

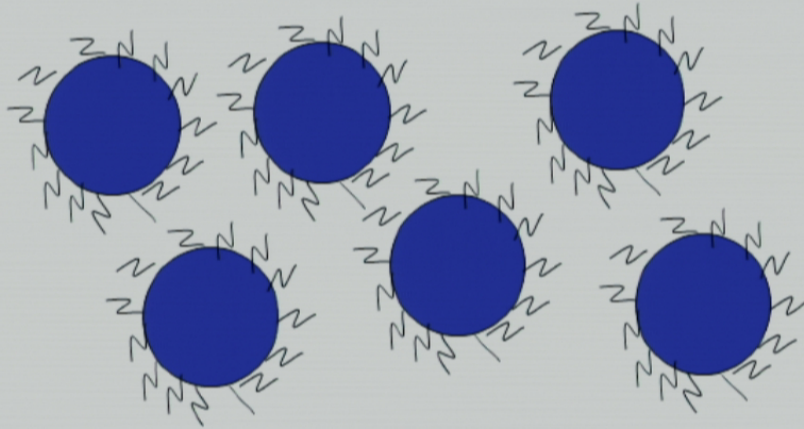
Title: Slow Melting and Fast Crystals

Date: Dec 05, 2013 01:40 PM

URL: <http://pirsa.org/13120015>

Abstract: This talk will focus on the behavior of colloidal crystals, and will describe both the nucleation and growth of crystals and their melting. The nucleation and growth of colloidal crystals is experimentally observed to be much faster than expected theoretically or through simulation. The discrepancy can be as much as 10^{150} ! I will describe some new experiments that suggest a possible reason for this. I will also describe the melting of colloidal crystals formed with highly charged particles that form a Wigner lattice. I will show that this melting resembles a second-order phase transition, and follows the prediction of Born for a catastrophic collapse of the elastic constant.

Colloidal Particles



Stability:

Short range repulsion

Sometimes a slight charge

Colloid Particles are:

•Big

• $\sim a \sim 1$ micron

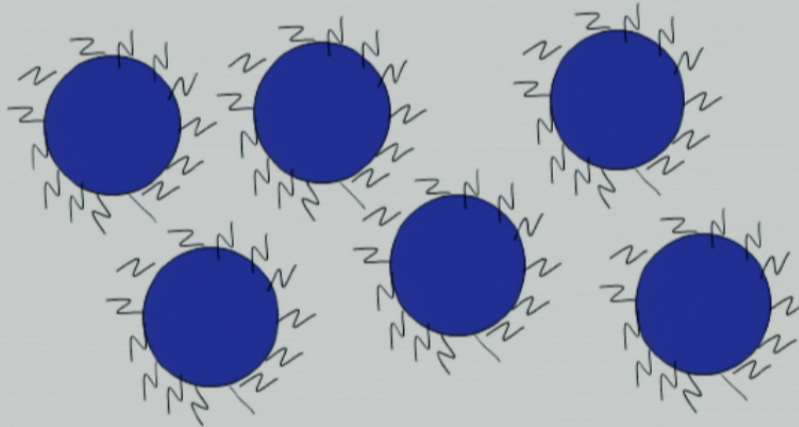
•Can “see” them

Slow

• $\tau \sim a^2/D \sim$ ms to sec

•Follow individual particle dynamics

Colloidal Particles



Stability:

Short range repulsion

Sometimes a slight charge

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•Big

• $\sim a \sim 1$ micron

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Slow

• $\tau \sim a^2/D \sim$ ms to sec

•Follow individual particle dynamics

Model: Colloid $\rightarrow$ Atom

Pusey-Van Megen colloidal hard spheres

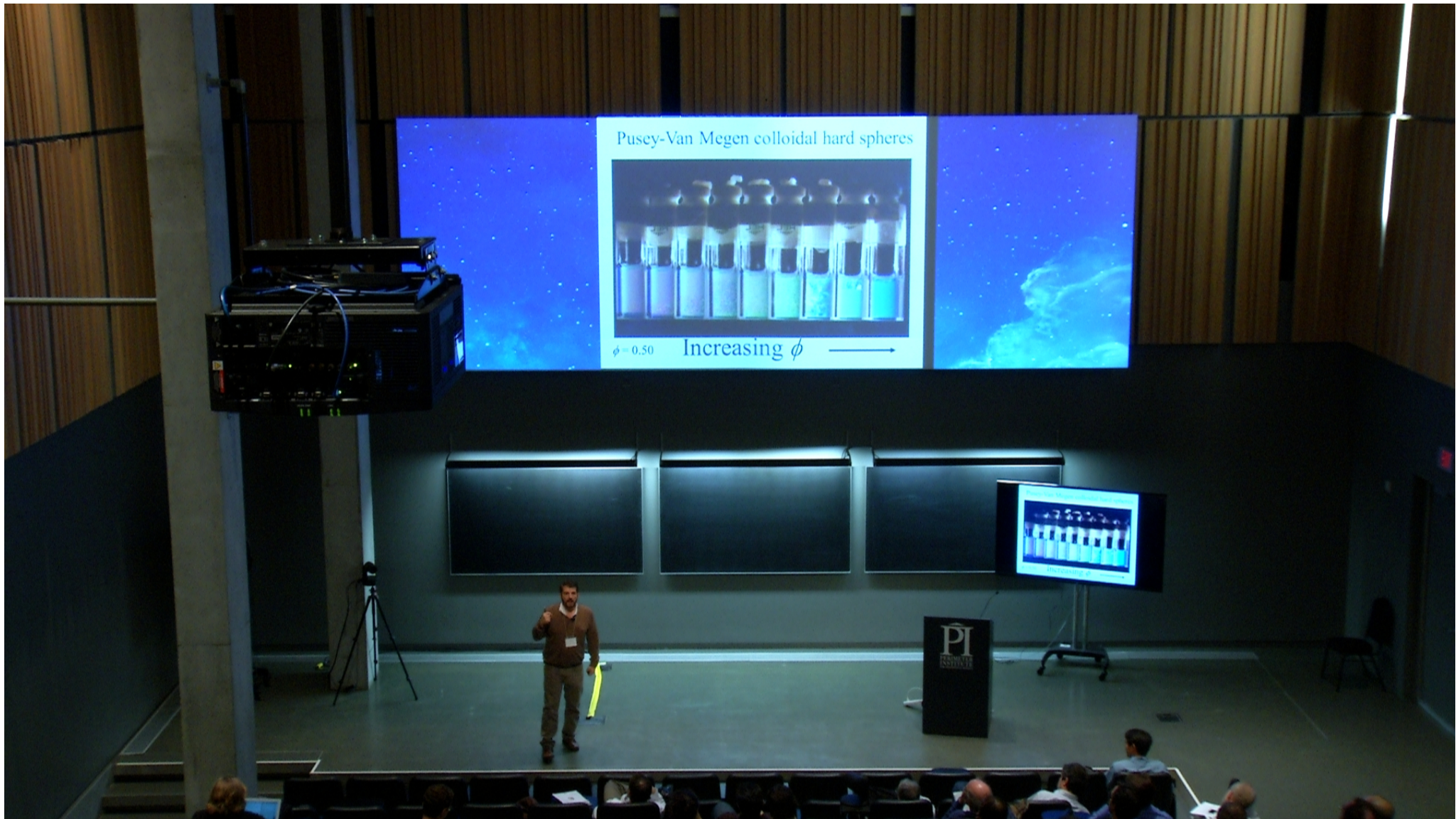


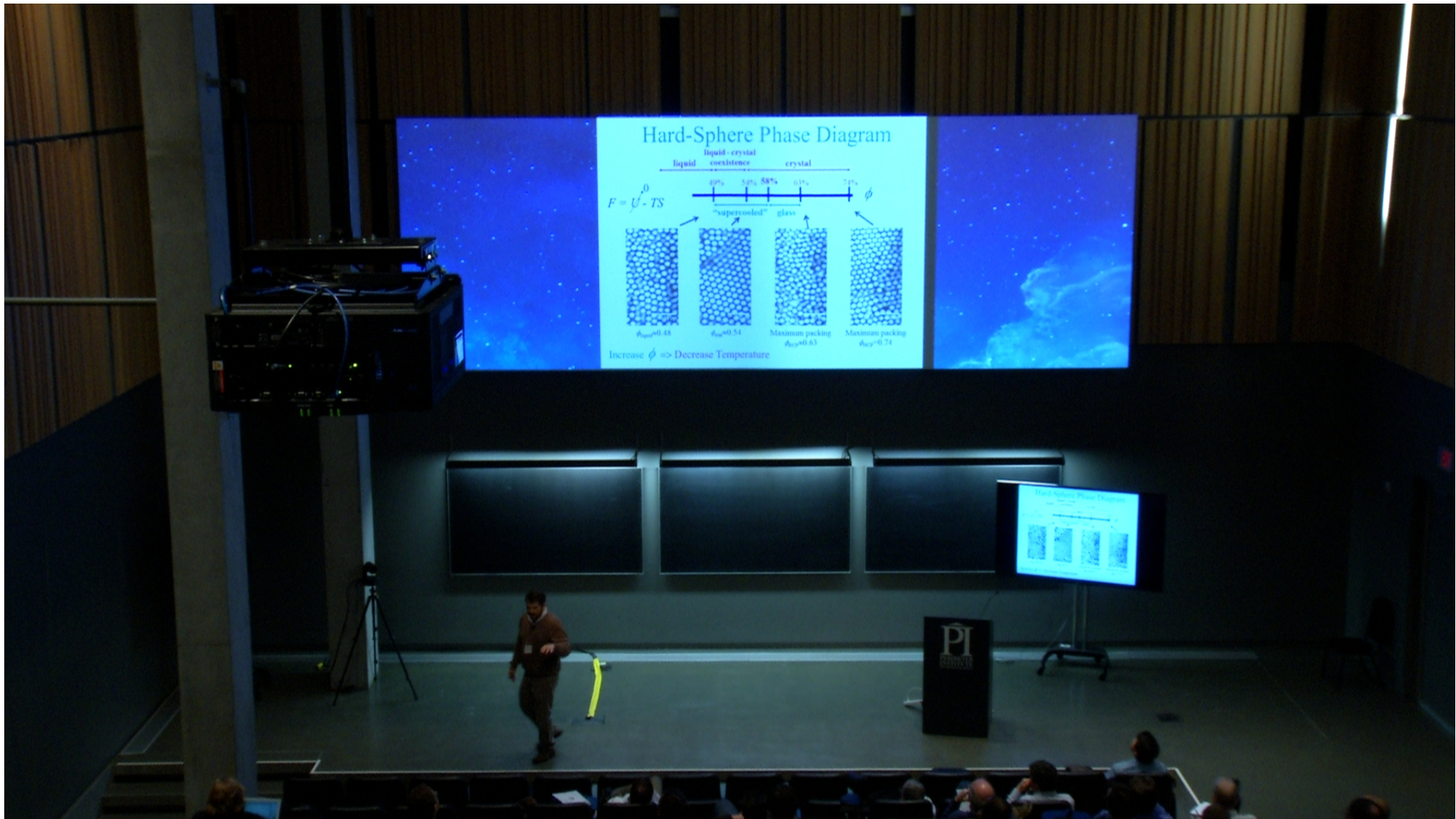
$\phi = 0.50$ Increasing ϕ $\longrightarrow$

Pusey-Van Megen colloidal hard spheres

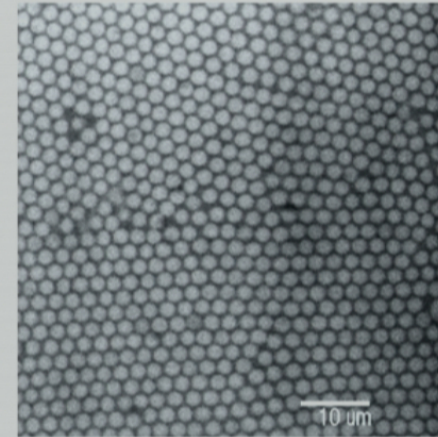
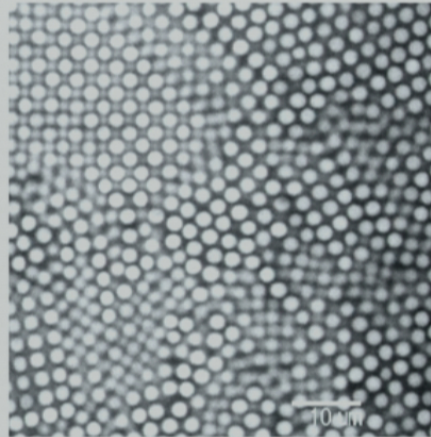
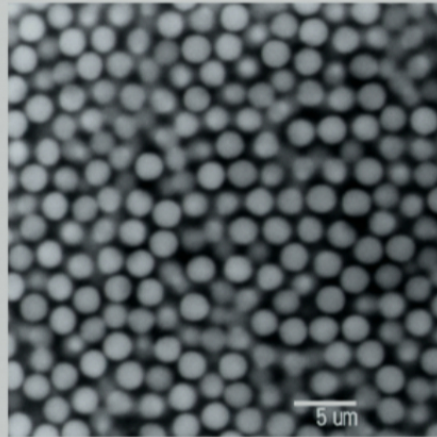


$\phi = 0.50$ Increasing ϕ $\longrightarrow$



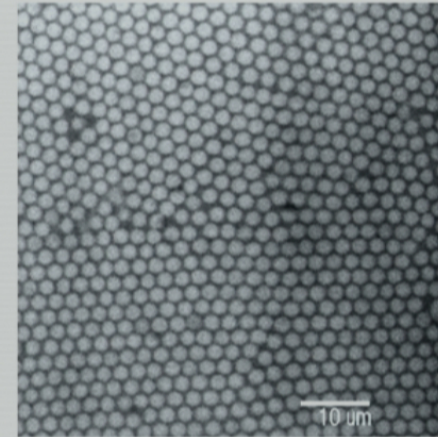
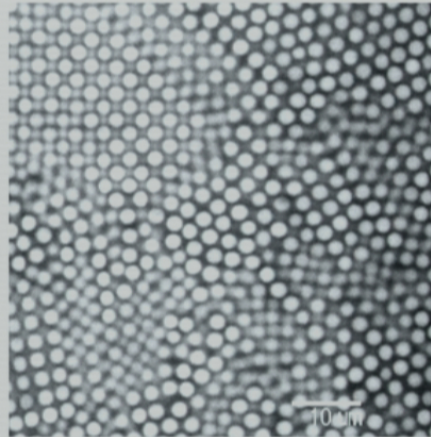
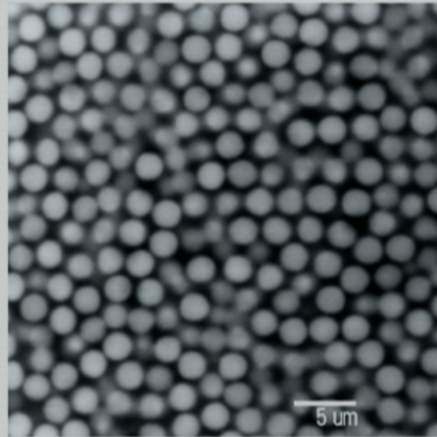


How do colloidal crystals form?

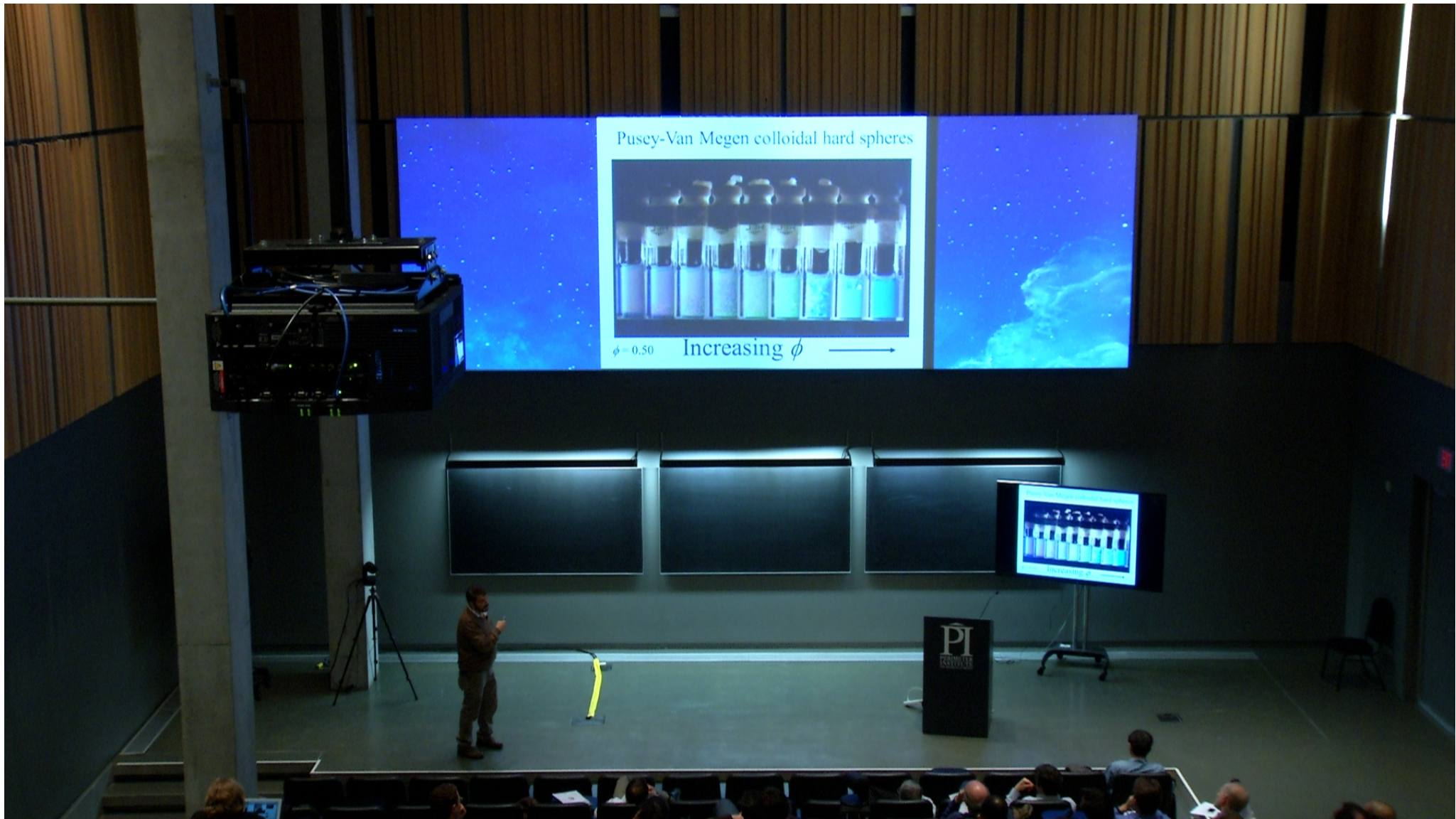


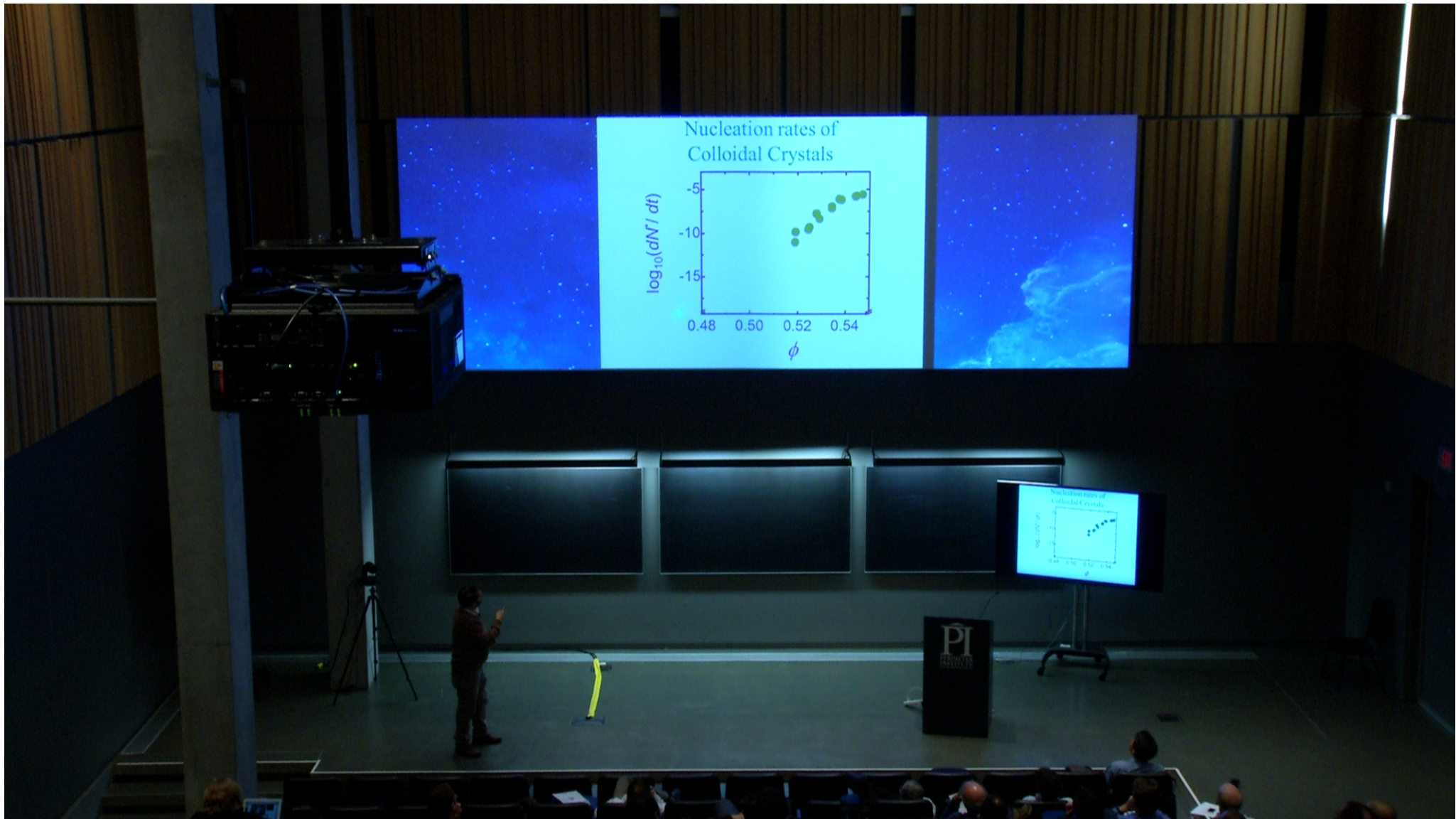
2.3 μm diameter PMMA spheres

How do colloidal crystals form?

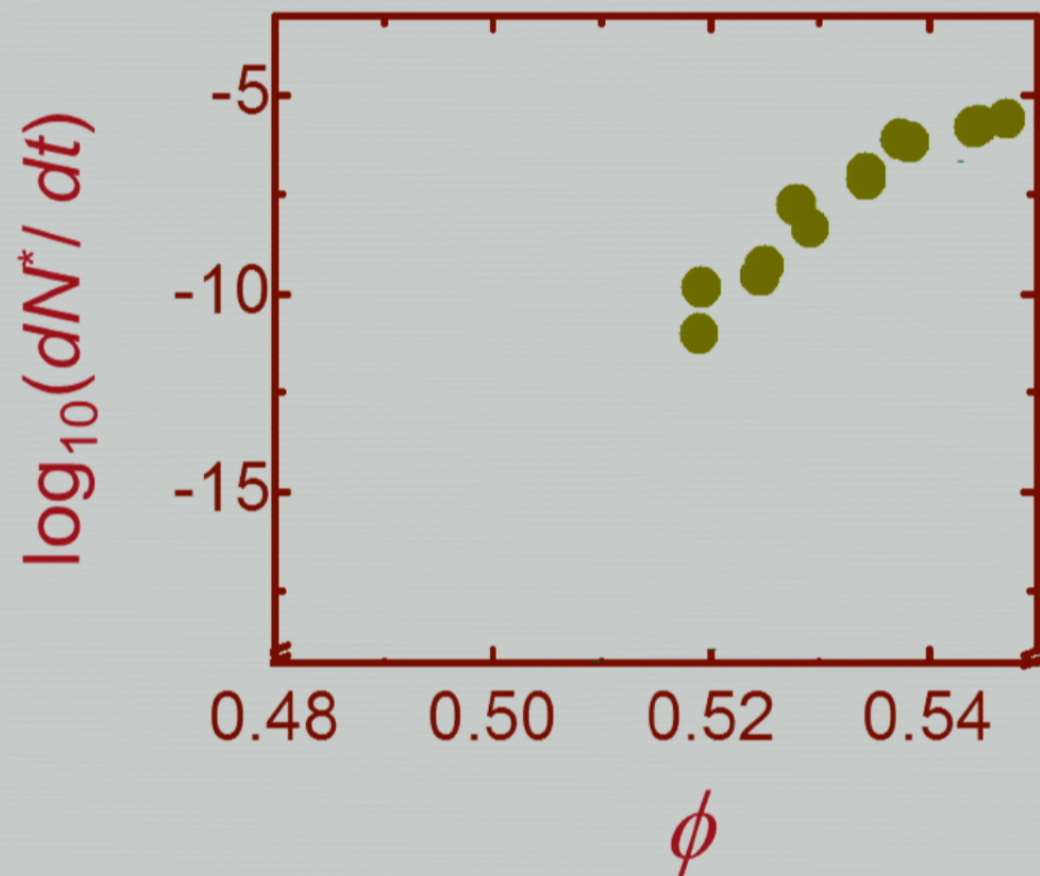


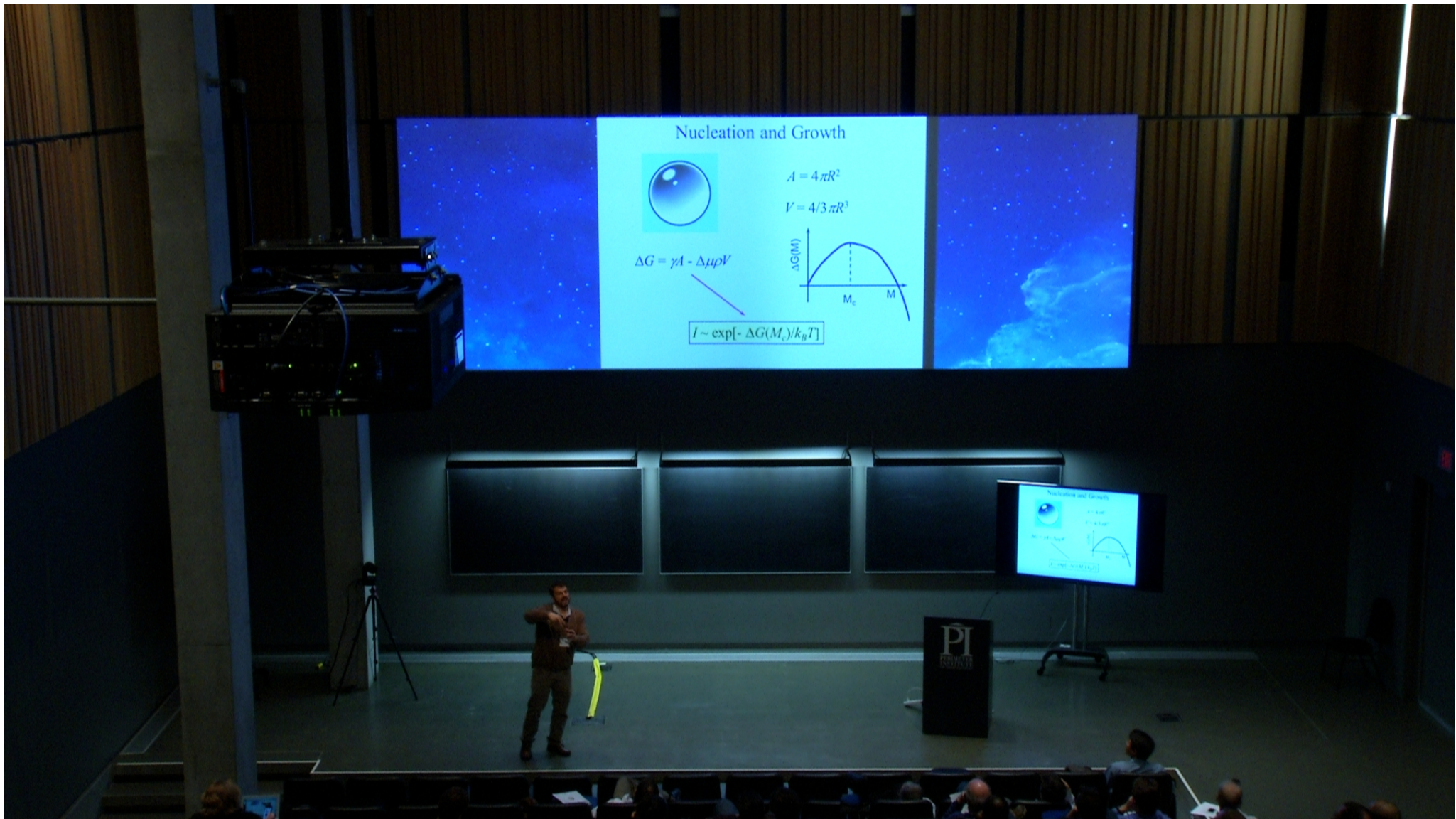
2.3 μm diameter PMMA spheres





Nucleation rates of Colloidal Crystals





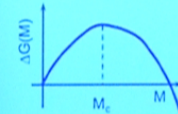
Nucleation and Growth



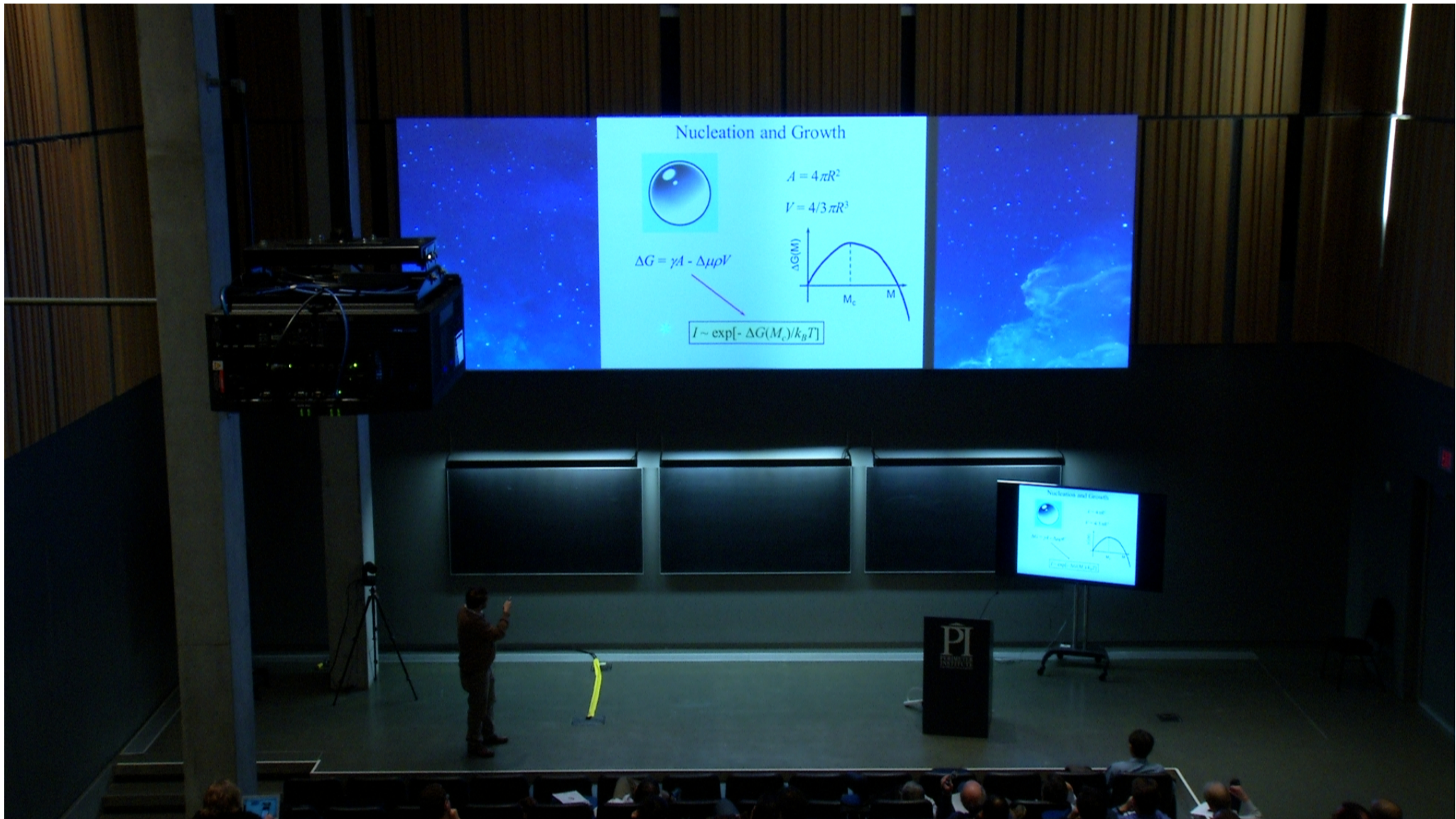
$$A = 4\pi R^2$$

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

$$\Delta G = \gamma A - \Delta\mu pV$$



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



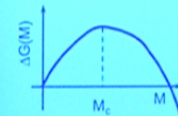
Nucleation and Growth



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

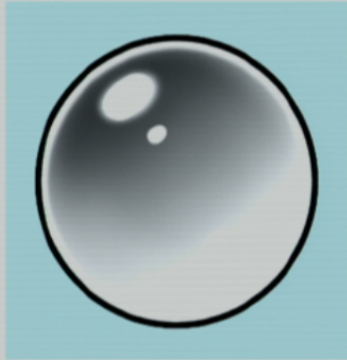
$$V = \frac{4}{3}\pi R^3$$

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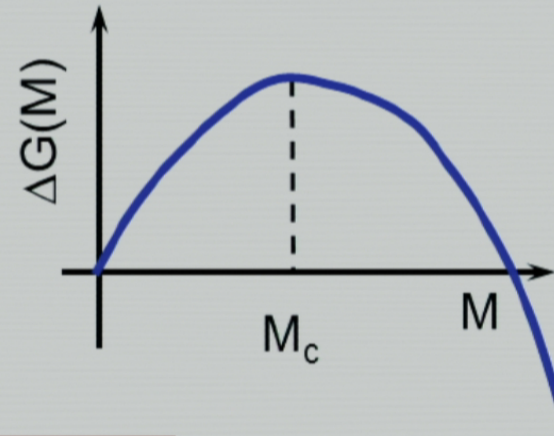
Nucleation and Growth



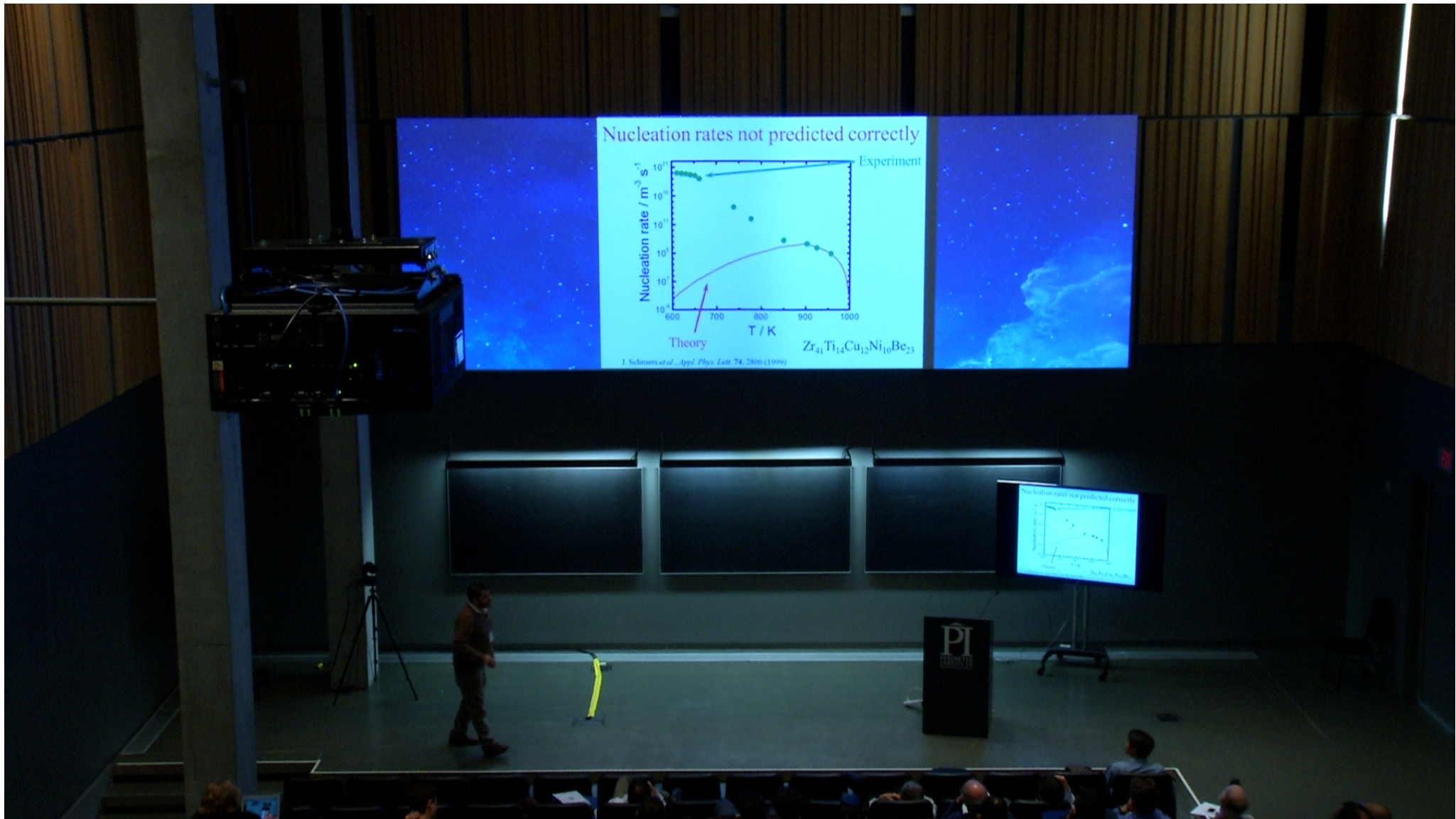
$$A = 4\pi R^2$$

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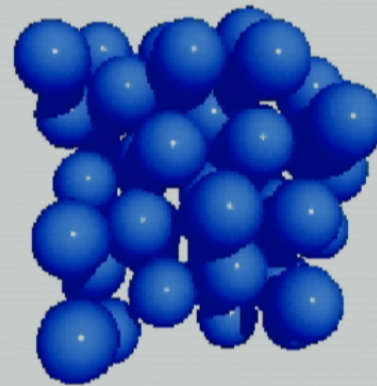
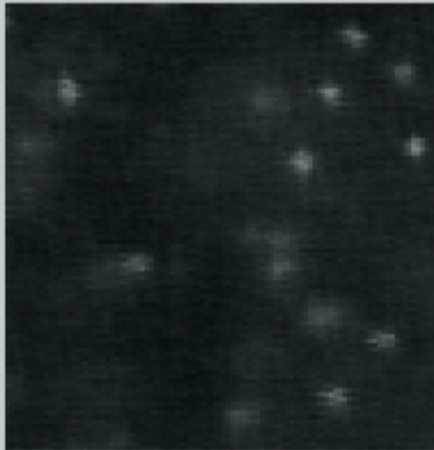
$$\Delta G = \gamma A - \Delta\mu\rho V$$



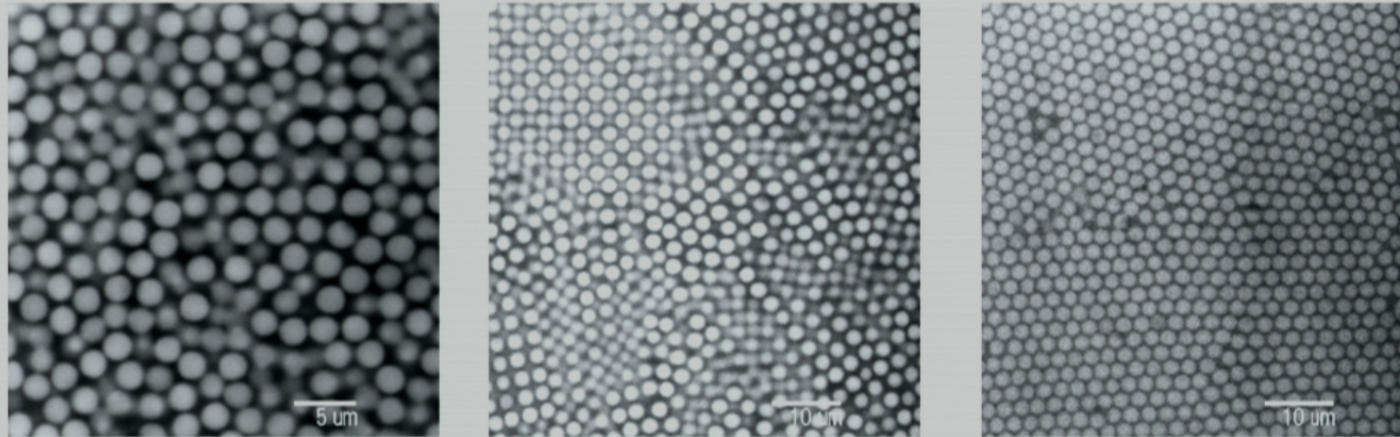
$$I \sim \exp[-\Delta G(M_c)/k_B T]$$



Brownian Motion in Real Time

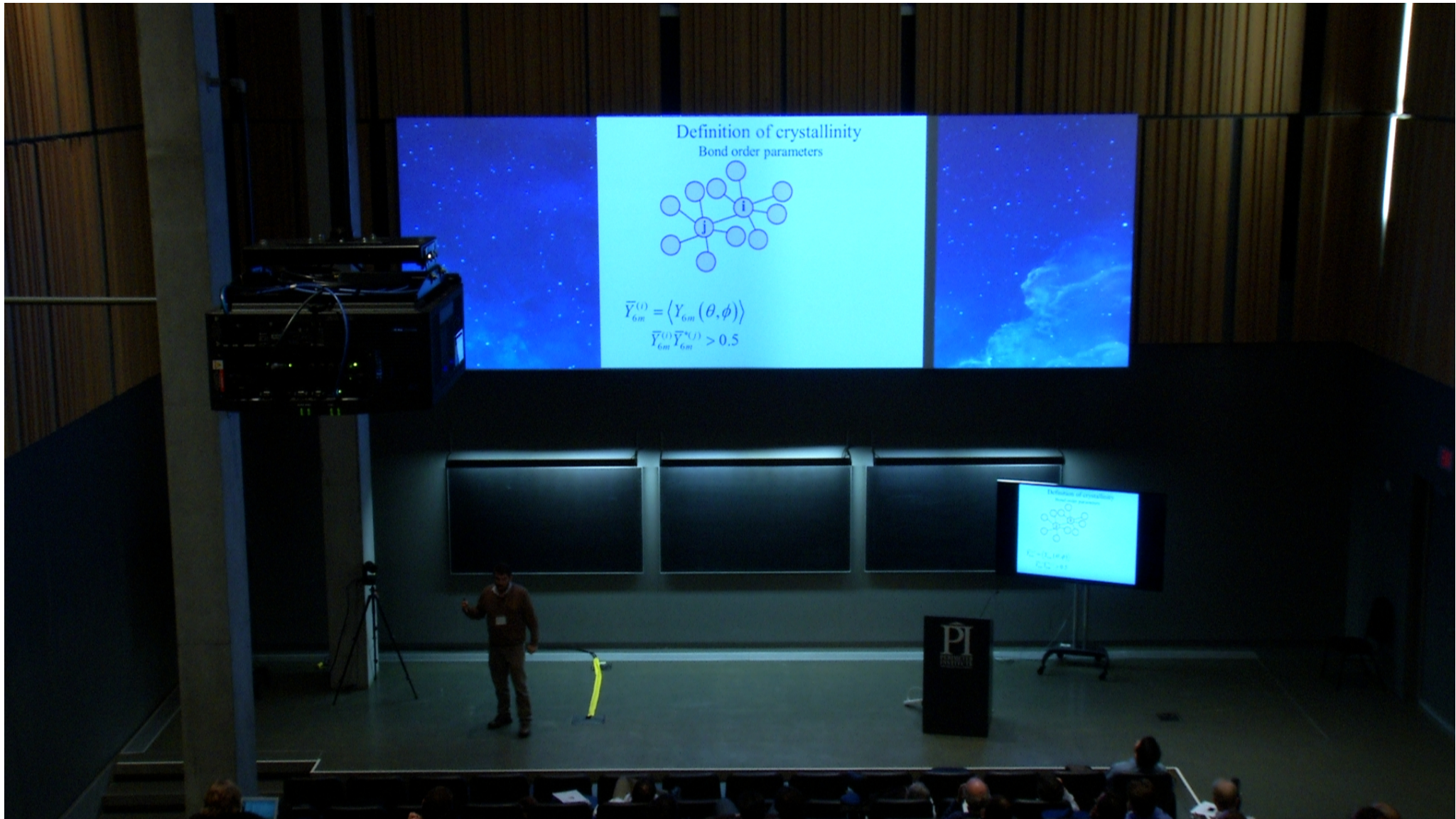


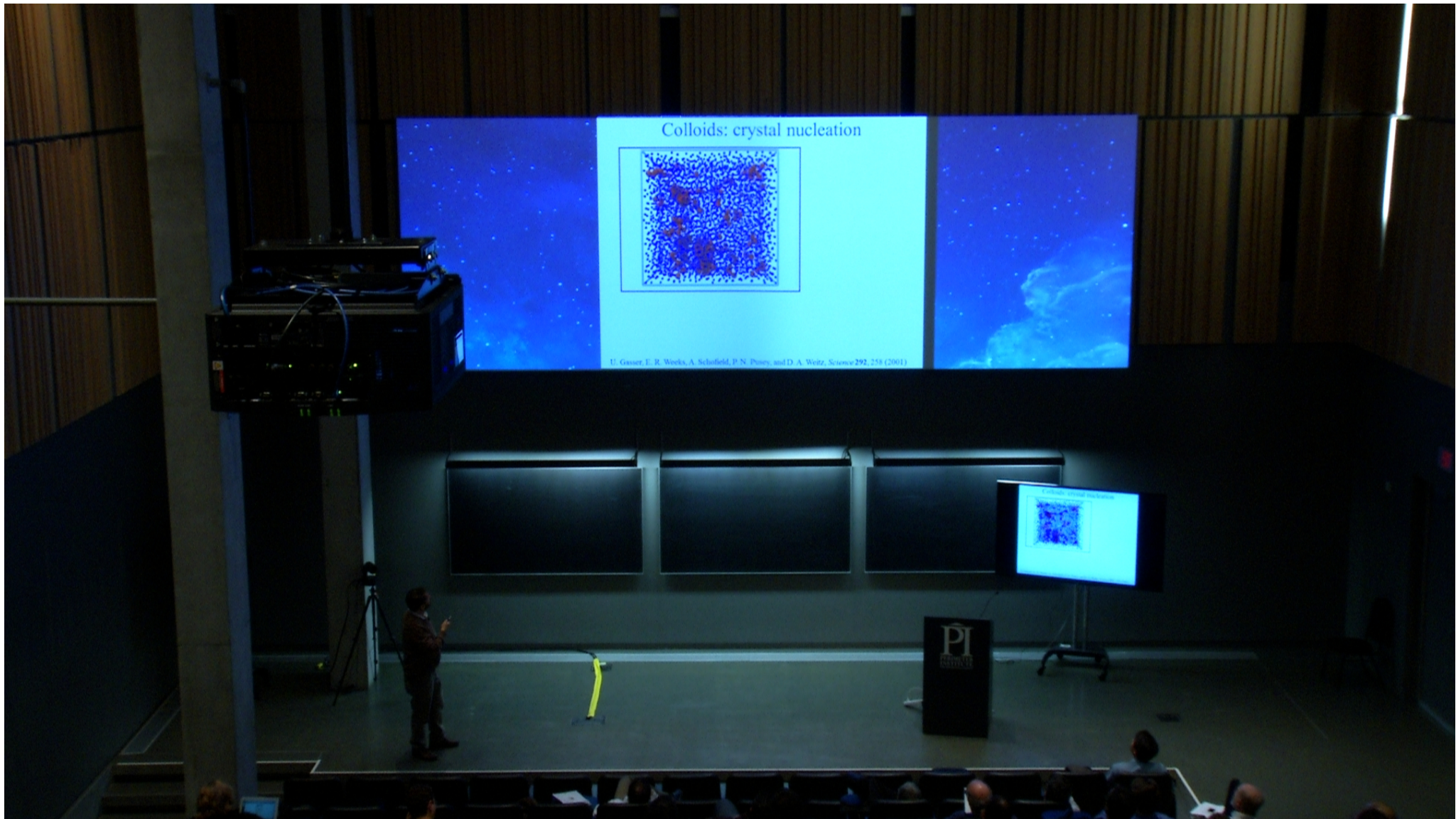
How to Identify Crystals

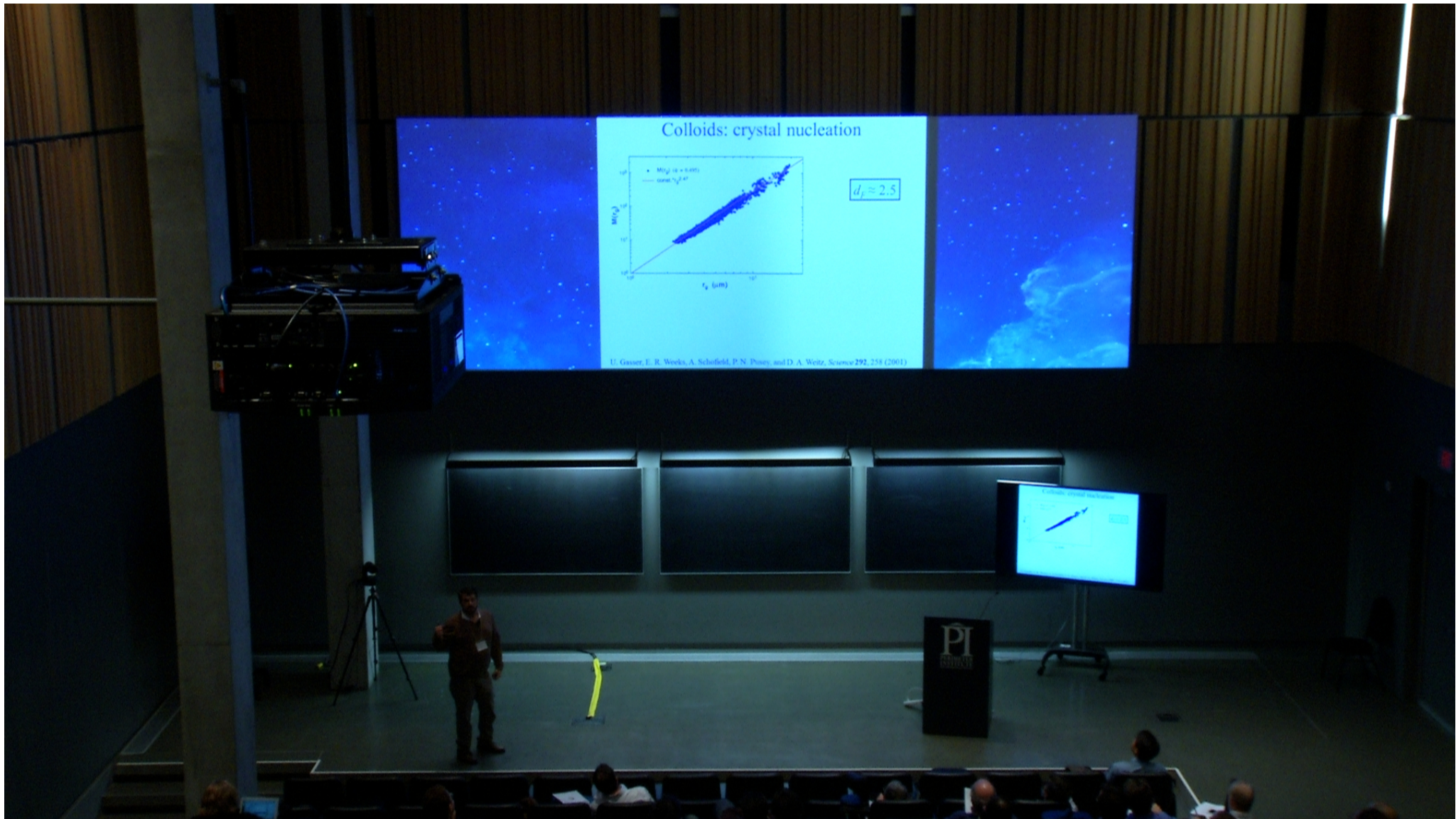


2.3 μm diameter PMMA spheres

Must identify incipient crystal nuclei

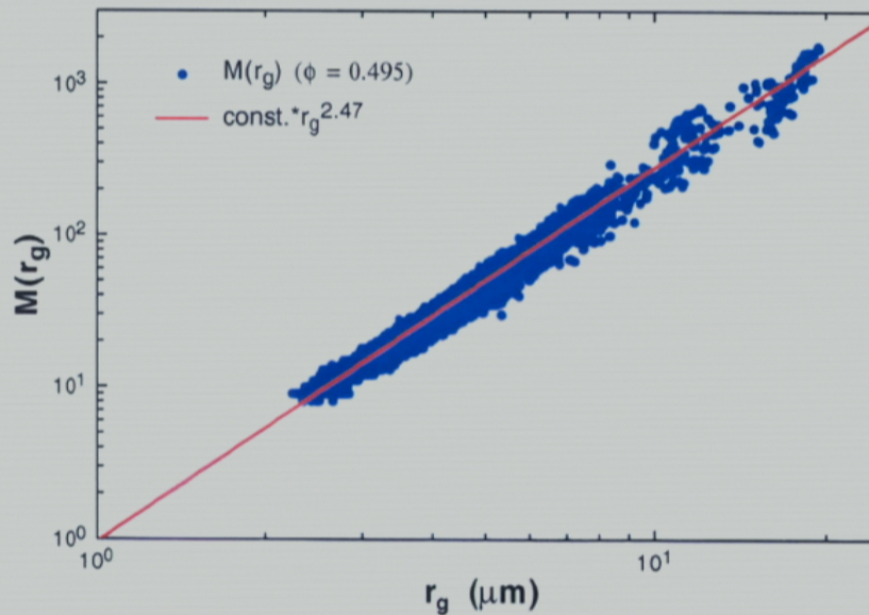






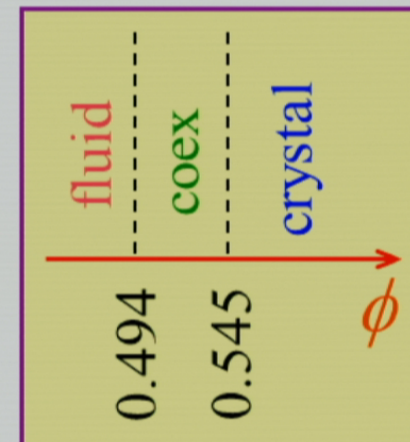


Colloids: crystal nucleation



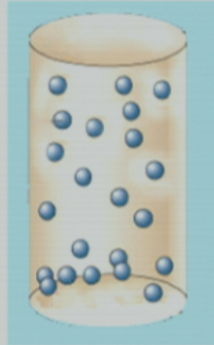
$$d_F \approx 2.5$$

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



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

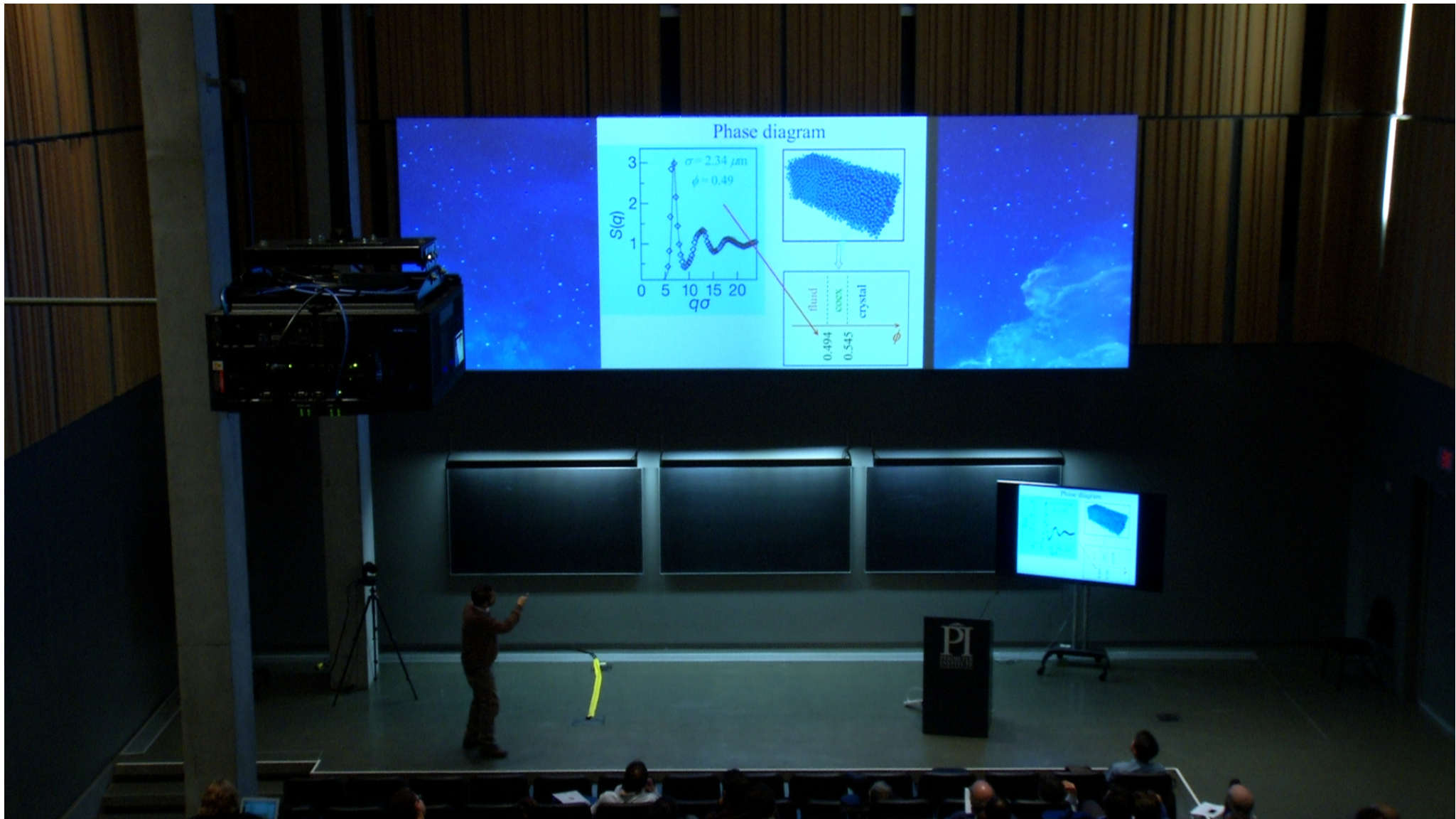
Colloidal suspension



$$\sigma \sim 2.3 \text{ mm}$$

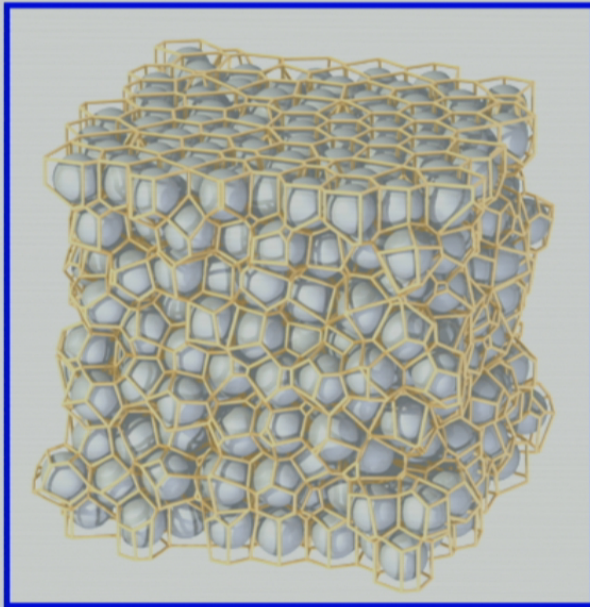
PMMA (polymethylmethacrylate)

PHSA (poly-12-hydroxystearic) “hairs”

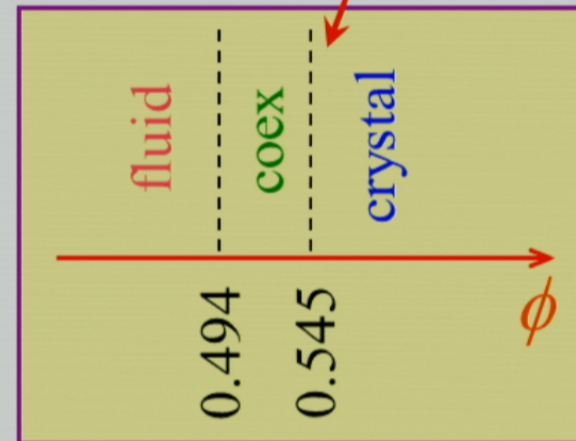
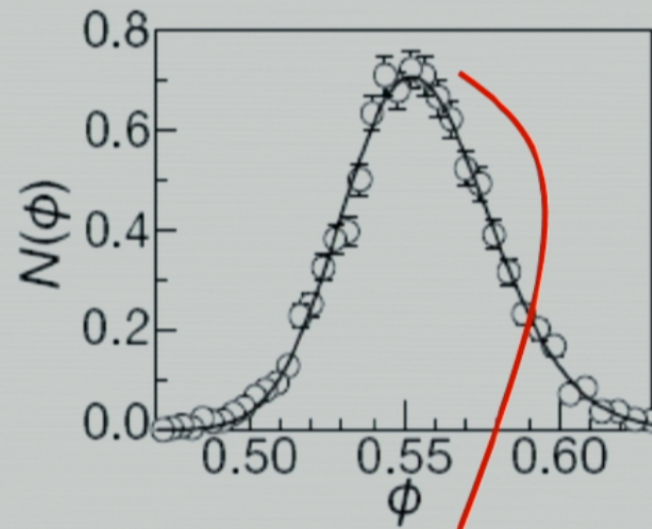


Phase behavior

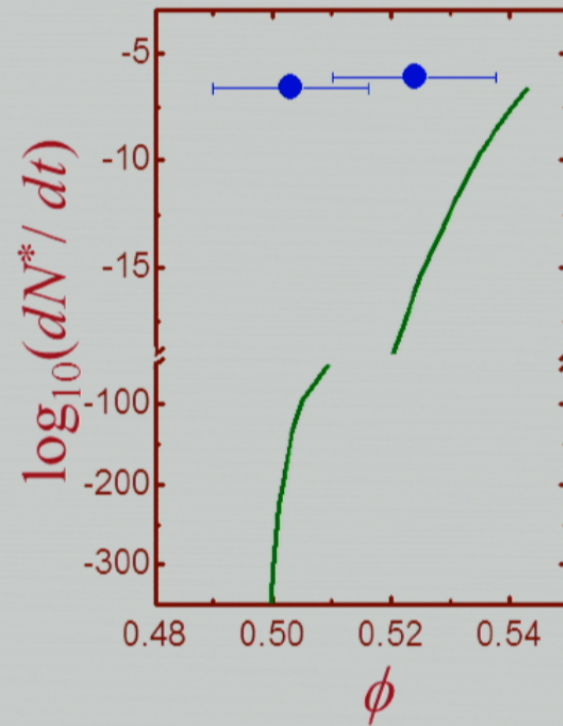
Voronoi tessellation



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

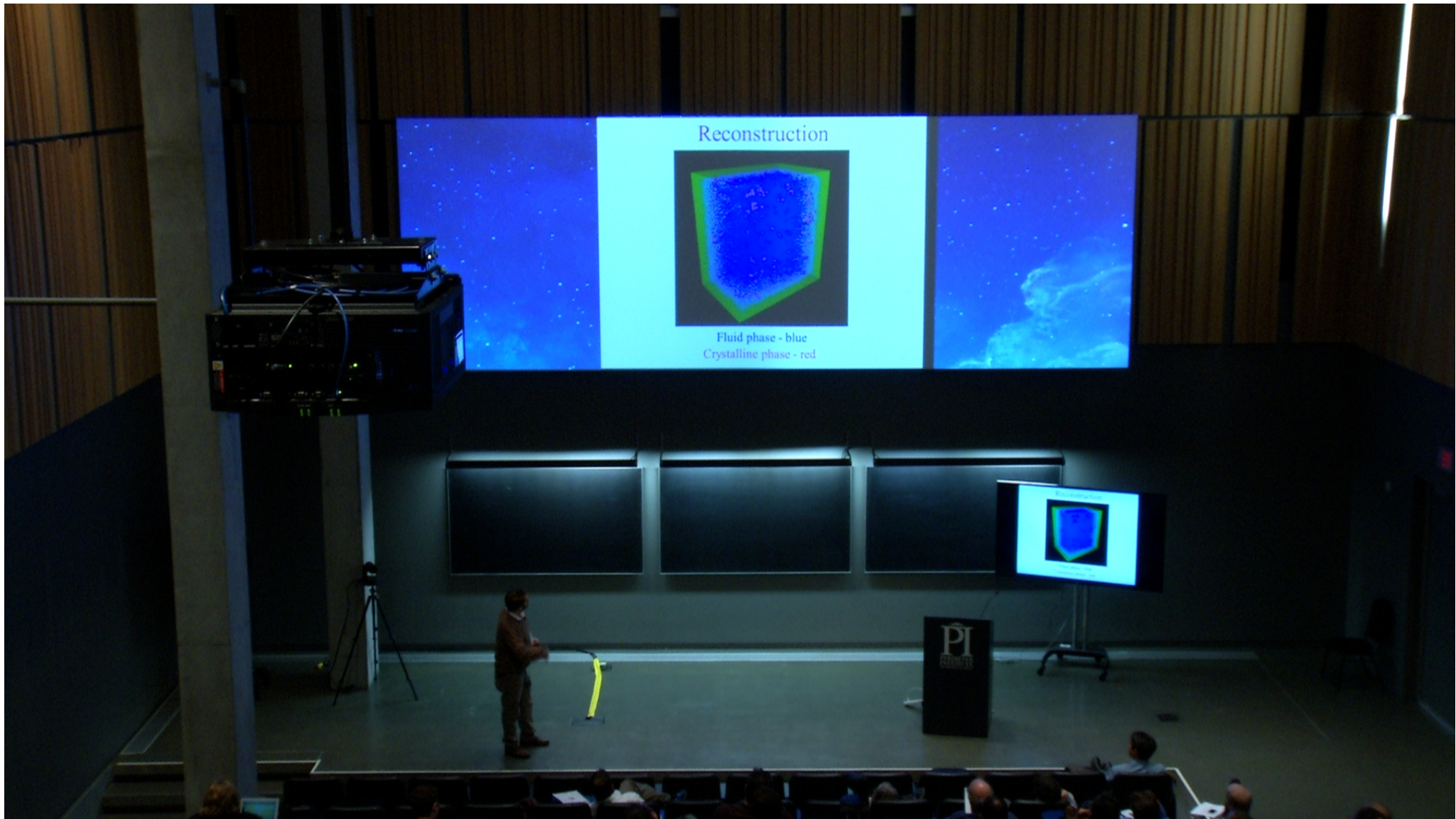


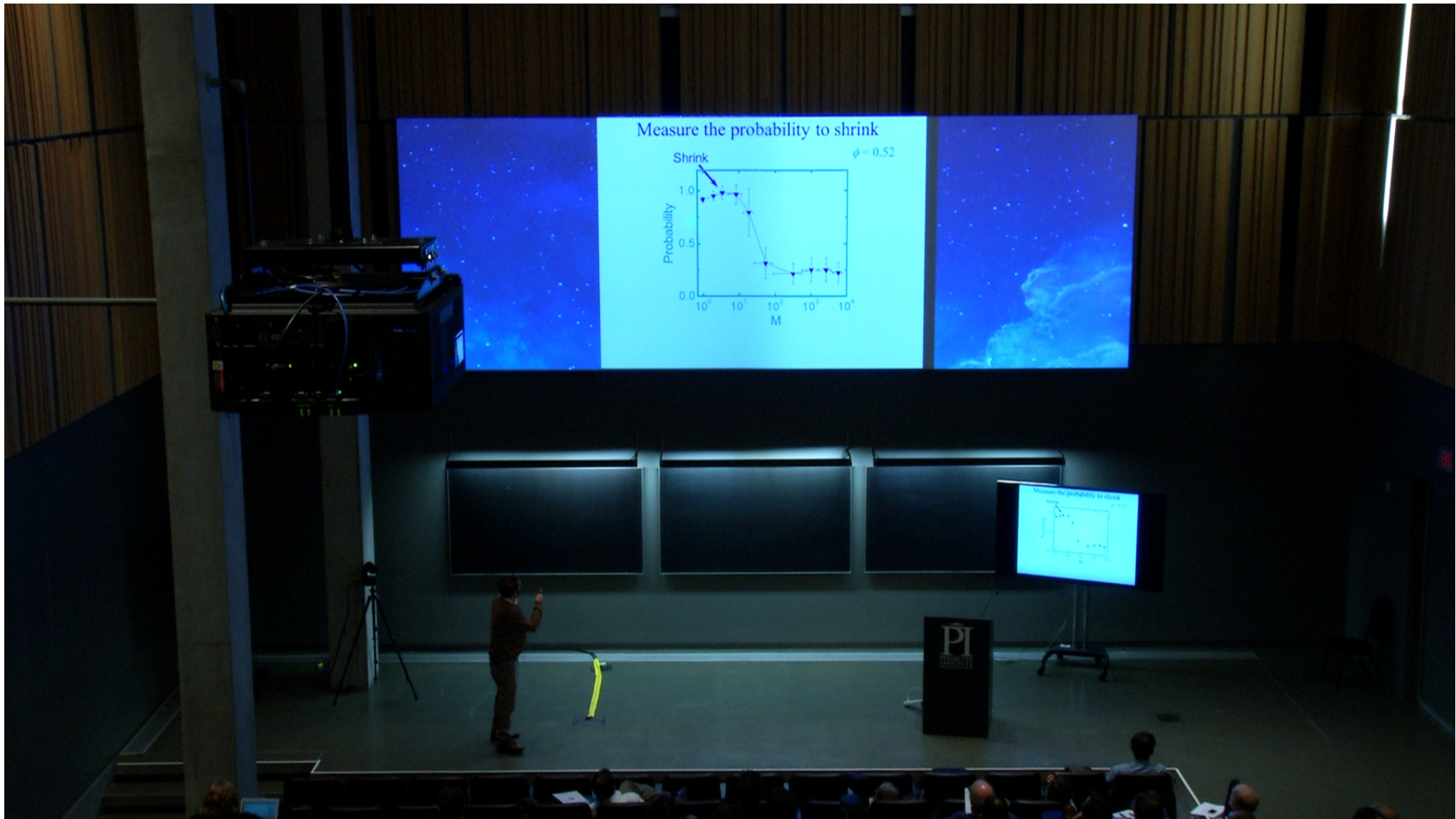
Nucleation rates

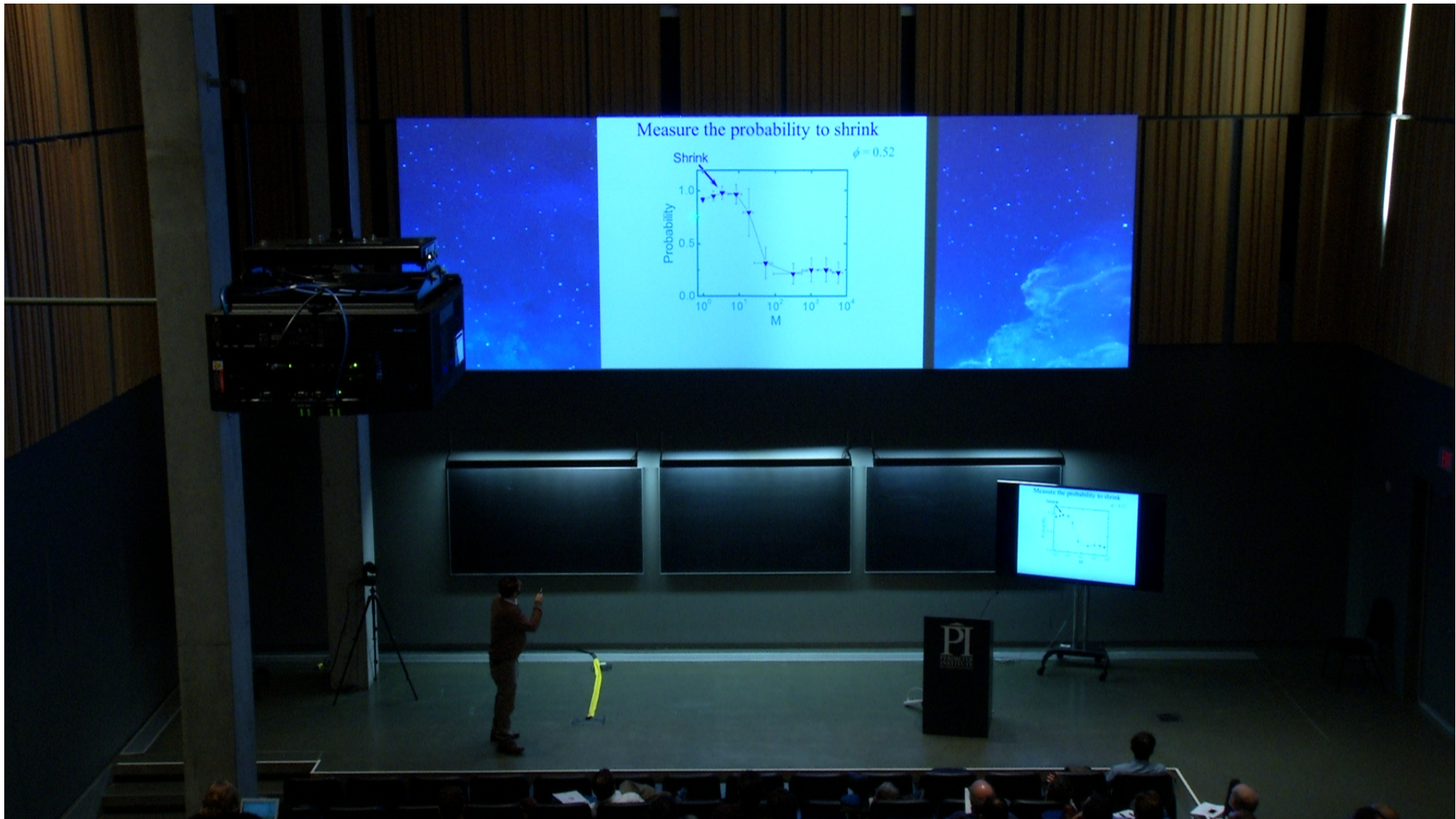


$10^{150}!!$

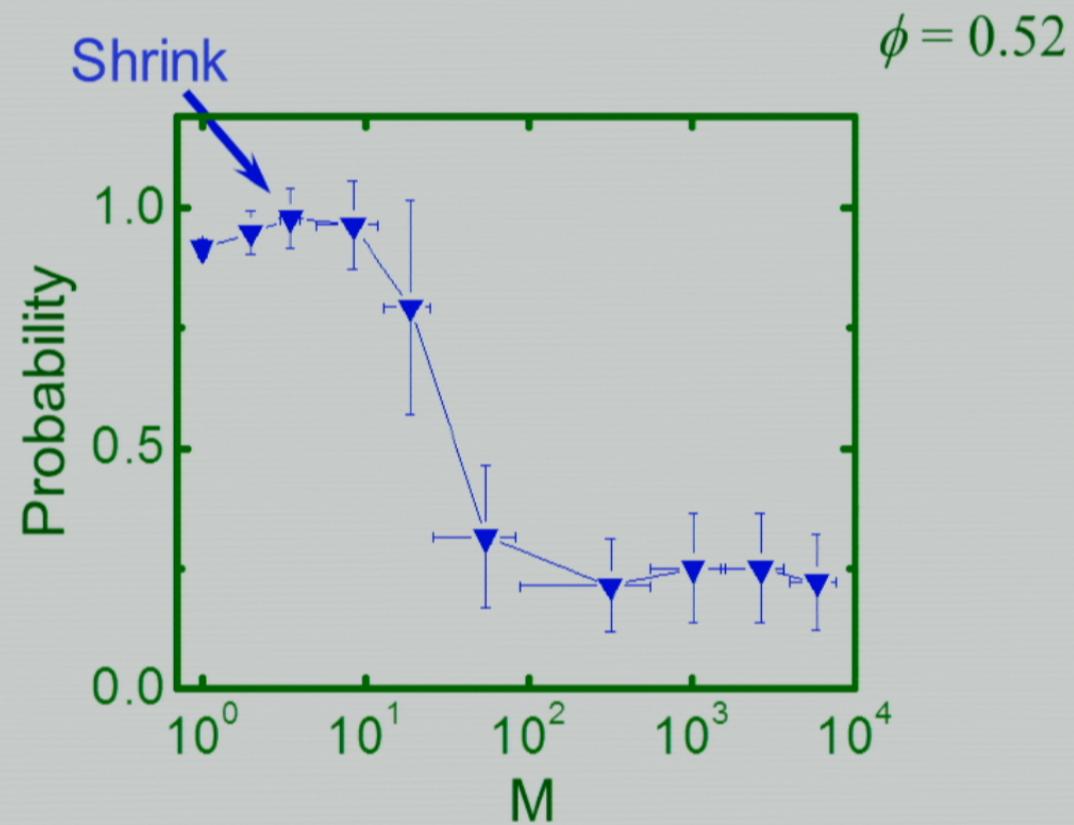
Auer & Frenkel, *Nature* **409**, 1020 (2001)



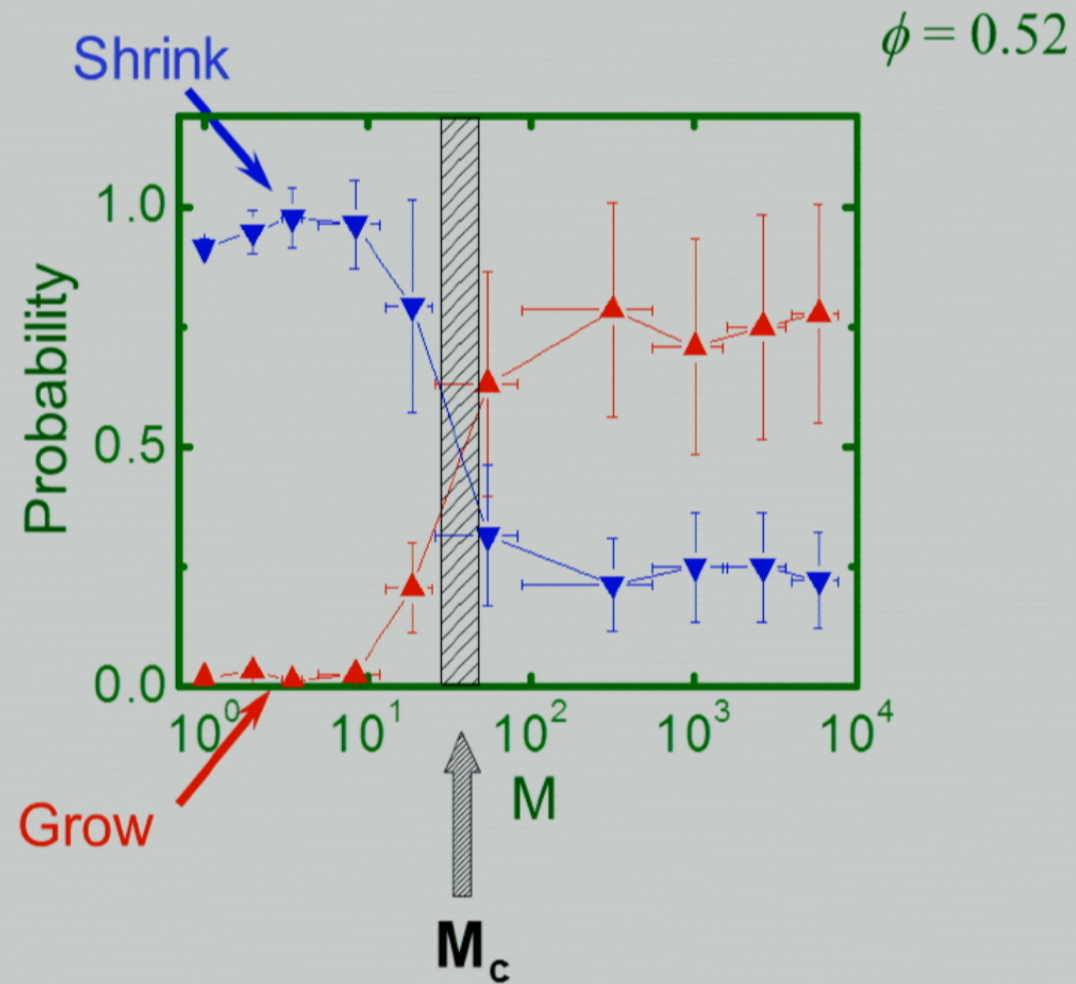


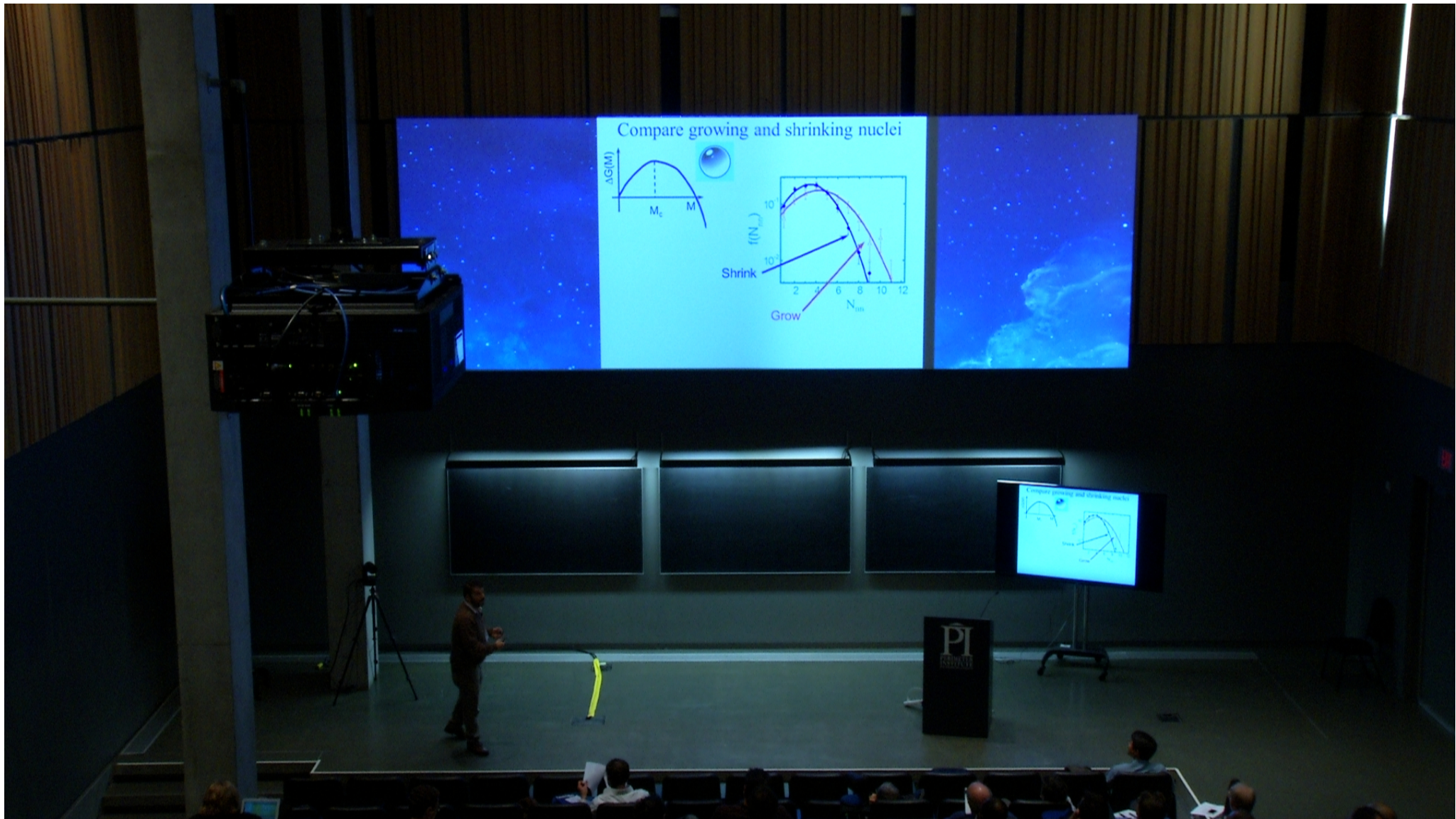


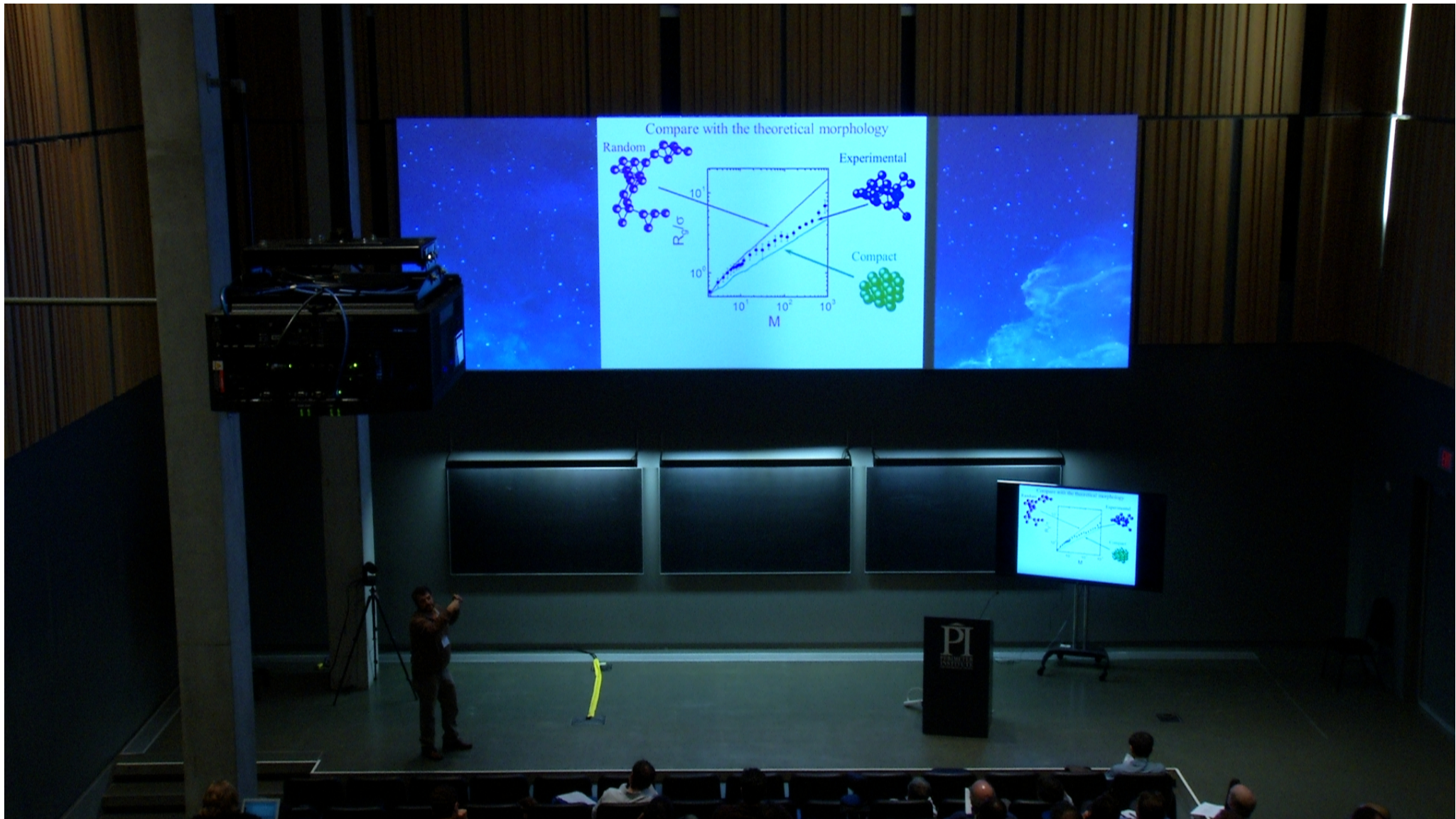
Measure the probability to shrink

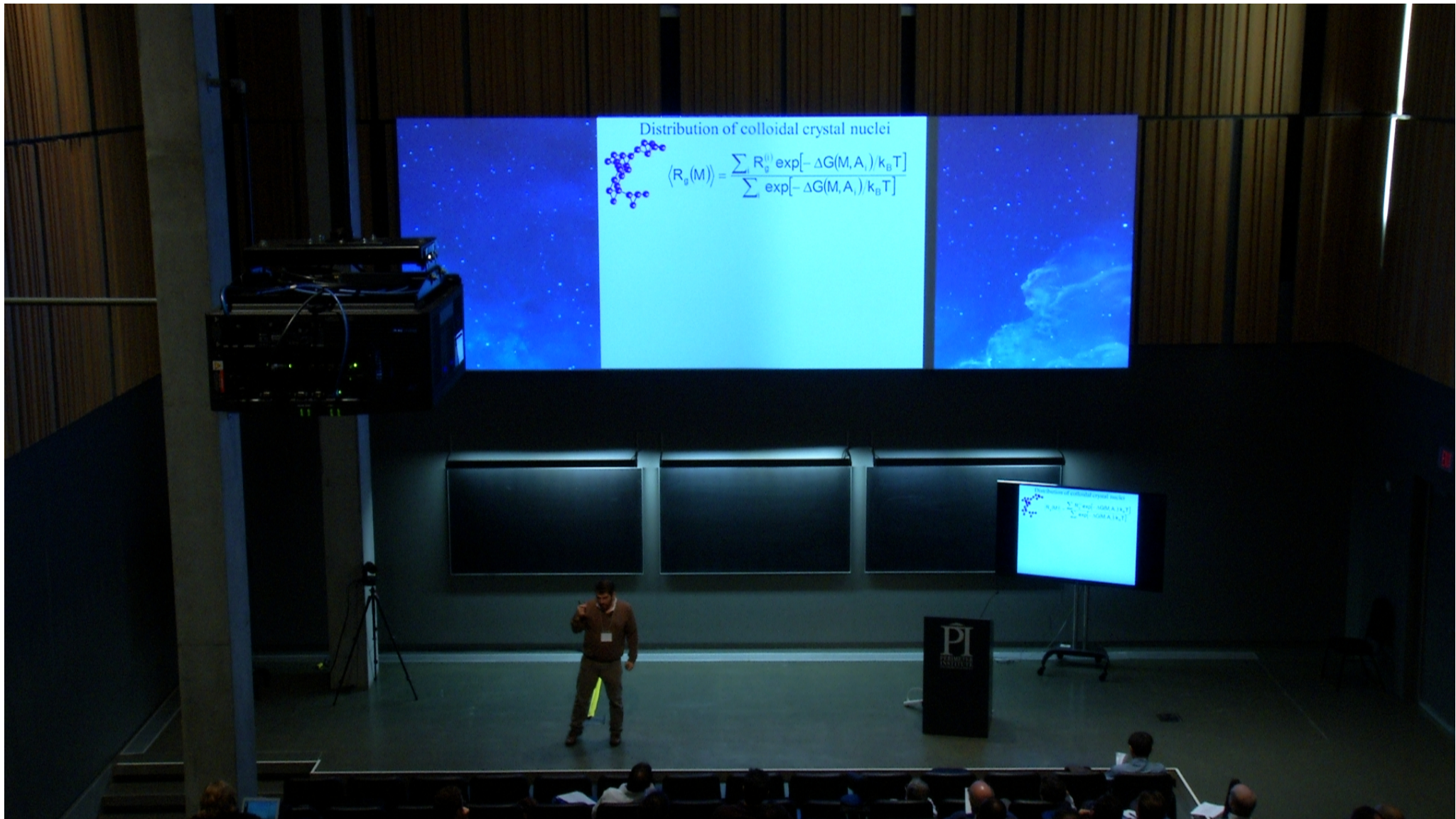


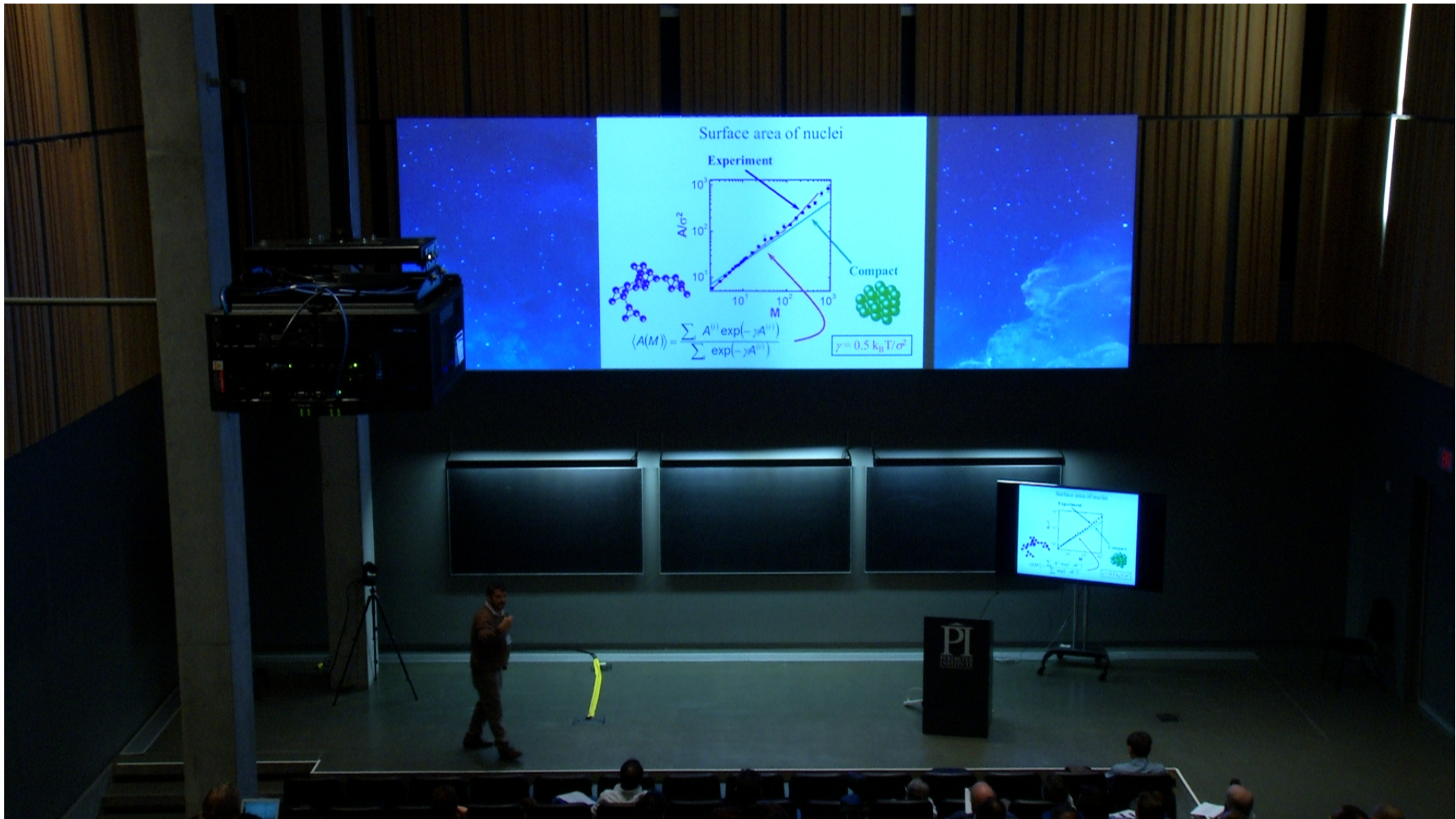
Measure the critical mass

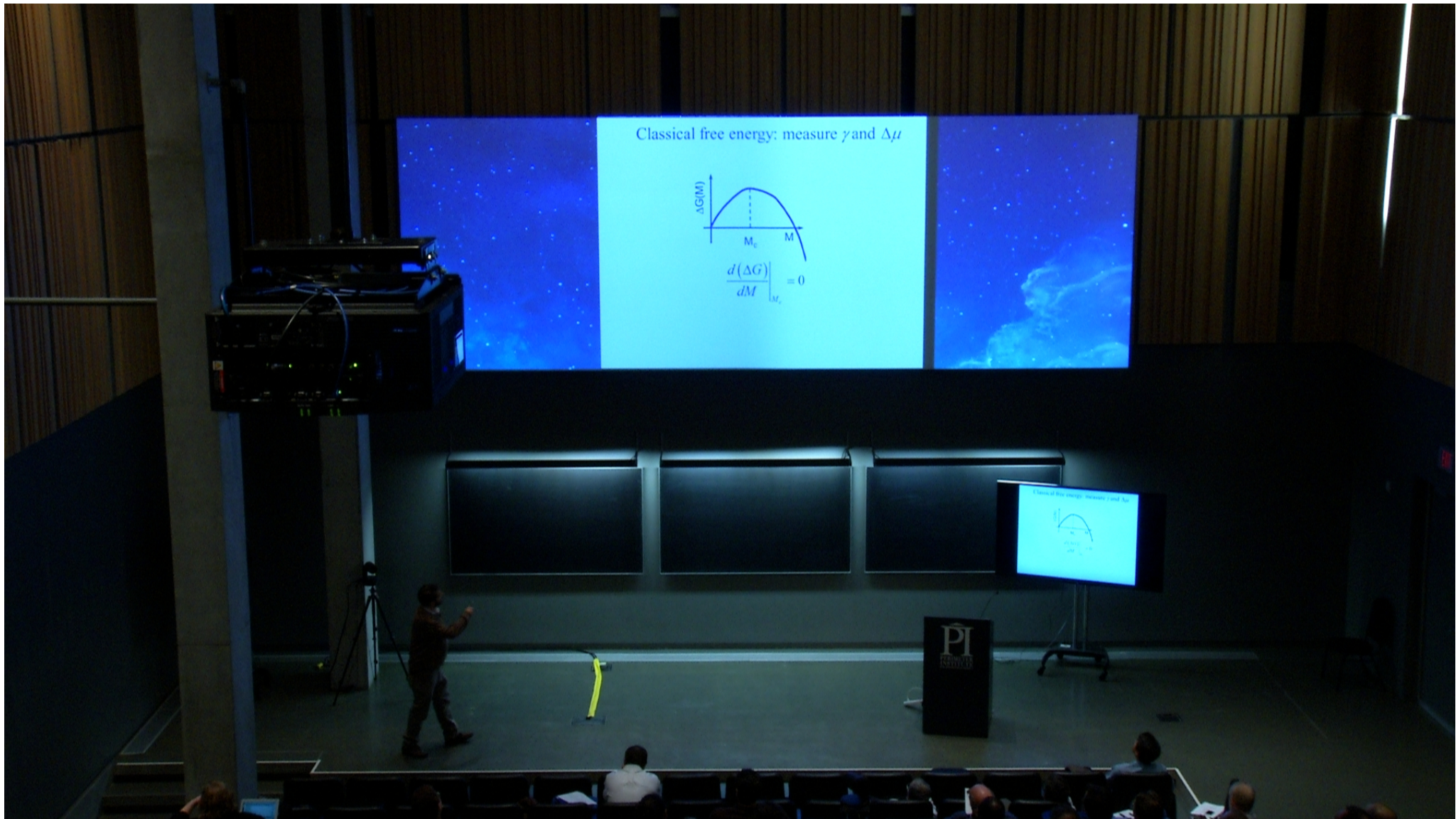




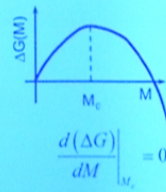


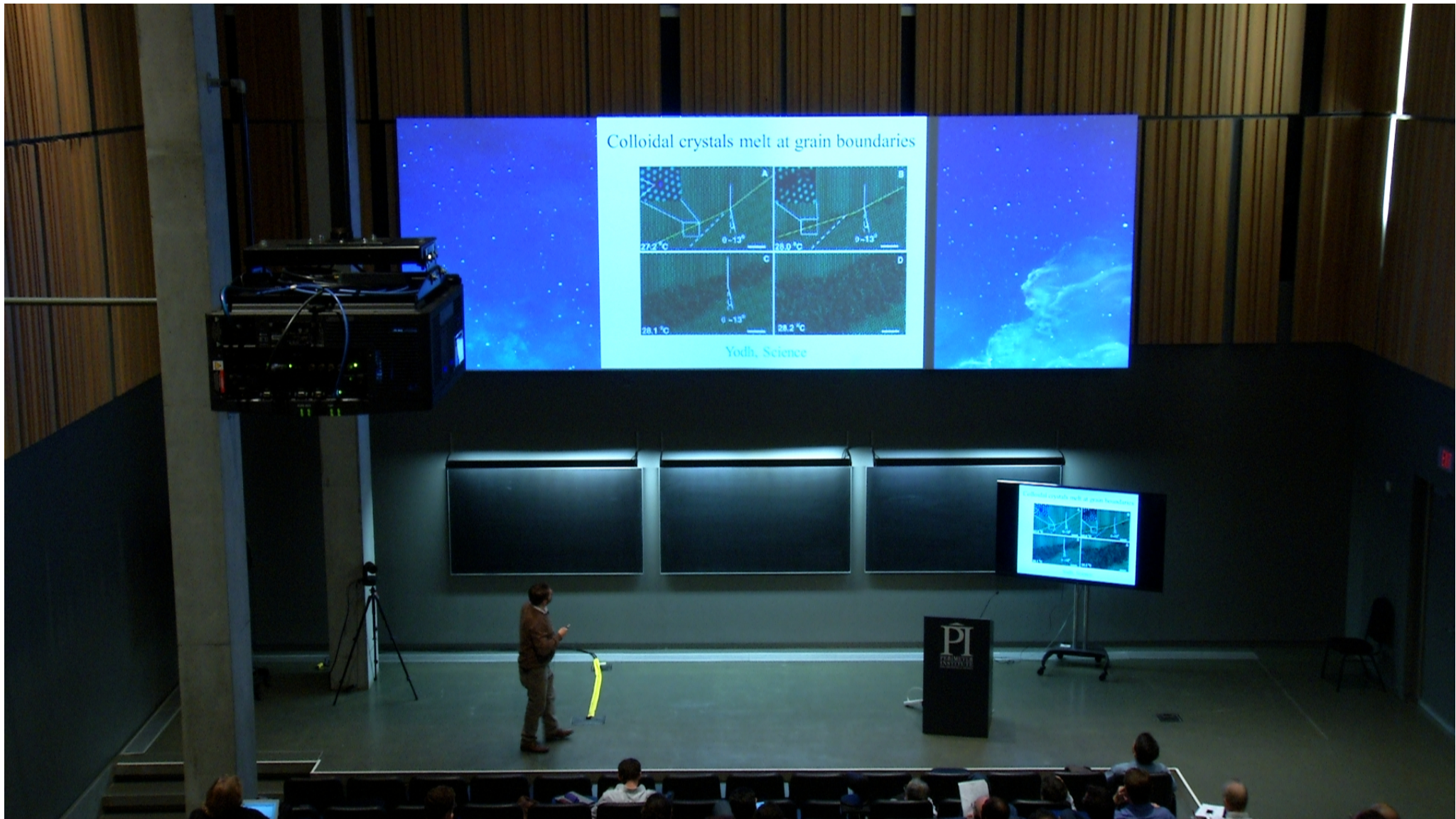


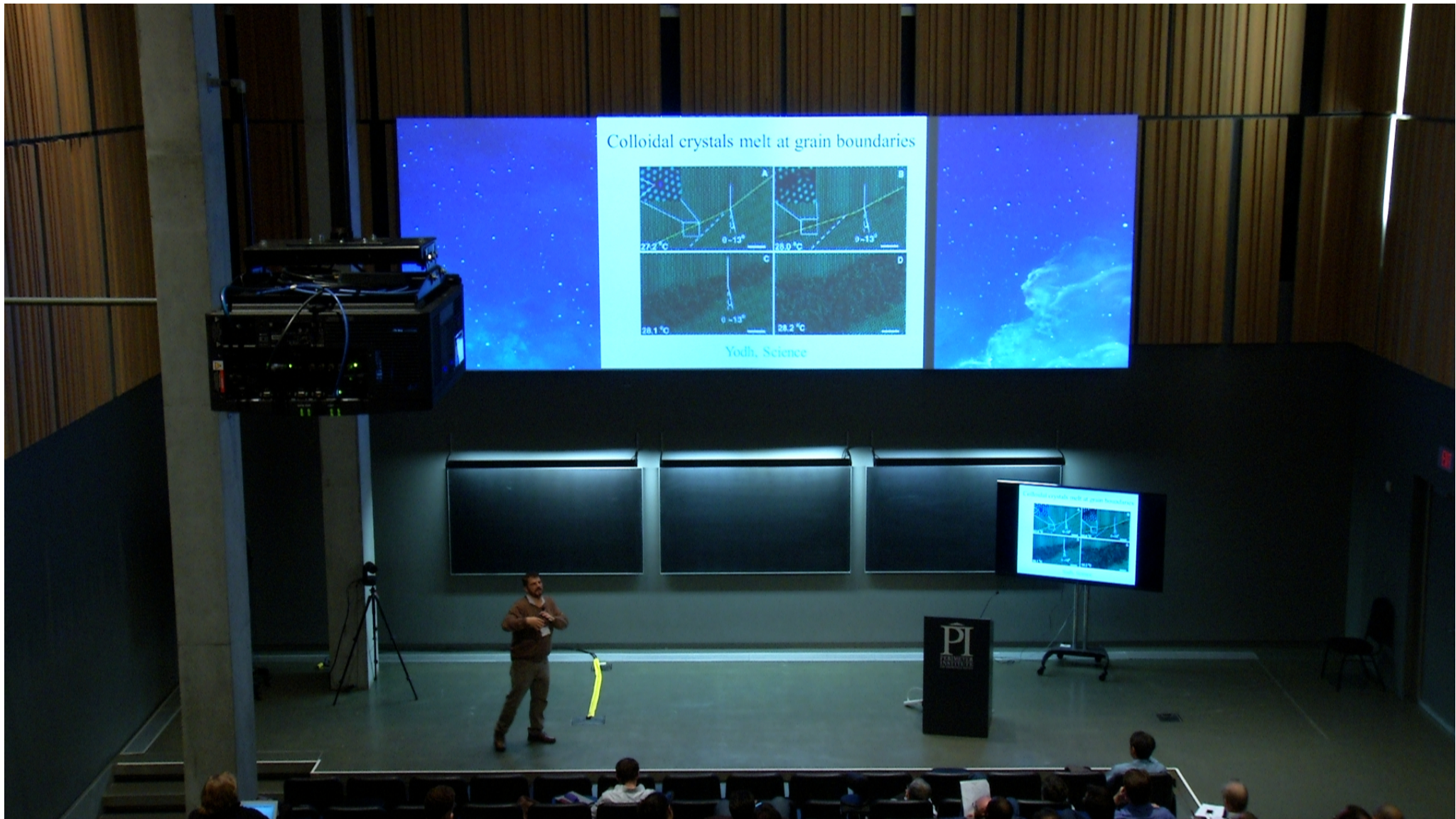




Classical free energy: measure γ and $\Delta\mu$





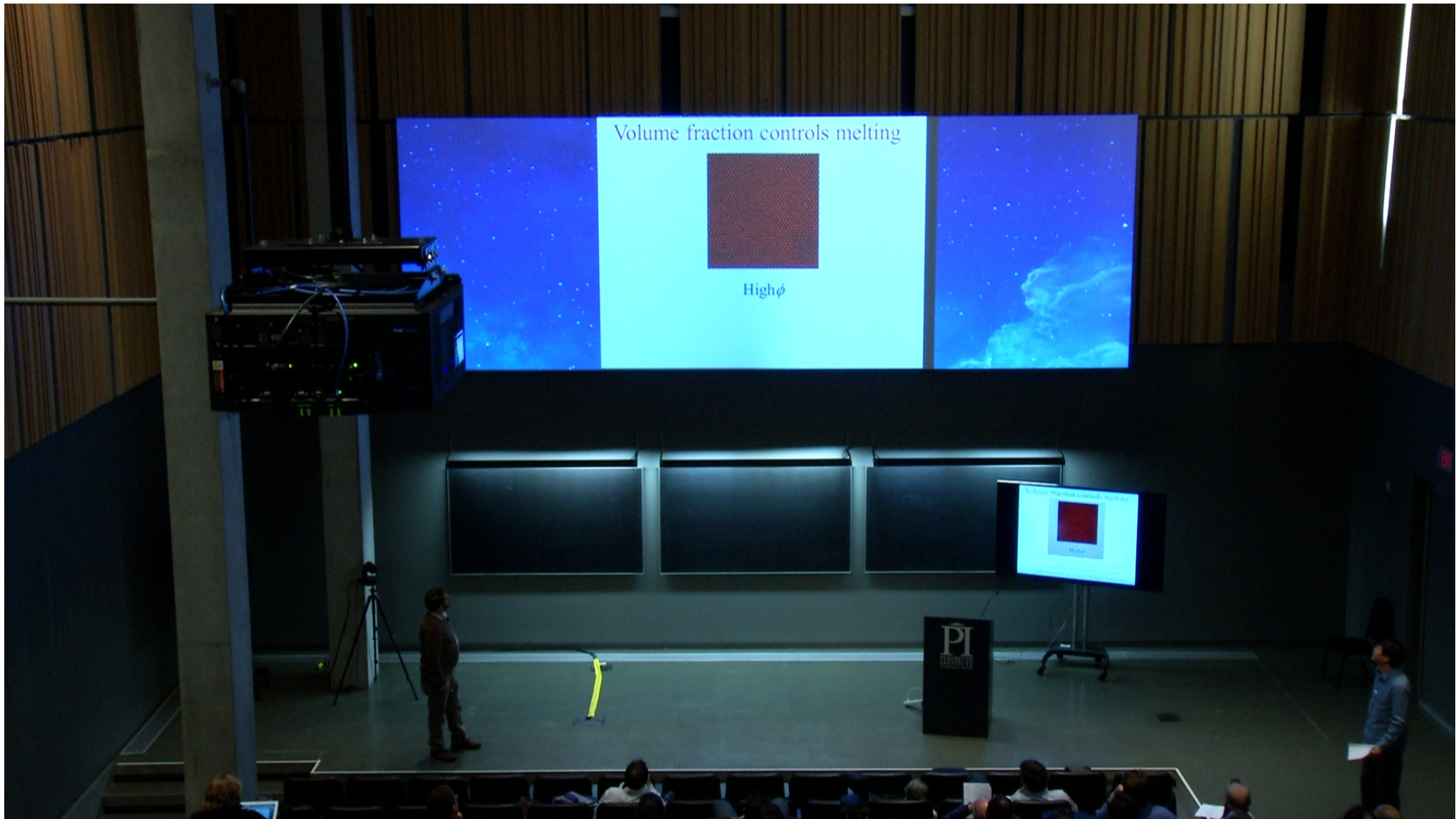


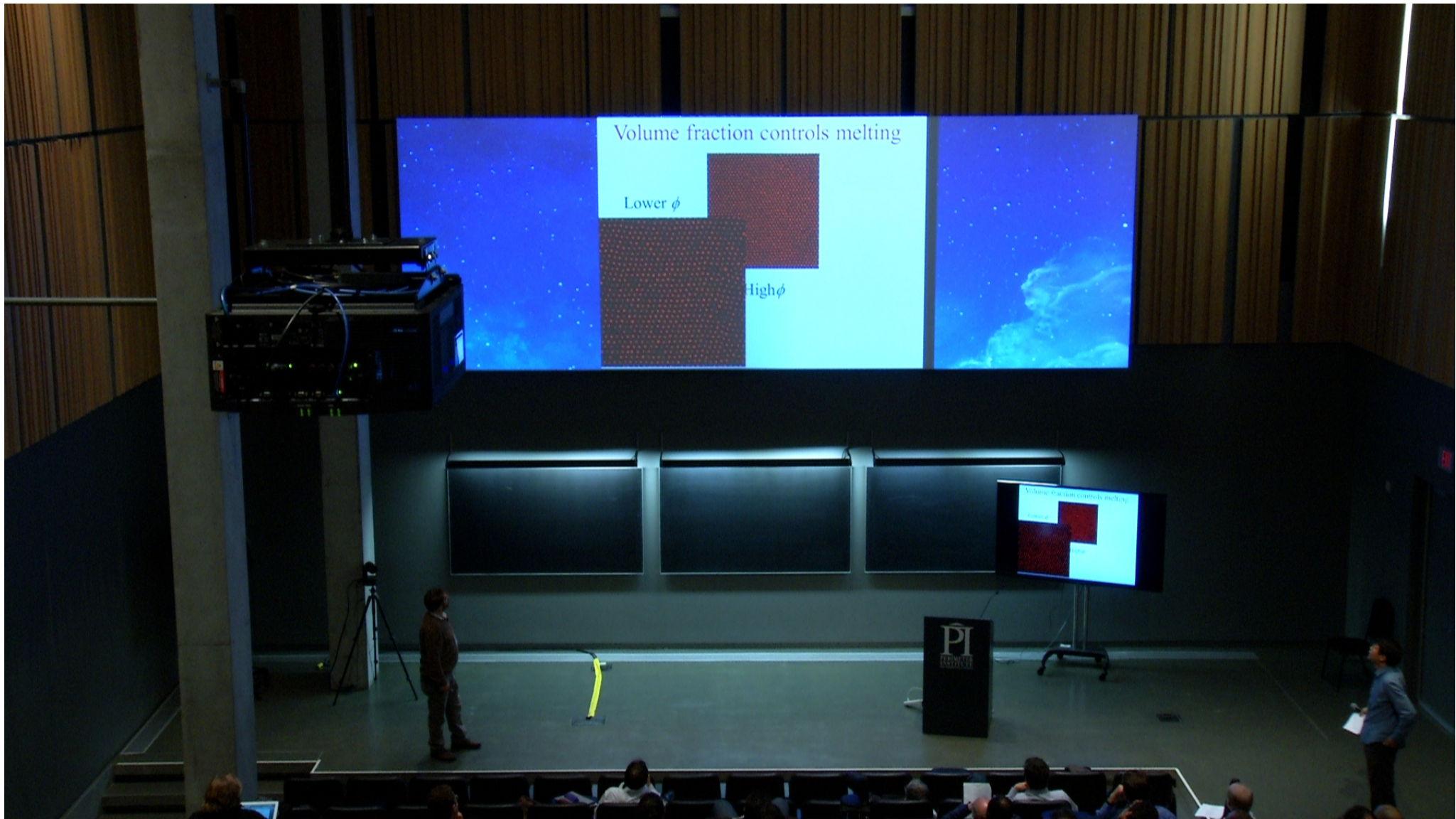
What if there are no interfaces?

Born melting:

- Elastic catastrophe
- Elastic modulus goes to zero, and crystal melts

But how does this actually occur??



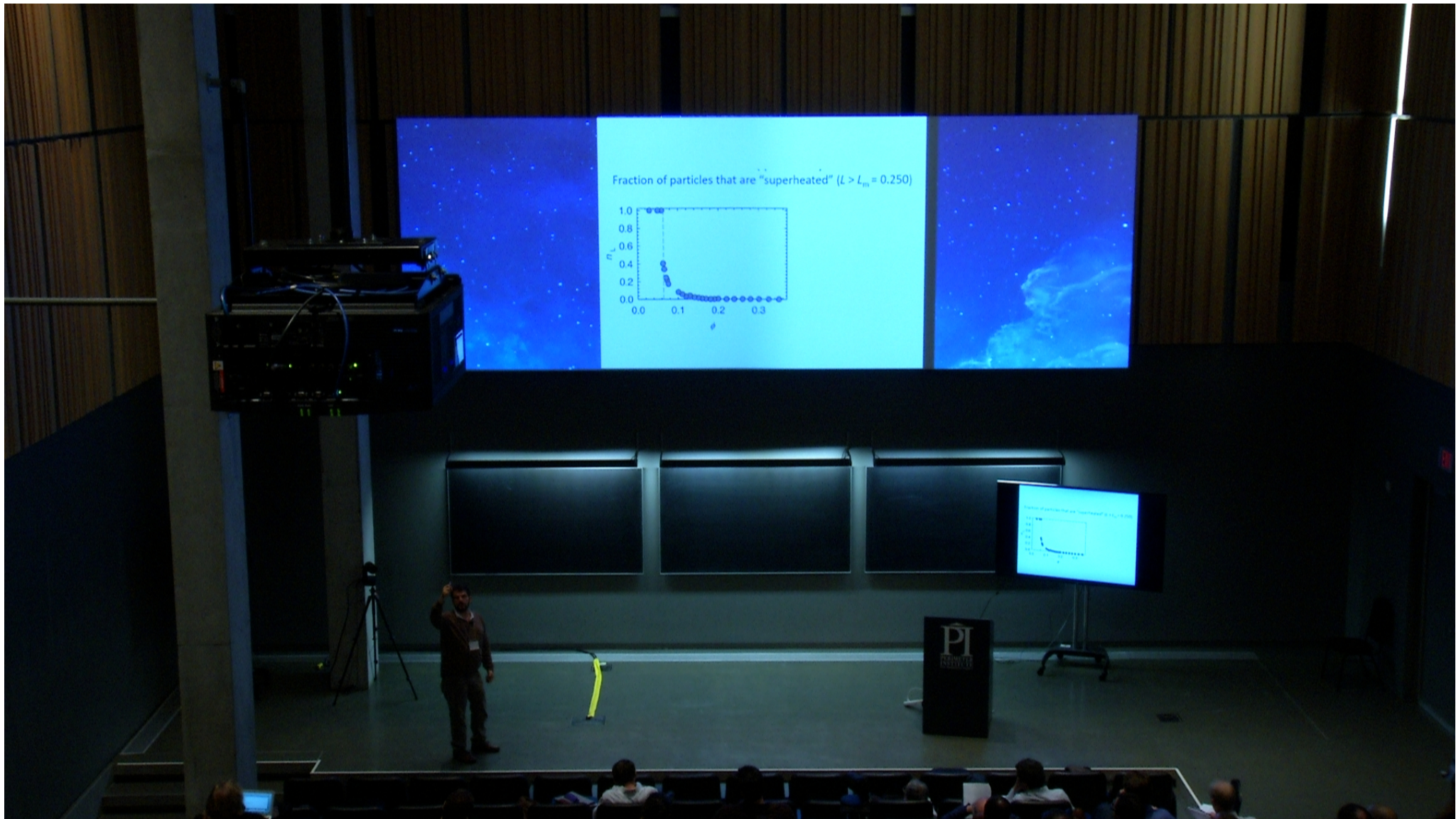


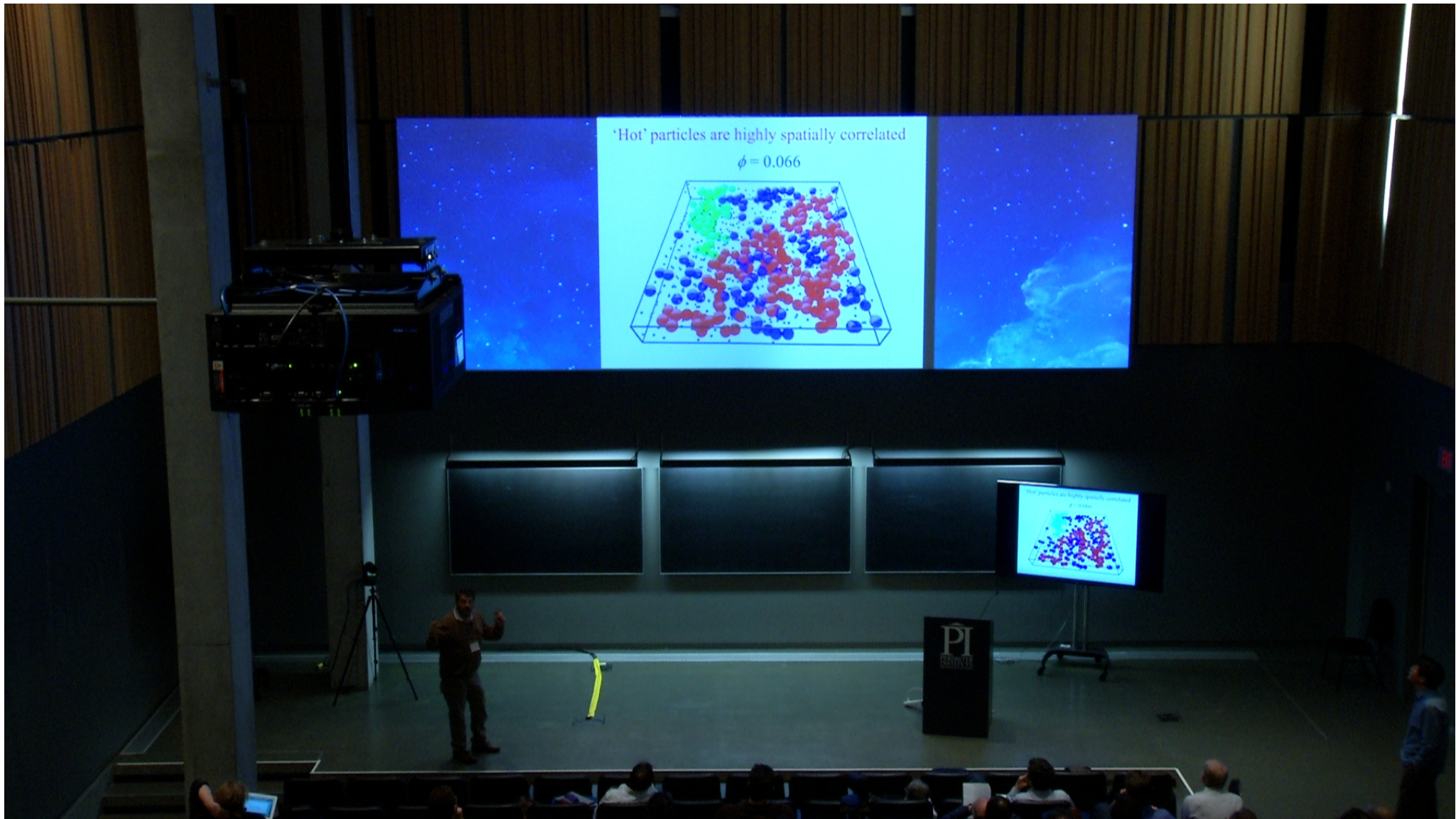
Volume fraction controls melting

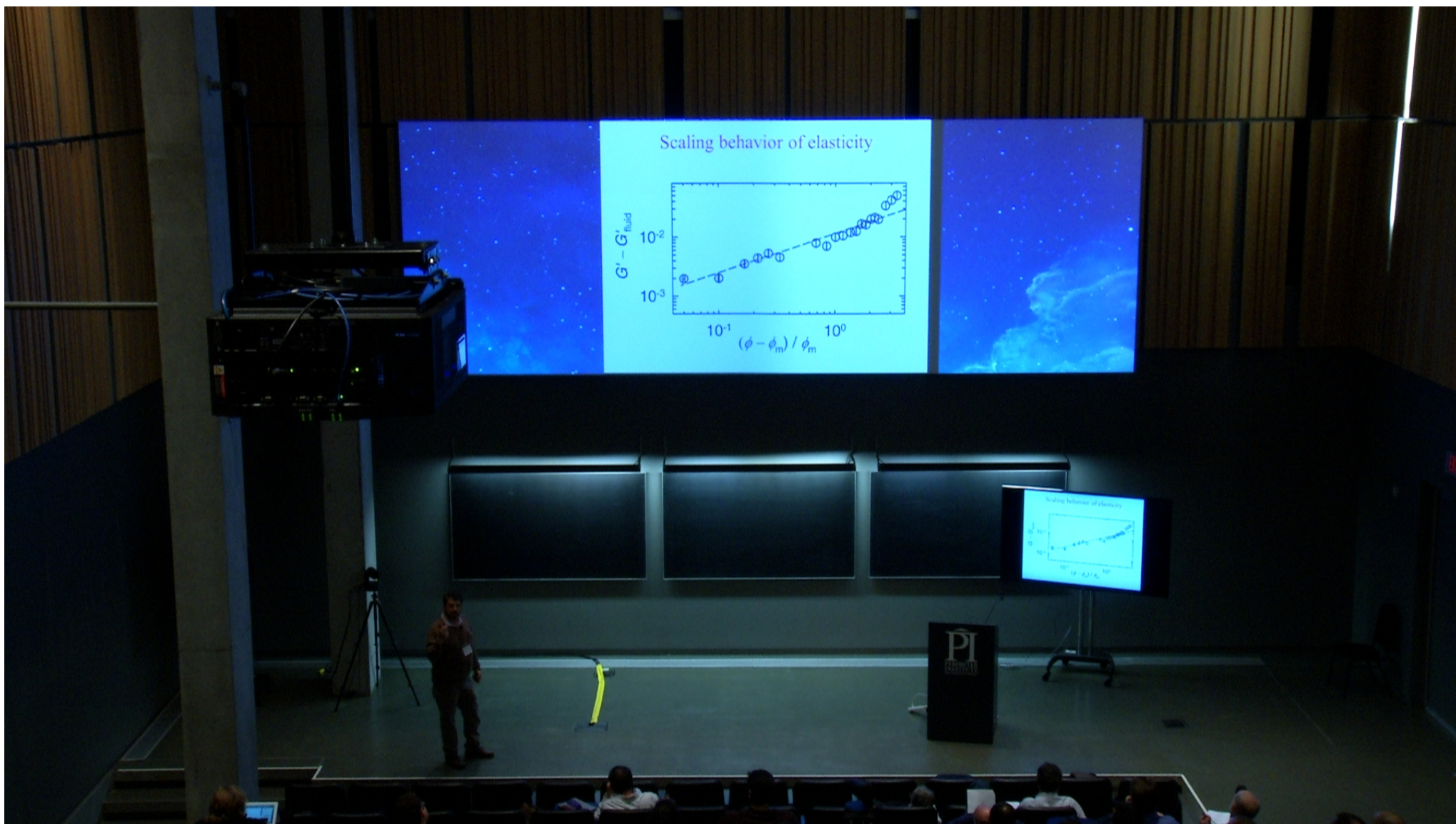
Lower ϕ

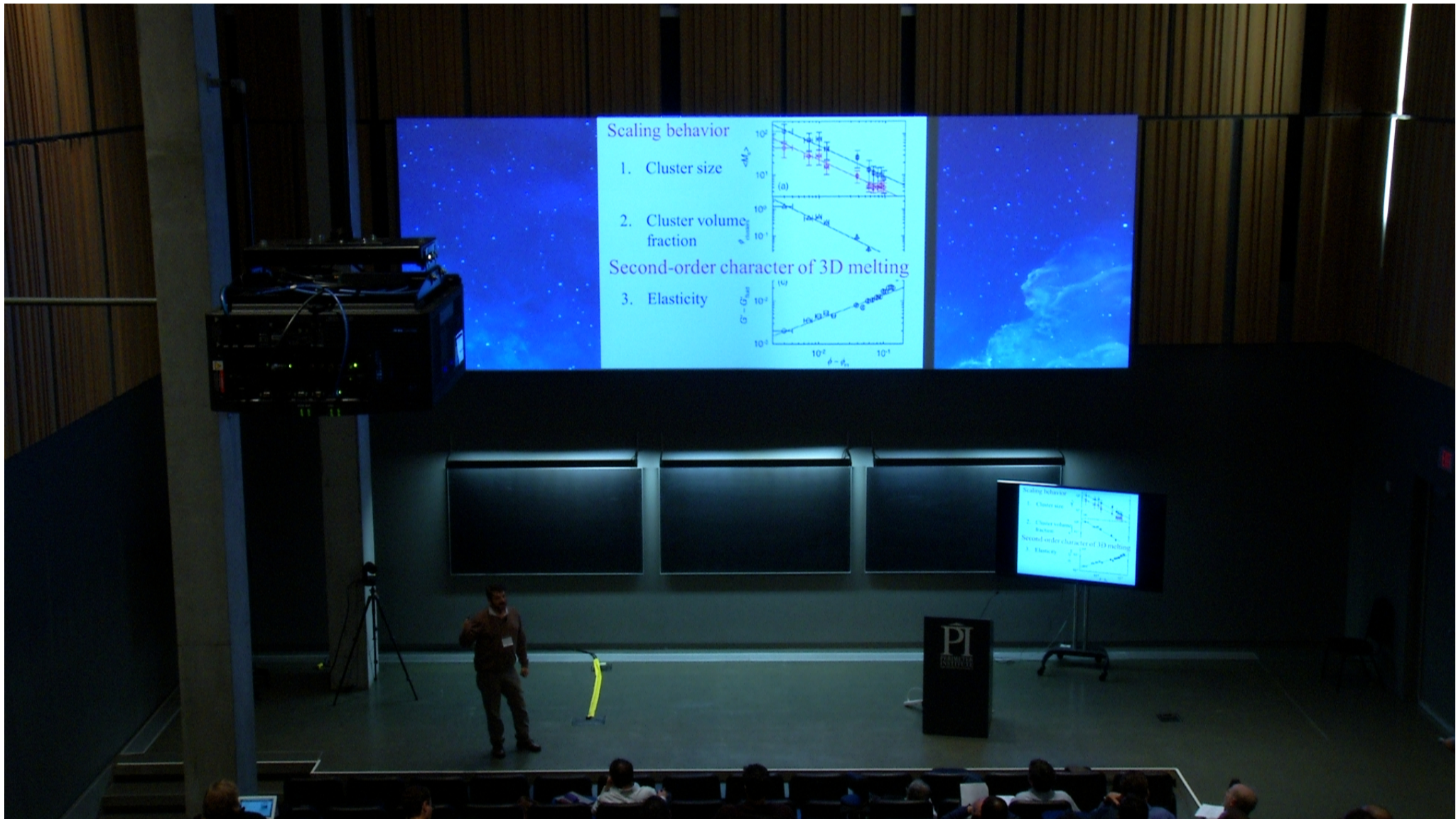
Lowest ϕ

High





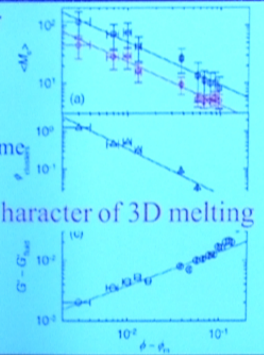




Scaling behavior

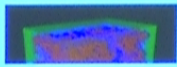
1. Cluster size
2. Cluster volume fraction
3. Elasticity

Second-order character of 3D melting









Conclusions

- Colloidal crystal nuclei are disordered
- Added entropic contribution to free energy
- Crystal melting has 2nd order character

Thank you for your attention



Fast crystal nucleation