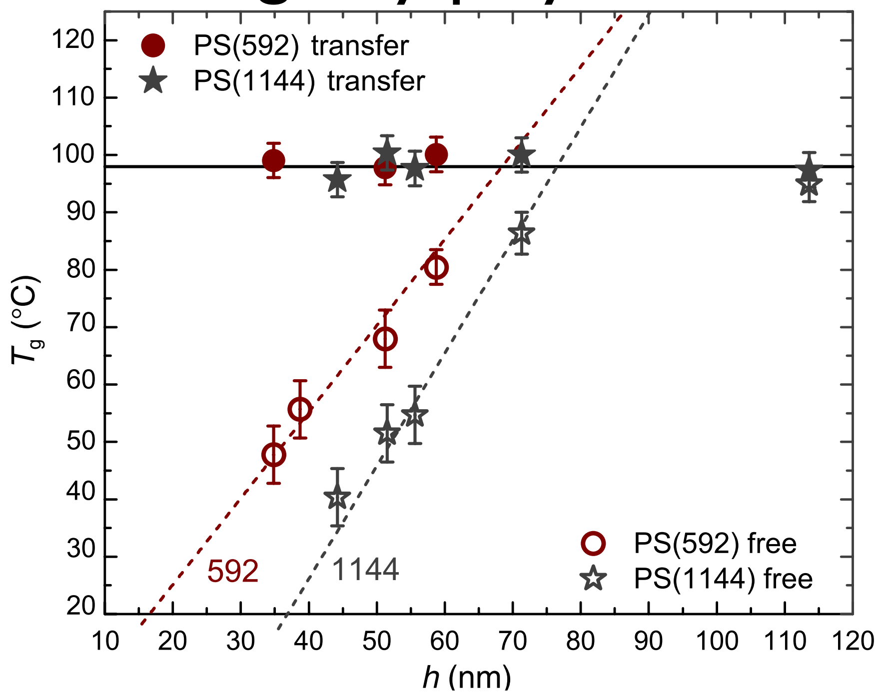
Structural Signatures of Mobility in Jammed and Glassy Systems

Andrea J. Liu
Department of Physics & Astronomy
University of Pennsylvania

Lisa Manning	Syracuse
Sam Schoenholz	UPenn
Ekin Dogus Cubuk	Harvard
Brad Malone	Harvard
Tim Kaxiras	Harvard
Joerg Rottler	U British Columbia
Rob Riggleman	UPenn
Jennifer Rieser	UPenn
Doug Durian	UPenn
Daniel Sussman	UPenn
Carl Goodrich	UPenn
Sid Nagel	UChicago

Free Surfaces

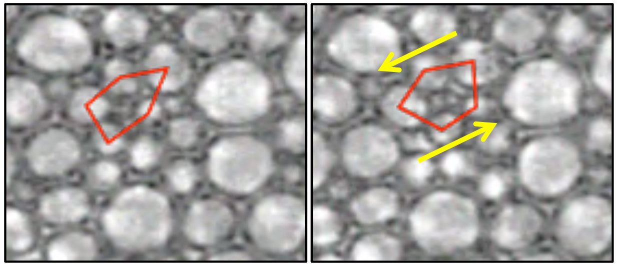
thin glassy polymer films



- experiments see thin mobile layer of about 5-10 particle diameters
- no structural quantity has been identified with gradients on this length scale

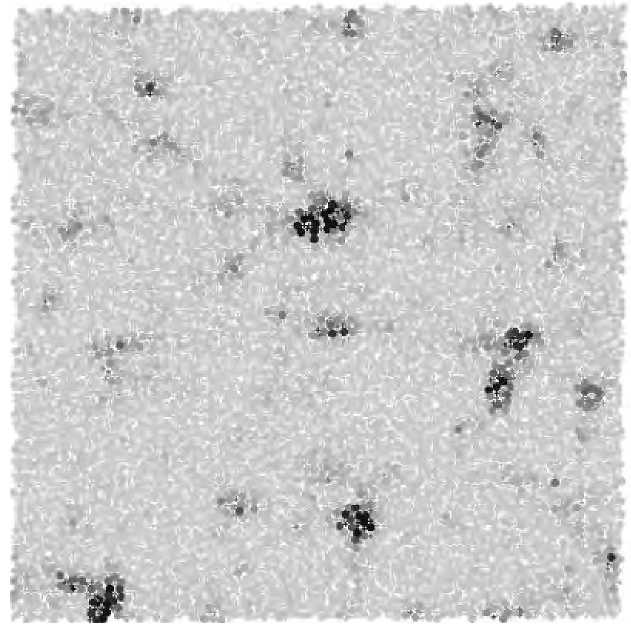
Courtesy of O. Baumchen et al. PRL (2012)

Localized Rearrangements in Disordered Solids



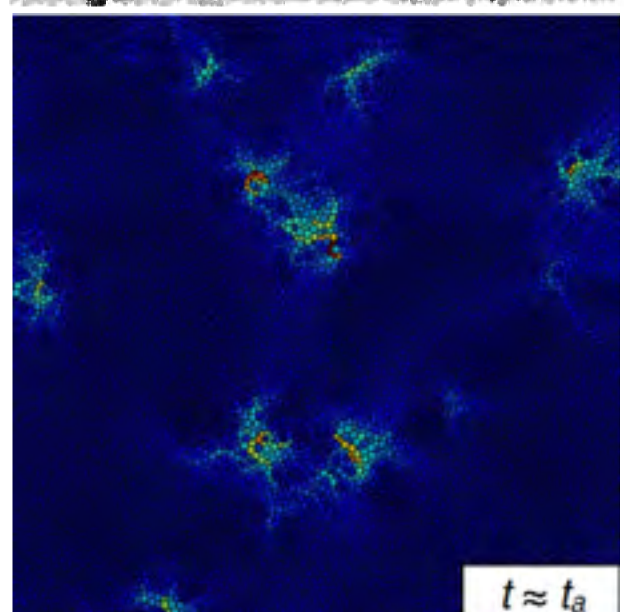
shaving cream

Courtesy of DJ Durian



2D binary Lennard-Jones

sheared glass



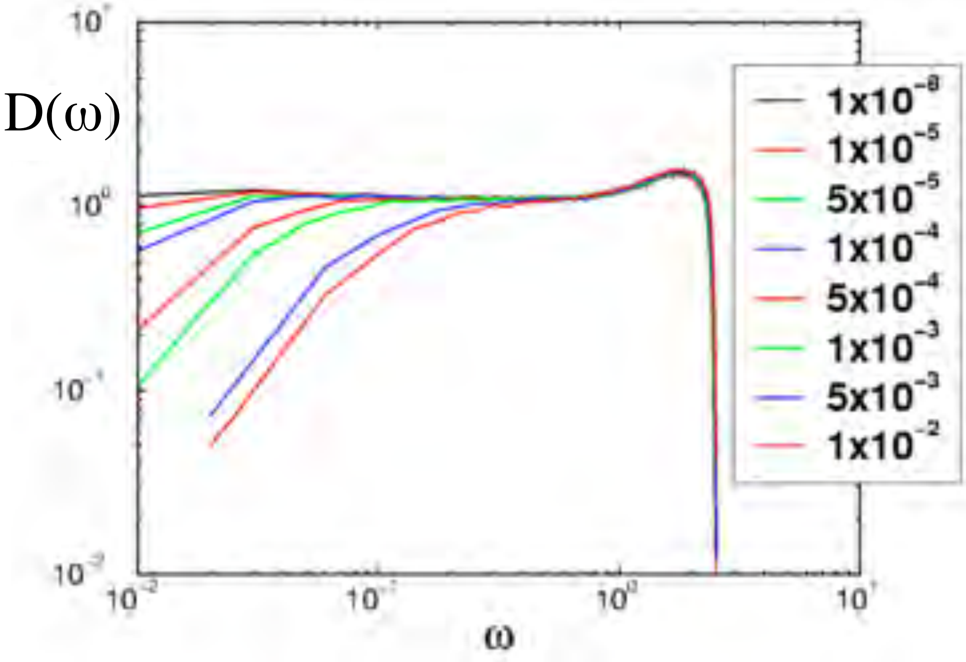
supercooled liquid

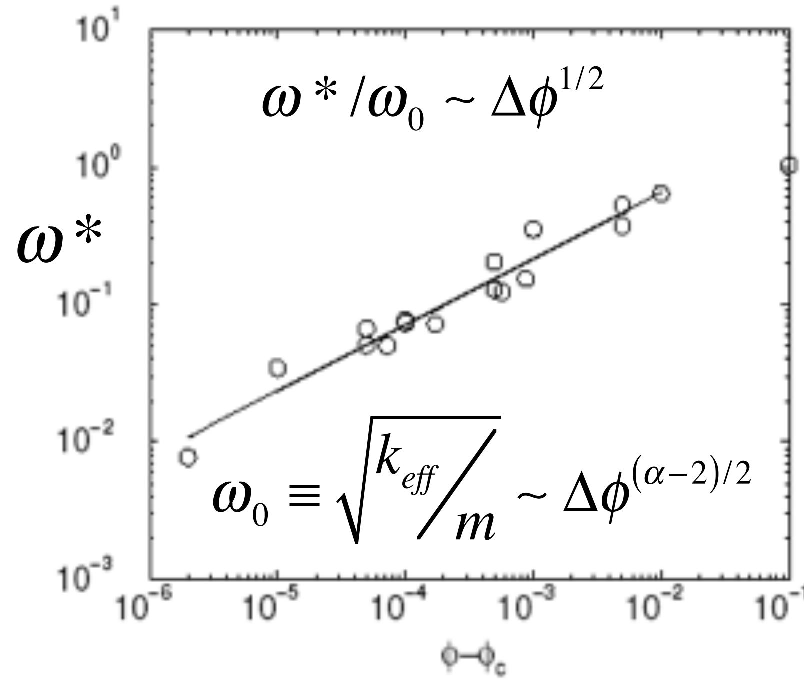
Keys, et al PRX (2011)

- Aim: identify population of "flow defects," analogous to dislocations in crystals, where rearrangements are likely to occur
- Standard structural quantities fail to predict these

Starting Point: Vibrations in Sphere Packings

L. E. Silbert, A. J. Liu, S. R. Nagel, PRL **95**, 098301 ('05)





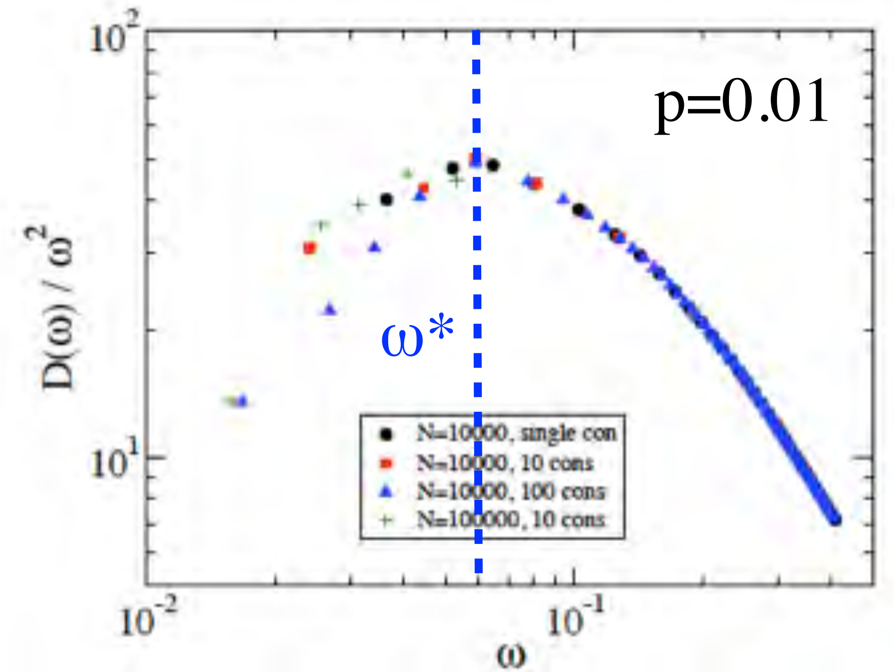
- New class of excitations originates from soft modes at Point J

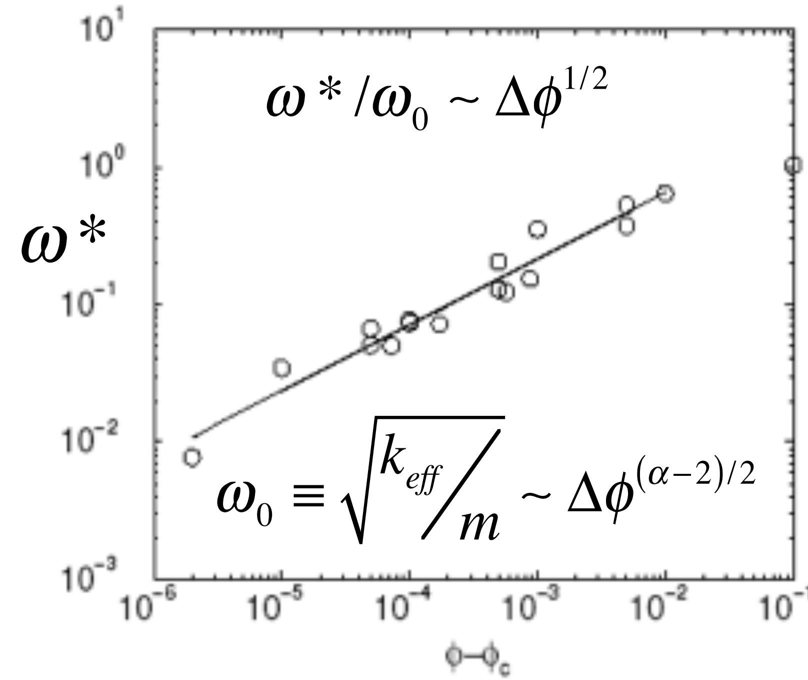
  M. Wyart, S.R. Nagel, T.A. Witten, EPL **72**, 486 (05)

- Related to diverging length scales $\ell_L \simeq c_L/\omega^*$ $\ell_T \simeq c_T/\omega^*$

Starting Point: Vibrations in Sphere Packings

L. E. Silbert, A. J. Liu, S. R. Nagel, PRL **95**, 098301 ('05)





- New class of excitations originates from soft modes at Point J

  M. Wyart, S.R. Nagel, T.A. Witten, EPL **72**, 486 (05)

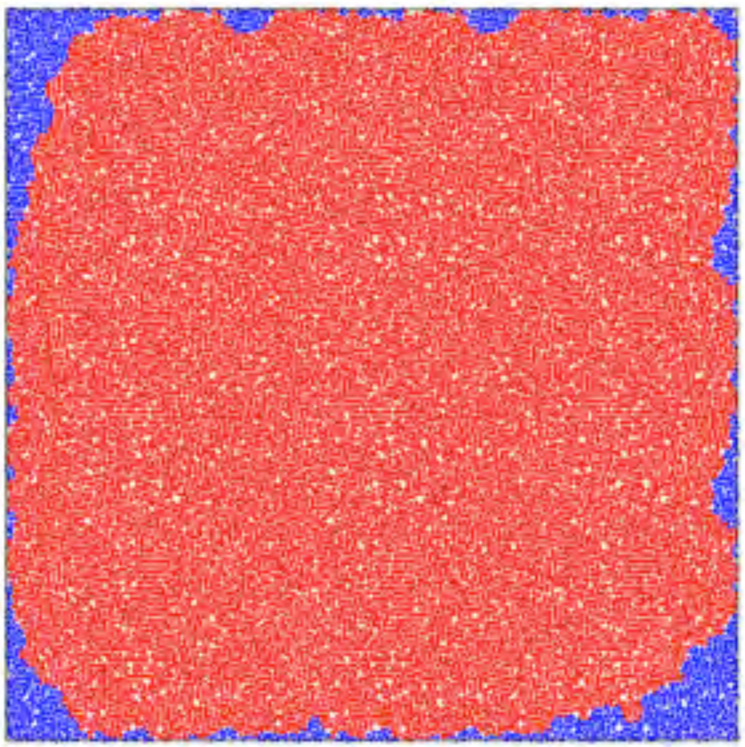
- Related to diverging length scales $\ell_L \simeq c_L/\omega^*$
  $\ell_T \simeq c_T/\omega^*$

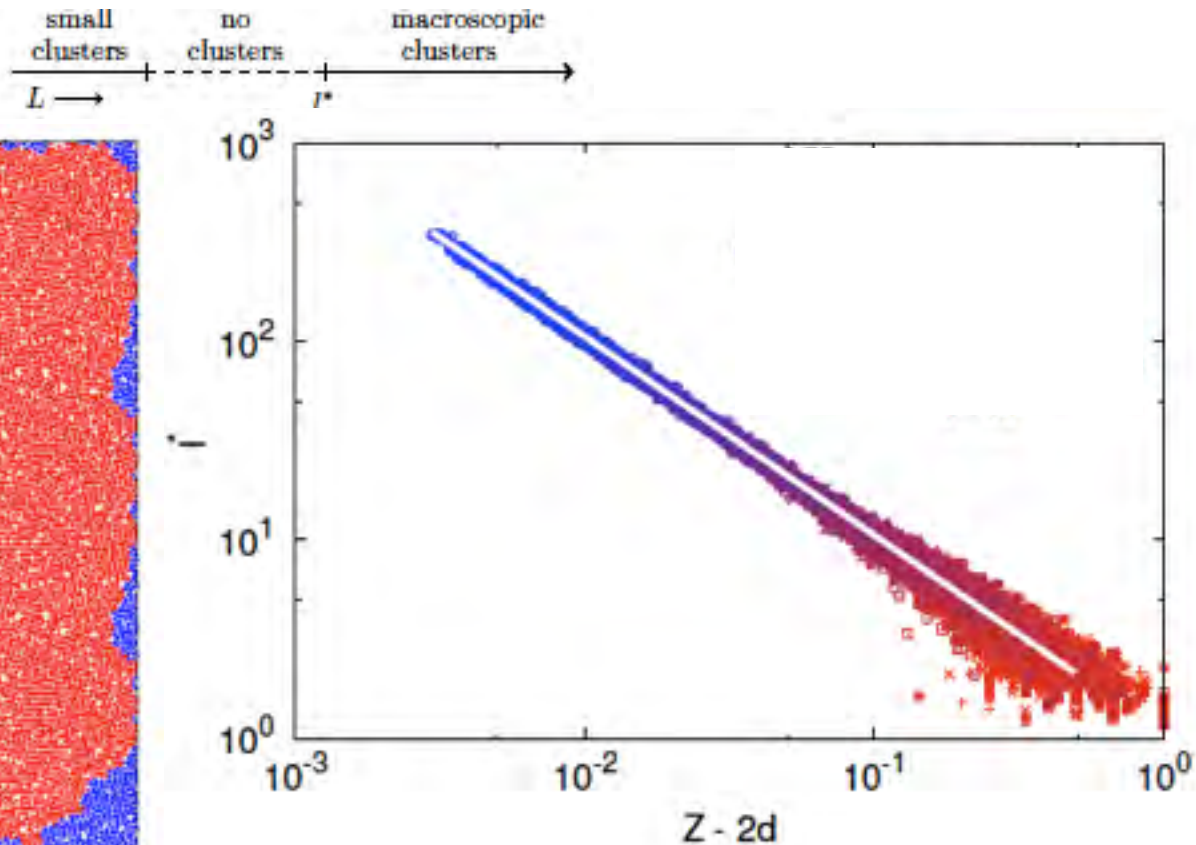
Stability to Boundary Cutting: ℓ_L

M. Wyart, S.R. Nagel, T.A. Witten, EPL **72**, 486 (05)

Size of smallest macroscopic rigid cluster for system with a free boundary of any shape or size

Goodrich, Ellenbroek, Liu Soft Matter (2013)





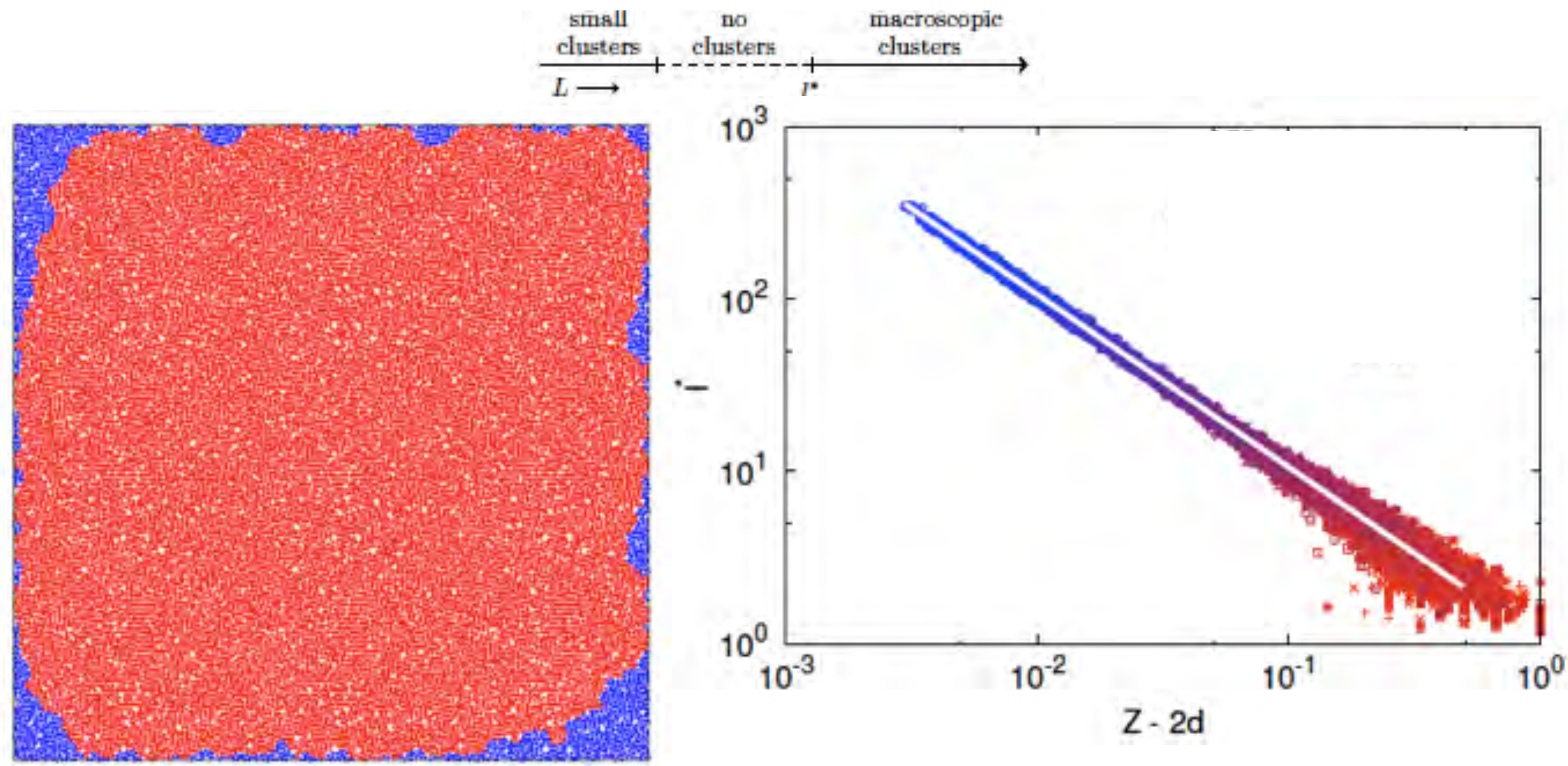
- ℓ_L diverges at Point J as expected from scaling argument

Stability to Boundary Cutting: ℓ_L

M. Wyart, S.R. Nagel, T.A. Witten, EPL **72**, 486 (05)

Size of smallest macroscopic rigid cluster for system with a free boundary of any shape or size

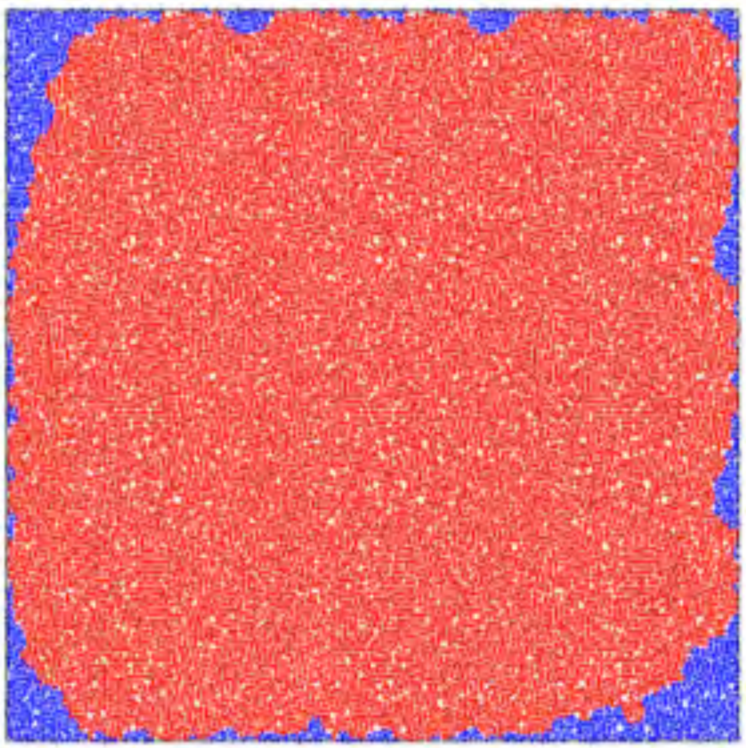
Goodrich, Ellenbroek, Liu Soft Matter (2013)

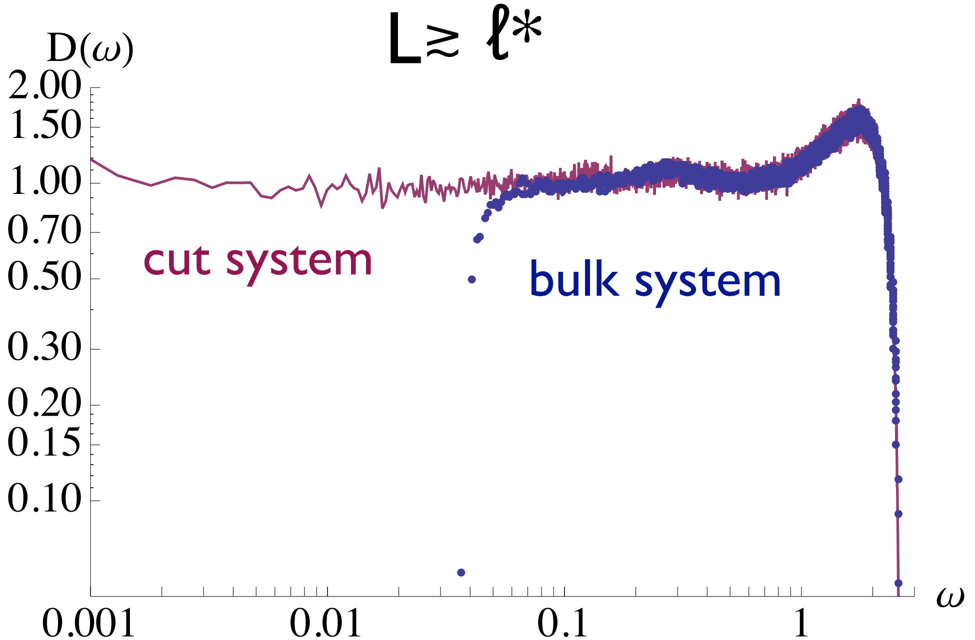


- ℓ_L diverges at Point J as expected from scaling argument

Free Surfaces

Goodrich, Liu, Nagel, Soft Matter (2013)



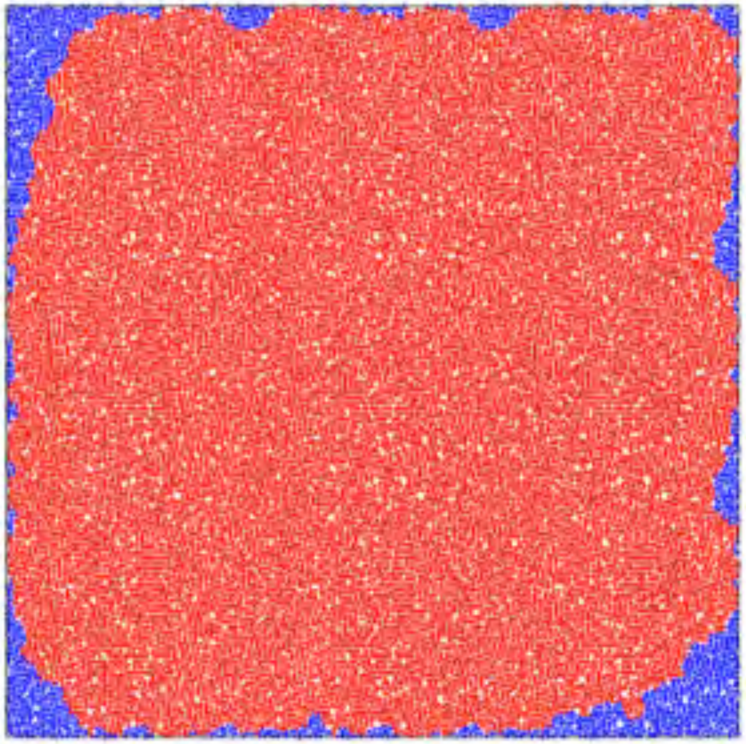


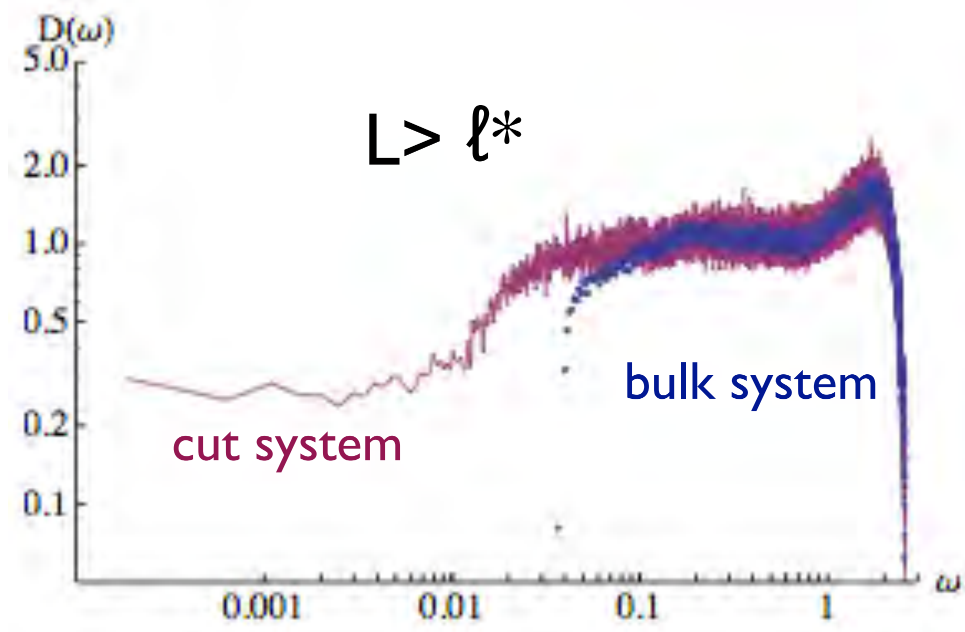
Daniel Sussman, Carl Goodrich

- There are zero frequency modes localized to the surface to within particle diameter
- There are also extra low frequency modes in excess of surface plane wave modes (Rayleigh waves, etc)

Free Surfaces

Goodrich, Liu, Nagel, Soft Matter (2013)

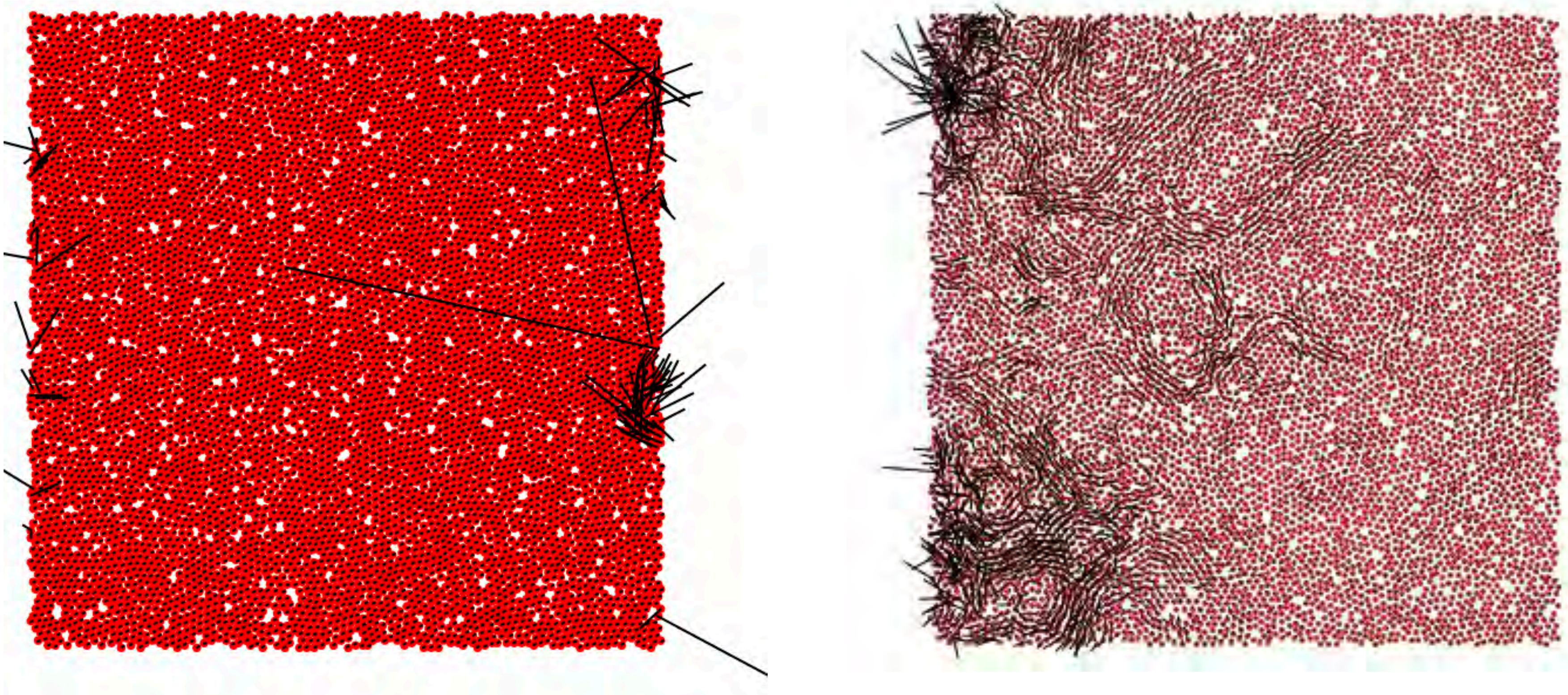




Daniel Sussman, Carl Goodrich

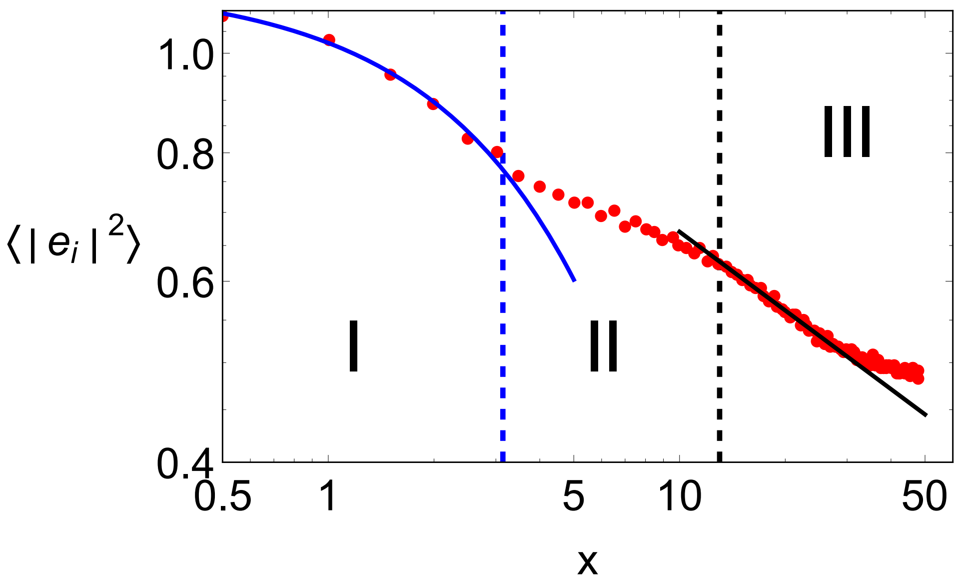
- There are zero frequency modes localized to the surface to within particle diameter
- There are also extra low frequency modes in excess of surface plane wave modes (Rayleigh waves, etc)

Low-Frequency Surface Modes are Localized to Surface



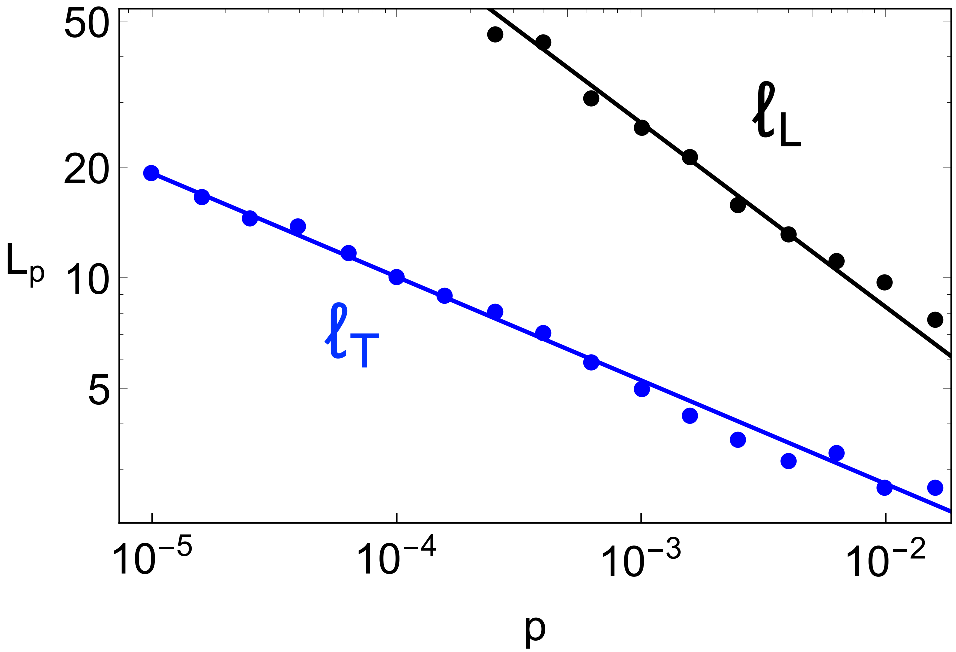
- Measure polarization vector magnitude vs distance from surface

Penetration Depth of Surface Localized Modes



- Three regimes for decay of polarization vector magnitude
- Regime I consistent with exponential decay
- Regime III independent of pressure
- Extract crossover lengths separating Regimes I & II and II&III

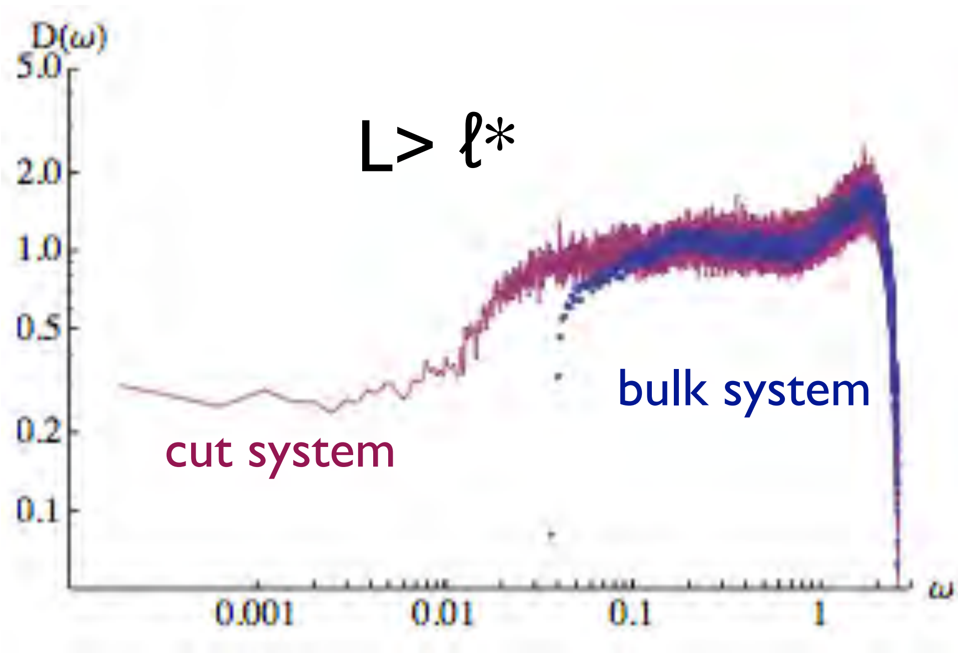
Penetration Depth of Surface Localized Modes

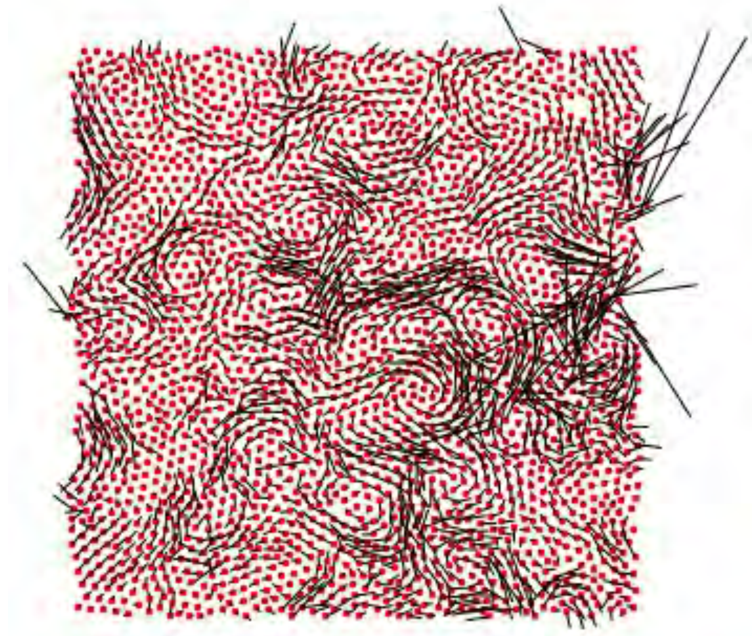


- Regime I/II crossover scales as ℓ_T which diverges at jamming transition as $p^{-1/4}$
- Regime II/III crossover scales as ℓ_L which diverges at jamming transition as $p^{-1/2}$
- Consistent with response to local bond perturbations (Lerner, During, Wyart, Soft Matter (2014))

Low frequency surface modes penetrate into system much further than particle diameter. Can this explain glassy thin films?

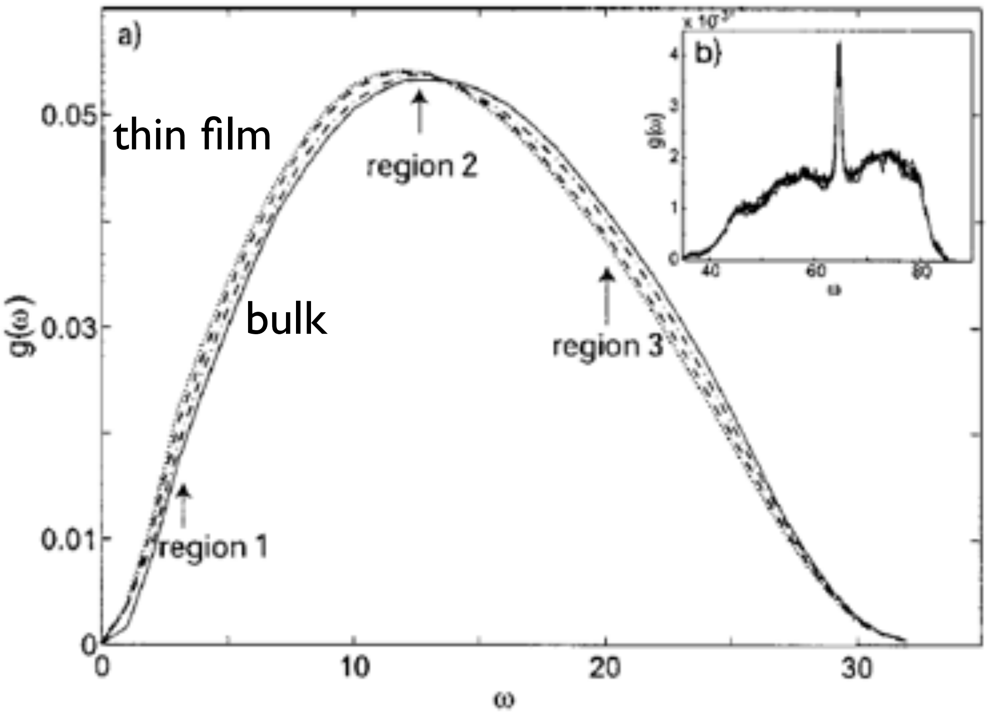
Problem:



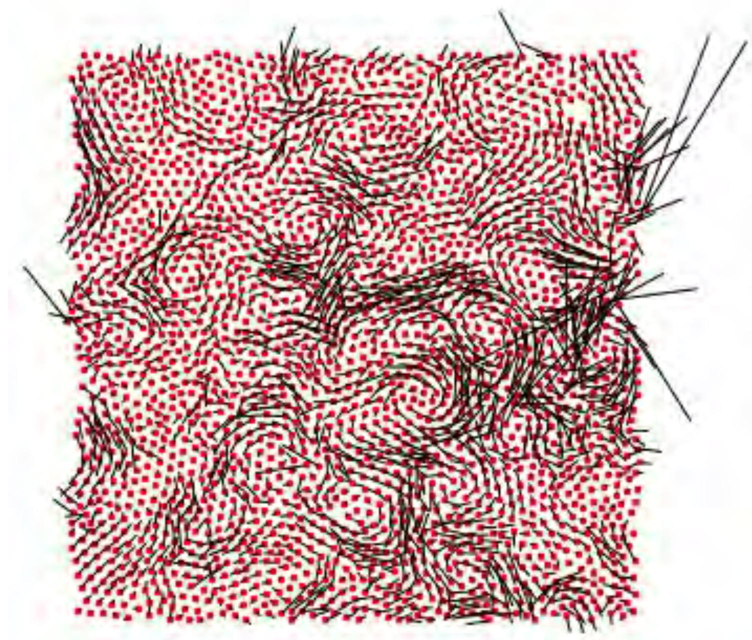


- In polymer thin films (or Lennard-Jones glasses), the surface localized modes lie in the same frequency range as the bulk modes so no clean separation of surface from bulk modes
- But low frequency modes still show high polarization near surface

Problem:

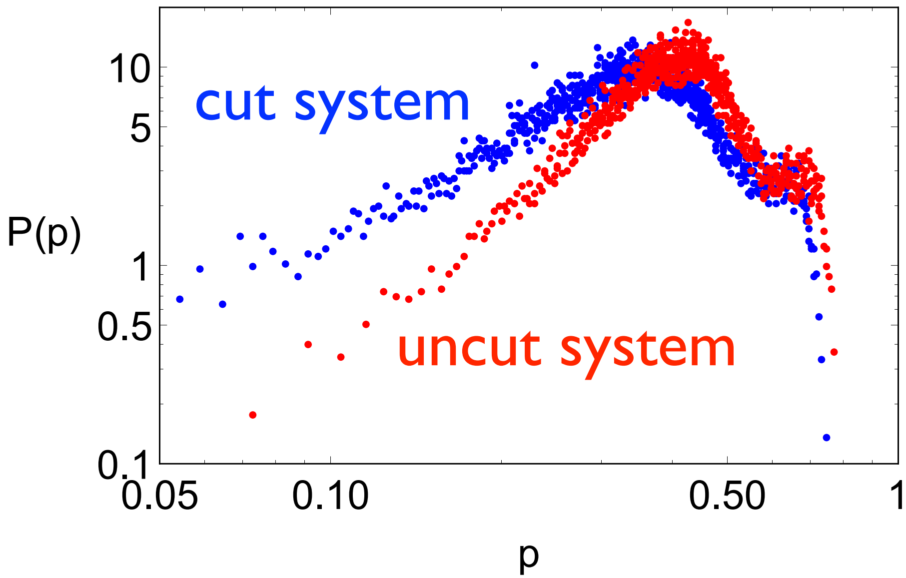


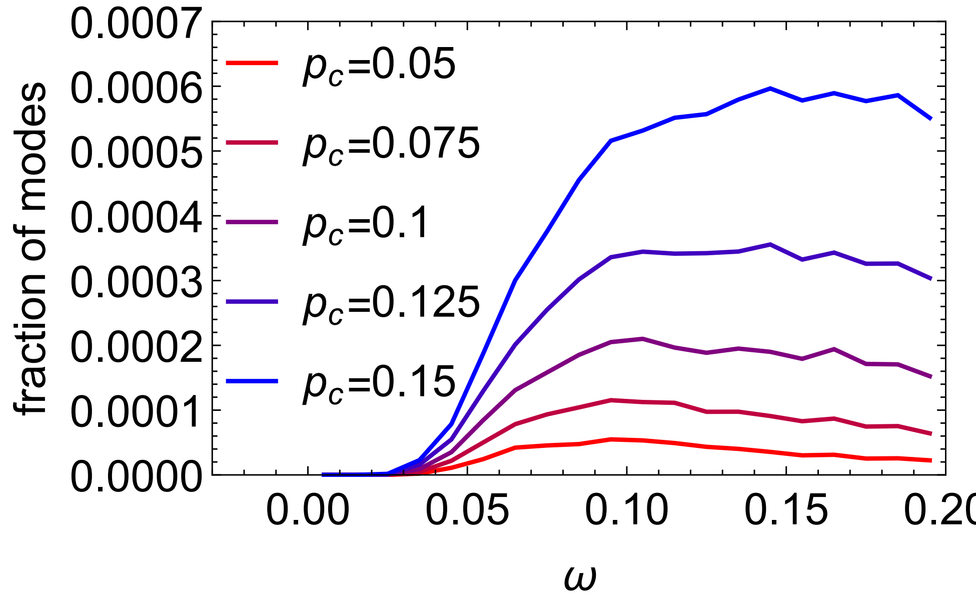
Jain and de Pablo, J Chem Phys (2004)



- In polymer thin films (or Lennard-Jones glasses), the surface localized modes lie in the same frequency range as the bulk modes so no clean separation of surface from bulk modes
- But low frequency modes still show high polarization near surface

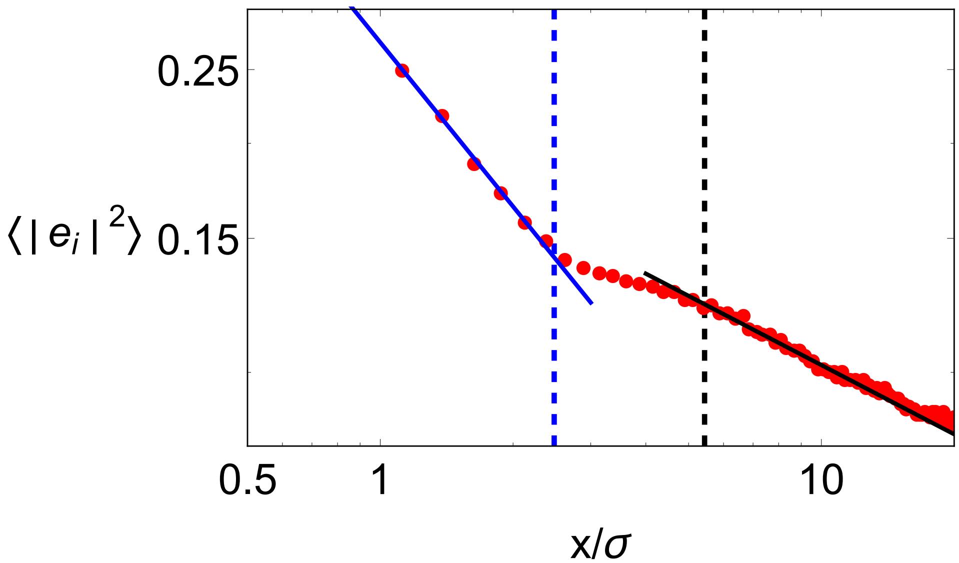
Focus on low-participation-ratio modes near ω*





- Cut system has more low participation-ratio modes than uncut system
- Low participation ratio modes most prevalent near ω*
- So look at these modes

Polarization Profile in Lennard-Jones Glass

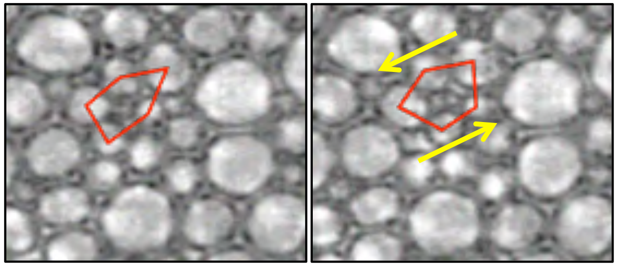


- Regime III has same form as for harmonically-repulsive spheres
- Regime I/II crossover consistent with $\ell_T \simeq c_T/\omega^*$
- Regime II/III crossover consistent with $\ell_L \simeq c_L/\omega^*$

- Polarization vector magnitude decays on scale of 5-10 particle diameters
- Consistent with observed thickness of mobile layer in thin glassy films
- High amplitude regions of low-frequency quasi localized modes are structural signature of mobile surface layer

D. Sussman, C. P. Goodrich, A. J. Liu, S. R. Nagel

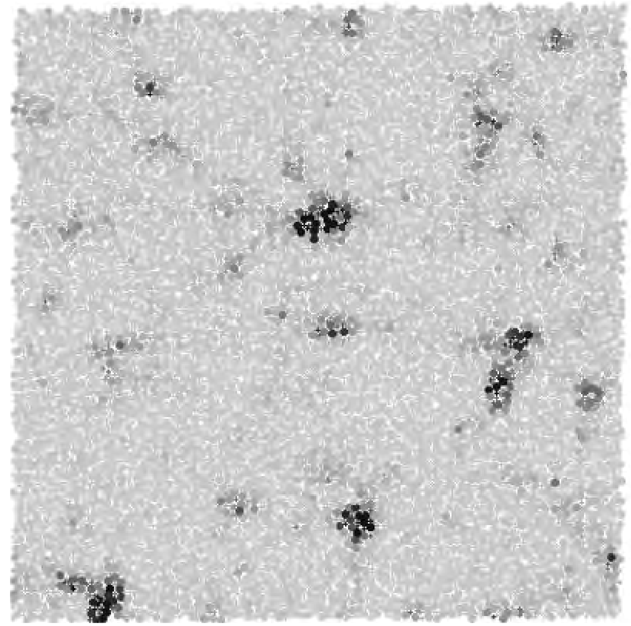
Localized Rearrangements in Glasses and Supercooled Liquids



shaving cream

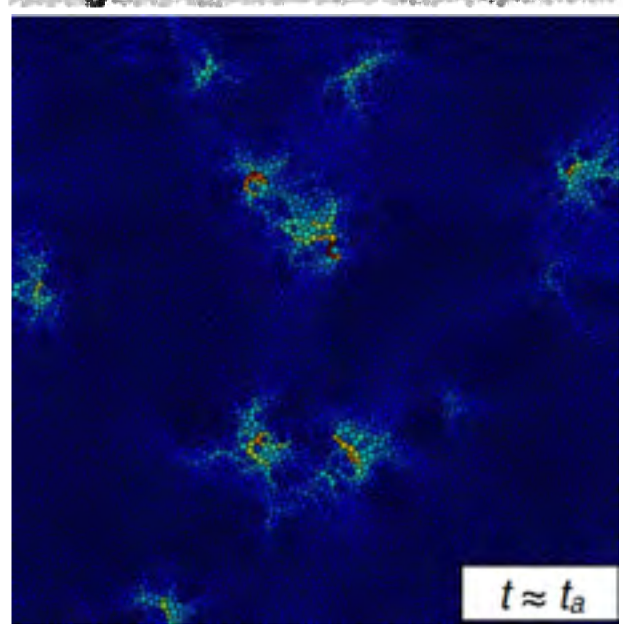
Courtesy of DJ Durian

- Aim: identify population of "flow defects," analogous to dislocations in crystals, where rearrangements are likely to occur
- Standard structural quantities fail to predict these



2D binary Lennard-Jones

sheared glass

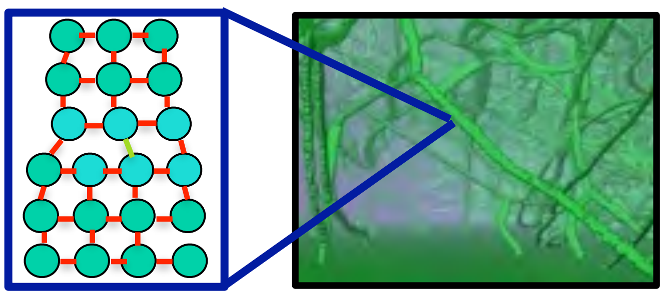


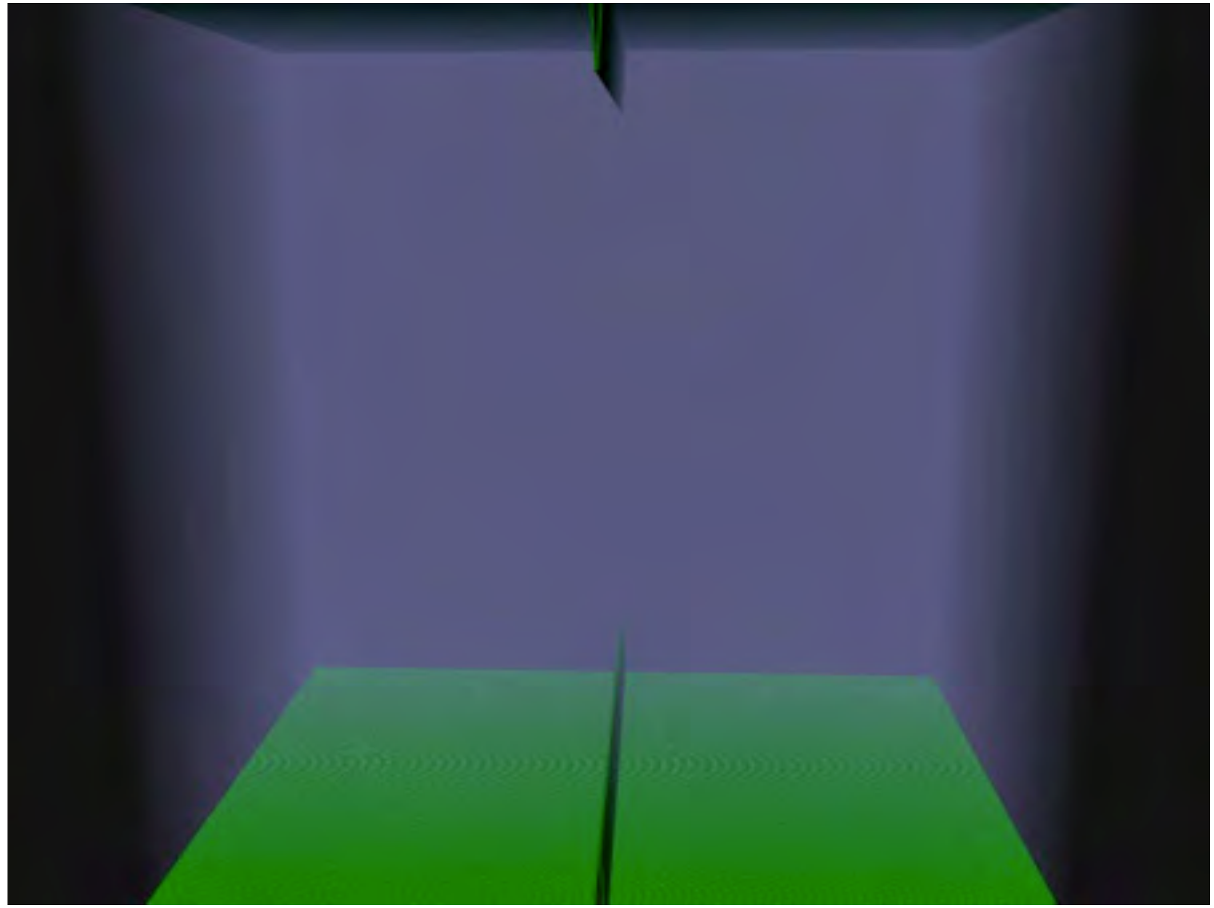
supercooled liquid

Keys, et al PRX (2011)

How Crystals Flow

In crystalline packings, localized rearrangements occur at dislocations

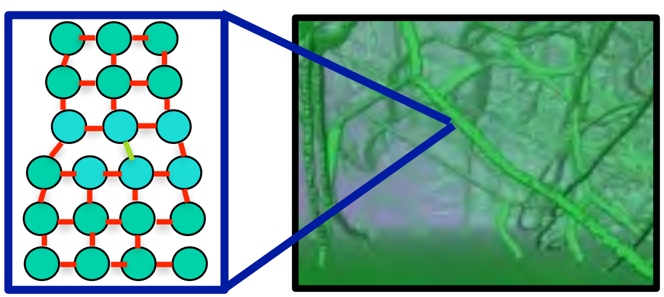


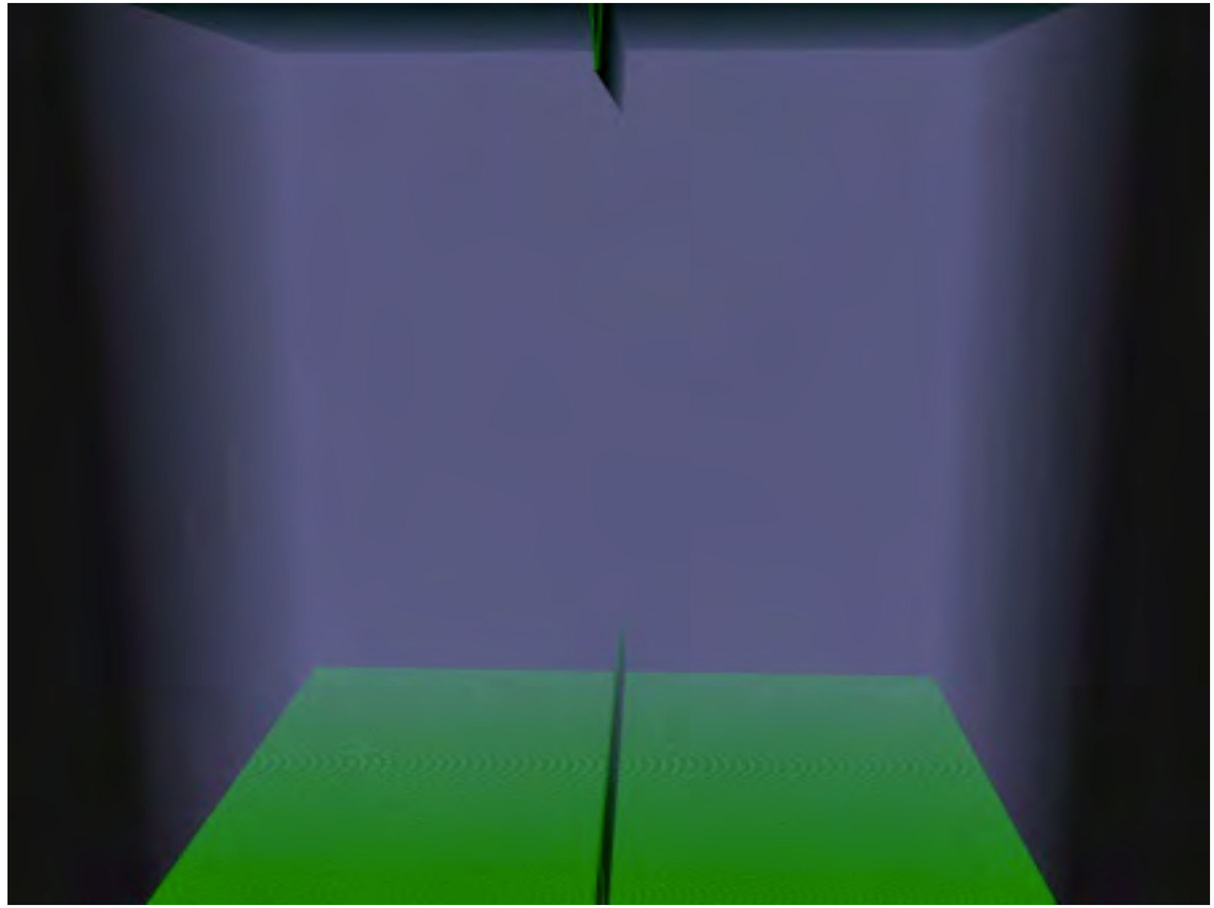


Courtesy of F Abraham

How Crystals Flow

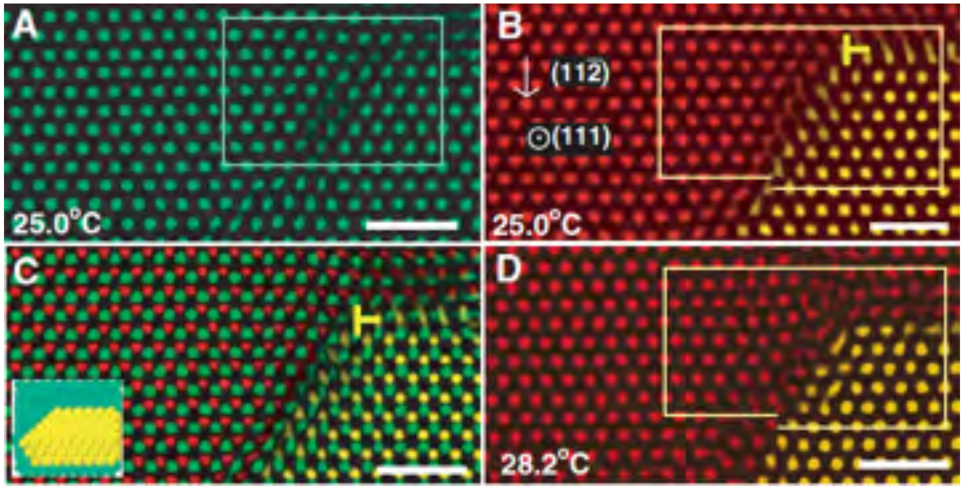
In crystalline packings, localized rearrangements occur at dislocations



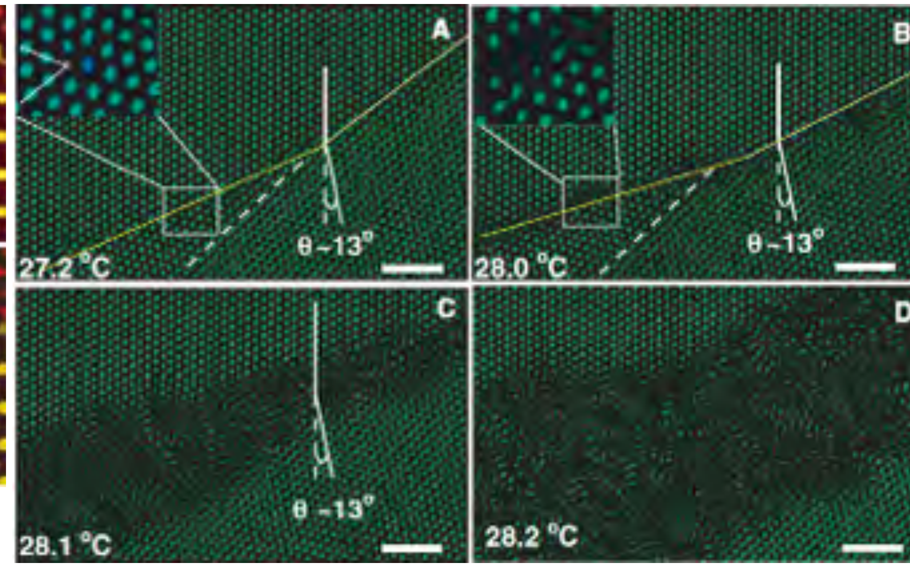


Courtesy of F Abraham

How Crystals Pre-Melt



Alsayed et al. Science (2005).

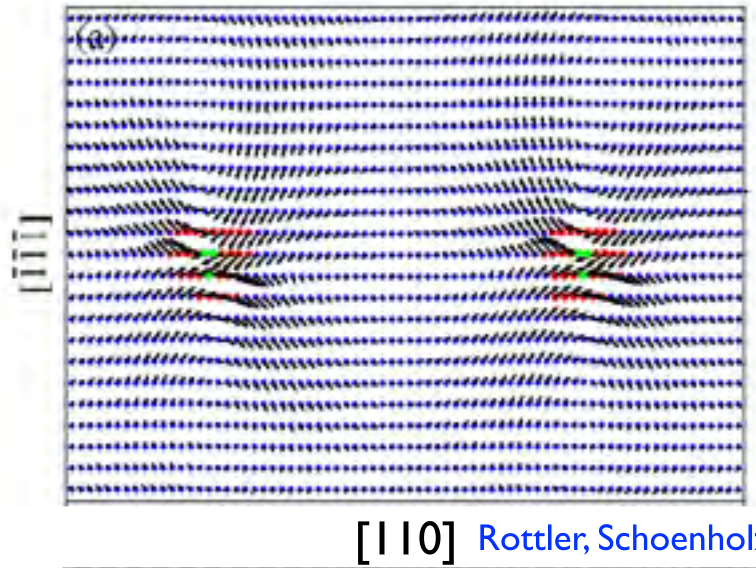


- Premelting also occurs at dislocations and grain boundaries
- Dislocations vulnerable to rearrangement under mechanical load or temperature

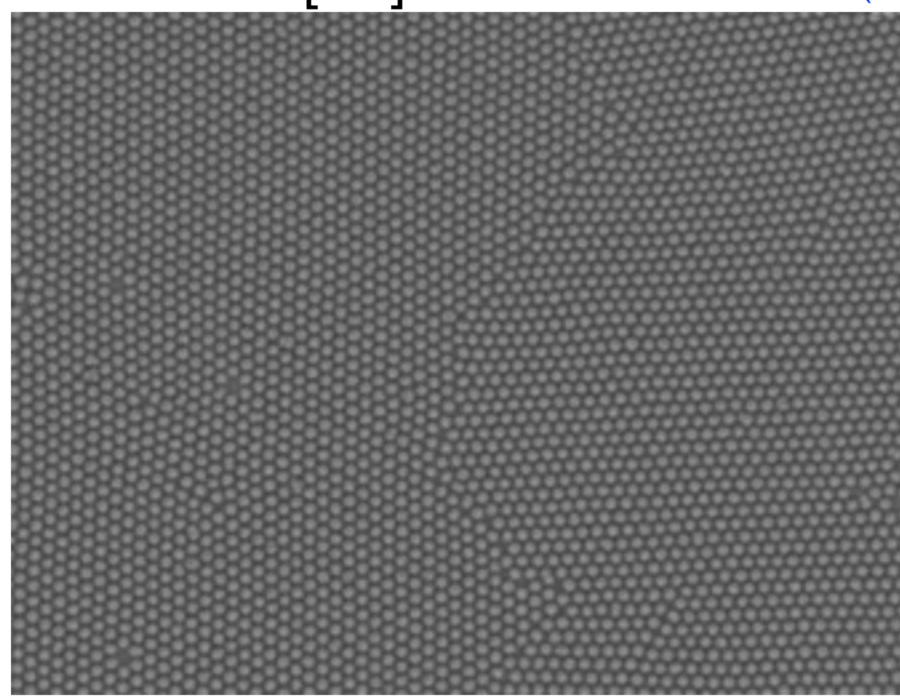
Look at Quasilocalized Modes in Crystals

- Quasilocalized modes localize to flow defects (dislocations and grain boundaries but not vacancies) because these scatter sound most effectively

- look at quasi localized modes in disordered systems



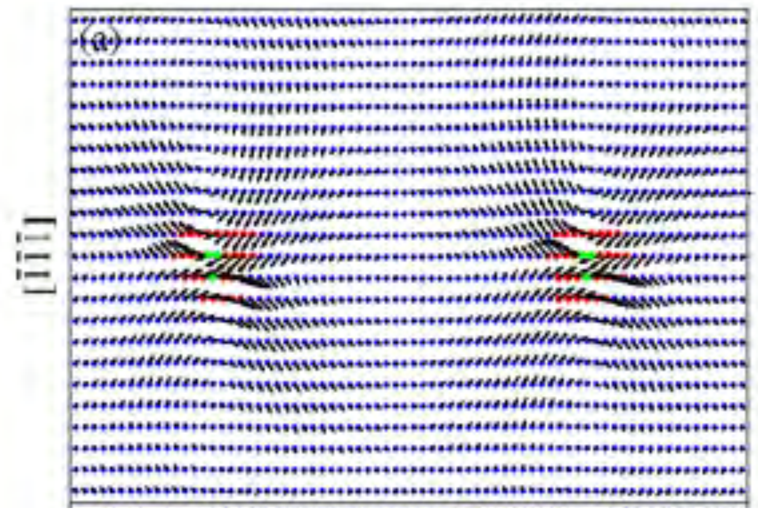
Rottler, Schoenholz, Liu PRE (2014)



Chen, Still, Schoenholz, Aptowicz, Schindler, Maggs, Liu, Yodh, PRE 88, 022315 (2013)

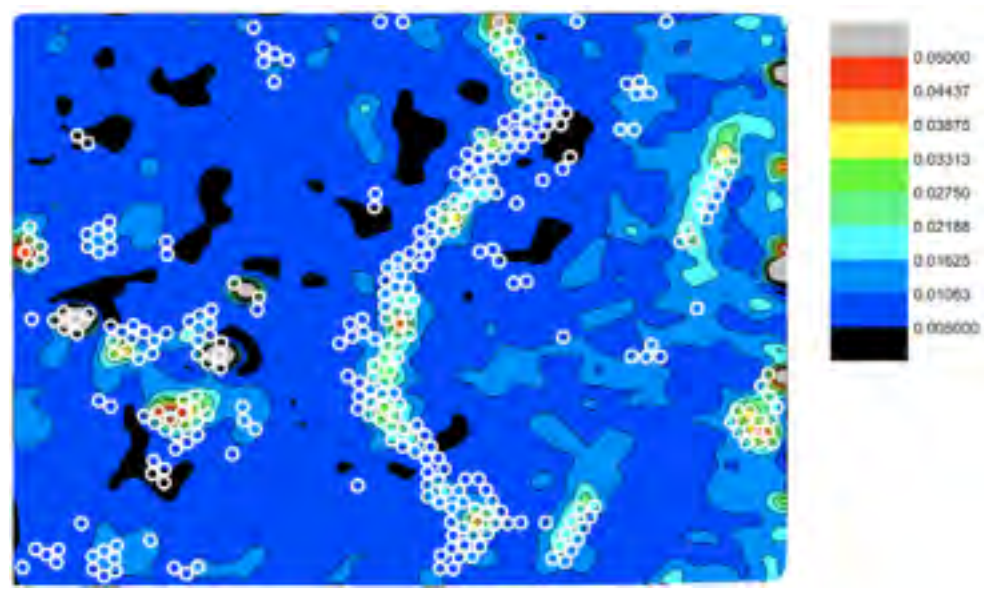
Look at Quasilocalized Modes in Crystals

- Quasilocalized modes localize to flow defects (dislocations and grain boundaries but not vacancies) because these scatter sound most effectively



[110] Rottler, Schoenholz, Liu PRE (2014)

- look at quasi localized modes in disordered systems

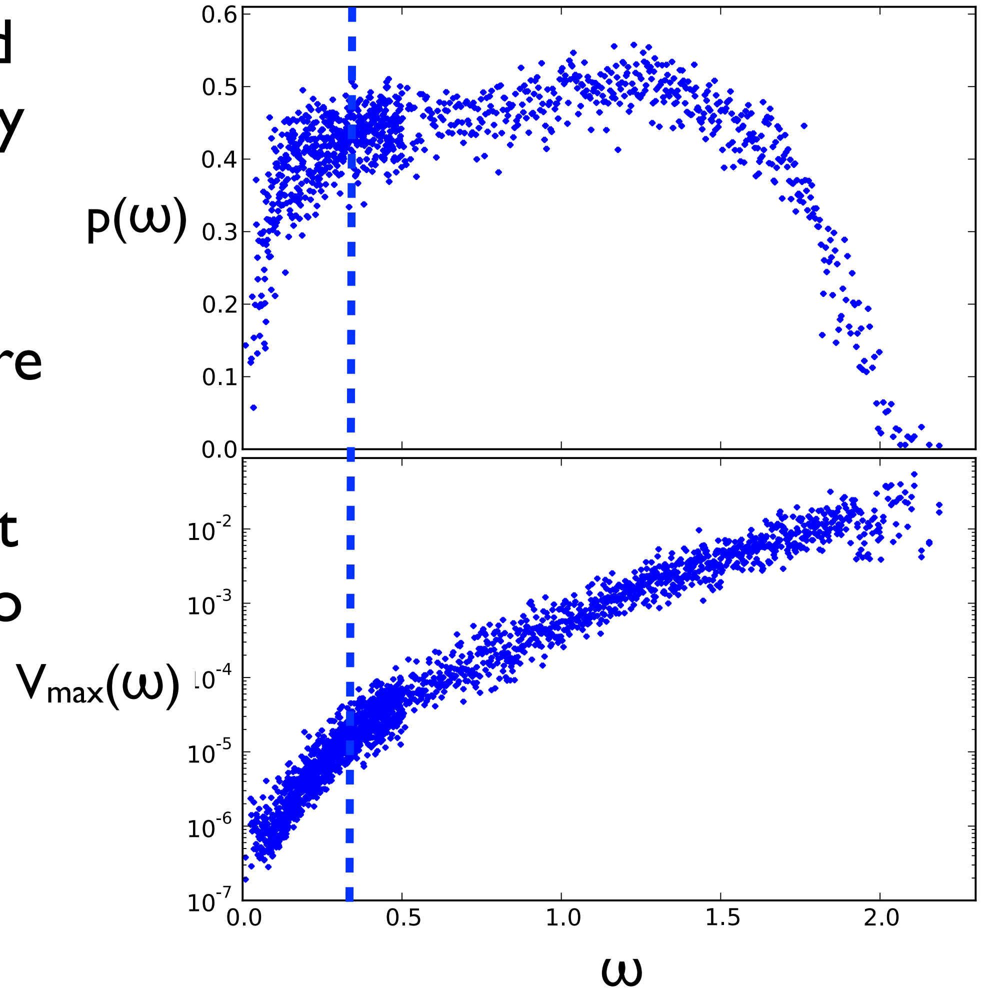


Chen, Still, Schoenholz, Aptowicz, Schindler, Maggs, Liu, Yodh, PRE 88, 022315 (2013)

Anharmonicity

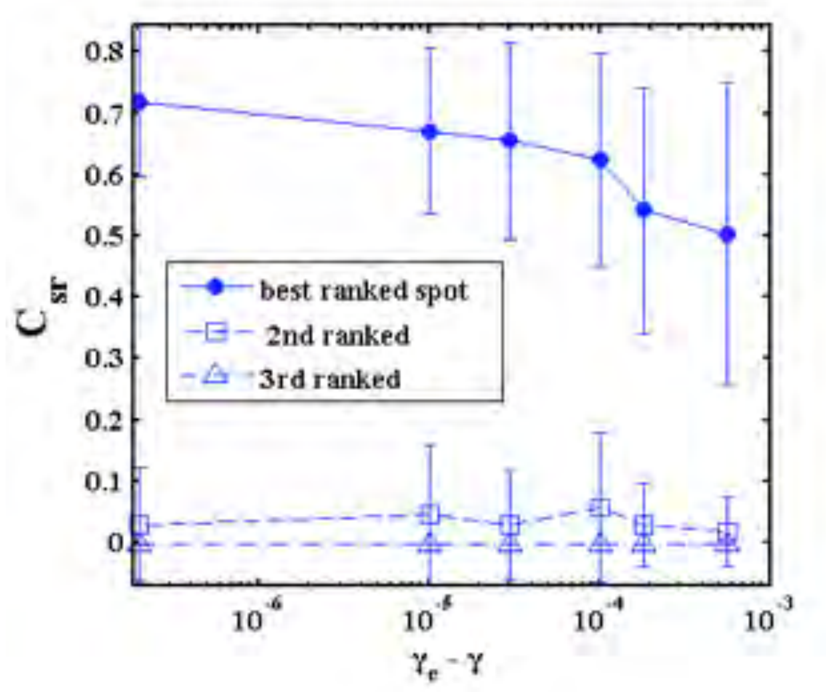
N. Xu, Vi Vitelli, A. J. Liu, S. R. Nagel, EPL **90**, 56001 (2010).

- Low-frequency quasi-localized modes have the lowest energy barriers to rearrangement
  - Barriers are likely to be lower if rearrangements are localized
  - These are the modes most likely to go unstable due to thermal fluctuations or mechanical load
- So QLM likely to contain information about flow defects



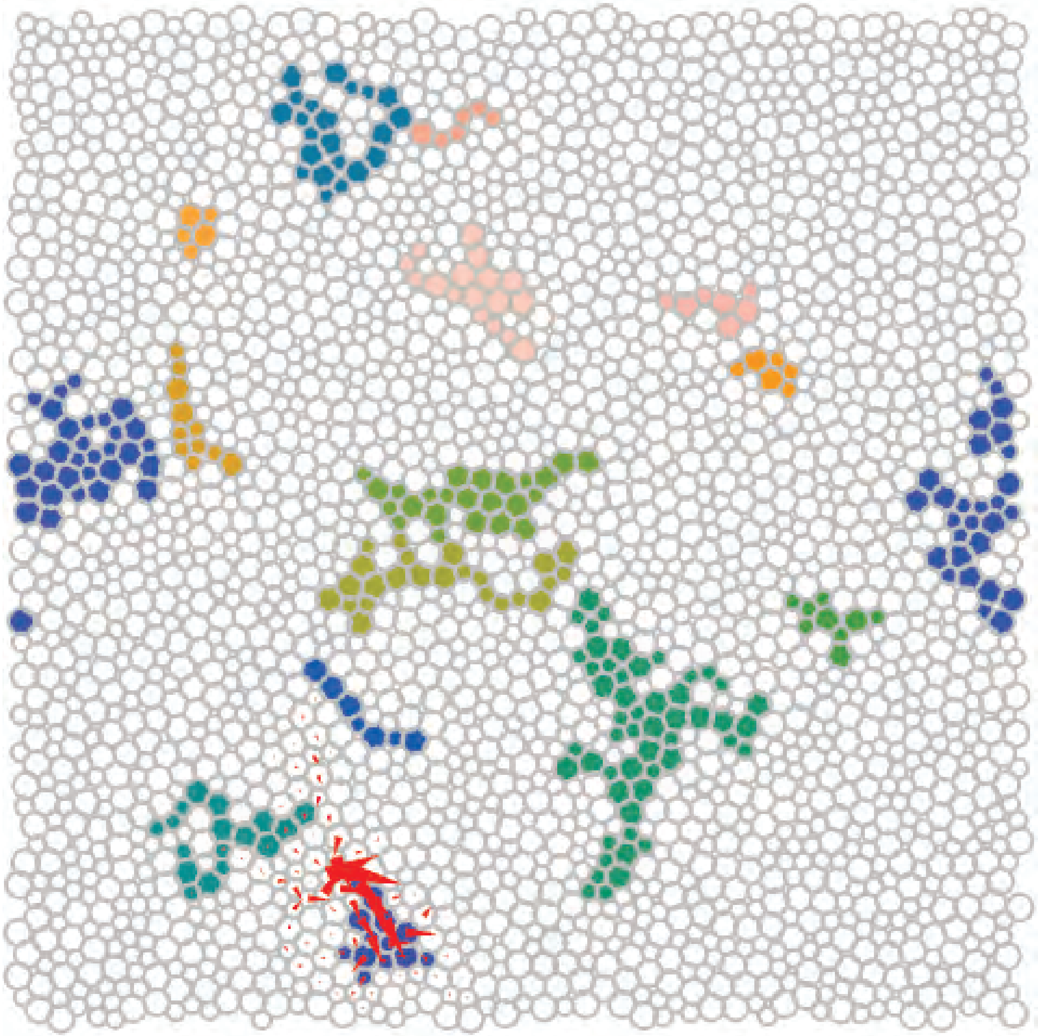
Carl P. Goodrich

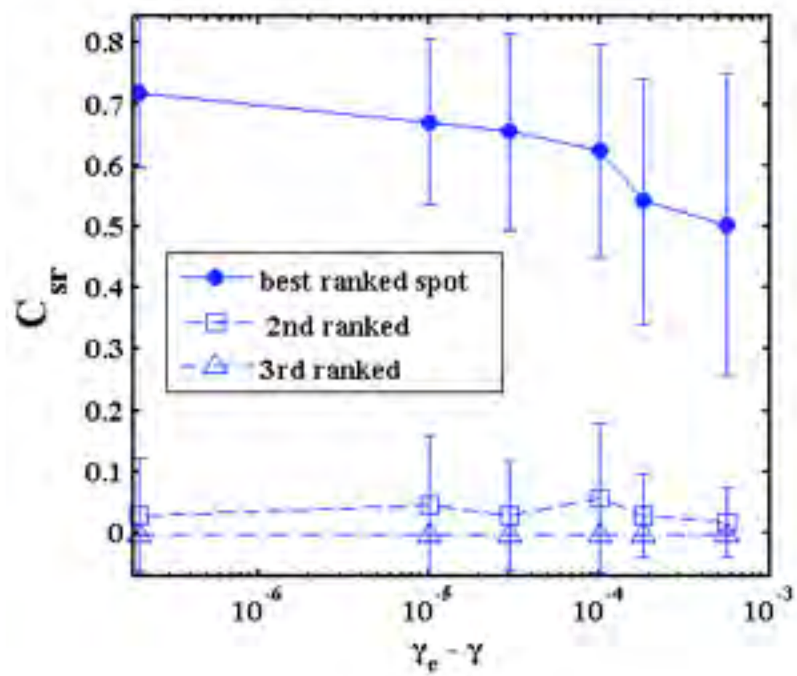
QLM Method of Identifying Flow Defects



M. L. Manning, A. J. Liu, Phys. Rev. Lett. 107, 108302 (2011)

QLM Method of Identifying Flow Defects





M. L. Manning, A. J. Liu, Phys. Rev. Lett. 107, 108302 (2011)

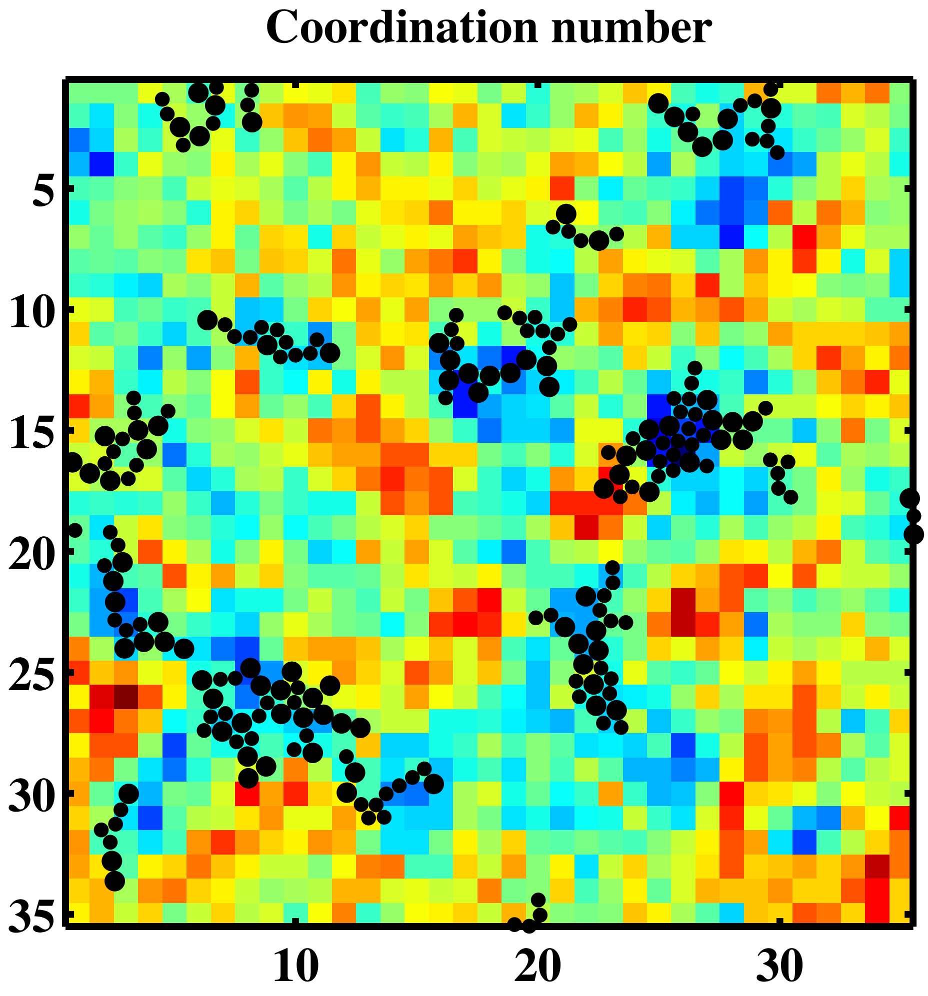
QLM Soft Spots Are Promising, But…

- To identify soft spots, need to
  - know interactions between particles precisely
  - quench system to obtain inherent structures
  - diagonalize dynamical matrix ($O(N^3)$)
- So this method cannot be applied to experimental data and is very slow even for simulation data

- We want a method for identifying regions vulnerable to rearrangement that relies on local structure alone

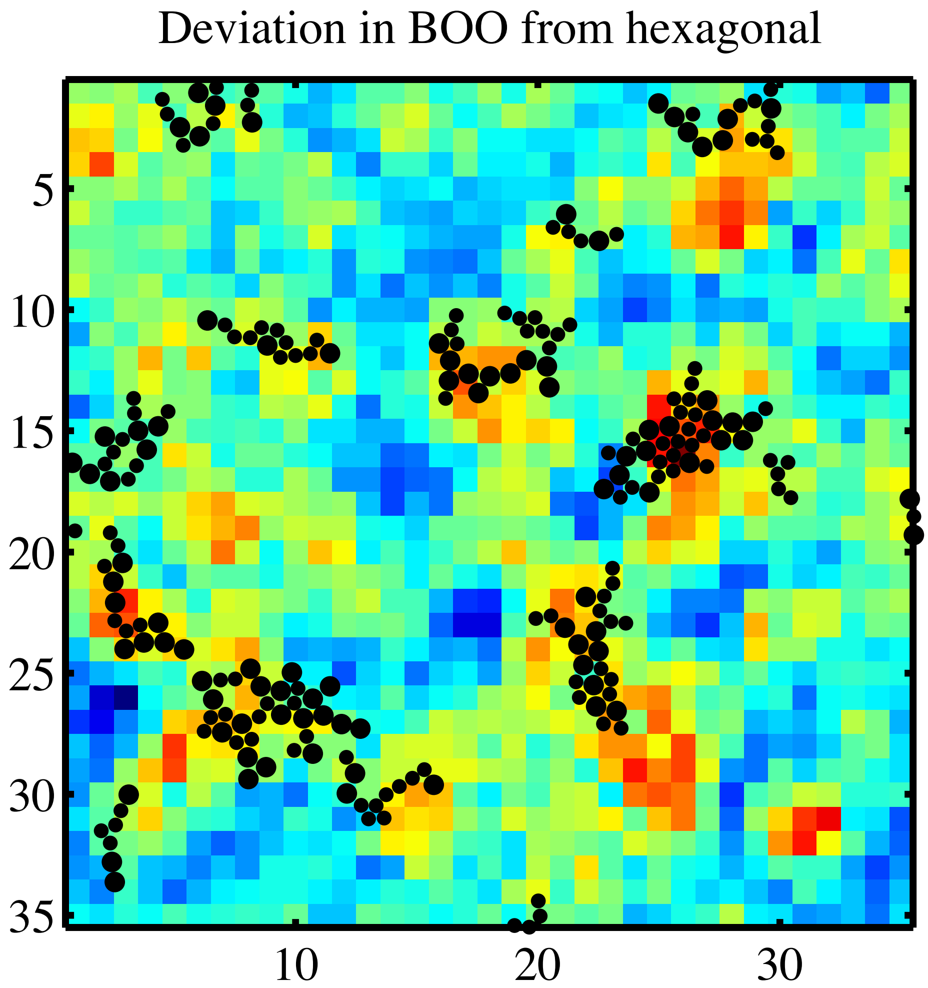
- Problem: all previous attempts have failed

Standard Structural Quantities Don't Tell Us Where Soft Spots Are



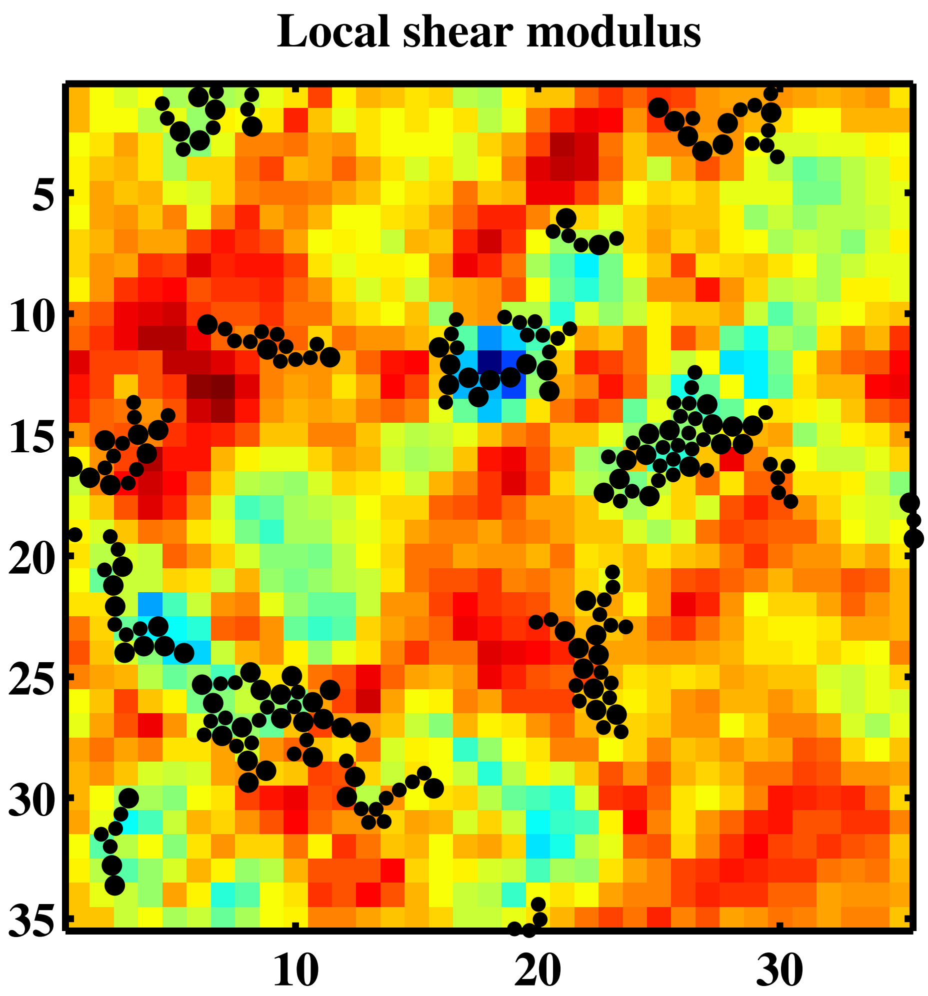
M. L. Manning, A. J. Liu, Phys. Rev. Lett. 107, 108302 (2011)

Standard Structural Quantities Don't Tell Us Where Soft Spots Are



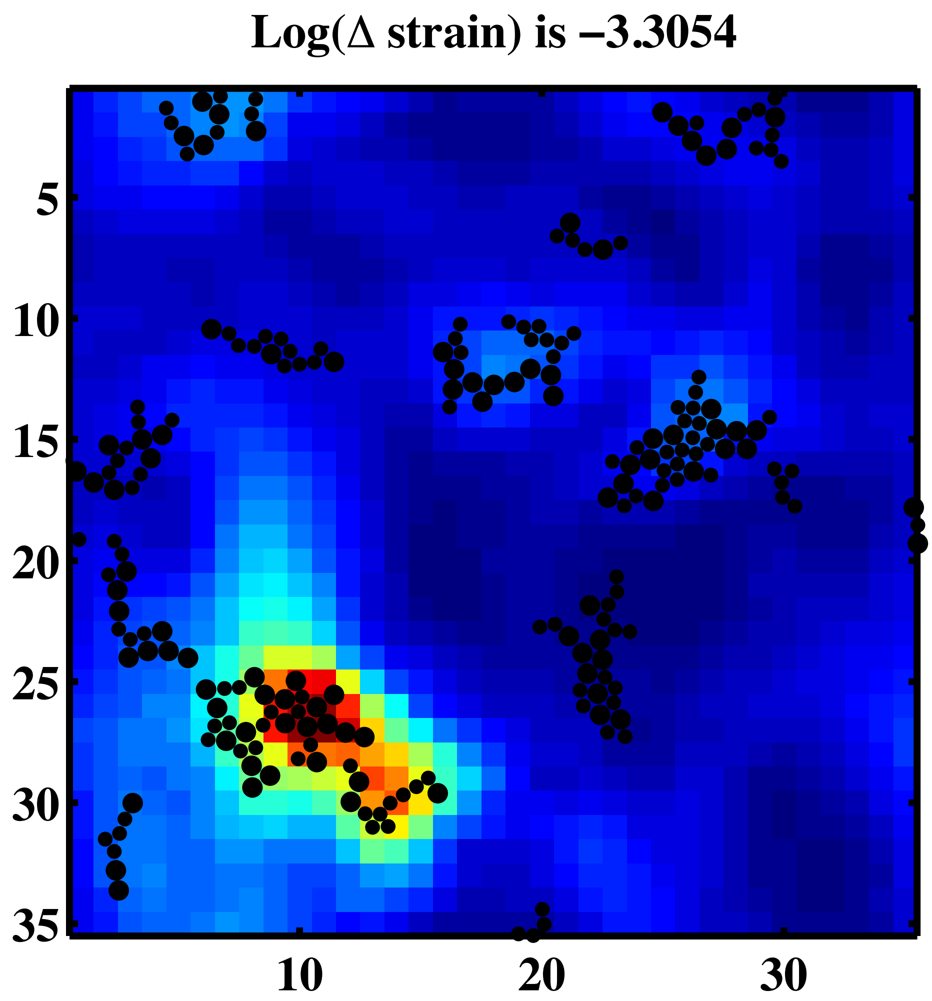
M. L. Manning, A. J. Liu, Phys. Rev. Lett. 107, 108302 (2011)

Standard Structural Quantities Don’t Tell Us Where Soft Spots Are



M. L. Manning, A. J. Liu, Phys. Rev. Lett. 107, 108302 (2011)

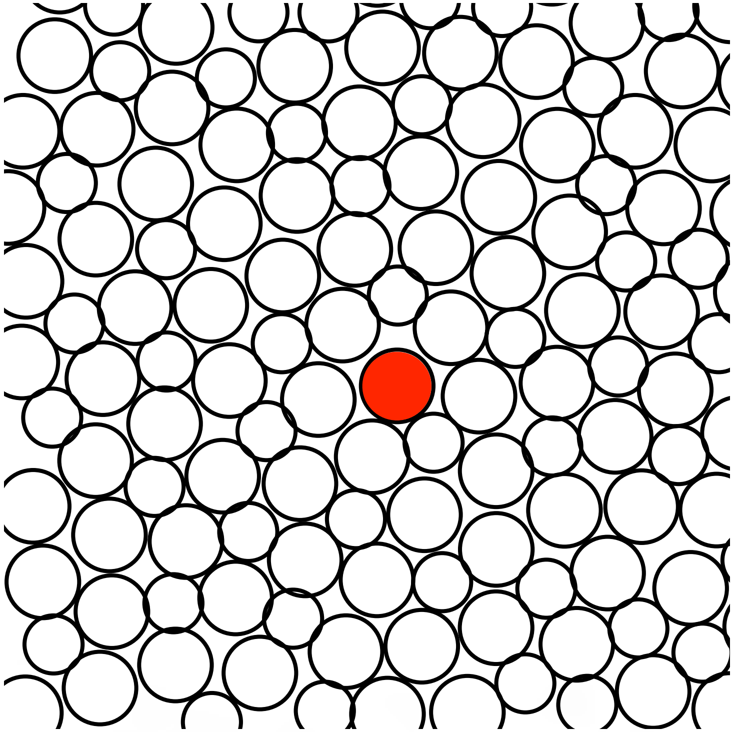
Standard Structural Quantities Don't Tell Us Where Soft Spots Are



M. L. Manning, A. J. Liu, Phys. Rev. Lett. 107, 108302 (2011)

Solution

- Don't just use one quantity to characterize structure
- Use MANY
- Introduce two families of functions



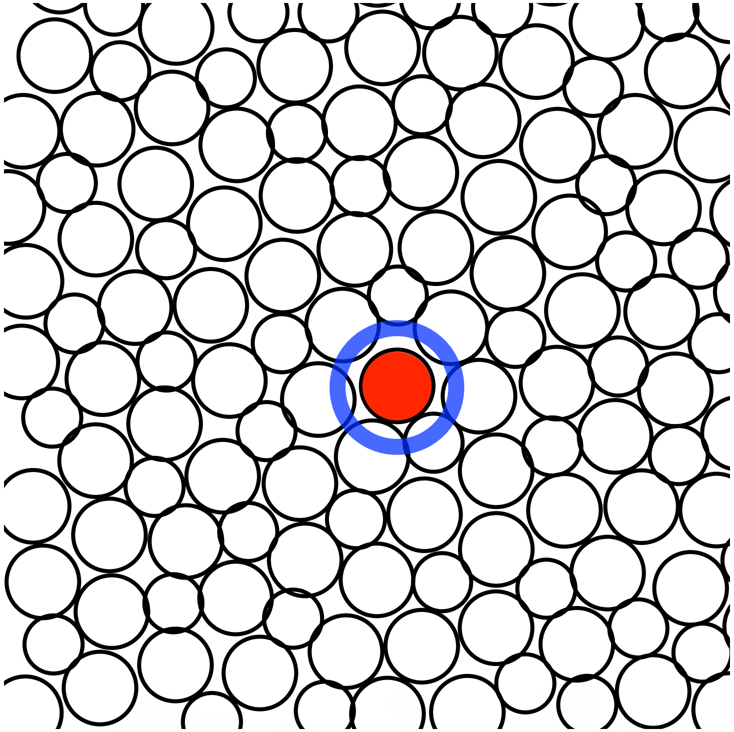
$$S_Y^X(i;\mu) = \sum_j e^{-(R_{ij}-\mu)^2/L^2}$$

$$Q_{YZ}^X(i;\xi,\lambda,\zeta) = \sum_j \sum_k e^{-(R_{ij}^2+R_{ik}^2+R_{jk}^2)/\xi^2}(1+\lambda\cos\theta_{ijk})^\zeta$$

Sam Schoenholz and Dogus Cubuk

Solution

- Don't just use one quantity to characterize structure
- Use MANY
- Introduce two families of functions



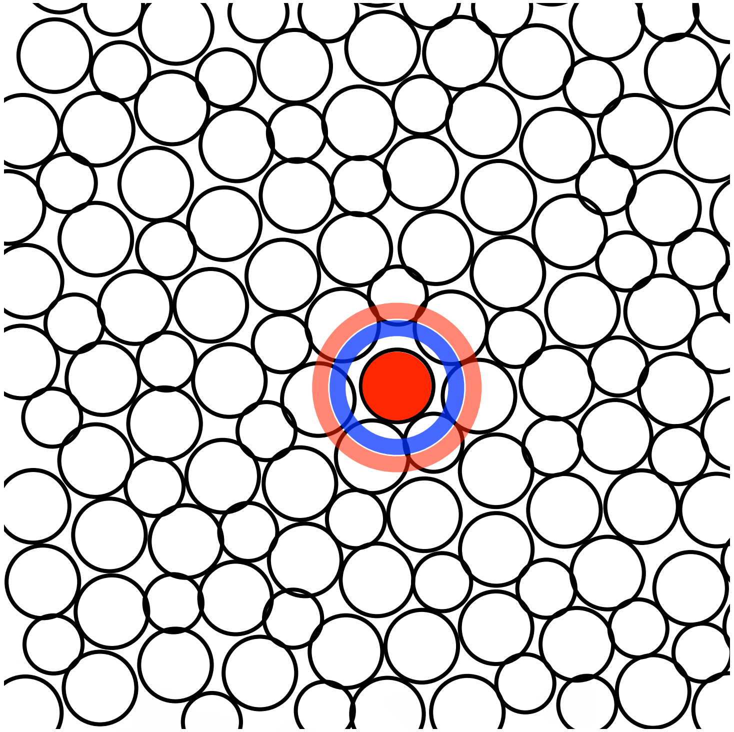
$$S_Y^X(i;\mu) = \sum_j e^{-(R_{ij}-\mu)^2/L^2}$$

$$Q_{YZ}^X(i;\xi,\lambda,\zeta) = \sum_j \sum_k e^{-(R_{ij}^2+R_{ik}^2+R_{jk}^2)/\xi^2}(1+\lambda\cos\theta_{ijk})^\zeta$$

Sam Schoenholz and Dogus Cubuk

Solution

- Don't just use one quantity to characterize structure
- Use MANY
- Introduce two families of functions



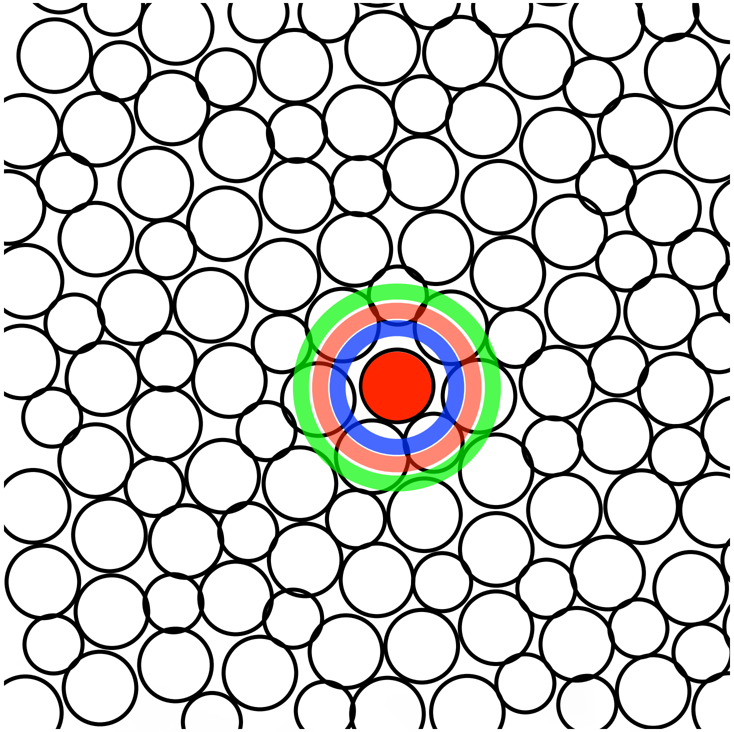
$$S_Y^X(i;\mu) = \sum_j e^{-(R_{ij}-\mu)^2/L^2}$$

$$Q_{YZ}^X(i;\xi,\lambda,\zeta) = \sum_j \sum_k e^{-(R_{ij}^2+R_{ik}^2+R_{jk}^2)/\xi^2}(1+\lambda\cos\theta_{ijk})^\zeta$$

Sam Schoenholz and Dogus Cubuk

Solution

- Don't just use one quantity to characterize structure
- Use MANY
- Introduce two families of functions



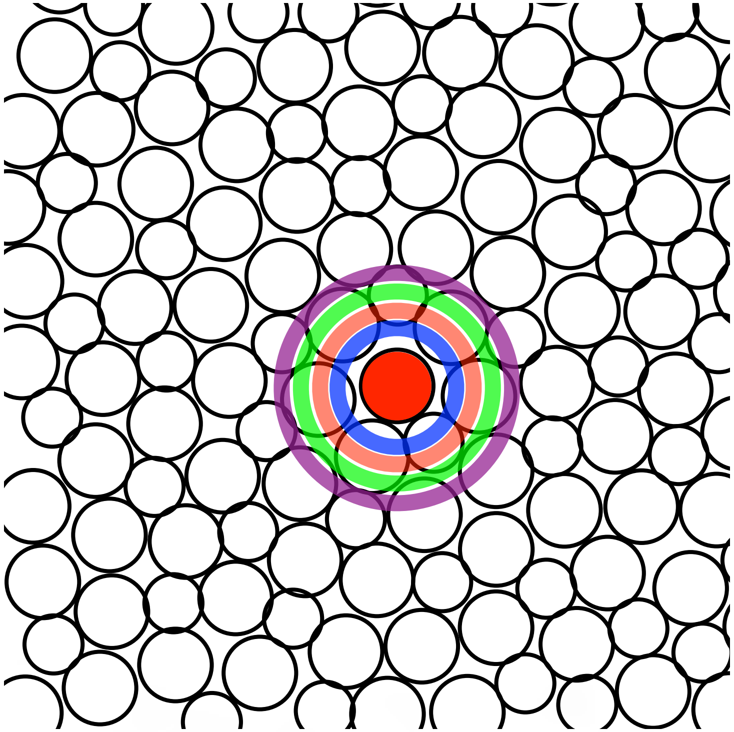
$$S_Y^X(i;\mu) = \sum_j e^{-(R_{ij}-\mu)^2/L^2}$$

$$Q_{YZ}^X(i;\xi,\lambda,\zeta) = \sum_j \sum_k e^{-(R_{ij}^2+R_{ik}^2+R_{jk}^2)/\xi^2}(1+\lambda\cos\theta_{ijk})^\zeta$$

Sam Schoenholz and Dogus Cubuk

Solution

- Don't just use one quantity to characterize structure
- Use MANY
- Introduce two families of functions



$$S_Y^X(i;\mu) = \sum_j e^{-(R_{ij}-\mu)^2/L^2}$$

$$Q_{YZ}^X(i;\xi,\lambda,\zeta) = \sum_j \sum_k e^{-(R_{ij}^2+R_{ik}^2+R_{jk}^2)/\xi^2}(1+\lambda\cos\theta_{ijk})^\zeta$$

Sam Schoenholz and Dogus Cubuk

Physical Meaning of Structure Functions

- First family measures density at radius r

$$S_Y^X(i;\mu) = \sum_j e^{-(R_{ij}-\mu)^2/L^2}$$

Radius to probe

Particle separation

Width of window

- Second family measures bond anticorrelation at radius r

$$Q_{YZ}^X(i;\xi,\lambda,\zeta) = \sum_j \sum_k e^{-(R_{ij}^2+R_{ik}^2+R_{jk}^2)/\xi^2}(1+\lambda\cos\theta_{ijk})^\zeta$$

Radius

Angular Resolution

Alignment/antialignment

Classify "softness"

- Have a set of structural variables for each particle i (values of S and Q at different values of μ, ξ, λ, ζ

$$S_Y^X(i;\mu) = \sum_j e^{-(R_{ij}-\mu)^2/L^2}$$

$$Q_{YZ}^X(i;\xi,\lambda,\zeta) = \sum_j \sum_k e^{-(R_{ij}^2+R_{ik}^2+R_{jk}^2)/\xi^2}(1+\lambda\cos\theta_{ijk})^\zeta$$

- Want to categorize each particle as soft (susceptible to rearrangement) or hard

- Use Support Vector Machines (SVM)

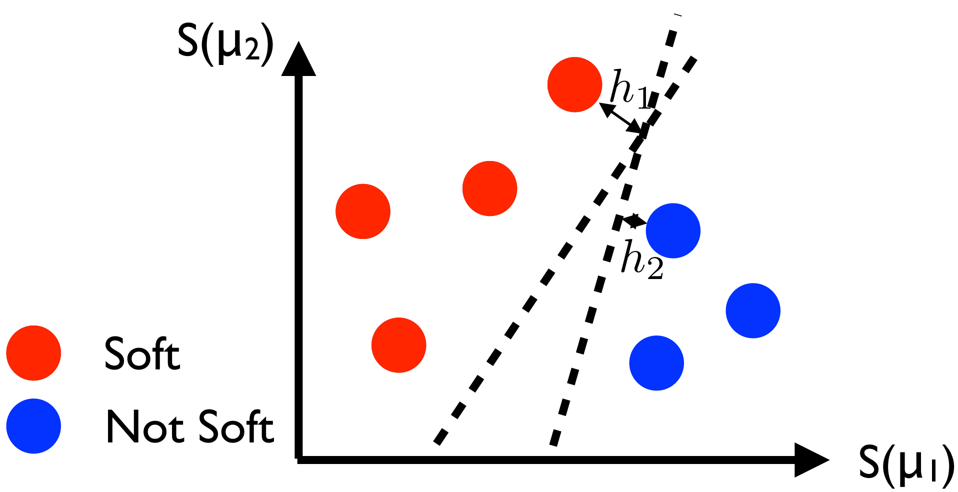
- Requires a "training set" with known classification

Classifying "softness"

Use D^2_{min} to find rearrangements

$$D^2_{\min}(i, \Delta t) = \sum_j \left[\boldsymbol{R}_{ij}(t + \Delta t) - \boldsymbol{\Lambda}_{\min}\boldsymbol{R}_{ij}(t)\right]$$

- Particle is "soft" if $D^2_{\min} > D^2_{\min,0} \approx \sigma^2_{AA}$
- Embed in space where each dimension is a structural variable
- Find dividing plane with maximum margin h
- Classify new data with dividing plane

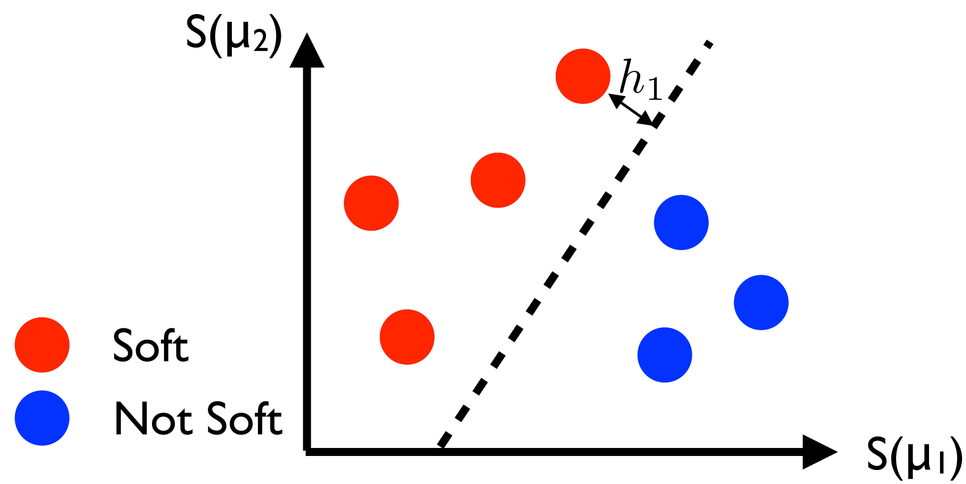


Classifying "softness"

Use D^2_{min} to find rearrangements

$$D^2_{\min}(i, \Delta t) = \sum_j \left[\boldsymbol{R}_{ij}(t+\Delta t) - \boldsymbol{\Lambda}_{\min}\boldsymbol{R}_{ij}(t)\right]$$

- Particle is "soft" if $D^2_{\min} > D^2_{\min,0} \approx \sigma^2_{AA}$
- Embed in space where each dimension is a structural variable
- Find dividing plane with maximum margin h
- Classify new data with dividing plane

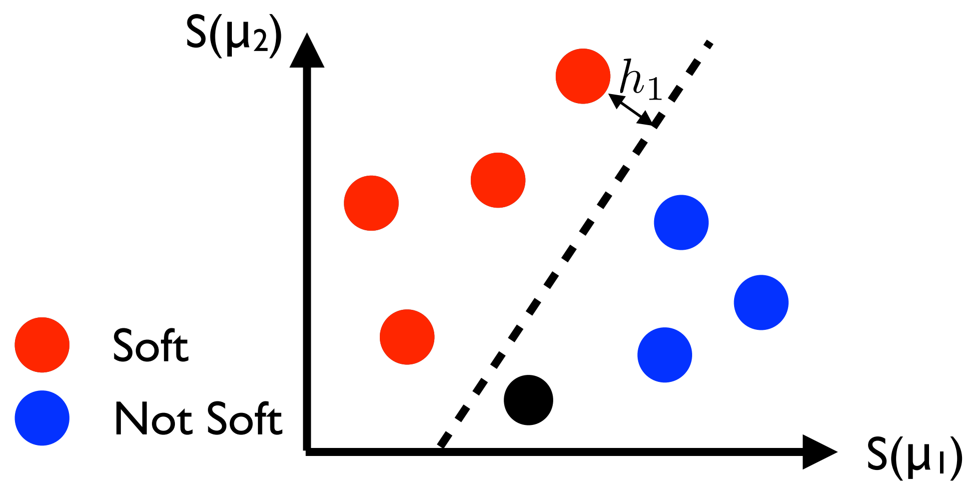


Classifying "softness"

Use D^2_{min} to find rearrangements

$$D^2_{\min}(i, \Delta t) = \sum_j \left[\boldsymbol{R}_{ij}(t+\Delta t) - \boldsymbol{\Lambda}_{\min}\boldsymbol{R}_{ij}(t)\right]$$

- Particle is "soft" if $D^2_{\min} > D^2_{\min,0} \approx \sigma^2_{AA}$
- Embed in space where each dimension is a structural variable
- Find dividing plane with maximum margin h
- Classify new data with dividing plane



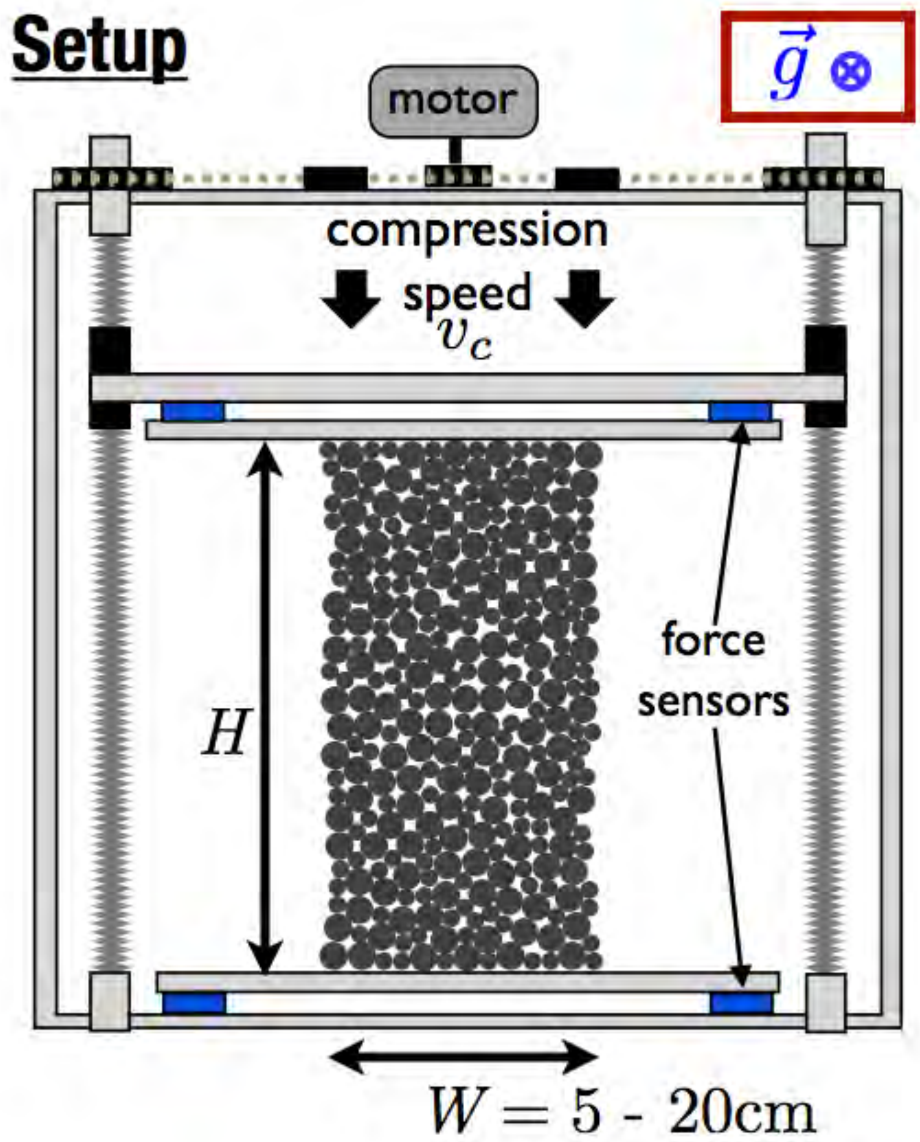
SVM Method

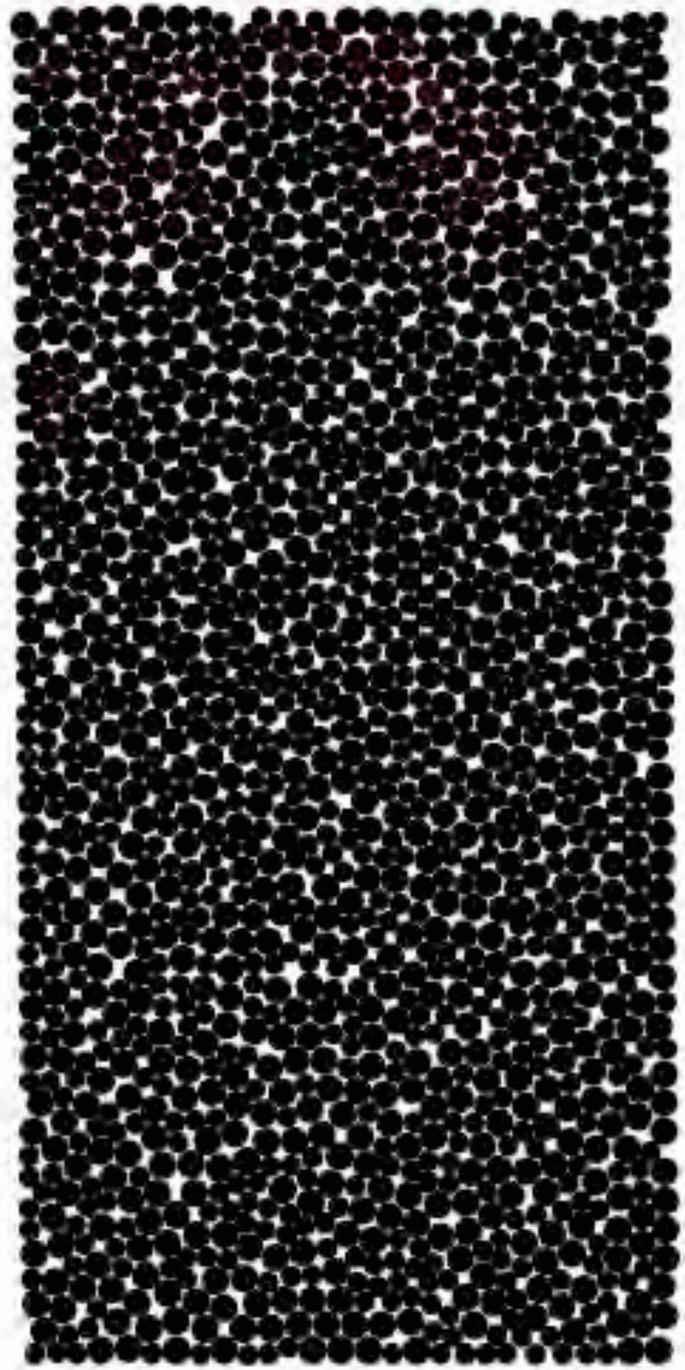
- Works better than QLM method
- Don't need to
  - quench system to obtain inherent structures
    - in fact, method works better because it can be applied to instantaneous snapshots
  - diagonalize dynamical matrix ($O(N^3)$)
    - method is $O(N)$
  - know interactions between particles precisely

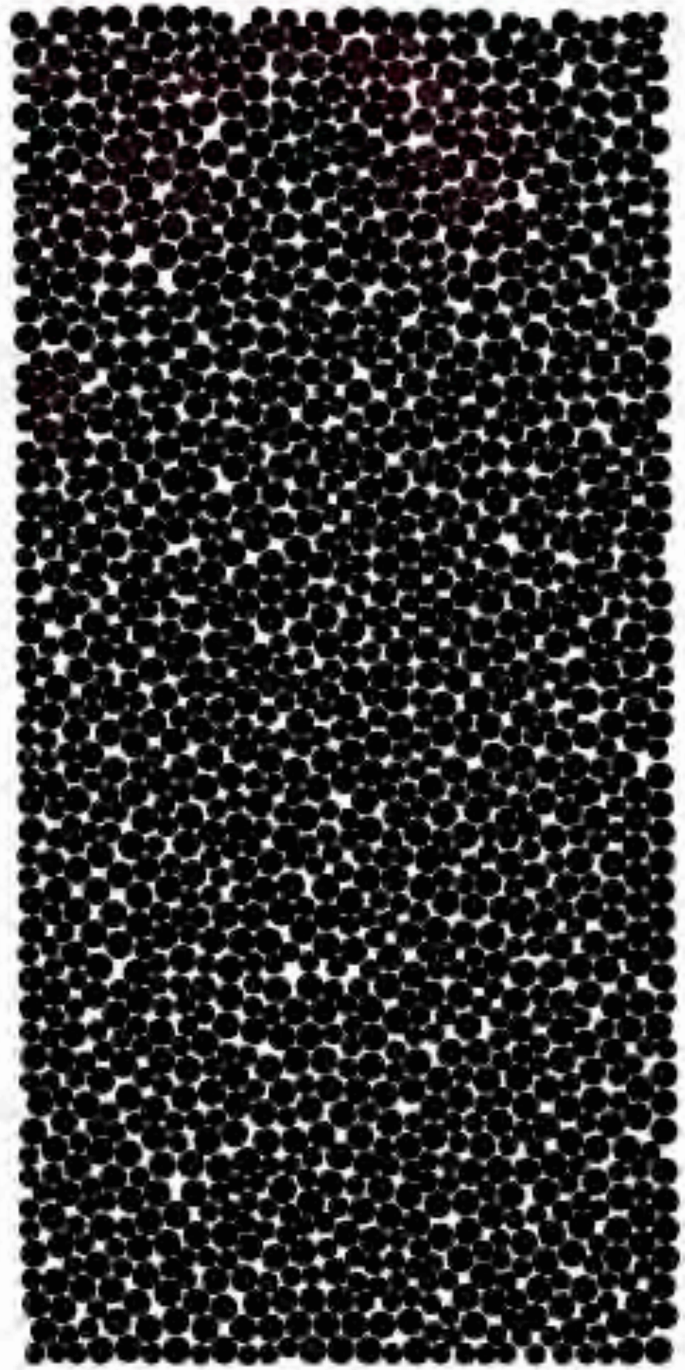
- Apply to experimental system

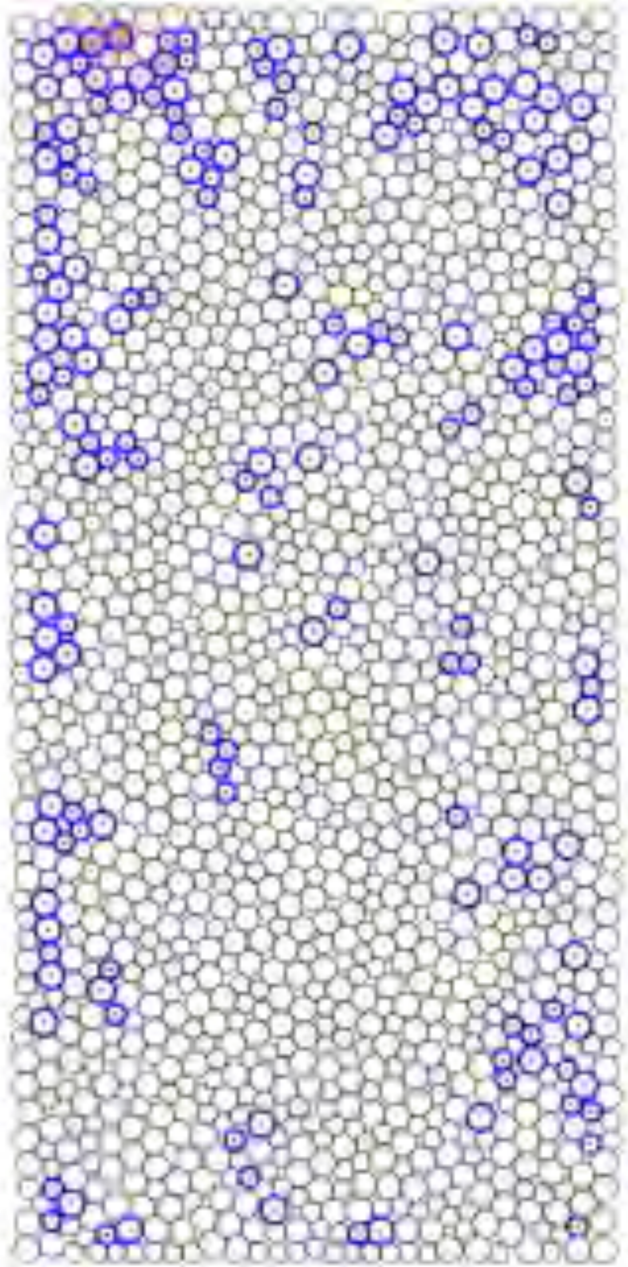
Compressed Granular Pillars

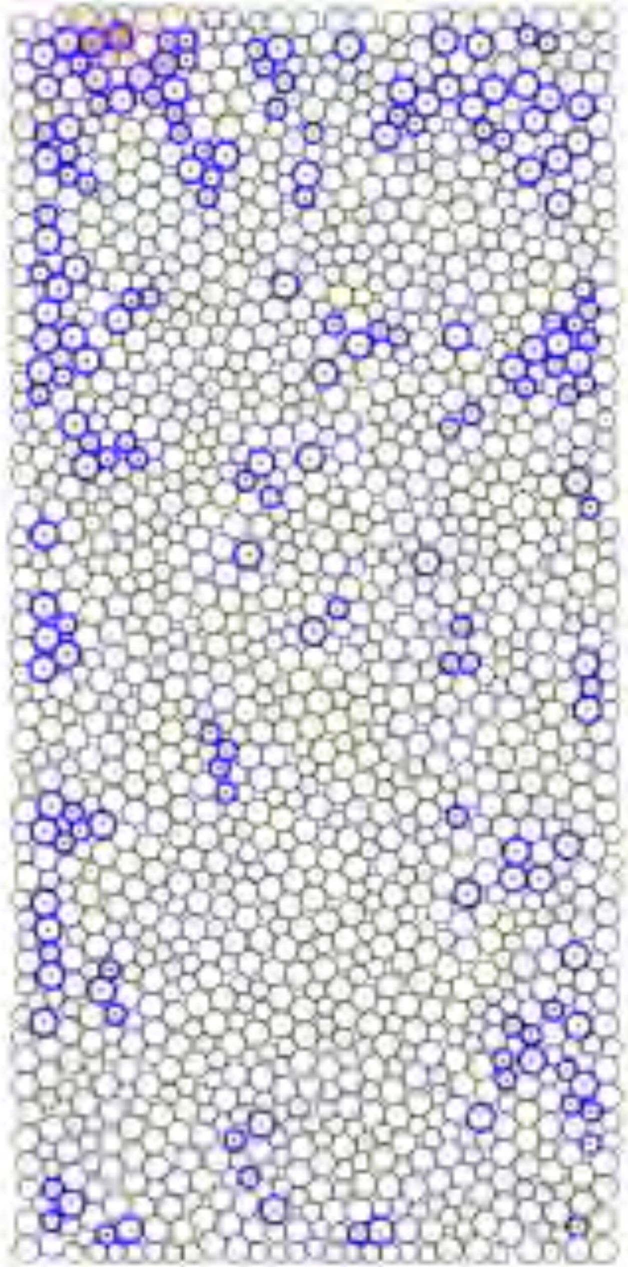
Jennifer Rieser, Doug Durian



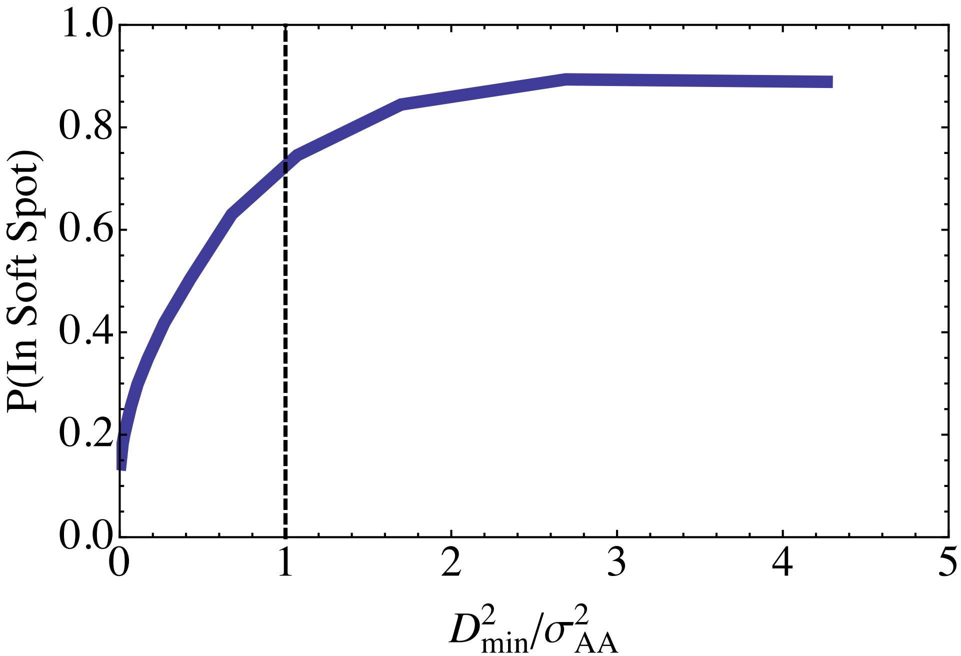






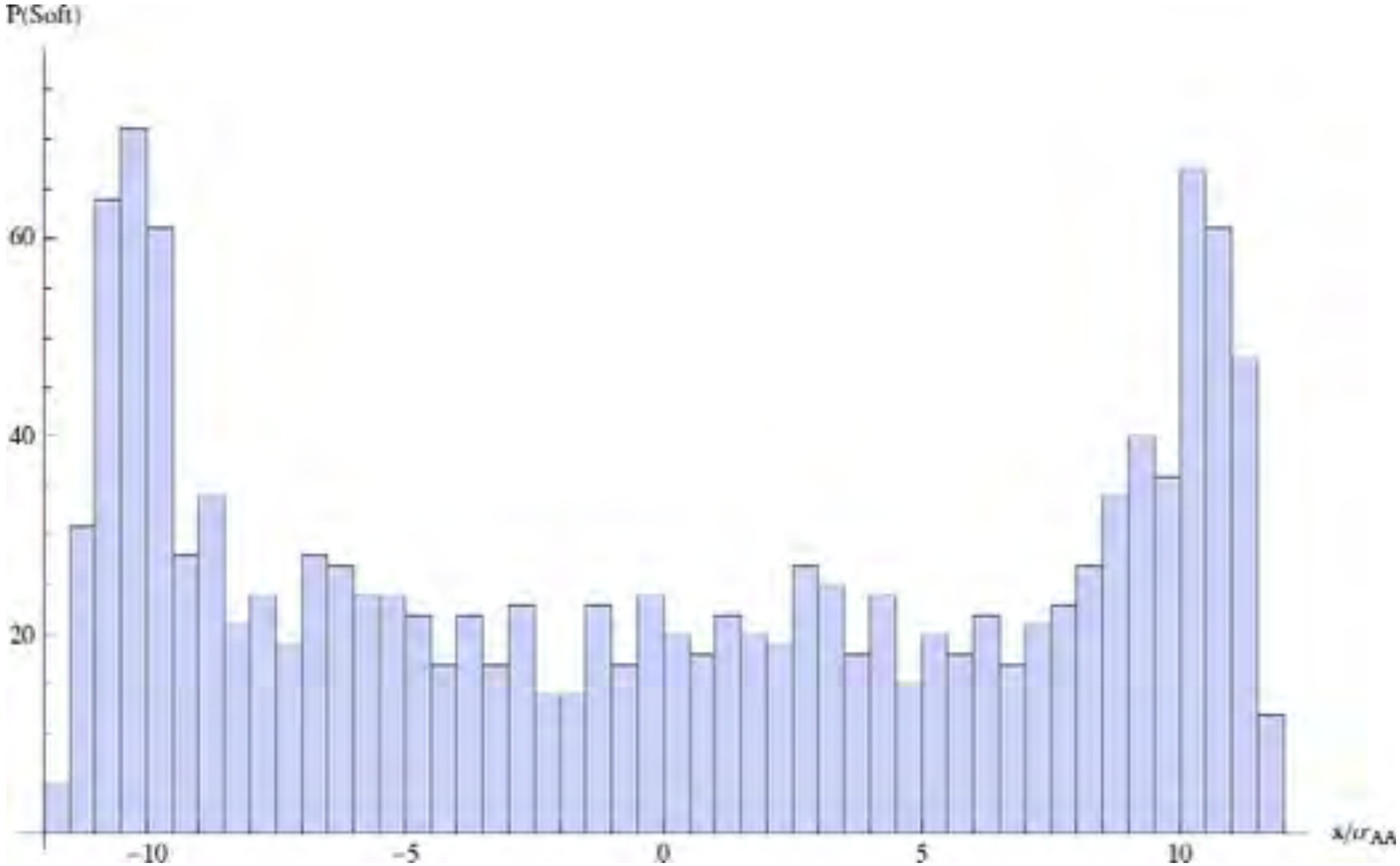


Compressed Granular Pillars



- 21% of system captures 80% of rearranging particles

Pillar Has Free Surfaces—Are There More Soft Particles There?



- Yes, number of soft particles is higher at surface
- Soft particles enhanced over range of ~ 5 particle diameters
- Granular pillars have "mobile layer" similar to that of glassy films

Tests of SVM method

(1) Sheared, thermal 2D Lennard-Jones glass

65:35 Kob-Andersen Lennard-Jones mixture

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

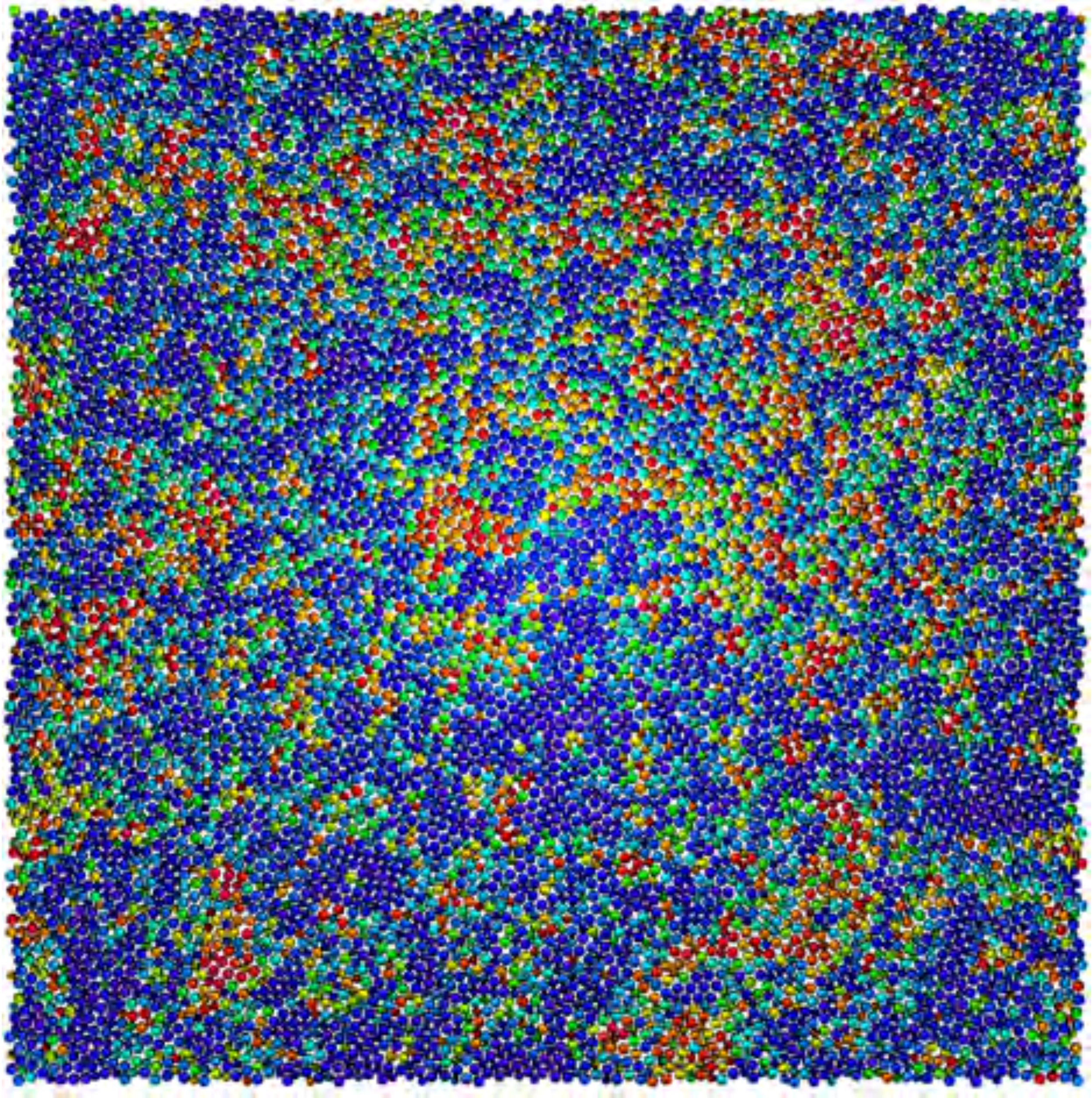
$$\sigma_{AA} = 1.0 \quad \sigma_{AB} = 0.88 \quad \sigma_{BB} = 0.8$$

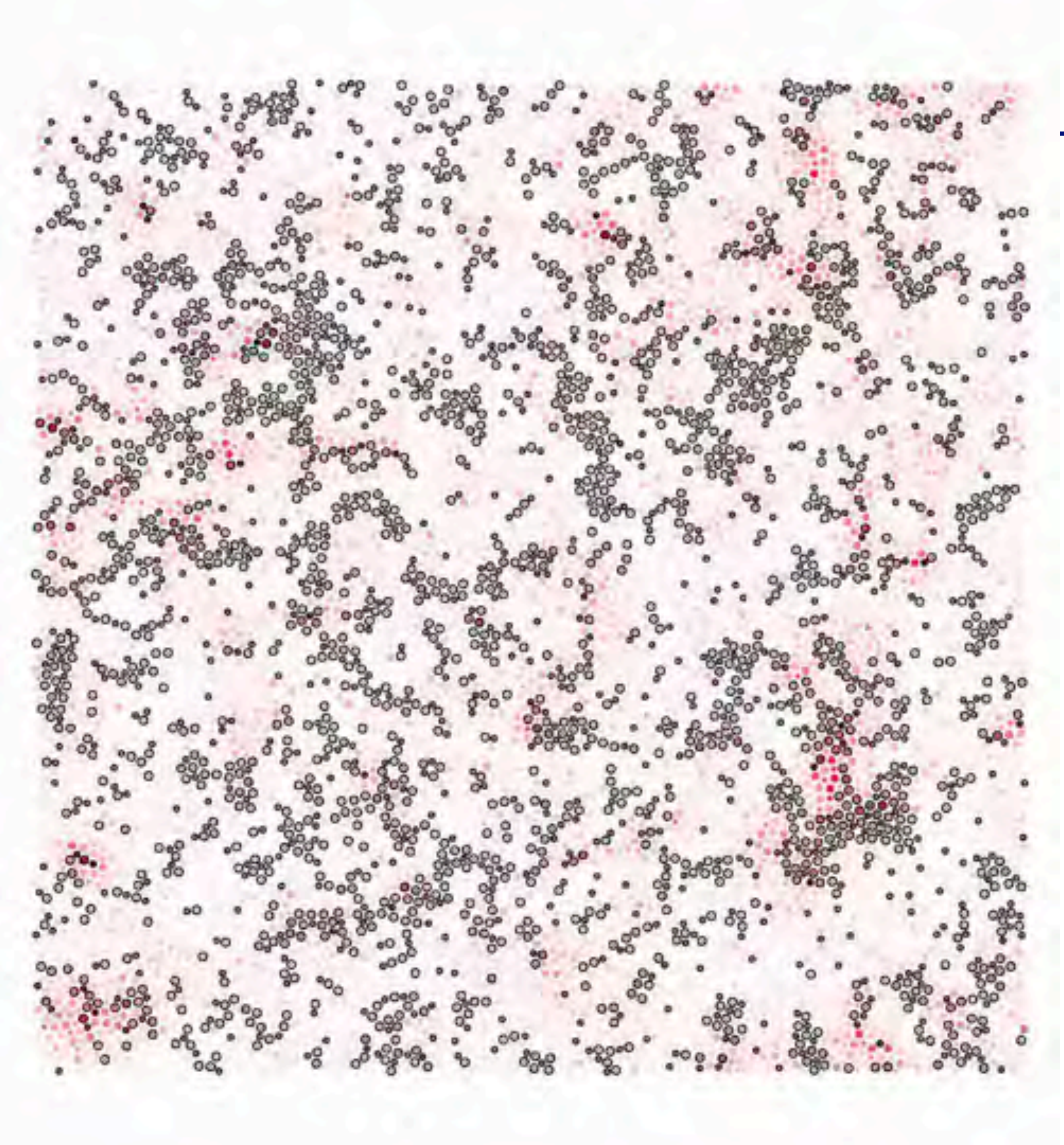
$$\epsilon_{AA} = 1.0, \quad \epsilon_{AB} = 1.5 \quad \epsilon_{BB} = 0.5.$$

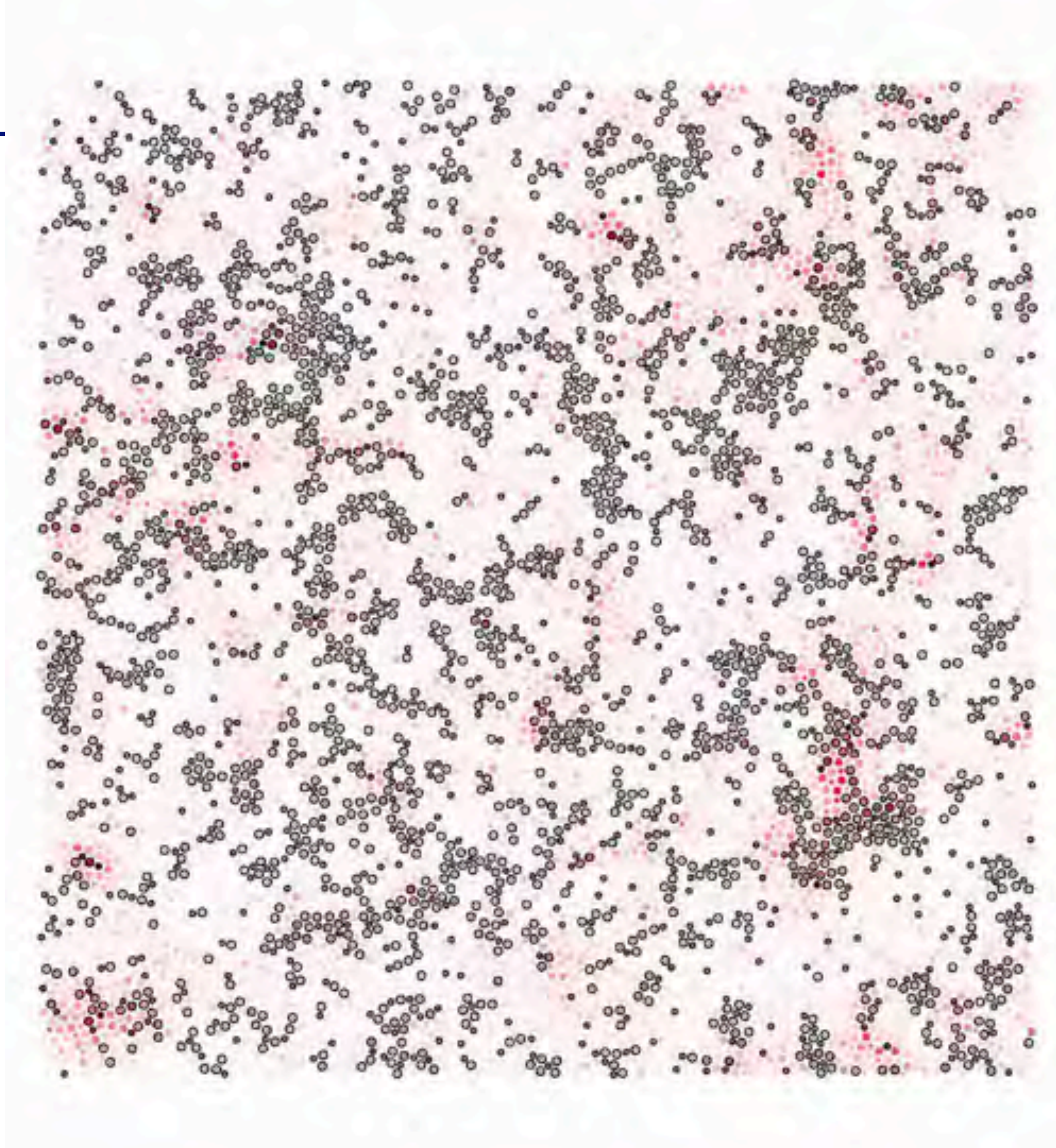
Characterized by Brüning *et al.* with T_g=0.33

$$T = 0.1, 0.2, 0.3, 0.4 \qquad \dot{\gamma} = 10^{-4}$$

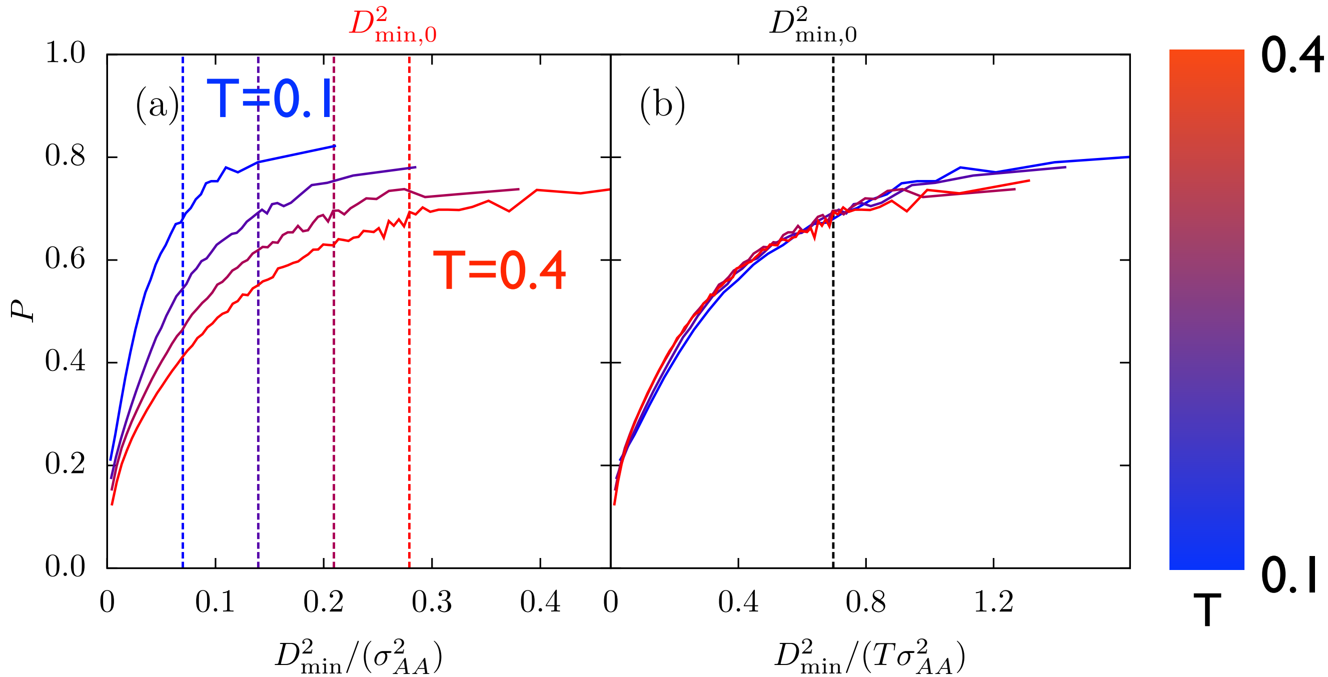
Softness Field





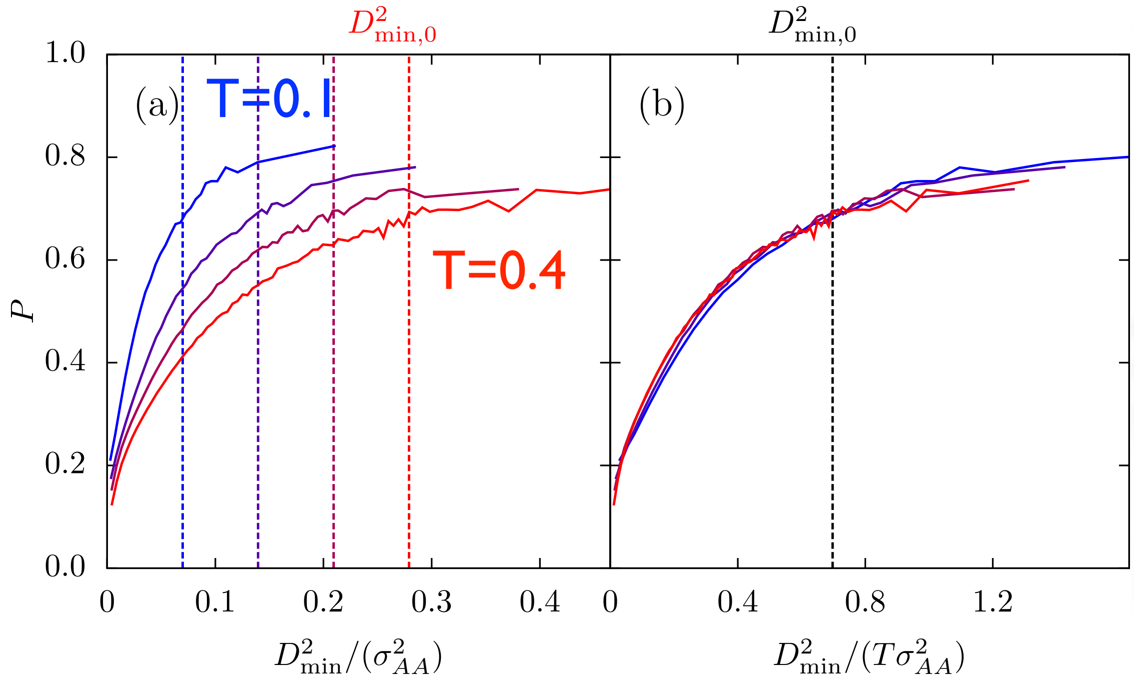


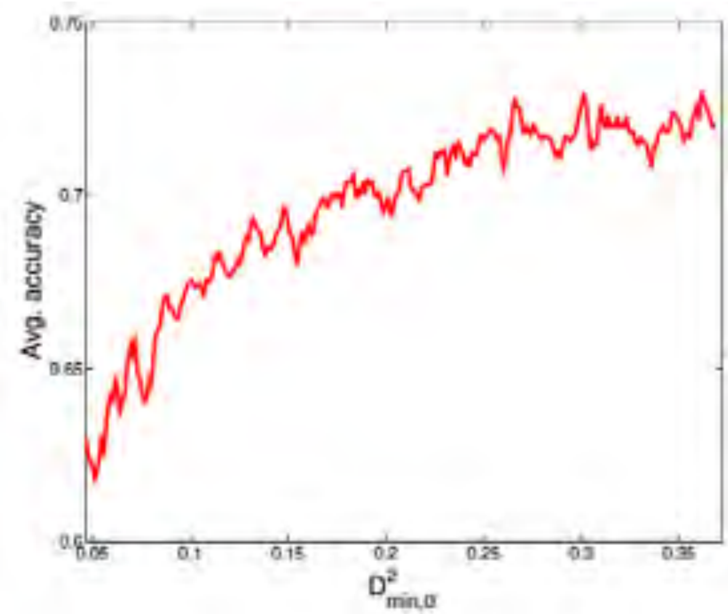
Sheared 2D Lennard-Jones glass



- 26% of system captures 73% of rearranging particles
- Works equally well at all temperatures, even above glass transition
- Accuracy insensitive to threshold

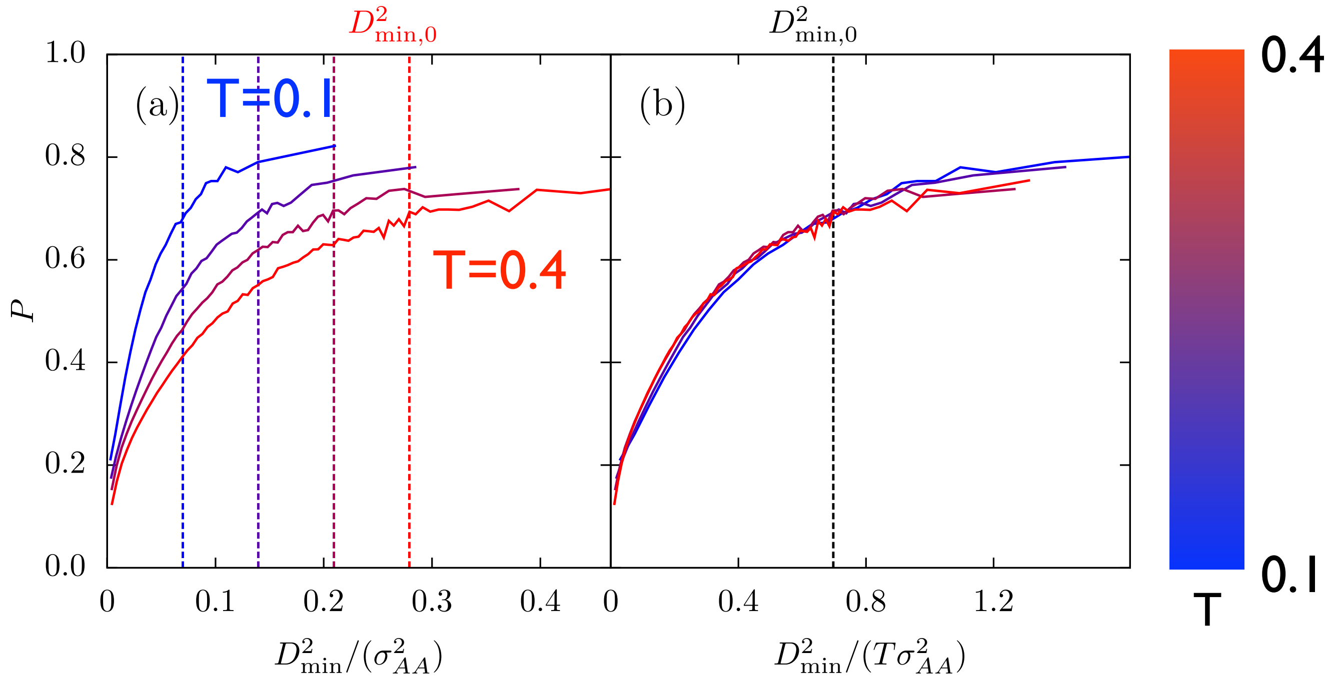
Sheared 2D Lennard-Jones glass





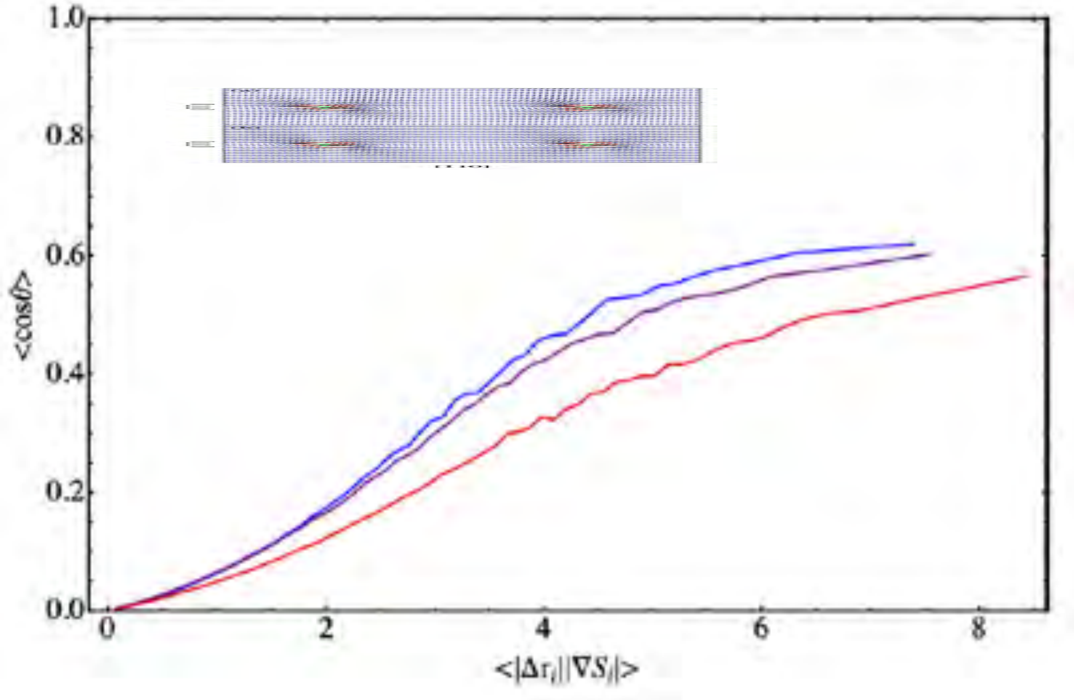
- 26% of system captures 73% of rearranging particles
- Works equally well at all temperatures, even above glass transition
- Accuracy insensitive to threshold

Sheared 2D Lennard-Jones glass

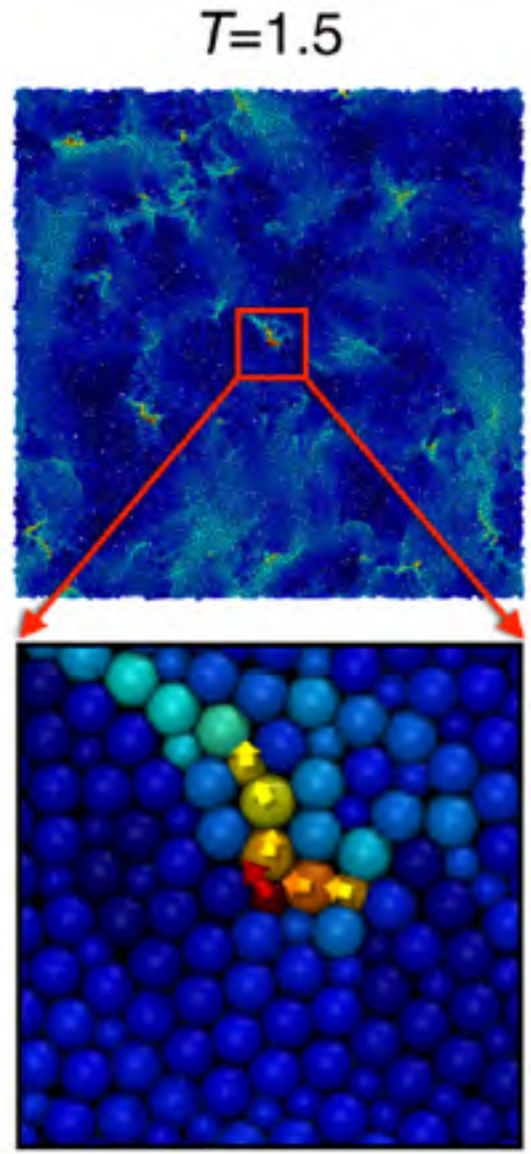


- 26% of system captures 73% of rearranging particles
- Works equally well at all temperatures, even above glass transition
- Accuracy insensitive to threshold

Particle Displacements correlate with softness gradient



- Rearranging particles tend to move in direction of increasing softness
- Promising as structural signature of facilitation



Keys, et al PRX (2011)

Tests of SVM method

(2) Quiescent, thermal 3D Lennard-Jones glass

65:35 Kob-Andersen Lennard-Jones mixture

$$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

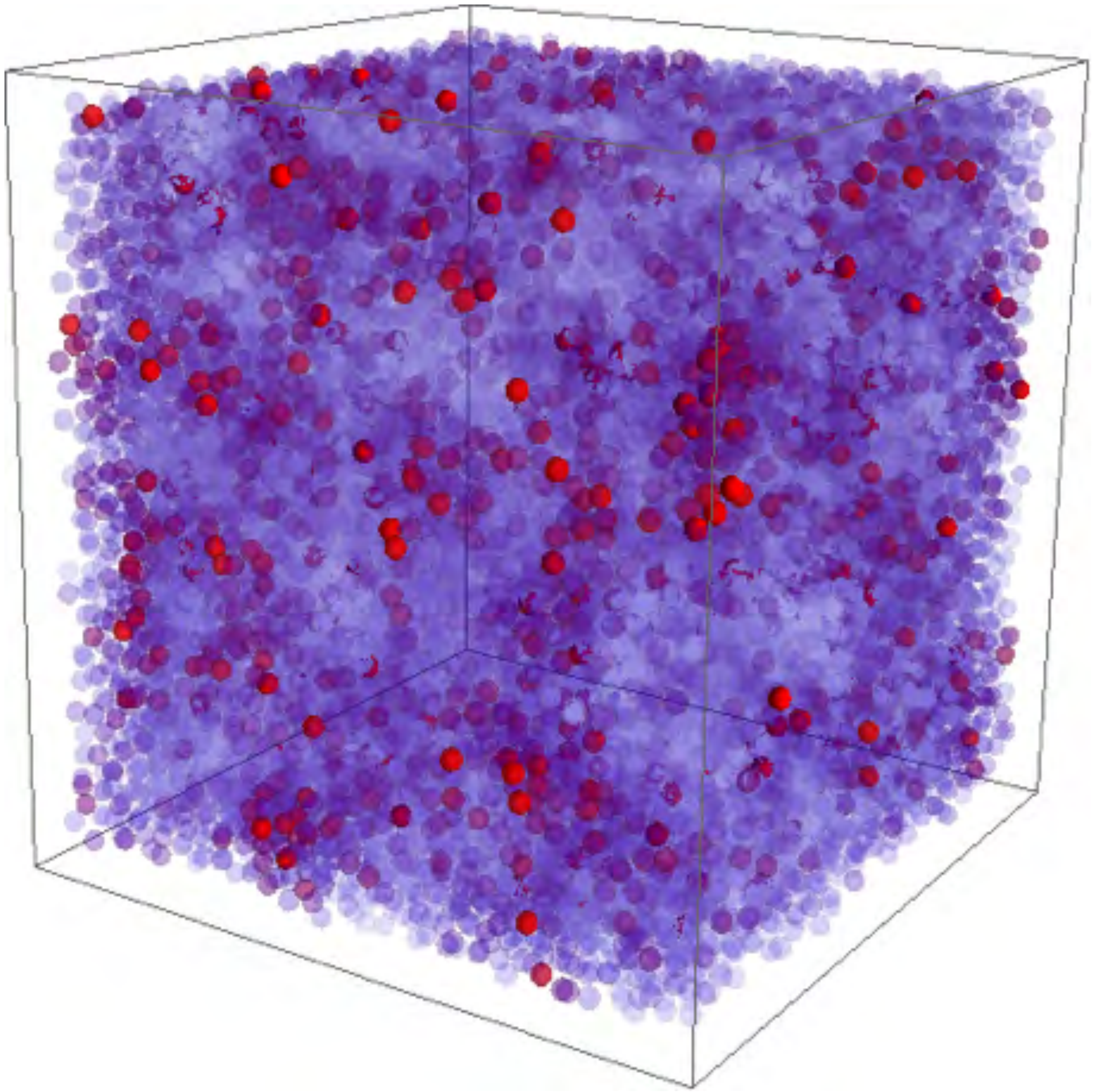
$$\sigma_{AA} = 1.0 \quad \sigma_{AB} = 0.88 \quad \sigma_{BB} = 0.8$$

$$\epsilon_{AA} = 1.0, \quad \epsilon_{AB} = 1.5 \quad \epsilon_{BB} = 0.5.$$

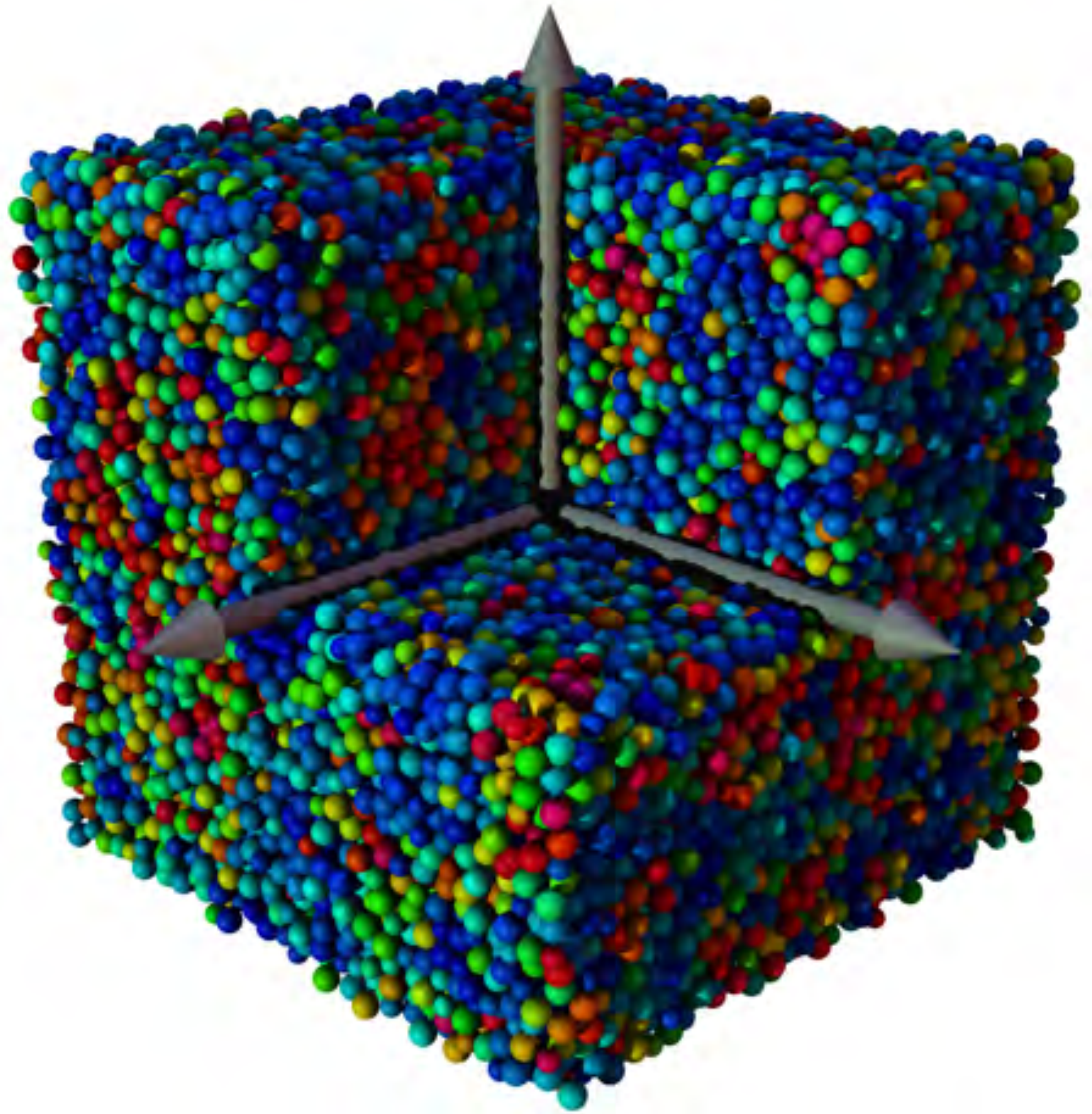
Characterized by Brüning *et al.* with T_g=0.58

$$T = 0.4, 0.5, 0.6$$

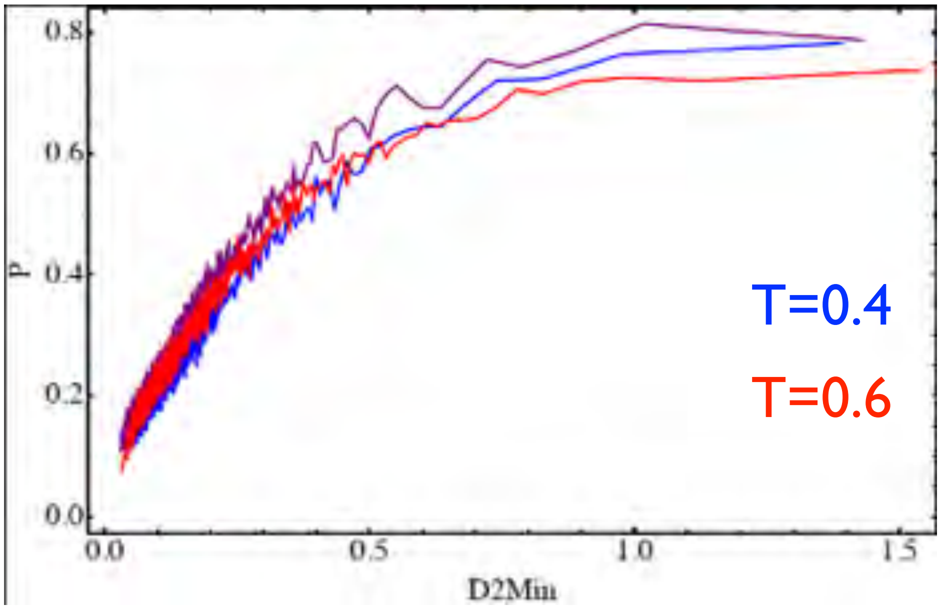
Rearrangements are localized

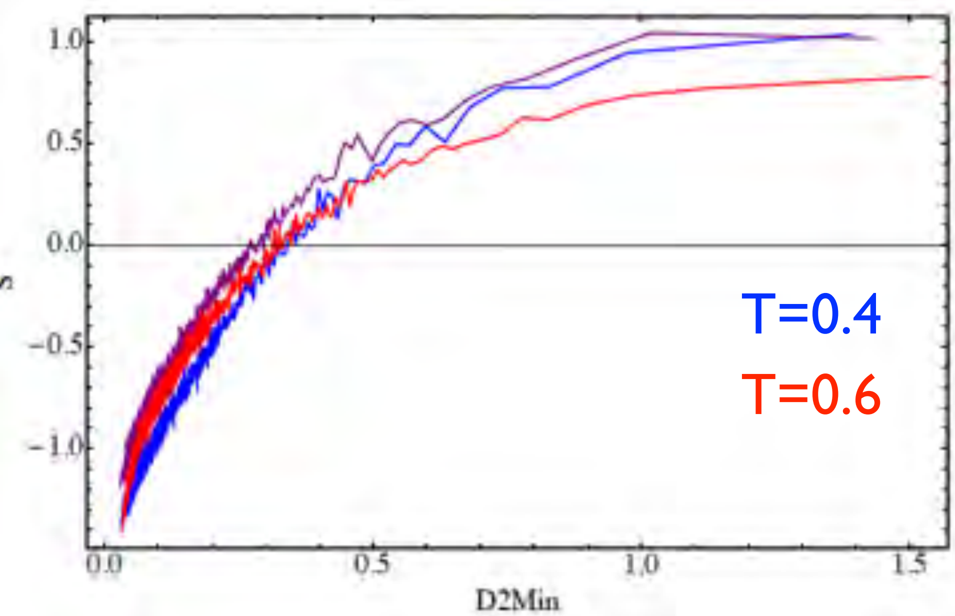


Softness Field



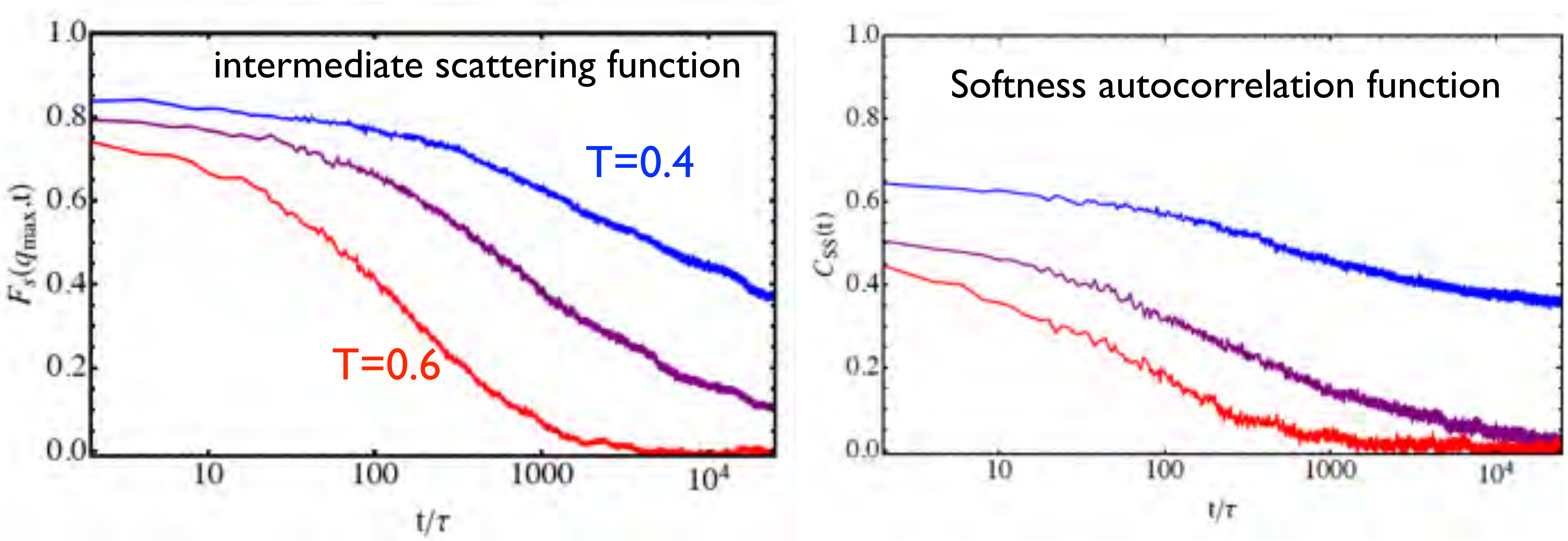
Rearranging Particles are Soft





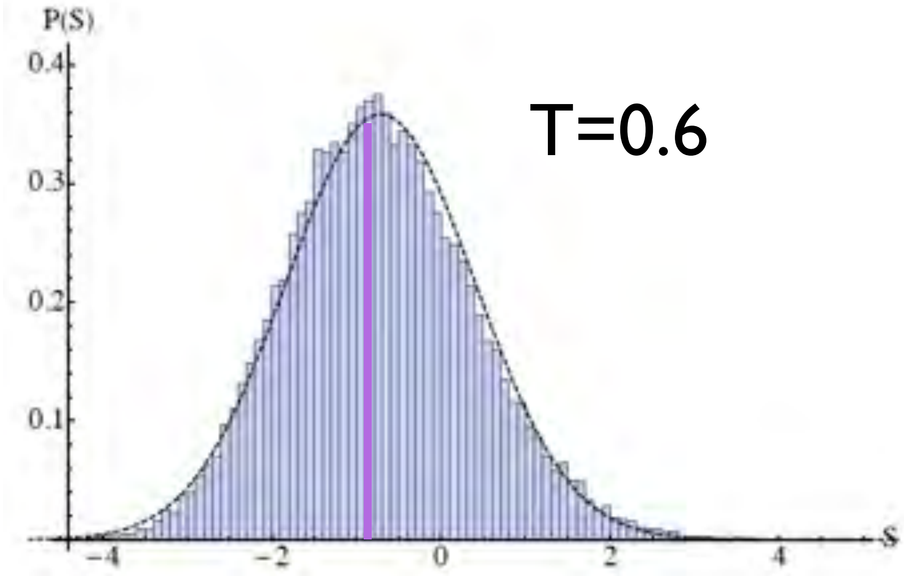
- Works well even at high temperatures (T_g=0.58)
  - At T=0.6, 24% of particles capture 72% of rearrangements (kinetic heterogeneities)
- average softness is high for rearranging particles
- Accuracy comparable in 2D and 3D

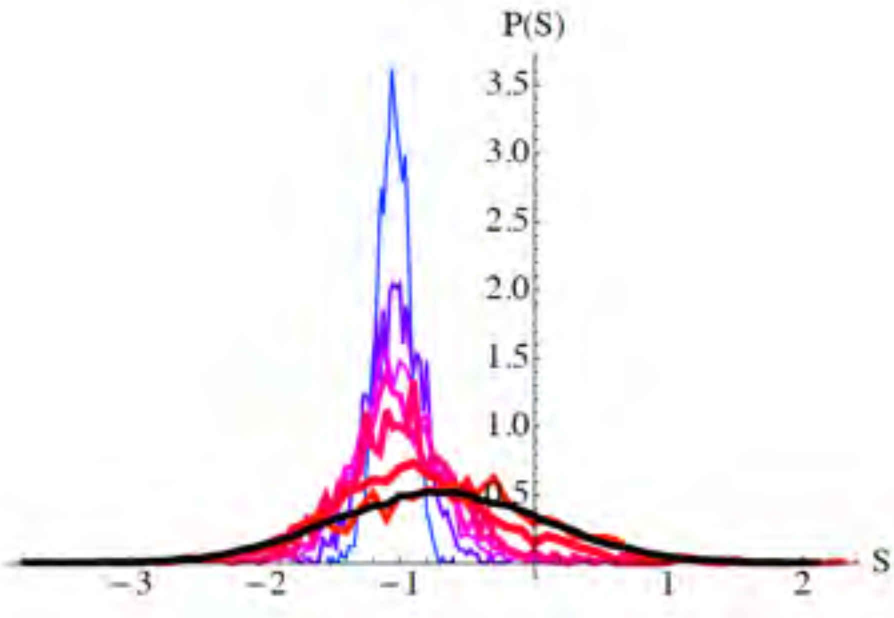
Softness Lifetime I



- Softness lifetime is comparable to relaxation time

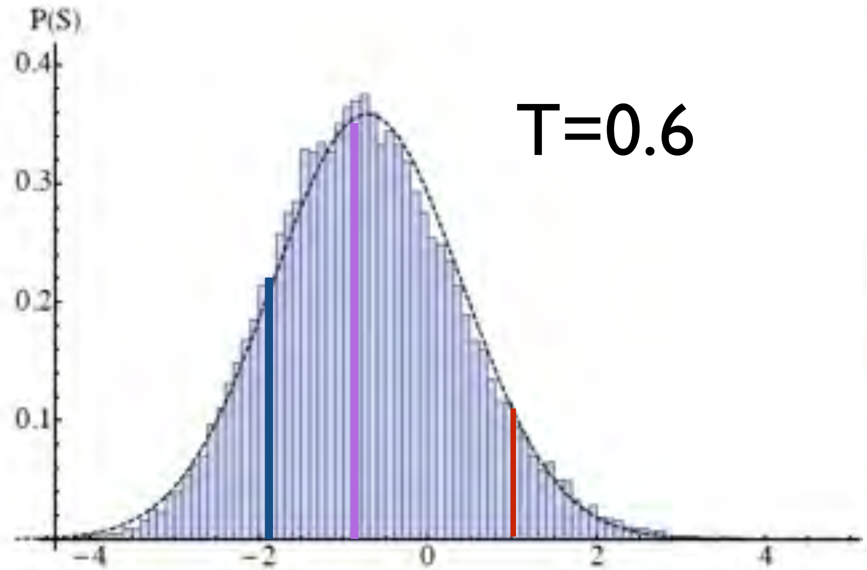
Softness Lifetime II

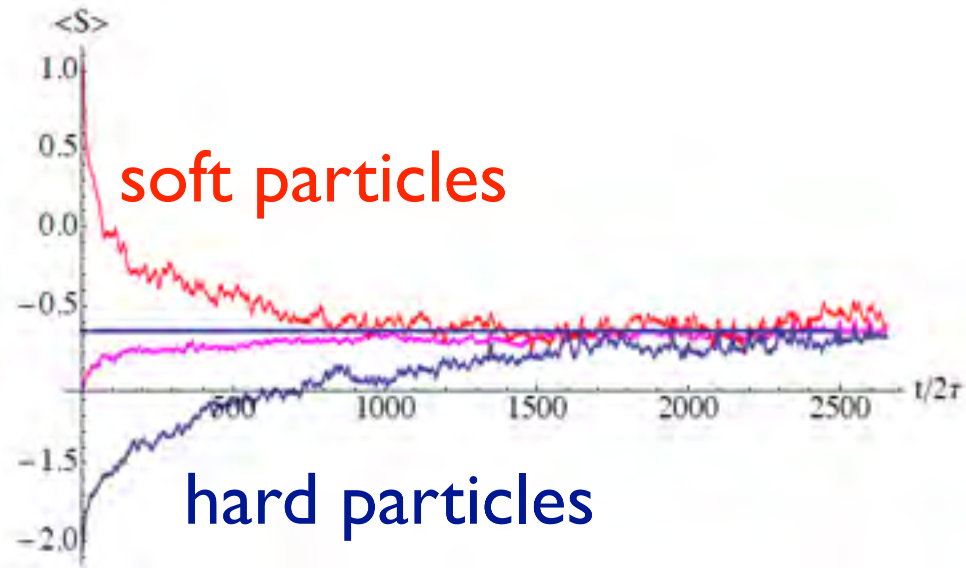


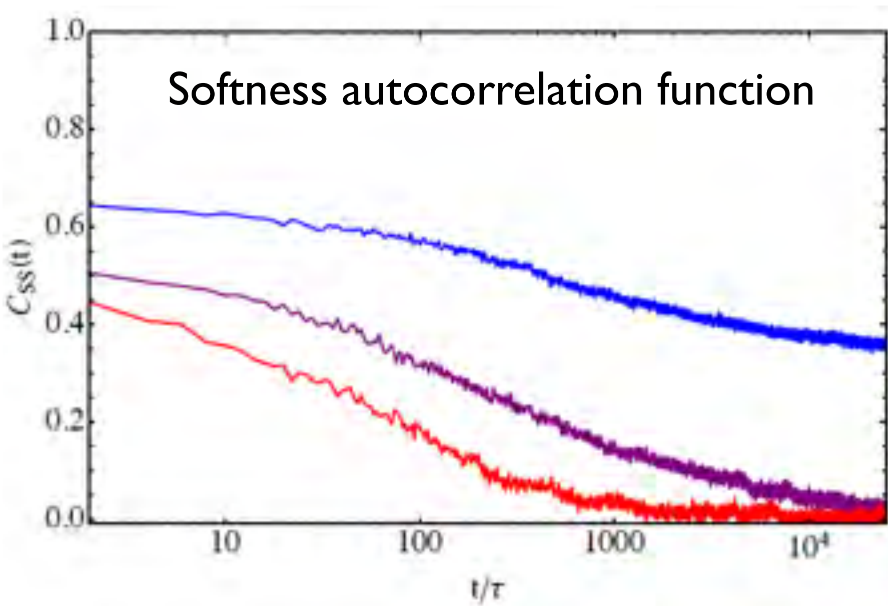


- Softness equilibrates over time to approach equilibrium softness distribution

Softness Lifetime III







- Soft particles equilibrate faster than hard particles
- Softness is promising as structural signature of kinetic heterogeneities

Dividing Surface Contains Physics

- Recall structural variables

$$S_Y^X(i;\mu) = \sum_j e^{-(R_{ij}-\mu)^2/L^2}$$

$$Q_{YZ}^X(i;\xi,\lambda,\zeta) = \sum_j \sum_k e^{-(R_{ij}^2+R_{ik}^2+R_{jk}^2)/\xi^2}(1+\lambda\cos\theta_{ijk})$$

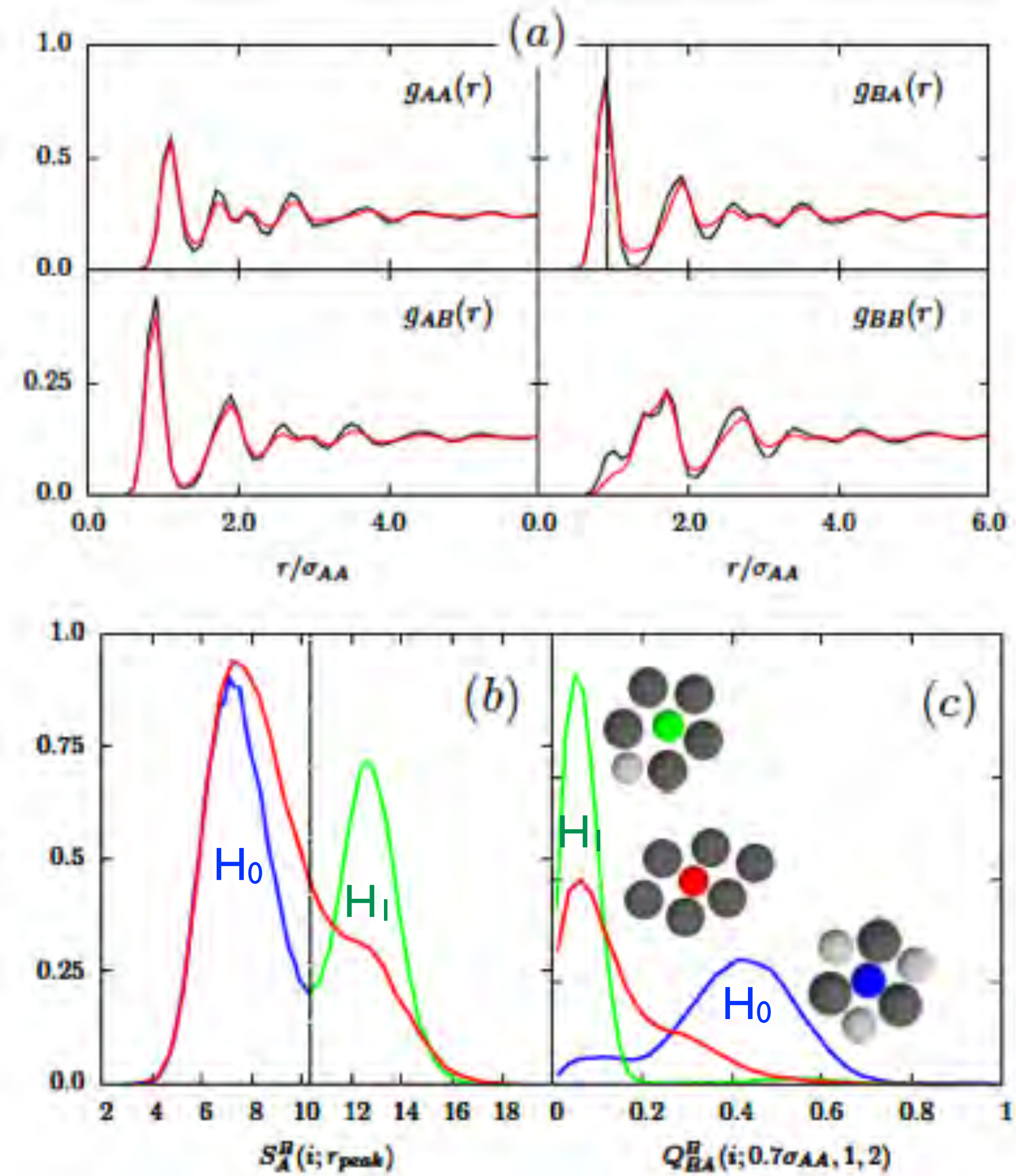
- S measures radial density

- Q measures relative bond orientation

- Note $g_{XY}(r) = \lim_{L\to 0} \frac{1}{N}\sum_{i=1}^{N} S_Y^X(i;r)/2\pi r$ so S corresponds to local g(r)

How are Soft Particles Different?

- Soft particles (red) are more "liquidlike" than system as whole
- S distinguishes between soft particles and H_1 particles but not soft and H_0
- Q distinguishes between soft and H_0 but not soft and H_1
- Need both S and Q (at least)



Conclusions

- Quasilocalized modes yields structural signatures of mobility near free surfaces and at flow defects
- Soft particles are structurally distinct, but in subtle ways that we can pick out using machine learning methods
- SVM method
  - Promising for identifying particles likely to rearrange under temperature or stress
  - Fast, and only requires positions of particles, not interactions
  - Works on experimental as well as simulation data!

QLM: Thanks to

Lisa Manning

Daniel Sussman

Carl Goodrich

Sid Nagel

DOE

SVM: Thanks to

Sam Schoenholz

Brad Malone

Dogus Cubuk

Tim Kaxiras

UPenn MRSEC

Jennifer Rieser

Joerg Rottler

Doug Durian