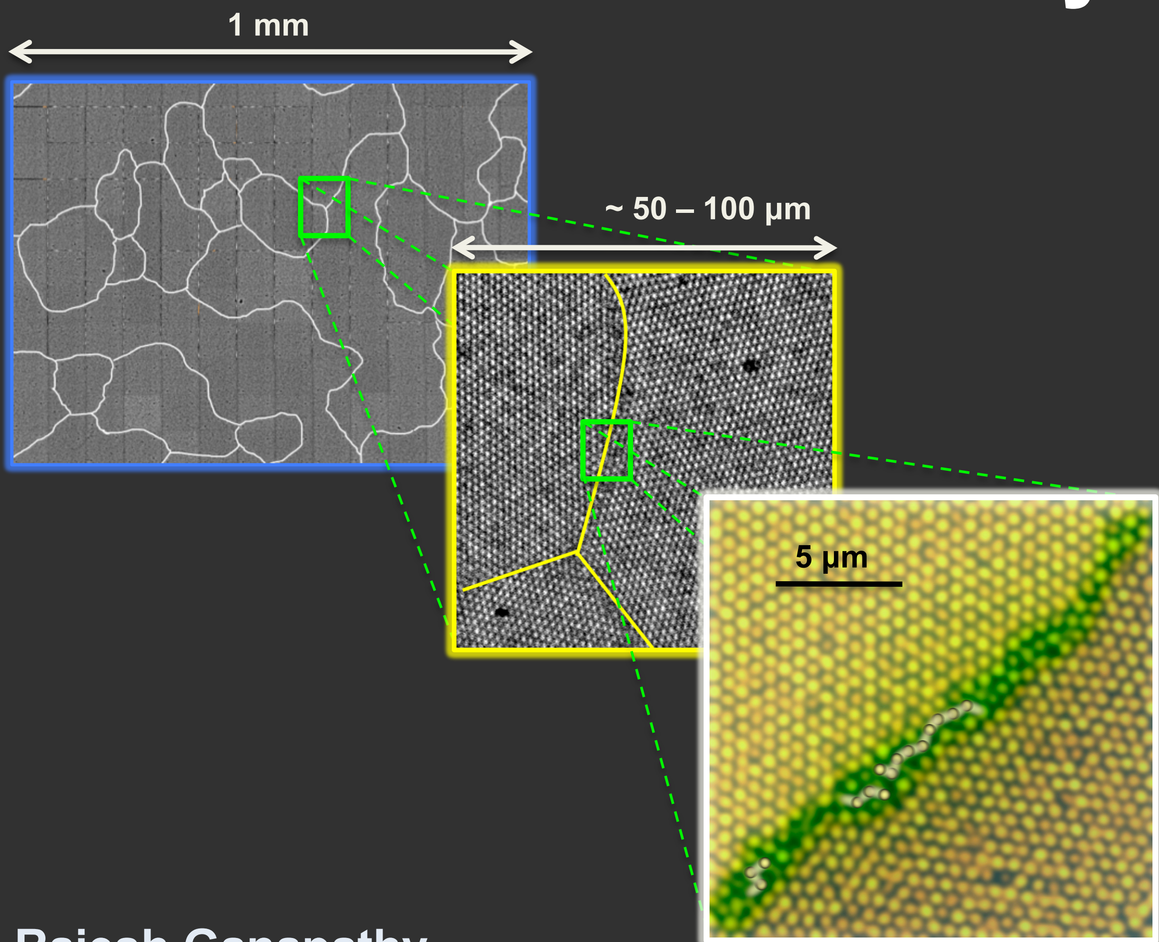
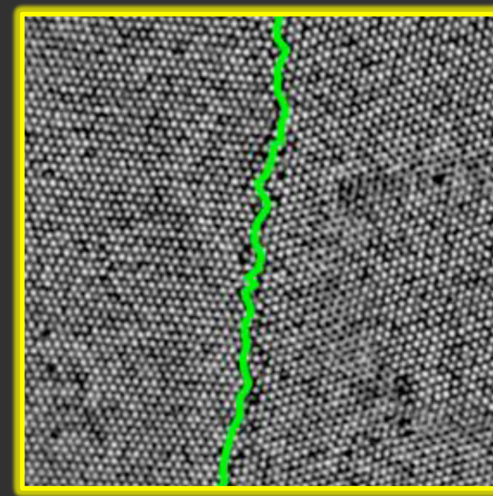
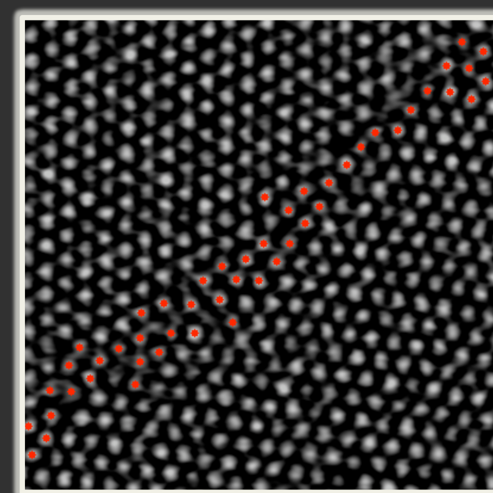
Grain Boundary Dynamics In Colloidal Crystals



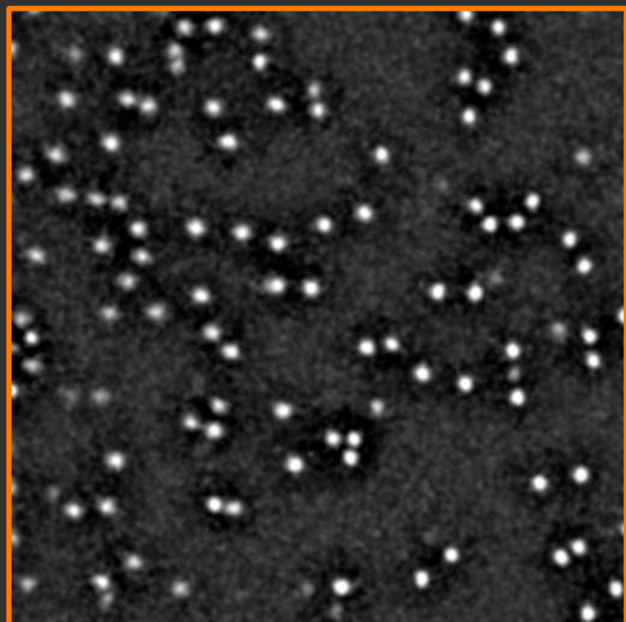




Rajesh Ganapathy
International Centre for Materials Science
JNCASR, Bangalore 560064

Collaborators: Hima Nagamansa (JNCASR), Shreyas Gokhale (IISc), Ajay Sood (IISc, JNCASR)

What Is A Colloidal Suspension?



Small objects suspended in a fluid

examples:

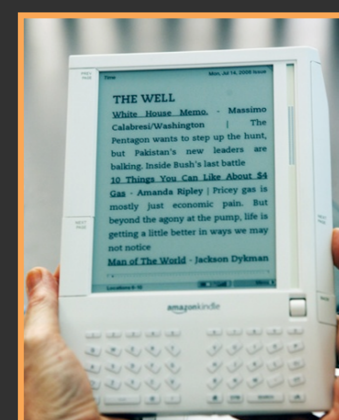
Milk – Fat particles in water

Tooth paste – Glass beads in water

Exhibit Brownian Motion

<u>INDUSTRIALLY IMPORTANT</u>

Coatings, electro-optical devices, lubricants, bio-rheology, etc.



Amazon Kindle e-book

Physics And Colloids?

- **Ising model of soft condensed matter:**

Particle number density is very large (typically $n_c \sim 10^{13}$/ml). Ideal for studying statistical mechanics phenomena.

- ❖ **Glasses**
- ❖ **Rheology – jamming, shear-thinning, shear-banding**
- ❖ **Phase transitions**

- **Models for atomic systems**

Thermal capillary waves

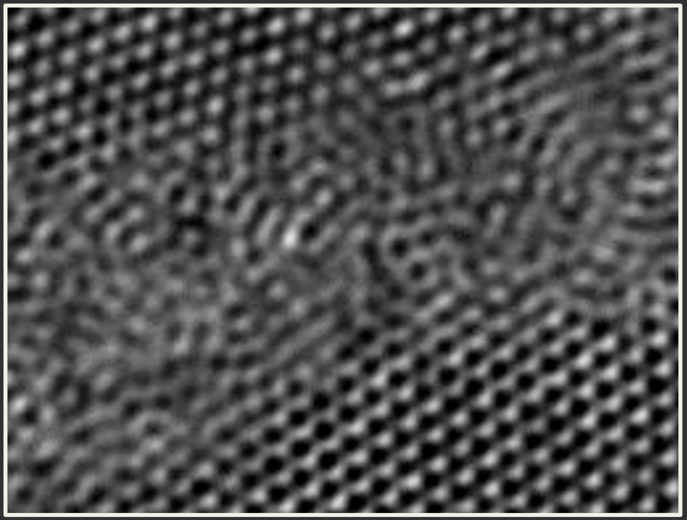
D. G. A. L. Aarts et al., Science 304, 847 (2005)

Premelting at Grain Boundaries

A. M. Alsayed et al., Science 309, 1207 (2005)

Epitaxial Growth

Rajesh Ganapathy et al., Science 327, 446 (2010)



Advantage

Study dynamics at single-particle resolution

Grain Boundaries

Grain Boundaries

Grain Boundaries (GBs): Structurally disordered interface that separates adjacent regions with different crystallographic orientation.

- ❖ GBs very crucial in deformation mechanisms, crack propagation, recrystallization kinetics, transport properties ….
- ❖ As grain sizes approach ~ nm dimensions, grain boundaries can occupy as much as ~ 30% - 40% of the material.

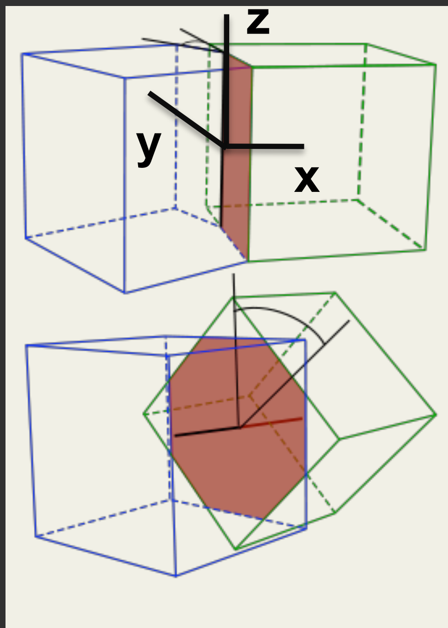
Enhance material properties by engineering GB architecture

(a) Alloying/ adding impurities

(b) Thermal + Mechanical Processing

Key: Microstructure and Dynamics of GBs

Quantifying Grain Boundaries



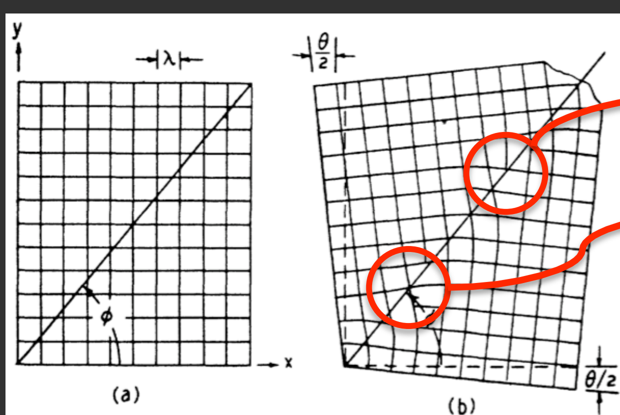
Define GB interface by five parameters

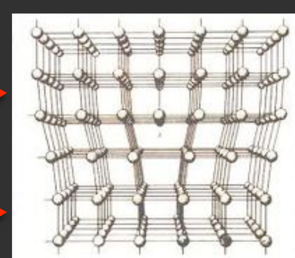
Θ, Ψ: Tilt angles (rotation axis in GB plane)
Φ: Twist angle (rotation axis perpendicular to GB Plane)
n_1, n_2: Interface surface normals

GB Classification

1) Low Angle GB (LAGB): Θ,Ψ,Φ < 12°
2) High Angle GB (HAGB):Θ,Ψ,Φ > 12°

Read-Shockley Model





LAGB: Planar array of discrete dislocations.

HAGB: Needs many dislocations.

Dislocation cores overlap leading to an continuous disordered interface

W. T. Read, W. Shockley, Physical Review 78, 275 (1950)

Motivation

Are HAGBs analogous to glasses?

❖ Brillouin (1898), Quincke (1905), Rosenhain (1913)

(to explain GB embrittlement observed at low temperatures)

M. Brillouin, Ann. Chem. Phys. 13, 77 (1898); G. Quincke, Proc. Roy. Soc. A 76, 431 (1905); W. Rosenhain, D. Ewen, J. Inst. Met. 10, 119 (1913).

❖ Ashby (1964): Bubble Raft experiments

M. F. Ashby, Surf. Sci. 31, 498 (1972)

❖ Wolf (2001), Warren (2009): Molecular Dynamics Simulations

D. Wolf, Curr. Opn. Sol. State Mat. Sci 5, 435 (2001)

H. Zhang, D. J. Srolovitz, J. F. Douglas, J. A. Warren, Proc. Nat. Acad. Sci., U.S.A. 106, 7735 (2009)

Glassy HAGBs – HAGB properties should be independent of Θ,Ψ,Φ as GB structure is isotropic

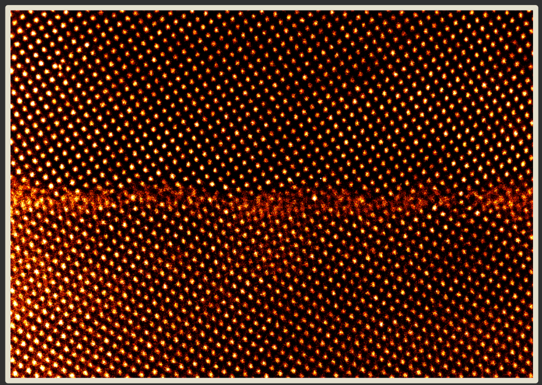
Experiments - HAGB properties depend on Θ,Ψ,Φ

Atomic experiments

High-Resolution Transmission Electron Microscopy (Limitations: Access to dynamics)

MD Simulations

Usually performed under external driving forces and/or at high temperatures.



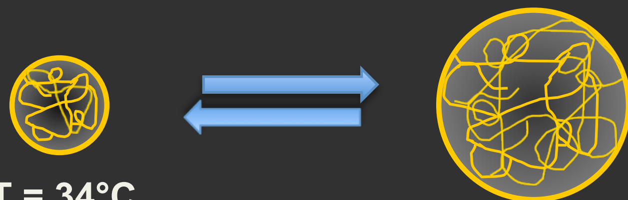
Ingredient 1: Realizing Colloidal GBs

Probe GB dynamics dependence with

(1) Mis-orientation angle (Φ,Ψ,θ)

(2) Temperature (T) (for colloids $1/\varphi_{Particle}$)

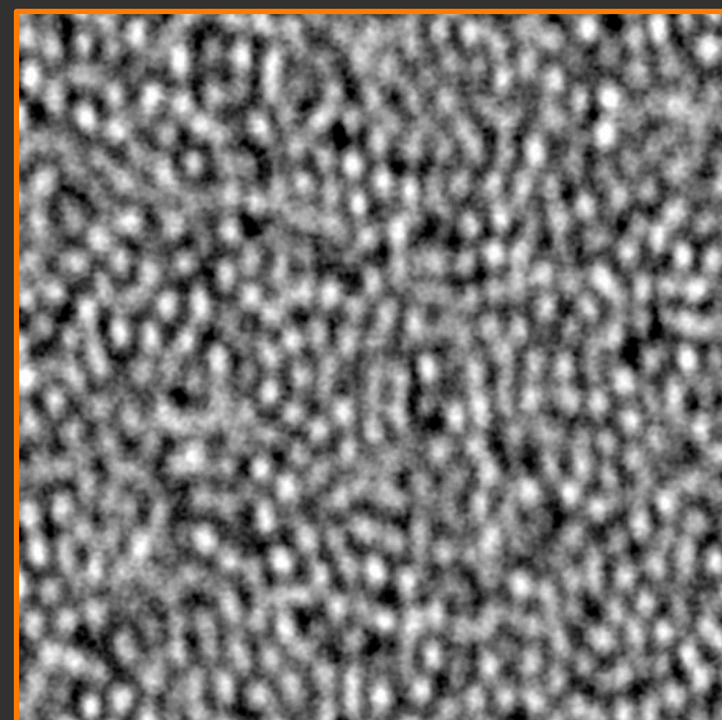
Colloids: PNIPA poly(N-isopropylacrylamide)



T = 34°C
Size ~ 350 nm

T = 27°C
Size ~ 620 nm
$\varphi_{Particle}$~ 70% at 27°C

Volume fraction can be changed in-situ



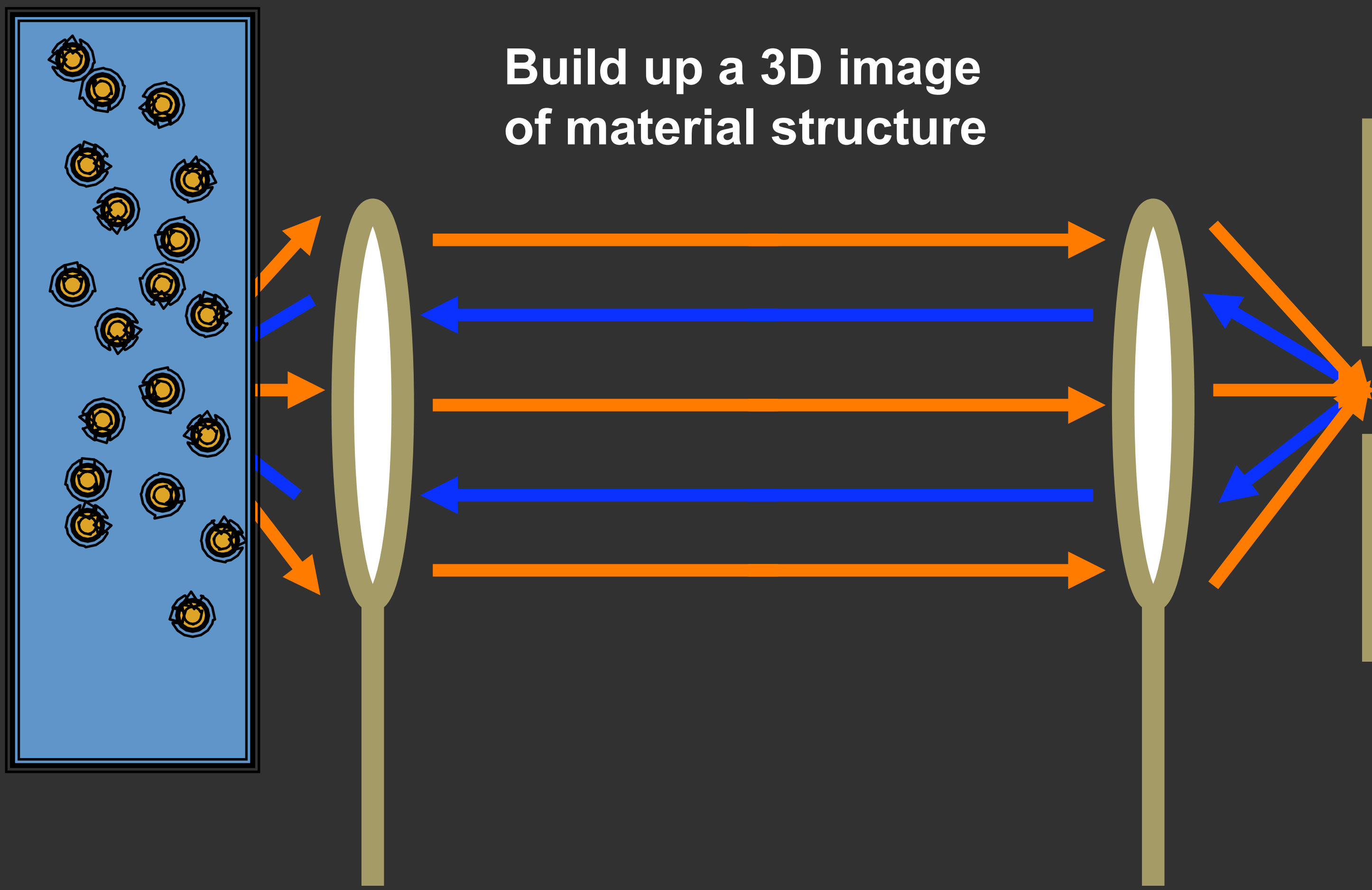
System: PNIPA-AAc Colloids
Rhodamine 6G Flurophore

Samples loaded in glass cells and sealed.
Crystal ~ 40 colloid layers thick.

Annealing sample yields distribution of Θ's

Ingredient 2: Imaging Colloidal GBs

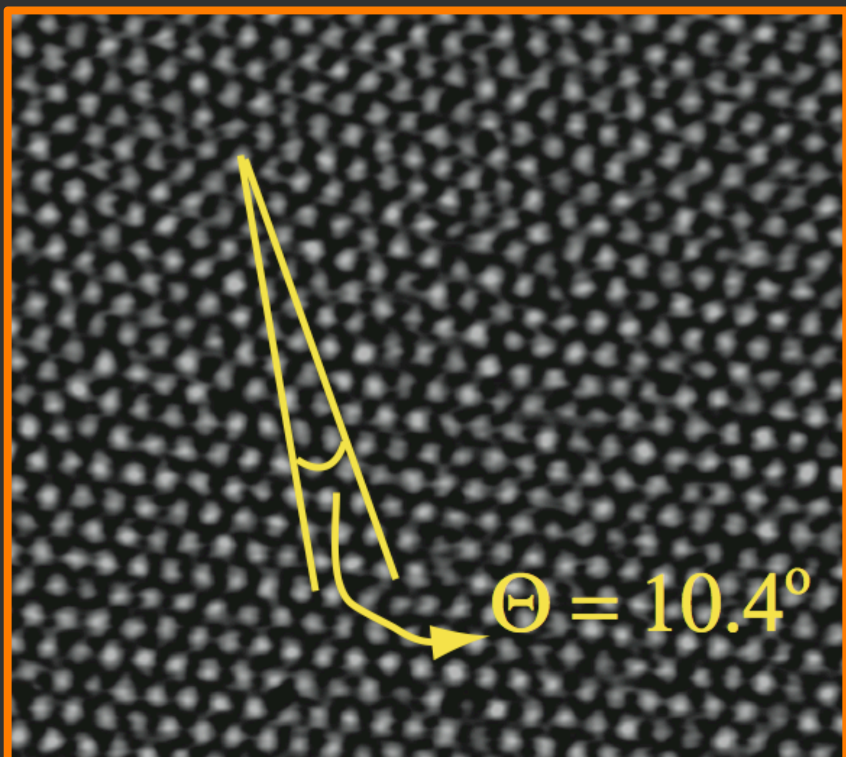
Confocal Microscopy



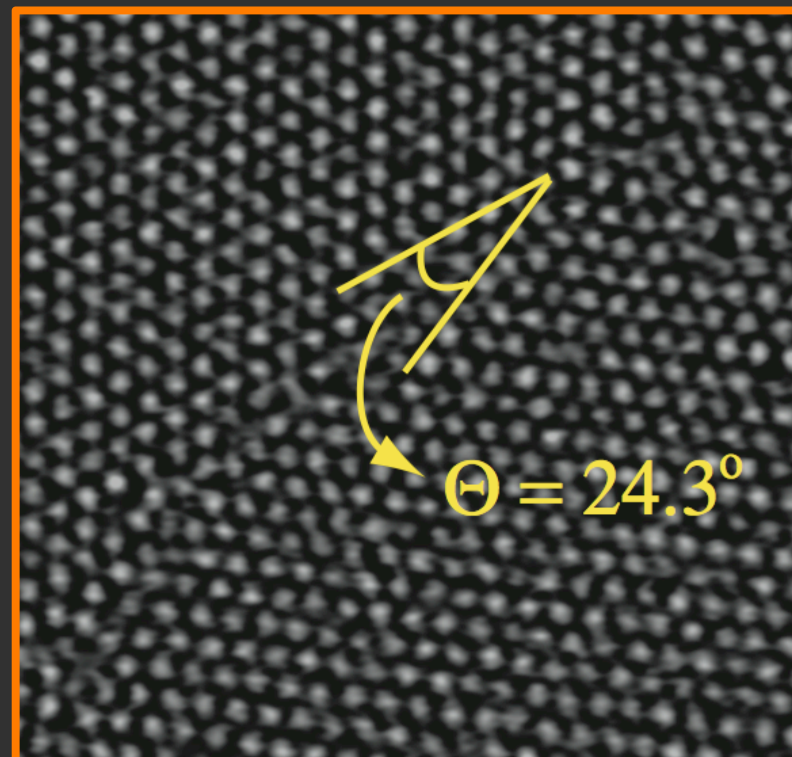
Colloidal Grain Boundaries

Pure Tilt Boundaries

LAGB



HAGB

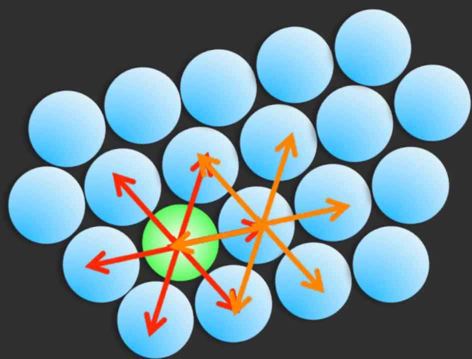


Annealing sample yields distribution of Θ's

Identifying GB Colloids

GB colloids have lower coordination number

- Use order-parameter sensitive to symmetry.



2D Halperin-Nelson Bond-Order Parameter

$$\psi_6(j) = (1/N)\Sigma_k \exp(6i\theta_{jk})$$

N: # of nearest-neighbors
j & k are nearest-neighbors if j-k bond length < 1.4σ

For dense amorphous regions ψ_6 can be high and hence insufficient to label GB colloids.

Look for # of ordered nearest-neighbors (N_o)

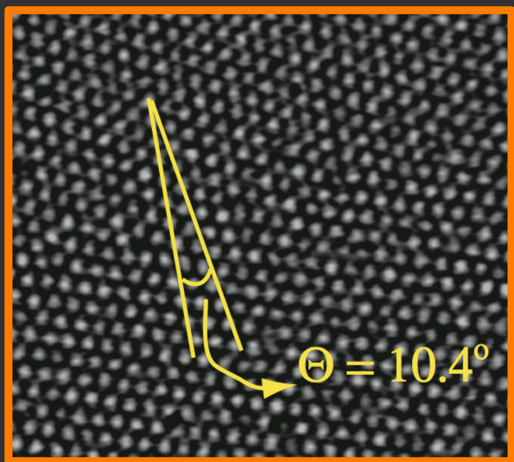
$$\psi_6(j)\psi_6(k)^* > 0.5$$

$N_o \geq 4$, particle is crystal-like
$N_o < 4$, particle is amorphous-like

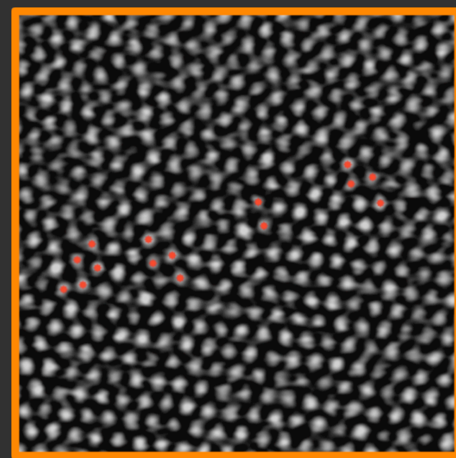
Particle may spend only part of the time as amorphous-like.
Particle has to spend at-least 50% of the time as amorphous-like to be labelled as GB colloid

GB Colloids

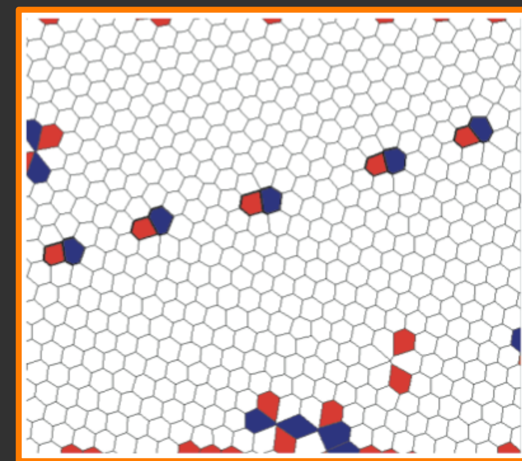
LAGB



Bond-order Analysis

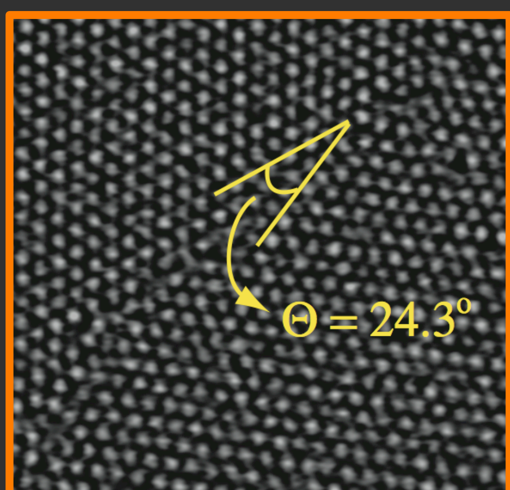


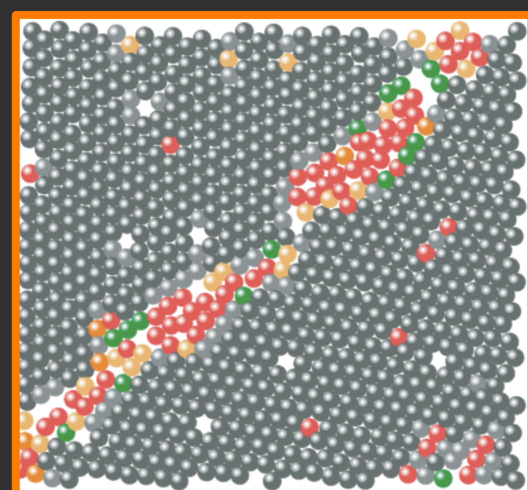
Voronoi Tessellation



Discrete Dislocation Cores

HAGB





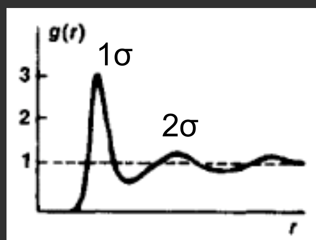
Particles color-coded as per N_o

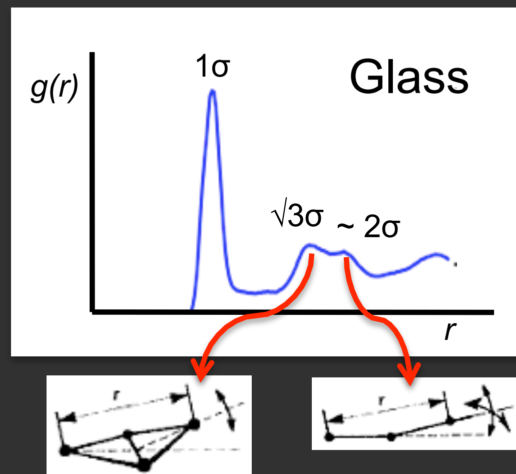
HAGB Structure

Quantify structure by radial pair-correlation function (PCF)

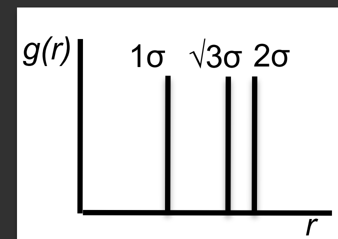
- measure the probability of finding a particle within a shell of radius r and thickness Δr

Liquid

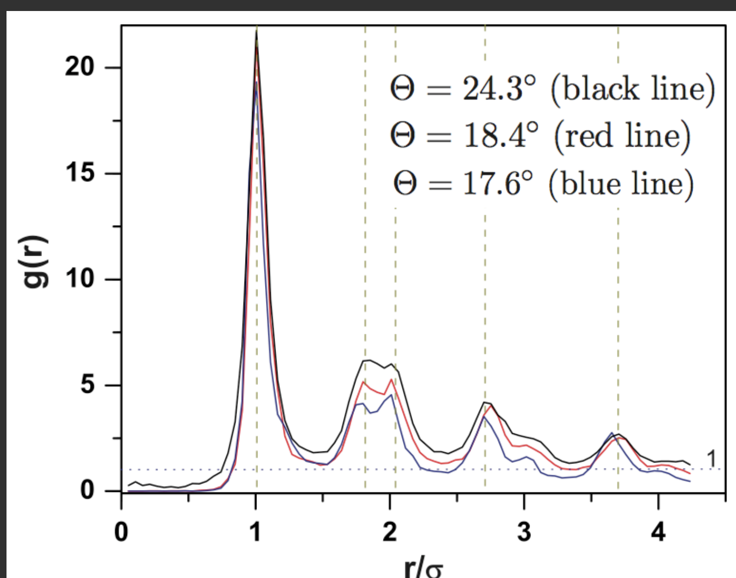




Crystal

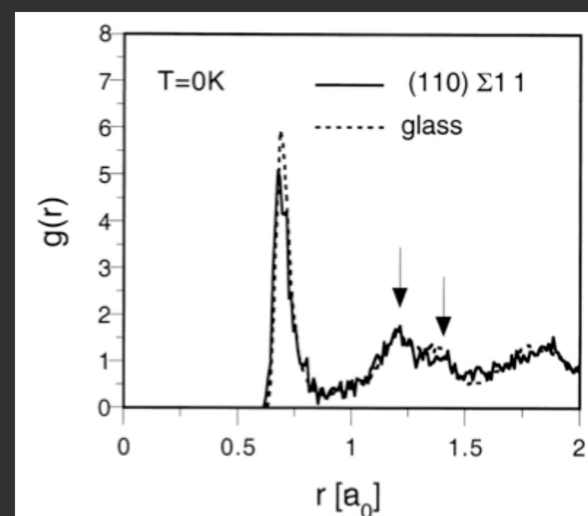


HAGB PCF



GB Width

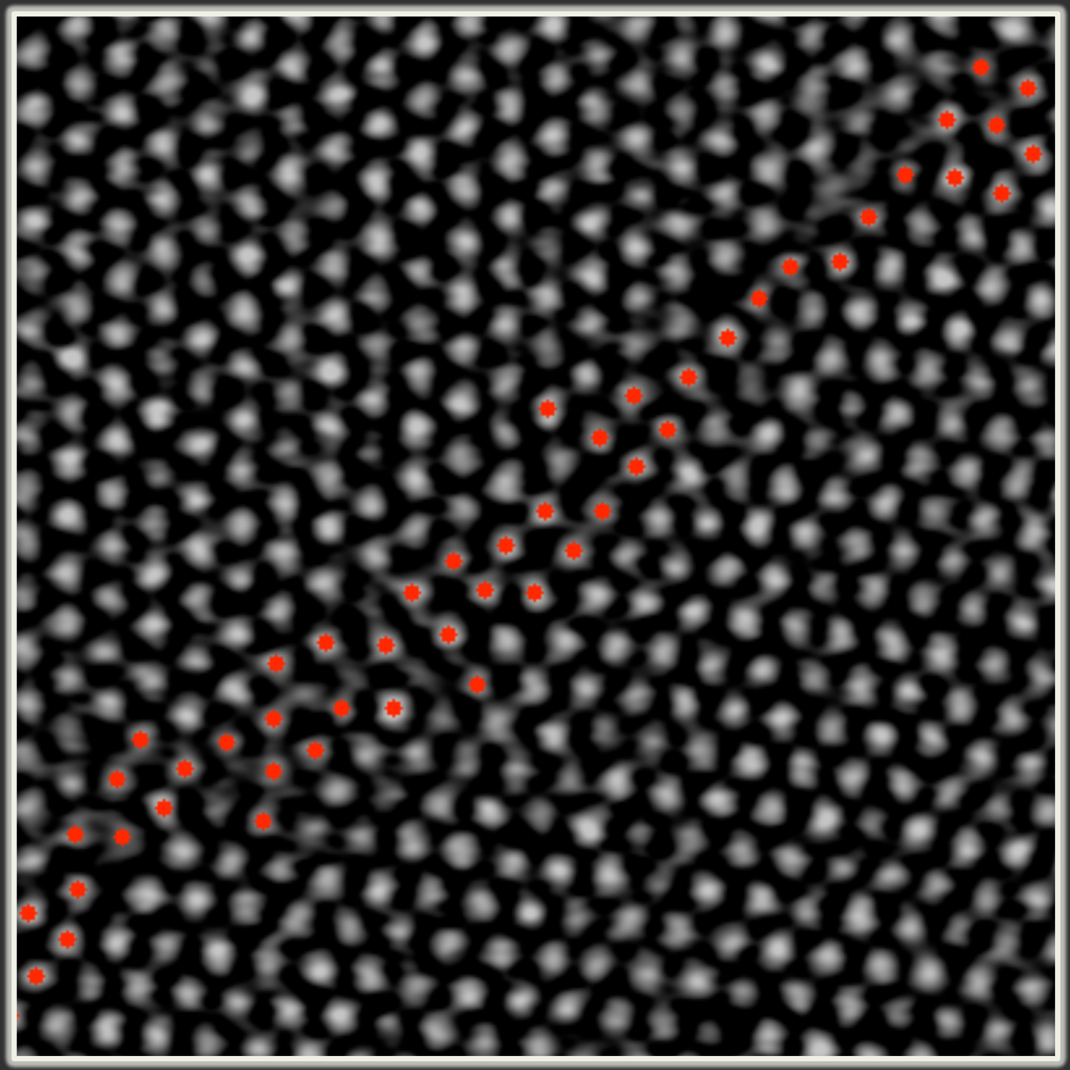
2.1 σ
1.8 σ
1.5 σ



D. Wolf, Curr. Opn. Solid State and Mat. Sci 5, 435 (2001)

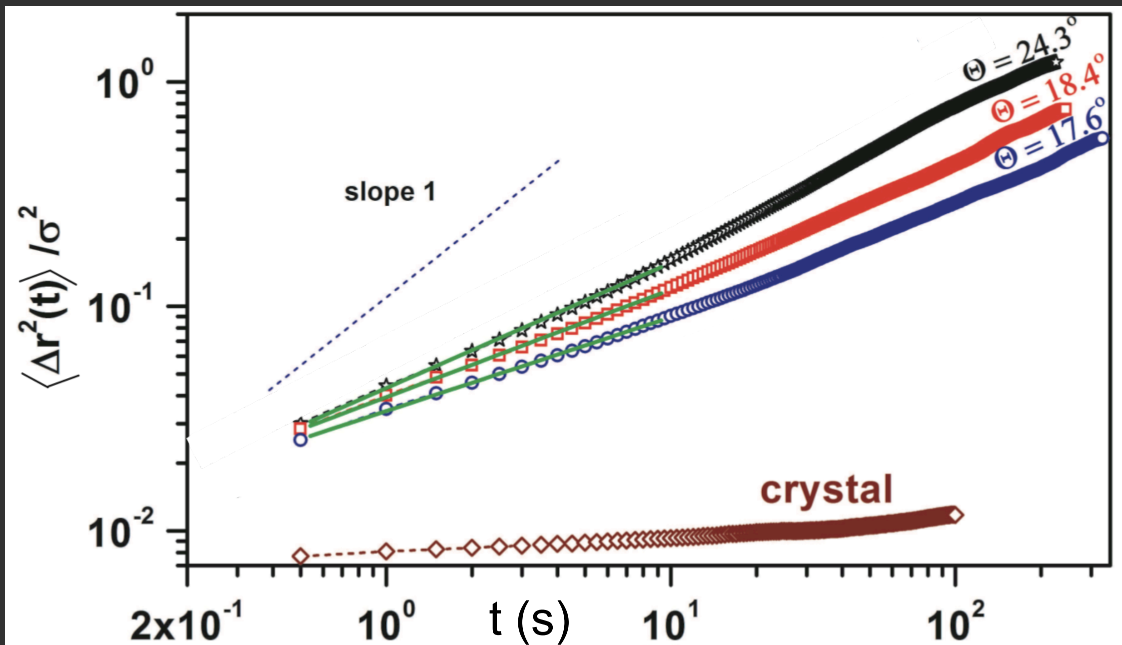
Hima Nagamanasa, Shreyas Gokhale, Rajesh Ganapathy, Ajay K Sood
*Proceedings of the National Academy of Sciences, U.S.A. **108**, 11323 (2011).*

HAGB Dynamics

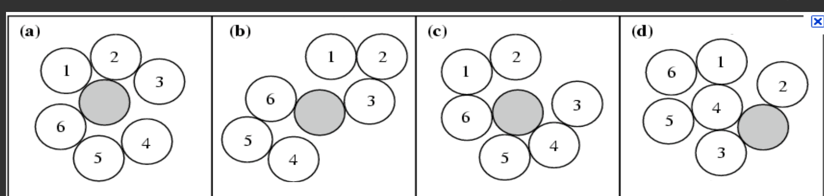


HAGB Dynamics – Mean Squared Displacement

Hima Nagamanasa, Shreyas Gokhale, Rajesh Ganapathy, Ajay K Sood
Proceedings of the National Academy of Sciences, U.S.A. ***108****, 11323 (2011).*

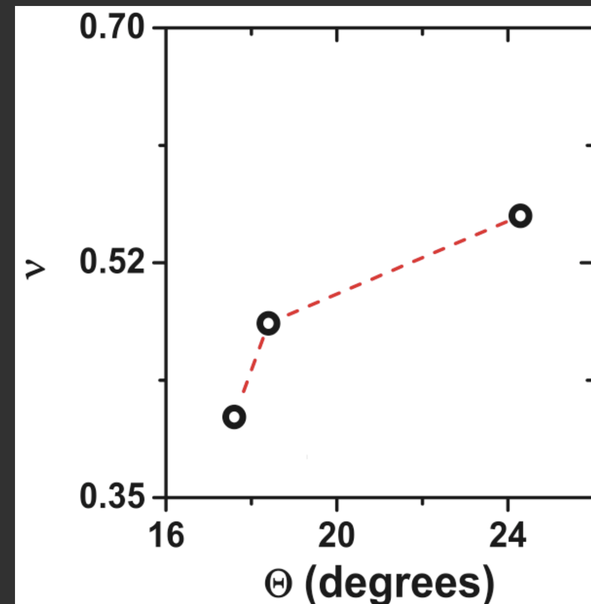


Glasses – Transient Cage Breaking



GB width increases as you near melting due to decrease in particle size

Fix Θ, change T



Systematic slowing down of dynamics for HAGBs with decreasing GB width

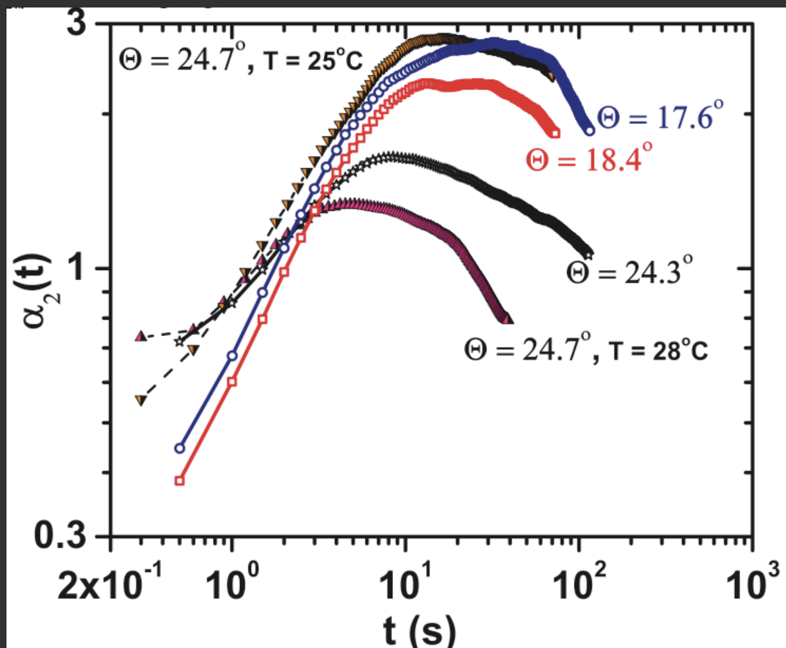
IS IT CONFINEMENT?

HAGB Dynamics – Non-Gaussian Displacements

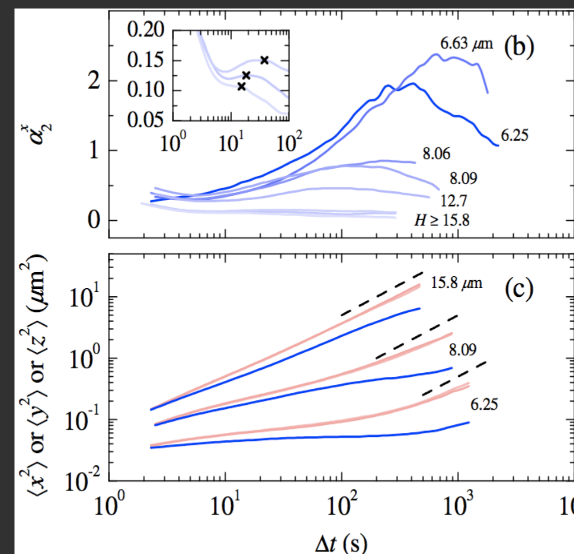
For glasses, particle displacements in the vicinity of the cage-breaking time are non-Gaussian

$\alpha_2(\Delta t) = (\langle \Delta r^4 \rangle / 2 \langle \Delta r^2 \rangle^2) - 1$

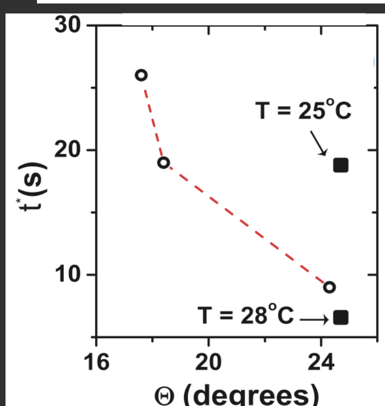
For diffusive behavior, $\alpha_2(t) = 0$

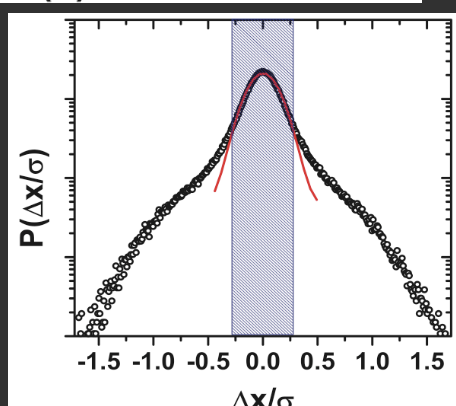


Confined Colloidal Glasses



Eric Weeks 2010 (Unpublished)



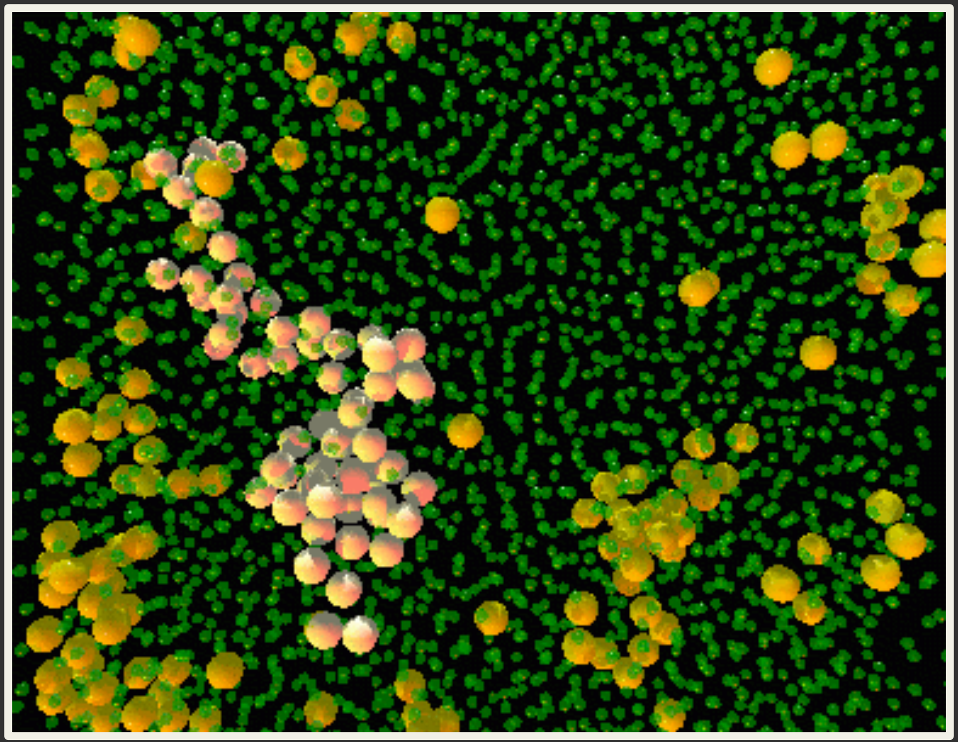


1. Misorientation angle-dependent confinement leads to slowing down dynamics
2. HAGBs become more glassy with decreasing Θ

Glasses - Cooperatively Rearranging Regions (CRRs)

Dramatic slowing down in dynamics as you approach the glass transition with no apparent change in structure.
CRRs – Pathway for structural relaxation in super-cooled fluids

Bulk Colloidal Glass



Eric Weeks – Emory University
http://www.physics.emory.edu/~weeks/lab/bumpy.html#1

CRRs grow in size as the glass transition is approached.

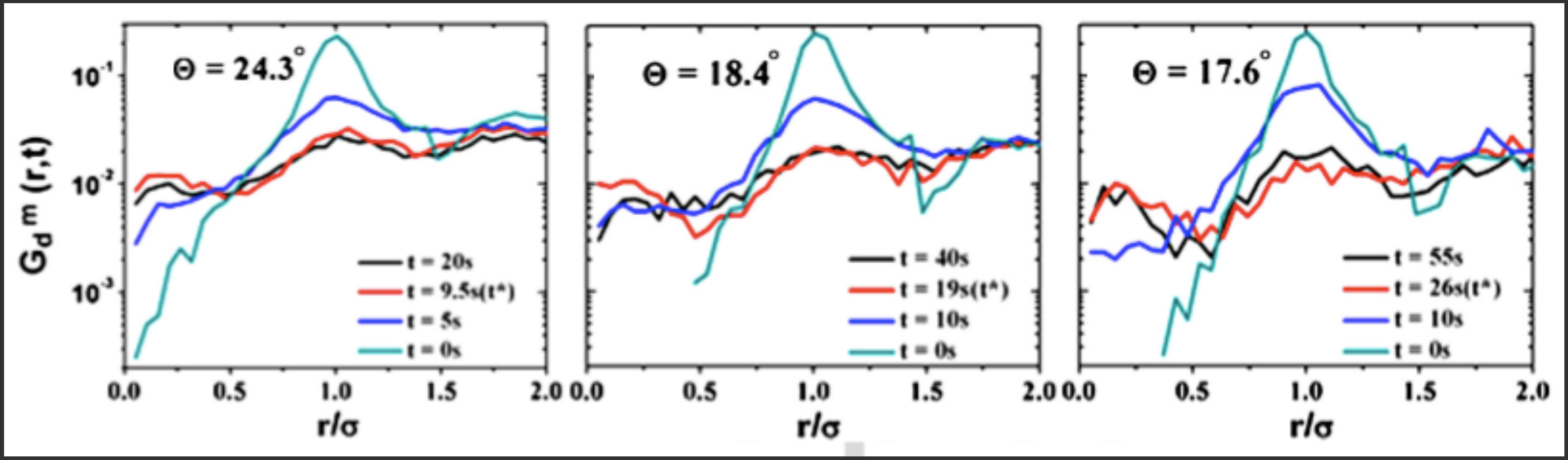
G. Adam, J. H. Gibbs, J. Chem. Phys. 43, 139 (1965)

HAGB Dynamics – Cooperative Motion

Distinct part of van Hove Correlation function quantifies particle replacements at cage breaking time *t**

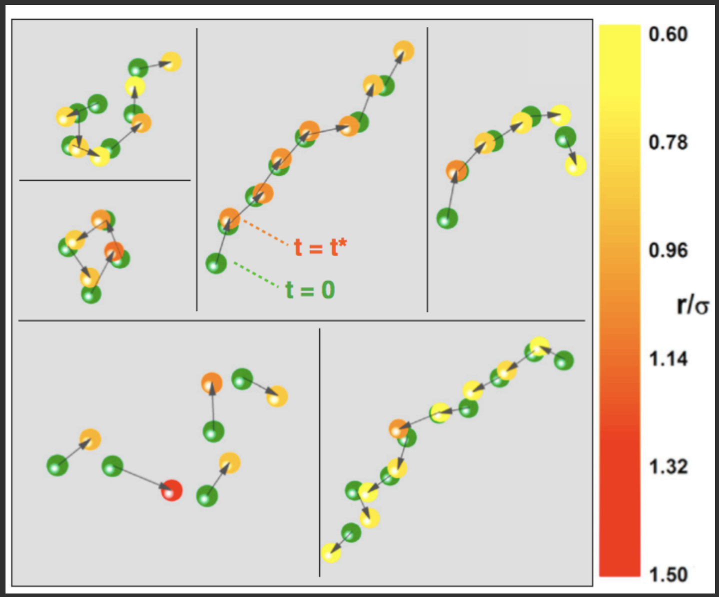
$$G_d^m(\mathbf{r},t) = N^{-1}\left\langle \sum_{j\neq i=1}^{N} \delta\left[\mathbf{r} + \mathbf{r}_j(0) - \mathbf{r}_i(t)\right] \right\rangle$$

top 10% most mobile particles

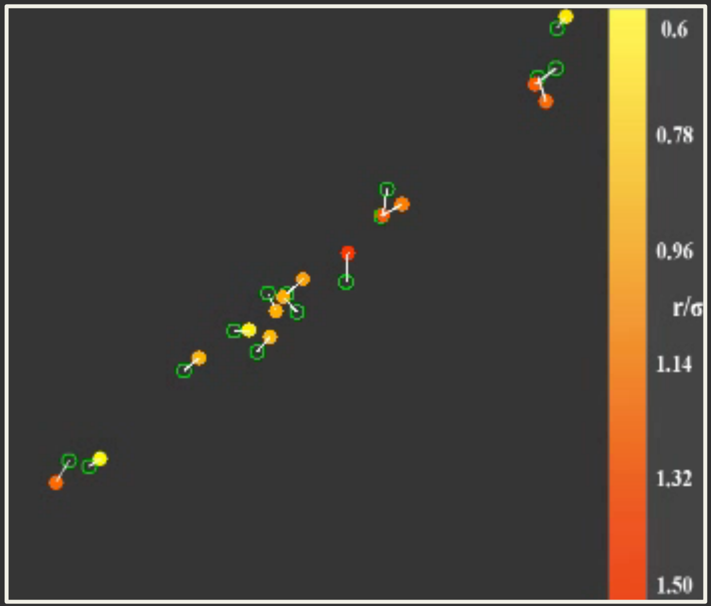


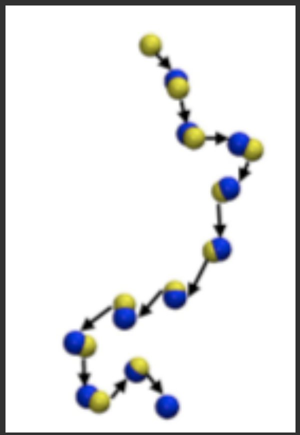
HAGB Dynamics – CRRs

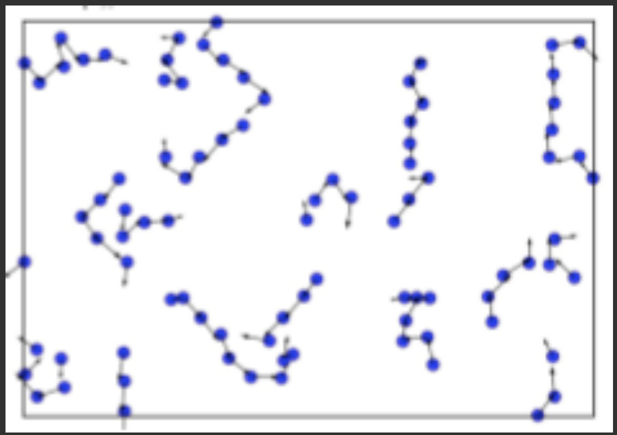
HAGB (Θ = 24.3°)



Displacement of the top 10% of most-mobile particles over time t*





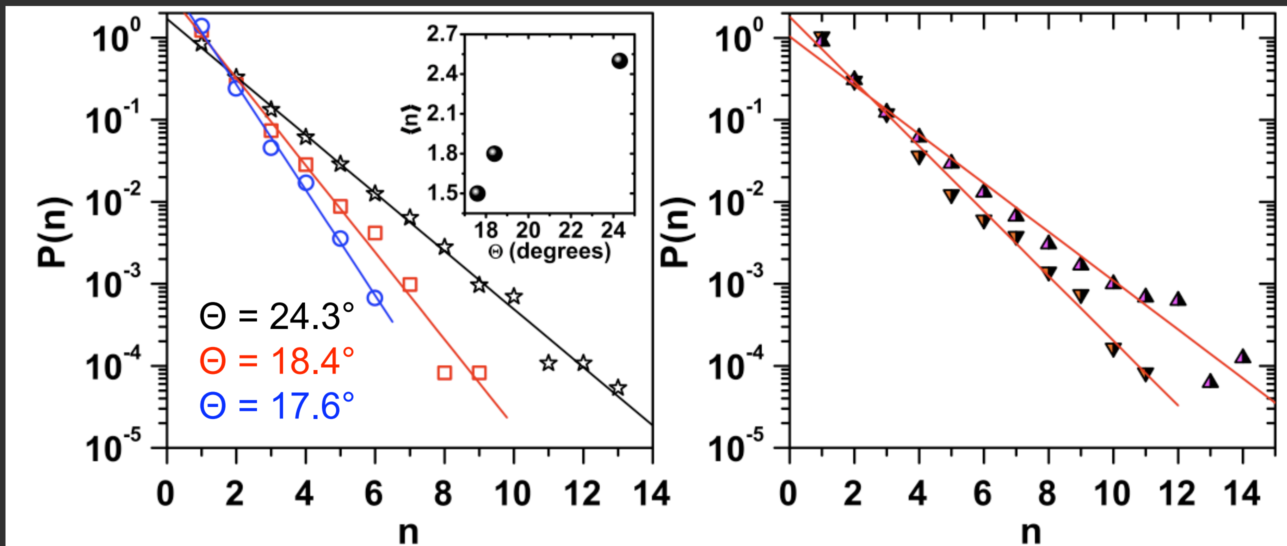


MD Simulations

H. Zhang, D. J. Srolovitz, J. F. Douglas, J. A. Warren, Proc. Nat. Acad. Sci., U.S.A. 106, 7735 (2009)

HAGB Dynamics – CRRs

Probability distribution of string lengths



CRR size increases with Θ

C. Donati, J. F. Douglas, W. Kob, S. J. Plimpton, P. H. Poole, S. H. Glotzer, Phys. Rev. Lett. 80, 2338 (1998)
H. Zhang, D. J. Srolovitz, J. F. Douglas, J. A. Warren, Proc. Nat. Acad. Sci., U.S.A. 106, 7735 (2009)

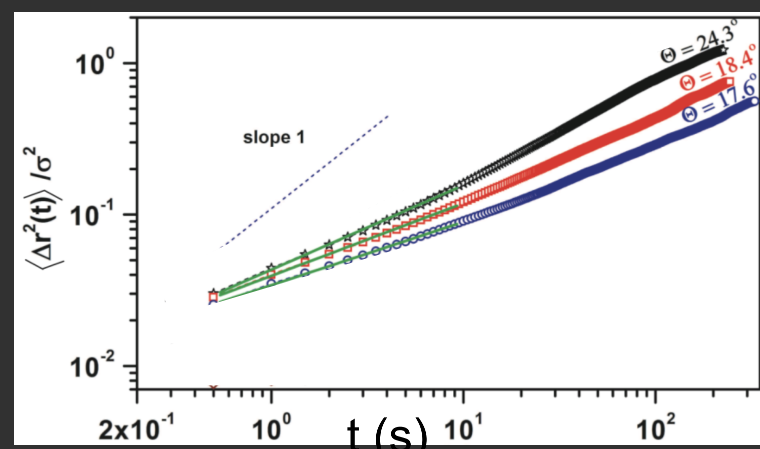
Recall

Dynamics become faster with increasing Θ

Adam Gibbs hypothesis

The size of CRRs decreases as dynamics become faster for bulk glasses

G. Adam, J. H. Gibbs, J. Chem. Phys. 43, 139 (1965)



GRAIN BOUNDARIES ARE CONFINED GLASSES

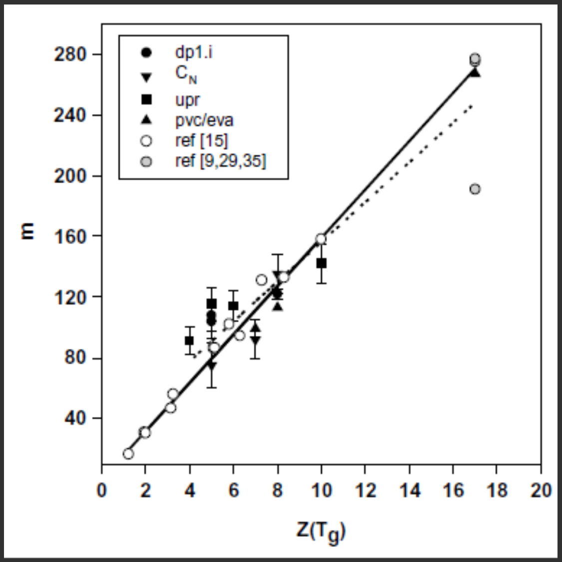
Confinement *Changes* Fragility

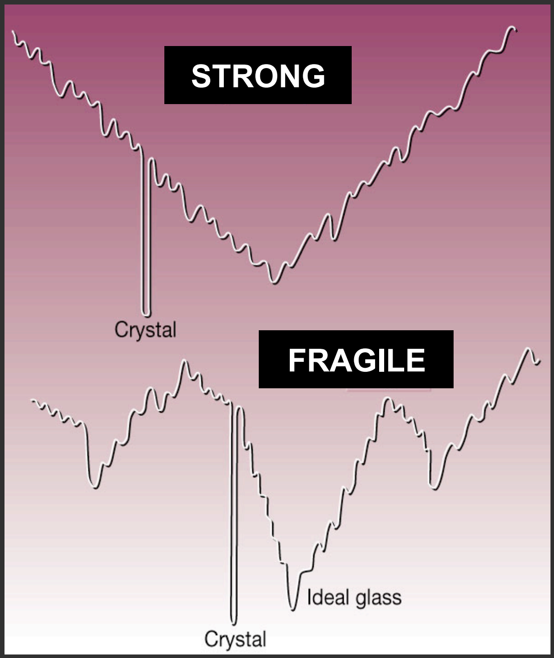
Fragility quantifies the deviation of the temperature dependence of viscosity from Arrhenius behavior

Angell CA, J Phys Chem Solids 49,863 (1988) .

Confinement can reduce fragility

R. A. Riggleman, K. Yoshimoto, J. F. Douglas, J. J. de Pablo Phys. Rev. Lett. 97, 045502 (2006)





Debenedetti PG, Stillinger FH, Nature 410, 259 (2001)

Size of CRRs increases with fragility

Saiter A, Saiter JM, Grenet J, Eur Poly J 42, 213 (2006)

Confinement reduces the fragility, which in turn results in a decrease in size of CRRs

Summary

- Direct observation of glassy dynamics at grain boundaries.
- Misorientation-angle dependent confinement imparts misorientaion angle dependent properties for HAGBs

Hima Nagamanasa, Shreyas Gokhale, Rajesh Ganapathy, Ajay K Sood
Proceedings of the National Academy of Sciences, U.S.A. ***108****, 11323 (2011).*

Acknowledgements

Grain Boundary & Shear

Hima Nagamanasa
ICMS, JNCASR

Shreyas Gokhale
Physics, IISc

Santhosh

Prof. Ajay K Sood
Physics, IISc

Prof. Bulbul Chakraborty (Brandeis)
Prof. Chandan Dasgupta (IISc)

Prof. CNR Rao

Financial support: ICMS, JNCASR