Formation of the Critical Nucleus in Phase Separating Polymer Blends

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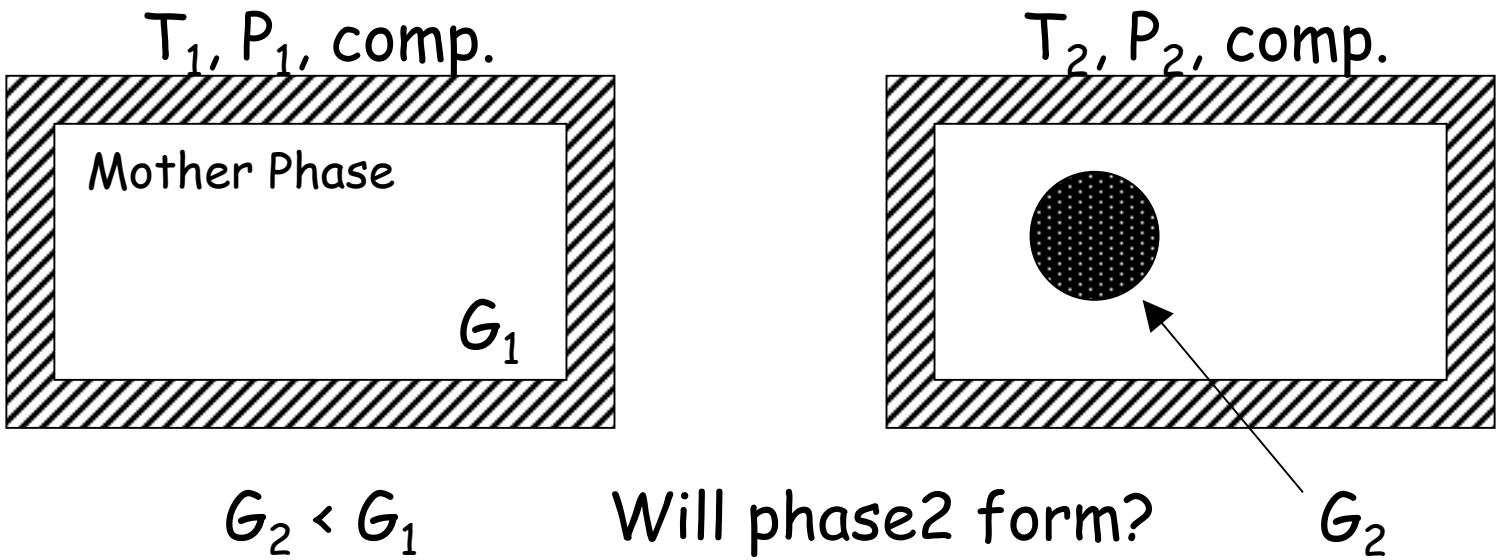
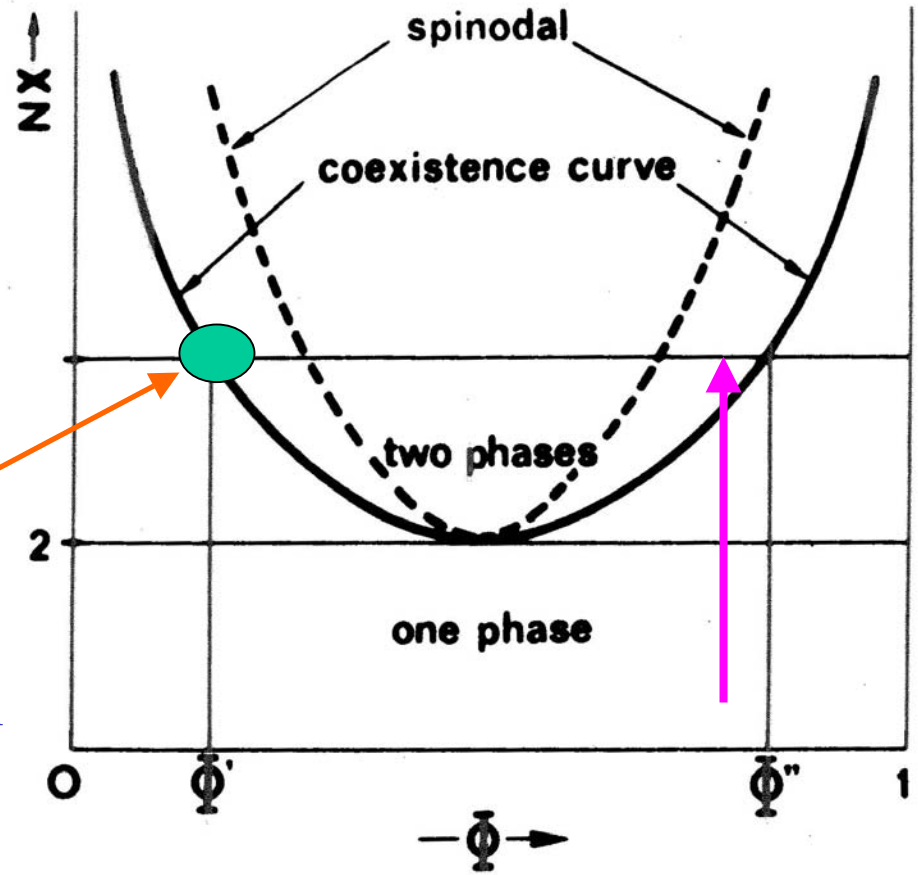
Nucleation



$G_2 < G_1$ Will phase2 form?

Answer: Depends (Gibbs), due to metastability of phase 1!
At any given time you can get either phase1 or phase2

Classical nucleation in polymer blends

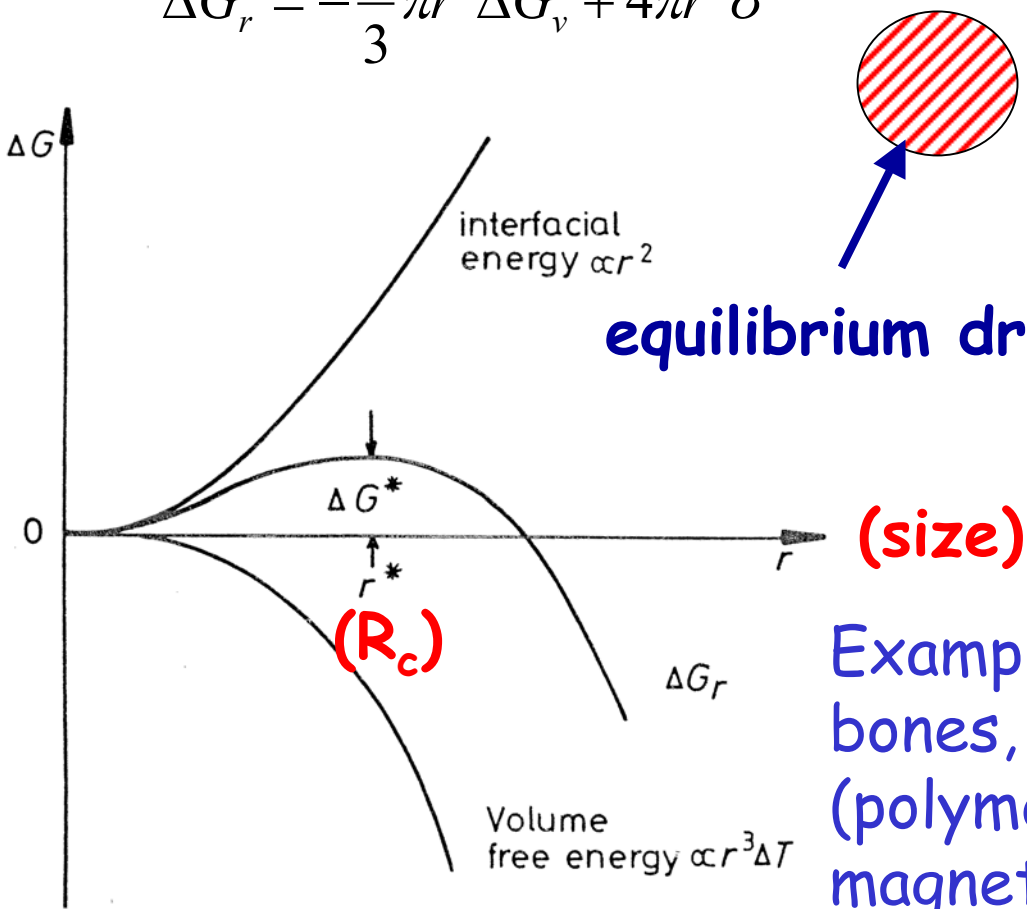


classical nucleus composition

1/T or P

Classical nucleation theory

$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \sigma$$



equilibrium droplet

(size)

Examples: clouds, rain, snow, bones, crystallization (polymorphs), boiling, melting, magnetization…

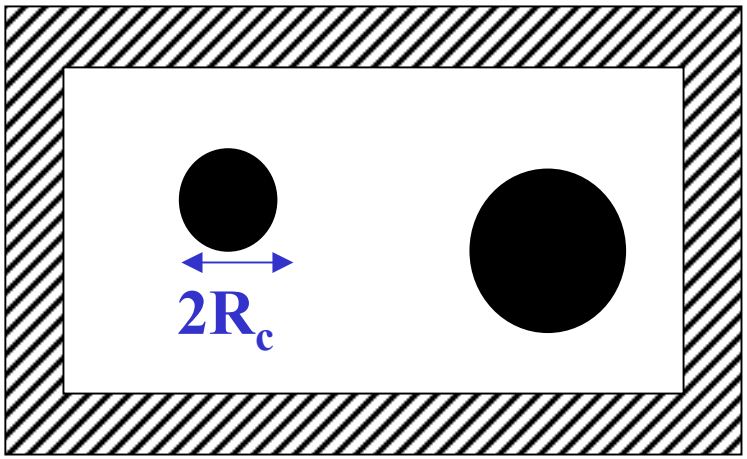
Questions about nucleation

1. How to look for the critical nucleus (prove that something is not there)?

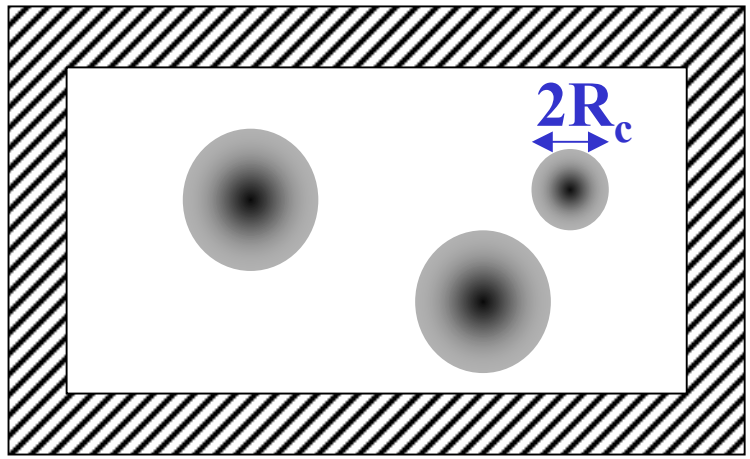
2. Why should the nucleus composition be that of the bulk at equilibrium (Ostwald's rule of stages)?

3. Why should the interface be sharp?

Liquid-liquid phase separation



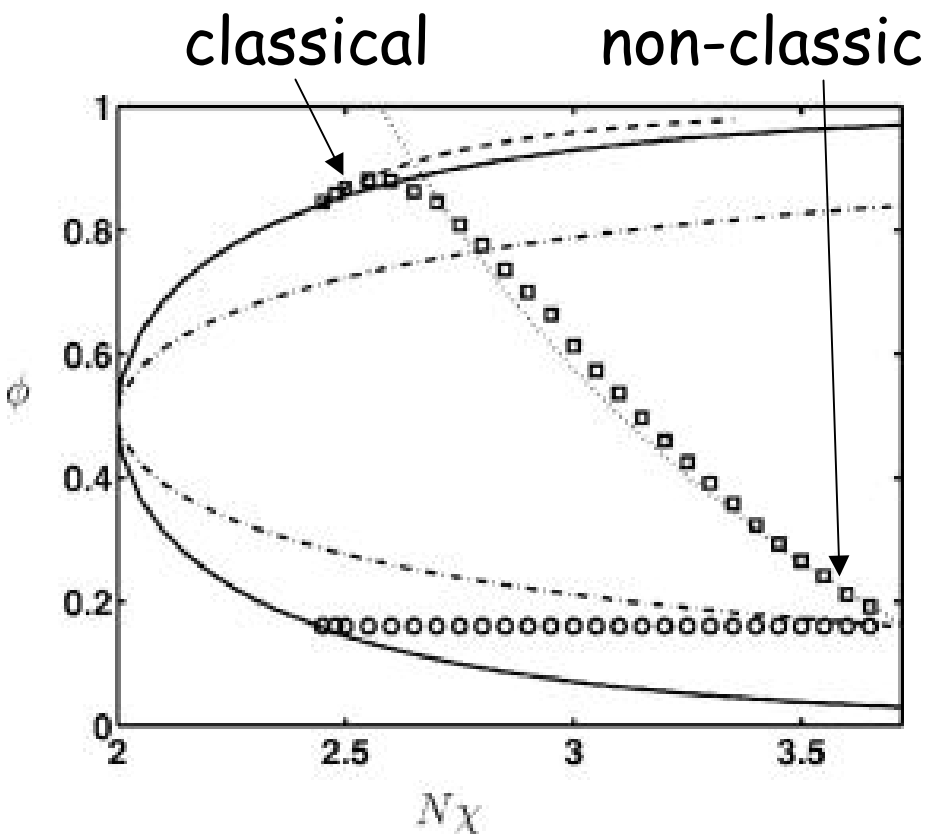
Gibbs

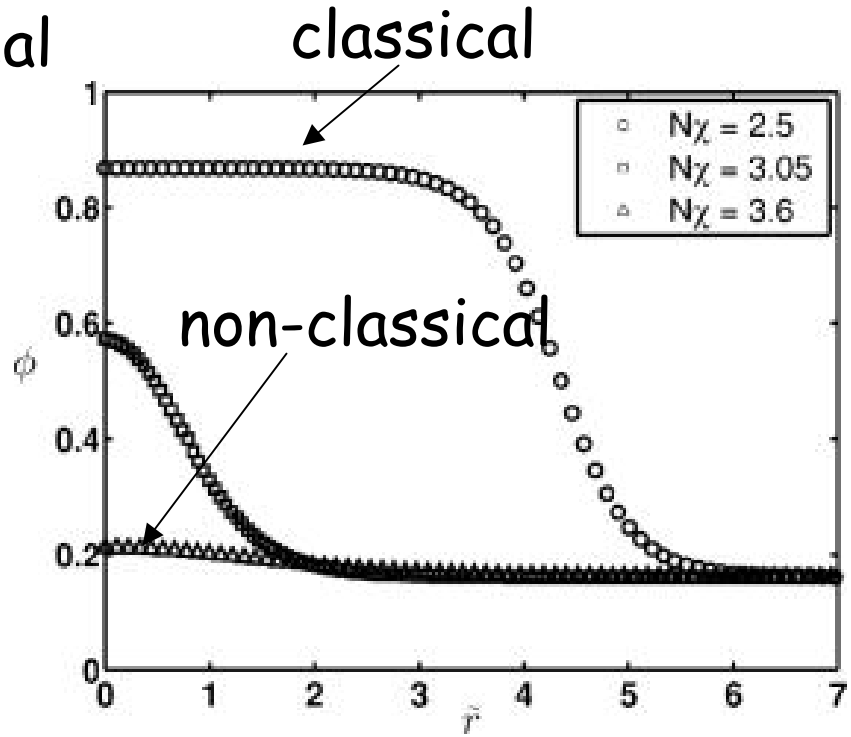


Cahn and Hilliard

Nuclei that have diffuse interfaces and composition that are not that of the bulk equilibrium phase can be computed exactly! (Cahn and Hilliard, J. Chem. Phys., 1955-prelude to spinodal decomposition)

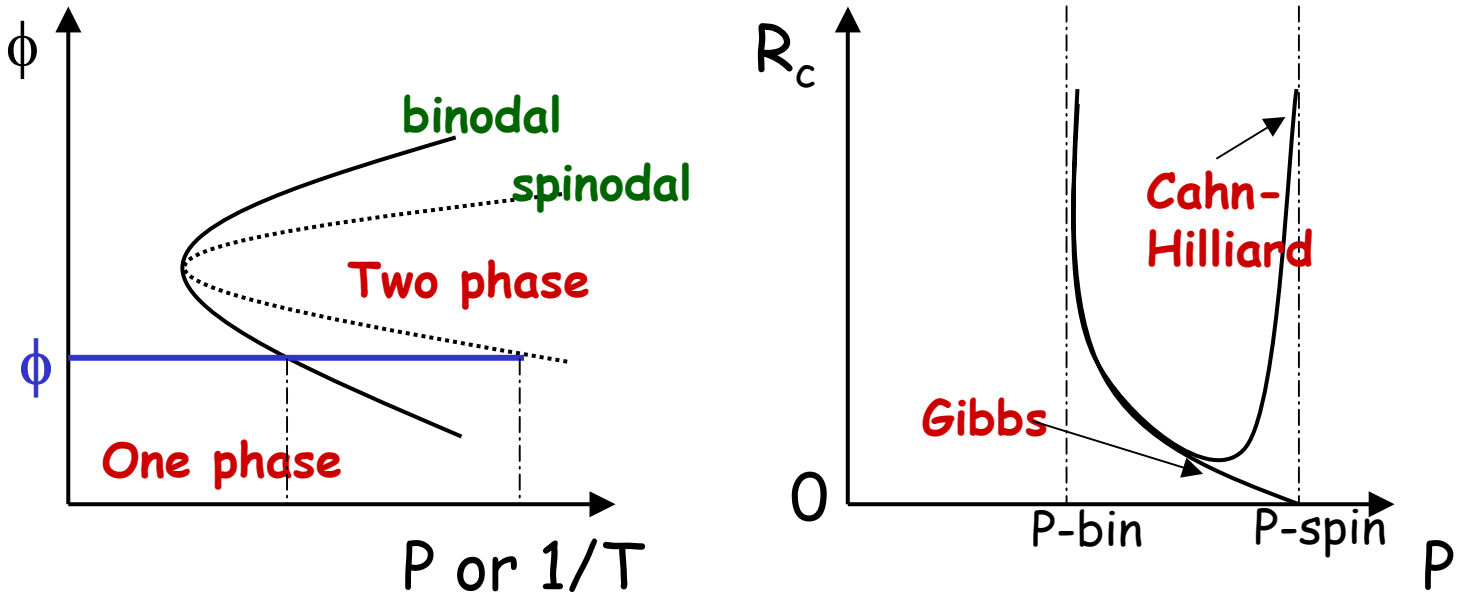
Theoretical Predictions





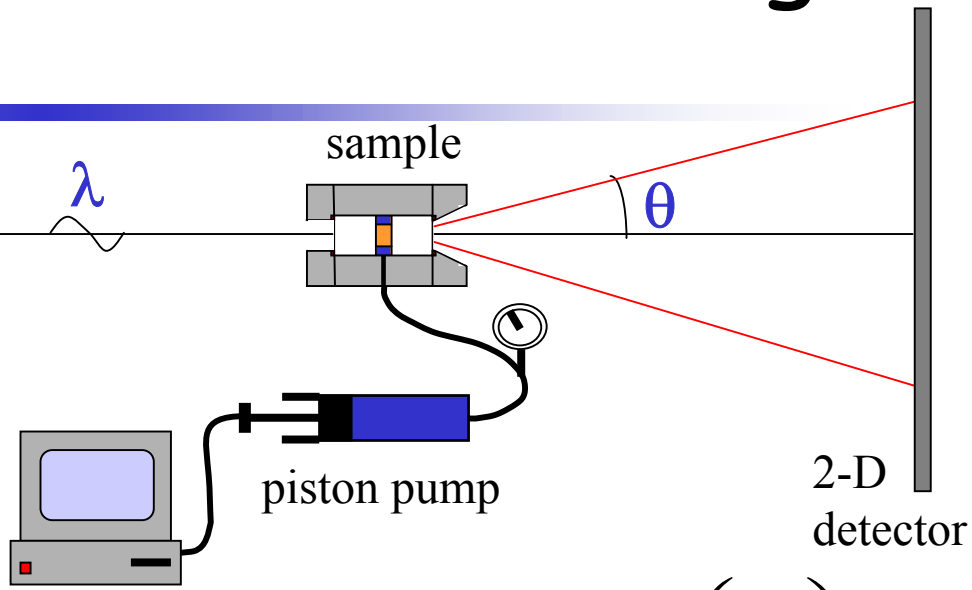
Self-consistent field calculations for polymer blends
Wood and Wang, J. Chem. Phys., 2002 (Cahn and Hilliard, 1950)

Predictions



Two classical theories give opposite results. No experimental data on initial stages of nucleation.

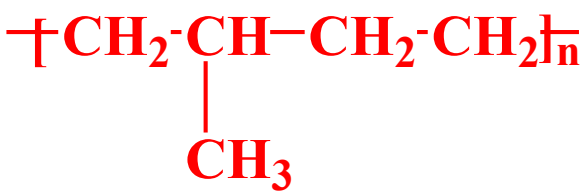
Small-angle neutron scattering



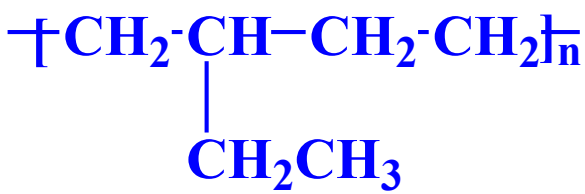
$$q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

If emerging structure is of size L~1/q, then scattering will increase at the corresponding q.

Materials



PM



PE

sample desig.	mol. wt. (kg/mol)	N	Rg (nm)
dPM	170	3360	16
hPE	220	4260	16

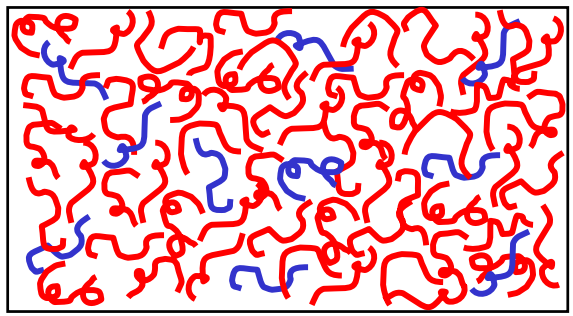
High vacuum anionic polymerization and high pressure catalysis polydispersity=1.03

Blends:

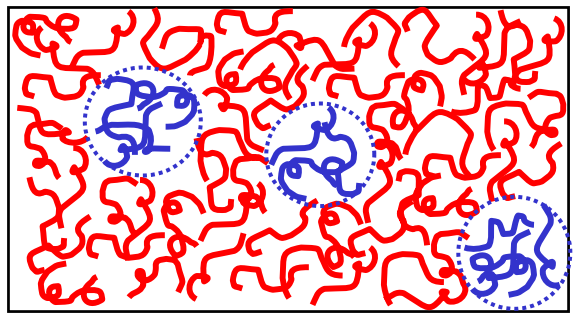
blend desig.	vol fr. of dPM
B2	0.16
B3	0.10

Polymers are amorphous liquids in the T,P range of interest.

Experiments on liquid mixtures



Metastable mixture
(one-phase)



Stable mixture
(two-phase)

Nucleation of A droplets

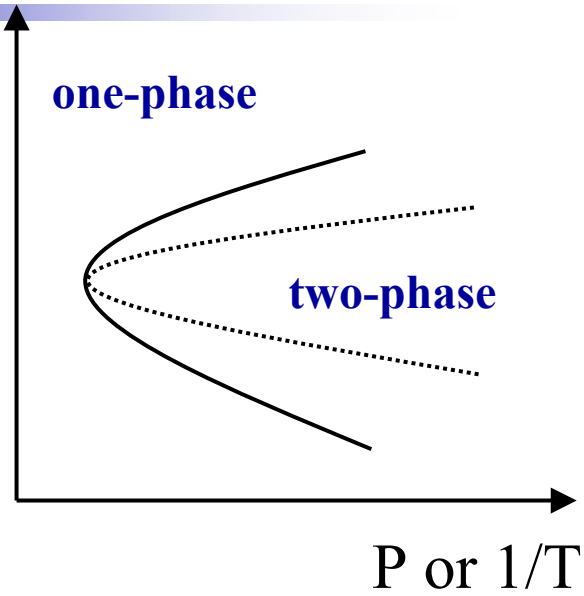
Krishamurthy and Goldburg (JCP 1982) write "Our observations of the very initial stages of nucleation were severely limited by our microscope technique, finite quench rates,... In our view, the same failing characterizes all previous experiments.

(Related experiments on crystallizing colloids by Weitz and Vekilov)

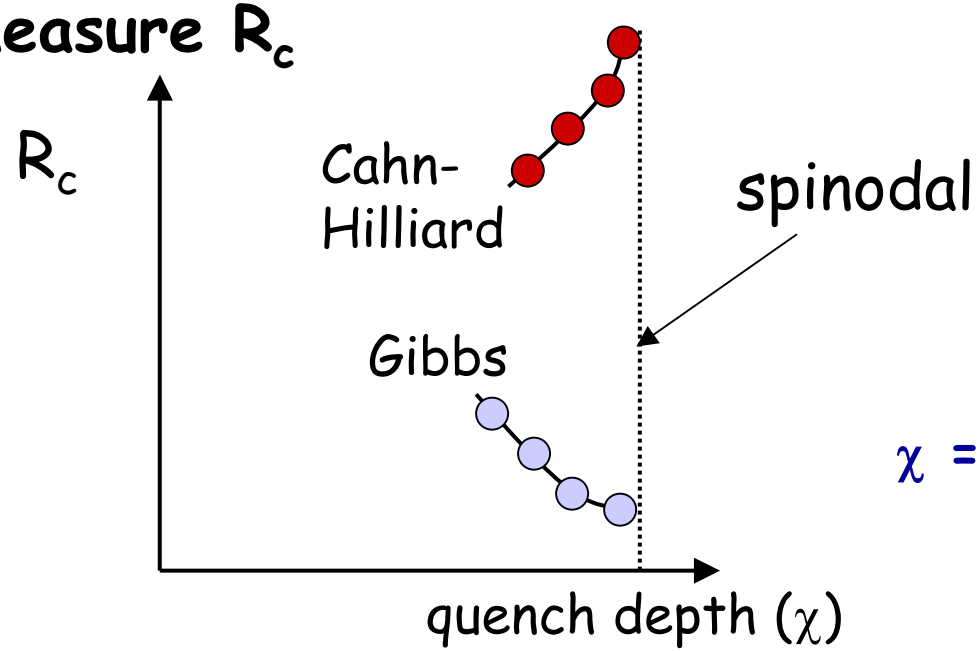
Outline of Work

1. Establish Equilibrium Thermodynamics

Lefebvre et al., Macromolecules, 2002
Lefebvre et al., Macromolecules, 2000

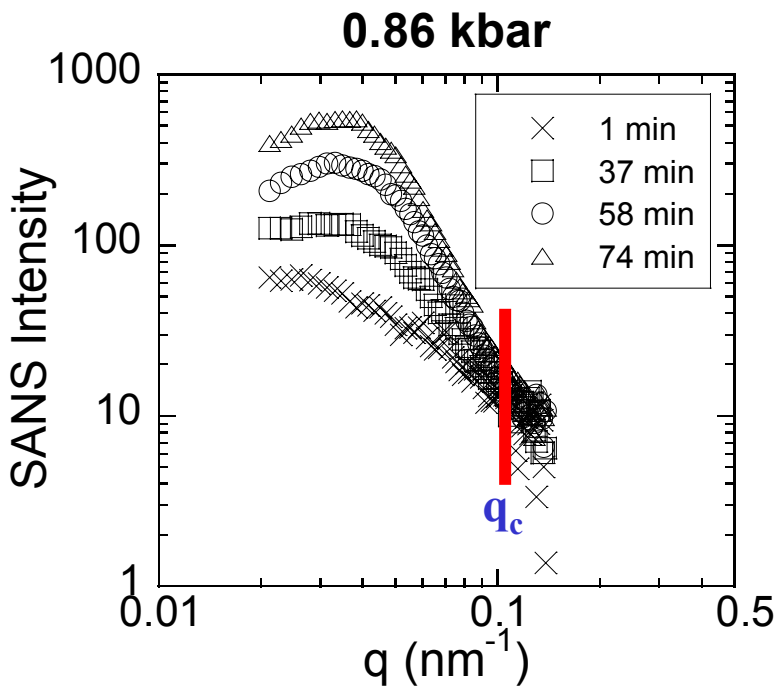


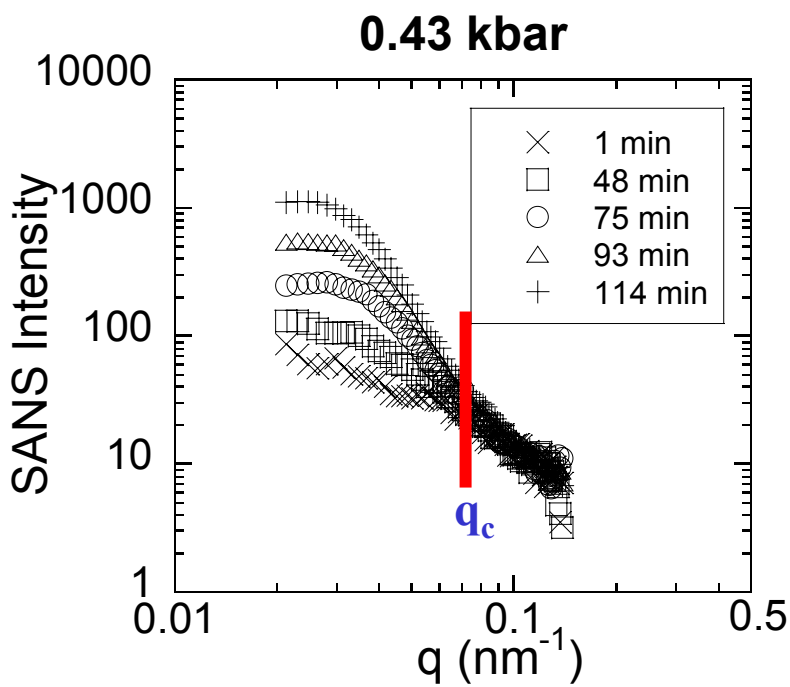
2. **Measure R_c**



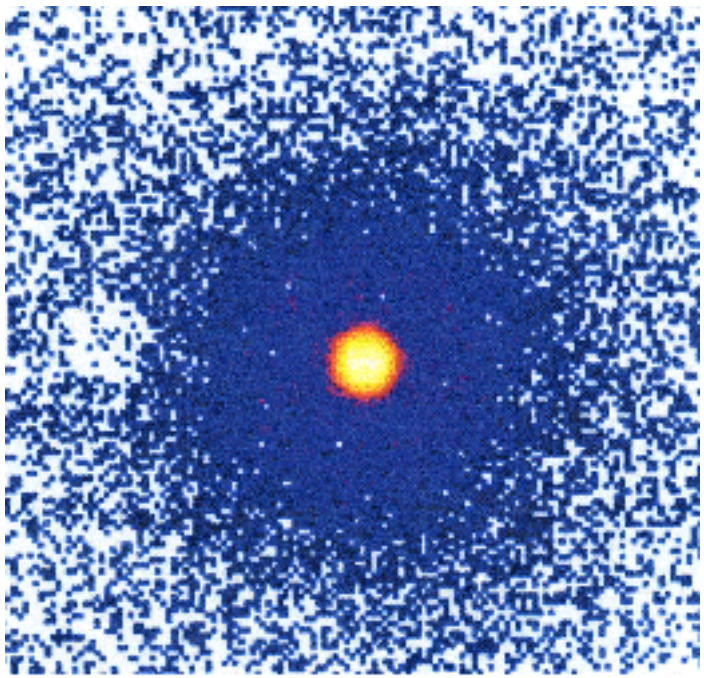
χ = Flory-Huggins interaction parameter

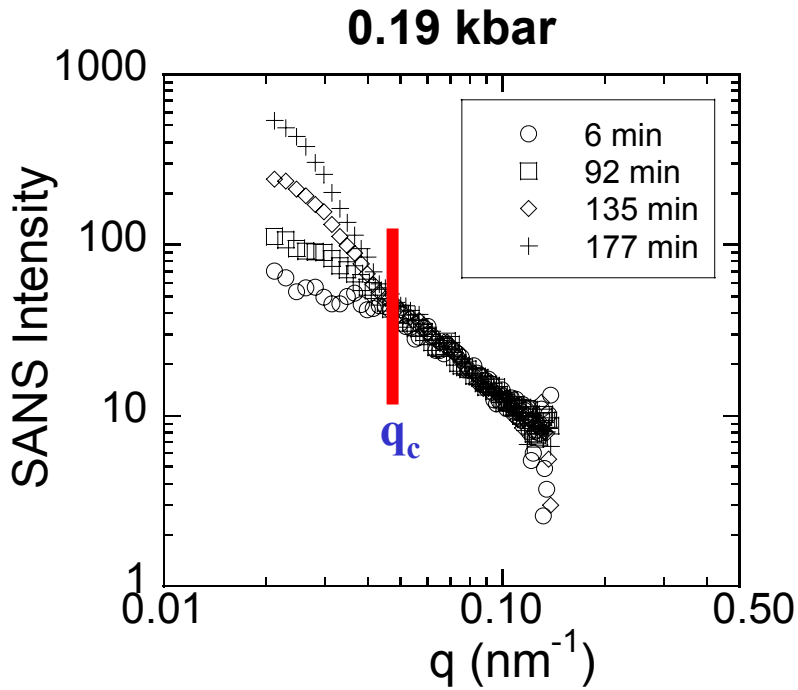
SANS profiles merge





Critical Nucleus Size

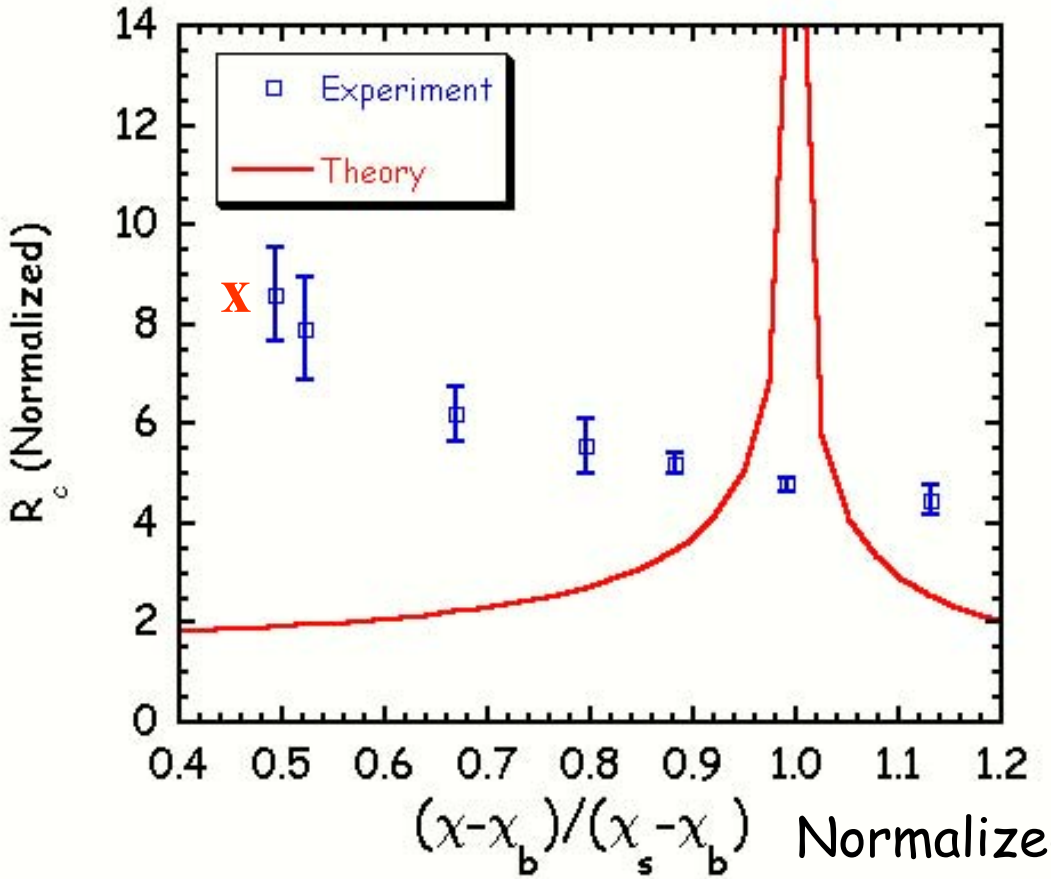




If none of the emerging structures are of size L then there will be no scattering increase at the corresponding q~1/L.

None of the growing structures are smaller than $R_c \sim 1/q_c$

Scaling of R_c with Quench Depth



No nucleation in 7-24 h for Q<0.48

$R_c = 2\pi/q_c$

Normalized quench depth, Q
Q=0 at binodal; Q=1 at spinodal

This result led to a lot of problems

Kurt Binder (a coauthor) withdraws his name from author list.

Example of positive review:

This paper presents very interesting new results that are purported to be relevant to homogeneous nucleation in polymers. The presented results are in fact a bit TOO INTERESTING. Indeed, ever since Prof. Balsara presented these results at last year's Polymer Physics Gordon Conference, the entire community has been puzzling over what artifacts could be responsible for their observations. To say that the results are controversial is a gross understatement, as even if the Cahn-Hilliard Theory is completely wrong, there is no reason to expect the critical nucleus size to increase as the system is moved AWAY from the spinodal!

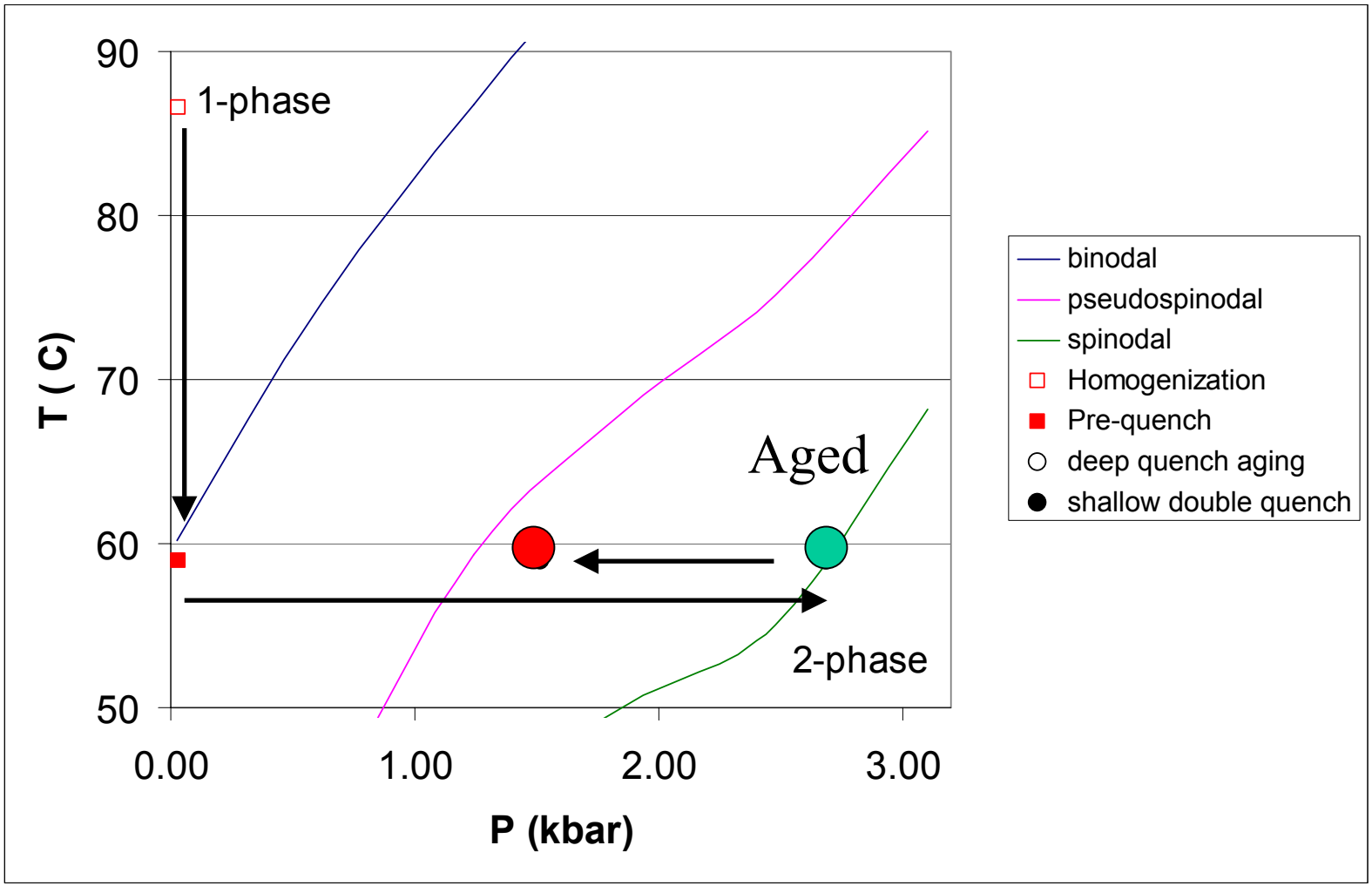
al Length and

ends.

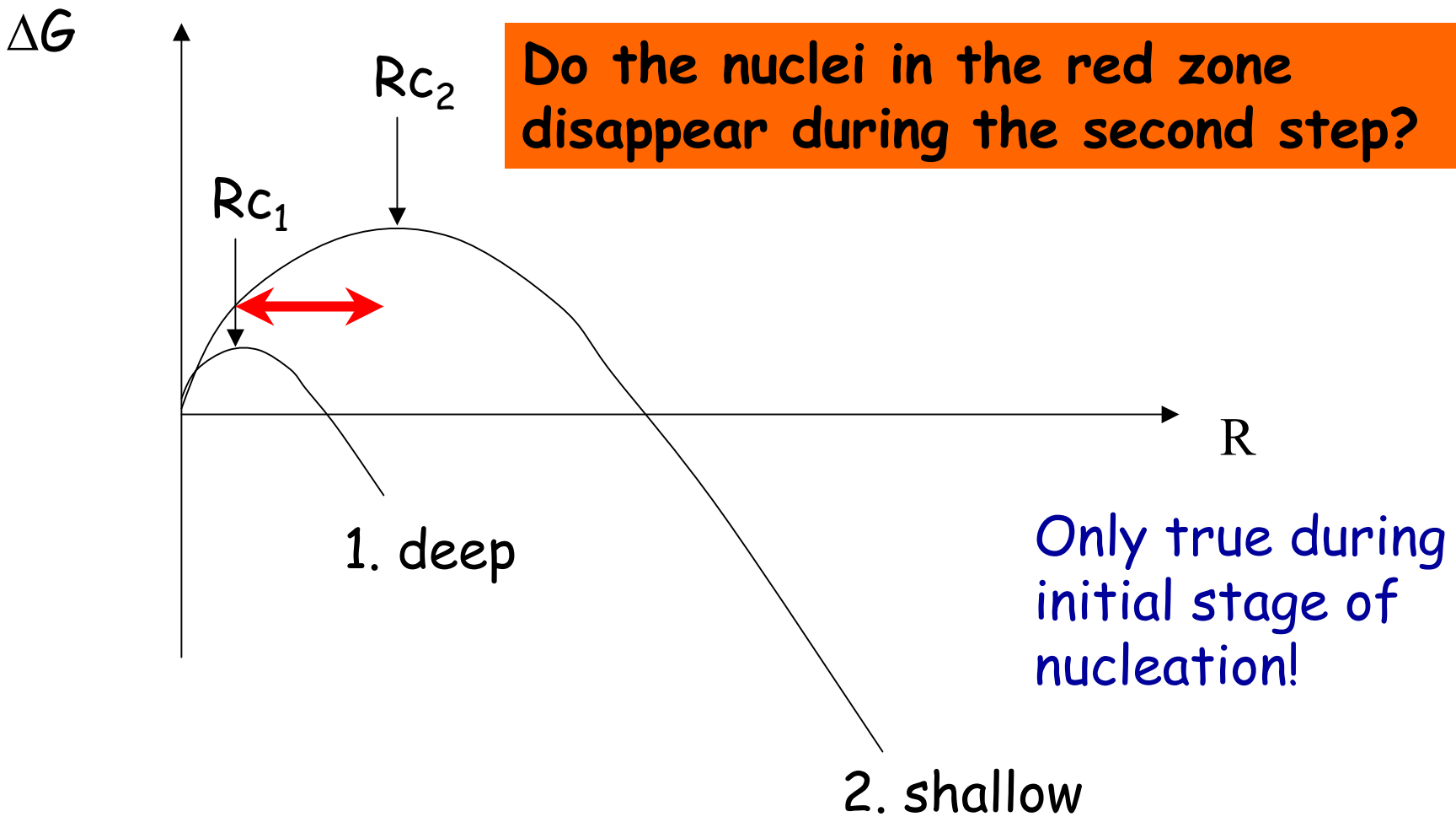
I still believe they are studying artifacts, but they now at least do a better job of describing what they did. I agree with the authors that, since they have not identified the artifacts in the past 2 years, it is time to publish the data and let the rest of the world figure out the meaning. I therefore recommend publishing the revised manuscript.

Published in J. Chem. Phys. (2002), 2 years after initial submission and 4 years after data were first presented at a seminar.

Aging Experiments



Aging Experiments



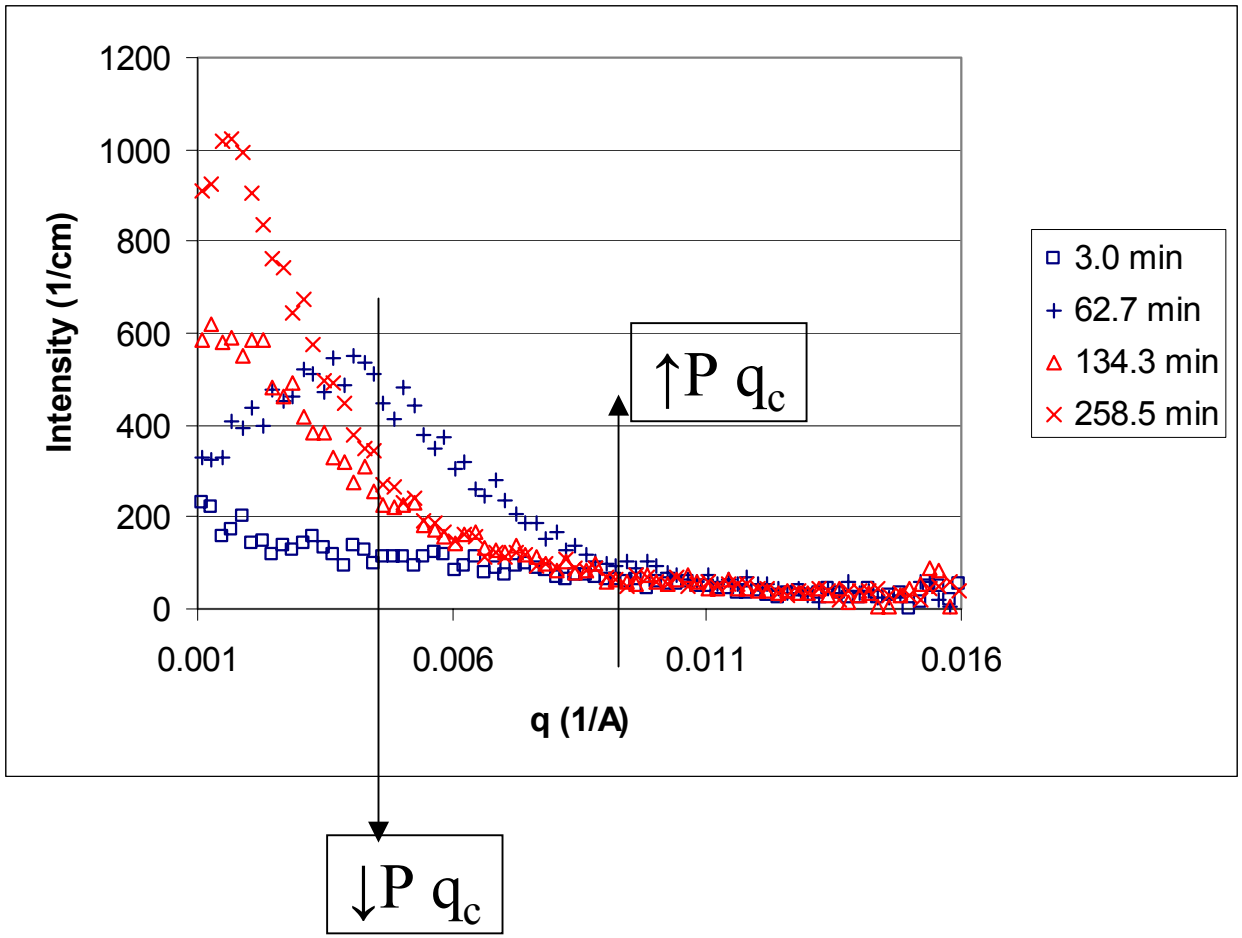
Do the nuclei in the red zone disappear during the second step?

Only true during initial stage of nucleation!

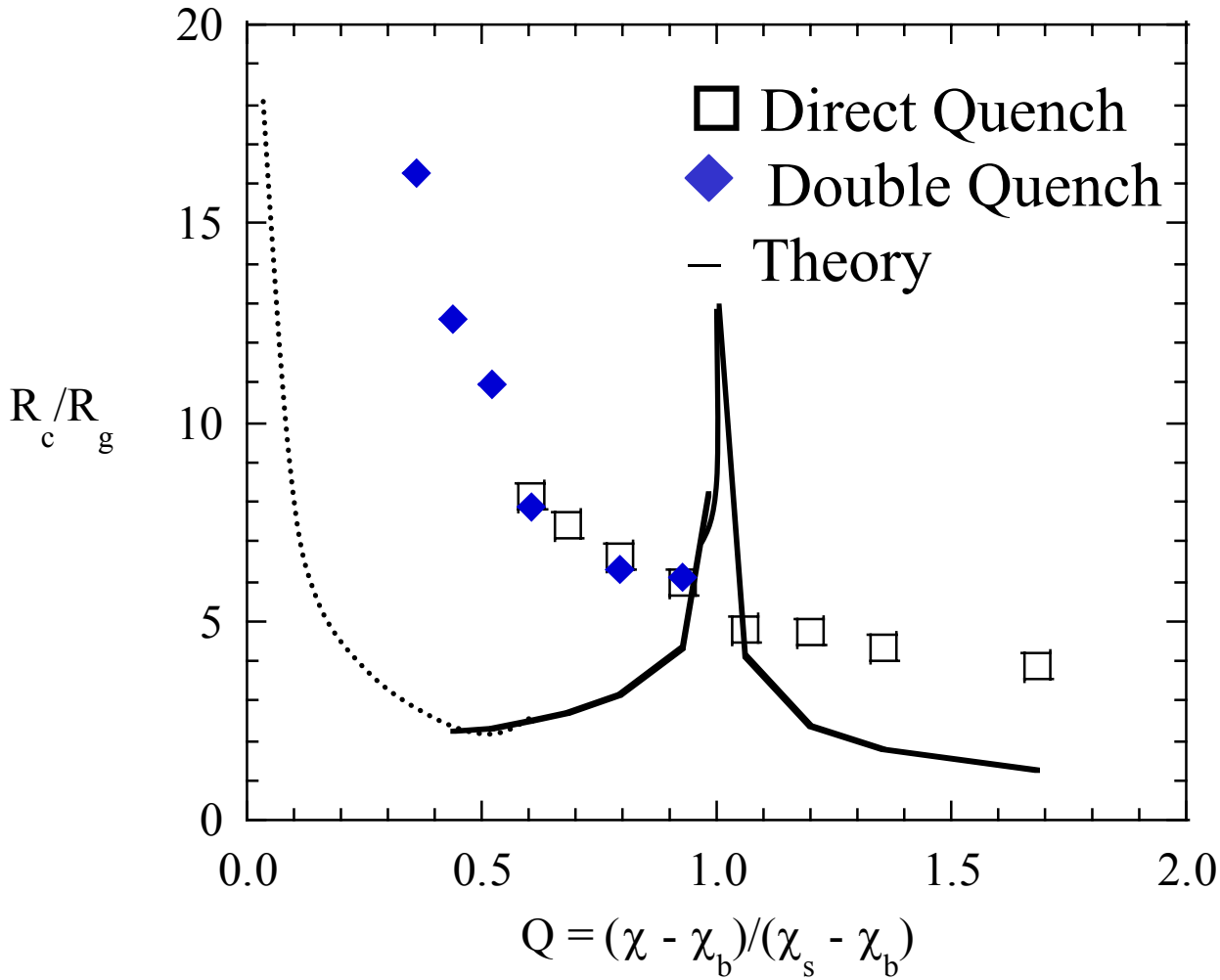
(1) 2.69 kbar aging: 69 min
(2) 1.52 kbar

1) Some nuclei dissolve after second quench.

2) $\downarrow P\ q_c$ agrees with direct nucleation data



Rc from direct and indirect quenches



David Chandler's Initial Reaction

In fall 2001, Albert Pan (DC's student) gave a graduate student seminar on "Nucleation of Ising magnets"

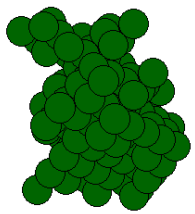
NPB: "Have you computed the structure factor during nucleation?"

Albert: "No".

DC: "Why would you care about the structure factor during nucleation!"....

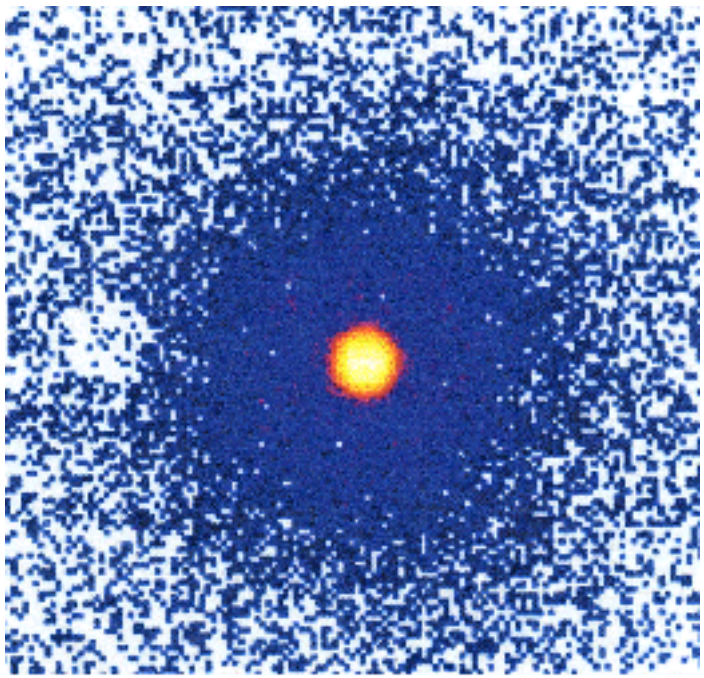
In fall 2003, I gave a seminar to DC's group.

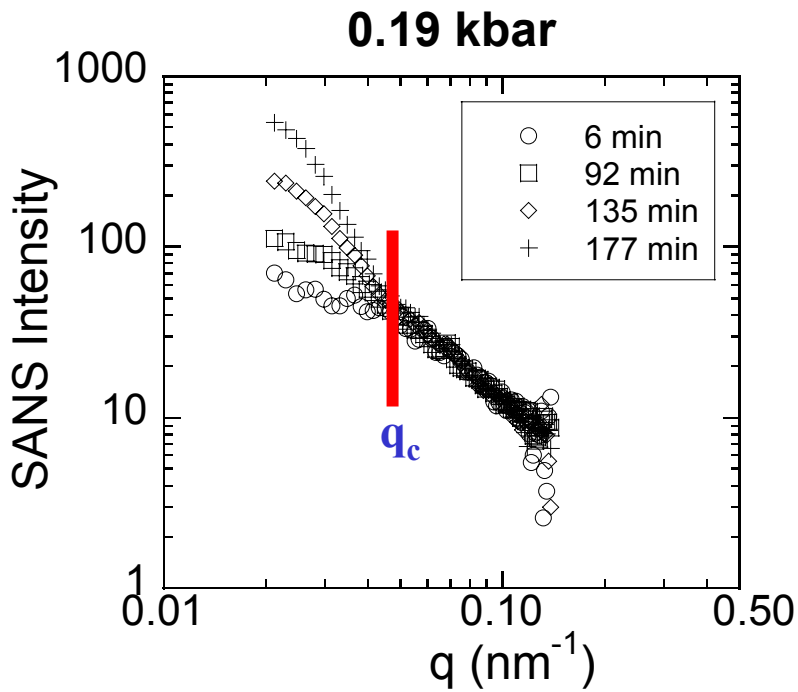
Albert Pan, David Chandler



Ising Model
T = 0.6Tc, h = 0.55, J = -1.
The critical nucleus is of size, N = 115 (giving kc = 2) formed at t = 75.

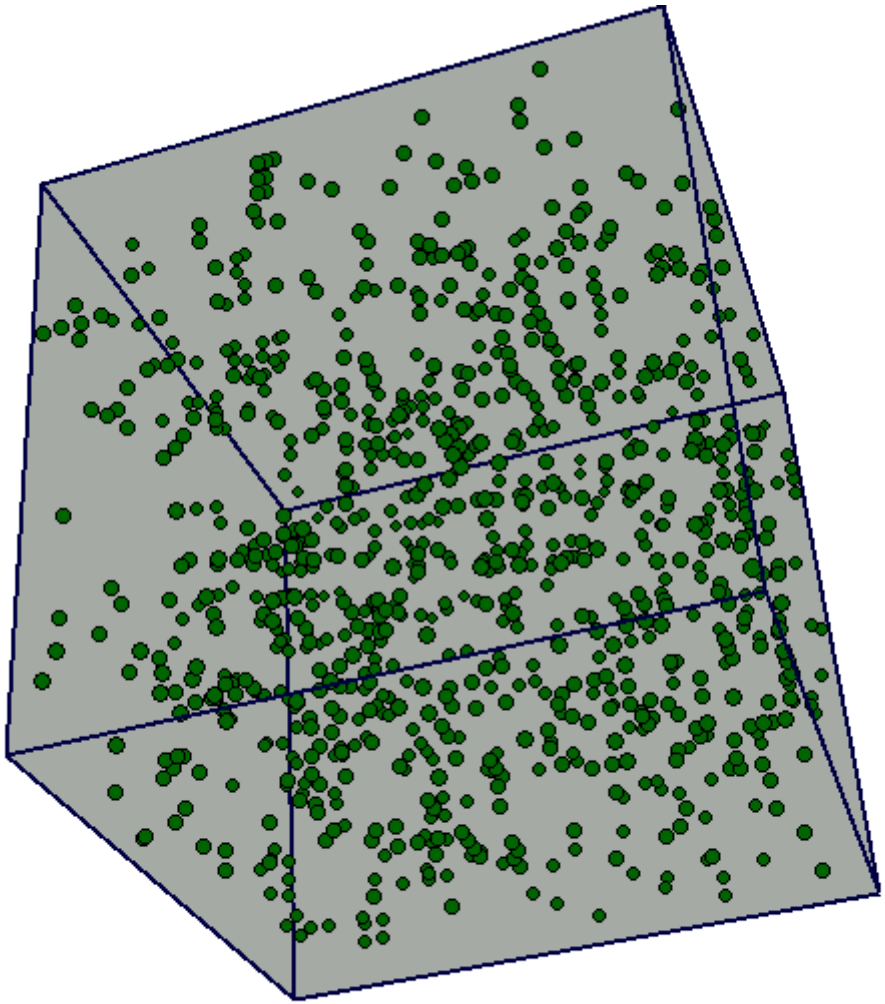
Critical Nucleus Signature





Our proposal might actually be universal!

Simulation



Pan, Chandler

Concluding Remarks

(1) Our proposal (J. Chem. Phys. 1999) that $R_c \sim 1/q_c$ looks promising.

(2) Critical nucleus size decreases monotonically with increasing quench depth near the spinodal.

(Bottom Line) Homogeneous nucleation occurs by a **collective** process via a coalescence of pre-existing concentration fluctuations. Only models such as the Ising model where concentration fluctuations are included explicitly seem appropriate. Predictions based on models that assume the presence of isolated nucleus in a structure-less matrix may not be relevant.