

Hexatic Molecular Orientational Order in a 2D Supercooled Liquid

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Abstract

The two-dimensional Lewis-Wahnström (2dLW) model of Ortho-terphenyl, a widely studied glass-forming liquid, is observed to form a supercooled phase dominated by hexatic molecular-orientational order. This ordering is mesoscopic and appears to persist as the liquid cools. While similar orientational ordering has been demonstrated in liquids of rigid polygons, why a preference for hexatic molecular orientational ordering exists in 2dLW is not obvious. The salient emergence of hexatic molecular orientational order suggests a relationship between local structure and supercooled dynamics in two-dimensional liquids. Here, we use molecular dynamics simulations to study molecular orientational ordering in the 2dLW system at a range of temperatures. We compute measures of liquid structure and closely examine the phase transition towards resolving mechanisms responsible for the onset of observed order.

The 2D Lewis-Wahnström Model

The Lewis-Wahnström model collapses each phenyl ring in Ortho-terphenyl to a single interaction site. We study a two-dimensional variant (2dLW) using Lennard-Jones potential centered at each site.

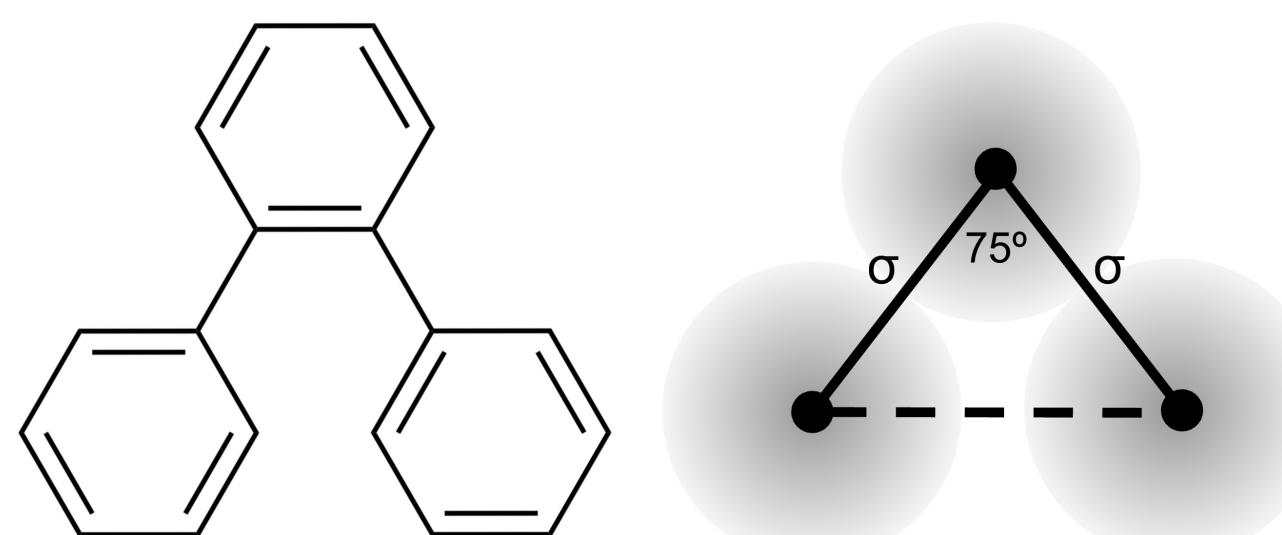


Figure: Skeleton model of Ortho-terphenyl (left) and the 2dLW model (right). Each circle represents a Lennard-Jones site. The apical angle is 75°. Lines denote rigid bonds, and the dashed line is a fictional bond used to maintain the apical angle. Here, the reduced unit σ represents a separation of 4.83 Å.

Molecular Dynamics

We simulate the dynamics of a 2dLW liquid using molecular dynamics simulations in the microcanonical (NVE) ensemble. We approximate the Hamiltonian of our system as the sum of total kinetic energy and pairwise potentials. Trajectories are obtained using velocity Verlet integration with a timestep of 0.001τ (in reduced Lennard-Jones time units). We enforce the geometry of 2dLW molecules using holonomic constraints via Lagrange multipliers calculated using an altered routine from the popular RATTLE algorithm [1]. The simulation domain was a square box of dimensions determined by a fixed reduced density of $\rho^* = 0.25$, and periodic boundary conditions.

$$\mathcal{H}(R) = \sum_{i=1}^N \frac{1}{2} m_i \dot{r}_i^2 + \mathcal{V}(R)$$

$$\mathcal{V}(R) = \sum_{i,j}^N \sum_{n,m}^3 4\epsilon \left[\left(\frac{\sigma}{r_{in,jm}} \right)^{12} - \left(\frac{\sigma}{r_{in,jm}} \right)^6 \right]$$

1,2 and 3 denote sites on any given pair of trimers, i,j .

Molecular Orientational Order

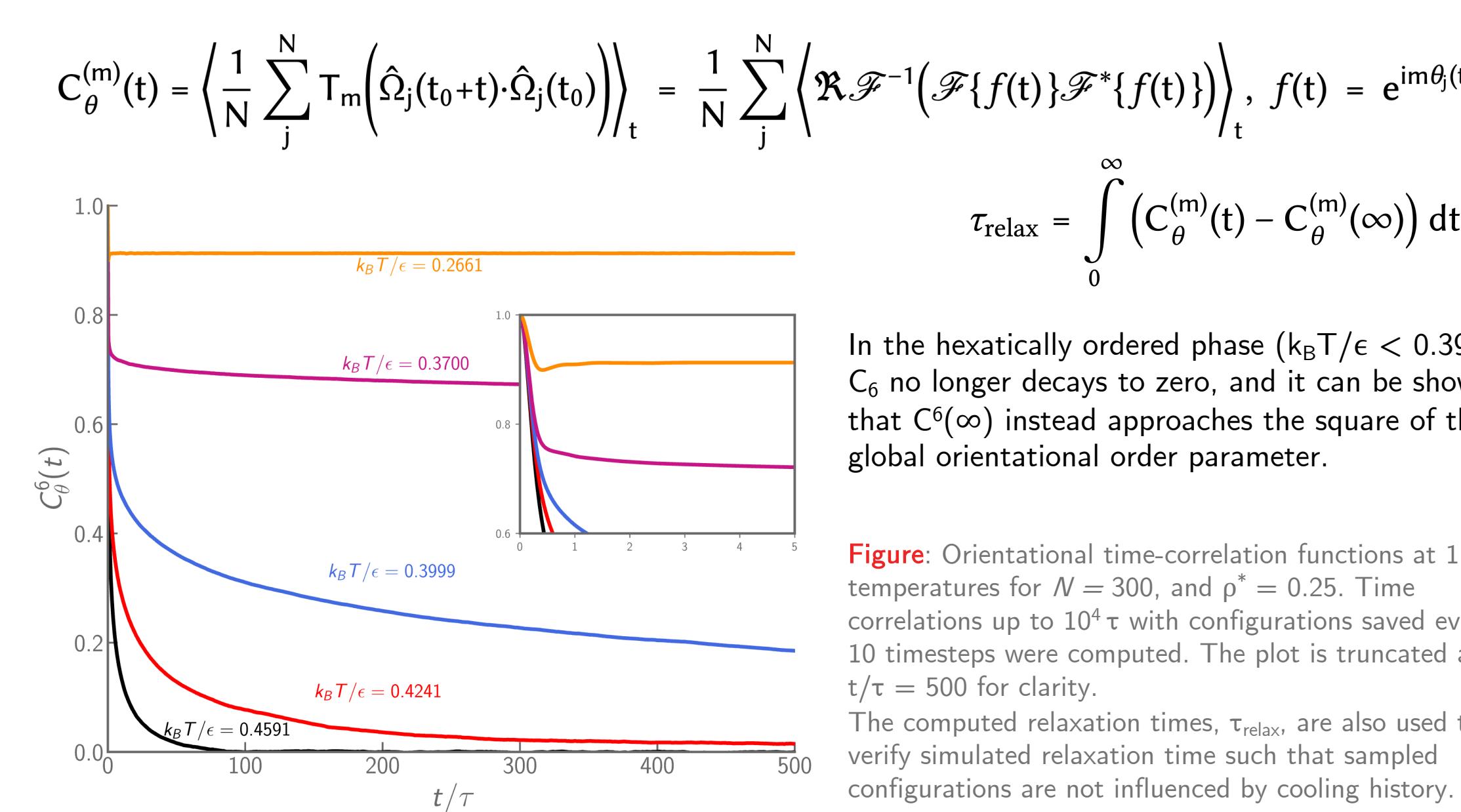
Molecular-orientational order, not to be confused with Bond-orientational order, describes the alignment of molecular symmetry axes with some common director. Orientational order can be described by the order parameter tensor (m in 2D), $\underline{Q}^{(m)}$, and the m -fold orientational order parameter, $|s_m|$. In an isotropic liquid, $|s_m| = 0$, while in a perfectly ordered liquid, $|s_m| = 1$.

$$\underline{Q}^{(m)} = \frac{1}{N} \sum_i^N \begin{bmatrix} \cos(m\theta_i) & \sin(m\theta_i) \\ \sin(m\theta_i) & -\cos(m\theta_i) \end{bmatrix}$$

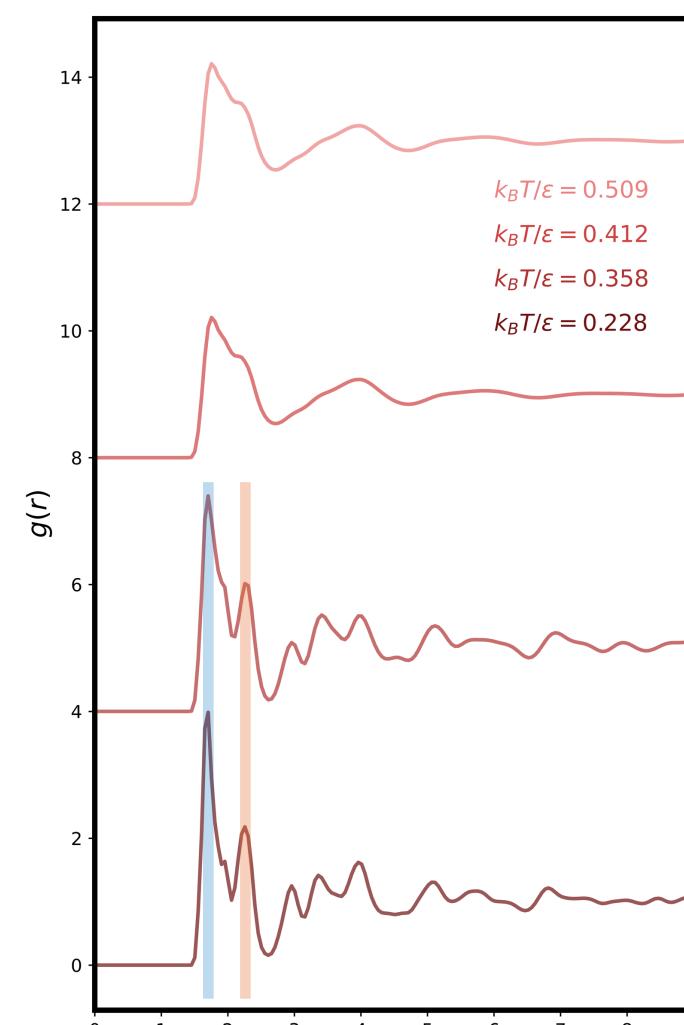
$$\langle |s_m| \rangle = \left\langle \left| \frac{1}{N} \sum_j^N e^{im\theta_j} \right| \right\rangle_t$$

Time Correlation Functions

Supercooled liquid dynamics are very slow. Time correlation functions show the timescale that liquids retain transient properties. Here, sixfold orientation becomes increasingly long-lived with cooling.

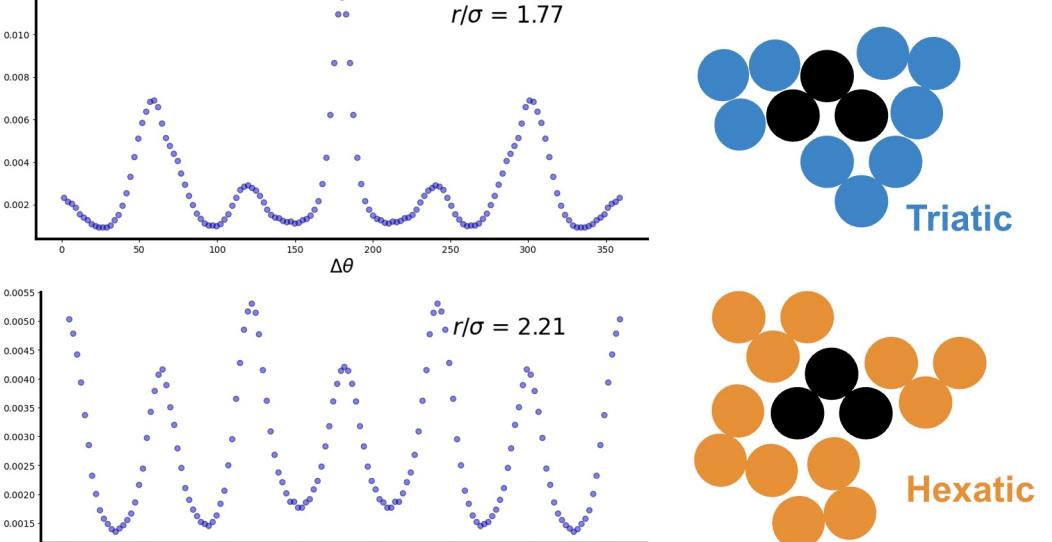


Local Structure



We study liquid structure using the radial pair distribution function, $g(r)$, which represents the relative likelihood of locating molecules separated by a given distance r . We observe an increase in local structure with decreasing temperature, and the formation of peaks in $g(r)$ corresponding to distinct nearest-neighbor relationships. The first and second peaks at supercooled temperatures (highlighted in the figure to the left) compose the closest 'shell' surrounding any given molecule. Crucially, we find a preference for **triatic** ordering relative to the central atom in the first peak, and **hexatic** ordering in the second peak.

Figure: Left: Radial distribution functions for $N = 300$ at four temperatures. 1st and 2nd peaks are highlighted.
Right: Snapshots of orientations about the first ($r/\sigma = 1.77$) and second ($r/\sigma = 2.21$) peaks. Probability densities of orientation relative to a central molecule are plotted for $N = 300$, averaged over 150τ .



An Isotropic→Hexatic Molecular-Orientational Phase Transition

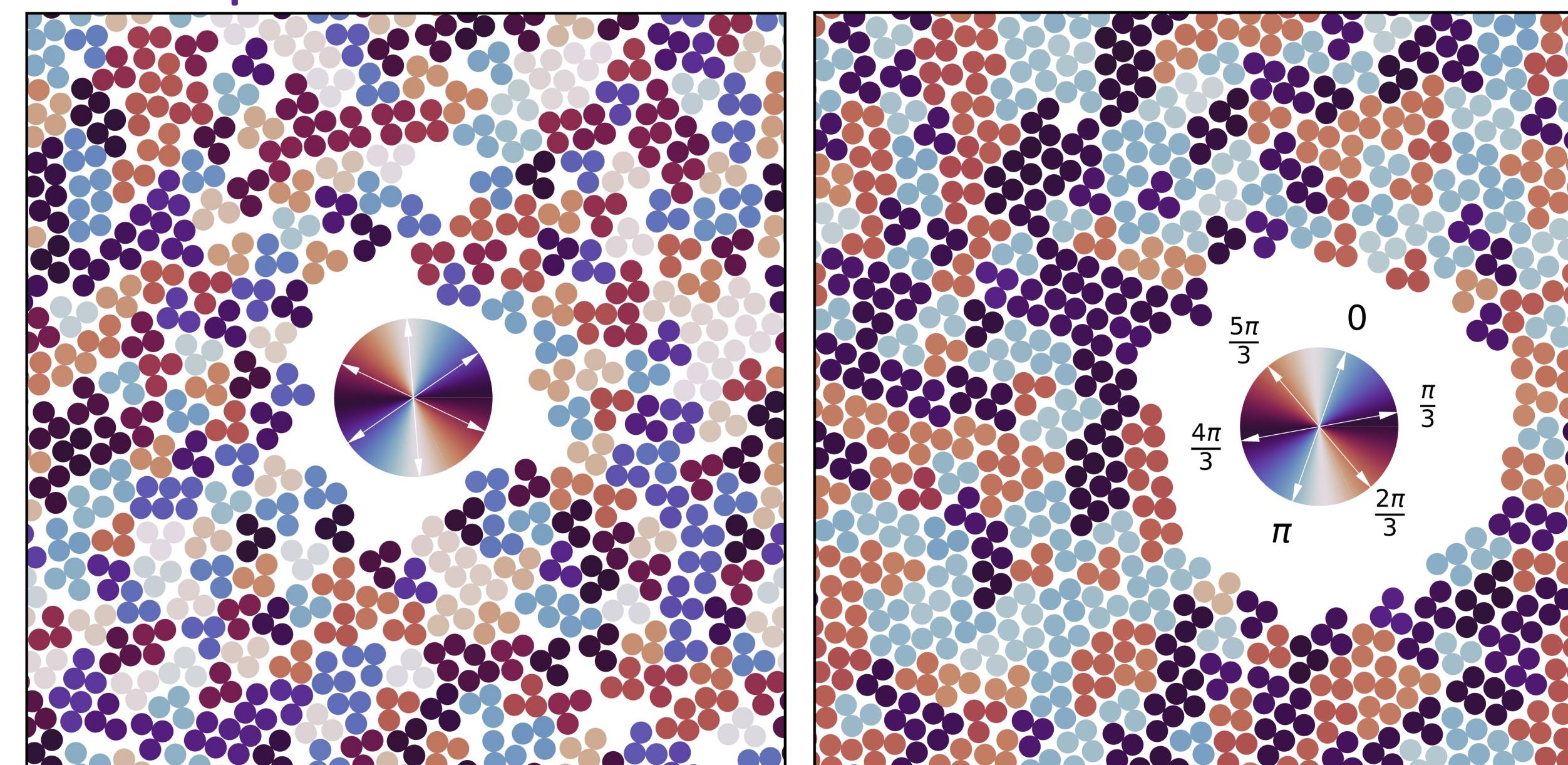
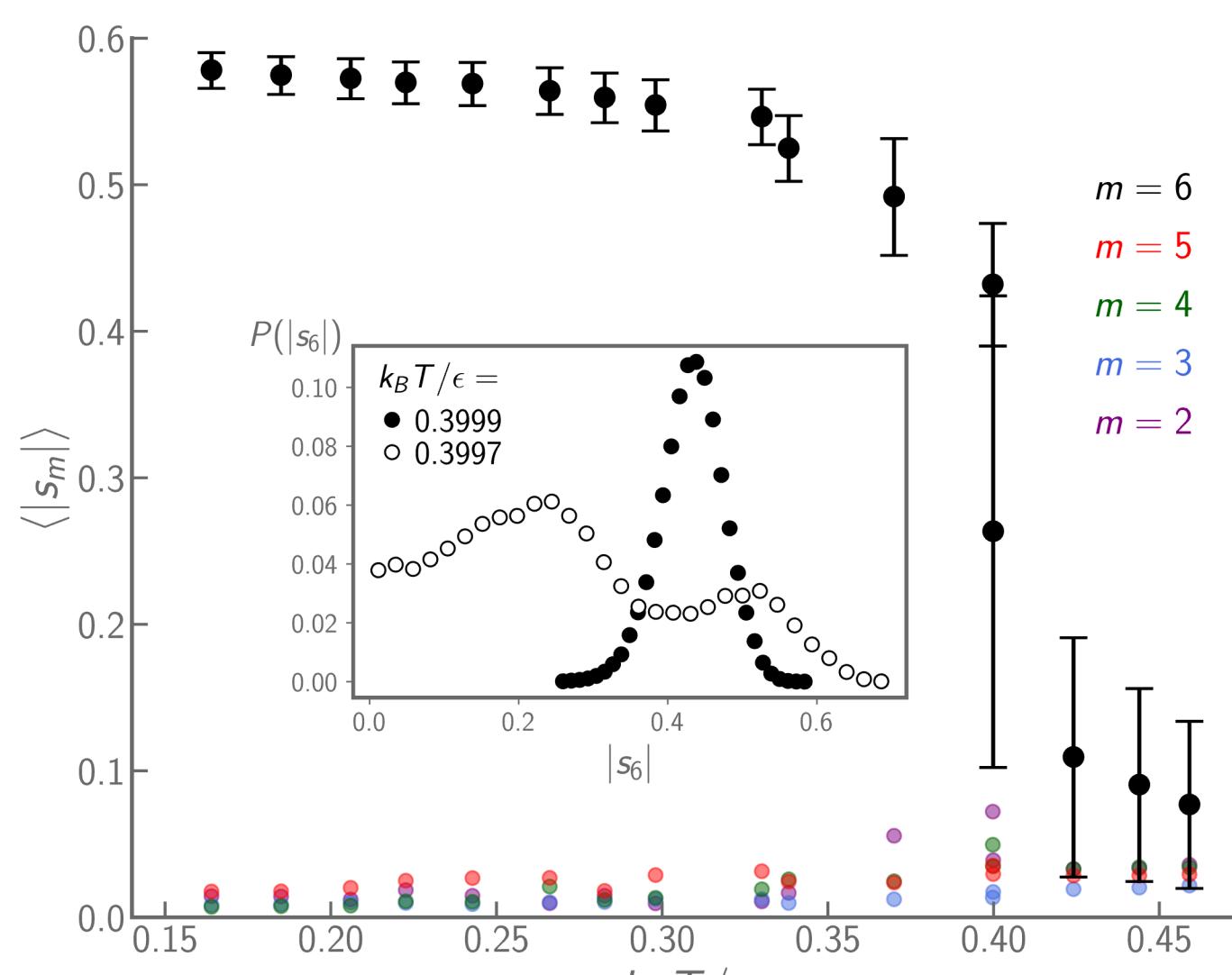


Figure: Images of a 2dLW liquid with $N = 300$ at temperatures $k_B T/\epsilon = 0.460$ (left) and $k_B T/\epsilon = 0.224$ (right). Trimers are shaded by orientation relative to the director (the eigenvector corresponding to the greatest eigenvalue of \underline{Q}^6 in each state). Isotropic character dominates on the left, while conspicuous hexatic ordering is present on the right.



With sufficient relaxation times, we observe a distinct phase transition from isotropic to hexatically ordered liquid around $k_B T/\epsilon = 0.3999$. Contrary to previous studies of 2dLW liquids where hexatic order appears to diminish below the glass transition, we observe persistent hexatic order as the liquid cools. Besides sixfold order, no significant orientational order is observed.

Figure: Left: Time-averaged molecular orientational order parameters ($m = 6, 5, 4, 3, 2$) for a system of $N=300$ 2dLW trimers at a range of temperatures. The error bars (omitted for $m < 6$) traverse ± 1 standard deviation from the mean. Averages are taken over 10^6 configurations. Inset contains probability densities of the sixfold order parameter at $k_B T/\epsilon = 0.3999$ and 0.3997.

Diffusion and Dynamical Heterogeneity

Liquid dynamics can be characterized by the temperature dependence of the diffusion constant. We confirm a dynamical crossover from VFT (supercooled liquid, plateau in $\Delta r^2(t)$) to Arrhenius behavior (glassy) with cooling below the transition temperature.

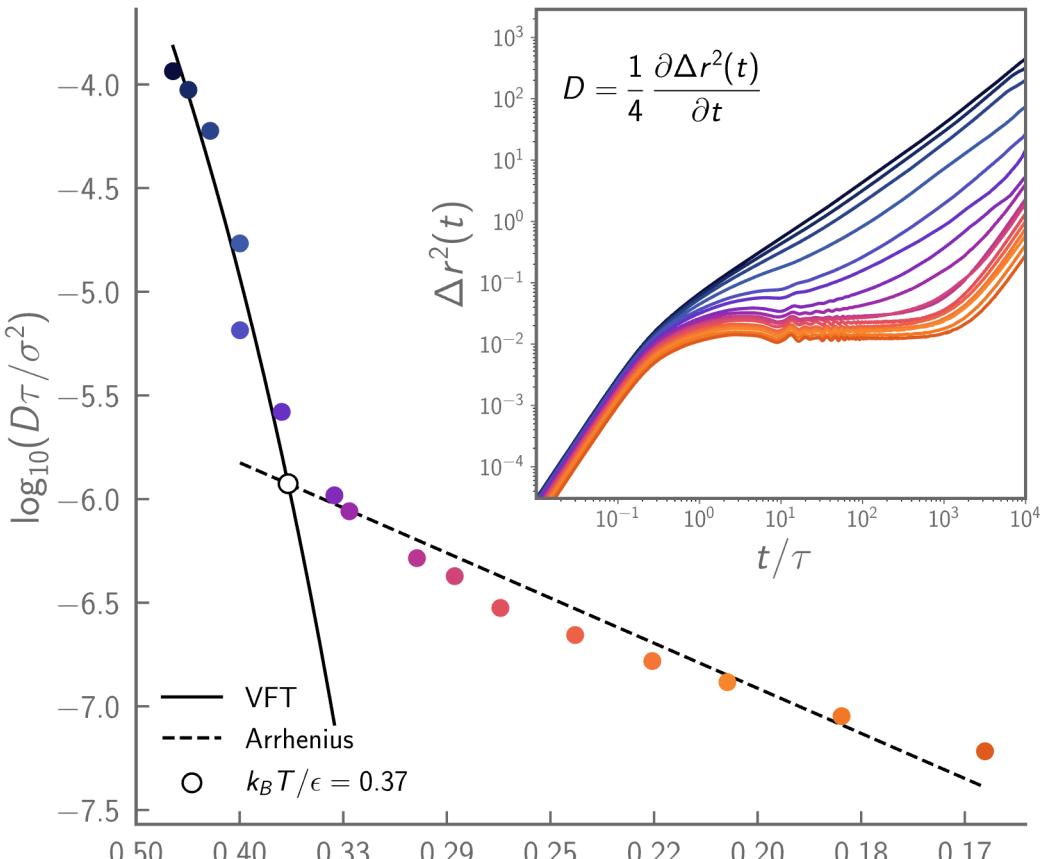
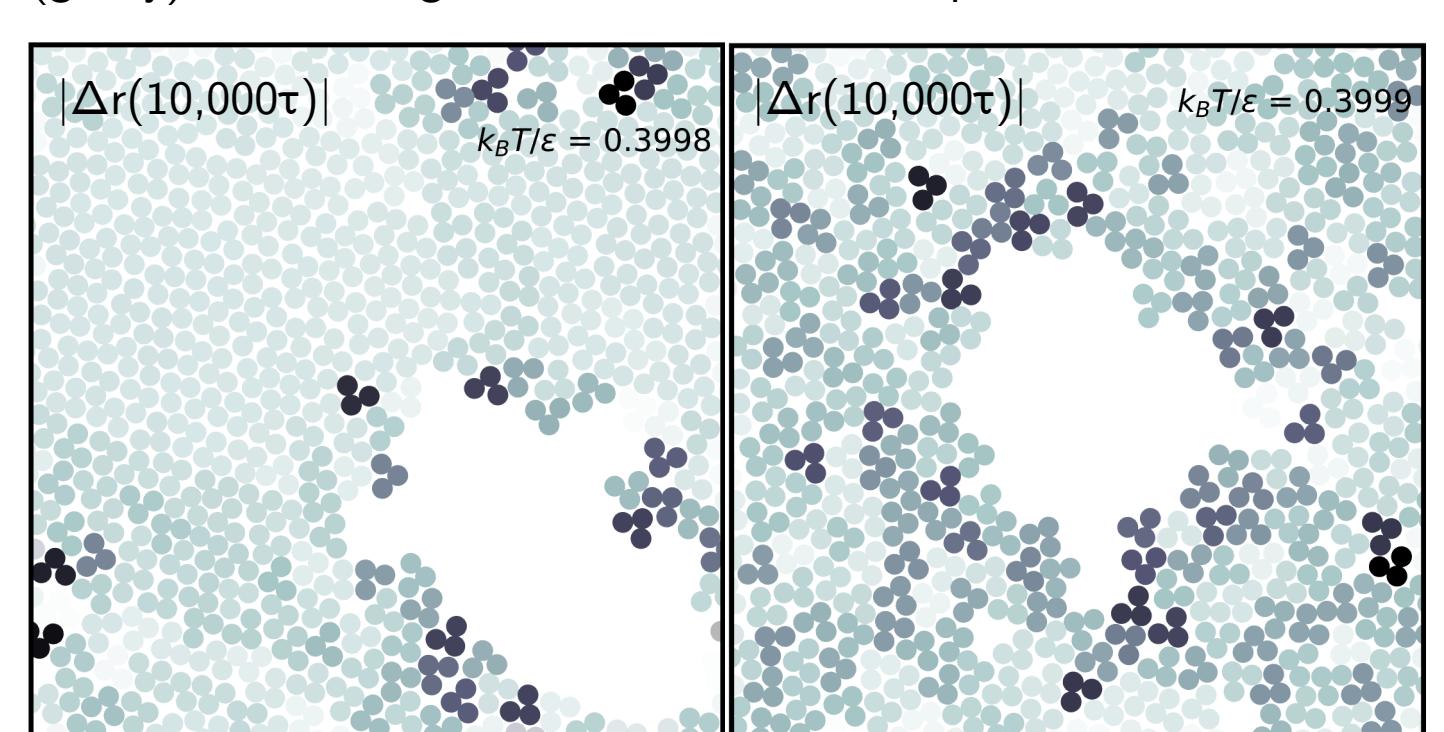


Figure: Above: Diffusion constants with temperature. VFT and Arrhenius equations are fitted. Left: Dynamical heterogeneity appears at the phase transition. Greater displacements are darker.

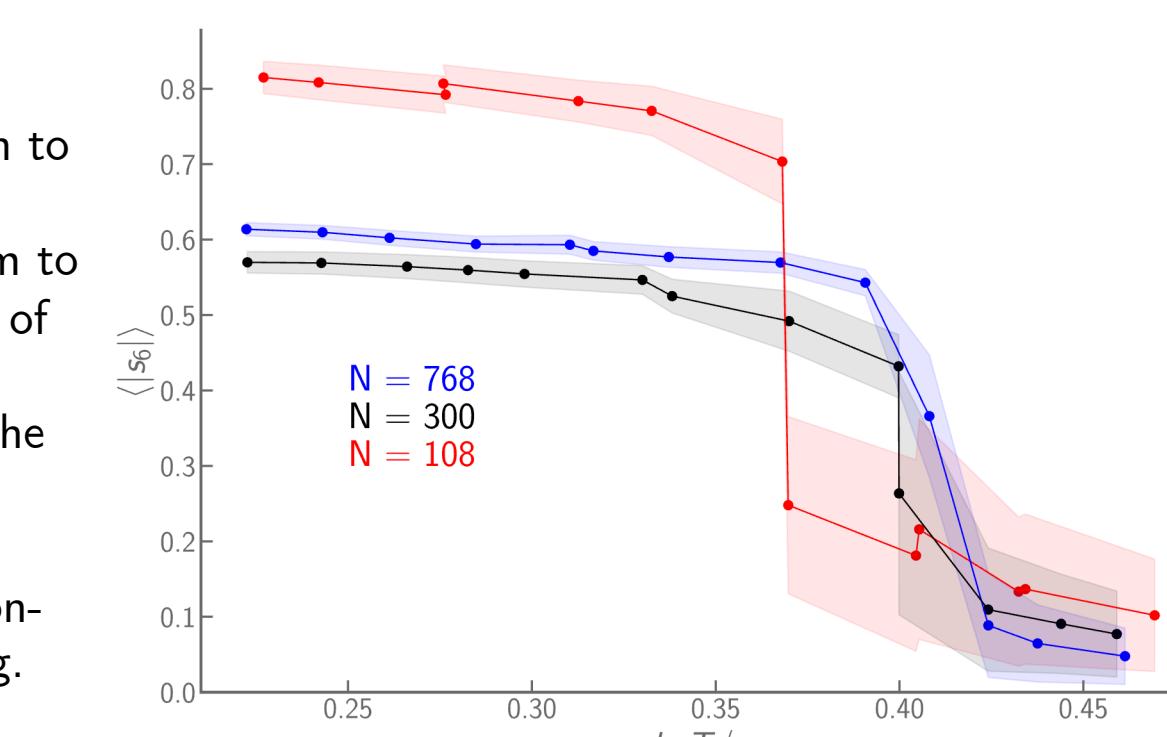
Large Fluctuations in Orientational Order

We observe large fluctuations in the sixfold order parameter at the phase transition. We also observe an apparent jump in total potential energy at the transition temperature. We hypothesize that the timeseries captures oscillations between coexisting phases, characteristic of a first-order phase transition. However, further simulations at the transition temperature are required to determine the order concretely. Still, such phenomena are promising indicators that the 2dLW system captures realistic liquid behaviors.

Figure: Left: $|s_6|$ timeseries at various temperatures. Crucially, the order parameter exhibits large fluctuations at the transition temperature, $k_B T/\epsilon = 0.3999$. Whether they are indeed oscillations between coexistent phases is unclear. At low temperatures, $|s_6|$ stabilizes at value between 0.57–0.60 with little variation in time.

Finite-Sized Scaling

Critical phenomena and correlation lengths are known to obey scaling laws with system size. Hence, we are interested in finite-sized scaling of our system and aim to study the change in $|s_6|$ with increasing N . The order of the transition may then be resolved. Preliminary simulations for $N = 108$ and $N = 768$ are shown in the figure (right). Importantly, we observe a qualitatively similar phase transition in each case. However, with small system sizes, the effect of cavitation may be non-trivial, which may explain the lack of expected scaling.



Scaled Particle Theory

It is possible to analytically predict phase transitions in two-dimensional liquids using **Scaled Particle Theory (SPT)**. To do this, we consider trimers composed of hard disks ($V=\infty$ for $r \leq \sigma$) with a 2dLW geometry. The fundamental idea of SPT is that the full equation of state for a 2D liquid can be extracted by computing the free energy cost associated with adding one additional molecule to a packed system at some orientation [3].

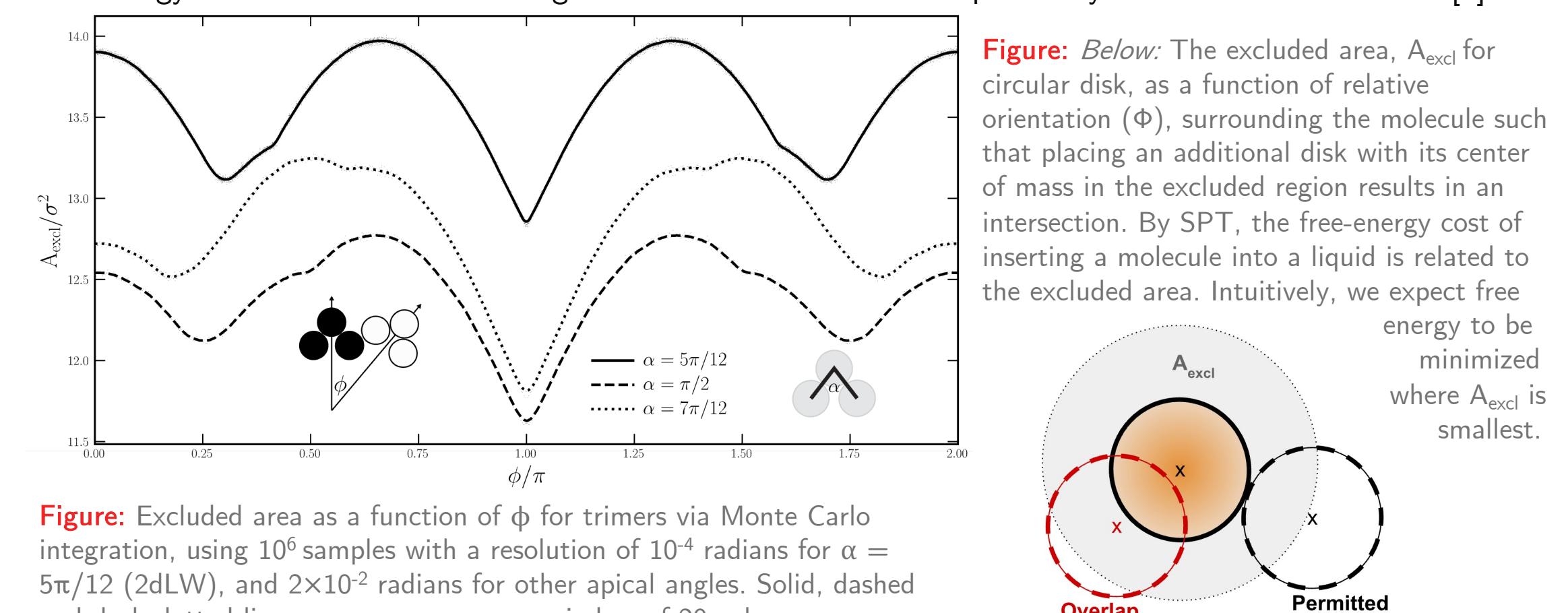


Figure: Below: The excluded area, A_{excl} for circular disk, as a function of relative orientation (Φ), surrounding the molecule such that placing an additional disk with its center of mass in the excluded region results in an intersection. By SPT, the free-energy cost of inserting a molecule into a liquid is related to the excluded area. Intuitively, we expect free energy to be minimized where A_{excl} is smallest.

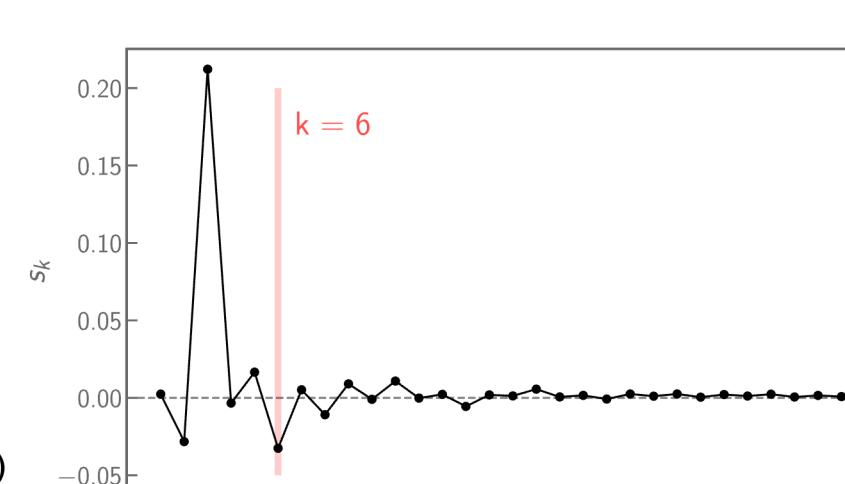


Figure: Excluded area as a function of ϕ for trimers via Monte Carlo integration, using 10^6 samples with a resolution of 10^{-4} radians for $\alpha = 5\pi/12$ (2dLW), and 2×10^{-2} radians for other apical angles. Solid, dashed, and dash-dotted lines are averages over a window of 20 values.

A Simple Preliminary Argument

For density ρ , orientational distribution $f(\Phi)$, relative orientation Φ , free energy per molecule φ , packing fraction η , and molecular area a : $\rho(\varphi) = \rho f(\varphi)$, $\eta = \rho a$, $A^{\text{SPT}}(\varphi) = A^{\text{excl}}(\varphi) - 2a$

The preferred $f(\Phi)$ is that with lowest free energy, and minimizes the free energy functional φ :

$$\varphi[f(\varphi)] = \int_0^{2\pi} f \ln(f) d\Phi - \ln(1-\eta) + \frac{\rho}{1-\eta} \mathcal{K}[f], \quad \mathcal{K}[f] = \frac{1}{2} \int_0^{2\pi} d\Phi d\Phi' f(\Phi)f(\Phi')A^{\text{SPT}}(\Phi-\Phi')$$

Rewriting in terms of Fourier coefficients, omitting constant terms:

$$A^{\text{SPT}}(\varphi) = \sum_k^{\infty} \cos(k\varphi), \quad s_k = \frac{1}{2\pi} \int_0^{2\pi} A^{\text{SPT}}(\varphi) \cos(k\varphi) d\varphi \quad f(\varphi) = \frac{1}{2\pi} \left[1 + \sum_{k \geq 1} f_k \cos(k\varphi) \right], \quad f_0 = 1 \quad \mathcal{K}[f] = \frac{1}{2} \sum_{k \geq 0} s_k f_k^2$$

It can be shown from the second variation of φ that the isotropic phase is no longer stable at sufficient η . Then, the free energy is minimized when s_k is most negative, with the corresponding coefficient f_k maximized. Computing s_k for the Monte-Carlo derived 2dLW A_{excl} , s_k is most negative for $k = 6$. So, $f(\varphi)$ ought to be dominated by f_6 – which possesses sixfold rotational symmetry.

In the limit of $N \rightarrow \infty$, we argue that this is sufficient to induce hexatic orientational order.

Conclusions & Outlook

Thus far, we have compelling evidence that the slow dynamics of a supercooled 2dLW liquid are coupled with the emergence of hexatic molecular orientational order. We require further analysis of the phase transition and critical phenomena, as well as continued investigation of finite-sized scaling. We also anticipate extracting equations of state from SPT using gradient-based optimization. Our preliminary results suggest that hexatic molecular orientational order in 2dLW is a direct result of its geometry. This relationship may be verified by generalizing our studies to arbitrary apical angles.

References

- [1] Hans C Andersen. Rattle: A "velocity" version of the shake algorithm for molecular dynamics calculations. *Journal of computational Physics*, 52(1):24–34, 1983.
- [2] Michael P Allen and Dominic J Tildesley. Computer simulation of liquids. Oxford university press, 2017.
- [3] Yuri Martínez-Ratón, Ariel Diaz-De Armas, and Enrique Velasco. Uniform phases in fluids of hard isosceles triangles: One-component fluid and binary mixtures. *Physical Review E*, 97(5):052703, 2018.
- [4] Ton, A. Dynamics of a Two-Dimensional supercooled liquid. Brown University digital repository, 2020.

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