynamically distinct domains, and a higher $F_B$ corresponds to a slower relaxing domain. It is of interest to
mention that it is the only theory as we know that does not connect the sharp slowing down of the structural relaxation under cooling to the growing of the length scale of the cooperative domain. It predicts that the diameter of the cooperative hopping domain maintains essentially constant between $T_g$ and $T_c$. Decreasing temperature condenses the molecular packing, which drastically raises the difficulty of the hopping process (increase of $F_B$). As a result, the structural relaxation is remarkably slowed down. Moreover, similar to the RFOT, the entropic barrier hopping theory also predicts that the size of the cooperative domain should be roughly constant (3~4 molecular size) among different materials, independent of the chemical structures and fragility.

2.2.1.4. Density fluctuation theory (a two-state model)

Density is the most widely used variable in the environment fluctuation models\textsuperscript{28,45–47}. The idea is that the fluctuations of density in the deeply supercooled liquid lead to a spatial distribution of density or packing at the intermediate length scale (a few nanometers). The molecules in a high-density region would move cooperatively and slowly, “solid-like”, while the molecules in a low-density region would relax independently and fast, “liquid-like”. In a simple vision, the overall system can be approximated by a two-state model (solid vs liquid)\textsuperscript{28}. This picture has been supported by the 4-Dimensional NMR (4D NMR) studies in a few glass-forming materials. The studies reveal that the dynamics of a supercooled liquid at $T$ close to $T_g$ is heterogeneous at nanometer length scale, and the motion of the molecules in the fast region can be orders of magnitude faster than the one in the slow regions\textsuperscript{69}. According to Ediger’s estimate,
the density contrast between the slow and fast regions needs to be ~2% to exhibit such
dynamic heterogeneity\textsuperscript{70}. This estimate is also in accord with De Gennes’ expectation\textsuperscript{28}.
Within the framework of the two-state model, the liquid domains would gradually
convert to solid clusters with decreasing temperature. Bakai\textsuperscript{57,58} provided a quantitative
picture for this conversion. He suggested that the solid fraction increases with cooling
from 0.15 (the percolation threshold of solid clusters) at some arbitrary high temperature
to ~0.5 at $T_c$, and to 0.85 at $T_g$, where the last percolated liquid network disappears\textsuperscript{27,57,58}.
Here it is important to emphasize that there might be two mechanisms to raise the
concentration of solid clusters: increase of the size and of the number. So far, however,
no two-state model has given a clear picture about which mechanism is dominant.

Moreover, the two-state model also provides a sound explanation to the puzzling
experimental phenomenon of decoupling between translational and rotational motions of
molecules in the supercooled liquids\textsuperscript{12,71,72}. It is known that the Stokes-Einstein (SE) and
Debye-Stokes-Einstein (DSE) relations are very useful to predict the molecular motions
in simple liquids\textsuperscript{73,74}:

\begin{align}
\text{SE: } D_T &= \frac{kT}{6\pi\eta r_H} \quad \text{(2.14)} \\
\text{DSE: } \tau_r &= \frac{4\pi\eta r_H^3}{3kT} . \quad \text{(2.15)}
\end{align}

Here $D_T$ is the translational diffusion coefficient, $\tau_r$ is the characteristic rotational
correlation time, $\eta$ is viscosity and $r_H$ is the hydrodynamic radius of diffusing molecules.
The product of $D_T$ and $\tau_r$ can be estimated by combining Eq. (2.14) and (2.15)

\begin{equation}
D_T\tau_r = \frac{2}{9} r_H^2 . \quad \text{(2.16)}
\end{equation}
Since $r_H$ has no explicit temperature dependence, the value of $D_T\tau_r$ should be temperature independent. However, this DSE-SE prediction fails for the deeply supercooled liquids$^{12,71,72}$, and the typical results are presented in Figure 2.3.

![Figure 2.3: Temperature dependence of $D_T\tau_r$, $(D_T\tau_r)_{DSE:SE}$ is the predicted value via the DSE-SE relation\textsuperscript{71} (Figure reprinted with permission from\textsuperscript{71}. Copyright (2010) by Rheologica Acta)](image)

As revealed by Figure 2.3, the translational motion is enhanced relative to the rotational one in the vicinity of $T_g$, where the product of $D_T$ and $\tau_r$ is a few orders higher than the prediction of the DSE-SE relation. This decoupling phenomenon can be easily understood via a two-state model. Let’s assume the supercooled liquid around $T_g$ consists of solid and liquid domains, and the motion of molecules in the former is orders of magnitude slower than that of the latter. For simplicity, the solid and liquid fractions are assumed to be equal, $x_s=x_l=1/2$. Another assumption is that the DSE-SE prediction is locally valid for every molecule no matter whether it is in the solid domain or in the liquid region.
So the average rotational correlation time is

\[<\tau_r> = \frac{1}{2}\tau_{rs} + \frac{1}{2}\tau_{rl} \approx \frac{1}{2}\tau_{rs}.\]  

(2.17)

Here \(\tau_{rs}\) and \(\tau_{rl}\) are the rotational correlation time of the molecules in the solid and liquid domains, respectively, and \(\tau_{rs} >> \tau_{rl}\). Likewise, the average translational diffusion coefficient can be expressed as

\[<D_T> = \frac{1}{2}D_{Ts} + \frac{1}{2}D_{Tl} \approx \frac{1}{2}D_{Tl}, \text{ since } D_{Tl} >> D_{Ts}.\]  

(2.18)

So \(<D_T> \cdot <\tau_r> \approx \frac{1}{4}\tau_{rs} \cdot D_{Tl} >> 1.\)  

(2.19)

In a word, the cause for the product of \(D_T\) and \(\tau_r\) in deeply supercooled liquids far exceeding the prediction of DSE-SE is the existence of a broad distribution of molecular mobility. \(<\tau_r>\) is ensemble-averaged relaxation time, determined more by the slow component of the distribution, whereas \(<D_T>\) is ensemble-averaged diffusion coefficient (inverse of relaxation time), dominated by the fast component.

2.2.2. Experimental observation

Dynamic heterogeneity is usually connected to molecular cooperativity at a relevant length scale. Within the framework of a two-state model, the solid cluster involves significant cooperative molecular motions, which greatly retard its dynamics to be orders of magnitude slower than that in the liquid domain. According to the entropic barrier hopping theory\(^{41}\), molecular cooperativity at nanometer scale is an intrinsic feature resulting from the structural correlation in the disordered materials. The motions
of molecules in these nanometer-scale domains are cooperatively slow or fast. In any case, molecular cooperativity is intimately bound up with dynamic heterogeneity and this fact (assumption) is the base of most experimental and theoretical approaches for studying the molecular cooperativity associated with the glass transition process \cite{8,12,17,22,28,30,41,46,68,69,75,76,77,78}. And the length scale of dynamic heterogeneity is usually used to quantify the cooperativity size \cite{8,12,17,22,28,30}. As described before, the density contrast for different regions, i.e. slowly or fast relaxing domains, might be only a few percent. It is too small for any diffraction method, e.g. X-ray diffraction, to detect \cite{79}. Thus the assignment is left to dynamic methods: Probing different cooperative regions is accomplished by observing domains with distinct mobility \cite{69,75-78}. It is known that the normal dynamic method is to measure the two-point correlation function. Normally, this function can be expressed as

\[
F^2 = \langle \delta A(0) \ast \delta A(t) \rangle .
\]  

(2.20)

Here \langle \rangle represents ensemble or time average, and \delta A(0) and \delta A(t) denote the fluctuation of local physical properties, such as density, modulus, orientation of molecules, etc., from its average value at time zero and t, respectively. In the case of structural relaxation of supercooled liquids, this function is usually described well by the Kohlrausch-Williams-Watts (KWW) equation \cite{80}, a stretched exponential, i.e. \(\exp(-(t/\tau_0)^\beta)\), \(0<\beta<1\). To interpret this non-exponential relaxation spectrum, two different scenarios are traditionally assumed \cite{69}. One is the heterogeneous scenario: the structural relaxation corresponds to a weighted sum of elementary processes. Each process has a correlation function, which exponentially decays in time but has different \(\tau_0\). The other one is the homogeneous scenario: the relaxation process has a natural non-exponential dependence,
i.e. the dynamics of each sub-ensemble is the same and intrinsically non-exponential. However, a two-point correlation function is not able to distinguish the two scenarios. To achieve this goal, a 4-point time-space correlation function must be measured, which can be expressed as

\[ F_4 = \langle \delta A(\mathbf{0}, t) \rangle \],

(2.21)

where \( \mathbf{0} \) and \( \mathbf{r} \) denote the position of the studied property (in this thesis, the letter in bold denotes a vector). This 4-point correlation function shows how two different positions in the sample dynamically correlate with each other at the time scale of \( t \). To study the structural relaxation, \( t \) should be set as \( \tau_\alpha \). If the homogeneous scenario is correct, \( F_4 \) would have no dependence on \( \mathbf{r} \). However, if the dynamics in supercooled liquids are spatially heterogeneous, \( F_4 \) will decay with \( \mathbf{r} \), from which the length scale of dynamic heterogeneities (or the dynamic correlation length) can be estimated. However, different experimental works as well as theoretical models show that the typical cooperativity length scale for the structural relaxation is about 1~4 nm. This means, to measure \( F_4 \), the experiments must be performed by using two probes whose distance are well controlled at nanometer scale to simultaneously measure the temporal fluctuation of physical properties at two positions in a liquid. This kind of measurement is not feasible for current technology. But an alternative way can be applied, which is to measure the dynamics of a selected sub-ensemble. If it is the same as the dynamics of the total ensemble, then the homogenous scenario is correct otherwise the heterogeneous scenario should be adopted. A typical example is the “reduced four-dimensional” exchange NMR (4DNMR) approach, where the orientation of the pre-selected molecules at four
subsequent points in time are probed. Here we would like to give a brief introduction to the working mechanism and the main results of this technique.

In this experiment, the spin of a particular nucleus, e.g. $^{13}\text{C}$, is excited by a Radio Frequency pulse. The NMR frequency ($\omega$) serves as an indicator for the orientation of the excited spin, and thus for the motion of the molecules. Figure 2.4 provides a schematic picture for the pulse sequences in 2DNMR and 4DNMR.

In a 2D experiment, the angular-dependent NMR frequencies are measured before ($\omega_1$) and after ($\omega_2$) the mixing time $t_m$ (Figure 2.4(a)). If the orientation of the molecule does not change, then $\omega_1 = \omega_2$. The 4D experiment can be approximately considered as a combination of two 2D setups plus a waiting time ($t_{mb}$) in the middle. The idea is that the slow molecules, whose orientation has no appreciable change during $t_{ma}$, are chosen through the first 2D setup. After the waiting time $t_{mb}$, whether those molecules are still slow is verified by comparing the NMR frequency before ($\omega_3$) and after ($\omega_4$) $t_{mc}$ in the second 2D setup. Figure 2.5 presents the experimental data for PVAc at $T=T_g+20\text{K}$, where the time periods are set as $t_m=t_{ma}=t_{mb}=t_{mc}=10\text{ms}$. As illustrated in Figure 2.5(a), significant off-diagonal contribution exists in the plot of $\omega_1$ versus $\omega_2$ for the overall
system in a 2DNMR experiment (without pre-selecting molecules). If the heterogeneous scenario is adopted, this plot of $\omega_1$ versus $\omega_2$ is shown to correspond to a broad distribution of rotational mobility (Figure 2.6), with a major part covering about 3 - 4 decades$^{69}$. In the 4DNMR experiment, slow molecules are pre-selected through the first 2DNMR (Figure 2.4(b)), and the plot of $\omega_3$ versus $\omega_4$ is nearly diagonal (Figure 2.5(b)). This result indicates that, if the molecules maintain their orientations during $t_{ma}$, they would most probably do so during $t_{mc}$. The remarkable difference between Figure 2.5 (a) and (b) clearly demonstrates that the homogeneous scenario is not correct; otherwise the plot of $\omega_1$ vs $\omega_2$ should be the same as that of $\omega_3$ vs $\omega_4$ no matter whether a sub-ensemble or the total ensemble is studied.

![Figure 2.5](image.png)

Figure 2.5: $^{13}$C NMR spectra of PVAc at 320K with $t_m = t_{ma} = t_{mb} = t_{mc} = 10\text{ms}$. (a) $\omega_1$ versus $\omega_2$ through a 2DNMR (Figure 2.4(a)); (b) $\omega_3$ versus $\omega_4$ through the second 2DNMR in a 4DNMR (Figure 2.4(b)).$^{69}$ (Figure reprinted with permission from $^{69}$. Copyright (2010) by Phys. Rev. Lett.)
An interesting question raised by Figure 2.5(b) is how long the slow molecules can remain slow. The same research group investigated this issue by increasing the waiting time $t_{\text{mb}}$ in Figure 2.4(b). And they found that the slow molecules turn to fast ones, or significantly changes its relaxation rate after a time period of about two relaxation processes\textsuperscript{75}. In other words, the dynamically heterogeneous domains, i.e. slow vs fast, are not a static picture, and they would inter-convert to each other at a time scale comparable to the structural relaxation time. The upcoming question is how large in space the dynamic heterogeneity is. To understand it, the authors added a new technique, so-called cross polarization (CP), to the previously used 4DNMR (Figure 2.4(b))\textsuperscript{10,11}. The use of CP is to transfer the magnetization of an excited $^{13}\text{C}$ to a neighbor one through the proton bath with a negligible transferring time in comparison to the rotational relaxation time of the molecules\textsuperscript{10}. The overall procedures can be described in the following way. The molecules in slow domains (Figure 2.7) are pre-chosen to be excited. By using the CP, the excited spins will diffuse through the slow domains and some of them will arrive at
the fast domains (Figure 2.7) with a diffusion coefficient \(D_{\text{spin}}\) measured independently. The time period \(t^*\) for the dynamics of the pre-selected sub-ensemble returns to that of the total ensemble is recorded. Thus, the product of \(D_{\text{spin}}\) and \(t^*\) can be used to extract the length scale of dynamic heterogeneity \(\xi_{\text{het}}\). A few glass-forming systems have been studied via this method and \(\xi_{\text{het}}\) was shown to be about 1 - 4 nm at T close to \(T_g\).

![Figure 2.7: A two-state vision of dynamic heterogeneity](image)

In addition to 4D NMR, photobleaching and dielectric non-resonant hole burning are also direct experimental methods to probe the dynamic heterogeneity in the supercooled liquids. In fact, the strategies of the two methods are quite similar. Here we will take the photobleaching method as an example to illustrate the working mechanism. In this approach, the supercooled liquid, mixed with a small amount of dye molecules, is illuminated by an intense unpolarized laser light. Under illumination, some of the dye molecules are permanently bleached (photo-peroxidated), and only the unbleached molecules are probed in the subsequent experiments. The dye molecules in more mobile regions are bleached with a higher efficiency than in slow regions, which
can be understood in a following way. The bleaching is attained by changing the conformation of the molecule from one state to another, e.g. from a planar dye molecule to a nonplanar peroxide. A more mobile region results from a lower-than-average local density, and dye molecules in this environment are more likely to undergo the conformational change required for the bleaching. In a regular photo-bleaching experiment, ~60% of the dye molecules are pre-bleached, which are mostly the ones in mobile regions. Then the orientations of the unbleached dye molecules are preferentially aligned in a particular direction by illuminating the sample with polarized light in a short time period. Afterwards the relaxation of the orientation of these molecules back to the isotropic state is probed. Since the unbleached dye molecules are mostly the ones in the slowly relaxing region, they exhibit longer relaxation time back to the isotropic stage than does the total ensemble without pre-bleaching. The experimental data from photobleaching experiments on OTP mixed with tetracene (dye) are presented in Figure 2.8. When $\Delta t$ (the waiting time after the bleaching) is short, the sub-ensemble remaining after photo-bleaching has a larger average relaxation time ($\tau_{\text{obs}}$) than the total ensemble ($\tau_C$). When $\Delta t$ is long enough, the dynamics of the sub-ensemble come back to the one of the total ensemble. The authors attributed this to the complete exchange of relaxation rate between the slow and fast regions at long waiting time.
Figure 2.8: Photobleaching experiment on OTP mixed with dye molecules (tetracene)\textsuperscript{12}, Δt is the waiting time after the bleaching, \( \tau_{\text{obs}} \) is the average relaxation time for the reorientation of the unbleached dye molecules, and \( \tau_C \) is the average relaxation time for the reorientation of the overall dye molecules without pre-bleaching. (Figure reprinted with permission from\textsuperscript{12}. Copyright (2010) by Ann. Rev. Chem. Phys.)

Furthermore, the observation of cooperative motions of colloid particles in the colloid systems near the jamming point is also considered as experimental evidence for cooperative molecular motions in supercooled liquids\textsuperscript{81,82}. However, the doubt of whether the colloid particles with a size of microns or submicron can accurately represent the motions of real molecules is difficult to clarify.
2.2.3. The cooperativity length scale

The length scale of molecular cooperativity or dynamic heterogeneity has been estimated via various experimental approaches, including direct methods, such as 4D NMR\textsuperscript{10,11} and Photobleaching\textsuperscript{78}, and indirect methods (model dependent), such as multipoint dynamic susceptibility function\textsuperscript{8,9} and thermodynamic method based on Fluctuation-dissipation theory\textsuperscript{7}. All these approaches provided a consistent estimate of cooperativity size, which is about 1-4 nm in different glass-forming materials. Moreover, some researchers tried to connect the cooperativity size estimated around $T_g$ to fragility, but no clear correlation has been found\textsuperscript{7,8,10}. One example, where the cooperativity size ($\xi$) is obtained via the multipoint dynamics susceptibility function\textsuperscript{8}, is presented in Figure 2.9. In this figure, $\chi^*(T_g)$ is the four point dynamic susceptibility at $T_g$, which is proportional to the cooperativity volume $\xi^3(T_g)$. And $\xi(T_g)/\alpha$ is the cooperativity length scale scaled by the size of the elementary structural units. Clearly, neither the cooperativity size nor the number of cooperative units around $T_g$ is directly correlated with fragility (Figure 2.9). This result is consistent with predictions of RFOT and the entropic barrier hopping theory.
Figure 2.9: (A) four point dynamic susceptibility $\chi^*_d(T_g)$ vs m, (B) $\xi(T_g)/a$ vs m, the meaning of $\chi^*_d(T_g)$ and $\xi(T_g)/a$ has been described in the text. (Figure reprinted with permission from\textsuperscript{8}. Copyright (2010) by Science)

Another important issue regarding the cooperativity length scale is its temperature dependence. According to the traditional cooperativity idea, the increase of the apparent activation energy upon decreasing temperature results from the increase of cooperativity size. Intuitively, the temperature dependence of the cooperativity length scale should follow that of $(E_A(T))^{1/3}$. In fact, most models (except the entropic barrier hopping theory) adopt a similar standpoint and connect the slowing-down of structural relaxation of supercooled liquid under cooling with the growing of the cooperativity size\textsuperscript{29,41,44}, although the detail mathematical expressions are distinct. Two examples (Adam-Gibbs theory and RFOT) have been presented in Section 2.2.1\textsuperscript{29,40,44}. On the experimental side, a few studies have been carried out on this issue. As a matter of fact, the 4D NMR approach is supposed to be one of the best candidates to tackle this issue because it is the least model-dependent experimental approach to study the dynamic heterogeneity or molecular cooperativity. However, due to the current technical limitation, it can only probe the dynamics in supercooled liquids in a narrow frequency window (0.001 ~ 10 s)\textsuperscript{83}. For most glass-forming materials, this frequency window corresponds to a rather
limited temperature range (less than 10K) in the vicinity of \( T_g \). Therefore, explicit messages about temperature dependence of molecular cooperativity are difficult to be obtained using this technique. Recently, Ediger and coworkers reported a 4D NMR study on glycerol, where the dynamic heterogeneity length scale (\( \xi_{\text{het}} \)) is shown to increase from 0.9±0.5 nm at \( T_g+18 \)K to 1.4±0.5 nm at \( T_g+10 \)K \(^{83}\). The reported temperature variation of \( \xi_{\text{het}} \) is, however, within the experimental error bar and hard to convince readers. Moreover, the work conducted by Berthier \textit{et al.} based on a 4 point dynamic susceptibility function shows that the cooperativity size exhibits very weak temperature dependence from \( T_g \) to about \( T_c \), and sharply decreases in high temperature region (Figure 2.10)\(^9\). (\( N_{\text{corr,T}} \) in Figure 2.10 is the number of molecules whose dynamics are correlated to a local fluctuation of enthalpy. \( N_{\text{corr,T}} \) is claimed to be approximately the square root of the number of molecules whose dynamics are correlated among themselves\(^9\). The latter is the molecular cooperativity discussed in this thesis and can only be estimated from the 4-point correlation function (Eq. (2.21))).
Figure 2.10: Number of molecules whose dynamics are correlated to a local fluctuation of enthalpy estimated by multi-point dynamic susceptibility function, $\lg \tau_0 = -12$, $\lg \tau(T_c) = -7$, and $\lg \tau(T_g) = 2$. (Figure reprinted with permission from. Copyright (2010) by Phys. Rev. E)

In addition, some researchers have connected the width of the first sharp diffraction peak in the static structure factor to the length scale of the structural correlation in the glass-forming materials, and the latter is assumed to be the cause of the molecular cooperativity in the structural relaxation. Specifically, according to the well-known Scherrer equation for microcrystalline samples, the width of Bragg peaks in diffraction patterns can be related to the average size of microcrystal. Similarly, the correlation length of disordered structures ($l_c$) in amorphous materials can be estimated by the expression,

$$l_c = \frac{2\pi}{\Delta Q}$$  \hspace{1cm} (2.22)
Here $\Delta Q$ is the half width at the half maximum of the first sharp diffraction peak in the static structure factor. The study of temperature dependence of $\Delta Q$ has been performed in several glass-forming materials\textsuperscript{87,88,89,90,91,92}. As illustrated in Figure 2.11, in some systems (PBD\textsuperscript{87}, and (AgI)$_{0.3}$(AgPO3)$_{0.7}$\textsuperscript{88} and glycerol\textsuperscript{92}, $\Delta Q$ slightly increases with temperature above $T_g$, i.e. $l_c$ weakly grows under cooling, but the trend (except (AgI)$_{0.3}$(AgPO3)$_{0.7}$) is far less than the predictions of most theories\textsuperscript{29,40,44}. In other materials, such as the (AgI)$_{0.5}$(AgPO3)$_{0.5}$\textsuperscript{88}, GeO\textsubscript{2}\textsuperscript{89}, GeSe\textsubscript{2}\textsuperscript{90} and OTP\textsuperscript{91}, $\Delta Q$ remains essentially constant in a large temperature window above $T_g$. Based on these diffraction data, the structural correlation length in supercooled liquids seems to have no strong temperature dependence above $T_g$ in general (Figure 2.11).

![Figure 2.11: Temperature dependence of $1/\Delta Q$ in different materials, the black line denotes $\xi$ predicted by the Adam-Gibbs theory, the red line represents $E_A(T)^{1/3}$, which serves as a intuitive reference for the cooperativity size according to the traditional cooperativity idea, and the blue line shows $\xi$ predicted via the RFOT.](image-url)
2.3. Molecular cooperativity in the fast collective vibrations

In addition to the structural relaxation, the collective vibrations in the pico-second time scale, the so-called boson peak, is also a common dynamic feature for all the glass-forming materials. It is known that the low-frequency (GHz-THz) acoustic region of vibrational density of states $g(\nu)$ in crystals can be well described by the Debye model, which predicts that $g(\nu) \propto \nu^2$. However, all disordered materials exhibit strong deviations from this prediction. Two extra contributions exist in this GHz-THz (pico-second time scale) region of the excitation spectra presented as $g(\nu)/\nu^2$ vs $\nu$ (Figure 2.12), measured by light or neutron scattering: (i) an anharmonic relaxation-like contribution, the so-called fast relaxation which appears as a broad quasielastic scattering (QES) and dominates the low frequency region (normally below 200GHz), and (ii) a harmonic vibration contribution, which arises as a broad inelastic peak, namely boson peak.

![Figure 2.12](image-url)  
Figure 2.12: A schematic plot of the low frequency spectra of amorphous materials presented as $g(\nu)/\nu^2$ vs $\nu$. 

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2.3.1. Theoretical models

Despite decades of study, the microscopic nature of the boson peak is still in debate. (i) According to the soft potential model (SPM), the vibrations in the boson peak are specified as localized (or quasi-localized) vibrational modes of soft (defect-like) regions in the disordered structure, e.g. interstitial atoms\textsuperscript{98,99,100}. Specifically, these interstitial atoms vibrate collectively and form soft harmonic oscillators. These harmonic oscillators elastically interact with each other and are stabilized by anharmoncity. This modifies the vibrational density of states and results in the formation of the boson peak. (ii) The model proposed by Schirmacher and coworkers attribute the boson peak to the scattering of acoustic waves by the fluctuations of elastic constants in the disordered structures\textsuperscript{18,101,102,103}. Briefly, the elastic constants fluctuates spatially in amorphous materials. This will strongly scatter and damp the high frequency acoustic modes, reduce their mean free path and shift them to the low frequency region. As a result, the vibrational density of states is changed and the boson peak arises. It is of interest to mention that the work conducted by Ramos \textit{et al.} shows the presence of the boson peak in the orientational glass of ethanol, i.e. a crystalline lattice with disordered molecular orientations\textsuperscript{104}. This result indicates that only fluctuation in molecular orientations (or the so induced fluctuation in elastic constants) is enough to render the excess low-frequency modes and the formation of the boson peak. In other words, this work provides a strong support for the elastic-constant-fluctuation model. (iii) Duval and others proposed a blob model. Specifically, the disordered materials are considered to consist of many blobs at nanometer scale which are separated by low-density boundaries. The vibrations of the
boson peak are specified as vibration modes of the blobs\textsuperscript{19}. If this model is true, a characteristic peak around 0.3-0.6 Å\textsuperscript{-1}, corresponding to the dimension of the nano blobs, would appear in the static structure factor measured via X-ray or Neutron diffraction. However, such experimental evidence has never been reported. (iv) Finally, the boson peak has been ascribed to the specific chemical structure of the studied materials. For example, the boson peak vibrations in SiO\textsubscript{2} have been specified as coupled rotations of several SiO\textsubscript{4} tetrahedra\textsuperscript{105}. In the case of chalcogenide glasses, the boson peak has been connected to vibrations of the layered structures\textsuperscript{106}. However, Sokolov and coworkers found that the boson peak shape (Figure 2.13, where the boson peak spectra are normalized by both the peak amplitude and position) in amorphous materials with different chemical structures are rather universal\textsuperscript{107}. Clearly, the model based on the specific chemical structures is at odds with Sokolov and coworkers’ finding.

Figure 2.13: Boson peak spectra normalized by peak amplitude and position for different materials\textsuperscript{107}: 1-As\textsubscript{2}S\textsubscript{3}; 2-Bi\textsubscript{4}Si\textsubscript{3}O\textsubscript{2}; 3-SiO\textsubscript{2}; 4-B\textsubscript{2}O\textsubscript{3}; 5-Li\textsubscript{2}O and 6-GeS\textsubscript{2}. (Figure reprinted with permission from\textsuperscript{107}. Copyright (2010) by Solid State Commun.)
Although the microscopic nature of the boson peak remains a subject of active discussions, it is usually described as a cooperative motions of groups of molecules and is related to some characteristic correlation (or heterogeneity) length ($\xi$) about a few nanometers in the disordered structure\textsuperscript{17,19-24}. According to the blob model, $\xi$ defines the characteristic correlation length of the density fluctuation, i.e. the blob size\textsuperscript{19}. In the elastic-constant-fluctuation model\textsuperscript{20,23}, $\xi$ is specified as the correlation length of elastic constants fluctuations, i.e. the length scale of elastic heterogeneity. The simulation studies by Barrat \textit{et al.} and L. E. Silbert \textit{et al.} describes $\xi$ as a length scale below which homogeneous elastic continuum approximation for deformation breaks down\textsuperscript{108,109,110,111}, i.e. $\xi$ is a length scale to separate the affine and non-affine deformation. In fact, the physical nature of $\xi$ in the elastic-constant-fluctuation model\textsuperscript{20,23} and the simulation studies\textsuperscript{108-111} are quite similar: both characterizing the spatial fluctuation of elastic properties in the disordered structure.

Let’s take the elastic-constant-fluctuation model for example to elucidate how the structural correlation length is connected to the boson peak spectra. According to this model\textsuperscript{20,23,101-103}, when the wavelength of the acoustic modes is comparable to the length scale of fluctuations of elastic constants, the acoustic modes are strongly scattered by the fluctuation and become quasi-localized to form the vibrational modes at the boson peak. The above picture has been supported by both experimental\textsuperscript{112} and simulation works\textsuperscript{113}. Therefore, the wavelength of the sound modes at the boson peak can be used to present the characteristic length scale of elastic heterogeneity, and thus the correlation length of the underling structural fluctuations,
Here $V_T$ and $\nu_{BP}$ are transverse sound velocity and boson peak frequency, respectively. It is of interest to mention that, according to literature, $\lambda_{BP}$ for several network glasses has been shown to be 2-3 nm\textsuperscript{17,113,114}, which is of the same order of magnitude as the cooperativity length scale involved in the structural relaxation\textsuperscript{27}. In Eq. (2.23), the transverse sound velocity is applied because the boson peak vibrations have been demonstrated by a few approaches to have mostly transverse-like nature\textsuperscript{17,18,112,115,116,117,118,119,120}. A convincing argument is based on the study of the depolarization ratio, i.e. the ratio of the depolarized to the polarized light scattering intensities, in the boson peak frequency range. The value is shown to be rather high in many disordered materials\textsuperscript{115-120}. Especially in the case of organic systems, it is about 0.6-0.7\textsuperscript{115-118}, which is approaching the limit of pure transverse vibrations (0.75) in an isotropic medium, but far away from the value of the pure longitudinal vibrations (0).

In some approaches\textsuperscript{17,18,29}, $\xi$ is thought to be directly equal to $\lambda_{BP}$, but a coefficient $S$ (close to 1) is assumed in others\textsuperscript{19-21,108,121}

$$\xi = \frac{V_T}{V_{BP}} .$$

(2.24)

For example, in a simple approach, the boson peak vibrations can be assumed as torsion or spherical modes of nano-blobs (or spherical particles), which contains $\sim$100 molecules, in the disordered materials. The size of the blobs can be expressed as,

$$l = 0.85 \frac{V_T}{V_s} \text{ (torsion mode); } l = 0.7 \frac{V_T}{V_s} \text{ (spherical mode)},$$

(2.25)
where $v_t$ ($v_s$) is the frequency of the torsion (spherical) mode of the blobs. Thus, the pre-factor $S$ in Eq. (2.24) would be 0.85 and 0.7 for the two cases, respectively. This approach has been supported by the low frequency Raman data of nanocrystals\textsuperscript{121}.

2.3.2. Experimental evidence

The direct experimental evidence for the cooperative molecular motion involved in the boson peak vibrations has been provided by using inelastic neutron scattering\textsuperscript{122}. According to the theory proposed by Carpenter and Pelizzari, the momentum transfer ($Q$) dependence of the dynamic structure factor $S(Q,E)$ at a fixed energy change ($E$) in disordered systems can be expressed as\textsuperscript{123},

$S(Q,E) \propto Q^2$, for totally uncorrelated motion.

$S(Q,E) \propto Q^2 S(Q,0)$, for correlated motion, e.g. sound waves.

Here $S(Q,0)$ is the static structure factor. The low energy vibrational spectrum of PBD measured by inelastic neutron scattering\textsuperscript{122} is presented in Figure 2.14, where the boson peak is located around 2meV. The corresponding static structure factor and the dynamic structure factor at two different $E$ are shown in Figure 2.15(a) and (b). The peak at 1.5 Å\textsuperscript{-1} in the static structure factor is related to the intermolecular distance. As revealed by Figure 2.15(b), a clear peak exists at ~1.5 Å in the dynamic structure factor at $E=1$meV, which is near the boson peak energy (marked in Figure 2.14). But this peak disappears at $E=6$ meV, that far exceeds $E_{BP}$. This result clearly demonstrates that the vibrations in the boson peak region involve significant inter-molecular cooperativity.
Figure 2.14: Boson peak spectrum of PBD obtained by neutron scattering\textsuperscript{122}, the arrow marks the position of the boson peak. (Figure reprinted with permission from\textsuperscript{122}. Copyright (2010) by Phys. Rev. Lett.)

Figure 2.15: (a) Static structure factor and (b) dynamic structure factor of PBD at two different energy change $E$ (1meV and 6meV), obtained by neutron scattering\textsuperscript{122}. (Figure reprinted with permission from\textsuperscript{3}. Copyright (2010) by Phys. Rev. Lett.)

Besides, indirect evidence supporting the idea that the vibrations at the boson peak involve molecular or structural cooperativity has been provided by Sokolov and coworkers\textsuperscript{17}. They demonstrated a linear correlation between the wavelength of the transverse acoustic modes at the boson peak and the structural correlation length.
estimated from the static structure factor as defined by Eq. (2.22) for different glass-forming materials (Figure 2.16), where the coefficient is close to 1\(^ {17} \),

\[ l_c = 2\pi / \Delta Q = (0.9 \pm 0.11)V_T / V_{BP} \]  

(2.26)

An intuitive explanation to the above correlation can be made in the following way. The elastic constants fluctuations, induced by the structural heterogeneity, strongly scatter and localize the acoustic modes, especially for the acoustic modes whose wavelength is comparable to the length scale of structural heterogeneity. This affects the density of vibrational states and result in the formation of the boson peak. Therefore, the wavelength of the vibration modes at the boson peak can reflect the correlation length of the structural fluctuation.

Figure 2.16: \( l_c \) vs \( \lambda_{BP} \), here \( V_T \) is the transverse sound velocity, \( c \) is velocity of light, and \( W_{max} \) is the maximum position of boson peak spectrum in unit of Å\(^{-1} \). Numbers represent different materials: 1~PMMA, 2~SiO\(_2\), 3~GeO\(_2\)-5.4% Na\(_2\)O, 4~SFI, 5~FI, 6~BaSF64, 7~LaSF9. (Figure reprinted with permission from\(^ {17} \). Copyright (2010) by Phys. Rev. Lett.)
2.4. The connection between the structural relaxation and the boson peak vibrations

It is known that the structural relaxation and the boson peak vibrations in the glass-forming materials have a huge difference in time window, e.g. the former, happening at pico-second time scale, is normally 12-15 orders of magnitude slower than the latter around $T_g$. In addition, the natures of the two processes are rather distinct. The former is a relaxation process, whereas the latter is vibrational motions. However, the recent studies on glass-forming materials revealed that the two processes have intimate connections\(^{18,24,25,27-30,36}\). First, Sokolov and coworkers have shown that a stronger system, i.e. a material that has lower fragility, would exhibit more pronounced boson peak (relative to the QES) at $T_g$\(^{18,24}\). They also demonstrated that the boson peak amplitude in different systems around $T_g$ relative to the corresponding Debye level inversely correlates with fragility\(^{24}\). Second, Buchenau and Zorn discovered a correlation between the temperature variations of $\ln(\tau_a)$ and that of the mean square displacement of fast molecular motions at nano to pico second time scale in selenium\(^{124}\). Recently, Larini and coworkers demonstrated that this correlation is quite universal among different materials\(^{25}\). They suggested that the glass transition in different glass-forming materials happens only when the mean square displacement of the fast motions exceeds a universally critical value. In other words, analogous to melting of crystals, a “Lindemann criterion” also applies for softening of glass. Third, it has been shown in several glass-forming materials that the boson peak vibrations become over-damped by the relaxation process around $T_c$\(^{36}\), which is a characteristic temperature to mark the crossover from liquid-like to solid-like dynamics for the structural relaxation on a molecular level.
(Figure 2.1). Last but not least, some researchers speculate that the characteristic length scale involved in boson peak vibrations is closely related to the cooperativity length scale in the structural relaxation\textsuperscript{27-30}. For example, Wolynes and coworkers showed that the excitations in the boson peak are just the domain wall motions of the entropic droplets\textsuperscript{29,30}, thus the characteristic length scale associated with the boson peak vibrations would be in accord with the cooperativity size in the structural relaxation; In a recent article, de Gennes suggested that the size of the solid clusters in the two-state model for the structural relaxation can be estimated by the wavelength of the sound modes at the boson peak\textsuperscript{28}. In one word, the boson peak vibrations and the structural relaxation are two closely related rather than independent processes, and this fact should be taken into account by every theory which attempts to describe the dynamics of glass-forming materials.

2.5. Research objectives

As discussed at the very beginning of this chapter, the steep temperature dependence of the structural relaxation time or viscosity in supercooled liquids cannot be explained by any simple-liquid theory. A widely adopted idea is to attribute this temperature dependence to the cooperativity involved in molecular motions. Two intuitive consequences are rendered by this idea. First, a material involving larger cooperativity would exhibit much stronger temperature variations of structural relaxation time around $T_g$, i.e. higher fragility. However, this statement seems contradictive to the experimental results. Second, the cooperativity size should drastically grow with
decreasing temperature to explain the sharp slowing down of the structural relaxation (or increase of $E_A$). Nevertheless, this point is not very clear as seen from currently available experimental data. In addition, it is well known that both decreases of free volume and thermal energy in a supercooled liquid under isobaric cooling would slow down the dynamics. But the relationship between the molecular cooperativity and the two contributions to the variations of $\tau_\alpha$ remains essentially unexplored. Moreover, the collective vibrations at pico-second time scale, is also described as a cooperative process, and some researchers speculate that the cooperativity length involved in the boson peak vibrations is related to that for the structural relaxation. Thorough experimental work is required to verify this speculation.

In summary, a few questions can be formulated from this chapter: (1) Do the boson peak vibrations involve the same size of cooperative molecular motions as the structural relaxations? (2) What is the relationship between the cooperativity length scale and fragility among different glass-forming materials? (3) How are the two contributions (volume and thermal energy) to the temperature variations of $\tau_\alpha$ connected to cooperativity size? (4) How does the cooperativity size vary with temperature?

In this work, we performed light scattering experiments on various glass-forming materials to estimate $\xi$ from the boson peak spectra (Eq. (2.23)) and try to tackle all the above questions. Before getting into the experimental details, we would like to give a brief introduction to some basic principles of light scattering.
2.6. Basic principles of light scattering

When light impinges on a particle, given the size of the particle is much smaller than the wavelength of the light, an electric dipole moment ($\mathbf{P}$) would be induced in the particle. The oscillation of this dipole moment with time would radiate light out to a direction different from the incoming one. This phenomenon is commonly known as the light scattering process\textsuperscript{125,126,127}. Here, the amplitude and polarization of the electric field of the scattered light strongly depend on the dielectric property of the particle. This scattering process can be schematically presented by Figure 2.17, where $\mathbf{k}_i$ is the wave vectors of the incident light, $\mathbf{k}_f$ is the wave vector of the scattered beam, $\mathbf{q}$ is the scattering wave vector, and $\theta$ is the scattering angle. According to the rule of vector operation,

$$\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i.$$  \hspace{1cm} (2.27)

Normally, the energy of the scattered light does not change much relative to that of the incident beam. In that case,

$$|\mathbf{k}_f| = |\mathbf{k}_i|.$$  \hspace{1cm} (2.28)

Combining Eq. (2.27) and (2.28), one obtains

$$|q| \approx 2\pi |\mathbf{k}_i| \sin \frac{\theta}{2} = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2}.$$  \hspace{1cm} (2.29)

Here $\lambda$ is the wavelength of light in vacuum, and $n$ is the refractive index of the medium for the scattering process.
It is known that a light beam can pass through pure water without much scattering, while enormous scattering can be caused by introducing dusts to the water. To elucidate the underlying physics, let’s assume that a plane wave is propagating through a medium (Figure 2.18). The medium can be considered to consist of many small scattering volumes $V^*$ with a linear dimension much smaller than $\lambda$. As illustrated in Figure 2.18, the scattered light observed away from the medium is a superposition of the lights radiated from all $V^*$s by summing up the electric field. If the medium is optically homogeneous, i.e. no fluctuation of dielectric constant, one always can find a volume $V_2^*$ along the wave front (AB), which radiates a light having the electric field with the same polarization and amplitude as the light radiated from $V_1^*$, but opposing phase (the optical path difference $|OC| = \lambda/2$). Clearly, the lights from $V_1^*$ and $V_2^*$ cancel one another when arriving at the observer. Following the above argument, it is not difficult to conclude that no scattering
can be observed at any non-zero scattering angle when light propagates in an optically homogeneous system.

Figure 2.18: Scattering of a plane wave in a medium. $k_i$ and $k_f$ are wave vectors of the incoming and scattered light beams, respectively. The line A-B is the wave front of the incoming beam. $\theta$ is the scattering angle. $V^*_1$ and $V^*_2$ represent scattering volumes with a linear size much smaller than the wavelength of the light. $|OC|$ is the optical path difference between the observed lights scattered from $V^*_1$ and $V^*_2$.

But if the dielectric constant in the medium is heterogeneous, the light radiated from $V^*_1$ and $V^*_2$ do not have electric fields with the same amplitude or polarization, so they will not completely cancel one another. Thus, noticeable scattering can be observed at non-zero angles.

In real materials, the dielectric constants fluctuate not only in space but also with time. The latter is caused by motions of molecules in the materials, such as thermal motions. Both spatial and temporal fluctuation of dielectric constants will scatter light. In
particular, unlike the spatial fluctuation of dielectric constants, the temporal one not only changes the direction of the scattered light relative to the incident one, but also alters its frequency. Thus, the scattered light would have a distribution of intensity as a function of the frequency shift \( \nu = \nu_i - \nu_f \) relative to the incident light, which can be generally expressed as

\[
I(\vec{q}, \nu) = \left[ \frac{I_0 \pi^2 V}{L^2 \lambda^4 N^* \varepsilon_0^2} \right] \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt < \delta\varepsilon(\vec{q}, 0) \delta\varepsilon(\vec{q}, t) > \exp(i2\pi \nu t),
\]

(2.30)

where \( I_0 \) is the intensity of the incident light, \( V \) is the volume of the system, \( L \) is distance of observation, \( N^* \) is the number density of the scattering particles or volumes, such as \( V^* \) in Figure 2.18, \( \varepsilon_0 \) is the average dielectric constant, the bracket \(< >\) denotes ensemble average, and \( \delta\varepsilon(q,t) \) is the fluctuation of dielectric constant in reciprocal space, which is Fourier transformed from real space

\[
\delta\varepsilon(q,t) = \int d^3\vec{r} \delta\varepsilon(\vec{r}, t) \exp(i\vec{q} \cdot \vec{r}),
\]

(2.31)

where \( \delta\varepsilon(r,t) \) is the fluctuation of dielectric constant in real space, which denotes the deviation of dielectric constant from its average value at an arbitrary time and position.

As shown in Eq. (2.30), the intensity of scattered light is inversely proportional to \( \lambda^4 \). This indicates that light with longer wavelength would be scattered less, which explains why the sky and the ocean look blue.

Normally, the light scattering spectra consist of three components, elastic, quasielastic and inelastic scatterings, which can be qualitatively illustrated in Figure 2.19.
Since the frequency shift of the scattered light is caused by molecular motions in the medium, the components in the light scattering spectra can provide useful information about molecular dynamics of the studied materials. The elastic scattering, also called Rayleigh scattering, appears as a central peak in the spectrum. This scattering process involves zero frequency shifts. So it does not result from the temporal fluctuation of the dielectric constant, and only provides information on the static structure.

Quasielastic scattering, also named the Rayleigh wing, presents a broadening of the elastic line. It is related to anharmonic molecular motions, such as translational and rotational relaxation processes. Usually, several relaxation processes with distinct characteristic correlation times contribute to the quasielastic scattering. To better illustrate each individual process, the light scattering data are presented as a susceptibility function,

$$\chi'(\nu, \tilde{q}) = I(\nu, \tilde{q})/(n(\nu) + 1).$$

(2.32)
where \( n(\nu) = \left[ \exp(h\nu/kT)-1 \right]^{-1} \) is the Bose temperature factor and \( I(\nu) \) is the measured intensity. A schematic susceptibility spectrum is displayed in Figure 2.20. Similar to the mechanical loss (\( G''' \)) and dielectric loss (\( \varepsilon'' \)) spectra, each peak in the susceptibility spectrum corresponds to one relaxation process, and the peak position marks the characteristic correlation time (frequency) of the process. In principle, all these relaxation processes would contribute to the quasielastic scattering, i.e. the broadening of the elastic line in Figure 2.19, but play different roles at different time scales. For example, the broadening at high frequency (GHz~THz) is usually dominated by the fast relaxation process, which has been mentioned in Section 2.3 as intimately connecting with the boson peak vibrations.

![Figure 2.20: A schematic plot of the susceptibility spectrum.](image)

The inelastic peaks in the light scattering spectra (Figure 2.19) are often related to vibrational motions of molecules. The propagation of the vibrational modes in the medium forms elastic waves. Normally, the elastic waves can be separated into two types: longitudinal and transverse waves. The vibrational direction of the molecules is
parallel to the propagation direction for the longitudinal wave, but perpendicular for the transverse wave.

Acoustic and optical modes are typical examples of vibrational motions of molecules. Here, we take a simple crystalline system, where each primitive cell contains two types of atoms, as an example to illustrate the difference between the two modes (Figure 2.21). In the case of optical modes, neighboring atoms are moving against each other while keeping the center of the mass fixed. For acoustic modes, the motion of one atom follows that of the previous one along the direction the propagation of the elastic wave. The dispersion relations of the two modes can be calculated by applying classical Newton mechanics, and is qualitatively displayed in Figure 2.22. (The dispersion relation presents the wave vector ($K$) dependence on the angular vibrational frequency ($\omega$) of the elastic wave.) As seen from Figure 2.22, the significant $K$ dependence of $\omega$ exists in the low $K$ range for the acoustic modes, but in high $K$ range for optical modes. In any scattering experiment, the vibrational modes can be probed only when $K$ is equal to the scattering wave vector $q$. Since the wavelength of the laser light in normal light scattering experiments is usually several hundreds of nanometers, that is, ~1000 times larger than the lattice constant ($a$), the accessible value of $q$ are usually below thousandths of $2\pi/a$. Such a small range of accessible $q$ (the marked region in Figure 2.22) has two consequences for the normal light scattering experiments. First, only acoustic modes exhibit appreciable $q$ dependence of vibrational frequency. Second, a huge frequency difference exists between the acoustic and optical vibrational modes probed. For most materials, the acoustic mode lies in 1~50GHz, and it is often probed by the Brillouin
spectroscopy. The optical modes are located at much higher frequency (~10THz), which are usually measured using Raman spectroscopy.

Figure 2.21: Optical vs acoustic vibrational modes\textsuperscript{128}, + and – denote the two types of neighboring atoms. The vertical arrows indicate the vibrational direction of the atoms, dashed lines represent the equilibrium position of the atoms, and the horizontal arrows show the propagation direction of the elastic waves.

Figure 2.22: Dispersion curves of acoustic and optical vibrational modes (angular frequency ($\omega$) vs the wave vector of the elastic wave ($K$))\textsuperscript{128}, here $M_1$ and $M_2$ are the masses of the two types of atoms in Figure 2.21, and $a$ is the lattice constant. The red rectangle marks the $q$ range which is accessible in normal light scattering experiments.
As discussed above, for normal light scattering experiments, only acoustic modes form well defined elastic waves with a clearly q-dependent vibrational frequency. These elastic waves are also called acoustic waves or sound waves. The velocity \( V \) of the propagating acoustic waves, i.e. sound velocity, can be estimated from the frequency \( \nu \) of Brillouin peaks measured using Brillouin spectroscopy

\[
V_{L,T} = \frac{\nu_{L,T}}{2\pi / q} = \frac{\lambda \nu_{L,T}}{2n \sin(\theta/2)}. \tag{2.33}
\]

In this formula, \( \theta \) denotes the scattering angle, the subscripts \( L \) and \( T \) represent longitudinal and transverse acoustic waves, respectively. Normally, the sound velocities are related to the elastic properties of the material as,

\[
\rho V_T^2 = G, \quad \rho V_L^2 = M, \quad B = M - \frac{4}{3}G. \tag{2.34}
\]

Here \( \rho \) is mass density, \( G \) is shear modulus, \( M \) is longitudinal modulus and \( B \) is bulk modulus.

Normally, in a light scattering spectrum, the inelastic peaks corresponding to vibrational motions of the molecules often appear in pair on both size of the Rayleigh line with equal frequency shift (Figure 2.23). The peak at energy-loss side, i.e. the frequency (energy) of the scattered light is lower than that of the incident beam, is called Stokes line, while the counterpart on the energy-gain side is named anti-Stokes line\(^{129} \). According to the quantum mechanics, the vibrational states of the molecules are quantized in terms of energy. The Stokes line corresponds to exciting of molecules from a lower-energy
vibrational state to a higher-energy one. And the excitation energy is absorbed from light. The ani-Stokes line denotes that molecules transit back from higher-energy vibrational state to a lower-energy one and lose energy to the light. Since the probability of transferring energy from materials to the electromagnetic field is much smaller than the reverse case\textsuperscript{129}, the intensity of Stokes line is stronger than the anti-Stokes line. The intensity ratio of the two lines is related to the energy difference ($\Delta \nu$) of the two vibrational states as\textsuperscript{129}

\[ \frac{I_s}{I_{AS}} = \exp(h\Delta \nu / kT) . \] (2.35)

At room temperature, $kT$ is about 25meV (6THz). For acoustic vibrations, $h\nu$ (1~50GHz) is too small in comparison to $kT$, hence the Stokes and anti-Stokes Brillouin modes do not exhibit appreciable difference in intensity. But the energy of optical modes are often comparable to or even larger than $kT$, thus a significant intensity difference would arise between Stokes and anti-Stokes Raman modes. In our study, the intensity difference between Stokes and anti-Stokes Raman modes is used as an extra means to estimate the temperature of the studied materials (Eq. (2.35)) in addition to reading temperature value from the temperature controller.
Figure 2.23: A schematic picture for Stokes and anti-Stokes lines.
CHAPTER III

EXPERIMENTAL DETAILS

In this chapter, detailed information on the light scattering setup, experimental conditions and samples is presented.

3.1. Light scattering setup

Figure 3.1: The light scattering setup used in our study, the arrows along the lines indicate the light path.
As shown in Figure 3.1, a 90-degree scattering geometry is applied in our study. Specifically, the light emitted from the laser chamber is divided by a splitter to two beams: a major one is used to illuminate the sample (solid line) and the other functions as a reference for aligning the Brillouin spectrometer (dash line). A polarization rotator and a polarizer are inserted in sequence between the beam splitter and the optical cryostat, where the samples are located. The polarizer controls the polarization of the incident light and the polarization rotator is to adjust the intensity of the incident light suitable for the studied material. The linearly polarized light after the polarizer is focused by Lens I to illuminate the sample, and the scattered light at 90 degrees is collected for analysis. For Brillouin measurement, the reflection mirror after Lens II is removed and an analyzer is inserted in between Lenses II and III. Applying Lenses II and III in a pair is to obtain a parallel beam between the two lenses and allow other optical components, such as polarizer, reflection mirror, etc., to be used in between. In our experiments, the polarization of the analyzer is fixed along vertical direction, and the polarized and depolarized Brillouin spectra are obtained by setting the polarization of the polarizer vertical and horizontal, respectively. To measure the boson peak spectra, a reflection mirror is inserted after Lens II (Figure 3.1), which reflects the scattered light to the Raman spectrometer sitting on a neighboring optical table. The pair of lenses (II and IV) has a similar function as that of (II and III). The internal optical components in the Raman spectrometer can work as an analyzer with a vertical polarization. Therefore, the polarized and depolarized Raman spectra can be measured in a similar way as the Brillouin spectra.
There are two major advantages by using the setup shown in Figure 3.1. First, for each material, both Raman and Brillouin spectra were measured at the same condition, even at the same spot of the sample, simply by inserting or removing the reflection mirror. Second, the sample cell was designed to have two parallel surfaces and aligned along the angle bisector of the scattering angle. It is called symmetrical scattering, having the advantage to estimate the sound velocity of the materials without knowing its refractive index. Here we take the symmetric scattering at 90-degree scattering angle as an example to elucidate this point. As shown in Figure 3.2, the actual scattering process is happening inside the sample, the wave vectors of the light beam before and after scattering are along NS and SN’, respectively. Based on Eq. (2.29), the scattering wave vector is equal to

\[ q = \frac{4\pi n}{\lambda} \sin \frac{\angle NSS'}{2}, \]  

(3.1)

Here \( n \) is the refractive index of the material and \( \lambda \) is wavelength of the light, and \( \angle NSS' \) is the internal scattering angle. As we discussed before (Eq. (2.33)), the sound velocity of the acoustic wave can be estimated by measuring the frequency of the corresponding Brillouin peaks

\[ V_{L,T} = \frac{2\pi}{q} V_{L,T} = \frac{V_{L,T} \lambda}{2n \sin \frac{\angle NSS'}{2}}. \]  

(3.2)

Based on the plane geometry, one can obtain the following relations

\[ \angle NSS' = \angle SN' N + \angle SNN', \]  

(3.3)

\[ \angle BN' N = \angle N' NA', \]  

(3.4)

\[ \angle SN' N = \angle SN' B + \angle BN' N, \]  

(3.5)

\[ \angle SNN' = \angle SNA' - \angle N' NA'. \]  

(3.6)
Taking Eq. (3.4) - (3.6) into Eq. (3.3), one obtains

\[ \angle NSS' = \angle SN' B + \angle SNA'. \] (3.7)

According to the Snell’s law,

\[
\begin{align*}
nsin \angle SN' B &= \sin \angle B' N'O' \\
n\sin \angle SNA' &= \sin ANO.
\end{align*}
\] (3.8)

In addition, the sample is aligned along the angle bisector of the scattering angle (90°), thus

\[ \angle B' N'O' = \angle ANO = 45°. \] (3.9)

Taking Eq. (3.9) into Eq. (3.8), one obtains

\[
\begin{align*}
\angle SN' B &= \angle SNA' = \frac{\angle NSS'}{2} \\
\sin \frac{\angle NSS'}{2} &= \sin \angle SN' B = \sin \angle SNA' = \frac{\sin 45°}{n}.
\end{align*}
\] (3.10)

Finally, one can estimate the sound velocity of the materials without knowing its refractive index by combining Eq. (3.10) and Eq. (3.2)

\[ V_{L,T} = \frac{v_{L,T} \lambda}{2n \sin \frac{\angle NSS'}{2}} = \frac{v_{L,T} \lambda}{2 \sin 45°} = \frac{v_{L,T} \lambda}{\sqrt{2}}. \] (3.11)
3.2. Light scattering devices

In this section, we will briefly describe all the devices used in the study such as laser, spectrometers and cryostat.

3.2.1. Laser

A continuous-wave, diode-pumped solid-state laser (Verdi-2 from Coherent) with a wavelength of 532nm is employed in our experiments. The power applied on the sample is normally 50 to 200 mW. By using etalon inside the laser cavity, a single-mode
lasing is achieved. It is extremely narrow in frequency (the full width of half maximum is ~ 100 MHz) and highly stable to ensure experiments lasting days.

In comparison to the Ar+ ion laser used for other projects in our lab, the solid-state laser produces much less heat. The complex cooling system required by the ion laser is not needed. Normally, a small internal cooling fan is efficient enough to maintain the work of the solid-state laser for days.

3.2.2. Spectrometers

In fact, the basic function for all the light scattering spectrometers are more or less the same: measuring the intensity of the scattered light as a function of the frequency shift. The main differences among different spectrometers are the frequency window it can scan and also the spectral resolution. Here we will briefly describe the working principles and the scanning frequency windows of Brillouin and Raman spectrometer used in our study.

3.2.2.1. Brillouin spectrometer

A tandem Fabry-Perot interferometer (Sandercock model) is used in our work to acquire the Brillouin spectra. Before describing this Sandercock model interferometer, we would like to introduce some basic principles of the Fabry-Perot interferometer (FP). As shown in Figure 3.3, a FP interferometer consists of two plane dielectric mirrors held parallel to one another. The inner surface of the mirrors is highly reflecting
(reflectivity~98%). When light gets in to the cavity formed by the two mirrors, it will be reflected back and forth. The wavelength of the light which can transmit through the cavity must fulfill the following relation\textsuperscript{126,130},

\[
m\frac{\lambda}{2} = L, \tag{3.12}
\]

Here \(m\) is an integer, and \(L\) is the space between the two mirrors, which is usually much larger than the wavelength of the light.

Figure 3.3: A schematic graph of a Fabry-Perot interferometer.

For a given space \(L\), the transmittance of the incident light as a function of the wavelength can be expressed as\textsuperscript{130},

\[
T = \frac{T_0}{1 + (4F^2 / \pi^2) \sin^2(2\piL / \lambda)}, \tag{3.13}
\]

where \(T_0\) is the maximum possible transmission determined by losses in the system, and \(F\), namely finesse, is a quality factor depending primarily on the reflectivity and flatness.
of the mirrors. A schematic plot of the transmission function expressed as Eq. (3.13)) is presented in Figure 3.4.

![Figure 3.4: Transmission function (Eq. (3.13)) of one FP\textsuperscript{130}, \( \Delta \lambda \) is the FSR (Eq. (3.14)), \( \lambda_m, \lambda_{m+1} \) and \( \lambda_{m+2} \) are the lights which can pass through the FP by satisfying Eq. (3.12). \( \delta \lambda \) is the width of the transmission peaks defined by Eq. (3.15).](image)

Clearly, any light with a wavelength satisfying Eq. (3.12) can pass through the FP, and this is the reason why many transmission peaks arise in Figure 3.4. The wavelength difference of the successive peaks (\( \Delta \lambda \)) is called free spectral range (FSR), which can be estimated as

\[
\Delta \lambda = \frac{\lambda^2}{2L}.
\]  

(3.14)

Moreover, in practice, the transmission peak always has a certain width, which is related to the Finesse of the FP as

\[
\delta \lambda = \frac{\Delta \lambda}{F}.
\]  

(3.15)
Higher $F$ leads to narrower width. In fact, $F$ can not be very high due to the fact that no mirror is perfectly flat or has 100% reflection. In our case, $F \approx 100^{1/30}$.

To understand how FP scans the scattered light as a function of frequency, let’s assume that the incoming light has a certain distribution of wavelength $(\lambda^*-d\lambda < \lambda < \lambda^*+d\lambda^*)$. At a proper space $L$, only the light with wavelength of $\lambda^*$ can pass through the FP by satisfying Eq. (3.12) and be detected by the detector. Then by varying $L$, the whole spectra within $\lambda^*-d\lambda$ to $\lambda^*+d\lambda^*$ could be swept. Here a key issue, which should be kept firmly in mind by every experimentalist when using a FP interferometer, is that the FSR must be wide enough to cover the spectral range of the incident light. Otherwise, the signal desired for a particular wavelength, e.g. $\lambda_{m+1}$ in Figure 3.4, would be also contributed by lights outside the FSR ($\Delta\lambda$) via satisfying Eq. (3.12), such as $\lambda_{m+2}$ and $\lambda_m$ in Figure 3.4. Therefore, an interferometer with larger FSR is always desired. There exists a means of increasing the effective free spectral range the spectrometer can scan at a fixed resolution by using two Fabri-Perot interferometers with different FSRs in series (a tandem FP). The mirror space in the two FPs is $L_1$ and $L_2$, respectively. To pass through the two FPs, the wavelength of the incoming light ($\lambda_m$) must satisfy

$$m \frac{\lambda_m}{2} = L_1$$
$$n \frac{\lambda_m}{2} = L_2 .$$

(3.16)

Here both $m$ and $n$ are integers. But the first neighbor of $\lambda_m$, i.e. $\lambda_{m+1}$ in Fig. 3.4, would be suppressed by FP$_2$ after it is transmitted from FP$_1$. This subtraction can be illustrated in Figure 3.5. The same would happen to the second neighbor $\lambda_{m+2}$. 

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Figure 3.5: A schematic plot of the transmission function for light passing through FP$_1$, FP$_2$ and a tandem FP (a pair of FP$_1$ and FP$_2$), respectively.

The question is which neighbor of $\lambda_m$ can be transmitted through both FP$_1$ and FP$_2$. Here we provide a mathematic derivation to answer this question, assuming that the ratio of $L_1$ to $L_2$ is $r/s$, where $r$ and $s$ are both integers and do not have any common divisor except 1. Since $\lambda_m$ satisfies Eq. (3.16), the ratio of $m/n$ should fulfill the following relation

$$\frac{m}{n} = \frac{L_1}{L_2} = \frac{r}{s}. \quad (3.17)$$

In addition, since $\lambda_{m+1}$, $\lambda_{m+2}$, ... $\lambda_{m+i}$ are successive neighbors of $\lambda_m$, which can pass through FP$_1$. Thus
\[(m + i) \frac{\lambda_{m+i}}{2} = L_1, \quad (3.18)\]

where \(i\) is an integer.

In order to pass through FP\(_2\) as well, \(\lambda_{m+i}\) must satisfy

\[L_2 \left( \frac{\lambda_{m+i}}{2} \right) = N. \quad (3.19)\]

Here \(N\) is an integer, too.

Taking Eq. (3.16) - Eq. (3.18) into Eq. (3.19), one obtains

\[n + \frac{i^* s}{r} = N. \quad (3.20)\]

Clearly, \(i\) must be a multiple of \(r\) to assure Eq. (3.20) is correct, which means only the neighbors \(\lambda_{m+r}, \lambda_{m+2r}, \lambda_{m+3r}, \ldots\) can pass through both FP\(_1\) and FP\(_2\). Therefore, the frequency range a tandem FP (FP\(_1 + \) FP\(_2\)) can scan is enlarged by \(r\) times in comparison to that of FP\(_1\).

In our experiment, the tandem FP is a Sandercock model, which can be schematically illustrated in Figure 3.6. The light passes through the tandem FP three times before arriving at the detector, by which the signal to noise ratio is substantially improved. The ratio of \(L_1/L_2\) is set as 20/19, hence the final spectral range the spectrometer can scan is enlarged by 20 times with respect to only using FP\(_1\). The variations of the two spaces (\(\delta L_1\) and \(\delta L_2\)) are performed simultaneous through a translational stage. The angle (\(\theta\)) between FP\(_1\) and FP\(_2\) is designed as \(\cos(\theta)=19/20\) to keep the ratio of \(\delta L_1/\delta L_2\) the same as \(L_1/L_2\). In other words, the ratio of \(L_1/L_2\) always maintains constant even during changing the spaces of FPs. So in the following discussion, we would only refer to the space of FP\(_1\) (\(L_1\)).
Figure 3.6: A schematic graph of a tandem Fabry-Perot interferometer (Sandercock model)\textsuperscript{130}, which contains two FPs.

Now let’s take a real example to illustrate how this Sandercock model interferometer records the spectrum. Assuming $L_1$ is 3mm and setting the wavelength of the laser light is 532nm, the frequency window the tandem FP can scan is

$$
\Delta \nu = 20 \frac{\Delta \lambda}{\lambda} \nu = 20 \frac{c}{2L} = 1000(\text{GHz}),
$$

(3.21)

where $\nu$, $\lambda$ and $c$ are the frequency, wavelength and velocity of the original laser light, respectively. The frequency of the original laser light is always set as the center of the spectra, e.g. the central line in Figure 3.7. Therefore, the scattered light within the frequency shift (-1000 to 1000 GHz) can be probed by varying $L_1$. (In the following text, the probed or scanned frequency always denotes the frequency shift of the scattered light relative to the original laser light.) At a given $L_1$, the probed frequency can be expressed as
\[ \delta \nu = \frac{\delta L}{L} \nu . \]  

In fact, we normally scan \( \delta L_1 \) in a range (-260 to 260 nm), so the obtained spectra only span from -50 GHz to +50 GHz. Moreover, in the central part of the spectra, about 5% of the spectra in frequency are blocked due to the limited Finesse. Therefore, the final scanning frequency range is \( \pm (2.5 \text{ to } 50 \text{ GHz}) \) when setting \( L_1 \) as 3 mm. For practical purpose, we usually measure Brillouin spectra at three FSRs (three \( L_1 \): 0.4 mm, 3 mm and 15 mm), and the corresponding scanned frequency ranges are 19 to 380 GHz, 2.5 to 50 GHz and 0.5 to 10 GHz on both sides of the central line, respectively. Since each FSR is uniquely defined by the space \( (L_1) \) at a given laser wavelength, for simplicity, we only refer to the space instead of the scanned frequency range for every specific FSR in the following discussion, e.g. at \( L_1=3 \text{ mm} \), we call it 3 mm FSR.

As discussed before, once the incident beam has a distribution of frequency larger than the frequency range the tandem FP can scan, signals inside and outside this range by satisfying Eq. (3.12) are mixed up. To block the undesired signal, an interference filter (band pass filter) is added after the Sandercock interferometer. Two interference filters have been employed in our study, and their bandwidth are \( \sim 1 \text{ THz} \) and \( \sim 150 \text{ GHz} \), respectively. The wider bandwidth filter is used for 3 mm and 0.4 mm FSRs, while the narrower filter is only applied for 15 mm FSR. Normally, the filter modifies the transmission function of the light. One example is displayed in Figure 3.7, where the spectrum of white lamp at 0.4 mm FSR with 1 THz filter is presented. The spectrum of white lamp is supposed to be flat, but it is clearly modified when light passing through the filter (Figure 3.7). To correct this filter-induced feature, we normalized the spectrum
of samples by that of white lamp $I(v)/I(v)_{WL}$. It has been noticed that this filter effect is not significant for 3mm and 15mm FSRs, so the above white lamp calibration is only performed for 0.4mm FSR.

![White Lamp spectrum](image)

**Figure 3.7:** A spectrum of white lamp at 0.4 mm FSR with the 1 THz filter, the central line represents the frequency of the original laser light.

Recording of the spectrum by varying $\delta L_1$ from -260nm to 260nm is not continuous. It is discrete as 1024 steps via a multi-channel analyzer card. As a result, the spectrum at a given FSR is composed by 1024 data points, and each point represents the signal at a particular frequency (more accurately, a narrow frequency window). Taking 3mm FSR as an example, the scanned frequency range is -50 to 50 GHz, so each data point in the Brillouin spectrum would be a summed intensity in a narrow frequency window ~0.1GHz. The spectral resolution of the Brillouin spectrum is mostly determined by the Finesse of the interferometer. In our case, it is about 1/100 of the swept frequency range at a given FSR. In our Brillouin spectrometer, an avalanche photodiode (APD) is employed as a detector.
By combining the spectra probed at 0.4, 3 and 15 mm FSRs together, a broad spectrum spanning from 0.5 GHz to 380 GHz is obtained. One example of a jointed susceptibility spectrum of low molecular weight PS is presented in Figure 3.8, where the highest frequency part (black) is acquired by Raman spectroscopy.

Figure 3.8: A combined susceptibility spectrum of PS with $M_w = 580$ g/mol measured by depolarized light scattering. The black curve is obtained by Raman spectroscopy, and the red, green and blue curves are acquired via the Brillouin spectroscopy at 0.4, 3 and 15 mm FSRs, respectively.

3.2.2.2. Raman spectrometer

The main part of the Raman spectrometer is a Jobin Yvon T64000 triple-monochromator, where three monochromators are arranged in series (Figure 3.9\textsuperscript{131}).
As shown in Figure 3.9, the whole spectrometer is composed by three monochromators. The first one consists of 5 components: Slits 1 and 4, Grating 2, Regular reflecting mirror 3 and Concave mirrors A and B. Items 4, 5, 6, 7, C and D constitute the second monochromator. The rest of the items form the last monochromator. The pair of the concave mirrors in each monochromator is used to image the entrance slit onto the exit one. To better illustrate this point, let’s take the first monochromator as an example. Firstly, Concave mirror A is applied to make the divergent beam coming from Slit 1 (entrance slit) to be parallel. Afterwards the parallel beam is spatially dispersed by Grating 2 in terms of frequency, and then it is focused by Concave mirror B onto Slit 4 (exit slit). The first two monochromators in the spectrometer are designed in a subtractive mode. Briefly, Grating 2 and 6 are set to spatially disperse the incident light.
in an opposite way. It means, after passing through the first two monochromators, the lights are refocused on Slit 8, i.e. converge back to one line instead of many lines which are spatially dispersed in terms of frequency. As a result, the first two monochromators work as a band pass filter, and the transmitted light is further spatially dispersed by the third monochromator. A narrow exit slit (not shown in Figure 3.9) is used afterwards to allow a narrow band of light to pass through and be probed by the detector. This design has a prominent advantage that it can strongly suppress the stray light and push the lower limit of the probed Raman spectra down to ~3cm$^{-1}$. (Note: 1cm$^{-1}$ = 30GHz.)

Another important component of the Raman spectroscopy is the detector, which is a (1024×256 pixels) CCD camera in our case. The number of pixels of the CCD camera determines the spectral resolution, which is roughly 15GHz. Normally, liquid nitrogen is used to cool down the detector, which can dramatically improve the signal to noise ratio. In comparison to the avalanche photodiode used in Brillouin spectrometer, the CCD camera can record a wide spectrum (about 500 cm$^{-1}$) at one time, which provides much faster and more accurate measurement.

In this study, we are mainly interested in the Boson Peak spectrum and some particular Raman modes. So the Raman spectrometer is mostly applied for the frequency range: 100GHz to 50 THz, although in principle, it can be used for fluorescence measurement at much higher frequency. By combining it with the Brillouin spectroscopy at 3 different FSRs, the molecular dynamics in a rather wide frequency window from 1GHz to 50THz can be studied (see, e.g. Figure 3.8).
3.2.3. Cryostat

The sample is placed in a Janis ST-100 cryostat with four optical windows for light scattering experiments. The vacuum is maintained inside the cryostat during the low temperature measurements to prevent moisture condensation on the optical windows. The temperature of the samples is controlled with an accuracy of ~ 1K by connecting a PID temperature controller to the cryostat. Moreover, Stokes and anti-Stokes Raman spectra are recorded as an additional method to estimate the temperature of the sample. In our studies, it has been noticed that the temperature estimated from Stokes and anti-Stokes Raman spectra always agree well with the value displayed by the temperature controller.

3.3. Samples and experimental conditions

In this work, we studied more than 30 different glass-forming materials, and measurements at both ambient condition and elevated pressure were performed.

3.3.1. Samples

Most of the materials used in our studies were purchased from commercial sources: Glycerol, Salol, Ortho terphenyl (OTP), Cumene, Sorbitol, Propylene glycol (PG), Di(propylene glycol) (DPG), Tri(propylene glycol) (TPG) and Poly(propylene glycol) (PPG) with Mw=4,000 g/mol, Mn=3,500g/mol were bought from Sigma-Aldrich; Polyisoprene (PIP) with Mw=2,450 g/mol, Mn=2,410g/mol, Poly(vinyl acetate) (PVAc)
with $M_w=184,100$ g/mol, $M_n=61,600$ g/mol, Polycarbonate (PC) with $M_w=60,000$ g/mol, Polysulfone (PSF) with $M_w=60,000$ g/mol, Plexiglas (Poly(methyl methacrylate)) (PMMA), Poly(ethylene terephthalate) (PET) with $M_w=30,000$ g/mol and two polystyrene (PS) samples (PS-0.5K: $M_w=580$ g/mol, $M_n=540$ g/mol and PS-1K: $M_w=1100$ g/mol, $M_n=990$ g/mol) were purchased from Scientific Polymer; Poly(methyl phenyl siloxane) (PMPS) with $M_w=25,600$ g/mol, $M_n=15,800$ g/mol, Poly(n-butyl methacrylate) (PnBMA) with $M_w=18,200$ g/mol, $M_n=17,500$ g/mol, Poly(t-butyl methacrylate) (PtBMA) with $M_w=1,950,000$ g/mol, $M_n=1,500,000$ g/mol, Poly(n-hexyl methacrylate) (PnHMA) with $M_w=32,000$ g/mol, $M_n=30,000$ g/mol, Poly(lauryl methacrylate) (PLMA) with $M_w=29,000$ g/mol, $M_n=27,000$ g/mol and two other PS samples: PS-5K with $M_w=5100$ g/mol, $M_n=4800$ g/mol and PS-200K with $M_w=223,000$ g/mol, $M_n=200,600$ g/mol were purchased from Polymer Source; GE Silicones SE54 (Poly(dimethyl siloxane) (PDMS) with $M_w=818,000$ g/mol, $M_n=538,000$ g/mol) was bought from General Electric Company; Polyisobutylene (PIB-3K) with $M_w=3,580$ g/mol, $M_n=3280$ g/mol was purchased from Polymer Standard service; other two PIB samples: PIB-0.3K with $M_n=300$ g/mol and PIB-20K with $M_n=20000$ g/mol was synthesized in Akron U (in Dr. Puskas’ lab); Ca-K-NO3 (CKN) was prepared in our group.

3.3.2. Sample cells

Two optical sample cells have been employed in our experiments. One is for measurement at ambient pressure, and the other is used for pressure study. The ambient
one is a homemade cell, which has two parallel sapphire windows to allow light to pass through. As shown in Figure 3.10, a silicon rubber O-ring is inserted in between the two windows. The so formed internal cavity is used for filling samples and has a disk-like shape with the thickness of ~ 1mm and the diameter of ~ 1cm. The surface of the silicone O-ring is coated by Teflon to ensure no chemical reaction with the samples. All the studied materials are loaded at room temperature (RT). If the sample is in a liquid state at RT, the filled cell would be directly placed in the optical cryostat (Figure 3.10) to be cooled down to a desired temperature for light scattering measurement. If the materials are powder-like solids, before placed in the cryostat for measurements, the filled cell must be preheated in a conventional oven to ensure the inside solid powders melt.

![Figure 3.10: The optical cell for ambient measurement.](image)

By using a commercial anvil pressure cell from D’Anvils, hydrostatic pressure up to 1.5GPa was applied to the studied materials. The basic parts of the pressure cell are displayed in Figure 3.11. A piece of stainless steel with a drilled hole in the center
functions as a gasket, which is caught between two anvils. In our experiments, both
diamond and moissanite are used as anvil materials. The samples are loaded in the
internal cavity formed by the gasket and the two anvils. The thickness of the gasket is ~
0.3mm and the diameter of the central hole is ~ 0.36mm, so only a small amount of
samples (~ 0.03 micron liters) is required for pressure study. Photos of components in the
pressure cell are shown in Figure 3.12, where quarter coins are presented to illustrate the
size of the components. The pressure is applied by tightening the three screws, which are
located symmetrically in the backing plates to hold the cell. To ensure the pressure inside
the sample is homogeneous, the initially loaded materials must be in liquid state. All the
procedures for loading samples, increasing or releasing the pressure are performed at
room temperature, details of which can be found in Ref. 97.

![Diagram of pressure cell](image)

Figure 3.11: Basic parts of the pressure cell\textsuperscript{97}.
The precise measurement of the applied pressure is crucial in pressure studies. Here we use the ruby fluorescence method, which is a well established technique\cite{97,133,134,135}. At ambient condition, Ruby has two strong fluorescence peaks located at $R_1$ (694.2 nm) and $R_2$ (692.7 nm), respectively. Both of them would shift to higher wavelength with pressure. Normally $R_1$ line is stronger and sharper, and its shift is conventionally used for estimating pressure. The detail expression can be found in Ref. 97 as

$$P(\text{GPa}) = \frac{1904}{7.665} \left[1 + \left(\frac{\Delta \lambda}{\lambda_0}\right)^7 - 1\right], \quad (3.23)$$

where $\lambda_0$ is the wavelength of $R_1$ line at ambient pressure, and $\Delta \lambda$ is the wavelength shift. It is important to mention that the wavelength of $R_1$ line also varies markedly with temperature, so Eq. (3.23) is only valid for pressure estimate at constant temperature. This requires us to measure the fluorescence of the pressurized ruby and non-pressurized one at the same temperature to obtain $\Delta \lambda$. For this purpose, we inserted one ruby with a linear size about 20 um inside the pressure cell along with the sample, and glued another piece of ruby on the surface of one backing plate, which can be seen in Figure 3.12(c).
The Raman spectroscopy is used to measure the R₃ line of the two rubies at each temperature. Moreover, the fluorescence spectrum of a mercury lamp is also measured. By comparing it to the standard spectrum of mercury, the shift of the spectrometer due to improper zero-calibration can be estimated. By taking the shift of spectrometer into account, more precise estimate of pressure can be achieved.

3.3.3. Experimental conditions and data analysis

In this study three types of experiments were performed: (A) deep in the glassy state at ambient pressure, (B) deep in the glassy state at elevated pressure; (C) above Tₓ at ambient pressure.

3.3.3.1. Deep in the glassy state at ambient pressure

The spectra of PIB, PIP, PMPS, glycerol, PG, DPG, TPG, PPG, salol, OTP and sorbitol were measured at T=140K. The spectra of Cumene, CKN, PC, PVAc, PSF, PET, PDMS, PMMA, PnBMA, PtBMA, PnHMA, PLMA and PS were measured at T=80K.

To estimate ξ from Eq. (2.23), both the boson peak frequency (Raman spectra) and transverse sound velocity (Brillouin spectra) are required. As an example, Figure 3.13(a) exhibits the Raman spectrum for OTP at 140K (100K below Tₓ), which is presented as a spectral density Iₙ(ν),
\[
I_n(\nu) = \frac{I(\nu)}{\nu[n(\nu)+1]},
\]

(3.24)

Here \(n(\nu)=[\exp(h\nu/kT)-1]^{-1}\) is the Bose temperature factor and \(I(\nu)\) is the measured intensity. For quantitative analysis, the spectra were fitted by a previously proposed expression\(^{136}\):

\[
I_n(\nu) = \frac{AV_0}{\nu_0^2 + \nu^2} + B \exp\left\{-\frac{[\ln(\nu/\nu_{BP})]^2}{2W^2}\right\},
\]

(3.25)

In Eq. (3.25), the first term describes the quasi-elastic scattering (QES), presented by a Lorentzian function with a free fitting parameter \(\nu_0\) (the width of the QES). The second term describes the boson peak approximated by a log-normal function, where \(B\), \(W\) and \(\nu_{BP}\) are the fitted amplitude, width and frequency of the boson peak, respectively. Both terms in Eq. (3.25) are assumed to be statistically independent. The so obtained boson peak frequency takes into account the contribution from QES. Here we need to emphasize that, once the measurement is performed deep in a glassy state, there is little difference (less than 5%) whether \(\nu_{BP}\) is obtained from Eq. (3.25) or taken as the apparent peak position. Taking OTP (Figure 3.13(a)) as an example, the apparent \(\nu_{BP}\) is 510GHz, and the fitted value is 520GHz. The difference is only 2%. For consistency, Eq. (3.25) is used to fit the spectra for all the materials measured deep in the glassy state and obtain \(\nu_{BP}\) to estimate \(\xi\).

The Brillouin spectra were fitted by a Lorentzian function to obtain the peak frequency \(\nu_T\) (an example for OTP is shown in Figure 3.13(b)). The longitudinal and transverse sound velocity \(V_{L,T}\) are estimated from \(\nu_{L,T}\) by using Eq. (3.11) as\(^{137}\),
\[ V_{L,T} = \frac{v_{L,T} \times \lambda}{2 \times \sin(90^\circ / 2)} = \frac{v_{L,T} \times \lambda}{\sqrt{2}}. \] (3.26)

Here \( \lambda \) is the wavelength of light. All the results of the fits and the literature data are presented in Table 4.1 in Chapter IV.

Figure 3.13: (a) Depolarized Raman spectrum presented as a spectral density defined in Eq. (3.24) and (b) Brillouin spectrum of OTP measured at \( T=140K \). Solid lines present fit to Eq. (3.25) in (a) and to a simple Lorentzian function in (b). LM and TM denote the longitudinal and transverse Brillouin modes, respectively.

3.3.3.2. Deep in the glassy state at elevated pressure

Seven materials have been studied in this case: PIP, PS-0.5K, PMPS, PIB-3K, glycerol, OTP and cumene. The experiments are performed at constant temperature (\( T=140K \) for all the materials except Cumene (\( T=100K \))). Pressures (starting from 1 atm) up to 1.5GPa are applied. The boson peak frequency, amplitude as well as the sound velocities are estimated in the same way as the one described in Section 3.3.3.1. In the pressure study, the intensity of the quasielastic scattering (\( I_{QES} \)) is also analyzed. As
discussed in Chapter II and also seen in Figure 3.13(a), the QES usually dominates the spectra below 200GHz, but its statistics is not as good as that of the boson peak. For an accurate analysis of $I_{QES}$, we integrate the spectra in a certain frequency range. The so obtained $I_{QES}$ reduces the statistical error. For most of the materials studied here, the integration frequency range is from 100 to 200 GHz, but it was from 250 to 350 GHz for glycerol and from 200 to 300 GHz for PIB. (These two materials are weak light scatterers and only Raman data are available. At the same time, relatively high $\nu_{BP}$ in these two materials allows analysis of the QES spectra at higher frequency.) As an example, we plot the pressure-induced variations of $I_{BP}$, $I_{QES}$, sound velocity and $\nu_{BP}$ for PS-0.5K in Figure 3.14.
Figure 3.14: Variations of (a) the boson peak amplitude, (b) QES intensity, (c) sound velocity and (d) boson peak frequency with pressure in PS-0.5K at 140K. Here the boson peak amplitude and QES intensity are normalized by the value at ambient pressure.
The obtained sound velocity can be used to estimate the variations of density with pressure in the samples. According to earlier works, the pressure-induced variations of density can be expressed as

\[
\left( \frac{\partial \rho}{\partial P} \right)_T = \left( \frac{\partial \rho}{\partial P} \right)_S + \alpha \rho \left( \frac{\partial T}{\partial P} \right)_S.
\] (3.27)

Here \( \alpha \) is thermal expansion coefficient, \( \rho \) is density and \( S \) is entropy. The right-hand side of Eq. (3.27) can be rewritten in terms of the measured sound velocities

\[
\left( \frac{\partial \rho}{\partial P} \right)_T = \frac{1}{V_L^2} \cdot \frac{4}{3} \frac{V_T^2}{C_p} \cdot \frac{\alpha^2 T}{C_p}.
\] (3.28)

Here \( C_p \) is the specific heat. Thus, the pressure-induced change in density, \( \Delta \rho(P) \), can be estimated by integrating the right-hand side of Eq. (3.28). The second term in Eq. (3.28), \( \alpha^2 T/C_p \), is much smaller than the first one. For example, the ratio of the second term to the first one for PS at 140K and ambient pressure is \( \sim 0.08 \), and it does not change much with pressure. So, we assume that the second term provides additional 8% of the first term for all the samples independent of pressure. This assumption will add an extra error \( \sim 1\% \) to the final estimated density.

It is worth to emphasize that using Eq. (3.28) we can only estimate the density change (\( \Delta \rho(P) \)) relative to the one (\( \rho_0 \)) at ambient pressure and the experimental temperature. To get the absolute density at the elevated pressure, the value of \( \rho_0 \) is required. However, the literature data for density of most of the studied samples are only available around \( T_g \) and above. Thus, to estimate \( \rho_0 \), we extrapolated the density from \( T_g \) to the experimental temperature deep in the glassy state using thermal expansion.
coefficient in the glassy state. This procedure provides additional uncertainty ~1% for
the calculated absolute density.

In general, the final accuracy for the estimated density, presented in a relative scale
\((\rho(P)/\rho_0)\) is better than 2%. One example for PS-0.5K is displayed in Figure 3.15.

![Graph showing variation of density with pressure in PS-0.5K.](image)

**Figure 3.15:** Variation of density with pressure in PS-0.5K, \(\rho_0\) is the density at ambient
pressure and 140K.

3.3.3.3 Above \(T_g\) at ambient pressure

Three samples: OTP, glycerol and PIB were chosen as representatives to study the
temperature effect on \(\xi\). The investigated temperature range for glycerol is 180 to 235K
(0.95 to 1.25 \(T_g\)), for OTP is 230K to 265K (0.95 to 1.1 \(T_g\)) and for PIB is 180K to 260K
(0.95 to 1.3 $T_g$). The sound velocity is estimated in the same way as the one for experiments deep in the glassy state. The analysis strategy for the boson peak is slightly different, and details are discussed in Chapter VI.
CHAPTER IV

MOLECULAR COOPERATIVITY FOR DIFFERENT GLASS-FORMING MATERIALS

4.1. Introduction

Currently, understanding the microscopic mechanism governing the glass transition process is one of the central issues in the condensed matter physics. The sharp slowing down of the structural relaxation in the supercooled liquids upon approaching $T_g$ is unlikely to be explained by any simple-liquid theory. After enormous endeavors on both theoretical and experimental sides have been devoted to this topic, most researchers came to the conclusion that the structural relaxation in supercooled liquids involves significant molecular cooperativity. Briefly, groups of molecules move together in a supercooled state, which will greatly retard the dynamics. Intuitively, the structural relaxation of a system with larger cooperativity size would be slowed down more dramatically, i.e. would have higher fragility. However, the recent experimental results seem to be at odds with this intuitive expectation$^{7,8,9,11}$.

In addition to the structural relaxation, the collective vibration at the boson peak is also described as a cooperative molecular motion. Many researchers even speculated that the cooperativity length scales involved in the two processes are closely related. For
example, within the framework of the Random first-order transition theory, Wolynes and coworkers show that the vibrational modes of the domain walls of the entropic droplets constitute the boson peak, where the entropic droplets denote the cooperatively relaxing domains. Thus the characteristic length scale of the collective vibrations should be defined in a similar way as the cooperativity size of molecular motions in the structural relaxation \(^{29,30}\). Furthermore, de Gennes has explicitly pointed out that the wavelength of the acoustic modes localized in the boson peak can represent the size of the solid clusters in his two-state model designed for the structural relaxation \(^{28}\). However, no experimental data have been provided to verify the above speculation.

In this chapter, we presented the characteristic length scale (\(\xi\)) estimated from the boson peak spectra using light scattering for a huge number of glass-forming. \(\xi\) is found to agree well with the dynamic heterogeneity length scale for the structural relaxation estimated by 4D NMR. This agreement supports the speculation that the boson peak vibrations and the structural relaxation involve a similar length scale for molecular cooperativity.

We examined the relationship between \(\xi\) and fragility among various glass-forming materials, and did not find a clear correlation. Nevertheless, a further analysis reveals a proportional correlation between \(\xi^3\) and the activation volume \(\Delta V^\#\), i.e. the pressure dependence of the structural relaxation time. This correlation was demonstrated to be valid for different chemical species, and also for the same chemical species with different molecular weight or under densification. Finally, a theoretical justification for the observed correlation is provided within the framework of the random first-order transition theory.
4.2. Experimental

The main experimental work in this chapter is to estimate $\xi(T_g)$ for different glass-forming materials. For this purpose, we need to obtain both boson peak frequency and transverse sound velocity at $T_g$. However, many fragile materials, such as CKN, PS, PC, etc., do not exhibit clear boson peak around $T_g$, because the strong quasielastic scattering overlaps with the boson peak. Therefore, a reliable analysis of $\nu_{BP}$, and thus $\xi$, is not accessible for these materials at $T_g$. In our studies, an alternative method, i.e. performing the measurement deep in the glassy state, is utilized. For most materials, the experimental temperature is set as $\sim T_g-100 K$. At such temperature, the boson peak is quite pronounced since the fast relaxation process (QES) is dramatically suppressed. It is known that both the boson peak frequency and the sound velocity would slightly vary with temperature below $T_g$, but the ratio of these two parameters has been shown to maintain constant in previous works$^{142}$. This indicates that $\xi$ does not change with temperature in the glassy state. The underlying physics might be that, once a material is cooled down into a glassy state, it will fall out of the equilibrium and the structure is essentially frozen in the experimental time window. Thus, the structural correlation length or cooperativity length scale would have no explicit temperature variations. In this work, the light scattering experiments for all the materials were performed deep in the glassy state to obtain the boson peak spectra and sound velocity, and thus $\xi$ can be estimated from Eq. (2.23). All the results are presented in Table 4.1. The detailed information on samples, experimental setups and procedures, including measurements at ambient pressure and at elevated pressure, has been provided in Chapter III.
Table 4.1: Data for all the materials presented in Chapter IV.

<table>
<thead>
<tr>
<th>Systems(^a)</th>
<th>m</th>
<th>(T_g) (K)</th>
<th>(dT_g/\text{d}P) (K/GPa)</th>
<th>(\alpha_t) (\times 10^{-4}) K(^{-1})</th>
<th>(\alpha_t) (\times 10^{-4}) K(^{-1})</th>
<th>(V_T) (km/s)</th>
<th>(\nu_{\text{HP}}) (GHz)</th>
<th>(\xi) (nm)</th>
<th>(\Delta V^g) (nm(^3))</th>
<th>(V_m\text{ at }T_g) (nm(^3))</th>
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</thead>
<tbody>
<tr>
<td>1. (\text{B}_2\text{O}_3)</td>
<td>32</td>
<td>520</td>
<td>200</td>
<td>3.3</td>
<td>0.7</td>
<td>1.44</td>
<td>810</td>
<td>1.78</td>
<td>0.172</td>
<td>0.129</td>
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<tr>
<td>2. (\text{As}_2\text{S}_3)</td>
<td>36</td>
<td>455</td>
<td>150</td>
<td>3.3</td>
<td>0.74</td>
<td>1.9</td>
<td>1340</td>
<td>1.42</td>
<td>0.056</td>
<td>0.115</td>
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<td>3. glycerol</td>
<td>50</td>
<td>191</td>
<td>35</td>
<td>4.8</td>
<td>1</td>
<td>2.35</td>
<td>1740</td>
<td>1.35</td>
<td>0.051</td>
<td>0.107</td>
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<td>4. glycerol (P=1 Gpa)</td>
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<td>223</td>
<td>27</td>
<td></td>
<td></td>
<td>1.49</td>
<td>828</td>
<td>1.80</td>
<td>0.246</td>
<td>0.298</td>
</tr>
<tr>
<td>5. Se</td>
<td>62</td>
<td>305</td>
<td>130</td>
<td>3.54</td>
<td>1.29</td>
<td>0.94</td>
<td>510</td>
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<td>168</td>
<td>37</td>
<td>3.8</td>
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<td>1150</td>
<td>1.38</td>
<td>0.0623</td>
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<td>195</td>
<td>80</td>
<td>6.1</td>
<td></td>
<td>1.41</td>
<td>795</td>
<td>1.77</td>
<td>0.163</td>
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<td></td>
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<td>828</td>
<td>1.80</td>
<td>0.246</td>
<td>0.298</td>
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<td>9 Salol</td>
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<td>1.2</td>
<td>1.27</td>
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<td>2.19</td>
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<td>1.2</td>
<td>1.63</td>
<td>960</td>
<td>1.70</td>
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<td>0.476</td>
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<td>267</td>
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<td>4.6</td>
<td>1.2</td>
<td>2.11</td>
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<td>PIB-0.3K (Mn=300)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>1.55</td>
<td>660</td>
<td>2.35</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>1.75</td>
<td>750</td>
<td>2.33</td>
<td></td>
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<td>240</td>
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<td>1.9</td>
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<td>204</td>
<td>6.4</td>
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<td>1.54</td>
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Table 4.1: Data for all the materials presented in Chapter IV (continued).

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<td>1.4</td>
<td>465</td>
<td>3.08</td>
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<td>(P=0.3 GPa)</td>
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<td>PMMA</td>
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<td>367</td>
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<td>1.56</td>
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<tr>
<td>28.</td>
<td>PC</td>
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<td>5.8</td>
<td>1.08</td>
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*The references for the literature data in this table can be found in Ref. 22.*

4.3. Results and discussions

In this section, we will perform explicit analysis to the cooperativity size estimated from the boson peak spectra for various materials.
4.3.1. Comparison of the characteristic length scale of the boson peak vibrations and that of the structural relaxation

As discussed in Chapter II, the cooperativity length scale of the structural relaxation in glass-forming materials has been estimated by several approaches, including both direct and indirect methods\(^7\)\(^{-}11\),\(^7\)\(^8\). Among all these approaches, 4D NMR is the least model-dependent and provides the most straightforward information about cooperativity in molecular motions. Specifically, the time period \(t^*\) and diffusion coefficient \(D_{\text{spin}}\) for spins to diffuse out of slow-relaxing domains are directly and independently measured\(^10\). Subsequently, the length scale of the slow-relaxing domain (dynamic heterogeneity) can be estimated. All the other approaches are highly model-dependent and involve many unjustified assumptions. For example, the thermodynamic method developed by Donth et al. is based on the Adam-Gibbs theory\(^40\), where all the cooperative rearranging regions (CCR) are assumed to fluctuate independently. In addition, Donth et al. also made many other crude assumptions\(^7\). For example, the fluctuation of thermodynamic quantities, e.g. \((\Delta T)^2\), in the CRR at nanometer scales can be estimated from bulk properties in the same way as in macroscopic systems, the imaginary part of the complex heat capacity around \(T_g\) as a function of temperature must obey Gaussian distribution, the jump of the isochoric heat capacity across \(T_g\) can be represented by that of the isobaric heat capacity multiplied by a universal constant for different materials regardless of their chemical structures, etc. To make a reliable comparison between the cooperativity length scales in the structural relaxation and in the boson peak vibrations, we chose the dynamic heterogeneity length scale estimated using 4D NMR as a reference. As shown in Table
4.2, the two length scales are in good agreement with one another. This result supports the idea\textsuperscript{27-30} that the structural relaxation and the boson peak vibrations reflect the same spatial cooperativity in molecular motions. As discussed above, the NMR studies estimate the characteristic length scale of slowly relaxing regions in glass-forming liquids. In a simple two-state (liquid-like and solid-like) model\textsuperscript{28}, these regions represent the solid-like clusters. Dynamically heterogeneous regions have different properties, including variations in e.g. Debye-Waller factor\textsuperscript{143} and elastic constants. When the temperature decreases below \( T_g \), the structure freezes and these regions (slow and fast) define the length scale of structural fluctuations, including fluctuations in elastic constants. The latter lead to scattering of the acoustic waves and a change of the vibrational density of states. Especially when the acoustic waves have a wavelength comparable to the length scale of the elastic constants fluctuations, they are strongly damped to form the quasi-localized vibrational modes in the boson peak. As a result, the same length scale appears in the boson peak vibrations.

Strictly speaking, the length scales estimated from 4D NMR and from the boson peak spectra denote the size of heterogeneities in terms of mobility and elastic constants, respectively. The main assumption in this thesis as well as in many other works\textsuperscript{8-12,17,22,28-30,41,46,68,75-79} is that these heterogeneities result from or are intimately connected to cooperative molecular motions at a relevant length scale. Thus the length scale of heterogeneity can be used to represent the size of cooperativity. In the rest of the thesis, we refer to \( \xi \) (estimated from the boson peak) as the cooperativity size, which in reality is the length scale of the elastic heterogeneities.
Table 4.2: Cooperativity size estimated from boson peak spectra and from 4D NMR$^{10,11}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\xi$ (BP) (nm)</th>
<th>$\xi_{het}$ (4D NMR) (nm)</th>
</tr>
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<tr>
<td>Glycerol</td>
<td>1.4±0.1</td>
<td>1.3±0.5</td>
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<tr>
<td>Sorbitol</td>
<td>1.5±0.1</td>
<td>2.5±1.2</td>
</tr>
<tr>
<td>OTP</td>
<td>2.5±0.2</td>
<td>2.5±1</td>
</tr>
<tr>
<td>PVAc</td>
<td>2.9±0.2</td>
<td>3.4±1</td>
</tr>
</tbody>
</table>

4.3.2. The correlation of $\xi$ with fragility and other parameters

In this section, we will examine the relationship between $\xi$ and fragility as well as other parameters. The discussions are performed among different materials, polymers with different molecular weight and materials at elevated pressures.

4.3.2.1. Different chemical species

According to the traditional cooperativity idea, the cooperativity size should positively correlate with fragility ($m$) among different materials, i.e. larger $\xi$ corresponds to higher $m$. To verify this idea, we first carried out experiments for several polymers. And the result presented in Figure 4.1 indeed supports the idea.
Figure 4.1: $\xi$ vs m for polymers, the full names of polymers are, PS: polystyrene; PC: Polycarbonate; PMPS: Poly(methyl phenyl siloxane); PVAc: Poly(vinyl acetate); PIP: Polyisoprene and PIB: Polyisobutylene. The molecular weight of these polymers is presented in Chapter III.

However, the correlation fails when we compare chemically different materials, including polymers and small molecules, covalent-, ionic- and hydrogen- bonding systems (Figure 4.2). There might exist a general trend as shown by the arrow in Figure 4.2, i.e. higher fragility corresponds to larger $\xi$, but systems such as CKN, DBP, sorbitol, glycerol and PG, clearly deviate downwards from the trend. This result is consistent with earlier data in Refs. 7, 8 and 10. Furthermore, Figure 4.2 also reveals another interesting phenomenon that polymers have relatively larger $\xi$ than non-polymeric materials. This result can be understood in a following way. Once a liquid is cooled down to a supercooled state, the free volume available to the individual molecule (repeat unit in the case of polymer) is substantially reduced. Then the motion of each molecule can only be realized by moving neighbors out of the way. In other words, the constraint coming from
neighbors is the physical origin of the cooperativity in molecular motions. Compared to non-polymeric systems, the motions of repeat units in polymers are not only impeded by inter-chain neighbors, but also intra-chain neighbors, e.g. a local rotation of one repeat unit without changing its position would be highly constrained by the chemically bonded neighbors along the chain. Consequently, polymers are expected to have greater molecular cooperativity than non-polymeric materials.

![Figure 4.2: ξ vs m for various glass-forming materials. The arrow denotes a rough trend.](image)

As shown in Table 4.1, the pressure dependence of the glass transition temperature (dT_g/dP) of those materials deviating downward in Figure 4.2 is much smaller (~50K/GPa) in comparison to others (~200K/GPa). This difference is better illustrated in Figure 4.3, where the same materials CKN, DBP, sorbitol, glycerol and PG are at the bottom of the figure. The similarity between Figure 4.2 and 4.3 suggests that the
failure of the correlation between $\xi$ and $m$ among various glass-forming materials might be due to the difference of their sensitivity of the structural relaxation to pressure.

Figure 4.3: $dTg/dP$ of the materials presented in Figure 4.2.

A usual approach to study the pressure dependence of the structural relaxation is to consider it as a volume-activated process

$$\tau_\alpha(T,P) = \tau_\alpha(T,0) \exp\left(\frac{P\Delta V^*}{k_B T}\right), \quad (4.1)$$

where $\Delta V^*$ is the activation volume, $k_B$ is the Boltzmann constant and $\tau_\alpha(T,0)$ is the relaxation time at ambient pressure. In this approach $\Delta V^*$ is the key parameter, which characterizes the pressure sensitivity of $\tau_\alpha$. It can be treated as the excess volume needed for a single relaxation event. From Eq. (4.1), $\Delta V^*$ can be expressed as

$$\Delta V^* = k_B T \left(\frac{\partial \ln \tau}{\partial P}\right)_{\tau}. \quad (4.2)$$
The direct way to estimate $\Delta V^\#$ is to measure the structural relaxation time at various pressures at constant temperature. The work was only performed in a small number of materials\textsuperscript{13}, because the required facility is not widely available. In fact, there is an alternative way to estimate $\Delta V^\#$ at $T_g$ by knowing fragility and $dT_g/dP$ of the materials, both of which are readily accessible in the literature. Here we would like to give a brief introduction to this alternative method.

Since we discuss supercooled liquids at $T_g$, which are equilibrium or quasi-equilibrium systems, the three variables ($P$, $T$ and $V$) are mutually related through a unique equation of state. In other words, once any two of them are known, the last one will be fixed. Thus, the relaxation time can be defined by any two of the three variables, and the following equation is fulfilled

$$f (\ln \tau_\alpha(P,T), P, T) \equiv 0 .$$  \hspace{1cm} (4.3)

Here $f()$ is a function defining the relationship among $\ln \tau_\alpha$, $P$ and $T$. Since $\ln \tau$, $P$ and $T$ satisfy Eq. (4.3), the following differential equation would be valid

$$\left( \frac{\partial \ln \tau_\alpha}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_{\ln \tau} \left( \frac{\partial T}{\partial \ln \tau} \right)_P = -1 .$$  \hspace{1cm} (4.4)

Taking Eq. (4.2) into Eq. (4.4) and considering the equation at $T=T_g$, one obtains

$$\Delta V^\#(T_g) = -k_B T_g \left( \frac{\partial \ln \tau_\alpha}{\partial T} \right)_P .$$  \hspace{1cm} (4.5)

Combining the definition of fragility (Eq. (2.2)) and Eq. (4.5), one obtains

$$\Delta V^\#(T_g) = k_B m \left( \frac{dT_g}{dP} \right) \ln 10 .$$  \hspace{1cm} (4.6)
Thus, the activation volume at $T_g$ of all the materials studied in this work can be estimated by knowing $dT_g/dP$ and $m$ from literature. All the results are presented in Table 4.1. (For simplicity, $\Delta V^\# (T_g)$ is denoted as $\Delta V^\#$ in the rest of this thesis.) As seen from Figure 4.4, the magnitude of $\Delta V^\#$ is of the same order of the molecular (or repeat unit) volume $V_m$. ($V_m$ is the molecular volume calculated using $V_m=M/(\rho \times N_A)$, where $M$ is the molecular weight of the structural unit, $\rho$ is the density and $N_A$ is the Avogadro’s number. In the case of small molecules, one molecule is taken as the structural unit. For polymers, we define each monomer as the structural unit. For covalent bonding or ionic bonding systems, we consider the structural unit based on the chemical formula.) Recently, Paluch et al. reported a positive correlation between $\Delta V^\#$ and $V_m$ in a series of hydrogen bonding materials, where larger $\Delta V^\#$ corresponds to bigger $V_m^{144}$. However, as illustrated in Figure 4.4, such correlation is not valid among various types of glass-forming materials. It even fails when only van der Walls small molecule systems are considered. For example, $V_m$ of DBP (NO.10) is more than twofold larger than that of cumene (NO.12), while the latter one has even bigger activation volume. Moreover, Figure 4.4 reveals another interesting phenomenon that polymers have larger $\Delta V^\#$ than non-polymeric systems. This result might indicate that the chemical bonds along the polymer chain hold neighboring units together during the structural relaxation, and thus a larger activation volume is required for a relaxation event.
Figure 4.4: Activation volume ($\Delta V^\#$) versus molecular size ($V_m$). Squares and spheres denote non-polymeric and polymeric materials, respectively. Numbers represent different materials displayed in Table 4.1, and the definition of $V_m$ is presented in the text.

A comparison of Figure 4.2 and 4.4 suggests that a material with a larger $\xi$ would have bigger $\Delta V^\#$, such as polymers vs non-polymeric materials. Subsequently, we find a correlation (Figure 4.5) between $\xi$ versus $\Delta V^\#$ for all the materials we were able to analyze. Approximation of this correlation by a linear function (Figure 4.5(a)) presents a power-law relationship $\xi^\gamma \propto \Delta V^\#$ with the exponent $\gamma = 3.3 \pm 0.3$. This relationship suggests that the activation volume is proportional to the cooperativity volume. When we plot the data in a linear scale in Figure 4.5(b), indeed a good linear relationship between $\xi$ and $(\Delta V^\#)^{1/3}$ arises. And the interception at y axis of the linear fitting is negligibly small (0.19nm), which further justifies the proportional relationship between $\xi^3$ and $\Delta V^\#$. Furthermore, the slope of the linear fitting in Figure 4.5(b) is $2.9 \pm 0.2$, which indicates that the activation volume required for a single relaxation event to occur at $T \sim T_g$ is only
a few percent of the cooperativity volume, $\Delta V^\# \approx 3-5%\xi^3$. According to the 4D NMR study, the slow and fast relaxing domains in the supercooled liquid are not permanent structures and the lifetime of the slow domain is comparable to the main structural relaxation time\textsuperscript{5}. In addition, the slow and fast domains observed in NMR are specified as solid and liquid clusters in the two-state model proposed by de Gennes, where the density of solid clusters is thought to be a few percent higher than the surrounded liquid\textsuperscript{28}. By considering the 4D NMR results and also de Gennes’ two-state model, we proposed a phenomenological picture to the observed correlation (Figure 4.5). Each solid cluster (the slowly relaxing domain) is one cooperatively relaxing unit, and the structural relaxation is realized by melting of the solid cluster to liquid (consistent with the 4D NMR result that the lifetime of the slow domain is comparable to $\tau_\alpha$). $\Delta V^\#$ is the excess volume required for the solid cluster to expand and melt. Intuitively, a bigger solid cluster needs a larger excess volume, which explains the observed proportional relationship (Figure 4.5). Moreover, the solid cluster just needs to expand ~2-5% (the ratio of $\Delta V^\#/\xi^3$) to melt. This is in agreement with the general expectation\textsuperscript{28} that the density of the materials normally changes a few percent across the glass transition region. It is also consistent with Ediger’s estimate that a few percent density differences among different domains can cause orders of magnitude differences in mobility in the supercooled liquids around $T_g$ as observed by 4D NMR (Figure 2.6 and Ref. 70).
4.3.2.2. Polymers with different molecular weight

As illustrated in Figure 4.2, polymers have larger cooperativity length scale than non-polymeric materials. It would be interesting to see how $\xi$ changes systematically from a small molecule to a polymer. Particularly, three systems have been studied in our work: PS, PIB and PPG. As revealed in Figure 4.6, when increasing the degree of polymerization (DP), $\xi$ sharply rises in PS, first increases and then saturates around DP=30 for PPG, but remains almost constant in the case of PIB.

Figure 4.5: Correlation between the cooperativity size $\xi$ and the activation volume $\Delta V^\#$ presented in (a) a double-logarithmic scale; (b) linear scale. Numbers denote materials displayed in Table 4.1. The linear fits in (a) gives $\lg(\xi)=0.48+0.3\times\lg(\Delta V^\#)$, and in (b) gives $\xi=0.18+2.9\times(\Delta V^\#)^{1/3}$. 
It is known that polymers can be roughly categorized to two groups in terms of their molecular weight dependence of the structural relaxation properties. In one group, such as PS and PMMA, both $T_g$ and fragility drastically increase with molecular weight. In the other one, such as PDMS and (poly propylene oxide) PPO, fragility remains constant (or does not vary much) and $T_g$ only slightly increases with molecular weight. Recently, Sokolov and coworkers proposed a scenario by considering the chain rigidity or stiffness to explain this diverse behavior$^{145}$. Specifically, for flexible polymers, such as PDMS and PPO, the motions of different parts of the polymer chain become decoupled on a short distance along the backbone. Thus, the relaxation properties of a flexible polymer would be similar to those observed in oligomers and do not change much with molecular weight. By contrast, high chain rigidity would impose significant constraint on the motions of individual parts of the chain and make them move cooperative. So increasing molecular
weight of a rigid polymer like PS would enlarge the molecular cooperativity and cause a sharp increase of the activation energy required for a relaxation event. As a result, both $T_g$ and $m$ significantly increase. This scenario provides a sound explanation to the steep rise of $\xi$ with molecular weight in PS (Figure 4.6). PIB has rather low $T_g$ (200K)\textsuperscript{145}, which indicates that it is a flexible polymer. According to the proposed scenario, the motion of different parts of a flexible chain is relatively decoupled, and thus the cooperativity size will not change much with molecular weight. This is indeed what has been observed for PIB (Figure 4.6). However, the scenario can not explain the molecular weight dependence of $\xi$ in PPG. PPG has the same chemical structure as PPO (a typical flexible polymer) except the end groups. Moreover, Miller’s work suggests that the energy barrier for rotation about the backbone in PPG is only one third of that of PIB\textsuperscript{146}, so PPG is even more flexible than PIB. Nevertheless, its cooperativity length scale sharply rises with increasing DP at least from 1 to 30 (Figure 4.6). In fact, not only $\xi$, $m$ and $T_g$ also have appreciable change at the initial stage of increasing molecular weight (Figure 4.8). As a matter of fact, the scenario proposed by Sokolov et al. is established on polymers only having van der Walls interactions. However, as illustrated in Figure 4.7, the nature of intermolecular interaction in PPG gradually changes from H-bonds to van der Walls force when increasing DP from monomer (propylene glycol) to polymer. As shown in Figure 4.2, hydrogen bonding materials (PG, glycerol and sorbitol) have the smallest cooperativity length scale among different types of glass-forming materials, and much smaller than the van der walls materials, e.g. PG vs OTP. We speculate that the changing of the intermolecular interaction with molecular weight in the case of PPG might be the cause of the increase of $\xi$, although the underlying physics are not clear yet.
If our speculation is right, the increase of $\xi$ should be only remarkable at the initial stage of increasing DP. When a chain already contains tens of repeat units, the concentration of hydrogen bonds would be too small to appreciably influence the dynamics of the system. And further increasing molecular weight will not significantly affect its relaxation properties, including the cooperativity size. This is supported by the saturation of $\xi$ around DP=30 in PPG (Figure 4.6).

![Chemical structures of PPG with different molecular weight.](image)

Figure 4.7: Chemical structures of PPG with different molecular weight.
Figure 4.8: DP vs m and T_g in PPG, all the parameters are scaled by the value of the monomer (PG): m=53 and T_g=168K.

We presented the data of the activation volume and $\xi$ for PS and PPG with different molecular weight in Figure 4.9. As revealed by the slope of the linear fit, the proportional relationship between $\xi^3$ and $\Delta V^#$ approximately holds in the two polymers when varying molecular weight. Unfortunately, the molecular weight dependence of $dT_g/dP$ for PIB is not available in literature, so we are not able to estimate $\Delta V^#$ for PIB with different molecular weight. But it is known that both fragility and $T_g$ of PIB have only slight changes with molecular weight, we would expect that $dT_g/dP$ is not sensitive to molecular weight either. Thus, as a product of m and $dT_g/dP$, $\Delta V^#$ will not have strong molecular weight dependence. This agrees with the variation of $\xi$ (Figure 4.6). The above discussions reveal that the previously discovered correlation between cooperativity size and activation volume (Figure 4.5) is generally valid for various polymers with different
molecular weight, although the molecular weight dependence of the relaxation properties, such as fragility, $T_g$, and $\xi$, in those polymers are quite diverse (Figure 4.6 and Ref. 145).

![Diagram](image-url)

**Figure 4.9:** $\Delta V^\#$ vs $\xi$ in PS (▲) and PPG (●) with different molecular weight, the dash line presents a linear fitting of the data presented in a double logarithm scale.

4.3.2.3. Materials at elevated pressure

It is known that both the sound velocity and the boson peak frequency would increase with pressure due to a simple hardening effect$^{137,147,148,149,150,151}$. Examples in PIP are presented in Figure 4.10 and 4.11.
Figure 4.10: Brillouin scattering spectra of PIP at 140K at different pressures: (a) Transverse modes; (b) Longitudinal modes. Symbols – experimental data and lines are the fits by a Lorentzian function.

Figure 4.11: Depolarized light scattering spectra of PIP presented as a spectral density (Eq. (3.24)) at T=140K and three different pressures indicated in the plot, symbols are experimental data and lines are fits to Eq. (3.25).
We have performed pressure studies in seven different glasses. The variations of boson peak frequency ($\nu_{BP}$), boson peak amplitude ($I_{BP}$) and the quasielastic scattering intensity ($I_{QES}$) with pressure for all the materials are presented in Figure 4.12. Here $\nu_{BP}$ and $I_{BP}$ are fitted to Eq. (3.25), and $I_{QES}$ is an integration of the spectral density spectra in a fixed frequency window, where the QES contribution is dominating. Details can be found in Chapter III. $\nu_{BP}$, $I_{BP}$ and $I_{QES}$ are all important parameters to characterize properties of the fast dynamics in amorphous materials. Briefly, $I_{BP}$ and $I_{QES}$ denote the strength of the collective vibrations and the fast relaxation, respectively. The value of $\nu_{BP}$ is related to the cooperativity size via Eq. (2.23). As illustrated in Figure 4.12, applying pressure always shifts boson peak to higher frequency, and decreases both the boson peak amplitude and the quasielastic intensity. However, the pressure-induced variations of all the parameters ($\nu_{BP}$, $I_{BP}$ and $I_{QES}$) in glycerol and OTP are significantly weaker than in other materials. In other words, the fast dynamics in glycerol and OTP is much less sensitive to pressure in comparison to most other materials. Moreover, as shown in Figure 4.13, these two materials also have the least pressure-induced variations of coopreativity length scale. Comparison of Figure 4.12 and 4.13 suggests that the systems where the characteristic length scale $\xi$ is insensitive to densification would exhibit weak variations of the fast dynamics with pressure. So, there might be a direct connection between variations of the structure at the intermediate length scale, i.e. nanometer scales, and variations of the fast dynamics.
Figure 4.12: Pressure variations of (a) the boson peak frequency, (b) the boson peak amplitude and (c) the QES intensity at T=140K (except cumene where T=100K). The values are normalized by the values at ambient pressure (except PMPS, where data are normalized by the value at P=0.05 GPa).
Figure 4.13: Pressure-induced variations of $\xi$, the values of $\xi$ are scaled by the values at ambient pressure (except PMPS, for which $\xi$ is scaled by the value at $P=0.05$ GPa).

It is worth to mention that the observed strong decrease of $\xi$ under pressure in most materials is consistent with the simulation work conducted by Wyart et al.\textsuperscript{152,153}. In their work, $\xi$ is specified as a length scale below which the homogeneous elastic continuum approximation for deformation breaks down and structural heterogeneity becomes important. As predicted by the simulation work, $\xi$ should decrease with pressure as

$$\xi \propto P^{-1/4}.$$ \hspace{1cm} (4.7)

Following Eq. (4.7), we fit the experimental data by a power law

$$\xi \propto P^{-x}.$$ \hspace{1cm} (4.8)

The example of PMPS is shown in Figure 4.14 and a fit to Eq. (4.8) provides an exponent of 0.1. The exponents fitted for other materials are presented in Table 4.3.
Except OTP and glycerol, x varies from 0.05 to 0.1 among the studied materials, and it is smaller than the predicted value 1/4. So there is only qualitative agreement between the simulation work and our experimental results, but both suggest that densification would reduce the structural correlation length at the nanometer scale in glassy materials.

Figure 4.14: Pressure dependence of $\xi$ in PMPS, the curve presents a power-law fit to Eq. (4.8).
Table 4.3: Parameters of the materials in the pressure study.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_g$ (K)$^a$</th>
<th>$dT_g/dP$ (K/GPa)$^a$</th>
<th>$a$</th>
<th>$d_m/dP$ (GPa$^{-1}$)</th>
<th>$x$</th>
</tr>
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<tbody>
<tr>
<td>PMPS</td>
<td>247</td>
<td>280</td>
<td>100c</td>
<td>0</td>
<td>0.10</td>
</tr>
<tr>
<td>PS-0.5K</td>
<td>253</td>
<td>260</td>
<td>72d</td>
<td>-60</td>
<td>0.06</td>
</tr>
<tr>
<td>PIP</td>
<td>201</td>
<td>178</td>
<td>62c</td>
<td>-40</td>
<td>0.06</td>
</tr>
<tr>
<td>PIB-3K</td>
<td>195</td>
<td>240</td>
<td>46c</td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>Cumene</td>
<td>126</td>
<td>86</td>
<td>93h</td>
<td>-60</td>
<td>0.06</td>
</tr>
<tr>
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<td>260</td>
<td>81c</td>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>Glycerol</td>
<td>185</td>
<td>40</td>
<td>53c</td>
<td>+35</td>
<td>0.00</td>
</tr>
</tbody>
</table>

$^a$ Parameters are obtained from Ref. 13.

Here the intriguing questions are why the two materials (OTP and glycerol) behave so differently from others (Figure 4.12 and 4.13). It cannot be ascribed to a difference in intermolecular forces, since glycerol is a hydrogen bonding system, but OTP is a van-der-Waals bonding material, the same as cumene. It cannot be attributed to the difference between polymers and small molecules, either. Cumene and PS-0.5K should be considered as small molecule systems, but exhibit the same behavior as polymers. It also cannot be explained by the distinction of pressure-induced density change among the materials. As illustrated in Figure 4.15, although glycerol has much smaller pressure-induced variations of density compared to other materials, OTP behaves quite similar to others. (Detailed procedures for estimating density of materials under pressure can be found in Chapter III and Ref. 137.) Same comparisons can be
made to $T_g$, $dT_g/dP$, fragility and its sensitivity to pressure ($d\eta/dP$). As shown in Table 4.3, none of those parameters is responsible for the observed diverse behavior of pressure dependence of fast dynamics and $\xi$ among the studied materials (Figure 4.12 and 4.13). So far, we have no clear understanding for this diversity.

![Figure 4.15: Pressure-induced variations of density at 140K for all the studied materials except cumene (100K), $\rho_0$ is the density at ambient pressure.](image)

In 2005, Roland et al. published a comprehensive review article\textsuperscript{13}, which summarized the recent achievements in the studies of the pressure effect on the structural relaxation in supercooled liquids. According to this article, fragility should significantly decrease with pressure for most glass-forming materials. Moreover, the value of $dT_g/dP$ also drops with pressure, although the detailed pressure dependence is material dependent\textsuperscript{13,154}. Therefore, as a product of $\eta$ and $dT_g/dP$ (Eq.4.6), $\Delta V^#$ should be dramatically reduced by densification in most glass-forming materials, which agrees with the observed pressure-induced variations of $\xi$ in most of the studied systems.
(Figure 4.13). However, OTP and glycerol are exceptions: fragility increases in glycerol and remains constant for OTP (Table 4.2). More specifically, as seen in Table 4.1, fragility of glycerol increases about 20% from ambient pressure to 1 GPa, while $dT_g/dP$ decreases 23%. Thus, the pressure-induced variations of the two parameters cancel one another. As a result, $\Delta V^#$ is insensitive to pressure, which is in agreement with the behavior of $\xi$ (Fig. 4.13). In the case of OTP, fragility remains constant up to 0.8 GPa, and $dT_g/dP$ only has a slight decrease up to 0.1 GPa. Although the experimental data of $dT_g/dP$ at high pressure is not available for OTP, we would not expect a strong pressure dependence of $\Delta V^#$ in this material. Again, it is in accord with the variation of $\xi$ (Fig. 4.13). In Figure 4.16, we plot the pressure dependence of the cooperativity length scale and the activation volume for four systems, whose pressure data of $m$ and $dT_g/dP$ are available in literature. The slope of the linear fit demonstrates that the proportional relationship between $\xi^3$ and $\Delta V^#$ holds for these materials under densification.
Figure 4.16: Pressure dependence of $\xi$ and $\Delta V^\#$, the solid line presents a linear fit.

In Figure 4.17, we summarized all the experimental data of $\xi$ and $\Delta V^\#$ at $T_g$ for different materials, polymers with different molecular weight and systems under pressure. As shown in the figure, the cooperativity volume of a glass-forming material is always proportional to its activation volume, regardless of the chemical structure, the molecular weight and the external pressure. It seems that the observed correlation is a general feature for glass-forming systems.
Figure 4.17: $\xi$ vs $\Delta V^#$ in a double-logarithmic scale, the linear fit (the dashed line) gives $\lg(\xi)=0.48+0.3\times\lg(\Delta V^#)$. Numbers represent the glass-forming systems listed in Table 4.1. Solid squares (■) stands for different systems at ambient condition; Solid spheres (●) and triangles (▲) present molecular weight effect on $\xi$ for PPG and PS, respectively; Empty squares (□), spheres(○), triangles(△) and diamonds(◇) denote pressure dependence of $\xi$ in PMPS, PS(LMW), PIP and glycerol, respectively.

4.3.3. Difference between $\xi$ estimated from neutron scattering and light scattering spectra

As mentioned in Chapter II, light scattering and inelastic neutron scattering are two usual tools to measure the boson peak spectra in glass-forming materials. Since the neutron facility is not as widely available as the light scattering facility, the Raman
spectroscopy is more often used to study the boson peak. It is known that neutron
scattering spectroscopy probes the vibrational density of states, \( g(\nu) \), directly. By contrast,
the measured Raman scattering intensity \( I(\nu) \) is proportional to the vibrational density
of states multiplied by the light-to-vibrations coupling coefficient, \( C(\nu) \):

\[
I(\nu) = \frac{C(\nu) g(\nu)[n(\nu) + 1]}{\nu}.
\]

(4.9)

Here \( n(\nu) \) is the Bose temperature factor. Direct comparisons of the Raman spectra to
inelastic neutron scattering data have shown that \( C(\nu) \) varies almost linearly with
frequency around the boson peak\textsuperscript{157,158,159}. Due to this coupling coefficient, the boson
peak measured by Raman scattering presented as a spectral density (Eq. (3.24)) will shift
to a higher frequency in comparison to that measured using neutron scattering (the
neutron scattering spectra are presented as a reduced vibrational density of states, \( g(\nu)/\nu^2 \)).
A typical example is shown in Figure 4.18.
Fig 4.18: Comparison of the boson peak spectra measured by inelastic neutron (□) and Raman (○) scattering of PIB-3K at 140 K and P=1 atm. The neutron data are presented as a reduced vibrational density of states, \( g(\nu) / \nu^2 \), and the Raman data are displayed as a spectral density \( I(\nu) / ((n(\nu)+1)*\nu) \).

Since the cooperativity length scale is estimated by dividing the transverse sound velocity by the boson peak frequency (Eq. (2.23)), this shift of \( \nu_{BP} \) (Figure 4.18) leads to higher \( \xi \) estimated from the neutron data than from the Raman spectra. By comparing \( \xi \) estimated from the neutron and Raman spectra among different materials and materials under pressure, we found that this shift is quite universal (Figure 4.19). The ratio of \( \xi_{\text{neutron}} / \xi_{\text{light}} \) is 1.3 ± 0.1, whose variation is much smaller than that of \( \xi \) (a factor of 3 in Figure 4.17). This comparison suggests that \( \xi \) estimated from neutron data should also hold a one-third-power-law relationship with \( \Delta V^\# \) similar to what has been presented in Figure 4.17, but the whole set of data points would be systematically shifted along y axis.
by a factor of ~1.3. As discussed in Chapter II, $\xi$ is expected to be not directly equal to $V_T/V_{BP}$ but with a pre-factor $S$\textsuperscript{19,21,108,121},

$$\xi = S \frac{V_T}{V_{BP}}.$$  \hfill (4.10)

The pre-factor $S$ is model dependent, but close to 1. For example, if the boson peak vibrations are specified as torsion modes of nanometer-size particles, $S$ is equal to 0.85\textsuperscript{121}, while a value of 0.7 is assumed if the collective vibrations are spherical modes\textsuperscript{121}. If true, assuming $S=1$ in our analysis would result in an overestimation of $\xi$ by about 20 -30%. However, as discussed before, using Raman spectra instead of neutron data leads to an underestimation of the cooperativity size (~30%), which approximately compensates the overestimation induced by assuming $S=1$. As a result, $\xi$ estimated as the ratio of the sound velocity to the boson peak frequency acquired from Raman spectra might be closer to the true value than estimated from the neutron data. This might explain why $\xi$ obtained in our work agrees well with the 4D NMR result (Table 4.2). However, in any case, we do not insist on the absolute value of $\xi$ estimated in our approach, as long as there is no good model describing the boson peak vibrations.
Figure 4.19: Comparison of cooperativity length scale estimated from Raman scattering and inelastic neutron scattering: (a) different materials at ambient pressure\textsuperscript{160}, (b) PIB at 140K at different pressures\textsuperscript{151}.

4.3.4. A theoretical justification

In this section, we present a theoretical justification of the observed proportional relationship between the cooperativity volume and the activation volume within the framework of the random first-order transition theory (RFOT)\textsuperscript{29}. The basic idea of this model can be described in the following way. In a high temperature liquid, e.g. above the equilibrium melting temperature, two molecules (repeat units in the case of polymer) do not stay with each other for any significant time, i.e. the time scale for molecular collision and permutation is comparable. The system is dynamically similar to a dense gas. When the material is supercooled to $T_A$, i.e. a characteristic temperature marking the crossover
between the Arrhenius and the non-Arrhenius temperature dependence of $\tau_\alpha$ (see Chapter II), molecules start to reside with each other for much longer time. And hundreds of consecutive collisions happen within nearly the same set of molecules. When temperature is low enough, molecules are stuck in cages formed by neighbors, which are locally long-living structures in comparison to the time scale of collisions. These long-living structures are named “entropic droplets”. Molecules mostly perform harmonic vibrations within these entropic droplets, just like being confined in small crystals or nuclei. In analogy to crystallization, the transition from liquid to entropic droplets is considered to be a first order transition, but it is a random first order transition, because the liquid is frozen into a set of droplets, which are randomly distributed in space and might have amorphous internal packing. According to the classic nucleation theory, two factors compete with each other: creating new surface requires energy and impedes the formation of nucleus, while a lower Gibbs free energy in the crystalline state facilitates the process. Likewise, the transition from liquid to entropic droplets is determined by two competing terms. On one hand, the increasing size of droplet would raise the surface mismatch penalty between the droplet and the external circumstance. On the other hand, the configurational entropy of the droplet increases with its size. As a result, the free energy change during the formation of one droplet can be presented as

$$\Delta F(N)\big|_{T_\alpha T_\beta} = \gamma \sqrt{N} - T s_c N ,$$

(4.11)

where $N$ is the number of molecules in a droplet, $s_c$ is the configurational entropy per molecule, and $\gamma$ is a constant related to Lindemann ratio and characterizes the mismatch penalty. Detailed derivation of Eq. (4.11) can be found in Ref. 29. To form a stable droplet, the two competing factors must cancel one another, i.e. free energy itself must be
continuous during the transition. This means $\Delta F = 0$. Taking this into Eq. (4.11), one obtains the size of a stable droplet

$$N^* = \frac{\gamma^2}{T^2 s_c^2}.$$  

(4.12)

Wolynes and coworkers argued that the size of a droplet will not grow any more at a given temperature when it reaches $N^*$, because all thermodynamically relevant bulk liquid states are accessible at $N^*$, and the entropic term in Eq. (4.11) has no further increase with growing of the size.²⁹

Since two factors compete with each other in Eq. (4.11), a maximum in free energy as a function of $N$ would appear. The dependence of $F$ on $N$ can be schematically presented in Figure 4.20.

Figure 4.20: Free energy of forming an entropic droplet.
The maximum in Figure 4.20 defines the energy barrier towards forming the stable droplet. It is similar to the nucleation barrier of forming the critical nucleus, beyond which the nucleus can grow spontaneously. The maximum ($\Delta F^\#$) can be obtained by setting the derivative of $\Delta F$ with respect to $N$ as zero

$$\Delta F^\# = \frac{\gamma^2}{4Ts_c}.$$  \hspace{1cm} (4.13)

The relaxation of an entropic droplet must overcome the energy barrier $\Delta F^\#$, which can be specified as the barrier for the structural relaxation

$$\tau_a = \tau_0 \exp(\Delta F^\# / k_B T).$$ \hspace{1cm} (4.14)

By taking the derivative of $\ln \tau_a$ with respect to pressure, one obtains the activation volume, given that $\gamma$ has no appreciable pressure dependence,

$$\Delta V^\#(T) = -\frac{\gamma^2}{4Ts_c^2} \left. \frac{\partial s}{\partial P} \right|_T.$$ \hspace{1cm} (4.15)

According to Maxwell’s relations,

$$-\left. \frac{\partial S}{\partial P} \right|_T = \left. \frac{\partial V}{\partial T} \right|_P.$$ \hspace{1cm} (4.16)

A further development of Eq. (4.16) leads to

$$-\left. \frac{\partial S}{\partial P} \right|_T = \alpha V,$$ \hspace{1cm} (4.17)

where $\alpha$ is the thermal expansion coefficient of the supercooled liquid.

Applying Eq. (4.17) to each droplet one obtains

$$-\left. \frac{\partial s_c}{\partial P} \right|_T = \frac{\alpha V^*}{N^*}.$$ \hspace{1cm} (4.18)
Here $V^*$ is the volume of the entropic droplet. At a given temperature, $V^*$ can be roughly expressed as

$$V(T)^* = (\xi(T))^3.$$  \hfill (4.19)

Combining Eqs. (4.12), (4.15), (4.18) and (4.19), one obtains

$$\frac{\Delta V^*(T)}{(\xi(T))^3} = \frac{1}{4} \alpha T.$$ \hfill (4.20)

When applying the above equation to materials at $T_g$, one obtains

$$\frac{\Delta V^*(T_g)}{\xi(T_g)^3} = \frac{1}{4} \alpha_l T_g,$$ \hfill (4.21)

where $\alpha_l$ is the thermal expansion coefficient of the supercooled liquid around $T_g$.

It is important to point out that $S$ is the total entropy in Maxwell’s relations (Eq. (4.16)), whereas $s_c$ (Eq. (4.18)) is the configurational entropy, which is the difference between the total entropy and the vibrational one. Traditionally, the configurational entropy can be estimated as the entropy difference between supercooled liquid and its crystalline counterpart at a given temperature. Likewise, to correct the error induced by using the configurational entropy instead of the total one in Eq. (4.18), one could modify the expansion coefficient in Eq. (4.21) by subtracting the crystalline value from the liquid one as

$$\frac{\Delta V^*(T_g)}{\xi(T_g)^3} = \frac{1}{4} \Delta \alpha T_g,$$ \hfill (4.22)

where $\Delta \alpha$ is the difference of the expansion coefficient between a supercooled liquid and its crystalline counterpart at $T_g$. It is known that the glassy and the crystalline expansion coefficients of the materials around $T_g$ are quite similar, and both are much smaller than
the value of the supercooled liquid. Therefore, we can substitute the glassy expansion coefficient ($\alpha_g$) for the crystalline value, given that the former is more widely available in literature. (In later analyses and discussions, $\Delta\alpha$ always denotes the difference of expansion coefficient between the liquid state and the glassy state around $T_g$.)

Simha and Boyer collected the liquid and glassy expansion coefficients for a large number of polymers as well as small molecule systems and found both $\alpha_l T_g$ and $\Delta\alpha T_g$ were approximately constant$^{161}$. As illustrated in Figure 4.21, although the two products are not exactly constant, the variations among different materials are not significant, only a factor of 2 to 3. It is one order of magnitude smaller than the variations of $\Delta V^\#$ or $\xi^3$ (Figure 4.17). Thus, the RFOT provides a theoretical justification (Eqs. (4.21) or (4.22)) to the proportional relationship we discovered between $\Delta V^\#$ and $\xi^3$. Moreover, if we scale $\Delta V^\#/\xi^3$ by $1/4\alpha_l T_g$ or $1/4\Delta\alpha T_g$ (Figure 4.22), the ratio appears to be close to 1, especially for $1/4\alpha_l T_g$, which gives an average value of 1.002. Thus, Figure 4.22 strongly supports the prediction of RFOT (Eq. (4.21) or Eq. (4.22)).
Figure 4.21: (a) $\alpha_l T_g$ and (b) $\Delta \alpha T_g$ for various materials, here $\alpha_l$ and $\Delta \alpha$ are thermal expansion coefficient of supercooled liquid and the difference of expansion coefficient between the liquid and the glassy state at $T_g$, respectively. All values are presented in Table 4.1.
4.4. Conclusion

In this chapter, we estimated the cooperativity length scale (length scale of elastic heterogeneities) from boson peak spectra in various glass-forming materials. The obtained values agree well with the dynamic heterogeneity length scale of structural relaxation estimated by 4D NMR. This comparison suggests that the boson peak vibrations and the structural relaxation involve a similar length scale of cooperative molecular motions. In other words, they are two different types of motions for the same group of molecules. It is worth to mention that the light scattering is performed in a glassy state, while the 4D NMR is conducted in a supercooled state around $T_g$. We argue that the frozen dynamic heterogeneities of the structural relaxation in the glassy state define the length scale of the structural fluctuations, including fluctuations of elastic
constant. The latter scatter and damp the acoustic modes, which modifies the density of vibrational state and causes the formation of the boson peak. As a result, the length scale of dynamic heterogeneities in the supercooled state around $T_g$ appears in the boson peak vibrations deep in the glassy state.

We examined the relationship between $\xi$ and fragility. The analysis shows that the positive correlation suggested by the traditional cooperativity idea does not exist among different types of glass-forming materials. A further analysis reveals a one-third-power-law correlation between $\xi$ and the pressure dependence of the structural relaxation time, i.e. the activation volume ($\Delta V^\#$), among various materials around $T_g$. In other words, $\Delta V^\#$ is proportional to $\xi^3$. This proportional relationship is further demonstrated to be valid for polymers with different molecular weight and for materials under pressure. It seems to be a general feature for all glass-forming systems. To explain this correlation, we proposed a phenomenological picture that the cooperative region (a solid cluster) is one relaxation unit, and $\Delta V^\#$ is the extra volume required for each solid cluster to relax. A more solid theoretical justification is provided by using the random first-order transition theory. To our surprise, the prediction of RFOT agrees with the experimental data even on a quantitative level.

Moreover, we found that $\xi$ is normally larger in polymers than in non-polymeric materials. We argued that the neighbors along the polymer chain add extra hindrance, i.e. intra-chain constraint, to the molecular motions, which enlarges the molecular cooperativity.
CHAPTER V
THE ROLE OF MOLECULAR COOPERATIVITY IN THE TEMPERATURE DEPENDENCE OF THE STRUCTURAL RELAXATION TIME AROUND TG

5.1. Introduction

In contrast to the expectation of the traditional cooperativity idea, our experimental results (Figure 4.2) as well as the results of others’ studies \(^{7,8,10}\) reveal that there is no clear correlation between the cooperativity size and fragility among different glass-forming materials. However, in the previous chapter, we demonstrate a general correlation between \(\xi^3\) and the activation volume. The latter characterizes the pressure dependence of the structural relaxation time at constant temperature (Eq. (4.2)), which only presents the volume contribution to the temperature variations of \(\tau_\alpha\). In this chapter, the two contributions (volume and thermal energy) to the variations of \(\tau_\alpha\) are discussed separately. The analysis shows that only the volume contribution correlates with \(\xi\), whereas the energetic one is more dependent on the chemical structure of the studied materials and does not exhibit a direct correlation with the molecular cooperativity.

As mentioned in Chapter IV, polymers seem to have larger \(\xi\) than non-polymeric materials (Figure 4.2). We argued that it is the intra-chain constraint that enlarges the cooperativity size. However, there must be some other structural parameters which also
control the cooperativity size in polymers, because a large diversity in $\xi$ has been observed among the studied polymers. In Section 5.3.3, we particularly compare $\xi$ among 16 polymers and find that a polymer with larger characteristic ratio ($C_{\text{int}}$) involves more repeat units in one cooperative domain. This result suggests a direct connection between the molecular cooperativity involved in the structural relaxation and the coil size of the polymer chains.

5.2. Experimental

This chapter is a continuation of Chapter IV. All details of experimental setup, procedures and conditions can be found in the previous two chapters. The parameters for different materials discussed in this chapter are summarized in Table 5.1.

Table 5.1: Parameters for all the materials discussed in Chapter V.

<table>
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<tr>
<th>Systems$^a$</th>
<th>m</th>
<th>$E_V/E_p$</th>
<th>$m_V$</th>
<th>$\alpha_1$ ($10^{-4}$ $K^{-1}$)</th>
<th>$\kappa_1$ ($10^5$ bar$^{-1}$)</th>
<th>$\xi$ (nm)</th>
<th>$\xi/V_m^{1/3}$</th>
<th>$(\xi^*Q)/2\pi$</th>
<th>$\xi/V_{\text{bead}}^{1/3}$</th>
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<tbody>
<tr>
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<td></td>
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Table 5.1: Parameters for all the materials discussed in Chapter V (continued).

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<td>45</td>
<td>7</td>
<td>4.6</td>
<td>2.50</td>
</tr>
<tr>
<td>12. Cumene</td>
<td>90</td>
<td>57</td>
<td>6.2</td>
<td>2.19</td>
<td>3.75</td>
<td>5.39</td>
</tr>
<tr>
<td>13. CKN</td>
<td>93</td>
<td>3.5</td>
<td>1.3</td>
<td>1.70</td>
<td>2.18</td>
<td>5.09</td>
</tr>
<tr>
<td>14. Sorbitol</td>
<td>93</td>
<td>0.87</td>
<td>81</td>
<td>4.6</td>
<td>1.50</td>
<td>2.56</td>
</tr>
<tr>
<td>15. PIB-3K</td>
<td>46</td>
<td>34</td>
<td>6.18</td>
<td>2.31</td>
<td>5.10</td>
<td>3.49</td>
</tr>
<tr>
<td>16. PnBMA</td>
<td>56</td>
<td>6.4</td>
<td>2.25</td>
<td>3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17. PIP</td>
<td>62</td>
<td>0.76</td>
<td>47</td>
<td>6.16</td>
<td>3.2</td>
<td>2.23</td>
</tr>
<tr>
<td>19. PS-0.5K</td>
<td>72</td>
<td>0.52</td>
<td>37</td>
<td>6.9</td>
<td>2.61</td>
<td>4.76</td>
</tr>
<tr>
<td>21. PS-200K</td>
<td>140</td>
<td>0.66</td>
<td>90</td>
<td>5.5</td>
<td>5.6</td>
<td>3.34</td>
</tr>
<tr>
<td>22. PPG</td>
<td>83</td>
<td>0.67</td>
<td>55</td>
<td>7</td>
<td>2.06</td>
<td>4.49</td>
</tr>
<tr>
<td>23. PVAc</td>
<td>95</td>
<td>0.6</td>
<td>57</td>
<td>7.13</td>
<td>5</td>
<td>2.88</td>
</tr>
<tr>
<td>24. PDMS</td>
<td>100</td>
<td>8.62</td>
<td>7.9</td>
<td>2.53</td>
<td>5.25</td>
<td></td>
</tr>
<tr>
<td>25. PMPS</td>
<td>100</td>
<td>0.52</td>
<td>52</td>
<td>4.7</td>
<td>3.36</td>
<td>5.79</td>
</tr>
<tr>
<td>27. PMMA</td>
<td>103</td>
<td>5.2</td>
<td>4.7</td>
<td>2.54</td>
<td>4.87</td>
<td></td>
</tr>
<tr>
<td>28. PC</td>
<td>132</td>
<td>5.8</td>
<td>5.1</td>
<td>3.18</td>
<td>4.50</td>
<td>6.23</td>
</tr>
<tr>
<td>8. TPG</td>
<td>71</td>
<td>0.83</td>
<td>59</td>
<td>5.8</td>
<td>1.80</td>
<td>2.69</td>
</tr>
<tr>
<td>9 Salol</td>
<td>68</td>
<td>36</td>
<td>7.3</td>
<td>2.48</td>
<td>3.79</td>
<td>3.16</td>
</tr>
<tr>
<td>10. DBP</td>
<td>75</td>
<td>63</td>
<td>7.5</td>
<td>1.47</td>
<td>1.96</td>
<td>3.74</td>
</tr>
</tbody>
</table>

*For consistency, the materials are listed in the same sequence as in Table 4.1.*
5.3. Results and discussions

In this section, we will discuss why the cooperativity size does not exhibit a clear correlation with fragility among different glass-forming materials.

5.3.1. Failure of the correlation between $\xi$ and $m$

As discussed in Chapter II, both decrease in thermal energy and free volume with cooling would slow down the structural relaxation of the supercooled liquids\textsuperscript{13-16}. Therefore, fragility, i.e. the steepness of the temperature variations of $\tau_\alpha$ around $T_g$ at constant pressure can be separated to two terms\textsuperscript{13}

$$m = m_V + \frac{1}{k_B \ln 10} \frac{\alpha_i}{\kappa_i} \Delta V^*.$$

(5.1)

Here $\alpha_i$ and $\kappa_i$ are thermal expansion coefficient and compressibility of the supercooled liquid around $T_g$, respectively. $m_V$ is the isochoric fragility defined in Eq. (2.3), which characterizes the temperature variations of $\tau_\alpha$ at constant volume, i.e. the purely energetic contribution to fragility. The second term presents the variations of $\tau_\alpha$ with pressure (volume) at constant temperature, i.e. the volume contribution to fragility. (For simplicity, the second term is denoted as $m - m_V$ in the following discussion.) Here we would like to provide a brief derivation to Eq. (5.1). Since the supercooled liquid around $T_g$ is equilibrium or quasi-equilibrium, the structural relaxation time can be defined by any two of the three thermal variables (V, T and P), which are mutually related through a unique equation of state. Thus, the following expression is valid.
\[ \log \tau_{a} = f\left(\frac{T_{g}}{T}, P\left(\frac{T_{g}}{T}, V\right)\right). \]  

(5.2)

A total differential of Eq. (5.2) gives that,

\[ d \log \tau_{a} = \frac{\partial \log \tau_{a}}{\partial T_{g}} \left(\frac{T_{g}}{T}\right) dT_{g} + \frac{\partial \log \tau_{a}}{\partial P} \left(\frac{T_{g}}{T}\right) dP + \frac{\partial P}{\partial V} \left(\frac{T_{g}}{T}\right) dV. \]  

(5.3)

Combining the definition of fragility (Eq. (2.2)) and Eq. (5.3), one obtains,

\[ m = \frac{\partial \log \tau_{a}}{\partial T_{g}} \left|_{p,T=T_{s}} \right. = \frac{\partial \log \tau_{a}}{\partial T_{g}} \left|_{v,T=T_{s}} \right. - \frac{\partial \log \tau_{a}}{\partial P} \left|_{p,T=T_{s}} \right. \frac{T_{g}}{T} \left|_{v,T=T_{s}} \right. \]  

(5.4)

One can expand \( \frac{\partial P}{\partial T_{g}} \left|_{V,T=T_{g}} \right. \) as

\[ \frac{\partial P}{\partial T_{g}} \left|_{V,T=T_{g}} \right. = \frac{\partial V}{\partial T} \left|_{p,T=T_{g}} \right. = -T_{g} \frac{\partial V}{\partial T} \left|_{p,T=T_{g}} \right. = -T_{g} \alpha. \]  

(5.5)

Taking Eq. (5.5) into Eq. (5.4), one obtains

\[ m = \frac{\partial \log \tau_{a}}{\partial T_{g}} \left|_{p,T=T_{s}} \right. = \frac{\partial \log \tau_{a}}{\partial T_{g}} \left|_{v,T=T_{s}} \right. + T_{g} \frac{\alpha}{\kappa} \frac{\partial \log \tau_{a}}{\partial P} \left|_{p,T=T_{s}} \right. \]  

(5.6)
Finally, Eq. (5.1) can be obtained by taking the definition of $m_V$ (Eq. (2.3)) and $\Delta V^*$ (Eq. (4.5)) into Eq. (5.6). All the values of $m$ and $m_V$ are presented in Table 5.1, and $m_V$ is calculated through Eq. (2.4) by knowing the values of $m$ from the literature.

Figure 5.1 shows that only the volume contribution ($m-m_V$) to fragility has a direct correlation with $\xi$ among the studied materials, roughly as $m-m_V \propto \xi^3$, whereas the energetic one ($m_V$) does not. To further elucidate this point, a particular series of materials: monomer (PG), dimmer (DPG), trimmer (TPG) and 70mer of polypropylene glycol were studied. The reason to choose this series of materials is that the two contributions to fragility have substantially distinct dependence on the degree of polymerization in PPG. As shown in Figure 5.2, $m-m_V$ significantly increases with molecular weight, while $m_V$ remains constant. The analysis of light scattering data shows that the cooperativity volume ($\xi^3$) also drastically increases with molecular weight, and the trend approximately follows that of $m-m_V$ (Figure 5.2). This result clearly demonstrates that only the volume contribution to fragility directly correlates with molecular cooperativity.
Figure 5.1: (a) $\xi$ versus $m-m_V$; (b) $\xi$ versus $m_V$, both (a) and (b) are presented in a double-logarithmic scale. The linear fit (the dash line) in (a) gives a slope as $0.32\pm0.05$. Numbers represent different materials listed in Table 5.1.

Figure 5.2: Molecular weight dependence of cooperative volume $\xi^3$ ($\blacktriangledown$), isochoric fragility $m_V$ ($\bullet$) and volume contribution to fragility $m- m_V$ ($\blacktriangle$) in polypropylene glycol (PPG).
The result presented in Figure 5.1 and 5.2 can be explained by the underlying physics of the two contributions to fragility. On the one hand, $m_m V$ characterizes the volume or pressure dependence of the structural relaxation time and is defined by

$$\frac{\alpha}{\kappa} \Delta V^* \text{ (Eq. (5.1))}.$$ 

As shown in Figure 5.3, the ratio of $\alpha / \kappa$ at $T_g$ does not vary much among different glass-forming materials. It only changes by a factor of 2~3, which is one order of magnitude smaller than the variations of $\Delta V^*$ (Figure 4.17). Thus the value of $m_m V$ is mostly determined by the activation volume, which has been shown to be proportional to the cooperativity volume in the previous chapter. Therefore, $m_m V$ directly correlates with $\xi$.

![Figure 5.3: Ratio of $\alpha / \kappa$ for different glass-forming materials around $T_g$.](image)

On the other hand, $m_V$ denotes the thermal variation of the structural relaxation at constant volume. Apparently, it depends on the chemical structure of the studied systems,
such as the type of the intermolecular interactions (e.g. hydrogen-bonding, ionic or van-der-Waals interactions) and intra-molecular degrees of freedom (e.g. rotational energy barriers in polymers). Therefore, \( m_V \) will not exhibit a straightforward correlation with the cooperativity size (Figure 5.1(b) and 5.2). To better elucidate this point, the studied materials were separated into three categories as shown in Figure 5.4: van der Waals systems, pure hydrogen bonding systems and materials where both van der Waals interaction and H-bonds are important. All the van der Walls forming systems, except DBP (NO. 10), are at the top of the graph, i.e. larger \( \xi \) at a given \( m_V \). The pure hydrogen bonding materials stay at the bottom, while the materials involving both van der Walls force and H-bonds sit in between the other two groups. This comparison indicates that much higher activation energy is required for a given size of cooperative domain to relax in hydrogen-bonding materials at the isochoric condition than in van-der-Waals systems. This result can be explained by the well-known fact that the H-bonds are much stronger intermolecular interaction than the van der Walls force. Here the only exception is DBP (NO.10), which is a van der Walls material without any H-bonds but sits at the bottom of Figure 5.4. This might be due to its relatively rigid chemical structure, i.e. two C=O groups are symmetrically bonded to a phenyl ring in ortho positions, which would cause a big energetic barrier for intra-molecular motions.
From the above discussion, we can conclude that the volume contribution to fragility is roughly determined by the activation volume, thus directly correlates with the cooperativity size. But the energetic contribution strongly depends on the chemical structure of the studied systems, thus does not have a straightforward correlation with molecular cooperativity among different types of glass-forming materials. For example, at the same value of $m_V$, a hydrogen bonding system would have smaller $\xi$ than a van der Walls material (Figure 5.4).

5.3.2. Number of elementary structural units in the cooperative region

In most theoretical approaches, the molecular cooperativity is discussed in terms of the number of correlated units instead of the length scale or volume. So we
normalize $\xi$ by the size of some elementary structural unit ($l_0$) to compare the experimental results with predictions of different models. However, there exists controversy about how to choose the elementary structural units. For example, one OTP molecule consists of three benzene rings, which are covalently bonded. It is hard to decide whether one benzene ring or the whole molecule should be counted as a structural unit. To alleviate the bias caused by the choice of the structural unit, three strategies are adopted to perform the analysis. (1) Each individual molecule is taken as a structural unit, whose volume ($V_m$) is defined in Chapter IV. And $l_0$ is set as $(V_m)^{1/3}$. (2) $l_0$ is defined as $2\pi/Q$, where $Q$ is the wave vector of the first intense peak of the static structure factor measured by neutron or X-ray diffraction. (3) The third one is the structural unit suggested by Wolynes et al., namely “bead”, which constitutes the entropic droplets.\(^{67}\)

As shown in Figure 5.5(a) (d) and (g), regardless of the scaling strategy, the number of cooperative structural units ($\xi/l_0$) is rather similar for most materials, i.e. scatters in a range 3~6, and does not depend on fragility. This result is consistent with the work conducted by Berthier et al. based on the multipoint dynamic susceptibility function\(^9,68\), which shows that the dynamically cooperative domain is about 4-6 molecule size and is independent of fragility. It also agrees with the predictions of the Random first-order transition theory\(^{29,30}\) and the entropic barrier hopping theory\(^{41}\), where $\xi/l_0$ is suggested to be approximately universal (~4-6 (RFOT) and ~3-4 (entropic barrier hopping theory)) for glass-forming systems. It is of interest to mention that this scaling indicates that each individual cooperative domain contains approximately ~100 structural units, which is far bigger than the value predicted by the Adam-Gibbs theory, where the number of particles in one cooperative rearranging region ($z^*$) is expected to be smaller than 10\(^{44,64,65}\).
Figure 5.5: Number of elementary structural units ($\xi/l_0$): (a), (b) and (c) are $\xi / (V_m)^{1/3}$ vs $m$, $m - m_V$ and $m_V$, respectively; (d), (e) and (f) are $\xi^* Q/2\pi$ vs $m$, $m - m_V$ and $m_V$, respectively; (g), (h) and (i) are $\xi / (V_{\text{bead}})^{1/3}$ vs $m$, $m - m_V$ and $m_V$, respectively. The definitions of $V_m$, $Q$ and $V_{\text{bead}}$ have been described in the text. Numbers represent the materials listed in Table 5.1.

Furthermore, by comparing Figure 5.1(a) with Figure 5.5(b), (e) and (h), we found that it is the cooperativity size rather than the cooperativity number, i.e. the number of structural units in a cooperative domain, that correlates with volume contribution to fragility. A simple explanation is that $m-m_V$ among different systems is roughly determined by $\Delta V^*$, thus it is directly connected to the cooperativity length scale. However, scaling the cooperative length scale by the size of the structural units, which is
remarkably distinct among different materials (Table 5.1 and Ref. 22), would cloud the above connection.

5.3.3. Cooperativity size in polymers

In Table 5.2, we presented the cooperativity size for 16 polymers. $\xi$ changes from 2 nm (PPG) to 3.9 nm (PtBMA), nearly a factor of 2, which means the cooperativity volume can vary almost an order of magnitude among different polymers. As a general trend, the rigid polymers seem to have relatively larger cooperativity size than the flexible ones. For example, $\xi$ of rigid polymers such as PSF, PC and PS are all above 3 nm, whereas flexible ones like PDMS, PPG and PIB have cooperativity length scale close to 2 nm. But it is worth to emphasize that the chain stiffness is not the only parameter to determine $\xi$. For example, PDMS and PMMA have significantly different flexibility, but nearly the same value of $\xi$; PMPS is a typical example of flexible polymers, but its cooperativity size is even larger than that of PS and PC.
Table 5.2: Data of polymers.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Full name</th>
<th>ξ ( ^\text{c} ) (nm)</th>
<th>C\textsuperscript{inf} ( ^\text{a} )</th>
<th>N\textsubscript{BB} ( ^\text{b} )</th>
<th>V\textsubscript{m} ( ^\text{c} ) (nm(^3))</th>
<th>V\textsubscript{S} ( ^\text{d} ) (nm(^3))</th>
<th>( ξ/(V\textsubscript{m})^{1/3} )</th>
<th>( ξ/(V\textsubscript{S})^{1/3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSF</td>
<td>Polysulfone</td>
<td>3.64</td>
<td>2.2</td>
<td>20/4</td>
<td>0.592</td>
<td>0.065/0.326</td>
<td>4.33</td>
<td>9.05/5.29</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
<td>3.09</td>
<td>2.4</td>
<td>12/2</td>
<td>0.352</td>
<td>0.070/0.422</td>
<td>4.37</td>
<td>7.48/4.11</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
<td>2.98</td>
<td>4.2</td>
<td>10/6</td>
<td>0.240</td>
<td>0.101/0.168</td>
<td>4.79</td>
<td>6.4/5.4</td>
</tr>
<tr>
<td>PS-0.5K</td>
<td>Polystyrene</td>
<td>2.62</td>
<td>5</td>
<td>2</td>
<td>0.166</td>
<td>0.415</td>
<td>4.77</td>
<td>3.51</td>
</tr>
<tr>
<td>PIP</td>
<td>Polyisoprene</td>
<td>2.23</td>
<td>5</td>
<td>4/2</td>
<td>0.114</td>
<td>0.143/0.286</td>
<td>4.60</td>
<td>4.27/3.39</td>
</tr>
<tr>
<td>PPG</td>
<td>Poly(propylene glycol)</td>
<td>2.06</td>
<td>5.4</td>
<td>3</td>
<td>0.096</td>
<td>0.173</td>
<td>4.49</td>
<td>3.69</td>
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<tr>
<td>PDMS</td>
<td>Poly(dimethyl siloxane)</td>
<td>2.53</td>
<td>6.1</td>
<td>2</td>
<td>0.112</td>
<td>0.341</td>
<td>5.25</td>
<td>3.62</td>
</tr>
<tr>
<td>PIB -3K</td>
<td>Polyisobutylene</td>
<td>2.31</td>
<td>6.6</td>
<td>2</td>
<td>0.093</td>
<td>0.307</td>
<td>5.09</td>
<td>3.42</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
<td>2.54</td>
<td>7.7</td>
<td>2</td>
<td>0.142</td>
<td>0.547</td>
<td>4.86</td>
<td>3.1</td>
</tr>
<tr>
<td>PnBMA</td>
<td>Poly(n-butyl methacrylate)</td>
<td>2.25</td>
<td>8</td>
<td>2</td>
<td>0.225</td>
<td>0.899</td>
<td>3.70</td>
<td>2.33</td>
</tr>
<tr>
<td>PVAc</td>
<td>Poly(vinyl acetate)</td>
<td>2.88</td>
<td>9.4</td>
<td>2</td>
<td>0.121</td>
<td>0.569</td>
<td>5.83</td>
<td>3.48</td>
</tr>
<tr>
<td>PS-200K</td>
<td>Polystyrene</td>
<td>3.34</td>
<td>10</td>
<td>2</td>
<td>0.168</td>
<td>0.839</td>
<td>6.06</td>
<td>3.54</td>
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<tr>
<td>PMPS</td>
<td>Poly(methyl phenyl siloxane)</td>
<td>3.36</td>
<td>10</td>
<td>2</td>
<td>0.195</td>
<td>0.974</td>
<td>5.79</td>
<td>3.39</td>
</tr>
<tr>
<td>PnHMA</td>
<td>Poly(n-hexyl methacrylate)</td>
<td>2.05</td>
<td>10.9</td>
<td>2</td>
<td>0.280</td>
<td>1.52</td>
<td>3.13</td>
<td>1.78</td>
</tr>
<tr>
<td>PtBMA</td>
<td>Poly(t-butyl methacrylate)</td>
<td>3.88</td>
<td>12</td>
<td>2</td>
<td>0.231</td>
<td>1.39</td>
<td>6.33</td>
<td>3.48</td>
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</table>
Table 5.2: Data of polymers (continued).

<table>
<thead>
<tr>
<th>PLMA</th>
<th>Poly(lauryl methacrylate)</th>
<th>2.47</th>
<th>13.4</th>
<th>2</th>
<th>0.422</th>
<th>2.83</th>
<th>3.29</th>
<th>1.74</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>Polyethylene</td>
<td>6.8</td>
<td>2</td>
<td>0.052</td>
<td>0.176</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a $C_{inf}$ is the characteristic ratio of the polymer. The value of $C_{inf}$ for most polymers is obtained from Ref.164, except PS-0.5K and PtBMA, where $C_{inf}$ is found in Ref. 165 and 166, respectively. (The molecular weight of all the polymers except (PS-0.5K) are high enough, and all the relaxation properties, such as $T_g$, $m$ and $\xi$, have no further variations with increasing degree of polymerization. The detailed molecular weight of all the polymers is presented in Chapter III.)

b $N_{BB}$ and $N_{BB}^*$ are real and effective number\textsuperscript{164} of backbone bonds per repeat unit.

c $V_m$ is the volume of one repeat unit.

d $V_s$ is the volume of a statistic segment defined in Eq. (5.7).

According to the entropic barrier hopping theory proposed by Schweizer and coworkers\textsuperscript{41}, the diameter of each correlated hopping domain is about 3~4 structural unit size. Particularly, Schweizer et al. suggest that the structural units in polymers are statistical segments rather than repeat units. And the volume of this segment can be estimated as\textsuperscript{41},

$$V_s = C_{inf} \frac{V_m}{N_{BB}}.$$  \hspace{1cm} (5.7)

Here $C_{inf}$ is the characteristic ratio of the polymer, $V_m$ is the volume of one repeat unit and $N_{BB}$ is the number of backbone bonds per repeat unit. First, we count $N_{BB}$ as the real number of backbone bonds, e.g. $N_{BB}=10$ for PET. The so obtained $V_s$ is presented in Table 5.2. As illustrated in Figure 5.6, the ratio of $\xi/(V_s)^{1/3}$ for most of the studied polymers is consistent with the proposed value ~3-4\textsuperscript{41}, and many of them are almost exactly at the middle line ($\xi/(V_s)^{1/3}=3.5$). But there are two groups of polymers deviating
significantly. The first one presents polymers with rigid phenyl ring in the backbone and rather low $C_{inf}$: PSF, PC and PET. As suggested by Wu, the phenyl ring, carbon carbon double bond and triple bond are too rigid, and one should count the effective $N_{BB}$ without including these rigid bonds\textsuperscript{164}. The recalculated values of $\xi/(V_m)^{1/3}$ are displayed by (●) in Figure 5.6. The new values are indeed closer to the proposed value, especially for PC and PIP. According to the simulation work by S. Leon \textit{et al.}\textsuperscript{167}, the value of $N_{BB}$ for PC is \~1.5, which is even smaller than the effective $N_{BB}$ (2) suggested by Wu. This brings the scaling (▲) even closer to the expected value. The points for PSF and PET remain much higher than 3.5 even after scaling by the effective $N_{BB}$. It is possible that, the same as for PC, the effective value suggested by Wu still overestimates $N_{BB}$. The second group is poly(n-alkyl methacrylate) with very long side chains and rather high $C_{inf}$. The deviation increases with the length of the side group: PLMA > PnHMA > PnBMA. In these polymers, the side group becomes dominant in the repeat unit in terms of volume (mass). For example, the side group is about 6 times larger than the backbone unit in the case of PLMA, and it is just like a short PE chain. In addition, both fragility and $T_g$ of those polymers approach the values of PE with increasing the length of the side group (Figure 5.7). The above comparisons indicate that the segmental dynamics of the long-side-group poly(n-alkyl methacrylate) might be dominated by the motions of PE-like side groups. Following this line, we re-normalize $\xi$ of those polymers by the size of statistical segment of PE. Indeed, this new scaling (♦) brings the deviated points much closer to the expected value (Figure 5.6). Based on the above discussions, it seems that the prediction of the entropic barrier hopping theory that the cooperative domain in polymers involves approximately universal number of statistic segments is generally valid\textsuperscript{41}. 143
Figure 5.6: $\xi/(V_S)^{1/3}$ versus $C_{inf}$ for polymers, the dash line serves as a guide line at $\xi/(V_S)^{1/3}=3.5$. $V_S$ is estimated based on Eq. (5.7) from N_B: (■) real value, (○) the effective value suggested by Wu$^{164}$ and (▲) the value obtained in the simulation work$^{167}$. (♦) $V_S$ is volume of the statistical segment of PE.
Figure 5.7: (a) $T_g$ and (b) fragility of Poly(n-alkyl methacrylate) with different lengths of side group\textsuperscript{168}. The dash lines denote the values of PE\textsuperscript{168,169}.

As seen from Table 5.2, the number of backbone bonds per repeat unit in most polymers is rather similar ($N_{BB}=2$). Therefore, $V_S$ would be defined by the product of $C_{inf}$ and $V_m$ according to Eq. (5.7). As discussed above, the ratio of $\xi/(V_S)^{1/3}$ is approximately constant according to the entropic barrier hopping theory. Consequently, the number of repeat units in the cooperative region ($\xi^3/V_m$) is mostly determined by the characteristic ratio of the polymers. Indeed, a nice positive correlation arises between $\xi/(V_m)^{1/3}$ and $C_{inf}$ among the studied samples in Figure 5.8. Even very rigid polymers: PET, PC and PSF
also obey the trend. The only exceptions are poly(n-alkyl methacrylate) with long side
groups. As discussed above, the structural relaxation of those polymers might be dominat-
ed by the PE-like side groups, so it would make more sense to normalize $\xi$ by $V_m$ of PE
rather than their own values. As shown in Figure 5.8, indeed, this modification brings the
deviated points back to the trend. It is of interest to mention that the value of $\xi/(V_S)^{1/3}$ is
3.9 when extrapolating the trend to $C_{inf} = 1$. This is consistent with the prediction of the
entropic barrier hopping theory about colloidal systems that the cooperative domain is 3 -
4 colloidal particle size$^{41}$. (To some extent, the colloidal systems can be approximated as
freely jointed chains with $C_{inf} = 1$.)

As discussed above, the entropic barrier hopping theory provides a qualitative
explanation to the correlation presented in Figure 5.8. In fact, there is another way to
interpret it without assuming any model. In polymer melts, chains form Gaussian coils
and the mean square end-to-end distance of the chain is defined as,

$$< R_{ee}^2 >= C_{inf} nl^2, \quad (5.8)$$

where $n$ is number of repeat units per chain, and $l$ is the average length of backbone
bonds.

Moreover, the radius of gyration of the Gaussian coil is connected to the end-to-
end distance by,

$$< R_g^2 >= \frac{< R_{ee}^2 >}{6}. \quad (5.9)$$

From Eq. (5.8) and (5.9), $C_{inf}$ defines the coil size of a polymer chain at a given
molecular weight. Therefore, a larger $C_{inf}$ means more chains interpenetrating each other
in the volume of $R_g^3$, i.e. a lower Self-Concentration. It is known that, for a given repeat
unit, only two of the nearest neighbors are covalently bonded with it. A natural outcome of a lower Self-Concentration is that the non-chemically bonded nearest neighbors are more likely from other chains rather than from the own chain of the given repeat unit. Thus, to realize the motion of this repeat unit, more inter-chain neighbors must be moved out of the way. As a result, more chains are involved in a single relaxation event, which clearly would enlarge the cooperativity size.

Figure 5.8: $\xi/(V_m)^{1/3}$ versus $C_{inf}$ for polymers, the dash line serves as a guide for the trend. Circles and squares denote the scaling of $\xi$ by the repeat-unit size of the studied polymers and by that of PE, respectively.
5.4. Conclusion

In this chapter, the volume contribution \((m-m_V)\) and the energetic contribution \((m_V)\) to fragility are discussed separately. The analysis demonstrates that only the volume contribution directly correlates with the cooperativity size among various materials, whereas the energetic one does not. We argued that the former is determined by the activation volume, which has been demonstrated in Chapter IV to be proportional to the cooperativity volume regardless of the chemical structure of the studied materials. Therefore, \(m-m_V\) is directly connected to \(\xi\). On the other hand, \(m_V\) is more dependent on the chemical structure of the studied materials, e.g. the type of the inter-molecular interactions and the intra-molecular rotational barrier, and thus has no clear correlation with \(\xi\) among different systems. This explains the failure of the earlier attempts to find a direct connection between the overall fragility and \(\xi\). In addition, scaling \(\xi\) by the size of elementary structural units reveals that it is the cooperativity size rather than the cooperativity number that directly correlates with \(m - m_V\).

Moreover, we compared the cooperativity size of 16 polymers. Scaling \(\xi\) by the size of the statistical segment proposed by Schweizer et al. leads to a quite universal number \(~3.5\), which agrees with the prediction of the entropic barrier hopping theory. The analysis also reveals that a polymer with higher \(C_{inf}\) would involve more repeat units in one cooperative domain. We speculate that it is the mutual penetration of the chains that facilitate the molecular cooperativity.

An interesting result has been observed in poly(n-alkyl methacrylates) with long side groups that their elementary structural unit, fragility and \(T_g\) are quite similar to that
of PE. This result suggests that the structural relaxation in these polymers might be dominated by the motions of the PE-like side groups instead of the backbones.
CHAPTER VI
TEMPERATURE DEPENDENCE OF MOLECULAR COOPERATIVITY

6.1. Introduction

One of the core concepts of the traditional cooperativity idea is that the sharp slowing down of the structural relaxation in supercooled liquids under cooling results from the growing of the cooperativity size. Following this idea, many theoretical approaches predict that $\xi$ should drastically increase with decreasing temperature, although the detailed mathematical expression is model dependent. For example, the widely cited Adam-Gibbs theory predicts that the number of particles in a cooperative rearranging region ($z^*$) grows with cooling as $T/(T-T_0)$ (Eq. (2.6))$^{44,64,65}$, where $T_0$ is the VFT temperature$^{32-34}$. According to the Random first-order transition theory, the diameter of the entropic droplets varies with temperature as $T^{1/3}/(T-T_K)^{2/3}$, where $T_K$ is the Kauzmann temperature$^{29}$. It is of interest to mention that, in contrast to the above theories, the entropic barrier hopping theory (so far the only one as we know) suggests that the size of the correlated hopping domain remains essentially constant from $T_\text{g}$ to $T_c$,$^{41}$ where $T_c$ is the cross-over temperature$^{36,39}$. On the experimental side, the temperature dependence of the cooperativity size remains a controversial issue. The work conducted by Berthier et al. shows that the cooperativity size has very weak temperature
dependence from \( T_g \) to about \( T_c \), and the drastic decrease of \( \xi \) with \( T \) occurs at much higher temperatures (Figure 2.10). The author of a 4D NMR study on glycerol contend that the dynamic heterogeneity length scale (\( \xi_{\text{het}} \)) increases about 50\% from \( T_g+20\text{K} \) to \( T_g+10\text{K} \). However, the observed temperature variation of \( \xi_{\text{het}} \) is within the experimental error bars and not convincing. As discussed in Chapter II, some researchers have connected the width of the first sharp diffraction peak (\( \Delta Q \)) in the static structure factor to the structural correlation length \(^{17,85,86}\). The latter is assumed to be related to the molecular cooperativity for the structural relaxation. The analysis of the X-ray and neutron diffraction data of different materials shows that \( \Delta Q \) either remains constant \(^{88-91}\) or slightly increases \(^{87,88,92}\) with increasing temperature above \( T_g \) (Figure 2.11). This result indicates that the structural correlation length is not sensitive to temperature in the investigated temperature range (Figure 2.11).

It would be of interest to see how \( \xi \) estimated from the boson peak spectra changes with temperature. In this chapter, we analyzed the light scattering data of several glass-forming materials. The analysis shows that \( \xi \) does not exhibit significant temperature variation above \( T_g \) in the studied temperature range. Some preliminary understanding of this result is provided.

6.2. Experimental

Glycerol, OTP and PIB were chosen to perform the temperature study of \( \xi \). Each material exhibit clear a boson peak in the light scattering spectrum around \( T_g \), which
enables reliable analysis of $v_{\text{BP}}$. The investigated temperature range for glycerol is 180 to 235K (0.95 to 1.25 $T_g$), for OTP is 230K to 265K (0.95 to 1.1 $T_g$) and for PIB is 180K to 260K (0.95 to 1.3 $T_g$). In the case of glycerol, the transverse sound velocity is not accessible above 235K, whereas for OTP and PIB, the boson peak starts to overlap strongly with the quasielastic scattering (QES) at high temperature, which can be evidenced in Figure 6.1. The values of $T_c$ of the three materials are 285K (glycerol), 290K (OTP) and 270K (PIB)$^{36}$, respectively, always above the studied temperature ranges.

![Figure 6.1: Temperature dependence of the shape the boson peak spectra of OTP.](image)

As illustrated in Figure 6.1, the boson peak becomes less and less readily distinguishable with increasing temperature above $T_g$. To provide a more reliable estimate of $v_{\text{BP}}$, we
applied three different analysis schemes. The first scheme is the same as the one used for the measurements deep in the glassy state (details can be found in Chapter III). In brief, Eq. (3.25) was used to fit the spectra, where the QES part is described by a Lorentzian function, with a width as a free fitting parameter ($\nu_0$), and the boson peak part is described by a Log normal function. The second scheme is similar to the first one, but the value of $\nu_0$ is fixed rather than using a free fitting parameter. $\nu_0$ is set as 400GHz for glycerol, 150 GHz for OTP and 240GHz for PIB (about one third of the corresponding $\nu_{BP}$, as suggested by Ref. 142). In the third strategy, we normalize both the amplitude and position of the boson peak so that the high frequency tails of the boson peaks at different temperatures overlap with each other. (One example is presented in Figure 6.1). The frequency used for normalizing the peak is $\nu_{BP}$. Results from the three schemes are displayed in Figure 6.2. The values of $\nu_{BP}$ estimated in different ways differ little in comparison to the uncertainty resulting from the fitting. To estimate $\xi$, we use an average value of $\nu_{BP}$ from the three schemes.
Figure 6.2: Temperature dependence of the estimated boson peak frequency using three different schemes described in the text: (□) Scheme 1, (○) Scheme 2 and (△) Scheme 3 for (a) glycerol (b) OTP and (c) PIB. The error bars result from fitting by using Eq. (3.25).

It is known that the propagation of the acoustic wave is gradually damped by the structural relaxations in the supercooled liquids with increase of temperature. As a reflection in the spectra, the width of the Brillouin peaks becomes increasingly broader. In order to take this damping effect into account, a Damped Harmonic Oscillator (DHO) function is often used to fit the Brillouin peaks to obtain the frequency of the acoustic waves

\[ I(\nu) = I_0 \frac{\Gamma^2}{(\nu^2 - \nu_0^2)^2 + (2\Gamma)} , \tag{6.1} \]

where \( I(\nu) \) is the measured intensity, \( I_0 \) is a constant, \( \nu_0 \) is the fitted frequency of the acoustic waves without damping, which is used to estimate the sound velocity, and \( \Gamma \) is the half width of the peak at half maximum, which characterizes the degree of damping. In fact, the studied temperature range for the chosen materials is not far away from \( T_g \), and no significant broadening is observed for the Brillouin peaks. As illustrated in Figure 154.
6.3(a), the Lorentzian function provides quite similar fittings as the DHO function. Especially, when normalized by the value at $T_g$, the temperature variations of the Brillouin frequency fitted by the two functions are almost the same (Figure 6.3(b)). For simplicity, only the Lorentzian function is applied to estimate the transverse sound velocity for further discussions.

![Figure 6.3: Temperature variations of the Brillouin frequency of transverse acoustic waves in glycerol: (a) $\nu_T$ and (b) $\nu_T/\nu_T(T_g)$. Squares and spheres denote the results fitted by Lorentzian function and Damped Harmonic Oscillator function, respectively.](image)

6.3. Results and discussions

As shown in Figure 6.4, the cooperativity size (as the ratio of $V_T/\nu_{BP}$) remains approximately constant with temperature within the experimental error bar for both OTP and glycerol. It slightly decreases for $\text{B}_2\text{O}_3$: ~12 % from $T_g$ to $2T_g$. In the case of PIB, $\xi$ weakly rises: ~15% from $T_g$ to $1.3\ T_g$. In summary, $\xi$ of the studied materials does not
exhibit strong variations in the investigated temperature range. This result is clearly at odds with the expectation of the traditional cooperativity idea that it is the growing of the cooperativity size that causes the sharp slowing down of dynamics, or the rising of the apparent activation energy, i.e. $E_A = \frac{\partial \ln(\tau_0)}{\partial (1/T)}$, in supercooled liquids under cooling.

According to this idea, the cooperativity volume should drastically increase with decreasing temperature, following the behavior of $E_A(T)$, or $\xi(T) \propto (E_A(T))^{1/3}$. The explicit temperature dependence of $E_A$ can be obtained by combining the VFT equation (Eq. (2.1)) and the definition of $E_A(T)$

$$E_A(T) = B \left( \frac{T}{T - T_0} \right)^2 \propto \left( \frac{T}{T - T_0} \right)^2 . \quad (6.2)$$

In Figure 6.5, we compare $(E_A(T))^{1/3}$ acquired from Eq. (6.2) with $\xi(T)$ estimated from the boson peak spectra for glycerol, OTP and $B_2O_3$. Clearly, the temperature dependence of $\xi$ is too weak to follow that of $(E_A(T))^{1/3}$. 

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Figure 6.4: Temperature dependence of $\xi$ in (a) Glycerol, (b) OTP, (c) PIB and (d) $\text{B}_2\text{O}_3$. The data of $\text{B}_2\text{O}_3$ are obtained from Ref. 170.
Figure 6.5: Temperature dependence of $\xi_T$, $(E_A(T))^{1/3}$ and $(\Delta V^\#)^{1/3}$ in (a) glycerol, (b) OTP and (c) $\text{B}_2\text{O}_3$. Squares (■): $\xi$ obtained from boson peak; spheres (●): $(\Delta V^\#)^{1/3}$; dash line: $(E_A(T))^{1/3}$, which is acquired from Eq. (6.2); solid line: $\xi$ predicted by the Adam-Gibbs theory (Eq. (2.12)); dotted line: $\xi$ predicted by RFOT. The parameters used for model predictions are presented in Table 6.1. The data for $\xi$ in $\text{B}_2\text{O}_3$ are taken from Ref. 170. The data of $\Delta V^\#$ in glycerol and OTP are obtained from Ref. 171 and Ref. 172, respectively. The value $\Delta V^\#$ at T$_g$ is not available in literature, and we obtain it by extrapolating the experimental data down to T$_g$ and assuming the temperature variation of $\Delta V^\#$ follows that of $E_A$. All the data are normalized by the values at T$_g$.

Table 6.1 Parameters used for model predictions.

<table>
<thead>
<tr>
<th>Systems</th>
<th>$T_0$ or $T_K$ (K)</th>
<th>$T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>glycerol</td>
<td>111</td>
<td>191</td>
</tr>
<tr>
<td>OTP</td>
<td>169</td>
<td>246</td>
</tr>
<tr>
<td>$\text{B}_2\text{O}_3$</td>
<td>263</td>
<td>520</td>
</tr>
</tbody>
</table>

* the values of $T_0$ or $T_K$ are obtained from Ref. 173
As discussed in Chapter II, many theoretical approaches follow the traditional cooperativity idea and connect the increase of $E_A$ to the growing of cooperativity size. For example, the Adam-Gibbs theory predicts that the structural relaxation time of supercooled liquid can be expressed as

$$\tau_a = \tau_0 \exp\left(\frac{z^*(T)\Delta \mu}{T}\right),$$

(6.3)

where $z^*(T)$ is the number of elementary structural units in a cooperative rearranging region (CRR) at a given temperature. $\Delta \mu$ is the energy barrier required for the cooperative rearrangement per structural unit, which is assumed to be temperature independent. $\tau_0$ is a constant. Combining Eqs. (6.2) and (6.3) as well as the VFT equation (Eq. (2.1)), one obtains

$$E_A(T) = z^*(T)^2 \frac{\Delta \mu^2}{B}.$$  

(6.4)

Therefore, the length scale of CRR is connected to $E_A$ through a one sixth power

$$\xi_{AG} \propto (E_A(T))^{1/6}.$$  

(6.5)

According to the Random first-order transition theory, the temperature dependence of the diameter of the entropic droplets can be approximated as

$$\xi_{RFOT} \propto \frac{T^{1/3}}{(T - T_K)^{2/3}},$$

(6.6)

where $T_K$ is the Kauzmann temperature that is assumed to be equal to $T_0$. Combining Eqs. (6.6) and (6.2), one obtains

$$\xi_{RFOT} \propto \left(\frac{E_A(T)}{T}\right)^{1/3}.$$  

(6.7)
Since the temperature variation of $1/T$ is much weaker than that of $E_A(T)$ (Eq. (6.2)), the temperature dependence of the size of the entropy droplet is mostly determined by that of $E_A$.

In Figure 6.5, we plot the prediction of $\xi(T)$ of the Adam-Gibbs theory (Eq. (6.5)) and of the RFOT (Eq. (6.7)). Clearly, $\xi(T)$ estimated from boson peak spectra does not follow the predictions.

As demonstrated in Chapter IV, the cooperative volume is proportional to the activation volume among different glass-forming materials around $T_g$. In Figure 6.5, we present the experimental data of $(\Delta V^\#(T))^{1/3}$ for OTP and glycerol, which drastically increase with decreasing temperature. Obviously, the proportional relationship between $\xi^3$ and $\Delta V^\#$ does not hold any more when changing temperature. As a matter of fact, the temperature variation of $\Delta V^\#$ is closely related to that of $E_A(T)$. From the definition of $\Delta V^\#$ (Eq. 4.2), one can derive the following relationship

$$\Delta V^\# \propto \frac{E_A(T)}{T} \left. \frac{\partial T}{\partial P} \right|_{T_e(T)} .$$

(6.8)

According to the study of Huang et al.\textsuperscript{155}, $\left. \frac{\partial T}{\partial P} \right|_{T_e(T)}$ does not vary much with temperature.

Therefore, the temperature dependence of $\Delta V^\#$ is mostly determined by $E_A(T)$. This is supported by Figure 6.6.
Figure 6.6: Comparison of temperature dependence of the activation volume and the apparent activation energy, the data of $\Delta V^\#$ in glycerol and OTP are taken from Ref. 171 and 172, respectively. $E_A$ is estimated by Eq. (6.2).

In conclusion, the temperature variation of $\xi$ estimated from the boson peak contradicts the expectation of the traditional cooperative idea as well as the predictions of the Adam-Gibbs theory and the RFOT theory. It also causes the failure of the correlation between the activation volume and the cooperative volume (Figure 6.5). Based on the above discussions, all these contradictions and failures can be reduced to one statement: $\xi$ estimated from boson peak is insensitive to temperature, which is at odds with a sharp increase of the apparent activation energy with cooling. Here we want to emphasize that this is a very puzzling result. So far, we do not have a clear understanding of this result, but we would like to provide some preliminary ideas, which might be helpful for resolving this puzzle.
Owing to the way the fragility plot is constructed (e.g. Figure 6.7), all the viscosity or relaxation time curves for glass-forming materials intersect at two points: one is at $T_g$, where $\log \eta \approx 13$ ($\eta$ is in Poise), or $\log \tau_\alpha \approx 3$ ($\tau_\alpha$ is in seconds); the other is at very high temperature ($T_g/T \to 0$), where all liquids have $\log \eta \approx -4$ (Ref.174) or $\log \tau_\alpha \approx -14$.

(The two intersecting points are marked in Figure 6.7.) As illustrated in Figure 6.7, if a liquid has a higher slope at $T_g$, i.e. higher fragility, it will have a smaller slope at very high temperatures, i.e. lower $E_A$ at high $T$. By noticing this fact, Novikov and Sokolov found an inverse correlation between the high-temperature apparent activation energy ($T_g/T \to 0$), denoted as $E_H$, and fragility, which is shown in Figure 6.8\textsuperscript{175}. A linear fitting to this correlation gives that

$$\frac{E_H}{T_g} = \frac{(19.2)^2 \ln 10}{m}.$$

By definition, the apparent activation energy at $T_g$ can be expressed as

$$E_A(T_g) = \frac{\partial \ln \tau_\alpha}{\partial (1/T)} \bigg|_{T_g} = T_g m \ln 10.$$

Combining Eqs. (6.9) and (6.10), one obtains

$$\frac{E_A(T_g)}{E_H} = \left(\frac{m}{19.2}\right)^2.$$

Clearly, the change of the apparent activation energy in a supercooled liquid from high temperatures to $T_g$ strongly depends on fragility, and a more fragile system would exhibit larger variation. For example, in PS ($m=140$), the ratio of $E_A(T_g)/E_H$ is ~50, while for SiO$_2$ ($m=20$), it is about 1. The difference of $E_A(T_g)/E_H$ between fragile and strong systems is almost 2 orders of magnitude.
Figure 6.7: Fragility plots. The two intersecting points are marked. (Figure reprinted with permission from 5. Copyright (2010) by Nature)

Figure 6.8: $T_g/E$ vs $m^{175}$, where $E$ is the high-temperature apparent activation energy. The data points correspond to different glass-forming materials: BeF$_2$, SiO$_2$, NBS715, NBS711, DGG1, BSC, propanol, B$_2$O$_3$, glycerol, ethanol, salol, propylene carbonate, OTP, TNB, toluene, ZBLAN20. The solid line presents a linear fit to Eq. (6.9). (Figure reprinted with permission from 175. Copyright (2010) by Phys. Rev. E)
On the other hand, our results in Chapter V (Figure 5.6) and Berthier et al.’s work\textsuperscript{8,9} as well as the predictions of the RFOT\textsuperscript{29} and the entropic barrier hopping theory\textsuperscript{41} all suggest that the cooperativity number, i.e. the number of molecules in a cooperative domain, at $T_g$ among different materials is rather universal (its variation is at least one order of magnitude smaller than that of $E_A(T_g)/E_H$). And this number is fragility independent. As a general expectation, the cooperativity number at high temperatures ($T_g/T \to 0$) should be some arbitrarily small value, e.g. 1, and not depend on fragility. Therefore, the ratio of the cooperative number at $T_g$ to that at high temperatures would not vary much among different systems and does not correlate with fragility. By contrast, as discussed above, the temperature variation of $E_A$ (Eq. (6.11) is strongly material and fragility dependent. Obviously, by no means can the temperature variations of molecular cooperativity follow that of $E_A$. In other words, the core concept of the traditional cooperativity idea that the increase of $E_A$ with cooling results from the growing of the molecular cooperativity is questionable. As illustrated in Figure 6.4, our analysis based on the boson peak spectra shows that $\xi$ is not very sensitive to temperature above $T_g$ in the studied temperature range. It is consistent with the results of other experimental work, such as the study of temperature variations of $\Delta Q$ (Figure 2.11) and the work based on the multipoint dynamic susceptibility function (Figure 2.10). In addition, it also agrees with the prediction of the entropic barrier hopping theory\textsuperscript{41}. Base on these experimental results and the above discussions, we speculate that, in a certain temperature range, e.g. between $T_g$ and $T_c$, the temperature variations of $E_A$ are not (at least not only) caused by the change of the cooperativity size. There might be other mechanisms. For example, the energy barrier required for the cooperative rearrangement per structural unit, i.e. $\Delta \mu$, in
the Adam-Gibbs theory (Eqs. (6.3) and (6.4)) might increase with cooling rather than being constant as initially proposed. It will significantly raise $E_A$. In fact, this view is consistent with the standpoint of the entropic barrier hopping theory$^{41}$. According to this theory, the size of the cooperative hopping domain remains essentially constant (3~4 molecule size) between $T_g$ and $T_c$. When decreasing $T$ towards $T_g$, molecules are packed more and more compactly. This raises the difficulty of the cooperatively hopping process, i.e. increasing the hopping energy barrier ($F_B$), and drastically slows down the dynamics.

Before closing the discussion of this chapter, we would like to bring up an issue that the pre-factor $S$ in Eq. (2.23) ($\xi = S(V_T/V_{BP})$) might also vary with temperature. As predicted by the elastic constant fluctuation model proposed by Schirmacher et al.$^{20}$, increasing the amplitude of the elastic constant fluctuations would decrease $S$. In general, lowering the temperature of an equilibrium liquid would reduce the amplitude of fluctuations. As a result, $S$ will increase with cooling. Nevertheless, this effect is modest, i.e. the variation of $S$ from $T_c$ to $T_g$ is just a few percent$^{18}$. If the prediction is right, $\xi$ estimated in our work as a ratio of $V_T$ to $v_{BP}$ should be modified and slightly increase with decreasing temperature. However, we want to emphasize that, in any case, this modification is not significant and the previous conclusion that the temperature dependence of the cooperativity size is too weak to follow that of the apparent activation energy is still valid.
6.4. Conclusion

In this chapter, we presented the temperature dependence of the cooperativity size, estimated as the ratio of transverse sound velocity to the boson peak frequency, above $T_g$ for several materials. No strong variation has been observed in the studied temperature range. This result qualitatively agrees with the work based on the 4-point dynamic susceptibility function and the diffraction data for various glass-forming materials, as well as the prediction of the entropic barrier hopping theory. However, the traditional cooperativity idea as well as most theoretical models expects that the cooperativity size should drastically increase with cooling in order to explain the strong temperature variations of the apparent activation energy. Obviously, our result is at odds with this popular expectation. In the discussion section, we clearly demonstrate that the temperature variations of the molecular cooperativity by no means can follow that of $E_A$. Briefly, the change of the cooperative number between high temperatures and $T_g$ is rather similar among different materials and is definitely independent of fragility, while the temperature variation of $E_A$ is strongly material and fragility dependent. Based on our experimental data and others’ work, we speculate that there might be a different mechanism, which is more responsible for the increase of $E_A$ with cooling from $T_c$ to $T_g$. For example, the energy barrier required for a cooperative relaxation event per molecule might rise with cooling.
CHAPTER VII
SUMMARY

Despite decades of studies, understanding the glass transition phenomenon remains a challenge. Most researchers attribute the sharp slowing down of the structural relaxation in the supercooled liquids approaching the glass transition temperature to the cooperativity involved in the molecular motions. Moreover, the boson peak vibrations are also described as cooperative molecular motions in many models. Many researchers even speculate that the cooperativity length scales involved in the structural relaxation and the boson peak vibrations are intimately connected. In this study, we performed light scattering experiments on various glass-forming materials and estimated the cooperativity length scale ($\xi$) from the boson peak spectra. (Strictly speaking, $\xi$ is the length scale of elastic heterogeneities.).

In Chapter IV, we presented $\xi$ acquired deep in the glassy state for different materials. The value agrees well with the dynamic heterogeneity length scale for structural relaxation estimated using 4-D NMR around $T_g$. We speculate that the frozen dynamic heterogeneities in the glassy state define the length scale of the structural fluctuations, including fluctuations of elastic constants. The latter strongly scatter and damp the acoustic modes with a comparable wavelength, which leads to the formation of
the boson peak. As a result, the same cooperativity length scale appears in both the structural relaxation and the boson peak vibrations.

We examined the relationship between $\xi$ and fragility. In contrast to the expectation of the traditional cooperativity idea, we found no clear correlation exists between the two parameters among various materials. A further analysis reveals that the activation volume, i.e. the pressure dependence of the structural relaxation time, is proportional to the cooperativity volume among all the materials we were able to analyze. This correlation has been further demonstrated to be valid for polymers with different molecular weight and for materials under densification. It seems to be a general feature for all glass-forming systems. A theoretical justification of the observed relationship between $\xi^3$ and $\Delta V^*$ is provided using the random first-order transition theory (RFOT). To our surprise, the prediction of RFOT agrees reasonably well with the experimental data even on a quantitative level.

Moreover, we found that $\xi$ is normally larger in polymers than in non-polymeric materials. We speculate that the intra chain connectivity adds extra hindrance, i.e. intra-chain constraint, to the motions of repeat units, which enlarges the cooperativity size in polymers.

In Chapter V, the two contributions to fragility: the volume contribution ($m-m_V$) and the energetic contribution ($m_V$) are discussed separately. The analysis shows that only the volume contribution directly correlates with the cooperativity size among different materials, whereas the energetic one does not. We argued that the former is determined by the activation volume, and thus is directly connected to $\xi$. However, $m_V$ is more dependent on the chemical structure of the studied materials, e.g. the type of the inter-
molecular interactions and the intra-molecular rotational barrier, and thus has no straightforward correlation with the molecular cooperativity. This explains the failure of the earlier attempts to find a direct connection between the overall fragility and the cooperativity size. In addition, scaling $\xi$ by the size of elementary structural units reveals that it is the cooperativity size rather than the cooperativity number that directly correlates with $m - m_V$.

Moreover, we compared $\xi$ among 16 polymers and found that a polymer with higher characteristic ratio ($C_{\text{inf}}$) would involve more repeat units in one cooperative domain. This result suggests a direct connection between the molecular cooperativity involved in the structural relaxation and the coil size of the polymer chains. We speculate that it is the strong chain interpenetration in a high-$C_{\text{inf}}$ polymer that enlarges the molecular cooperativity.

In Chapter VI, we presented studies of the temperature dependence of $\xi$ in several materials above $T_g$. No strong variation has been observed in the studied temperature range. This observation contradicts the expectation of the traditional cooperativity idea as well as most of theoretical models that the cooperativity size should drastically increase with cooling to explain the sharp increase of the apparent activation energy. We provided experimental evidences to show that this expectation is questionable. Briefly, the variations of $E_A$ between high temperatures and $T_g$ among different systems are substantially distinct and strongly depend on fragility, while the behavior of the cooperativity number is rather material and fragility independent. Our results based on the boson peak indicate that the cooperativity size does not vary much in the studied temperature range. It agrees with the work based on the multipoint dynamic susceptibility
function and the diffraction data of various glass-forming materials, as well as the prediction of the entropic barrier hopping theory. We speculate that the growing of the cooperativity size might not be the major cause of the increase of $E_A$ with cooling in a certain temperature range close to $T_g$. There might be other mechanisms.
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