The Pennsylvania State University The Graduate School College of Engineering

### LIQUID TO SOLID WITHOUT ORDER: HINDERED MOTION IN GLASSY MATERIALS

A Dissertation in Chemical Engineering by Yuxing Zhou

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### Abstract

Glasses are non-equilibrium disordered solids that constitute a wide range of natural and engineered materials, including silicate glasses, plastics, colloidal suspensions and foams. Despite decades of research, the nature of the glass transition, whereby liquids transform to glasses under rapid cooling or compressing, is still a matter of debate. According to many leading glass theories, the dramatic slowing down of dynamics with decreasing temperature or increasing concentration— a key signature of the glass transition— is attributed to some underlying growing length scale. While a number of methods have been proposed, identifying the length scale relevant to the sluggish dynamics in glass-forming liquids remains elusive, since, after all, glasses are defined not by a common feature they share, but rather something they all lack: order.

In this thesis, we combine computational and theoretical approaches to study the dynamics and structures in glass-forming colloidal hard spheres, which is the simplest model glass-former and theoretically more tractable, as well as realistic polymer systems. First, we develop a novel crystal-avoiding method to suppress crystallization while preserving the dynamics of monodisperse hard spheres, which allows us to probe the long-time dynamics of the system in metastable equilibrium and offers new opportunities to examine the effect of size polydispersity. Then, we introduce a purely geometric criterion for the glass transition in monodisperse hard spheres, based on potentially caged particles that are restricted to neighbor rearrangement. We also propose a graph theory-based method combining Voronoi tessellation and graph isomorphism to explicitly enumerate distinct inherent structures and thereby obtain the structural entropy. We find a finite structural entropy at the glass transition volume fraction for both hard disks and hard spheres. When applied to identify locally preferred structures, the graph method reveals growing icosahedral clusters in random dense hard spheres, whose lifetime increases significantly as the system is densified. Finally, we expose the hidden correlation lengths in glass-forming systems from the dynamical response to external perturbations – pinned particles in colloidal hard spheres and free surfaces in polymer thin films. We find the correlation lengths obtained in both systems increase moderately as the glass transition is approached and correlate to the unperturbed structural relaxation times, as predicted by some theories.

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## Chapter 1 | Introduction

Glasses or amorphous solids constitute a range of solid materials ranging from window glasses, plastics (polymers) and colloidal suspensions to metallic glasses, foams and granular materials. The most common way to make a glass is to cool a liquid fast enough so that crystallization is avoided below the melting temperature. The liquid first becomes a supercooled liquid in metastable equilibrium. As cooling proceeds, motions of atoms or molecules in the supercooled liquid become increasingly slow, until at some temperature, the so-called glass transition temperature  $T_{\rm g}$ , the liquid can no longer be equilibrated within the experimental time scale, and a glass is formed. Understanding the nature of glass and the glass transition is widely accepted as a deep, interesting and fundamental problem in condensed matter physics and materials science. However, the consensus does not extend much further. Despite decades of intense research, there still lacks a coherent and elegant approach to the glass problem. Since the glassy state is ubiquitous in both nature and engineered materials, the final resolution of the glass problem may have a broad implication on many areas, such as food processing, drug release and organic semiconductors.

Glass-forming liquids display extremely slow dynamics and disordered structures. One of the central questions about glass and the glass transition is whether the spectacular glassy dynamics are associated with one or more length scales. The quest for length scales in glass-forming liquids arises naturally as a temptation to treat the glass transition in analogy to well-studied critical phenomena, where the critical slowing down is characterized by a diverging correlation length. However, there is no obvious way to define a static order parameter for the glass transition— conventional measures of structure, such as radial distribution function and structure factor, show very little difference, if any, between glass and liquid. Identifying the relevant length scale in glass-forming liquids is crucial for understanding the key aspects of the glass phenomena, including the dramatic slowdown in dynamics without any apparent structural change, the structural origin of dynamical heterogeneity, and the breakdown of the Stokes-Einstein relation.

In this thesis, we apply a variety of theoretical and computational methods to study the relation between dynamics and structures of glass-forming systems, including simple hard/soft-sphere models and realistic polymeric systems. Our aim is to seek the relevant length scales that may be associated to the glassy dynamics. The thesis is organized as follows.

In this chapter, the phenomena of the glass transition and some leading glass theories are introduced. In Chapter 2, the avoidance of crystallization in glassforming liquids is discussed, which is a matter that is often taken for granted in glass theories and most simulations. A novel crystal-avoiding method is developed to suppress crystallization while preserving the dynamics, which allows us to study monodisperse hard- and soft-sphere systems in metastable equilibrium.

In Chapter 3, a purely geometric criterion for the colloidal glass transition is introduced. We identify topologically caged (T1-inactive) particles as those that cannot gain or lose any Voronoi neighbors by moving within their free volumes while others are held fixed. For glass-forming hard-sphere fluids, we find that all particles become caged at random close packing, while caged particles start to percolate at the colloidal glass transition accompanying a diverging correlation length. The growth of the percolation length seems consistent with the dynamical correlation length associated to the spatially heterogeneous dynamics in supercooled liquids.

In Chapter 4, we propose a graph theory-based method to explicitly enumerate the inherent structures for both hard disks and hard spheres and thereby obtain the configurational entropy, which is related to the length scale of the so-called cooperatively rearranging regions (CRR) in thermodynamic glass theories, such as Adam-Gibbs (AG) theory and random first-order transition (RFOT) theory. We also use the graph method to identify local structures in glass-forming hard-sphere systems, which reveals an increase of icosahedral order that is locally preferred and long-lived when approaching the glass transition.

Finally, we study the effect of external perturbations on the dynamics and expose the length scales for colloidal hard spheres with periodically pinned particles (Chapter 5) and polymer thin films with free surfaces (Chapter 6). Proposals for future studies and some preliminary results are presented in Chapter 7.

### 1.1 Phenomenology

The most common way to make a glass, as has been practiced by glassblowers for thousands of years, is to cool down a melt fast enough so that nucleation and growth of crystalline order do not have time to happen. Below the melting temperature, a supercooled liquid is in metastable equilibrium compared to the crystal phase, which, if it exists, is the true thermodynamic equilibrium. As cooling proceeds, the dynamics in the supercooled slows down rapidly. until at some temperature  $T_{\rm g}$ , when the longest relaxation time of the system exceed the experimental time scale set by the inverse of the cooling rate, the system falls out of equilibrium with respect to the metastable state and becomes a glass. Below the glass transition temperature, many glass properties, such as specific volume or enthalpy, deviate from the supercooled line, but changes slowly towards the (metastable) equilibrium values at a slow rate depending on the thermal history, a phenomenon known as "aging". This observed glass transition, albeit quite sharp in most cases, is not a bona fide phase transition such as the solid/liquid/gas transition, but rather a dynamical crossover that depends on the cooling rate or observation time. A schematic of the glass transition is shown in Figure 1.1.

As the glass transition is approached from high temperature, a class of glass formers called "fragile" liquids display super-Arrhenius temperature dependence of viscosity or structural relaxation time; that is, the effective activation energy itself increases with decreasing T. Furthermore, the dynamics of a supercooled liquid not only slows down dramatically but inhomogeneously. This phenomenon is referred to as dynamical heterogeneity. In a supercooled liquid, there exist spatially correlated domains that can be faster or slower than the mean dynamics by orders of magnitude, the size and strength of which are both temperature and time dependent. In striking contrast to the dynamical anomalies in the glass transition, the structure of glasses and supercooled liquids is apparently the same as liquids at high temperatures. Both dynamic heterogeneity and dramatic slowdown of dynamics without obvious structural change are recognized as central aspects of the glass transition, and are the focus of intense research in the last decades. In



Figure 1.1: Schematic of the liquid-glass transition at constant pressure. Specific volume or enthalpy of the system is shown as a function of temperature.

this section, several important experimental observations on glass formation and their implications are discussed.

#### 1.1.1 Slow Dynamics

The experimental glass transition is now widely accepted as a dynamical crossover through which a liquid falls out of equilibrium in the observation time fixed by some operational convention. A common definition of the glass transition temperature for a liquid is the temperature at which the viscosity of the system reaches  $\eta = 10^{13}$ poise =  $10^{12}$  Pa·s, or roughly a relaxation time  $\tau \sim 10^2-10^3$  s, according to the Maxwell model,  $\tau = \eta/G_{\infty}$ , where  $G_{\infty} \sim 1$ –10 GPa is the instantaneous (infinity frequency) shear modulus and is almost constant that varies little with temperature. Note that the viscosity criterion usually does not apply for polymers, since the viscosity is highly molecular weight dependent while  $T_{\rm g}$  is not. In this case, the relaxation time criterion is still valid for segmental time but not for the terminal relaxation time.

The temperature dependence of viscosity for a variety of glass formers are shown in Figure 1.2. In this well-known "Angell" plot, the slope of a curve at a given



Figure 1.2:  $T_{\rm g}$ -scaled Arrhenius plots of viscosity for typical strong and fragile liquids. Different functions are used to fit the data: VFT equation (solid line), DF parabolic form (dotted line) and MCT power law (dashed line). (Adapted from ref. [1])

temperature is related to the corresponding activation energy  $\Delta$  in the Arrhenius equation,

$$\tau = \tau_0 \exp\left[\frac{\Delta}{k_{\rm B}T}\right],\tag{1.1}$$

where the prefactor  $\tau$  is some vibrational time scale ~  $10^{-13}$  s and  $k_{\rm B}$  is the Boltzmann constant. The fragility *m* is commonly defined as the steepness at  $T_{\rm g}$  [2],

$$m = \frac{\partial \log \tau}{\partial (T_{\rm g}/T)} \Big|_{T=T_{\rm g}}.$$
(1.2)

It is clear that for strong glass formers (small m) like SiO<sub>2</sub> and GeO<sub>2</sub>, the activation energy  $\Delta$  is almost constant throughout the temperature range of interest, and therefore the slowing dynamics as the temperature is lowered is due to the fact that thermal energy becomes smaller so that the rearrangements take longer time to overcome the energy barrier. On the other hand, fragile liquids (large m), such as o-terphenyl (OTP) and toluene, deviate strongly from the Arrhenius behavior,



Figure 1.3: Normalized activation energy  $\Delta(T)$  as a function of  $T_A/T$  for differently glass-forming liquids. (Adapted from ref. [4])

suggesting an increasing activation energy with decreasing temperature. There is in general agreement that the non-Arrhenius temperature dependence implies cooperative motions of multiple atoms or molecules, with the size of rearranging particles associated to the energy barrier [3].

The temperature dependence of activation energy  $\Delta$ , defined as  $\Delta(T) = k_{\rm B}T \log(\tau/\tau_0)$ , is shown as a function of  $T_{\rm A}/T$  in Figure 1.3, where  $T_{\rm A}$  is the temperature above which relaxation time has simple Arrhenius dependence. As the glass transition is approached, the energy barrier remains the same for strong liquids such as SiO<sub>2</sub> and GeO<sub>2</sub>, while the barrier increases by a factor of 2–3 for fragile liquids such as OTP and toluene. In contrast to the dramatic change in the relaxation time, the energy barrier of a supercooled liquid increases moderately as temperature is lowered. If we assume the activation energy and some length scale (e.g., size of CRRs) are related through a power law,  $\Delta \sim \xi^{\psi}$ , the moderate change of barrier implies the growth of any associated length scale may also be small.

Many fitting functions, either empirical or theory-based, have been used to describe the non-Arrhenius relaxation behavior. Proposed almost a century ago, the Vogel-Fulcher-Tammann (VFT) equation [5–7] is undoubtedly the most frequently used:

$$\tau/\tau_0 = \exp\left(\frac{BT_0}{T - T_0}\right),\tag{1.3}$$

where B and  $T_0$  are material-dependent parameters. When  $T_0 = 0$  and  $B \to \infty$ ,

the usual Arrhenius law is recovered. According to VFT, relaxation time of a fragile liquid diverges at nonzero temperature  $T_0 < T_{\rm g}$ , which is usually interpreted as the hallmark of an ideal glass transition in thermodynamic glass theories, such as Adam-Gibbs theory and RFOT theory.

The fragility evaluated from Eq. 1.2 then becomes

$$m = \kappa \left( 1 + \frac{\kappa}{B} \right), \tag{1.4}$$

where  $\kappa = \log(\tau(T_g)/\tau_0)$ . The fragility is therefore inversely proportional to B as  $m \sim 1/B$ , given that  $\tau(T_g)$  is fixed to be 100 s and  $\tau_0$  does not vary significantly for different substances. Based on the VFT fits shown in Figure 1.2, strong liquids such as SiO<sub>2</sub> and GeO<sub>2</sub> have very large  $B \sim 10^{12}$ , corresponding to a fragility  $m = \kappa \approx 20$  [8]; whereas fragile liquids have small B and hence large fragility indices, e.g., B = 4.9, m = 81 for OTP and B = 4.2, m = 94 for K<sup>+</sup>Ca<sup>2+</sup>NO<sub>3</sub><sup>-</sup> [8].

Alternatively, the relaxation time of a wide range of materials can be equally well fit to a parabolic form

$$\log(\tau/\tau_{\rm o}) = \left(\frac{J}{T_{\rm o}}\right)^2 \left(\frac{T_{\rm o}}{T} - 1\right)^2,\tag{1.5}$$

as suggested by dynamical facilitation (DF) theory [9], where J is an energetic barrier,  $\tau_{\rm o}$  is the relaxation time of the liquid at the  $T_{\rm o}$ , and  $T_{\rm o}$  is the onset temperature below which this form holds. Unlike VFT, the parabolic form is only singular at T = 0, which suggests no thermodynamic glass transition.

However, the VFT or parabolic form in general fails to account for the relaxation times of fragile liquids at higher temperatures. Instead, a power law fit

$$\tau/\tau_0 = \left(\frac{T - T_{\rm c}}{T_{\rm c}}\right)^{-\gamma},\tag{1.6}$$

captures the initial stages of supercooling as predicted by mode-coupling theory (MCT). Because of its mean field nature, the singularity at  $T_{\rm c} > T_{\rm g}$  in ideal MCT is usually avoided in real systems as a result of activated or hopping process [3].

There are other functions that yield similarly good fits in the temperature range accessible with current experimental or simulation techniques, it is therefore difficult to distinguish between leading theories. Nevertheless, as one of the central questions in the glass transition, non-Arrhenius temperature dependence should be a key aspect captured in any successful glass theory.

#### 1.1.2 Two-Step Relaxation Process

One common way to study the dynamics of a system is to measure the mean-square displacement (MSD) defined as

$$\left\langle r^{2}(t)\right\rangle = \frac{1}{N} \sum_{i=1}^{N} \left\langle (\boldsymbol{r}_{i}(t) - \boldsymbol{r}_{i}(0))^{2} \right\rangle$$
(1.7)

where  $\mathbf{r}_i(t)$  is the position of particle *i* at time *t* and the brackets  $\langle ... \rangle$  denotes ensemble or initial time average. At short times, particles translate ballistically between collisions and  $\langle r^2(t) \rangle \sim t^2$  is expected. On long time scales, the motion of particles are governed by the diffusion process. In Einstein's seminal work on Brownian motion, the MSD is related to the diffusivity *D* and the time elapsed *t* as

$$\left\langle r^2(t) \right\rangle = 2dDt,$$
 (1.8)

where d is the spatial dimension. In supercooled liquids, however, the ballistic and diffusive regimes are separated by a subdiffusive regime or a plateau at low temperatures (see Figure 1.4). The length of the subdiffusive regime increases as temperature decreases, which is often interpreted as particles spending more and more time in the cages formed by their nearest neighbors before they can escape.

The dynamics can also be characterized by dynamical correlation functions. For glass-forming liquids, the self (coherent)-intermediate scattering function  $F_{\rm s}(\mathbf{k}, t)$  is commonly used, which can be measured by inelastic neutron or X-ray scattering. Mathematically,  $F_{\rm s}(\mathbf{k}, t)$  is defined as the spatial Fourier transform of the self-part of the van Hove function  $G_{\rm s}(\mathbf{r}, t)$ , which correlates positions of the same particle separated by time interval t,

$$G_{\rm s}(\boldsymbol{r},t) = \frac{1}{N} \left\langle \sum_{j=1}^{N} \delta[\boldsymbol{r} + \boldsymbol{r}_j(0) - \boldsymbol{r}_j(t)] \right\rangle, \qquad (1.9)$$

where  $\delta(x)$  is the delta function. Therefore, the self-intermediate scattering function

can be written as

$$F_{\rm s}(\boldsymbol{k},t) = \frac{1}{N} \left\langle \sum_{j=1}^{N} \exp[i\boldsymbol{k} \cdot (\boldsymbol{r}_j(t) - \boldsymbol{r}_j(0))] \right\rangle, \qquad (1.10)$$

where  $\boldsymbol{k}$  is the wave vector usually chosen as the first peak of static structure factor  $S(\boldsymbol{k})$  For isotropic systems like liquids, one can average over the wave vector angle so that the self-intermediate scattering function only depends on the magnitude  $k = |\boldsymbol{k}|$ , which finally leads to

$$F_{\rm s}(k,t) = \frac{1}{N} \left\langle \sum_{j=1}^{N} \frac{\sin(kr_j(t))}{kr_j(t)} \right\rangle, \text{ for } d = 3,$$
(1.11)

$$F_{\rm s}(k,t) = \frac{1}{N} \left\langle \sum_{j=1}^{N} J_o(kr_j(t)) \right\rangle, \text{ for } d = 2,$$
 (1.12)

where  $J_0(x)$  is the zeroth-order Bessel function of the first kind. The above expressions for  $F_s(k,t)$  can be readily evaluated in simulations from particle trajectories.

Similar to the time-dependence of MSD,  $F_{\rm s}(k,t)$  also shows different relaxation behaviors as the glass transition is approached. At high temperatures, the decay of  $F_{\rm s}(k,t)$  as a function of time follows a simple exponential form  $F_{\rm s}(k,t) = \exp(-t/\tau)$ , where  $\tau$  is the characteristic time. In the case of exponential decay,  $\tau$  is identical to the structural or  $\alpha$ -relaxation time,  $\tau_{\alpha}$ , usually defined as the time such that  $F_{\rm s}(k,\tau_{\alpha}) = 1/e$ . In the supercooled regime, however, after the initial decay, which is also observed in high T as a result of ballistic collisions, the correlation function develops a plateau in a log-time representation, whose length increases with decreasing temperature, before eventually decays to zero at long enough times (see Figure 1.4). Conventionally, the fast (above the plateau) and slow (below the plateau) relaxation processes are called, respectively,  $\beta$  and  $\alpha$  relaxation. The decay of  $\alpha$  relaxation can be well described by a stretched exponential (also called Kohlrausch-Williams-Watts (KWW) law),

$$F_{\rm s}(k,t) = A \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right],\tag{1.13}$$

where  $\beta$  is the stretching exponent and is normally less than 1 for glassy dynamics. Note that in this case, the  $\alpha$ -relaxation time  $\tau_{\alpha}$  is different from  $\tau$ .



Figure 1.4: Mean-square displacement  $\langle r^2(t) \rangle$  (top) and self-intermediated scattering function  $F_s(q_0 = 7.2, t)$  (bottom) for A particles in a Kob-Andersen (KA) fluid [10] at different temperatures near the glass transition. Simulations are performed in the *NVE* ensemble with density  $\rho = 1.2$ .

The two-step relaxation in the dynamics is another hallmark of the glass transition. Although the cage interpretation is intuitive and sometimes useful, it is only a simplistic view. First, the dynamical heterogeneity observed in a supercooled liquid (see below) suggests that the structural relaxation is achieved via cooperative motions instead of individual particles escaping their cages independently. Second, the driven force for the uncaging process can be either energetic, i.e., a large energy barrier is overcome due to thermal fluctuation, or entropic, i.e., the rare low energy path through barriers is taken. It is unclear which scenario will dominate or whether it depends on the temperature. Finally, for mean-field systems without real space structure (i.e., no distance or neighboring particles), the plateau of the dynamical correlation function is also present at low temperatures, suggesting that there may be an alternative explanation of the two-step relaxation. For example, from the potential energy landscape viewpoint of the glass transition, the decreasing number of unstable saddle points with decreasing temperature is responsible for the two-step relaxation and slowing down in dynamics.

#### 1.1.3 Dynamical Heterogeneity

It is now well established from experiments [11–14] and simulations [15–17] that there exist spatially correlated fast and slow domains in supercooled liquids, dense colloidal suspensions and granular materials, known as dynamical heterogeneity (DH). In Figure 1.5, we show an example of DH for a binary mixture of hard disks in the vicinity of glass transition.

In experimental [18] and numerical [19] studies, the simplest way to characterize the dynamical heterogeneity is to consider the non-Gaussian parameter  $\alpha_2$ , defined as

$$\alpha_2(t) = \frac{d \langle r^4(t) \rangle}{(d+2) \langle r^2(t) \rangle^2} - 1,$$
 (1.14)

where d is the spatial dimension. The non-Gaussian parameter essentially measure the deviation of the distribution of particle displacements from Gaussian behavior.  $\alpha_2 = 0$  for perfect Gaussian distribution and larger  $\alpha_2$  value indicates stronger DH.

Dynamical heterogeneity is transient in the sense that the size of the most mobile or immobile clusters reaches the maximum at some intermediate time scale  $t^*$ , roughly corresponding to  $\alpha$  relaxation time  $\tau_{\alpha}$ . At too short or long enough times, motion of particles are primarily vibrational or diffusive, and their displacements follow a Gaussian distribution; no obvious DH can be observed.

To further quantify the spatial extent of mobile or immobile clusters, a fourpoint correlation function  $G_4(r;t)$  has been introduced [20–23], which quantifies the relaxation of density fluctuations at two points separated by distance r and time t. The dynamical susceptibility  $\chi_4(t)$  and dynamical correlation length  $\xi_d(t)$  are often extracted from the four-point correlation function in Fourier space, namely the dynamical structure factor,

$$S_4(q;t) = \frac{1}{N} (\langle W(\boldsymbol{q};t) \rangle \langle W(-\boldsymbol{q};t) \rangle - |\langle W(\boldsymbol{q};t) \rangle|^2), \qquad (1.15)$$



Figure 1.5: Particle displacements for a binary mixture of hard disks at  $\phi = 0.76$ . A third  $(x_A = 1/3)$  of disks are 1.4 times larger than the remaining disks. The time interval is chosen as 500 collisions per particle, about three times the relaxation time. Large displacements are shown in red while small are in blue.

$$W(\boldsymbol{q};t) = \sum_{i=1}^{N} \Theta[a - |\boldsymbol{r}_i(t) - \boldsymbol{r}_i(0)|] \exp[-i\boldsymbol{q} \cdot \boldsymbol{r}_i(0)], \qquad (1.16)$$

where N is the total number of particles and the  $\Theta(x)$  is Heaviside step function, which selects localized or immobile particles with displacements below a (often chosen as the plateau value of the  $\langle r^2 \rangle$ ). In the low-q limit,  $S_4(q;t)$  can be fit to an Ornstein-Zernike form,

$$S_4(q;t) = \frac{\chi_4(t)}{1 + (q\xi_d)^2}.$$
(1.17)

Like non-Gaussian parameter, the time-dependent dynamical susceptibility  $\chi_4(t)$ also displays a peak at  $t^* \sim \tau_{\alpha}$ . However, different time dependence of the dynamical correlation length  $\xi_d(t)$  have been reported in different investigations. Specifically,  $\xi_4(t)$  is found to grow monotonically with time [24], or reach a plateau and remain constant at longer time [25], or show a maximum value like dynamical susceptibility [26]. This inconsistency may arise from the difficulties involved in extracting  $\xi_d(t)$ , such as finite size effect. To avoid this potential problem, the dynamical correlation length is usually evaluated at  $t^*$  corresponding to the maximum of susceptibility  $\chi_4(t)$ . A number of studies [25–27] have shown that  $\xi_d$  increases considerably as glass transition is approached.

While the four-point correlation function by construction selects the localized particles, similar  $\chi_4$  and  $\xi_d$  values have been obtained for delocalized particles. Interestingly, more direct analyses of fast and slow domains in ref. [16] reveal different roles played by mobile and immobile particles. It is found that the characteristic time of mobile clusters (when spatial size reaches a maximum) is linear with the diffusion coefficient D/T, while the time scale of immobile clusters is related to the structural relaxation time  $\tau_{\alpha}$ . Thus the wide distribution of fast and slow particles has been argued to be responsible for the breakdown of the Stokes-Einstein relation,  $D/T \propto 1/\tau$ , in supercooled liquids [28, 29].

As previously mentioned, the increasing energy barrier for structural relaxation has been attributed to cooperative motions. Therefore, it is natural to study the correlation between relaxation time and dynamical length. On the one hand, Lačević et al. [26] show that a power law,  $\tau_{\alpha} \sim \xi_{\rm d}^{2.34}$ , is valid for WCA soft spheres above the MCT temperature  $T_{\rm c}$ , while Flenner and coworkers [25] find that exponential form,  $\tau_{\alpha} \sim \exp(A\xi_{\rm d})$ , provides a better description over larger range of data for binary hard-sphere mixtures. For bead-spring polymers, Starr et al. [16] show that the radius of gyration of mobile clusters and strings (a subset of mobile clusters with replacing particles)  $R_{\rm g}$  or the string size z, evaluated at some shorter time scale related to diffusion process, also correlate well with  $\tau_{\alpha}$  as  $\tau_{\alpha} \sim \exp(AR_{\rm g}^{1.3}/T)$ or  $\tau_{\alpha} \sim \exp(Az/T)$ . On the other hand, based on finite-size scaling analysis of Kob-Andersen model [10], Karmakar et al. [30] point out that the growth of relaxation time may not correlate with that of the dynamical length.

In summary, while the dynamical heterogeneity has been appreciated as a core aspect of glass phenomenon, which distinguishes supercooled liquids from hightemperature liquids, it remains elusive as to whether different measurements of dynamical length scale are equivalent; whether fast and slow particles have different local environments in structure; and most importantly, whether the DH is the origin or only a byproduct of slow dynamics.

#### **1.1.4** Configurational Entropy

One of the mysteries about glass transition is whether the dynamical slowdown is purely a kinetic arrest— no glass transition would occur if the system were cooled infinitely slowly (assuming crystallization can be avoided), or a manifestation of an underlying thermodynamic phase transition or ideal glass transition— the relaxation time diverges below some nonzero temperature and the system is in an *equilibrium* glass phase.

The configurational entropy  $S_c$  plays a central role in a number of thermodynamic approaches of glass transition. Traditionally, the configurational entropy is defined as the difference between the total entropy of a liquid and the vibrational entropy,

$$S_{\rm c} = S_{\rm t} - S_{\rm v}.$$
 (1.18)

Experimentally, the configurational entropy has been estimated from the excess entropy, defined as  $S_{\text{ex}} = S_{\text{t}} - S_{\text{CR}}$ , in which the vibrational entropy of the liquid is approximated by the entropy of the crystal,  $S_{\text{CR}}$ . The excess entropy can therefore be obtained from thermodynamic relation,

$$S_{\rm ex}(T) = \Delta S_{\rm m}(T_{\rm m}) + \int_{T_{\rm m}}^{T} \frac{\Delta C_{\rm p}}{T} dT, \qquad (1.19)$$

where  $\Delta C_{\rm p}$  is the difference between the heat capacities of liquid and crystal at T, and  $\Delta S_{\rm m}(T_{\rm m})$  is the melting entropy at the melting temperature  $T_{\rm m}$ . In 1948, Kauzmann observed that for many substances, including lactic acid, glucose and glycerol, the excess entropy decreases significantly with decreasing temperature and appears to vanish at some nonzero temperature by low-T extrapolation, This phenomenon is known as *Kauzmann's paradox* or *entropy crisis*. However, Kauzmann's himself did not believe the vanishing configurational entropy and resolved the problem by invoking a kinetic spinodal at  $T_{\rm sp} > T_{\rm K}$ , below which crystallization always occurs before a supercooled liquid could relax. It is Gibbs who first argued that the vanishing  $S_{\rm c}$  could be a signature of thermodynamic glass transition.

Inspired by the analytical solution of mean-field spin glasses, the physical significance of configurational entropy (called complexity in spin-glass model) can be understood in terms of metastable states in the free energy landscape. Formally,

the configurational entropy is a measure of the number of metastable states, i.e.,

$$S_{\rm c}(T) = \frac{k_{\rm B}}{N} \log \sum_{\alpha=1}^{\mathcal{N}} \delta(f_{\alpha} - f^*(T)), \qquad (1.20)$$

where  $\mathcal{N}$  denotes the number of states,  $f_{\alpha}$  is the free energy of state  $\alpha$  and  $f^*(T)$  is the characteristic free energy at a given temperature that satisfies the saddle-point equation,  $S'(f^*) = 1/T$ . The exact solution of *p*-spin model reveals a thermodynamic phase transition at  $T_{\rm K}$  (called  $T_{\rm s}$  in the *p*-spin). For  $T > T_{\rm K}$ , the equilibrium state consists exponentially large number of metastable states and the configurational entropy is finite. For  $T < T_{\rm K}$ , the equilibrium state is dominated by one of the free energy minima, whose number is sub-exponential; the configurational entropy gradually reduces with decreasing T.

In the mean-field model, the free energy barrier becomes infinite below the dynamic glass transition  $T_d > T_K$ ; therefore, the configurational and vibrational entropies can be sharply separated, and the metastable state can be well defined. However, the concept of metastable state is not so clear in real systems. For one thing, since the energy barriers are finite due to finite range interaction, a metastable state may be surrounded by many small minima that are irrelevant as metastable states. For another, different parts in a large system, far from each other, can rearrange independently and continuously, so the whole system represented as a single point in the phase space cannot be found vibrating within a global metastable state, but instead, is always on top of a barrier.

Nevertheless, at low enough temperatures, the metastable states in free energy landscape may be identified as the inherent structures (IS) in the potential energy landscape (PEL). First proposed by Stillinger and Weber [31,32], the configurational space can be unambiguously partitioned into a set of distinct basins, associated with the local minima of the PEL. Each configuration is connected to a inherent structure via a steepest descent path. Unlike free energy landscape, the shape of PEL is independent of temperature, but the exploration of PEL is strongly T-dependent. As a result, the configurational entropy defined in terms of PEL is related to the number of basins with a local minimum energy  $e_{\rm IS}(T)$  typical at T.

Following the PEL thermodynamic formalism, a number of simulations have been conducted to calculate the configurational entropy for various systems [33–35]. In most cases, thermodynamic integration of some macroscopic observable is evoked. For example, the total entropy of the liquid  $S_t$  in Eq. 1.18 can be evaluated from the equilibrium liquid equation of state (EoS), while the vibrational entropy  $S_v$ is obtained by constraining the system to a local energy minima. Alternatively, the vibrational entropy can be estimated by harmonic approximation. Note that although the total entropy is well defined, some ambiguity may arise in defining the vibrational contribution. In general, the obtained configurational entropy is found to decreases with decreasing temperature.

Unfortunately, this putative ideal glass transition is inaccessible to experiments or simulations, as the system will fall out of equilibrium at  $T_{\rm g} > T_{\rm K}$ , and the  $S_{\rm c}$  in the glassy state will remain almost constant as T decreases. Therefore, most work that reports vanishing configurational entropy at nonzero temperature are based on extrapolation. The validity of extrapolations into lower temperature or higher density regions has been criticized. For example, it has been argued that the ideal glass transition does not exist in 2d hard-disk systems by explicitly constructing an exponentially large number of packings [36]. Second, the identification of metastable state with inherent structures has been questioned [37], for reasons discussed above. A different numerical measurement of configurational entropy has been proposed recently [38], which does not require precise definitions of the free energy landscape and metastable states, and is conceptually closer to the theoretical definition. Interestingly, the configurational entropy obtained from this approach disappears discontinuously above some onset temperature, consistent with predictions from spin-glass model. Finally, while the idea that the system becomes extremely slow at low temperatures as a result of rarefaction of available states is an intriguing one, direct evidence of the fact that the structural rearrangement is driven by the configurational entropy is still lacking; there are other explanations of the sluggish dynamics in which thermodynamics is trivial [39]. In Chapter 3, we propose another way to compute the configurational entropy based on local structures in real space.

#### 1.1.5 Structural Property of glass transition

Over the past few decades, considerable effort been devoted to searching for the structural origin of glass transition. In conventional condensed matter systems, structures determines dynamics, and a sudden change in dynamical properties



Figure 1.6: Pair correlation function g(r) between A-A particles for a KA model at different temperatures. The structural change revealed by this standard correlation function is subtle as the glass transition is approached.

usually follows from a similar sudden change in structure, e.g., phase transition between liquid and crystal. However, in the glass transition, the dynamics slows down drastically without apparent structural change. For example, the radial distribution function (RDF) or pair correlation function which is the only measure of structure that is easy to access experimentally, displays little change when approaching to the glass transition from high temperature, as shown in Figure 1.6, for a Kob-Andersen (KA) model [10]. This rather discouraging result suggests that even if there exists some static length scale accompanying the glass transition, it is hidden in the apparently disordered structure, so that conventional tools are not effective to detect it. Therefore, delicate analyses of local properties are required to identify the underlying structural signature in glassy materials.

The free volume theory [40–42] is one of the theories that are rooted in the real space structures, which became popularized as a way to explain dynamical and mechanical changes in the glass transition. This theory assumes that molecular transport in a supercooled liquid relies motions of particles into voids formed by redistribution of the so-called "free volume", loosely defined as the remaining space not taken by molecules. As temperature is lowered (or density is increased), the free volume decreases due to the reduction of system volume, and eventually vanishes at some  $T_0$  (or  $\phi_0$ ), which is reminiscent to singularity appears in the VFT equation (Eq. 1.3). Indeed, the VFT equation can be derived based on the free volume distribution and thermal expansion coefficient. However, except for hard particles, which have a simple geometry, the free volume is not well defined in most systems and thus cannot be measured directly. The lack of a precise definition may give rise to some contradictory results. For example, in the traditional model, the total free volume is define as the system volume subtracted by the hard-core volume of particles. This suggests that the glass transition would not occur if temperature is lowered at a constant volume, which is certainly not true. The free volume model also fails in explaining the pressure-dependent behavior [43]. A more consistent treatment of free volume, such as the approach recently proposed based on the lattice model [44], may help clarity some ambiguities and misconceptions in this theory. Finally, although the free volume theory provides a reasonable explanation of the non-Arrhenius behavior of dynamics, the type of molecular motion is poorly defined in the model on the microscopic level. Thus it gives no prediction of dynamical heterogeneity— no causal link has been found between local free volume and local dynamics [45].

A different approach focuses on local structural motifs in glass-forming systems. Charles Frank first suggested about 60 years ago that the formation of energetically favored, fivefold symmetric icosahedra in supercooled liquids may suppress crystallization and lead to vitrification. The geometric frustration approach argues that the glass transition can be thought as "crystallization" of polyhedral motifs in curved space, where locally preferred structures (LPS) like icosahedron can tessellate but the growth of LPS is frustrated in Euclidean space as they cannot fill the space. Both experiments [46,47] and simulations [48–50] have revealed the existence of icosahedral or other polyhedral order in fluids of spherical particles, such as colloidal suspensions and metallic glasses. Furthermore, some studies suggest that icosahedral clusters tend to have slower dynamics than the rest of the system [51,52]. A key drawback of this proposal is that the prevalent local order is system-dependent (e.g., bicapped square antiprisms are locally favored in the KA model), and that it may be difficult to access in generic molecular glass formers such as polymers.

Another type of structural motif called medium-range crystalline order (MRCO) short-lived transient crystal-like ordering characterized by bond-orientational order has been associated to the dynamical heterogeneity and slow dynamics in polydisperse particle systems and a spin liquid [53, 54]. The splitting of the second
peak in the RDF is often used as the evidence of growing MRCO (see Figure 1.6). However, this scenario has been challenged by some contradictory results for moderately polydisperse disks [55], and the lack of growing MRCO in binary and highly polydisperse systems [56,57]. Moreover, a recent study suggests that the growth of MRCO could be a result of weakly first-order transition rather than glassiness [58].

One related question in establishing the link between structural and dynamic length scales is whether the dynamic heterogeneity has a purely structural origin. Using isoconfigurational ensemble, Widmer-Cooper et alshowed that the particle propensities, obtained by averaging over independent trajectories with the same initial configuration but different initial velocities, display considerable spatial variation, and hence demonstrated that the underlying initial structure does affect the DH [59]. However, in quest of an explicit structural criterion for mobile/immobile particles, local free volume and local potential energy failed badly [45], while LPS correlates only weakly to the local dynamics [60]. Recent studies suggest a strong correlation between irreversible structural reorganization and quasi-localized soft modes in binary mixture of 2d glass-formers [61, 62]. Machine learning methods have proven successful in predicting a *population* of particles that are susceptible to rearrangement at a later time from the local structural geometry alone [63], but the actual structural indicators for particle propensities remain unclear. It is probably as good as what we may expect for predicting dynamics from initial structure, as Wolfram [64] has pointed out that for some irreducible phenomena in complex systems, the future behavior cannot be obtained by an algorithm more efficient than solving the equations of motion.

More recently, a series of "order-agnostic" approaches have been developed [30, 65, 66], which capture the static amorphous order without *a priori* knowing the any specific local order. Among other proposals, the point-to-set correlation length [66, 67] characterizes the distance over which boundary conditions imposed by pinned particles affect the equilibrium structure of the remaining liquid.

Exploring the relationships between structure and dynamics is of great importance for understanding the glass phenomena. The correct length scale could serve as the order parameter in glass-forming systems, with which the glass problem may be studied within the framework of conventional second-order phase transitions. Also, recasting dynamic properties in terms of structure may provide new insights on predicting the glassy behavior. In this thesis, different approaches have been employed in search of the relevant length scales associated with glass transition.

## **1.2** Theories of the Glass Transition

Over the course of time many theories of the glass transition have been developed. The approaches by which these theories explain the slowing down of supercooled liquids with decreasing temperature vary radically. Some have a underlying thermodynamic origin, such as free-volume model [40], energy landscape description [68], Adam-Gibbs (AG) theory [69] and random first-order transition (RFOT) theory [70]. Others are purely based on dynamics, including the mode-coupling theory (MCT) [71], dynamical facilitation (DF) theory [39] and kinetically constraint model (KCM) [72]. Although each model can explain some aspects of the glass transition, there is no widely accepted resolution that can provides a coherent and elegant explanation of all the key features of glassy phenomena. One of the main difficulties arises from the large gap between the time scale required to discern leading theories and that accessible in current experiments or simulations. It is worth mentioning that some advanced simulation algorithms (e.g., swap Monte Carlo [73]) and experimental protocols (e.g., vapor deposition [74]) can prepare equilibrium samples for certain glass-formers at a temperature below the conventional  $T_{\rm g}$ , however, direct measurement of relaxation time still requires a long observation time, which exceeds the capability of current techniques. Despite relatively slow evolution of this field owing to these difficulties, emerging evidence of correlations between various properties in glass-forming liquids suggests that a general theory for the glass transition is possible. Several detailed reviews of glass theories can be found in the literature [3, 75, 76]. In this section, some popular glass theories are introduced with their advantages and limitations discussed.

### 1.2.1 Mode-Coupling Theory

First developed by Bengtzelius, Götze and Sjölander [71] in the 1980s, the modecoupling theory (MCT) is still regarded by many as the only established first principles approach to the glass transition. Essentially, MCT is an approximate solution of exact equations of slow motions derived from the Mori-Zwanzig projection operator formalism, i.e.,

$$\ddot{F}(q,t) + \Omega^2(q)F(q,t) + \int_0^t \left[ M^0(q,t-t') + \Omega^2(q)m(q,t-t') \right] \dot{F}(q,t')dt' = 0.$$
(1.21)

Here F(q,t) is the intermediate scattering function introduced previously;  $\Omega(q)$ is a microscopic frequency related to static structure factor S(q) via  $\Omega^2(q) = q^2 k_{\rm B}/(mS(q))$  with m the mass of the particles; and the kernel is split into a regular part  $M^0(q,t)$  and the main contribution m(q,t), describing respectively the dynamics of a normal liquid and a supercooled liquid. The regular part  $M^0(q,t)$ is often approximated by delta function corresponding to Newtonian friction,  $M^0(q,t) = v(q)\delta(t)$ , while the kernel m(q,t) is rather complicated. In the idealized version of MCT, it can be expressed as  $m(q,t) = \sum_{k+p=q} V(q; k, p)F(k,t)F(p,t)$ . Importantly, the vertices V(q; k, p) can be calculated from static structure factor S(q). In short, MCT gives the dynamics from the static information.

Owing to the nonlinear feedback mechanism of the MCT equations, the resulting  $F_{\rm s}(q,t)$  is strongly temperature-dependent even though the input S(q) is rather temperature insensitive. One of the main results from MCT is the existence of  $\beta$ -and  $\alpha$ -relaxation processes at low temperature— the development of a plateau in  $F_{\rm s}(q,t)$  in intermediate time scales, consistent with experimental and simulation observations (see Figure 1.4).

Another important prediction of the idealized MCT is the power law dependence of the relaxation time  $\tau$  or the inverse of diffusion constant D on temperature, with a singularity at  $T_c$ ,  $\tau \sim 1/D \sim (T - T_c)^{-\gamma}$ , which is reasonably good for the hardsphere model (although the calculated  $\phi_c \sim 0.52$  is lower than the experimental value between 0.58 and 0.59). However, the singularity is often avoided and instead manifests itself as a crossover in most real systems, as a result of thermal activated or hopping process neglected in the idealized theory. Even if the hopping processes are taken into consideration, a signature of the sharp transition still persists and gives rise to a dynamical anomaly in the relaxation behavior. This suggests that simply incorporating the hopping process in MCT below the critical temperature  $T_c$  is not adequate to correctly describe the relaxation of the system.

Although the diverging relaxation time in the simple version of MCT is originally viewed as a local caging phenomenon without any growing length scale, recent discovery of the connection between MCT and mean-field spin glasses [77], as well as the subsequent development of inhomogeneous MCT [78,79], suggest that MCT dynamical transition should be understood as a critical phenomenon accompanied by a diverging "dynamical" length scale  $\xi_{\rm d} \sim (T - T_{\rm c})^{-1/4}$ .

Despite the success in explaining various experimental and numerical results, there are several disturbing issues with MCT. For example, it has been shown by comparing Lennard-Jones and WCA potentials that structural information *not* encoded in the two-body density correlation S(k) may play a crucial role in the dynamics and thus cannot be captured by MCT [80]. In addition, increasing discrepancy between MCT and numerical results at higher dimensions d > 4suggests the success of MCT in d = 3 might be partially a coincidence and some modification of MCT is required [81].

### 1.2.2 Adam-Gibbs Theory

In the deeply supercooled regime below the onset temperature  $T_{\rm o}$  (empirically identified as the MCT  $T_{\rm c}$ ), structural relaxation is mainly achieved via activated process, whereby the system overcomes the barriers between neighboring basins of energy landscape. According to Adam-Gibbs (AG) theory [69,82], such relaxation process is associated to the so-called "cooperatively rearranging regions" (CRR). They define the typical CRR as the smallest region that can be rearranged independently from its surrounding. Assuming the typical number of particles within a CRR is zand is temperature dependent, while the number of locally stable states for a CRR is a constant  $\Omega$  of order unity, it follows that the number of global states a system of N particles can be found is  $\mathcal{N} = \Omega^{N/z}$ . Since the configurational entropy  $S_{\rm c}$  is a measure of number of states as discussed previously, we may write

$$S_{\rm c} = \frac{1}{N} \log \mathcal{N} = \frac{\log \Omega}{z}.$$
 (1.22)

Finally, assuming the activation energy scales with the size of CRR,  $\Delta \sim z$ , the relaxation time can be written as

$$\log \tau \sim \frac{\Delta}{T} \sim \frac{1}{TS_{\rm c}},\tag{1.23}$$

according to Arrhenius formula. Therefore, the increasing relaxation time is intimately related to the reducing  $S_{\rm c}$  as temperature is lowered, which is the main

result of AG theory. As an aside, the empirical VFT fit can be rationalized based on the assumption that the configurational entropy can be approximated by the excess entropy  $S_{\rm ex}$  between liquid and crystal, which vanishes at Kauzmann temperature  $T_{\rm K}$ . For several glass-forming liquid, the excess specific heat can be well fitted by  $\Delta C_{\rm p} = K/T$ , where K is a constant. Thus, the configurational entropy can be evaluated by integration the standard thermodynamics relation  $dS_c/dT = \Delta C_{\rm p}/T$ from  $T_{\rm K}$  to T, to obtain  $S_c = K/(1/T_{\rm K} - 1/T)$ . This finally leads to the VFT equation

$$\log \tau \sim \frac{T_{\rm K}/K}{T - T_{\rm K}}.\tag{1.24}$$

The Adam-Gibbs theory has enjoyed an enduring favor thanks to its elegance and simplicity. For one thing, AG theory provides a direct connection between the thermodynamics and dynamics in supercooled liquids, For another, also relates the fragility to the changing rate of excess specific heat,  $m \sim K$ , according to Eq. 1.2. However, the nature of CRR, arguably the most important concept in AG framework, remains unclear. What do CRRs look like microscopically? How do they relax independently? Why the number of configurations  $\Omega$  accessible to a typical CRR is constant and does not scale with CRR size? Some recent progress has been made to address these ambiguities in the AG theory. For example, based on dynamical heterogeneity it has shown that string-like mobile clusters in which particles move cooperatively may be a good candidate for CRR [16]. A "living polymerization" theory has been proposed [4] based on string-like clusters. Nevertheless, the dynamical nature of mobile/immobile strings seem to defeat the purpose of a thermodynamic explanation of the glass transition in AG theory.

### **1.2.3** Random First-Order Transition Theory

The random first-order transition (RFOT) theory [70] (also known as mosaic theory) is a real space interpretation of the mean-field theory of spin glasses. In the RFOT framework, a supercooled liquid below the onset temperature is decomposed into a set of "mosaic states". On length scales smaller than the typical size of a mosaic, particles cannot decorrelate from their original positions and the region is trapped in one state; whereas on larger length scales, the region can rearrange and explore other states. The free energy change of rearranging a region of size R comes from the entropic gain of visiting other available states, and the surface energy cost of

mismatch between a new state and the old surroundings, namely,

$$\Delta F = Y R^{\theta} - T S_{\rm c} R^d, \tag{1.25}$$

where Y is some generalized surface tension, d is the dimension of space and  $\theta \leq d-1$ . Therefore, the typical size of a CRR is obtained by letting  $\Delta F = 0$ ,

$$\xi(T) = \left(\frac{Y(T)}{TS_{\rm c}(T)}\right)^{\frac{1}{d-\theta}}.$$
(1.26)

For activated processes, the relaxation time is expected to scale with the energy barrier, which grows with mosaic size as  $\Delta \sim \xi^{\psi}$ . RFOT theory then predicts

$$\log \tau \sim \frac{1}{T} \left( \frac{Y(T)}{TS_{\rm c}(T)} \right)^{\frac{\psi}{d-\theta}}.$$
(1.27)

The original proposal based on renormalization group suggests  $\theta = d/2$  and  $\psi = \theta$  [70], which simplifies Eq. 1.27 to the familiar Adam-Gibbs relation assuming  $Y \sim T$ . However, some recent numerical works have predicted different values of  $\psi \approx 1$  and  $\theta = 0.3-2.3$  [16,83].

In both RFOT and AG scenarios, the super-Arrhenius slowdown comes from the growth of  $\xi$  or the size of CRR. Like AG theory, the RFOT theory predicts an ideal glass transition at  $T_{\rm K}$  associated with vanishing configurational entropy and a diverging length scale  $\xi$ . However, the RFOT provides a much clearer picture of the role played by configurational entropy and the nature of CRRs— a region smaller than  $\xi$  cannot rearrange to explore all its available states, because the surface energy penalty is larger than the entropic gain in getting out of its original state. Thus this explains why the number of states a CRR can explore,  $\Omega \sim 1$ , is independent of temperature, as assumed in AG theory. Furthermore, RFOT approach suggests a way to measure the growing mosaic or amorphous order using the so-called point-to-set correlation function, which has a purely static definition [66]. In Chapter 5, we introduced a related method to extract the static correlation length in hard spheres from dynamical response to the pinning field.

Historically, the RFOT theory is constructed based on the intrinsic mean-field glass transition (also called one-step replica symmetry breaking (1-RSB)), with a high-temperature ergodicity breaking transition at  $T_c$  and a low-temperature

thermodynamic transition at  $T_{\rm K}$ . According to the mean-field solution, for  $T > T_{\rm c}$ , the most probable states are unstable saddles of free energy landscape, which becomes marginally stable near  $T_{\rm c}$ , and the dynamics is exactly described by MCT equation. For  $T_{\rm c} > T > T_{\rm K}$ , system is trapped in one of the exponentially large number states because of the infinite energy barrier in the mean field, but the thermodynamics can still be described by the ensemble of these states, e.g., total free energy is given by  $f_{\rm liquid} = f_{\rm state} - TS_{\rm c}$ . For  $T < T_{\rm K}$ , the configurational entropy vanishes and the system is an ideal glass. However, in realistic systems, the free energy barriers are finite and ergodicity is restored by activated processes. Thus, the dynamical transition at  $T_{\rm c}$  is smeared out and appears as a crossover. Moreover, metastable states are no longer global and permanent in real systems, but have a finite size and lifetime as described in RFOT theory.

With additional modeling, the RFOT approach can also make a connection to a broad range of experimental data in glass-forming liquids and polymers [84]. However, there are some concerns about RFOT. For example, the concept of surface tension seems fuzzy for a domain containing only a few particles. In addition, the role played by dynamical heterogeneity in the RFOT framework and its relation to the mosaic or CRRs also remain unclear. Finally, the RFOT theory has been criticized for containing too many uncontrolled assumptions, so that one can always attribute the weakness of the theory as resulting from some approximation, as well as its mean-field foundations that may be destroyed by fluctuations in finite dimensions [85]. Indeed, analytical progress on a finite system where RFOT can be shown to hold is highly crucial but also challenging.

### **1.2.4** Frustration-Limited Domain Theory

Unlike MCT and AG/RFOT models, the frustration-limited domain (FLD) theory [86–88] focuses on the geometric origin of the glassy dynamics. The concept of frustration in general refers to the situation where the total energy function cannot be minimized by merely minimizing all local interactions. For supercooled liquids without quenched randomness, frustration arises from locally preferred structures that cannot tile space. For example, the locally preferred cluster of spheres in three dimensions is an icosahedron, however, forming a periodic icosahedral crystal is impossible since the five-fold rotational symmetry is incompatible with transitional symmetry. In the FLD picture, there is a crossover temperature  $T^* \sim T_c$  corresponding to the ordering transition of locally preferred structures in the absence of frustration; below  $T^*$ , the liquid is broken up into a patchwork of locally preferred domains whose size is limited by frustration. The associated correlation length  $\ell^*$  grows with decreasing temperature as  $(1-T/T^*)^{\nu}/K^{1/2}$ , where K is the a dimensionless parameter of the frustration strength and  $\nu$  is the exponent that governs the growth of  $L^*$  without frustration K = 0. The energy barrier associated with the rearrangement of these domains is predicted as

$$\Delta(T < T^*) = \Delta_{>} + \frac{AT^*}{K} \left(1 - \frac{T}{T^*}\right)^{4\nu}$$
(1.28)

where  $\Delta_{>}$  is the high-temperature energy barrier for vibrational motion and A is a positive constant [87]. This energy barrier naturally leads to the super-Arrhenius behavior with its variation related to dynamical heterogeneity, according to the FLD theory.

There are several similarities between FLD and RFOT scenarios, such as an onset temperature of some thermodynamic order, and the decomposition into domains that grow with decreasing temperature. However, the domain size is limited by configurational entropy in RFOT, and by long-range elastic energy that frustrate the locally preferred structure in FLD. Additionally, FLD predicts saturation of  $\ell^*$  and  $\Delta$  below a certain temperature far from  $T^*$ , and a reversion to a purely Arrhenius behavior known as fragile-to-strong crossover, also predicted by other models such as the shoving model [89], string model [4] and dynamical facilitation theory [90]. Consequently, no ideal glass transition at  $T_{\rm K}$  appears in the FLD theory. Finally, although the FLD is an appealing approach based on real space, it is in general difficult to identify locally preferred structures in glass-forming liquids except for simple spherical systems, and quantitative and testable predictions beyond scaling are still lacking.

# Chapter 2 | Avoiding Crystallization

It is believed by many that crystallization does not play an important role in the glass transition, provided that it can be avoided in supercooled liquids as assumed by most theories and models. However, for systems made of non-attractive monodisperse components, such as colloidal suspension of hard spheres, the supercooled metastable state is obscured by two competing phenomena: a rapid, first-order crystallization under slow compression, and an out-of-equilibrium glass transition under fast compression. Therefore, the equilibration of one-component colloidal systems in metastable state is a subtle question. While particles with polydisperse diameters are often used in order to avoid or delay the crystallization, the effect of size polydispersity on the glass transition dynamics is still a matter of debate. To address this problem, we introduce a crystal-avoiding method that can effectively suppresses the crystallization while preservation the dynamics, which allows us to probe the long-time dynamics of metastable monodisperse hard-sphere liquids. We also extend this method to purely repulsive soft spheres. Some complications related to soft spheres are discussed.

## 2.1 Phase Diagram of Hard Spheres

Colloidal hard-sphere systems have been studied intensively in experiments, simulations and theory, because of their theoretic simplicity, well-defined geometry and the ability to model a number of physical systems with more complicated potentials. As an analogy to the temperature in molecular liquids, the control parameter in a hard-sphere system is the volume fraction  $\phi = \pi \rho \sigma^3/6$ , where  $\sigma$  is the particle diameter, while temperature only serves as a scaling factor of the time unit. The



Figure 2.1: Phase diagram in the pressure-volume fraction plane for hard-sphere systems. Similar to molecular systems shown in Figure 1.1, hard-sphere systems exhibits a first-order liquid to solid thermodynamic transition and a dynamical glass transition under fast compression.

phase diagram for the hard-sphere system is depicted in Figure 2.1. By varying the volume fraction, monodisperse hard spheres display a fluid phase below the freezing transition  $\phi_{\rm f} \approx 0.494$ , and a liquid-crystal coexistence regime between  $\phi_{\rm f}$  and the melting transition  $\phi_{\rm m} \approx 0.545$ . Above the melting volume fraction  $\phi_{\rm m}$ , the system exhibits a crystal phase that can be densified until  $\phi \approx 0.74$ , which corresponds to the close packing of face-centered cubic (fcc) crystal. Under rapid compression, on the other hand, the hard-sphere system may remain disordered in metastable equilibrium above the freezing point until it falls out of equilibrium with further compression and becomes a glass . Depending on the compression protocol, such as compression rate and, the maximum volume fraction of a disordered hard-sphere system can achieve, known as the random close packing (RCP) is approximately  $\phi_{\rm RCP} \approx 0.64$ . While it is possible to generate a random packing of hard sphere at  $\phi < \phi_{\rm RCP}$ , in order to explore the metastable branch of the phase diagram and study the properties in the vicinity of the glass transition, one needs to equilibrate the initially non-equilibrium system while being caution not to allow crystallization to occur, which is not trivial for hard spheres.

### 2.2 Crystallization and Metastability

In general, liquids undergo a first-order phase transition at the melting temperature  $T_{\rm m}$ . The thermodynamically stable state below  $T_{\rm m}$  is the ordered crystal phase associated with a lower free energy. In this regard, an equilibrium supercooled liquid is a metastable phase and can be probed only if the liquid relaxation time is shorter than that of crystallization. The formation of crystal within a supercooled liquid is usually considered as a two-step process: *nucleation* and *crystal growth*. The system has to first form some stable nuclei larger than a critical size, and then grow them to be a considerable part of the sample. The nucleation process is dominated by the competition between surface tension and free energy gain, while the growth of crystal is limited by the viscosity of the background liquid as well as the mismatch between contacting crystallites. As a result, the crystallization rate is dominated by the slowest process, nucleation or crystal growth.

The metastability of supercooled state relies on the difference between the relaxation time of liquid and the nucleation time. The temperature dependence of nucleation time usually shows a minimum at a certain temperature below  $T_{\rm m}$ , while the relaxation time is a monotonic function that increases with decreasing temperature. Therefore, if the nucleation time and relaxation time do not cross, it is possible to equilibrate the supercooled liquid to an arbitrarily low T with a nonlinear cooling protocol. However, there are systems exhibiting a kinetic spinodal at  $T_{\rm sp} > 0$ , below which the relaxation time excesses the nucleation time and equilibration of the supercooled liquid becomes impossible. Close to the spinodal, the difference between polycrystal and glass is somewhat blurred. In this case, the relaxation time of the supercooled liquid cannot really diverge at a finite temperature and the ideal glass transition predicted by some theories is always intervened by crystallization.

The existence of kinetic spinodal is not necessarily a serious problem if the kinetic spinodal is in the low temperature regime far from the experimental glass transition, since theories explaining the slow dynamics by the underlying phase transition do not need the transition to actually happen. However, difficulties may arise in studying the supercooled system if the kinetic spinodal is close to the melting point and thereby buries the metastable state. The colloidal suspension of monodisperse hard spheres falls into this category. In Figure 2.2, we show the crystal



Figure 2.2: Crystal nucleation time (disk) and liquid relaxation time (square) as a function of volume fraction for monodisperse hard spheres. Three regions separated by the relaxation and nucleation times are indicated.

nucleation time and the liquid relaxation time as a function of volume fraction for monodisperse hard spheres. The nucleation time date is taken from Ref. [91], while the  $\alpha$  relaxation time is obtained from the self-intermediate scattering function  $F_{\rm s}(k_0,t)$  (see Eq. 1.12), with  $k_0 = 6.5$  corresponding to the the first peak in the structure factor S(k). The metastable hard-sphere liquid is simulated using our crystal-avoiding method, as will be introduced in the following section. It is evident that the relaxation time exceeds the nucleation time at  $\phi \approx 0.57$ , above which the metastable branch is inaccessible with conventional simulation method.

To suppress crystallization and explore the metastable regime in the vicinity of the hard-sphere glass transition, a strategy widely used in both experiments and simulations is to introduce a small amount of polydispersity in particle sizes. The size polydispersity  $\delta$  is conventionally defined as the fractional standard deviation of particle diameter,  $\delta = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (\sigma_i - \overline{\sigma})^2} / \overline{\sigma}$ . As polydispersity increases, the freezing and melting points moves towards higher volume fractions. The fact that polydispersity can destabilize the crystal phase can be understood as follows. For monodisperse spheres above the melting volume fraction, the ordered crystal have higher entropy because of larger free volume for local motions, and therefore lower free energy, compared to the disordered metastable fluid. When polydisperse is introduced, random distribution of different particle sizes results higher packing efficiency than packing on a crystal lattice. It is found via computer simulation that for  $\delta \ge 0.08$ , crystallization without fractionation is effectively suppressed [92]. At larger polydispersity and volume fraction, coexistence of multiple solid phases is predicted from free energy calculation [93], the size fractionation requires motion of particles over large distance to form and therefore occurs on a much longer time scale, which is recently observed in Monte Carlo simulations with unphysical swap moves [73]. In this case, a relatively large polydispersity  $\delta 0.23$  is used to avoid crystal formation.

However, a large polydispersity not only complicates dynamic properties of hard spheres, such as dynamical heterogeneity, but may alter the glass transition as a result of the partial localization.effect of large and small particles [94]. In contrast, monodisperse hard-sphere system is the simplest glass former and is theoretically more tractable. Therefore, it would be attractive to find a way to carry out molecular dynamics (MD) simulations of monodisperse hard-sphere fluids in which crystallization was somehow suppressed. To this end, we propose a novel crystal-avoiding method that allows us to suppress crystallization without perturbing the dynamics significantly.

## 2.3 Bond-Orientational Order Parameters

To suppress crystallization in supercooled liquids, one needs to identify the occurrence of crystallization. While crystallization, as a first-order phase transition, is associated with an abrupt change in thermodynamic properties, such as potential energy and pressure, these macroscopic observables are found unsatisfying for detecting the early stage of crystal formation [95]. A widely used, more sensitive measure of crystalline order is the bond-orientational order parameter. Based on the angles between a center particle and its surrounding neighbors, the bond order parameter is independent of the specific crystal structure and invariant to translation and rotation of the whole system.

In two-dimensional disks, the global bond order parameter for hexagonal order [96] is defined as

$$\Psi_6 = \left| \frac{1}{N_{\rm b}} \sum_j \sum_k e^{6i\theta_{jk}} \right|,\tag{2.1}$$

where indices j and k run over all pairs of neighboring particles in the system,  $\theta_{jk}$  is the angle between the bond connecting the centers of disk j and k and the x

axis, and  $N_{\rm b}$  is the number of bonds in the system. The neighbors can be defined in various ways, such as Voronoi tessellation, fixed distance cutoff (e.g., the first minimum of pair correlation function g(r)) or a solid-angle based method [97]. By construction, for perfect hexagonal packing,  $\Psi_6 = 1$ , while  $\Psi_6 \sim 1/\sqrt{N_{\rm b}}$  for an ideal gas [98]. A caveat to the global order parameter is that it is possible to construct a system in which disks are mostly in hexagonal packing with a small  $\Psi_6$  value [98]. To avoid this problem, an averaged local order parameter has been proposed,

$$\psi_{6} = \frac{1}{N} \sum_{j}^{N} \left| \frac{1}{n_{\rm b}(j)} \sum_{k} e^{6i\theta_{jk}} \right|, \qquad (2.2)$$

where  $n_{\rm b}(i)$  is the number of neighbors of particle j. While the local order parameter is sensitive to local hexagonal order, it may fail to identify systems with substantial global orientational order but locally disordered. In practice, one needs to take both global and local order parameters into consideration in order to detect crystal formation more effectively.

As a natural generalization on the two-dimensional order parameter for 6-fold symmetry, the bond order parameter can be constructed in three dimensions based on spherical harmonics,  $Y_l^m(\theta_i, \varphi_i)$ , where  $\theta_i$  and  $\varphi_i$  are the polar and azimuthal angles or bond *i* relative to a fixed coordinate system [99]. A global order parameter is then defined as

$$Q_{l} = \left(\frac{4\pi}{2l+1} \sum_{m=-l}^{l} \left| \frac{1}{N_{\rm b}} \sum_{i=1}^{N_{\rm b}} Y_{l}^{m}(\theta_{i},\varphi_{i}) \right|^{2} \right)^{1/2}, \qquad (2.3)$$

where *m* and *l* are the order and degree of spherical harmonics. It can be shown that  $Q_l$  is independent of the reference coordinate system (see Appendix A for details). Depending on the choice of *l*,  $Q_l$  is sensitive to different types of ordering. For l = 6, which is used extensively in the literature,  $Q_6$  reaches its maximum value ( $Q_6 \approx 0.574$ ) for perfect fcc crystal, and also has high values for other typical crystals, such as body-centered cubic (bcc,  $Q_6 \approx 0.511$ ), hexagonal close packing (hcp,  $Q_6 \approx 0.485$ ) and simple cubic (sc,  $Q_6 \approx 0.353$ ). For l = 4, a higher value is found for simple cubic than for other crystals. For a truly random distribution of bonds,  $Q_l = 1/\sqrt{N_b}$ , similar to that in two dimensions [95].

Likewise, a local measure of orientational order can be defined. First, an

averaged spherical harmonics is defined for each particle,

$$q_l^m(i) = \frac{1}{n_{\rm b}(i)} \sum_{j=1}^{n_{\rm b}(i)} Y_l^m(\theta_j, \varphi_j), \qquad (2.4)$$

where  $n_{\rm b}(i)$  is the number of nearest neighbors of particle *i*. Note that  $q_l^m(i)$  is a complex number. To make the quantity rotationally-invariant, the local order parameter is defined by summing all integer *m* from -l to *l* similar to the global one,

$$q_l(i) = \left(\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |q_l^m(i)|^2\right)^{1/2}.$$
(2.5)

Finally, the averaged local order parameter,  $q_l$ , for the whole system can be obtained,

$$q_l = \frac{1}{N} \sum_{i=1}^{N} q_l(i).$$
(2.6)

Notably, for a particle on the center of icosahedron cluster,  $q_6(i) \approx 0.663$ , which is higher than that for fcc crystal, although the maximum value of  $q_6$  for a considerably large system is still given by fcc since icosahedron cannot tile the space.

Another useful bond order parameter, which is also rotationally-invariant and sensitive to different orientational symmetries, is often considered [99]. For a given particle, such parameter is defined as

$$w_{l}(i) = \frac{\sum_{\substack{-l \leqslant m_{1}, m_{2}, m_{3} \leqslant l \\ m_{1} + m_{2} + m_{3} = 0}} \binom{l \quad l \quad l}{m_{1} \quad m_{2} \quad m_{3}} q_{l}^{m_{1}}(i) q_{l}^{m_{2}}(i) q_{l}^{m_{3}}(i)}{\left(\sum_{m=-l}^{l} |q_{l}^{m}(i)|^{2}\right)^{3/2}}, \qquad (2.7)$$

where the coefficients in parentheses is the Wigner 3j symbols. It is worth noting that  $w_6(i)$  has a very negative value for icosahedra (-0.170), about 13 times larger than that for fcc (-0.013), hcp (-0.012), bcc (0.013) and sc (0.013).

An improved local bond parameter that takes into account of the next-nearest neighbors has been proposed [100]. The only difference from the previous local bond parameter is that an additional average is performed on  $q_l^m(i)$  defined in Eq.

2.4,

$$\overline{q}_l^m(i) = \frac{1}{n_{\rm b} + 1} \sum_{j=0}^{n_{\rm b}} q_l^m(j), \qquad (2.8)$$

where j runs over all neighbors of particle i and itself. The corresponding new local order parameters,  $\overline{q}_l(i)$ ,  $\overline{q}_l$  and  $\overline{w}_l(i)$ , are then defined similarly following Eq. 2.5, Eq. 2.6, Eq. 2.7 with  $q_l^m(i)$  substituted with  $\overline{q}_l^m(i)$ . This coarse-grained local bond parameter is found more robust in distinguishing between liquid and different crystals.

It is sometimes convenient to assign particles as liquid-like or solid-like based on their local environment. One way is to choose a threshold for the local order parameter above which a particle is regarded as solid-like. Another commonly used method [101] is based on the structural similarity between a particle and its neighbors. From the complex vector  $q_6^m(i)$ , the correlation between particle *i* and *j* can be calculated from the scalar product

$$S_{ij} = \sum_{m=-6}^{6} q_6^m(i) q_6^{m*}(j).$$
(2.9)

Typically, two particles are considered connected if  $S_{ij} > 0.7$ , and if the number of connected neighbors  $n_c$  of particle *i* exceeds a certain threshold, e.g,  $n_c \ge 6$ , the particle is considered as solid-like.

Finally, we note that a similar bond order parameter, called Minkowski structure metrics [102], has been recently proposed to avoid the ambiguity of the neighborhood definition, such as the instability involved in Voronoi tessellation [103]. In this method, each bond spherical harmonics  $Y_l^m(\theta_j, \varphi_j)$  is weighted by the associated Voronoi facet area relative to the total Voronoi cell area, and hence improves the robustness of conventional bond order parameters.

## 2.4 Crystal-Avoiding Method

### 2.4.1 Monodisperse Hard Spheres

The simple form of hard-sphere potential leads to a special simulation algorithm called event-driven or discrete MD. In this algorithm, one recursively computes the collision time between each pair of spheres, proceeds the collision that happens



Figure 2.3: Schematic of the crystal-avoiding method. An MC move generated from a short MD trajectory of time  $\Delta t$  is accepted or rejected depending on the change of crystal bond order parameter. If the move is rejected, velocities of particles are randomized before next trial move.

first and updates positions of particles accordingly. A cell list is often employed to reduce the computational complexity. Note that the microcanonical (NVE) ensemble is sampled with this method.

For hard spheres, we have developed a crystal-avoiding (CA) MD simulation method based on hybrid Monte Carlo (MC), inspired by previous works [104–107]. Each MC move is generated from a short event-driven MD trajectory and accepted with a probability  $p = \min \{ \exp(-\gamma N \Delta \overline{q}_6), 1 \}$ , where N is the number of particles and  $\overline{q}_6$  is the local bond order parameter averaged over next-nearest neighbors [100] (or any other sensitive bond-order parameter that measures the crystallinity of the system). If the MC move is rejected, all particle velocities are reassigned from a Maxwell-Boltzmann distribution before the next trial move. We emphasize that the simulation time only advances when a trial is accepted; in this way, the particle dynamics can be reasonably reproduced despite the low acceptance rate. In short, the method essentially samples among those trajectories in phase space for which crystallization did not occur. If the duration of the trial trajectories and hence the time between velocity randomizations is larger than velocity autocorrelation time, the resulting dynamics should well represent the metastable fluid. If nucleation is rapid, this may lead to a low acceptance rate of trial moves. In practice, we choose the bias  $\gamma$  and trial trajectory length  $l_{\rm MD}$  for reasonably high acceptance rates and



Figure 2.4: Mean-squared displacements for monodisperse hard spheres using crystal-avoiding method (CA) and polydisperse systems with conventional MD (MD) at  $\phi = 0.55$ , 0.56, 0.57 and 0.58. Inset: pressure versus time at  $\phi = 0.57$  with different methods. Dotted line indicates corresponding pressure reported in Ref. [108].

fidelity to dynamics of polydisperse systems (see Table 2.1).

Fig.2.5 illustrates the dependence of the particle self-diffusion coefficient D on the crystal bias parameter  $\gamma$  and trial trajectory length  $l_{\rm MD}$ , for a dense system with  $\phi = 0.56$ . The self-diffusion coefficient is clearly insensitive to the value of  $\gamma$ (over this range, crystallinity is effectively suppressed). D depends weakly on  $l_{\rm MD}$ , until  $l_{\rm MD}$  becomes longer than the particle velocity autocorrelation time. For the largest values of  $\phi$  we study  $\phi \ge 0.57$ , to maintain a reasonable acceptance rate, we take smaller  $l_{\rm MD}$  values (10–20, see Table 2.1). This leads to slightly smaller values of D (by a factor of  $10^{0.15} \approx 1.4$ ), which is a small effect compared to the strong dependence of D on  $\phi$ .

We test the CA method by comparing to monodisperse and mildly polydisperse systems (Gaussian distributed diameters with  $\delta = 0.08$ ) at  $\phi = 0.57 > \phi_{\rm f}$  simulated with conventional MD. The inset to Fig. 2.4 shows that a monodisperse system under MD will crystallize spontaneously as indicated by an abrupt drop in pressure. The same monodisperse system simulated with the CA method maintains a constant pressure, indicating that crystallization is suppressed. Likewise, a polydisperse system under MD does not crystallize— but does display a lower constant pressure, as noted previously [91]. On the other hand, the mean-squared displacement (MSD) of systems simulated with the CA method are consistent with those of polydisperse



Figure 2.5: Dependence on  $\gamma$  and  $l_{\rm MD}$  of diffusion coefficients D at  $\phi = 0.56$ . The resulting dynamics is insensitive to  $\gamma$  and depends weakly on  $l_{\rm MD}$  (see main text).

Table 2.1: Parameters for crystal-avoiding MD simulation. MD trial length  $l_{\rm MD}$  is in unit of collisions per particle. The smaller  $l_{\rm MD}$  used for high  $\phi$  is a compromise between reproducing dynamics and high acceptance rate (see main text).

$\phi$	$\gamma$	$l_{\mathrm{MD}}$
< 0.50	0	-
0.50 - 0.53	0.25	40
0.54	0.50	40
0.55	0.50	40
0.56	1.00	40
0.57	1.20	20
0.58	1.20	10
$\geq 0.59$	1.50	10

systems under MD. Previous work suggests that MSD is insensitive to the amount of mild polydispersity [92] as long as the system is below glass transition, so we conclude the dynamics of metastable monodisperse fluids are well represented by our CA method.

### 2.4.2 Monodisperse Soft Spheres

While first proposed for hard-sphere systems, the crystal-avoiding method can be readily applied to soft potential systems. A soft-sphere system is often modeled by the purely repulsive Weeks-Chandler-Andersen (WCA) potential, which is a simpler alternative to the more realistic Lennard-Jones (LJ) potential. The WCA



Figure 2.6: (a) A snapshot of the low- $\bar{q}_6$  crystal phase. (b) A thin slab of the system with thickness around  $3\sigma$ . (c) Frank-Kasper  $\sigma$  phase projected along the c axis.

potential is the LJ potential truncated and shifted at the minimum energy, which reads

$$U_{\rm WCA}(r) = \begin{cases} 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + \epsilon, & r \leq 2^{1/6}\sigma \\ 0, & r > 2^{1/6}\sigma, \end{cases}$$
(2.10)

where  $\epsilon$  and  $\sigma$  are the characteristic energy and length parameters, respectively. In molecular dynamics simulations, it is convenient to define dimensionless (reduced) units based on the LJ/WCA potential. The reduced units chosen in this work are mass m, length  $\sigma$ , energy  $\epsilon$ , temperature  $\epsilon/k_{\rm B}$ , time  $\sqrt{m\sigma^2/\epsilon}$  and pressure  $\epsilon/\sigma^3$ .

Unlike the event-driven scheme for simulating hard spheres, MD simulation of soft spheres mostly adopts the Verlet algorithm with constant time-step. To extend our crystal-avoiding method to soft spheres, we incorporate the MC algorithm into the GROMACS package, a highly efficient MD simulation software, using shell scripts. While considerable disk read/write operations are involved in this approach, the overhead is negligible compared to the main computation cost.

In generally, we find the CA method also works for soft spheres for different densities and temperatures where system would crystallize with normal MD. However, we have encountered some complications in choosing the proper bond order parameter to signal soft-sphere crystals. Under certain conditions, an uncommon crystal phase, signaled by an abrupt drop in pressure, may be sampled with the CA method for WCA spheres (and possibly also for LJ systems). A snapshot for this crystal phase is shown in Figure 2.6. Such crystalline order has a similar or even lower bond order parameter,  $\overline{q}_6$ , than that for a liquid (see Figure 2.7(a)), which explains the failure of the CA method in suppressing the crystal.



Figure 2.7: (a) Distribution of local bond order parameter  $\overline{q}_6(i)$  for liquid and crystals. Note that this bond order parameter fails to distinguish liquid from the low- $\overline{q}_6$  crystal phase possible related to the Frank-Kasper  $\sigma$  phase. (b)  $w_6$ - $q_6$  plane for WCA system in different phases.



Figure 2.8: Phase diagram of the WCA potential in the density-temperature plane using (a) normal MD and (b) CA method with bond order parameter  $\overline{q}_6$  suppressed. Points shown in (a) are phase coexistence data from Ref. [109]. Solid Lines are isobaric melting curves. Dashed lines in (b) indicate the solid-liquid coexistence shown in (a).

A detailed analysis based on local bond parameters  $q_6$  and  $w_6$ , as shown in Figure 2.7, suggests that the unexpected crystal is closely related to the Frank-Kasper  $\sigma$  phase, which is a quasicrystal approximant. In addition, the isobaric melting temperature of the unknown phase is very close to that of the  $\sigma$  phase. Indeed, quasicrystals and their approximant have been observed in many soft matter systems, such as polymers [110] and colloidal micelles [111], as well as in computer simulations [112, 113].

To compare the quasicrystal phase with the ordinary fcc crystal, we construct the  $T - \rho$  phase diagram for WCA systems by melting a fcc crystal or a QC under constant pressure and observing the abrupt change in density. We note that although this rather crude approach may suffer from the limitations like finite-size effect and overheating, the results for solid-liquid coexistence are in good agreement with those obtained from some meticulous method [109]. As shown in Figure 2.8(b), fcc crystals are suppressed below the melting temperature by the CA method using bond order parameter  $\overline{q}_6$ , while a liquid-quasicrystal transition occurs at a lower temperature depending on the density.

While the formation of quasicrystal is interesting and deserve further investigations, our main focus here is the metastable liquid state and thus it is necessary to suppress both fcc and QC. We find that this can be achieved by replacing the single bond order parameter  $\bar{q}_6$  with a a linear combination of multiple order parameters. For example, an effective bond order parameter can be defined as

$$Q_{\text{eff}} = w_1 \overline{q}_6 + w_2 Q_6 + w_3 q_6, \qquad (2.11)$$

where  $w_1$ ,  $w_2$ ,  $w_3$  are constants. In general,  $\overline{q}_6$  is the most sensitive to local fcc order,  $Q_6$  is a more global measure and  $q_6$  gives signal to both crystal and QC. With properly adjusted coefficients, the effective order parameter can detect the occurrence of either fcc or QC, and hence the CA method can probe the metastable state of WCA soft spheres, at least in a time scale long enough to study the dynamics. We also check that different choices of coefficients can barely affect the results, as long as the system is in metastable equilibrium.

# Chapter 3 | Geometrical Criterion for the Hard-Sphere Glass Transition

To study the relationship between dynamics and structure in a glass-forming liquid, we introduce a purely geometric criterion for locally mobile particles in a dense hard-sphere fluid: namely, "T1-active" particles, which can gain or lose at least one Voronoi neighbor by moving within their free volume with other particles fixed. We obtain geometrical and dynamical properties for monodisperse hard-sphere fluids with  $0.40 < \phi < 0.64$  using a new "crystal-avoiding" MD simulation that effectively suppresses crystallization without altering the dynamics. We find that the fraction of T1-active particles vanishes at random close packing, while the percolation threshold of T1-inactive particles is essentially identical to the commonly identified hard-sphere glass transition,  $\phi_{\rm g} \approx 0.585$ .

## 3.1 Introduction

The dramatic slowing down and heterogeneity of dynamics in glass-forming liquids is related to growth of regions of particles that require collective rearrangements to relax. Despite substantial efforts, the structural origin of glass transition remains unclear. Widmer-Cooper et al., demonstrated that local Debye-Waller factor of a particle (corresponding to the short time dynamics or "rattling motion") is correlated with its dynamical propensity (characterizing long time dynamics or "cage-breaking" process) [114]. Both quantities were obtained from an isoconfigurational ensemble average, in which multiple simulations are performed with the same starting configuration and different realizations of thermal initial velocities. Hence both the Debye-Waller factor and the propensity only depend on the initial geometry. Similarly, recent numerical and experimental results suggest a strong correlation between irreversible structural reorganization and quasi-localized soft modes, which again reflect the local structure [17,62]. However, finding a local measure of the initial configuration that is causally connected to the dynamics has proven to be elusive [45].

In this paper, we propose a new, purely geometrical criterion that relates directly to the hard-sphere glass transition. By analogy to rearrangement processes in foams, we define "T1-active" particles as those that can either gain or lose a Voronoi neighbor by moving within their own free volumes, with other particles held fixed. When T1-inactive particles percolate, we may expect the system to become non-ergodic or glassy. In fact, we find that the percolation threshold of T1-inactive particles with the monodisperse hard-sphere glass transition, commonly reported at  $\phi_g \approx 0.585$  [91,92].

### 3.2 Method

Hard-sphere fluids have been intensively studied since they serve as the simplest model that exhibits a glass transition, and are well approximated by real colloidal suspensions. Geometric properties such as free volume and cavities can be defined rigorously and computed conveniently for hard-sphere systems [115]. However, monodisperse hard-sphere fluids crystallize readily at volume fractions  $\phi > \phi_{\rm f} \approx 0.494$ . To study the metastable fluid phase above  $\phi_{\rm g}$ , a small amount of polydispersity  $\delta$  (defined as the fractional standard deviation of particle diameter) is typically introduced to suppress crystallization. Recently, the extent to which polydispersity alters the dynamics near the glass transition has been debated [94,116,117]. Also, algorithms for computing free volume and related properties are most conveniently implemented for monodisperse hard-spheres (though extension to polydisperse spheres is possible) [115]. For these reasons, we carry out molecular dynamics (MD) simulations of monodisperse hard-sphere fluids with the crystal-avoiding introduced in Chapter 2.

To systems at or slightly above the glass transition, we observe a dramatic difference in the dynamics of monodisperse and slightly polydisperse systems. Fig. 3.1 compares the dependence of the apparent particle diffusion coefficient on



Figure 3.1: Dependence on equilibration time  $\tau_{\rm e}$  of diffusion coefficients  $D(t_{\rm e})$  at  $\phi = 0.58$  and  $\phi = 0.59$  with filled and empty symbols representing monodisperse and polydisperse systems, respectively. Inset: examples of obtaining  $D(t_{\rm e})$  from the slope of MSD in monodisperse systems at  $\phi = 0.59$  for different  $t_{\rm e}$ .

aging time  $t_e$  (time elapsed after the initial Lubachevsky-Stillinger configurations are generated, before the diffusion coefficient is measured). For  $\phi = 0.58$ , both monodisperse (filled symbols) and slightly polydisperse systems (open symbols) show no dependence of D on aging. For  $\phi = 0.59$ — slightly above the commonly reported colloidal glass transition of  $\phi_c = 0.585$  [91,92]— the monodisperse system shows a strong aging dependence of D, which continues to decrease with  $t_e$  as far as we can observe. (The inset shows two representative plots of  $\Delta r^2$  versus t for the monodisperse system for different aging times; values of D are extracted from the slopes of these plots.) The polydisperse system displays some aging dependence, but ultimately seems to settle to a finite value of D. This contrast between the sudden onset of strong aging in the monodisperse system and the more modest aging behavior of the polydisperse system suggests that the polydisperse glass transition is smeared or delayed due to small mobile particles, consistent with recent findings by Zaccarelli et al. [94].

For our simulations of metastable monodisperse hard-sphere fluids, we use the Lubachevsky-Stillinger algorithm [118] to prepare initial fluid configurations of N = 2000 hard spheres with  $\phi = 0.40$  to 0.61. Then, we use the CA method to equilibrate the systems until no obvious aging process is observed for the quantity of interest before collecting data. (For  $\phi \ge 0.59$ , data are collected after the longest equilibration time we can perform in spite of the aging.) The fraction of "crystalline

particles" is controlled to be less than 3%. (A particle *i* is deemed crystalline if it has  $N_c \ge 6$  neighbors with local bond order parameter  $d_6(i, j) > 0.7$ , see Ref. [101].) Polydisperse systems are also prepared using Lubachevsky-Stillinger algorithm with diameters normally distributed. Standard hard-sphere units are used: sphere diameter  $\sigma$ , sphere mass *m*, collision time  $\tau = \sigma \sqrt{m/(k_{\rm B}T)}$ .

## 3.3 Results

### 3.3.1 Particle Propensity and Neighbor Rearrangements

In this work, we are concerned with local geometries that permit particles to rearrange. Such rearrangements or "cage-breaking" events are often identified by comparing particle displacements to a threshold. As we shall show, such events can equally well be identified by counting the number of changed Voronoi neighbors. In this language, the "supercooling" (densification) of a hard-sphere fluid can be described as follows. For  $\phi < \phi_g$ , particles change neighbors frequently and irreversibly, and the system is ergodic. Above  $\phi_g$ , more and more neighbors are fixed during a given time, and ergodicity is broken. At  $\phi = \phi_J$ , the system is completely jammed, and no particle can change any neighbors.

To establish the connection between mobility and neighbor rearrangements, we compare the dynamic propensity  $\langle \Delta r_i^2 \rangle_{ic}$ , calculated following Ref. [59], and the total number of new Voronoi neighbors, defined as  $| \cup_j \mathbf{V}_{ij} |$ , where  $\mathbf{V}_{ij}$  is the set of new neighbors that particle *i* gained in the *j*th isoconfigurational run, starting from the same initial configuration. Here  $| \cup_j \mathbf{V}_{ij} |$  is a short-time measure of rearrangements, in that we take the isoconfigurational run length to be 25 times shorter than that used for the propensity, which is evaluated at the end of the caging regime [59]. Fig. 3.2 shows that the propensity and number of new neighbors are heterogeneously distributed and correlated with each other— indicating that cage-escape dynamics of particles can be predicted to some extent by the rearrangements of Voronoi neighbors over a much shorter time.

Having established that acquiring new and losing old Voronoi neighbors is correlated with cage escape and hence particle diffusion, we ask what could be the elementary local motions by which new neighbors are acquired and old ones lost, and what local particle arrangements promote or preclude these motions. We



Figure 3.2: Dynamic propensity (left) and number of new Voronoi neighbors (right) averaged at  $\phi = 0.58$  over 400 isoconfigurational runs of length  $125\tau$  and  $5\tau$  respectively. 20% of particles with the largest and smallest values are shown for clarity. Propensity timescale  $125\tau$  corresponds to the end of the caging plateau in the log-log plot of MSD (see Fig. 2.4).

consider the simplest class of local motions in which a single particle moves in its free volume, defined as the space within which its center can translate with other particles fixed.

### 3.3.2 Uncaged Particles

A sufficient condition for a given particle to gain a new Voronoi neighbor is that at least one of its "exclusion spheres", i.e., the neighboring particles that define its free volume, is *not* currently one of its Voronoi neighbors (see Fig. 3.4a). In such a case, by moving within its free volume the given particle can touch the exclusion sphere, which certainly then becomes a new Voronoi neighbor. This criterion implies that the circumcenter of the Delaunay tetrahedron formed by the new Voronoi neighbor and three other neighboring exclusion spheres must be farther than  $\sigma$  from the original position of the given particle. Therefore, a cavity (into which an new sphere can be added) must exist. When a cavity is present, a nearby particle can hop into the cavity to acquire a new neighbor, leaving behind a cavity for another particle to hop into, and so forth. Stringlike motion observed in experiments [12] and simulations [22, 59] seems to support this scenario. We call such a particle "uncaged", because it can move beyond its Voronoi cell without the aid of nearby



Figure 3.3: (a) Diffusion coefficient  $D(\phi)$  and uncaged particle fraction  $h(\phi)$ , versus volume fraction  $\phi$ . Inset: average number of cavities per particle. (b) T1-active fraction  $p_{T1}(\phi)$ . Inset:  $p_{T1}$  as  $\phi$  approaches  $\phi_0$  (random close packing). All dashed lines are power law fits. The error bars are smaller the size of the symbols.

particle motion.

To test this scenario, that uncaged particles contribute to neighbor rearrangements, we compute the fraction of uncaged particles  $h(\phi)$  and number of cavities as a function of  $\phi$  by extending the Sastry free volume construction [115] (see Fig. 3.3a). We find that cavities and hence uncaged particles become extremely rare, decreasing by four orders of magnitude as  $\phi$  approaches 0.53 or so. By contrast, the diffusion coefficient  $D(\phi)$  decreases much more gently with  $\phi$  in this range. Thus uncaged particles cannot be primarily responsible for local neighbor rearrangements and structural relaxation in glassy hard-sphere fluids. (Note that we do observe a small concentration of cavities (vacancies) in the *crystal* phase, which lead to vacancy diffusion.)

### 3.3.3 T1 Process

If the sufficient but not necessary condition of uncaged particles is rarely met, how can particles in dense glassy change Voronoi neighbors when there is no cavity to hop into? By analogy to the T1 process of structural rearrangement in two



Figure 3.4: 2D schematics of neighbor rearrangements. (a) A hopping particle (purple) initially surrounded by its Voronoi neighbors (gray) can hop into the cavity (white region), collide with a new neighbor (green), and leave behind a cavity. (b) T1 event in a 2D foam corresponding to a flip of one soap film (solid line). (c) A T1-active particle (blue) gains a new neighbor (green) in a T1 event; no cavity is required.

dimensional foams [119] (see Fig. 3.4b), we identify another way particles can change neighbors. A particle  $p_1$  with Voronoi neighbors  $p_2, p_3, p_4$  can acquire a new Voronoi neighbor  $p_5$ , if  $p_1$  is initially outside the circumsphere of the Delaunay tetrahedron formed by the four particles  $p_2-p_5$ , but is able to move inside the circumsphere to complete the T1 event. Note particle  $p_1$  may have  $p_5$  as a neighbor without being able to touch  $p_5$ . Through a reverse T1 event  $p_1$  can lose  $p_5$  as a neighbor.

The free volume of a given particle presents a set of cusps, each defined by three Voronoi neighbor particles. These cusps are the most favorable positions for a T1 event to occur. If a particle can either gain or lose a Voronoi neighbor while moving within its free volume, both it and the neighbor are marked as T1-active; otherwise, particles are T1-inactive.

The fraction of T1-active particles  $p_{T1}(\phi)$  as a function of  $\phi$  is shown in Fig. 3.3b.



Figure 3.5: Probability that a T1-inactive cluster spans the system as a function of T1-inactive fraction  $p_{\overline{T1}}$  for different system sizes; solid lines are fits to tanh function (see main text). Inset: volume fraction  $\phi$  versus T1-inactive fraction  $p_{\overline{T1}}$ . Four typical configurations in the vicinity of the glass transition are shown, with particles highlighted according to their T1-activities.

In the fluid region  $\phi < 0.5$ , almost all particles are T1-active. In the metastable region  $\phi > 0.5$ ,  $p_{T1}(\phi)$  decreases gently until ultimately vanishes near random close packing, as  $(\phi_0 - \phi)^{\zeta}$ , with  $\phi_0 = 0.6448 \pm 0.0001$  and  $\zeta = 0.65 \pm 0.02$ . In contrast, the diffusion coefficient appears to vanish at the glass transition, at  $\phi \approx 0.585$ , which is associated with the growth of domains of particles that must rearrange cooperatively. Evidently, particle diffusion does not cease because T1-active particles become rare. Instead, we focus on T1-inactive particles, which by definition are those that cannot undergo T1 events by the motion of any single particle in the system. In reality, of course, particles can move simultaneously so that a T1-inactive particle based on geometric analysis may change its neighbors within some time scale; however, a T1-active particle may not actually undergo a T1 process at the same time. Therefore, we argue that the actually T1-activity at short times may be represented by a static analysis.

For a T1-inactive particle to change Voronoi neighbors and contribute to structural relaxation, cooperative motion of at least two particles is required. Thus, formation of a network of T1-inactive particles could be related to the growth of cooperatively rearranging regions (CRRs). To this end, we study percolation of T1-inactive particles as volume fraction increases. We use particles that define the free volume of a given particle as its neighbors in the percolation problem. Spanning clusters (infinite in periodic boundary conditions) of T1-inactive particles are identified for many configurations over a range of  $\phi = 0.57$  to 0.61. The percolation threshold  $p_c$  and critical exponents are obtained from finite-size analysis.

Fig. 3.5 displays the percolation probability of T1-inactive clusters as a function of T1-inactive fraction  $p_{\overline{T1}}$ . The inset shows the linear relation between T1-inactive fraction  $p_{\overline{T1}}$  and the particle volume fraction  $\phi$ . Evidently, percolation of T1inactive particles occurs around  $p_{\overline{11}} = 0.232$ , or equivalently  $\phi = 0.59$ . To obtain the critical threshold and exponents, we perform finite-size scaling by fitting the percolation probability as a function of T1-inactive fraction to a tanh function  $\left(1 + \tanh\left[\left(p_{\overline{\text{T1}}} - p_{\text{c}}^{\text{eff}}(L)\right)/\Delta(L)\right]\right)/2$  for different system sizes L, as shown in Fig. 3.5. In the limit of an infinite system, the percolation probability would be a step function and the percolation transition occurs at  $p_{\rm c} = 0.232 \pm 0.002$ , which corresponds to  $\phi_{\rm c} \approx 0.586$ — essentially identical to the location of the "colloidal glass transition" often quoted as  $\phi_{\rm g} \approx 0.585$  [91, 92]. The critical exponents in our model for the correlation length  $[\xi \sim (\phi_c - \phi)^{-\nu}]$  and percolating cluster fraction  $[m \sim (\phi - \phi_c)^{\beta}]$  are  $\nu = 0.91 \pm 0.01$  and  $\beta = 0.50 \pm 0.02$ , consistent with standard percolation results  $\nu_0 \approx 0.88$  and  $\beta_0 \approx 0.41$  [120]. This suggests whatever spatial correlations in T1 activity are present are not strong enough to change the universality class.

In addition to our result that T1-inactivity percolates and the diffusion coefficient vanishes at the same volume fraction, we note that the scaling of the T1-inactive correlation length, combined with a power law fit for the vanishing diffusion coefficient  $[D \sim (\phi_c - \phi)^{-2.2\pm0.1}]$ , gives a dynamic scaling relation  $1/D \sim \xi^z$  with  $z \approx 2.4$ . Similar values of  $z \sim 2-5$  have been reported for power law relations between relaxation time and dynamic correlation length [25,26,121]. This is further evidence that T1-inactive clusters are dynamically relevant.

In fact, a percolation approach to the glass transition has been suggested before. Cohen and Grest studied percolation of liquid-like particles with free volumes above some arbitrary criterion [42]. This approach seemed ad hoc, because no significant difference in free volume distribution distinguishes the liquid and glassy states. In contrast, the T1 activity of a particle by definition is determined from the configuration, the evolution of which is in turn influenced by the dynamics.

Recently, another connection between the glass transition and percolation has

been reported [122]; namely, that the MCT glass transition  $\phi_c$  coincides with the divergence of the cluster size of fast moving particles, and the VFT-fitted  $\phi_0$  (close to  $\phi_{\rm RCP}$ ) coincides with the divergence of the cluster size of slow moving particles. Comparing this to the present work, we remark that fast and slow clusters are defined dynamically, based on observed particle mobility; both of them grow with increasing  $\phi$ , consistent with increasing collective motion. In contrast, T1-activity is a purely geometrical property describing the "possibility" of changing Voronoi neighbors for a given configuration; the fraction of T1-inactive particles increases with increasing  $\phi$ . The actual mobility of a particle in a given simulation is also influenced by the initial velocities, so there is no deterministic relation between T1-activity and mobility. That being said, an increasing number of T1-inactive particles, which cannot change their Voronoi neighbors by their individual motion, implies a growing degree of collective motion required for relaxation. The similar power law divergence of the dynamic correlation length and T1-inactive cluster length discussed above also suggests a connection between mobility and T1-inactive particles.

## 3.4 Conclusion

In this work, we employ a new crystal avoiding (CA) method to study glassy monodisperse hard-sphere fluids at  $\phi > \phi_{\rm f}$ . The CA method allows us to explore glassy monodisperse hard-sphere fluids at  $\phi > \phi_{\rm f}$ — for which equilibration has been a "subtle question" [123]— and offers new opportunities to examine the effect of polydispersity on dynamics. In searching for the relevant local rearrangements that permit particles to gain and lose Voronoi neighbors, we show that the number of uncaged particles vanishes too rapidly compared to the moderate slowing of diffusion, and so cannot be the primary means by which particles acquire new neighbors.

Instead, we propose that T1-active particles, identified based purely on geometry, are able to acquire and lose neighbors by single particle motion without cavities present, and are common enough to contribute to rearrangements, only becoming scarce near random close packing. Moreover, clusters of T1-inactive particles percolate at  $\phi \approx 0.586$ , remarkably close to the glass transition. These results suggest a close relation between T1-inactive clusters and slow dynamics in glassy

hard-sphere fluids. Establishing the same link for polydisperse systems and exploring the possible connection of T1-(in)active correlation length to the dynamic or static correlation lengths will be the subject of future work.

# Chapter 4 | Local Structures and Entropy From Graph Isomorphism

Configurational entropy plays a central role in thermodynamic scenarios of the glass transition. As a measure of the number of metastable states configurational entropy for a glass-forming liquid can be evaluated by counting distinct inherent structures. In this work, we propose a graph-theory based method to examine local structure and obtain the configurational entropy of hard-particle systems. Voronoi diagrams of associated clusters are classified using a graph isomorphism algorithm. The statistics of these clusters reveal structural motifs such as icosahedron-like order, and also allow us to calculate the structural entropy  $S_{\rm G}$ . We find the structural entropy of an *n*-particle subsystem grows linearly with *n*. Thus the structural entropy per particle can be obtained from the slope  $dS_{\rm G}/dn$ . Our results are consistent with previous values for configurational entropy obtained via thermodynamic integration. Structural entropies per particle are measured for hard-disk and hard-sphere polydisperse systems, and extrapolated for monodisperse hard disks, all of which are nonzero at the dynamic glass transition.

## 4.1 Introduction

As a liquid is quenched toward the glass transition temperature  $T_{\rm g}$  without crystallizing, the dynamics slows drastically without any apparent change in the liquid-like molecular structure. One of the fundamental questions regarding the glass transition is whether the dynamical phenomena have an underlying thermodynamic origin. Depending on the answer to this question, glass theories are divided into two points of view. A kinetic perspective, such as dynamical facilitation theory [90,124], claims the glass transition is a kinetic arrest, and should be understood at the dynamic level. Whereas, a thermodynamic scenario, such as random first-order transition (RFOT) theory [66, 70] attributes the increasing relaxation time to decreasing configurational entropy, which vanishes at a Kauzmann temperature  $0 < T_{\rm K} < T_{\rm g}$ , leading to a thermodynamic phase transition from fluid to glass state.

Considerable efforts have been made to calculate the configurational entropy, because of its central role in thermodynamic glass theories. Based on the idea that particle motions in a supercooled liquid can be decomposed into fast vibrations within the cage formed by its neighbors and slow cage-breaking rearrangements, the configurational entropy  $S_c$  has been calculated as the difference between the total entropy of the liquid S and the vibrational entropy  $S_v$ . While the total entropy can be readily obtained by thermodynamic integration of the pressure from the ideal gas to the glassy state, significant ambiguity arises in the definition of vibrational motions. As a result, the estimate of  $S_v$  depends on the method used to restrict structural rearrangement; these methods include harmonic approximation [34, 125, 126], perturbed Hamiltonian approach [33], and tether method [127].

We are interested in systems near a dynamic glass transition, defined operationally as the point at which in experiments or simulations it becomes extremely difficult to observe particle diffusion, and hence to equilibrate a liquid. As a system approaches a dynamic glass transition, ergodicity is effectively broken, and configuration space is partitioned into some number of distinct regions, with a given system trapped for increasingly long times in a single region. The configurational entropy  $S_c$  can therefore be defined by counting the number of distinct "inherent structures" [32, 128] of a glassy system.

These inherent structures can be defined in several ways. For jammed particles, inherent structures can be taken as the set of collectively jammed configurations at a given volume fraction. For particles interacting via smooth potentials, inherent structures have been defined as the set of local minima of the potential energy landscape at a given total energy, which can be found by minimizing the potential energy, starting from representative system configurations. Structures could also be defined in terms of free energy minima (called "pure states")— one of which may correspond to several energy minima separated by weak barriers [37]. (Counting free energy minima for such systems would be more relevant, but is much harder to do.)

Several previous authors have obtained values for  $S_c$  by explicitly counting inherent structures, with different heuristic methods for distinguishing different structures. For example, Xu *et al.* [129] study small jammed hard-disk systems, in which different inherent structures are distinguished by the eigenvalues of vibrational modes; Donev *et al.* [35] partition large hard-disk systems onto lattices and count the occurrence of sublattice configurations. In a related method [130, 131], volumes of basins in the potential energy landscape are measured; then the number of basins is the total volume of configurational space divided by the average basin volume. Despite these efforts, relation between configurational entropy, characterizing the number of basins in *dN*-dimensional landscape, and real space structures remains elusive.

For hard-sphere systems near the dynamic glass transition, conventional approaches to identifying inherent structures do not directly apply; there is no potential energy to minimize, and the system is not jammed. In this work, we present a new approach to identifying structures, and thereby reveal local geometric motifs and estimate the configurational entropy. We propose that a useful definition of structures for glassy hard-sphere fluids can be given in terms of the network of neighbor relationships, as defined by the Voronoi construction, because these remain essentially unchanged for very long times above the dynamic glass transition, even as particles rattle in their cages. Phase space for the broken-ergodicity dynamic glass is then partitioned into regions defined by distinct Voronoi network topologies.

To distinguish different neighbor networks, we classify the corresponding graphs using graph isomorphism algorithms, which reliably identify and uniquely label topologically distinct graphs. In this way, we can obtain the statistics of distinct structures, investigate prominent local clusters, and estimate the structural entropy. Our direct results for structural entropy are consistent with the configurational entropy inferred from thermodynamic integration. In this work we focus on the simple hard-particle systems, though our method can be applied to systems with any potential.


Figure 4.1: Two graphs are said to be isomorphic if they contain the same number of graph vertices connected in the same way. One possible isomorphism is shown in the diagram.

## 4.2 Method

We study hard-particle systems in the vicinity of the dynamic glass transition ( $\phi \approx 0.80$  in 2D and  $\phi \approx 0.58$  in 3D), defined by the apparent vanishing of the particle diffusivity [92, 132]. After initial preparation using the Lubachevsky-Stillinger (LS) algorithm [133], systems with packing fraction below the dynamic glass transition are equilibrated until no obvious aging is observed for the quantity of interest. Moderate size polydispersity (fractional standard deviation of particle diameter),  $\Delta = 0.13$  in 2D and  $\Delta = 0.08$  in 3D, is introduced to inhibit crystallization [92, 134] above the monodisperse freezing point ( $\phi_{\rm f} \approx 0.70$  in 2D and  $\phi_{\rm f} \approx 0.50$  in 3D).

We perform Voronoi tessellation to define the nearest-neighbor network for a given configuration of hard particles. For polydisperse systems, we use the radical plane construction to define the Voronoi network; this construction prevents Voronoi facets from intersecting particles, and yields a sensible neighbor network. In fact, the glass transition of binary soft disks has been studied in terms of the statistics of Voronoi cells [135], suggesting a close relation between amorphous structure and Voronoi network.

Since the total number of distinct graphs grows exponentially with number of particles, we are limited to relatively small systems with less than 30 particles in 2D and 20 particles in 3D. However, a strong finite size effect has been observed in small systems with periodic boundary conditions [136]; in particular, we find systems of certain "magic" sizes can develop crystalline order even when the density is below the freezing point. To avoid this problem, we consider small subsystems within a large system of size  $N \sim 10^5$ . For each large system, we examine many small



Figure 4.2: Snapshot of a polydisperse hard-disk system with 4 distinct graphs of n = 16 vertices shown in different colors. Corresponding canonical graphs of Voronoi clusters are shown with the same color. Graphs (1) and (2) are more common than (3) and (4).

subsystems (less than N to avoid double counting), whose centers are uniformly chosen from a square or cubic grid superimposed on the system. A fixed number of particles nearest to the center are selected to constitute the subsystem, which is then mapped to a graph with edges formed between Voronoi neighbors in the subsystem (see Figure 4.2,

Instead of comparing graphs with all their possible permutations of vertex labels, we exploit a powerful tool in graph theory – canonical labelling. Roughly speaking, two graphs are isomorphic if some relabelling vertices yields the same set of edges for both graphs (see Fig. 4.1). A canonical labelling of a graph then represents the whole isomorphism class of that graph. We automate the graph classification process by adapting NAUTY [137], a leading graph isomorphism solver, which produces a canonical graph that can be used to "name" any given graph.

The structural entropy measures the number of distinct topological states available to the subsystem of size n, defined as

$$S_{\rm G} = -\sum_{i} p_i \log(p_i), \qquad (4.1)$$

where  $p_i$  is the probability of finding distinct graph *i*. For large enough *n*,  $S_{\rm G}$  is expected to grow linearly with *n*. We estimate the structural entropy per particle  $S'_{\rm G}$  from the slope  $dS(n)_{\rm G}/dn$ .

#### 4.3 Results

#### 4.3.1 Local Structures in Hard-Sphere Systems

To begin with, we show that the seemingly oversimplified Voronoi graphs, which only contain topological information of clusters, are quite effective to identify local cluster structures. Because of the geometric constraints associated with non-overlapping particles in dense systems, a given graph can be almost uniquely mapped to a certain real-space structure, allowing for some degree of distortion by thermal fluctuations. Hence Voronoi graphs can be used to represent local clusters and reveal structural motifs.

As an example, we consider two configurations of monodisperse hard spheres in different phases— a supercooled liquid at  $\phi = 0.58$  (N = 2000) equilibrated by crystal-avoiding (CA) method [138] and a crystal at  $\phi = 0.71$  (N = 4000). Here we focus on local clusters built around each atom in the system with their first shell of Voronoi neighbors. Clusters obtained this way typically have a size of 12 to 17 particles (as opposed to the fixed subsystem size we use for entropy calculation).

We do notice a small fraction of misdetections of Voronoi neighbors because of the degeneracy of the Voronoi construction for highly symmetrical particle arrangements, especially for the ordered phase. To address this issue, modifications of the Voronoi construction have been used previously [139]. Here we simply remove a Voronoi bond if the area of the shared Voronoi facet is below a threshold, e.g.,



Figure 4.3: Most common cluster types in monodisperse hard-sphere systems for solid phase (a) and liquid phase (b). Central atoms of each cluster type are colored accordingly. Graph representations of selected clusters are shown with their number fractions indicated.

2-4% of the average Voronoi facet area (our results are robust within this range of threshold values).

As shown in Figure 4.3, FCC clusters dominate in the crystal, with less than 10% of HCP clusters appearing as a result of planar stacking defects. In contrast, many different structures are found in the disordered phase, with the most common ones being icosahedron-like (13A, 14A) and decahedron-like (15C) (see Ref. [140] for the established nomenclature of local clusters). However, compared to the few crystalline structures that dominate the system, even the most common structures (around each atom) in the amorphous systems are sparse, making up only about 10% of all the distinct structures found in that configuration, consistent with previous findings [46,51,141]. (The TCC method finds somewhat fewer icosahedron-based clusters [142], because that heuristic for local structures is more sensitive to fluctuations in interparticle distances.) Since these clusters cannot tile space, the central atoms of a given cluster type are unlikely to be neighbors of each other because of geometric frustration, as depicted in figure Figure 4.3(b). This frustration limits the concentration of the most common icosahedral and dodecahedral motifs.

To illustrate this point, Figure 4.4 highlights all involved atoms (not just the



Figure 4.4: Same configuration as Figure 4.3(b) with all involved atoms highlighted for each cluster type. Percentage indicates the fraction of cluster members. Cluster centers are darkened.

center atoms) for a given cluster type. As can be seen in the figure, clusters of each type pervade the system. Atoms involved in the three cluster types make up nearly 80% of the system, although most of them are shared among different clusters. We find similar results for disordered systems with mild polydispersity  $\Delta = 0.08$ . This suggests that any structural artifacts of our CA method for metastable monodisperse systems are small.

To explore the relation between local structures and dynamics, we compute the persistent time or lifetime for the three most common clusters, namely, 13A, 14A and 15C. Following Ref. [51], a single-particle function  $v_i(t)$  can be defined that equals 1 if particle *i* is at the center of a given type of cluster, and 0 if not. The autocorrelation function of  $v_i(t)$  can be computed as

$$\sigma(t) = \frac{1}{N} \sum_{i=1}^{N} \langle v_i(t) v_i(0) \rangle - \left(\frac{n_c}{N}\right)^2, \qquad (4.2)$$

where  $n_{\rm c} = \sum_{i=1}^{N} \langle v_i(0) \rangle$  is the average number of particles at the center of a



Figure 4.5: (a) Single-particle function  $v_i(t)$  at  $\phi = 0.58$  for selected common cluster types (see text for details). (b) Persistent times for different cluster types as a function of volume fraction. Inset: autocorrelation function  $\sigma(t)$  for 13A clusters.

given cluster. The persistent time of a given cluster can be defined as the time when  $\sigma(t)/\sigma(0)$  decays to 1/e. In Figure 4.5 (a), we show the time dependence of single-particle function  $v_i(t)$  for three typical particles that frequently appear at the center of each type of cluster. It is clear that icosahedron is more resistant to thermal fluctuation and local rearrangement than other clusters. As shown in Figure 4.5 (b), icosahedron clusters display the longest persistent time among others for monodisperse hard spheres, which increases rapidly as the glass transition is approached, in a similar manner as the structural relaxation time. However it is worth mentioning that the most immobile particles are not strongly correlated with icosahedra. The relation between dynamics and local structure on singleparticle level remains elusive [114]. Nonetheless, our results suggest that icosahedral order plays an important role in the slowing down of monodisperse hard spheres, consistent with previous studies on different potentials [51].

Several structure classification methods have been previously used in the literature. The shape matching approach [143] uses invariant harmonic descriptors to compare structures; the topological cluster classification (TCC) algorithm [142,144] compares a cluster with a library of known structures, using sophisticated detection routines. By comparison, our graph-theory based method is completely automated, with no need to identify important structures "by hand". The common neighbor analysis (CNA) [145] and Voronoi index [141] describe structures based on reduced information on the neighbor connectivity, and therefore are not always able to distinguish topologically different structures.

The patch method [65], recently developed for characterizing order in 2D glassy

systems, considers two patches as "congruent" if, by rotating one patch around its central particle, particles in the two patches correspond to each other within some distance cutoff. The patch method is more challenging in 3D because of the need to rotate independently on multiple axes to bring patches into correspondence. In addition, because congruency depends on the distance cutoff, a patch A may be congruent to patches B and C, without B being congruent to C, which makes defining equivalence classes and counting states potentially problematic.

Finally, a graph isomorphism technique similar to our present work has been previously used by Donev *et al.* to analyze the local contact network of jammed packings [146]. In that system, they find the dominant pattern to be open chains with very few tetrahedra, because of small contact number ( $Z \approx 6$ ); no calculation of graph entropy is performed.

#### 4.3.2 Structural Entropy for Hard Disks

Having established the connection between cluster structures and Voronoi graphs, we proceed to obtain the structural entropy of glassy hard-disk systems, by counting the number of topologically distinct local structures. A typical probability distribution of graphs for polydisperse hard disks is shown in Figure 4.6(a). The number of distinct graphs grows dramatically as the subsystem size n increases. Although only a few graph types dominate the configurations, the contribution from the tail of rare states to the structural entropy are collectively non-negligible.

For larger subsystems, the total number of distinct clusters unavoidably exceeds our maximum sample size (~ 10<sup>7</sup>), so that the entropy obtained from that sample is underestimated. Since the decay of the graph histogram does not follow a simple exponential form or a power law as indicated in Figure 4.6 (a), we do not know how to extend the distribution tail by fitting. Remarkably, we observe that the difference between entropy calculated from undersampled data and a sufficiently large sample,  $\Delta S_{\rm G}(\lambda) = S_{\rm G}(\lambda) - S_{\rm G}(\infty)$ , where  $\lambda = n_{\rm s}/n_{\rm d}$  is the sampling ratio of the total number of samples  $n_{\rm s}$  to the number of distinct clusters  $n_{\rm d}$ , is a universal function of the sampling ratio for different  $\phi$ , n and  $\Delta$  (see Figure 4.6(b)). We use this fact to construct a "correction curve", to infer the true value of the structural entropy from insufficiently sampled data.



Figure 4.6: (a) Probability distribution of distinct graphs (rank ordered) of different subsystem sizes for polydisperse hard disks at  $\phi = 0.74$ . Inset: a log-log plot. (b) Entropy difference  $\Delta S_{\rm G}$  (see main text) as a function of sampling ratio  $\lambda$  for different  $\phi$ , n and  $\Delta$  collapse onto a master curve. Solid line is an empirical fit of form  $f(x) = a_1 x^{b_1} + a_2 x^{b_2}$ . Inset: unshifted data of  $S_{\rm G}(\lambda)$ . (c) Structural entropy  $S_{\rm G}$  versus subsystem size n for polydisperse hard disks at  $\phi = 0.74$ . For subsystem size shown here, the corrected entropy estimated from a small sample size ( $n_{\rm s} = 10^4$ , filled red) agrees with that obtained from a larger sample ( $n_{\rm s} = 10^6$ , black), supporting the validity of the correction curve. Dashed line depicts the linear relation between  $S_{\rm G}$  and n.



Figure 4.7: Measured structural entropy per particle  $S'_{\rm G}$  as a function of packing fraction for polydisperse hard disks. Inset: equilibration times t dependence of  $S'_{\rm G}(\phi)$ , where  $\tau$  is the mean collision time.

Using the correction curve, we can estimate the value of  $S_{\rm G}(\infty)$  from the undersampled  $S_{\rm G}(\lambda)$  and its associated sampling ratio  $\lambda$ ; this works well as long as  $\lambda$  is not close to unity (we mainly use  $\lambda \sim 3$  for large n). As illustrated in Figure 4.6(c), the correction method successfully reproduces the sufficiently sampled entropy from a data set 100 times less well sampled.

Since the subsystems we study contains no more than 30 particles, the structural entropy for such a small region might be contaminated by surface effects. Fortunately, we find a good linear relationship between corrected  $S_{\rm G}$  and n for n > 12, shown in Figure 4.6(c). This suggests that the surface correction for subsystem entropy is negligible for relatively large n, and the slope  $dS_{\rm G}/dn$  gives a reasonable estimate for the entropy per particle  $S'_{\rm G}$ .

The measured  $S'_{\rm G}(\phi)$  with the longest equilibration time, defined as the time elapsed after the initial LS configurations are generated, are shown in Figure 4.7 as a function of volume fraction. About  $2 \times 10^6$  samples have been used to evaluate  $S_{\rm G}(n)$  before we apply the correction. Within the range of equilibration time studied (see inset of Figure 4.7), the structural entropy per particle quickly converges to its equilibrium value for  $\phi < 0.78$ . As the glass transition is approached, a strong aging effect is found for  $S'_{\rm G}$  because of slow structural relaxation. This aging of the structural entropy can be understand in terms of the landscape view of aging. During the rapid LS compression protocol, a hard-particle system at high  $\phi$  may be trapped in one of the basins typical for a lower density  $\phi_0 < \phi$  associated with larger structural entropy. The aging process allows the system to evolve until it



Figure 4.8: Comparison between structural entropy per particle  $S'_{\rm G}$  and configurational entropy  $s_{\rm c}$  from thermodynamic integration [36], for a bidisperse hard-disk mixture. The growth rates used in the LS algorithm are  $\gamma = 1 \times 10^{-4}$  and  $\gamma = 3.2 \times 10^{-6}$ , respectively.

explores the configuration space correctly drawn from the Boltzmann distribution at  $\phi$ . Our results suggest that the extremely large relaxation barrier in glassy systems eventually dominates the thermodynamic driving force, resulting in a structural entropy at high  $\phi$  higher than that for a system at lower  $\phi$  with the same equilibration time. This may be the reason for a higher value of  $S'_{\rm G}$  at  $\phi = 0.80$ compared to  $\phi = 0.78$ .

In spite of the aging process above  $\phi_{\rm g}$ , the difference between structural entropy for our two longest equilibration times is quite small. This suggests the equilibrated structural entropy of polydisperse hard-disk systems remains nonzero in the vicinity of glass transition, consistent with recent studies of the configurational entropy [36, 147, 148].

To compare our direct evaluation of the structural entropy with conventional determination of the configurational entropy by thermodynamic integration, we apply our method to a binary mixture of hard disks with diameter ratio 7:5 and mole fraction ratio 1:2. The configurational entropy for this system has been calculated [36], for which the vibrational entropy is estimated from single-occupation cell system. As shown in Figure 4.8, the structural entropy agrees with configurational entropy  $s_c$  at high  $\phi$ , indicating that Voronoi networks well represent the inherent structures of a system, and the structural entropy is essentially identical to the configurational entropy.

The discrepancy between the two calculations at low  $\phi$  arises from the differences

in defining vibrational motions. Since our structural entropy is calculated based on a Voronoi network, any motion that does not change the Voronoi neighbor is effectively "vibrational"; these motions are much larger in a dilute system. For the configurational entropy, on the other hand, the vibrational contribution depends on how far particles are allowed by the constraints to explore a single basin; these constrains are less sensitive to density variation (cell radius around one particle diameter is found sufficiently small to prevent particle rearrangements for the densities studied [36]). The ambiguity in defining vibrational motions vanishes in the high  $\phi$  limit, where both methods are rigorous and consistent with each other.

For binary mixtures, it is possible to assign different colors to the graph vertices associated with large and small particles. This scheme leads to larger structural entropy as each 1-color graph has many color combinations. However, we argue that the configurational entropy calculated from integrating the pressure did not take into account the "color difference", but only the effect of variation in particle size on the local geometry of the system, which are already encoded in the 1-color graph as seen in the structural entropy of polydisperse systems. We note similar argument has been made that when calculating the granular entropy of polydisperse soft disks, a constant  $\ln N!$  should be subtracted [131]. Therefore, the structural entropy obtained from 1-color graph is more suitable for the comparison here. Nevertheless, entropy of color graphs provides additional information about the arrangement of different species, discussed further below.

#### 4.3.3 Effect of Polydispersity on Structural Entropy

Since polydispersity is known to affect the glass transition [94, 149] and thus may alter the structural entropy, it is natural to ask what is the structural entropy of amorphous monodisperse systems. One may naively assume that the total configurational entropy is the sum of the configurational entropy for a monodisperse system, plus an ideal-gas polydispersity entropy (i.e. random assignment of diameter to each particle), which can be computed as the entropy of mixing n species ideally,  $S_{\text{mix}} = -\sum_n x_i \ln x_i$ , where  $x_i$  is the fraction of particle diameters lie in successive bins of width  $d\sigma$ . However, the random mixing assumption may not be valid at high densities, where systems may adopt some correlations between large and small disks in local arrangements to realize higher packing efficiency.



Figure 4.9: (a) Structural entropy per particle and (b) crystallinity  $\chi$  versus packing fraction  $\phi$  for hard-disk systems with varying polydispersities  $\Delta$ .

To see this, we recall that a 2-color structural entropy can be computed for binary systems as discussed above, which, compared to its 1-color counterpart, reveals information about the mixing of large and small particles. As an example, for  $\phi = 0.77$ , the 2-color and 1-color entropy per particle are  $S'_{2G} = 0.96$  and  $S'_{1G} = 0.67$ , respectively. Hence the difference  $S'_{2G} - S'_{1G}$  is about 0.29, which is considerably smaller than the entropy of ideal mixing at 1:2 ratio,  $\Delta S_{\text{mix}} \approx 0.64$ . In addition, we find that the value of random 2-color structural entropy, measured by randomly assigning the color of graph vertices as if particles were ideally mixed, is about 1.22, which is larger than the actual 2-color entropy. So simple assumption about the random mixing of small and large disks are not justified.

An alternative approach to circumvent the difficulty of calculating polydispersity entropy is to directly measure the  $S'_{\rm G}$  as a function of polydispersity for different densities, and extrapolate it to the monodisperse limit. In Figure 4.9(a), we show a family of curves of  $S'_{\rm G}$  versus  $\phi$  for polydispersity  $0 \leq \Delta \leq 0.16$ . For  $\Delta < 0.12$ , an abrupt drop in structural entropy around  $\phi = 0.70$  is due to the liquid-solid transition, which is also signaled by the increase of crystallinity, defined as the



Figure 4.10: (a) Structural entropy per particle as a function of polydispersity  $\Delta$  for different  $\phi$ . Solid lines are power law fits of form  $y = ax^{1.5} + b$  for  $\Delta \geq 0.12$  (filled points). (b) Extrapolated  $S_{\rm G}^{0'}$  for monodisperse disordered systems compared to measured  $S_{\rm G}'$  for monodisperse and polydisperse systems at equilibrium.

fraction of solid-like particles (shown in Figure 4.9(b)). As an extension from hard-sphere systems, a disk *i* is deemed solid-like if it has  $n_c \geq 6$  neighbors with local bond order parameter  $d_6(i, j) > 0.9$ . The structural entropy of crystals almost vanishes at the highest density, with a small residual entropy mainly from crystallographic defects. In contrast, for disordered systems with  $\Delta \geq 0.12$ , the structural entropy decreases only moderately as glass transition is approached.

To extrapolate the structural entropy from the high polydispersity region where crystallization is avoided to the monodisperse limit, we replot the same data of structural entropy shown in Figure 4.10(a), as a function of polydispersity for different  $\phi$ . It is evident that as the monodisperse limit is approached,  $S'_{\rm G}(\Delta)$ decreases smoothly for systems below the freezing density  $\phi_{\rm f}$ , whereas for  $\phi > \phi_{\rm f}$ , it deviates from the high polydispersity trend because of crystallization. We find that for disordered systems with  $\phi \leq 0.68$ ,  $S_{\rm G}(\Delta)$  follows a power law in the whole  $\Delta$  range studied, with exponent  $\alpha$  ranging from 1.6 to 1.4. This nonlinearity, or more specifically, the decreasing slope  $dS'_{\rm G}/d\Delta$  as  $\Delta \rightarrow 0$ , might result from the fact that when  $\Delta$  is too small compared to a certain threshold  $\Delta_0$ , the variance of particle size barely affects the Voronoi neighbor relation of the configuration and thus creates many fewer new graphs. Besides, the slightly decreased  $\alpha$  at higher density also suggests that the geometry of the system becomes more sensitive to the size difference as particles have more contacts, which in turn moves the threshold  $\Delta_0$  toward a lower value.

In practice, we fit  $S_{\rm G}'$  to a power law with a fixed exponent  $\alpha$  = 1.5, i.e.,



Figure 4.11: Structural entropy of disordered states measured using CA method (red diamonds) are in agreement with those extrapolated from high  $\Delta$  data (dashed line) for two "supercooled" densities:  $\phi = 0.70$  (top) and  $\phi = 0.72$  (bottom). Inset: crystallinity for systems sampled by CA method and conventional MD.

 $S'_{\rm G}(\Delta) = S^{0'}_{\rm G} + k\Delta^{1.5}$ , for  $0.12 \leq \Delta \leq 0.16$  and  $0.64 \leq \phi \leq 0.80$ . As depicted in Figure 4.10, the solid fitting curves are in good agreement with measured  $S'_{\rm G}$  for  $\phi \leq 0.68$ , and give decent estimates of the actual entropies in the monodisperse limit. Assuming the fit remains valid for disordered states at  $\phi \geq 0.70$ , we may take the parameter  $S^{0'}_{\rm G}$  as the structural entropy for disordered monodisperse systems. As presented in Figure 4.10(b)), the extrapolated monodisperse entropy  $S^{0'}_{\rm G}$  matches that of actual monodisperse systems below  $\phi_{\rm f}$ , and then instead of decreasing rapidly due to crystallization, it follows a smooth decay similar to polydisperse systems. As a result, even though the extrapolated monodisperse entropy is smaller than the polydisperse one, it exceeds that of a crystal, and is nonvanishing at the highest density studied.

We can further justify this extrapolation approach by exploiting the crystalavoiding method, which samples the metastable states that would otherwise crystallize. Compared to 3D hard spheres, it is more difficult to bypass crystallization in 2D systems, since nucleation is easier in low dimensions [118]. Also, the crystallinity



Figure 4.12: (a) Subsystem size dependence of raw and corrected structural entropy for polydisperse hard-sphere systems at different  $\phi$ . Linear fits of corrected  $S_{\rm G}$ versus *n* are shown in dashed lines. (b) Extracted entropy per particle  $S'_{\rm G}(\phi)$ . Inset: equilibration time dependece of  $S'_{\rm G}$  for  $\phi = 0.55 - 0.59$  (the last two curves are overlapping).

of metastable states is somewhat arbitrary, so one can always trade order for entropy to some extent. With these caveats, we show in Figure 4.11 the measured structural entropy of marginally "supercooled" metastable states ( $\phi = 0.70$  and  $\phi = 0.72$ ) sampled using the CA method. Crystallization is largely suppressed by the CA method, with  $\chi$  controlled below 6% for  $\phi = 0.70$ , and 12% for  $\phi = 0.72$ , as depicted in the insets of the figure. The agreement between entropy at low polydispersity obtained using the CA method and the extrapolated entropy is very encouraging, suggesting the validity of our extrapolation procedure.

#### 4.3.4 Structural Entropy for Hard Spheres

The same structural entropy calculation can be performed for 3D hard spheres. However, it is more challenging than for hard disks since there are many more topologically distinct states. Here we show preliminary results for hard-sphere systems near the glass transition ranging from  $\phi = 0.55$  to  $\phi = 0.60$ . As expected, the raw structural entropy soon becomes undersampled as subsystem size n > 15(see Figure 4.12(a)). We again find a correction curve to estimate the true entropy value from insufficiently sampled data for hard-sphere systems. For  $n \leq 16$ , we find a reasonably good linear relation between the corrected  $S_{\rm G}$  and n, from the slope of which we obtain the structural entropy per particle  $S'_{\rm G}$  as displayed in Figure 4.12(b). We have also checked the aging behavior, and make sure that the change in entropy, even though not completely settled for  $\phi > 0.58$ , is very small for longer equilibration times.

Similar to the hard-disk systems, the structural entropy per particle of polydisperse hard spheres decreases moderately as glass transition  $\phi_{\rm g} \approx 0.59$  is approached, after which it remains nonzero. Additional extensive simulations are required for detailed investigation, which is part of future work.

## 4.4 Conclusion

In this work, we propose a new graph-based approach to study the structure of glass-forming hard-particle systems. We show that the geometric motifs of local clusters can be revealed by classifying the corresponding Voronoi networks based on graph isomorphism. A wide spectrum of different cluster structures for amorphous hard-sphere systems are identified, including icosahedron-like and decahedron-like clusters. This suggests that complex structural information in real space is effectively encoded in the Voronoi network. By extensively enumerating topologically distinct graphs of subsystems with varying number of particles, we obtain the graph entropy per particle for polydisperse hard-disk systems. We also estimate the structural entropy per particle of disordered systems in the monodisperse limit, by fitting the entropy in the high polydispersity regime (where crystallization is fully suppressed) as a function of polydispersity to a power law. A good agreement is found between the extrapolated entropy and those measured using our crystal-avoiding method for selected densities. Furthermore, the structural entropy is found to be close to the conventional configurational entropy for a model binary mixture near glass transition. Finally, we apply the graph method to obtain the structural entropy of polydisperse hard-sphere systems. As for hard-disk systems, we find the structural

entropy per particle stops decreasing near glass transition, and exhibits a nonzero value. This indicates an exponential number of topologically distinct structures exist near glass transition in which a nonergodic system can be trapped. Whether this is also true for systems cooled infinitely slowly without crystallization— which would contradict the assumption that the configurational entropy vanishes for an ideal glass [69, 82, 150]— remains an intriguing possibility. (assuming that metastable states in free energy landscape are well represented by inherent structures, though this idea has been questioned [37, 38, 75]). Our graph-based method can be extended to systems with soft potentials or under confinement, as well as network glasses such as amorphous silica, which will be interesting for future studies.

# Chapter 5 | Static Lengths in Dense Hard Spheres Revealed by Pinning

In this chapter, we explore the static correlation lengths in glass-forming hardsphere liquids revealed by the response of dynamical properties (diffusion coefficient D and  $\alpha$  relaxation time  $\tau_{\alpha}$ ) to a regular array of pinned particles. By assuming a universal scaling form, we find data can be excellently collapsed onto a master curve, from which relative length scales can be extracted. By exploiting a crystal-avoiding simulation method that suppresses crystallization while preserving dynamics, we can study monodisperse as well as polydisperse systems. The static length obtained from dynamical property Q ( $\tau_{\alpha}$  and D) scales as  $\log Q \sim \xi_s^{\psi}$ , with  $\psi \approx 1$ .

#### 5.1 Introduction

The origin of sluggish motions in supercooled liquids is still a matter of debate. Under the general view of cooperative motion in glass-forming liquids, growing (or diverging) relaxation times should be associated with one or more growing (or diverging) length scales.

On the one hand, a dynamic correlation length, characterizing the growth of spatially heterogeneous dynamics as temperature decreases, can be extracted from multipoint space-time correlation functions [11, 25]. This correlation length depends on the delay time, and reaches its peak value near the alpha relaxation time  $\tau_{\alpha}$ . However, although the relaxation time and dynamic length both grow as the temperature decreases, it has been suggested they might not be directly related [30]. The question remains unsettled, whether dynamic heterogeneity is the origin or only a consequence of glassy dynamics.

On the other hand, many efforts have been made to identify a "hidden" static length responsible for the slow dynamics. Since it is difficult to identify any amorphous order parameter from the apparently unchanged structure during glass formation, static lengths are often computed either from spatial correlations of some *a priori* local order, such as icosahedrons [52], polytetrahedrons [151] or medium-range crystalline order [53], or by an "order-agnostic" approach, including the point-to-set (PTS) technique [66] and excess plastic modes analysis [152]. It is unclear whether static lengths estimated by different approaches agree with each other.

One of the most studied static lengths is the PTS length  $\xi_{\rm ps}$ . A general procedure [66, 153–155] of obtaining  $\xi_{\rm ps}$ , motivated by random first-order transition (RFOT) theory, is as follows. All particles in an equilibrated system outside of a spherical region of radius R are frozen, while the inner particles are allowed to relax in the presence of the frozen boundary. The RFOT theory predicts that for  $R \gg \xi_{\rm ps}$ , the subsystem inside the cavity should decorrelate from its initial state in favor of configurational entropy; whereas for  $R \ll \xi_{\rm ps}$ , the subsystem is trapped into the initial state due to the cost of surface tension (mismatch on the boundary). To measure whether the subsystem of radius R can eventually switch to a different state, the long time limit of an global overlap function  $Q_{\infty}(R)$  is introduced. The PTS length is defined as the radius for which  $Q_{\infty}(\xi_{\rm ps})$  falls below some small value.

Although defined by *static* overlap, the PTS length might be generally regarded as the characteristic length over which the boundary conditions imposed by pinning particles affect nearby particles. This interpretation suggests that we can reveal the static length from the response of some dynamic property (such as the particle self-diffusion coefficient) to an imposed pinning field.

In several recent works, the effect of pinned particles on structural relaxation has been studied in systems with soft potentials [156–159]. To extract the correlation length, these authors have made different theoretically motivated assumptions for how the structural relaxation time  $\tau_{\alpha}$  depends on pinning strength, such as  $\tau_{\alpha} \sim \exp(Ac)$  with c the pinning concentration [156, 158] or  $\ln \tau_{\alpha} \sim \exp(Bz)$  with z the distance from the wall [157, 159]. To distinguish from the "static" length extracted from overlap, the length obtained from relaxation time has been called "dynamic" in Ref. [157, 159]. In the present work, we refer such a length as "static" to emphasize its time-independent nature.

In this work, we use molecular dynamics (MD) simulation of monodisperse hard-sphere systems to learn how dynamical properties change as the pinning length scale varies, and extract static correlation lengths from scaling analysis without assuming a specific functional form. Two typical dynamical properties are examined in this work, namely the diffusion coefficient D and alpha relaxation time  $\tau_{\alpha}$ .

# 5.2 Method

The hard-sphere fluid is the simplest system that exhibits a glass transition, at a volume fraction  $\phi_{\rm g} \approx 0.59$  [91,160]. In experiments on colloidal hard-sphere suspensions, particles can be pinned using optical tweezers [161]. To avoid crystallization above the freezing point  $\phi_{\rm f} \approx 0.495$ , a moderate polydispersity in particle size s is usually introduced. However, polydispersity does alter the dynamics, especially in the vicinity of glass transition. For polydisperse hard spheres at high  $\phi$ , small particles may remain diffusive while large ones are almost arrested, so that the ideal monodisperse glass transition is smeared out [94].

To avoid this artifact, we exploit a crystal-avoiding (CA) hybrid Monte Carlo method that suppresses crystallization in monodisperse hard spheres while preserving the dynamics [138]. Although pinning some particles tends to frustrate crystallization, we find that the monodisperse hard-sphere system still crystallizes readily at low pinning concentrations (see Appendix B for details). To prevent crystallization and to be consistent across different pinning fractions, we employ the CA method for all simulations reported here.

## 5.3 Results

#### 5.3.1 Dynamics of Unperturbed Systems

We consider hard-sphere systems of N = 2000 particles for  $\phi$  ranging from 0.53 to 0.58. For each  $\phi$ , initial configurations are generated using the Lubachevsky-Stillinger algorithm and then equilibrated. For unpinned monodisperse systems, we calculate the self-diffusion coefficient D (extracted from the long-time limit of mean square displacement (MSD)) and alpha relaxation time  $\tau_{\alpha}$  (defined as the



Figure 5.1: Self-diffusion coefficient D and alpha relaxation time  $\tau_{\alpha}$  as a function of  $\phi$  for monodisperse and polydisperse system (s = 0.08). Dashed and solid lines are MCT fits. Inset: aging of diffusion coefficient D at  $\phi = 0.59$  as a function of equilibration time  $\tau_{\rm e}$ .

time at which the intermediate incoherent scattering function  $F_{\rm s}(q, \tau_{\alpha})$  equals 1/e, with q = 6.5 near the first peak in S(q), and compare to results for polydisperse systems (see Fig. 5.1).

The dramatic increases in both 1/D and  $\tau_{\alpha}$  are well described by a power-law divergence,

$$1/D \text{ or } \tau_{\alpha} \sim (\phi_{\rm c} - \phi)^{-\gamma},$$
 (5.1)

inspired by mode-coupling theory (MCT). We find for monodisperse systems,  $\phi_c = 0.586 \pm 0.003$ ,  $\gamma = 2.5 \pm 0.5$  for 1/D and  $\phi_c = 0.584 \pm 0.002$ ,  $\gamma = 2.6 \pm 0.4$ for  $\tau_{\alpha}$ . For our polydisperse system (s = 0.08), we have  $\phi_c = 0.586 \pm 0.001$ ,  $\gamma = 2.2 \pm 0.1$  for 1/D and  $\phi_c = 0.584 \pm 0.001$ ,  $\gamma = 2.4 \pm 0.2$  for  $\tau_{\alpha}$ . Although the MCT calculation for hard-sphere systems using the Percus-Yevick approximation gives a much smaller  $\phi_{c,MCT} \approx 0.52$  [162],  $\phi_c$  obtained here agrees well with the experimental glass transition in colloidal suspensions,  $\phi_g \approx 0.59$ . [91, 160]

Alternatively, the data can be equally well fit by an exponential form

$$1/D \text{ or } \tau_{\alpha} \sim \exp\left[A/(\phi_0 - \phi)\right].$$
 (5.2)

with  $\phi_0 = 0.605 \pm 0.006$  for 1/D and  $\phi_0 = 0.599 \pm 0.002$  for  $\tau_{\alpha}$  for the monodisperse system, and  $\phi_0 = 0.604 \pm 0.002$  for 1/D and  $\phi_0 = 0.599 \pm 0.001$  for  $\tau_{\alpha}$  for our polydisperse system. Although the dynamics appears barely altered by small polydispersity when the system is far from glass transition, strong aging is observed at



Figure 5.2: Confining length dependence of diffusivity for monodisperse and polydisperse systems (at  $\phi = 0.56$ ), for periodic array and random pinning.

 $\phi = 0.59$  in monodisperse systems (Fig. 5.1 inset); in contrast, aging in polydisperse systems at  $\phi = 0.59$  is much less pronounced, because of the decoupling of dynamics of small and large particles [94]. As we shall see below, the glass transition can also be induced by pinning particles even at  $\phi \ll \phi_{\rm g}$ , hence polydispersity should be expected to affect dynamics under pinning whenever the system becomes glassy. Indeed, we observe a weaker pinning effect on dynamics for polydisperse systems (see Fig. 5.2).

#### 5.3.2 Pinning Induced Glass Transition

While random pinning has been proposed as the best candidate for studying static correlation [67], we focus here on periodic array pinning, in which particles nearest to the corresponding nodes of a  $m \times m \times m$  grid are pinned, so that the pinning fraction is  $c = m^3/N$ . The confining length  $\ell_c$  is then defined as  $\ell_c = L/m$ , with Lthe system size. In this way,  $\ell_c$  is unaffected by variations that may arise by random pinning, as a result of fluctuations in the locations of pinned particles. Array pinning also avoids spatial heterogeneity induced by randomly pinned particles, that may mimic intrinsic dynamical heterogeneity. Some modified random pinning schemes [163, 164] have been used for similar purposes.

Fig. 5.2 compares the effect of pinning on diffusivity for monodisperse and polydisperse systems with array and random pinning at  $\phi = 0.56$ , as an example. It is evident that fluctuations in both particle sizes (polydispersity) and pinned particle positions (random pinning) diminish the liquid-glass transition.



Figure 5.3: Pinning effect on mean-squared displacement  $\langle \Delta r^2(t) \rangle$  and intermediate scattering function  $F_s(q_0, t)$  for monodisperse systems at  $\phi = 0.53$  and  $\phi = 0.57$ . The confining length  $\ell_c$  ranges from infinity down to  $1.39\sigma$  for  $\phi = 0.53$ , and from infinity down to  $2.04\sigma$  for  $\phi = 0.57$ . Dashed lines are fits described in main text.

To expose a static length using pinning, an array of particles are frozen in an equilibrated configuration, while the remaining unpinned particles are allowed to move. For each  $\phi$ , we vary the number of pinned particles  $m^3$  from zero up to the value at which the system is essentially frozen during the simulation. The confining length is related to m as  $\ell_c = \left(\frac{\pi N}{6\phi}\right)^{1/3}/m$ . For each  $\phi$  and m, MSD and  $F_s(q_0, t)$  are averaged over five independent initial configurations and at least five realizations of array pinning. (Since the center of mass of unpinned particles can diffuse due to collisions with pinned particles, all particle positions are calculated with respect to the mean position of the unpinned particles.)

Fig. 5.3 illustrates the pinning effect on MSD and  $F_s(t)$  for  $\phi = 0.53$  and  $\phi = 0.57$ . The array of pinned particles evidently hinder the motions of unpinned particles— the growth of  $\langle \Delta r^2(t) \rangle$  and decay of  $F_s(t)$  become slower with increasing m or decreasing  $\ell_c$ . Moreover, the pinning effect is more pronounced in the more dense system— a smaller value of m is sufficient to freeze the system— consistent with an increasing static length scale. In other words, the glass transition can also be induced by pinning particles in a dense liquid with  $\phi < \phi_g$  or  $T > T_g$ , which opens a new way to study the glass transition [165].



Figure 5.4: Normalized diffusion coefficient  $D(\ell_c, \phi)/D(\infty, \phi)$  and  $\alpha$  relaxation time  $\tau_{\alpha}(\ell_c, \phi)/\tau_{\alpha}(\infty, \phi)$ , for different  $\phi$  and confining length  $\ell_c$ . Raw data with error bars (one standard error) are in gray. Dashed lines are guides for the eye.

At high pinning concentration, our simulation time is unavoidably limited compared to the slow relaxation time. Nonetheless, we can estimate the diffusion coefficient D from the slope of a linear plot of MSD versus time assuming the diffusive region has been reached. Likewise, we can obtain the the alpha relaxation time  $\tau_{\alpha}$  as the time such that  $F_s(q_0, \tau_{\alpha}) = 1/e$  with the final decay fit to a stretched exponential. Since the configuration of unpinned particles is automatically in equilibrium after pinning [163, 166], the measured MSD and  $F_s(q_0, t)$  are correct equilibrium values, i.e., they do not show aging; and the accuracy of estimated Dand  $\tau_{\alpha}$  is only limited by the simulation time. In fact, our values for D and  $\tau_{\alpha}$  are reasonably robust, in that we find since no significant change in our results when we use longer runs at selected state points.

#### 5.3.3 Correlation Lengths From Dynamical Scaling

Having obtained D and  $\tau_{\alpha}$  for an array of values for  $\phi$  and confining length  $\ell_c$ , we can extract static correlation lengths  $\xi_s$  from a dynamic scaling assumption. For

 $\ell_c \gg \xi_s$ , unpinned particles can barely "feel" the presence of pinned particles, and dynamic properties are governed by the static correlation length  $\xi_s$ . As  $\ell_c$  decreases and becomes comparable to  $\xi_s$ , the dynamics crosses over from being governed by  $\xi_s$  to  $\ell_c$ .

Assuming this crossover behavior depends only on the ratio of characteristic lengths  $\ell_c/\xi_s$ , a given dynamic property Q at different  $\phi$  and  $\ell_c$  can be described by a scaling form

$$\frac{Q(\ell_{\rm c};\phi)}{Q(\infty;\phi)} = f\left(\frac{\ell_{\rm c}}{\xi_{\rm s}(\phi)}\right),\tag{5.3}$$

in which Q is either 1/D or  $\tau_{\alpha}$ , and f(x) is a dimensionless scaling function. A master curve can be constructed by horizontally shifting the curves of  $Q(\ell_c; \phi)/Q(\infty; \phi)$ plotted versus  $\log \ell_c$ . Up to an overall prefactor, the static length  $\xi_s(\phi)$  for each  $\phi$ can be determined from the corresponding shift factor.

To construct the master curve without knowing the form of f(x), we define the "smoothness" of a given set of n points as the arc length of its basis spline curve. A better collapse of our data (Fig. 5.4) with fewer twists and turns result in a smaller basis spline arc length. The master curve is obtained by horizontally shifting raw data points and numerically minimizing the arc length with respect to the shift factors ( $\phi_0 = 0.53$  is chosen as reference and left unshifted).

As shown in Fig. 5.4, normalized data for both D and  $\tau_{\alpha}$  collapse onto smooth master curves that span nearly four decades for diffusion coefficients and six decades for  $\alpha$  relaxation time, confirming our scaling assumption (Eq. 5.3). An analogous data collapse  $\tau_{\alpha}$  versus system size  $N^{1/3}$  has been previously reported in systems without pinning, using the static length obtained from the minimum eigenvalue of the Hessian matrix [167]. However, because of the rather weak dependence of  $\tau_{\alpha}$  on system size, the range of  $\tau$  spans less than one decade. We find that the diffusion coefficient and relaxation time become decoupled as the pinning concentration increases, consistent with recent reports [168]. Despite this behavior (related to the breakdown of the Stokes-Einstein relation, see below), we find that the scaling form Eq. 5.3 describes both the diffusion coefficients and relaxation times very well (see Fig. 5.4).

Based on RFOT theory and renormalization group method, Ref. [169] predicts  $\tau_{\alpha}$  with random pinning scales as  $\log \tau \sim 1/(c_{\rm K} - c)$  for high  $T > T_{\rm K}$ , where c is the pinning concentration and  $c_{\rm K}$  the "Kauzmann" concentration at which the



Figure 5.5: (a) Static lengths obtained from master curve construction of diffusion coefficient (triangles) and alpha relaxation time (diamonds) as a function of  $\phi$ ; dashed lines are power law fits. Also included are "Kauzmann" critical lengths (disks) extracted from fitting inspired by AG theory. (b) D and  $\tau_{\alpha}$  versus the static length  $\xi_{\rm s}$  obtained from the corresponding quantity, with  $\xi_{\rm s}^*$  at  $\phi = 0.53$  used as reference.

configurational entropy  $S_c$  vanishes. If we fit the raw data for  $\tau_{\alpha}$  at different  $\phi$  to this form and extract the static length as  $\xi_s \sim 1/c_K^3$ , the results are very close to those from our master curve construction (see Fig. 5.5). However, it is difficult to obtain robust values for  $\xi_s$  by this procedure, since the fitting parameters are so sensitive that we must exclude certain data at high pinning fractions to get reasonable values. In contrast, the master curve covers a wider range of data and is more robust.

As can be seen in Fig. 5.5(a), the static length  $\xi_s$  grows mildly by a factor of two or so over the range of  $\phi$  accessible to our simulations, comparable with previous observations in a wide variety of systems [27, 154, 170, 171]. Our results can be well fit by a power law,

$$\xi_{\rm s} \sim (\phi_{\rm s} - \phi)^{-\nu},\tag{5.4}$$

yielding  $\phi_{\rm s} = 0.593 \pm 0.001$ ,  $\nu = 0.32 \pm 0.01$  for *D*; and  $\phi_{\rm s} = 0.589 \pm 0.001$ ,  $\nu = 0.34 \pm 0.01$  for  $\tau_{\alpha}$ . Although the values for  $\phi_{\rm s}$  are slightly larger than our results for  $\phi_{\rm c}$  obtained from fitting the divergences in *D* and  $\tau_{\alpha}$ , they agree within statistical error. To see the relation between the static length and dynamics, we plot 1/D and  $\tau_{\alpha}$  versus  $\xi_s$  in Fig. 5.5 (b). The results can be fit either by a power-law form,  $Q \sim \xi_s^z$ , or by an activated scaling behavior,  $\log Q \sim k\xi_s^\psi$ , yielding  $z = 10.6 \pm 0.6$ ,  $\psi = 1.2 \pm 0.3$  for 1/D and  $z = 10.5 \pm 0.7$ ,  $\psi = 1.2 \pm 0.2$  for  $\tau_{\alpha}$ .



Figure 5.6: Comparison of static lengths obtained from scaling and master curves, and PTS lengths from configurational overlap. Static lengths are normalized by their values at  $\phi = 0.52$ .

Within the RFOT theory, scaling relations of the form  $\log \tau_{\alpha} \sim \xi_{\rm s}^{\psi}$  and  $\xi_{\rm s} \sim (1/S_{\rm c})^{1/(d-\theta)}$  are expected, where  $S_{\rm c}$  is the configurational entropy and d is the space dimension. While  $\psi \approx 1$  is generally quoted which agrees with our result, the value of exponent  $\theta$  is controversial, varying from 0.3 to 2.3. [16, 70, 83]. Nevertheless, by assuming the Kauzmann volume fraction  $\phi_{\rm K} \sim \phi_s$  and  $S_{\rm c} \sim (\phi_{\rm K} - \phi)^{\beta}$ , with  $\beta = 0.30 \pm 0.04$  approximated from a law-power fit of the  $S_{\rm c}(\phi)$  data in Ref. [33] (which also gives  $\phi(S_{\rm c} = 0) \approx 0.587 \sim \phi_{\rm s}$ ), we estimate  $\theta \approx 2.1$  for hard-sphere systems.

We note that the  $\xi_s$  obtained from D grows more slowly than the length obtained from  $\tau_{\alpha}$ , suggestive of the decoupling of 1/D and  $\tau_{\alpha}$  with increasing  $\phi$  (see Fig. 5.1), signaling the breakdown of the Stokes-Einstein relation. Since this breakdown can be qualitatively understood as the consequence of dynamic heterogeneity—Dis dominated by the mobile particles while  $\tau_{\alpha}$  results from the immobile ones the difference between  $\xi_s$  from D and  $\xi_s$  from  $\tau_{\alpha}$  may also arise from differently weighted averages of a spectrum of static lengths present in the system [66]. Despite the growing discrepancy between 1/D and  $\tau_{\alpha}$  and their corresponding  $\xi_s$ , the proportionality constants k in the relations  $\log 1/D \sim k\xi_s$  and  $\log \tau_{\alpha} \sim k\xi_s$  are nearly identical (assuming the two static length scales coincide at low  $\phi$ ).

We have also applied our methods to bidisperse particles, and compare the static lengths obtained from our scaling and master curves to PTS lengths obtained from configurational overlap. Following Ref. [27], we randomly pinned an equimolar binary mixture of N=2000 particles with a diameter ratio 6:5. We perform standard

event-driven MD for  $\phi = 0.52, 0.55, 0.56, 0.57$  and 0.58 and check that the pressures and diffusion coefficients are consistent with those reported in Ref. [27]. The resulting static lengths is shown in Fig. 5.6 as a function of  $\phi$ , which agree reasonably well with the PTS lengths previously reported. [27]

## 5.4 Conclusion

To conclude, we present a simple way of extracting static lengths based on the response of dynamic properties to an external pinning field. By exploiting a recently developed crystal-avoiding method, we simulate the monodisperse hard-sphere metastable fluids and calculate D and  $\tau_{\alpha}$  in the presence of a periodic array of frozen particles. We find a universal scaling description of dynamic crossover as a function of confining length  $\ell_c$  over the range of  $\phi$  studied. A master curve is constructed by optimizing its "smoothness", from which we extract static lengths  $\xi_s$  for both D and  $\tau_{\alpha}$ , which grow moderately with increasing  $\phi$  as the dynamics slows dramatically. The two  $\xi_s$  obtained for D and  $\tau_{\alpha}$  decouple at higher  $\phi$ , suggesting a distribution of static lengths in different regions of the system. Scaling relations between dynamical quantities and the static lengths of the form  $\tau_{\alpha} \sim \exp(k\xi_s^{\psi})$  and  $\xi_s \sim (\phi_s - \phi)^{1/(d-\theta)}$  with  $\psi \approx 1$  and  $\theta \approx 2$  are consistent with RFOT, but investigations at higher  $\phi$  are needed for more precise values. It would be interesting to apply our method to systems with soft potentials, and compare the results to static lengths obtained by other methods.

# Chapter 6 | Suppression of $T_{g}$ in Polymer Thin Films

Suppression of the glass transition temperature  $T_{\rm g}$  in polymer thin films is of great practical importance and theoretical significance. It is widely believed that such  $T_{\rm g}$  suppression results from enhanced segmental mobility at the free surface. To investigate these effects, we carry out united-atom molecular dynamics simulations on free-standing polystyrene thin films. Care has been taken to ensure consistent behavior between thin films and the bulk. The dilatometric  $T_{\rm g}$  inferred from the density versus temperature shows substantial reduction in thin films compared to the bulk even at high cooling rates. Furthermore, we find that dynamical  $T_{\rm g}$  shifts, obtained by collapsing temperature-dependent short-time dynamical properties onto a master curve, vary with film thickness just like the dilatometric  $T_{\rm g}$ . We apply the same data collapse procedure to dynamics of segments within a given distance from the free surface to obtain the local  $T_{\rm g}(z)$ , which reveals a mobile surface layer of about 4 nm larger than the Kuhn length (~ 1 nm).

## 6.1 Introduction

While the of the nature of the glass and the glass transition in bulk materials remains a subject of intense debate, nano-confinement effects on glass-forming polymer thin films have attracted a great deal of interest in recent years. This interest is largely driven by the importance of glassy thin films in engineering applications ranging from protective coatings to organic photovoltaics, as well as fundamental questions of glassy dynamics such as the origin of non-Arrhenius relaxation behavior, cooperative rearrangements, and dynamical heterogeneity.

Since the first observation of the confinement effect on glass transition temperature  $T_{\rm g}$  in supported polystyrene thin films by Keddie et al, a variety of experiments have shown considerable deviation of  $T_{\rm g}$  in polymer films from the bulk value, when the film thickness is below some tens of nanometers. While the average  $T_{\rm g}$  for supported thin films has been reported either increasing, decreasing or unchanged compared to the bulk depending on polymer chemistry, polymer-substrate interaction and sample preparation [172], there is a general consensus that  $T_{\rm g}$  is lower in free-standing films. This behavior is attributed to a highly mobile layer near the free surface. (One exception is for star-polystyrene thin films, for which the  $T_{\rm g}$  of free surface layer is slightly higher than the bulk probably because of higher packing densities of short-arm star-shaped molecules at the interface [173].)

Another important experimental finding is that the  $T_{\rm g}$  reduction in thin films depends strongly on the cooling rate. Based on ellipsometric measurements, Fakhraai and Forrest showed that for a 6 nm-thick polystyrene film supported by Pt coated SiN substrate, no appreciable suppression of  $T_{\rm g}$  can be observed for cooling rates larger than 90K/min (or 0.6 Hz) [174]. Their results appear to clarify some contradictions in the literature, such that thickness dependence of thin film  $T_{\rm g}$  is weak or even absent in calorimetric measurements with fast cooling rates [175], or dielectric spectroscopy measurements at high frequency [172, 176]. Similar cooling rate dependence of thin film  $T_{\rm g}$  have been observed in DSC measurements [177]. Investigations of dynamics near free surfaces also indicate that enhanced mobility is only observable at very long time scales or low frequencies [178].

In contrast to the extensive experimental literature, there are rather few atomistic MD simulations of the glass transition in polymer thin films, because it is computationally expensive to simulate systems with slow dynamics. Since the longest time accessible in MD simulations (~1 µs) is orders of magnitude smaller than in experiments, one would expect no thickness-dependence of  $T_{\rm g}$  according to Fakhraai and Forrest. Indeed, recent atomistic simulations on supported PS films [179] with a cooling rate of 10K/ns find the average  $T_{\rm g}$  determined from the temperature dependence of density is almost identical to the bulk value for films as thin as 2 nm.

On the other hand, enhanced mobility near a free surface is a common feature in coarse-grained simulations [180–183], atomistic MD simulations [179, 184, 185] and

lattice models [186] of thin films with a free surface. Results from these simulations often predict appreciable suppression of average or local  $T_{\rm g}$ , by extrapolating the segmental relaxation time to experimental time scale (e.g., 100 s) using VFT-like equations. It is unclear whether the disagreements in measured and simulated  $T_{\rm g}$  reduction arise from probing different relaxation processes (such as dipole moment relaxation, segmental mobility and density fluctuations) that are coupled with different characteristic time scales, since the robust correlation for bulk systems between  $T_{\rm g}$  and many dynamical processes may no longer hold for thin films [178, 187].

In addition to the slow  $\alpha$  relaxation, which is thought to involve collective motions by more than one particle, supercooled liquids also exhibit a short-time  $\beta$ relaxation process, which is thought to be related to motions of particles within their cages formed by neighboring particles, and often manifests as the plateau in the time-dependent mean-square displacement. From experimental observations that  $T_{\rm g}$  reduction in thin films is not appreciable at short time scales, one may expect the effect of a free surface on the  $\beta$  relaxation will be weak or even absent. However, contradictory and somewhat confusing results have been reported.

For example, measurements of structural relaxation in supported PMMA films [188] suggest that the free surface effect on the structural relaxation rate, which is possibly related to the  $\beta$  relaxation process, is *stronger* than on the local  $T_{\rm g}$  associated with  $\alpha$  relaxation. Moreover, simulations of freestanding PS film show that while the average  $\beta$  relaxation rate (based on orientational relaxation time of phenyl bonds) is the same for films and the bulk, the  $\beta$  process is *faster* in the center of the film than near the free surface, as opposed to the  $\alpha$  relaxation [185]. From these recent works, the response of  $\alpha$  and  $\beta$  relaxation processes to free surfaces, and the implications for  $T_{\rm g}$  reduction, remains unclear.

In this work, we perform united-atom molecular dynamics simulations on freestanding polystyrene films and investigate the effects of a free surface on thin film  $T_{\rm g}$ , inferred from a variety of film-average and local properties. The dilatometric  $T_{\rm g}$  inferred from film density versus temperature shows a noticeable thickness dependence, with a reduction of about 35 K for a 6 nm thick film— in contrast to the expectation from experiment of no  $T_{\rm g}$  reduction at high cooling rates. For the same cooling rates, we also obtain  $T_{\rm g}$  values by collapsing the temperature dependence of short-time dynamical properties for different films and bulk onto a master curve. The  $T_{\rm g}$  values obtained this way are generally consistent with the dilatometric  $T_{\rm g}$ .

We also extract the *local*  $T_{\rm g}$  from relaxation of monomers and chains at a given distance from the free surface, using a similar master curve approach. A mobile surface layer of about 4 nm with lower  $T_{\rm g}$  is observed, which agrees with the thickness of the mobile surface layer inferred from long-time relaxation in our simulations, as well as some experimental measurements [189, 190]. Our results suggest that while  $T_{\rm g}$  is most commonly associated with the relatively slow dynamics of  $\alpha$  relaxation, suppression of  $T_{\rm g}$  in thin films can also be revealed by short-time dynamics.

#### 6.2 Methods

We perform molecular dynamics simulations on a united-atom model of atactic polystyrene, with each chain consisting of 10 monomers ( $M_{\rm w} = 1040$  g/mol). These chains are quite short compared to most experimental systems. We use short chains to keep the simulation time manageable. We have checked for chain length dependence by simulating 20-mer systems for a few selected film thicknesses; we find results consistent with our 10-mer simulations. Each thin film system contains 384, 300, 192, 140, 110 or 80 chains, corresponding to a film thickness of approximately 28 nm, 22 nm, 14 nm, 10 nm, 8 nm or 6 nm at 500 K with box area fixed to  $5 \times 5$ nm<sup>2</sup>. The atactic chains are constructed by duplicating a single isotactic chain, turning off the improper dihedral potential that stabilizes the tetrahedral backbone carbon and equilibrating at high temperatures to randomize the tacticity, and then restoring the dihedral potential. Periodic boundary conditions are applied only in the x and y directions for free-standing films. Bulk systems consisting of 192 chains are also prepared with full periodic boundary conditions in all directions. To improve statistics, results are averaged over 5 to 20 independent runs depending on system size.

Thin film systems are equilibrated in the NVT ensemble at 500K until monomers have diffused farther than the average end-to-end distance, and then quenched from 500K to 200 K at a cooling rate of 5 K/ns. Bulk systems are equilibrated and quenched in the same way, except that the semi-isotropic NPT ensemble is used, with varying system dimension and zero pressure in the z direction only. The bulk system dimensions are fixed in x and y for consistency with the thin films, for which fixed x and y dimensions are necessary to keep the free surface from shrinking in response to surface tension. [173] Compared to cooling results from full 3d *NPT* simulations, we find the bulk densities are identical in the melt region; in the glassy state, the density is slightly higher in 3d *NPT* systems, since the system can contract laterally in response to the tensile stress caused by cooling, which the system with fixed transverse dimensions cannot do.

All simulations are carried out using the GROMACS package [191] with integration time step of 2 fs. Stochastic velocity rescaling thermostat ( $\tau_{\rm t} = 0.2$  ps) and the Berendsen barostat ( $\tau_{\rm p} = 0.5$  ps) are chosen for *NVT* and *NPT* ensembles. The united-atom force field we use for PS is adapted from the TraPPE-UA model, which has been shown to produce polymeric properties in good agreement with experimental values for simple polymer systems (e.g., PE [192] and iPP [193]).

However, it is found that for PS the UA model predicts a much faster dynamics (~ 40 times larger) compared to all-atom (AA) PS model [194], probably because of a relatively weak dihedral potential along the aliphatic backbone in the presence of phenyl ring [195]. To remedy this, we reparameterize the dihedral potential along the aliphatic backbone, as well as the improper dihedral used to maintain the sp<sup>3</sup> stereochemical configuration of the CH group, to match the corresponding dihedral distributions obtained from the AA model, using the standard Boltzmann inversion method (see Appendix C for the modified force field). The resulting modified UA PS model leads to about 10 times faster diffusivity than the AA model for all temperatures— which is fortunate, since the AA model dynamics is about 4.6 times slower than experiments [196].

In addition, the modified UA force field gives a slightly smaller bulk density than the original TraPPE UA model, only about 4% higher than the experimental values for PS with  $M_{\rm w} \sim 910$  g/mol at 0 MPa between 400 K and 500 K. This good agreement for the density contrasts with the relatively large deviations given by the AA model (density 7% too high), as well as another widely used UA model (18% too high) proposed by Lyulin et al [197, 198]. As a result, we do not need to boost the external pressure to match the experimental density as in previous works, [179, 197] which anyway is not possible for simulating films exposed to vacuum.

Usually, simulations use cutoff LJ interactions, and apply standard "dispersion corrections" to add back the average attractive energy of distant monomers. These

corrections contribute to the cohesive energy, and increase the density at a given pressure. (We included the standard dispersion correction for the benchmarking bulk simulations discussed above.) This approach works well for homogeneous 3d periodic systems. However, for systems with interfaces, computing these corrections is more involved. One must consider the actual configuration during the MD run and use some special treatments [199, 200]. Unfortunately, this nonuniform long range correction is not currently implemented in the GROMACS package.

To make a consistent comparison between the bulk and thin films, we turn off the dispersion correction and use a rather large cutoff distance of 1.8 nm for both bulk systems and thin films. While the bulk density without the long-range correction decreases by less than 1%, a consistent density value is now reached in the center of the film for all film thickness studied. We note that the density match is crucial for a proper comparison of dynamics between thin films and the bulk. For example, in a recent atomistic simulation study of supported PS films [184], the segmental dynamics of the middle layers of a rather thick film (14 nm) is noticeably faster than the corresponding bulk system. In contrast, we find in our simulations with the dispersion correction turned off that the segmental relaxation time of the middle layer in a 14 nm film is the same as the bulk.

Another issue we have encountered is that a free-standing film tends to develop spurious shear modes along the z direction, which are more pronounced in thick films near the free surfaces. This is probably due to the lack of sufficient friction in the xy plane, as the transverse area is anomalously small compared to the film thickness to keep the overall system volume manageable (see Appendix C for details). A closer examination reveals that particles in each layer tend to "drift" together, with their center of mass moving like a random walk. This shear-like motion cannot be corrected by removal of the center of mass motion of the entire system. To minimize this finite-size effect without increasing the box area, we subtract the lateral center of mass motion in each layer before analyzing the local dynamics.

For bulk systems, this shear-like motion is largely inhibited by the full periodic boundary conditions in a cubical box. However, small fluctuations of the center of mass do exist in each layer, which scales approximately with the number of particles in the layer N as  $\sqrt{N}$ . To make a consistent comparison between thin films and bulk systems, we apply the same corrections to bulk samples as for thin films. In practice, we divide the system into a number of layers of thickness about 0.7 nm, which is thin enough to subtract the average shear-like motion in each layer while still thick enough to containing plenty of particles for good statistics. We note that this artifact does not affect the measurement of translation-invariant properties, such as bond rotational dynamics.

#### 6.3 Results

## 6.3.1 $T_{g}$ From Temperature Dependence of Density

One way the glass transition reveals itself is a relatively sharp decrease in the thermal expansivity as the system solidifies. To observe this in simulation, we begin by obtaining the average density of a thin film, evaluated between two polymervacuum interfaces. To locate the interfaces, we fit the film density profile to an error function,

$$\rho(z) = \rho_{\rm b}/2 \left(1 + \operatorname{erf}\left((z - z_0)/\sigma\right)\right) \tag{6.1}$$

where  $z_0$  is the position of an interface,  $\rho_b$  is the plateau density well inside the film, and  $\sigma$  characterizes the interfacial width. This expression well describes the density profiles, as shown in Figure 6.1 for selected film thicknesses equilibrated at 500 K. The width of the interface is about 1 nm, which is expected to decrease at lower temperature.

We obtain the average density  $\overline{\rho}$  by averaging the density profile between the two free surfaces, defined by the inflection points of the profile (dashed lines in Figure 6.1). Also shown in Figure 6.1 is the bulk density at 500 K, which agrees with the plateau density  $\rho_{\rm b}$  of thin films. (This agreement depends on turning off the long-range corrections in the bulk simulations, as discussed above.)

It is also interesting to define an interior density  $\rho_0$  that characterizes the middle region of the film. Naively,  $\rho_0$  should be the same as the plateau density  $\rho_p$  from the fit. However, the error function profile may not fit well for non-equilibrium systems, as a result of faster aging near the free surface versus the middle of the film [201]. To avoid this potential problem, we define the interior density  $\rho_0$  as the average over the middle region in the thin film 1.5 nm away from each free surface, which is expected to give the bulk density for systems in equilibrium, given that the width of free surface is about 1 nm.



Figure 6.1: Snapshots of the bulk and thin films with selected thicknesses at 500 K (top) and the corresponding density profiles as a function of z position (bottom). Solid curves are fits Eq. 6.1). Film thickness h is defined as the distance between two free surfaces indicated by dashed lines (inflection point of density profile).

We perform the density calculation for each configuration collected every 40 ps during the cooling procedure. As shown in Figure 6.2(a), the average density for thin films is smaller than the bulk, and decreases with decreasing film thickness. This is simply a result of the contribution of the less-dense interfacial region, which is a larger fraction of a thinner film.

In contrast, the interior densities are essentially the same for all films and


Figure 6.2: (a) Average density  $\overline{\rho}$  and (b) interior density  $\rho_0$  as a function of temperature for different systems. The solid are nonlinear fits to Eq. (6.2).

the bulk in the liquid regime (T > 400 K) above the glass transition. In the glassy regime, the interior density of the thickest film is very close the the bulk, but *increases* systematically with *decreasing* film thickness (see Figure 6.2(b)). It appears that the interior of a thin film ages faster and thus becomes more dense, because of the nearby free surface. This observation suggests non-local effects of the free surface on dynamics that extends more than 1.5 nm into the interior.

In principle, we could probe the dynamical length scale over which the free surface accelerates aging within the film, by the depth to which the non-equilibrium local density is perturbed by the free surface. However, large spatial fluctuations and insufficient sampling of local density at low temperatures make accurate measurement during the cooling process difficult. Instead, we investigate the length scale of enhanced dynamics directly from short-time local dynamical properties, as discussed in the following section.

We determine the  $T_{\rm g}$  values of thin films and the bulk by fitting the density versus temperature to a function that smoothly transitions from a constant thermal expansivity in the glass to a higher value in the liquid. We use the following empirical form [202],

$$\rho(T) = w \left(\frac{M-G}{2}\right) \ln \left[\cosh\left(\frac{T-T_{\rm g}}{w}\right)\right] + (T-T_{\rm g}) \left(\frac{M+G}{2}\right) + c \qquad (6.2)$$

where w is the width of the transition, M and G are the slopes of melt and glass regions, and c is the density at  $T_{\rm g}$ . If we fit the data with w as free parameter, its value ranges from 40 to 100 K for different films. This is a much broader glass transition than seen in experiments, where w ranges from 2 to 5 K. [202, 203] This increased transition width may be due to smaller fragility at the relatively high  $T_{\rm g}$  probed in simulations with high cooling rate. In practice, we find that fixing the transition width w = 80 K yields good fitting results for thin films and the bulk, as shown in Figure 6.2.

We emphasize that the  $T_{\rm g}$  value is rather sensitive to the temperature range over which the fit is performed. It is important to ensure that fully developed glassy and melt regions are included in the fit. For example, fitting only the data from 300 K to 500 K for the thinnest films, where the system still remains partially liquid-like, would lead to a narrower transition, larger glassy thermal expansivity and hence higher  $T_{\rm g}$  value. Moreover, in the that temperature range, different choices of wmay vary  $T_{\rm g}$  considerably without significantly changing the fit quality. With these caveats in mind, we can obtain the thickness dependence of  $T_{\rm g}$  from the density versus temperature in simulations, in the same way as for typical dilatometric measurements.

Figure 6.3 shows dilatometric  $T_{\rm g}$  values obtained as a function of film thickness, from analyzing both the average density and the interior density of the films. We find the dilatometric  $T_{\rm g}$  from average density decreases substantially with decreasing film thickness, varying roughly as  $\Delta T_{\rm g} \sim 1/h$ . This 1/h dependence reflects the decreasing contribution to the average density of a mobile surface layer with low  $T_{\rm g}$ and roughly fixed thickness, to an increasingly thick film with essentially bulk-like properties.

In contrast, the  $T_{\rm g}$  reduction of the interior region is weaker than that of the whole film, and only substantially reduced for thinner films, because the outermost 1.5 nm of material has been eliminated from the average. Evidently some near-surface material deeper than 1.5 nm is still more mobile, with a lower  $T_{\rm g}$  than the bulk value, so that the dilatometric  $T_{\rm g}$  from the interior density still shows a modest decrease for the thinnest films. Qualitatively, this behavior is consistent with the relatively weak thickness dependence of the interior density versus temperature of Figure 6.2(b). By eliminating more surface material, e.g., the outermost 3.0 nm from each free surface, we find the  $T_{\rm g}$  of the middle layer becomes essentially the same as the bulk  $T_{\rm g}$  within the error bars, independent of the film thickness (no middle layer for the 6-nm film), as shown in Figure 6.3.

In short, we observe a dilatometric  $T_{\rm g}$  reduction of about 20 K and 36 K, respectively, for the interior region and the whole film of 6 nm. This is in contrast



Figure 6.3: Film thickness dependence of  $T_{\rm g}$  inferred from the change in the density. Different parts of thin films are considered, i.e., 0.0 nm (average density), 1.5 nm (interior density) and 3.0 nm from the two free surfaces. The solid lines are fits of data to  $\Delta T_{\rm g}(h) \sim 1/h$  and the dashed line corresponds to the bulk value. The error bars are calculated based on the standard errors of corresponding fits weighted by measurement errors.

to previous simulation results [179] and experimental predictions [174] for supported films on a neutral substrate, that no appreciable  $T_{\rm g}$  reduction can be observed at high cooling rates. Even if we take into account that the  $T_{\rm g}$  reduction in a supported film is about half as large as that of a freestanding film of same thickness, a  $T_{\rm g}$ reduction of about 10 K to 18 K in a 6-nm supported PS film is still significantly larger than one would expect based on the experimental value of 10 K for the same film thickness but with a cooling rate 12 decades slower.

On the other hand, we note that the magnitude of  $T_{\rm g}$  reduction we find is *smaller* than the experimental values for freestanding PS films obtained from ellipsometry and Brillouin light scattering (BLS) techniques [204], e.g., 70K for a 20-nm film. It is possible that this discrepancy is due to the different time scales probed in simulation ( $t \sim 0.1$  ns) and in experiments ( $t \sim 1$  s), such that the cooperative  $\alpha$  relaxation at long times may have additional contribution to  $T_{\rm g}$  reduction in thin films aside from the local short-time  $\beta$  relaxation. Interestingly, the thickness dependence of the  $T_{\rm g}$  reduction appears much closer to that determined from direct measurement of probe reorientation in PS films [189], e.g., 28 K for a 14-nm film.

We emphasize that our modified force field can reproduce the correct bulk  $T_{\rm g}$ 

rather quantitatively, suggesting that our united atom simulations are a reasonable representation of real PS. We note that our simulated bulk glass transition temperature  $T_{\rm g}^{\rm bulk} = 402$  K is comparable to previous simulation results for similar PS systems [179, 185]— and much higher than the nominal experimental  $T_{\rm g}$  of 374 K. But to compare our  $T_{\rm g}$  with experiment, we must account for the effects of our very short chains and very high cooling rate.

On the one hand,  $T_{\rm g}$  for low  $M_{\rm w} = 10^3$  PS is reduced by about 88 K, estimated from the extrapolation of experimental data using the Fox-Flory equation [205],  $T_{\rm g}(M_{\rm n}) = T_{\rm g}^{\infty} - K/M_{\rm n}$ , with  $K = 8.8 \times 10^4$  K g/mol. On the other hand, the fast cooling rate  $\gamma = 5 \times 10^9$  K/s in the simulation leads to an increase of  $T_{\rm g}$  by approximately 108 K, compared to a typical experimental cooling rate of about 1 K/s, according to the Vogel–Fulcher–Tammann–Hesse (VFTH) equation [206], log  $\gamma = A - B/(T_{\rm g} - T_0)$ , with A = 13.5, B = 570 K and  $T_0 = 333$  K. Given the typical experimental  $T_{\rm g}$  of about 374 K for high  $M_{\rm w}$  PS at small cooling rates [203, 205–207], the expected  $T_{\rm g}$  at simulation conditions is estimated as 394 K, in reasonable agreement with the simulation result of 402 K. Such corrections are not yet routinely applied in simulations of glassy polymers, but have been previously discussed for PS [208] and other polymer systems [209, 210].

### 6.3.2 $T_{\rm g}$ From Short-Time Dynamics

To explore the connection between  $T_{\rm g}$  and dynamics in film films, we measure different short-time dynamical properties for the same cooling runs and find the shifts  $T_{\rm g}$  from dynamical scaling. In brief, we find that a given short-time dynamical property versus temperature for different films and bulk samples collapses onto a master curve, after shifting the temperatures by an amount that depends on film thickness. From the temperature shifts we determine the suppression of  $T_{\rm g}$  relative to the bulk as displayed in Fig. 6.4, which shows similar thickness dependence as the dilatometric  $T_{\rm g}$  obtained above.

Now we describe in more detail what short-time dynamical properties we use to extract  $T_{\rm g}$  shifts versus film thickness, how those data are analyzed, and how the master curves are constructed. The dynamical property we examine first is the lateral monomer mean-square displacement (MSD), i.e., how far monomers can diffuse laterally in a given short time. As mentioned above, the effect of spurious



Figure 6.4: Film thickness dependence of  $T_{\rm g}$  obtained from data collapse of different short-time dynamical properties: backbone mean-square angular displacement (MSAD), monomer and chain center of mass mean-square displacement (MSD). The solid lines are fits to  $\Delta T_{\rm g}(h) \sim 1/h$ . Error bars are smaller than the symbols.

shear modes must be eliminated before measuring the monomer MSD. In Figure 6.5, we show both raw and corrected monomer MSD as a function of time for a 14 nm-thick film and the bulk, at T = 500 K and 400 K. We emphasize that although the effect of the shear modes on average MSD appears to be modest, it can significantly alter the apparent local dynamics in films (see Appendix C for details).

To extract a distance from observations of monomer MSD, we must choose an appropriate observation time  $t^*$ . Three dynamical regimes for an unentangled polymer melt can be identified for the monomer MSD: the initial ballistic regime with  $\langle r^2(t) \rangle \sim t^2$ , an intermediate subdiffusive regime with  $\langle r^2(t) \rangle \sim t^{0.66}$  corresponding to the Rouse-like motion of monomers within a chain, and the long-time diffusive regime with  $\langle r^2(t) \rangle \sim t$  as monomers diffuse farther than the chain end-to-end distance.

We choose an observation time  $t^*$  of 200 ps, which corresponds to monomer displacements of less than one monomer diameter, within the subdiffusive regime of chain dynamics over the temperature range of interest (see Figure 6.5). The meansquared displacement of monomers  $\langle r^2(t^*) \rangle$  are calculated for different starting times or, equivalently, different temperatures, along the cooling trajectory. The data are finally averaged over a short time interval of 1 ns to improve the statistics. We emphasize that our results for  $T_g$  shifts are insensitive to the choice of observation



Figure 6.5: Mean-square displacement of monomer center of mass as a function of time for a 14-nm thick film (black lines) and bulk (red lines), at 500 K and 400 K, before (dashed lines) and after (solid lines) removing the spurious shear mode described in the main text. The dashed lines represent the end-to-end distance  $R_{\rm ee} \approx 16.7$  Å and the average diameter of united atoms  $\sigma \approx 4.3$  Å, which is also close to a monomer size.

time  $t^*$ , over a wide range of short times from 100 to 400 ps, as discussed below.

Previous simulation studies [185,210,211] have estimated  $T_{\rm g}$  from the intersection of the melt- and glassy-state temperature dependences of short-time MSD. (This approach is similar to the way dilatometric  $T_{\rm g}$  is obtained from the intersection of asymptotic tangents to the density versus temperature curve.) However, it is difficult to locate precisely the "kink" in the temperature dependence of monomer MSD, as the transition between melt and glassy state is quite smooth (see Figure 6.6(a)).

Instead, we find that the temperature dependences of  $\langle r^2(t^*) \rangle$  for both thin films and the bulk follow the same functional form upon shifting the temperature by a thickness-dependent factor  $\Delta T(h)$ , which is directly related to  $T_{\rm g}$  reduction. To construct the master curve in a systematic way, we first fit the *T*-dependent  $\langle r^2(t^*) \rangle$  for the bulk system to a sixth-order polynomial g(T), and then obtain the shift factor  $\Delta T$  for each film thickness by fitting the *T*-dependent data to  $g(T + \Delta T)$ . Since the polynomial fit becomes significantly worse for T < 200 K or T > 500 K, we fit the thin film data lying within the temperature range so that 200 K  $< T + \Delta T < 500$  K by iteration.

As shown in the inset of Figure 6.6(a), the data collapse is excellent for all



Figure 6.6: Temperature dependence of average dynamical properties at  $t^* = 200$ ps for bulk and films of different thicknesses. (a) Mean-square displacement of monomer center of mass. (b) Mean-square angular displacement of CH<sub>2</sub>-CH<sub>2</sub> backbones. (c) Mean-square displacement of chain center of mass. Insets: Master curve of corresponding quantity as a function of temperature shifted by  $\Delta T(h)$ 

thin films and the bulk system. The resulting  $T_{\rm g}(h) - T_{\rm g}^{\rm bulk}$  varies strongly with film thickness as shown in Figure 6.4. These results agree quantitatively with the  $T_{\rm g}$  reduction inferred from the density versus temperature (see Figure 6.3). We note that this master curve construction method is more robust in obtaining  $T_{\rm g}$ reduction, as compared to fitting the temperature dependence of density, which is sensitive to the fitting procedure as discussed previously.

To investigate effect of the observation time  $t^*$  on our results, we vary  $t^*$  from 40 ps to 400 ps and perform the same data collapse procedure to obtain  $\Delta T_g$ . Note that the monomer MSD is always in the subdiffusive regime for this range of time at  $T \leq 500$  K, but monomers do become diffusive at higher T. We find that the data collapse is equally good for all  $t^*$  values, although the master curves do have different shapes for different  $t^*$ . The  $\Delta T_g$  values for different film thicknesses depend only weakly on  $t^*$ , as shown in Figure 6.7.

This insensitivity of  $\Delta T_{\rm g}$  to the choice of  $t^*$  not only demonstrates that our method is robust for obtaining  $T_{\rm g}$  in thin films, but suggests that a film of thickness h at temperature T looks dynamically the same as the bulk at higher temperature  $T + \Delta T_{\rm g}(h)$ , at least in the subdiffusive region. Indeed, recent bead-spring chain simulations of supported [212] and free-standing films [201] reveal similar dynamical behavior for films and the bulk at the same reduced temperature, i.e., intermediatetime monomer MSD versus  $T - T_{\rm c}$ , where  $T_{\rm c}$  is the mode-coupling theory (MCT) glass transition temperature obtained from a power law fit of relaxation time and



Figure 6.7: Average  $\Delta T_{\rm g}$  obtained from data collapse of monomer MSD observed at different time  $t^*$  for various film thicknesses.

the aging rate versus  $T - T_{\rm g}$ .

Monomer MSD is not the only dynamical property we can use to extract  $T_{\rm g}$ shifts from short-time dynamics. We perform the same data collapse method for other dynamical properties, including bond orientation dynamics and chain center of mass motion, and obtain corresponding  $\Delta T_{\rm g}$  values. In Figure 6.6(b) and (c), we show the original data and the master curves for mean-square angular displacement (MSAD) of backbones and the MSD of chain center of mass, for  $t^* = 200$  ps. The data collapse is very good for both quantities. The angular displacement for a given backbone vector  $\vec{v}_i$ , which connects two consecutive aliphatic CH<sub>2</sub> atoms separated by one CH atom, is calculated as  $\Delta \theta_i(t) = \arccos(\vec{v}_i(0) \cdot \vec{v}_i(t)/|\vec{v}_i(0))|^2)$ , By definition,  $\Delta \theta_i$  is bounded to the maximum value of  $\pi$  at long times. However, within the observation time  $t^* = 200$  ps, we observe no bond rotates more than 180° at the highest temperature 500 K.

The  $T_{\rm g}$  reduction obtained from backbone rotational motions (mean-square angular displacement) and chain center of mass translational motions (mean-square displacement) as a function of film thickness also are shown in Figure 6.4. In comparison to the  $\Delta T_{\rm g}$  previously obtained from monomer MSD, they agree with each other and also with the dilatometric  $T_{\rm g}$ , which further suggests that substantial  $T_{\rm g}$  reduction can be revealed by short-time measurements. We notice that the suppression is relatively weaker for the  $T_{\rm g}$  determined from bond orientational motions than from monomer MSD, while the chain translational motions shows



Figure 6.8: Same as Figure 6.6 except for *local* dynamical properties ( $t^* = 200$  ps) at different distances d from the free surface in a 14-nm film. Insets: Master curves of each dynamical property as a function of temperature shifted by  $\Delta T(d)$ .

stronger  $T_{\rm g}$  suppression. One may ask whether the difference in the average  $T_{\rm g}$  reduction for different dynamical properties arises from their distinct responses to the free surface, or from a differently weighted average of essentially the same local response.

To this end, we measure the *local* dynamics within a film as a function of the distance from the free surface, and apply the same data collapse approach to obtain the local  $T_{\rm g}$  reduction. We divide the system into several "reporting layers" about 0.7 nm thick, each containing a subset of the centers of mass of the monomers, backbones or chains. Objects in each layer are selected based on their average position during  $t^* = 200$  ps, which is sufficiently small so that monomers diffuse less than the layer thickness even at the highest temperature of 500 K. (Note that the position of the outermost "surface" layer defined this way will not coincide exactly with the PS-vacuum interface defined by inflection point in the density profile.)

As depicted in Figure 6.8, the layer-resolved monomer MSD, backbone MSAD and chain MSD are enhanced near the free surface compared to the bulk values. Overall, we find a good collapse of each dynamical property for different layers in the film of 14 nm. (For the outermost layer about 0.5 nm from the free surface, the low temperature dynamics slightly deviates from the master curve, probably because of a smaller density than the inner layers (see Figure 6.1), so the quantitative results for this layer should be interpreted with caution.)

Figure 6.9 shows results for the local  $T_{\rm g}(d)$  shift versus distance from the free surface d, obtained from data collapse of local short-time dynamics of the monomer MSD, backbone MASD, and chain MSD. Remarkably, the results are essentially



Figure 6.9: Suppression of local  $T_{\rm g}(d)$  as a function of the distance from the free surface d obtained from data collapse of different dynamical properties. The profile has been symmetrized over two halves of the film. Solid line is a guide to the eye.

identical for the different dynamical properties, in contrast to the average  $T_{\rm g}$  reduction shown in Figure 6.4. We argue that the local  $T_{\rm g}$  reduction might be more fundamental than the average  $T_{\rm g}$  reduction, and the seemingly inconsistent results can be reconciled as follows.

Given the successful collapse of local dynamics, the *T*-dependence of some local dynamical property can be described as  $\phi_i = g(T + \Delta T_i)$  for each layer *i*, with g(T) the functional form for the master curve. The average dynamics is then obtained by averaging over the local dynamics weighed by the mass of each layer  $\overline{\phi} = \langle \phi_i \rangle = \langle g(T + \Delta T_i) \rangle \approx g(T + \Delta \overline{T})$ , where the last approximation is suggested by the successful data collapse of average dynamics. It is thus clear that while the local  $T_g$  reduction is independent of the type of dynamical measurement, the data collapse of an average dynamical property might only be a good approximation so that the average  $T_g$  reduction obtained from the shift factor  $\Delta \overline{T}$  depends on the specific form of g(T).

The local  $T_{\rm g}$  profile of Figure 6.9 reveals a mobile surface layer of about 4 nm thick, beyond which bulk-like behavior is recovered in the middle of the film. This non-local effect of confinement on dynamics is consistent with the previous observation that the interior density can be affected by the free surface much farther away than the distance (~ 1 nm) at which the bulk density is recovered in an equilibrium system. As an aside, we find that results based on rotational dynamics of side groups, characterized by the vector between the C atom attached to the

backbone and the para-CH atom on the phenyl ring, are quantitatively similar to those based on the rotations of backbone tangents.

## 6.4 Long-Time Dynamics and Free Surface Size

To this point, all our local  $T_{\rm g}$  values, and the inferred range of influence of the free surface, have been based on short-time dynamical properties. Alternatively, we can investigate the range of influence of the free surface by analyzing the segmental autocorrelation function decay time, typically of order 1–1000 ns. We cannot extract isothermal autocorrelation functions at such long times from our rapid cooling scans. Instead, we fully equilibrate 14 nm films and bulk systems at different temperatures ranging from 500 K to 400 K, and then calculate the segmental relaxation time  $\tau$ . Here  $\tau$  is defined as the time when the autocorrelation function of the second Legendre polynomial  $P_2(t) = (3/2) \langle \cos^2 \theta(t) \rangle - 1/2$  decays to 1/e, where  $\theta(t)$  is the backbone angular displacement defined above.

Figure 6.10(a) displays an example of the autocorrelation function of local  $P_2(t)$  at different distances from the free surface for a 14 nm film at 400 K. These autocorrelation functions are well fit by the Kohlrausch-Williams-Watts (KWW) stretched exponential. We the obtain the local segmental relaxation time as a function of position in the film for each temperature, as shown in Figure 6.10(b). In the temperature range studied, the extent to which the long-time dynamics is perturbed by the free surface (3–5 nm) is similar to the range over which the local  $T_g$  obtained from short-time dynamics is perturbed. This 3–5 nm length scale is also consistent with the experimental value of 4–5 nm at 370K deduced from probe reorientation [189] and nanoparticle embedding measurements [190].

Moreover, we notice a moderate increase of the size of the mobile surface layer with decreasing T. According to the thermodynamic framework of glass transition, such as Adam-Gibbs (AG) theory [69] and random first-order transition (RFOT) theory [66,70]. the growing relaxation time below the activation temperature can be related to some growing correlation length  $\xi$  as  $\tau \sim \exp(\xi^{\psi}/T)$ , where the exponent  $\psi = d_{\rm f}$  in the AG theory and  $\psi = d_{\rm f} - \theta$  in the RFOT theory to recover the VFT form, and  $d_{\rm f}$  is the fractal dimension of the CRR (cooperatively-rearranging regions) or "mosaic droplet" for each scenario [16]. It has been proposed that the domain size affected by confinement by a free surface or fixed wall, might be controlled by



Figure 6.10: (a) Layer-resolved autocorrelation function of  $P_2$  for a 14-nm thin film at 400 K. The solid lines are to the KWW equation. (b) Local segmental relaxation time  $\tau$  versus distance from the free surface at different temperatures: 500 K, 480 K, 460 K, 440 K, 430K, 420 K, 410 K and 400 K (from lower to upper). Solid curves are fits to an error function; dashed lines are bulk values. The profile has been symmetrized over two halves of the film. (c) Bulk relaxation time  $\tau/\tau_0$  versus 1/T and  $(\xi/T)$ , normalized by values at  $T_0 = 500$  K. Solid line is a VFT fit while dashed line is a linear fit. Inset: correlation length versus temperature.

the cooperatively rearranging region (CRR) in the AG scenario [201] or the mosaic length scale.

To extract the size of the mobile surface layer  $\xi$ , we fit the local relaxation time profile to an error function  $\log \tau(d) = c_1 + c_2 \operatorname{erf}(d/\xi)$  (see Figure 6.10(b)), which we find gives better results for our data than the tanh function [201] or exponential form [213] used previously by other groups. From the inset of Figure 6.10(c), it is evident that the length scale  $\xi$  increases moderately with decreasing temperature, consistent with simulation results on bead-spring chains [181, 201].

Figure 6.10(c) displays a semi-log plot of the bulk relaxation time  $\tau$  as a function of inverse temperature 1/T, normalized by their values at  $T_0 = 500$  K. The non-Arrhenius behavior shown in the figure is typical for fragile glass formers, indicating an increasing activation energy barrier. We plot the same data but as a function of  $\xi(T)/T$ , and find a reasonably good linear relationship between the logarithm of the bulk relaxation time  $\log(\tau)$  and  $\xi(T)/T$ , This suggests a fractal dimension  $d_f \approx 1$  in the AG theory corresponding to string-like clusters, or  $\psi \approx 1$  in the RFOT scenario, consistent with values obtained for different systems using different methods [16, 83, 149, 171]. Clearly, data at lower temperature regime and with better statistics is needed before we can draw a firm conclusion as to the value of exponent, which is unfortunately challenging for atomistic simulations.

## 6.5 Conclusion

In this work, we perform extensive atomistic MD simulations on free-standing polystyrene films to investigate the effect of free surfaces on static and dynamical properties and hence on the glass transition temperature  $T_{\rm g}$ . We modify the TraPPE-UA potential to match the chain backbone dihedral distribution obtained from all-atom simulations, which leads to simulated bulk density and segmental dynamics close to the experimental values. Care has been taken in simulations to ensure consistent results between films and bulk. Despite the high cooling rate and short time scales probed, we find substantial suppression of the dilatometric  $T_{\rm g}$  in thin films inferred from the average film density versus temperature. The dilatometric  $T_{\rm g}$  reduction is much less when we measure only the density in the interior of the film, suggesting that the mobile surface layer is largely responsible for the  $T_{\rm g}$  reduction obtained from the average film density. We also extract both average and local  $T_{\rm g}$  values from dynamical properties. We find the temperature dependence of short-time dynamics, including monomer MSD, chain MSD and bond MSAD, collapses onto a master curve for different films and the bulk by shifting the temperature for each film thickness. The  $T_{\rm g}$  shifts obtained in this way from short-time dynamics averaged over the whole film exhibits similar film thickness dependence as the dilatometric  $T_{\rm g}$  from average density. Following the same procedure, we study the *local* dynamics of each layer in the film at short times, and obtain the associated local  $T_{\rm g}$  shift. The local  $T_{\rm g}$  reduction is as large as 80 K near the free surface, vanishes at a distance about 4 nm from the free surface, and is the same for all dynamical properties we investigated.

We also show a qualitative agreement between the mobile surface layer thickness based on local  $T_{\rm g}$  inferred from short-time dynamics, and from the range  $\xi$  of depth dependence of backbone orientational relaxation times. The latter-defined dynamical length  $\xi$  increases moderately with decreasing T, and scales with the bulk relaxation time as  $\log(\tau) \sim \xi/T$ , broadly consistent with both the AG and RFOT scenarios. Our work suggests that short-time measurements of static and dynamical properties consistently reveal appreciable free surface effects on both average and local  $T_{\rm g}$  in thin films.

# Chapter 7 | Future Work

## 7.1 Generalization of the T1-Activity Analysis

In Chapter 3, we explored the relation between T1-activity and dynamics in the simplest glass former, monodisperse hard spheres, with the aid of crystal avoiding method. Our main finding is that the T1-inactive particles percolate the whole system at the glass transition volume fraction. It is nature to ask whether this purely geometrical criterion is also applicable to other systems. such as polydisperse hard spheres and soft spheres.

Given that the T1-activity is defined based on the possibility of neighbor rearrangement for a given particle with all the others fixed, a general way to compute the T1-activity for any system is to actually run the MD simulation for a single particle with different initial velocities drawn from Maxwell-Boltzmann distribution while fixing all the other particles and observe whether neighbor rearrangement occurs for that particle. The trade-off for this generalization is a higher computational cost. For certain systems, such as polydisperse hard spheres and monodisperse soft spheres, however, it is possible to perform the purely geometrical analysis for T1-activity.

### 7.1.1 Polydisperse Hard Spheres

For polydisperse hard spheres, the same analysis of T1-activity can be applied, except that a new definition of Voronoi tessellation is needed to account for the size difference. One choice is the so-called radical plane construction. In this method,



Figure 7.1: Schematic of the radical plane construction.

the distance h between a point at  $\mathbf{x}$ , and a sphere at  $\mathbf{s}_i$  of radius  $r_i$  is defined as

$$h^{2} = \|\mathbf{x} - \mathbf{s}_{i}\|^{2} - r_{i}^{2}.$$
(7.1)

A set of points equidistant from two spheres i and j then defines a radical plane (see Figure 7.1), from which the familiar Voronoi tessellation can be performed, and geometrical properties such as free volume can be computed as before [115].

#### 7.1.2 WCA Soft Spheres

For point-like particles interacting via a soft potential, particle sizes are rigorously defined so that the free volume computation could be problematic. In this case, we may define the free volume relative to an energy level— the amount of energy available for a particle, which can be chosen as its current potential energy plus a kinetic energy boost of order  $kT_{\rm B}$ . The cusps of free volume, whereby we check if a particle can gain or lose a neighbor in hard spheres, can thus be defined for soft spheres as follows the furthest place a particle can move toward the plane of each triangle of nearest-neighbors along the path with minimized potential energy. In this way, the T1-activity can be defined for any form of potential.

Alternatively, a simpler method can be applied to monodisperse WCA soft sphere, in which we assign a single effective hard-sphere diameter for all particles



Figure 7.2: (a) Diffusion coefficients of soft spheres with varying densities and (b) n values. Power law fits are shown in solid lines.

based on the mean collision energy and perform the same T1-analysis as if they are hard spheres. Certainly, this will lead to some overlaps between particles and particles may left no cavity after being removed. In this case, we may simply assign those particles as T1-inactive.

For a generalized WCA potential of the form "n-2n",

$$U_{\text{WCA}}(r) = \begin{cases} 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{2n} - \left(\frac{\sigma}{r}\right)^n \right] + \epsilon, & r \leqslant 2^{1/n}\sigma \\ 0, & r > 2^{1/n}\sigma, \end{cases}$$
(7.2)

the effective hard-sphere diameter can be obtained following Ref. [214],

$$\sigma_{\rm HS} = \sigma \left(\frac{2}{1 + \sqrt{E_{\rm c}/\epsilon}}\right)^{1/n},\tag{7.3}$$

where  $\sigma$  and  $\epsilon$  are the length and energy scales, n is the "softness" of spheres (n = 6 for standard LJ/WCA and  $n = \infty$  for hard spheres), and  $E_c = \alpha(\rho, n)kT_B$  is the mean collision energy with coefficient  $\alpha$  that depends on density  $\rho$  and n. Note that  $E_c = 2kT_B$  for dilute hard spheres [215], which provides a reference for the value of  $\alpha$ .

To test this idea, we perform MD simulations on supercooled WCA soft spheres using our crystal-avoiding method with special care taken to forestall both crystallization and quasi-crystallization (see section 1.5). We obtain the diffusion coefficient from the time-dependent MSD at different temperatures, densities and



Figure 7.3: Rescaled diffison coefficients for hard spheres and soft spheres with different  $\rho$  and n.



Figure 7.4: (a) Number fraction and (b) percolation probability of T1-inactive particles as a function of temperature for soft spheres with  $\rho = 1.2$  and n = 6.

n values in the NVT ensemble (see Figure. 7.2). The coefficient of the collision energy,  $\alpha$ , is chosen for different n and  $\rho$  such that the rescaled diffusion coefficient  $D(T)/\sqrt{(T)}$  of soft spheres matches that of hard spheres. As shown in Figure 7.3, the diffusivities for different soft-sphere systems collapse onto to a master curve, slightly below the data for hard spheres, consistent with the results in [214]. We then conduct the T1-activity analysis based on the chosen effective hard-sphere diameter for each system. In Figure 7.4, we show the number fraction and percolation probability of T1-inactive particles as a function of temperature for n = 6,  $\rho = 1.2$ as an example. Moreover, we find that for all systems studied the percolation temperatures of T1-inactive particles,  $T_c$ , are in good agreement with the MCT glass transition temperatures,  $T_{MCT}$ , defined from power law fitting, as depicted in Figure 7.5. Our preliminary results suggest that our geometrical criterion of the glass transition based on T1-activities can be extended to monodisperse WCA soft



Figure 7.5: Correlation between the percolation temperature,  $T_c$ , and the MCT glass transition temperature,  $T_{MCT}$ , for various WCA systems.

spheres.

For monodisperse spheres with L-J potential, however, the diffusivity data cannot collapse onto the same master curve as for WCA spheres with a constant collision energy for all temperatures. This is probably because the effect of attractive interaction becomes increasingly important at lower temperatures, e.g., particles may be trapped in the potential well of a neighbors after the collision, so that the effective free volume is smaller. Indeed, different dynamical behaviors between WCA and LJ binary mixtures with almost identical radial distribution functions have been observed. In this case, a direct mapping between LJ system and monodisperse hard spheres may be oversimplified; the more involved analysis mentioned above may be needed.

## 7.2 Identifying Local Structures of Amorphous Silica Network

In Chapter 4, we introduced a graph-theoretic method to automatically classify the local structures in disordered hard spheres, and observed a relatively high fraction of icosahedral-like clusters than other types of clusters. Similar approach can be applied to study the structure of amorphous silica. The SiO<sub>2</sub> network can be generated using the BKS potential [216], a widely used potential that can reproduce the experimental structural properties, including bond angle, bond length and



Figure 7.6: Number fraction of prevalent local clusters for n = 2 as a function of temperature. Graphs shown on the right are labelled according to their ranks. Note that graph #7 and #12 correspond to the local structure of  $\alpha/\beta$ -quartz (the same for cristoballite and tridymite for n = 2) and coesite, respectively.

density [217]. In addition, the valence rule between Si and O atoms are largely satisfied under low cooling rates. Instead of using Voronoi tessellation, the nearest neighbors for a given atom can be defined by a fixed cutoff slightly larger than the average Si-O bond length (about 1.64 nm). Since O atoms only serve as bridges between Si atoms, we may focus on the Si atoms alone and define for each Si atom the associated graph consisting of neighbors at depth n. For a given n value, we can perform the canonical labeling on graphs and identify distinct local structures.

Preliminary results for n = 2 (including next-nearest neighbors of a center particle) show that there are about 1500 topologically distinct clusters, and certain structures containing five-membered rings appear more frequently than others; and their concentrations increase with decreasing temperature but flatten out as the simulated glass transition (~ 2700 K) is approached (see Figure 7.6). Moreover, these prominent structures do not belong to common crystal structures, such  $\alpha/\beta$ quartz,  $\beta$ -tridymite,  $\beta$ -cristobalite or coesite. Interestingly, however, there seems to be no difference in the persistent time or life time between prevalent structures and uncommon ones, in contrast to spherical systems, where the life time of locally preferred structures, e.g., icosahedra for hard spheres, is significantly longer. Given that SiO<sub>2</sub> is a typical strong glass-former while hard sphere are more fragile, this observation may suggest a connection between long-lived structures and fragility of glass-forming systems, We note that although the structure of  $SiO_2$  network has been characterized by the distribution of rings of a given size [217], our graph method captures the complete topological information about local environment since particles participating in the same ring can have different graphs. Even though a detailed ring size analysis for each particle, similar to the common-neighbor analysis (CNA), might provide similar structural information, the graph method can be extended to include higher level of neighbors, which could be challenging for ring size analysis.

# 7.3 Plasticization Effects on $T_{\rm g}$ From Short-Time Dynamics

In Chapter 6, we studied the glass transition in polystyrene thin films from atomistic simulations. We find that short-time dynamical properties, such as monomer MSD, collapse onto a master curve for different film thicknesses, from which the reduction of glass transition temperature can be obtained. We may apply the same technique to bulk PS with plasticizers and study the effect of plasticization on dynamics and  $T_{\rm g}$ . To do so, we focus on bulk PS systems consisting of 96 chains, each chain consists of 20 monomers. We select one or more chains to cut up into monomers and change them into ethylbenzene (EB) as the plasticizer, for which the inter/intramolecular interactions are well described by the TraPPE-UA potential. Having prepared systems with different weight fraction of EB,  $w_{\rm EB}$  ranging from 0 to 0.64, we equilibrate each system at 600 K for 20 ns before quenching it linearly from 600 K to 200 K in 80 ns, corresponding to a cooling rate of 5 K/ns. To improve statistics, final results are averaged over five independent runs for data point.

Following our previous study on PS thin films, we first determine the dilatometric  $T_{\rm g}$  from the change of thermal expansivity. As shown in Figure 7.7(a), the temperature-dependent density of systems with different EB concentrations are well described by the empirical fit previously used (Eq. 6.2). It is clear that the melt density is lowered by the plasticizer while the glassy density is slightly larger for higher  $w_{\rm EB}$ , as a result of delayed glass transition. As an aside, we find that the width of the transition appears unchanged by plasticization. In Figure 7.7(b).



Figure 7.7: (a) Temperature dependence of density for systems with different weight fractions of EB. Solid lines are empirical fits according to Eq. 6.2. (b) Suppression of  $T_{\rm g}$  obtained from density and mean-square displacement as a function of EB concentration. Also included are experimental data from DSC measurements.



Figure 7.8: Mean-square displacement of (a) PS monomers and EB and (b) PS monomers part for systems with different EB concentration  $w_{\rm EB}$ . Insets are data collapse obtained by sliding curves along the temperature axis.

substantial  $T_{\rm g}$  reductions is shown as a function of EB concentration, which suggests that the presence of small EB molecules will speed up dynamics of the PS/EB mixture and hence decrease the average glass transition temperature. We also find that the extent of  $T_{\rm g}$  suppression agree with experimental date from differential scanning calorimetry (DSC) measurements [218].

Alternatively, we may also obtain the shift in  $T_g$  from the change in dynamical properties. To this end, we first compute the monomer (or molecule) center of mass MSD, as an example, for the entire system including both PS and EB, as well as for PS only. In Figure 7.8, we show the MSD at a fixed time interval  $t^* = 200$  ps as a function of temperature, with varying plasticizer concentration. The same master curve construction as used in Chapter 6 is applied. We find excellent collapse for all our data as shown in the inset of Figure 7.8, which allows us to determine the suppression in  $T_{\rm g}$  from shift factor. Remarkably, for the entire system, the average  $T_{\rm g}$  reduction inferred from the temperature dependent of density agree with those obtained from data collapse of MSD, consistent with our thin-film study. Moreover, the dynamical scaling method allows us to isolate the contribution of plasticizers to the  $T_{\rm g}$  reduction by only focusing on the MSD of polymer chains. As also shown in Figure 7.7(b), We find a weaker plasticizer concentration dependence of  $T_{\rm g}$  for PS chains than for the mixture.

The success of data collapse for dynamical properties also suggests that the width of glass transition remains almost unchanged by the plasticizer EB. Admittedly, for other types of plasticizer, we may expect a broader or narrower transition in addition to the change of  $T_{\rm g}$ , where the dynamical scaling by simply shifting the temperature cannot collapse the data onto a master curve, and probably additional rescaling of temperature is needed.

# Appendix A Rotational-Invariance of Bond Order Parameter

Here we give a brief proof to show that the global bond order parameter  $Q_l$  is rotationally invariant, i.e., independent of the coordinate system in which bond vectors  $v_i$  are measured; the same arguments apply to other types of bond order parameters. According to Eq. 2.3, the bond order parameter  $Q_l$  can be written as

$$\begin{aligned} Q_l^2 &= \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \left| \frac{1}{N_{\rm b}} \sum_{i=1}^{N_{\rm b}} Y_l^m(\theta_i, \varphi_i) \right|^2 \\ &= \frac{1}{N_{\rm b}^2} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \left( \sum_{i=1}^{N_{\rm b}} Y_l^m(\theta_i, \varphi_i) \sum_{i=1}^{N_{\rm b}} Y_l^{m*}(\theta_i, \varphi_i) \right) \\ &= \frac{1}{N_{\rm b}^2} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \left( \sum_{i=1}^{N_{\rm b}} Y_l^m(\theta_i, \varphi_i) \sum_{i=1}^{N_{\rm b}} Y_l^{m*}(\theta_i, \varphi_i) \right) \\ &= \frac{1}{N_{\rm b}^2} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \left( \sum_{i=j}^{N_{\rm b}} Y_l^m(\theta_i, \varphi_i) Y_l^{m*}(\theta_j, \varphi_j) + \sum_{i\neq j}^{N_{\rm b}} Y_l^m(\theta_i, \varphi_i) Y_l^{m*}(\theta_j, \varphi_j) \right) \\ &= \frac{1}{N_{\rm b}^2} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \left( \sum_{i=1}^{N_{\rm b}} |Y_l^m(\theta_i, \varphi_i)|^2 + \sum_{i\neq j}^{N_{\rm b}} Y_l^m(\theta_i, \varphi_i) Y_l^{m*}(\theta_j, \varphi_j) \right) \\ &= \frac{1}{N_{\rm b}^2} \frac{4\pi}{2l+1} \left( \sum_{i=1}^{N_{\rm b}} \sum_{m=-l}^{l} |Y_l^m(\theta_i, \varphi_i)|^2 + \sum_{i\neq j}^{N_{\rm b}} \sum_{m=-l}^{l} Y_l^m(\theta_i, \varphi_i) Y_l^{m*}(\theta_j, \varphi_j) \right) \\ &= \frac{1}{N_{\rm b}} + \frac{1}{N_{\rm b}^2} \sum_{i\neq j}^{N_{\rm b}} P_l(\cos \gamma_{ij}), \end{aligned}$$
(A.1)

where  $\gamma_{ij} = \vec{v}_i \vec{v}_j = \cos \theta_i \cos \theta_j + \sin \theta_i \sin \theta_j \cos (\phi_i - \phi_j)$ , is the angle between bond i and j, and  $Y^*$  is the complex conjugate of Y. Since the angle between each pair of bonds is rotationally invariant, the bond order parameter  $Q_l$  as a function of  $\gamma_{ij}$  is also rotationally invariant.

To reach the last line, we have used the fact that spherical harmonics form an complete, orthonormal basis for a (2l + 1)-dimensional subspace, which leads to

$$\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |Y_l^m(\theta_i, \varphi_i)|^2 = 1,$$
(A.2)

and also the spherical harmonic addition theorem,

$$P_{l}(\cos\gamma_{ij}) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_{l}^{m}(\theta_{i},\phi_{i})Y_{l}^{m*}(\theta_{j},\phi_{j}), \qquad (A.3)$$

where  $P_l(x)$  is the *n*th-degree Legendre polynomial.

# Appendix B Validation of Crystal-Avoiding Method for Pinned Systems

While pinned particles can to some extent frustrate crystallization in monodisperse hard spheres, a high pinning fraction is required. To illustrate this, we perform standard event-driven MD for monodisperse systems with N = 2000 particles at  $\phi = 0.56$  as an example. Periodic array pinning is applied with the number of pinned particles  $m^3$  ranging from 0 to 7<sup>3</sup>. As shown in Fig.B.1, crystallization can be observed within simulation time for  $m \leq 5$ , suggesting that crystal-avoiding (CA) method is necessary to suppress crystallization for small pinning concentrations.

To show that the dynamics is preserved by CA method in pinned systems, as we have demonstrated previously for unpinned systems [138], we compare the MSD of monodisperse hard spheres at  $\phi = 0.56$  with that of slightly polydisperse systems (s = 0.08) with the same pinning concentration. As shown in Fig. B.2, CA method barely affect the dynamics for pinned systems for m < 5. Deviation between monodisperse and polydisperse systems is observed for  $m \ge 5$ , possibly due to the increasing partial localization of large and small particles in polydisperse systems as pinning induced glass transition is approached.

For m > 5, the dynamics of monodisperse systems obtained with CA method can be justified by directly comparing to that obtained without the CA method, since crystallization is fully suppressed in this case as a result of strong pinning effect. As shown in Fig. B.3, the MSD is almost identical between systems with and without CA method for high pinning concentrations. In fact, when crystallization is fully suppressed, the crystal-avoiding MD effectively becomes standard MD since every MC move is accepted.



Figure B.1: Time-dependent crystallinity  $\chi(t)$ , defined as the number fraction of crystal-like particles (see Ref. [138] for details), for monodisperse systems at  $\phi = 0.56$  with varying pinning concentration. Five pinning realizations for each m were performed.



Figure B.2: A comparison of MSD between polydisperse systems (solid lines) and monodisperse systems (dashed lines) for different pinning concentrations at  $\phi = 0.56$ . CA method is applied for monodisperse systems.



Figure B.3: MSD of monodisperse systems with CA method (dashed line) and standard MD (solid line) for high pinning fractions at  $\phi = 0.56$ .

# Appendix C Simulation Details on PS Thin Films

### C.1 Correction for Spurious Shear Modes

Because of the relatively small box area and correspondingly large fluctuation of the center of mass position of each layer, a simulated "tall" thin film ("tall" = transverse dimensions small relative to film thickness) tends to develop shear-like motion along the z direction. This artifact cannot be completely eliminated by removal of the center of mass motion of the entire system. In Figure C.1 we show two snapshots of a 22 nm film separated by  $\Delta t = 16$  ns. In addition to the self-diffusion of polymer segments in each layer, shear-like motions develop across the film.

This collective motion can be a combination of different modes that satisfy a zero total center of mass motion of the system. For example, the lowest mode is a linear lateral velocity profile along the z axis, which leads to a quadratic MSD profile for the layer center of mass as a function of height, as shown in Figure C.2. For higher shear modes, the velocity gradient is larger and the mode less likely to develop because of the larger shear stress. However, it is difficult to theoretically predict the magnitudes of different modes and their contributions to the apparent shear-like motion, in order to remove them analytically.

To correct this artifact, we divided the system into layers about 0.7 nm thick, and remove the center of mass motion of each layer before analyzing the local dynamics. Figure C.2 compares the raw monomer MSD, corrected monomer MSD and layer center of mass MSD as a function of z position for a 22 nm thin film at 500 K. Finally, we verified that this shear-like motion is suppressed by a system



Figure C.1: Example of the shear modes developed in a 22-nm film. Colors are based on the chain positions in the z direction in the initial frame.



Figure C.2: Lateral MSD of monomers at  $t^* = 200$  ps as function of z position before and after the removal the layer center of mass motion. The MSD of center of mass of each layer is well fit to a quadratic function, indicating a linear velocity profile across the z direction. Dashed line is the bulk value with layer center of mass motion removed, which agrees with the value at the center of the film.

with a larger transverse area, while the corrected MSD profile is not affected by the transverse area, as shown in Figure C.3 for a 10 nm thick film with different box areas. To keep computational time manageable, rather than increasing the transverse area for thick films we fix the transverse area of the system, and use this technique to eliminate the spurious collective shear-like motions.



Figure C.3: Effect of box area on the lateral MSD of layer center of mass and the corrected lateral MSD of monomer at  $t^* = 200$  ps.

## C.2 Force Field Modification and Validation

The force field used in this work is adapted from the TraPPE-UA model for polystyrene, [219, 220] modified to match the backbone dihedral distribution obtained from all-atom simulations. We also find it necessary to modify the improper dihedral that maintains the tetrahedral arrangement around the carbon connected to the phenyl ring, and to add a torsional potential along the bond joining the phenyl ring to the backbone following previous works [198, 221], in order to match all-atom results. In Table C.1 we present the modifications to the TraPPE-UA dihedral potentials. All other bonded and nonbonded potential parameters are the same as in Ref. [219].

A comparison of dihedral distributions, pair distribution functions and densities among different force fields are shown in Figure C.4. The modified TraPPE potential used in this work improves the agreement with all-atom results for structural properties. For the bulk density, both the original TraPPE potential and the modified one show good agreement with experimental data.

$V(\phi) = c_1[1 + \cos(\phi)] + c_2[1 - \cos(2\phi)] + c_3[1 + \cos(3\phi)] + c_4[1 - \cos(4\phi)]$				
proper dihedral	$c_1 \; (kJ/mol)$	$c_2 \; (kJ/mol)$	$c_3 \; (kJ/mol)$	$c_4 \; (kJ/mol)$
$CH_x$ - $CH$ - $CH_2$ - $CH_y$	5.77	-1.23	11.33	1.01
$CH_x$ - $CH$ - $C_{aro}$ - $CH_{aro}$	0	-2.09	0	0
improper dihedral	$c_1 \; (kJ/mol)$	$c_2 \; (kJ/mol)$	$c_3 \; (kJ/mol)$	$c_4 \; (kJ/mol)$
$CH_x$ - $CH$ - $C_{aro}$ - $CH_y$	0	3.28	-14.73	-3.36

Table C.1: Modified Dihedral Potential for Atactic Polystyrene



Figure C.4: Comparison between different force fields for PS. (a) Probability distributions of dihedral angles along the backbone  $CH_x$ -CH- $CH_2$ - $CH_y$ . (b) Probability distributions of improper dihedral angles around the tetrahedron carbon  $CH_x$ -CH- $C_{aro}$ - $CH_y$ . (c) Total pair distribution functions of  $CH_2$ - $CH_2$  groups. (d) Temperature dependence of bulk densities at P = 1.0 bar with dispersion correction applied. Also shown are experimental data from Zoller and Walsh [222].

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## Vita

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- Yuxing Zhou, Scott T. Milner, "Short-time dynamics reveal  $T_{\rm g}$  suppression in simulated polystyrene thin films", submitted.
- Jiawei Luo<sup>\*</sup>, Yuxing Zhou<sup>\*</sup>, Scott T. Milner, Carlo G. Pantano, Seong H. Kim, "Change in IR spectral features of silica and silicate glasses due to thermal and mechanical stress: Molecular dynamics study of correlation between peak position and bond parameters", submitted. [\*First authorship shared]
- Yuxing Zhou, Scott T. Milner, "Structural entropy of glassy systems from graph isomorphism", *Soft Matter*, 2016, **12**, 7281-7288.
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