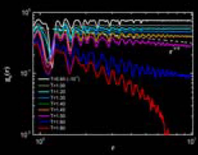
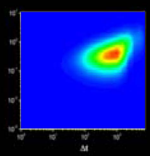
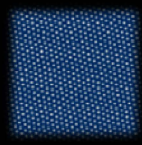
Glassy Dynamics in 2D Melting

Search for links between structure and dynamics

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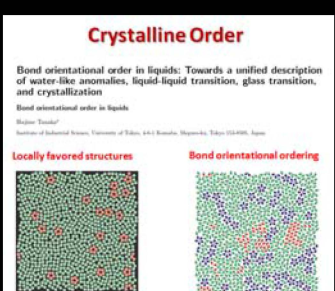
Center for Soft Condensed Matter Physics & Interdisciplinary research

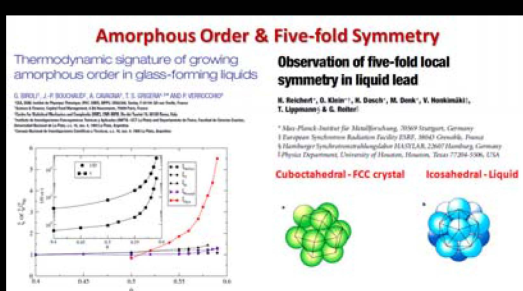
Collaborators: Wende Tian, Suzhou; Yilong Han, HUST

The Puzzling Glass Transition

- **Glass transition: dynamics becomes progressively slower and heterogeneous, with little structural change**
- **Connection between structure and dynamics: a central problem in glass research**



Tanaka, EPJE, 2012



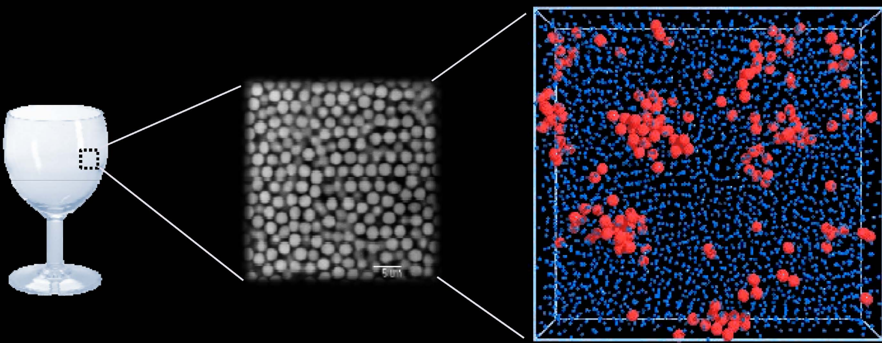
Biroli et al. Nat. Phys. 2009
Charbonneau et al. PRL, 2012

Reichert et al. Nature (2000)

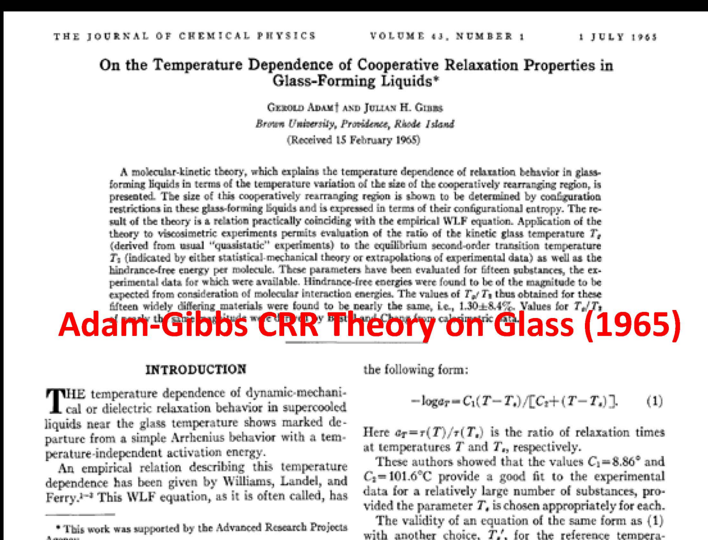
Structure and Dynamical Heterogeneity (DH)

DH: spatial - temporal correlation of the dynamics

Weeks and Weitz et al. Science 2000



Red: top 10% fast particles



THE JOURNAL OF CHEMICAL PHYSICS VOLUME 43, NUMBER 1 1 JULY 1965

On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids*

GEROLD ADAM† AND JULIAN H. GIBBS
Brown University, Providence, Rhode Island

(Received 15 February 1965)

A molecular-kinetic theory, which explains the temperature dependence of relaxation behavior in glass-forming liquids in terms of the temperature variation of the size of the cooperatively rearranging region, is presented. The size of this cooperatively rearranging region is shown to be determined by configuration restrictions in these glass-forming liquids and is expressed in terms of their configurational entropy. The result of the theory is a relation practically coinciding with the empirical WLF equation. Application of the theory to viscosimetric experiments permits evaluation of the ratio of the kinetic glass temperature T_g (derived from usual "quasistatic" experiments) to the equilibrium second-order transition temperature T_2 (indicated by either statistical-mechanical theory or extrapolations of experimental data) as well as the hindrance-free energy per molecule. These parameters have been evaluated for fifteen substances, the experimental data for which were available. Hindrance-free energies were found to be of the magnitude to be expected from consideration of molecular interaction energies. The values of T_g/T_2 thus obtained for these fifteen widely differing materials were found to be nearly the same, i.e., 1.30±8.4%. Values for T_g/T_2 [illegible] calorimetric data.

INTRODUCTION

THE temperature dependence of dynamic-mechanical or dielectric relaxation behavior in supercooled liquids near the glass temperature shows marked departure from a simple Arrhenius behavior with a temperature-independent activation energy.

An empirical relation describing this temperature dependence has been given by Williams, Landel, and Ferry.[1-3] This WLF equation, as it is often called, has the following form:

$$-\log a_T = C_1(T-T_s)/[C_2+(T-T_s)]. \quad (1)$$

Here $a_T=\tau(T)/\tau(T_s)$ is the ratio of relaxation times at temperatures T and T_s, respectively.

These authors showed that the values $C_1=8.86°$ and $C_2=101.6°C$ provide a good fit to the experimental data for a relatively large number of substances, provided the parameter T_s is chosen appropriately for each.

The validity of an equation of the same form as (1) with another choice, T_s', for the reference tempera-

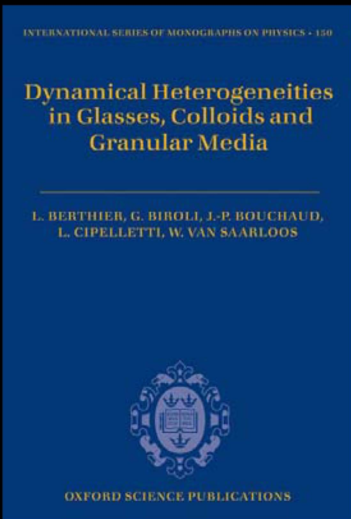
* This work was supported by the Advanced Research Projects Agency.

Adam-Gibbs CRR Theory on Glass (1965)

CRRs grow too large to move in exp. time window

1. Dynamical arrest and glass transition;
2. Dynamical Length Scale

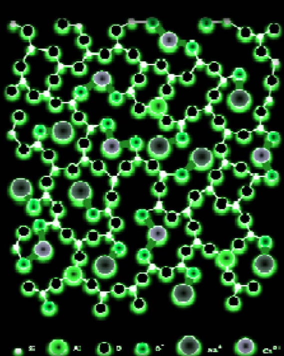
Dynamical Heterogeneity: "The Book"

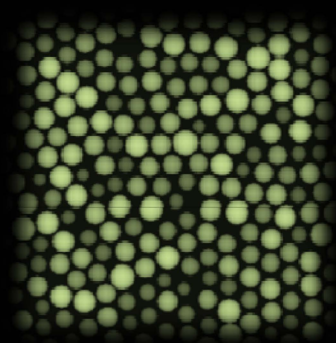


"In this book, we survey the most recent research dealing with glassy physics … with an emphasis on the key role played by heterogeneities in the dynamics of glass."

Oxford Sci. Pub. 2012

Colloids as Model Systems to Study Glass Transition

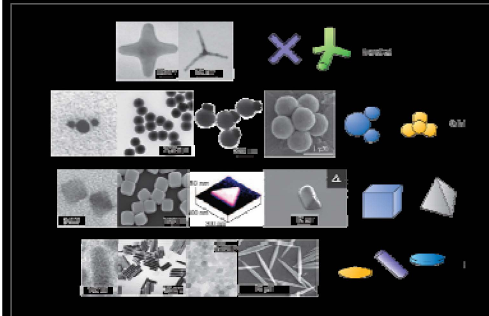




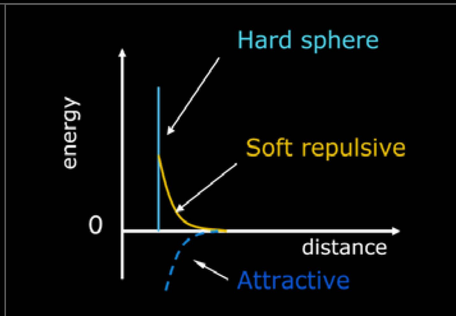
Smith and Tanaka

Colloids Model Systems

Shape



Interaction

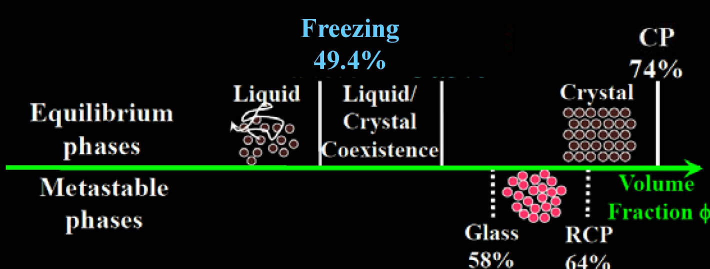


Glotzer et al. Nat. Mat. 2011

Colloids: Packing-driven Phase Transition

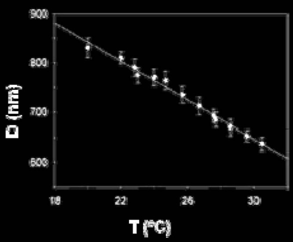
- Molecular Glass: Temperature T

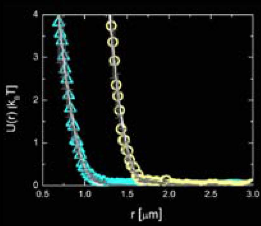
- Colloidal Glass: Packing fraction ϕ



Temperature-driven: Microgel Colloid

Use T to tune packing
Soft-repulsive interaction

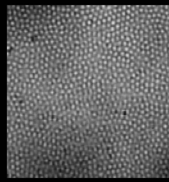




Melting of colloidal crystal

T =26.7°C
(crystal)

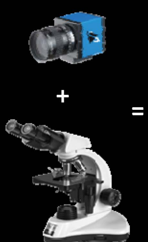
T =28.3°C
(liquid)

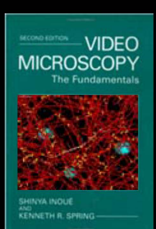


Han et al. PRE (2007)

Experimental Tool & Data Analysis

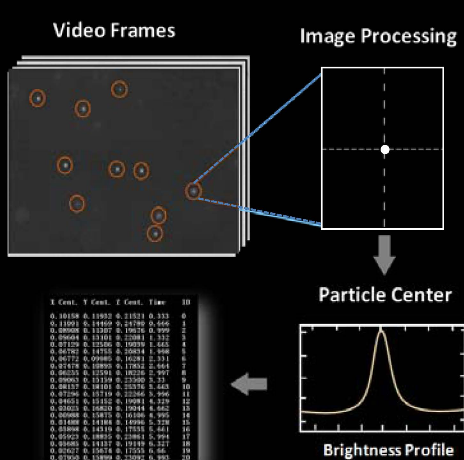
Video Microscopy



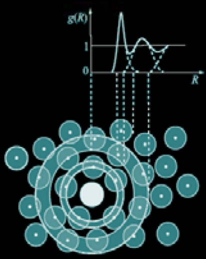


Two colloids (D ~ 3 μm) in water
(Brownian motion)

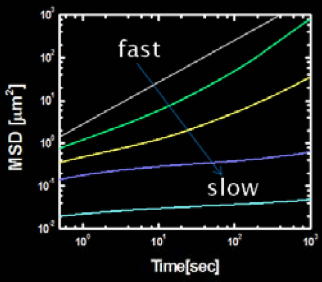
Particle Tracking



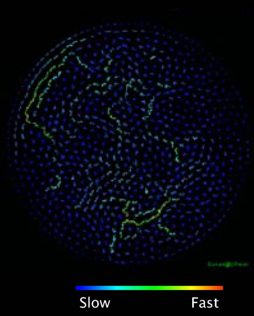
Structural and Dynamical Properties



Pair Correlation Function, g(r)

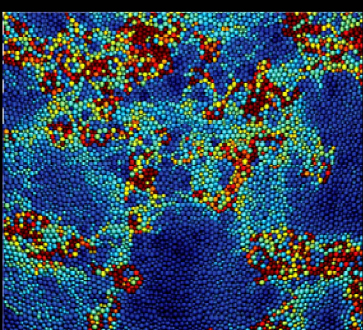


Mean Squared Displacement, MSD



Cluster Size & DH

Dynamics and Dynamical Heterogeneity



MD simulation of LJ glass
red-fast particles   blue-slow particles

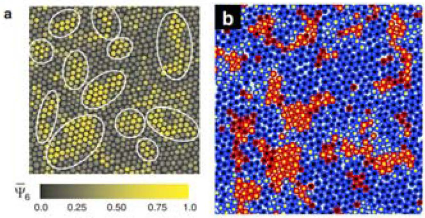
- Speeds of particles vary in time and space
- Cooperative and clustering

Connection: Structure and Dynamics ?

Correlation between Dynamic Heterogeneity and Medium-Range Order in Two-Dimensional Glass-Forming Liquids

PRL 2009

Takeshi Kawasaki, Takeaki Araki, and Hajime Tanaka*
Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo 153-8505, Japan



Medium Range Order
and
Glassy Dynamics

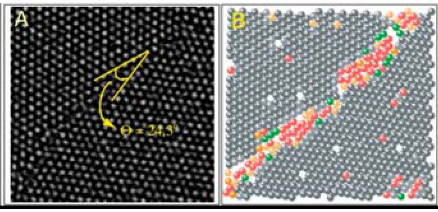
Confined glassy dynamics at grain boundaries in colloidal crystals

PNAS 2012

K. Hima Nagamanasa[a,1], Shreyas Gokhale[b,1], Rajesh Ganapathy[c,2], and A. K. Sood[b,c]

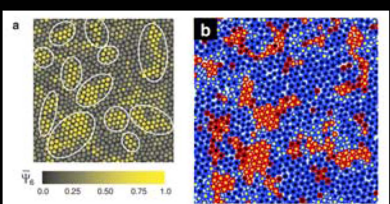
[a]Chemistry and Physics of Materials Unit, Jawaharlal Nehru Center for Advanced Scientific Research, Jakkur, Bangalore 560064, India; [b]Department of Physics, Indian Institute of Science, Bangalore 560012, India; and [c]International Center for Materials Science, Jawaharlal Nehru Center for Advanced Scientific Research, Jakkur, Bangalore 560064, India

Grain boundary
and
Glassy Dynamics

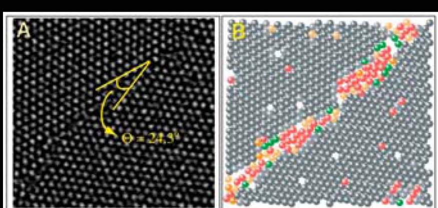


Open Questions

Medium Range Order



Grain boundary and Defects



Defects & Order ⟺ **Glassy Dynamics**

Can we learn glassy dynamics from melting of crystal?

Crystal melting

↓

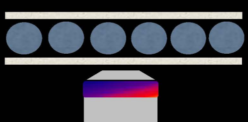
Lose order and produce defects

↓

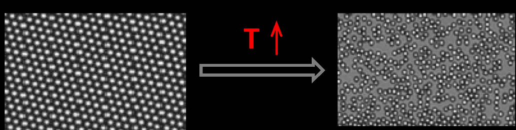
Glassy dynamics

Experiments: T-responsive Colloids

2D sample cell



Temperature control



Crystal **Liquid**

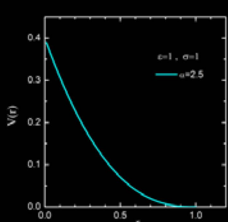
- 800 nm microgel particles
- N ~ 10^6 particles, 2D triangular lattice

MD Simulations

Zhang et al. Nature (2009)

Soft Sphere:

$$V(r)=\begin{cases}0 & r>\sigma \\ \dfrac{\varepsilon}{\alpha}\left(1-\dfrac{r}{\sigma}\right)^{\alpha} & r\le\sigma\end{cases}$$



- α = 2.5, fits well the interaction of colloids
- N ~10^3 - 10^5 particles, 2D triangular lattice, PBC

2D Melting

- **Classical Topic** in condensed matter physics
- **Debated** widely
- **KTHNY Theory: Solid-Hexatic-Liquid**, two-step melting (Kosterlitz-Thouless-Halperin-Nelson-Young)

Previous effort
static structure, orientational order parameter, order of transition…

Our focus
glassy dynamics, dynamical heterogeneity …

Krauth, Phys. Rev. Lett. 2011, 2015

Characteristics of KTHNY 2D melting

Two-step transition: Solid → Hexatic → Liquid

3D	Solid	Liquid
Translation	long	short
Orientation	long	short

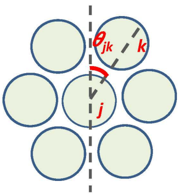
2D	Solid	Hexatic	Liquid
Translation	quasi-long	short	short
Orientation	long	quasi-long	short

KTHNY Theory and Orientational Order

Solid→Hexatic→Liquid

Orientational Order Parameter

$$\psi_{6j} = \frac{1}{n_j}\sum_{k=1}^{n_j} e^{i6\theta_{jk}}$$

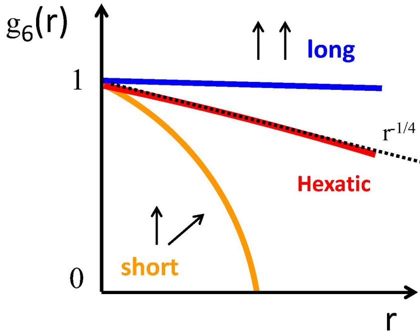


Perfect crystal $\psi_6 = 1$

Disorder $\psi_6 = 0$

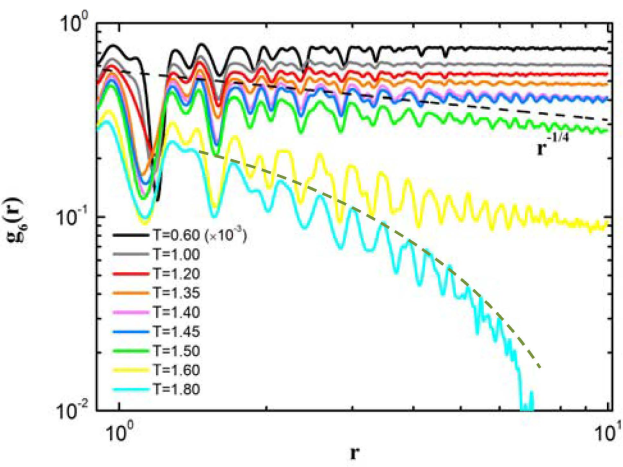
Order Parameter Correlation

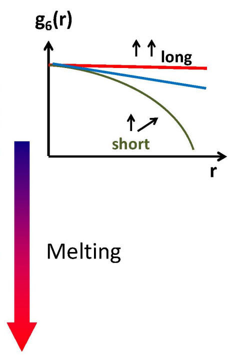
$$g_6(r) = <\psi^*_{6i}(r_i)\psi_{6j}(r_j)>$$



Results: Orientational Correlation Function, $g_6(r)$

Typical 2D Melting Behavior: Solid – Hexatic – Liquid

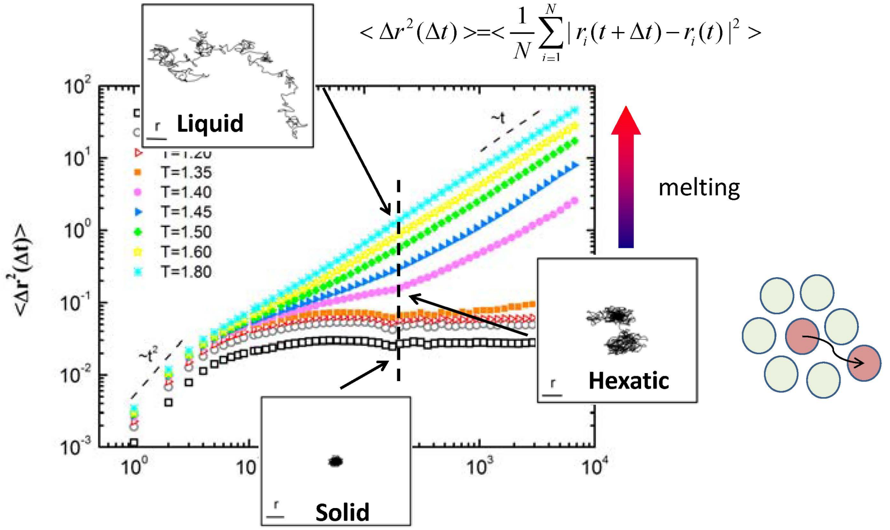




Results: Mean Square Displacement

Hallmarks of Glassy Dynamics in the Hexatic Phase

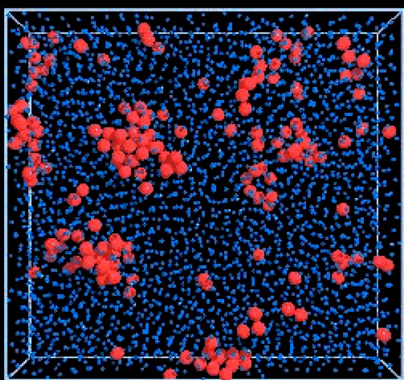
$$<\Delta r^2(\Delta t)> = < \frac{1}{N}\sum_{i=1}^{N} |r_i(t+\Delta t) - r_i(t)|^2 >$$



Dynamical Heterogeneity (DH)?

Spatial - temporal correlation of the dynamics

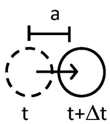
Weeks & Weitz, Science (2000)



How to quantify DH?

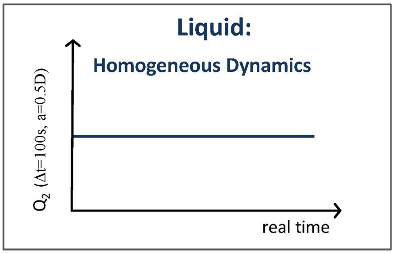
Quantify Dynamical Heterogeneity

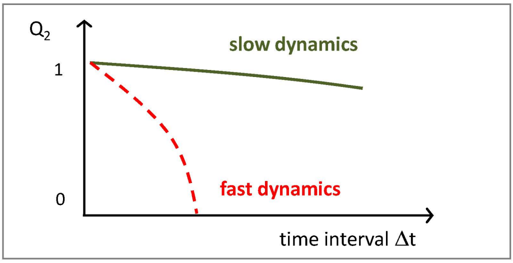
Self-overlap function, Q_2

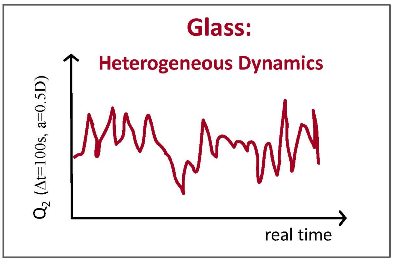


$$Q_2(\Delta t, \mathrm{a}) = \frac{1}{N}\sum_{i=1}^{N}\exp\left(-\frac{\Delta r_i(\Delta t)^2}{2\mathrm{a}^2}\right)$$

$$Q_2(\Delta t, a) = \begin{cases} 1 & if \quad \Delta r < a \\ 0 & otherwise \end{cases}$$







Q_2 fluctuates: Dynamical Heterogeneity

Quantify Dynamical Heterogeneity:

Four Point Susceptibility – χ_4

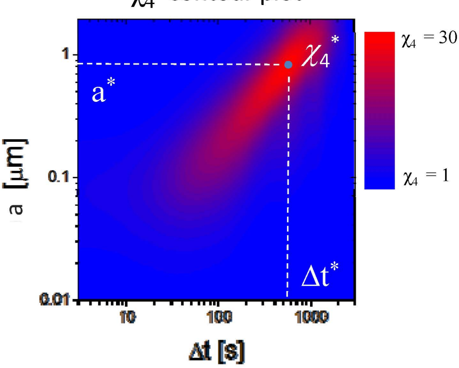
Mathematically, χ_4 is the fluctuation of overlap function, $Q_2(\Delta t, a)$:

$$\chi_4(\Delta t, a) \equiv N\left(\left\langle Q_2(\Delta t, a)^2\right\rangle - \left\langle Q_2(\Delta t, a)\right\rangle^2\right)$$

a length scale Δt time scale

N number of particles

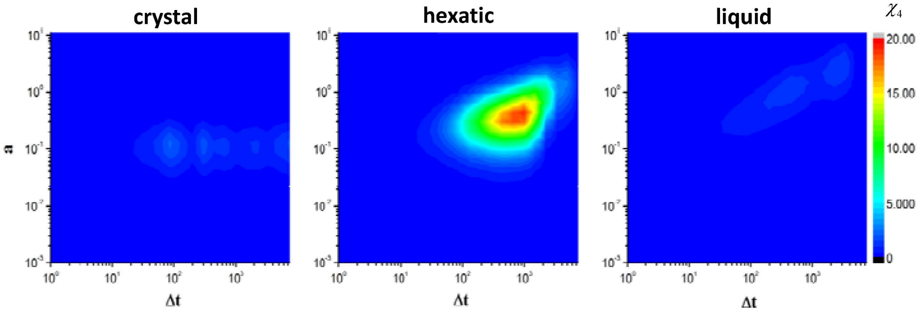
χ_4 contour plot



Phys. Rev. Lett. 95, 265701 (2005); Nature Physics 3, 260 (2007)

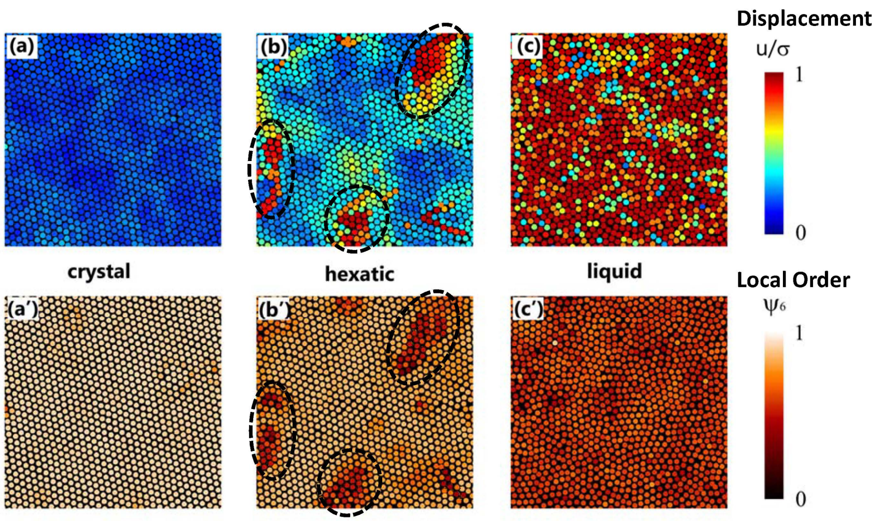
Dynamical Heterogeneity in 2D Melting:
4-point susceptibility

$$Q_2(\Delta t, a) = \frac{1}{N}\sum_{i=1}^{N}\exp\left(-\frac{\Delta r_i(\Delta t)^2}{2a^2}\right) \qquad \chi_4(a,\Delta t) = N[<Q_2(a,\Delta t)^2> - <Q_2(a,\Delta t)>^2]$$



- Strong dynamical heterogeneity at intermediate phase

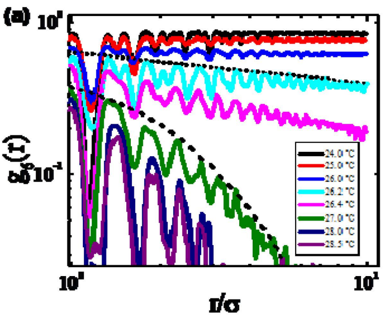
Connections : Local Structures &Dynamics



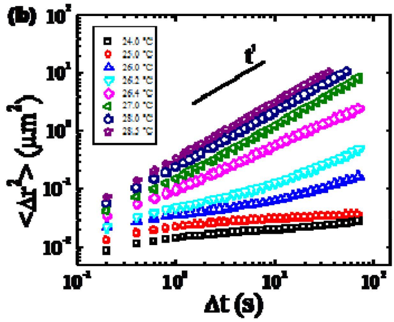
Colloidal Experiments

Orientational Order and Dynamics

Orientational Correlation Function, g_6



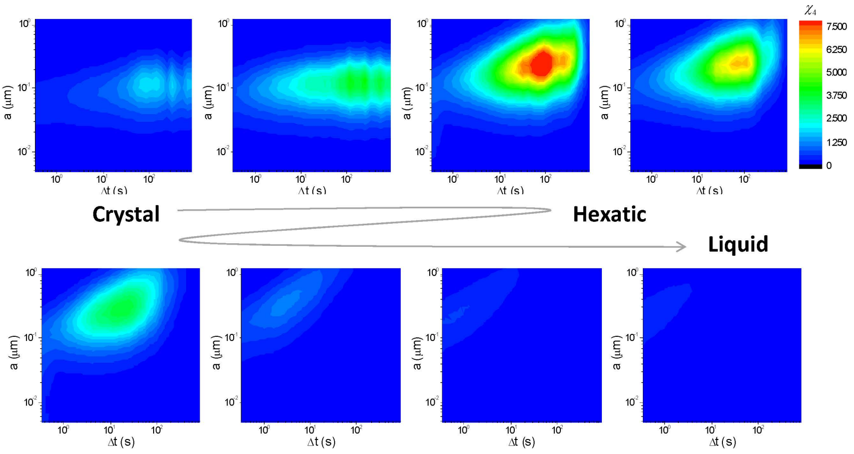
Mean Square Displacement, MSD



- **Power law/expn. decay: typical 2D melting**
- **Glassy behavior at intermediate phase**

Colloidal Experiments

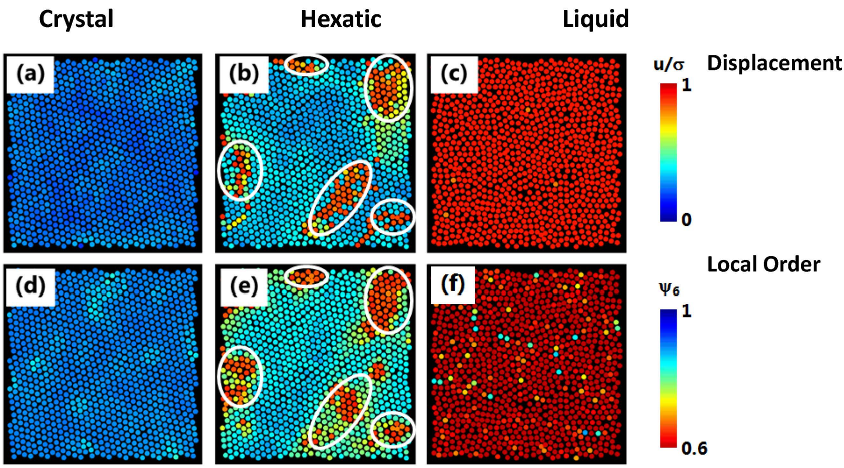
Heterogeneity: Four-point susceptibility



- **Strong dynamical heterogeneity at intermediate phase**

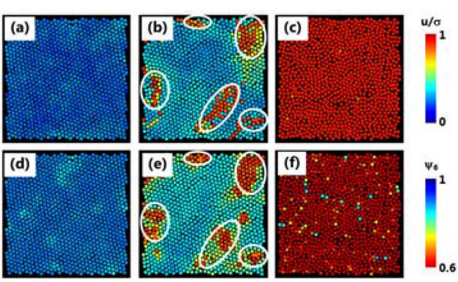
Colloidal Experiments

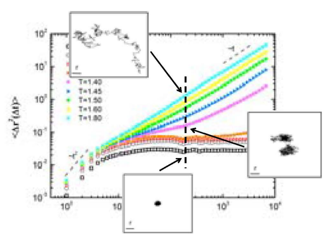
Connections between Dynamics and Local Structures

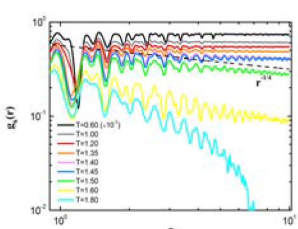


Summary

- **Glassy dynamics**: slow, caging dynamics, dynamical heterogeneity… consistent with AG picture
- **Connections:** between defects, local structures and dynamics







Future Work: Spatial Correlation and Length Scale?

S_2 Excess Entropy:

$$s_2 = -\pi k_B \rho \int_0^\infty (g(r)\ln g(r) - (g(r)-1)) r dr$$

$$C_{s_2}(r = |\vec{r}_i - \vec{r}_j|) = < s_{2i}(\vec{r}_i) s_{2j}(\vec{r}_j) >$$

Dynamics:

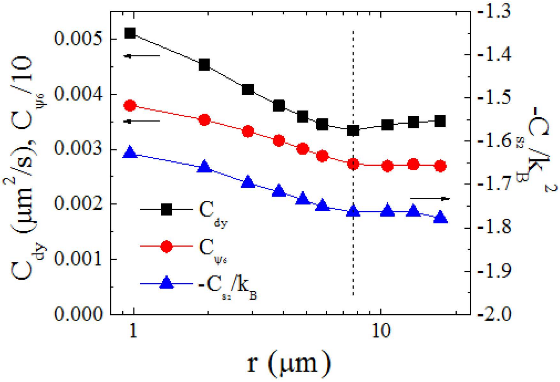
$$C_{dy}(r = |\vec{r}_i - \vec{r}_j|) = < \Delta r_i \Delta r_j > / \Delta t$$

Orientational Order:

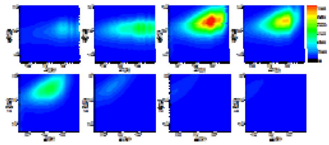
$$C_{\psi_6}(r = |\vec{r}_i - \vec{r}_j|) = < (1-\psi_{6i}(\vec{r}_i))(1-\psi_{6j}(\vec{r}_j)) >$$

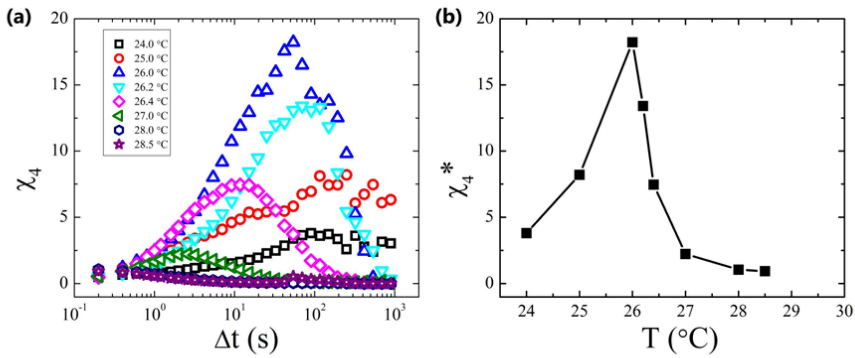
Tong et al. Phys. Rev. E (2015)
Zheng et al. Nat. Commun.(2014)
Zhang et al. Phys. Rev. Lett.(2013)

Future Work: Spatial Correlation and Length Scale?



Future Work: Dynamical Length Scale from DH?





Thank you！

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