Nucleation and growth of hard-sphere colloidal crystals

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Toshi Kani	Yokohama	Peter Pusey	Edinburgh

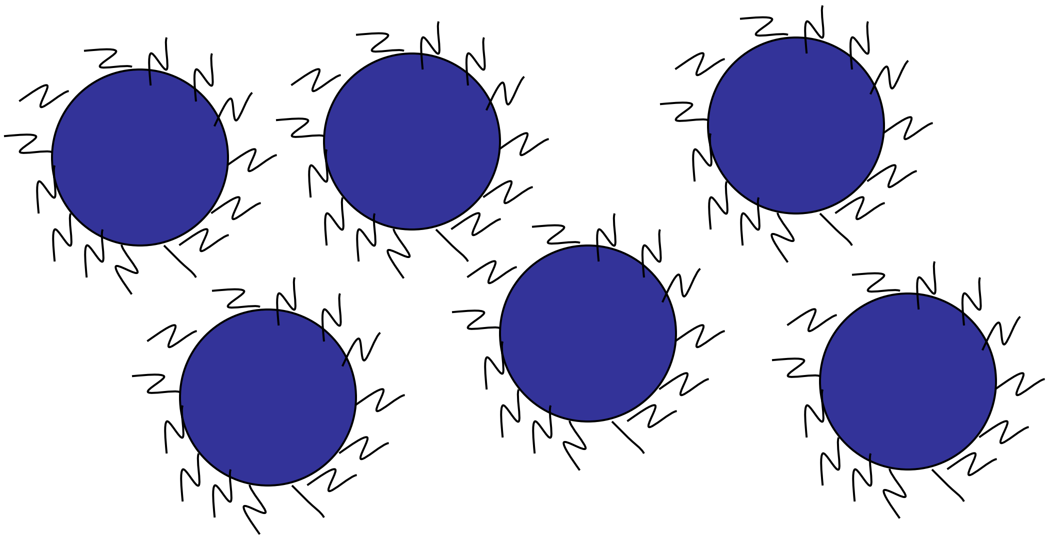
1. Hard-sphere colloid nucleation
2. Nucleation of Yukawa particles

NSF, MRSEC, NASA

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

NAG2010 7/29/10

Colloidal Particles



Stability:

Short range repulsion

Sometimes a slight charge

Colloid Particles are:

•Big

•~ a ~ 1 micron

•Can "see" them

Slow

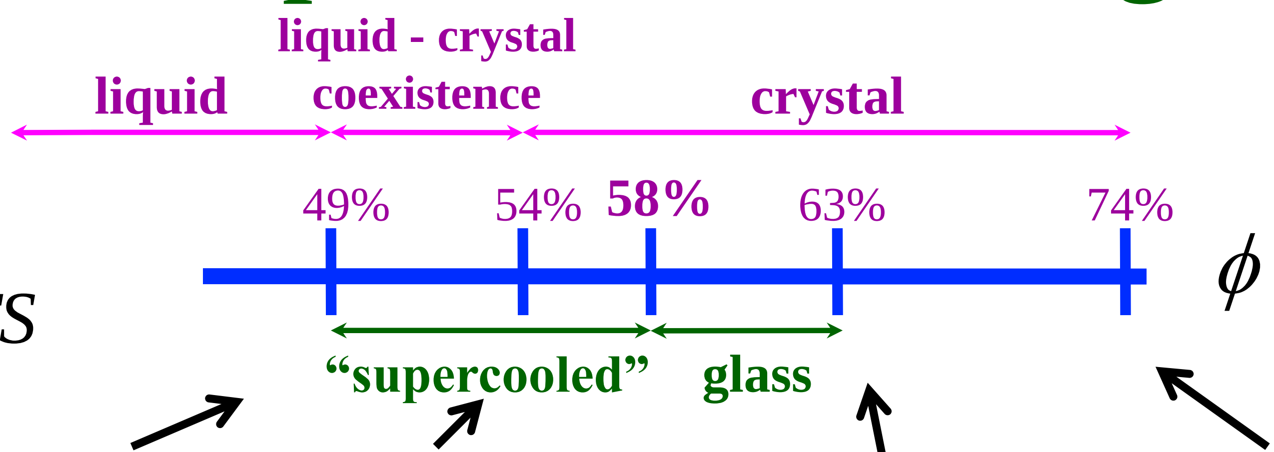
• $\tau \sim a^2/D$ ~ ms to sec

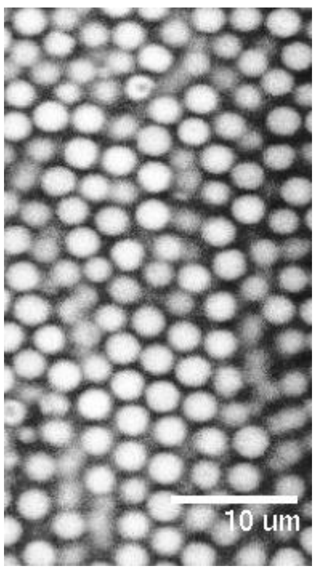
•Follow individual particle dynamics

Model: Colloid → Atom

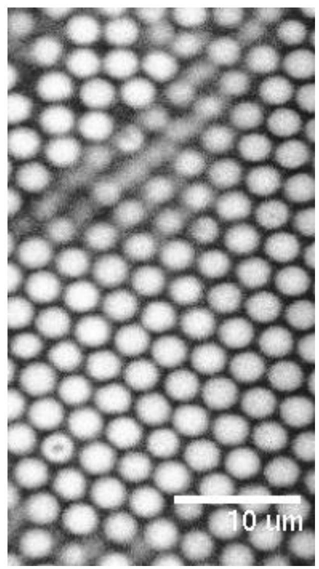
Hard-Sphere Phase Diagram

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

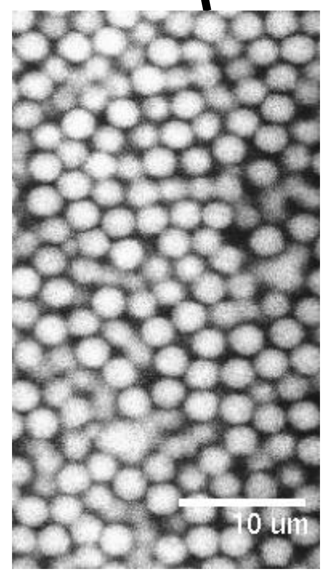




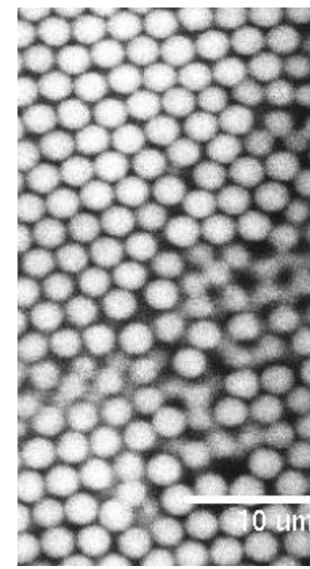
$\phi_{liquid} \approx 0.48$



$\phi_{xtal} \approx 0.54$



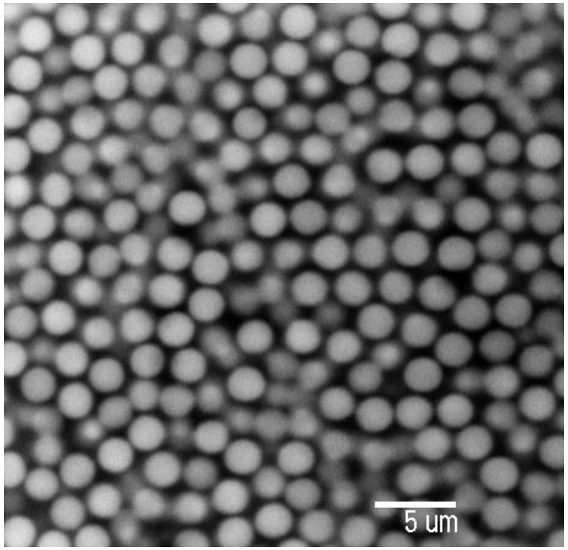
Maximum packing
$\phi_{RCP} \approx 0.63$

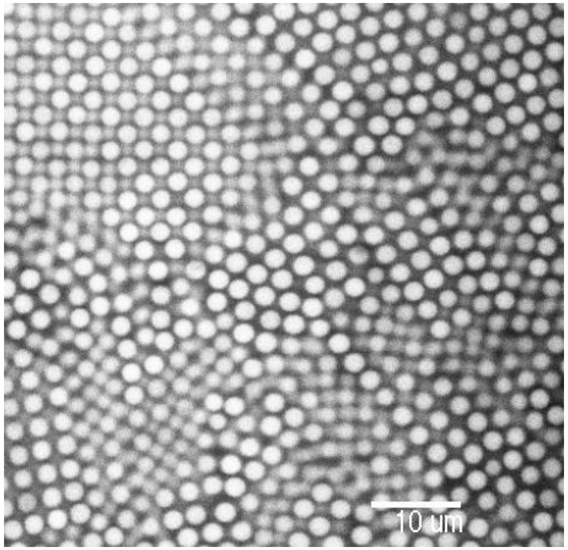


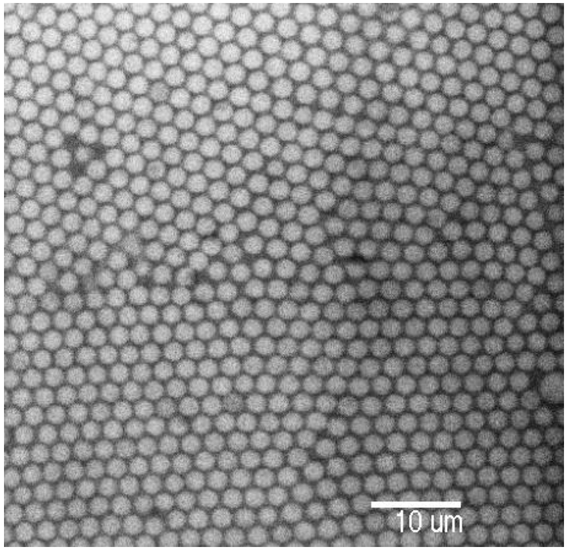
Maximum packing
$\phi_{HCP} = 0.74$

Increase ϕ => Decrease Temperature

How do colloidal crystals form?

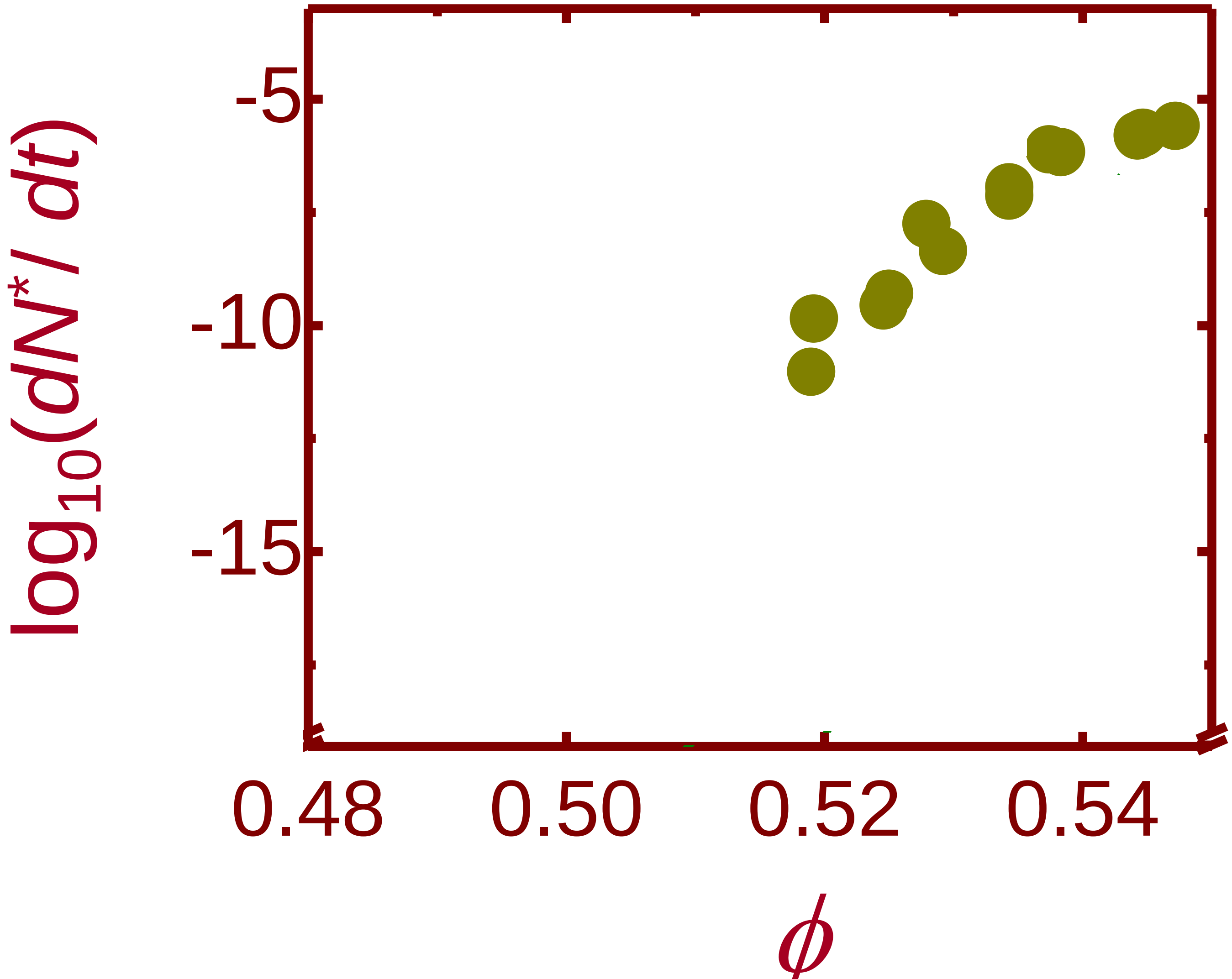




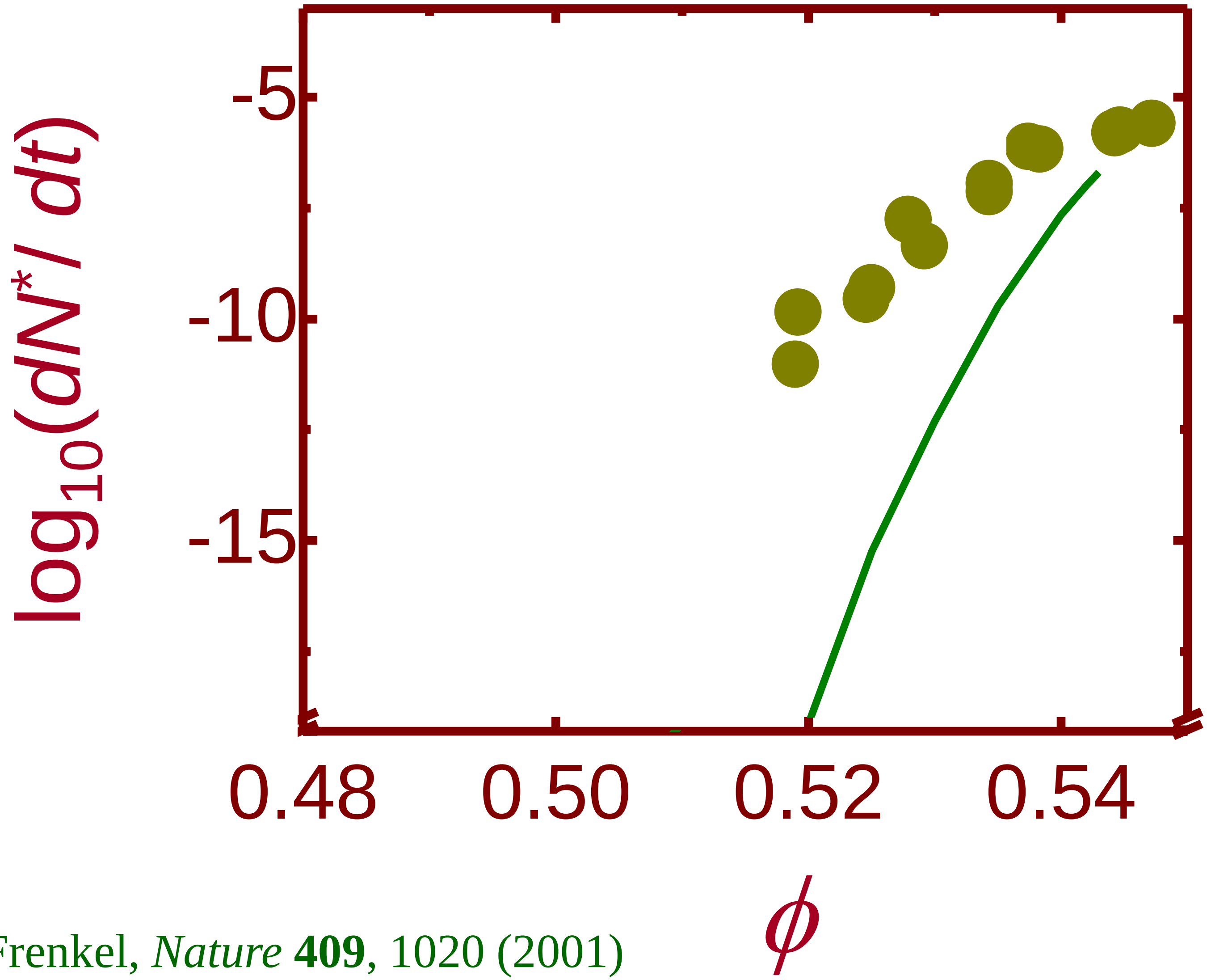


2.3 μm diameter PMMA spheres

Nucleation rates of Colloidal Crystals

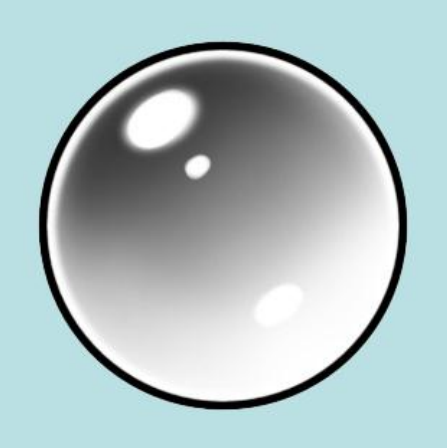


Nucleation rates of hard-sphere colloidal crystals



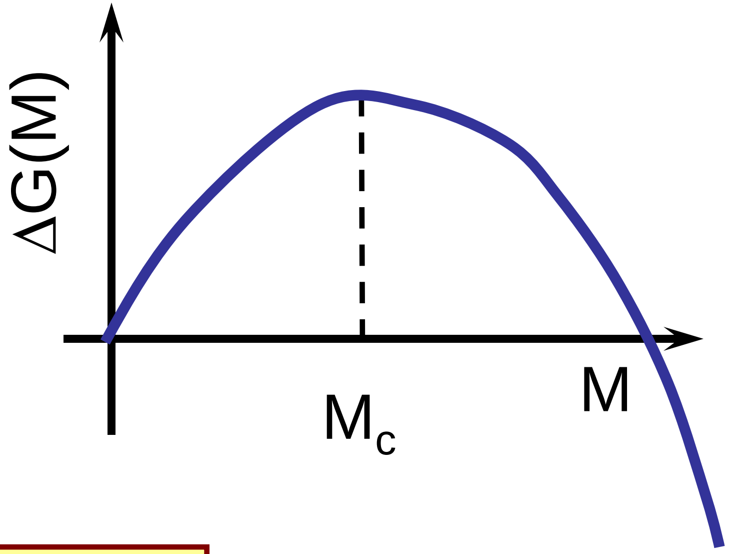
Auer & Frenkel, *Nature* **409**, 1020 (2001)

Nucleation and Growth



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

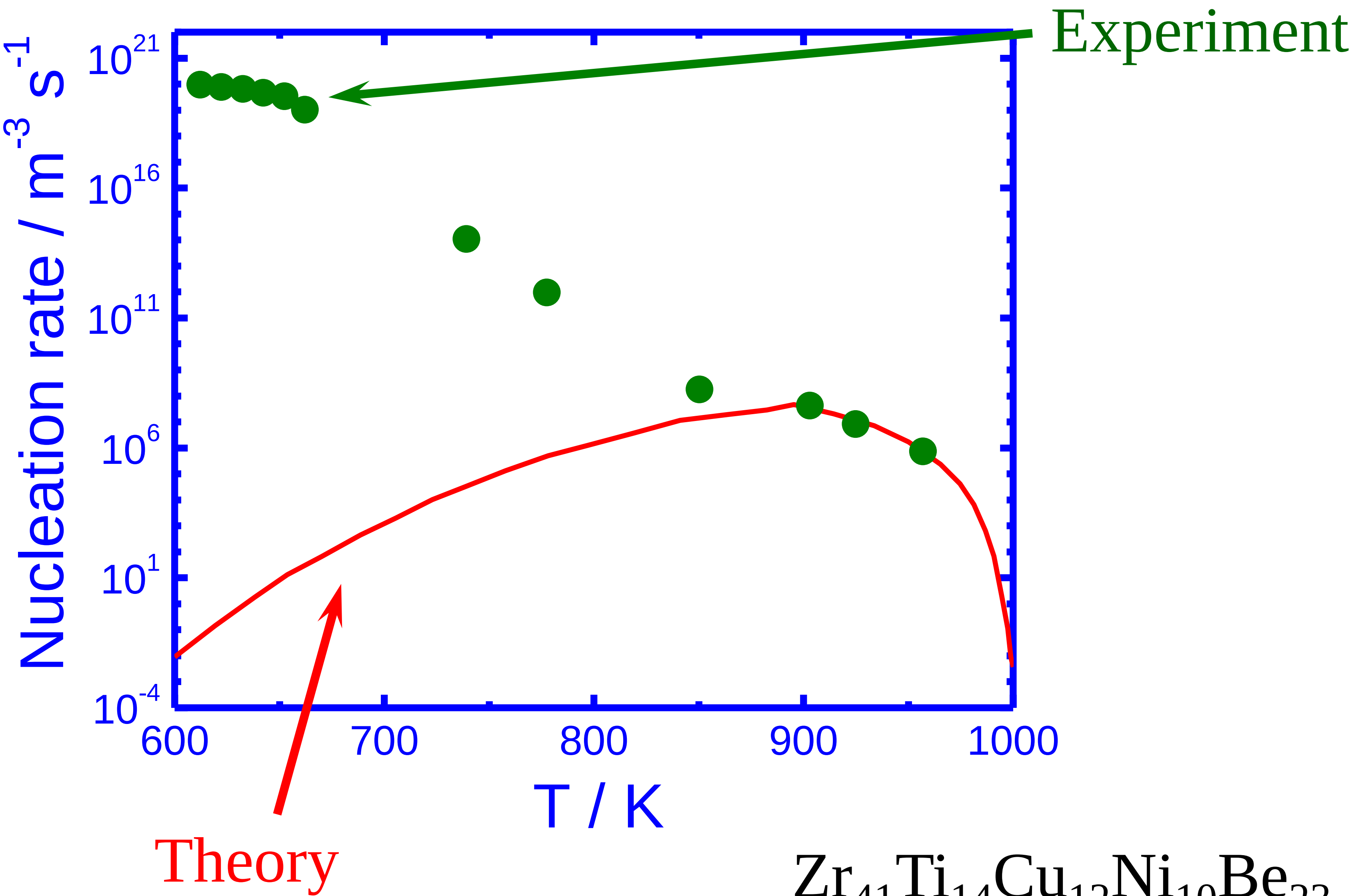
$$V = 4/3\pi R^3$$



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

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

Nucleation rates not predicted correctly



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

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

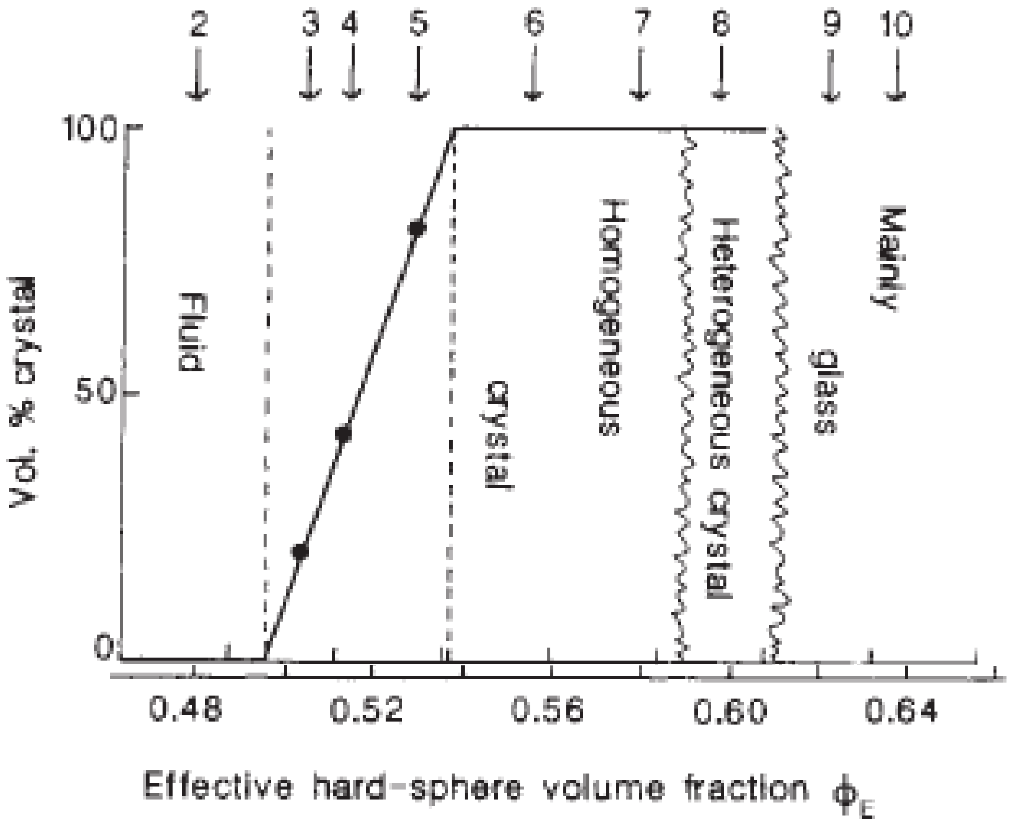
Pusey-Van Megen colloidal hard spheres

← Increasing ϕ

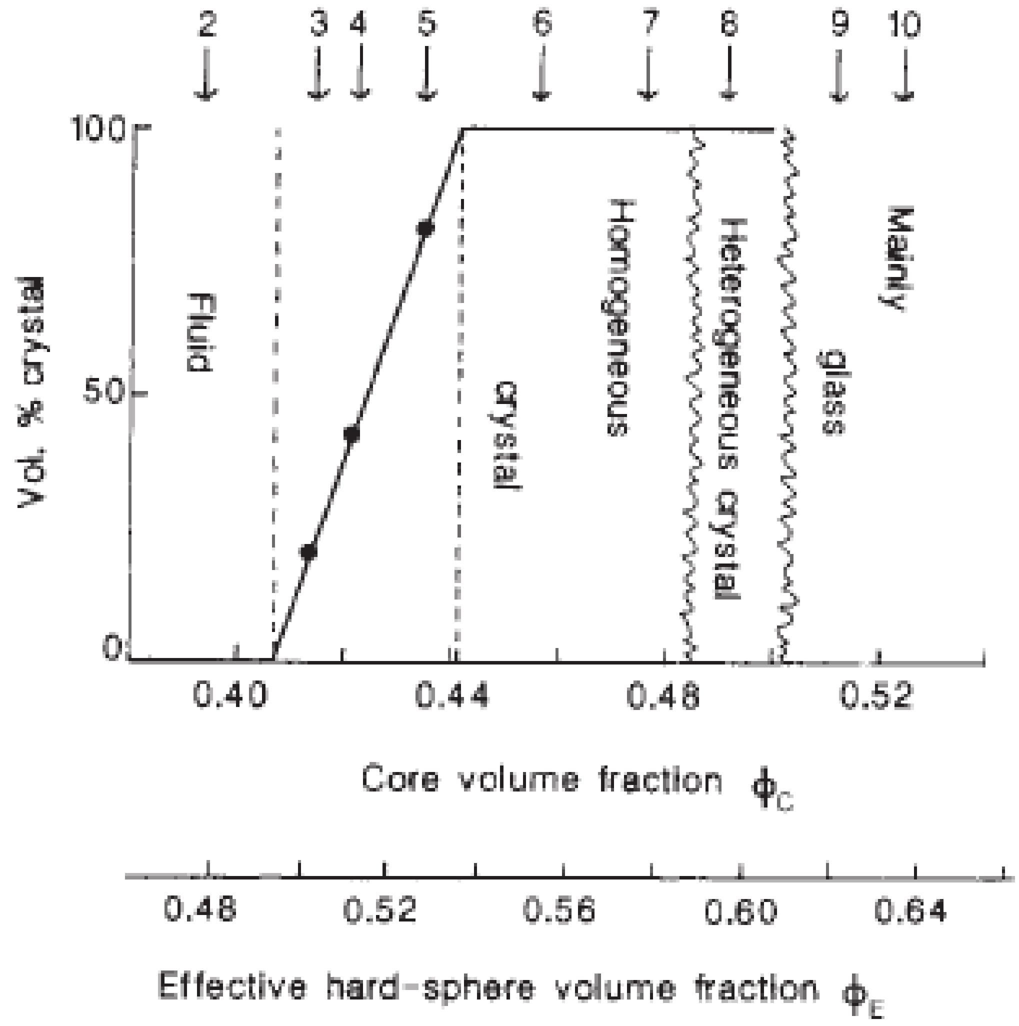
Pusey-Van Megen colloidal hard spheres

$\phi = 0.50$ Increasing ϕ →

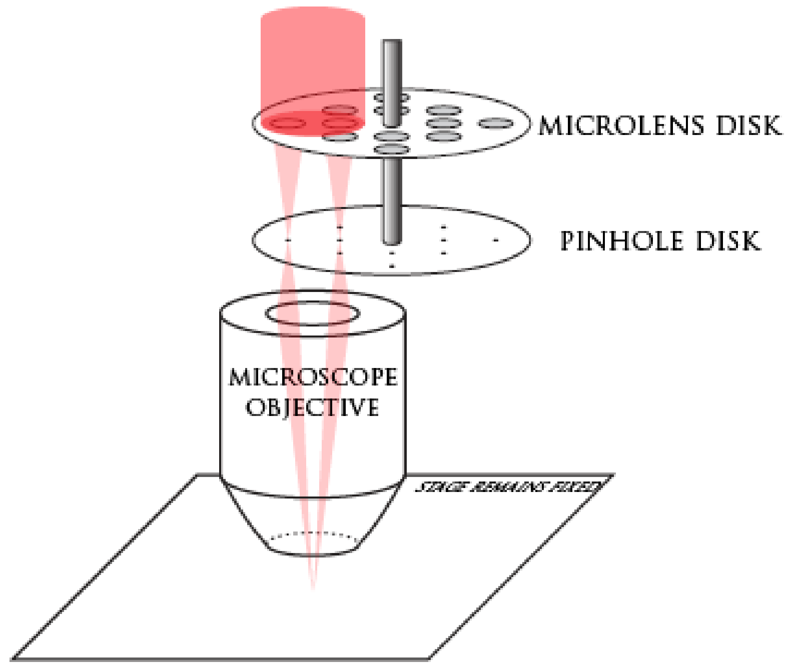
Pusey-Van Megen colloidal hard spheres

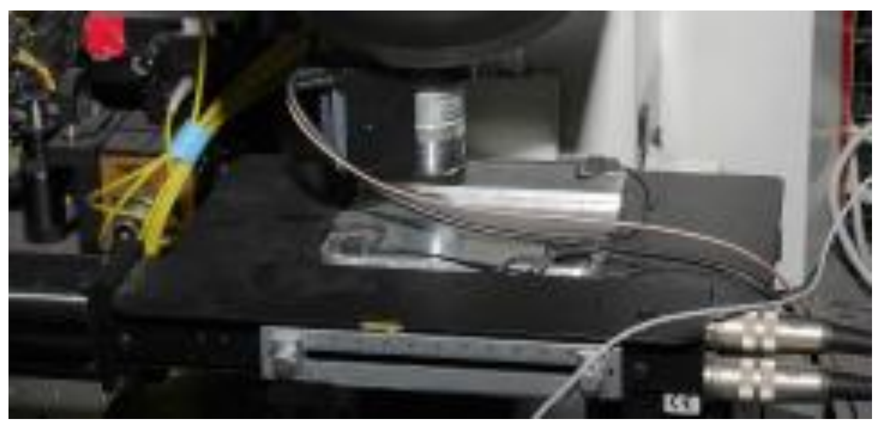


Pusey-Van Megen colloidal hard spheres



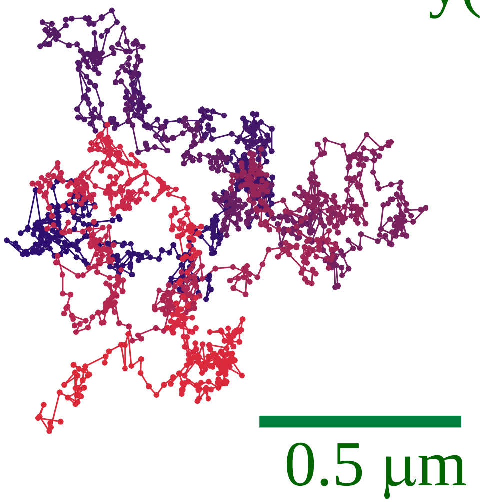
Confocal Microscopy

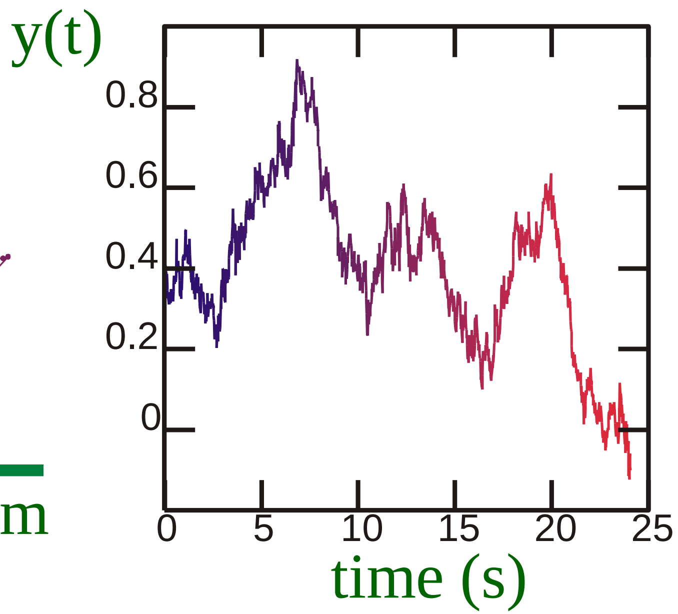


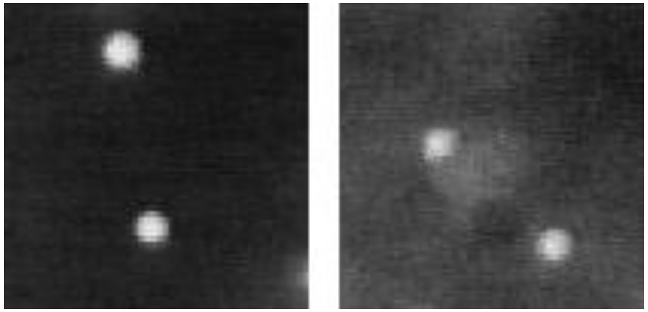


Brownian Motion

(2 μm particles, **dilute** sample)

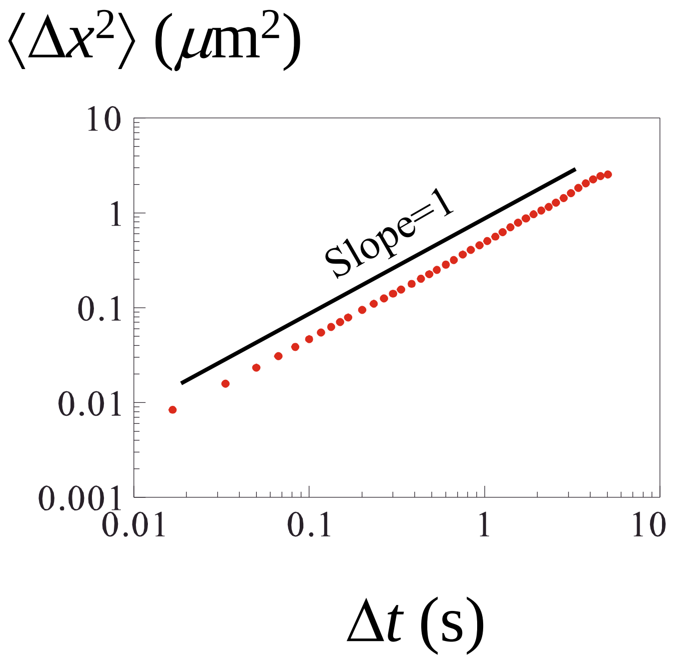




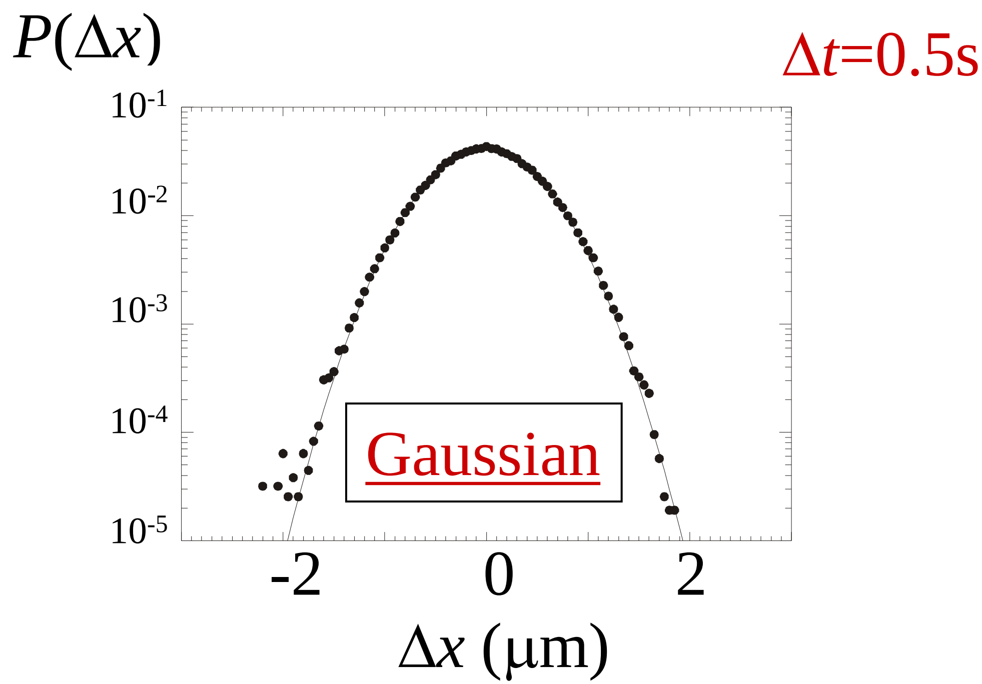


Diffusion: **dilute** samples

Mean square displacement:



Displacement distribution function:



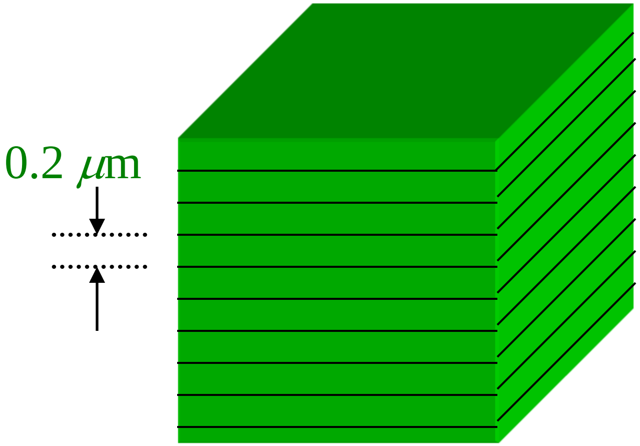
Leads to normal diffusion: $\langle \Delta x^2 \rangle = 2Dt$

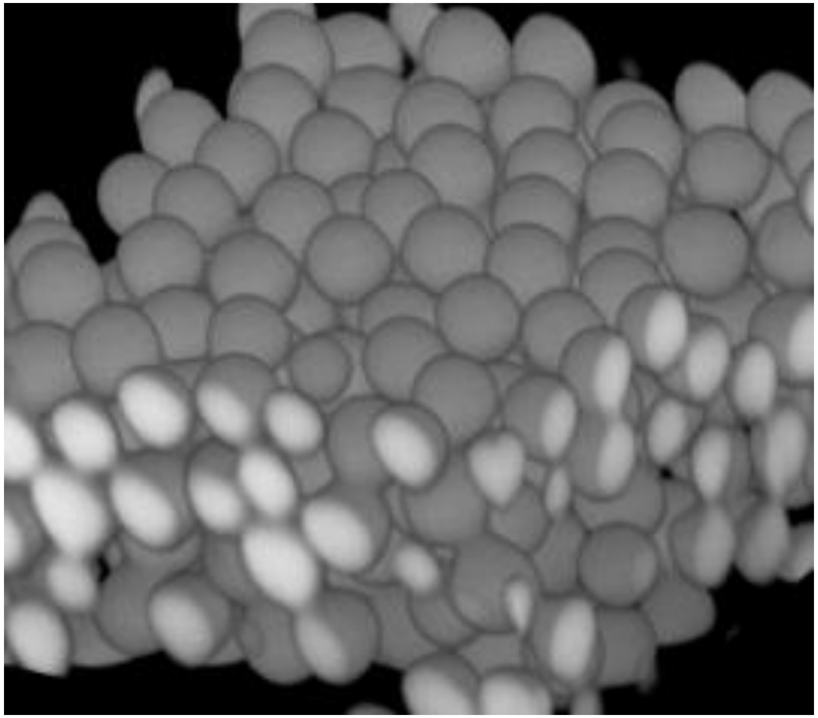
$$D = \frac{k_B T}{6\pi\eta a}$$

Particle size a

viscosity η

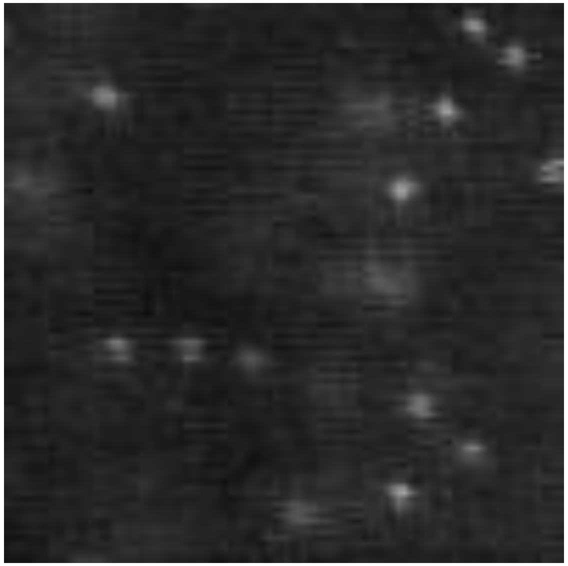
Confocal microscopy for 3D pictures

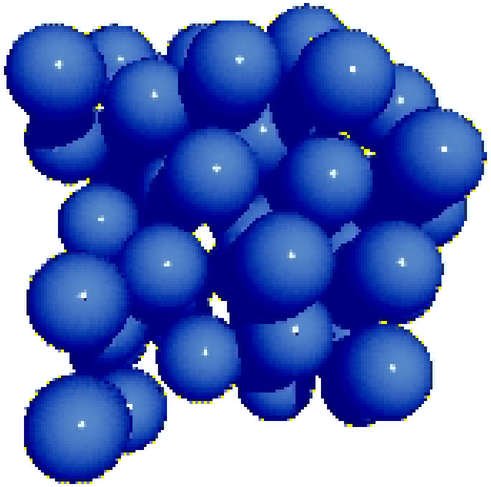




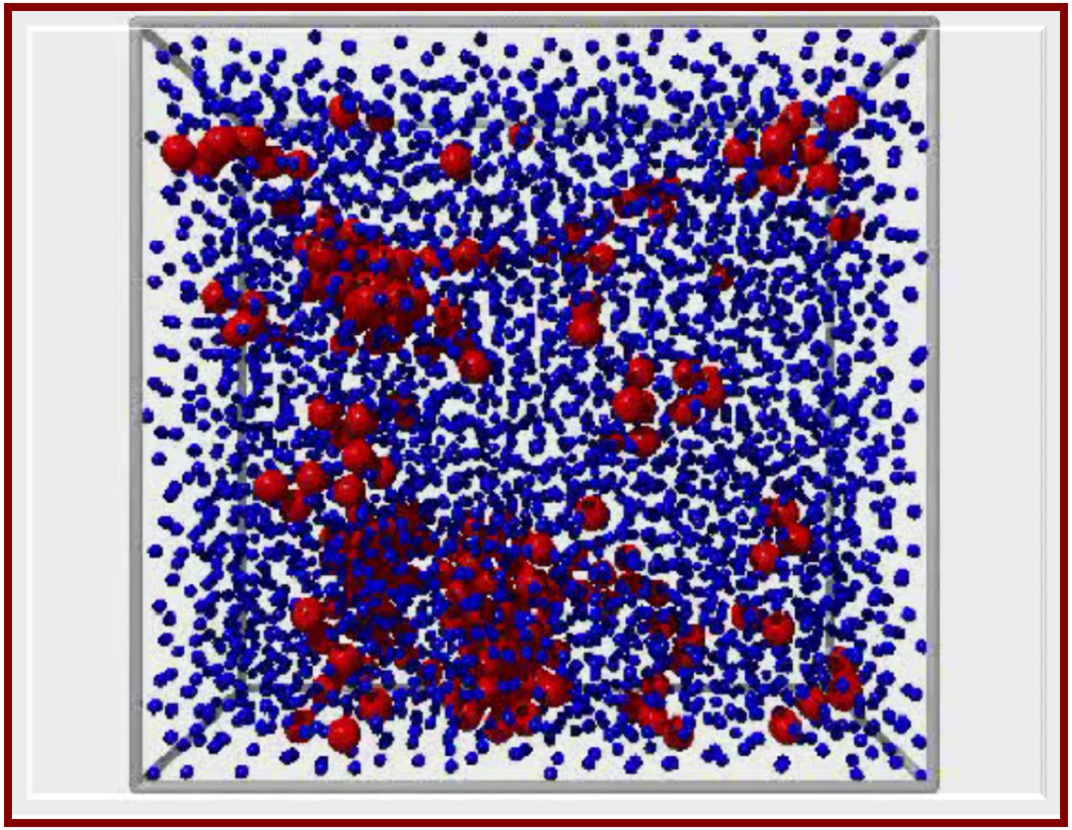
Scan many slices,
reconstruct 3D image

Brownian Motion in Real Time





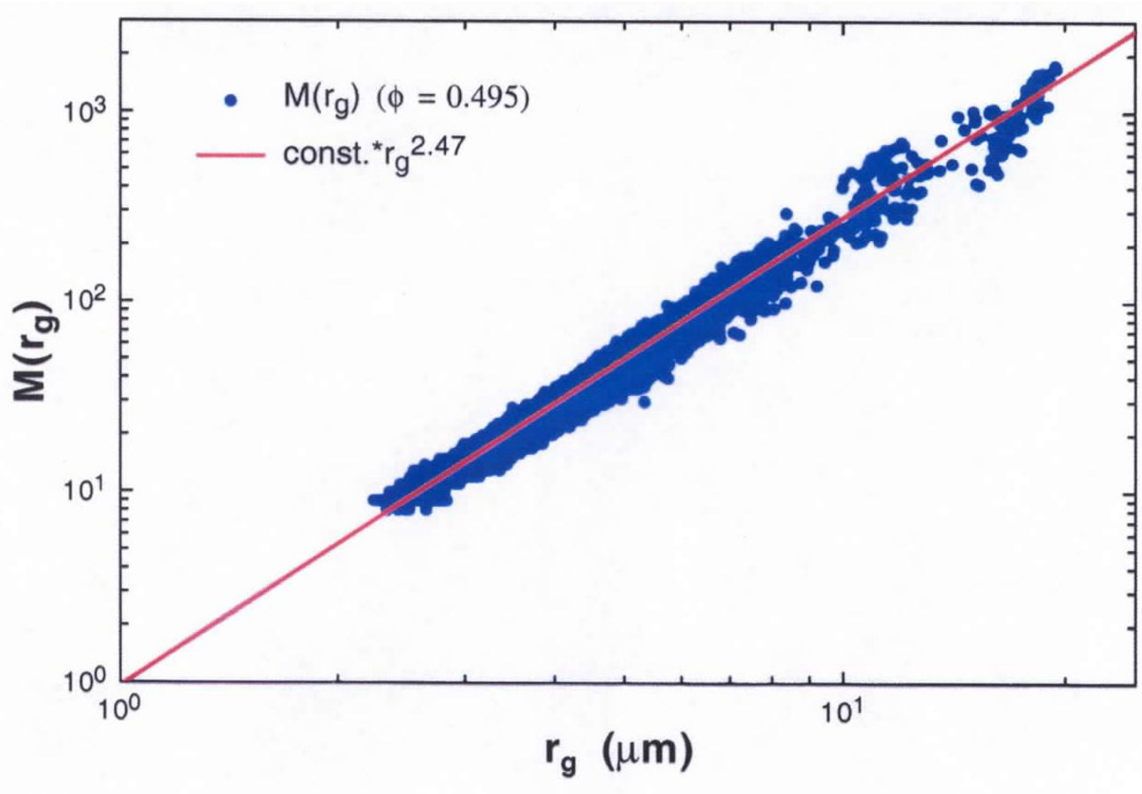
Colloids: crystal nucleation



Nucleation rates much faster than predicted

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

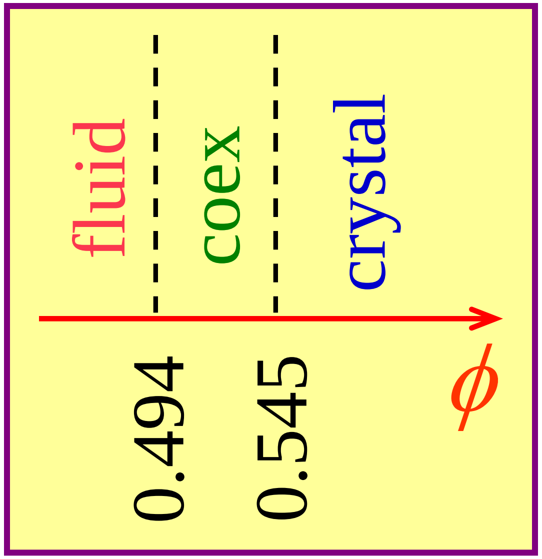
Colloids: crystal nucleation



$d_F \approx 2.5$

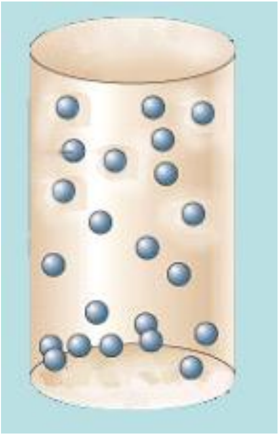
$\phi = 0.42$ instead of $\phi = 0.494$

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) “hairs”

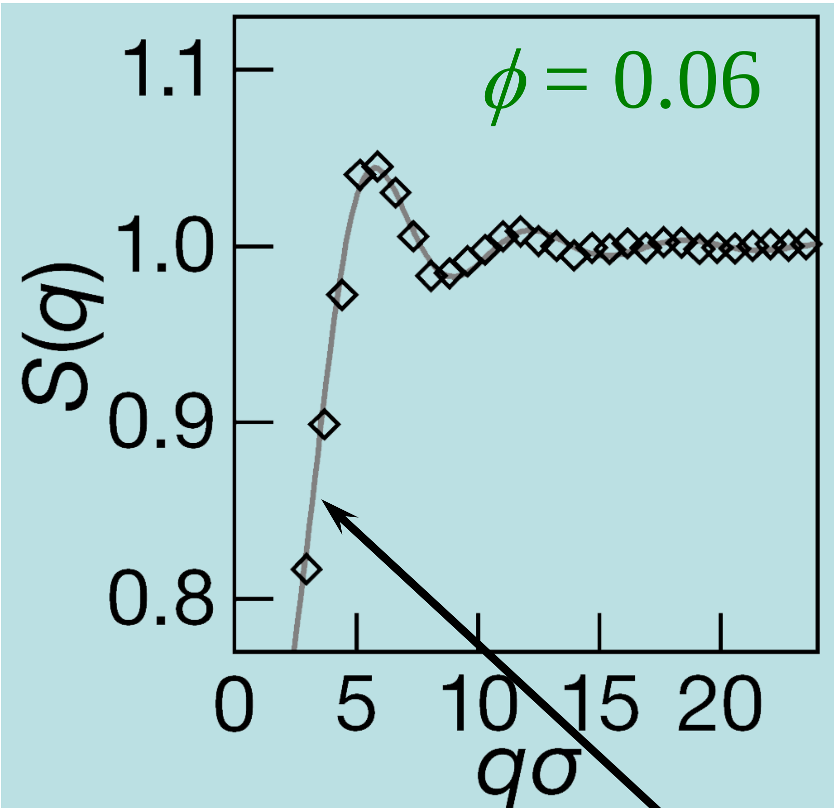
Fluorescent

Decalin + tetrachloroethylene

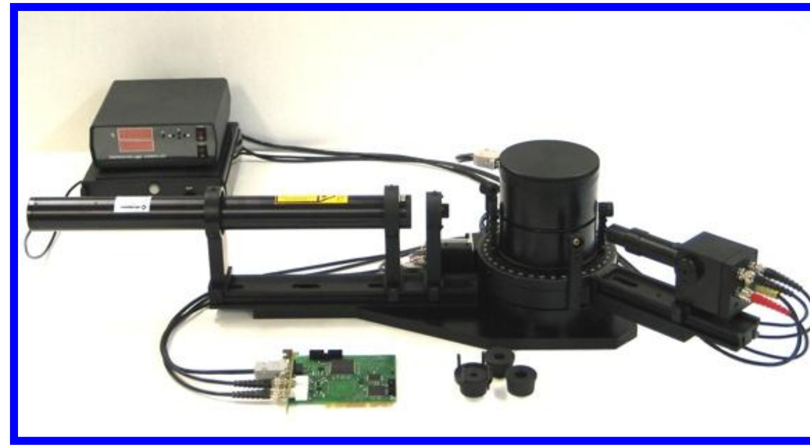
Confirm HS behavior

- Fluid structure
- Phase diagram
- Lattice constant

Fluid structure



Percus-Yevick



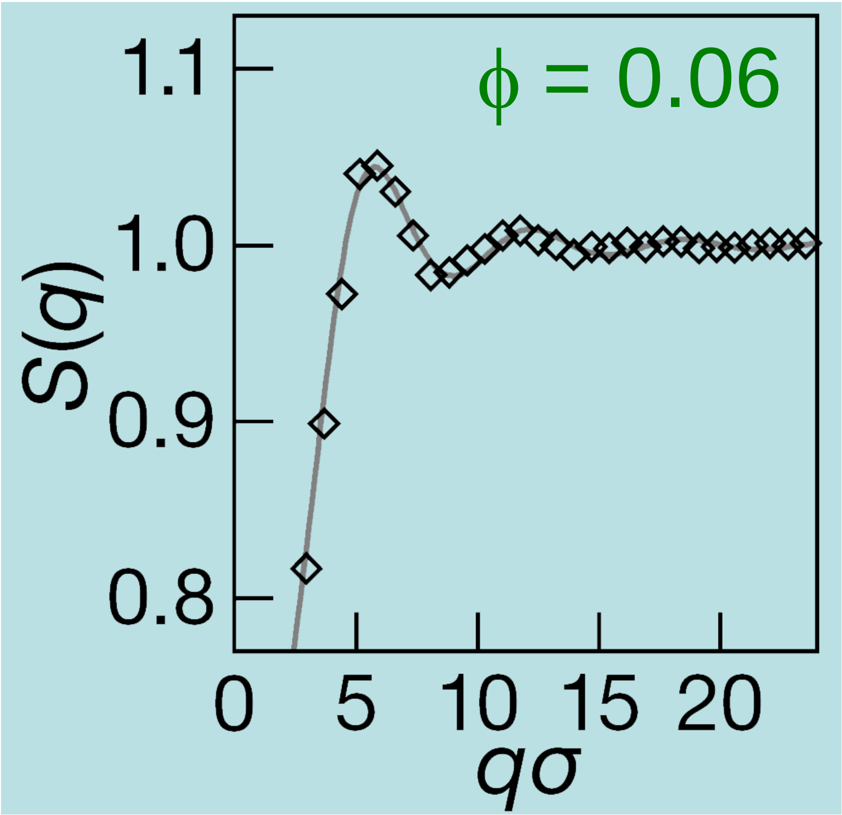
Dynamic Light Scattering

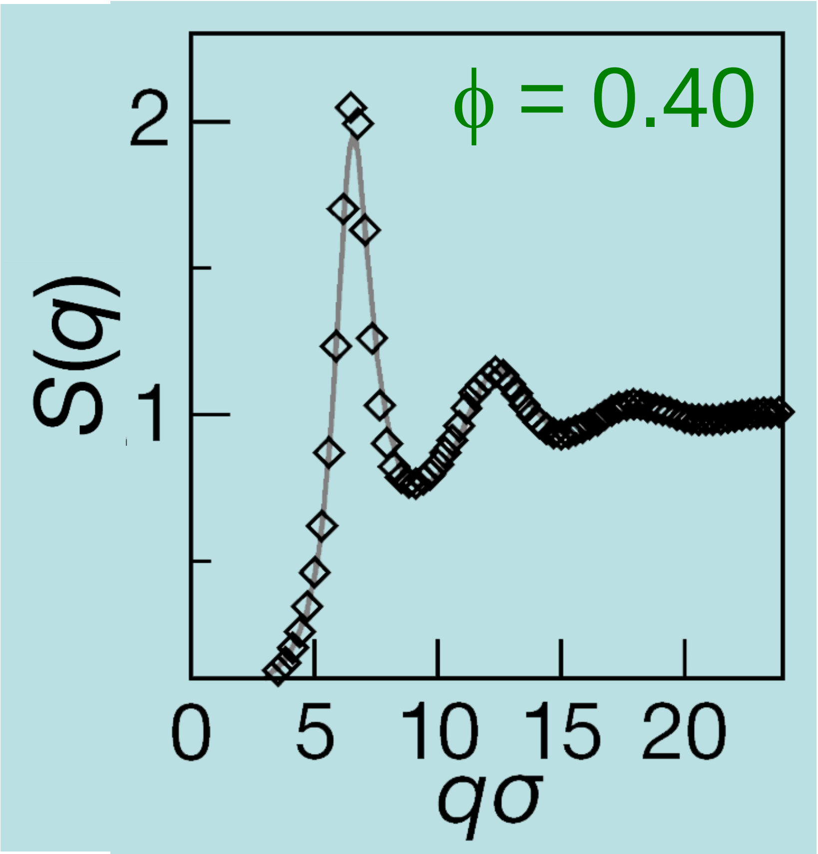
$\phi = 5\times10^{-4}$

$\sigma = 2.33\ \mu m$

$\sigma = 2.36\ \mu m$

Fluid structure



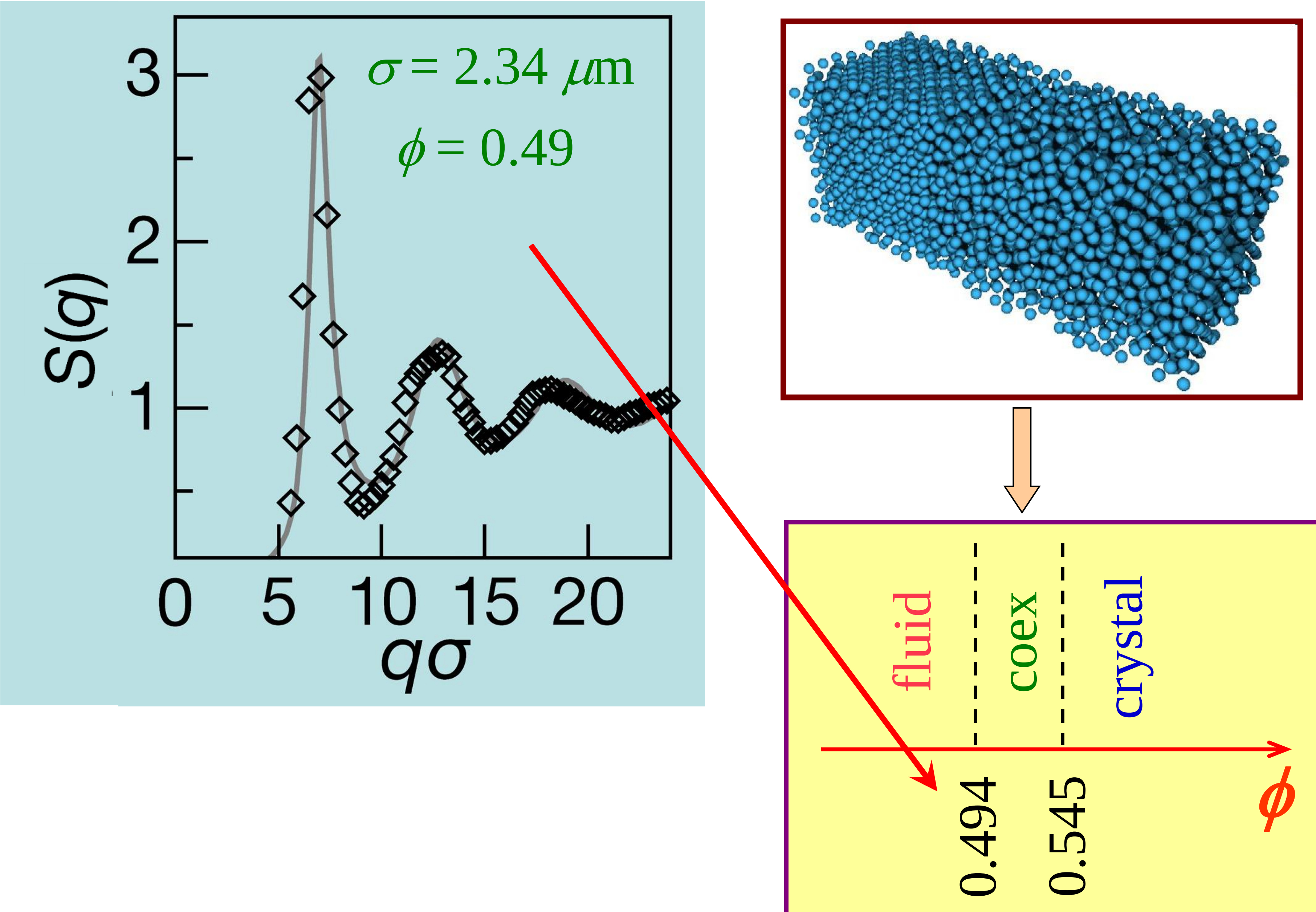


$\sigma = 2.36\ \mu\text{m}$

Confirm HS behavior

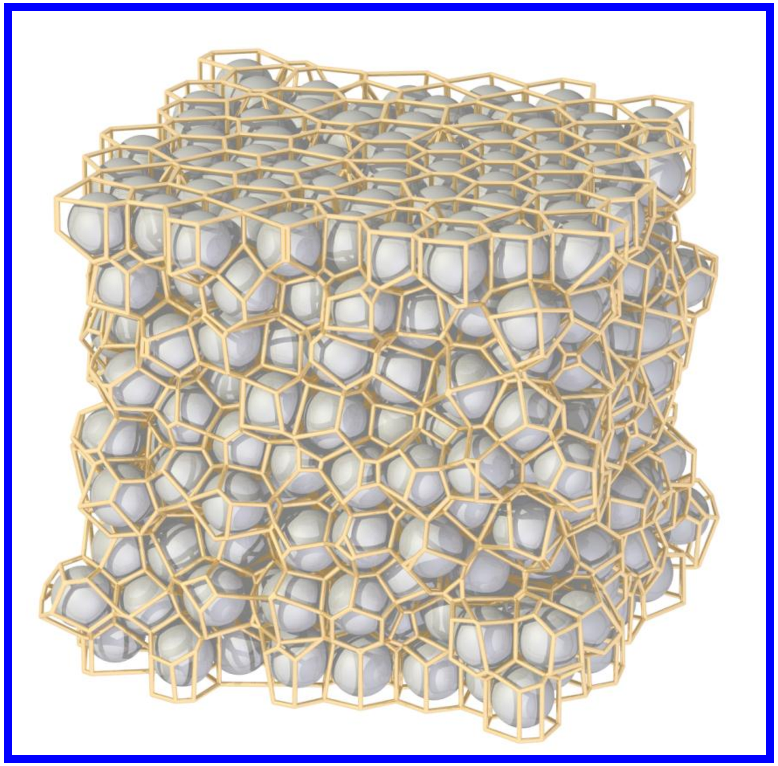
- Fluid structure ✓
- Phase diagram
- Lattice constant

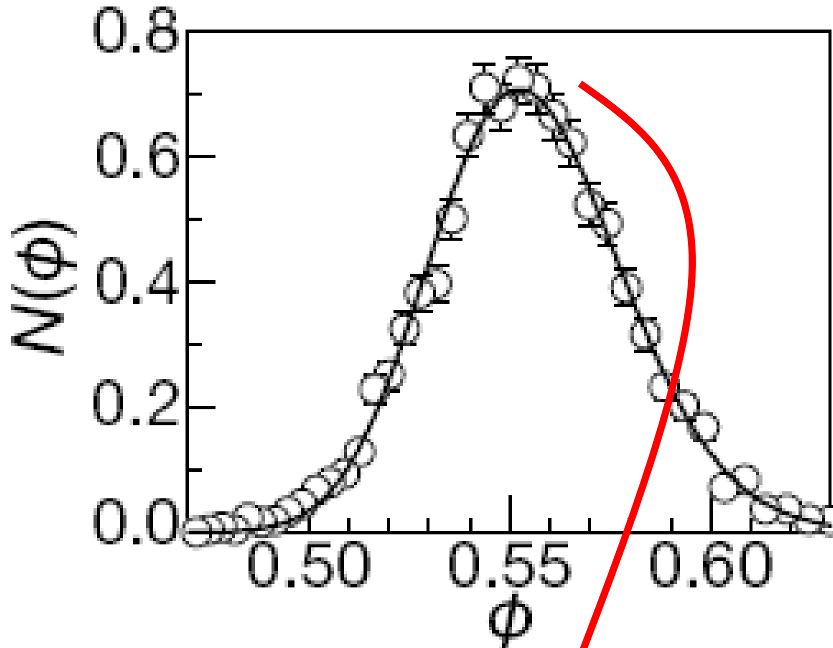
Phase diagram

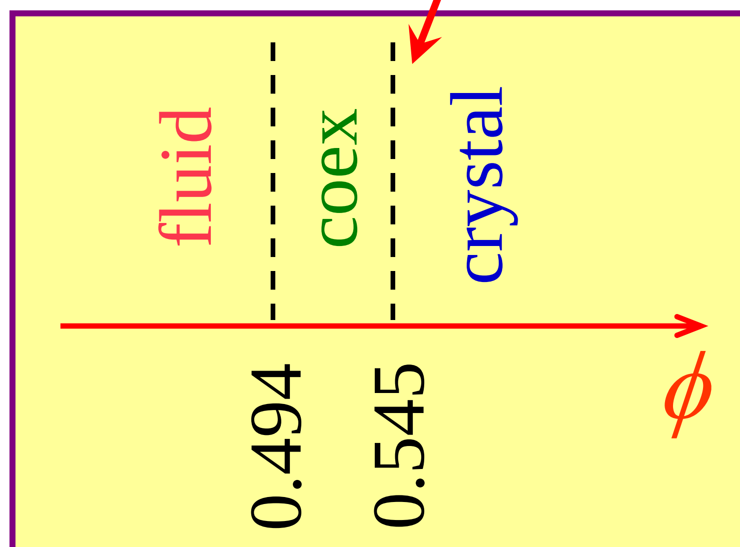


Phase behavior

Voronoi tesselation





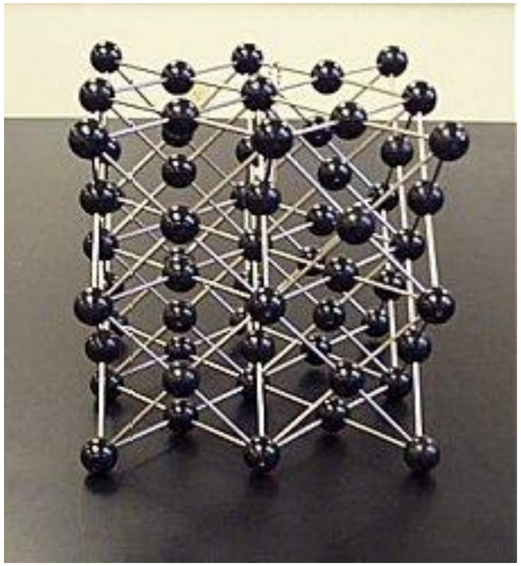


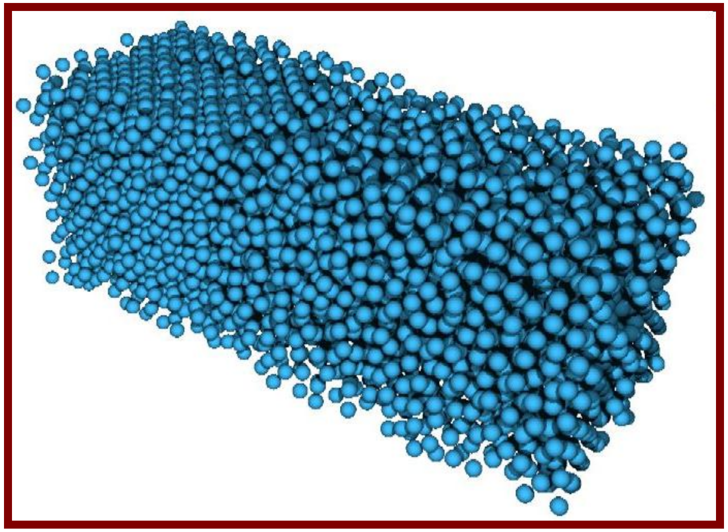
$$\phi = \frac{\pi\sigma^3/6}{\text{Voronoi volume}}$$

Confirm HS behavior

- Fluid structure ✓
- Phase diagram ✓
- Lattice constant

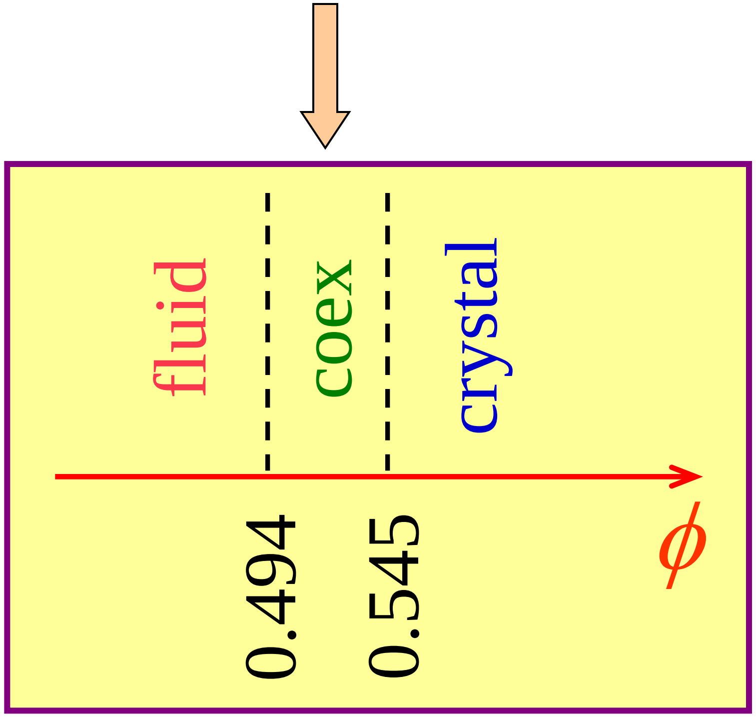
Lattice constant





$$\left(3\sqrt{2}\cdot 0.545/\pi\right)^{-1/3}\sigma = 1.11\sigma$$

Experiment: 1.1±0.01 σ

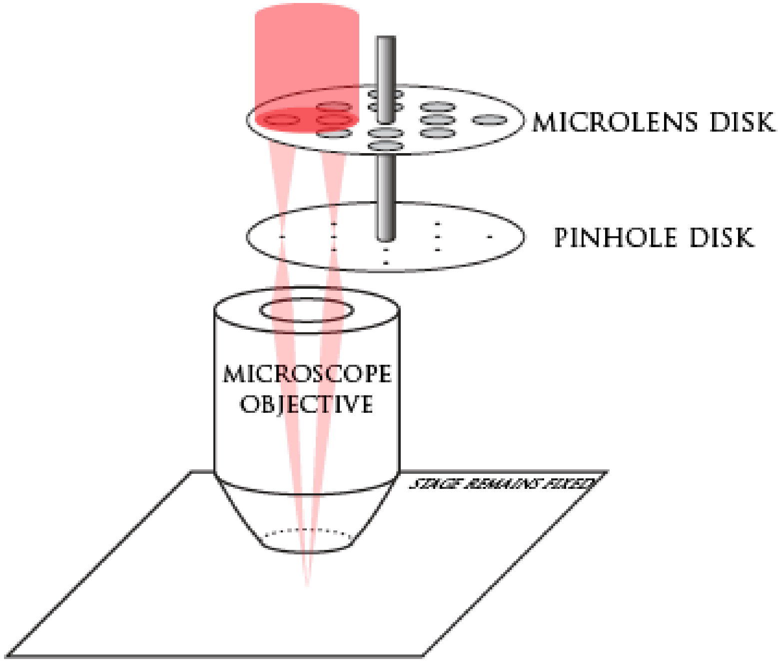


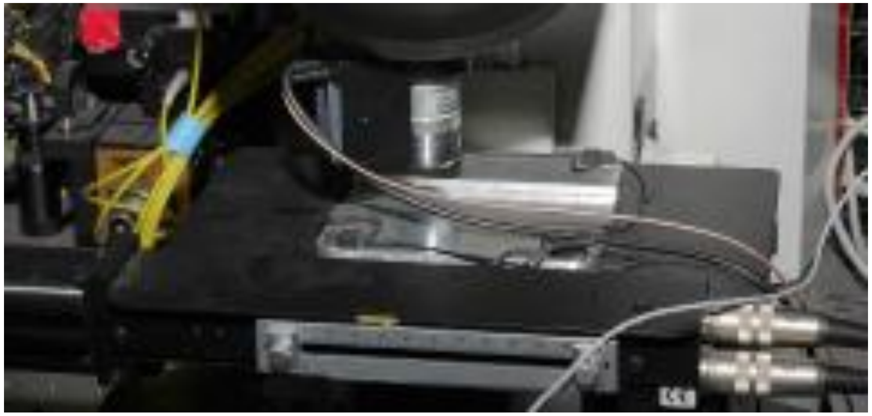
Confirm HS behavior

- Fluid structure ✓
- Phase diagram ✓
- Lattice constant ✓

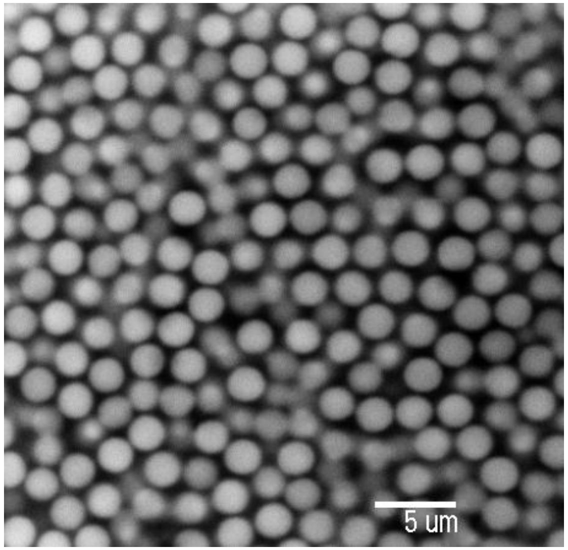
Particles are hard spheres

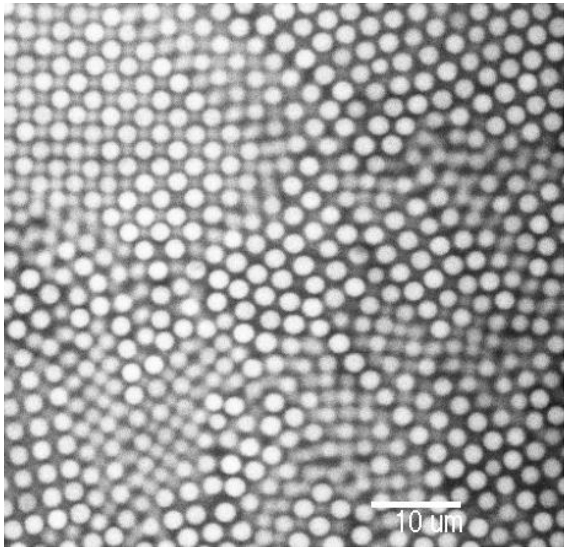
Confocal Microscopy

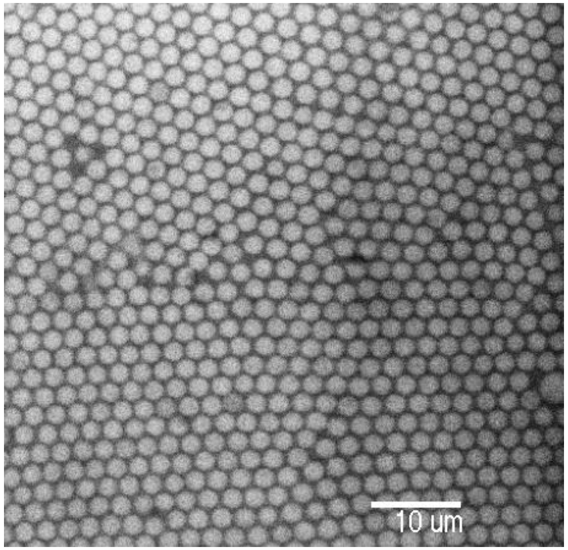




How to Identify Crystals





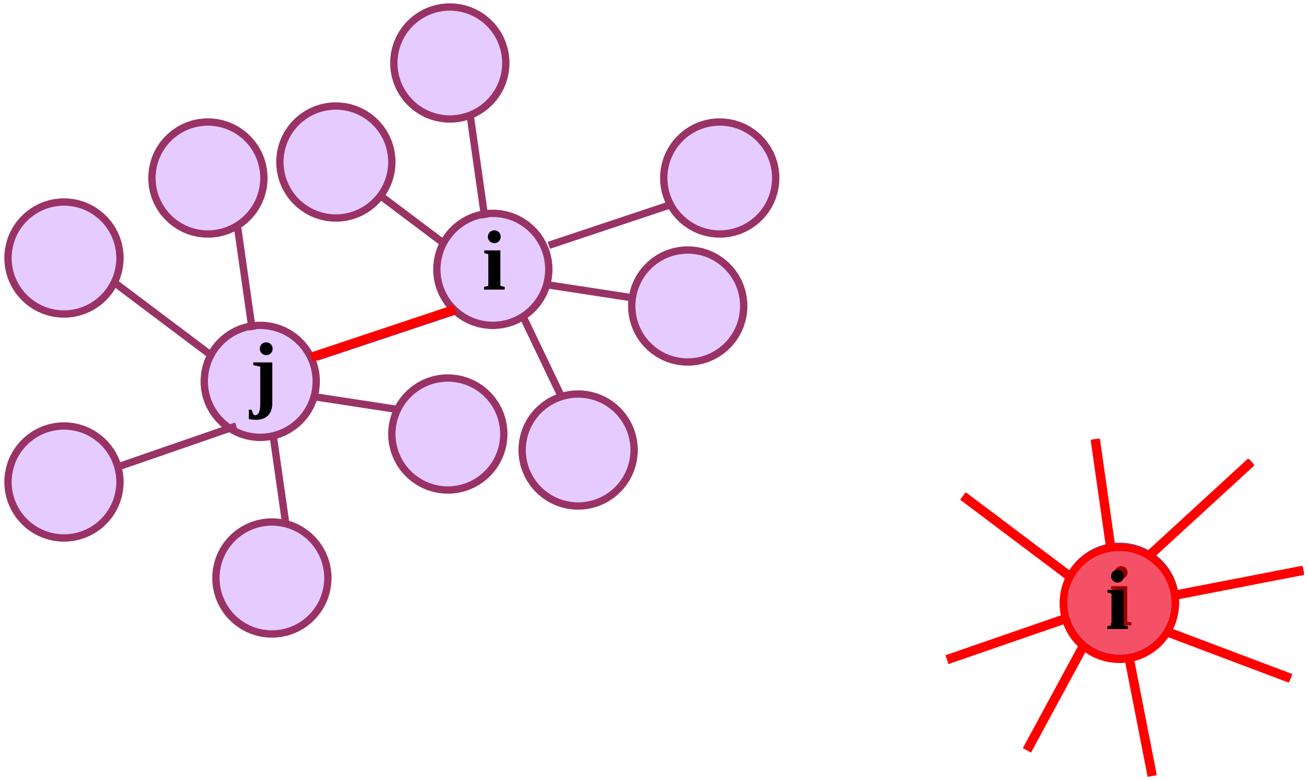


2.3 μm diameter PMMA spheres

Must identify incipient crystal nuclei

Definition of crystallinity

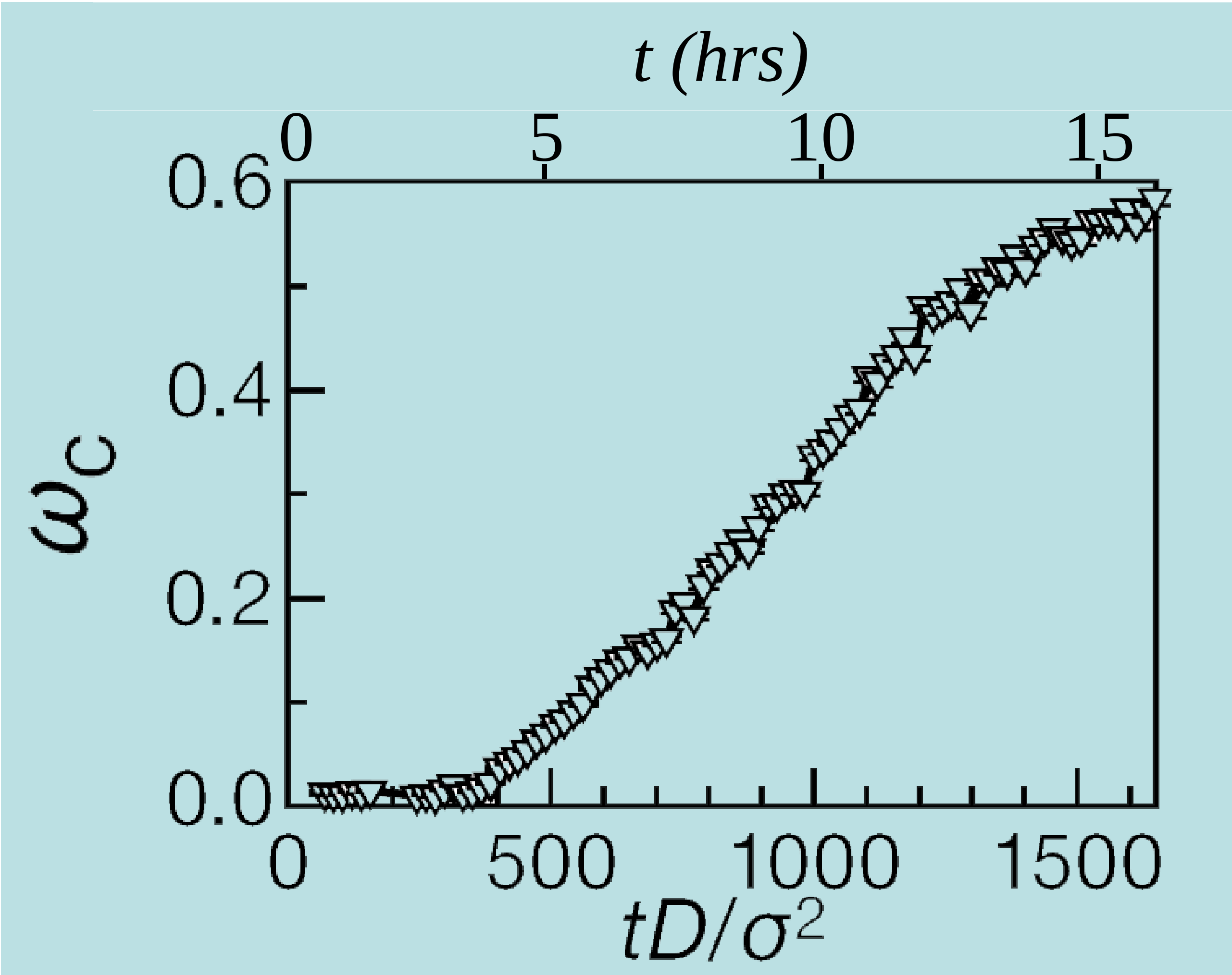
Bond order parameters



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

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

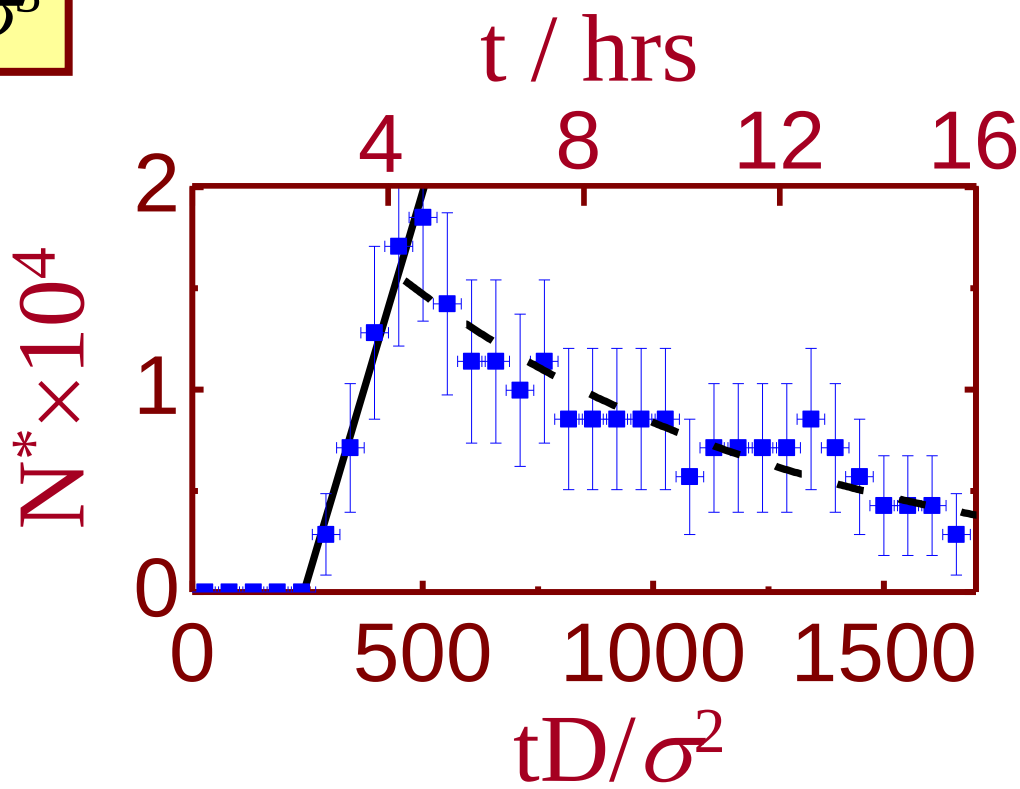
Growth of crystalline phase



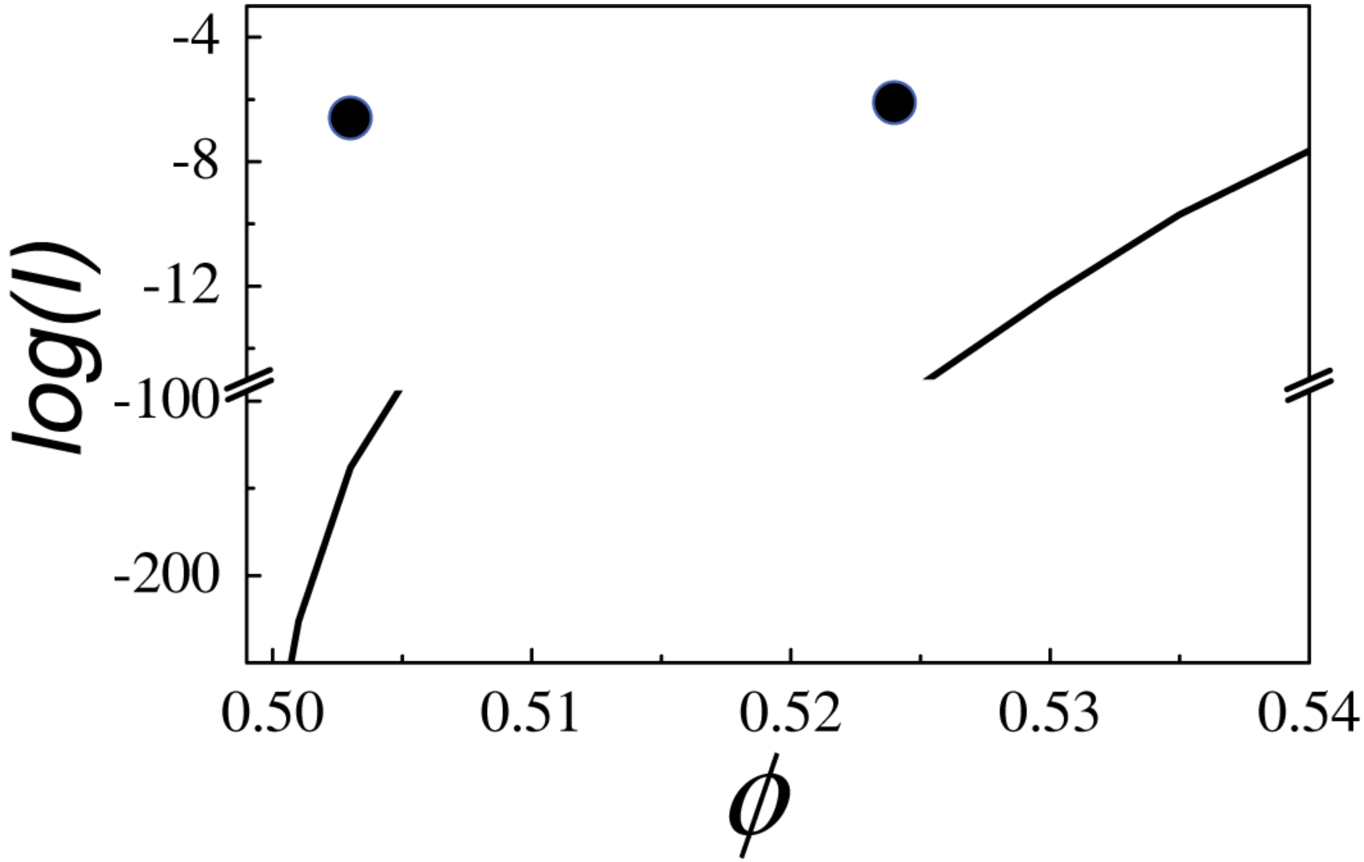
Measure nucleation rates

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

$\phi = 0.52$



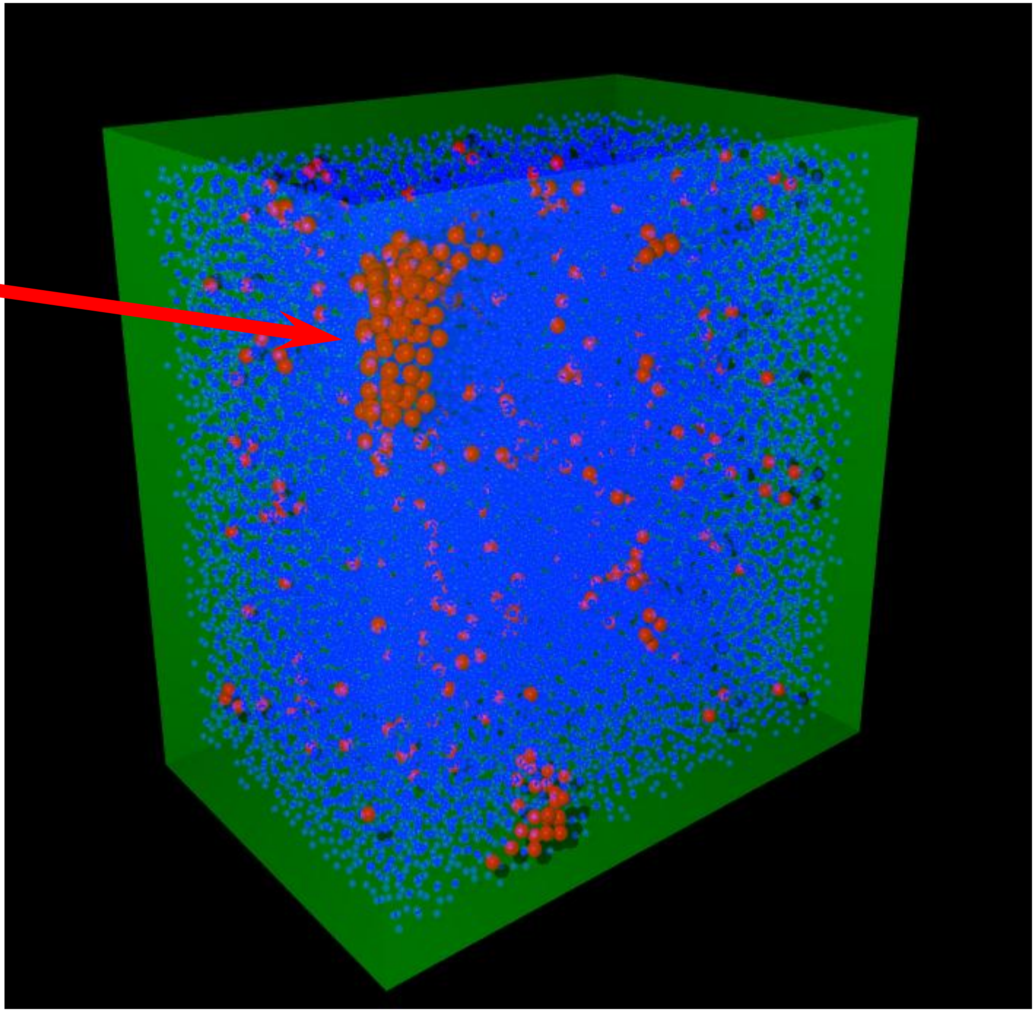
Nucleation rates



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

Reconstruction

Nucleus



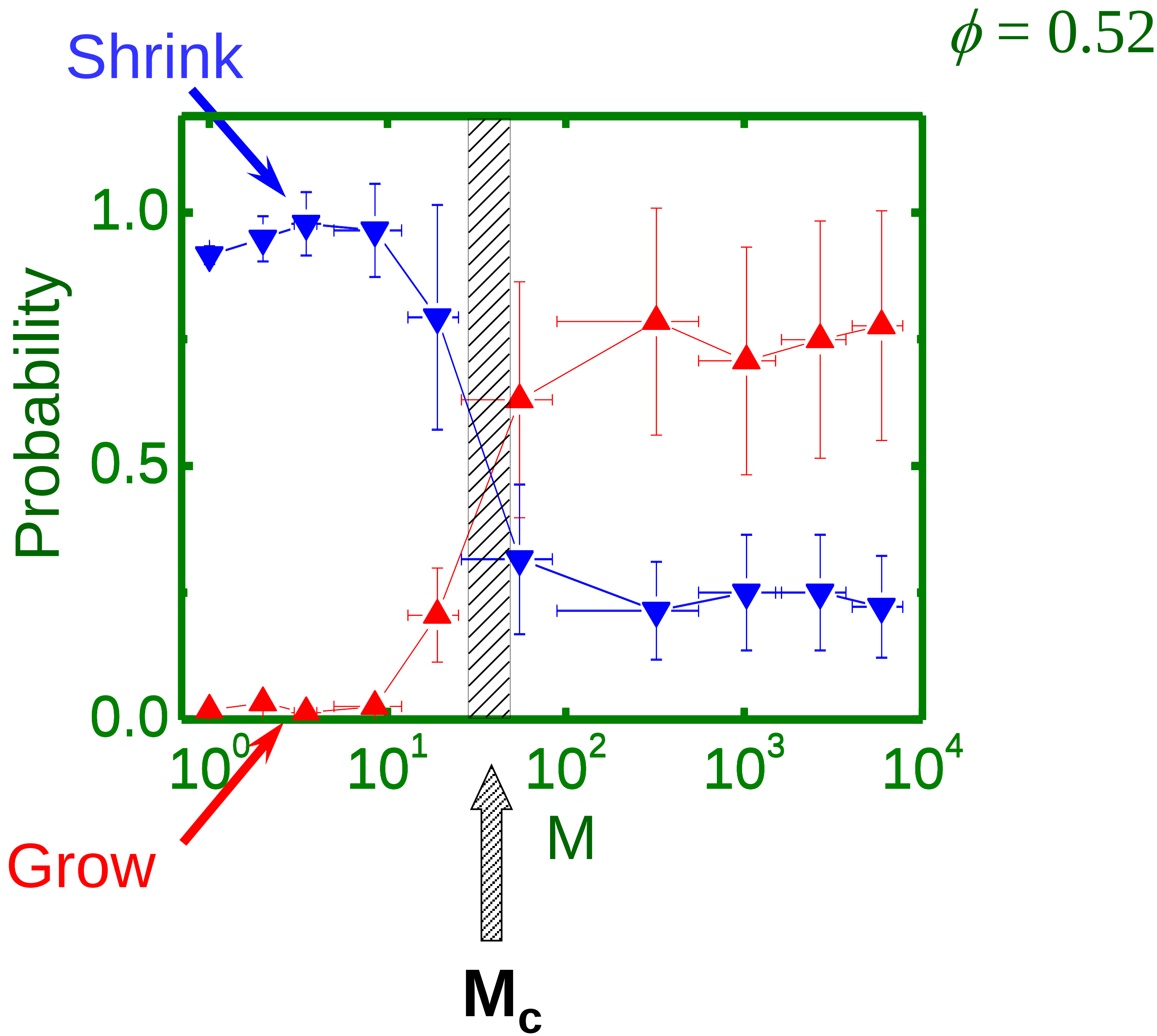
Fluid phase - blue

Crystalline phase - red

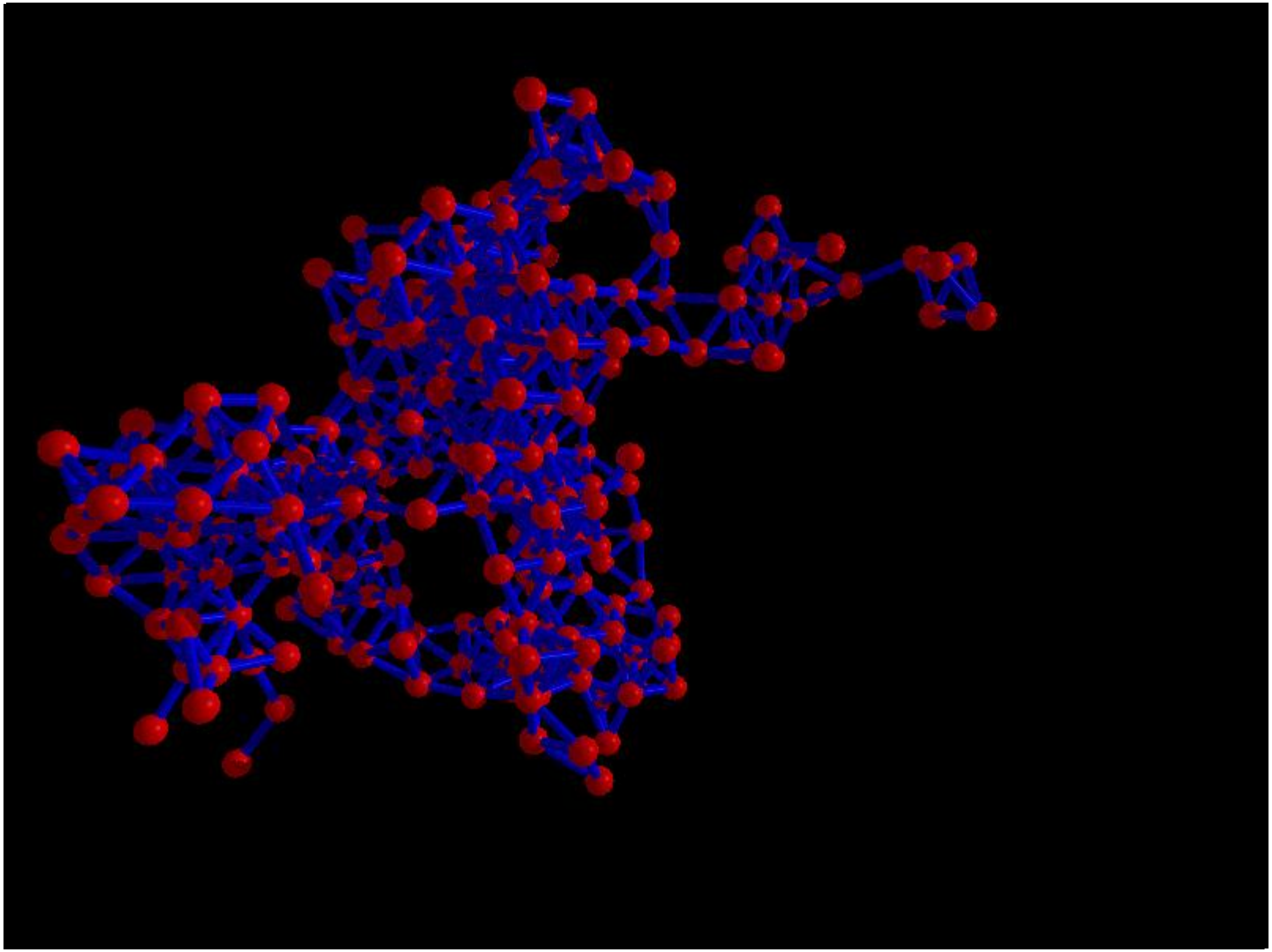
Measure the probability to shrink

Measure the probability to grow

Measure the critical mass

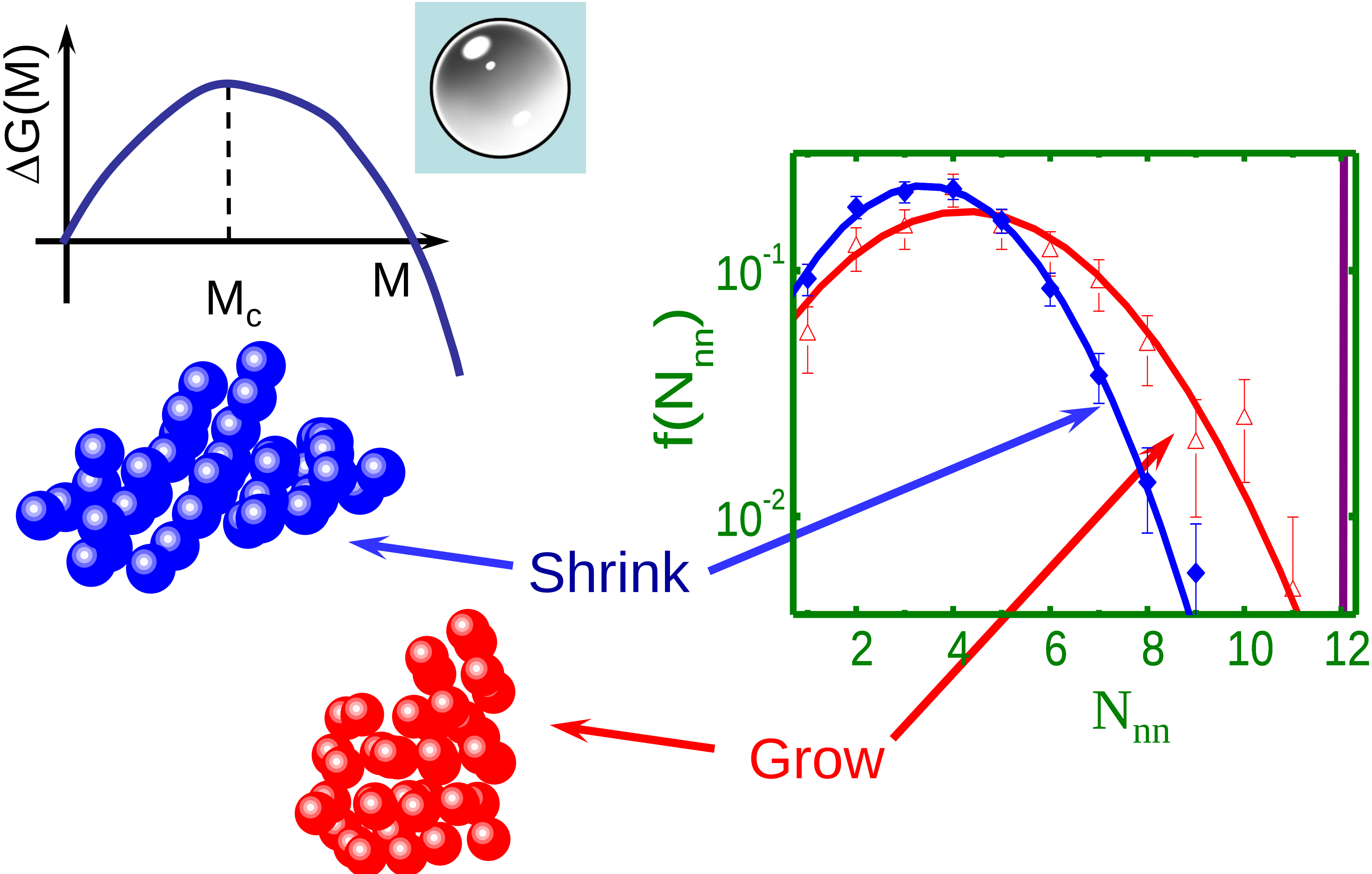


Stepwise formation of an overcritical nucleus



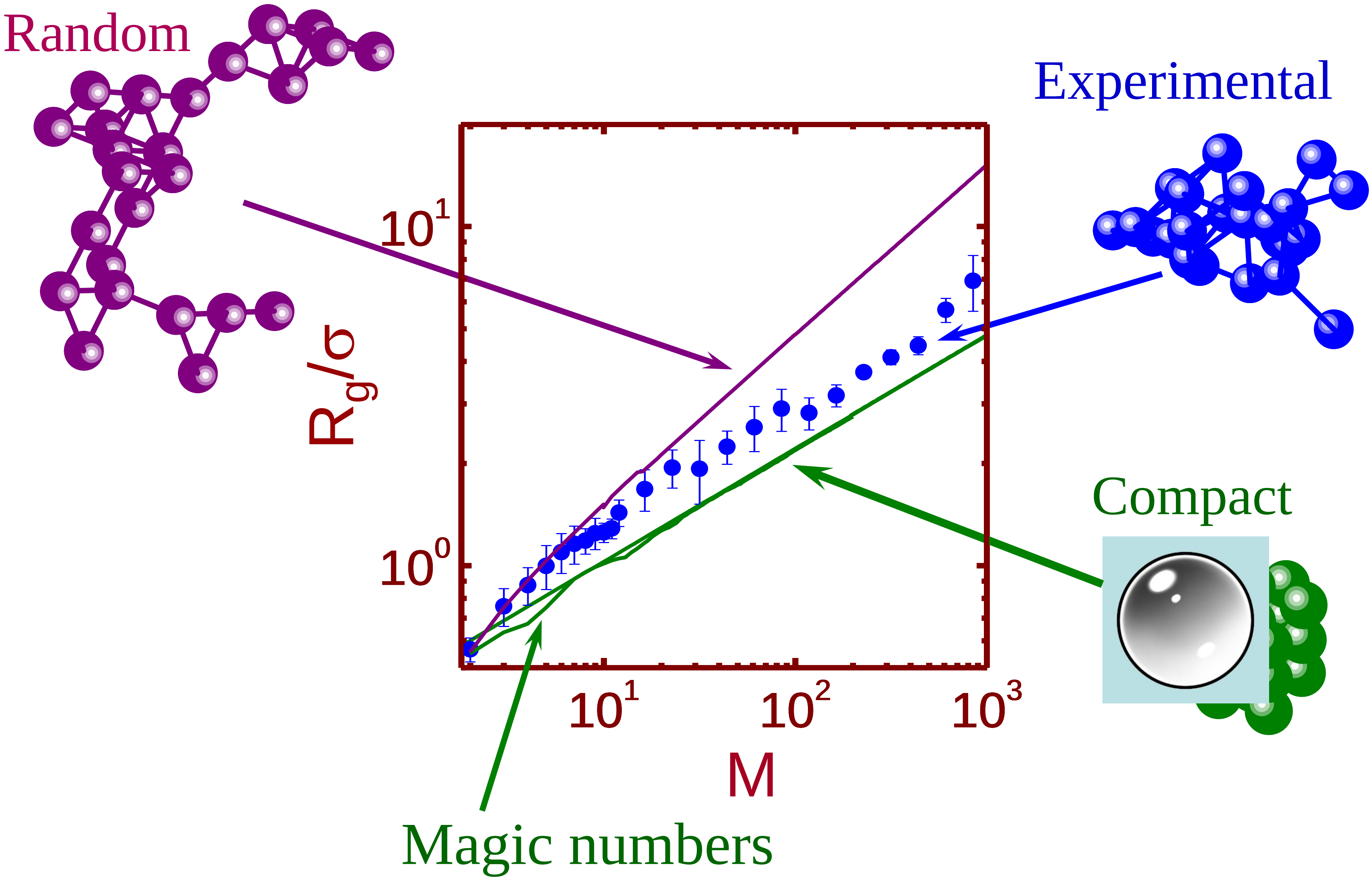
3 hrs

Compare growing and shrinking nuclei

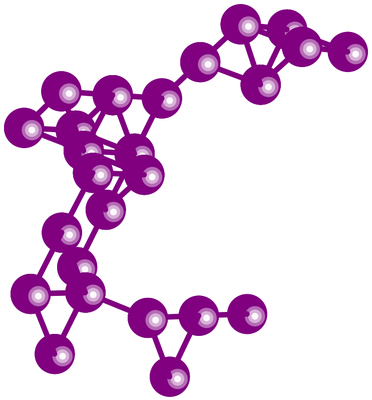


Not only mass matters

Compare with the theoretical morphology



Distribution of colloidal crystal nuclei

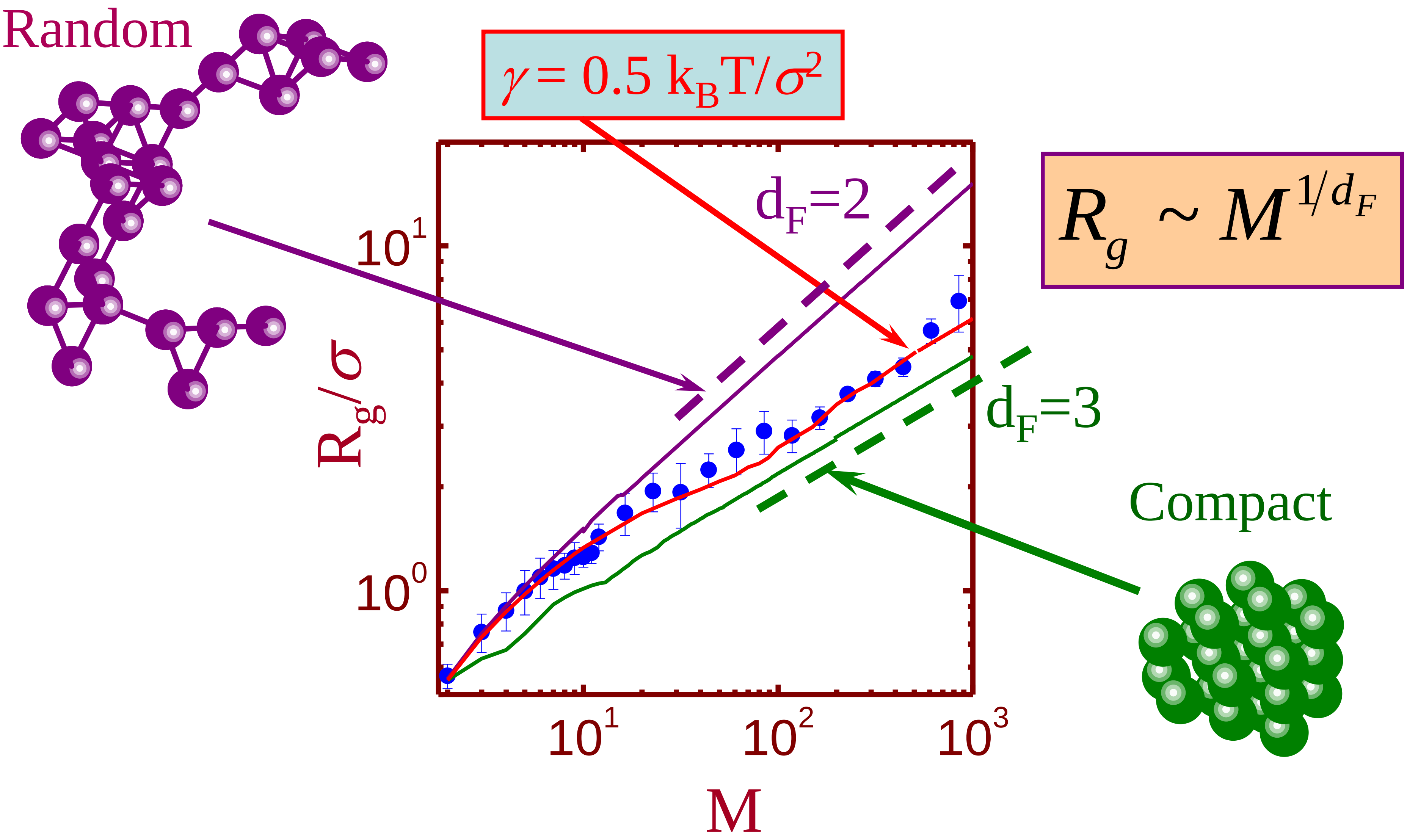


$$\langle R_g(M)\rangle = \frac{\sum_i R_g^{(i)} \exp\left[-\Delta G(M, A_i)/k_B T\right]}{\sum_i \exp\left[-\Delta G(M, A_i)/k_B T\right]}$$

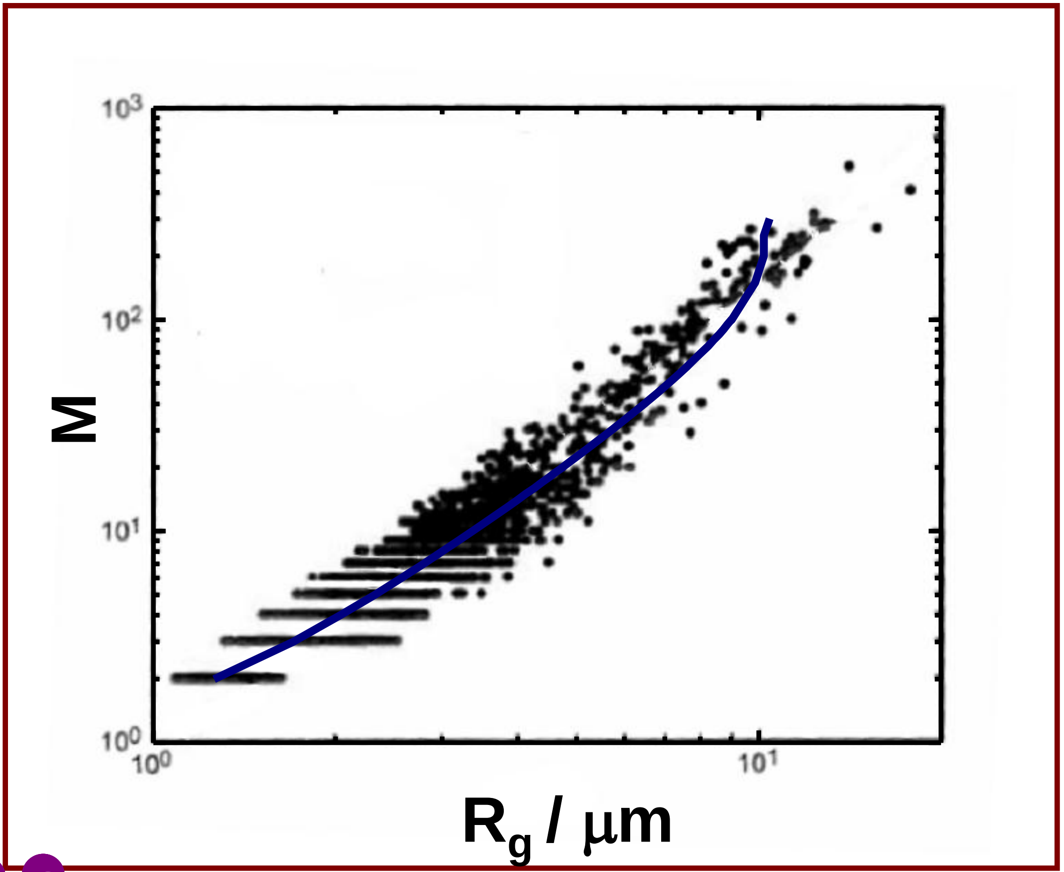
$$\Delta G = \gamma A_i - \Delta\mu M$$

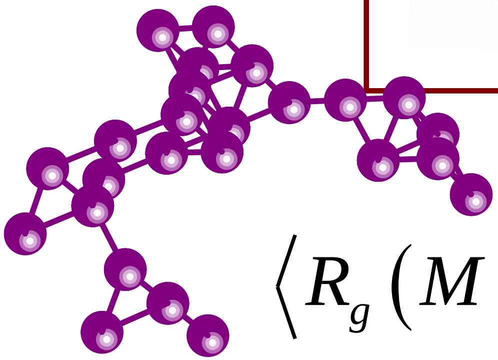
$$\langle R_g(M)\rangle = \frac{\sum_i R_g^{(i)} \exp\left(-\gamma A_i / k_B T\right)}{\sum_i \exp\left(-\gamma A_i / k_B T\right)}$$

Nuclei adopt different morphologies



Morphology of nuclei: Charged colloids



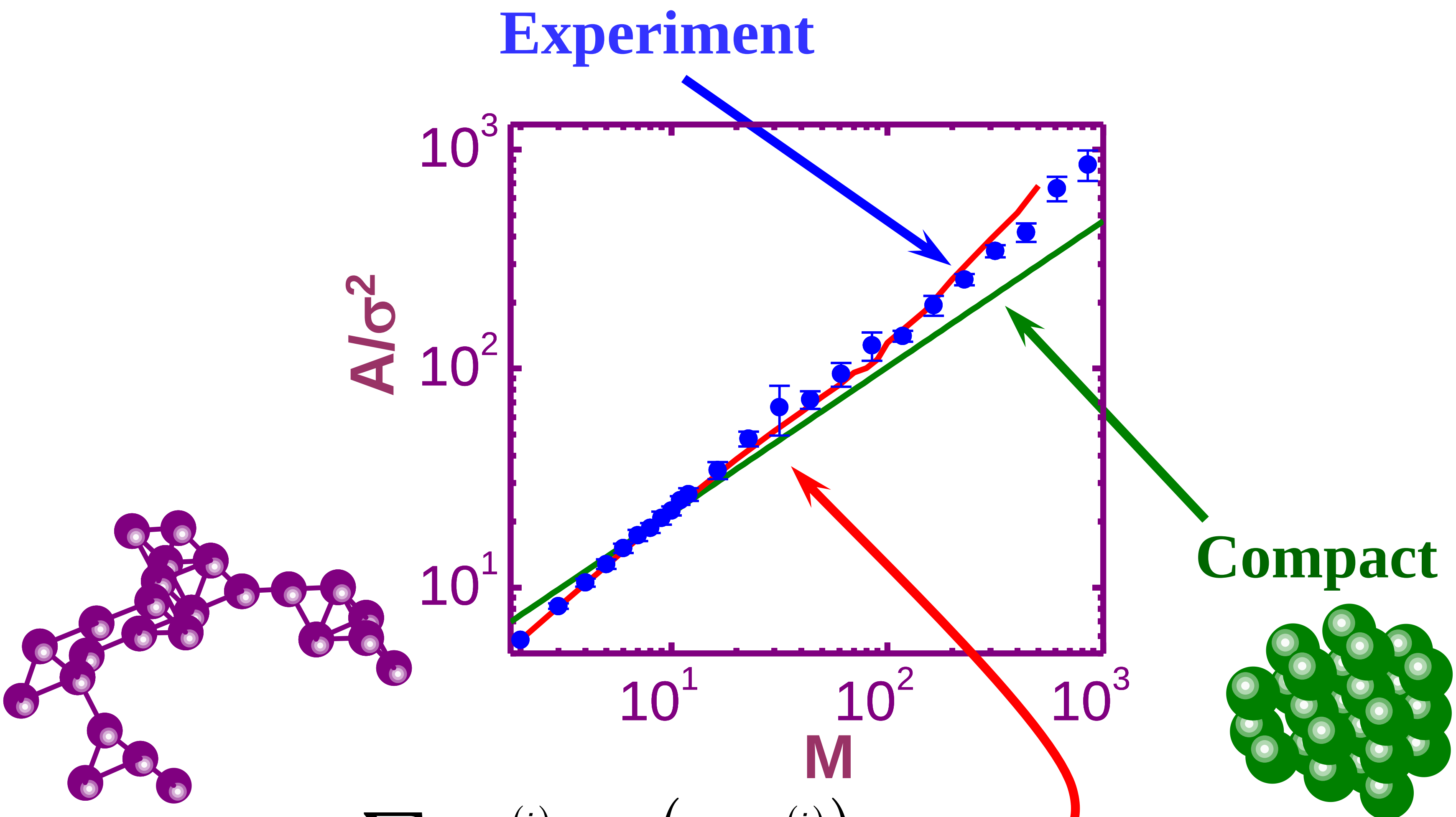


$$\left\langle R_g(M)\right\rangle = \frac{\sum_i R_g^{(i)} \exp\left(-\gamma A^{(i)}\right)}{\sum_i \exp\left(-\gamma A^{(i)}\right)}$$

$\gamma = 0.1\ k_B T/\sigma^2$

U. Gasser et al., *Science* **292**, 258 (2001)

Surface area of nuclei

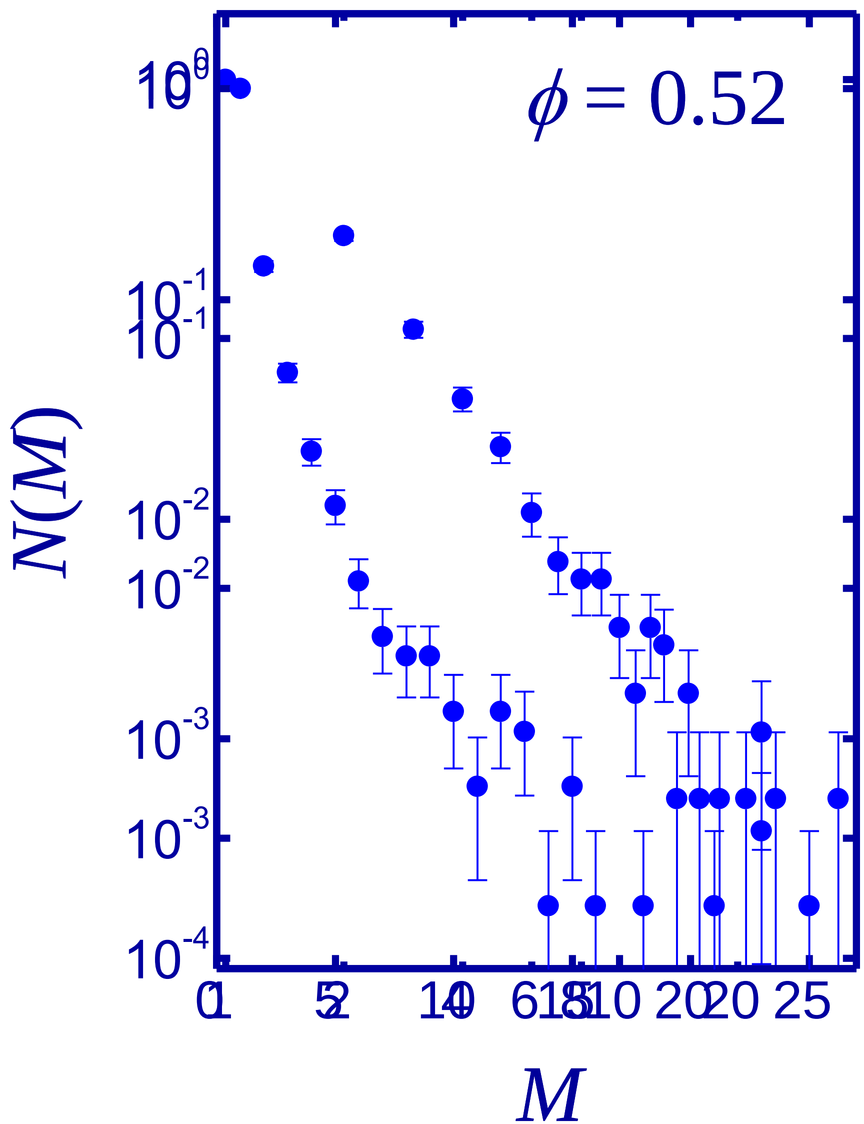


$$\langle A(M) \rangle = \frac{\sum_i A^{(i)} \exp\left(-\gamma A^{(i)}\right)}{\sum_i \exp\left(-\gamma A^{(i)}\right)}$$

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

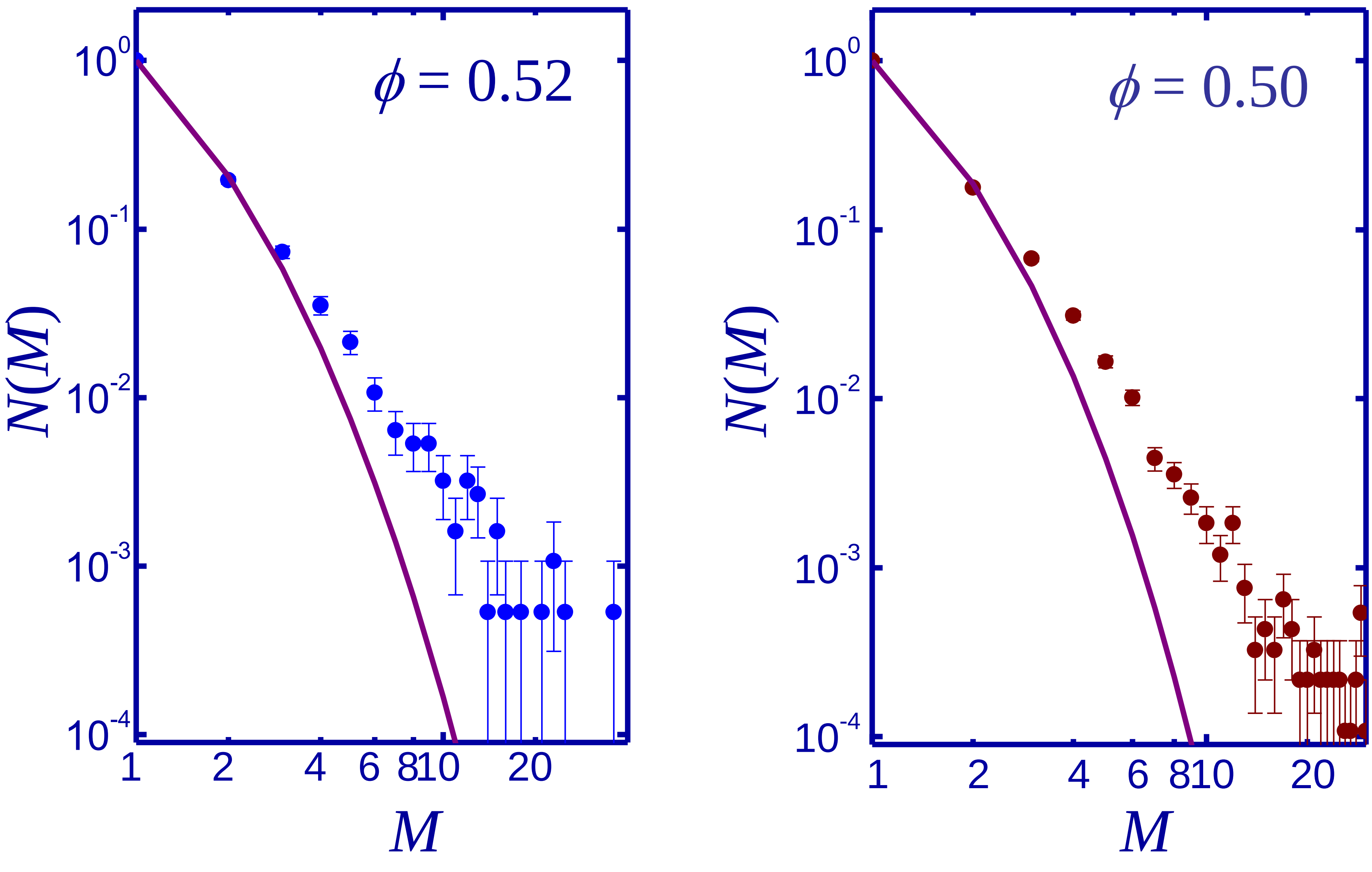
Does morphology alter the free energy?

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



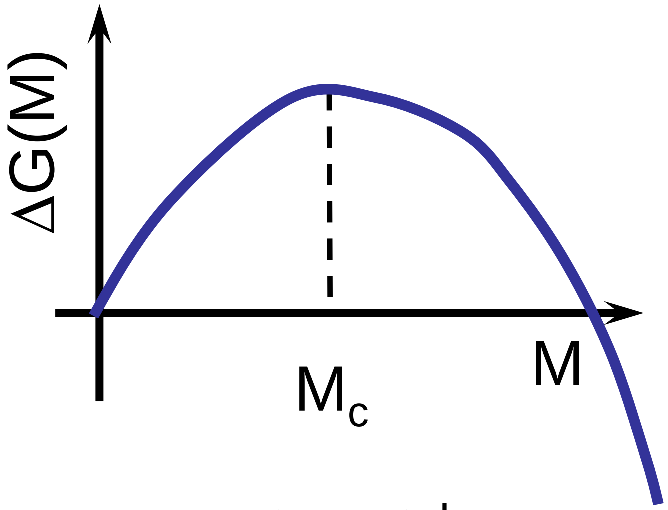
Size distribution of nuclei

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



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

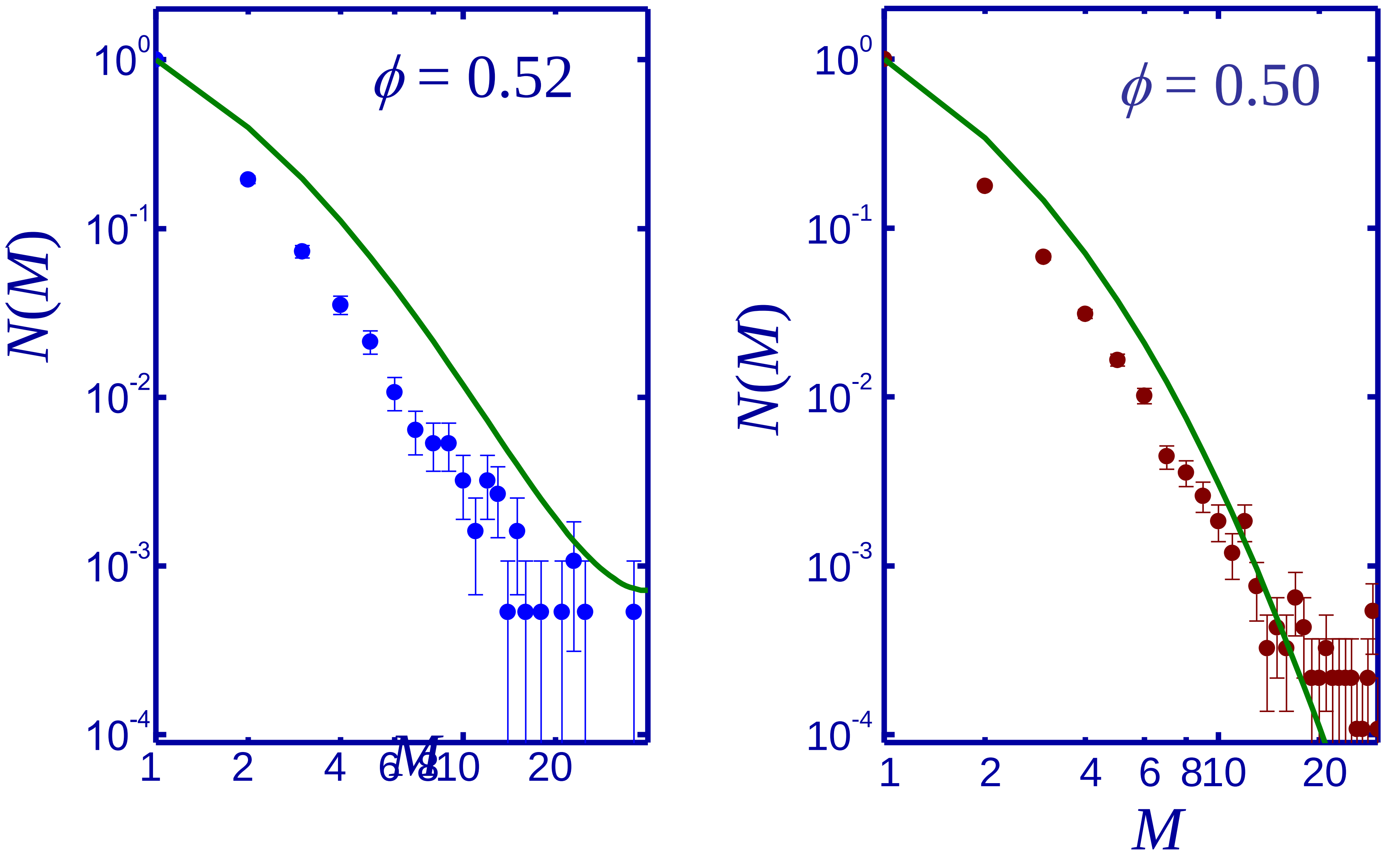
$$\Delta G = \pi M^{2/3} 0.545^{-2/3} \sigma^2 \gamma - \Delta\mu M$$



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

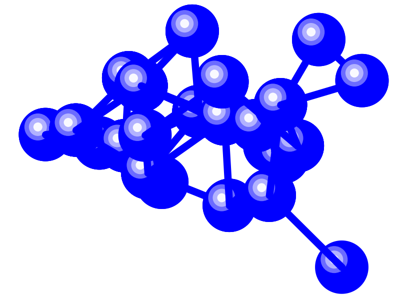
$$\Delta\mu = \frac{2\pi}{3} \sigma^2 \gamma M_c^{-1/3} \cdot 0.545^{-2/3}$$

Size distribution of nuclei

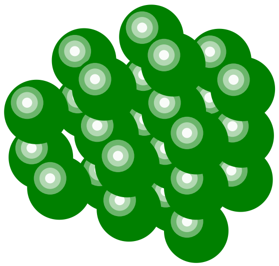


Introduce morphological entropy

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



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



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

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

$\gamma = 0.5\ k_B T/\sigma^2$	(Morphology)
$M_c = 40 \pm 10$	(Growth probablity)

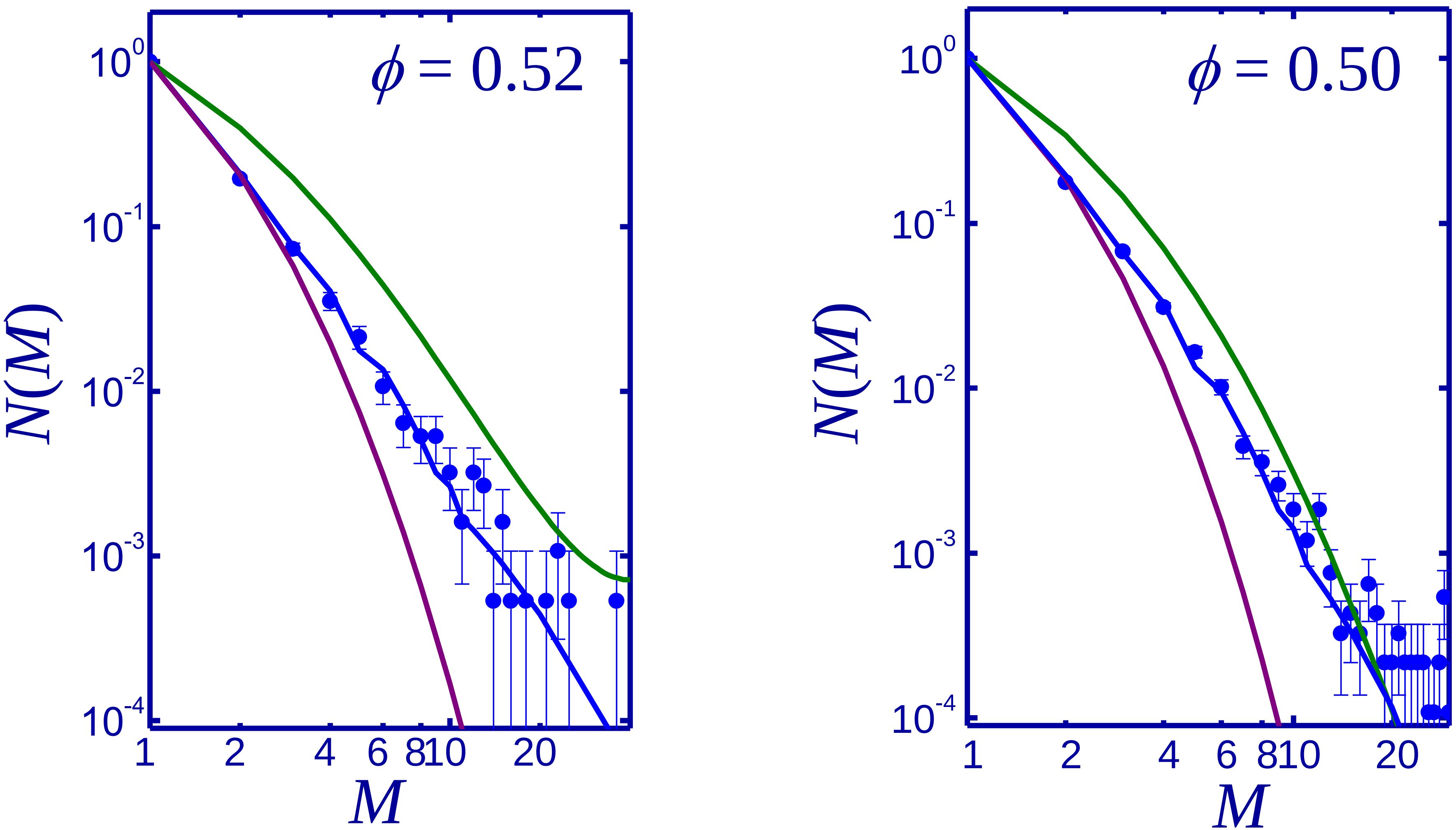
$$\left.\frac{d(\Delta G)}{dM}\right|_{M_c} = 0$$

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

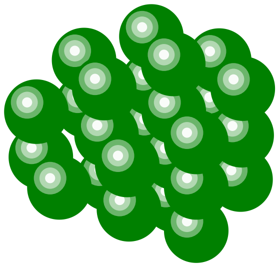
Test the modified free energy

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

$\tau = 1.25 \pm 0.25$



The full free energy



$\phi = 0.52$

$\tau = 1.25$

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

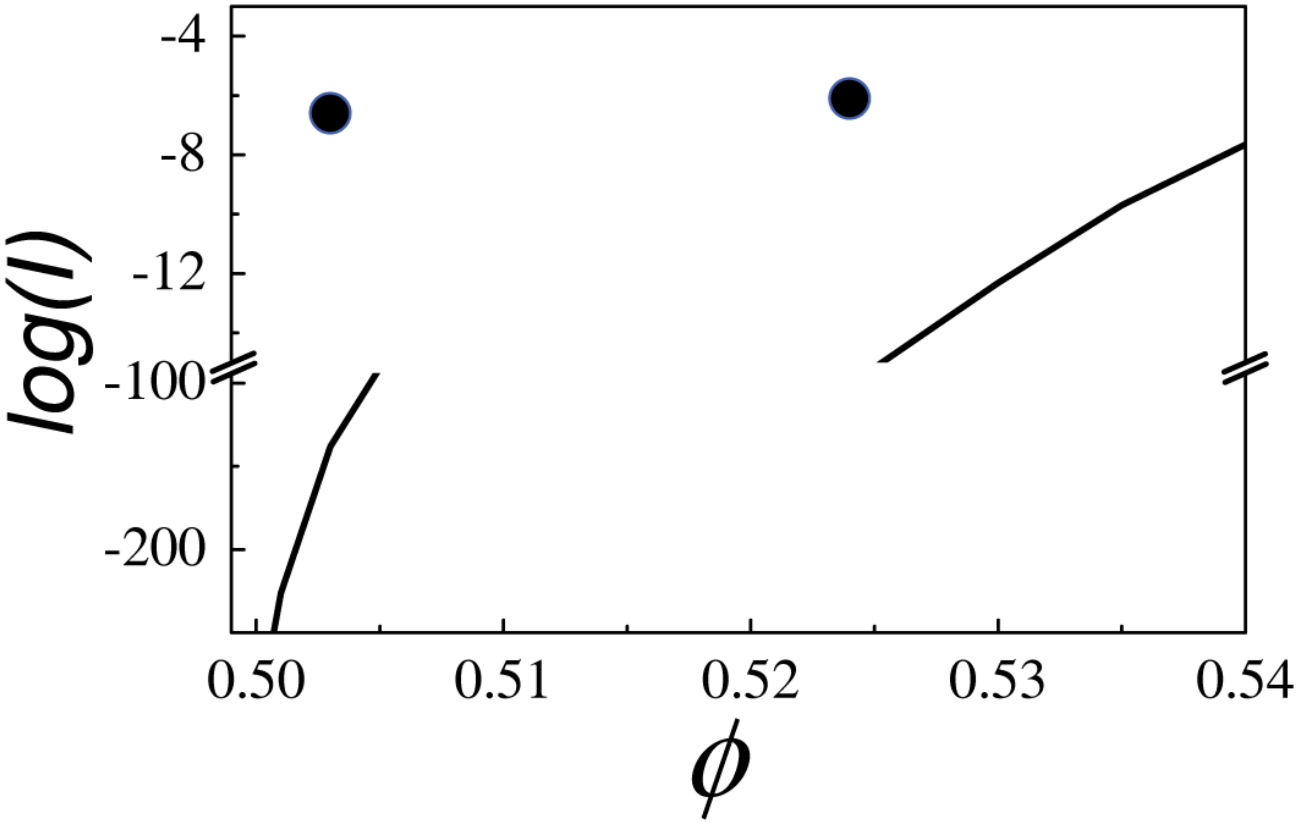
$$\Delta G(M) = 0.5 A(M) - 0.44 M + k_B T\, 1.25 \ln M$$

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

$\Delta\mu$ (fit)

Test predicted nucleation rates

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

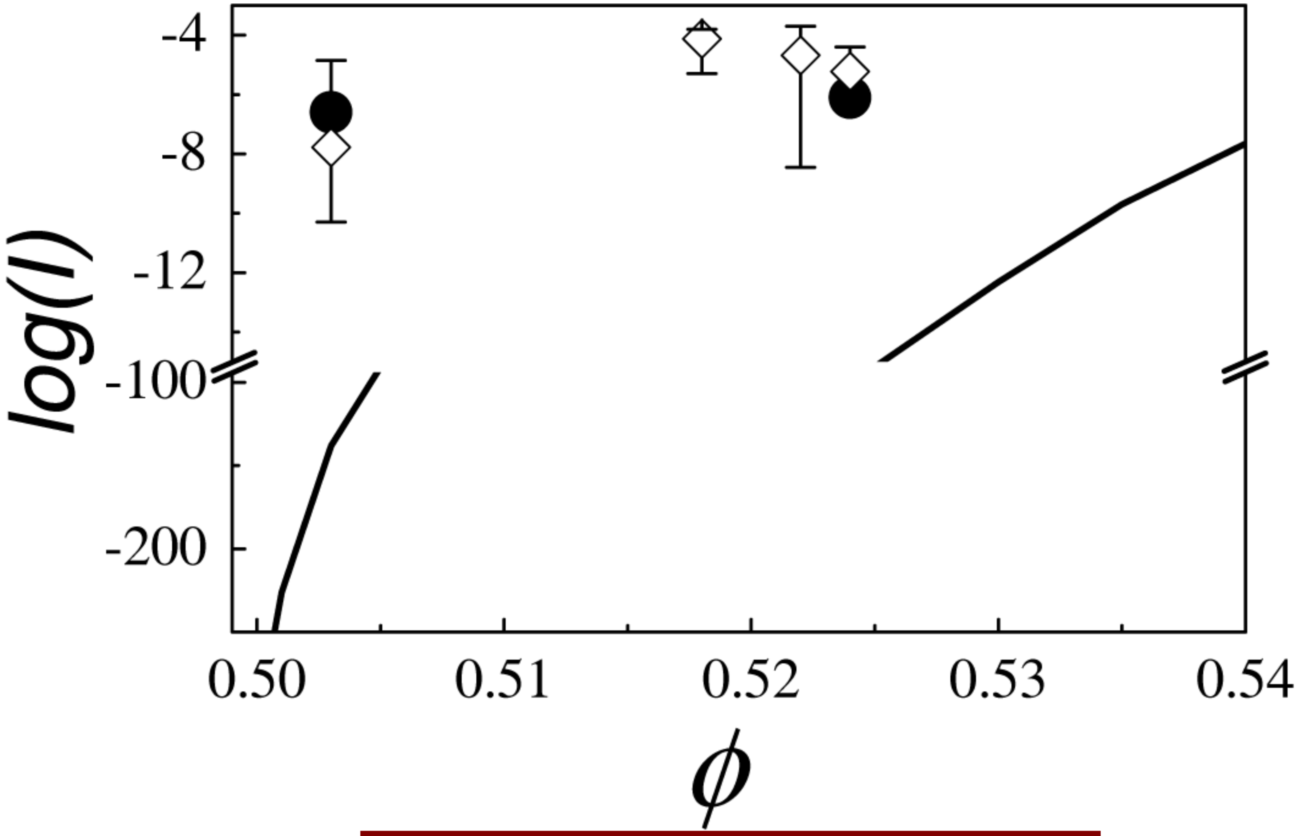


$$I \sim \exp[-\Delta G(M_c)/k_B T]$$

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

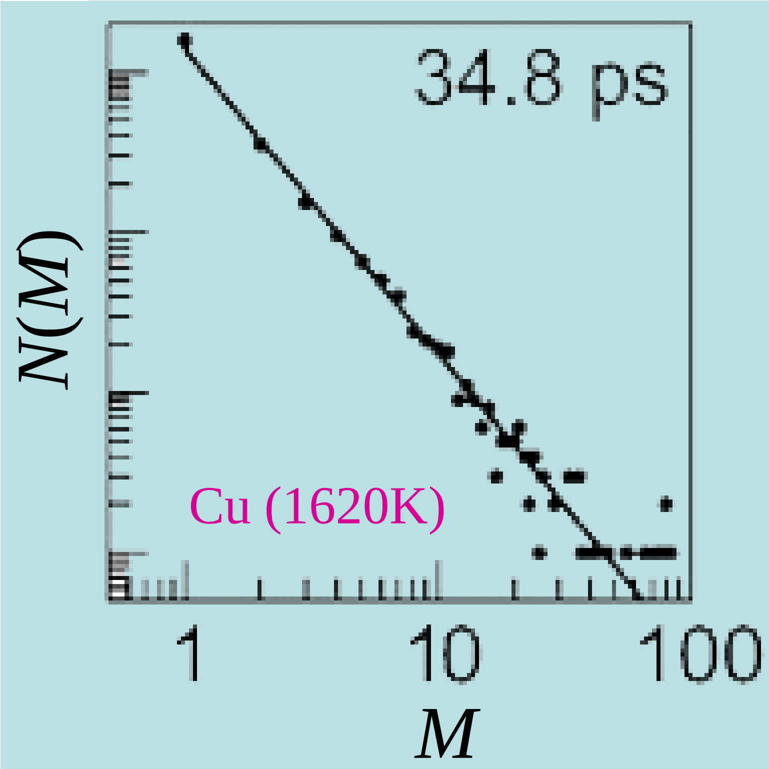
γ(Au) ~ 0.2 kT/σ^2

γ(Al) ~ 0.2 kT/σ^2

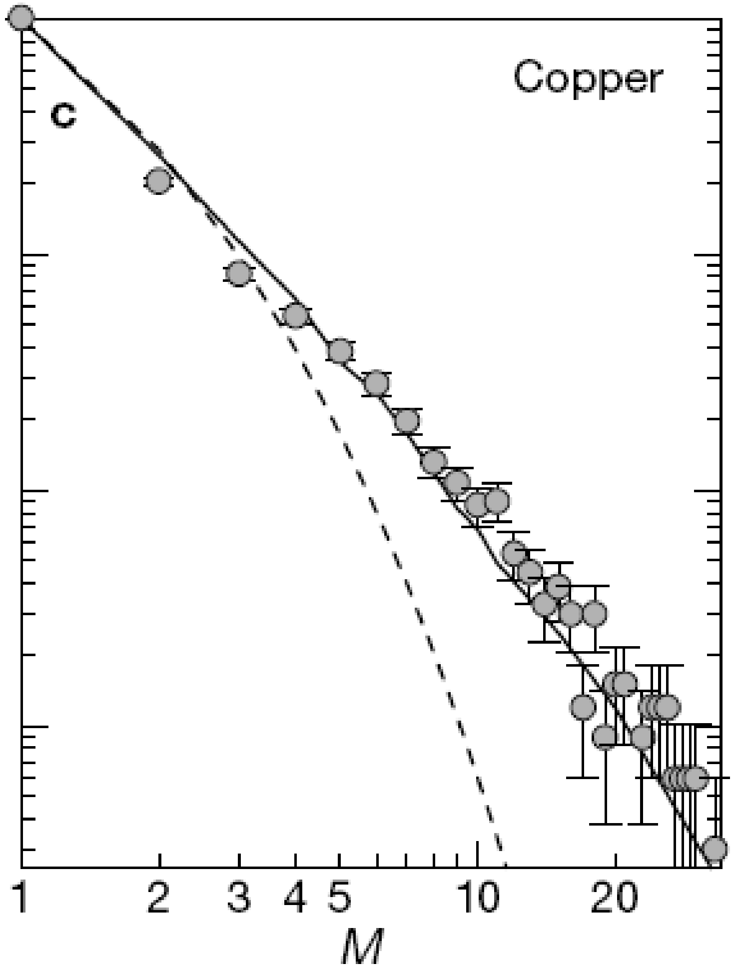
γ(Charged) ~ 0.1 kT/σ^2

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

Simulation of nucleation of Cu crystals



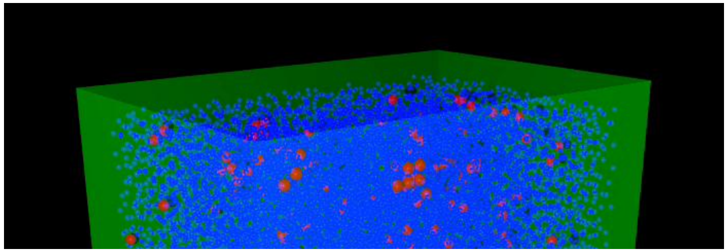
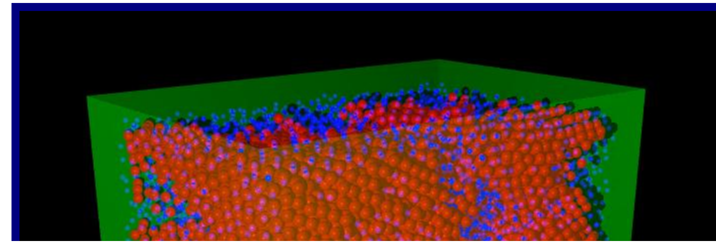
L. Zheng *et al.*, *JCP* **127**, 164503 (2007)



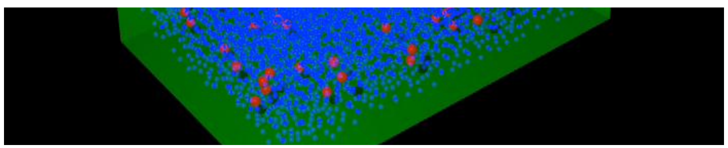
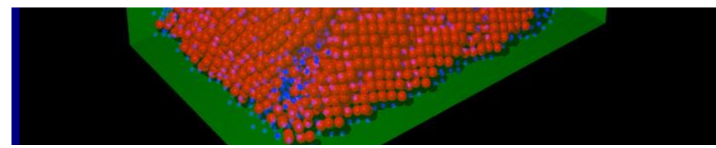
Power-law distribution

Fit with free energy using crystal entropy

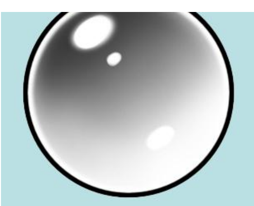
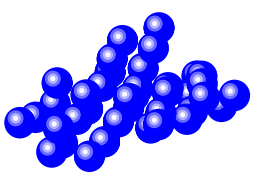
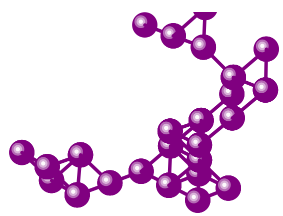
Conclusions

- Colloidal crystal nuclei are disordered
- Added entropic contribution to free energy

Thank you for your attention

Fast crystal nucleation