Colloidal Glasses

Dave Weitz Harvard

Hans Wyss	TUEindhoven	Jaci Conrad	Houston
Frans Spaepen	Harvard	Eric Weeks	Emory
Dave Reichmann	Columbia	Christoph Eisenman	Munich
Johan Mattsson	Leeds	Param Dhillon	Berkeley
Chanjoong Kim	Kent State	Veronique Trappe	Fribourg
Al Fernandez-Nieves	GIT	Zhibing Hu	Texas St.

- Relaxation in supercooled colloidal liquiuds
- Flow of colloidal glasses
- Microgel glasses → analogy to molecular glasses

NSF, MRSEC, NASA

http://www.seas.harvard.edu/projects/weitzlab

KITP 6/25/10

Colloidal Crystals & Glasses

Dave Weitz Harvard

Elie Sloutskin	Bar Ilan	Peter Lu	Harvard
Hans Wyss	TUEindhoven	Jaci Conrad	Houston
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Chanjoong Kim	Kent State	Veronique Trappe	Fribourg
Al Fernandez-Nieves	GIT	Zhibing Hu	Texas St.

- Crystal nucleation in colloidal hard spheres
- Relaxation in supercooled colloidal liquiuds
- Flow of colloidal glasses
- Microgel glasses → analogy to molecular glasses

NSF, MRSEC, NASA

http://www.seas.harvard.edu/projects/weitzlab

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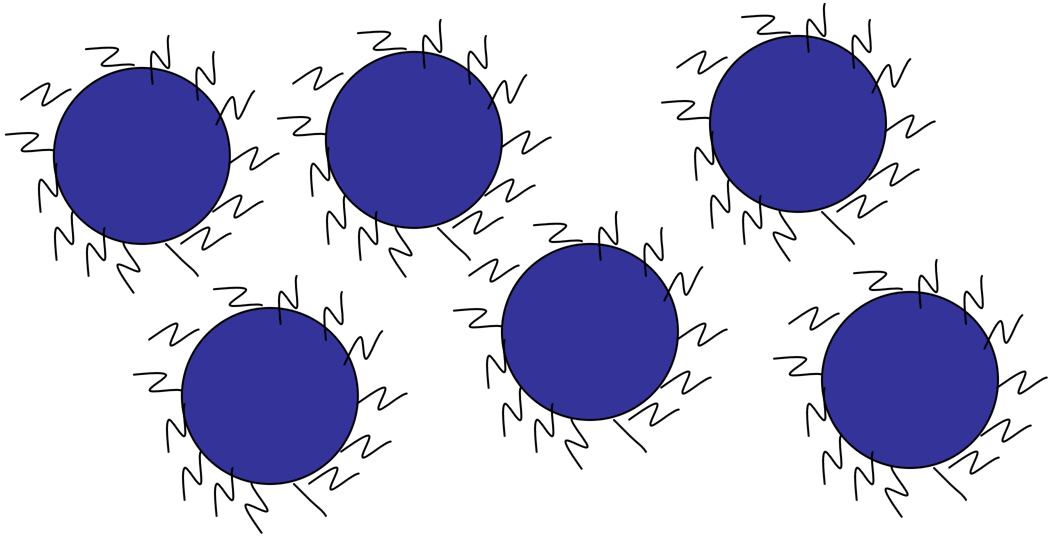
Colloidal Particles



Stability:

Short range repulsion

Sometimes a slight charge

Colloid Particles are:

•Big

•~ a ~ 1 micron

•Can "see" them

Slow

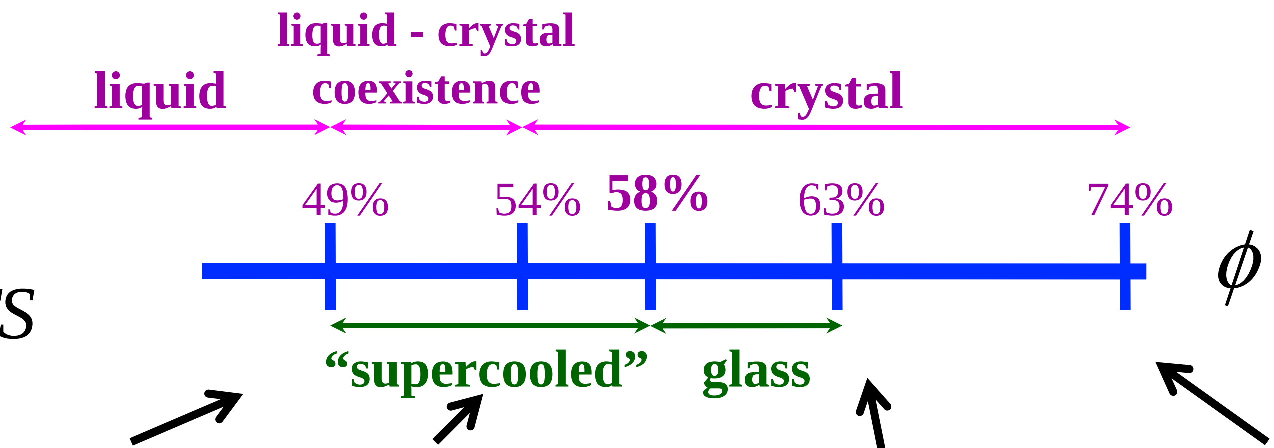
• $\tau \sim a^2/D$ ~ ms to sec

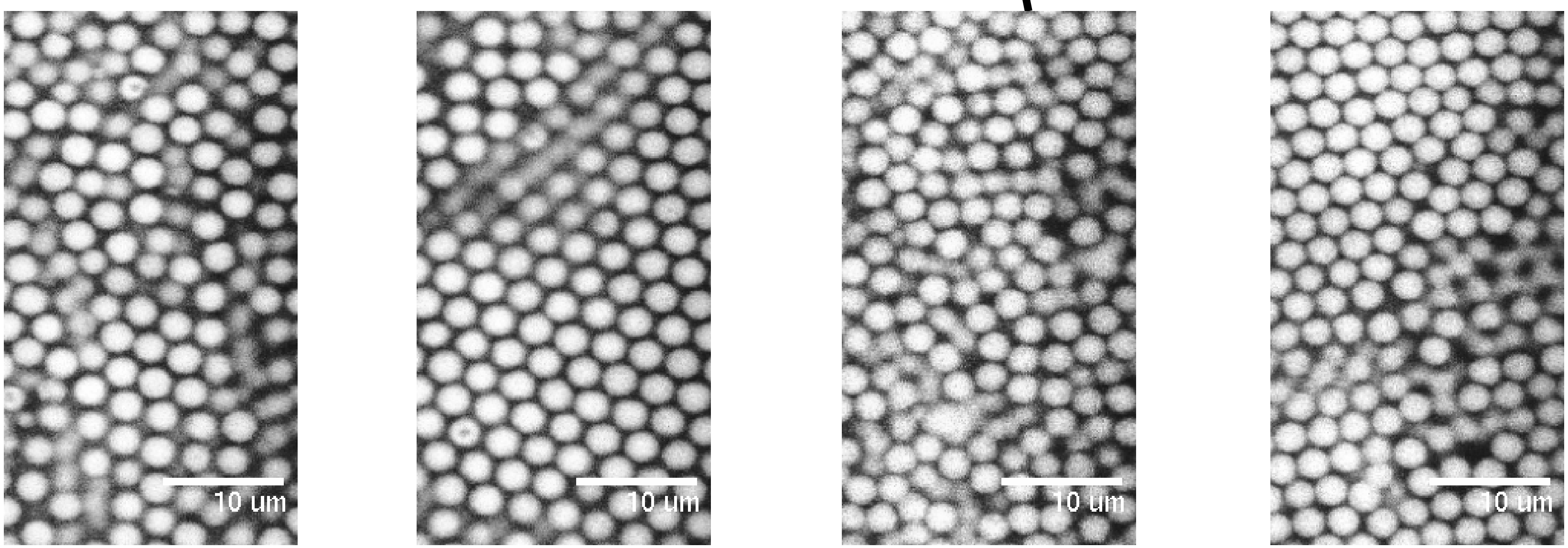
•Follow individual particle dynamics

Model: Colloid → Atom

Hard-Sphere Glasses

$F = U - TS$ (with $U \to 0$)





$\phi_{liquid} \approx 0.48$

$\phi_{xtal} \approx 0.54$

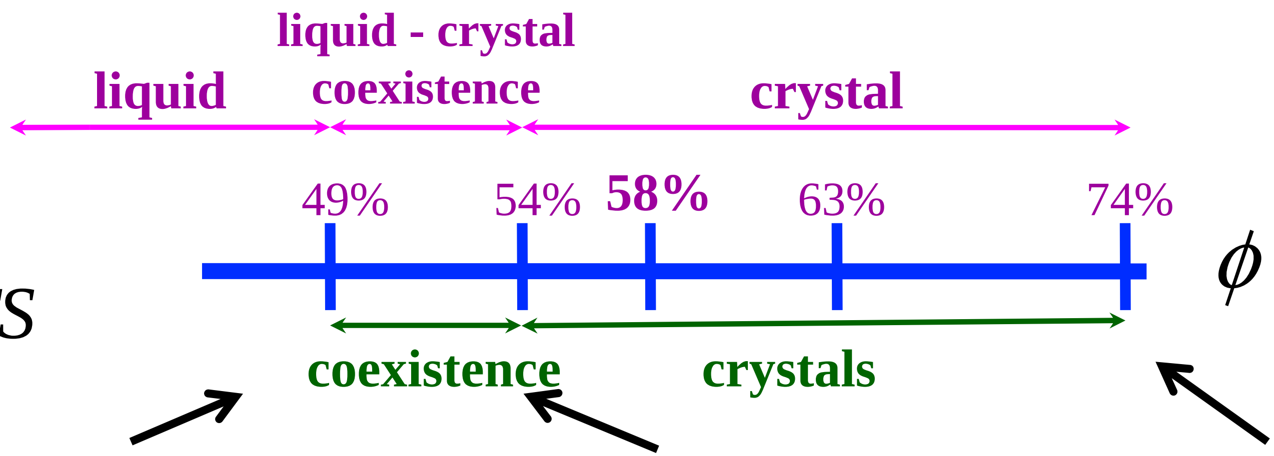
Maximum packing $\phi_{RCP} \approx 0.63$

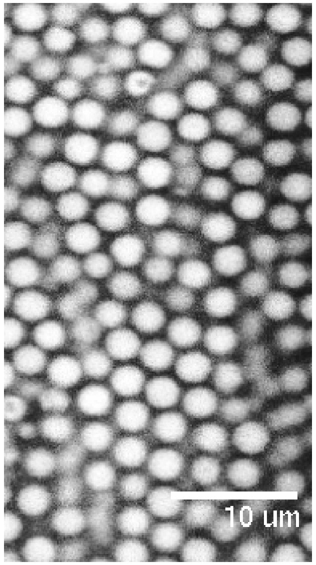
Maximum packing $\phi_{HCP} = 0.74$

Increase ϕ => Decrease Temperature

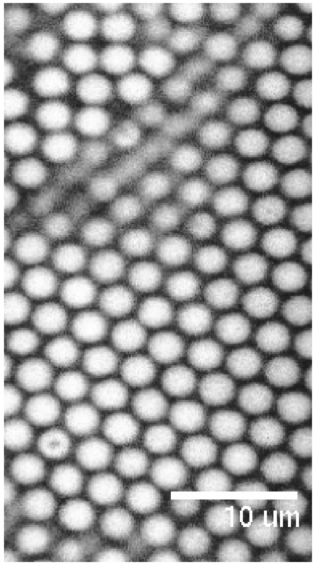
Hard-Sphere Crystals

$F = \cancelto{0}{U} - TS$

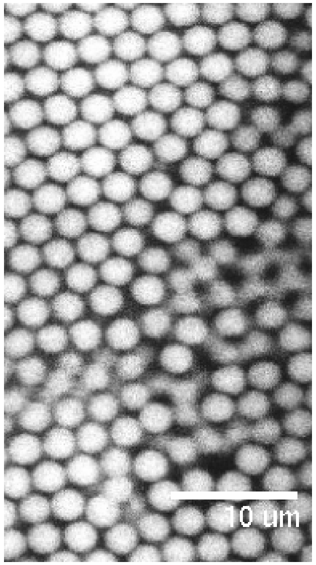




$\phi_{liquid} \approx 0.48$



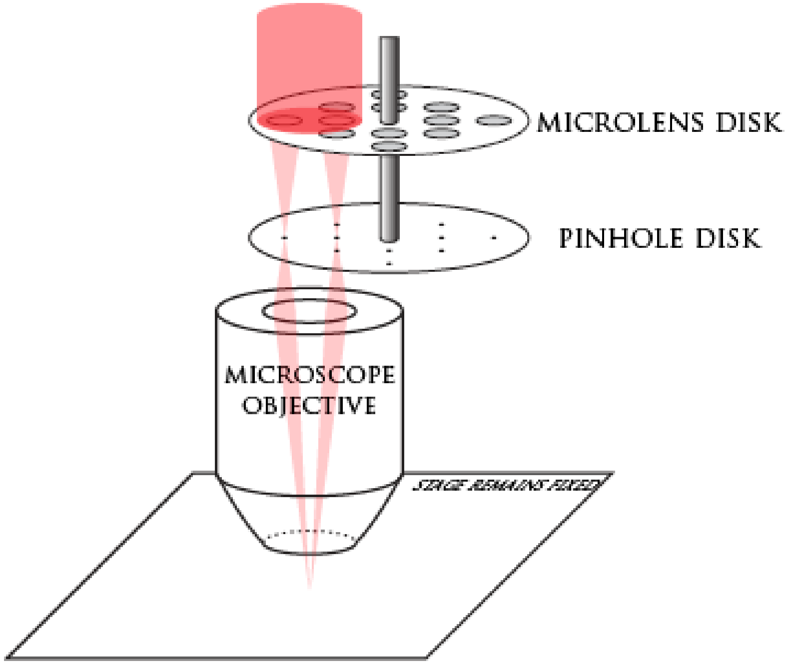
$\phi_{xtal} \approx 0.54$



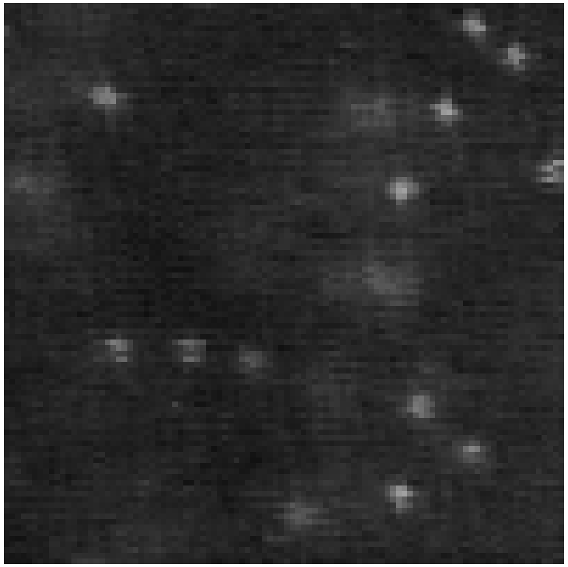
Maximum packing
$\phi_{HCP} = 0.74$

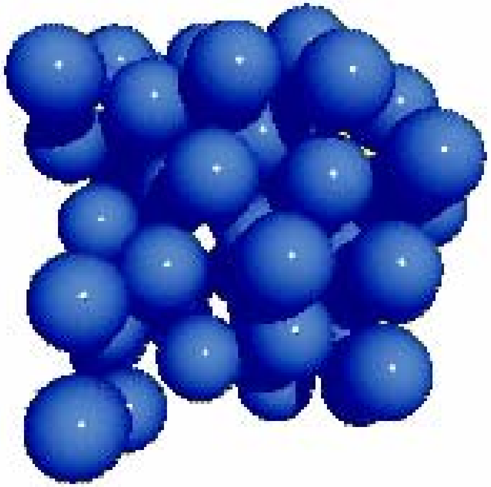
Increase ϕ => Decrease Temperature

Confocal Microscopy



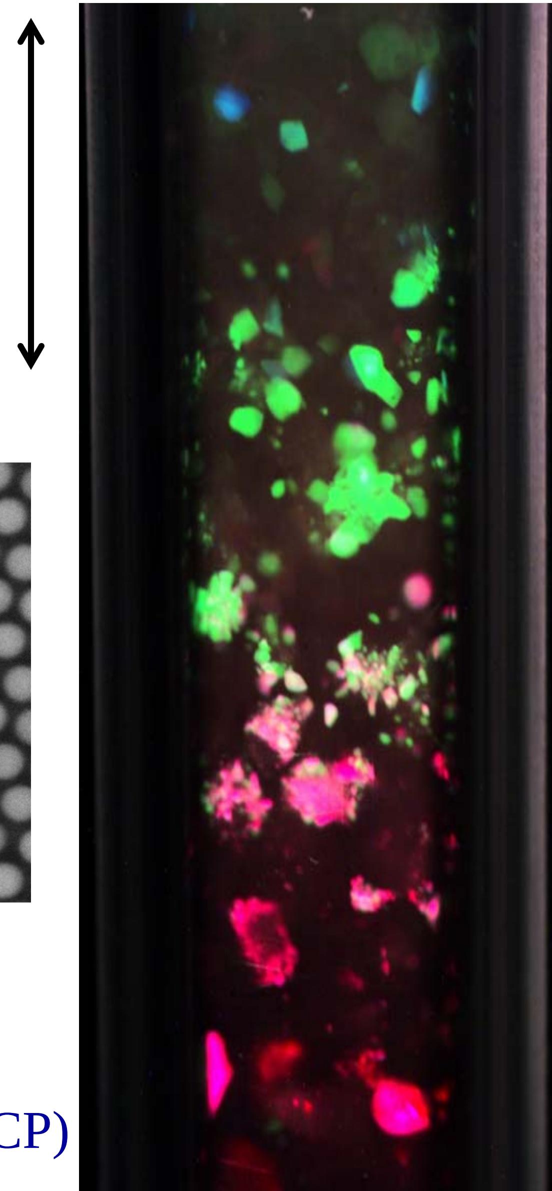
Brownian Motion in Real Time

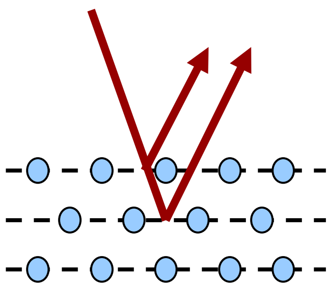


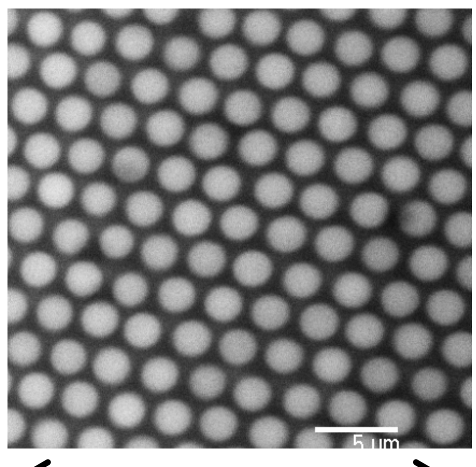


Colloidal Crystals

1 cm





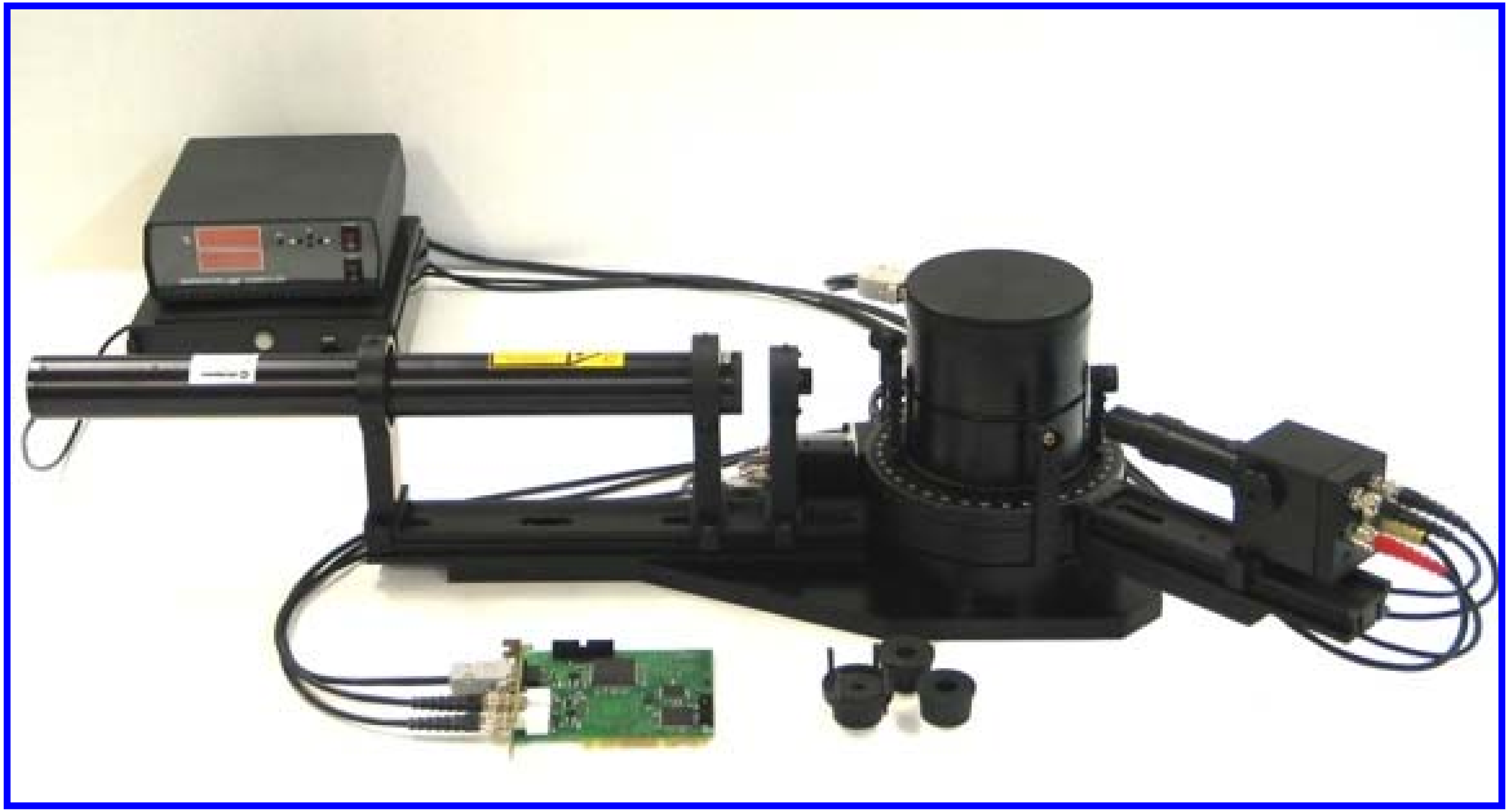


25 µm

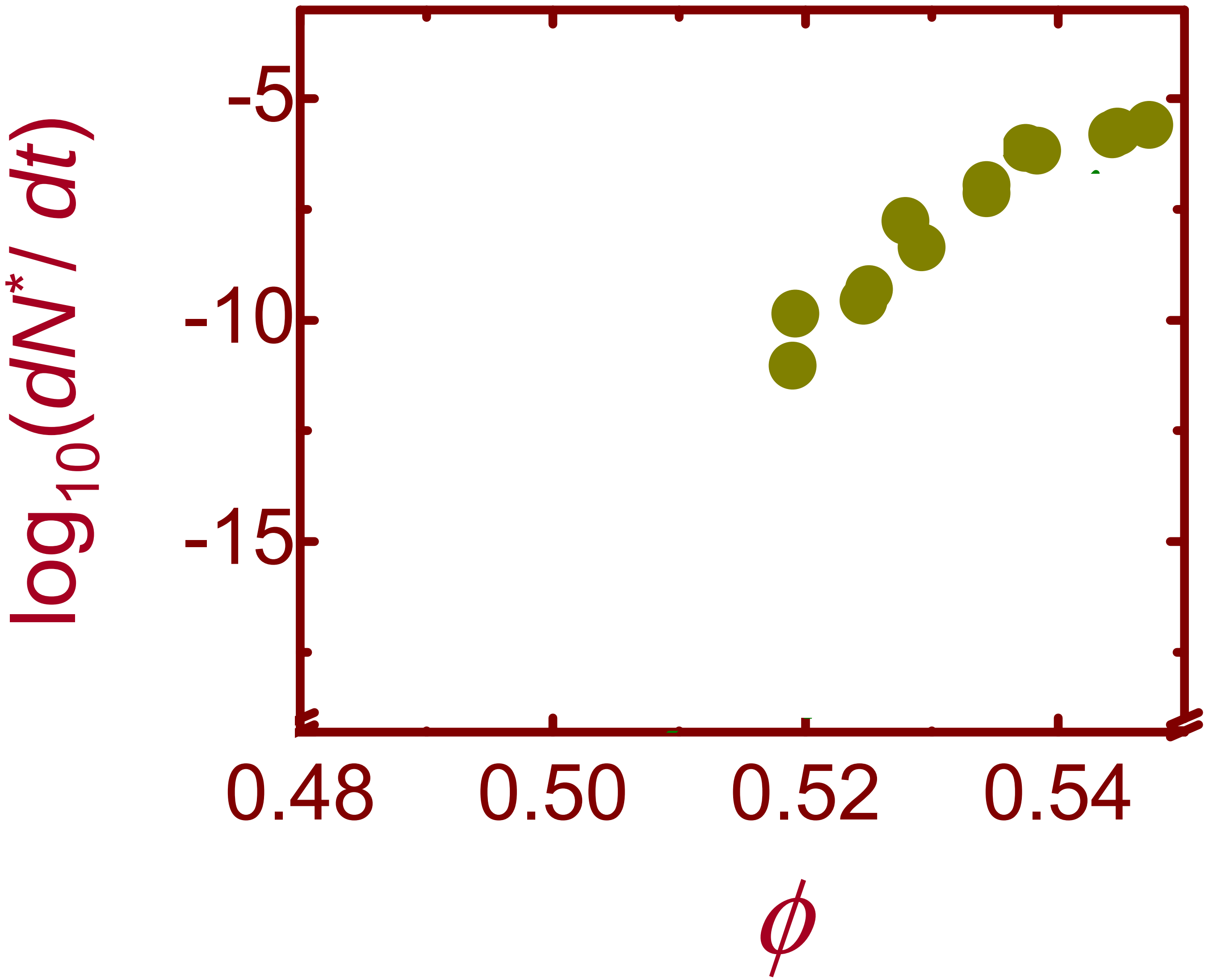
Bragg scattering of visible light

Hexagonal close-packed layers (FCC/HCP)

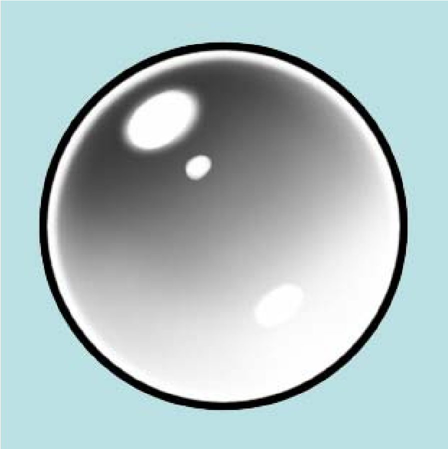
X-ray scattering → light scattering



Nucleation rates of Colloidal Crystals

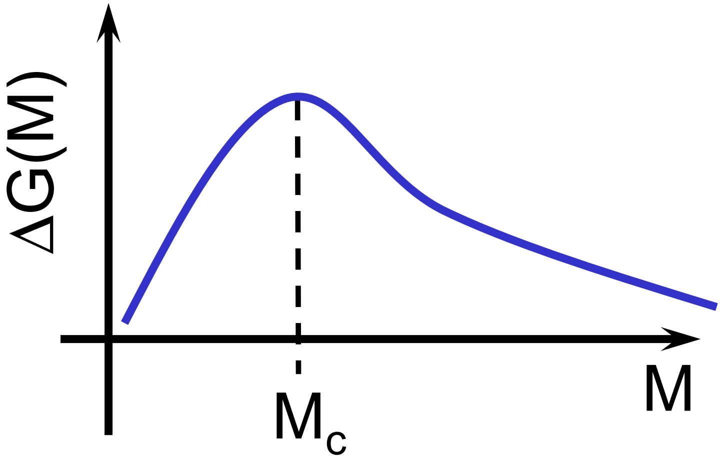


Nucleation and Growth



$$A = 4\pi R^2$$

$$V = 4/3\pi R^3$$

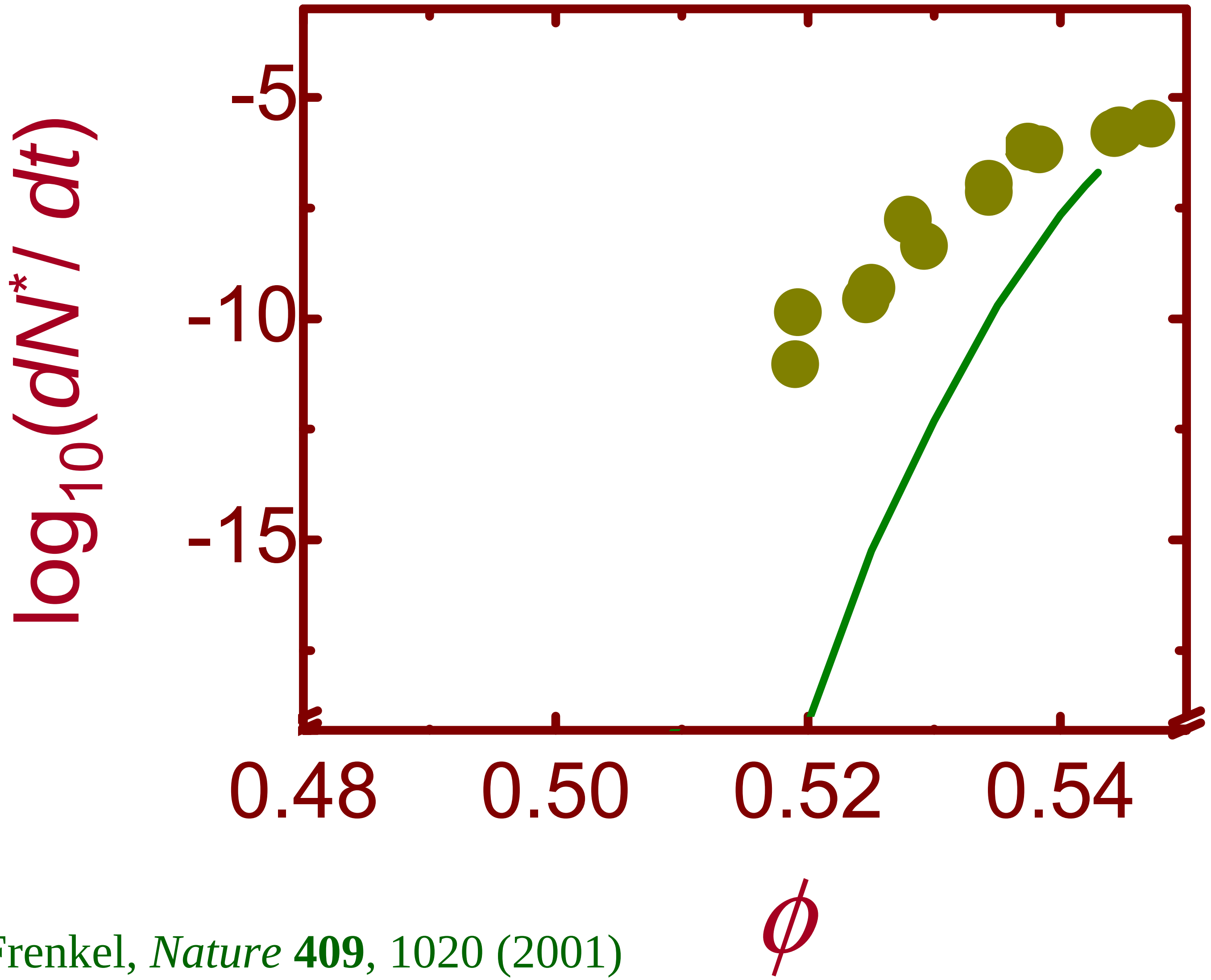


$$\Delta G = \gamma A - \Delta\mu\rho V$$

$$I \sim \exp[-\,\Delta G(M_c)/k_B T]$$

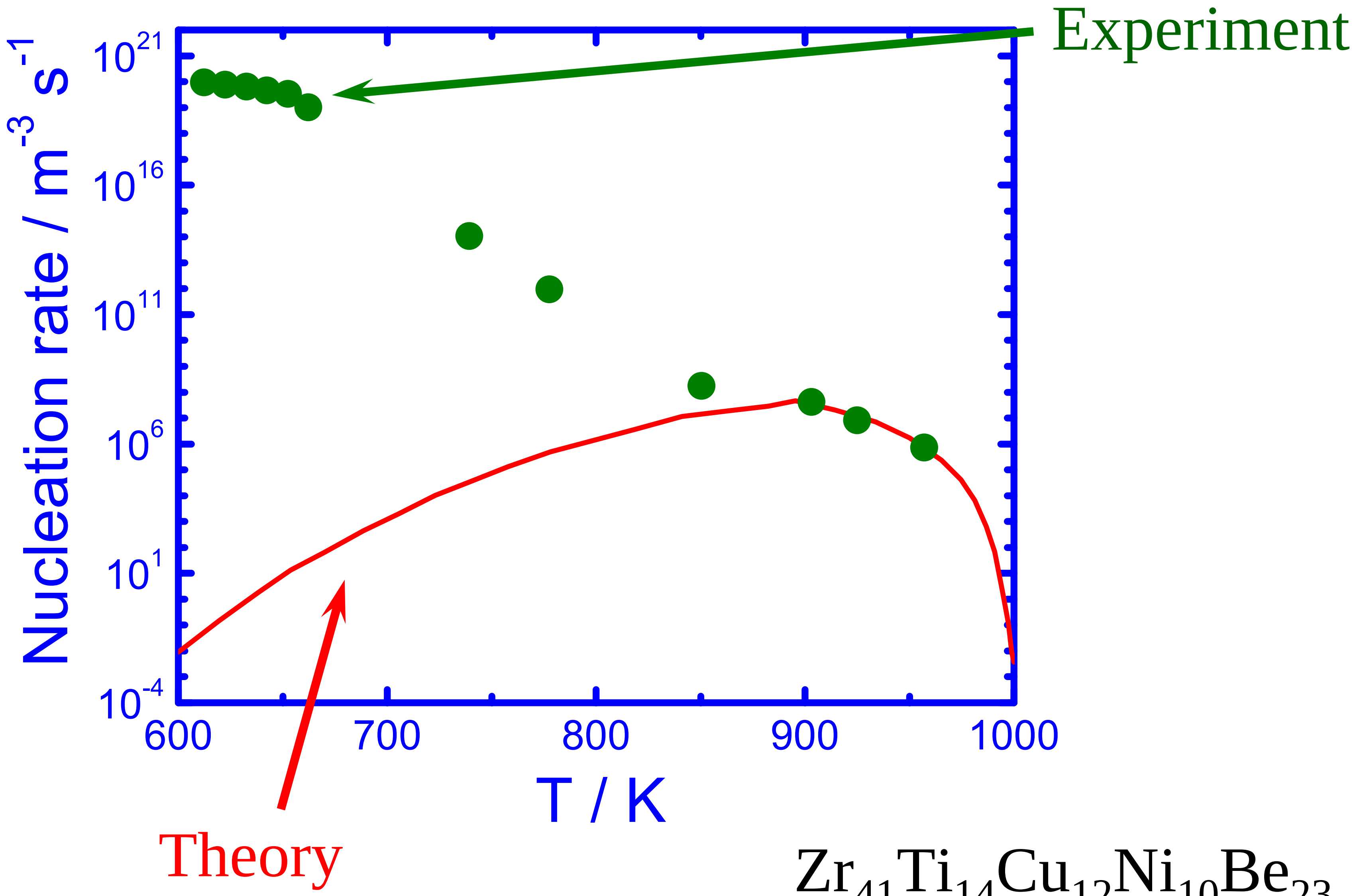
Nucleation rates not predicted correctly

Colloidal Crystals



Auer & Frenkel, *Nature* **409**, 1020 (2001)

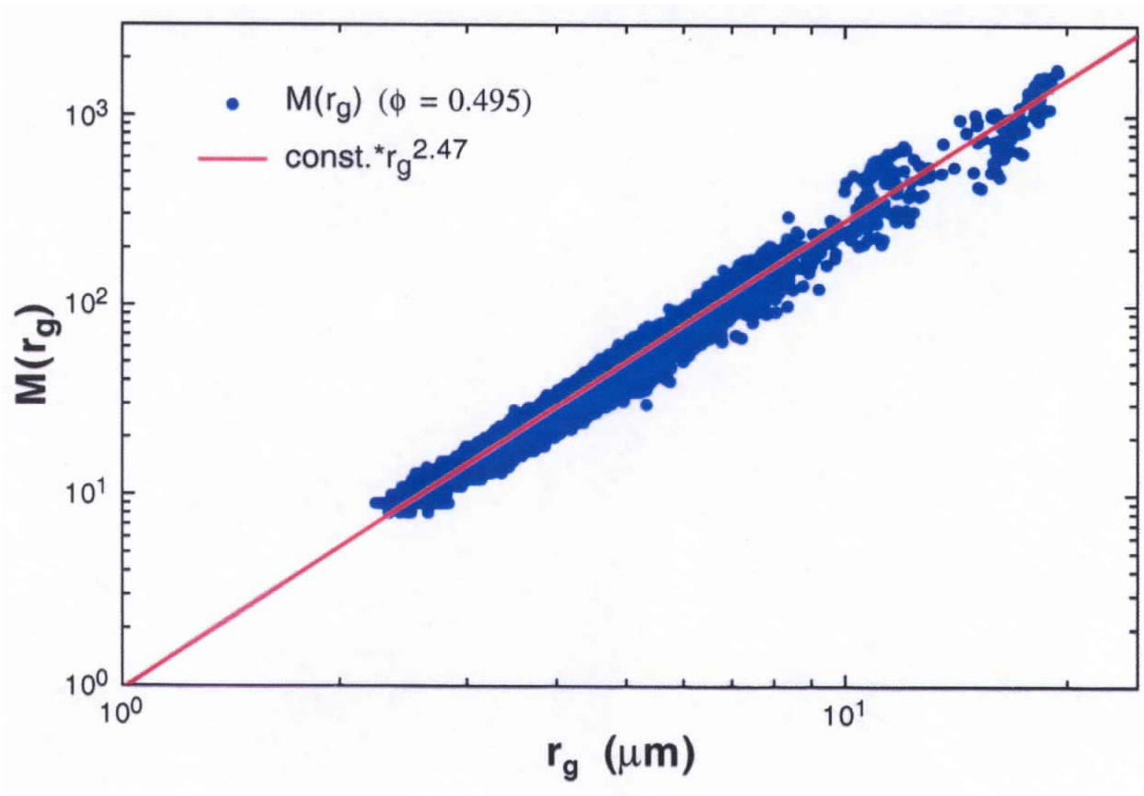
Nucleation rates not predicted correctly



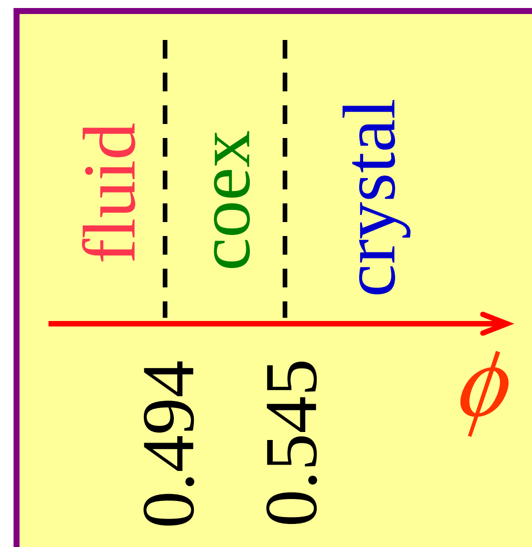
$Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$

J. Schroers *et al.*, *Appl. Phys. Lett.* **74**, 2806 (1999)

Charge effects on crystal nucleation



$d_F \approx 2.5$

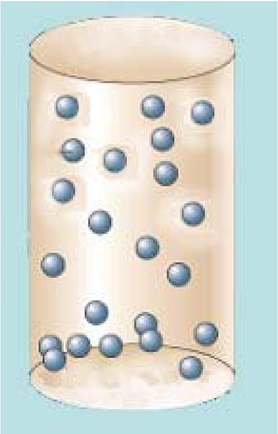


$\phi_c = 0.42$ instead of $\phi_c = 0.495$

Soft potential – (ϕ, T)

U. Gasser, E. R. Weeks, A. Schofield, P. N. Pusey, and D. A. Weitz, *Science* **292**, 258 (2001)

Colloidal suspension



$\sigma \sim 2.3$ mm

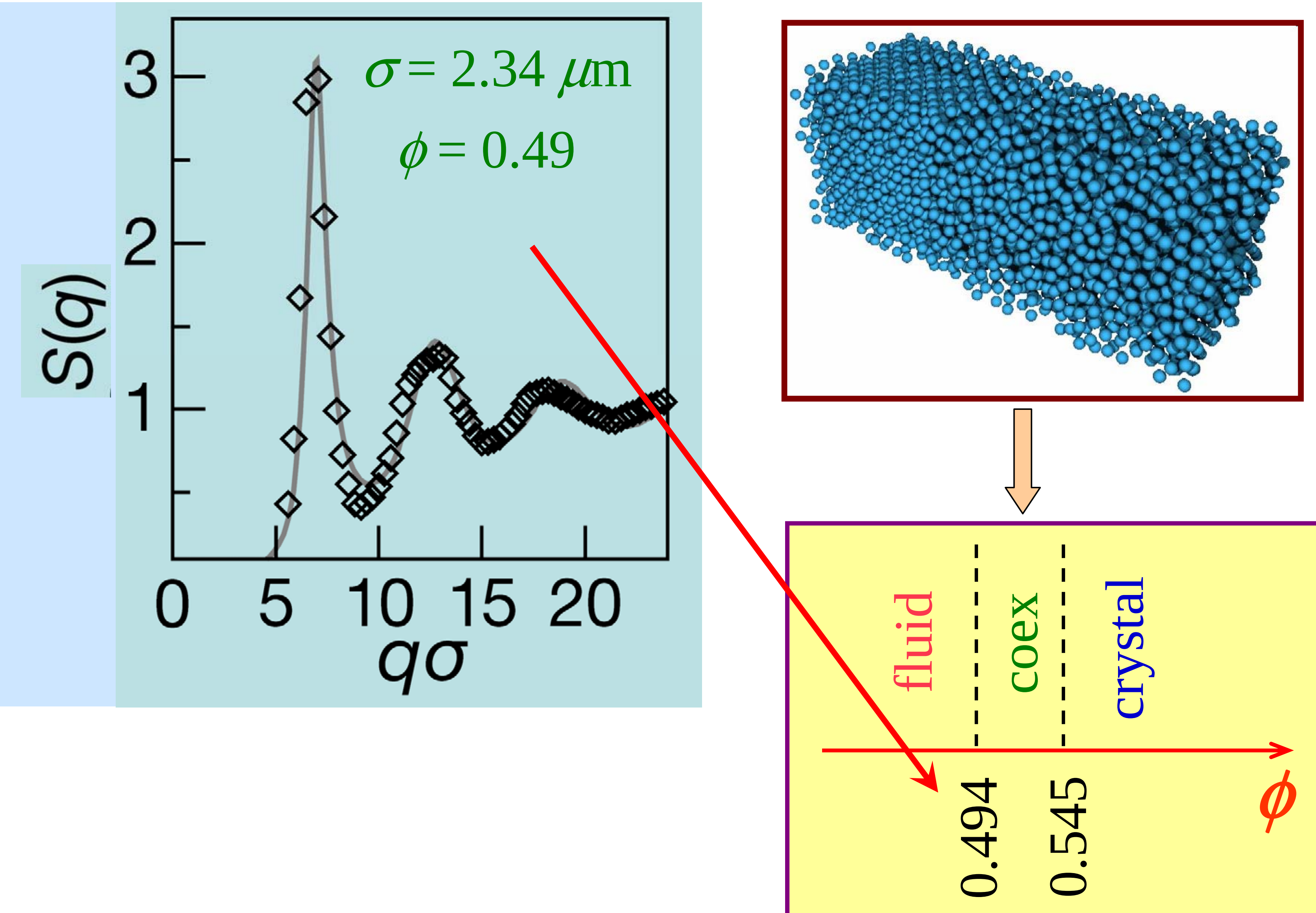
PMMA (polymethylmethacrylate)

PHSA (poly–12–hydroxystearic) for steric stabilization

Fluorescent

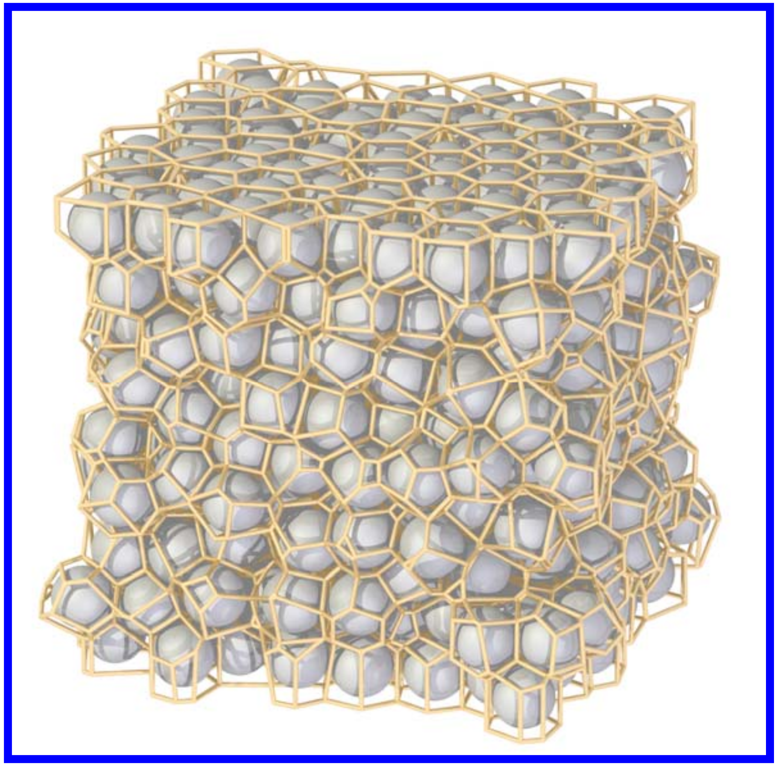
Decalin + tetrachloroethylene

Phase diagram

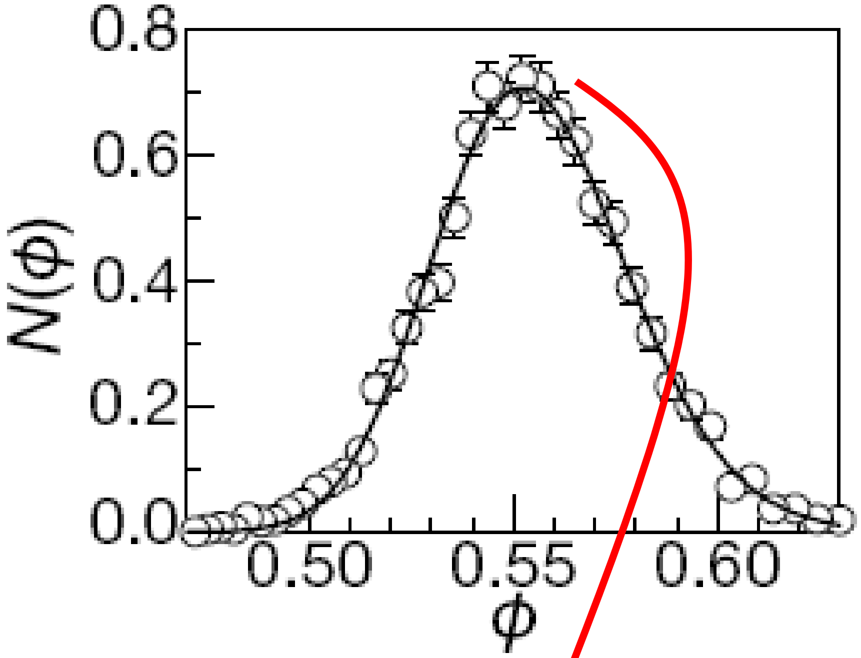


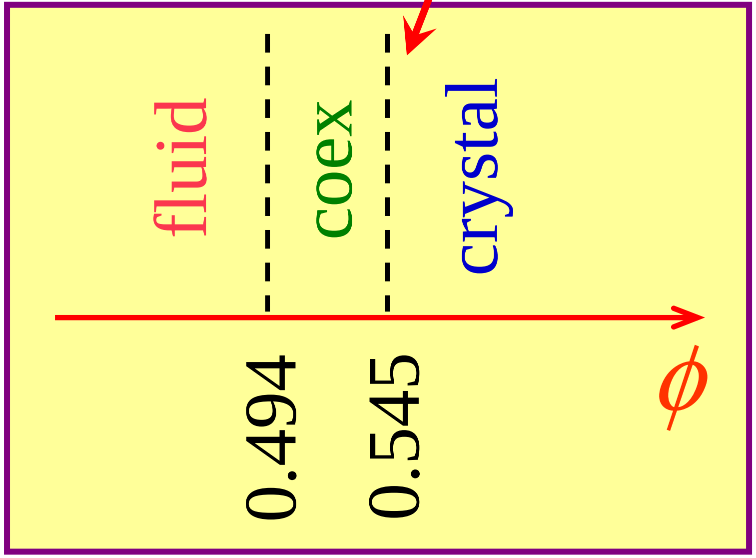
Phase behavior

Voronoi tesselation



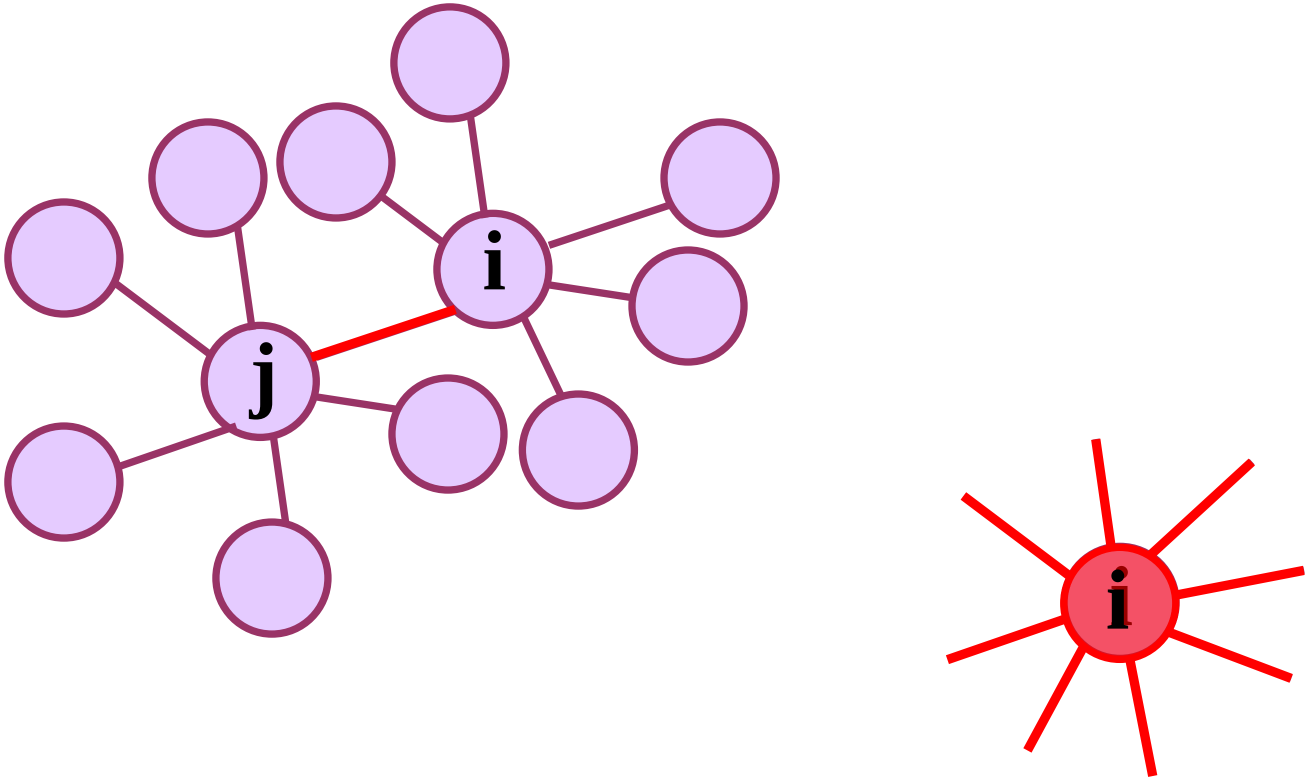
$$\phi = \frac{\pi\sigma^3/6}{\text{Voronoi volume}}$$





Definition of crystallinity

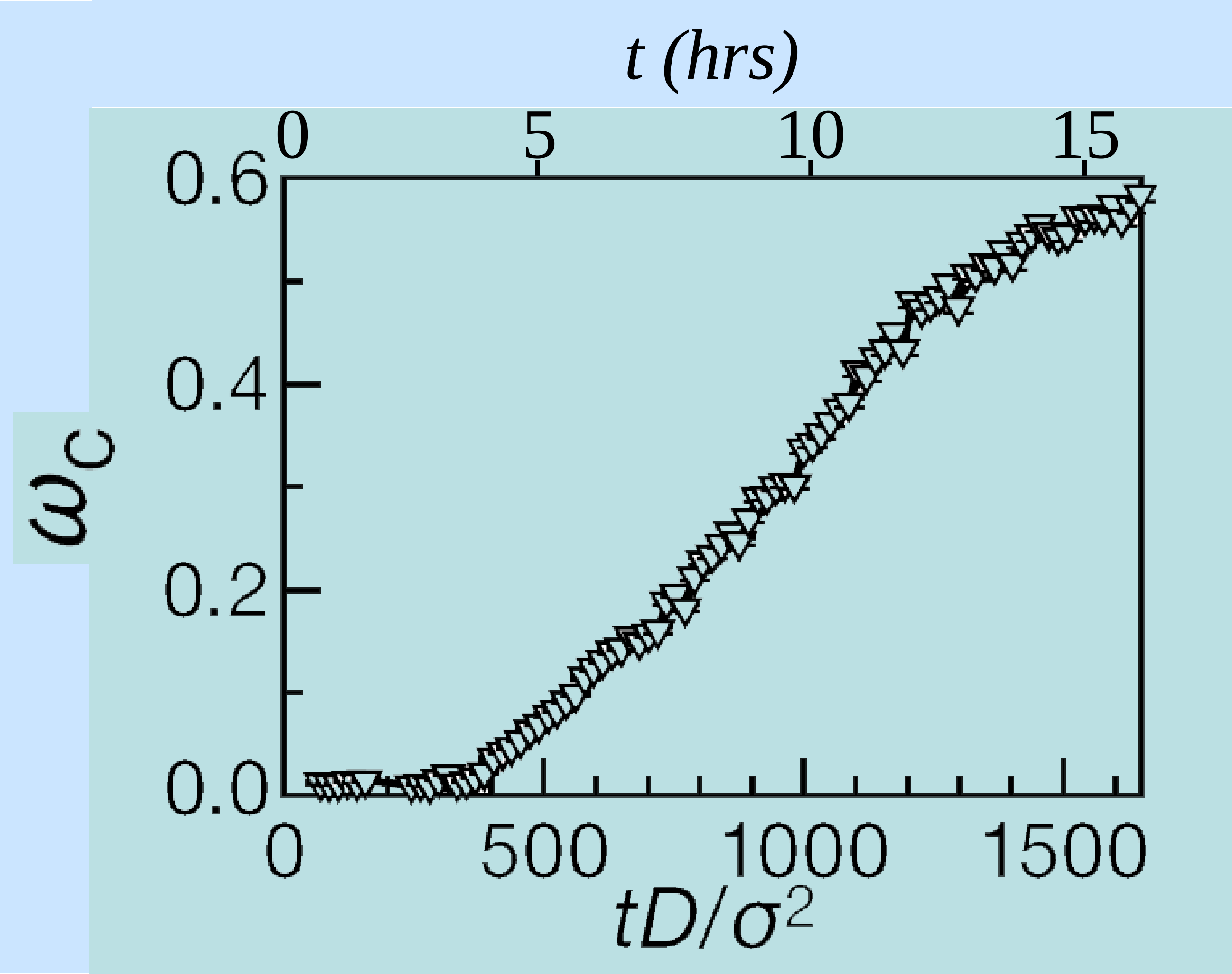
Bond order parameters



$$\overline{Y}_{6m}^{(i)} = \left\langle Y_{6m}\left(\theta,\phi\right)\right\rangle$$

$$\overline{Y}_{6m}^{(i)}\overline{Y}_{6m}^{*(j)} > 0.5$$

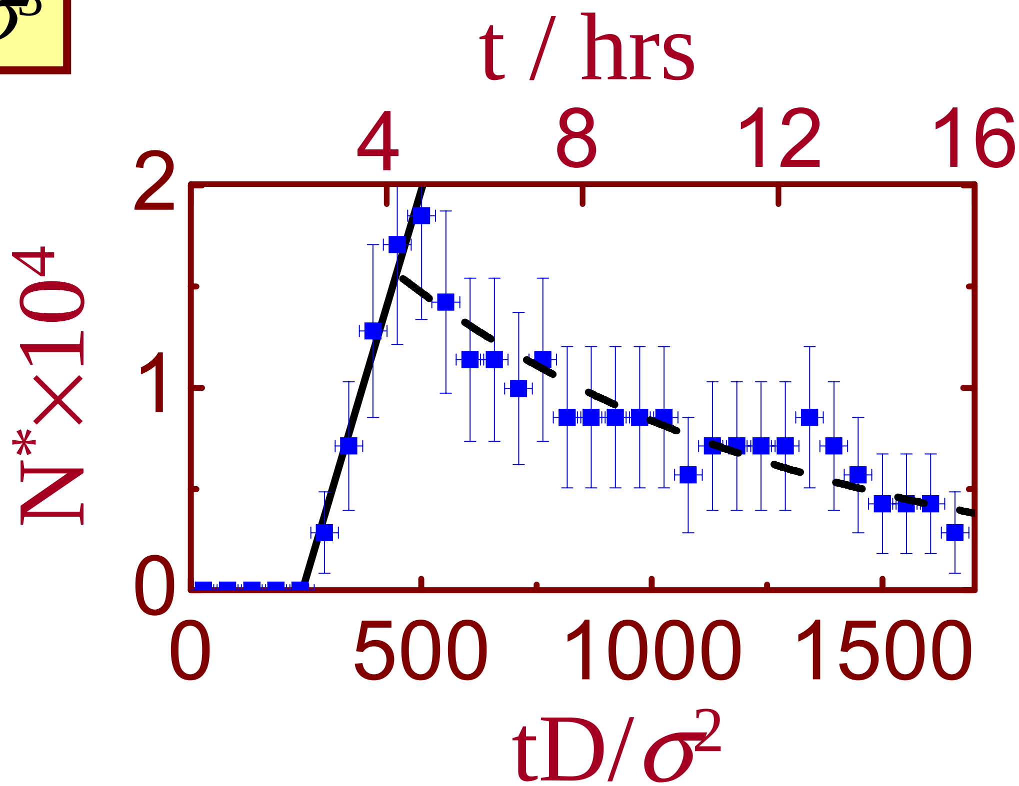
Growth of crystalline phase



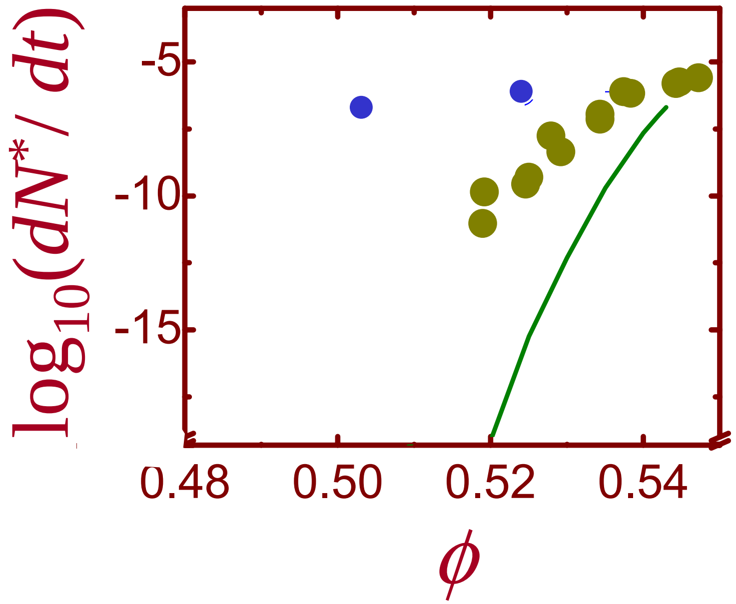
Measure nucleation rates

$N^* \equiv N/\sigma^3$

$\phi = 0.52$

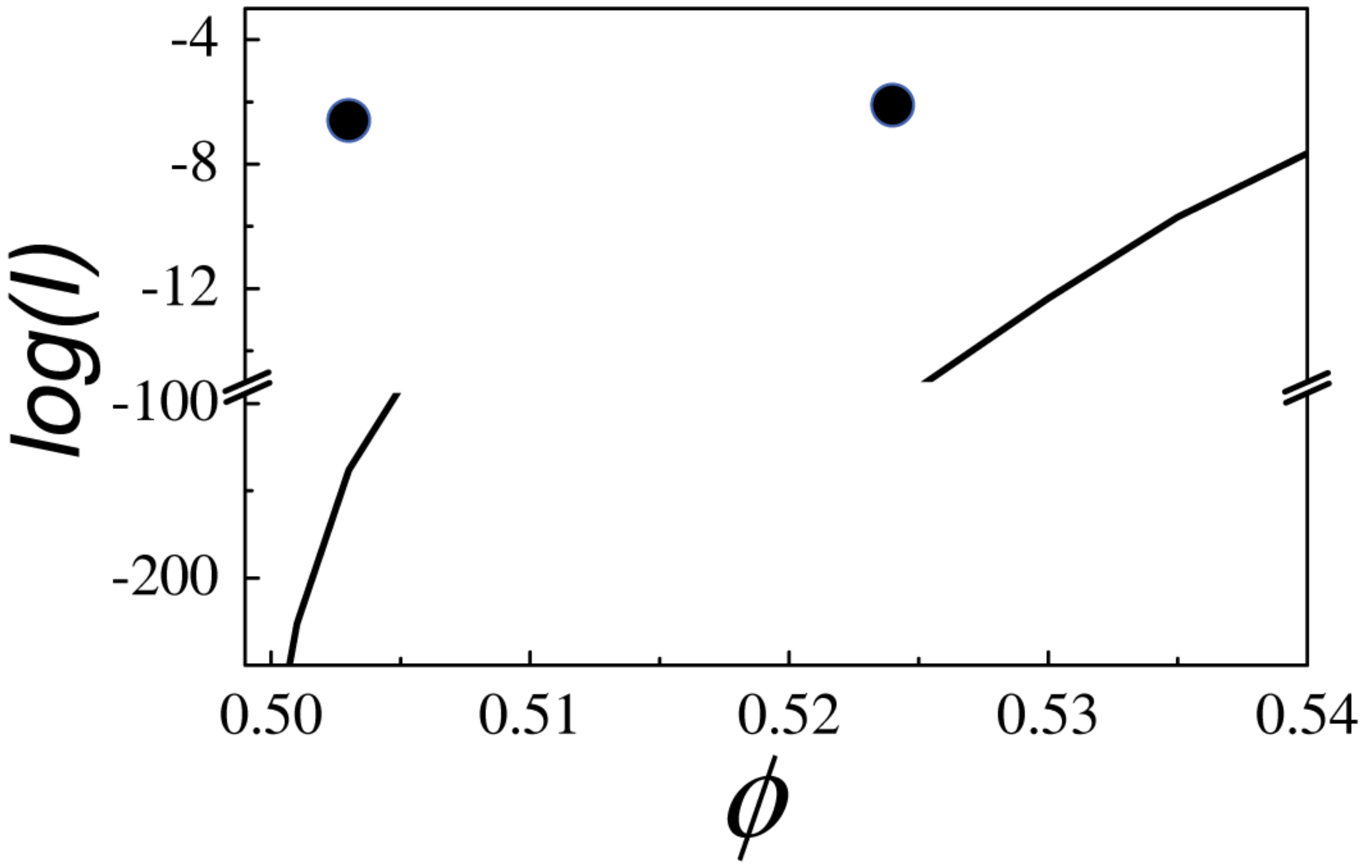


Nucleation rates



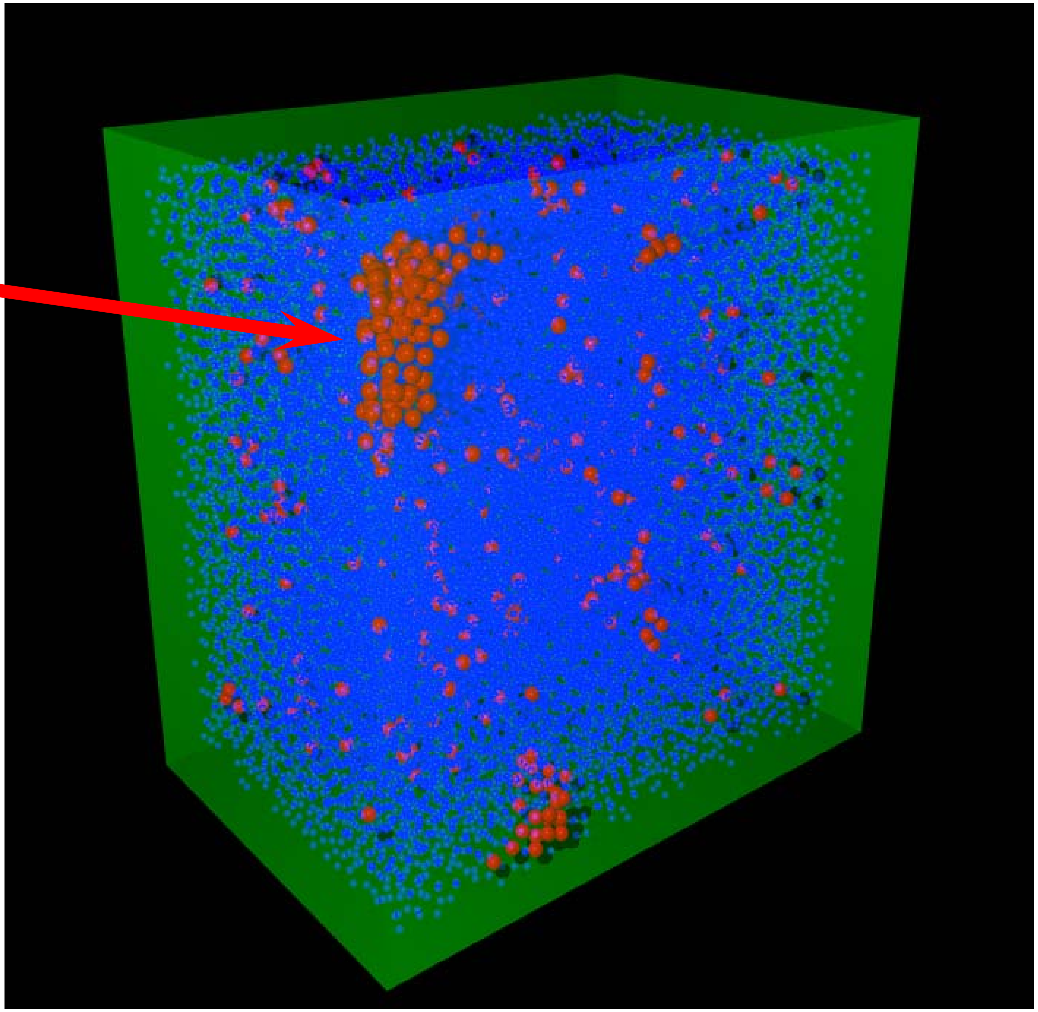
Auer & Frenkel, *Nature* **409**, 1020 (2001)

Nucleation rates



Auer & Frenkel, *Nature* **409**, 1020 (2001)

Reconstruction



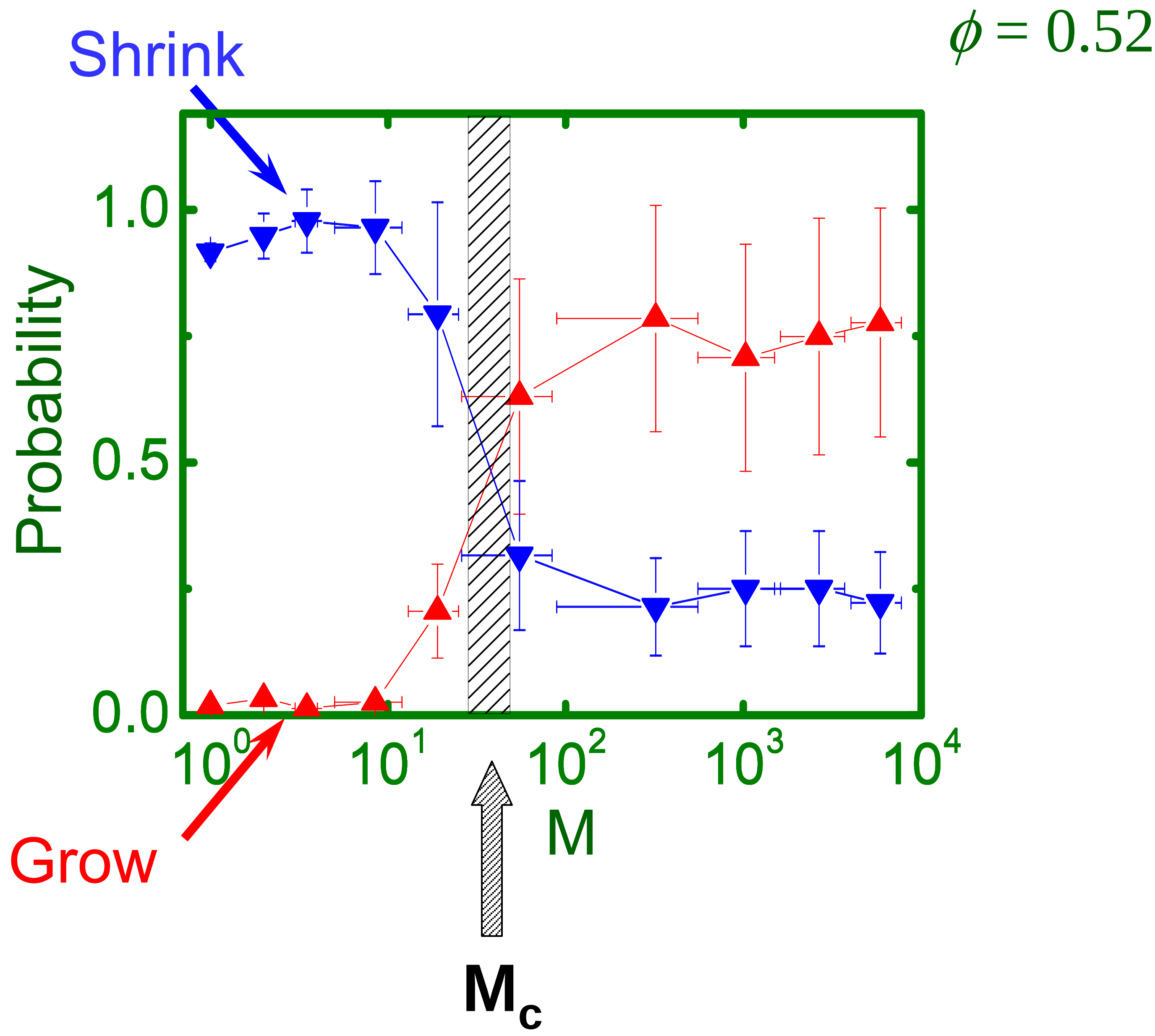
Fluid phase - blue

Crystalline phase - red

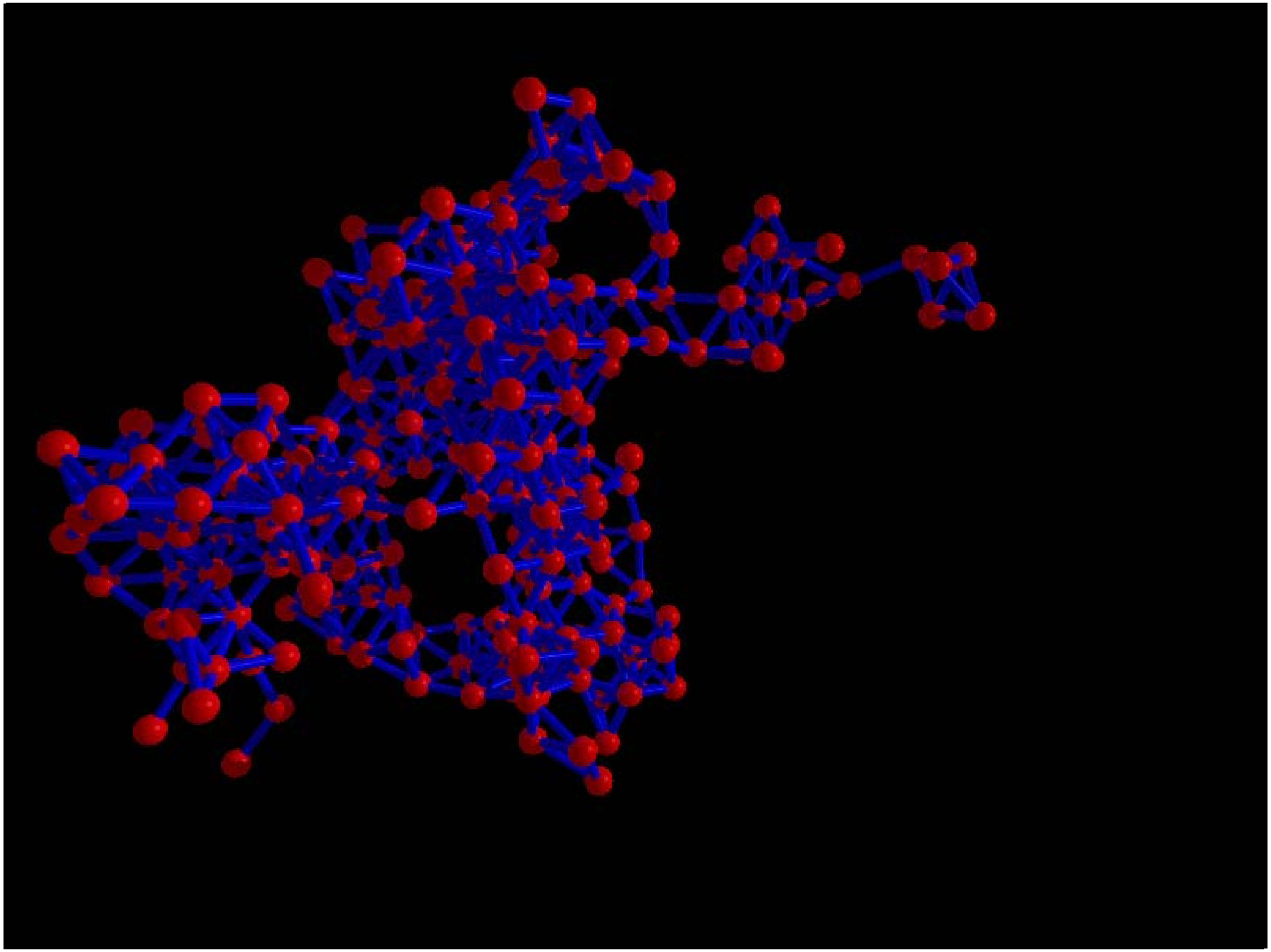
Measure the probability to shrink

Measure the probability to grow

Measure the critical mass

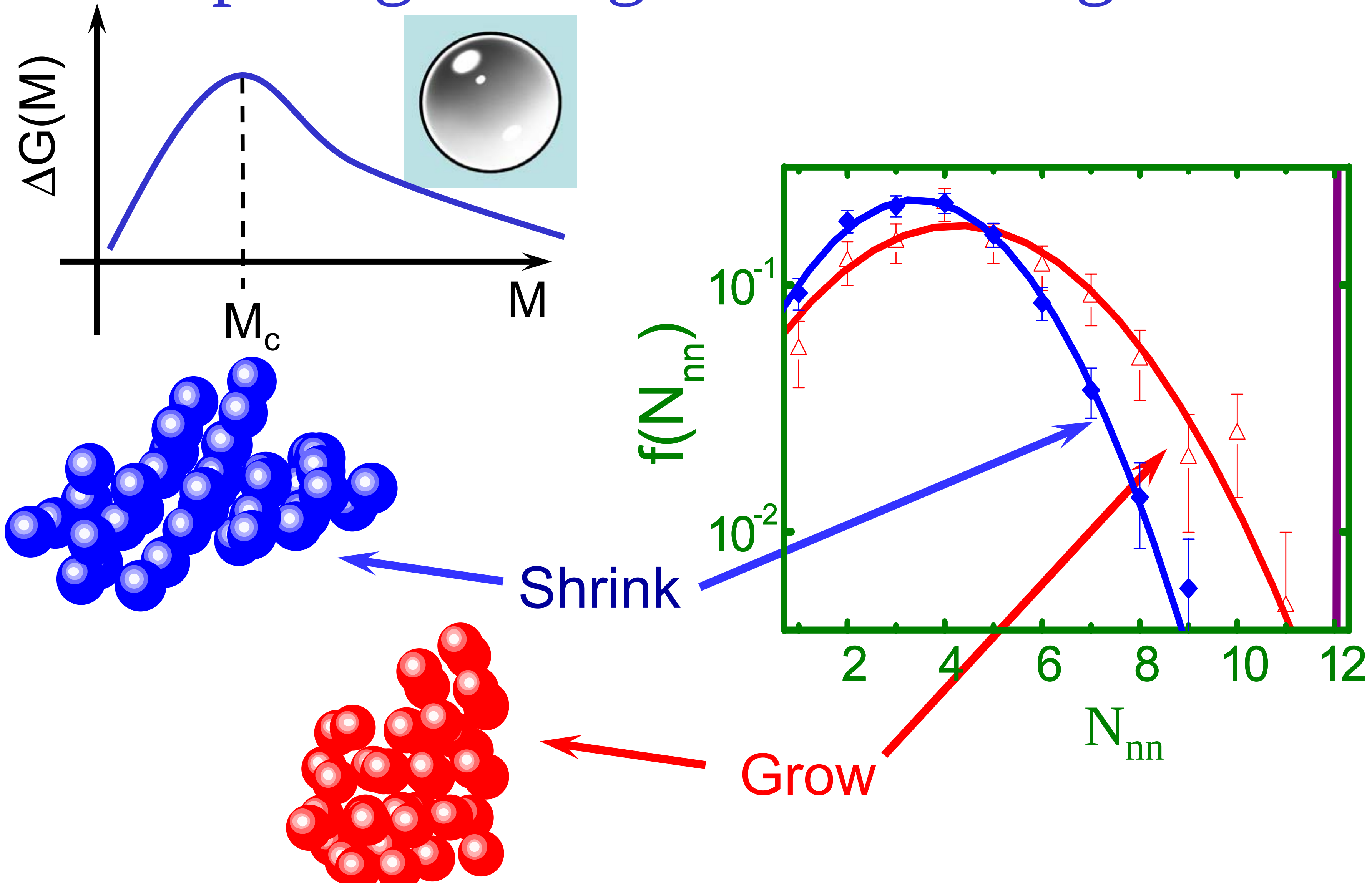


Stepwise formation of an overcritical nucleus



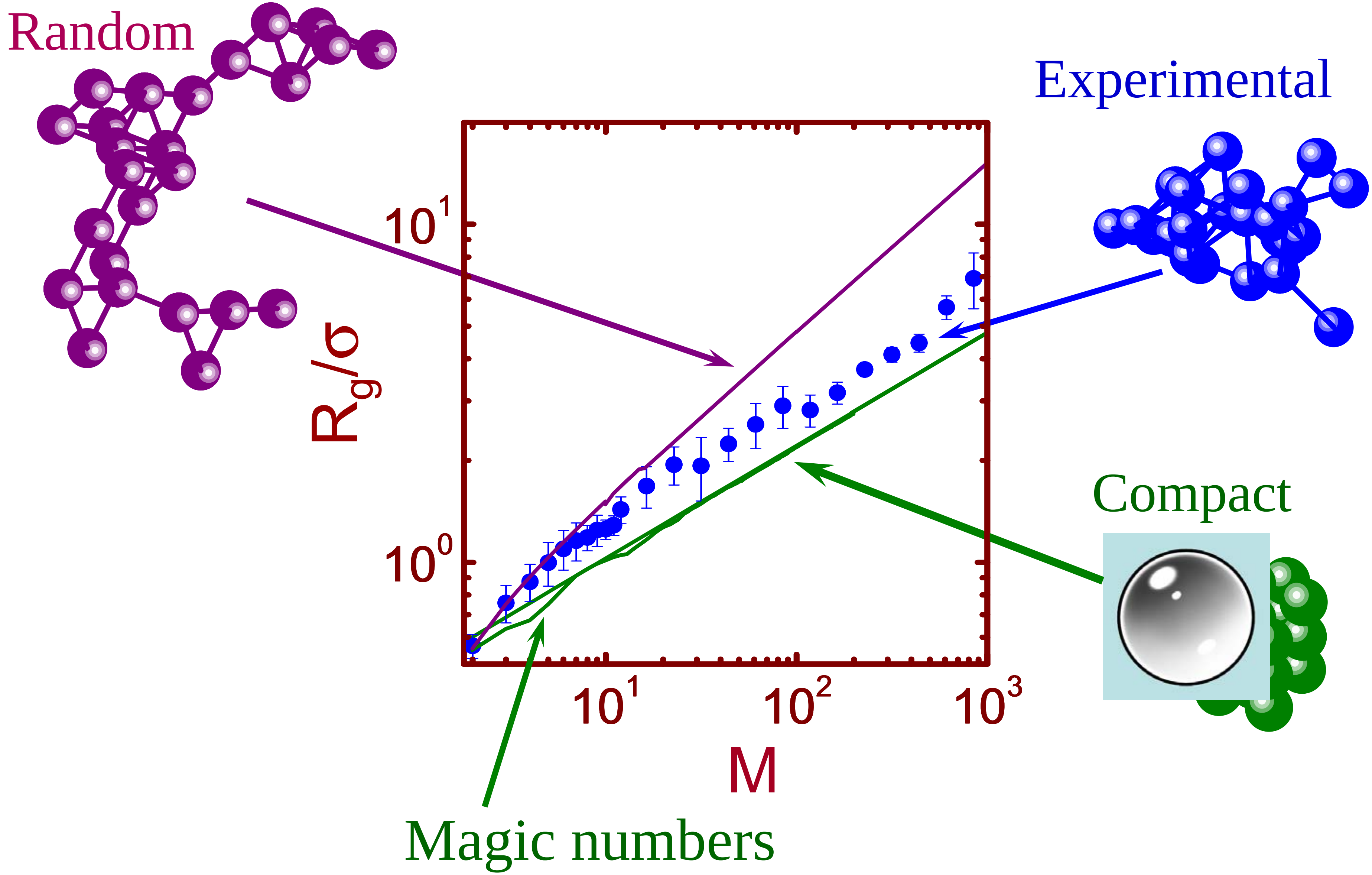
3 hrs

Compare growing and shrinking nuclei

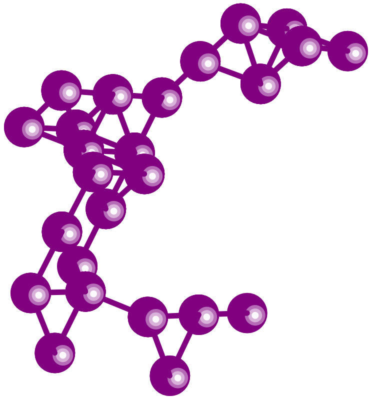


Not only mass matters

Compare with the theoretical morphology



Distribution of colloidal crystal nuclei

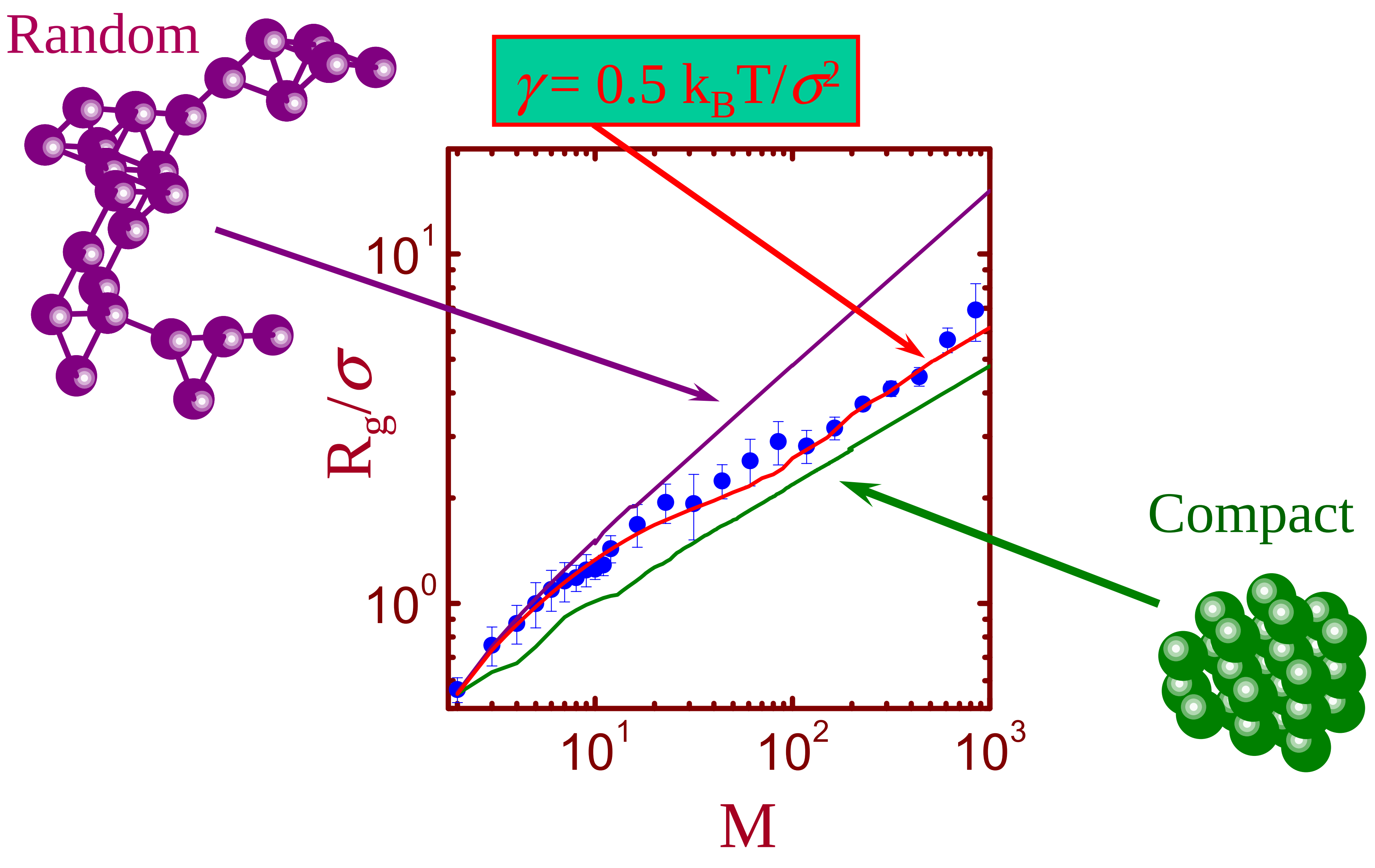


$$\left\langle R_g(M)\right\rangle = \frac{\sum_i R_g^{(i)} \exp\left[-\Delta G(M, A_i)/k_B T\right]}{\sum_i \exp\left[-\Delta G(M, A_i)/k_B T\right]}$$

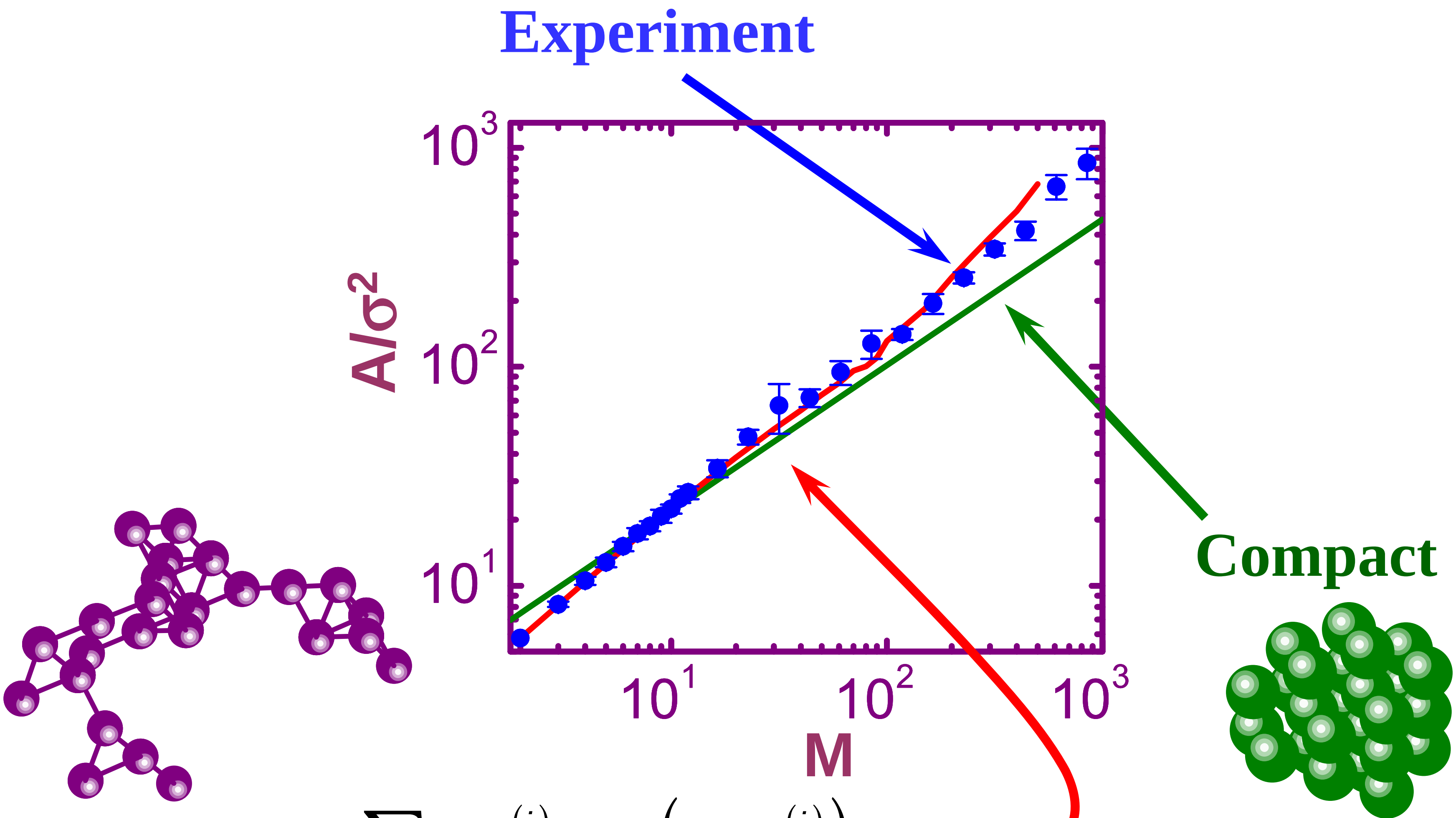
$$\Delta G = \gamma A_i - \Delta\mu M$$

$$\left\langle R_g(M)\right\rangle = \frac{\sum_i R_g^{(i)} \exp\left(-\gamma A_i / k_B T\right)}{\sum_i \exp\left(-\gamma A_i / k_B T\right)}$$

Nuclei adopt different morphologies



Surface area of nuclei

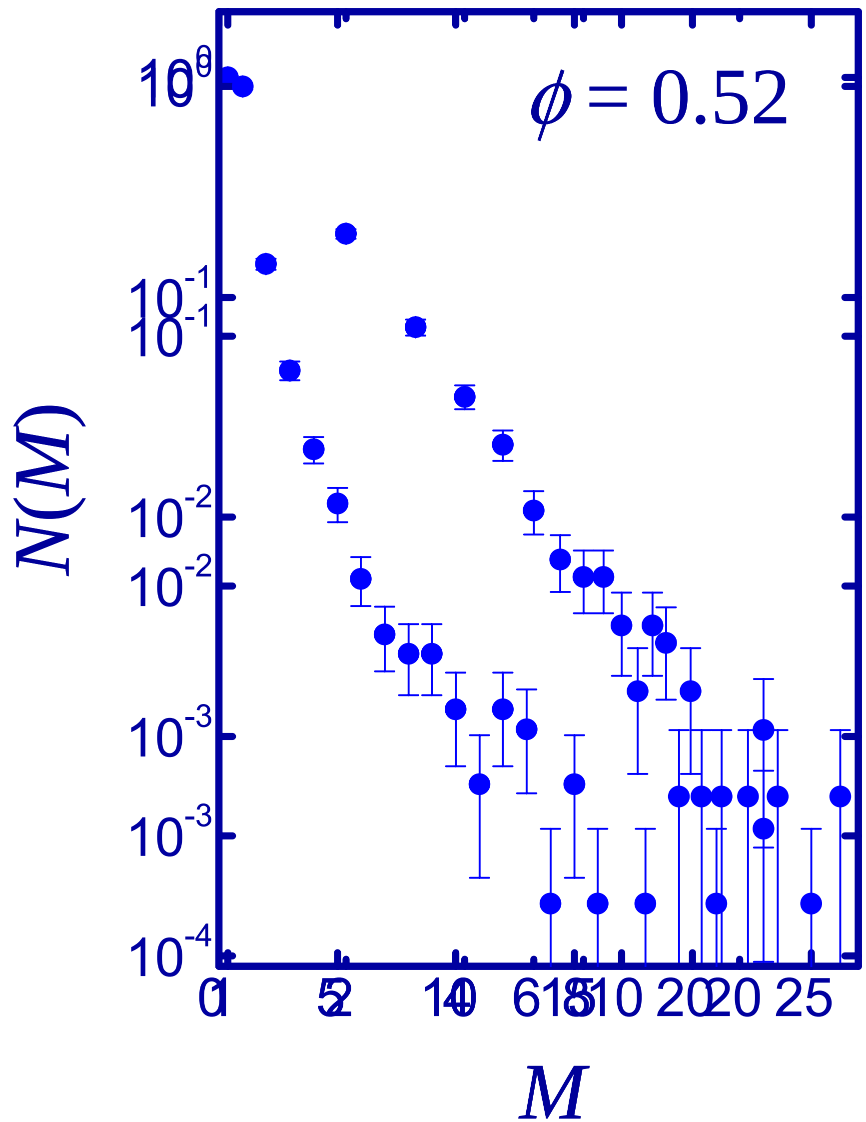


$$\langle A(M) \rangle = \frac{\sum_i A^{(i)} \exp\left(-\gamma A^{(i)}\right)}{\sum_i \exp\left(-\gamma A^{(i)}\right)}$$

$\gamma = 0.5\ k_B T/\sigma^2$

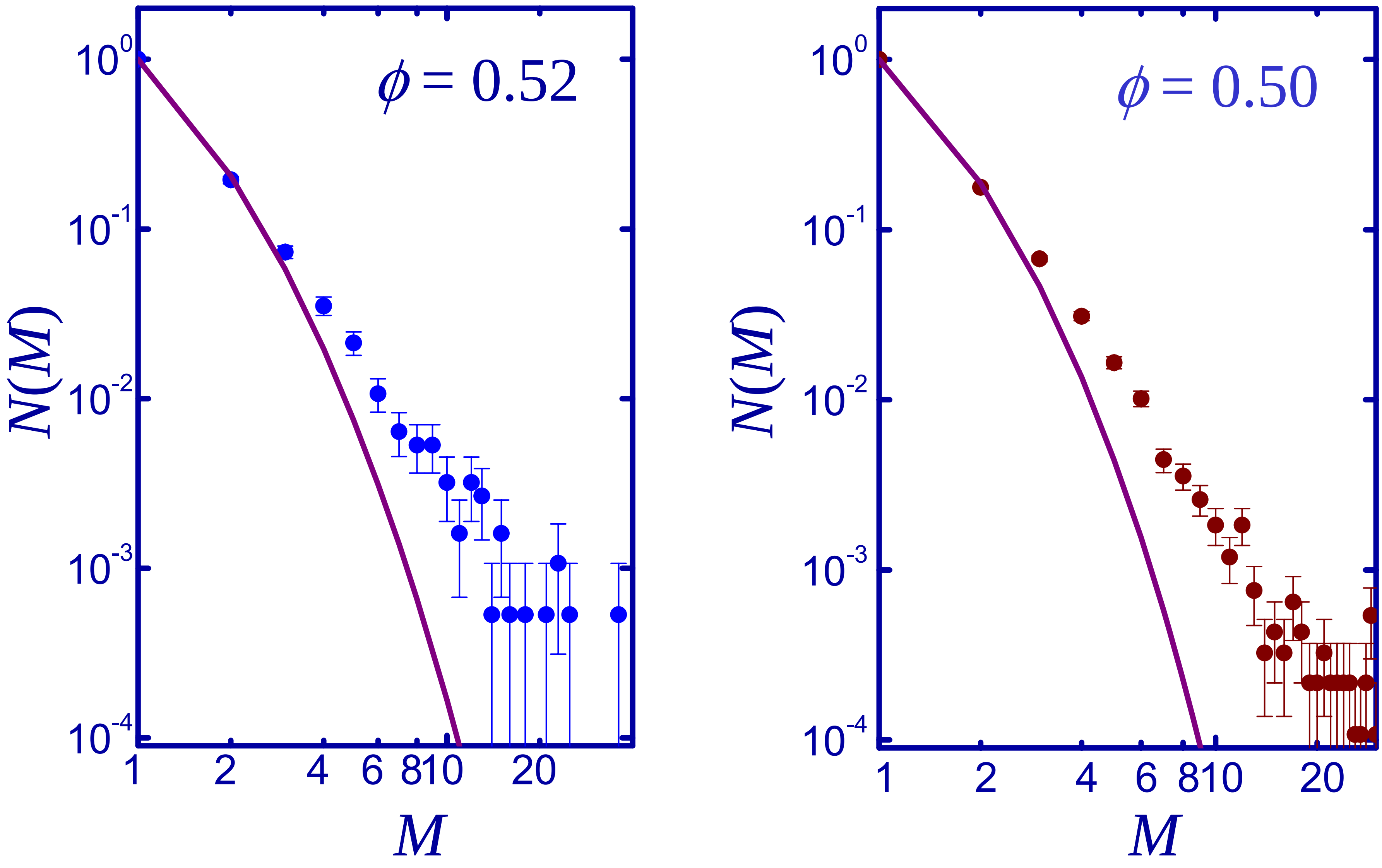
Does morphology alter the free energy?

$$N(M) \propto \exp(-\Delta G/k_B T)$$



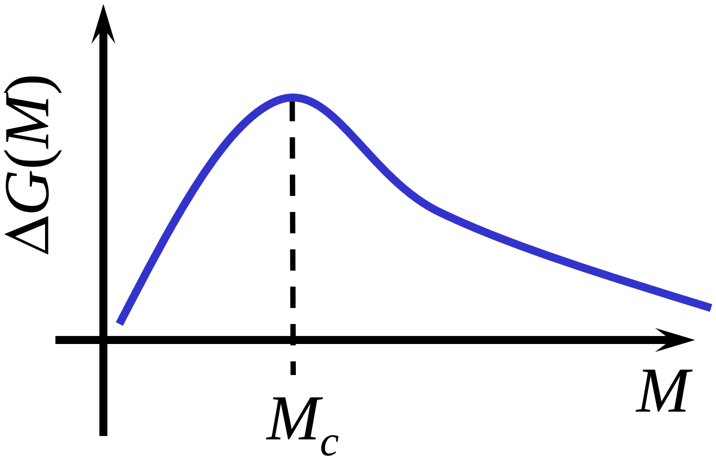
Size distribution of nuclei

$$N(M) \propto \exp(-\Delta G/k_B T)$$



Classical free energy: measure γ and $\Delta\mu$

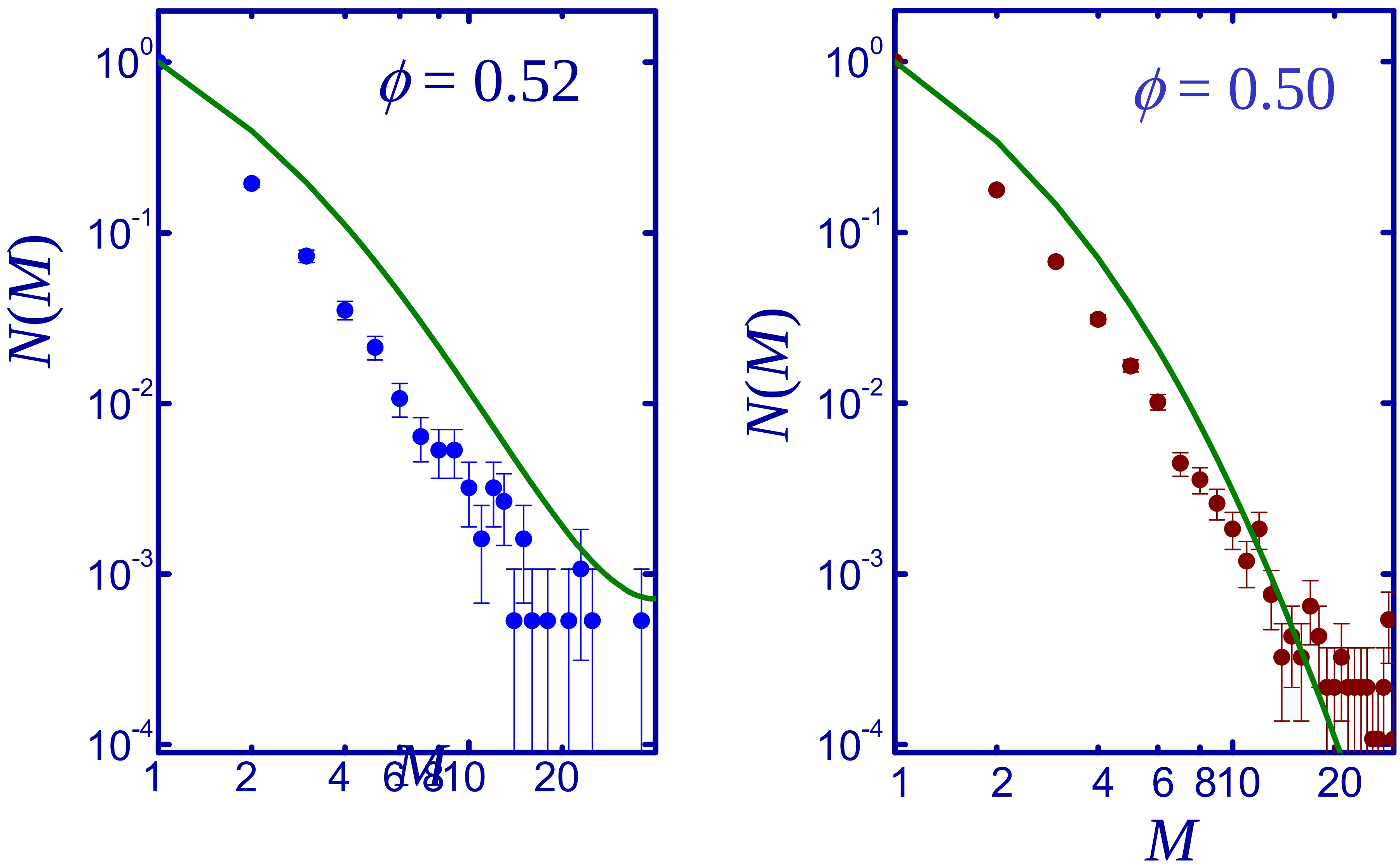
$$\Delta G = \pi M^{2/3} 0.545^{-2/3} \sigma^2 \gamma - \Delta\mu M$$



$$\left.\frac{d(\Delta G)}{dM}\right|_{M_c} = 0$$

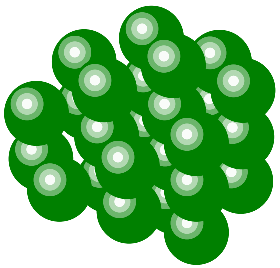
$$\Delta\mu = \frac{2\pi}{3}\sigma^2 \gamma M_c^{-1/3} \cdot 0.545^{-2/3}$$

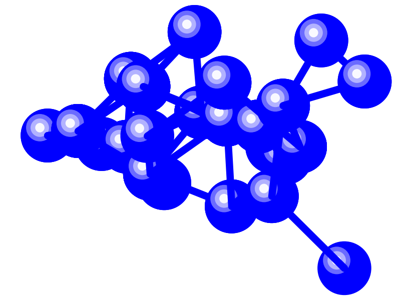
Size distribution of nuclei



Introduce morphological entropy

$$\Delta G = \gamma A - \Delta\mu M + ?$$





$$\Omega \sim e^{A_M M} M^{\tau}$$

$$S = k_B \ln\Omega = A_M{}' M + k_B \ln M^{\tau}$$

$$\Delta G = \gamma A - \Delta\mu' M + k_B T \ln M^{\tau}$$

$\gamma = 0.5\, k_B T/\sigma^2$ (Morphology)

$M_c = 40 \pm 10$ (Growth probablity)

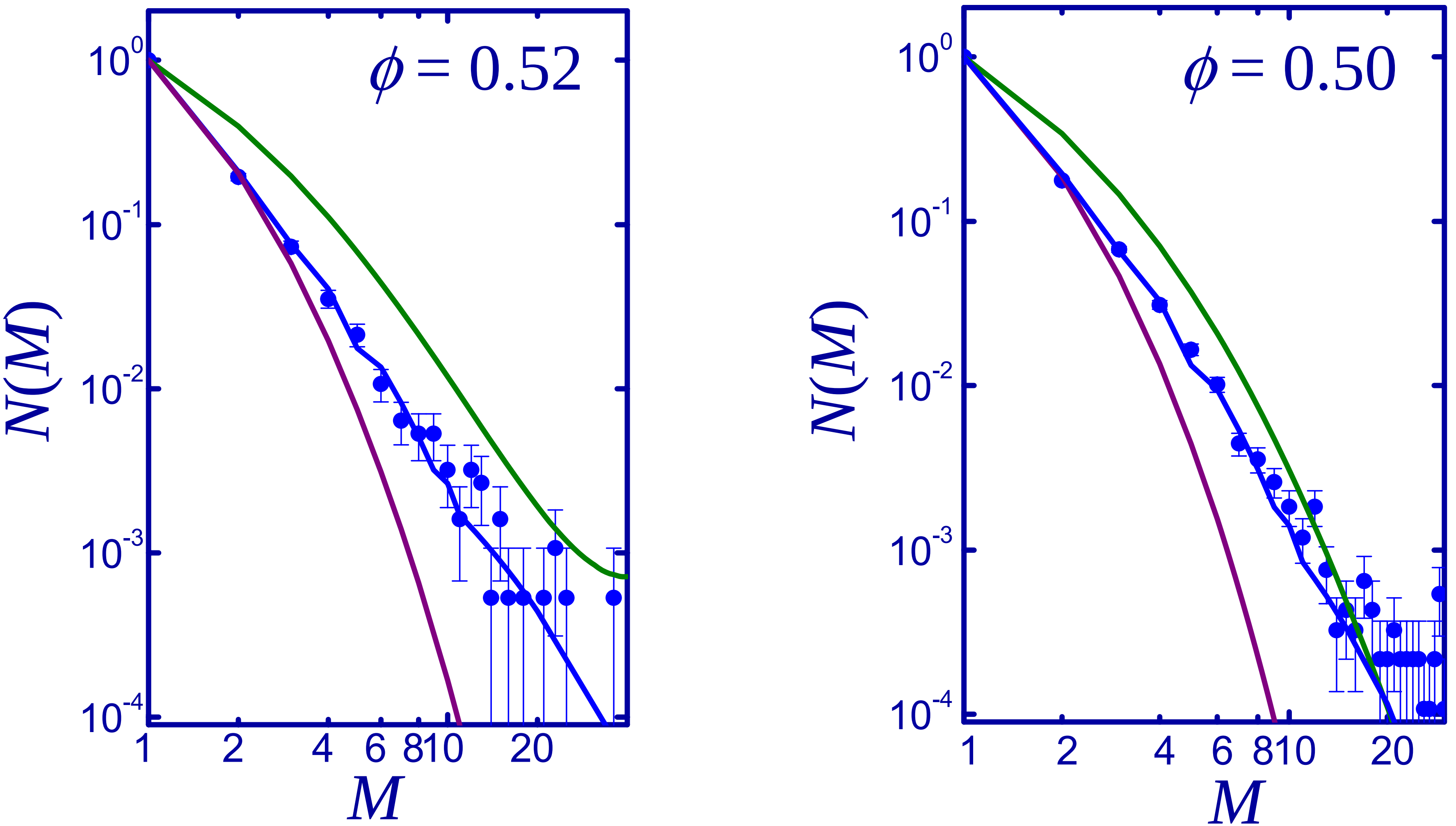
$$\left.\frac{d(\Delta G)}{dM}\right|_{M_c} = 0$$

Eddington, Kiang, Stauffer & Walker, *PRL* **26**, 820 (1971)

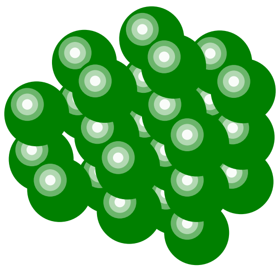
Test the modified free energy

$$\Delta G = \gamma A - \Delta\mu M + k_B T \ln M^{\tau}$$

$\tau = 1.25 \pm 0.25$



The full free energy



$\phi = 0.52$

$\tau = 1.25$

$$\Delta G(M) = \gamma A(M) - \Delta\mu M + \tau k_B T \ln M$$

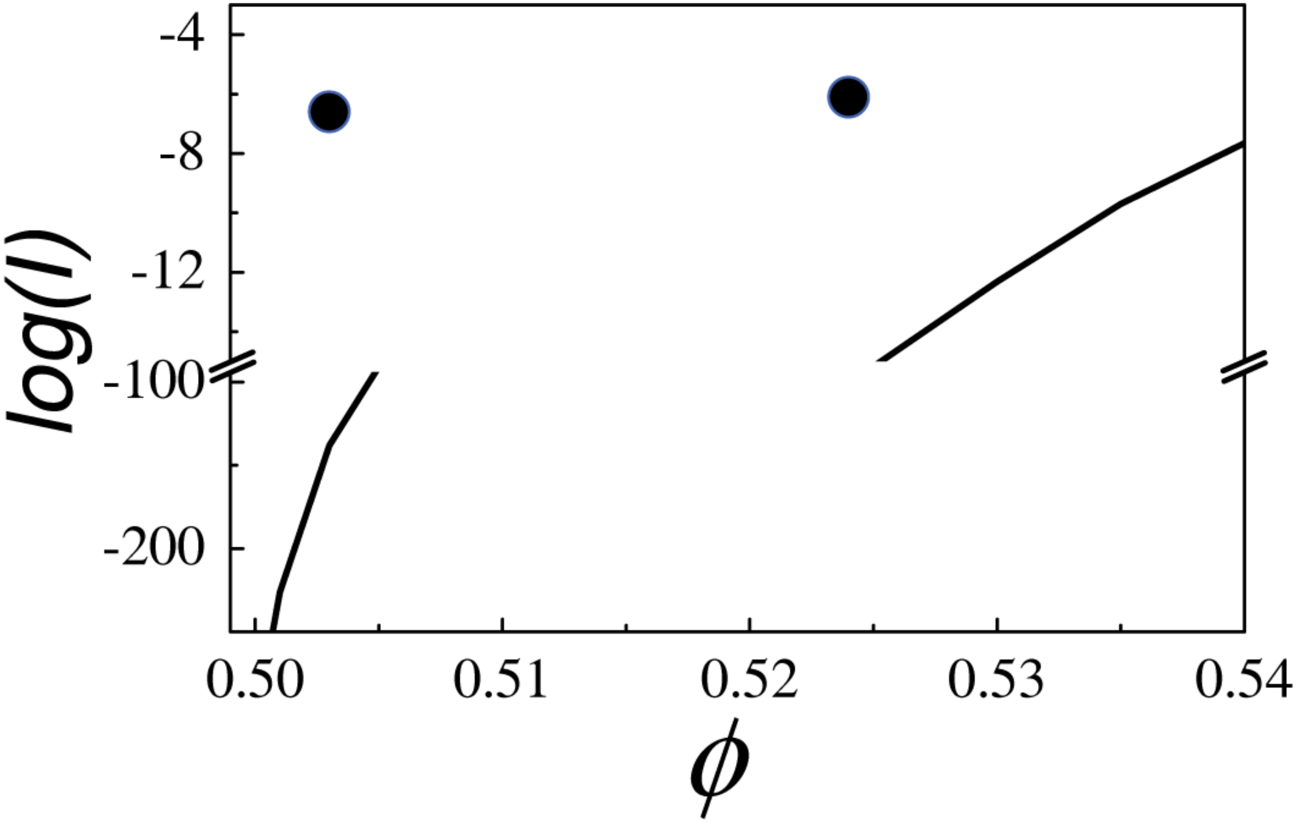
$$\Delta G(M) = 0.5 A(M) - 0.44 M + 1.25 k_B T \ln M$$

$\gamma = 0.5\, k_B T/\sigma^2$ (Morphology)

$\Delta\mu$ (fit)

Test predicted nucleation rates

$$\Delta G = \gamma A - \Delta\mu\rho V$$

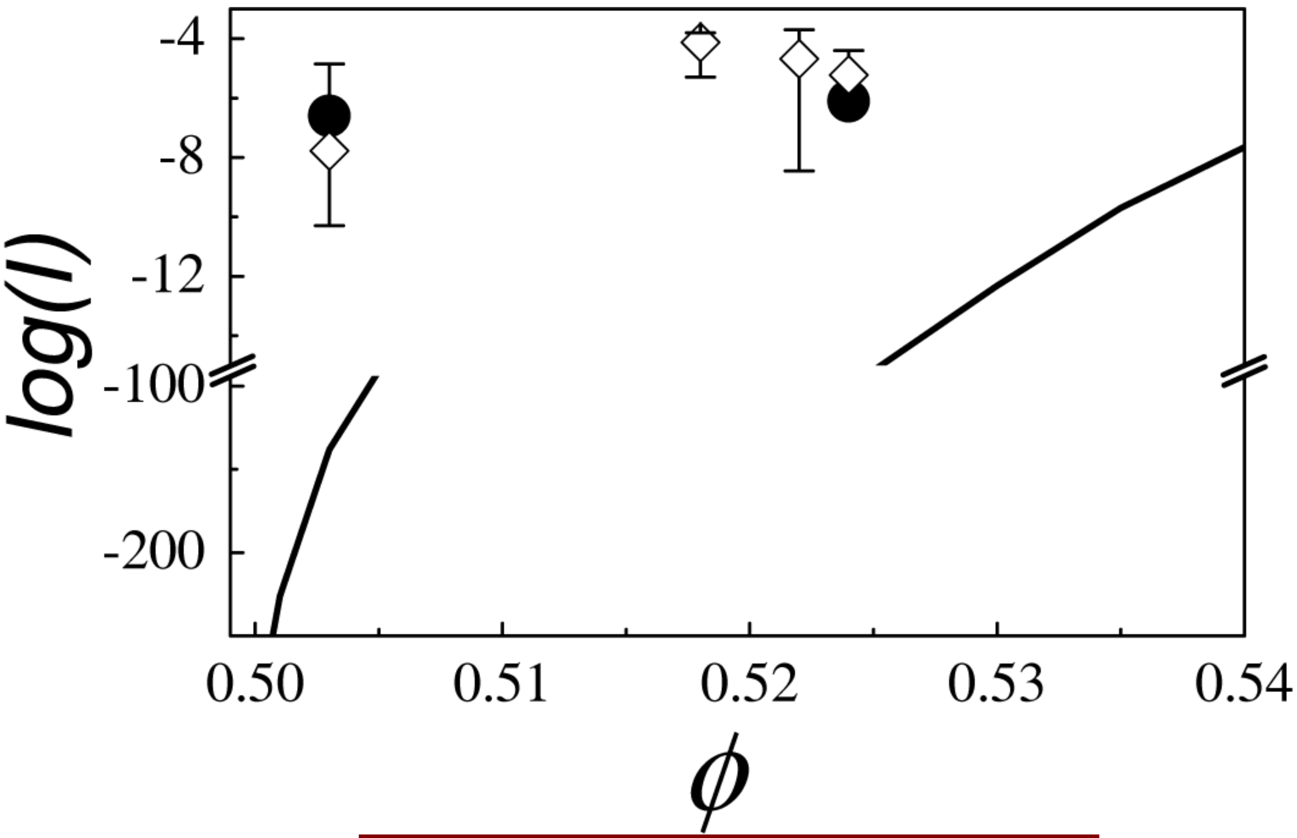


$I \sim \exp[-\Delta G(M_c)/k_B T]$

Test predicted nucleation rates

$$\Delta G = \gamma A - \Delta\mu\rho V$$

$$\Delta G = \gamma A - \Delta\mu\rho V + k_B T \ln M$$



$$I \sim \exp[-\Delta G(M_c)/k_B T]$$

Morphology of nuclei in *atomic* materials

<u>Solid-Liquid Tensions</u>

γ(Hard) ~ 0.5 kT/σ^2

γ(Ga) ~ 0.5 kT/σ^2

γ(Hg) ~ 0.3 kT/σ^2

γ(Cu) ~ 0.3 kT/σ^2

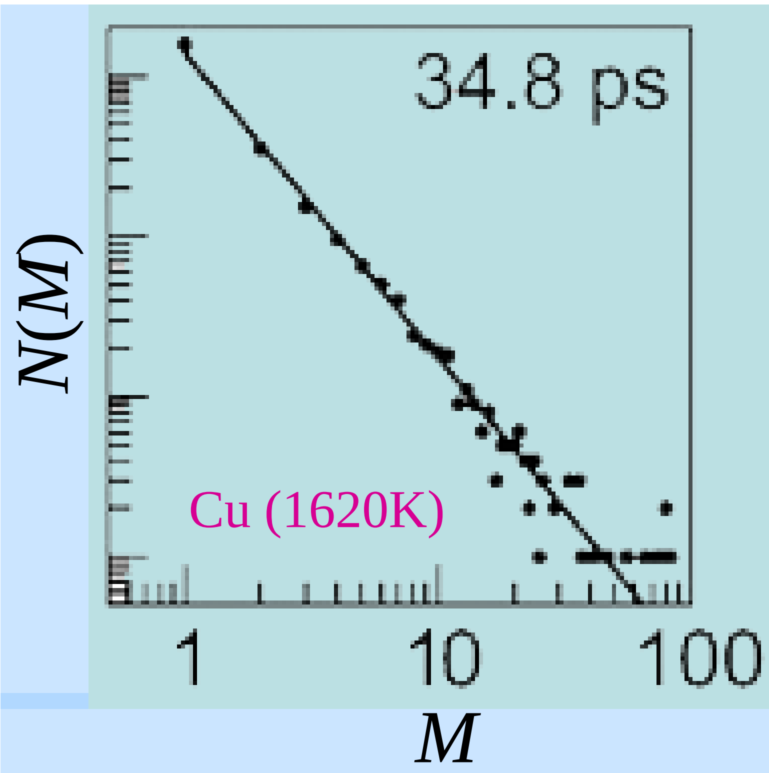
γ(Au) ~ 0.2 kT/σ^2

γ(Al) ~ 0.2 kT/σ^2

γ(Charged) ~ 0.1 kT/σ^2

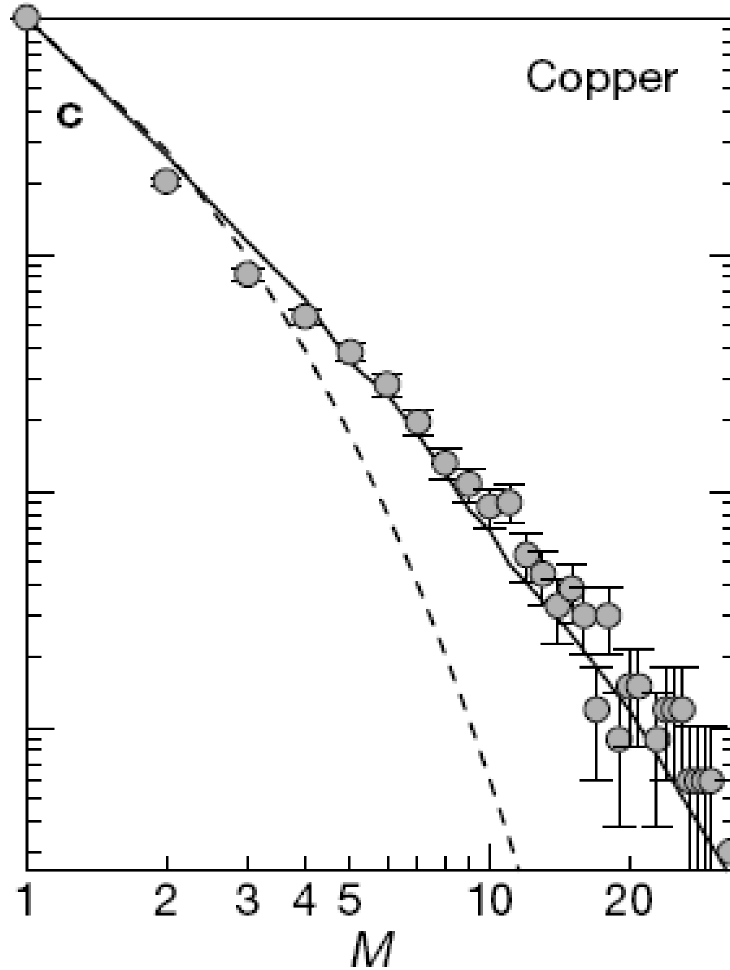
B. Vinet et al., *J. Coll. Interf. Sci* **255**, 363 (2002)

Simulation of nucleation of Cu crystals



L. Zheng *et al.*, *JCP* **127**, 164503 (2007)

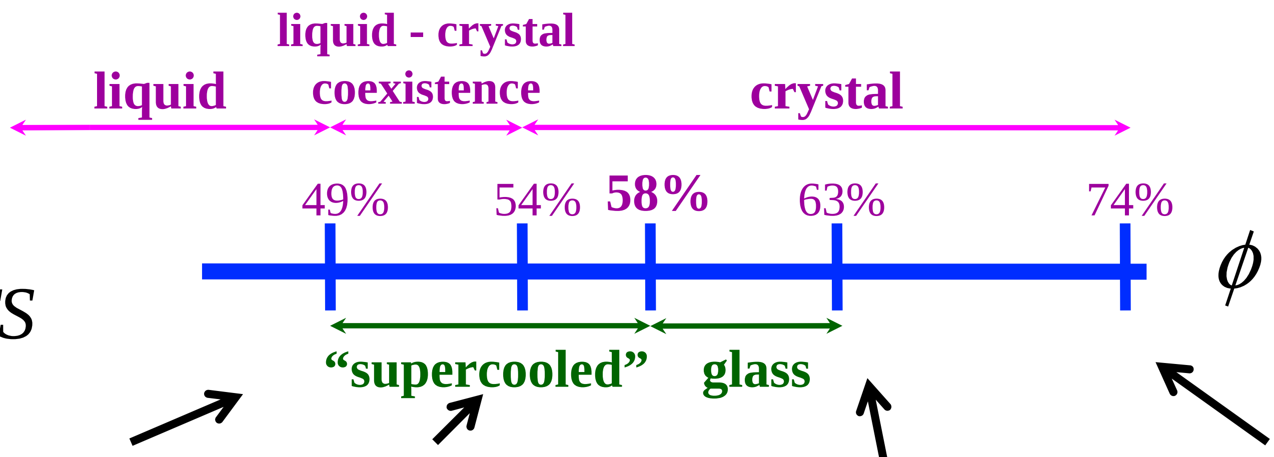
Power-law distribution

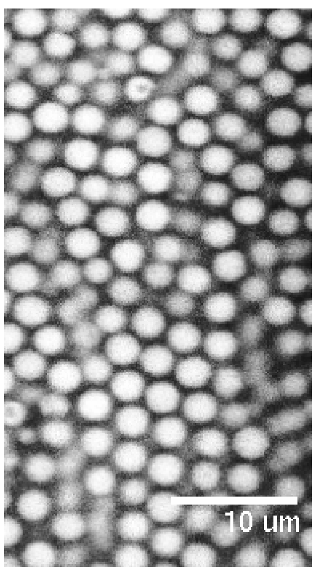


Fit with free energy using crystal entropy

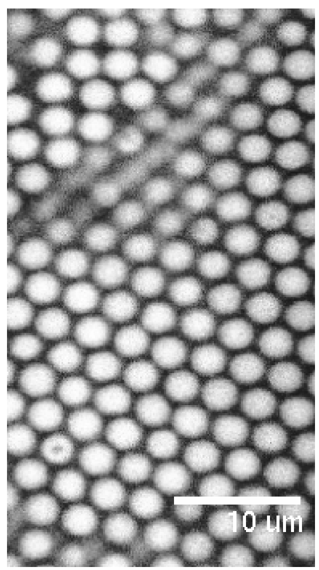
Hard-Sphere Glasses

$$F = \cancel{U}^{\,0} - TS$$

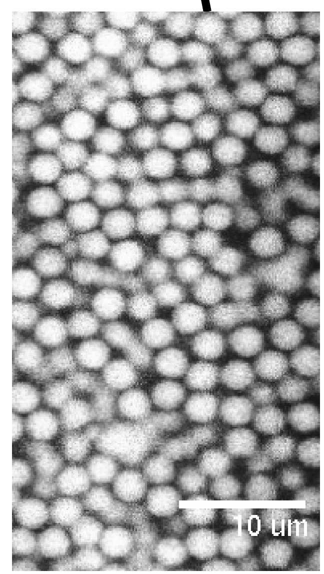




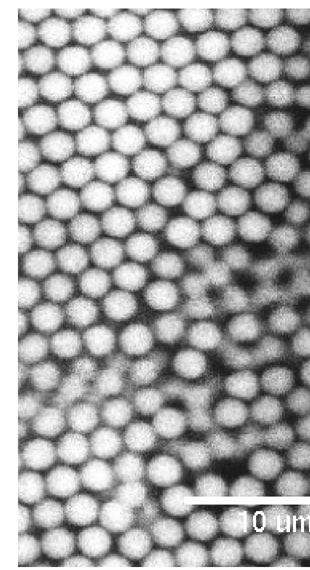
$\phi_{liquid} \approx 0.48$



$\phi_{xtal} \approx 0.54$



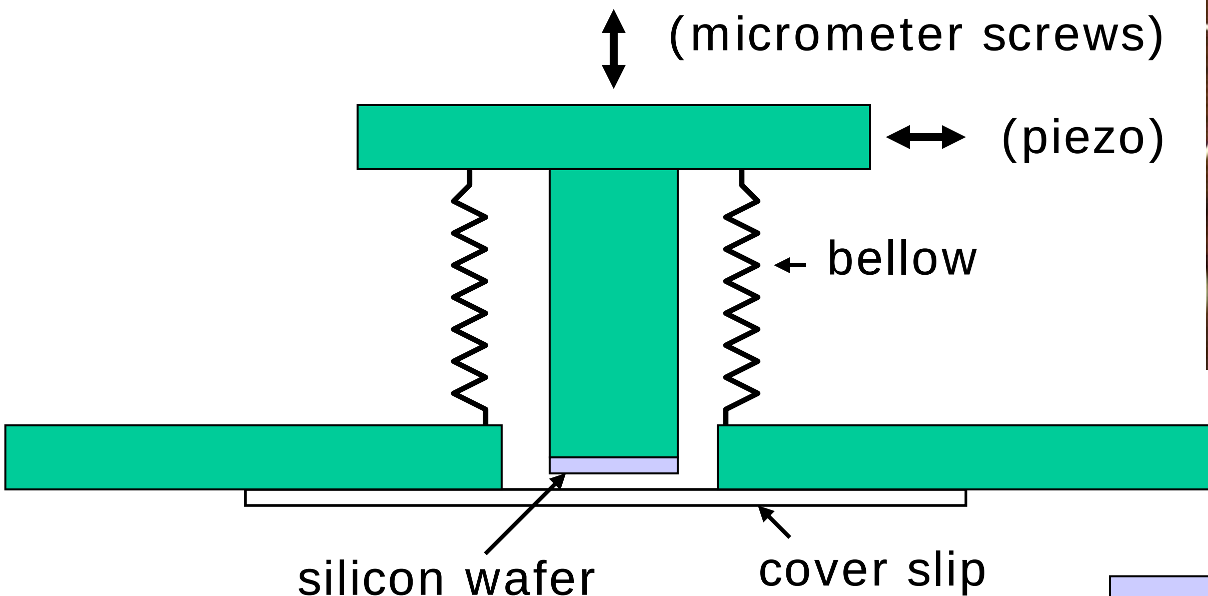
Maximum packing
$\phi_{RCP} \approx 0.63$

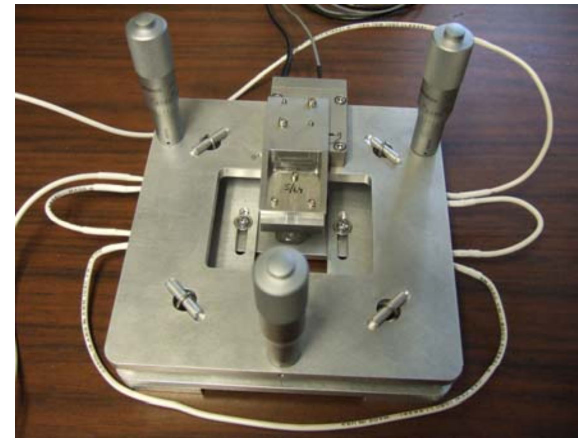


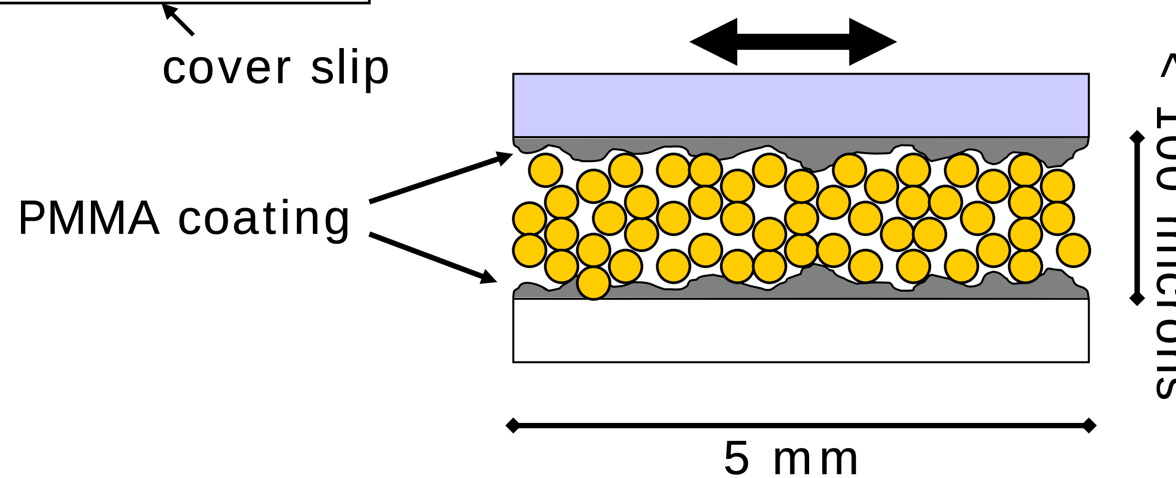
Maximum packing
$\phi_{HCP} = 0.74$

Increase ϕ => Decrease Temperature

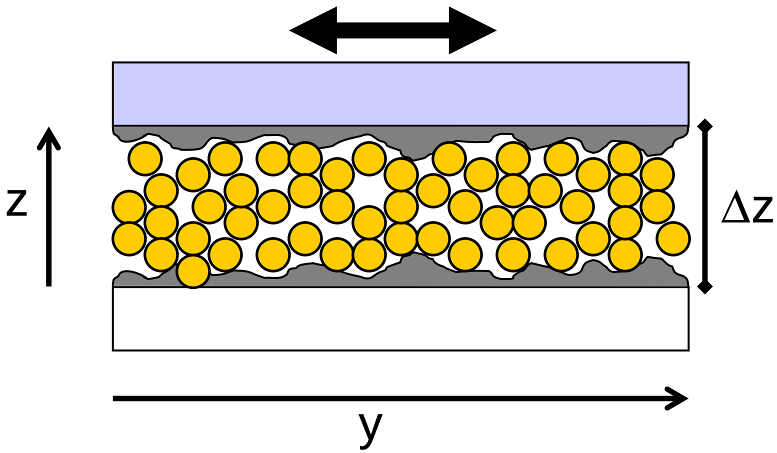
Shear cell

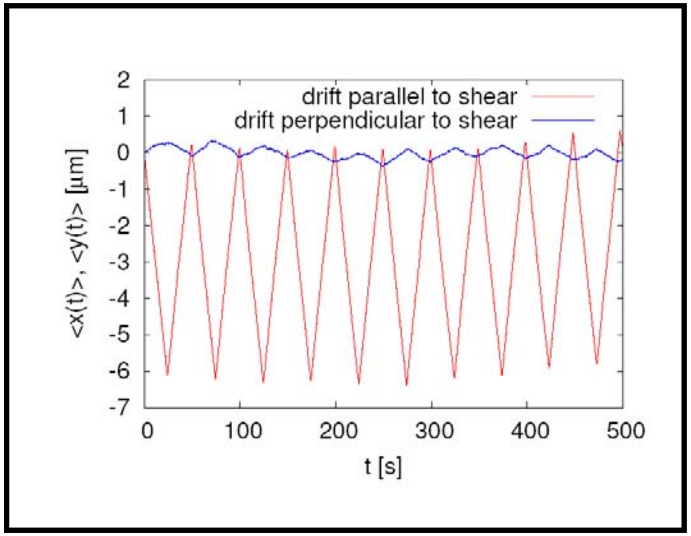

(micrometer screws)
(piezo)
bellow
silicon wafer
cover slip

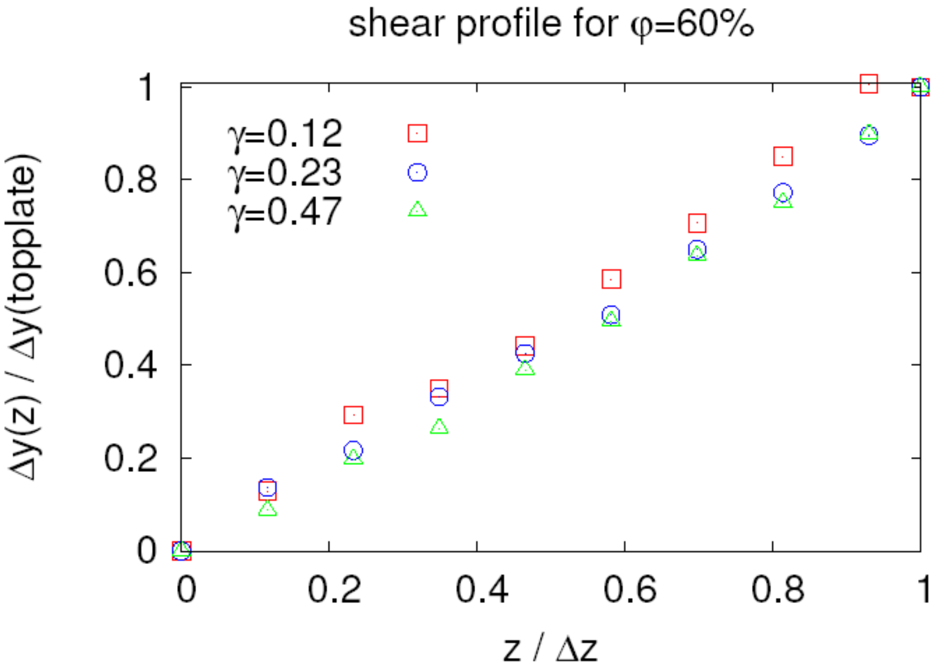



PMMA coating
< 100 microns
5 mm

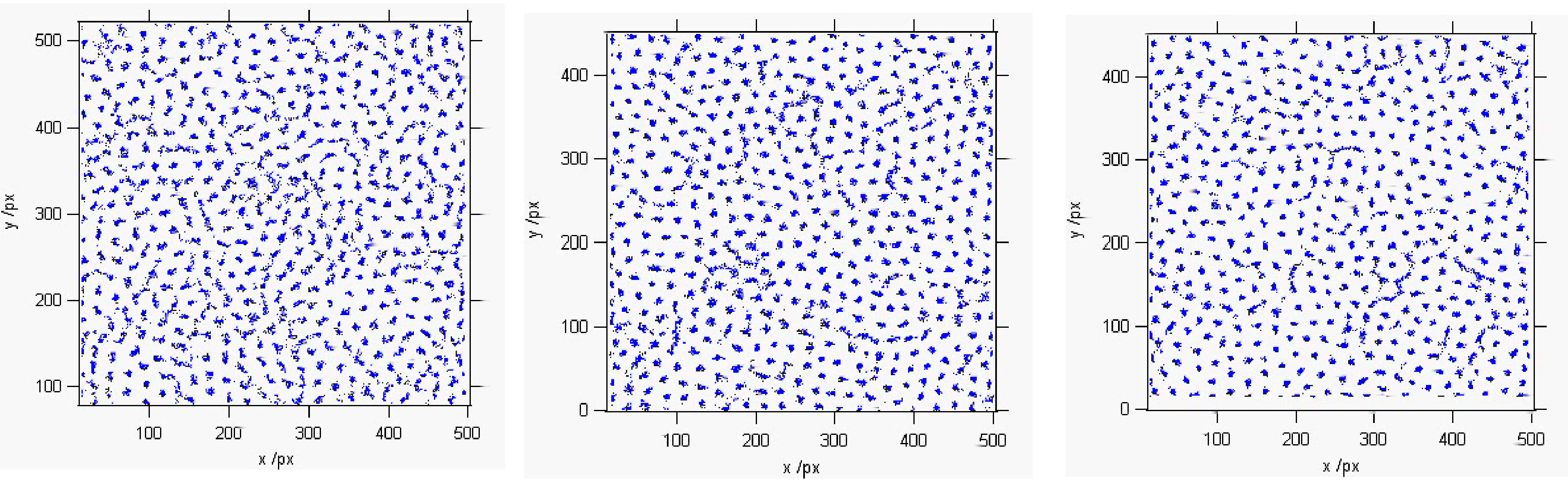
Shear profile



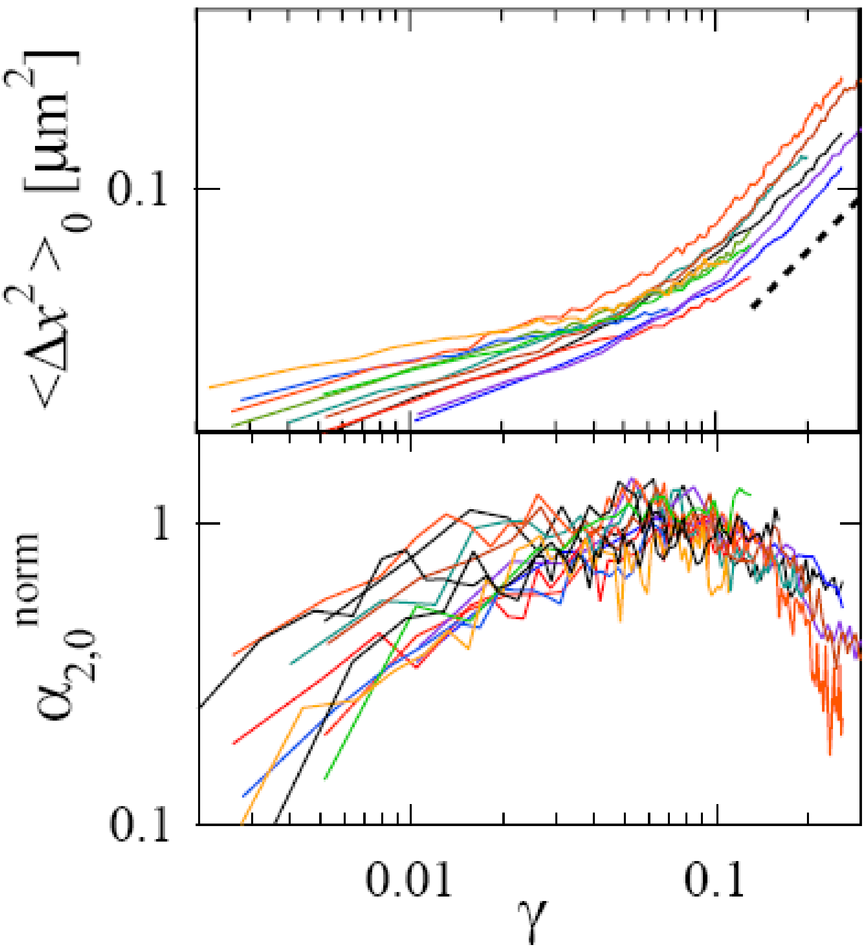




Glasses : Collective relaxations

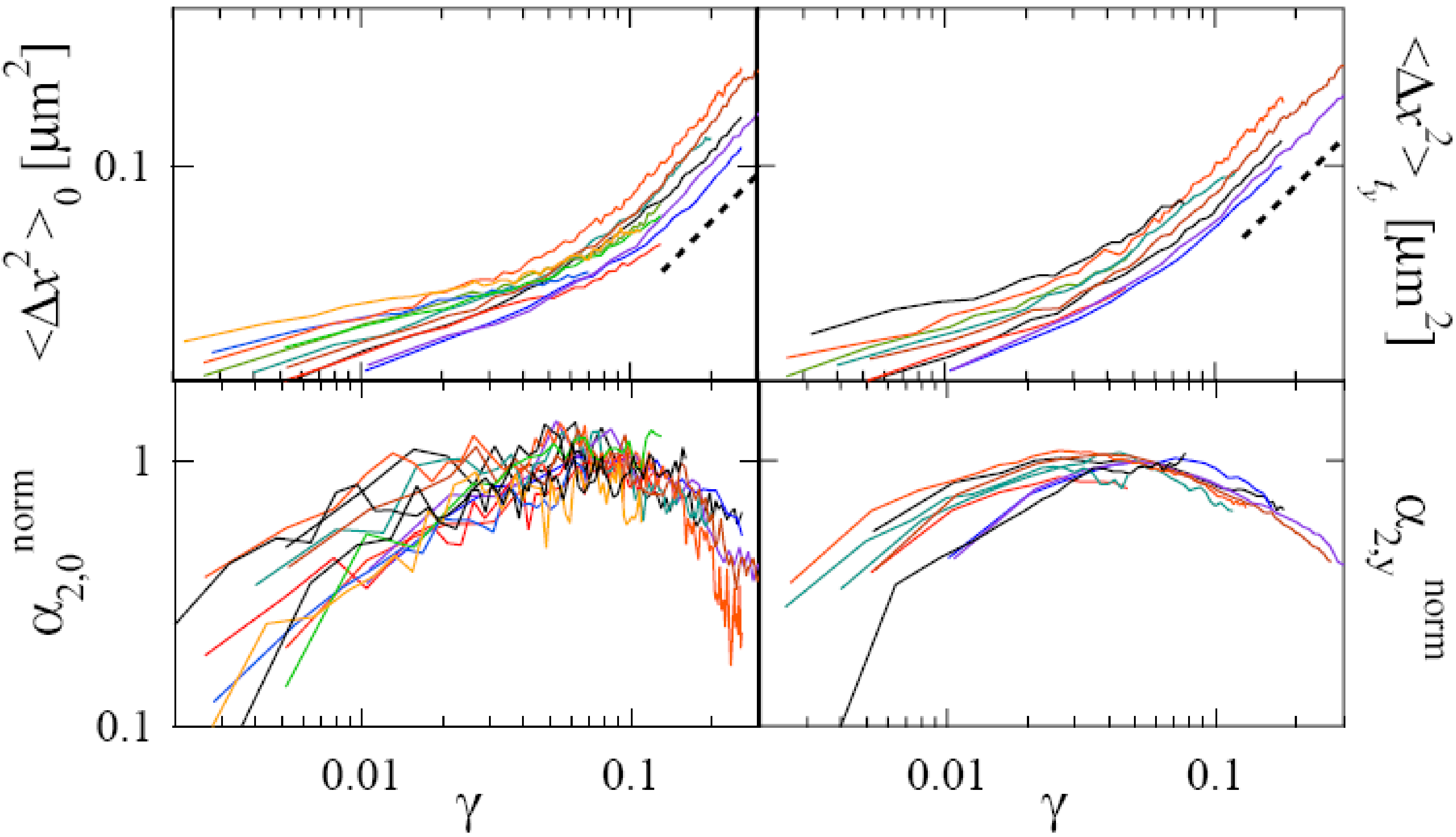


Yield strain ALWAYS required for flow



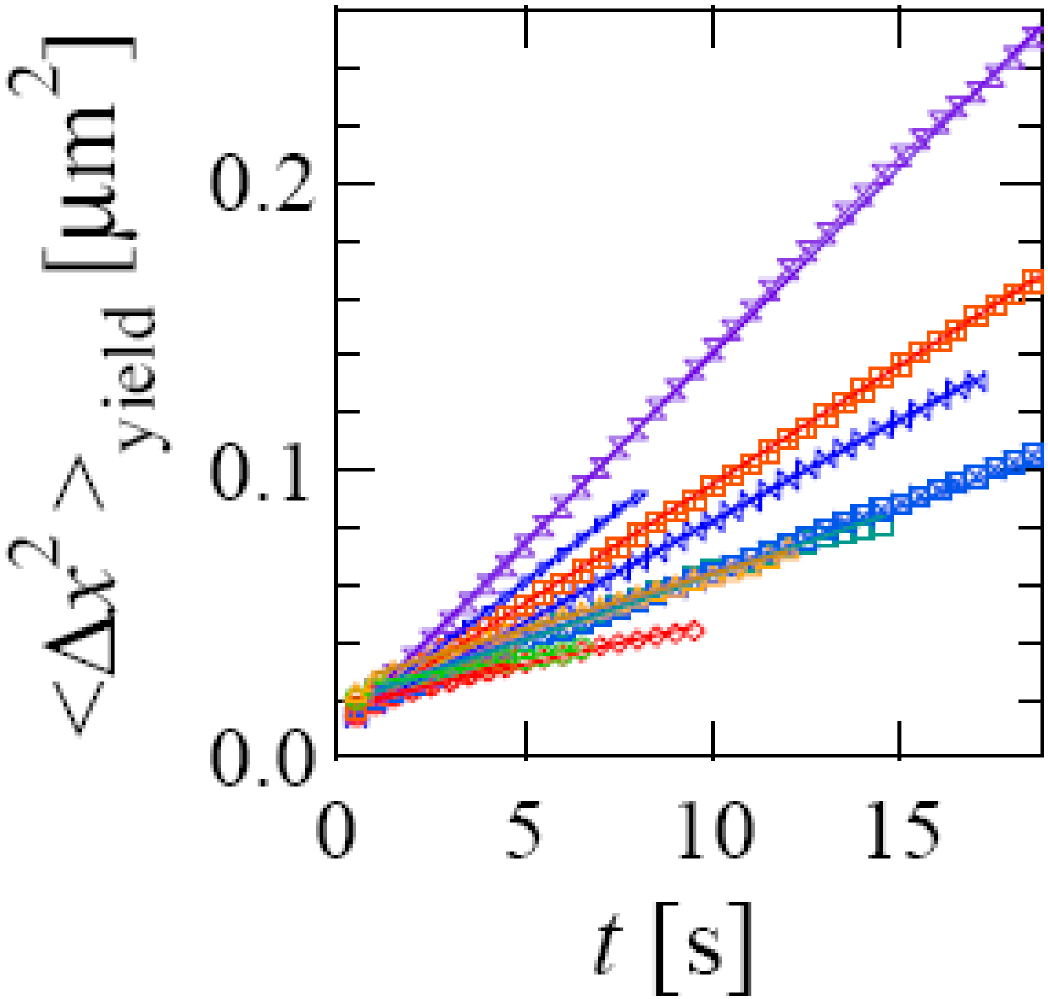
Beginning of shear

Yield strain ALWAYS required for flow



Beginning of shear After yield strain

Glasses : Shear strain network



Diffusion coefficient

$$D = k_{\mathrm{B}}T/6\pi\eta r$$

$$k_{\mathrm{B}}T \rightarrow \frac{4\pi}{3} r^3 \eta \dot{\gamma}$$

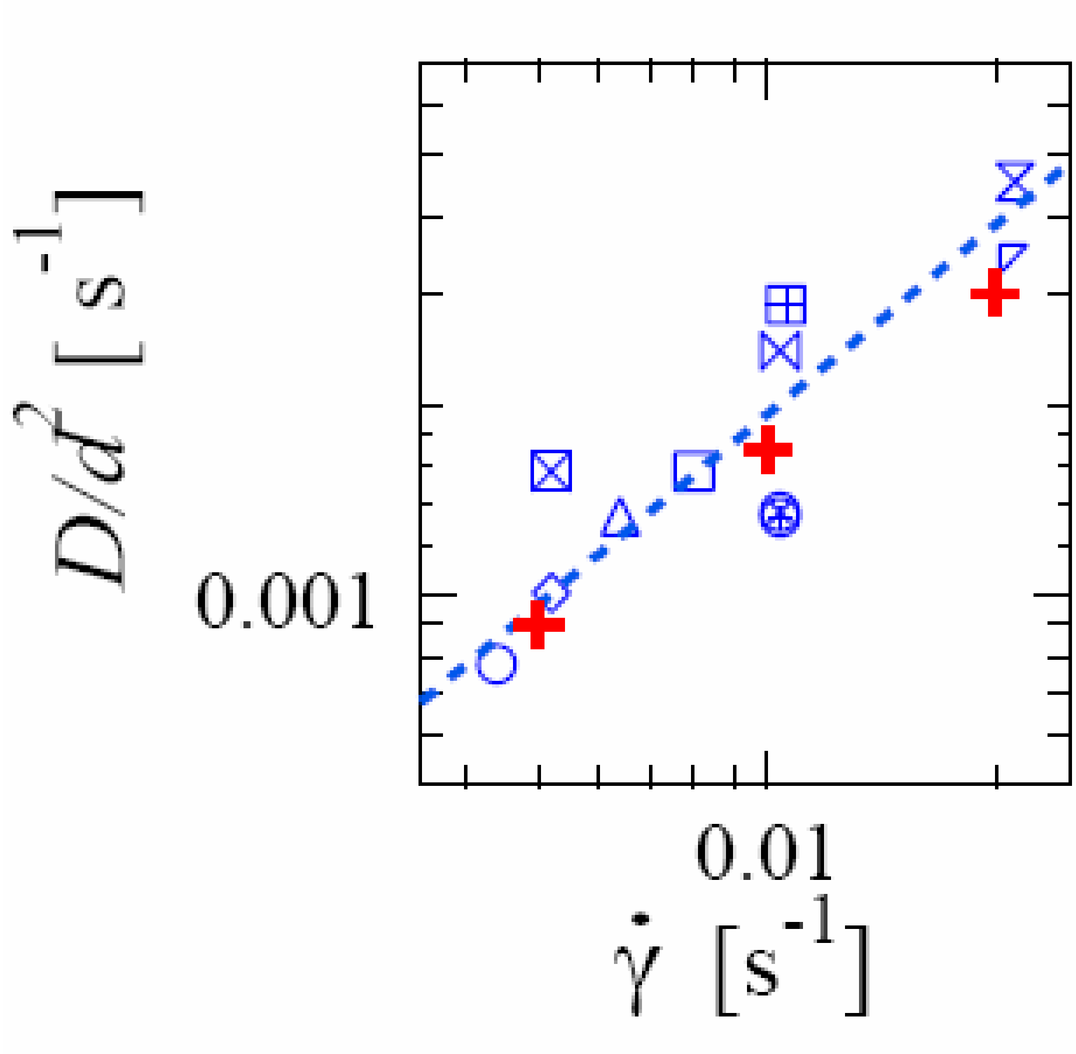
Shear energy

$$D = \frac{2}{9} r^2 \dot{\gamma}$$

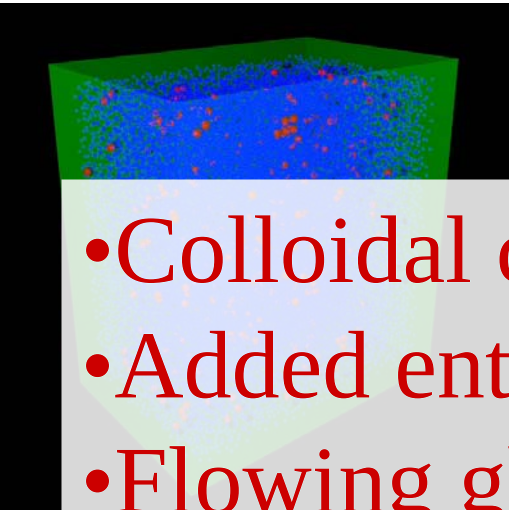
Effective diffusion coefficient depends on shear rate

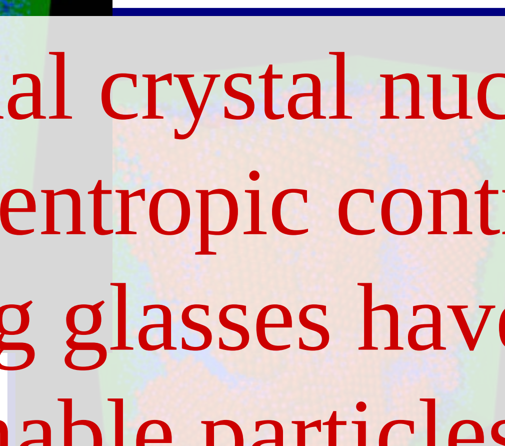
$$D = \frac{2}{9} r^2 \dot{\gamma}$$

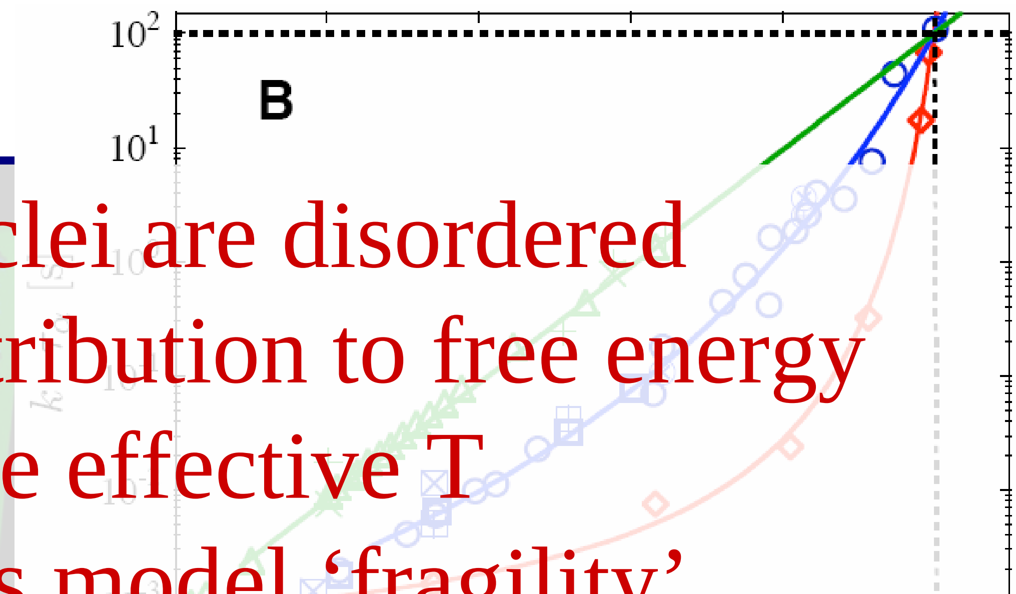
V ~ 4 particles



Conclusions

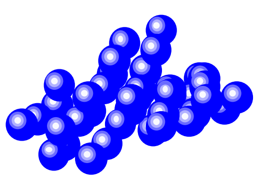


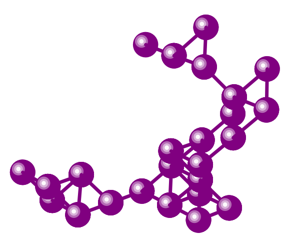




- Colloidal crystal nuclei are disordered
- Added entropic contribution to free energy
- Flowing glasses have effective T
- Deformable particles model ‘fragility’

Thank you for your attention





Fast crystal nucleation