Excitations, Emergent Facilitation and Glassy Dynamics in Supercooled Liquids

Muhammad R. Hasyim[1], Kranthi K. Mandadapu[2]

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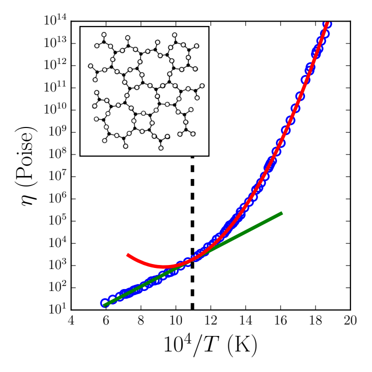

Viscosity of boron oxide (B_2O_3) (Tweer, Simmons, and Macedo, *J. Chem. Phys.*, 1970).

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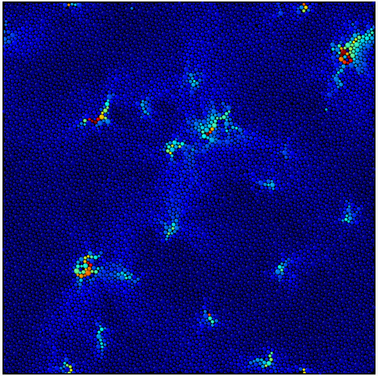

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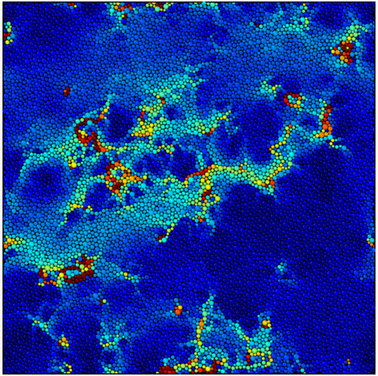

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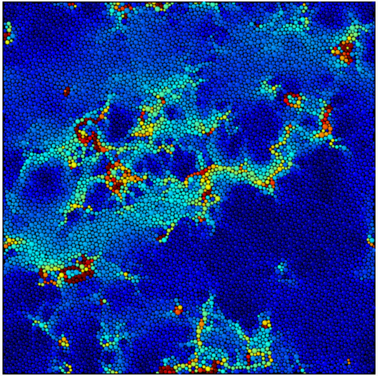

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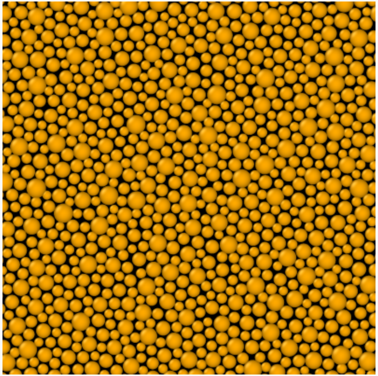
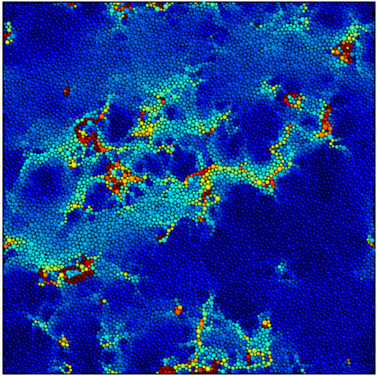


It is not obvious from the structure where the heterogeneity is coming from!

Central Question

How to understand the dramatic slowdown and dynamical heterogeneity of supercooled liquids?

Dynamics



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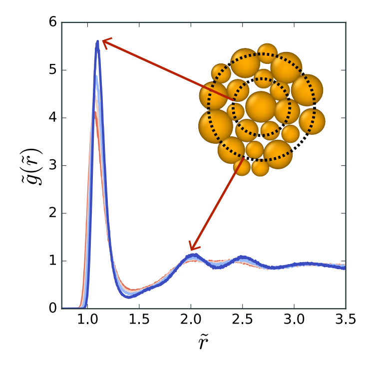

Radial distribution function (RDF). Data sweeps across **4 decades in relaxation time**.

A Dynamics-Based Perspective: Dynamical Facilitation Theory

DF theory (Chandler and Garrahan, *Annu. Rev. Phys. Chem*, 2010) can explain glassy dynamics **without knowledge of local structure** with two key ideas:

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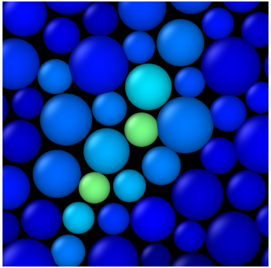

Energy Cost J_σ

Below the onset temperature T_o, localized excitations drive glassy dynamics! (Keys, et al. *Phys. Rev. X* 2011)

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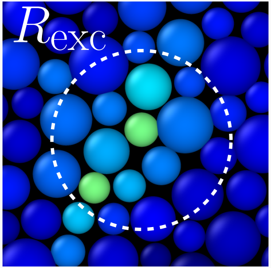

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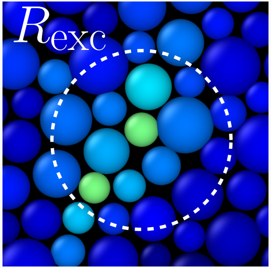

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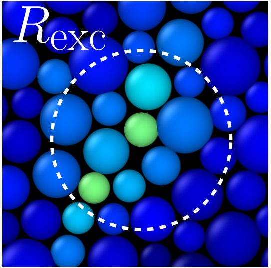

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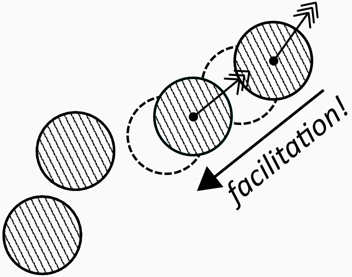

Excitations facilitate the creation and relaxation of another excitation close by.

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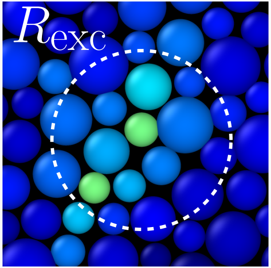

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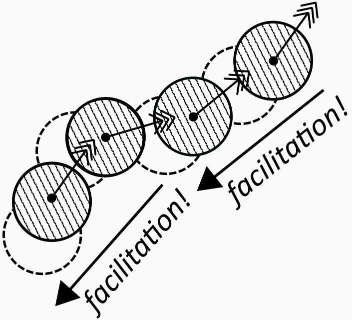

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Origin of Excitations

The inherent **structure and elasticity (solid-like)** of supercooled liquids $\leftrightarrow$ localized excitations!

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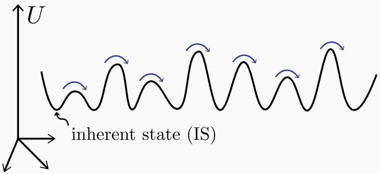

Glassy dynamics is hopping between energy minima (inherent states) (Stillinger and Weber, *Phys. Rev. A* 1982)

1. Inherent states '=' amorphous solids

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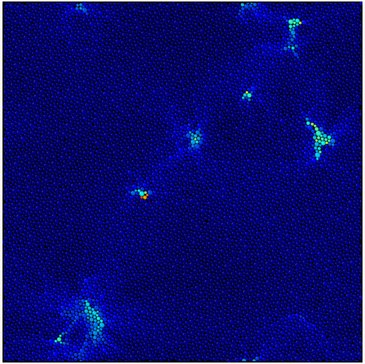

Excitations of a model glass former, detected by the initial dynamic heterogeneity.

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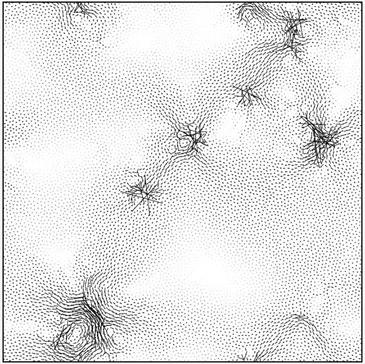

The displacement vector field due to excitations in the liquid.

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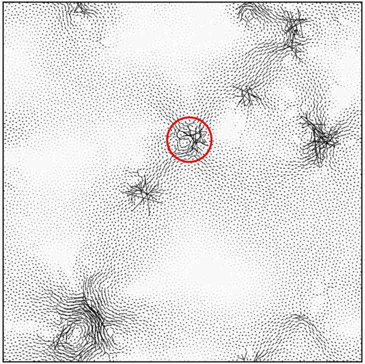

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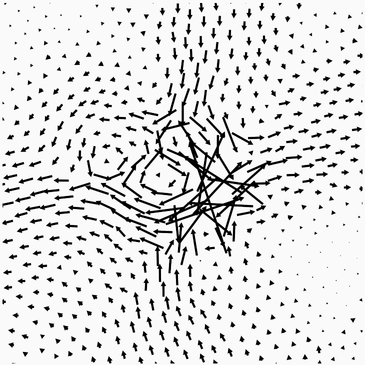

An excitation reorganizes the surrounding solid medium.

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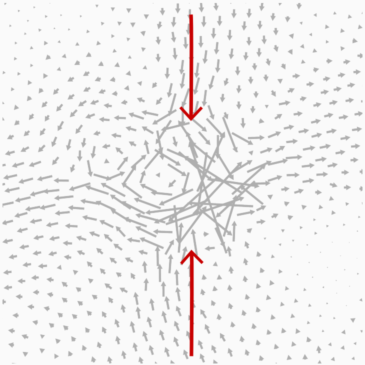

In one axis, there's compressive flow.

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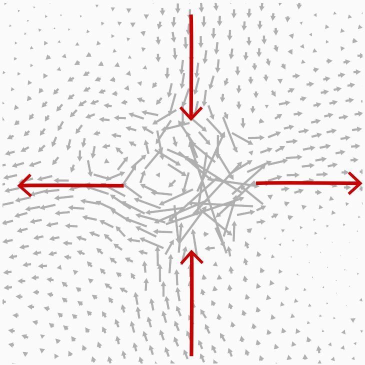

In another axis, there's extensile flow.

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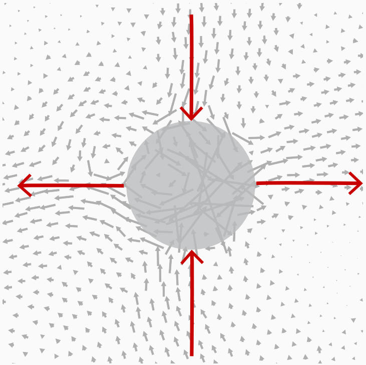

Compressive + extensile flow = **a pure shear deformation** (Lemaitre, *PRL* 2014).

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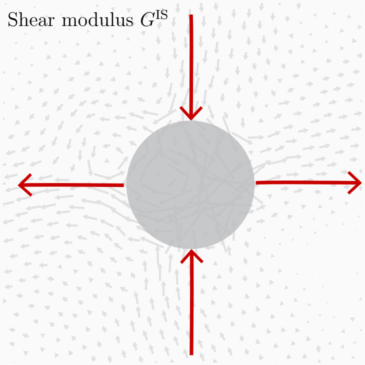

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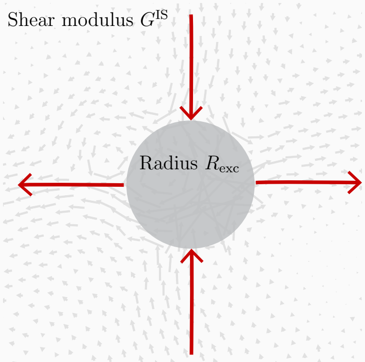

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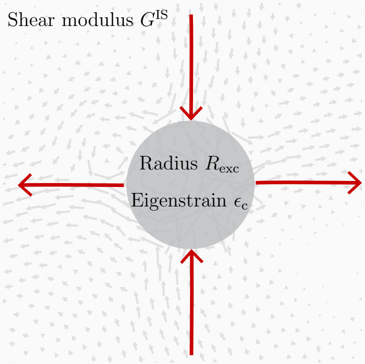

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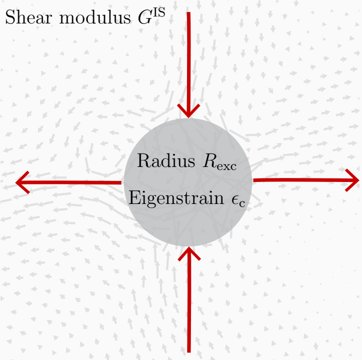

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2. The linear theory of elasticity:

Excitation Energy Cost J_σ

$$\Delta F^{\ddagger}(T) = G^{\mathrm{IS}}(T)\left(\pi R_{\mathrm{exc}}^2\right)\epsilon_c^2 \quad \text{(in 2D)}$$

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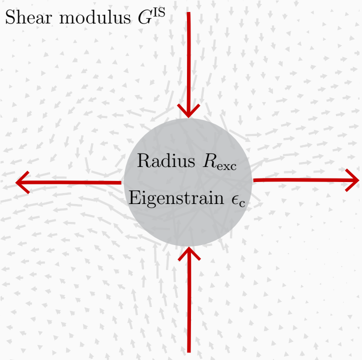

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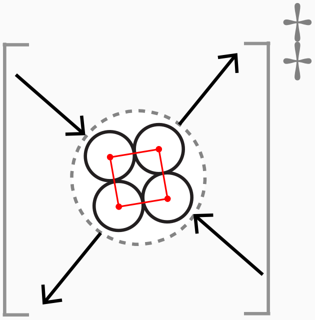

A structural motif underlie the localized pure shear, e.g., T1 transition in 2D.

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4. Compute R_{exc} and ϵ_c from structural info, e.g., the radial distribution function.

A Theory of Localized Excitations: Numerical Results

Glass Former	Measured[‡] J_σ	Predicted[†] J_σ
Poly-(12,0), ($\varepsilon = 0.2$)	1.710(2)	1.77(2)
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Poly-(18,0), ($\varepsilon = 0.0$)	6.69(1)	10.2(6)
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Poly-(10,6), ($\varepsilon = 0.1$)	1.365(2)	1.56(3)
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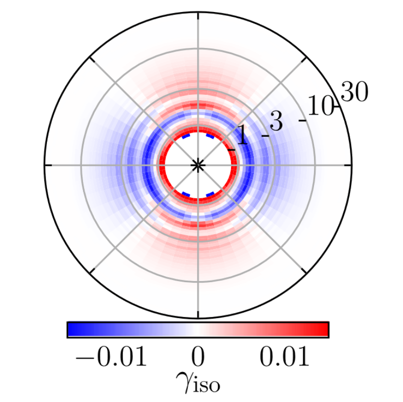

Strain profile from MD simulations (Chacko, et. al. *Phys. Rev. Lett.* 2021)

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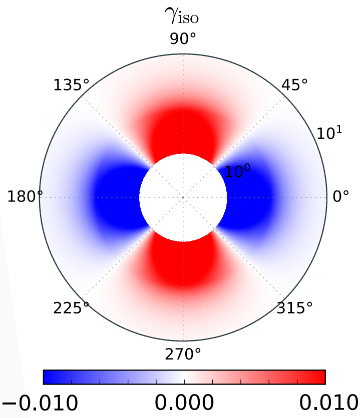
- Strain profile also matches qualitatively with those observed in literature.



From linear theory of elasticity

A Theory of Onset Temperature in 2D

Inherent–State Melting and the Onset of Glassy Dynamics in Two-Dimensional Supercooled Liquids

Dimitrios Fraggedakis,[1,*] Muhammad R. Hasyim,[1,‡] and Kranthi K. Mandadapu[1,2,†]

[1] *Department of Chemical & Biomolecular Engineering, University of California, Berkeley, CA 94720*
[2] *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720*

(Dated: April 18, 2022)

Below the onset temperature T_o, the equilibrium relaxation time of most glass-forming liquids exhibits glassy dynamics characterized by super-Arrhenius temperature dependence. In this supercooled regime, the relaxation dynamics also proceeds through localized elastic excitations corresponding to hopping events between inherent states, i.e., potential-energy minimizing configurations of the liquid. Despite its importance in distinguishing the supercooled regime from the high-temperature regime, the microscopic origin of T_o is not yet known. Here, we construct a theory for the onset temperature in two dimensions and find that inherent-state melting transition, described by the binding-unbinding transition of dipolar elastic excitations, delineates the supercooled regime from the high-temperature regime. The corresponding melting transition temperature is in good agreement with the onset temperature found in various two-dimensional atomistic models of glass formers. We discuss the predictions of our theory on the displacement and density correlations of two-dimensional supercooled liquids, which are consistent with observations of the Mermin-Wagner fluctuations in recent experiments and molecular simulations.

Keywords: Two-dimensional glassy dynamics, Kosterlitz-Thouless transition, excitations, geometric charges

D. Fraggedakis, M.R. Hasyim, K.K. Mandadapu, *PNAS* 120 (14) e2209144120 (2023)

A Theory of Dynamical Facilitation: The Role of Revertibility

$\beta J_\sigma = 1$ (High-T)

Origin of Glassy Behavior
A combination of **emergent constraints** and **revertibility** of dynamics.

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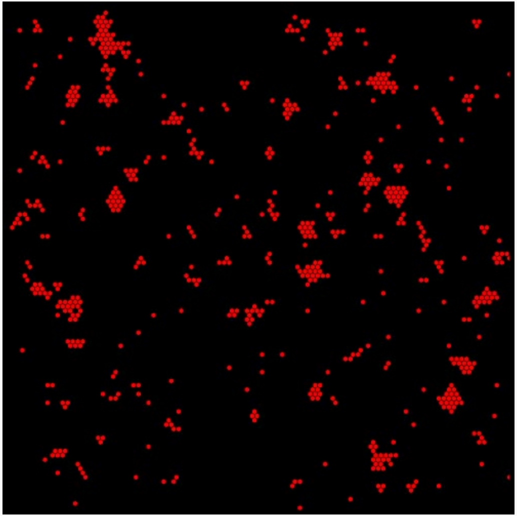

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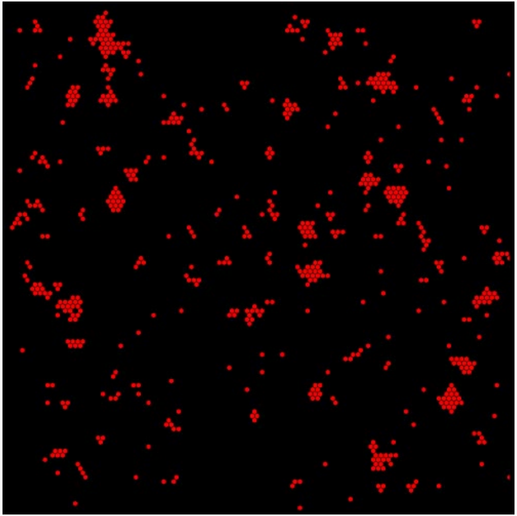

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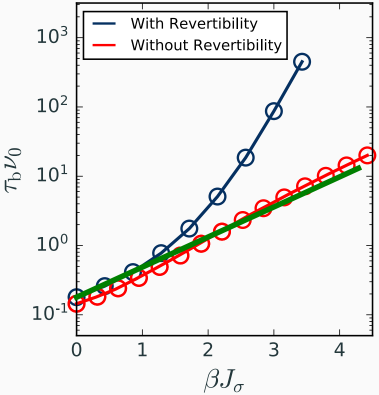

Relaxation time data when revertibility is turned off (red markers) along with an Arrhenius timescale $\tau_{\mathrm{arr}} \sim e^{\beta J_\sigma}$.

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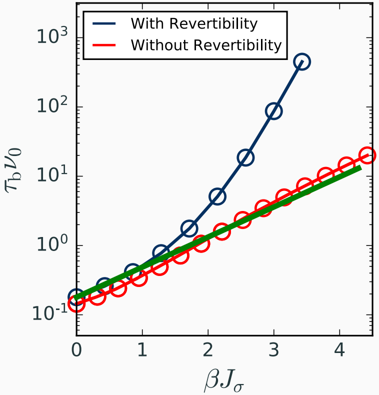
A Theory of Dynamical Facilitation: The Role of Revertibility

$\beta J_\sigma = 1$ (High-T)



Relaxation time data when revertibility is turned off (red markers) along with an Arrhenius timescale $\tau_{\text{arr}} \sim e^{\beta J_\sigma}$.

Origin of Glassy Behavior

A combination of **emergent constraints** and **revertibility** of dynamics.

1. **Emergent Constraints:** Dynamics only persist in a few spots of the liquid.
2. **Revertibility:** Within an active region, excitations can go back and forth, wasting time in the process.

No revertibility, no super-Arrhenius behavior.