Small Angle Neutron Scattering Studies of the Initial Stages of Phase Separation

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NSF (indirect 1995-2003)
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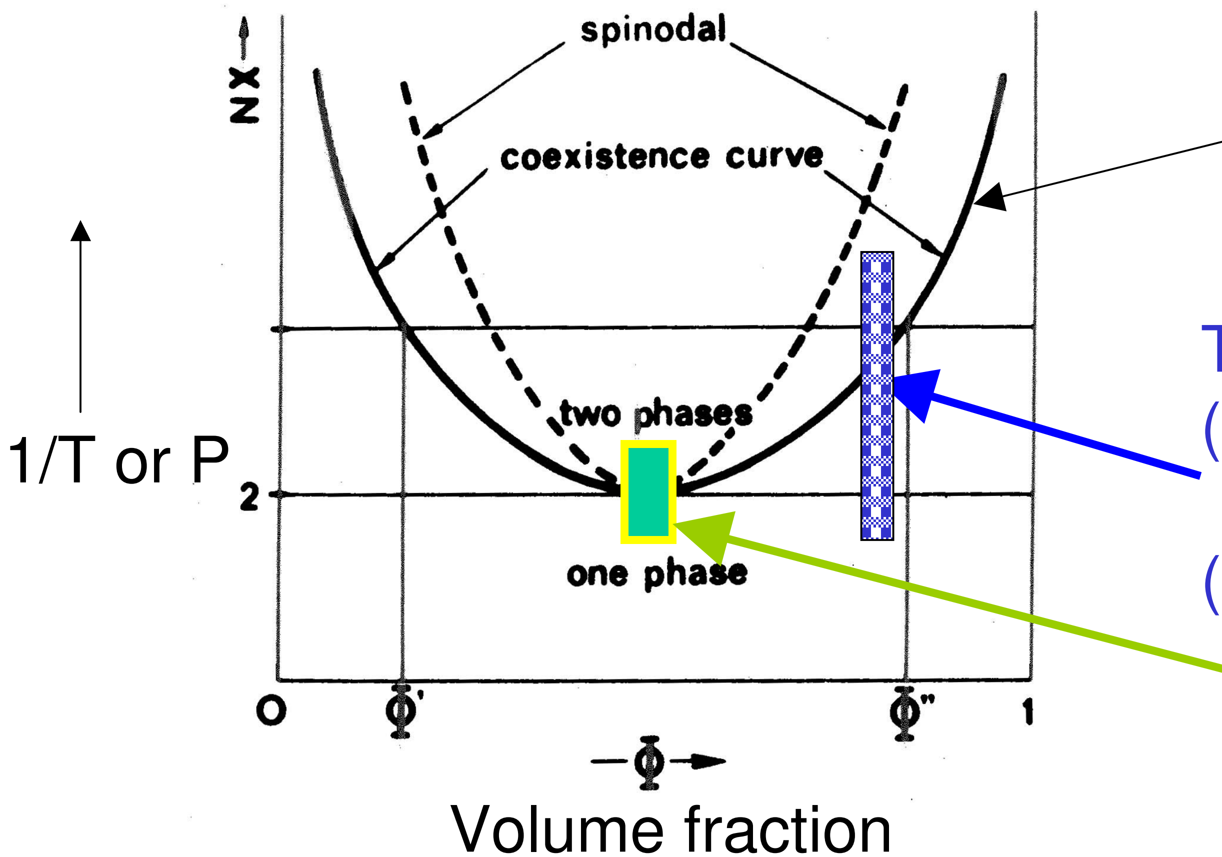
Phase diagram of liquid (polymer) mixtures



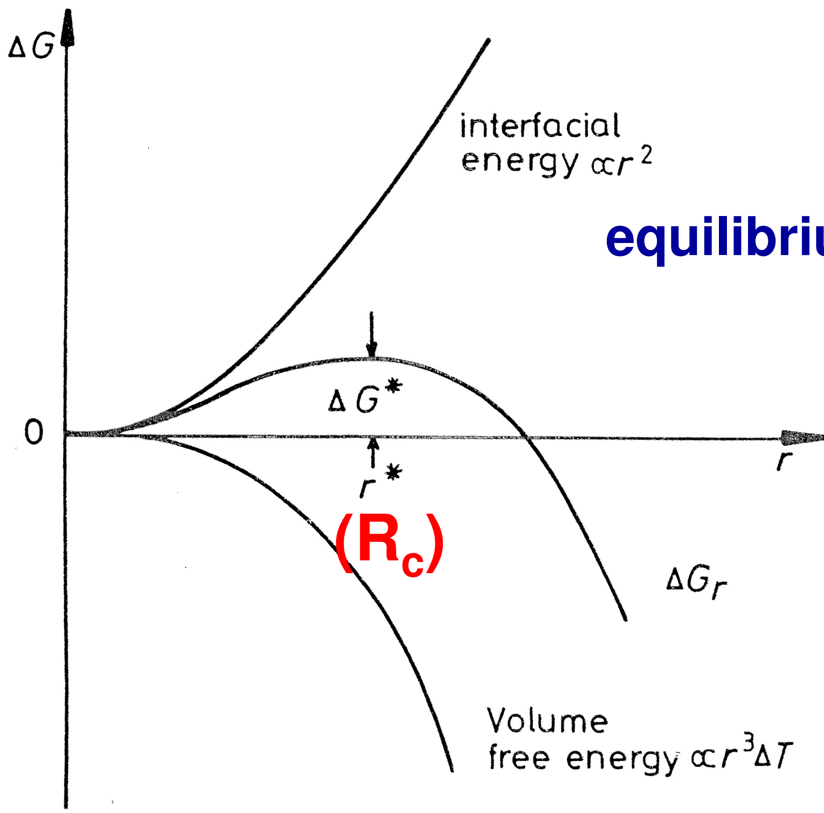
Two Mechanisms:
(1) Nucleation (off-critical systems)
(2) Spinodal Decomposition (critical systems)

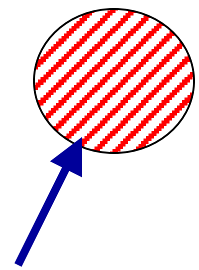
Question: Is there any difference between the 2 mechanisms?

John Cahn

1. Classical nucleation theory

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



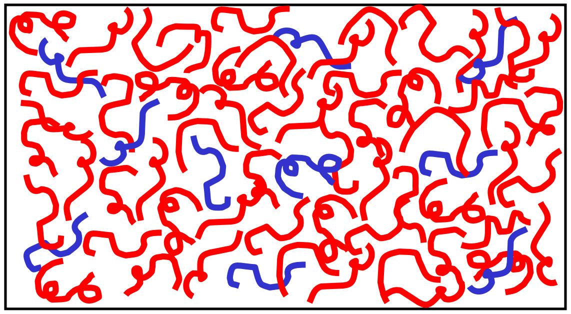


equilibrium droplet in an infinite "ocean"

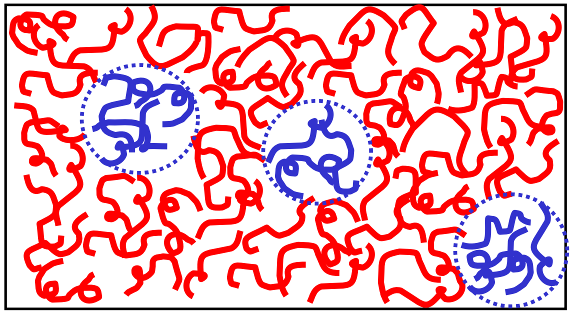
(size)

Examples: clouds, rain, snow, bones, crystallization, boiling, melting, magnetization, phase separation…

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.

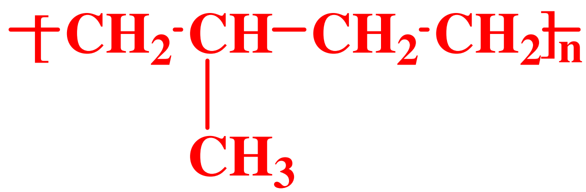
Questions about nucleation

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

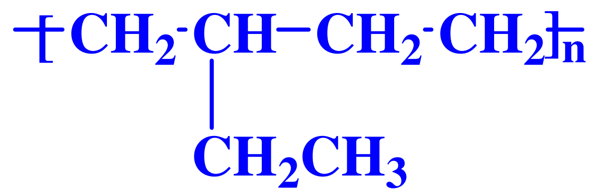
2. Can scattering (a powerful tool for studying critical systems) be used to study nucleation?
If nuclei are infinitely dilute, then scattering will not work.

3. Theory is remarkably silent about measuring R_c.
Find each cluster and determine the probability of growth/decay (experiments by Weitz and Vekilov).

Materials



PM



PE

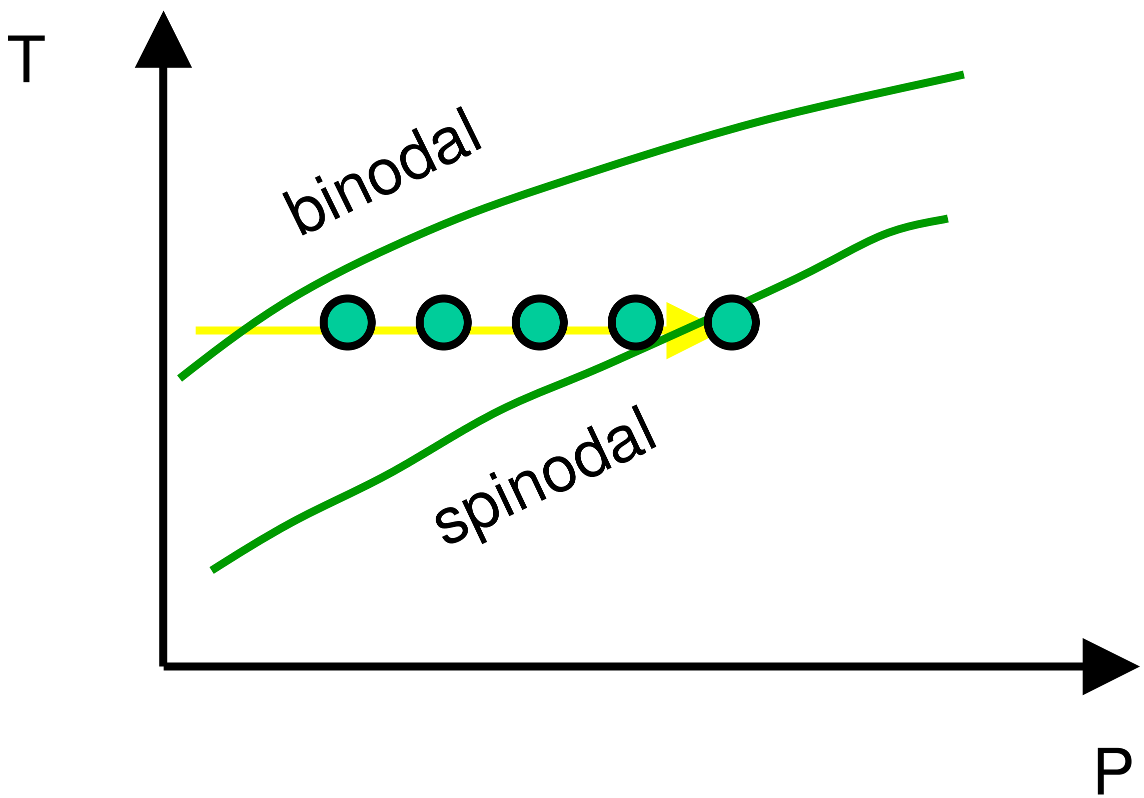
sample desig.	mol. wt. (kg/mol)	N	Rg (nm)
dPM	145	2055	15.2
hPE	195	2350	15.5

Blends:

blend desig.	vol fr. of dPM
B5	0.49 (critical)
B4	0.20 (off-critical)

B1, B2, B3 are also off-critical blends (JCP, 2002)

Pressure Quench (off-critical)



Anneal above the binodal at P=0.

Quench in two steps to final (T,P).

Phase separation triggered by the pressure quench.

Determination of binodal and spinodal: Lefebvre, et al., Macromolecules, 2002

Salient Features of our Experiments

1. Molecular motion is extremely slow (τ~0.1 s) and completely understood (non-glassy).

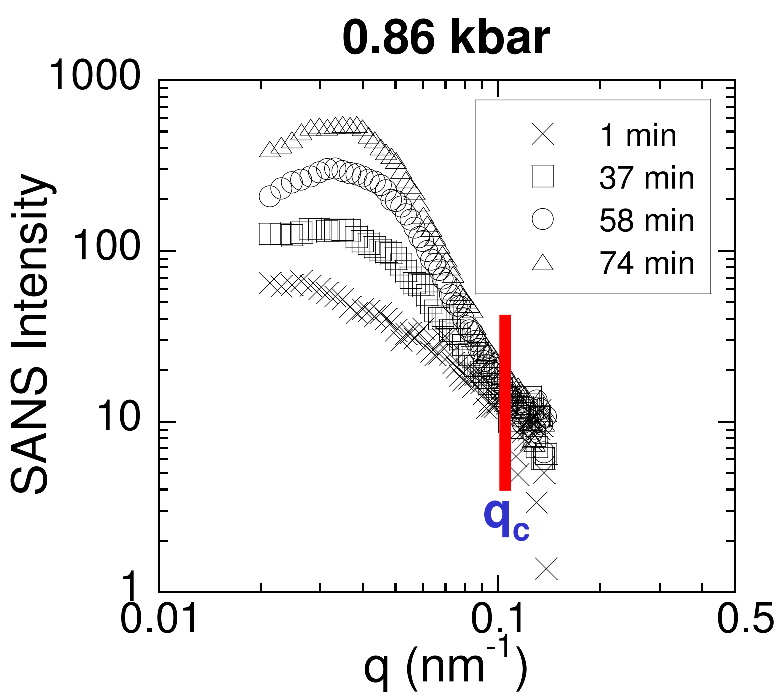
2. Robust models for equilibrium thermodynamics are available; expressions for R_c can be easily derived:

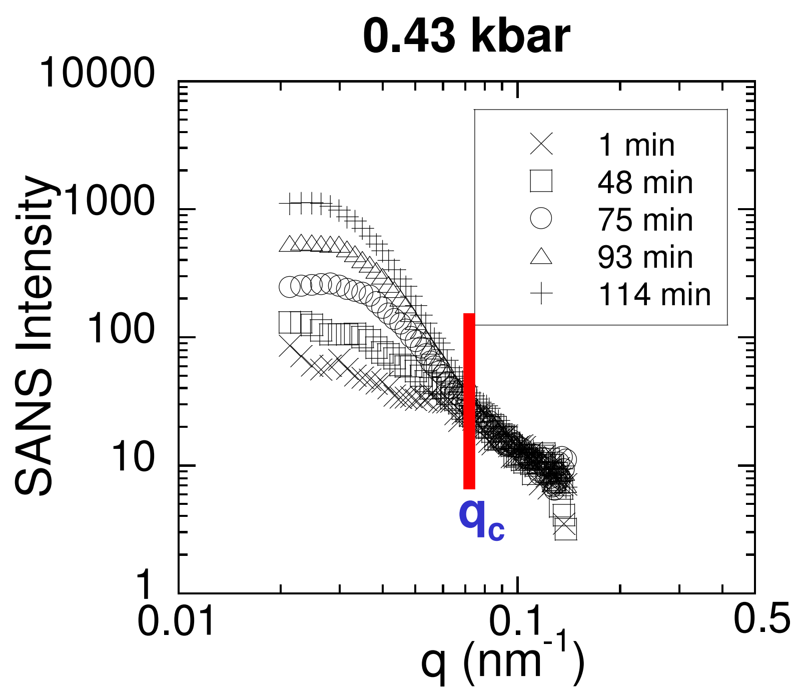
$$\left(\frac{R_g}{R_c}\right)^2 = \left(\frac{2\chi N}{0.73}\right)^2 \phi(1-\phi)\left(\frac{1}{2} - \frac{1}{2}\sqrt{1-\frac{2}{\chi N}} - \phi\right)\left(\sqrt{1-\frac{2}{\chi N}}\right)$$

3. Nucleation triggered by pressure quench (faster and cleaner than temperature quench).

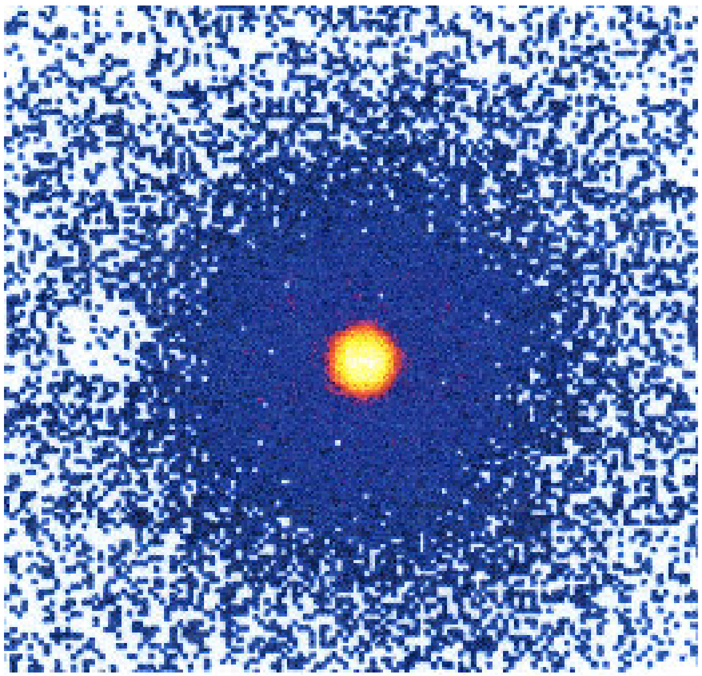
4. Deuterium labeling enables detection of initial clustering by SANS.

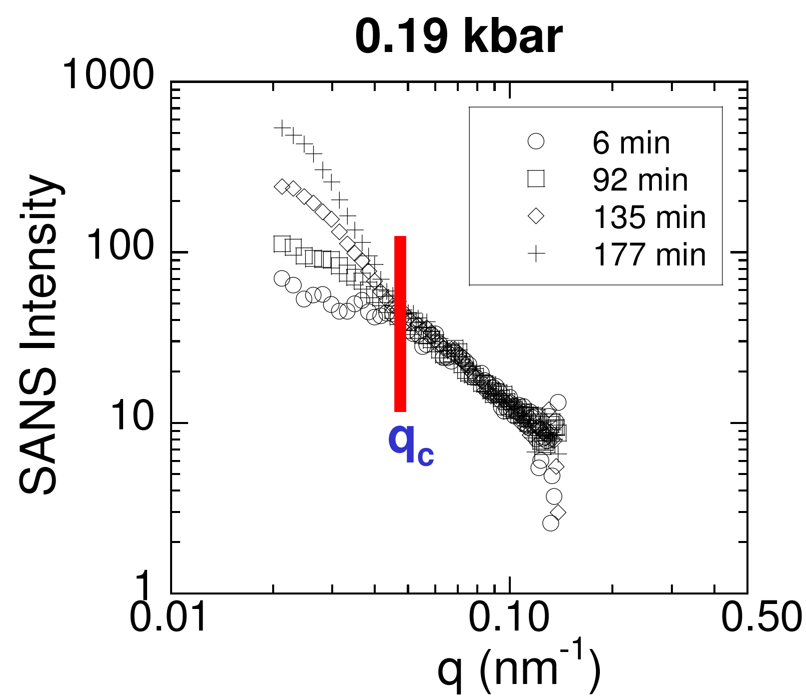
SANS profiles merge





Scattering Signature of Critical Nucleus

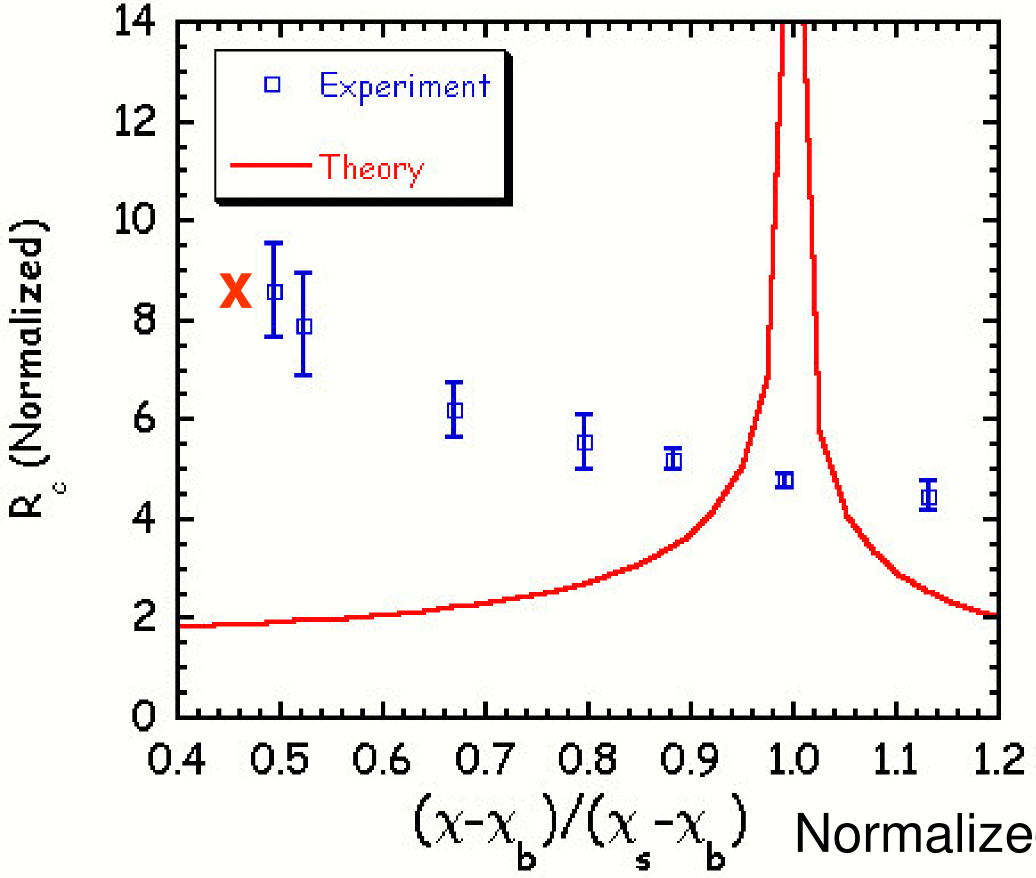




If none of the emerging structures are of size L then there will be no scattering increase at the corresponding q~1/L.

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 $\kappa < 0.48$

$R_c = 2\pi / q_c$

Normalized quench depth, κ

$\kappa = 0$ at binodal; $\kappa = 1$ at spinodal

This result led to a lot of problems

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

Example of positive review:

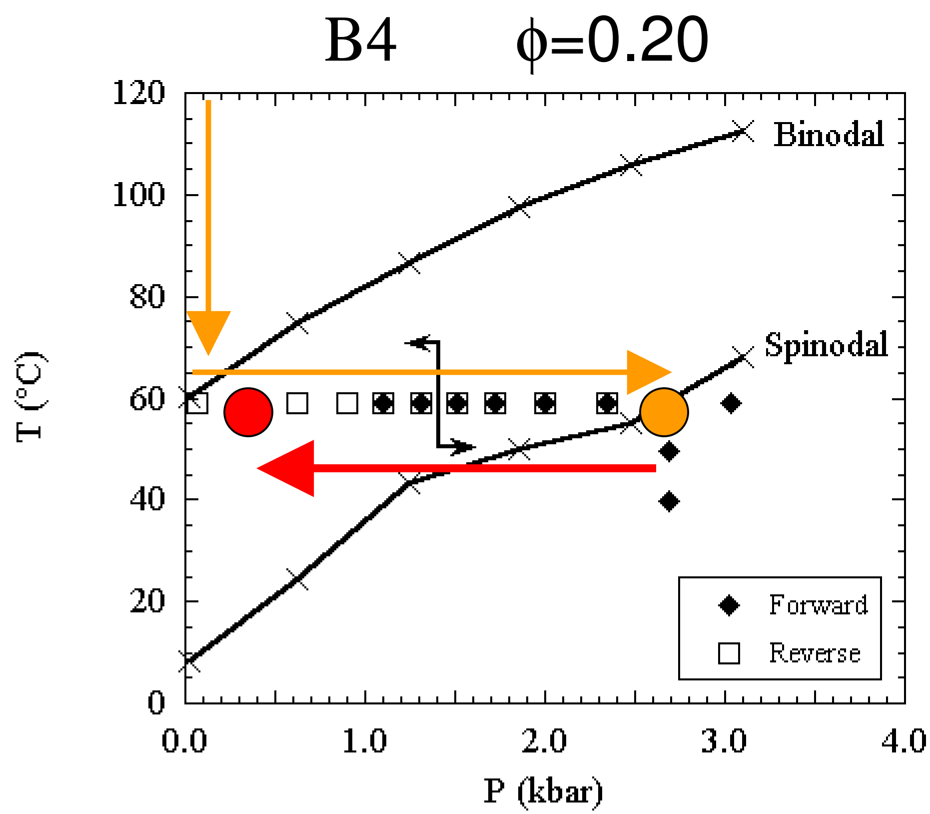
This paper presents very interesting new results that are purported to be relevant to homogeneous nucleation in polymers. The presented results are in fact a bit TOO INTERESTING. Indeed, ever since Prof. Balsara presented these results at last year's Polymer Physics Gordon Conference, the entire community 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.

Perturbing Metastable Systems



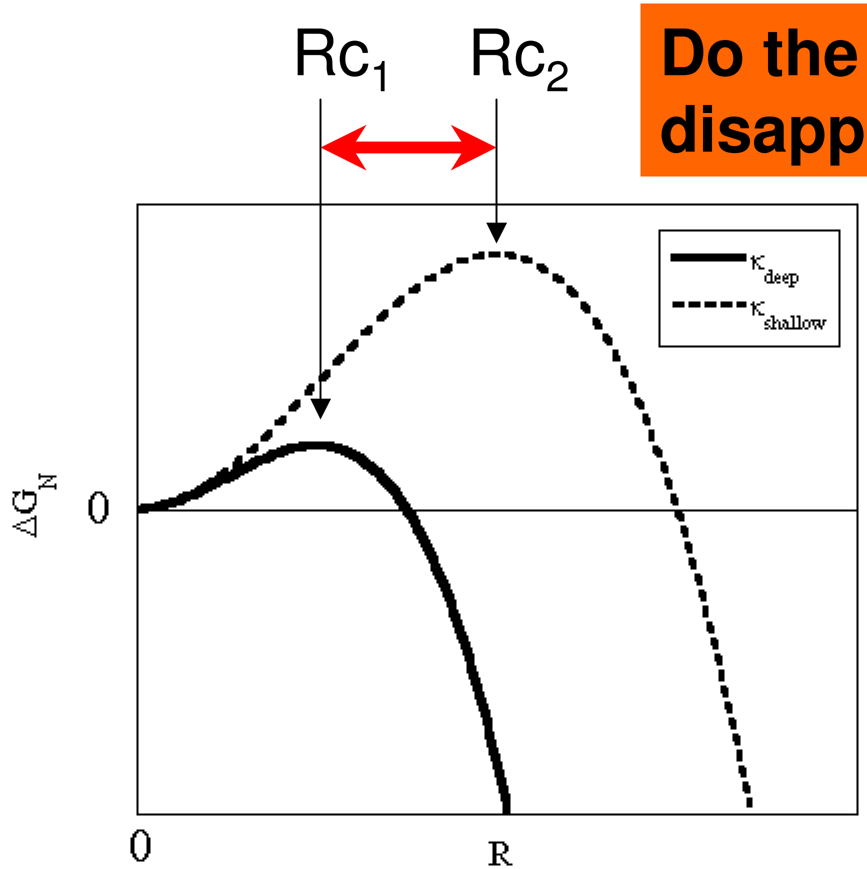
Anneal above the binodal at P=0.

Quench in two steps to $\kappa(T_1,P_1) = \kappa_{age}$.

Phase separation triggered by the pressure quench.

Quench to $\kappa(T_2,P_2)$
$T_2=T_1$, $P_2<P_1$

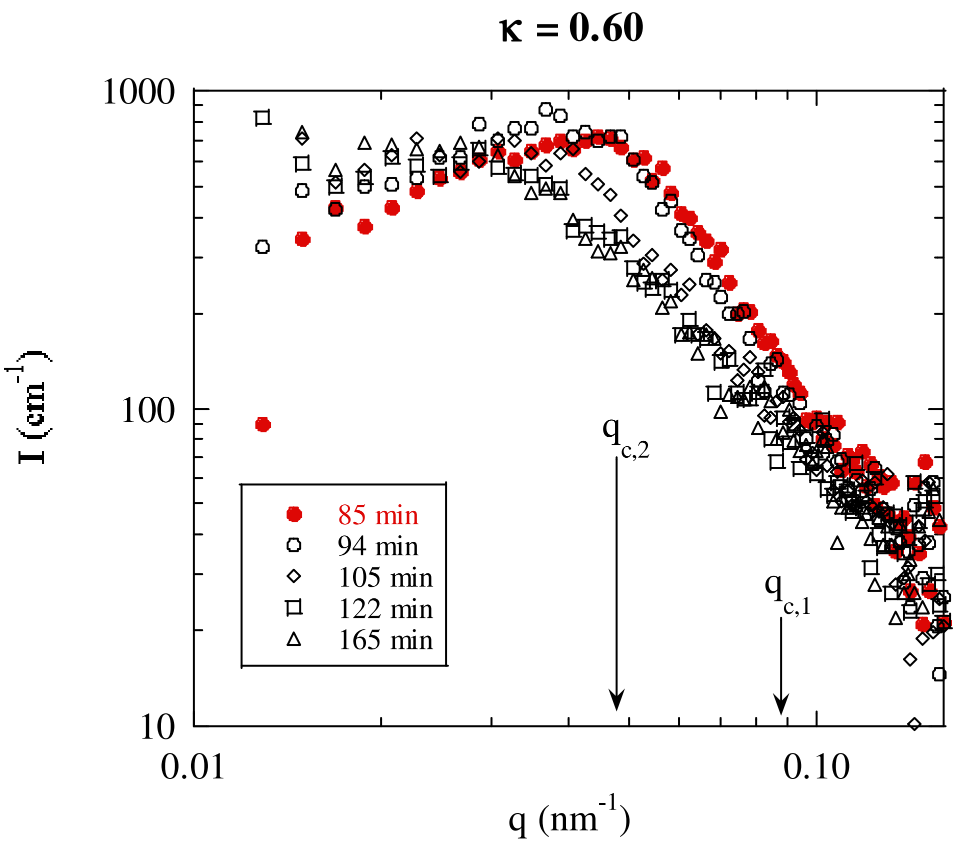
Aging Experiments

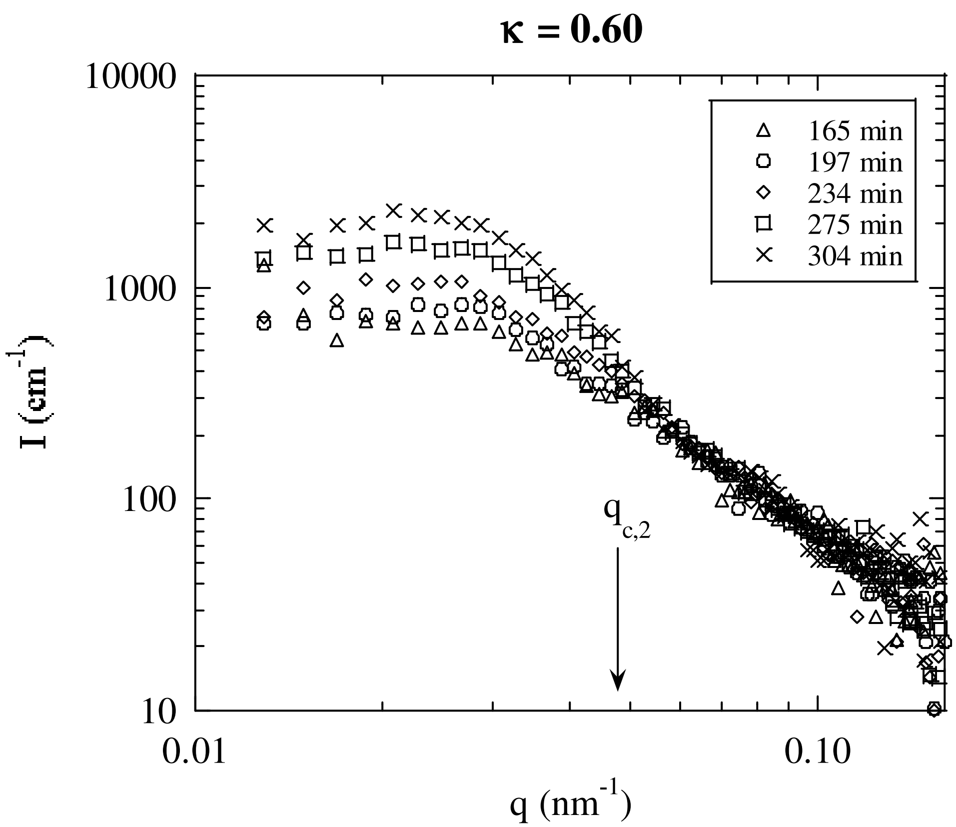


Do the nuclei in the red zone disappear during the second step?

Only true during initial stage of nucleation!

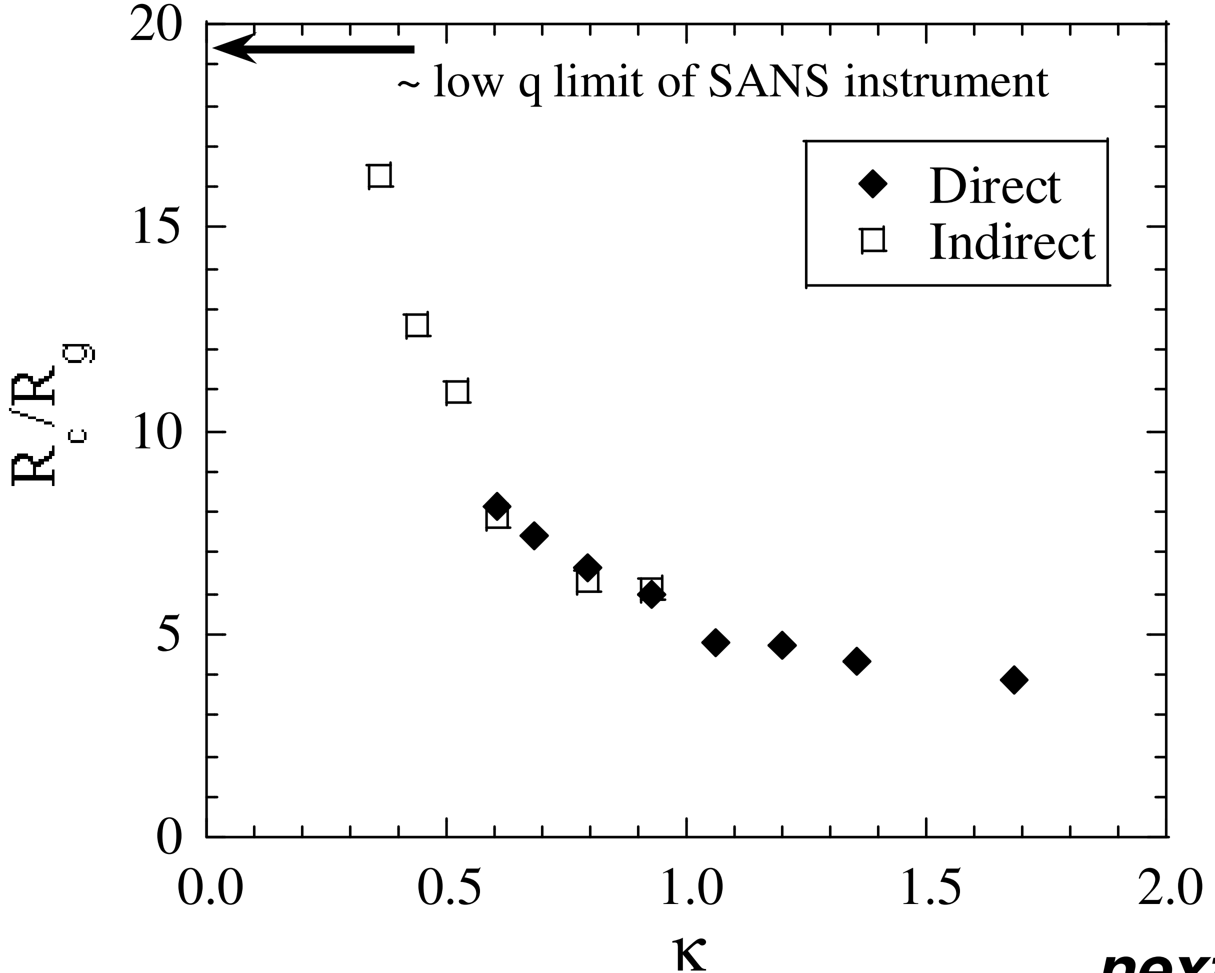
(1) 2.69 kbar aging: 90 min
(2) 1.52 kbar





1) Small nuclei disappear immediately after second quench (left).
2) Subsequently (right), $q_{c,2}$ agrees with direct nucleation data to 1.52 kbar

R_c from direct and indirect quenches



next step-simulations

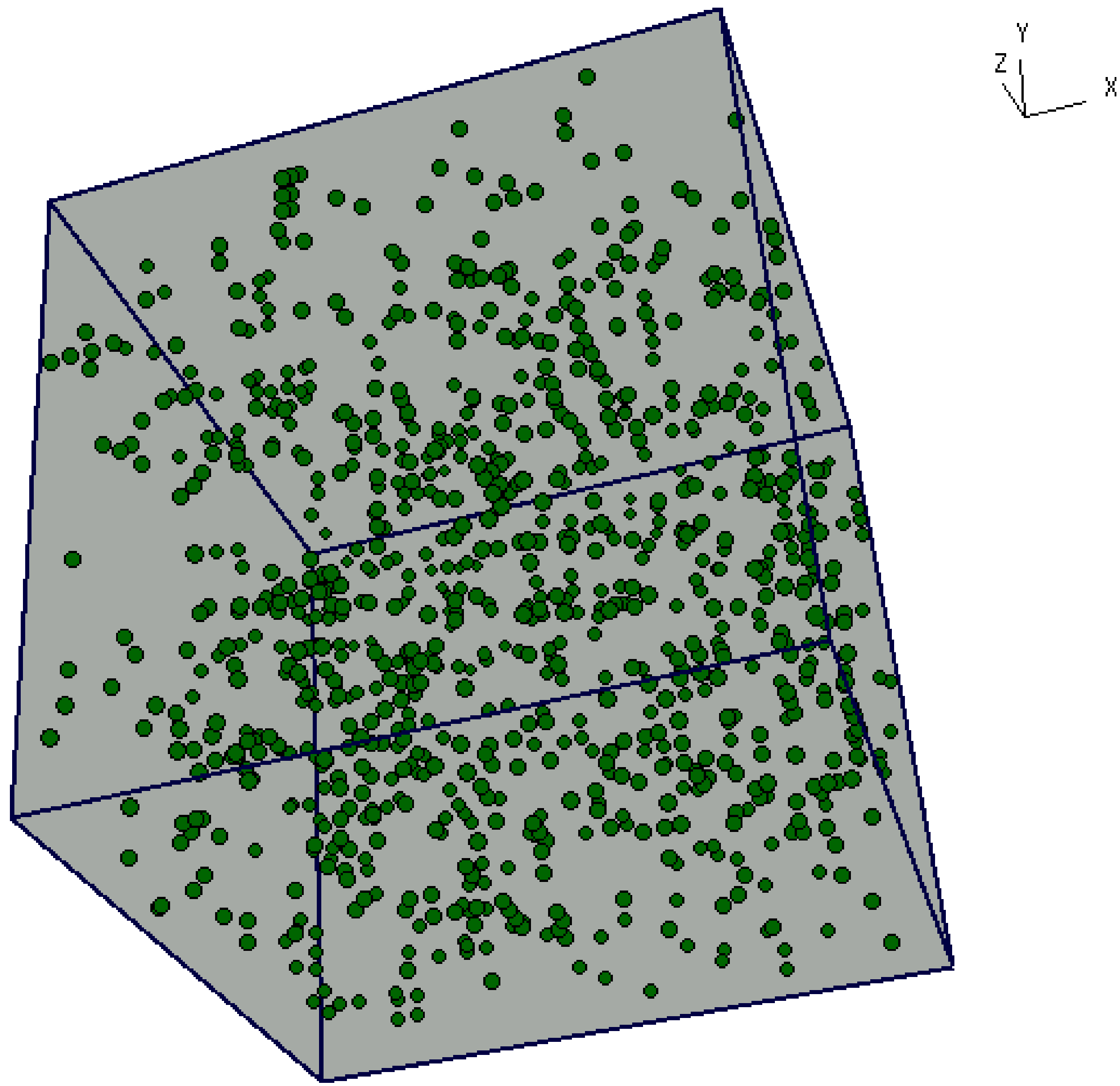
Simulations

Ising Model

All spins are up initially.

An external downward field with magnitude h is imposed at $t=0$ ($J=-1$).

Dark box shows spin down domains.



Pan, Chandler simluations of nucleation in an Ising magnet

David Chandler's Initial Reaction

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

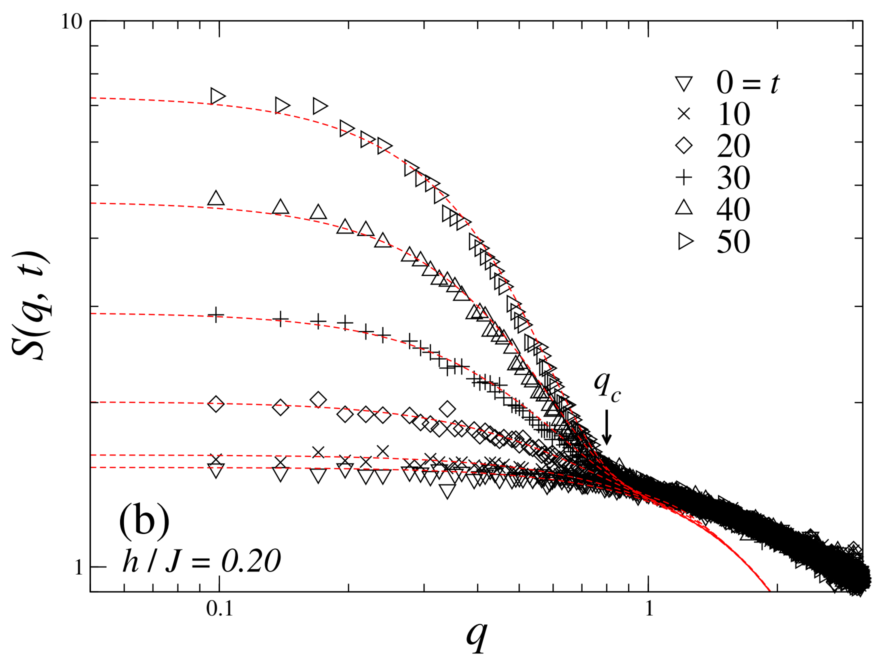
NPB: "Have you computed the structure factor during nucleation?"

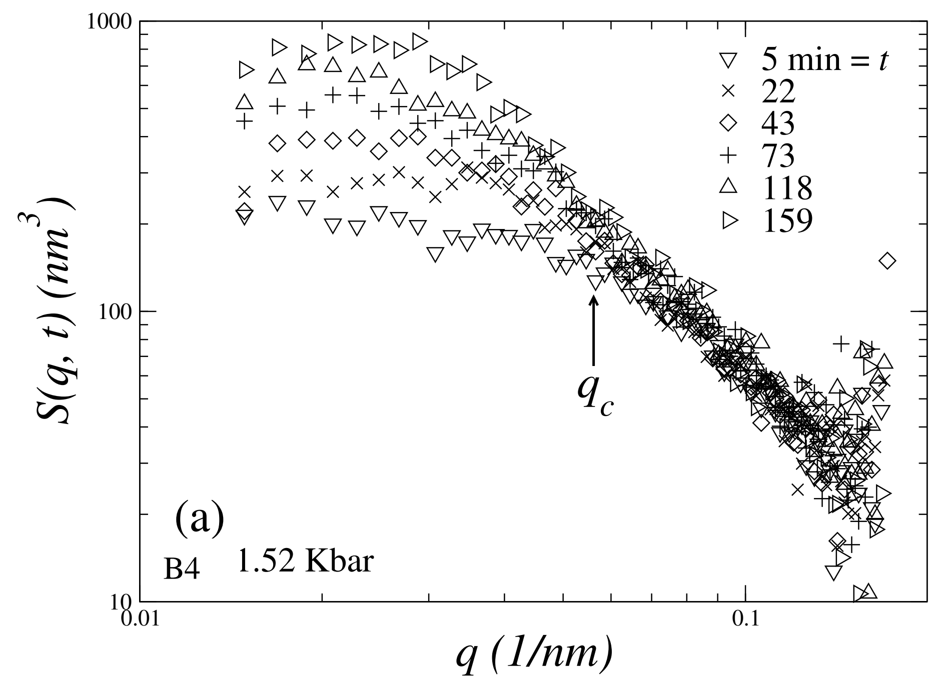
Albert: "No".

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

In fall 2003, I gave a seminar to DC's group....tells Albert to compute the structure factor.

Simulation & Experiment

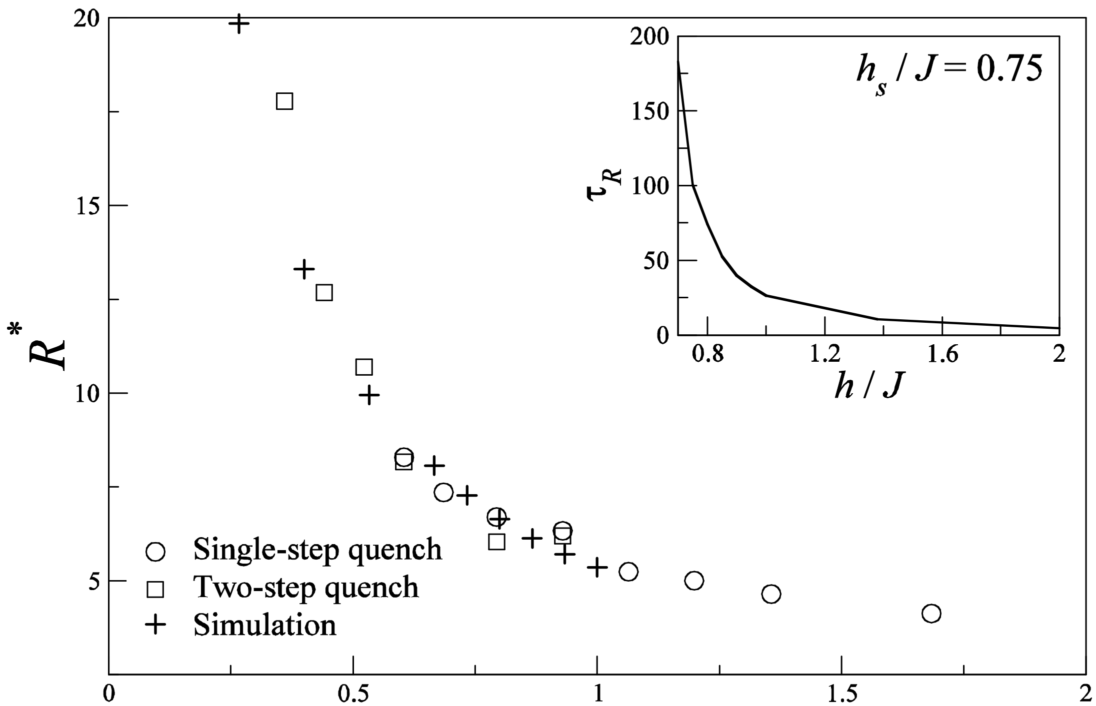




$q_c = 2\pi/R_c$

Comparing Nucleation Simulation and Experiments

R_c/R_g



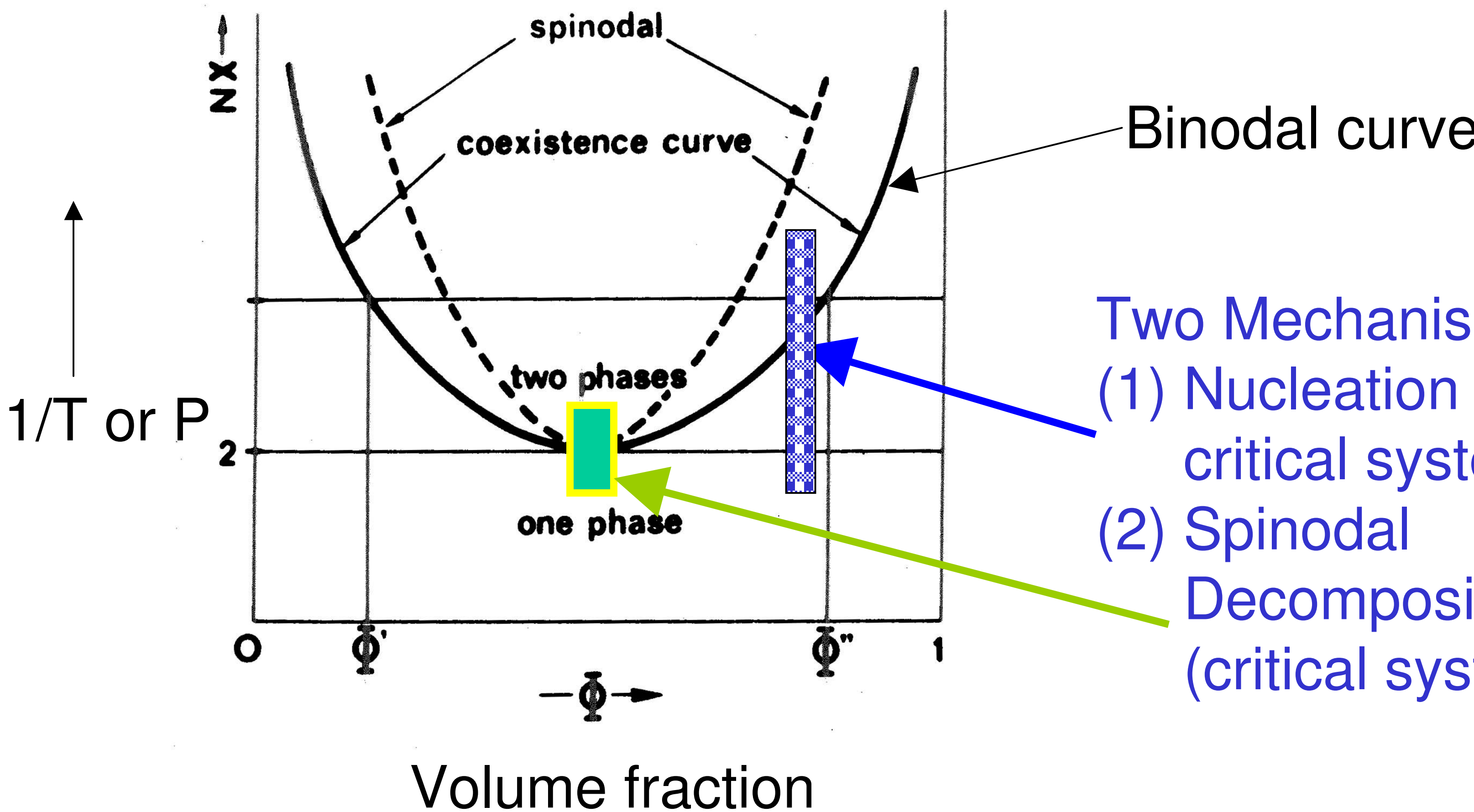
Reduced quench depth, κ

Ising model:

Spinodal at $h_s/J=0.75$

Binodal at $h_s/J=0$

2. Spinodal Decomposition



Two Mechanisms:

(1) Nucleation (off-critical systems)

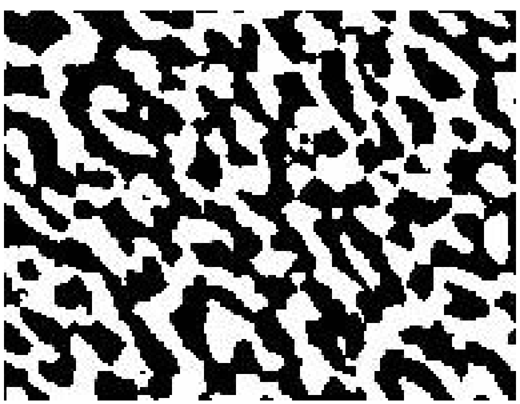
(2) Spinodal Decomposition (critical systems)

2. Spinodal Decomposition (John Cahn)

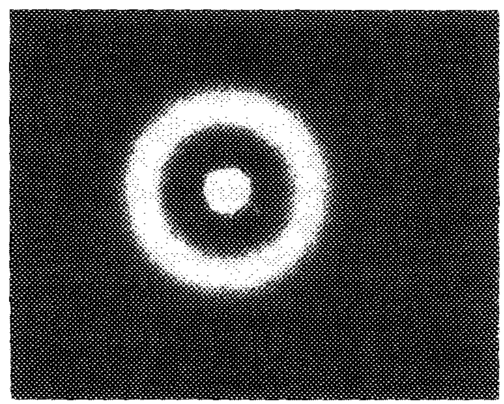
Phase separation in critical binary liquid mixtures.

$$\frac{\partial c}{\partial t} = k_1 \frac{\partial^2 c}{\partial x^2} - k_2 \frac{\partial^4 c}{\partial x^4}$$

$$c - c_0 = \exp[R(q)t]\cos[qx]$$



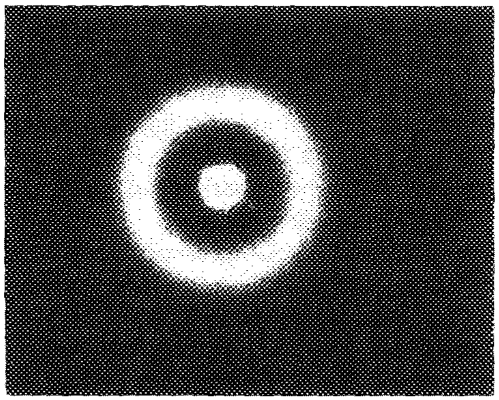
position space



reciprocal space

ring size independent of time

Two key scattering vectors

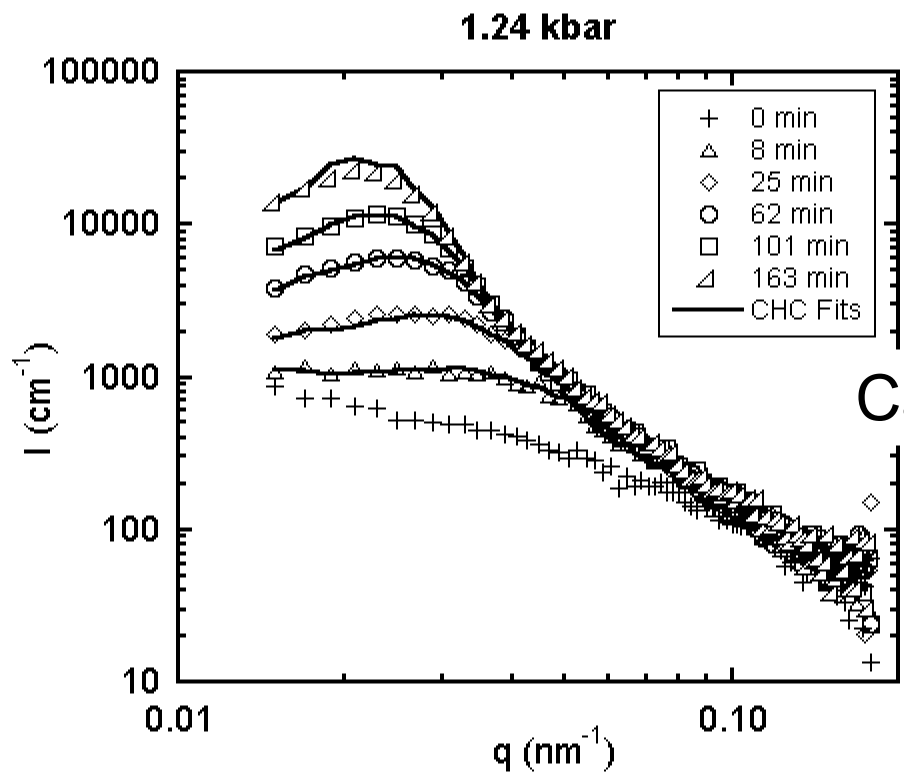


$$c - c_0 = \exp[R(\beta)t]\cos[\beta x]$$

(1) q_m: fastest growing length scale (R_{max}) results in a scattering peak

(2) q_c: critical size of growing structures ($R>0$ only for $q<q_c$) results in a merging of high q scattering ($q_m=2^{1/2}q_c$)

Typical SANS Data

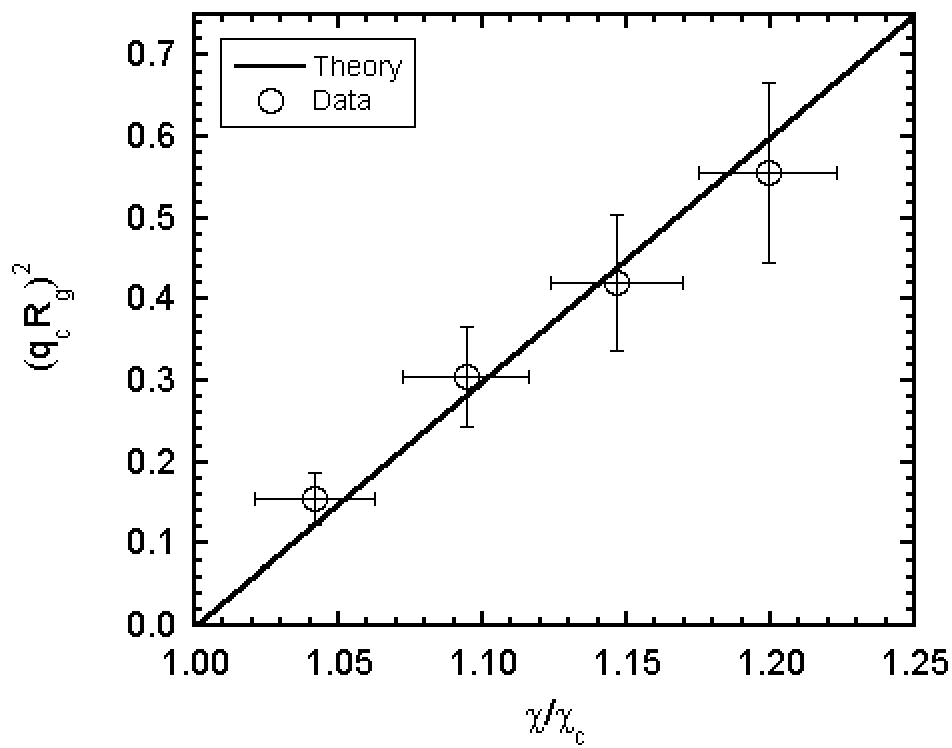


Cahn-Hilliard-Cook Analysis

$$I(q,t) = I_T(q) + [\ I_0(q)-I_T(q)\ ]\exp[\ 2R(q)t\ ]$$

I_0,I_T,R at each q are fitting parameters.

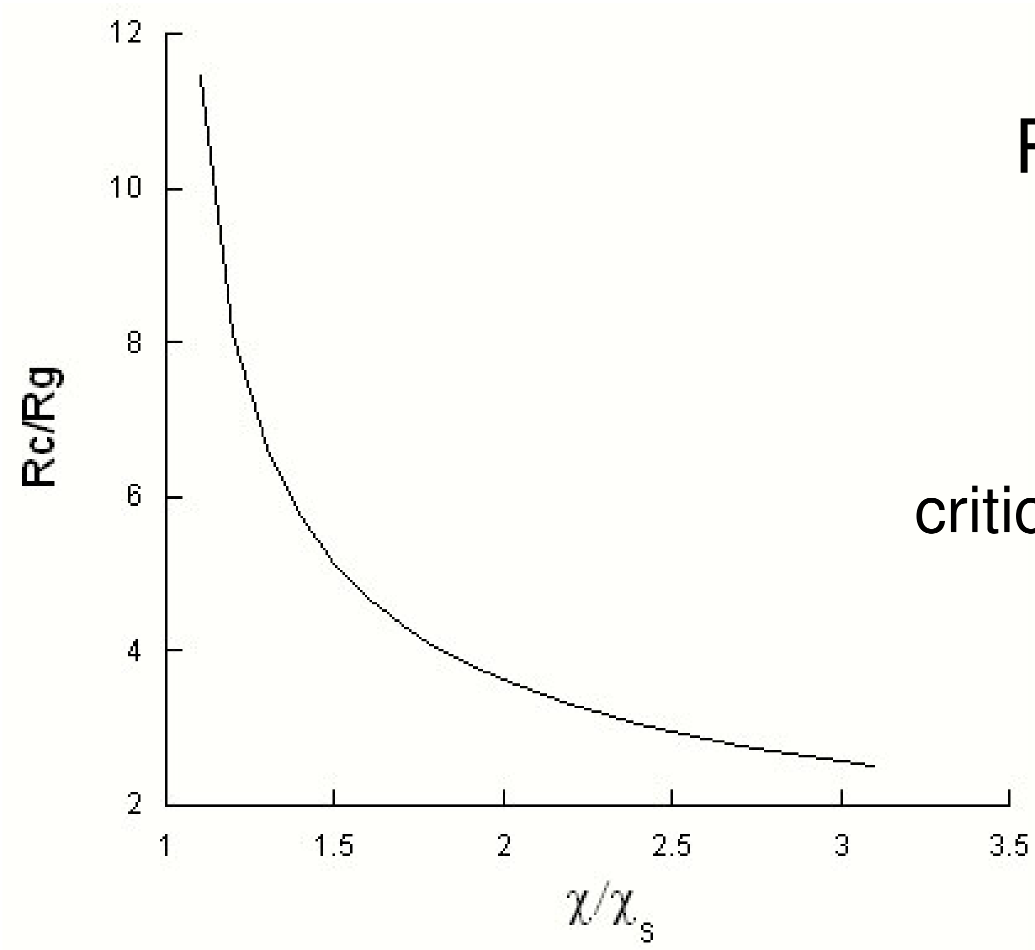
Dependence of q_c on Quench Depth



Remarkable agreement with theory (JCP, 2005)

$$[q_c R_g]^2 = 3[\chi(T,P)/\chi_c(P) - 1]$$

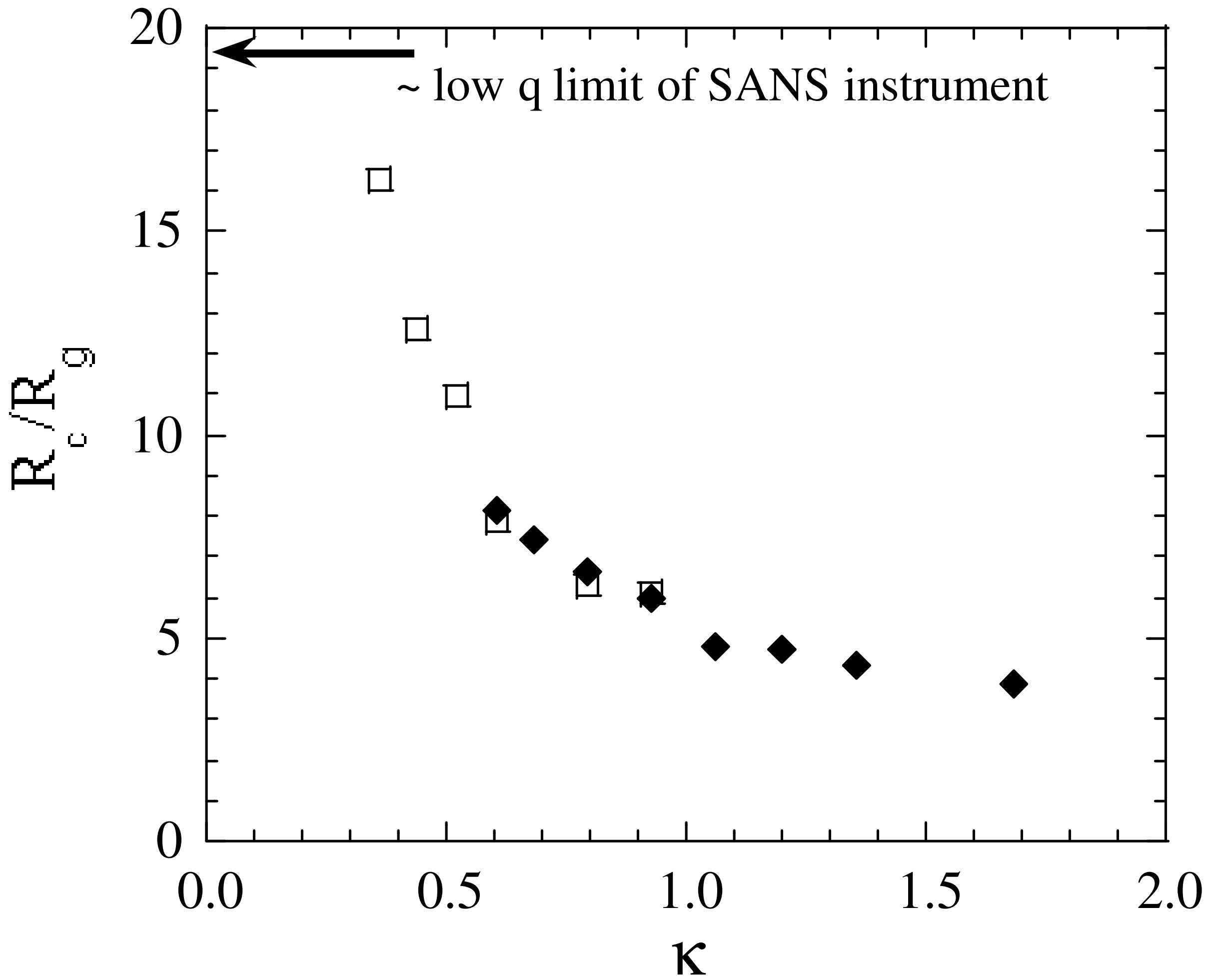
Dependence of R_c on quench depth



$R_c = 2\pi/q_c$

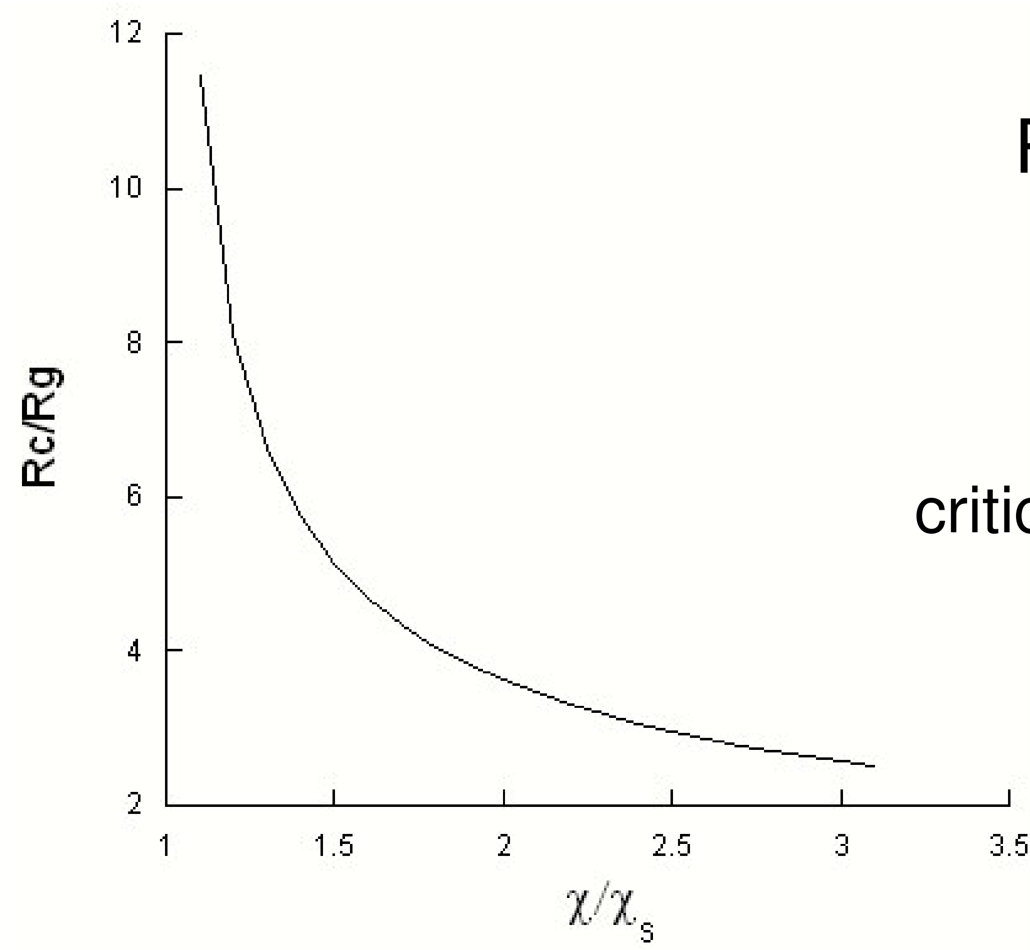
critical systems

R_c from nucleation studies



off-critical systems

Dependence of R_c on quench depth



$R_c=2\pi/q_c$

critical systems

Concluding Remarks

(1) Scattering signature of the critical nucleus is proposed $R_c \sim 2\pi/q_c$ (first proposed signature).

(2) Simple nucleation models do not agree with experiments. Ising simulations do.

(3) No qualitative difference in the initial stages of phase separation in critical and off-critical quenches.

There appears to be no important difference in the mechanism of phase separation inside and outside the spinodal.

August 29, 2005

Memo to: Mike Rowe and Jack Rush
From: Setab Knarf

Dear Drs. Rowe and Rush:

I am a youngish scientist/engineer fresh out of graduate school contemplating my future. The world looks complicated today, so I have examined the historical records available through the Freedom of Information Act and spotted your names on the list of individuals who have “Succeeded against all odds.” Would you be so kind as to advise me on a few career choices?

My greatest concern is to make sizable amounts of money. Based on the impact of your work I have concluded that you two must be exceedingly rich. Searching through the government records I repeatedly discovered your names, heading or involved in high-level committees that make recommendations regarding the allocation of huge amounts of money. Your recommendations seem to be highly regarded, well most of them, and I can only assume you have been nicely compensated for this work. My business classes didn’t deal with this type of entrepreneurial activity and I wondered whether you could recommend a self-help manual or something comparable.

I am really puzzled about your activities with “cold neutrons.” Presumably producing this is your specialty Dr. Rowe as I have noticed you are from Canada. I’ve found thousands upon thousands of scientific and technological references to this product. How do you market this item? I must admit I am perplexed about the economics. Authors, including some very successful ones publishing in top-drawer journals and magazines, thank your facility for providing this commodity at no cost! Here again you guys must be very clever. All that impact at no cost! Perhaps Dr. Rush, a New Yorker, handles the murky finances.

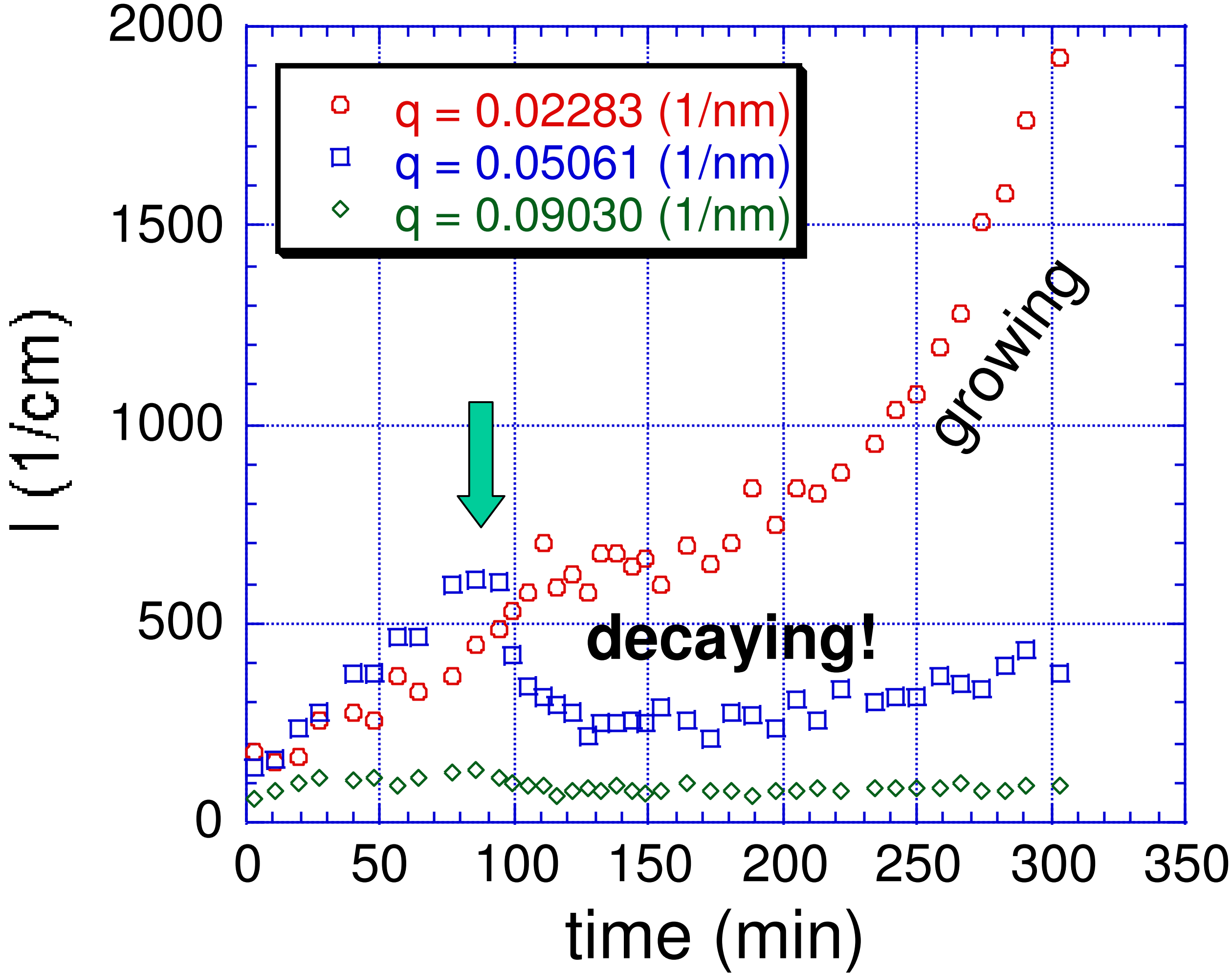
When I look back on my own career I hope to reflect on a fraction of the impact you two have brought society. As usual, any advice would be appreciated.

Sincerely,Setab Knarf
Admiring and appreciative friend and colleague

Neutrons for the rest of us

We, the non-neutron specialists, wish Mike and Jack a happy retirement!

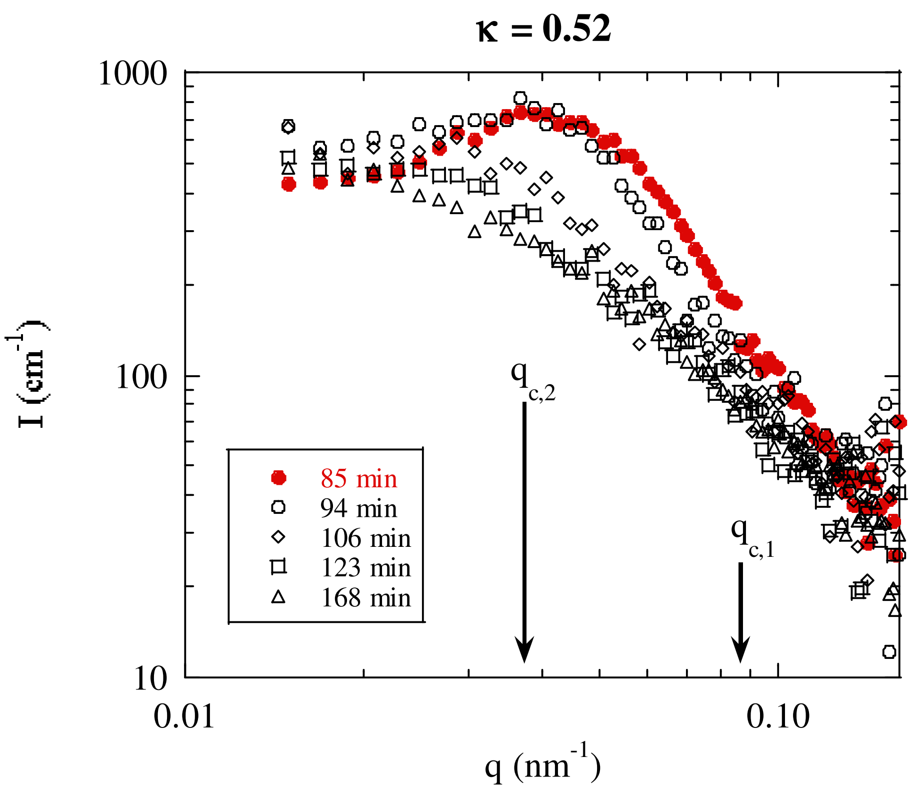
(1) 2.69 kbar aging: 90 min
(2) 1.52 kbar

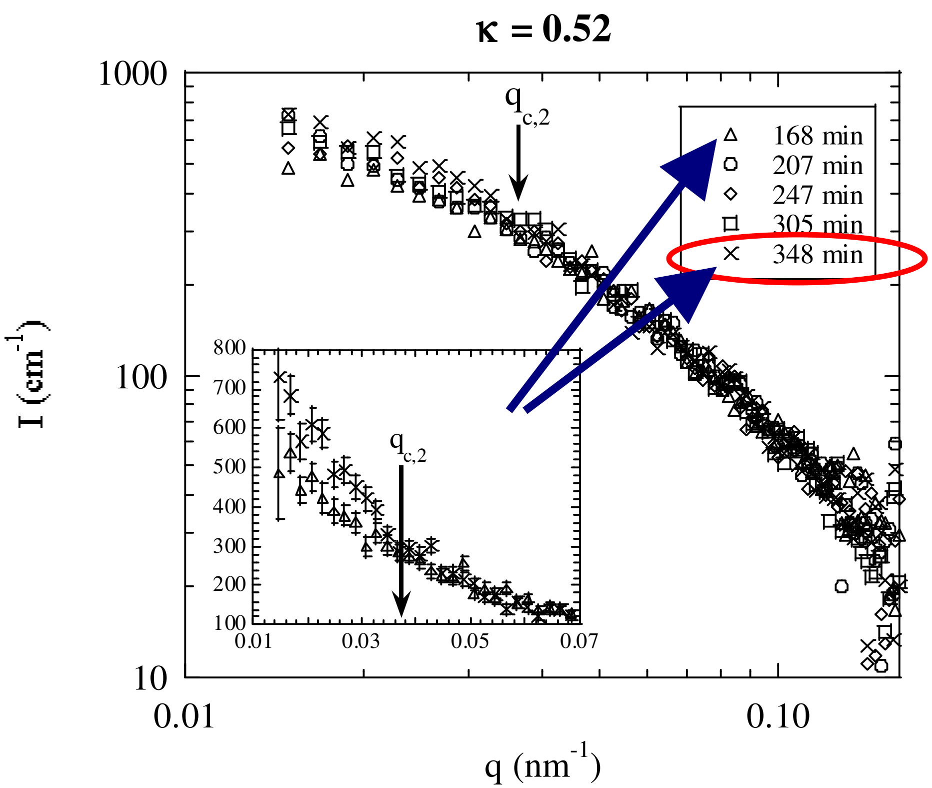


q_c (2.69)= 0.087 nm^{-1}

q_c (1.52)= 0.047 nm^{-1}

(1) 2.69 kbar aging: 90 min ($3\tau_e/4$)
(2) 1.31 kbar

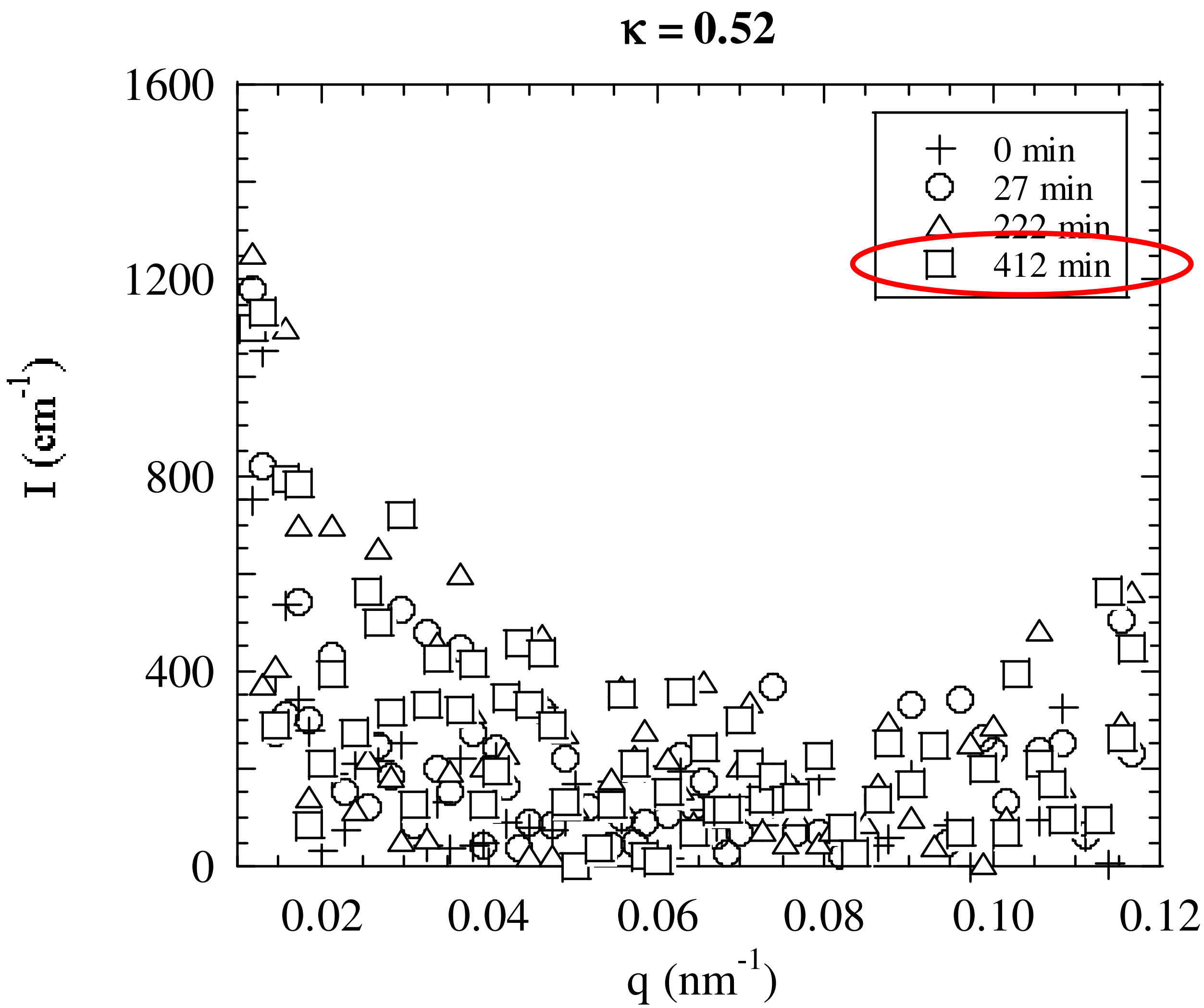




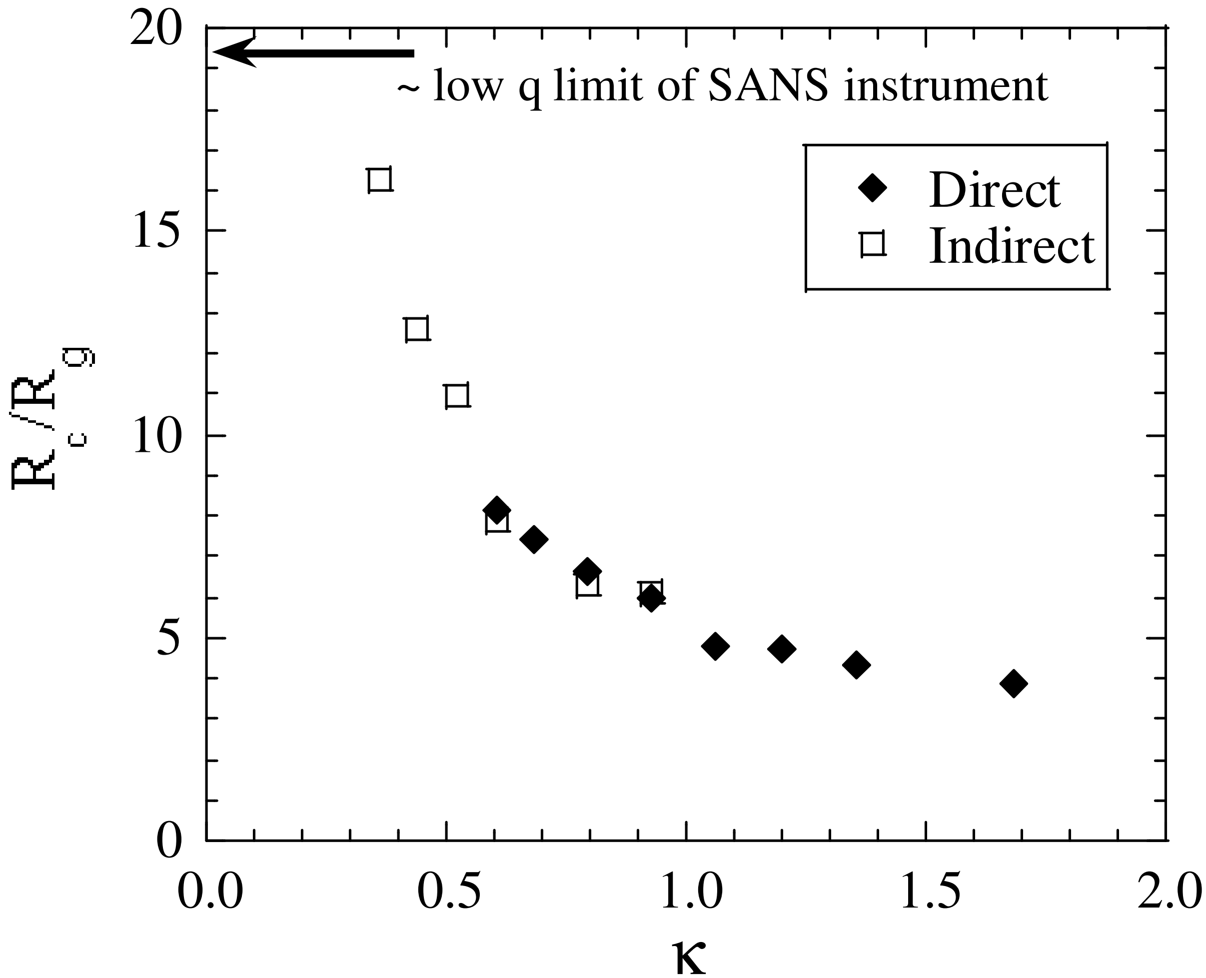
1) Phase separation triggered at 1.31 kbar!

2) $q_{c,2}$ agrees with **extrapolation!**

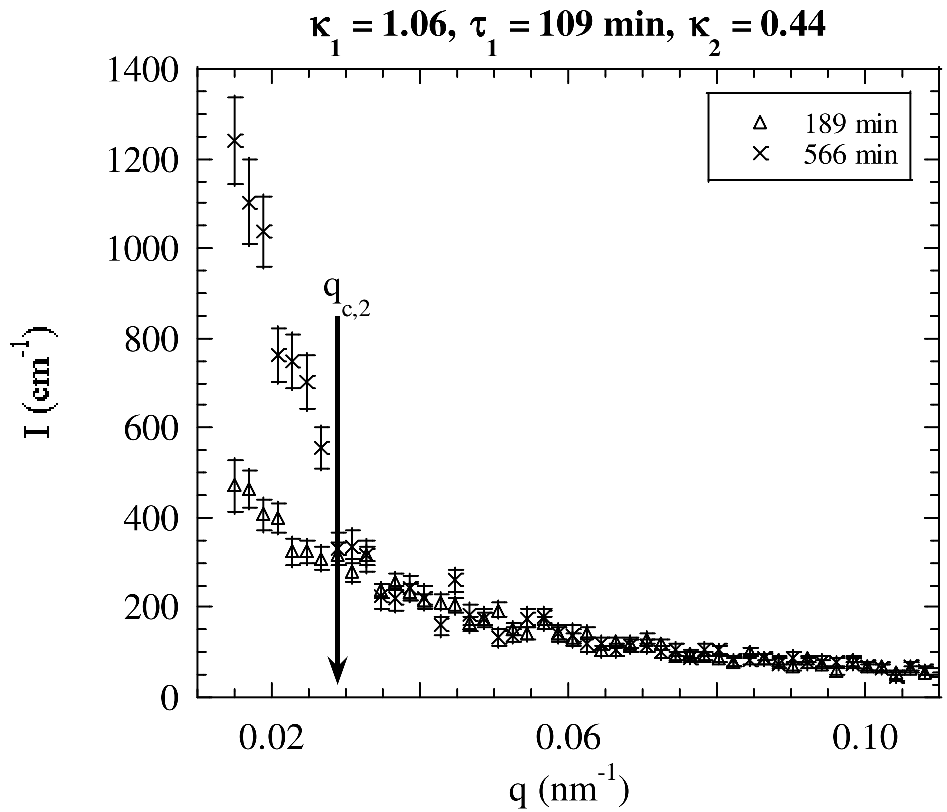
Direct Quench to 1.31 kbar does not nucleate



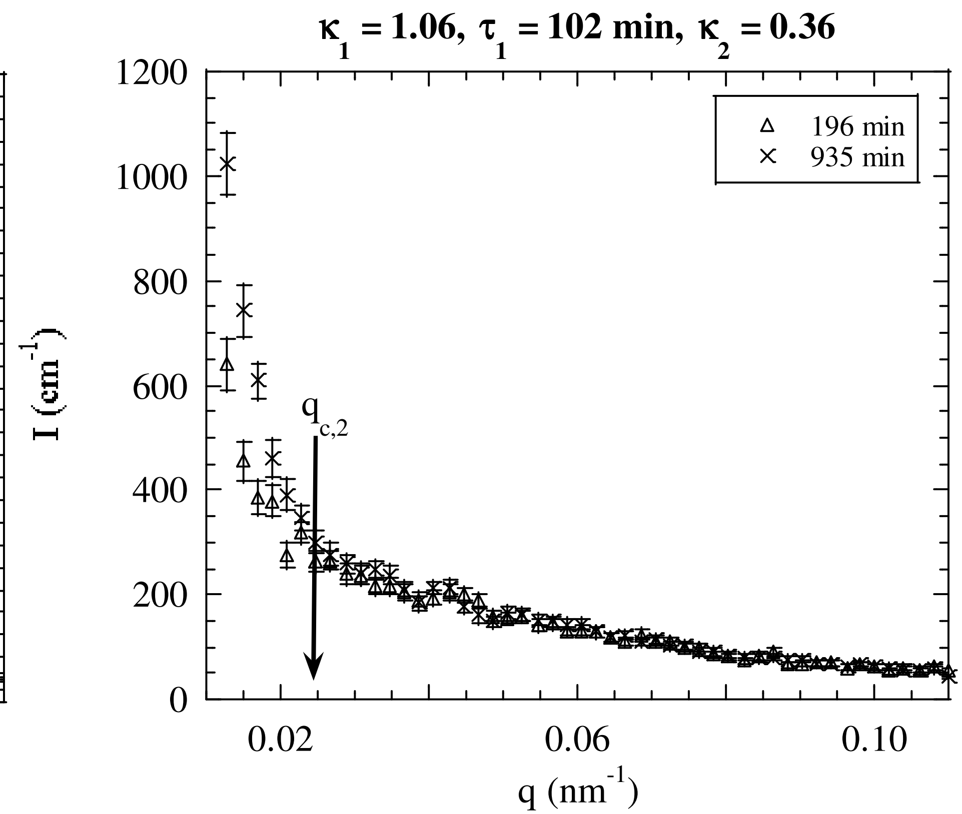
R_c from direct and indirect quenches



2.69 kbar aging: $\tau_1 < \tau_{nucl}$ = 120 min

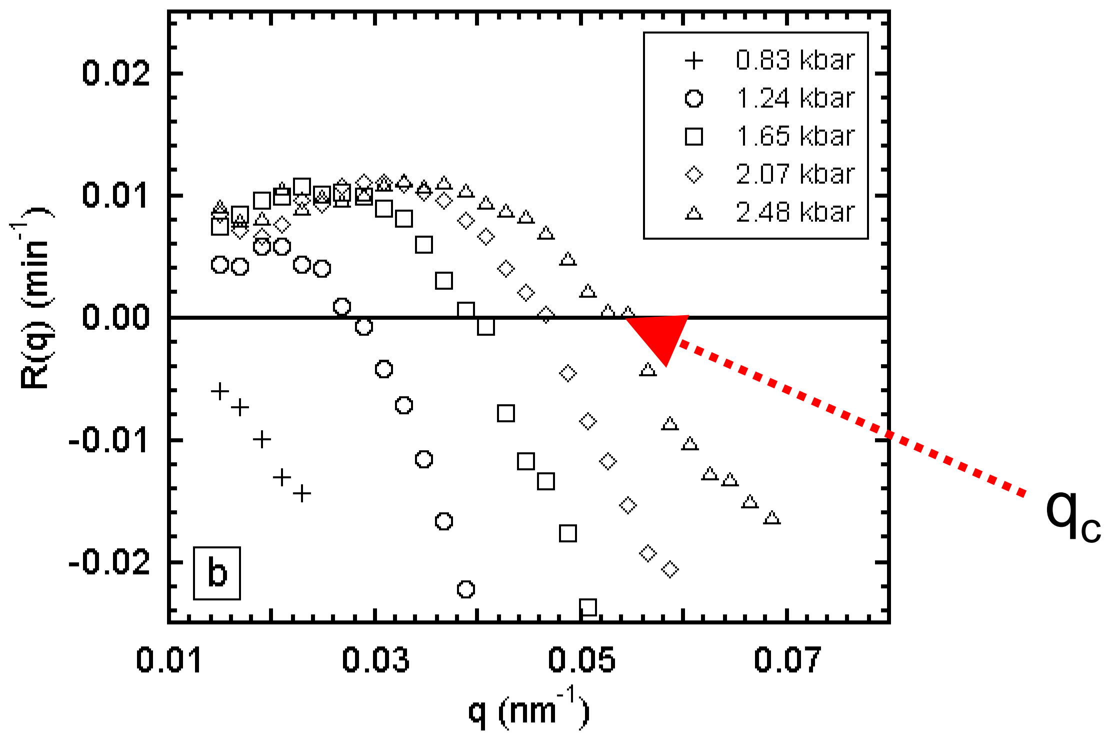


P = 1.10 kbar



P = 0.90 kbar

Critical Scattering Vector



merge point analysis gives similar q_c

The Answer

Does Conventional Nucleation Occur During Phase Separation in Polymer Mixtures?

No.

Financial Support:
NSF
ACS PRF

Experimental Data

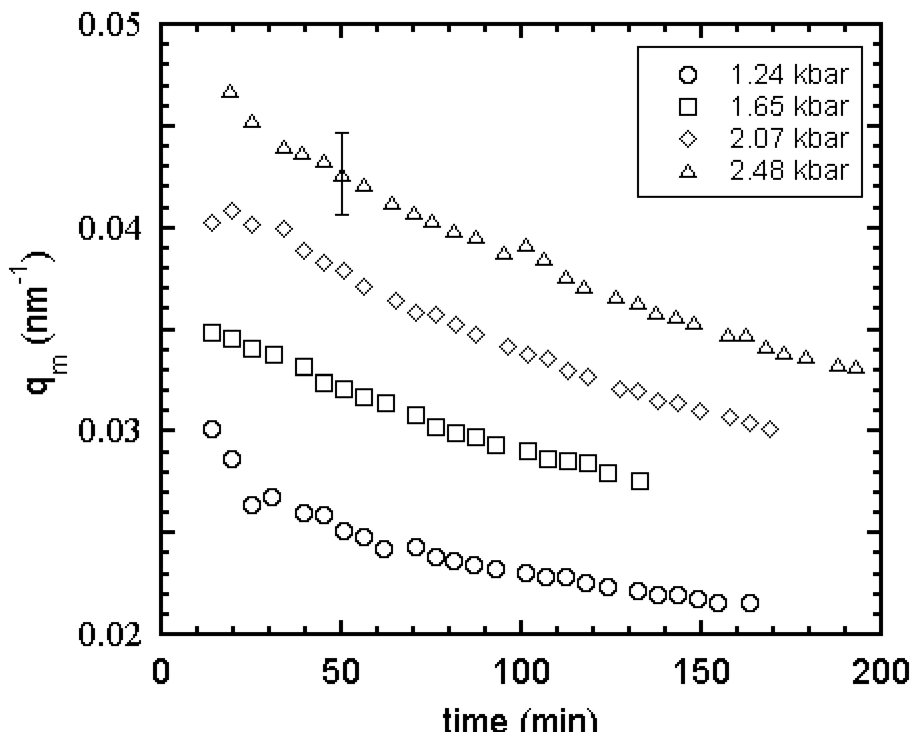
We are certain that we are studying the ***initial stages*** on spinodal decomposition because:

(1) Tracked the evolution a scattering peak from the initial structure factor (Random Phase Approximation).

(2) Reasonable agreement with the Cahn-Hilliard-Cook model.

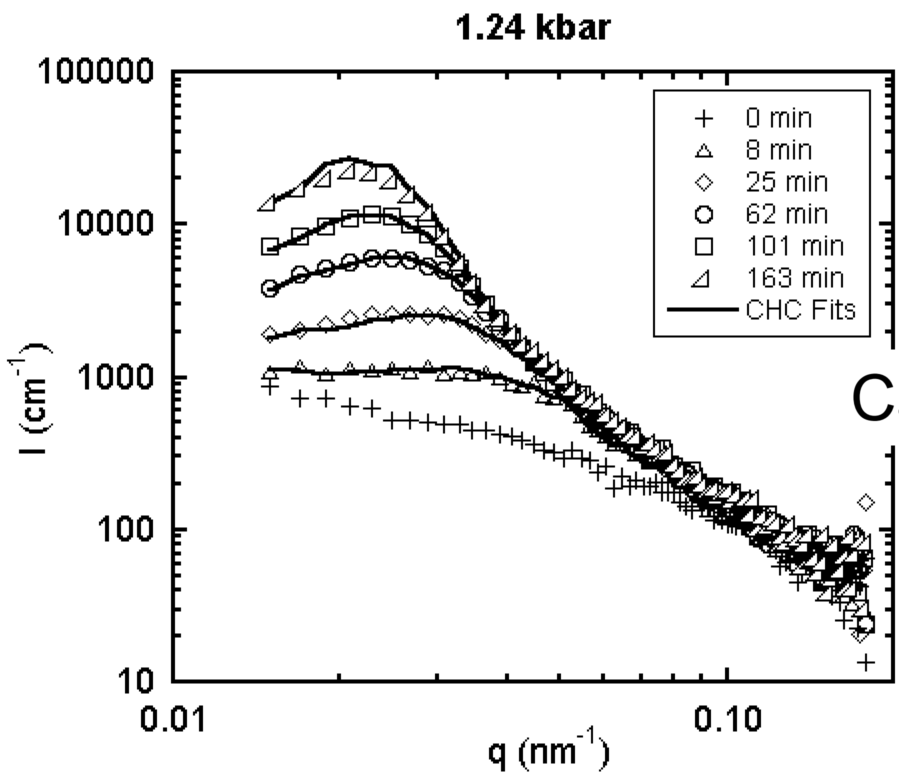
(3) Spectacular agreement between theory and experiment for q_c (signatures at a given quench depth and quench depth dependence of q_c).

q_{peak} versus time



q_m is a monotomically decreasing function of time. Coarnesing begins immediately after the quench and continues throughout the initial stages of spinodal decomposition.

Typical SANS Data

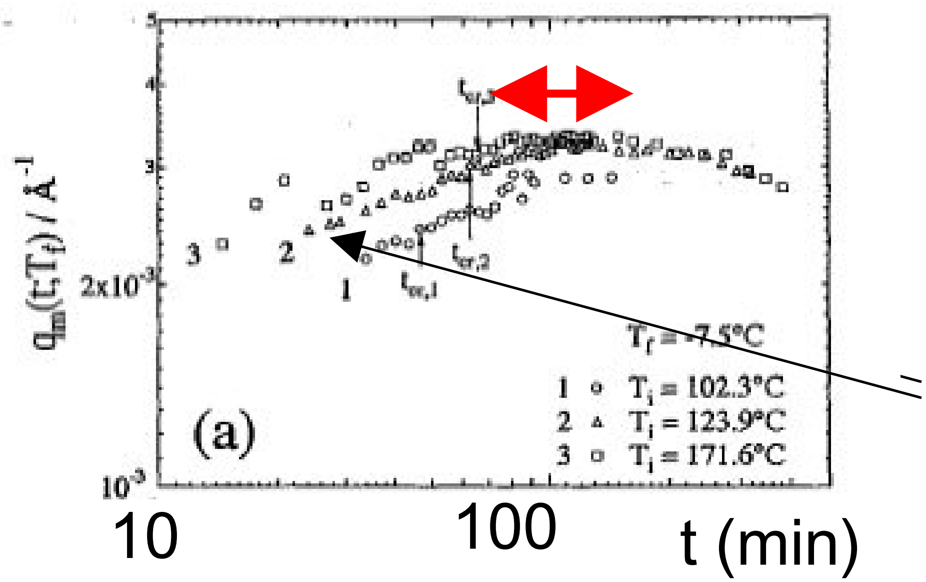


Cahn-Hilliard-Cook Analysis

$$I(q,t) = I_T(q) + [\ I_0(q)-I_T(q)\ ]\exp[\ 2R(q)t\ ]$$

I_0,I_T,R at each q are fitting parameters.

Data of Jinnai et al.



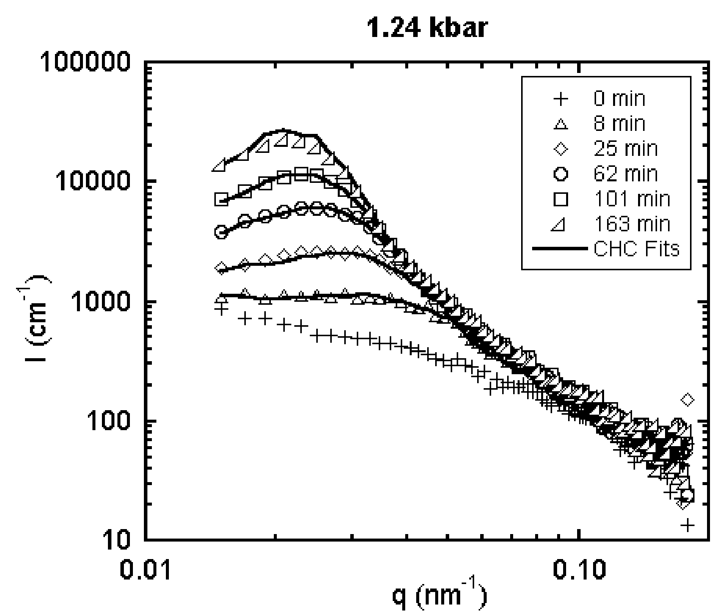
"Actually it took finite time to cool the specimen…"

Early time data at lower quench depth.

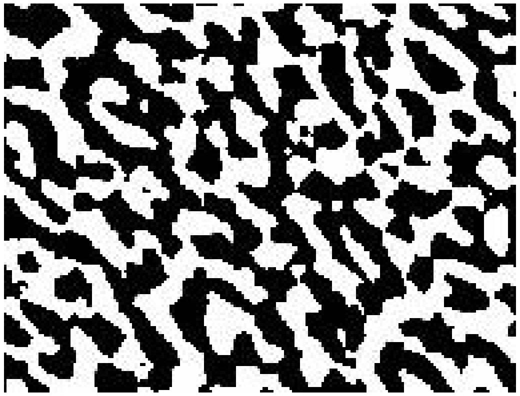
We suggest that the "plateau" is simply a cross-over from the cooling artifact to the initial stages where coarsening occurs continuously.

Main Conclusion on Spinodal Decomposition

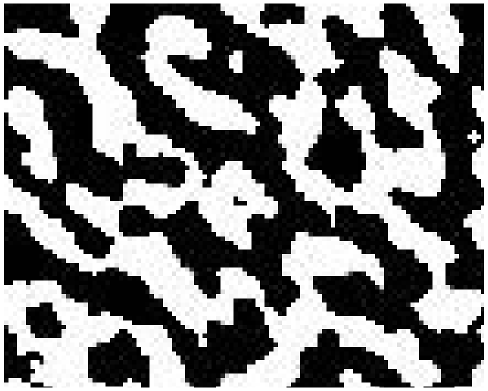
Non-linear theory of the initial stages is probably needed for analyzing early stage data, especially near $q=q_{peak}$ (not at q_c).



Coarsening Occurs at Later Stages



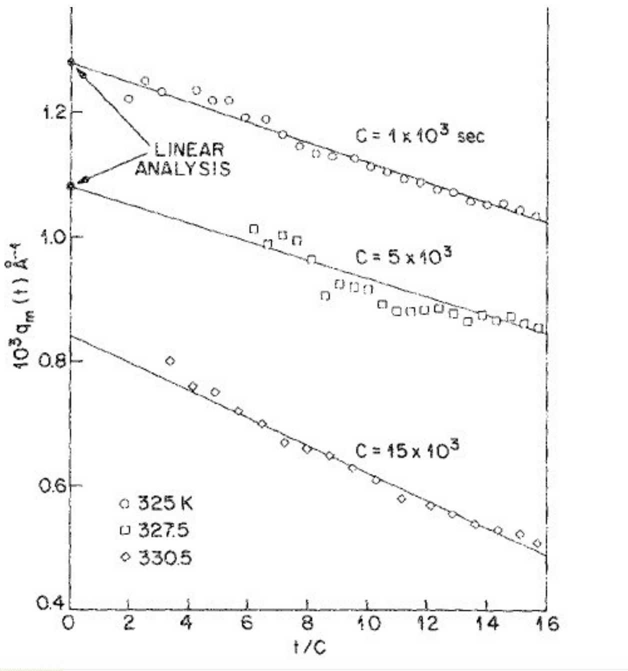
Initial structure

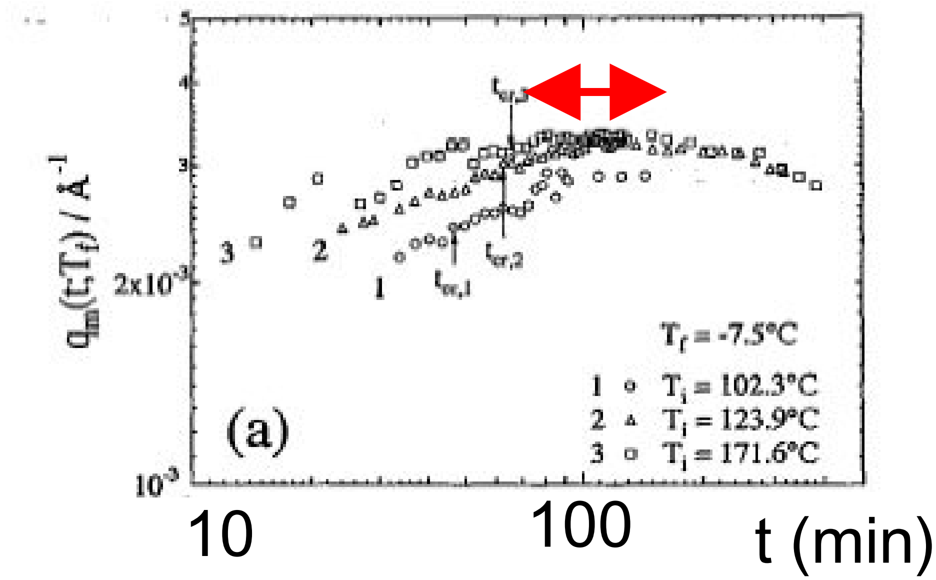


Late time structure

Late stage coarsening mechanisms are well established (interfacial effects, hydrodynamics, etc.)

No data with time independent q_{peak}





Jinnai, Hasegawa, Hashimoto, Han, JCP, 1989

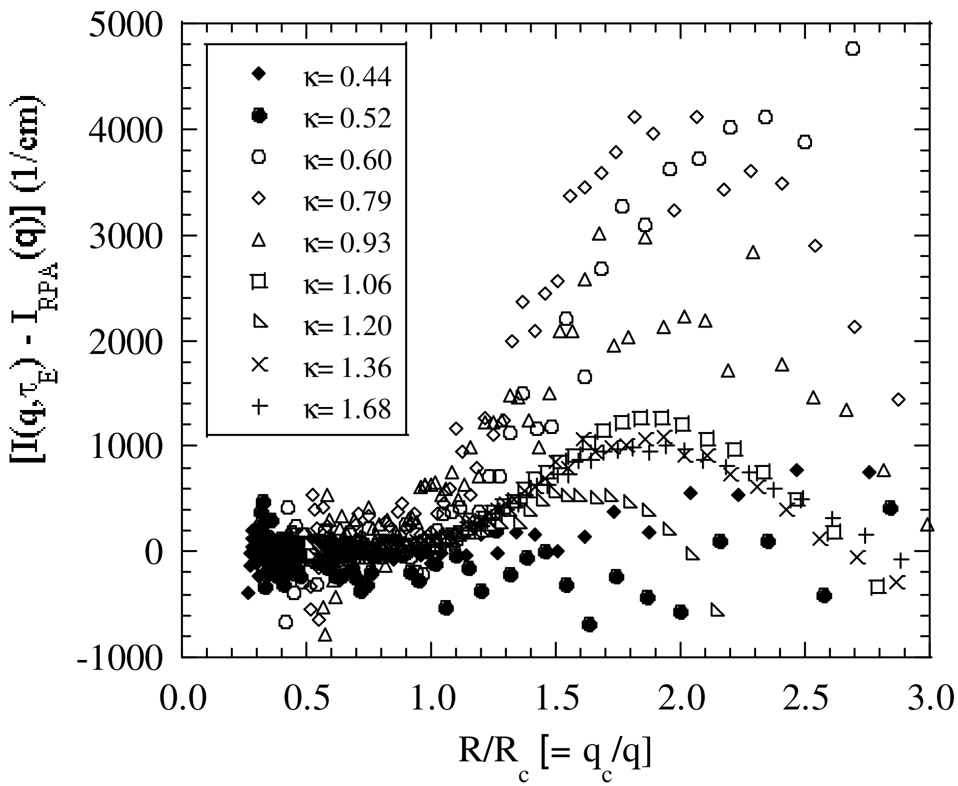
Bates, Wiltzius JCP, 1989:

"In none of our measurements have we observed our scattering peak to be stationary…despite… q_{peak} *was well within experimental resolution."*

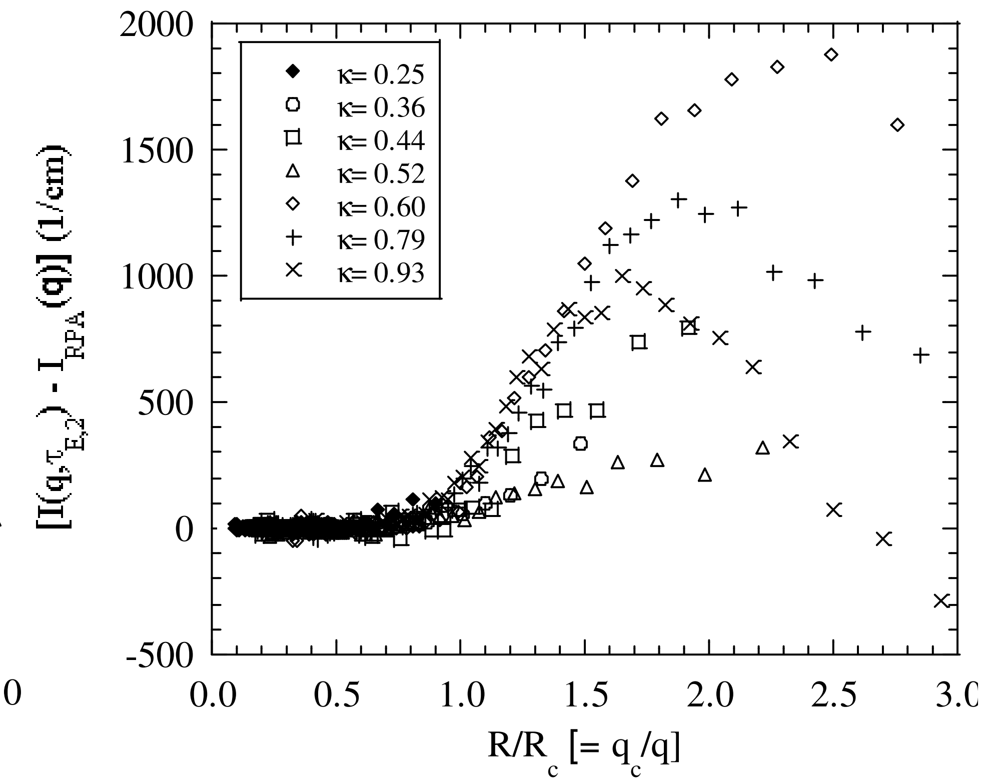

Tim
Amy


Tim

Structure of B4 at $t=\tau_{nucl}$

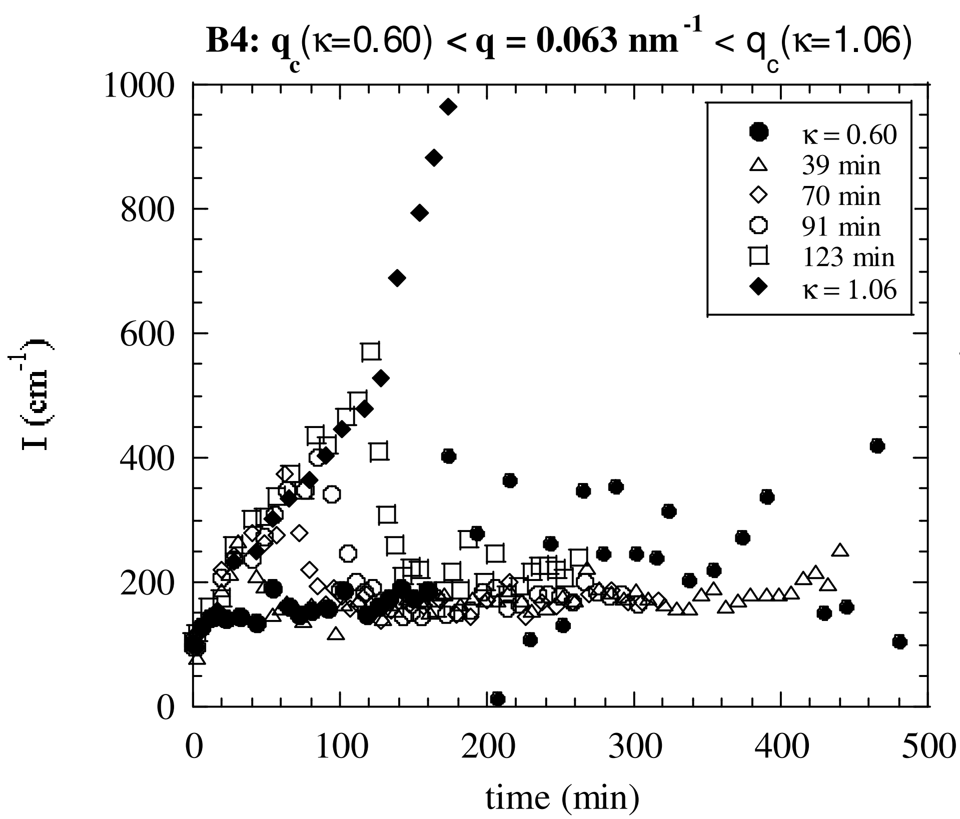


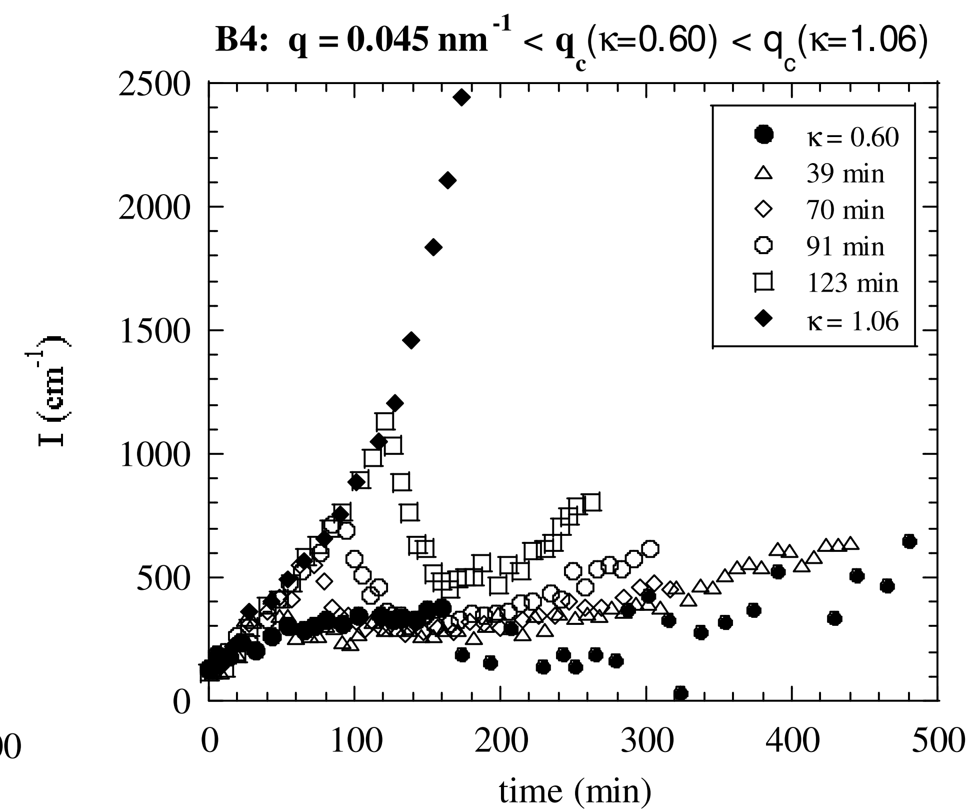
Direct Quenches



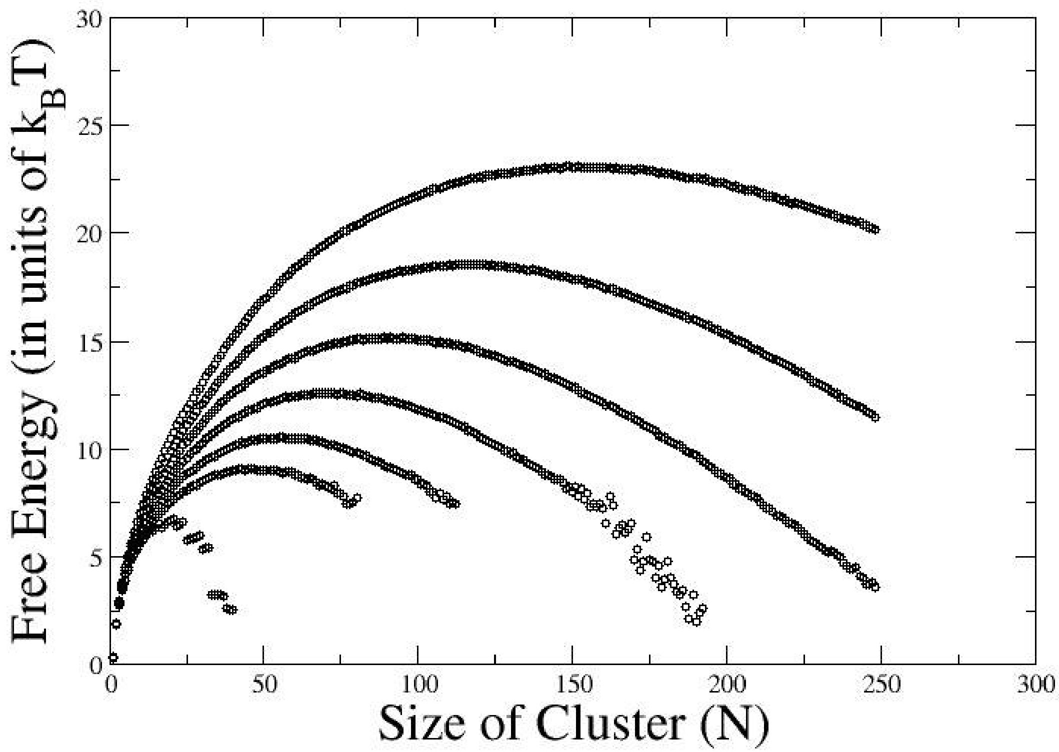
Indirect Quenches

Effect of Age time, τ_1



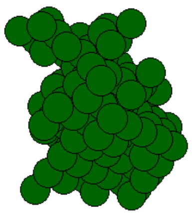


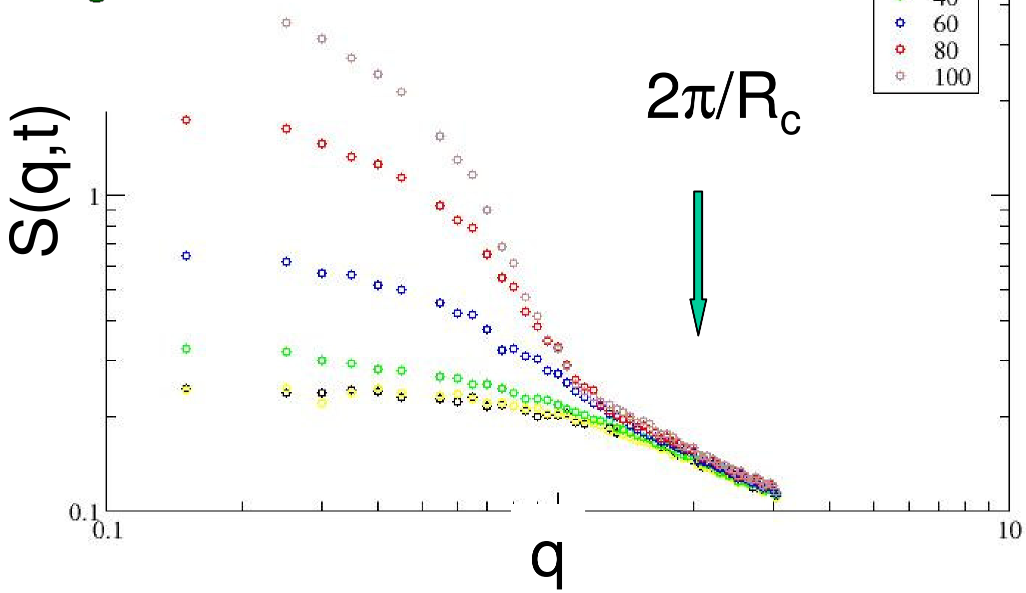
Ising Spinodal



at h=0.8
N is not an appropriate order parameter.

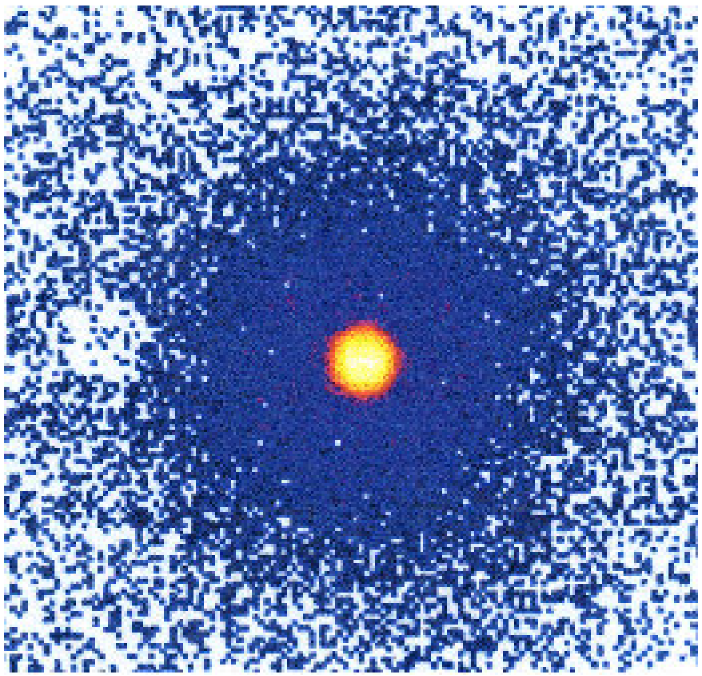
Albert Pan, David Chandler

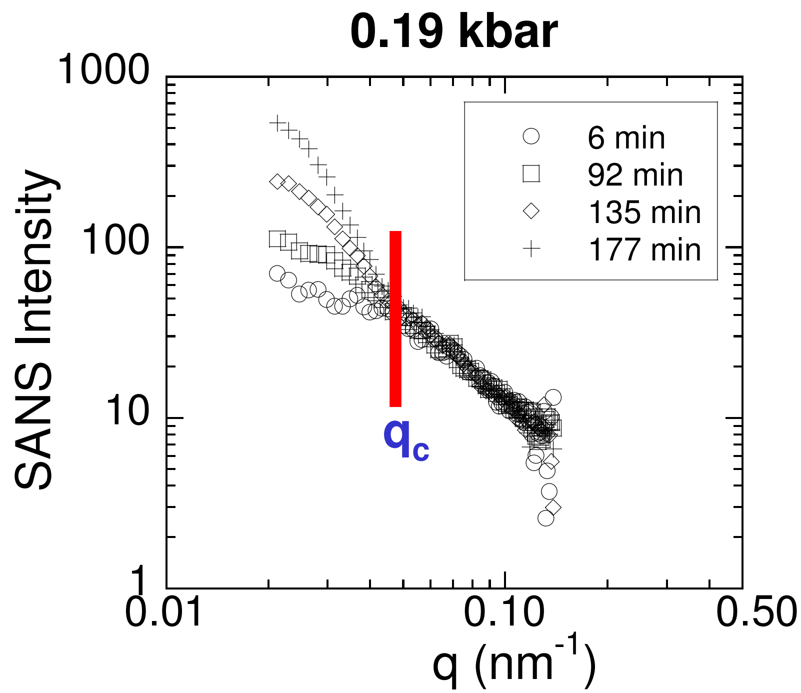




Ising Model
T = 0.6Tc, h = 0.55, J = -1. The critical nucleus is of size, N = 115 (giving kc = 2) formed at
t = 75.

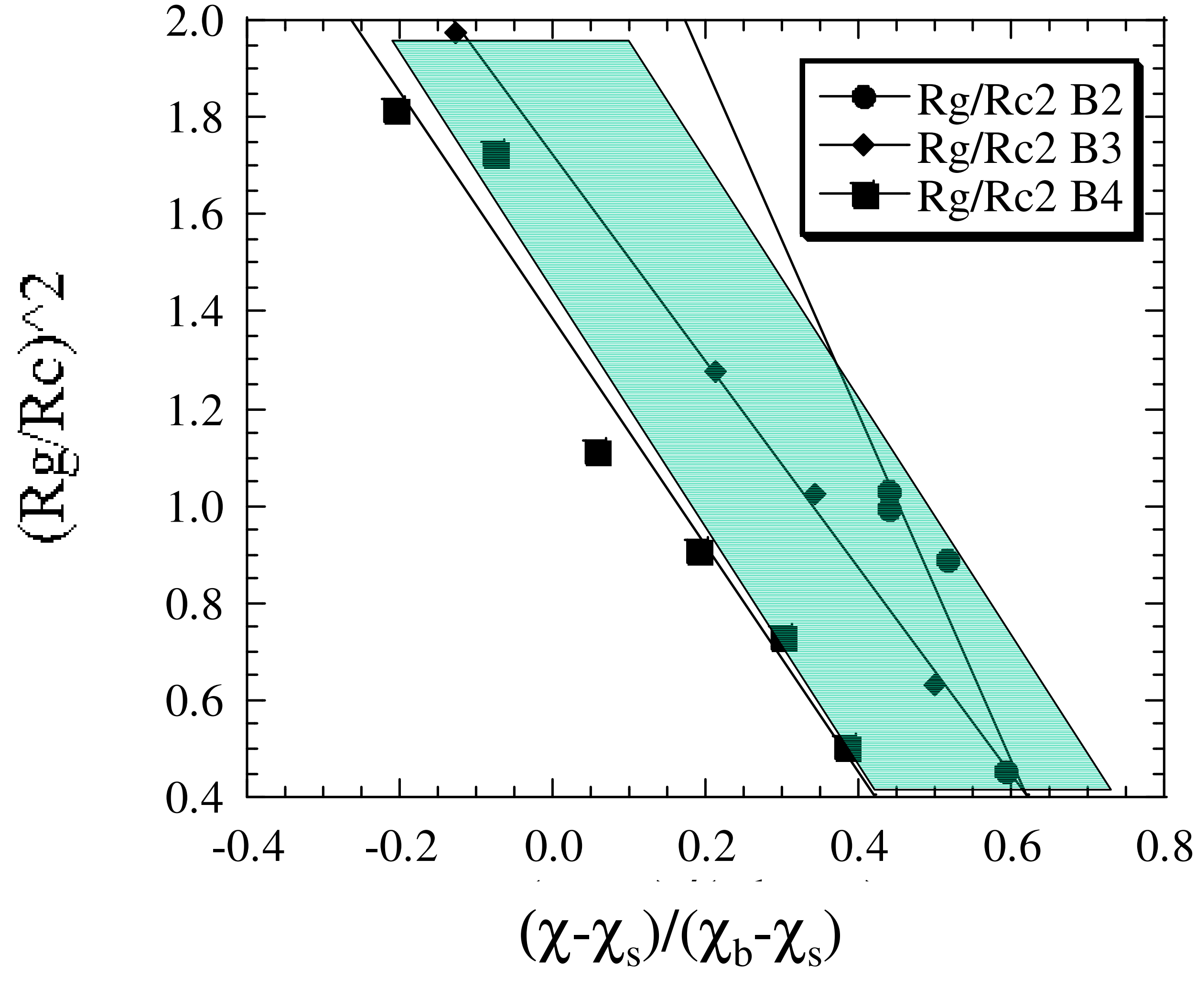
Critical Nucleus Signature





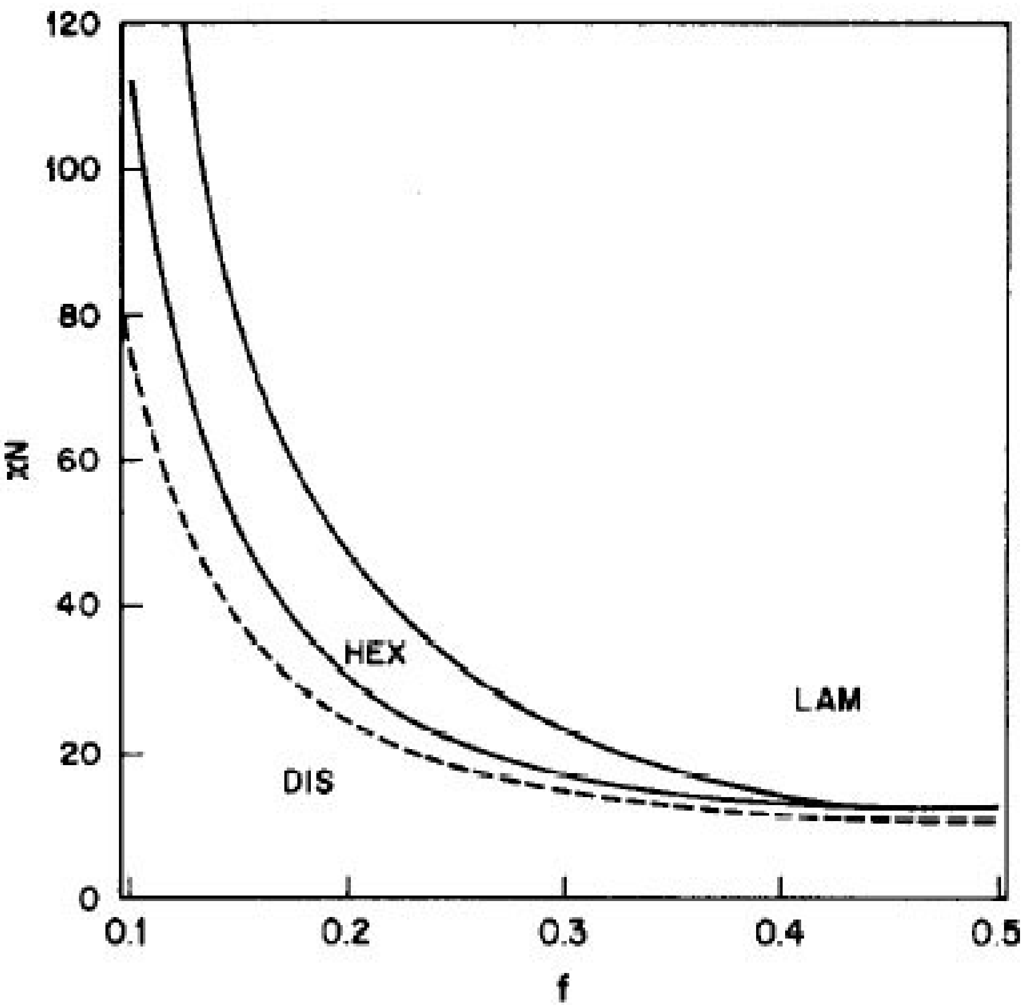
Our proposal might actually be universal!

Partial collapse of data



Fluctuation effects in the theory of microphase separation in block copolymers

Glenn H. Fredrickson and Eugene Helfand
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

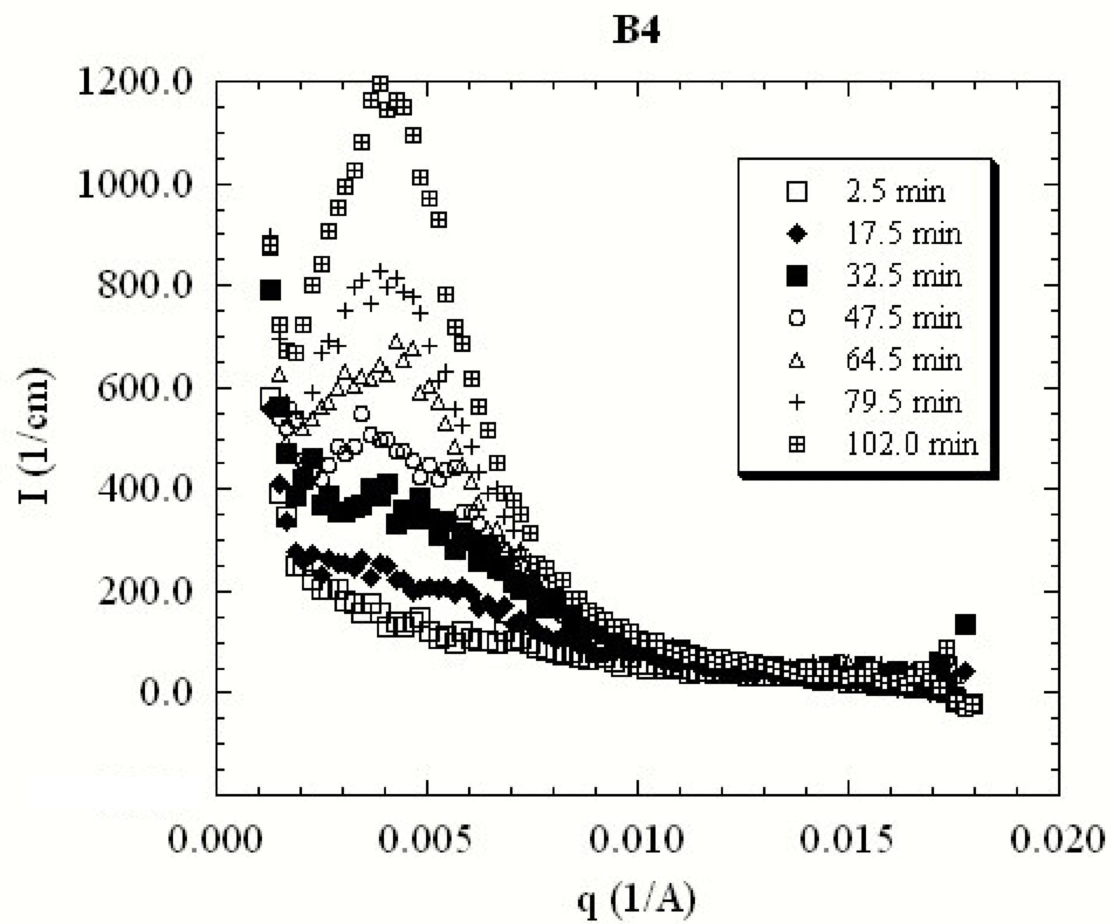


$N=10^4$

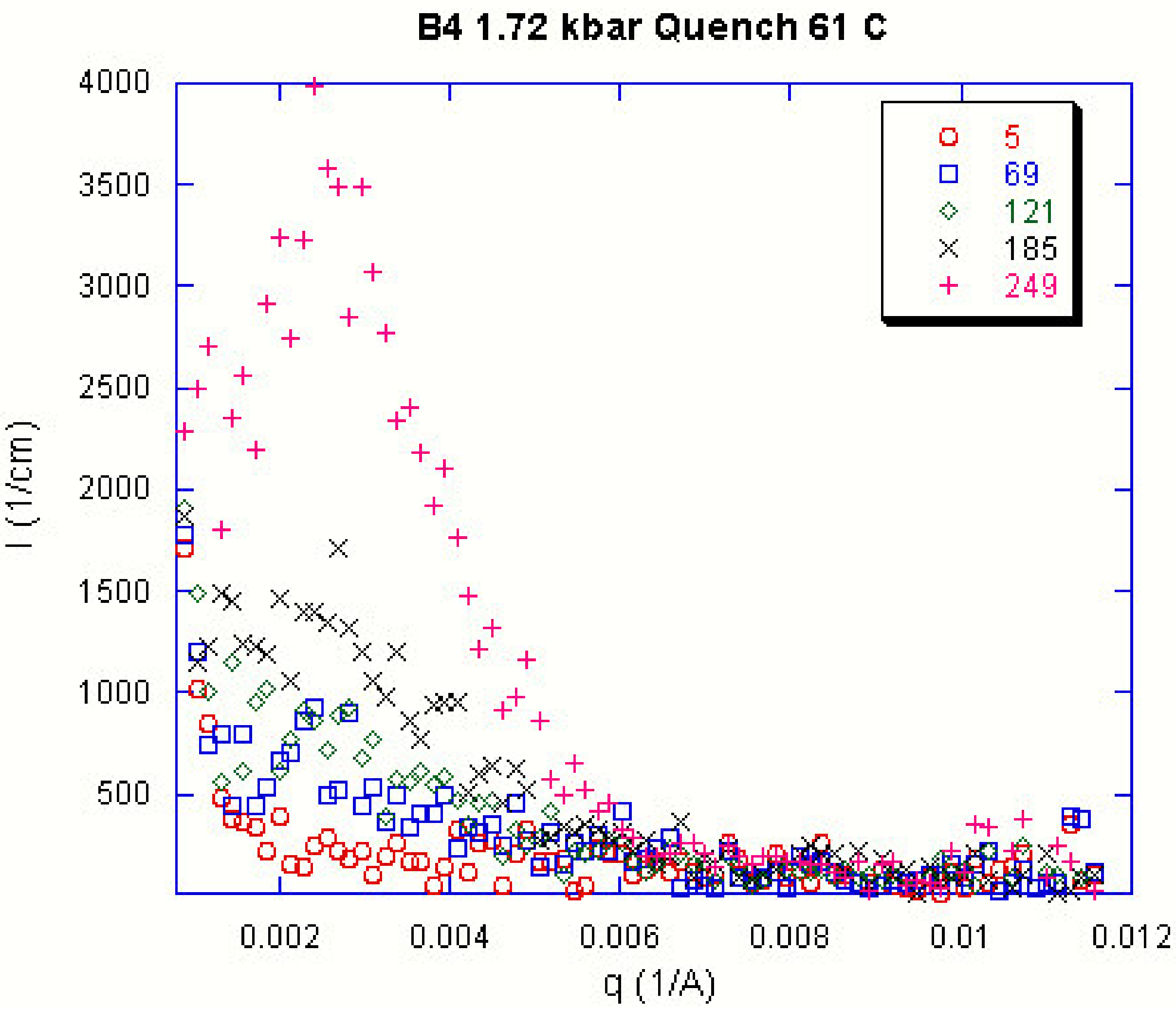
Fluctuation corrections are too large for theory!

J Chem Phys 1987.

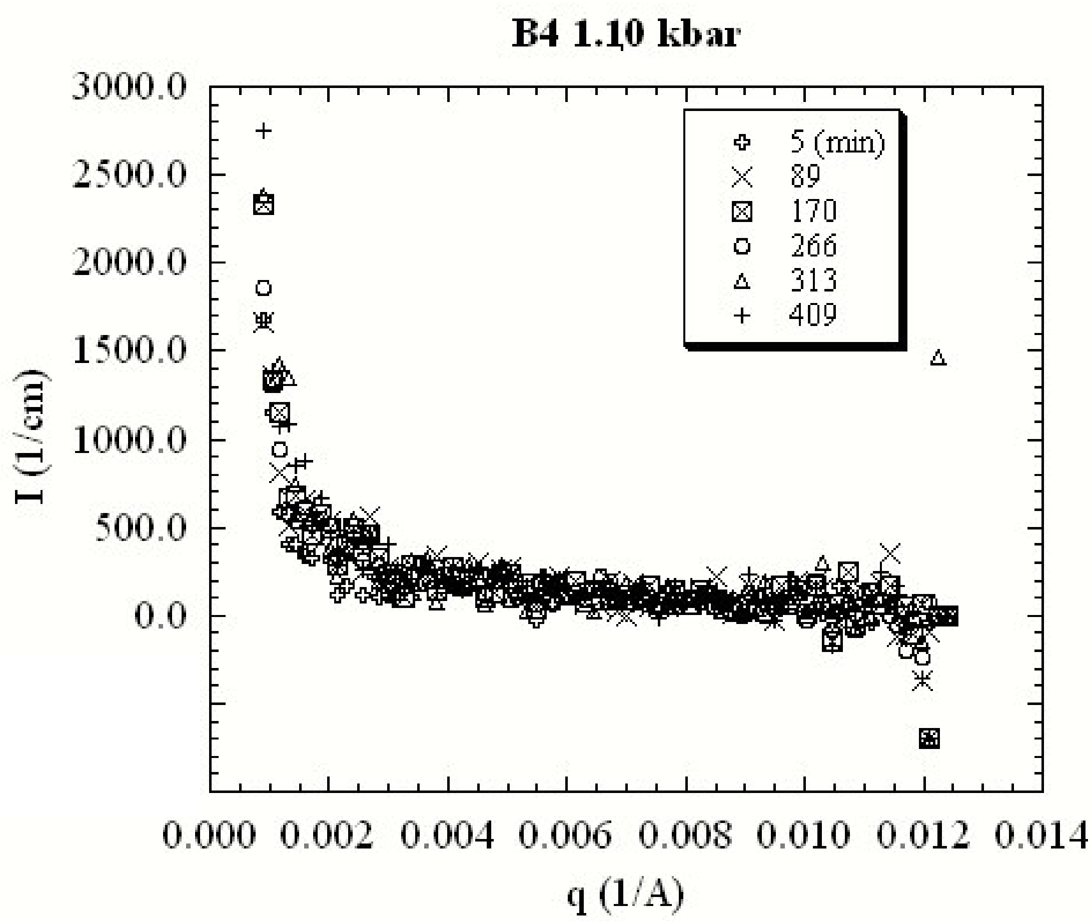
Nucleation during deep quench (2.69 kbar)



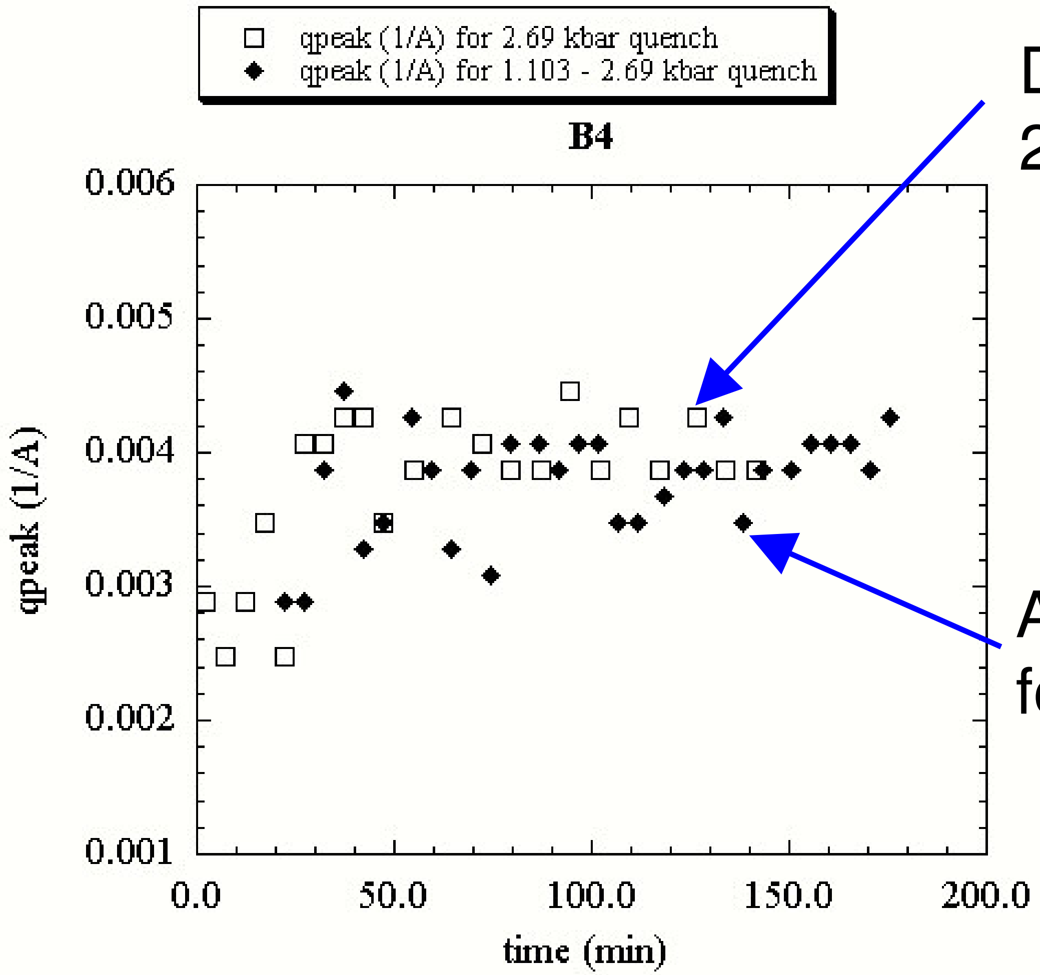
Nucleation near the edge of metastability



Nucleation beyond the metastability



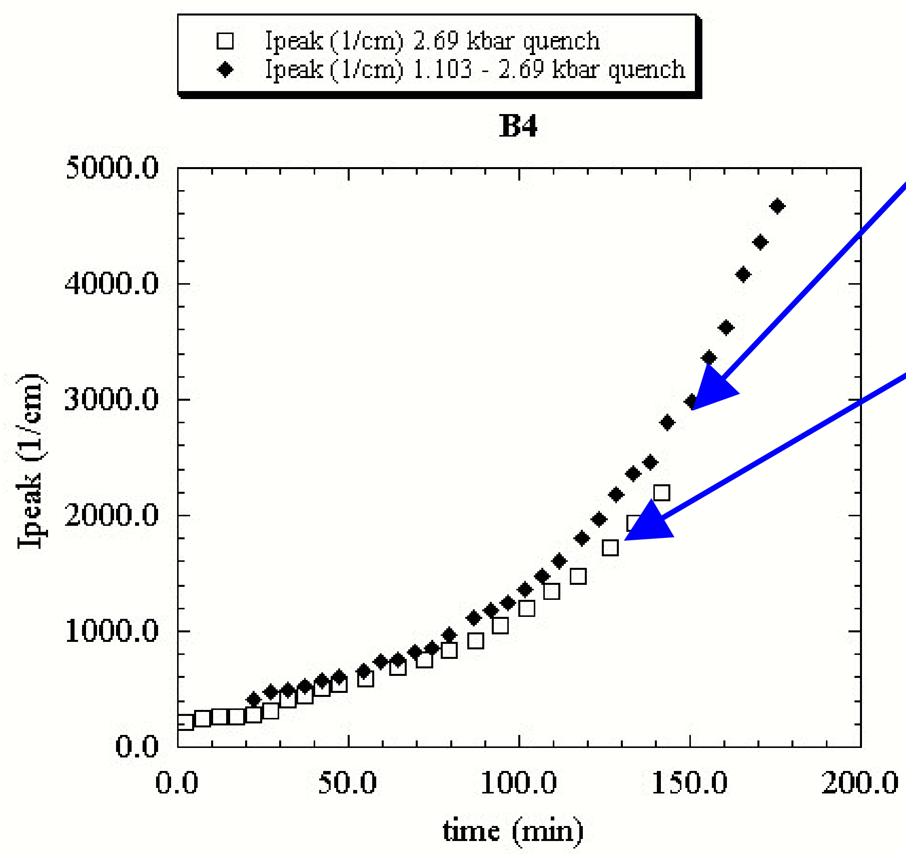
Effect of Aging



Direct quench to 2.69 kbar

After aging at 1.10 kb for 400 min

No effect of aging



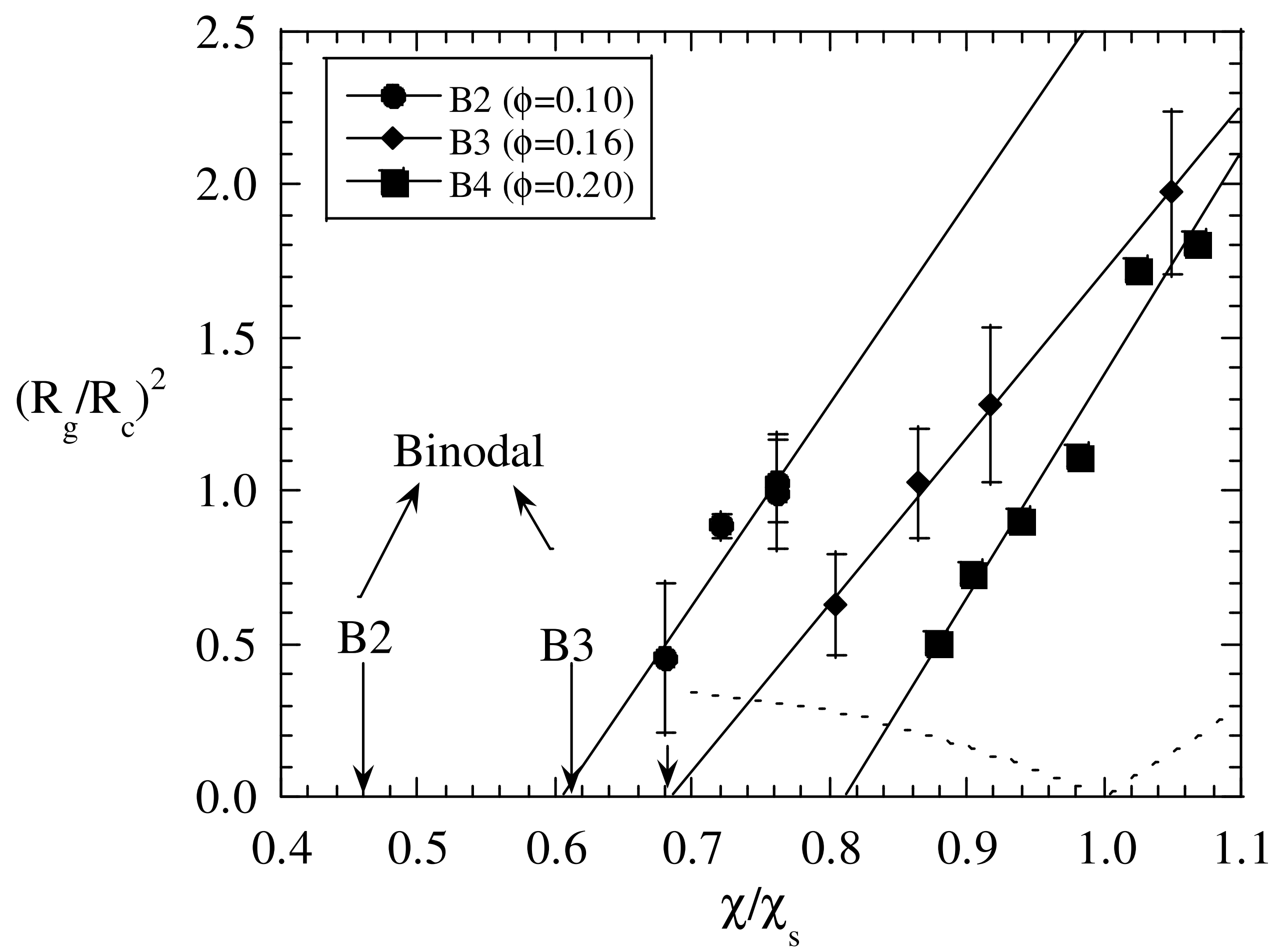
After aging for 400 min at 1.1 kbar

Direct quench to 2.69 kbar

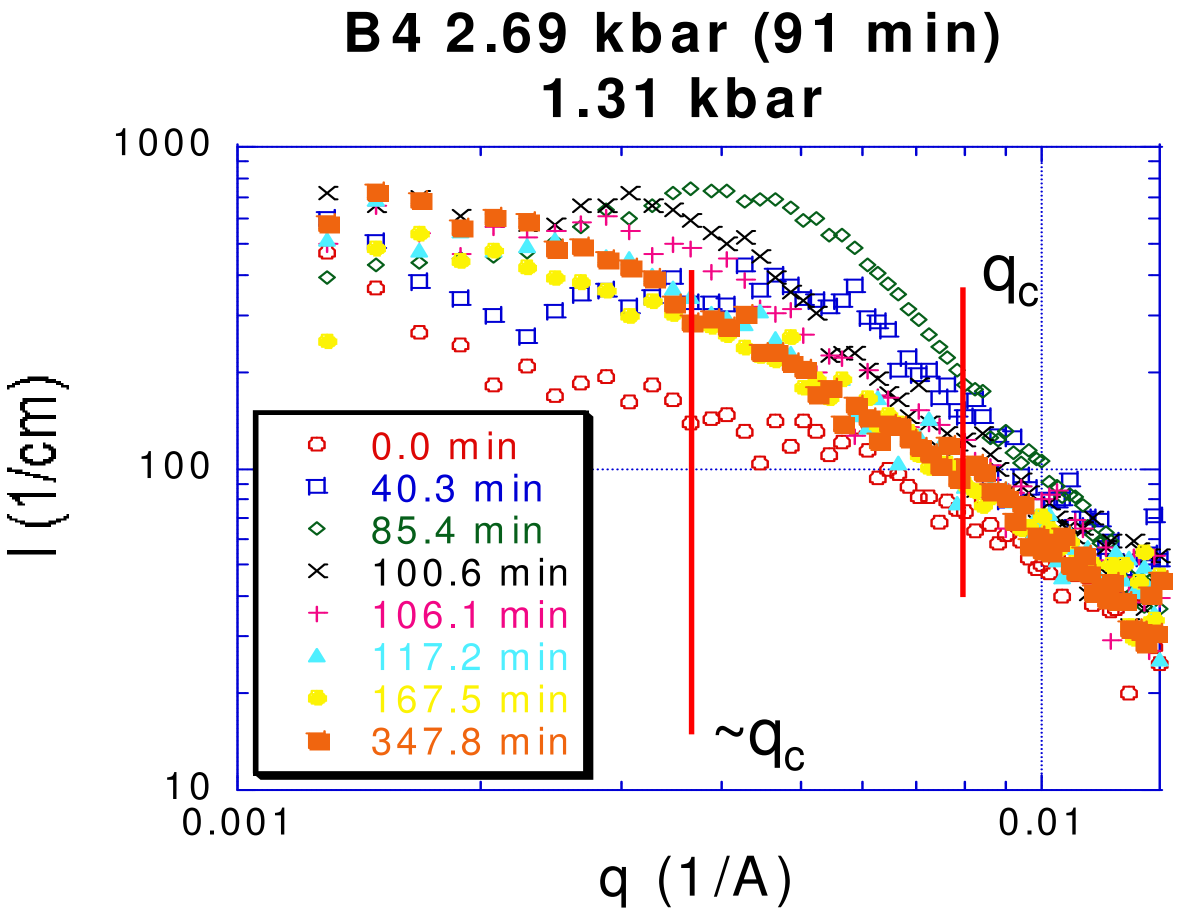
Within reproducibility

R_c=12.8 nm (aged)
R_c=11.6 nm (direct)

Added points to B4



Complete data set



Concluding Remarks

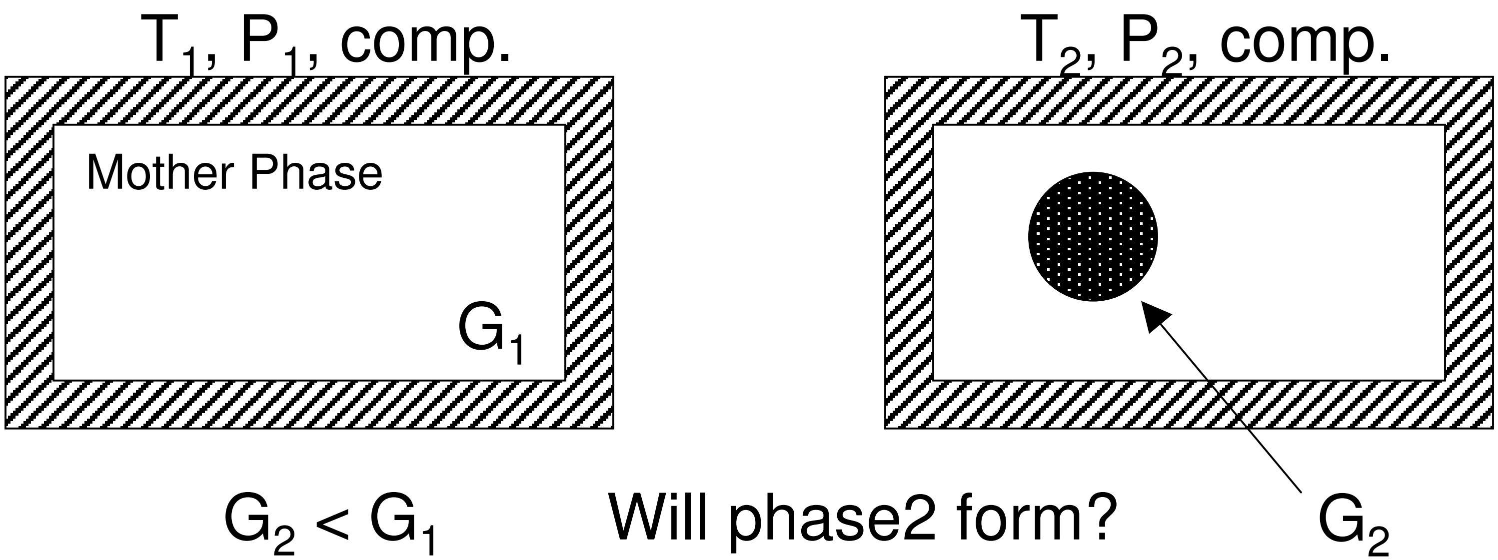
(1) The merging of the SANS profiles is a signature of the critical nucleus and its size $R_c=1/q_c$.

(2) Critical nucleus size decreases monotonically with increasing quench depth and is finite at the spinodal.

(3) Spinodal (critical opalecscence and τ_{nuc}->0) appears to have no dynamic significance.

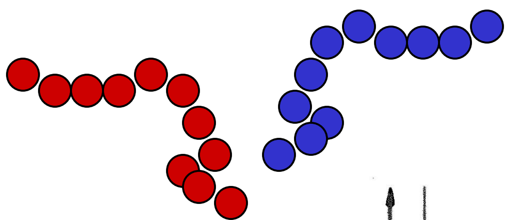
(4) Existence of a well-defined metastability limit.

Nucleation



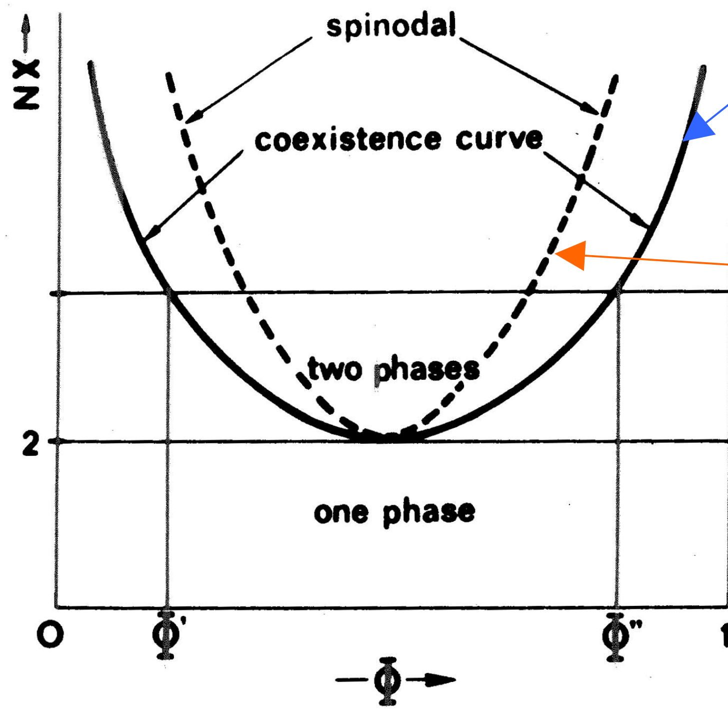
Answer: Depends (Gibbs), due to metastability of phase 1!
At any given time you can get either phase1 or phase2

Conventional wisdom (Flory, Huggins theory)



N=3000

Binodal curve (cloud point)



Spinodal curve (change of phase transition mechanism or "off-critical" opalescence)

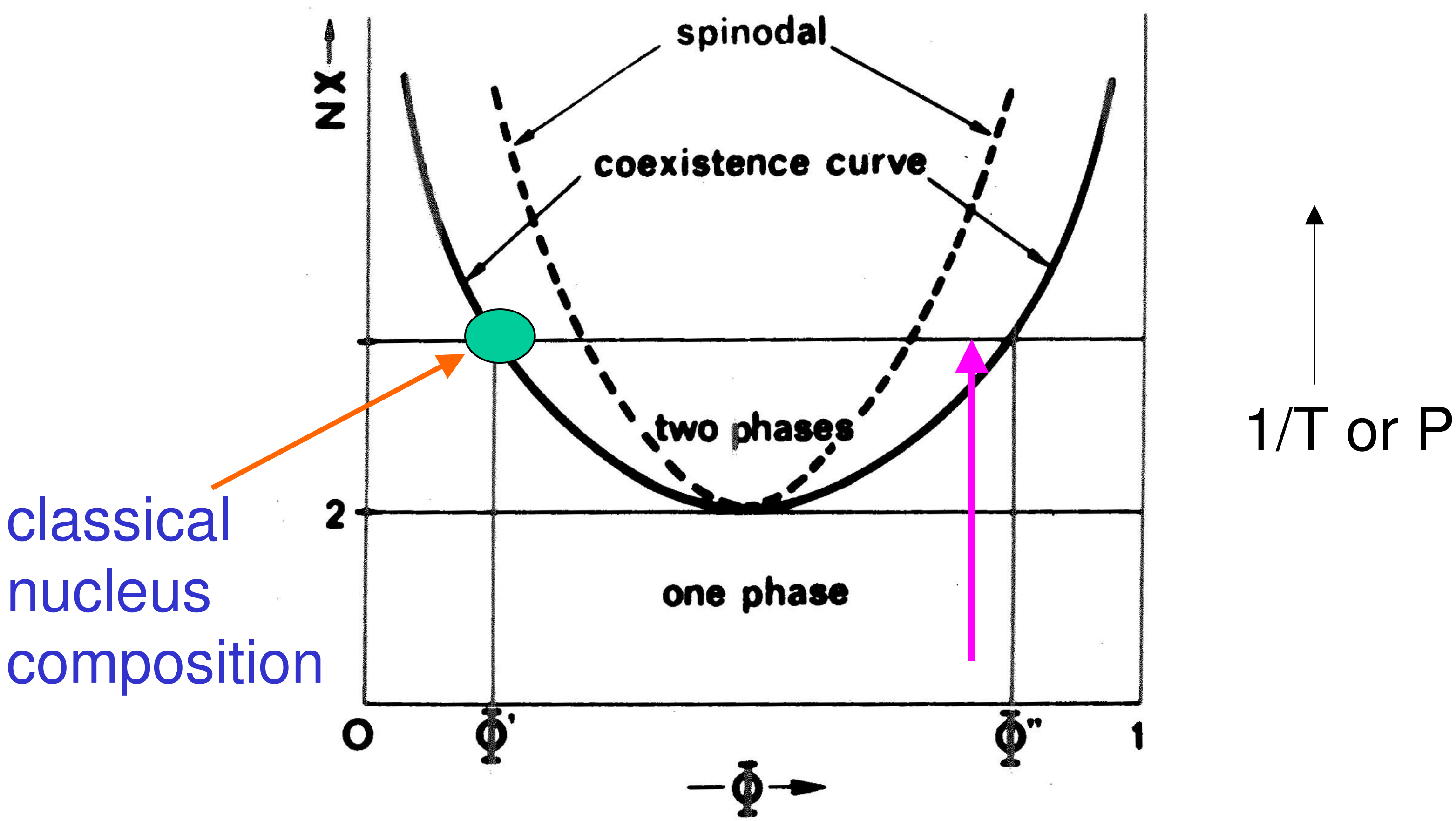
Gi~1/N, de Gennes

$\chi(T,P)\,N$

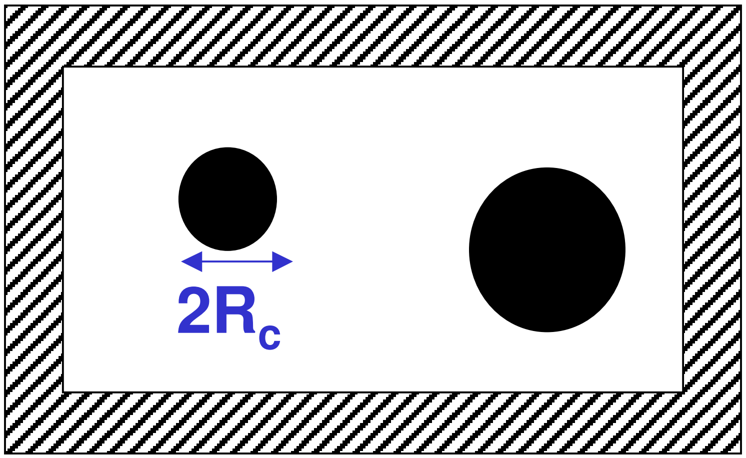
monomer-monomer interactions

Volume fraction, ϕ

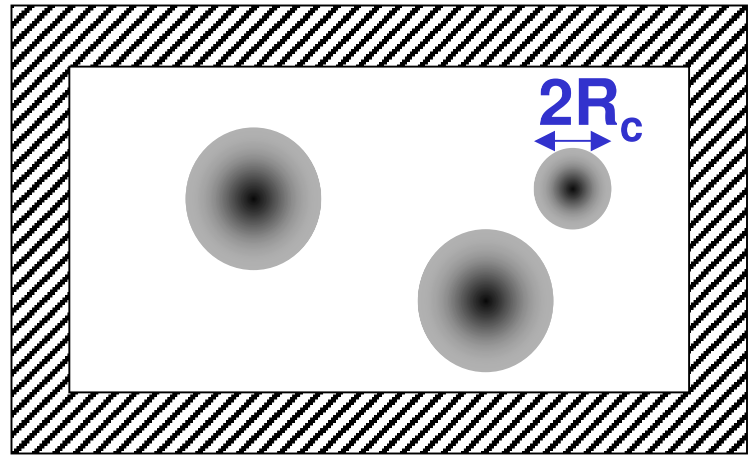
Classical nucleation in polymer blends



Liquid-liquid phase separation



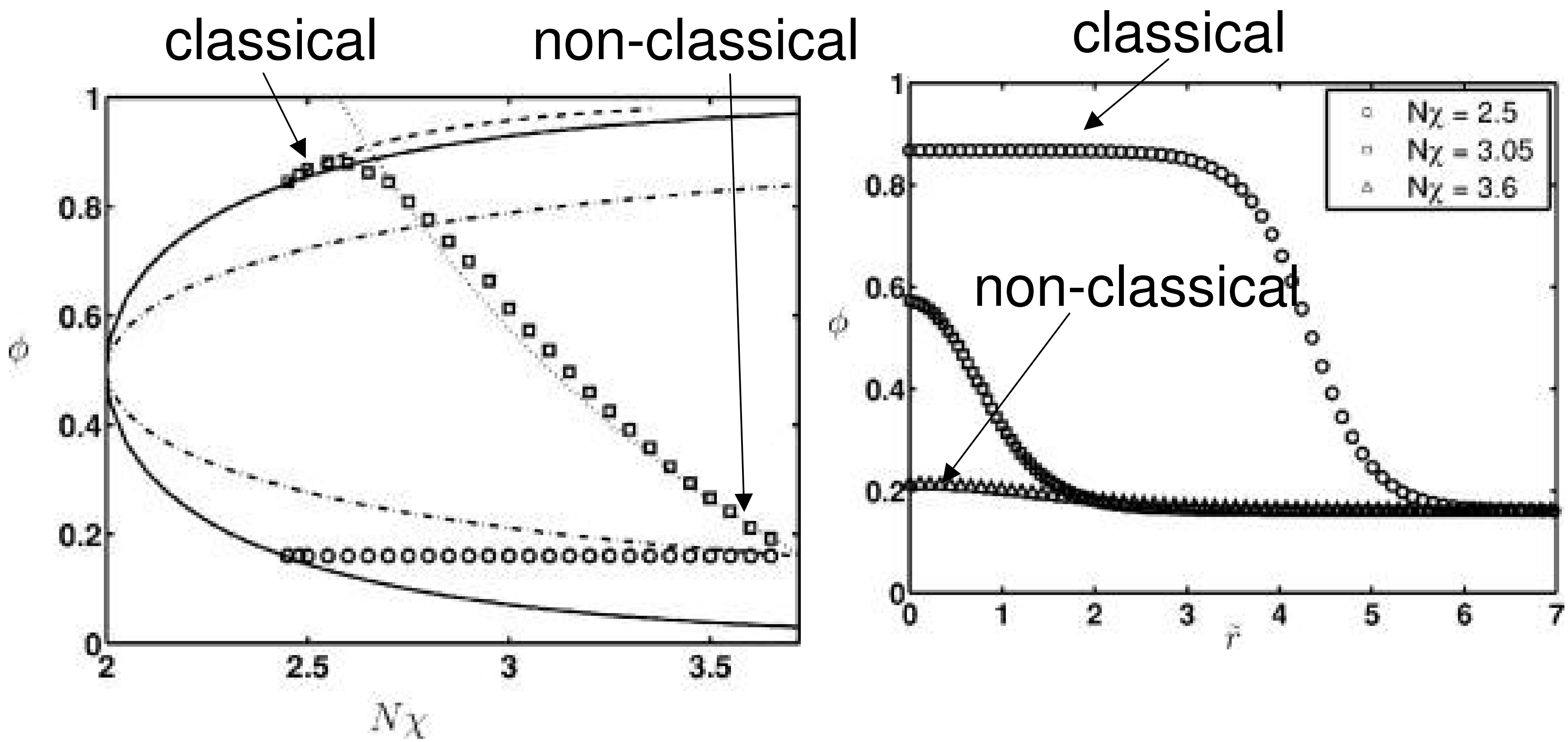
Gibbs



Cahn and Hilliard

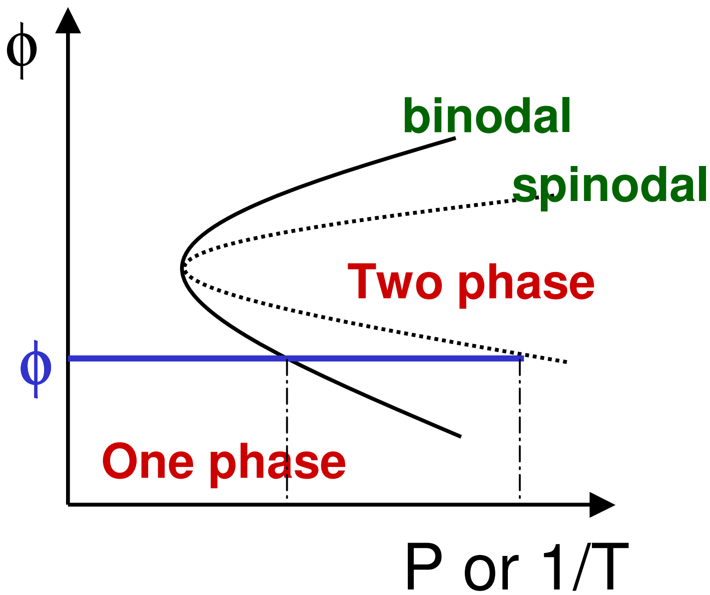
Nuclei that have diffuse interfaces and composition that are not that of the bulk equilibrium phase can be computed exactly! (Cahn and Hilliard, J. Chem. Phys., 1955-prelude to spinodal decomposition)

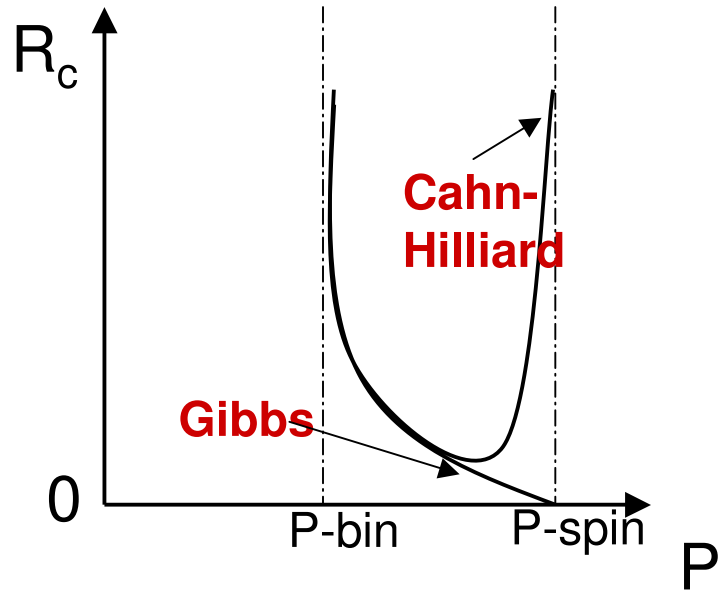
Predictions



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

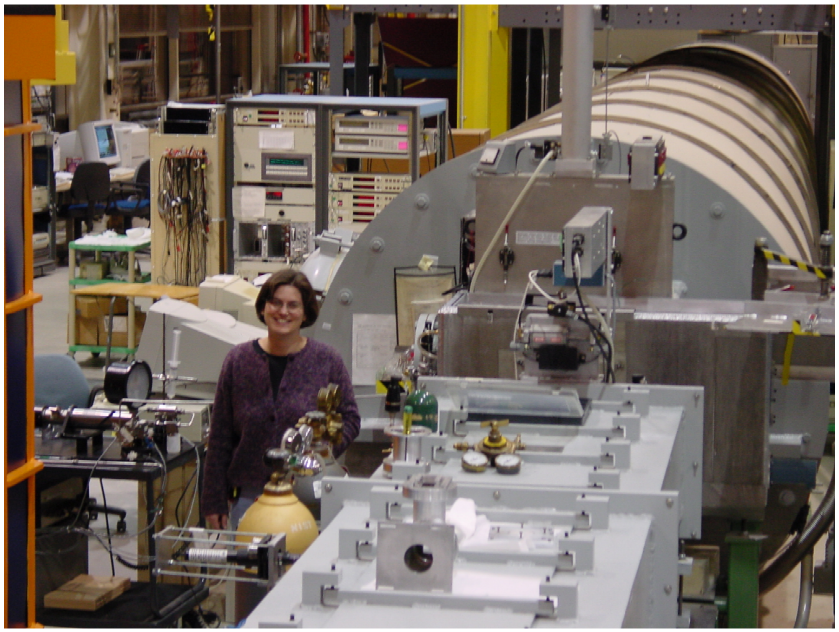
Predictions

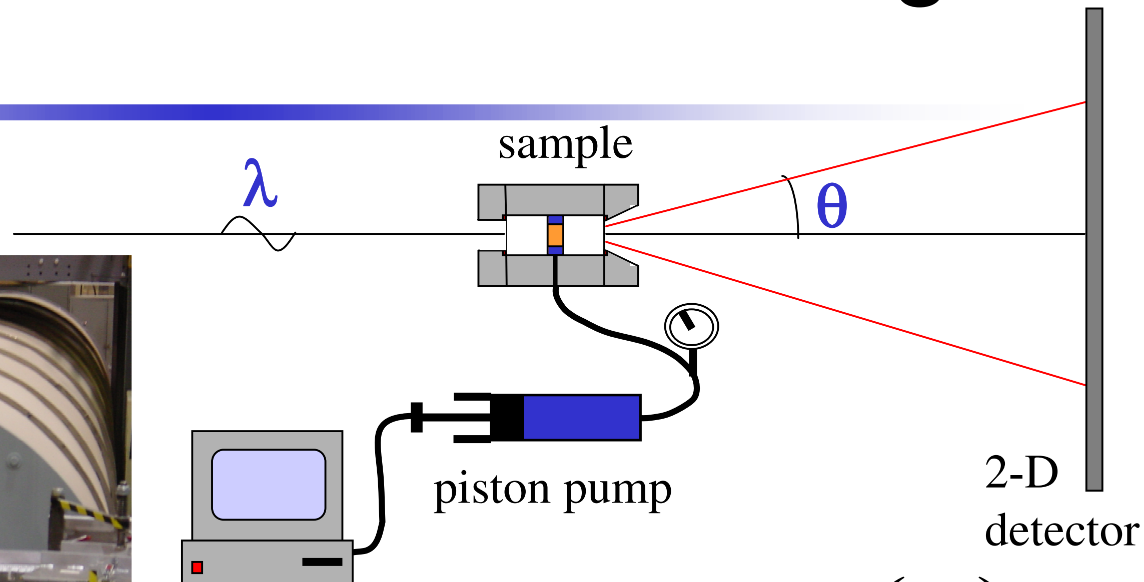




Two classical theories give opposite results. No experimental data on initial stages of nucleation.

Small-angle neutron scattering

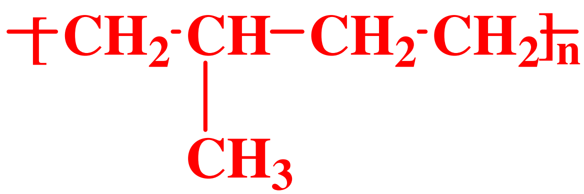




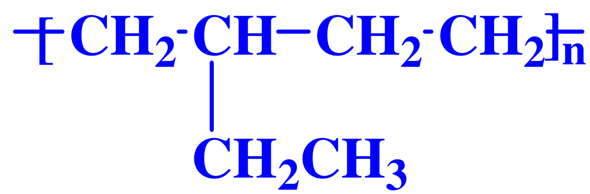
$$q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

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

Materials (Amy)



PM



PE

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

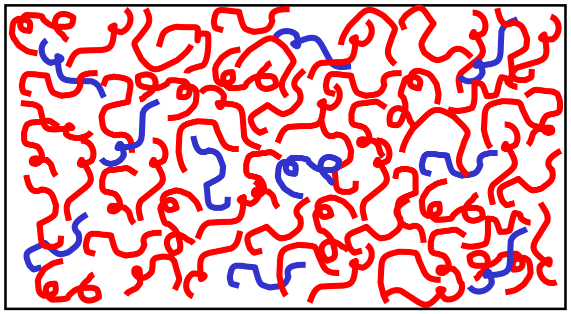
High vacuum anionic polymerization and high pressure catalysis polydispersity=1.03

Blends:

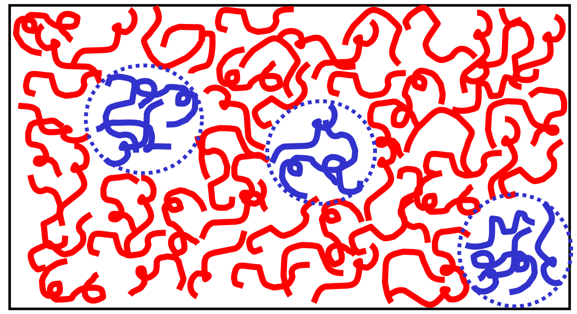
blend desig.	vol fr. of dPM
B2	0.16
B3	0.10

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.

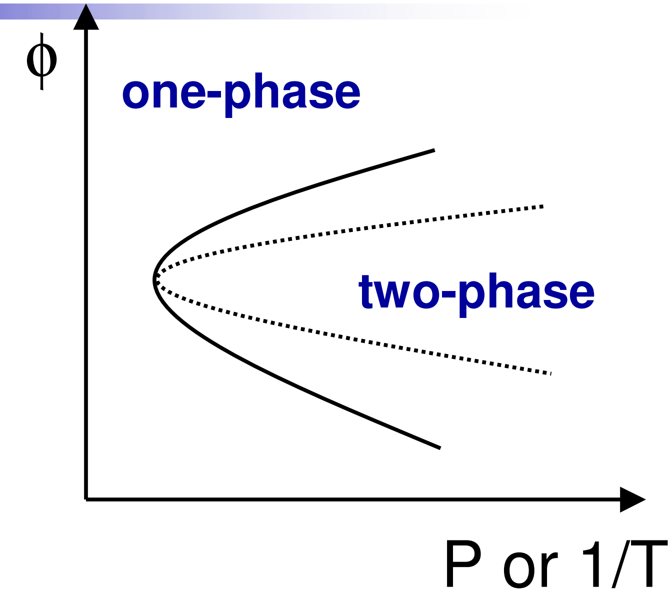
(Related experiments on crystallizing colloids by Weitz and Vekilov)

Outline of Work

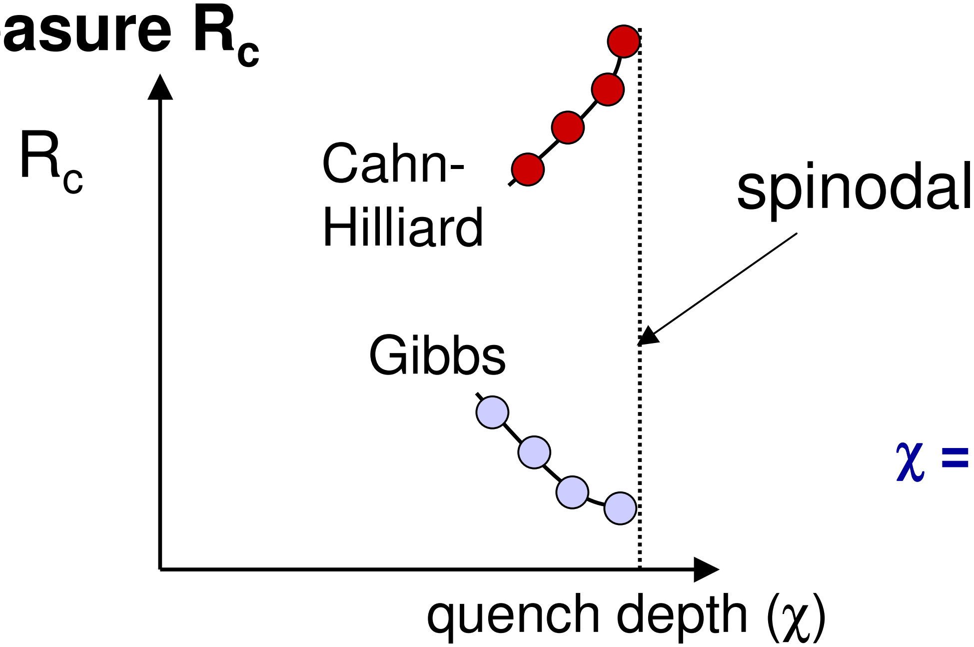
1. Establish Equilibrium Thermodynamics

   Lefebvre et al., Macromolecules, 2002

   Lefebvre et al., Macromolecules, 2000

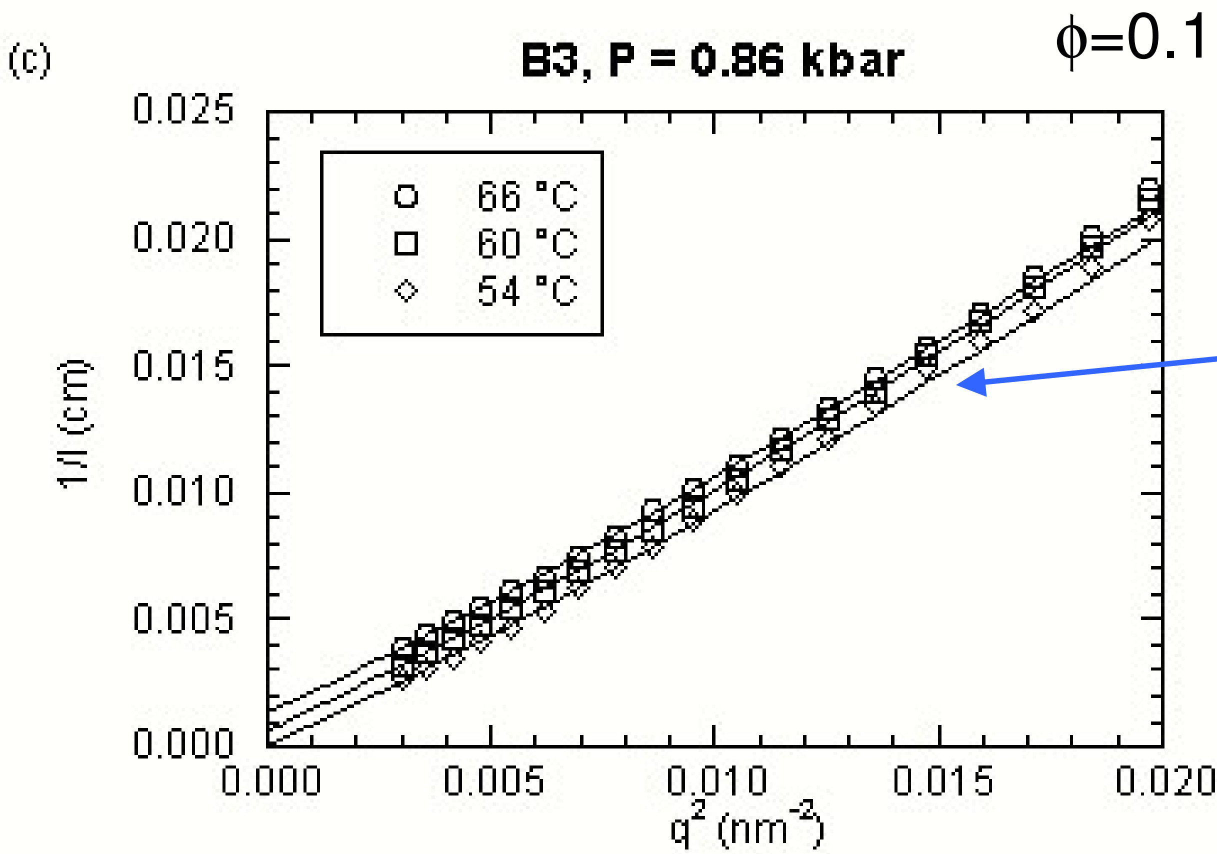


2. **Measure R_c**



χ = Flory-Huggins interaction parameter

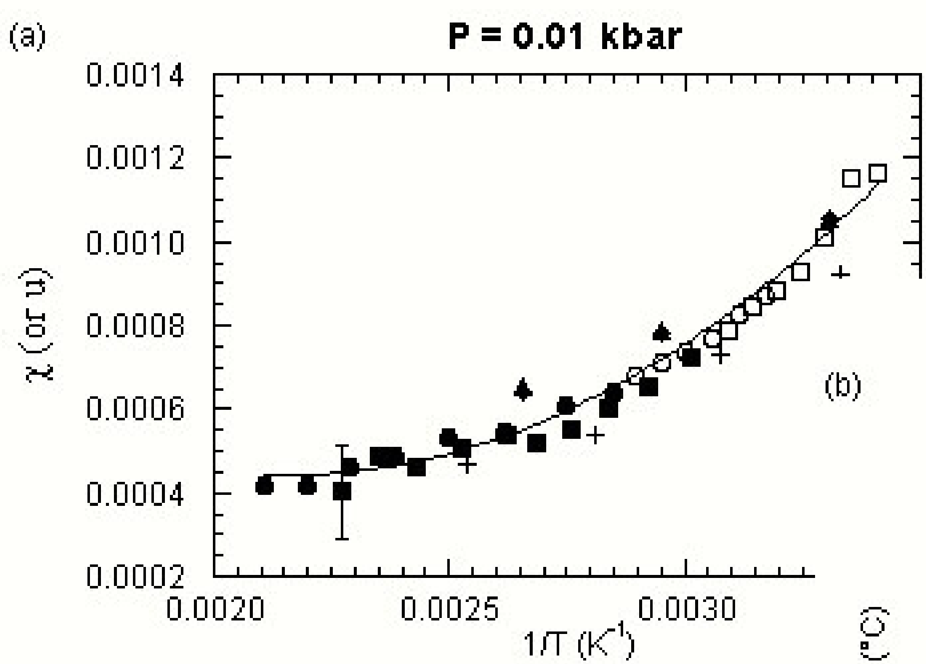
Typical SANS data in the **metastable** region

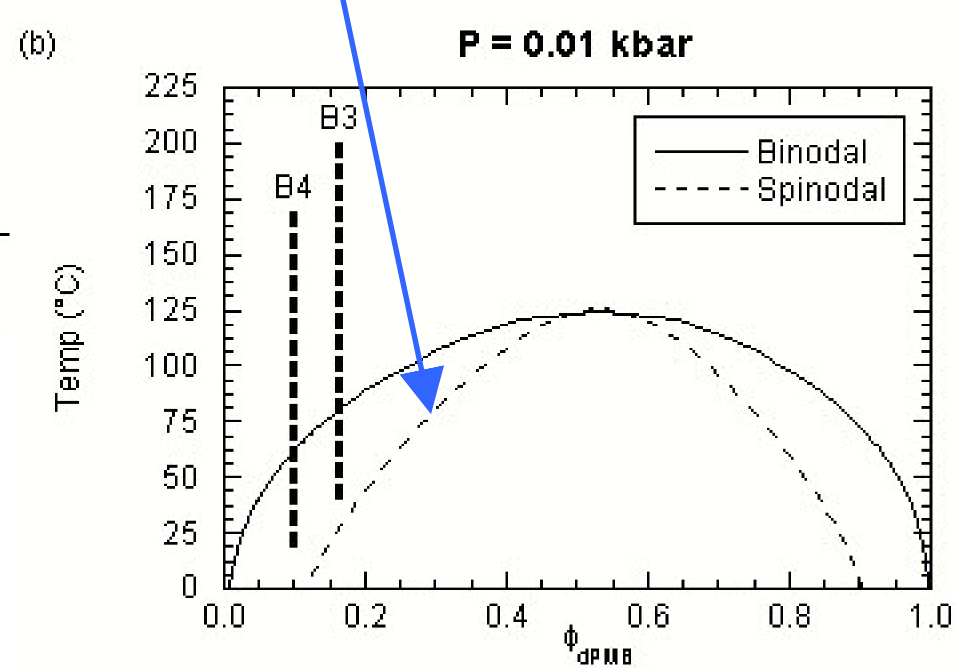


Random phase approximation fit gives χ.

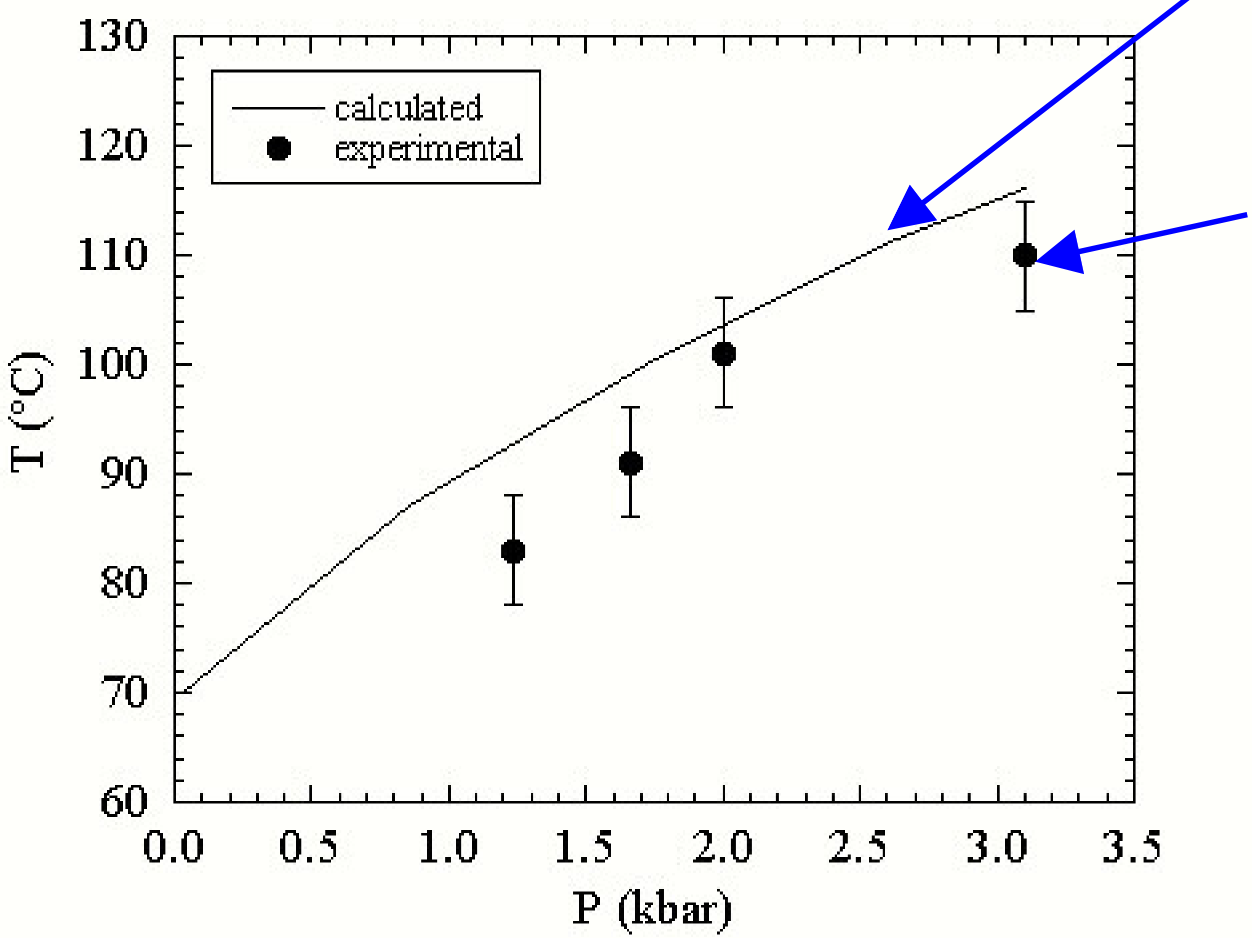
Spinodal Determination

Divergence of I(q) at q=0 or
Flory-Huggins calculations





Binodal Determination

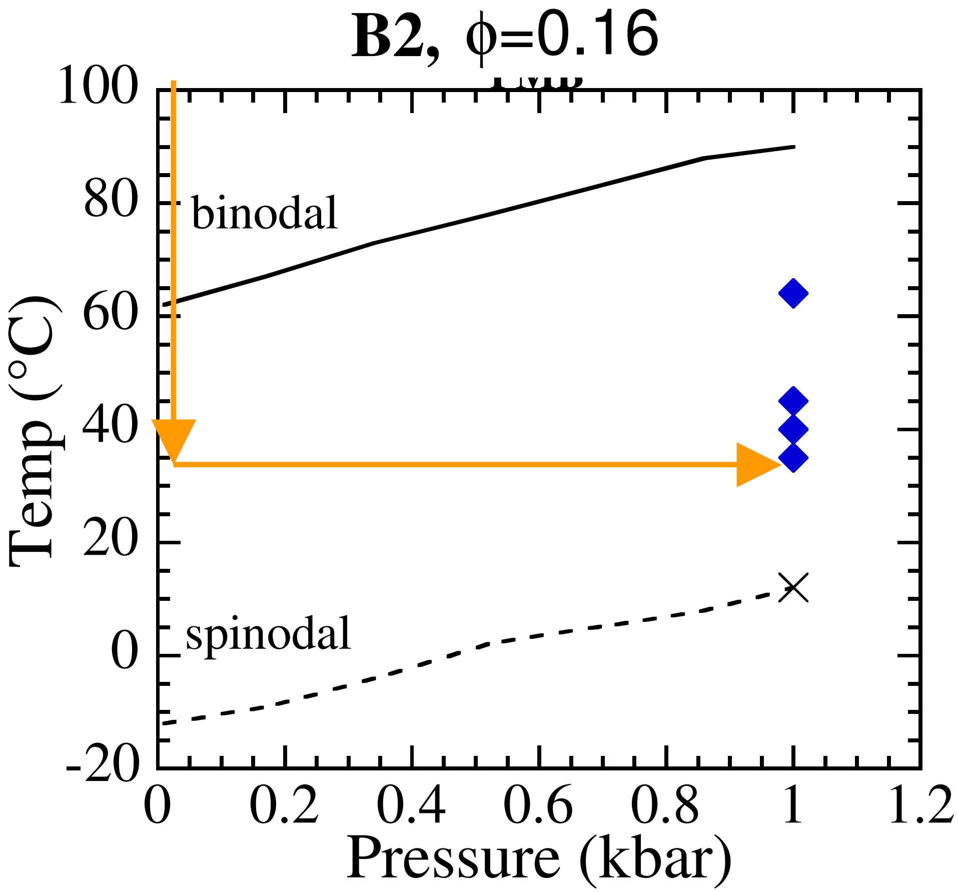


Flory-Huggins calculations.

Dissolution T at given P

Cannot use "cloud point" due to nucleation barriers.

Typical Protocol

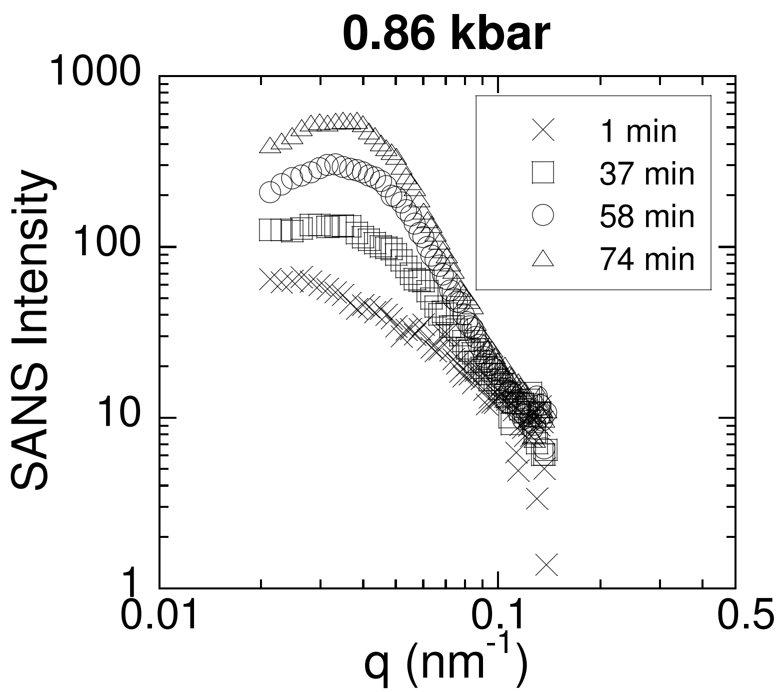


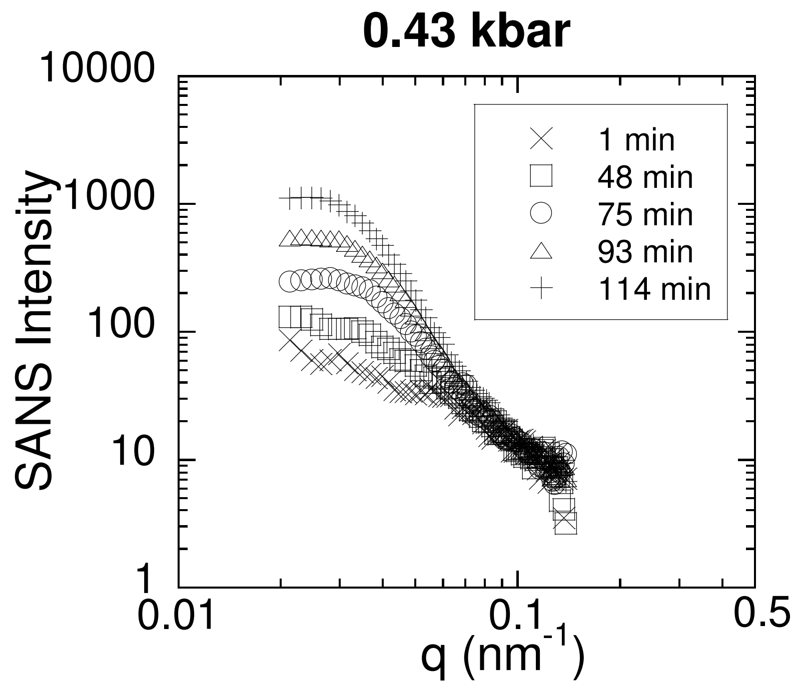
Anneal above the binodal at P=0.

Quench in two steps to final (T,P).

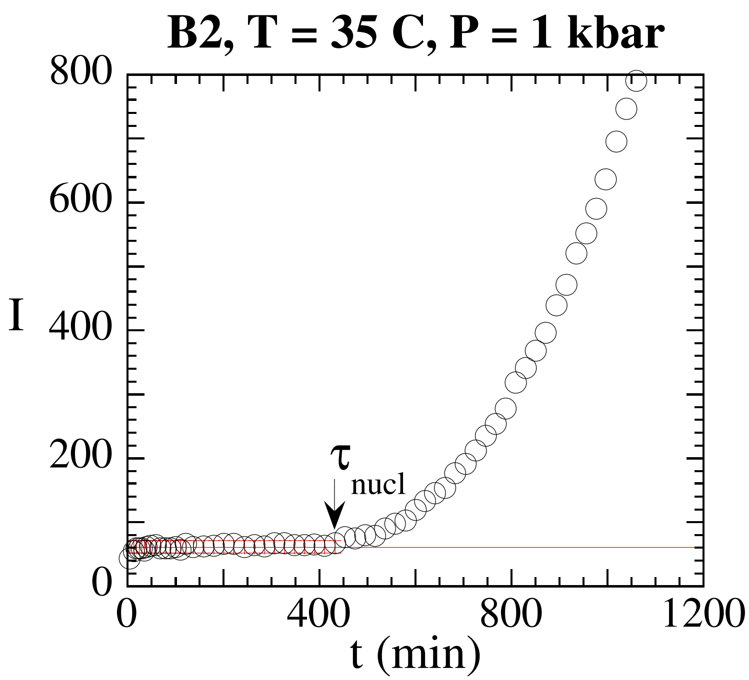
Phase separation triggered by the pressure quench.

SANS profiles



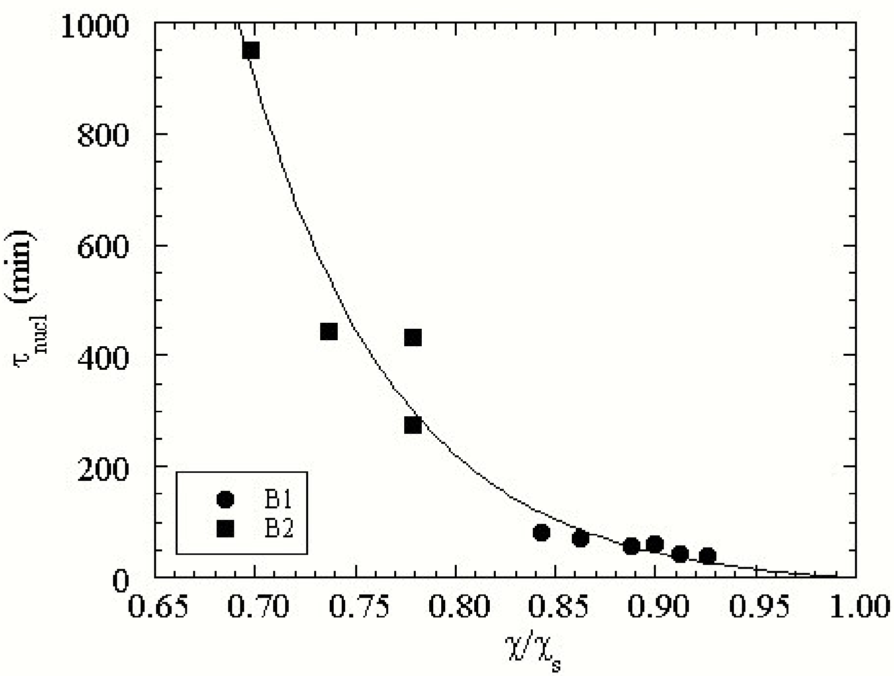


Nucleation Time Scale

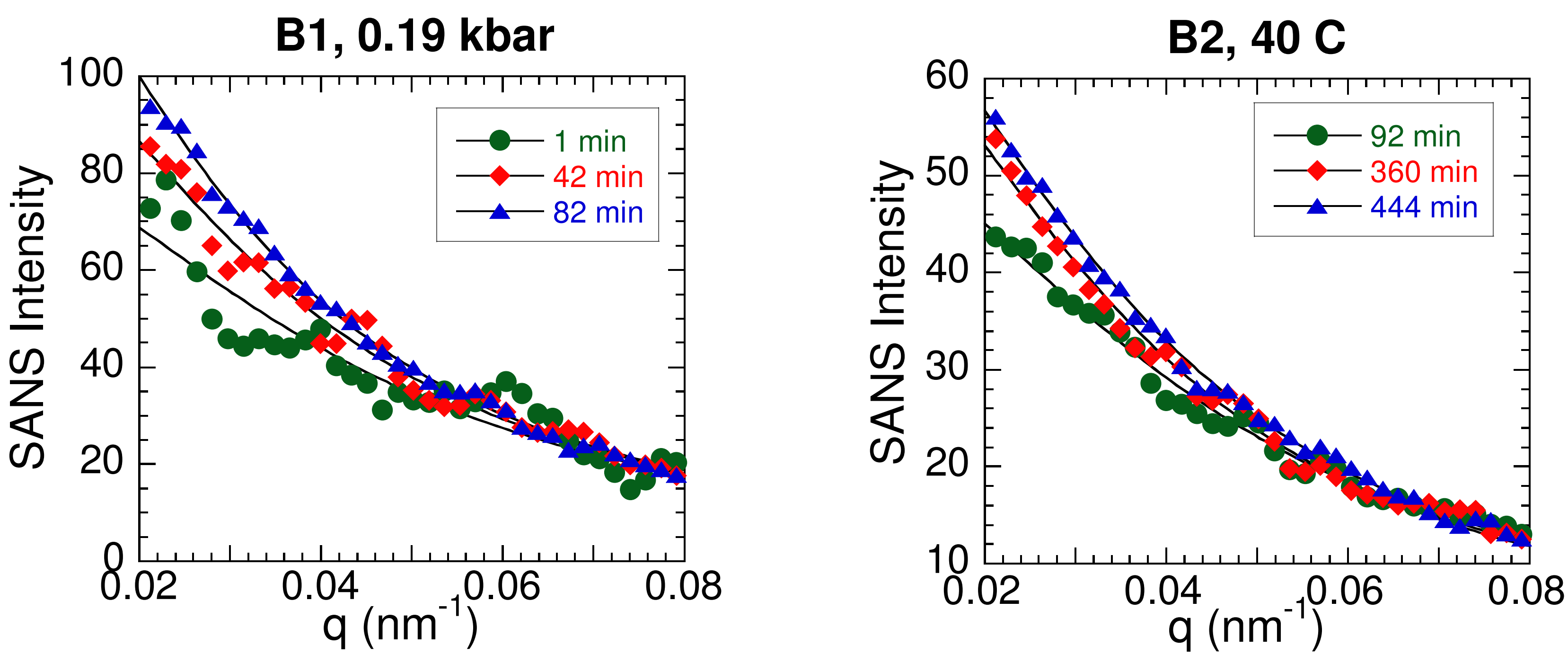


$$\frac{\tau_{nucl}}{\tau_0} = e^{-B\left(\frac{\chi}{\chi_s}-1\right)} - 1$$

τ_0 = 16.2 min
B = 13.4

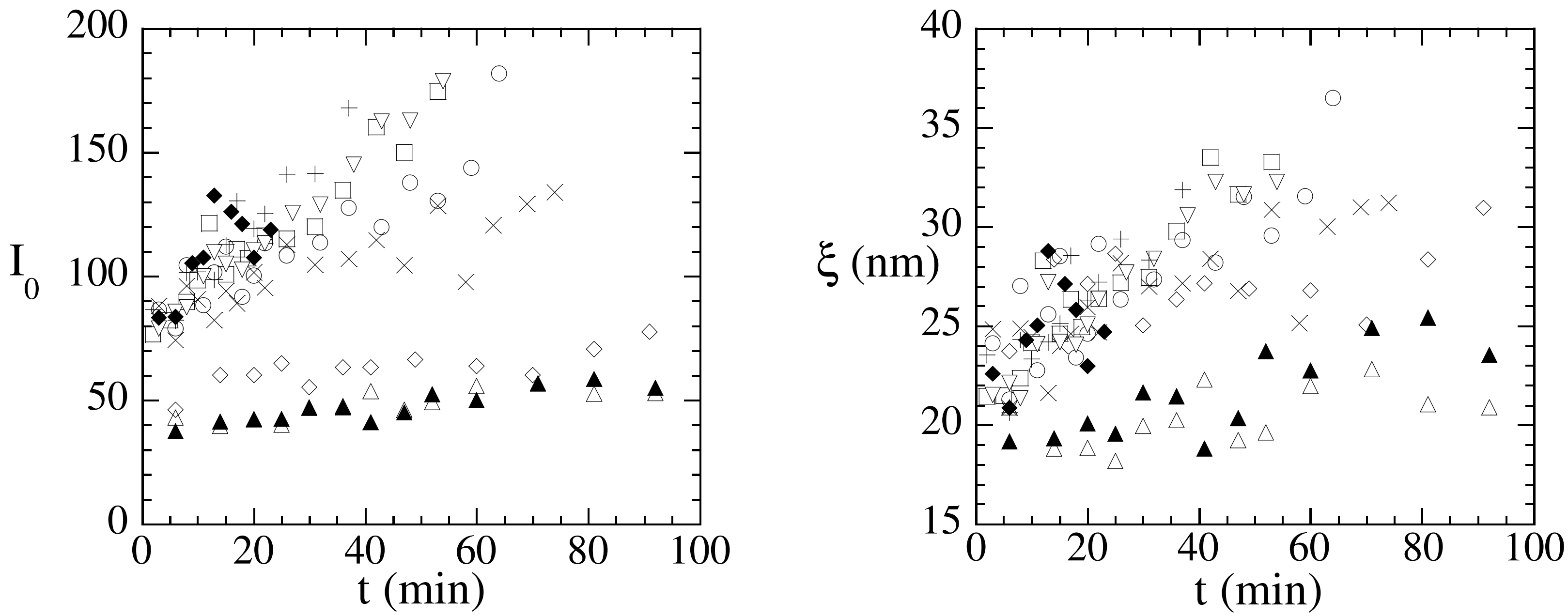


Analysis of SANS data

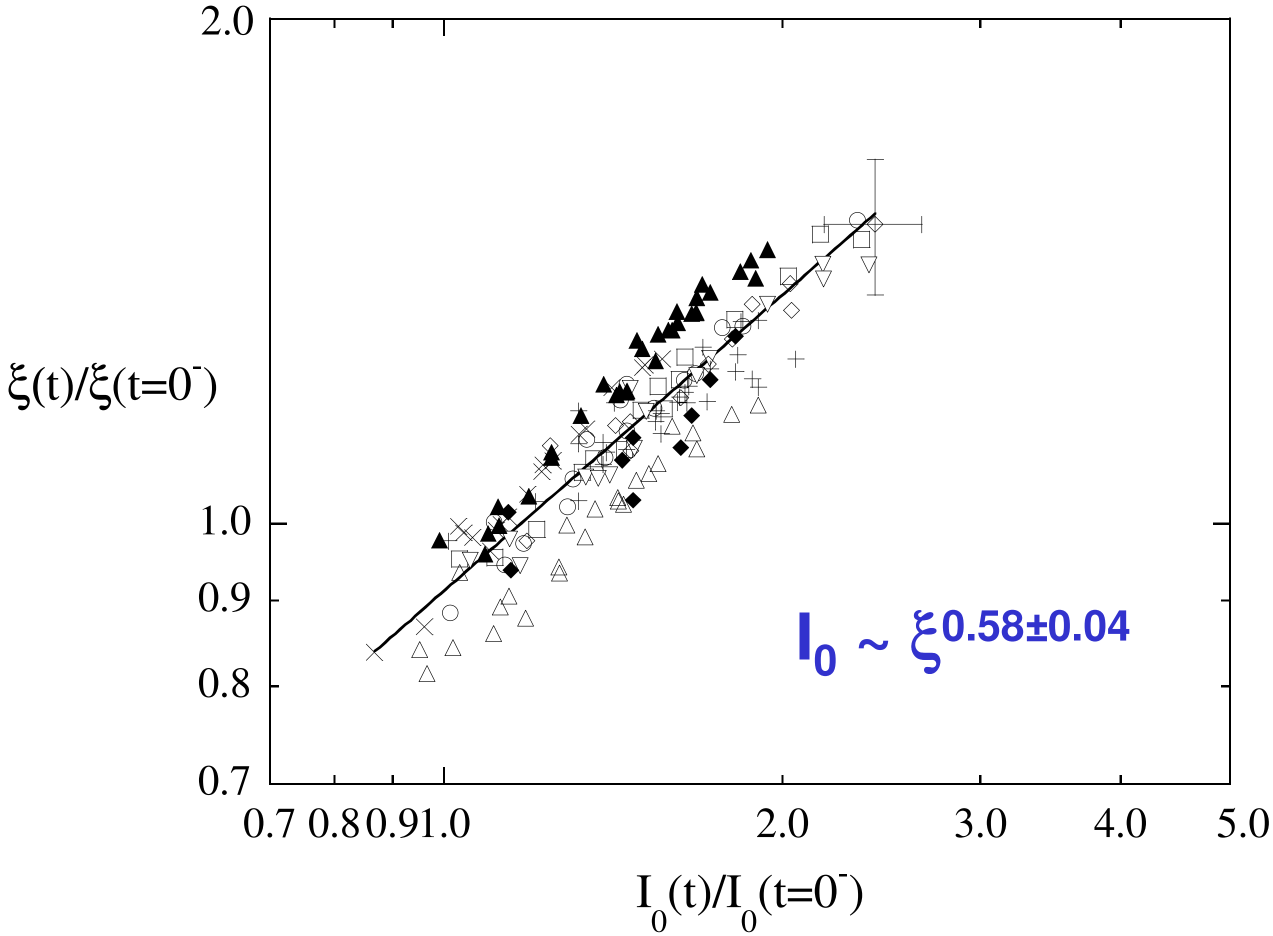


$I = I_0/[1+(q\xi)^2]$ Ornstein Zernike

Ornstein-Zernike parameters

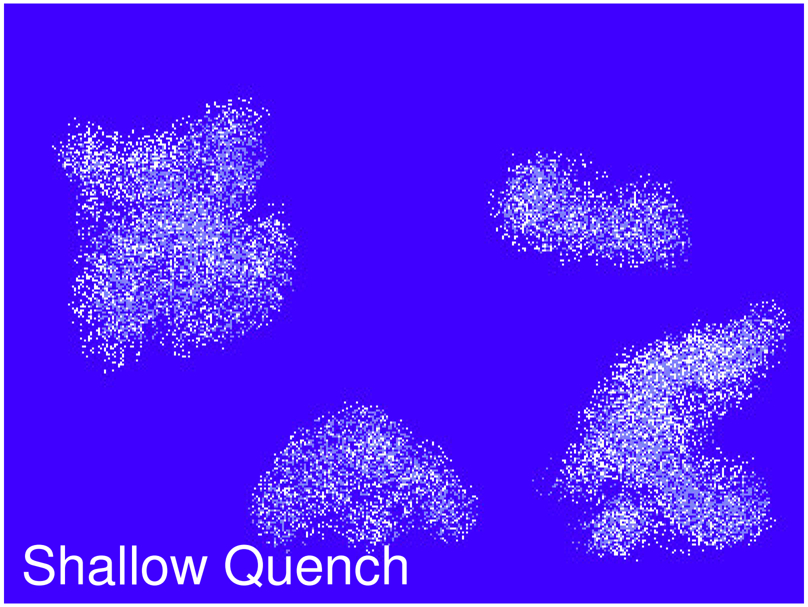


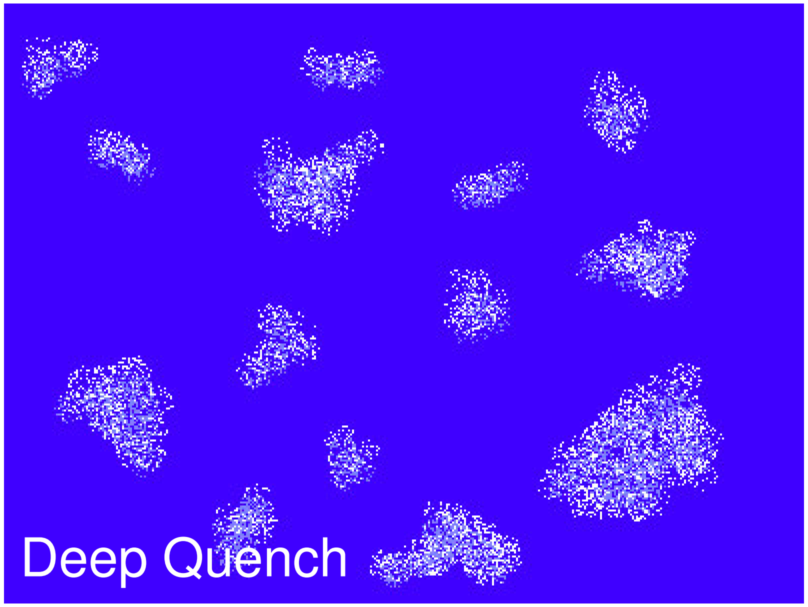
Relationship between I_0 and ξ



Mean-field concentration fluctuations $I_0 \sim \xi^{2!!}$ check

Diffuse self-similar structures at all quenches





<u>Problem:</u>

Classical theory-self similar nuclei at all quench depths (drops).

Cahn-Hilliard theory-more diffuse nuclei as you approach the spinodal.