ANOMALOUS DYNAMICS IN GLASSY COLLOIDAL LIQUIDS

by

Ryan Cedric Roberts

A dissertation submitted to the Chemical and Biomolecular Engineering Department, Cullen College of Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

> Chair of Committee: Jacinta C. Conrad Co-Chair of Committee: Jeremy C. Palmer Committee Member: Lars C. Grabow Committee Member: Pradeep Sharma Committee Member: Greg C. Morrison

> > University of Houston December 2020

Copyright 2020, Ryan Cedric Roberts

Acknowledgements

I gratefully acknowledge support from my family and friends, mentorship and guidance from my advisors Jacinta Conrad and Jeremy Palmer, and scientific feedback from collaborators, Ramanan Krishnamoorti, and Suresh Narayanan. I also thank my labmates, particularly Maxwell Smith, Nayoung Park, Renjie Chen and Ryan Poling-Skutvik for their mentorship and friendship, and my committee members for their guidance.

Abstract

A liquid that is slowly cooled below the melting temperature usually undergoes a first-order transition to a crystal with long-range periodic order. Rapid cooling, by contrast, may suppress nucleation and result in a glass transition, in which the liguid viscosity and relaxation time appear to diverge despite the structure remaining liquid-like. With decreasing temperature, liquid dynamics become spatially and temporally heterogeneous as the system segments into ephemeral regions of relatively mobile and immobile particles. In this work, we use molecular dynamics simulations of model, colloidal glass-formers to probe anomalous dynamics of glassy liquids. In one investigation, we probe anomalous dynamics of dilute, hard sphere tracers within supercooled liquid and glass matrices with varying interparticle attraction strength. We find that tracers with diameters that are 35% of the matrix diameter exhibit anomalous dynamics indicative of competing relaxation mechanisms. This competition is associated with particular time and length scales that increase as the dominant interactions within the matrix are modulated from repulsive to attractive. As a result, tracer trajectories in attractive systems are more compact than trajectories in repulsive systems, reflecting the underlying rearrangements of the matrices. Further, we simulate tracers of this characteristic size in glasses with no long-time matrix rearrangement and find that vitrification does not prohibit tracer rearrangement. In fact, tracers are delocalized in repulsive glasses but localized in attractive glasses. This localization in attractive systems is heterogeneous in space and time because of the smaller matrix fluctuations in attractive systems, allowing the matrix structure to more strongly determine tracer dynamics. In another investigation, we examine the dynamics of polydisperse hard spheres confined between parallel hard walls separated by varying length H. We find a minimum in relaxation time at an intermediate H that is incommensurate with average particle size, coinciding with a change from square to hexatic crystalline ordering in confined monodisperse hard spheres. Glassy slowdown in systems with commensurate H is correlated with growing hexatically ordered domains, whereas no strong correlation between dynamics and crystalline ordering is observed for incommensurate H. Thus, dynamics can be driven by local ordering, but this relation is sensitive to confinement.

Table of Contents

A	ckno	wledgements	iii
A	bstra	ct	iv
Ta	able o	of Contents	vi
\mathbf{L}^{i}	ist of	Tables	viii
Li	ist of	Figures	ix
1	Inti	oduction	1
	1.1	Introduction to the glass transition	1
	1.2	Dynamics leading up to the glass transition	3
	1.3	Simulation methodology	5
2	Tra	cer Transport Probes Relaxation and Structure of Attractive and	
	Rep	oulsive Glassy Liquids	10
	2.1	Introduction	10
	2.2	Results and Discussion	12
	2.3	Conclusions	20
3	Tracer Transport in Attractive and Repulsive Supercooled Liquids		
	and	Glasses	22
	3.1	Introduction	22
	3.2	Methods	24
		3.2.1 Model systems	24
		3.2.2 Cage analysis	27

		3.2.3	Isoconfigurational ensemble	28
		3.2.4	Trajectory shape analysis	29
	3.3 Results and Discussion			30
		3.3.1	Matrix dynamics	30
		3.3.2	Tracer dynamics	33
		3.3.3	Effects of matrix caging	36
		3.3.4	Structural determinism of tracer dynamics	40
		3.3.5	Consequences for tracer exploration	45
	3.4	Concl	usions	47
4	Dvr	namics	s of Polydisnerse Hard-Snheres Under Confinement	50
Т	<i>1</i> J	Intro		50
	4.1	Introc		90
	4.2	Metho	pds	52
	4.3	Resul	ts and Discussion	56
	4.4	Concl	usions	66
5	Cor	clusio	ons and future work	68
	5.1	Conclusions		
	5.2	2 Future work		70
		5.2.1	Effect of Gaussian polydispersity on phase behavior of confined	
			hard spheres	70
		5.2.2	Long-wavelength fluctuations in confined hard spheres	70
		5.2.3	Connection between dynamic heterogeneity and precursors to	
			nucleation in thin water films	72
	5.3	List of	f publications	74
Re	References			

List of Tables

3.1	Liquid and glass matrices examined in this study.	26
3.2	Cage size r_{cage} for tracers in each matrix	37

List of Figures

1.1	Dependence of liquid entropy S at constant pressure, where $T_{\rm m}$ is the	
	melting temperature, $T_{ m g}$ is the experimental glass transition tempera-	
	ture, and $T_{ m K}$ is the Kauzmann temperature. \ldots \ldots \ldots \ldots	2
1.2	MSDs $\Delta r^2(t)$ of supercooled, polydisperse hard spheres for $\phi = 0.55$,	
	0.56, 0.57, 0.58, 0.59, 0.60 (increasing ϕ from blue to yellow). The black	
	line indicates a diffusive scaling.	4
2.1	Mean-square displacement $\langle \Delta ilde{r}^2 angle$ for (a) matrix species A and (b-f) trac-	
	ers (δ indicated in panels) in the RGM (red) and the AGM (blue). Ar-	
	rows show the timescale at which the tracer $\langle \Delta ilde{r}^2 angle$ in mobile (solid) and	
	immobile (dashed) matrices diverge.	13
2.2	(a) Non-Gaussian parameter α_2 as a function of time τ for matrix	
	species A in RGM (red) and AGM (blue). (b) Non-Gaussian parame-	
	ter α_2 as a function of τ for tracers of size δ = 0.2, 0.35, and 0.5 in RGM	
	(red shades) and AGM (blue shades)	16
2.3	Tracer $F(\tilde{q},\tau)$ (a)–(b) for $\delta = 0.35$ and varying wavevector \tilde{q} and (c)–	
	(d) for varying δ and \tilde{q} at which logarithmic decay appears \tilde{q}^{*} ((a)–(b)	
	black dashed lines). Tracer $F(\tilde{q},\tau)$ in the AGM and the RGM are blue	
	and red, respectively. Matrix $F(6.7, \tau)$ are shown in black. \ldots \ldots \ldots	18
2.4	Trajectories for tracers with δ = 0.35 in the (a) RGM and (b) AGM. (c)–	
	(e) Trajectory M versus $R_{ m g}$ in the RGM (red) and AGM (blue). Dashed	
	and dotted lines are power laws of two and three, respectively. (insets)	
	Probability distribution functions for $R_{ m g}$ at $5000 au_{ m cg,\delta}$	19

3.1	(a) Rendering of a configuration with tracers (red) in a matrix of A	
	(green) and B (blue) particles. (b) Tracer trajectories 360τ in duration	
	within $G_{0.20}.$ (c) Two-dimensional projection of a tracer trajectory 800τ	
	in duration illustrating tracer cage rearrangement.	24
3.2	State diagram from Ref. 107 for the model square-well glass former.	
	Symbols denote the locations of the liquid (L) and glass (G) matrices	
	investigated in this study. Arrows denote hypothetical protocols for	
	preparing glasses from the ergodic liquids.	26
3.3	Non-Gaussian parameter α_2 for tracer particles in each matrix as a	
	function of normalized time scale τ . Arrows indicate the maximum in	
	$lpha_2$ and the corresponding lag time of the maximum $ au^*$. Arrows are	
	color-coded according to their respective matrices.	28
3.4	Self-intermediate scattering function $F_s(q,\tau)$ for $q\sigma_{\rm BB}$ = 6.7 for matrix	
	particle species A in each system.	31
3.5	Mean-square displacement Δr^2 for matrix species A (a) for all matri-	
	ces with $\phi = 0.610$ and (b) for glasses with $\phi = 0.635$ compared to the	
	corresponding liquids with $\phi = 0.610$. The black solid line indicates a	
	power-law slope of one.	32
3.6	Mean-square displacement Δr^2 for (a) tracers in matrices with ϕ =	
	0.610 and tracers in glasses with ϕ = 0.635 and the corresponding liq-	
	uids. Arrows indicate the time scales at which (a) $\Delta r^2_{\rm G_{0.20}} \approx \Delta r^2_{\rm L_{0.35}}$	
	and (b) $\Delta r^2{}_{ m G_{0.35}}$ and $\Delta r^2{}_{ m G_{1.05}}$ qualitatively diverge. \ldots \ldots \ldots	34
3.7	(a) Normalized CDP \tilde{x}_{12} versus previous displacement magnitude \tilde{r}_{01}	
	for tracers in matrices with $\phi = 0.610$ and (b) for tracers in glasses	
	with $\phi = 0.635$ and in the liquids. Shaded regions indicate statistical	
	uncertainty. The black solid lines have a slope of -0.5	38

3.8	Tracer dynamic susceptibility χ_4 (a) in matrices with ϕ = 0.610 and (b)	
	in glasses with $\phi = 0.635$ and the liquids. Wavevectors maximize the	
	peak in χ_4 and are $q\sigma_{\rm BB}$ = 2.0, 2.5, 1.6, 2.8, 3.0, and 3.0 for L _{0.35} , L _{1.05} ,	
	$G_{0.20}, HSG_{1.00}, G_{0.35}, and \ G_{1.05},$ respectively. $\ldots \ldots \ldots \ldots \ldots$	39
3.9	Tracer structural variance $\sigma_{ m DP}^2$ of the dynamic propensity $ m DP_i$ distribu-	
	tion. (a) $\sigma^2_{\rm DP}$ for tracers in matrices with ϕ = 0.610. (b) $\sigma^2_{\rm DP}$ for tracers	
	in glasses with $\phi = 0.635$ and in the corresponding liquids. Shaded	
	regions indicate statistical uncertainty.	41
3.10) Fraction of tracer fluctuations due to initial structure $R_{\rm c}$. (a) $R_{\rm c}$ for	
	tracers in matrices with $\phi = 0.610$. (b) $R_{\rm c}$ for tracers in glasses with	
	$\phi = 0.635$ and in the corresponding liquids. Shaded regions indicate	
	statistical uncertainty.	42
3.11	Static structure factor $S(q)$ for all matrix particles in each system	43
3.12	Radial distribution function $g(r)$ for all matrix particles in each system.	
	The first, second, and third sharp peaks at small r arise from B – B,	
	A–B, and A–A nearest neighbors, respectively. The black line indicates	
	g(r) = 1.	44
3.13	B Fractional contribution of isoconfigurational fluctuations due to struc-	
	ture $R_{\rm c}$ for matrix particles in each system. Shaded regions indicate	
	statistical uncertainty. The reported $R_{ m c}$ values were computed by aver-	
	aging $n_{\rm s}$ independent configurations (Table 3.1) $\ldots \ldots \ldots \ldots$	45
3.14	Tracer dynamical variance $\Delta_{c,norm}^{iso}$ of the dynamic propensity DP_i dis-	
	tribution for each system. Shaded regions indicate statistical uncer-	
	tainty.	46

- 4.6 Correlation length scales associated with (a) ξ_6 and (b) ξ_4 for particles within the contact layers adjacent to the walls as a function of relaxation time τ_{xy} . Solid lines are fits to the relation $\tau_{xy} = B \exp(C\xi_l)$, where B and C are positive constants and ξ_l is either ξ_4 or ξ_6 64

Chapter 1: Introduction

1.1 Introduction to the glass transition

Glasses are metastable materials that lack long-range crystalline order but exhibit solid-like elastic properties. When cooled slowly, liquids exhibit a first-order thermodynamic phase transition to a crystal at the melting temperature $T_{\rm m}$, and the disordered liquid structure gives way to periodic order (Fig. 1.1). However, crystallization can be avoided by cooling the liquid over a time scale shorter than the nucleation time but longer than the relaxation time τ , resulting in a metastable supercooled liquid^{1,2}. Upon further cooling, the liquid eventually falls out of equilibrium as the relaxation time becomes larger than the experimental time scale^{3,4}. Beyond this point, molecules no longer rearrange significantly, and the heat capacity c_p appears to discontinuously decrease. The experimental glass transition temperature $T_{\rm g}$ is often defined as the intersection of the entropy S curves when extrapolated from the liquid and glass regimes^{4,5}.

Liquid dynamics can be measured experimentally through the shear viscosity η , which can be related to relaxation time through the Maxwell model $\eta = G_{\infty}\tau$, where G_{∞} is the shear modulus¹. The dramatic slowdown when approaching the glass transition is strongly material-dependent. Liquids are commonly classified according to the sensitivity of η to changes in T through fragility, which can be seen in a plot of $\log(\eta)$ versus $1/T^6$. The growth of η with 1/T in "strong" liquids is nearly Arrhenius and thus follows the equation:

$$\eta = A \exp(\frac{E}{k_{\rm B}T}),\tag{1.1}$$

where E is the activation energy, $k_{\rm B}$ is Boltzmann's constant, and A is a T-



Figure 1.1: Dependence of liquid entropy S at constant pressure, where $T_{\rm m}$ is the melting temperature, $T_{\rm g}$ is the experimental glass transition temperature, and $T_{\rm K}$ is the Kauzmann temperature.

independent constant³. The activation energy is given by $\frac{d \log(\eta)}{d(1/T)}$ and is nearly independent of *T*. Strong glass-forming liquids like silica SiO₂ often have threedimensional networks arising from directional bonding^{7,8}.

In "fragile" liquids, by contrast, the increase in η is super-Arrhenius (faster than exponential). Many polymers, organic molecules such as toluene, or Lennard-Jones liquids are fragile glass-formers with non-directional interactions that do not form networks³. Empirically, the Vogel-Fulcher-Tamman (VFT) has been shown to describe $\eta(T)$ in fragile liquids:

$$\eta = A \exp(\frac{B}{T - T_0}),\tag{1.2}$$

where B and T_0 are constants^{4,9}. Note that this equation reduces to the Arrhenius case when $T_0 = 0$. This particular super-Arrhenius dependence implies that η and τ diverge at a finite temperature T_0 , which is often identified with the so-called Kauzmann temperature T_K . At this temperature, the S curves of the supercooled liquid and crystal would intersect if equilibrium could be maintained for infinitely slow supercooling (Fig. 1.1)¹⁰. Maintaining the respective c_p of the liquid and crystal for $T \rightarrow 0$ would violate the third law of thermodynamics, forming the based of the so-called Kauzmann paradox. To ensure positive S, Kauzmann suggested a lower limit to T_g , which has been identified as T_0 in some theories which posit an ideal glass transition at $T_0^{11,12}$.

1.2 Dynamics leading up to the glass transition

A variety of materials can form glasses, including silica, polymers¹³, and metals¹⁴. Yet despite the ubiquity of these materials, a microscopic theory describing glass formation remains the subject of debate^{1,6,15}. Thus, it is illustrative to examine the dynamics of a prototypical glass-former. Thermalized hard spheres, in which particles interact through discontinuous, excluded-volume interactions, provide a simple model in that the free energy of the system does not have an enthalpic component and is determined entirely by entropy¹⁶. The thermodynamic control parameter is the particle volume fraction ϕ :

$$\phi = \frac{\sum_{i} V_{\rm s,i}}{V_{\rm sys}},\tag{1.3}$$

where $V_{\rm s,i}$ is the volume of the *i*th particle and $V_{\rm sys}$ is the system volume^{16,17}. For $\phi \rightarrow 0$, the system behaves as an ergodic fluid. On increasing to $\phi = 0.494$, fluid and liquid coexist until $\phi = 0.545$, after which the crystal exists as a single phase¹⁸. Introducing polydispersity (a distribution of particle diameters) can bypass nucleation to produce a 'supercooled' liquid that exhibits an experimental glass transition around $\phi_{\rm g} \approx 0.58^{16,17,19}$.

Like other glass-formers, the hard sphere glass transition exhibits a lack of marked structural changes upon supercooling. More specifically, there is no development of long-range structural order in the glass that is detectable in commonly used two-point structural correlation functions such as the radial distribution function and static structure factor 20,21 . To gain insight, we turn to dynamical correlation functions such as the single-particle mean-square displacement (MSD):

$$\Delta r^2 = \frac{1}{N} \sum_i \langle ||\mathbf{r}_i(t) - \mathbf{r}_i(0)||^2 \rangle, \qquad (1.4)$$

where N is the total number of particles, and \mathbf{r}_i is the position vector of the *i*th particle. For normal liquids $\phi \lesssim 0.5$, liquid dynamics scale ballistically $\Delta r^2 \sim t^2$ for t with a few interparticle collisions, and then scale diffusively $\Delta r^2 \sim t$ for t at which collisions dominate dynamics (Fig. 1.2). For large ϕ , a plateau region develops between the ballistic and diffusive regimes that lengthens with increasing ϕ , indicative of a two-step particle relaxation that is a characteristic of all glass-formers²². This plateau arises from the localization of particles within transient 'cages' formed by nearest neighbors, and particle rearrangement in strongly supercooled systems only occurs when the neighbors of a particle rearrange²³⁻²⁵.



Figure 1.2: MSDs $\Delta r^2(t)$ of supercooled, polydisperse hard spheres for $\phi = 0.55$, 0.56, 0.57, 0.58, 0.59, 0.60 (increasing ϕ from blue to yellow). The black line indicates a diffusive scaling.

On long time scales, all particles rearrange in the ergodic supercooled liquid, and particle displacements follow diffusive Gaussian statistics. However, dynamics are non-Gaussian on time scales near the end of the caging regime, with the strongest non-Gaussian behavior arising near the α -relaxation (the upturn in the MSD)^{17,26,27}. Displacements with the smallest magnitudes approximately follow a Gaussian distribution, corresponding to particles 'rattling' within neighbor cages. The tails of these distributions, by contrast, are 'fatter' than Gaussian, and have been identified with particles that have undergone cage-rearrangement^{17,27}. Thus, particles are segmented into relatively mobile and immobile populations, and further examination of particle trajectories reveals particles interchange between these populations, with extended periods of immobility interrupted by rearrangements beyond the caging length scale^{27–29}.

Particle dynamics are therefore spatially and temporally heterogeneous as dynamics vary from particle to particle. Extensive experimental and simulation evidence reveals that heterogeneous dynamics are correlated in space and time, with groups of particles rearranging collectively^{30–33}. Closer to the glass transition, the length scale of these correlations grows, and theories of the glass transition have postulated that the separation between mobile regions²⁹ or size of the correlated regions^{11,34,35} control the dynamic slowdown. Whether a static or dynamic length scale controls the dynamic slowdown on approach to the glass transition remains a topic of investigation.

1.3 Simulation methodology

Molecular dynamics (MD) is a computational technique to simulate the trajectory of a particle system that obeys the rules of classical mechanics, allowing us to calculate equilibrium or non-equilibrium properties of the system³⁶. Following the laws of statistical mechanics, we can estimate thermodynamic, structural, and dynamical averages from the trajectory³⁷.

We initialize a system by inputting particles within a cubic simulation cell and assigning each particle with initial momenta sampled from the Maxwell-Boltzmann distribution. We use classical force fields to model interparticle attractions and repulsions, which are single-body or pair-wise interactions in our simulations. The system potential energy is then

$$U(\mathbf{r}^N) = \sum_j \sum_{j>i} u(r_{ij}) + \sum_i v(\mathbf{r}_i), \qquad (1.5)$$

where N is the number of particles, r_{ij} is the pairwise interparticle separation distance, u is the pairwise potential, v is the single-body potential, and \mathbf{r}^N is a 3Ndimensional vector containing the positions of each particle. For the glass-forming systems we use, the pairwise interactions are discrete, which must be contrasted with continuous potentials.

For systems consisting of particles that interact through continuous potentials, we can follow the time evolution of the system by numerically solving Newton's equations of motion. To solve Newton's equations of motion, we require the net force acting on a particle

$$\mathbf{F}_{i} = m_{i} \frac{d^{2} \mathbf{r}_{i}(t)}{dt^{2}} = -\frac{\partial}{\partial \mathbf{r}_{i}} U, \qquad (1.6)$$

where $\mathbf{r}_i(t) = (x_i(t), y_i(t), z_i(t))$ is the position vector for particle *i* at time *t*, *U* is the system potential energy, m_i is the particle mass, and \mathbf{F}_i is the net force acting on the particle. Future particle positions and coordinates are then calculated by finite difference integration using a discrete timestep dt. The velocity-Verlet integration is commonly used to update positions and velocities for each timestep ³⁶

$$\mathbf{r}_{i}(t+dt) = \mathbf{r}_{i}(t) + \mathbf{v}_{i}(t)dt + \frac{\mathbf{F}_{i}(t)}{2m}dt^{2}$$
(1.7)

and

$$\mathbf{v}_{i}(t+dt) = \mathbf{v}_{i}(t) + \frac{\mathbf{F}_{i}(t) + \mathbf{F}_{i}(t+dt)}{2m}$$
(1.8)

For systems with discrete potentials, however, the timestep-based MD algorithm is not suitable. Consider the hard sphere interaction, in which a particle of diameter σ_i cannot overlap its volume with the volume of another particle with diameter σ_i

$$u(r_{ij}) = \begin{cases} \infty & r_{ij} \le \frac{\sigma_i + \sigma_j}{2} \\ 0 & r_{ij} > \frac{\sigma_i + \sigma_j}{2} \end{cases}$$
(1.9)

where the interaction distance for the hard sphere repulsion is given by the sum of the particle radii at contact. Evolving the system via conventional MD is possible, but requires a small timestep and the determination of events during the timestep, which is computationally demanding³⁸.

By recasting the dynamics to consist of a series of events (e.g., collisions) between pairs of particles, event-driven molecular dynamics (EDMD) provides an analytical method to integrate the equations of motion for systems interacting by discrete potentials³⁹. These events change particle properties, specifically the velocities of the particle pairs. The event-driven algorithm consists of the following cyclical steps³⁹:

- 1. Event testing all particles and particle pairs are tested to determine when the next collisions will occur, and the events are added to a list
- 2. Event sorting the next event is determined
- 3. Ballistic motion particles are free-streamed until the next event time
- 4. Event execution the exit properties for interacting particles are calculated
- 5. Events update determine the next events for the particles that underwent an event and add those events to the list
- 6. Return to step two until end of simulation

This algorithm requires the definition of event rules. For our studies, we consider two types of interparticle events: hard sphere collision and square-well attractions. For collisions between smooth hard spheres, the exit velocities for a pair of particles undergoing a perfectly elastic collision are given by the following⁴⁰

$$\mathbf{v}_{i}' = \mathbf{v}_{i} - m_{i}^{-1} \mu_{ij} (\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij}) \hat{\mathbf{r}}_{ij}$$

$$\mathbf{v}_{j}' = \mathbf{v}_{j} + m_{i}^{-1} \mu_{ij} (\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij}) \hat{\mathbf{r}}_{ij}$$
(1.10)

where \mathbf{v}_i is the velocity vector, $\hat{\mathbf{r}}_{ij}$ is the unit of the interparticle separation vector $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, and $\mu_{ij} = (m_i^{-1} + m_j^{-1})^{-1}$ is the reduced mass. We also consider particles that interact by square-well attractions

$$u(r_{ij}) = \begin{cases} \infty & r_{ij} \le \frac{\sigma_i + \sigma_j}{2} \\ \varepsilon & \frac{\sigma_i + \sigma_j}{2} < r_{ij} \le \lambda \frac{\sigma_i + \sigma_j}{2} \\ 0 & r_{ij} > \lambda \frac{\sigma_i + \sigma_j}{2} \end{cases}$$
(1.11)

where ε is the depth of the square-well attraction and λ is the range of the attraction. For two particles approaching each other that reach $r_{ij} = \lambda \frac{\sigma_i + \sigma_j}{2}$, the momentum impulse increases the kinetic energy of each particle by ε^{40} . Similarly, the energies of separating particles decrease by ε .

The natural units for the colloidal models we study here are given by the typical mass m and diameter σ of the particles and the energy of interparticle interactions. Dimensional analysis then yields the units of time as $\sqrt{\frac{m\sigma^2}{E}}$, where E is the typical energy scale. For hard spheres, the thermal energy $k_{\rm B}T$ sets the energy scale. For square-well interactions, it is the well depth ε . In colloidal of latex nanospheres with diameters ranging from one to ten microns, the typical time scale is $10^{-5} - 10^{-3}$ seconds⁴¹.

Boundary conditions in our simulations are either hard walls or periodic. The potential governing hard wall-particle events is similar to the hard sphere potential in that the particle volume cannot overlap with the infinitely thin wall. For an elastic hard wall-particle interaction, the exit particle velocities are $\mathbf{v}'_i = (\mathbf{v}_{i,\parallel}, -\mathbf{v}_{i,\perp})$, where $\mathbf{v}_{i,\parallel}$ and $\mathbf{v}_{i,\perp}$ are the incoming particle velocity components in the directions parallel and perpendicular to the plane of the wall, respectively.

Periodic boundary conditions are used to mimic infinitely sized systems along a particular dimension. This boundary condition is identical to replicating the entire system along each face of the simulation cell. A particle that exits through one face of the simulation cell is immediately replaced by an identical particle at the opposite face with identical momentum. However, the explicit simulation of the replicas is unnecessary; periodicity is maintained by transforming the coordinates of the exiting particle to the coordinates of the hypothetical incoming particle.

The following chapters investigate anomalous dynamics within supercooled liquids: Chap. 2 focuses on the role of interparticle attractions on the transport of dilute penetrants in supercooled liquids and Chap. 3 addresses the effect of long-time rearrangement and matrix structure on the transport of dilute, non-absorbing penetrants. Finally, Chap. 4 examines the role of locally ordered regions on the dynamics of confined hard sphere liquids.

Chapter 2: Tracer Transport Probes Relaxation and Structure of Attractive and Repulsive Glassy Liquids

This chapter was previously published by ACS Publishing: Roberts, R. C.; Poling-Skutvik, R.; Palmer, J. C.; Conrad, J. C.;, *The Journal of Physical Chemistry Letters* 2018, **9**, 3008-3013.

2.1 Introduction

Confined transport within slowly relaxing and structurally disordered matrices governs important processes in physical and biological systems. Controlling the dispersion of particles within polymer matrices, which underpins the functional properties of polymer nanocomposites,⁴² requires understanding how the dynamics of nanoparticles in solutions and melts^{43,44} relate to those of the polymer matrix.⁴⁵ At smaller size scales, transport of penetrating gas molecules into supercooled or glassy polymer matrices^{46,47} governs the efficacy of membrane separation processes.^{48,49} Finally, migration and transport in crowded biological systems^{50–56} depends on the relaxations of the surrounding crowders. In each process, competition between the relaxations of a disordered matrix and the dynamics of the confined particles can lead to anomalous transport. Although this competition must depend on the structure and nature of the surrounding matrix relaxations, the coupling between tracer transport properties and matrix relaxations remains poorly understood despite its relevance for many physical transport processes.

One of the most intensely studied models of a slowly relaxing system is a dense suspension of colloidal spheres with repulsive interactions. Increasing the sphere volume fraction induces a transition from an ergodic liquid to an arrested glass, driven by entropic crowding.^{57,58} Approaching this transition, dynamics become heterogeneous in space and time^{59,60} and relaxations occur when particles escape the cages formed by their neighbors, leading to collective stringlike rearrangements.^{17,61} Weak attractions between particles melt the repulsive glass⁶², whereas stronger interactions lead to the formation of an attractive glass in which dynamics are controlled by caging and interparticle bonds^{63–67} and in which collective relaxations are more compact.^{68,69} Recent studies on a repulsive colloidal model system reveal that tracers of a critical, relative size can exhibit anomalous logarithmic dynamics, arising from the competition between tracer localization within voids and escape through collective matrix relaxations.⁷⁰ Nevertheless, fundamental understanding of how attractive interactions between matrix particles,⁷¹ which are present in all molecular systems, influence tracer transport is critical for advancing most practical applications.

We use event-driven molecular dynamics simulations to show that tracer dynamics within attractive and repulsive glassy matrices with equal packing fractions and long-time diffusivities are remarkably sensitive to differences in matrix structure and dynamics. The tracer dynamics, characterized through the mean-square displacement and the non-Gaussian parameter, depend on tracer size and interactions between matrix particles. Further, they reveal signatures of cage rearrangements in repulsive liquids and, additionally, the competition between bond formation and breaking in attractive liquids. Anomalous, logarithmic tracer dynamics signal a crossover from diffusion within the matrix void space to diffusion coupled to the glassy matrix dynamics, and occurs on different length scales in repulsive and attractive matrices. As a result of this coupling, the shape of tracer trajectories is different between the two matrices: fractal-like in the repulsive matrix but more compact in the attractive. The sensitivity of tracer dynamics to the confining environment can be exploited to probe subtle differences in the structure of glassy matrices with varying interactions and provides insight into their distinct relaxation processes.

2.2 Results and Discussion

We first examine the dynamics of the two isodiffusive matrices in the absence of tracers. The matrices have identical packing fractions ($\phi = 0.61$) and consist of a 50:50 binary AB mixture of species (N = 1372 particles total) with a hard-core diameter ratio $\sigma_{AA}:\sigma_{BB} = 1.2:1$ chosen to prevent crystallization.⁷² The matrix components have unit mass (m = 1) and interact through a short-range square-well potential with depth u_0 and width Δ_{ij} satisfying $\Delta_{ij}/(\sigma_{ij} + \Delta_{ij}) = 0.03$ for each pair type i, $j \in A, B$, where $\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj})$. Following convention, we adopt units in which Boltzmann's constant k_B is equal to unity and report length, temperature, and time in terms of σ_{BB} , u_0/k_B , and $\sigma_{BB}(m/u_0)^{1/2}$, respectively. To account for thermal contributions to tracer dynamics, we introduce a normalized time $\tau = tD_0/D_{ref}$, where t is the nominal simulation time, $D_0 = \sigma_{BB}\sqrt{T/m}$ is the thermal diffusivity at T, and D_{ref} is the reference value of D_0 at T = 1.

The high-temperature (T = 1.05) repulsive glassy matrix (RGM) and lowtemperature (T = 0.35) attractive glassy matrix (AGM) are ergodic and exhibit nearly equal long-time diffusivities $D_{\rm rep}/D_0 \approx D_{\rm att}/D_0 \approx 6.5 \pm 0.8 \times 10^{-7}$ for species A (Fig. 2.1(a)), similar to the isodiffusive behavior observed in liquids with density anomalies.^{73,74} Both matrices recover these diffusive dynamics on a time scale $\tau \approx 10^4$, indicating that cage escape controls the final relaxation. On intermediate time scales, however, the matrices exhibit different relaxation processes. Particles in the RGM are caged by their neighbors beginning at $\tau \approx 10^0$, with a near-constant normalized mean-squared displacement (MSD, $\langle \Delta \tilde{r}^2 \rangle = \langle \Delta r^2 \rangle / \sigma_{\rm BB}^2$) indicating a localization length of $\sqrt{\langle \Delta \tilde{r}^2 \rangle} = 0.14$. Conversely, the AGM's MSD exhibits only a weak plateau corresponding to a localization length of $\sqrt{\langle \Delta \tilde{r}^2 \rangle} = 0.04$ before increasing as a powerlaw with an exponent less than 1, i.e., MSD ~ τ^{β} , $\beta < 1$. Particle motions in the AGM are more localized due to interparticle bonds,⁷⁵ so that the extended subdiffusive regime reflects a competition between repulsive caging and attractive bonding.⁷⁶ Thus, matrix dynamics on intermediate time scales are controlled by caging in the RGM but by both caging and bonding in the AGM.



Figure 2.1: Mean-square displacement $\langle \Delta \tilde{r}^2 \rangle$ for (a) matrix species A and (b-f) tracers (δ indicated in panels) in the RGM (red) and the AGM (blue). Arrows show the timescale at which the tracer $\langle \Delta \tilde{r}^2 \rangle$ in mobile (solid) and immobile (dashed) matrices diverge.

The different intermediate-time relaxation processes in the AGM and RGM significantly influence the dynamics of confined tracers. We add a small number $(N_t = 10)$ of tracer particles with diameter σ_t to the matrices and characterize their equilibrium dynamics through their MSD (Fig. 2.1(b)-(f)). The tracers are assigned unit mass and interact with the matrix and other tracer particles through purely repulsive hard-sphere interactions. For small tracers of relative size $\delta = \sigma_t / \sigma_{AB} = 0.20$, the MSDs in both the RGM and AGM exhibit a crossover from ballistic motion on short time scales ($\tau \leq 10^{0}$) to diffusive motion on time scales $\tau > 10^{2}$ (Fig. 2.1(b)). The crossover time is nearly identical in the two matrices, indicating that this transition is controlled by hard-sphere steric interactions between tracer and matrix particles. By contrast, the dynamics of larger tracers depend on matrix interactions. In the RGM, the MSD for tracers of size $\delta \geq 0.30$ exhibits an incipient subdiffusive plateau (Fig. 2.1(c)) whose height decreases and duration increases with increasing tracer size (Fig. 2.1(d)-(f)). In the AGM, this subdiffusive plateau is slightly flatter (i.e., the MSD increases less steeply with lag time), and of greater height and longer duration than that in the RGM for tracers of comparable size. Notably, these differences between tracer dynamics are opposite those of the matrix particle (Fig. 2.1(a)).

The higher intermediate-time plateau in tracer MSDs through the AGM suggests that the tracers explore larger void spaces in the AGM relative to the RGM. To more directly probe the effects of instantaneous matrix structure on tracer dynamics, we simulate tracer dynamics in 'frozen' matrix configurations extracted from equilibrium trajectories. Tracer size controls how the structure of the frozen matrix affects their dynamics. The MSDs of small tracers ($\delta = 0.20$) in the frozen and mobile matrices, whether repulsive or attractive, are nearly indistinguishable, indicating that they move easily through the interstitial voids and do not strongly couple to matrix relaxations. Larger tracers, by contrast, exhibit pronounced differences in their dynamics in mobile and immobile matrices that depend on matrix interactions. In the RGM, the tracer MSD in the mobile matrix diverges from that in the immobile matrix before the onset of the plateau (at τ ca. 10^{-1}), indicating that matrix relaxations affect tracer dynamics even on relatively short times. Tracers in the mobile RGM are not fully caged, and their dynamics are subdiffusive over roughly a decade in τ . In the AGM, however, the divergence between tracer MSDs in the mobile and immobile matrices occurs approximately two orders of magnitude later in time (τ ca. 10¹). This result suggests that attractive bonds between matrix particles generate a cage that relaxes very slowly compared to tracer diffusion, so that tracer particle dynamics are dominated by sampling of arrested cages on short- to intermediate time scales. Because the local environment is more heterogeneous in the AGM (Fig. 2.1), the trajectories of individual tracers therein likewise exhibit a broader distribution of relaxation behaviors. Thus while exploration of cages appears to be the dominant mechanism controlling the average tracer dynamics within the AGM, other processes may also play a role. Together, these comparisons indicate that tracer dynamics are affected both by the (instantaneous) structure of glassy matrices and the dynamics of their relaxation processes, leading to tracer dynamics that qualitatively differ from those of the surrounding matrix.

The pronounced difference between the subdiffusive exponents for tracers in the RGM and AGM suggests that local relaxation processes affect tracer diffusion. We characterize the time scales associated with these processes by computing the non-Gaussian parameter $\alpha_2 = 3 \langle \Delta \tilde{r}^4 \rangle / 5 \langle \Delta \tilde{r}^2 \rangle^2 - 1$ as a function of lag time. The shape and relaxation times identified by α_2 differ between the RGM and AGM (Fig. 2.2(a)). The α_2 for the RGM exhibits the classic behavior expected for a supercooled colloidal liquid ⁵⁹, attaining a local maximum at τ ca. 10⁴, the timescale at which the matrix particle dynamics become diffusive and cages are disrupted (Fig. 2.1(a)). The α_2 for the AGM, however, first exhibits a shoulder at τ ca. 10 and then reaches a maximum near $\tau \leq 10^4$. The broad maximum in α_2 for the AGM is consistent with the idea that rearrangements in glassy attractive liquids occur over a broader range of time scales ⁶⁸ and hence, likely, length scales than those of a glassy repulsive liquid.

The α_2 values for the tracers are smaller than those obtained for their corresponding matrices (Fig. 2.2(b)), and exhibit a maximum at a particular time scale τ shorter than the time scale in the matrix. The time scale corresponding to maximum non-Gaussianity increases with increasing tracer size. For small tracers of size $\delta = 0.20$, α_2 attains a maximum near τ ca. 1 in both the RGM and AGM. The greater height



Figure 2.2: (a) Non-Gaussian parameter α_2 as a function of time τ for matrix species A in RGM (red) and AGM (blue). (b) Non-Gaussian parameter α_2 as a function of τ for tracers of size $\delta = 0.2, 0.35$, and 0.5 in RGM (red shades) and AGM (blue shades).

and width of the maximum of the tracer α_2 in the AGM indicate that the tracer dynamics in the AGM are slightly more heterogeneous than in the RGM. When $\delta = 0.35$, the shapes of the tracer α_2 in the RGM and AGM become dissimilar. In the RGM, the maximum in α_2 increases in height and width with increasing tracer size; it remains approximately Gaussian in shape but shifts to larger τ (~ 10² at $\delta = 0.50$). By contrast, α_2 in the AGM becomes increasingly broad as δ increases. For all tracer sizes, α_2 increases rapidly up to $\tau \sim 10^0$, and then increases more slowly to reach a maximum that shifts to greater τ as δ is increased; this evolution reflects broad coupling to cage relaxations occurring on these time scales. Thus the α_2 measurements reveal heterogeneous tracer dynamics on distinct time scales that depend both on tracer size and matrix interactions, with increasing coupling to matrix dynamics as the tracer size is increased.

To gain insight into the length scales over which tracer dynamics are coupled to matrix relaxations, we examine the collective intermediate scattering functions (ISF, $F(\tilde{q},\tau)$). From the ISF, it is clear that tracer dynamics depend on tracer size, matrix interactions, and length scale $2\pi/\tilde{q}$, where $\tilde{q} = q\sigma_{\rm BB}$ is the normalized scattering wave vector (Fig. 2.3). We first scrutinize the dynamics of tracers of size $\delta = 0.35$ as a function of \tilde{q} in the different matrices. At low \tilde{q} , the ISF of a tracer in the RGM decays nearly exponentially (Fig. 2.3(a)). At $\tilde{q} \approx 3.5$, however, $F(\tilde{q}, \tau)$ exhibits a logarithmic decay over two orders of magnitude in time for nearly its entire relaxation process. The onset of the logarithmic dynamics occurs at approximately the time scale at which the matrix relaxes and is close to the time scale ($\tau \approx 1$) at which the tracer α_2 attains a maximum; these comparisons suggest that these logarithmic dynamics arise when the tracers become transiently localized. Similar logarithmic decay is observed for tracers of size $\delta \leq 0.40$ in the RGM and in the AGM (Fig. 2.3(b)), but not for tracers with size ratio $\delta = 0.50$.

Logarithmic relaxations in glassy systems are usually interpreted as a consequence of competing arrest mechanisms.^{75,77–81} Because the matrix relaxations are not logarithmic, the logarithmic dynamics of the tracers do not reflect competing arrest mechanisms in the matrix but instead indicate a crossover between local processes controlling their dynamics. Similar crossovers have been proposed for other confined transport systems. Partially-pinned particles exhibit logarithmic behavior, for example, as they undergo a crossover from localized to glassy dynamics.^{82,83} Closer to our work, the extended logarithmic dynamics observed in Ref. 70 were attributed to two competing processes, transient localization and matrix crowding. Hence we posit that the length scale of the logarithmic dynamics reflects the length scale on which tracer dynamics become coupled to the slow relaxations of the matrix.²

The value of \tilde{q} where logarithmic decay appears, \tilde{q}^* , depends on tracer size and matrix interactions.⁷⁰ In both matrices, \tilde{q}^* increases with tracer size (Fig. 2.3(b), (c)), indicating that relaxation processes compete on smaller length scales. Furthermore,

²In contrast to the study of Ref. 70, which examined tracer diffusion in liquids and in glasses and also observed extended logarithmic relaxations, we examine only liquids, as the use of isodiffusive matrices allows us to remove effects arising from the long-time dynamics. Thus in our study the self-and collective ISFs do not decouple, because both matrices are ergodic on long time scales.



Figure 2.3: Tracer $F(\tilde{q}, \tau)$ (a)–(b) for $\delta = 0.35$ and varying wavevector \tilde{q} and (c)–(d) for varying δ and \tilde{q} at which logarithmic decay appears \tilde{q}^* ((a)–(b) black dashed lines). Tracer $F(\tilde{q}, \tau)$ in the AGM and the RGM are blue and red, respectively. Matrix $F(6.7, \tau)$ are shown in black.

for a fixed tracer size the wavevector of the logarithmic dynamics is smaller in the AGM than in the RGM. Two mechanisms may explain the decrease in relaxation length scales with increasing tracer size: larger tracers more frequently contact surrounding matrix particles and less frequently encounter fluctuations in the matrix large enough for the tracer to enter. Both mechanisms reduce the mobility of tracers and, because the matrix relaxations do not change with tracer size, lead to a decrease in the length scale corresponding to logarithmic decay. Indeed, tracers of

size $\delta = 0.5$ exhibit the multistep relaxations characteristic of deeply supercooled colloids,⁷⁶ but no logarithmic decay is observed at any \tilde{q} . Our data also indicate that tracers in the AGM couple to relaxations on larger length scales than those in the RGM, attributable to the slower dynamics of the AGM on intermediate time scales $(10^0 \leq \tau \leq 10^4, \text{ Fig. 2.1(a)})$. The fact that the tracer dynamics are logarithmic over different length scales in the RGM and AGM suggests that the tracers couple to the different mesoscale relaxation processes of the two matrices.



Figure 2.4: Trajectories for tracers with $\delta = 0.35$ in the (a) RGM and (b) AGM. (c)–(e) Trajectory M versus $R_{\rm g}$ in the RGM (red) and AGM (blue). Dashed and dotted lines are power laws of two and three, respectively. (insets) Probability distribution functions for $R_{\rm g}$ at $5000\tau_{{\rm cg},\delta}$.

In glassy colloidal liquids, the morphology of mesoscale relaxations depends on matrix interactions — relaxing regions in attractive glasses are reported to be more compact than those in repulsive glasses.^{68,69} To assess whether the shape of relaxing regions affects the ability of tracers to explore space, we directly visualize the tracer trajectories, coarse-graining over a time scale, $\tau_{cg,\delta}$, that for a given δ removes cage exploration processes and the effects of thermal diffusion. For tracers of size $\delta = 0.2$, we choose $\tau_{cg,0.2} = 0.05$ for both matrices. For larger tracers, we use $\tau_{cg,\delta} = \tau_{cg,0.2} (\tau_{cage,\delta} / \tau_{cage,0.2})$ to remove the effects of cage exploration, where $\tau_{cage,\delta}$ is chosen to satisfy $\langle \Delta \tilde{r}^2(\tau_{\text{cage},\delta}) \rangle / \sigma_t^2 = 1.0$. Representative trajectories for tracers of size $\delta = 0.35$ have distinct morphologies in the two matrices (Fig. 2.4(a), (b)). Tracer trajectories are tenuous and fractal-like in the RGM but more compact in the AGM. We characterize this difference in shape by examining the tracer trajectory mass M, calculated as the number of boxes of size $\langle \Delta \tilde{r}^2(\tau_{cg,\delta}) \rangle$ (the square-root of the tracer MSD at the coarse-grained time scale, $\tau_{cg,\delta}$) needed to cover the trajectory, as a function of the trajectory radius of gyration $R_{g}^{84,85}$. The mass of tracer trajectories in the RGM scales as a power-law with $R_{\rm g}$, i.e., $M \sim R_{\rm g}^{d_{\rm f}}$, and the resultant long-time fractal dimension $d_{\rm f} \approx 2.0$ is approximately independent of the tracer size. This fractal scaling of the tracer trajectories corresponds to free diffusion and is expected for both matrices, which are ergodic on long time scales. For tracer trajectories in the AGM, however, M is larger than that in the RGM at a given $R_{\rm g}$; likewise, the instantaneous slope is larger and does not approach the expected terminal scaling with $R_{\rm g}$ of 2.0 on accessible time scales. Thus, tracer trajectories in the AGM are more compact than those in the RGM on similar length and time scales.

2.3 Conclusions

Our simulations reveal that the spatiotemporally heterogeneous dynamics in glassy liquids of varying matrix particle interactions alter the dynamics of hardsphere tracers. The tracers couple to relaxation processes in repulsive and attractive matrices on distinct time and length scales. As a result, tracers exhibit trajectories of different shape in the two matrices, indicating that matrix interactions alter the ability of tracers to explore space within a slowly relaxing matrix. Because dispersing particles within slowly-relaxing matrices with varying interactions appear in settings ranging from the crowded cytoplasm inside cells to natural soils in the environment to artificial fiber nanocomposites and membranes, these results provide insight into the coupling between particle transport and matrix dynamics across a wide range of scientifically and technologically relevant processes.

Chapter 3: Tracer Transport in Attractive and Repulsive Supercooled Liquids and Glasses

This chapter was previously published by AIP Publishing LLC: Roberts, R. C.; Poling-Skutvik, R.; Conrad, J. C.; Palmer, J. C.;, *The Journal of Chemical Physics* 2019, **151**, 194501.

3.1 Introduction

The transport of dilute small molecules or particles within disordered media affects the delivery of drug molecules encapsulated in hydrogels,^{86,87} the efficacy of polymeric gas separation membranes in capturing carbon dioxide or purifying natural gas,^{88,89} and the movement of DNA through the crowded cytoplasm during transformation and transcription.^{90–92} In these processes, penetrant dynamics may couple to the structure and/or to the slow relaxations of the surrounding matrix. As an example, increasing the density of an arrested, disordered matrix leads to anomalous diffusion at a critical density or localization at higher densities.^{93,94} Likewise, matrix mobility affects gas diffusion in polymeric membranes^{95–97} and the transport of cytoskeletal and cytoplasmic constituents within the cell.^{90,98} Understanding the effects of matrix structure and dynamics on penetrant transport, however, remains a persistent challenge.

Recent progress has been made in understanding tracer transport in complex matrices using well-controlled colloidal models. Anomalous tracer dynamics and localization have been observed in model disordered media consisting of colloidal particles fixed in gel-like⁹⁹ and liquid configurations.^{100,101} Similarly, tracer dynamics have also been shown to be coupled to matrix motion, crossing over from localized to diffusive behavior as the matrix relaxes.^{102,103} This coupling, however, depends on the relative time scales between tracer and matrix dynamics and also the nature of the matrix relaxations. It is unclear, for example, how the onset of non-ergodic, glassy dynamics^{33,104} may influence this coupling. Moreover, it is also unclear how tracer coupling is affected by the nature of the matrix relaxations, which can be qualitatively altered by modulating the interactions between matrix particles.^{105,106}

In this study, we use event-driven molecular dynamics (MD) to investigate the transport of tracer particles in a model colloidal glass-former consisting of a squarewell fluid with short-ranged attractions.^{105,107} In the supercooled liquid regime, this system exhibits reentrant dynamics characterized by a marked increase in the liguid's relaxation time upon heating or cooling. Whereas heating produces a "repulsive" glassy liquid in which relaxations are hindered by steric interactions between particles, cooling results in an "attractive" glassy liquid where relaxations are frustrated by long-lived interparticle bonds.^{105,107} Distinct glasses can be prepared by further heating or cooling of the repulsive and attractive liquids, respectively, and by compression. Here, we examine the dynamics of tracer particles of a critical size, known to exhibit anomalous transport, ^{102,103} embedded in these liquid and glass matrices. We find that tracer transport is affected both by intermediate- and long-time matrix dynamics as well as by the matrix structure. Intriguingly, sufficiently large local fluctuations in arrested matrices that do not relax on long time scales can allow tracers to escape cages and recover diffusive behavior. In strongly quenched matrices, however, tracer dynamics are primarily determined by the structure of matrix cages. Our results identify the relative contributions of matrix structure and dynamics on tracer motions in attractive and repulsive glassy matrices and thus provide a framework to understand transport processes in slowly-relaxing materials.


Figure 3.1: (a) Rendering of a configuration with tracers (red) in a matrix of A (green) and B (blue) particles. (b) Tracer trajectories 360τ in duration within G_{0.20}. (c) Twodimensional projection of a tracer trajectory 800τ in duration illustrating tracer cage rearrangement.

3.2 Methods

3.2.1 Model systems

Event-driven MD simulations were performed to investigate the transport behavior of tracer particles in glassy matrices.²⁴The matrices were modeled using a wellstudied equimolar binary (AB) glass-forming mixture that exhibits reentrant dynamics. ^{105,108,109} Following Refs. 105,109,110, the matrix species were assigned unit masses (m = 1) and a hard-core diameter ratio of σ_{AA} : $\sigma_{BB} = 1.2$:1 to frustrate crystallization (Fig. 3.1). The matrix particles interacted through a short-range square-well potential with depth $u_0 = 1$ and width $\Delta_{ij} = 0.03(\sigma_{ij} + \Delta_{ij})$ for each pair type $i, j \in A, B$, where $\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj})$. In the discussion to follow, we adopt conventional simulation units in which Boltzmann's constant $k_B = 1$ and σ_{BB} , u_0/k_B , and $\sigma_{BB}(m/u_0)^{1/2}$ are the fundamental measures of length, temperature, and time, respectively. To account for the influence of temperature on particle dynamics, we also define a thermal time scale $\tau = tD_0/D_{ref}$, where t is the nominal simulation time, $D_0 = \sigma_{BB}\sqrt{k_BT/m}$ is the thermal diffusivity at temperature T, and D_{ref} is the reference value of D_0 at T = 1.¹⁰⁷

We examined tracer dynamics in matrices with N = 1372 particles at six different state points specified by $\{\phi, T\}$, where ϕ is the volume fraction of matrix particles (Fig. 3.2, Tbl. 3.2). For notational convenience, we refer to these samples as L_T or G_T (liquid or glass, respectively), where T is the sample temperature. We considered two ergodic liquid states at $\phi = 0.610$ with approximately equal long-time diffusion coefficients D_i/D_0 : a high-temperature repulsive glassy liquid ($L_{1.05}$) and a lowtemperature attractive glassy liquid ($L_{0.35}$), where D_i is the nominal diffusion coefficient. ¹⁰³ Two glasses were also prepared at the same temperatures ($G_{1.05}, G_{0.35}$) and increased matrix volume fraction $\phi = 0.635$. Similarly, a glass ($G_{0.20}$) with $\phi = 0.610$ was prepared at T = 0.20, a lower temperature than the attractive glassy liquid. Finally, we also studied a hard-sphere glass at $\phi = 0.610$ and T = 1.00 (HSG_{1.00}), which is equivalent to a square-well glass in the high-temperature limit (Fig. 3.2).

We embedded $N_{\rm t} = 10$ tracers into each supercooled liquid or glass matrix. Interactions between the matrix and tracer particles were modeled using purely repulsive, hard-sphere collisions. The diameter of the tracer $\sigma_{\rm tt}$ was chosen such

Matrix	State	Т	ϕ	t_w^{-1}	$n_{ m s}^{2}$	$n_{ m c,iso}^{3}$	$n_{ m t,iso}^4$
$L_{0.35}$	Liquid	0.35	0.610	_	5	50	80
$L_{1.05}$	Liquid	1.05	0.610	_	5	50	80
$G_{0.35}$	Glass	0.35	0.635	$8.1 imes10^5$	20	100	80
$G_{1.05}$	Glass	1.05	0.635	$8.7 imes10^5$	20	100	80
G _{0.20}	Glass	0.20	0.610	$8.0 imes10^5$	10	100	80
$HSG_{1.00}$	Glass	1.00	0.610	$1.7 imes 10^6$	5	50	80

Table 3.1: Liquid and glass matrices examined in this study.

that $\delta_t = \sigma_{tt}/\sigma_{AB} = 0.35$, which is approximately the size ratio where tracers exhibit anomalous dynamics and couple to matrix fluctuations and relaxations.^{102,103} Larger tracers exhibit dynamics similar to matrix particles, whereas smaller tracers can traverse through interstitial voids and thus are largely unaffected by matrix fluctuations.^{102,103}



Figure 3.2: State diagram from Ref. 107 for the model square-well glass former. Symbols denote the locations of the liquid (L) and glass (G) matrices investigated in this study. Arrows denote hypothetical protocols for preparing glasses from the ergodic liquids.

The supercooled liquid matrices were equilibrated at their respective T and ϕ . The glass matrices, by contrast, were prepared by first incrementally compressing the system to a volume fraction of $\phi = 0.610$ by increasing the particle radii. The systems were then equilibrated in the NVT ensemble at T = 0.55. Following equilibration, the samples were either instantaneously thermally quenched to their final temperature by rescaling the particle velocities (G_{0.20} and HSG_{1.00}) or compressed to $\phi = 0.630$ in increments of $\Delta \phi = 0.010$, followed by additional compression to $\phi = 0.635$ in a single step of $\Delta \phi = 0.005$, and then thermally quenched (G_{0.35} and G_{1.05}). After each compression increment, the glasses were simulated for 10τ at constant ϕ and T to relax compression-induced stresses. This protocol was employed in earlier studies, 107,110 where it was shown to not qualitatively affect dynamics beyond the microscopic regime. 110 For the HSG_{1.00} sample, the attractive square-well interactions were removed after the thermal quench. All glasses were subsequently aged for a waiting time $t_w \gg \tau_{\text{max}}$ (Tbl. 3.1), producing t_w -invariant trajectory data up to the maximum observation time ($\tau_{\text{max}} \approx 10^5$). 107 Statistical properties were calculated by averaging over trajectories computed for $n_s = 5-20$ independent samples prepared for each type of matrix using the protocols described above.

3.2.2 Cage analysis

To characterize the restriction of tracer particle motions by the matrices, we performed cage analysis using the method of Doliwa and Heuer.^{31,111} Their method is based on the assumption that the sequential displacements of caged particles will be directionally anticorrelated. Consider an initial displacement of a caged particle $\Delta \vec{r}_{01} = \vec{r}(\Delta t) - \vec{r}(0)$ over a time interval Δt on which $\Delta \vec{r}_{01}$ is comparable to the characteristic cage size, where \vec{r} is the particle's position vector. Because the neighbor cage restricts further motion along $\Delta \vec{r}_{01}$, the displacement over the next time interval $\Delta \vec{r}_{12} = \vec{r}(2\Delta t) - \vec{r}(\Delta t)$ should, on average, be anticorrelated. The displacement $\Delta \vec{r}_{12}$ can be projected onto the unit vector of the preceding displacement $\Delta \vec{r}_{01}$, yielding the caging displacement projection (CDP) $x_{12} \equiv \Delta \vec{r}_{12} \cdot \frac{\Delta \vec{r}_{01}}{|\Delta \vec{r}_{01}|}$, which is parallel to $\Delta \vec{r}_{01}$. For a caged particle, the ensemble-averaged CDP $\langle x_{12} \rangle$ is negative and its magnitude grows with $|\Delta \vec{r}_{01}|$. In hard-sphere supercooled liquids, $\langle x_{12} \rangle = -c|\Delta \vec{r}_{01}|$ for small displacements where the cage has not been broken. Larger magnitudes of the proportionality constant c indicate greater displacement memory during caging.³¹ For larger, cage-breaking displacements, by contrast, $\langle x_{12} \rangle$ is independent of $|\Delta \vec{r}_{01}|$.¹¹²

In analyzing tracer dynamics, we first compute the non-Gaussian parameter for

particle displacements $\alpha_2(\Delta t)$ (Fig. 3.3). The maximum in $\alpha_2(\Delta t)$ signifies the time scale τ^* on which the per-particle variance in tracer dynamics due to caging and matrix rearrangement is greatest. 26,113 We use $\Delta t = \tau^*$ as the time interval for computing tracer displacements $\Delta \vec{r}_{01}$ and $\Delta \vec{r}_{12}$. 112 The magnitudes of tracer displacements at τ^* vary across different matrices. To account for this variation, we report normalized quantities $\tilde{x}_{12} \equiv \mathscr{C}^{-1}\langle x_{12}\rangle$ and $\tilde{r}_{01} \equiv \mathscr{C}^{-1}|\Delta \vec{r}_{01}|$, where \mathscr{C} is the square-root of the tracer mean-square displacement Δr^2 at lag time τ^* .



Figure 3.3: Non-Gaussian parameter α_2 for tracer particles in each matrix as a function of normalized time scale τ . Arrows indicate the maximum in α_2 and the corresponding lag time of the maximum τ^* . Arrows are color-coded according to their respective matrices.

3.2.3 Isoconfigurational ensemble

We performed simulations in the isoconfigurational ensemble (IE) to isolate the effects of matrix structure on particle dynamics. In this approach, an ensemble of separate simulations are run over a fixed time interval. Each simulation starts from the same initial particle configuration, but with a different set of randomly-assigned momenta.¹¹⁴ For each matrix system, we analyzed $n_{c,iso} = 50 - 100$ configurations (Tbl. 3.1) extracted from independently-prepared samples prepared using the procedures described in Section 3.2.1. Each of the $n_{c,iso}$ configurations was used to initialize $n_{t,iso} = 80$ short MD trajectories. Initial particle momenta for the MD trajectories were randomly drawn from the Maxwell-Boltzmann distribution at set temperature T.^{114,115} Isoconfigurational averages $\langle ... \rangle_{iso}$ were computed from statistics collected from the MD trajectories. Specifically, to characterize the mobility of individual particles, we calculated the dynamic propensity $DP_i(t) = \langle \frac{(\vec{r}_i(t) - \vec{r}_i(0))^2}{\Delta r_i^2} \rangle_{iso}$, where Δr_i^2 is the ensemble-averaged mean-square displacement (MSD) of the *i*th particle. This quantity is the second moment of the particle displacement distribution, computed by averaging over the trajectories of particle *i*. When each particle's mobility is equal to the average mobility $\langle \Delta r_i^2 \rangle_{iso}$, DP_i will be unity.^{116,117} Thus, examination of this quantity for all particles provides insight into the spatial distribution of dynamic heterogeneity.

3.2.4 Trajectory shape analysis

To characterize the shapes of tracer rearrangements, we calculated the mass M of a trajectory as a function of its radius of gyration $R_{\rm g}$. This analysis is performed by overlaying the trajectory on a cubic lattice composed of unit cells with edge length $\sigma_{\rm tt}$. The trajectory mass M is evaluated by assigning each cell unit mass and summing over the unique cells visited by the trajectory.^{85,118} To remove the effects of the initial ballistic motion, we coarse-grain the trajectories over a time scale $\tau_{\rm cg}$ such that $\langle \Delta r^2(\tau_{\rm cg}) \rangle = \sigma_{\rm tt}^2$ for tracers within a given matrix. The trajectories are then re-sampled to ensure that successive frames are separated by a time interval $\tau_{\rm cg}$. From the coarse-grained trajectories, we compute the radius of gyration $R_g = \sqrt{\frac{1}{n_{\rm ng}} \sum_{i=1}^{n_{\rm cg}} (\vec{x}_i - \vec{x}_{\rm avg})^2}$, where $n_{\rm cg}$ is the number of coarse-grained points in the trajectory, \vec{x}_i is the position of the *i*th coarse-grained point, and $\vec{x}_{\rm avg} = \frac{1}{n_{\rm cg}} \sum_{i=1}^{n_{\rm cg}} \vec{x}_i$ is the mean position.

3.3 Results and Discussion

3.3.1 Matrix dynamics

We first characterize the dynamics of the different glassy matrices through the ensemble-averaged mean-square displacement (MSD) Δr^2 (Fig. 3.5), focusing on the intermediate-time and long-time dynamics of the large matrix particles. The intermediate-time dynamics are influenced by cage rattling and interactions between matrix particles, whereas long-time dynamics are controlled by the ability of the matrix to relax when particles escape their local cages. Generally, the MSDs exhibit the expected behavior for glassy matrices: ^{105,107,119} intermediate relaxations are suppressed in attractive matrices relative to those in comparable repulsive matrices and long-time relaxations are suppressed in vitrified samples. Similar behaviors can be observed in the matrices' self-intermediate scattering functions, $F_s(q,\tau) = \langle \frac{1}{N_i} \sum_{k=1}^{N_i} \exp[-j\vec{q} \cdot (\vec{r}_k(\tau) - \vec{r}_k(0))] \rangle$, where $q = |\vec{q}|$ is the wavevector magnitude, $j = \sqrt{-1}$, N_i is the number of particle species *i*, and the brackets indicate an ensemble average (Fig. 3.4). Detailed comparisons between different matrices reveal further insights into relaxation processes of glassy matrices.

The MSD of the large matrix particles in $L_{1.05}$ is approximately constant on lag times $\tau \approx 10^0$ to 10^3 , indicating interparticle caging (Fig. 3.5(a)). By contrast, Δr^2 for $L_{0.35}$ exhibits a small plateau at $\tau \approx 10^{-1}$ followed by an increasing, subdiffusive power-law $\Delta r^2 \approx \tau^{\beta}$ that extends to $\tau \approx 10^3$, where $\beta \approx 0.32$. The small plateau corresponds to the length scale of interparticle bond formation, whereas the power-law region signifies a transition from dynamics dominated by bonding at small τ to dynamics dominated by caging at larger τ .¹⁰⁵ The smaller values of Δr^2 indicate that particles in $L_{0.35}$ are more localized than those in $L_{1.05}$, likely due to the formation of interparticle bonds.¹²⁰ Thus, on intermediate time scales the liquids have different relaxation mechanisms. On long time scales, however, the liquids exhibit nearly-



Figure 3.4: Self-intermediate scattering function $F_s(q,\tau)$ for $q\sigma_{\rm BB} = 6.7$ for matrix particle species A in each system.

identical dynamics. The MSD for both $L_{0.35}$ and $L_{1.05}$ scales linearly with τ at long times, indicating normal diffusive dynamics. The crossover to diffusive dynamics occurs on similar time and length scales in both liquid matrices and indicates the terminal relaxation of the matrix as particles escape from their local cages.

Next, we examine the dynamics of the glassy matrices ($G_{0.20}$ and $HSG_{1.00}$) with the same ϕ as the two supercooled liquids. The $G_{0.20}$ and $HSG_{1.00}$ glasses exhibit dynamics on intermediate time scales similar to the corresponding liquids ($L_{0.35}$ and $L_{1.05}$), but do not relax on long time scales (Fig. 3.5(a)). The Δr^2 of the hard-sphere glass $HSG_{1.00}$ exhibits a plateau on intermediate time scales, similar to the one observed for the repulsive liquid $L_{1.05}$. The smaller plateau height in $HSG_{1.00}$ relative to that in $L_{1.05}$ indicates that thermal fluctuations in the repulsive liquid slightly increase the local cage size. Likewise, Δr^2 of the attractive glass $G_{0.20}$ resembles that of the liquid $L_{0.35}$, exhibiting a small plateau followed by a power-law increase with



Figure 3.5: Mean-square displacement Δr^2 for matrix species A (a) for all matrices with $\phi = 0.610$ and (b) for glasses with $\phi = 0.635$ compared to the corresponding liquids with $\phi = 0.610$. The black solid line indicates a power-law slope of one.

time. The power-law exponent in this increasing region is $\beta \approx 0.11$, smaller than the exponent $\beta \approx 0.32$ for the corresponding $L_{0.35}$ liquid matrix. This behavior indicates that matrix rearrangements are restricted on intermediate length and time scales due to the stronger attractions between particles in $G_{0.20}$.

Two glassy matrices $G_{0.35}$ and $G_{1.05}$ can also be produced by compressing from $\phi = 0.610$ to 0.635. This increase in ϕ leads to suppressed plateaus in Δr^2 on intermediate time scales and prevents the matrix from fully relaxing on long time scales. The Δr^2 of $G_{1.05}$ displays an intermediate-time plateau that is suppressed relative to the plateau for the liquid $L_{1.05}$ (Fig. 3.5(b)) because of the higher matrix density of $G_{1.05}$. The MSD of $G_{0.35}$ exhibits a small shoulder at $\tau \approx 10^{-1}$, qualitatively similar to but quantitatively lower than the one observed for $L_{0.35}$, which arises from attractive bond formation. On time scales $\tau \gtrsim 10^2$, the MSD of $G_{0.35}$ exhibits a long-time

plateau that contrasts with the extended power law observed on long time scales for the Δr^2 of L_{0.35}. The plateau indicates that particles in G_{0.35} remain caged on long time scales, whereas the extended power-law in L_{0.35} indicates that bond rearrangement and cage escape occur on similar time scales. Thus, comparison of the MSDs for G_{0.35} and G_{1.05} with those of L_{0.35} and L_{1.05} reveals that increasing matrix ϕ results in caging-driven arrest.

3.3.2 Tracer dynamics

Differences in packing fraction and interparticle interactions influence fluctuations and relaxations in the six matrices, leading to distinct dynamics. The dynamics of tracers of a critical relative size, $\delta_t = 0.35$, 102,103,121 within a slowly-relaxing matrix are affected both by caging within matrix voids and matrix relaxations and fluctuations. 102,103,121 We thus anticipate that differences in matrix structure and dynamics will alter the motions of confined tracer particles, providing insight into the nature of the transport processes in these matrices. 102,103

After initial ballistic motion, tracers of relative size $\delta_t = 0.35$ relax differently on intermediate and long time scales in different matrices (Fig. 3.6). The tracers embedded in the $L_{0.35}$ and $L_{1.05}$ matrices exhibit subdiffusion on intermediate time scales $10^{-1} \leq \tau \leq 10^3$. Diffusive dynamics are recovered on long time scales $\tau \gtrsim 10^3$, with tracers in $L_{1.05}$ exhibiting a higher diffusivity. The transition from ballistic motion to subdiffusive dynamics reflects the onset of caging by the matrix particles. The value of the MSD at the crossover to subdiffusive behavior is greater for $L_{0.35}$ than in $L_{1.05}$, indicating that tracers explore larger voids in $L_{0.35}$.¹⁰³ The logarithmic slope β of the tracer MSD in the subdiffusive regime ($\Delta r^2 \sim t^{\beta}$), however, is smaller for $L_{0.35}$ than for $L_{1.05}$, reflecting smaller matrix fluctuations on these time scales (Fig. 3.5). The larger voids and slower tracer relaxations in $L_{0.35}$ are due to subtle changes in matrix structure arising from the strong attractive bonds between the matrix particles.^{103,122,123} To obtain insight into the effects of temperature-induced matrix arrest on tracer dynamics, we compare tracer MSDs in $L_{0.35}$ and $L_{1.05}$ to those in $G_{0.20}$ and $HSG_{1.00}$. Tracer dynamics in $HSG_{1.00}$ are subdiffusive for time scales $10^{-1} \leq \tau \leq 10^3$ and diffusive for long time scales $\tau \gtrsim 10^3$ (Fig. 3.6(a)). In the subdiffusive regime, the tracer MSD of $HSG_{1.00}$ has a slightly smaller slope and magnitude for a given τ relative to $L_{1.05}$. Furthermore, diffusive dynamics are recovered later in time in $HSG_{1.00}$ and the terminal diffusivity is smaller. These behaviors suggest that tracer dynamics in $L_{1.05}$ are faster and less localized than in $HSG_{1.00}$ and that tracer cage escape occurs on shorter time scales in $L_{1.05}$ due to its liquid-like relaxations.



Figure 3.6: Mean-square displacement Δr^2 for (a) tracers in matrices with $\phi = 0.610$ and tracers in glasses with $\phi = 0.635$ and the corresponding liquids. Arrows indicate the time scales at which (a) $\Delta r^2_{G_{0.20}} \approx \Delta r^2_{L_{0.35}}$ and (b) $\Delta r^2_{G_{0.35}}$ and $\Delta r^2_{G_{1.05}}$ qualitatively diverge.

Tracer dynamics within the attractive matrices $L_{0.35}$ and $G_{0.20}$ exhibit distinct features not present in $L_{1.05}$ and $HSG_{1.00}$, reflecting the effects of attractive bonds between the matrix particles. The tracer MSDs Δr^2 in $L_{0.35}$ and $G_{0.20}$ are subdiffusive and nearly identical for time scales $10^{-1} \le \tau \le 10^1$, but diverge for $\tau > 10^1$. In the subdiffusive regime $(10^{-1} \le \tau \le 10^1)$, the slopes of the MSDs of L_{0.35} and G_{0.20} are smaller than those of L_{1.05} and HSG_{1.00}. The MSD of tracers in L_{0.35} transitions from subdiffusive to diffusive scaling, becoming fully diffusive for $\tau > 10^3$. By contrast, the Δr^2 of tracers in G_{0.20} scale subdiffusively, appearing to tend towards recovering diffusive behavior on time scales longer than those readily accessible in simulation. This extended subdiffusion arises from the increased role of matrix interparticle bonding, which reduces matrix fluctuations and increases the residence time of tracers in matrix cages.

Comparison of matrix and tracer MSDs reveals dynamic coupling on intermediate time scales and suggests that these processes can facilitate tracer transport. Tracer dynamics in $\mathrm{HSG}_{1.00}$ are diffusive on time scales exceeding $au\gtrsim 10^3$, even though the matrix itself does not relax. This behavior sharply contrasts with the lack of tracer diffusion in $G_{0.20}$ even on much longer time scales of $\tau \sim 10^5$. The matrix Δr^2 of HSG_{1.00} is an order of magnitude larger than that of G_{0.20} (Fig. 3.5(a)), indicating that intermediate-time-scale fluctuations are larger in the repulsive glass. Hence, thermal 'cage rattling' in $HSG_{1.00}$ allows tracers to escape and diffuse but is suppressed in $G_{0.20}$ due to the presence of attractive bonds. Tracer dynamics begin to recover diffusive behavior in $G_{0.20}$ on long time scales, when rare fluctuations in the matrix occur that allow tracers to escape. The long-time tracer dynamics in the arrested glasses $G_{0.20}$ and $HSG_{1.00}$ qualitatively differ from those in the completely frozen attractive and repulsive matrices examined in Ref. 103. Whereas tracers are localized in cages at long times in frozen matrices, the intermediate-time fluctuations of arrested glasses allow for long-time tracer relaxation and cage escape. This relaxation occurs on longer time scales within $G_{0.20}$ than in HSG_{1.00} because $G_{0.20}$ exhibits smaller matrix fluctuations and hence more closely approximates the environment encountered in completely frozen matrices.

Comparison of transport within attractive $G_{0.20}$ and repulsive HSG_{1.00} glasses with the corresponding liquids ($L_{0.35}$ and $L_{1.05}$, respectively) reveals how changes in matrix relaxation processes due to temperature-induced vitrification affect tracer dynamics. Insights into how compression-induced vitrification influences tracer dynamics can be obtained by examining the glasses $G_{0.35}$ and $G_{1.05}$. Densification reduces the magnitude of the tracer MSDs in glasses at the onset of subdiffusion, relative to all other matrices, reflecting the smaller cages formed at higher ϕ . In addition, the logarithmic slopes of the tracer Δr^2 in $G_{0.35}$ and $G_{1.05}$ for a given τ are smaller than those of the other matrices and diffusive dynamics are not recovered on long time scales. This reduction in tracer mobility on intermediate and long time scales appears to be primarily a trivial consequence of increased matrix density.

The nature of the interactions between matrix particles in $G_{0.35}$ and $G_{1.05}$ also affects tracer dynamics. The tracer Δr^2 in $G_{0.35}$ and $G_{1.05}$ are nearly identical up to $\tau \lesssim 10^2$. This result is in sharp contrast with the marked differences in short- and intermediate time tracer dynamics in the lower-density glasses ($G_{0.20}$ and HSG_{1.00}). One possible explanation is that increasing matrix density may lead to more uniform cages in attractive and repulsive glasses that are accessible to tracers of this size on short time scales. For $\tau \gtrsim 10^2$, however, the tracer MSDs remain subdiffusive but begin to diverge, with tracers in $G_{0.35}$ exhibiting slower dynamics than in $G_{1.05}$. This result suggests that tracer dynamics are still sensitive to differences in cage rattling in $G_{1.05}$ and $G_{0.35}$ (Fig. 3.5(b)), but only on longer time scales.

3.3.3 Effects of matrix caging

Tracers in all matrices exhibit subdiffusive behavior on intermediate time scales $10^{-1} \leq \tau \leq 10^3$, suggesting that they are transiently caged by the matrix (Fig 3.6). To further investigate the effect of matrix caging on tracer dynamics, we calculate the tracer CDP \tilde{x}_{12} as a function of the initial displacement magnitude \tilde{r}_{01} for lag times τ^* . For a particle trapped in a harmonic well, \tilde{x}_{12} varies linearly with \tilde{r}_{01} with a slope

of c = 0.5, indicating that the second displacement $\Delta \vec{r}_{12}$ is anti-correlated with the initial displacement $\Delta \vec{r}_{01}$.¹²⁴ The slope c is the extent to which a particle is "dragged back" (this phenomenon henceforth referred to as backdragging) as a fraction of its initial displacement \tilde{r}_{01} .³¹ For matrix particles in glassy liquids, by contrast, \tilde{x}_{12} varies linearly with \tilde{r}_{01} for small displacements, but deviates from this initial linear behavior for \tilde{r}_{01} beyond a length scale \tilde{r}_{cage} identified as the characteristic cage size.^{31,111,125,126}

Matrix	$r_{\rm cage}^{5}$
$L_{0.35}$	$0.69 {\pm} 0.04$
$L_{1.05}$	$0.31 {\pm} 0.02$
$G_{0.35}$	$0.75 {\pm} 0.05$
$G_{1.05}$	$0.75 {\pm} 0.05$
$G_{0.20}$	$0.72{\pm}0.03$
$HSG_{1.00}$	$0.38{\pm}0.02$

Table 3.2: Cage size r_{cage} for tracers in each matrix.

For all tracers, the CDP linearly decreases for small displacements, indicating that they are caged by the matrices up to a length scale \tilde{r}_{cage} (Fig. 3.7). The cage length scale depends upon the matrix and varies between 0.3 and 0.8 (in units of σ_{BB}) (Tbl. 3.2). The slopes c, which reflect the extent of backdragging for tracers in each matrix, are ≥ 0.4 , near the harmonic limit of c = 0.5 and are similar for all tracers for $\tilde{r}_{01} < \tilde{r}_{cage}$. The similar values of c indicates that tracers vibrate nearly harmonically within their cages, suggesting that collisions of the tracers with the matrix dominate dynamics up to \tilde{r}_{cage} .

Tracers with displacements larger than \tilde{r}_{cage} escape their cages and rearrange into new positions. Steeper slopes for the tracer CDP \tilde{x}_{12} in the rearrangement regime indicate enhanced backdragging. For tracers within the repulsive liquid L_{1.05} and glass HSG_{1.00}, \tilde{x}_{12} is approximately constant for $\tilde{r}_{01} > \tilde{r}_{cage}$, indicating that the extent of backdragging does not increase beyond \tilde{r}_{cage} (Fig. 3.7(a)). For the other matrices, by contrast, \tilde{x}_{12} continues to decrease with increasing \tilde{r}_{01} for $\tilde{r}_{01} > \tilde{r}_{cage}$,



Figure 3.7: (a) Normalized CDP \tilde{x}_{12} versus previous displacement magnitude \tilde{r}_{01} for tracers in matrices with $\phi = 0.610$ and (b) for tracers in glasses with $\phi = 0.635$ and in the liquids. Shaded regions indicate statistical uncertainty. The black solid lines have a slope of -0.5.

but not as sharply as in the small-displacement regime. This behavior indicates that tracers are dragged back, but not as far as predicted from linear extrapolation from the harmonic region.¹¹² Similar behavior has also been observed in the rearrangement regime for probe particles in Laponite clay gels.^{127,128} Analyses of simple model systems show that such deviations from linearity are observed if the matrix is heterogeneous on the scale of the tracers or the relaxation rate of the probe particle is spatially dependent.¹²⁸ Accordingly, the behavior of \tilde{x}_{12} for L_{0.35}, G_{0.20}, G_{0.35}, and G_{1.05} indicates heterogeneity in tracer dynamics for length scales beyond \tilde{r}_{cage} and within these matrices.^{103,122,123} Comparison of the slopes for different matrices suggest that backdragging outside of the local cage is enhanced by stronger matrix bonding (e.g., G_{0.20} vs. L_{0.35}). Further, the fact that the \tilde{x}_{12} slopes are similar for G_{0.35} and G_{1.05} but different for the other matrices (L_{0.35}, L_{1.05}, and HSG_{1.00}) indicates that matrix



Figure 3.8: Tracer dynamic susceptibility χ_4 (a) in matrices with $\phi = 0.610$ and (b) in glasses with $\phi = 0.635$ and the liquids. Wavevectors maximize the peak in χ_4 and are $q\sigma_{BB} = 2.0, 2.5, 1.6, 2.8, 3.0, and 3.0$ for L_{0.35}, L_{1.05}, G_{0.20}, HSG_{1.00}, G_{0.35}, and G_{1.05}, respectively.

density, not matrix interparticle interactions, is the dominant factor controlling the extent of backdragging in the rearrangement regime.

To directly quantify tracer dynamical heterogeneity arising from differing matrix interparticle interactions, we calculated the dynamic susceptibility $\chi_4(q,\tau)$ at the wavevector magnitude q for which the peak in χ_4 is maximized (Fig. 3.8(a) and (b)). The dynamic susceptibility is the variance of tracer self-dynamics, defined as $\chi_4(q,\tau) \equiv N_t(F_s^2(q,\tau) - [F_s(q,\tau)]^2)$. For all matrices, χ_4 exhibits a peak whose location and width corresponds to the maximum and persistence of tracer dynamic heterogeneity, respectively. Comparison of the χ_4 widths reveals that the persistence of the tracer dynamic heterogeneity varies across the different matrices, increasing such that $L_{1.05} < HSG_{1.00} < G_{0.20}$. Based on the tracer CDPs for these matrices, we posit that the increase in tracer dynamic heterogeneity persistence may be associated with larger cages \tilde{r}_{cage} (e.g., larger in HSG_{1.00} than in L_{1.05}; Tbl. 3.2) and enhanced backdragging (e.g., in G_{0.20} vs. HSG_{1.00}) in the rearrangement regime.

3.3.4 Structural determinism of tracer dynamics

The susceptibility χ_4 reveals that the dynamics of the embedded tracer particles are temporally heterogeneous. To quantify the structural and dynamical contributions to this heterogeneous behavior, we performed simulations in the isoconfigurational ensemble. Because this analysis allows a particle's capacity for motion to be characterized for a given initial configuration, it enables the spatial distribution of dynamics in a given system to be linked to the system's structure¹¹⁴ without requiring correlations to specific structural metrics (e.g., free volume, potential energy, etc.) to be established, which has proven to be extremely challenging.^{129,130} In this ensemble, total tracer dynamical fluctuations can be expressed as $\Delta_{c,norm} = \sigma_{DP}^2 + \Delta_{c,norm}^{iso}$.^{131–133} The first term $\sigma_{DP}^2 = \langle (DP_i)^2 \rangle - 1$ is the structural variance, where $\langle ... \rangle$ is the ensemble average over all $n_{c,iso}$ configurations, $n_{t,iso}$ trajectories, and N_t tracer particles. This variance is a measure of fluctuations in the tracer dynamic propensity DP_i . The second term $\Delta_{c,norm}^{iso} = \langle DP_{2,i} - (DP_i)^2 \rangle$ is the dynamical variance, where $DP_{2,i} = \frac{\langle (\vec{r}_i(t) - \vec{r}_i(0))^4 \rangle_{iso}}{\langle \Delta r_i^2 \rangle_{iso}^2}$. This variance quantifies the spread in DP_i between different isoconfigurational trajectories.

In $L_{0.35}$ and $L_{1.05}$, the tracer structural variance σ_{DP}^2 increases up to and peaks at $\tau \approx 10^1$, corresponding to the time at which tracers experience maximum structural determinism (Fig. 3.9(a)). On longer time scales, σ_{DP}^2 decreases and reaches a value near zero at $\tau \approx 10^3$, approximately the lag time at which tracer dynamics become diffusive in the MSD Δr^2 (Fig. 3.6). The structural variance σ_{DP}^2 is larger and attains a maximum at a larger lag time τ for tracers within $L_{0.35}$ compared to $L_{1.05}$. Strictly positive values of σ_{DP}^2 arise from particle-to-particle variations in dynamic propensity. Hence, the larger values of σ_{DP}^2 indicate that tracer relaxation times are more broadly distributed in $L_{0.35}$, which is a consequence of the structural



Figure 3.9: Tracer structural variance $\sigma_{\rm DP}^2$ of the dynamic propensity DP_i distribution. (a) $\sigma_{\rm DP}^2$ for tracers in matrices with $\phi = 0.610$. (b) $\sigma_{\rm DP}^2$ for tracers in glasses with $\phi = 0.635$ and in the corresponding liquids. Shaded regions indicate statistical uncertainty.

heterogeneity arising from strong interparticle bonds in this matrix. The existence of greater structural heterogeneity in $L_{0.35}$ than in $L_{1.05}$ is evidenced by the shorter first peak in matrix static structure factor S(q), which indicates reduced translational ordering (Fig. 3.11). Similar evidence can be found by inspecting the matrix radial distribution function g(r) (Fig. 3.12).

To understand the effects of matrix arrest on structural determinism in tracer dynamics, we compare the structural variances in $L_{0.35}$ and $L_{1.05}$ to those in $G_{0.20}$ and HSG_{1.00} (Fig. 3.9(a)). The tracer σ_{DP}^2 in HSG_{1.00} exhibits a larger peak at a larger τ than in $L_{1.05}$. The structure of the nearly arrested HSG_{1.00} matrix obstructs tracer rearrangement, leading to a broader DP_i distribution. Surprisingly, σ_{DP}^2 is greater in attractive than repulsive arrested matrices $\sigma_{DP,HSG_{1.00}}^2 < \sigma_{DP,G_{0.20}}^2$, and the disparity in σ_{DP}^2 between $L_{0.35}$ and $G_{0.20}$ is much larger than the disparity between



Figure 3.10: Fraction of tracer fluctuations due to initial structure R_c . (a) R_c for tracers in matrices with $\phi = 0.610$. (b) R_c for tracers in glasses with $\phi = 0.635$ and in the corresponding liquids. Shaded regions indicate statistical uncertainty.

 $L_{1.05}$ and $HSG_{1.00}$. These observations suggest that arrest by bonding in attractive matrices results in local environments that are highly structurally heterogeneous compared to those in the repulsive matrices.

In the higher-density matrices (G_{0.35} and G_{1.05}), $\sigma_{\rm DP}^2$ increases steeply for tracers for $\tau \lesssim 10^3$, appearing to plateau or even slightly decrease on longer time scales (Fig. 3.9(b)). On time scales exceeding 10^3 , $\sigma_{\rm DP}^2$ increases very gradually or decreases slightly for tracers within G_{0.35} and G_{1.05}, respectively. The strong initial increase in $\sigma_{\rm DP}^2$ indicates heterogeneous local environments and a broad distribution of tracer relaxation times. This increase is similar to that observed in the lower-density, strongly arrested glass G_{0.20}. The common feature of G_{0.20}, G_{0.35}, and G_{1.05} is that matrix rattling is suppressed on intermediate to long time scales, indicated by the low values of the matrix MSD (Fig. 3.5). Thus, reduced matrix fluctuations appear to lead to an



Figure 3.11: Static structure factor S(q) for all matrix particles in each system. increase in structural determinism in the tracer dynamics.

Finally, to characterize the relative importance of structure for tracer dynamics, we examine the relative contribution of $\sigma_{\rm DP}^2$ to total tracer fluctuations within each matrix via the structural ratio $R_{\rm c} = \sigma_{\rm DP}^2 / \Delta_{\rm c,norm}$, where $R_{\rm c}$ is the fractional contribution of isoconfigurational fluctuations due to structure. ^{131,132} For tracers in all matrices, $R_{\rm c}$ is approximately constant on short time scales $\tau \lesssim 10^1$ but varies depending on matrix (Fig. 3.10(a) and (b)). This behavior suggests that the relative contributions from matrix structure are fixed on these time scales but depend on matrix density and interactions between matrix particles. The values of $R_{\rm c}$ for matrix particles are larger than those of the corresponding tracers (Fig. 3.13) for all matrices, indicating that structural contributions are more important for the matrix dynamics than for tracer dynamics. For $\tau \gtrsim 10^2$, $R_{\rm c}$ for tracers in L_{1.05}, L_{0.35}, and HSG_{1.00} decay towards zero as tracer dynamics become diffusive (Fig. 3.6) and χ_4 peaks (Fig. 3.8(a)). Collectively, these observations suggest that relatively large dynamical ma-



Figure 3.12: Radial distribution function g(r) for all matrix particles in each system. The first, second, and third sharp peaks at small r arise from B-B, A-B, and A-A nearest neighbors, respectively. The black line indicates g(r) = 1.

trix fluctuations in these matrices allow tracers to escape their local cage so that matrix structure no longer affects tracer dynamics. By contrast, the values of R_c for $G_{0.20}$, $G_{0.35}$, and $G_{1.05}$ continue to increase for $\tau \gtrsim 10^2$. The absence of tracer diffusion within these matrices on these time scales suggests that tracers are partially or fully localized and thus their dynamics are strongly influenced by matrix structure. This interpretation is consistent with the nearly constant dynamical variances $\Delta_{c,norm}^{iso}$ for $G_{0.20}$, $G_{0.35}$, and $G_{1.05}$ on intermediate to long time scales (Fig. 3.14). Sufficiently strong vitrification, whether through attractive bonding ($G_{0.20}$) or increased matrix density ($G_{0.35}$ and $G_{1.05}$), reduces dynamical matrix fluctuations and thereby hinders the ability of tracers to escape their cages. As a result, tracer dynamics in highly vitrified matrices are more strongly influenced by matrix structure.



Figure 3.13: Fractional contribution of isoconfigurational fluctuations due to structure R_c for matrix particles in each system. Shaded regions indicate statistical uncertainty. The reported R_c values were computed by averaging n_s independent configurations (Table 3.1)

3.3.5 Consequences for tracer exploration

To characterize tracer exploration within each matrix, we analyze the scaling of the tracer trajectory radius of gyration R_g as a function of its mass M. Comparison of the trajectory shapes for tracers within attractive and repulsive matrices reveal that the nature of interactions between matrix particles influences tracer exploration (Fig. 3.15). For tracers within $L_{1.05}$ and $HSG_{1.00}$, M scales approximately as a power law for large R_g ($R_g > 0.5$, long times). The logarithmic slope d_f in this region defines the fractal dimension, which is approximately 2.0 in both matrices. This value corresponds to the limit of free diffusion that is expected for tracers at long times (large R_g) in all matrices in which tracer dynamics are ergodic. For tracers within $L_{0.35}$ and $G_{0.20}$, by contrast, the instantaneous value of d_f is larger than 2.0. This



Figure 3.14: Tracer dynamical variance $\Delta_{c,norm}^{iso}$ of the dynamic propensity DP_i distribution for each system. Shaded regions indicate statistical uncertainty.

result indicates that the trajectories in attractive matrices are more compact than those within repulsive matrices, with a fractal dimension that approaches that of a geometric solid (i.e., $d_f = 3$). The nearly indistinguishable mass scaling of the arrested and liquid matrices suggests that it is matrix interparticle interactions and not dynamical arrest that leads to the difference between attractive and repulsive matrices.

Lastly, we examine the role of matrix density on tracer trajectory shape by comparing the fractal scaling of tracer trajectories in $G_{0.35}$ and $G_{1.05}$ to $L_{0.35}$ and $L_{1.05}$ (Fig. 3.15(b)). The slopes in the glasses are larger than those in the corresponding liquid, illustrating that tracer trajectories within the glasses have larger fractal dimensions than those within the liquids. Thus, tracer trajectories in $G_{0.35}$ and $G_{1.05}$ are less extended in space, indicating that tracers explore cages for longer periods of time and rearrange over smaller distances as matrix density is increased.



Figure 3.15: Mass *M* of tracer trajectories as a function of radius of gyration R_g as calculated by box-counting (a) in matrices with $\phi = 0.610$ and (b) in glasses with $\phi = 0.635$ and in the liquids. Black dotted and dashed lines indicate fractal scalings of three and two, respectively.

3.4 Conclusions

We used event-driven MD to investigate the dynamics of dilute, hard-sphere tracers in attractive and repulsive liquid matrices with similar long-time relaxations and in analogous attractive and repulsive glass matrices prepared via thermal quenching or compression. Comparison of the matrix and tracer MSDs revealed the effects of matrix dynamics on tracer dynamics. Although tracers within glasses were less mobile than tracers within the corresponding liquids, matrix arrest was insufficient to guarantee tracer localization. Through cage analysis, we determined whether tracers are caged for small displacements and characterized the heterogeneity of tracer cage rearrangements for large displacements. This analysis revealed that increasing matrix density ϕ from 0.610 to 0.635 (G_{0.35}, G_{1.05}) or enhancing attractions (G_{0.20}, $L_{0.35}$) increased the tracer dynamic heterogeneity within these matrices relative to the repulsive matrices with $\phi = 0.610$ ($L_{1.05}$, HSG_{1.00}). The tracer dynamic susceptibility revealed that tracer dynamics were spatiotemporally heterogeneous, as also shown through cage analysis. By performing simulations in the isoconfigurational ensemble and calculating the dynamic propensity, we quantified the structurallyinduced heterogeneity of tracer dynamics and the extent to which tracer dynamics were determined by matrix structure. This analysis revealed that strong arrest of the matrix, driven by attractive bonding or high density, enhanced structural determinism. Finally, the mass scaling of tracer trajectories revealed that increasing matrix attractions or matrix density leads to more compact tracer trajectories. These results collectively reveal how the spatial and temporal heterogeneity in matrices is reflected in the dynamics of embedded tracers.

Our simulations also demonstrate that tracers are able to diffuse on long time scales through glass matrices if the matrix fluctuations are sufficiently large. This result has interesting implications for understanding the ability of tracers to penetrate dense, slowly-relaxing matrices, suggesting that fluctuations above a critical size can facilitate transport even in matrices that do not fully relax on long time scales. The findings from our study also motivate future work in a number of different directions. Whereas our investigation focused on understating equilibrium tracer dynamics, penetrant transport in most practical settings is driven by a chemical potential gradient and hence occurs under nonequilibrium conditions. Although much work has been done towards understanding nonequilibrium transport through rigid matrices, ^{134–136} it remains unclear how these processes are influenced by structural fluctuations and slow matrix relaxations. Additionally, fluctuations within the matrices studied here are isotropic due to the bulk nature of the samples imposed through the use of periodic boundary conditions. Experimental studies of supercooled liquids and glasses show, however, that fluctuations in these system can become anisotropic

by imposing different boundary conditions.^{137,138} This scenario has been encountered, for example, when examining the dynamics of confined supercooled liquids in porous media^{139,140} and glasses prepared through vapor deposition onto surfaces.¹⁴¹ An intriguing future line of inquiry would be to investigate how anisotropic fluctuations in these systems affects the dynamic coupling of tracer and matrix particles. Lastly, we investigated small particles in the isolated tracer limit. For asymmetric hard-sphere binary mixtures, both reentrant melting of the large-particle glass and vitrification of the small particles were observed upon increasing small-particle density.^{142,143} How matrix interactions affect and, in turn, are affected by tracers at high concentrations has not yet been studied. We anticipate that these outstanding questions can be addressed using computational approaches similar to those employed in this study.

Chapter 4: Dynamics of Polydisperse Hard-Spheres Under Confinement

This chapter was previously published by Taylor & Francis Group: Roberts, R. C.; Marioni, N.; Palmer, J. C.; Conrad, J. C., *Molecular Physics* 2020, 1-9.

4.1 Introduction

The underlying mechanisms responsible for the dramatic slowing of dynamics by many orders of magnitude upon compression or cooling of dense liquids are incompletely understood and intensely debated^{4,34}. Near the glass transition, particles are trapped in long-lived cages formed by their neighbors, and are able to relax only when the cages rearrange. Phenomenologically, this relaxation is viewed as a twostep process involving movement within and escape from the cage formed by the neighbors^{6,144,145}. This coupling to neighbor configuration suggests that the surrounding structure is a strong determinant of glassy dynamics. How the nature of the cages and their relaxations depend on the structure of the liquid remain open questions. The length scale and structural motifs associated with these relaxations are thought to be non-local^{130,131}. Indeed, upon cooling or compressing the dynamics of liquids become increasingly heterogeneous in space and time. These spatial heterogeneities are thought to be connected to a growing length scale over which dynamics are correlated^{146–148}.

Confining a liquids inside a thin geometry modifies the dynamics and introduces a competing length scale H, characterizing the extent of confinement.^{149–152}. For hard-sphere fluids under weak confinement ($H \gtrsim 5$ particle diameters) the dynamics slow monotonically as the confinement length scale is decreased ^{137,152}. In stronglyconfined hard-sphere systems ($H \lesssim 5$ particle diameters), by contrast, the relaxation times can depend non-monotonically on the separation between the walls^{137,153–157}. At high particle densities, this non-monotonic behavior can lead to multiple glass transitions¹⁵⁴, as predicted by mode-coupling theory¹⁵³. Notably, the glass transition line for polydisperse hard spheres exhibits oscillations whose period is of the order of the particle diameter¹⁵⁴, strongly intimating that the competition between layering and local packing drives the unusual dynamical re-entrance observed in these systems.

For certain glass-forming systems, bond-orientational order has been shown to be connected to dynamics. Numerical simulations of 2-D polydisperse hard disks, for example, reveal that transient clusters of highly-ordered particles are correlated with dynamical heterogeneity¹⁵⁸. In several systems, the clusters associated with such medium-range crystalline order (MRCO) are hexatically-ordered in 2-D^{159,160} or hexagonally-ordered in 3-D^{133,161,162}. Whereas the static and dynamic length scales have been shown to grow similarly for 2-D glasses with MRCO, this behavior is not observed in other 2-D glass formers^{163,164}. In strongly confined systems, MRCO is enhanced within the layers of particles that form near the confining walls¹⁶⁵. When the confinement length scale is commensurate with particle size, particles within the layers typically adopt hexatic order parallel to the walls. By contrast, incommensurate geometries tend to promote square ordering^{166–168}. While these earlier studies show that MRCO is amplified by strong confinement, they have not explored its link to dynamics.

In this study, we use molecular dynamics (MD) simulations to investigate the connection between local structural ordering and the unusual re-entrant dynamics observed for polydisperse hard-sphere liquids confined in small slit pores. Despite the polydisperse nature of these systems, the particles in the contact layers adjacent to the confining walls exhibit pronounced local ordering, whose symmetry changes as the wall separation becomes incommensurate with the average particle size. Particles in commensurate geometries largely exhibit hexatic local order, whereas square local order is also observed in systems where the confinement length scale is incommensurate with particle size. The static correlation length associated with hexatic local order is found to increase logarithmically with the relaxation time, in agreement with predictions from 2-D random first-order theory¹² and models based on locally-favored structures³⁵. Square ordering, by contrast, is short-ranged and not associated with a growing length scale even for incommensurately-packed systems in which square ordering is most prevalent. This observation suggests that square order is strongly geometrically frustrated for all levels of confinement studied here. For incommensurate geometries, neither hexatic nor square ordering are associated with a growing length scale. This striking result indicates that the connection between bond-orientational order and dynamical slowing can be altered by varying confinement.

4.2 Methods

Event-driven MD simulations were performed to investigate the behavior of polydisperse hard-spheres confined in slit-shaped pores consisting of two parallel walls separated by distance H along the z-axis of the cell. Periodic boundary conditions were imposed along the x- and y-axes parallel to the walls to model an infinite slab geometry. Each of the N = 10976 particles in the system was assigned unit mass and a hard-core diameter σ_i randomly sampled from a Gaussian distribution. The average of the distribution was set to $\bar{\sigma} = 1$ and the standard deviation s was chosen to modulate particle polydispersity (PDI). Following convention, we adopt units in which Boltzmann's constant $k_{\rm B} = 1$, and $\bar{\sigma}$ and $t = \bar{\sigma} (m/k_{\rm B}T)^{1/2}$ are the fundamental measures of length and time, respectively^{19,154}. All simulations were performed in the microcanonical (NVE) ensemble, with initial particle momenta randomly drawn from the Maxwell-Boltzmann distribution with specified temperature T = 1.

We investigated the static and dynamic properties of the confined hard-spheres

at various state points specified by $\{s, \phi, H\}$, where ϕ is the particle volume fraction. For PDI s = 0.15, we examined ranges $0.47 \le \phi \le 0.51$ and $2.00 \le H \le 3.00$. For s = 0.05, we considered $2.00 \le H \le 3.00$ at a single volume fraction $\phi = 0.51$. The systems were prepared by incrementally compressing an initial confined liquid-like configuration at $\phi = 0.45$ to achieve the final H and ϕ . The compression steps were performed in increments of $\Delta \phi = 0.01$, following each step by a short MD simulation (10t) at constant ϕ to relax compression-induced stresses. After compression, the systems were equilibrated until their properties became invariant with sample age. The sample age was measured as the waiting time t_w , defined as the time elapsed since the end of the final compression step.

For all systems, we computed the mean 2-D Mermin order parameters averaged over particles in the wall contact layers¹⁶⁹

$$\psi_l = \frac{1}{N_{\text{wall}}} \sum_{j=1}^{N_{\text{wall}}} \psi_l^j \tag{4.1}$$

where

$$\psi_l^j = \frac{1}{n_j} \sum_{k=1}^{n_j} e^{il\theta_{jk}}, \tag{4.2}$$

 N_{wall} is the number of particles in the wall contact layers, n_j is the number of nearest neighbors of particle j, $i = \sqrt{-1}$, l is a positive integer indicating the orientational symmetry, $\theta_{jk} = \cos^{-1} [\mathbf{\hat{i}} \cdot \mathbf{r}_{jk} | \mathbf{r}_{jk} |^{-1}]$ is the angle between the *x*-axis and the in-plane interparticle separation vector $\mathbf{r}_{jk} = \mathbf{r}_j - \mathbf{r}_k$, $\mathbf{\hat{i}}$ is the unit vector along the *x*-axis, and $\mathbf{r}_j = \{x_j, y_j\}$ is the in-plane particle position vector for particle *j*. The contact layers were identified by computing the density profile along the *z*-axis perpendicular to the walls

$$\rho(z) = \frac{1}{N\Delta z} \sum_{j=1}^{N} \delta(z - z_j), \qquad (4.3)$$

where z_j is the out-of-plane particle coordinate and Δz is the bin width. Particles with *z*-coordinates lying between the first two minima in $\rho(z)$ nearest to each wall were defined as belonging to the contact layers. Equation 4.2 was evaluated by taking the sum over the nearest neighbors of the central particle j that lie within the same layer and a cutoff separation distance of r = 1.34, which approximately encompasses the first coordination shell.

We monitored ψ_4 and ψ_6 , which are sensitive to square and hexatic ordering, respectively. The order parameter $\psi_4 = 1$ for perfect long-range square ordering, whereas $\psi_6 = 1$ for systems with perfect long-range hexatic ordering. For disordered systems, $\psi_4 \rightarrow 0$ and $\psi_6 \rightarrow 0$ as $N \rightarrow \infty$, but they take on small positive values near zero in finite systems due to fluctuations. Systems with appreciable square and/or hexatic ordering (i.e., $\psi_4 \ge 0.05$ and/or $\psi_6 \ge 0.05$) were considered equilibrated when the Mermin order parameters became invariant with sample age (within statistical uncertainty). This invariance was observed for t_w ranging from 20000 – 100000. For the remaining (disordered) systems, equilibration was monitored by computing the the pore-averaged mean-square displacement (MSD)

$$\Delta r^{2}(t) = \frac{1}{N} \sum_{k=1}^{N} \left(\mathbf{r}_{k}^{2}(t) - \mathbf{r}_{k}^{2}(0) \right)^{2}$$
(4.4)

as a function of sample age. The systems were considered equilibrated when the MSDs computed over different time periods became statistically invariant with respect to sample age. This criterion was met for t_w ranging from 200 – 30000 simulation time units, depending on the state conditions.

Following equilibration, the simulations were extended to generate a production phase, during which trajectories were saved for subsequent analysis. The duration of the production phase was typically a factor of 10 longer than the equilibration period. Statistical properties at each state point were computed by averaging over $N_{\rm s} = 5, 10$, or 20 independent simulations, depending on the PDI, each initiated from a different particle configuration prepared using the procedures described above. The correlation lengths ξ_l associated with *l*-fold symmetry were estimated by computing the in-plane spatial correlation functions for the 2-D Mermin parameters

$$g_l(r) = \frac{L^2}{2\pi r \Delta r N_{\text{wall}}(N_{\text{wall}}-1)} \sum_{j \neq k} \delta(r - |\mathbf{r}_{jk}|) \psi_l^j \psi_l^{k*}$$
(4.5)

where L is the length of the simulation cell in the direction parallel to the walls, Δr is the histogram bin width, and $\psi_l^j \psi_l^{k*} = \operatorname{Re}(\psi_l^j)\operatorname{Re}(\psi_l^k) + \operatorname{Im}(\psi_l^j)\operatorname{Im}(\psi_l^k)$. Equation 4.5 was evaluated for l = 4,6 to analyze the extent of square and hexatic ordering in the contact layers, respectively. The correlation lengths for both symmetries were extracted by fitting an exponential

$$f(r) = A \exp[-2r/\xi_l] \tag{4.6}$$

to the envelope of $g_l(r)/g(r)$, where g(r) is the in-plane radial distribution function computed by evaluating Eq. 4.5 with the product $\psi_l^j \psi_l^{k*}$ omitted ^{170,171}. An exponential fitting function was used because the usual Ornstein-Zernike (OZ) expression, which predicts power-law decay r^{-n} , is derived for isotropic systems, whereas the confined systems studied here are anisotropic¹⁷².

To characterize the relaxation dynamics, we calculated $S_{00}^{(s)}(q,t)$, which is the selfpart of the first component of the matrix

$$S_{\mu\nu}(q,t) = \frac{1}{N} \langle \rho_{\mu}(\mathbf{q},t)^* \rho_{\nu}(\mathbf{q},0) \rangle \tag{4.7}$$

indexed by non-negative integers μ , ν . Equation 4.7 is a generalization of the intermediate scattering function to systems confined in one dimension, with associated density fluctuations

$$\rho_{\mu}(\mathbf{q},t) = \sum_{j=1}^{N} \exp[iQ_{\mu}z_{j}(t)]e^{i\mathbf{q}\cdot\mathbf{r}_{j}(t)}.$$
(4.8)

Here, $\mathbf{q} = \{q_x, q_y\}$ is the wavevector with norm q, $Q_{\mu} = 2\pi\mu H^{-1}$ is a discrete

wavenumber, and $\mathbf{r}_j = \{x_j, y_j\}$ and z_j are the in- and out-of-plane particle coordinates, respectively.



4.3 Results and Discussion

Figure 4.1: (a) Pore-averaged $S_{00}^{(s)}(q_{xy}\bar{\sigma} = 3.3,t)$ in the direction parallel to the walls for $\{s,\phi\} = \{0.15,0.50\}$ and varying H. (b) Inverse relaxation time τ_{xy}^{-1} as a function of H for systems with s = 0.15 and different ϕ . The relaxation times are defined via $S_{00}^{(s)}(q_{xy}\bar{\sigma} = 3.3, \tau_{xy}) = 1/e$.

We first examine the dynamics of strongly confined liquids parallel to the direction of confinement through the intermediate scattering function $S_{00}^{(s)}(q_{xy}\bar{\sigma}=3.3,t)$ at the wave-vector corresponding to a length scale of approximately two particle diameters (Fig. 4.1(a)). For wall separations $2 \le H \le 3$, $S_{00}^{(s)}(q_{xy}\bar{\sigma}=3.3,t)$ fully decays to zero on time scales accessible with simulation. We define the in-plane, pore-averaged relaxation time scale τ_{xy} via $S_{00}^{(s)}(q_{xy}\bar{\sigma}=3.3,\tau_{xy}) = 1/e$. The out-of-plane dynamics also fully relax, but the terminal relaxations are not diffusive due to the confinement imposed along the this direction and thus are not discussed further.

The in-plane relaxation dynamics depend non-monotonically on the wall separation H (Fig. 4.1(b)). At a volume fraction of $\phi = 0.47$, the inverse relaxation time τ_{xy}^{-1} depends only weakly on H. Near $H \approx 2.1$, τ_{xy}^{-1} exhibits a weak local maximum, and near $H \approx 2.3$ it exhibits a modest local minimum. Thus, highly confined, disperse suspensions exhibit re-entrant dynamics. These local extrema become more pronounced as ϕ is increased to 0.51. Our results are qualitatively similar to those of Ref.¹⁵⁴, which reported re-entrant diffusivities, extracted from the long-time limit of the ensemble-averaged mean-square displacements, for strongly confined suspensions of polydisperse hard spheres.

To gain insight into the changes in the underlying microstructure that are responsible for these unusual re-entrant dynamics, we first examine the number density profiles along the direction perpendicular to the walls, $\rho(z)$. The evolution of $\rho(z)$ with increasing ϕ varies markedly with the wall separation H. For H = 2.20, $\rho(z)$ does not strongly depend upon ϕ (Fig. 4.2(a)). Two layers form near the walls in all systems, and $\rho(z)$ is slightly enhanced near the pore center at z = 0 as ϕ is increased. Increasing the wall separation slightly to H = 2.34 leads to a stronger enhancement in density near the pore center with increasing ϕ (Fig. 4.2(b)). Systems confined at H = 2.50, however, show pronounced variation in $\rho(z)$ with ϕ (Fig. 4.2(c)). Three layers form in these systems. Further, as ϕ is increased the local maxima and minima respectively increase and decrease in height, indicating that layering becomes more pronounced. An additional increase in the wall separation, to H = 3.00, reveals three layers whose density profiles do not strongly vary with ϕ (Fig. 4.2(d)), as for H = 2.00.

The evolution in $\rho(z)$ with H indicates a change in the ordering of particle layers within the pore. For commensurate wall separations H, the ratio $H/\bar{\sigma}$ takes integer values and particles organize into close-packed layers^{167,173}. Incommensurate wall separations are those for which $H/\bar{\sigma}$ takes on non-integer values, disrupting



Figure 4.2: Number density profiles $\rho(z)$ in the direction perpendicular to the confining walls for (a) H = 2.20, (b) H = 2.34, (c) H = 2.50, and (d) H = 3.00 and volume fractions ϕ denoted in the legend. Each system has a polydispersity of s = 0.15.

the close-packed layers. For our systems, the development of incommensurate packing (between H = 2.20 and H = 2.34, Fig. 4.2(a,b)) coincides with the minimum in τ_{xy}^{-1} (Fig. 4.1). The development of incommensurate packing was observed to correlate with slow dynamics and larger nonergodicity parameters in Ref. 174, suggesting that motion in the confining plane is obstructed by such packings. For H = 2.20, however, relaxation times increase markedly without the formation of incommensurate layers, suggesting additional mechanisms for dynamical slowing.

To explore other mechanisms leading to dynamical slowing, we examine the local structure of particles in layers. Previous studies of monodispersed particles $^{166-168,175}$ have shown that fully developed incommensurate packings for nearly half-integer values of $H/\bar{\sigma}$ are accompanied by a change in the in-plane local crystal structure. In monodisperse systems, increasing the wall separation from 2 to 3 particle diameters at $\phi \approx 0.50$ drives a transition in the in-plane order from $2\Delta \rightarrow 3\Box \rightarrow 3\Delta$, where Δ and \Box indicate hexatic and square order, and the integers indicate the number of distinct particle layers ¹⁶⁸. Although our systems are polydisperse, we hypothesize that the change in commensurability in our system is also accompanied by a change in the the local structure of the particles.

To scrutinize the evolution of local structure in our systems, we calculate ψ_4^j and ψ_6^j (Eq. 4.2) for particles within the layers nearest to the wall (Fig. 4.3(a)). Particles within the contact layers adjacent to the walls are colored according to the magnitudes of the local Mermin order parameters (Eq. 4.2) with dark blue and dark red indicating $\psi_6 = 1$ and $\psi_4 = 1$, respectively. Particles with $\psi_6 \approx \psi_4 \approx 0$, or not within the wall contact layers, are colored white. The parameters ψ_4^j and ψ_6^j are local variants of the spatially averaged 2-D Mermin parameters (Eq. 4.1) that characterize the extent of square and hexatic order in the coordination environments of individual particles, respectively. We first examine a low-dispersity system (PDI 5%, s = 0.05) with $\phi = 0.51$, whose structure is expected to closely mimic that of confined monodisperse spheres. The phase behavior of unconfined bulk systems was found to be qualitatively similar to the monodisperse limit below a threshold particle polydispersity^{176,177}. This threshold is larger for confined than unconfined particles^{19,154}. In our confined systems, increasing the wall separation from H = 2.20 to 3.00 leads to changes in the predominant local order in the wall contact layers (Fig. 4.3(b-e)). For


Figure 4.3: Renderings of systems with $\phi = 0.51$ in the directions (a) parallel and (b-i) perpendicular to the confining walls. Systems with (b-e) s = 0.05 and (f-i) s = 0.15. Wall separations are (b,f) H = 2.20, (c,g) H = 2.34, (a,d,h) H = 2.50, and (e,i) H = 3.00.

H = 2.20 particles primarily exhibit hexatic local order. For H = 2.34 local hexatic and square order coexist, whereas for H = 2.50 local square order is dominant. Finally, at H = 3.00 the particles near the wall again exhibit primarily hexatic local order. These observations indicate that the extent of hexatic local ordering is re-entrant. Hexatic local order is more prevalent in strongly confined systems for which packing is commensurate. Square ordering becomes more prevalent in incommensurate packings as a mechanism by which particles resolve frustration in ordering, forming BCC-like local arrangements in the direction perpendicular to the pore walls.

The transition from hexatic to square local order observed in our simulations with s = 0.05 is consistent with the $2\Delta \rightarrow 3\Box$ transition observed for monodisperse hard spheres over this range of wall separations¹⁶⁸. Further, the coexistence of square and hexatic motifs in H = 2.34 is analogous to two-phase coexistence between 2Δ and $3\Box$ observed from the free energy calculations of Ref.¹⁶⁸. Indeed, despite the

modest dispersity, all systems with s = 0.05 fully crystallize on the simulated time scales.

Re-entrance in the extent of hexatic order is also observed with increasing wall separation when the dispersity is increased to 15% (Fig. 4.3(f-i)). The fraction of particles with locally square order increases as H is increased from 2.00 to 2.50, and then decreases for larger wall separations. The size of ordered regions is smaller, however, in higher-dispersity than in lower-dispersity systems. In contrast to the 5% dispersity system at H = 2.50, large regions of locally square order are not found in the 15% dispersity sample. This result is consistent with earlier observations that dispersity reduces the length scale associated with MRCO¹⁶⁵. Collectively, our results indicate that these length scales are strongly sensitive to the extent of confinement in polydisperse systems.



Figure 4.4: (a) Hexatic correlation function $g_6(r)/g(r)$ for H = 2.05, s = 0.15 and ϕ denoted in the legend. (b) Square correlation function $g_4(r)/g(r)$ for H = 2.50. Dashed lines are error-weighted fits to the function envelopes to decaying exponentials (Eq. 4.6).

To extract the characteristic length scales associated with hexatic and square local order, we calculate the correlation functions $g_6(r)/g(r)$ and $g_4(r)/g(r)$, respectively (Fig. 4.4). The envelope of each correlation function can be fit using a decaying exponential (Eq. 4.6) to extract static correlation lengths associated with square and hexatic order (ξ_4 and ξ_6 , respectively). The hexatic length scale ξ_6 grows steeply with ϕ for 2.00 $\leq H \leq 2.34$ and 2.70 $\leq H \leq 3.00$, the systems with commensurate packing (Fig. 4.5(a)). For systems with strongly incommensurate packing (H = 2.50 and 2.55), however, ξ_6 is nearly independent of ϕ . For these systems, particles of average size cannot organize into hexagonal layers parallel to the confining walls at these high volume fractions^{167,168}. Thus, hexatic ordering is frustrated by the competition between in-plane and out-of-plane packing within incommensurately-packed systems. In addition, ξ_6 exhibits re-entrance as the wall separation H is increased for all ϕ . This structural re-entrance follows the dynamic re-entrance observed in our simulations (Fig. 4.1) and in earlier studies^{154,157}.

By contrast, the square correlation length ξ_4 does not grow strongly with ϕ for any H (Fig. 4.5(b)). The prevalence of square ordering increases with ϕ for H = 2.50 and H = 2.55, but this behavior is not associated with an increase in the static correlation length ξ_4 . Instead, it manifests as an increase in the exponential prefactor A (Eq. 4.6). In the conventional OZ formalism, A is a local analytic function unrelated to the static correlation length 172 . This behavior indicates that square ordering is primarily local. The local nature of square ordering likely arises from its greater susceptibility to frustration 158,162 , which has been attributed to mechanical instabilities associated with this type of order in confined hard-spheres 178 .

The relatively small magnitudes of ξ_6 and ξ_4 for H = 2.50 compared to the values at other H indicate that square and hexatic ordering compete in these systems. Examination of the local order parameters for H = 2.50 provides additional support for this idea. The absence of well-defined hexatic and square regions indicates that



Figure 4.5: Correlation length scales associated with (a) ξ_6 and (b) ξ_4 for particles within the contact layers adjacent to the walls as a function of H. Error bars reflect uncertainties in ξ_l from fits of the envelopes of $g_l(r)/g(r)$ to decaying exponentials (Eq. 4.6).

no one type of order is dominant and that the development of local crystalline motifs is frustrated (Fig. 4.3(h)). The relative dominance of square ordering for H = 2.50at s = 0.05 (Fig. 4.3(d)) suggests that increasing polydispersity facilitates competition between domains with different local order, which has been observed for bulk systems^{176,179}.

To directly assess the role of hexatic ordering on the slowing of dynamics, we examine the dependence of the in-plane relaxation time τ_{xy} on ξ_6 . For wall separations that lead to approximately commensurate packing (H = 2.00, 2.34, and 3.00), ξ_6 increases logarithmically with τ_{xy} (Fig. 4.6). A similar dependence of the relaxation time on the hexatic length scale was also observed in simulations of 2-D polydisperse particle, binary metal, driven granular, and binary spin systems exhibiting MRCO^{158,160,162}. This behavior is consistent with scaling arguments for the relax-



Figure 4.6: Correlation length scales associated with (a) ξ_6 and (b) ξ_4 for particles within the contact layers adjacent to the walls as a function of relaxation time τ_{xy} . Solid lines are fits to the relation $\tau_{xy} = B \exp(C\xi_l)$, where B and C are positive constants and ξ_l is either ξ_4 or ξ_6 .

ation time derived from 2-D random first-order theory (RFOT)¹². The RFOT framework predicts that, below a threshold temperature (or above a threshold density, for hard spheres), a glassy liquid can be described as a mosaic of distinct domains that rearrange cooperatively and are separated by well-defined interfaces^{12,34}. In this low-temperature (or high-density) regime, the relaxation time increases exponentially with the domain size. For the hexatic ordering in our confined systems, the predicted scaling would imply that $\tau_{xy} = B \exp(C\xi_l)$, where B and C are positive constants, which is consistent with our simulation data. Similar scaling is also predicted by the locally-favored structure model for vitrification of Ref. 35. In addition to ξ_4 and ξ_6 , several other structural metrics were also analyzed, but were found to exhibit only weak correlations with τ_{xy} for the systems examined here (Fig. 4.7). These comparisons collectively suggest dynamical slowing in quasi-2-D systems with



commensurate layering is driven by hexatic ordering.

Figure 4.7: (a) Data from Fig. 4.6(a). Correlation of τ_{xy} with the (b) local particle volume fraction and the (c) averages and (d) standard deviations of the particle diameter distributions. Solid and dashed lines correspond to contact and incommensurate layers, respectively.

By contrast, ξ_6 is nearly independent of τ_{xy} for H = 2.50, which exhibits incommensurate packing (Fig. 4.6(a)). For this system, hexatic ordering does not appear to drive dynamical slowing, suggesting a different crystalline symmetry or mech-

anism is responsible. Because local square order is enhanced in this system (Fig. 4.3(h)), we also examine the scaling of ξ_4 with τ_{xy} . Interestingly, ξ_4 is smaller for H = 2.50 compared to H = 2.00, 2.34, and 3.00, which likely occurs due to greater disorder in the incommensurate packing for this wall separation. Nonetheless, we find that ξ_4 does not significantly increase with τ_{xy} for any wall separation (Fig. 4.6(b)), suggesting square ordering is not strongly associated with dynamical slowing. Our results show that the relaxation time increases logarithmitically with the static correlation length associated with hexatic MRCO in commensurate system with $H \approx 2.50$. Whether dynamical slowing in this system is associated with a growing static correlation length or a different underlying physical mechanism remains an open question.

4.4 Conclusions

In this study, we investigated the connection between local structural ordering and the unusual re-entrant dynamics observed for polydisperse hard-sphere liquids confined in small slit pores. At low polydispersity, hexatic and square local order dominate in systems with commensurate and incommensurate packings, respectively. At higher polydispersities, the competition between hexatic, square, and liquid-like order is more pronounced, consistent with the reduction in MRCO observed in unconfined liquids as dispersity is increased.

For commensurate packings with $H \leq 2.34$, we found that the static correlation length associated with local hexatic order increased logarithmically with the relaxation time scale, in agreement with the prediction from 2-D random first-order theory. By contrast, square ordering was short-ranged and was not associated with a growing length scale. The short-ranged square ordering and lack of well-defined ordered domains indicated that incommensurately-packed systems were more geometrically frustrated than commensurately-packed systems. For H = 2.50, the growth of MRCO was frustrated, yet dynamical slowing with increasing ϕ persisted. Together, these results suggest that a growing static length scale associated with bond orientational order can contribute to dynamical slowing in strongly-confined hardspheres. Moreover, they show that the influence of bond-orientational order on dynamical slowing may be altered by slight changes in the extent of confinement.

Our analysis revealed a growing length scale associated with hexatic local order for systems with commensurate packing. For the incommensurately-packed, strongly frustrated systems, a growing length scale has yet to be identified. It is of interest to ask whether other dynamic and static length scales¹⁶⁴, such as the dynamical correlation length¹⁴⁶ or point-to-set length scale^{180,181}, and/or the structural entropy^{165,182} also exhibit re-entrance that correlates with the dynamics. Further, the connection between local structure and dynamics in polydisperse liquids may be affected by the nature of the particle size distribution (e.g. Gaussian versus Pareto-distributed particle sizes^{183,184})¹⁷¹. Future investigations in these areas are expected to provide additional insight into how the mechanisms for dynamical slowing differ in 2-D, quasi-2-D, and 3-D systems.

Chapter 5: Conclusions and future work

5.1 Conclusions

In this work, we presented investigations into the often-encountered scenario of anomalous, slow dynamics within supercooled liquids and glasses. To probe the physics of these systems, we performed MD simulations to study (1) the dynamics of dilute, hard sphere tracers within model liquid and glass matrices and (2) the evolution of ordered domains with dynamic slowdown in confined hard spheres. To understand the role of interparticle interactions on non-absorbing tracer dynamics, the matrix dynamics were tuned from attractive to repulsive by varying T. This system is similar to the dense phase of liquid-liquid phase-separated solutions of oppositely charged macromolecular species¹⁸⁵, in which the attractions between the macromolecules may be tuned from strong to weak¹⁸⁶. With increasing tracer size, we found that tracer dynamics became slower and more like the glassy dynamics of the underlying liquid matrices, exhibiting anomalous logarithmic decay in the intermediate scattering function at a critical size of $\delta \approx 0.35$. Despite the long-time attractive and repulsive liquid diffusivities being approximately equal, the anomalous dynamics of the tracers extended for larger length and time scales within the attractive matrices. This coupling to distinct time and length scales suggested that the liquid dynamics in the caging regime alter tracer dynamics, manifesting in more compact tracer trajectories in the attractive systems.

We extended this work by simulating hard sphere tracers of the critical size $\delta \approx 0.35$ in attractive and repulsive glasses, finding that dynamic arrest in the glass matrices further slowed tracer dynamics and that tracers were localized in attractive glasses. However, arrest did not guarantee tracer localization in the case of

hard sphere glasses, for which tracers became diffusive on simulation time scales. Further investigation revealed that tracers in attractive systems were more strongly caged and that caging length scales were more heterogeneous compared to repulsive counterparts, suggesting that heterogeneity in attractive systems strongly influenced tracer dynamics. Using the isoconfigurational ensemble, we found that structural heterogeneity in attractive systems played a stronger role in determining tracer dynamics in the caging regime, indicating that the larger fluctuations during the caging regime in repulsive systems resulted in greater coupling between matrix dynamics and tracer dynamics. Conversely, the smaller caging fluctuations of attractive systems resulted in more static cages, allowing matrix void structure to control tracer fluctuations.

Finally, we investigated the role of local bond-orientational order on the dynamic slowdown of supercooled hard spheres confined between two parallel hard plates with varying plate separation H. On decreasing H, the system exhibited a minimum diffusivity at an intermediate $H \approx 2.34$, corresponding to a switch from incommensurate to commensurate packing in the direction perpendicular to the confining walls. For commensurate packings (H < 2.34 and H = 3.00), relaxation times in the direction parallel to the walls increase exponentially with the correlation length of hexatically ordered domains, which increases in size with increasing ϕ . For incommensurate packings H = 2.50, square and hexatically ordered domains coexist, but neither increase exponentially with correlation lengths of these domains. Thus, we found that a static length scale associated with bond-orientational order can contribute to dynamic slowdown in confined hard sphere liquids, but also that the dependence on bond-orientational order varies with slight changes in confining length scale.

5.2 Future work

5.2.1 Effect of Gaussian polydispersity on phase behavior of confined hard spheres

Recently, Monte Carlo algorithms with 'swap' moves involving the exchange of particle diameters was shown to circumvent the kinetic barriers limiting particle rearrangement^{187,188}. For some size-polydisperse supercooled liquids, Swap Monte Carlo (SMC) allows for the preparation of supercooled configurations that would require in excess of millions of years of CPU time to prepare otherwise¹⁸³. For other liquids that are more prone to local crystalline ordering, SMC allows for the equilibration of complex crystal structures in strongly polydisperse systems^{189,190}. Particle size distributions in many of these crystallizing systems are unimodal and are similar to the experimental size distributions in colloidal glass-formers^{133,191,192}. Thus, simulation and experimental investigations using these model supercooled liquids require knowledge of the thermodynamic equilibrium phase behavior in order to avoid crystallization.

Avoiding crystallization is particularly important for confined liquids in which confining walls may decrease the freezing volume fraction^{166,168}. Utilizing SMC to uncover the equilibrium phase behavior of polydisperse hard spheres under confinement would be a step towards the planning of future investigations. Specifically, comparing the phase behavior of hard spheres with Gaussian-distributed diameters to systems with power law or multimodal-distributed diameters would be useful.

5.2.2 Long-wavelength fluctuations in confined hard spheres

The investigation in Chap. 4 is concerned with the crossover from three to two dimensional liquids in the limit of strong confinement^{154,174,193}. Relatedly, investigations into supercooled liquids have examined the existence of long-wavelength density fluctuations in supercooled liquids and glasses, a phenomena first predicted



Figure 5.1: Cage-irrelevant portion of the mean square displacement M^{CI} for varying periodic system side length L. The black dashed line is a fit to a logarithmic scaling function. Parallel hard walls in this system are separated by H = 2.0 average particle diameters..

for two dimensional crystals^{194–199}. Fluctuations in low dimensions ($d \le 2$) add up independently, allowing the amplitude of fluctuations between particles on a lattice to increase without bound as the distance between the particles increases; the amplitude is bounded for higher dimensions ($d \ge 3$) because displacements must be correlated and cannot add up independently^{169,200,201}. Confined polydisperse hard spheres provide a model to investigate systems with dimensions 2 < d < 3.

Utilizing the SMC method introduced in section 5.2.1, we have conducted preliminary investigations of long-wavelength fluctuations in confined polydisperse hard spheres. By distributing particle diameters according to $P(\sigma) = \frac{A}{\sigma^3}$ (A is constant) to avoid crystallization, we have confirmed long-wavelength fluctuations in these systems (Fig. 5.1). The signature of these fluctuations in two dimensions is a logarithmic increase in the cage-irrelevant portion of the MSD M^{CI} with the periodic side length of the simulation cell $L^{195,196}$. Further investigation along these lines would illuminate the influence of these long-wavelength fluctuations on the glass transition.



Figure 5.2: Dynamic susceptibility χ_4 for oxygen atoms with centers initially within layers that are three angstroms in thickness. The surface layer (yellow) that includes the liquid-vacuum interface. Only periodic directions are utilized in the calculations.

5.2.3 Connection between dynamic heterogeneity and precursors to nucleation in thin water films

In Chap. 4, we demonstrated an exponential dependence between relaxation time in commensurately confined hard spheres and hexatic ordering, which is the closepacked structure for two dimensional isotropic interactions. Being close-packed, this packing differs qualitatively from the tetrahedral ordering characteristic of networkforming liquids such as silica or water^{202–204}. However, ice-like ordering was recently shown in bulk supercooled TIP4P/Ice water²⁰⁵ to slow the dynamics of surrounding water molecules¹¹⁶. Moreover, local drops in molecular mobility, a direct result of dynamic heterogeneity, preceded the formation of ice-like clusters.

We ask whether similar mobility reduction could precede ice-like ordering in confined water and how confinement may alter ordering within supercooled water. Following Fitzner et al., we may quantify the magnitude and time scale of maximum dynamic heterogeneity in water confined along one direction using the dynamic susceptibility χ_4 (Chap. 3)¹¹⁶. However, this calculation is complicated by the dynamic gradient in the direction perpendicular to the confining surfaces^{206,207}. To resolve this complication, we introduce a layer-resolved calculation of χ_4 and identify the time scale the maximum for each layer. We have performed this calculation for freestanding thin films of supercooled TIP4P/Ice at 230 K, revealing that the time scale and extent of dynamic heterogeneity increases towards the center of the film (Fig. 5.2). Once these time scales are identified, we can identify regions of mobile and immobile particles and investigate connections with local ordering²⁰⁴ in free-standing films²⁰⁸ and films deposited on substrates²⁰⁹.

5.3 List of publications

- Ryan C Roberts, Ryan Poling-Skutvik, Jeremy C Palmer, and Jacinta C Conrad. Tracer transport probes relaxation and structure of attractive and repulsive glassy liquids. *The Journal of Physical Chemistry Letters* 9(11):3008–3013, 2018.
- Ryan Poling-Skutvik, Ryan C Roberts, Ali H Slim, Suresh Narayanan, Ramanan Krishnamoorti, Jeremy C Palmer, and Jacinta C Conrad. Structure dominates localization of tracers within aging nanoparticle glasses. *Journal of Physical Chemistry Letters* 10(8):1784–1789, 2019.
- Ryan C Roberts, Ryan Poling-Skutvik, Jacinta C Conrad, and Jeremy C Palmer. Tracer transport in attractive and repulsive supercooled liquids and glasses. *Journal of Chemical Physics* (Editor's Pick) 151(19):194501, 2019.
- Ryan C Roberts, Nico Marioni, Jeremy C Palmer, and Jacinta C Conrad. Dynamics of polydisperse hard-spheres under strong confinement. *Molecular Physics*, 2020.

References

- Cavagna, A. Supercooled liquids for pedestrians. *Physics Reports* 2009, 476, 51–124.
- [2] Angell, C. A. Structural instability and relaxation in liquid and glassy phases near the fragile liquid limit. *Journal of Non-Crystalline Solids* 1988, 102, 205– 221.
- [3] Ediger, M. D.; Angell, C. A.; Nagel, S. R. Supercooled liquids and glasses. The Journal of Physical Chemistry 1996, 100, 13200–13212.
- [4] Karmakar, S.; Dasgupta, C.; Sastry, S. Length scales in glass-forming liquids and related systems: a review. *Reports on Progress in Physics* 2015, 79, 016601.
- [5] Debenedetti, P. G.; Truskett, T. M.; Lewis, C. P.; Stillinger, F. H. Theory of supercooled liquids and glasses: Energy landscape and statistical geometry perspectives; Advances in Chemical Engineering; Academic Press, 2001; Vol. 28; pp 21 – 79.
- [6] Debenedetti, P. G.; Stillinger, F. H. Supercooled liquids and the glass transition. Nature 2001, 410, 259–267.
- [7] Ciarella, S.; Biezemans, R. A.; Janssen, L. M. Understanding, predicting, and tuning the fragility of vitrimeric polymers. *Proceedings of the National Academy of Sciences of the United States of America* 2019, 116, 25013–25022.
- [8] Yildirim, C.; Raty, J.-Y.; Micoulaut, M. Revealing the role of molecular rigidity on the fragility evolution of glass-forming liquids. *Nature Communications* 2016, 7, 1–6.

- [9] Stickel, F.; Fischer, E. W.; Richert, R. Dynamics of glass-forming liquids. I. Temperature-derivative analysis of dielectric relaxation data. *The Journal of Chemical Physics* 1995, 102, 6251–6257.
- [10] Kauzmann, W. The nature of the glassy state and the behavior of liquids at low temperatures. *Chemical Reviews* 1948, 43, 219–256.
- [11] Adam, G.; Gibbs, J. H. On the temperature dependence of cooperative relaxation properties in glass-forming liquids. *The Journal of Chemical Physics* 1965, 43, 139-146.
- [12] Kirkpatrick, T. R.; Thirumalai, D.; Wolynes, P. G. Scaling concepts for the dynamics of viscous liquids near an ideal glassy state. *Physical Review A* 1989, 40, 1045–1054.
- [13] Baschnagel, J.; Varnik, F. Computer simulations of supercooled polymer melts in the bulk and in confined geometry. *Journal of Physics: Condensed Matter* 2005, 17, R851.
- [14] Na, J. H.; Corona, S. L.; Hoff, A.; Johnson, W. L. Observation of an apparent first-order glass transition in ultrafragile Pt-Cu-P bulk metallic glasses. Proceedings of the National Academy of Sciences of the United States of America 2020, 117, 2779–2787.
- [15] Biroli, G.; Garrahan, J. P. Perspective: The glass transition. The Journal of Chemical Physics 2013, 138, 12A301.
- [16] Hunter, G. L.; Weeks, E. R. The physics of the colloidal glass transition. *Reports on Progress in Physics* 2012, 75, 066501.
- [17] Weeks, E. R.; Crocker, J. C.; Levitt, A. C.; Schofield, A.; Weitz, D. A. Three-

Dimensional Direct Imaging of Structural Relaxation Near the Colloidal Glass Transition. *Science* **2000**, *287*, 627–631.

- [18] Pusey, P. N.; Van Megen, W. Phase behaviour of concentrated suspensions of nearly hard colloidal spheres. *Nature* 1986, 320, 340–342.
- [19] Zaccarelli, E.; Valeriani, C.; Sanz, E.; Poon, W.; Cates, M.; Pusey, P. Crystallization of hard-sphere glasses. *Physical Review Letters* 2009, 103, 135704.
- [20] van Blaaderen, A.; Wiltzius, P. Real-space structure of colloidal hard-sphere glasses. Science 1995, 270, 1177–1179.
- [21] Leheny, R. L.; Menon, N.; Nagel, S. R.; Long Price, D.; Suzuya, K.; Thiyagarajan, P. Structural studies of an organic liquid through the glass transition. *The Journal of Chemical Physics* **1996**, *105*, 7783–7794.
- [22] Kob, W.; Andersen, H. C. Testing mode-coupling theory for a supercooled binary Lennard-Jones mixture I: The van Hove correlation function. *Physical Review E* 1995, 51, 4626.
- [23] Gotze, W.; Sjogren, L. Relaxation processes in supercooled liquids. *Reports on Progress in Physics* 1992, 55, 241.
- [24] Schweizer, K. S.; Yatsenko, G. Collisions, caging, thermodynamics, and jamming in the barrier hopping theory of glassy hard sphere fluids. *The Journal* of Chemical Physics 2007, 127, 164505.
- [25] Charbonneau, P.; Ikeda, A.; Parisi, G.; Zamponi, F. Dimensional study of the caging order parameter at the glass transition. Proceedings of the National Academy of Sciences of the United States of America 2012, 109, 13939–13943.
- [26] Kob, W.; Donati, C.; Plimpton, S. J.; Poole, P. H.; Glotzer, S. C. Dynamical

heterogeneities in a supercooled Lennard-Jones liquid. *Physical Review Letters* **1997**, *79*, 2827.

- [27] Chaudhuri, P.; Gao, Y.; Berthier, L.; Kilfoil, M.; Kob, W. A random walk description of the heterogeneous glassy dynamics of attracting colloids. *Journal* of Physics: Condensed Matter 2008, 20, 244126.
- [28] Gokhale, S.; Ganapathy, R.; Nagamanasa, K. H.; Sood, A. Localized excitations and the morphology of cooperatively rearranging regions in a colloidal glassforming Liquid. *Physical Review Letters* **2016**, *116*, 068305.
- [29] Keys, A. S.; Hedges, L. O.; Garrahan, J. P.; Glotzer, S. C.; Chandler, D. Excitations are localized and relaxation is hierarchical in glass-forming liquids. *Physical Review X* 2011, 1, 021013.
- [30] Perera, D. N.; Harrowell, P. Consequences of kinetic inhomogeneities in glasses. *Physical Review E* 1996, 54, 1652.
- [31] Doliwa, B.; Heuer, A. Cage effect, local anisotropies, and dynamic heterogeneities at the glass transition: A computer study of hard spheres. *Physical Review Letters* 1998, 80, 4915.
- [32] Russell, E. V.; Israeloff, N. Direct observation of molecular cooperativity near the glass transition. *Nature* 2000, 408, 695–698.
- [33] Kegel, W. K.; van Blaaderen, A. Direct observation of dynamical heterogeneities in colloidal hard-sphere suspensions. *Science* 2000, 287, 290–293.
- [34] Berthier, L.; Biroli, G. Theoretical perspective on the glass transition and amorphous materials. *Reviews of Modern Physics* 2011, 83, 587-645.
- [35] Tanaka, H. Two-order-parameter description of liquids. I. A general model

of glass transition covering its strong to fragile limit. *The Journal Chemical Physics* **1999**, *111*, 3163–3174.

- [36] Frenkel, D.; Smit, B. <u>Understanding molecular simulation: from algorithms to</u> <u>applications</u>; Elsevier, 2001; Vol. 1.
- [37] Allen, M. P. "Introduction to molecular dynamics simulation." Computational soft matter: from synthetic polymers to proteins 2004, 23, 1–28.
- [38] Allen, M. P.; Frenkel, D.; Talbot, J. Molecular dynamics simulation using hard particles. *Computer physics reports* 1989, 9, 301–353.
- [39] Bannerman, M. N.; Sargant, R.; Lue, L. DynamO: a free \calO (N) general event-driven molecular dynamics simulator. *Journal of computational chemistry* 2011, 32, 3329-3338.
- [40] Bannerman, M. N. DynamO. 2015 (accessed November 24, 2020).
- [41] Kodger, T. E.; Lu, P. J.; Wiseman, G. R.; Weitz, D. A. Stable, fluorescent polymethylmethacrylate particles for the long-term observation of slow colloidal dynamics. *Langmuir* 2017, 33, 6382–6389.
- [42] Kumar, S. K.; Benicewicz, B. C.; Vaia, R. A.; Winey, K. I. 50th Anniversary Perspective: Are Polymer Nanocomposites Practical for Applications? *Macromolecules* 2017, 50, 714–731.
- [43] Grabowski, C. A.; Mukhopadhyay, A. Size Effect of Nanoparticle Diffusion in a Polymer Melt. *Macromolecules* 2014, 47, 7238–7242.
- [44] Poling-Skutvik, R.; Krishnamoorti, R.; Conrad, J. C. Size-Dependent Dynamics of Nanoparticles in Unentangled Polyelectrolyte Solutions. ACS Macro Letters 2015, 4, 1169–1173.

- [45] Cai, L.-H.; Panyukov, S.; Rubinstein, M. Mobility of Nonsticky Nanoparticles in Polymer Liquids. *Macromolecules* 2011, 44, 7853–7863.
- [46] Zhang, R.; Schweizer, K. S. Correlated Matrix-Fluctuation-Mediated Activated Transport of Dilute Penetrants in Glass-Forming Liquids and Suspensions. *The Journal of Chemical Physics* 2017, 146, 194906.
- [47] Zhang, K.; Meng, D.; Muller-Plathe, F.; Kumar, S. K. Coarse-Grained Molecular Dynamics Simulation of Activated Penetrant Transport in Glassy Polymers. Soft Matter 2018, 14, 440–447.
- [48] Geise, G. M.; Lee, H.-S.; Miller, D. J.; Freeman, B. D.; McGrath, J. E.;
 Paul, D. R. Water Purification by Membranes: The Role of Polymer Science.
 Journal of Polymer Science Part B: Polymer Physics 2010, 48, 1685–1718.
- [49] Sanders, D. F.; Smith, Z. P.; Guo, R.; Robeson, L. M.; McGrath, J. E.; Paul, D. R.;
 Freeman, B. D. Energy-Efficient Polymeric Gas Separation Membranes for a Sustainable Future: A Review. *Polymer* 2013, 54, 4279–4761.
- [50] Lee, S.-H.; Bardunias, P.; Su, N.-Y.; Yang, R.-L. Behavioral Response of Termites to Tunnel Surface Irregularity. *Behavioral Processes* 2008, 78, 397–400.
- [51] Roosen-Runge, F.; Hennig, M.; Zhang, F.; Jacobs, R. M. J.; Sztucki, M.; Schober, H.; Seydel, T.; Schreiber, F. Protein Self-Diffusion in Crowded Solutions. Proceedings of the National Academy of Sciences of the United States of America 2011, 108, 11815–11820.
- [52] Di Rienzo, C.; Piazza, V.; Gratton, E.; Beltram, F.; Cardarelli, F. Probing Short-Range Protein Brownian Motion in the Cytoplasm of Living Cells. *Nature Communications* 2014, 5, 5891.

- [53] Angelini, T. E.; Hannezo, E.; Trepat, X.; Marquez, M.; Fredberg, J. J.; Weitz, D. A. Glass-Like Dynamics of Collective Cell Migration. Proceedings of the National Academy of Sciences of the United States of America 2011, 108, 4714–4719.
- [54] Schötz, E.-M.; Lanio, M.; Talbot, J. A.; Manning, M. L. Glassy Dynamics in Three-Dimensional Embryonic Tissues. *Journal of the Royal Society Interface* 2013, 10, 20130726.
- [55] Garcia, S.; Hannezo, E.; Elgeti, J.; Joanny, J.-F.; Silberzan, P.; Gov, N. S. Physics of Active Jamming During Collective Cellular Motion in a Monolayer. Proceedings of the National Academy of Sciences of the United States of America 2015, 112, 15314–15319.
- [56] Gravish, N.; Gold, G.; Zangwill, A.; Goodisman, M. A. D.; Goldman, D. I. Glass-Like Dynamics in Confined and Congested Ant Traffic. Soft Matter 2015, 11, 6552–6561.
- [57] Stevenson, J. D.; Schmalian, J.; Wolynes, P. G. The Shapes of Cooperatively Rearranging Regions in Glass-Forming Liquids. *Nature Physics* 2006, 2, 268– 274.
- [58] Garrahan, J. P.; Chandler, D. Geometrical Explanation and Scaling of Dynamical Heterogeneities in Glass Forming Systems. *Physical Review Letters* 2002, 89, 035704.
- [59] Kob, W.; Donati, C.; Plimpton, S. J.; Poole, P. H.; Glotzer, S. C. Dynamical Heterogeneities in a Supercooled Lennard-Jones Liquid. *Physical Review Letters* 1997, 79, 2827–2830.
- [60] Pastore, R.; Pesce, G.; Sasso, A.; Pica Ciamarra, M. Cage Size and Jump Pre-

cursors in Glass-Forming Liquids: Experiment and Simulations. *The Journal* of *Physical Chemistry Letters* **2017**, *8*, 1562–1568.

- [61] Donati, C.; Douglas, J. F.; Kob, W.; Plimpton, S. J.; Poole, P. H.; Glotzer, S. C. Stringlike Cooperative Motion in a Supercooled Liquid. *Physical Review Letters* 1998, 80, 2338–2341.
- [62] Foffi, G.; Dawson, K. A.; Buldyrev, S. V.; Sciortino, F.; Zaccarelli, E.; Tartaglia, P. Evidence for an Unusual Dynamical-Arrest Scenario in Short-Ranged Colloidal Systems. *Physical Review E: Statistical, Nonlinear, and Soft Matter Physics* 2002, 65, 050802(R).
- [63] Reichman, D. R.; Rabani, E.; Geissler, P. L. Comparison of Dynamical Heterogeneity in Hard-Sphere and Attractive Glass Formers. *The Journal of Physical Chemistry B* 2005, 109, 14654–14658.
- [64] Pham, K. N.; Petekidis, G.; Vlassopoulos, D.; Egelhaaf, S. U.; Poon, W. C. K.; Pusey, P. N. Yielding Behavior of Repulsion- and Attraction-Dominated Colloidal Glasses. *Journal of Rheology* 2008, 52, 649–676.
- [65] Zaccarelli, E.; Poon, W. C. K. Colloidal Glasses and Gels: the Interplay of Bonding and Caging. Proceedings of the National Academy of Sciences of the United States of America 2009, 106, 15203–15208.
- [66] Koumakis, N.; Petekidis, G. Two Step Yielding in Attractive Colloids: Transition from Gels to Attractive Glasses. Soft Matter 2011, 7, 2456–2470.
- [67] van de Laar, T.; Higler, R.; Schoën, K.; Sprakel, J. Discontinuous Nature of the Repulsive-to-Attractive Colloidal Glass Transition. *Scientific Reports* 2016, 6, 22725.

- [68] Zhang, Z.; Yunker, P. J.; Habdas, P.; Yodh, A. G. Cooperative Rearrangement Regions and Dynamical Heterogeneities in Colloidal Glasses with Attractive Versus Repulsive Interactions. *Physical Review Letters* 2011, 107, 208303.
- [69] Brown, Z.; Iwanicki, M. J.; Gratale, M. D.; Ma, X.; Yodh, A. G.; Habdas, P. Correlated Rearrangements of Disordered Colloidal Suspensions in the Vicinity of the Reentrant Glass Transition. *Europhysics Letters* 2016, 115, 68003.
- [70] Sentjabrskaja, T.; Zaccarelli, E.; De Michele, C.; Sciortino, F.; Tartaglia, P.;
 Voigtmann, T.; Egelhaaf, S. U.; Laurati, M. Anomalous Dynamics of Intruders in a Crowded Environment of Mobile Obstacles. *Nature Communications* 2016, 7, 11133.
- [71] Parmar, A. D. S.; Sastry, S. Kinetic and Thermodynamic Fragilities of Square Well Fluids with Tunable Barriers to Bond Breaking. *The Journal of Physical Chemistry B* 2015, 119, 11243–11252.
- [72] Zaccarelli, E.; Foffi, G.; Sciortino, F.; Tartaglia, P. Activated Bond-Breaking Processes Preempt the Observation of a Sharp Glass-Glass Transition in Dense Short-Ranged Attractive Colloids. *Physical Review Letters* 2003, 91, 108301.
- [73] Coslovich, D.; Ikeda, A. Cluster and Reentrant Anomalies of Nearly Gaussian Core Particles. Soft Matter 2013, 9, 6786–6795.
- [74] Bertolazzo, A. A.; Barbosa, M. C. Phase Diagram and Thermodynamic and Dynamic Anomalies in a Pure Repulsive Model. *Physica A* 2014, 404, 150–157.
- [75] Dawson, K.; Foffi, G.; Fuchs, M.; Gotze, W.; Sciortino, F.; Sperl, M.; Tartaglia, P.; Voigtmann, T.; Zaccarelli, E. Higher-Order Glass-Transition Singularities in Colloidal Systems with Attractive Interactions. *Physical Review E* 2000, 63, 011401.

- [76] Zaccarelli, E.; Foffi, G.; Dawson, K. A.; Buldyrev, S. V.; Sciortino, F.; Tartaglia, P. Confirmation of Anomalous Dynamical Arrest in Attractive Colloids: A Molecular Dynamics Study. *Physical Review E: Statistical, Nonlinear,* and Soft Matter Physics **2002**, 66, 041402.
- [77] Sciortino, F.; Tartaglia, P.; Zaccarelli, E. Evidence of a Higher-Order Singularity in Dense Short-Ranged Attractive Colloids. *Physical Review Letters* 2003, 91, 268301.
- [78] Moreno, A. J.; Colmenero, J. Logarithmic Relaxation in a Kinetically Constrained Model. *The Journal of Chemical Physics* 2006, 125, 016101.
- [79] Moreno, A. J.; Colmenero, J. Relaxation Scenarios in a Mixture of Large and Small Spheres: Dependence on the Size Disparity. *The Journal of Chemical Physics* 2006, 125, 164507.
- [80] Mayer, C.; Sciortino, F.; Likos, C. N.; Tartaglia, P.; Löwen, H.; Zaccarelli, E. Multiple Glass Transitions in Star Polymer Mixtures: Insights from Theory and Simulations. *Macromolecules* 2009, 42, 423–434.
- [81] Gnan, N.; Das, G.; Sperl, M.; Sciortino, F.; Zaccarelli, E. Multiple Glass Singularities and Isodynamics in a Core-Softened Model for Glass-Forming Systems. *Physical Review Letters* 2014, 113, 258302.
- [82] Kim, K.; Miyazaki, K.; Saito, S. Slow Dynamics in Random Media: Crossover from Glass to Localization Transition. *Europhysics Letters* 2009, 88, 36002.
- [83] Kurzidim, J.; Coslovich, D.; Kahl, G. Dynamic Arrest of Colloids in Porous Environments: Disentangling Crowding and Confinement. *Journal of Physics:* Condensed Matter 2011, 23, 234122.

- [84] Zierenberg, J.; Fricke, N.; Marenz, M.; Spitzner, F. P.; Blavatska, V.; Janke, W. Percolation Thresholds and Fractal Dimensions for Square and Cubic Lattices with Long-Range Correlated Defects. *Physical Review E* 2017, 96, 062125.
- [85] Saberi, A. A. Fractal Structure of a Three-Dimensional Brownian Motion on an Attractive Plane. *Physical Review E: Statistical, Nonlinear, and Soft Matter Physics* 2011, 84, 021113.
- [86] Hadjiev, N. A.; Amsden, B. G. An assessment of the ability of the obstructionscaling model to estimate solute diffusion coefficients in hydrogels. *Journal of Controlled Release* 2015, 199, 10–16.
- [87] Li, J.; Mooney, D. J. Designing hydrogels for controlled drug delivery. Nature Reviews Materials 2016, 1, 1–17.
- [88] Baker, R. W. Future directions of membrane gas separation technology. Industrial & Engineering Chemistry Research 2002, 41, 1393–1411.
- [89] Paul, D. R.; Robeson, L. M. Polymer nanotechnology: nanocomposites. *Polymer* 2008, 49, 3187–3204.
- [90] Ellis, R. J. Macromolecular crowding: an important but neglected aspect of the intracellular environment. Current Opinion in Structural Biology 2001, 11, 114–119.
- [91] Nakano, S.-i.; Miyoshi, D.; Sugimoto, N. Effects of molecular crowding on the structures, interactions, and functions of nucleic acids. *Chemical Reviews* 2014, 114, 2733–2758.
- [92] Regan, K.; Wulstein, D.; Rasmussen, H.; McGorty, R.; Robertson-Anderson, R. M. Bridging the spatiotemporal scales of macromolecular transport in crowded biomimetic systems. *Soft Matter* **2019**, *15*, 1200–1209.

- [93] Höfling, F.; Franosch, T.; Frey, E. Localization transition of the threedimensional Lorentz model and continuum percolation. *Physical Review Letters* 2006, 96, 165901.
- [94] Jin, Y.; Charbonneau, P. Dimensional study of the dynamical arrest in a random Lorentz gas. *Physical Review E* 2015, 91, 042313.
- [95] Cohen, M. H.; Turnbull, D. Molecular transport in liquids and glasses. The Journal of Chemical Physics 1959, 31, 1164–1169.
- [96] Müller-Plathe, F. Diffusion of penetrants in amorphous polymers: A molecular dynamics study. *The Journal of Chemical Physics* 1991, 94, 3192–3199.
- [97] Gusev, A. A.; Suter, U. W. Dynamics of small molecules in dense polymers subject to thermal motion. *The Journal of Chemical Physics* 1993, 99, 2228–2234.
- [98] Hwang, J.; Kim, J.; Sung, B. J. Dynamics of highly polydisperse colloidal suspensions as a model system for bacterial cytoplasm. *Physical Review E* 2016, 94, 022614.
- [99] Alcázar-Cano, N.; Delgado-Buscalioni, R. A general phenomenological relation for the subdiffusive exponent of anomalous diffusion in disordered media. *Soft Matter* 2018, 14, 9937–9949.
- [100] Schnyder, S. K.; Spanner, M.; Höfling, F.; Franosch, T.; Horbach, J. Rounding of the localization transition in model porous media. *Soft Matter* 2015, *11*, 701– 711.
- [101] Skinner, T. O.; Schnyder, S. K.; Aarts, D. G.; Horbach, J.; Dullens, R. P. Localization dynamics of fluids in random confinement. *Physical Review Letters* 2013, 111, 128301.

- [102] Sentjabrskaja, T.; Zaccarelli, E.; De Michele, C.; Sciortino, F.; Tartaglia, P.;
 Voigtmann, T.; Egelhaaf, S. U.; Laurati, M. Anomalous dynamics of intruders in a crowded environment of mobile obstacles. *Nature Communications* 2016, 7, 1–8.
- [103] Roberts, R. C.; Poling-Skutvik, R.; Palmer, J. C.; Conrad, J. C. Tracer transport probes relaxation and structure of attractive and repulsive glassy liquids. *The Journal of Physical Chemistry Letters* 2018, 9, 3008–3013.
- [104] Weeks, E. R.; Crocker, J. C.; Levitt, A. C.; Schofield, A.; Weitz, D. A. Threedimensional direct imaging of structural relaxation near the colloidal glass transition. *Science* 2000, 287, 627–631.
- [105] Zaccarelli, E.; Foffi, G.; Dawson, K. A.; Buldyrev, S.; Sciortino, F.; Tartaglia, P. Confirmation of anomalous dynamical arrest in attractive colloids: A molecular dynamics study. *Physical Review E* 2002, 66, 041402.
- [106] Pham, K. N.; Puertas, A. M.; Bergenholtz, J.; Egelhaaf, S. U.; Moussaud, A.; Pusey, P. N.; Schofield, A. B.; Cates, M. E.; Fuchs, M.; Poon, W. C. Multiple glassy states in a simple model system. *Science* 2002, 296, 104–106.
- [107] Zaccarelli, E.; Poon, W. C. Colloidal glasses and gels: The interplay of bonding and caging. Proceedings of the National Academy of Sciences of the United States of America 2009, 106, 15203–15208.
- [108] Dawson, K. A. The glass paradigm for colloidal glasses, gels, and other arrested states driven by attractive interactions. *Current Opinion in Colloid & Interface Science* 2002, 7, 218–227.
- [109] Zaccarelli, E.; Löwen, H.; Wessels, P.; Sciortino, F.; Tartaglia, P.; Likos, C. Is there a reentrant glass in binary mixtures? *Physical Review Letters* 2004, 92, 225703.

- [110] Zaccarelli, E.; Sciortino, F.; Tartaglia, P. Numerical study of the glass-glass transition in short-ranged attractive colloids. *Journal of Physics: Condensed Matter* 2004, 16, S4849.
- [111] Doliwa, B.; Heuer, A. The origin of anomalous diffusion and non-Gaussian effects for hard spheres: analysis of three-time correlations. *Journal of Physics: Condensed Matter* 1999, 11, A277.
- [112] Weeks, E. R.; Weitz, D. Subdiffusion and the cage effect studied near the colloidal glass transition. *Chemical Physics* 2002, 284, 361–367.
- [113] Shell, M. S.; Debenedetti, P. G.; Stillinger, F. H. Dynamic heterogeneity and non-Gaussian behaviour in a model supercooled liquid. *Journal of Physics: Condensed Matter* 2005, 17, S4035.
- [114] Widmer-Cooper, A.; Harrowell, P. On the study of collective dynamics in supercooled liquids through the statistics of the isoconfigurational ensemble. *The Journal of Chemical Physics* 2007, 126, 154503.
- [115] Widmer-Cooper, A.; Harrowell, P.; Fynewever, H. How reproducible are dynamic heterogeneities in a supercooled liquid? *Physical Review Letters* 2004, 93, 135701.
- [116] Fitzner, M.; Sosso, G. C.; Cox, S. J.; Michaelides, A. Ice is born in low-mobility regions of supercooled liquid water. *Proceedings of the National Academy of Sciences of the United States of America* 2019, 116, 2009–2014.
- [117] Sosso, G. C.; Colombo, J.; Behler, J.; Del Gado, E.; Bernasconi, M. Dynamical heterogeneity in the supercooled liquid state of the phase change material GeTe. *The Journal of Physical Chemistry B* 2014, 118, 13621–13628.

- [118] Russell, D. A.; Hanson, J. D.; Ott, E. Dimension of strange attractors. *Physical Review Letters* 1980, 45, 1175.
- [119] Perera, D. N.; Harrowell, P. Origin of the difference in the temperature dependences of diffusion and structural relaxation in a supercooled liquid. *Physical Review Letters* 1998, 81, 120.
- [120] Dawson, K.; Foffi, G.; Fuchs, M.; Gotze, W.; Sciortino, F.; Sperl, M.; Tartaglia, P.; Voigtmann, T.; Zaccarelli, E. Higher-order glass-transition singularities in colloidal systems with attractive interactions. *Physical Review E* 2000, 63, 011401.
- [121] Poling-Skutvik, R.; Roberts, R. C.; Slim, A. H.; Narayanan, S.; Krishnamoorti, R.; Palmer, J. C.; Conrad, J. C. Structure dominates localization of tracers within aging nanoparticle glasses. *The Journal of Physical Chemistry Letters* 2019, 10, 1784–1789.
- [122] Krekelberg, W. P.; Ganesan, V.; Truskett, T. M. Free volumes and the anomalous self-diffusivity of attractive colloids. *The Journal of Physical Chemistry B* 2006, 110, 5166–5169.
- [123] Krekelberg, W. P.; Mittal, J.; Ganesan, V.; Truskett, T. M. How short-range attractions impact the structural order, self-diffusivity, and viscosity of a fluid. *The Journal of Chemical Physics* 2007, 127, 044502.
- [124] Heuer, A.; Kunow, M.; Vogel, M.; Banhatti, R. D. Backward correlations and dynamic heterogeneities: A computer study of ion dynamics. *Physical Review* B 2002, 66, 224201.
- [125] Weeks, E. R.; Weitz, D. Properties of cage rearrangements observed near the colloidal glass transition. *Physical Review Letters* 2002, 89, 095704.

- [126] Gebremichael, Y.; Vogel, M.; Glotzer, S. Particle dynamics and the development of string-like motion in a simulated monoatomic supercooled liquid. *The Journal of Chemical Physics* 2004, 120, 4415–4427.
- [127] Oppong, F. K.; Rubatat, L.; Frisken, B. J.; Bailey, A. E.; de Bruyn, J. R. Microrheology and structure of a yield-stress polymer gel. *Physical Review E* 2006, 73, 041405.
- [128] Rich, J. P.; McKinley, G. H.; Doyle, P. S. Size dependence of microprobe dynamics during gelation of a discotic colloidal clay. *Journal of Rheology* 2011, 55, 273–299.
- [129] Widmer-Cooper, A.; Harrowell, P. On the relationship between structure and dynamics in a supercooled liquid. *Journal of Physics: Condensed Matter* 2005, 17, S4025.
- [130] Widmer-Cooper, A.; Harrowell, P. Free volume cannot explain the spatial heterogeneity of Debye–Waller factors in a glass-forming binary alloy. *Journal of Non-Crystalline Solids* 2006, 352, 5098–5102.
- [131] Berthier, L.; Jack, R. L. Structure and dynamics of glass formers: Predictability at large length scales. *Physical Review E* 2007, 76, 041509.
- [132] Tong, H.; Tanaka, H. Revealing hidden structural order controlling both fast and slow glassy dynamics in supercooled liquids. *Physical Review X* 2018, 8, 011041.
- [133] Leocmach, M.; Tanaka, H. Roles of icosahedral and crystal-like order in the hard spheres glass transition. *Nature Communications* 2012, 3, 1–8.
- [134] He, S.; Palmer, J. C.; Qin, G. A non-equilibrium molecular dynamics study of

methane transport in clay nano-pores. *Microporous and Mesoporous Materials* **2017**, *249*, 88–96.

- [135] Gubbins, K. E.; Liu, Y.-C.; Moore, J. D.; Palmer, J. C. The role of molecular modeling in confined systems: impact and prospects. *Physical Chemistry Chemical Physics* 2011, 13, 58–85.
- [136] Maginn, E. J.; Bell, A. T.; Theodorou, D. N. Transport diffusivity of methane in silicalite from equilibrium and nonequilibrium simulations. *The Journal of Physical Chemistry* 1993, 97, 4173–4181.
- [137] Nugent, C. R.; Edmond, K. V.; Patel, H. N.; Weeks, E. R. Colloidal glass transition observed in confinement. *Physical Review Letters* 2007, 99, 025702.
- [138] Hunter, G. L.; Edmond, K. V.; Weeks, E. R. Boundary mobility controls glassiness in confined colloidal liquids. *Physical Review Letters* 2014, 112, 218302.
- [139] Faraone, A.; Liu, L.; Mou, C.-Y.; Yen, C.-W.; Chen, S.-H. Fragile-to-strong liquid transition in deeply supercooled confined water. *The Journal of Chemical Physics* 2004, 121, 10843–10846.
- [140] Richert, R. Dynamics of nanoconfined supercooled liquids. Annual Review of Physical Chemistry 2011, 62, 65–84.
- [141] Ediger, M. D. Perspective: Highly stable vapor-deposited glasses. The Journal of Chemical Physics 2017, 147, 210901.
- [142] Sentjabrskaja, T.; Jacob, A. R.; Egelhaaf, S. U.; Petekidis, G.; Voigtmann, T.; Laurati, M. Binary colloidal glasses: linear viscoelasticity and its link to the microscopic structure and dynamics. *Soft Matter* **2019**, *15*, 2232–2244.
- [143] Laurati, M.; Sentjabrskaja, T.; Ruiz-Franco, J.; Egelhaaf, S. U.; Zaccarelli, E.

Different scenarios of dynamic coupling in glassy colloidal mixtures. *Physical Chemistry Chemical Physics* **2018**, *20*, 18630–18638.

- [144] Angell, C. A. Formation of glasses from liquids and biopolymers. Science 1995, 267, 1924–1935.
- [145] Ediger, M. D. Spatially heterogeneous dynamics in supercooled liquids. Annual Review of Physical Chemistry 2000, 51, 99–128.
- [146] Lačević, N.; Starr, F. W.; Schrøder, T. B.; Glotzer, S. C. Spatially heterogeneous dynamics investigated via a time-dependent four-point density correlation function. *The Journal of Chemical Physics* 2003, 119, 7372–7387.
- [147] Berthier, L.; Biroli, G.; Bouchaud, J.-P.; Cipelletti, L.; El Masri, D.; L'Hôte, D.; Ladieu, F.; Pierno, M. Direct experimental evidence of a growing length scale accompanying the glass transition. *Science* 2005, 310, 1797–1800.
- [148] Karmakar, S.; Dasgupta, C.; Sastry, S. Growing length and time scales in glassforming liquids. Proceedings of the National Academy of Sciences of the United States of America 2009, 106, 3675–3679.
- [149] Löwen, H. Colloidal soft matter under external control. Journal of Physics: Condensed Matter 2001, 13, R415–R432.
- [150] Kritikos, G.; Vergadou, N.; Economou, I. G. Molecular dynamics simulation of highly confined glassy ionic liquids. *The Journal of Physical Chemistry C* 2016, 120, 1013–1024.
- [151] Ellison, C. J.; Torkelson, J. M. The distribution of glass-transition temperatures in nanoscopically confined glass formers. *Nature Materials* 2003, 2, 695– 700.

- [152] Eral, H. B.; van den Ende, D.; Mugele, F.; Duits, M. H. G. Influence of confinement by smooth and rough walls on particle dynamics in dense hard-sphere suspensions. *Physical Review E* 2009, 80, 061403.
- [153] Lang, S.; Boţan, V.; Oettel, M.; Hajnal, D.; Franosch, T.; Schilling, R. Glass transition in confined geometry. *Physical Review Letters* 2010, 105, 125701.
- [154] Mandal, S.; Lang, S.; Gross, M.; Oettel, M.; Raabe, D.; Franosch, T.; Varnik, F. Multiple reentrant glass transitions in confined hard-sphere glasses. *Nature Communications* 2014, 5, 4435.
- [155] Lang, S.; Schilling, R.; Krakoviack, V.; Franosch, T. Mode-coupling theory of the glass transition for confined fluids. *Physical Review E* 2012, *86*, 021502.
- [156] Lang, S.; Schilling, R.; Franosch, T. Mode-coupling theory for multiple decay channels. Journal of Statistical Mechanics: Theory and Experiment 2013, 2013, P12007.
- [157] Mittal, J.; Truskett, T. M.; Errington, J. R.; Hummer, G. Layering and positiondependent diffusive dynamics of confined fluids. *Physical Review Letters* 2008, 100, 145901.
- [158] Kawasaki, T.; Araki, T.; Tanaka, H. Correlation between dynamic heterogeneity and medium-range order in two-dimensional glass-forming liquids. *Physi*cal Review Letters 2007, 99, 215701.
- [159] Watanabe, K.; Tanaka, H. Direct observation of medium-range crystalline order in granular liquids near the glass transition. *Physical Review Letters* 2008, 100, 158002.
- [160] Hu, Y.-C.; Tanaka, H.; Wang, W.-H. Impact of spatial dimension on structural ordering in metallic glass. *Physical Review E* 2017, 96, 022613.

- [161] Gasser, U.; Schofield, A.; Weitz, D. A. Local order in a supercooled colloidal fluid observed by confocal microscopy. *Journal of Physics: Condensed Matter* 2002, 15, S375–S380.
- [162] Tanaka, H.; Kawasaki, T.; Shintani, H.; Watanabe, K. Critical-like behaviour of glass-forming liquids. *Nature Materials* 2010, 9, 324–331.
- [163] Xu, W.-S.; Sun, Z.-Y.; An, L.-J. Effect of attractions on correlation length scales in a glass-forming liquid. *Physical Review E* 2012, *86*, 041506.
- [164] Tah, I.; Sengupta, S.; Sastry, S.; Dasgupta, C.; Karmakar, S. Glass transition in supercooled liquids with medium-range crystalline order. *Physical Review Letters* 2018, 121, 085703.
- [165] Watanabe, K.; Kawasaki, T.; Tanaka, H. Structural origin of enhanced slow dynamics near a wall in glass-forming systems. *Nature Materials* 2011, 10, 512-520.
- [166] Pieranski, P.; Strzelecki, L.; Pansu, B. Thin colloidal crystals. *Physical Review Letters* 1983, 50, 900.
- [167] Neser, S.; Bechinger, C.; Leiderer, P.; Palberg, T. Finite-size effects on the closest packing of hard spheres. *Physical Review Letters* 1997, 79, 2348.
- [168] Fortini, A.; Dijkstra, M. Phase behaviour of hard spheres confined between parallel hard plates: manipulation of colloidal crystal structures by confinement. *Journal of Physics: Condensed Matter* 2006, 18, L371–L378.
- [169] Mermin, N. D. Crystalline order in two dimensions. *Physical Review* 1968, 176, 250.
- [170] Russo, J.; Tanaka, H. Assessing the role of static length scales behind glassy

dynamics in polydisperse hard disks. *Proceedings of the National Academy of Sciences of the United States of America* **2015**, *112*, 6920–6924.

- [171] Berthier, L.; Charbonneau, P.; Ninarello, A.; Ozawa, M.; Yaida, S. Zerotemperature glass transition in two dimensions. *Nature Communications* 2019, 10, 1508.
- [172] Campanino, M.; Ioffe, D.; Velenik, Y. Ornstein-Zernike theory for finite range Ising models above T c. *Probability Theory and Related Fields* 2003, 125, 305– 349.
- [173] Varnik, F.; Franosch, T. Non-monotonic effect of confinement on the glass transition. Journal of Physics: Condensed Matter 2016, 28, 133001.
- [174] Mandal, S.; Lang, S.; Boţan, V.; Franosch, T. Nonergodicity parameters of confined hard-sphere glasses. Soft Matter 2017, 13, 6167–6177.
- [175] Fontecha, A. B.; Schöpe, H. J.; König, H.; Palberg, T.; Messina, R.; Löwen, H. A comparative study on the phase behaviour of highly charged colloidal spheres in a confining wedge geometry. *Journal of Physics: Condensed Matter* 2005, 17, S2779–S2786.
- [176] Fasolo, M.; Sollich, P. Equilibrium phase behavior of polydisperse hard spheres. *Physical Review Letters* 2003, 91, 068301.
- [177] Tong, H.; Tan, P.; Xu, N. From crystals to disordered crystals: A hidden orderdisorder transition. *Scientific Reports* 2015, 5, 15378.
- [178] Nygård, K.; Sarman, S.; Kjellander, R. Packing frustration in dense confined fluids. *The Journal of Chemical Physics* 2014, 141, 094501.
- [179] Sollich, P.; Wilding, N. B. Crystalline phases of polydisperse spheres. *Physical Review Letters* 2010, 104, 118302.
- [180] Biroli, G.; Bouchaud, J.-P.; Cavagna, A.; Grigera, T. S.; Verrocchio, P. Thermodynamic signature of growing amorphous order in glass-forming liquids. *Nature Physics* 2008, 4, 771–775.
- [181] Hocky, G. M.; Markland, T. E.; Reichman, D. R. Growing point-to-set length scale correlates with growing relaxation times in model supercooled liquids. *Physics Review Letters* 2012, 108, 225506.
- [182] Baranyai, A.; Evans, D. J. Direct entropy calculation from computer simulation of liquids. *Physical Review A* 1989, 40, 3817–3822.
- [183] Ninarello, A.; Berthier, L.; Coslovich, D. Models and algorithms for the next generation of glass transition studies. *Physical Review X* 2017, 7, 021039.
- [184] Zhang, K.; Dice, B.; Liu, Y.; Schroers, J.; Shattuck, M. D.; O'Hern, C. S. On the origin of multi-component bulk metallic glasses: Atomic size mismatches and de-mixing. *The Journal of Chemical Physics* 2015, 143, 054501.
- [185] Sing, C. E.; Perry, S. L. Recent progress in the science of complex coacervation. Soft Matter 2020, 16, 2885–2914.
- [186] Ou, Z.; Muthukumar, M. Entropy and enthalpy of polyelectrolyte complexation: Langevin dynamics simulations. The Journal of chemical physics 2006, 124, 154902.
- [187] Grigera, T. S.; Parisi, G. Fast Monte Carlo algorithm for supercooled soft spheres. *Physical Review E* 2001, 63, 045102.
- [188] Berthier, L.; Coslovich, D.; Ninarello, A.; Ozawa, M. Equilibrium sampling of hard spheres up to the jamming density and beyond. *Physical Review Letters* 2016, 116, 238002.

- [189] Bommineni, P. K.; Varela-Rosales, N. R.; Klement, M.; Engel, M. Complex crystals from size-disperse spheres. *Physical Review Letters* 2019, 122, 128005.
- [190] Jung, G.; Petersen, C. F. Confinement-induced demixing and crystallization. *Physical Review Research* 2020, 2, 033207.
- [191] Brambilla, G.; El Masri, D.; Pierno, M.; Berthier, L.; Cipelletti, L.; Petekidis, G.; Schofield, A. B. Probing the equilibrium dynamics of colloidal hard spheres above the mode-coupling glass transition. *Physical Review Letters* 2009, 102, 085703.
- [192] Brambilla, G.; El Masri, D.; Pierno, M.; Berthier, L.; Cipelletti, L.; Petekidis, G.; Schofield, A. Brambilla et al. reply. *Physical Review Letters* 2010, 104, 169602.
- [193] Mandal, S.; Spanner-Denzer, M.; Leitmann, S.; Franosch, T. Complex dynamics induced by strong confinement – From tracer diffusion in strongly heterogeneous media to glassy relaxation of dense fluids in narrow slits. *The European Physical Journal Special Topics* 2017, 226, 3129–3156.
- [194] Flenner, E.; Szamel, G. Fundamental differences between glassy dynamics in two and three dimensions. *Nature Communications* 2015, 6, 1–6.
- [195] Shiba, H.; Yamada, Y.; Kawasaki, T.; Kim, K. Unveiling dimensionality dependence of glassy dynamics: 2D infinite fluctuation eclipses inherent structural relaxation. *Physical Review Letters* 2016, 117, 245701.
- [196] Illing, B.; Fritschi, S.; Kaiser, H.; Klix, C. L.; Maret, G.; Keim, P. Mermin–
 Wagner fluctuations in 2D amorphous solids. *Proceedings of the National Academy of Sciences of the United States of America* 2017, 114, 1856–1861.

- [197] Zhang, B.; Cheng, X. Long-wavelength fluctuations and static correlations in quasi-2d colloidal suspensions. Soft Matter 2019, 15, 4087–4097.
- [198] Li, Y.-W.; Mishra, C. K.; Sun, Z.-Y.; Zhao, K.; Mason, T. G.; Ganapathy, R.; Ciamarra, M. P. Long-wavelength fluctuations and anomalous dynamics in 2dimensional liquids. Proceedings of the National Academy of Sciences of the United States of America 2019, 116, 22977–22982.
- [199] Flenner, E.; Szamel, G. Viscoelastic shear stress relaxation in two-dimensional glass-forming liquids. Proceedings of the National Academy of Sciences of the United States of America 2019, 116, 2015–2020.
- [200] Peierls, R. Bemerkungen über umwandlungstemperaturen. Helvetica Physica Acta 1934, 7, 81.
- [201] Mermin, N. D.; Wagner, H. Absence of ferromagnetism or antiferromagnetism in one-or two-dimensional isotropic Heisenberg models. *Physical Review Letters* 1966, 17, 1133.
- [202] Shi, R.; Russo, J.; Tanaka, H. Common microscopic structural origin for water's thermodynamic and dynamic anomalies. *The Journal of Chemical Physics* 2018, 149, 224502.
- [203] Shi, R.; Tanaka, H. Impact of local symmetry breaking on the physical properties of tetrahedral liquids. Proceedings of the National Academy of Sciences of the United States of America 2018, 115, 1980–1985.
- [204] Shi, R.; Russo, J.; Tanaka, H. Origin of the emergent fragile-to-strong transition in supercooled water. Proceedings of the National Academy of Sciences of the United States of America 2018, 115, 9444–9449.

- [205] Espinosa, J. R.; Vega, C.; Sanz, E. Ice-water interfacial free energy for the TIP4P, TIP4P/2005, TIP4P/Ice, and mW models as obtained from the Mold integration technique. *The Journal of Physical Chemistry C* 2016, 120, 8068– 8075.
- [206] Zhang, W.; Douglas, J. F.; Starr, F. W. Dynamical heterogeneity in a vapordeposited polymer glass. *The Journal of Chemical Physics* 2017, 146, 203310.
- [207] Li, S.-J.; Qian, H.-J.; Lu, Z.-Y. A comparative study on the dynamic heterogeneity of supercooled polymers under nanoconfinement. *Physical Chemistry Chemical Physics* 2019, 21, 15888–15898.
- [208] Haji-Akbari, A.; Debenedetti, P. G. Computational investigation of surface freezing in a molecular model of water. *Proceedings of the National Academy* of Sciences of the United States of America 2017, 114, 3316–3321.
- [209] Haji-Akbari, A.; Debenedetti, P. G. The effect of substrate on thermodynamic and kinetic anisotropies in atomic thin films. *The Journal of Chemical Physics* 2014, 141, 024506.