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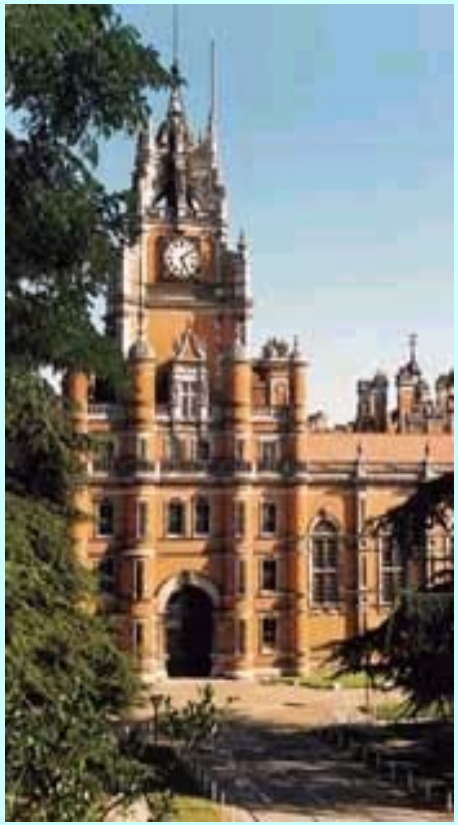

Critical Phase Separation and Spinodal Decomposition in Solid Helium Mixtures

Brian Cowan

Malcolm Poole, John Saunders

Phase Separation in Solid ^{3}He/^{4}He Mixtures

Introductory overview

Phase Separation in Solid ^{3}He/^{4}He Mixtures

- 1st order phase transition with conserved order parameter

Phase Separation in Solid ^{3}He/^{4}He Mixtures

- 1st order phase transition with conserved order parameter

  order parameter is density – number of particles fixed
  -- unlike ferromagnet etc.

  This is a beautiful and simple(?) system for studying a prototypical phase transition

Phase Separation in Solid ^{3}He/^{4}He Mixtures

- 1st order phase transition with conserved order parameter
- Processes occur over measurable timescales – so can study dynamics of the transition

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Liquids – time scales ~ ns
Solids – time scales ~ years
Solid helium – quantum exchange → hours

$$D = Ja^2$$

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  At these low temperatures all impurities will be stuck to the walls

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Crystals grown at constant pressure as Fraass and Simmons, Phys. Rev. B, **36** 97 (1987) – X-ray diffraction.

No dislocations or other nucleation points

Phase Separation in Solid ^{3}He/^{4}He Mixtures

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- Ideal model system

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Test ground for studying nucleation, kinetics, spinodal decomposition, criticality, and generic features of 1st order transitions.

– aerosols, vapour condensation, polymer melts, metal alloys, etc.

Phase diagram – binary alloy

- Simple mean field model

  ε_{33}, ε_{44}, ε_{34}. – nearest neighbour interactions

  Single important parameter

  $\varepsilon = \varepsilon_{34} - (\varepsilon_{33} + \varepsilon_{44})/2$

  $\varepsilon > 0$ favours phase segregation at $T = 0$

- Regular solution model

  More general – longer range interactions

  – but still single important parameter ε.

Phase diagram – binary alloy

- Simple mean field / regular solution model

At finite temperatures minimise $F = E - TS$

$E_m = sx(1-x)\,\varepsilon$ $\qquad \varepsilon = \varepsilon_{34} - (\varepsilon_{33} + \varepsilon_{44})/2$

$S_m = k\{x\ln x + (1-x)\ln(1-x)\}$ $\qquad s =$ nº of neighbours

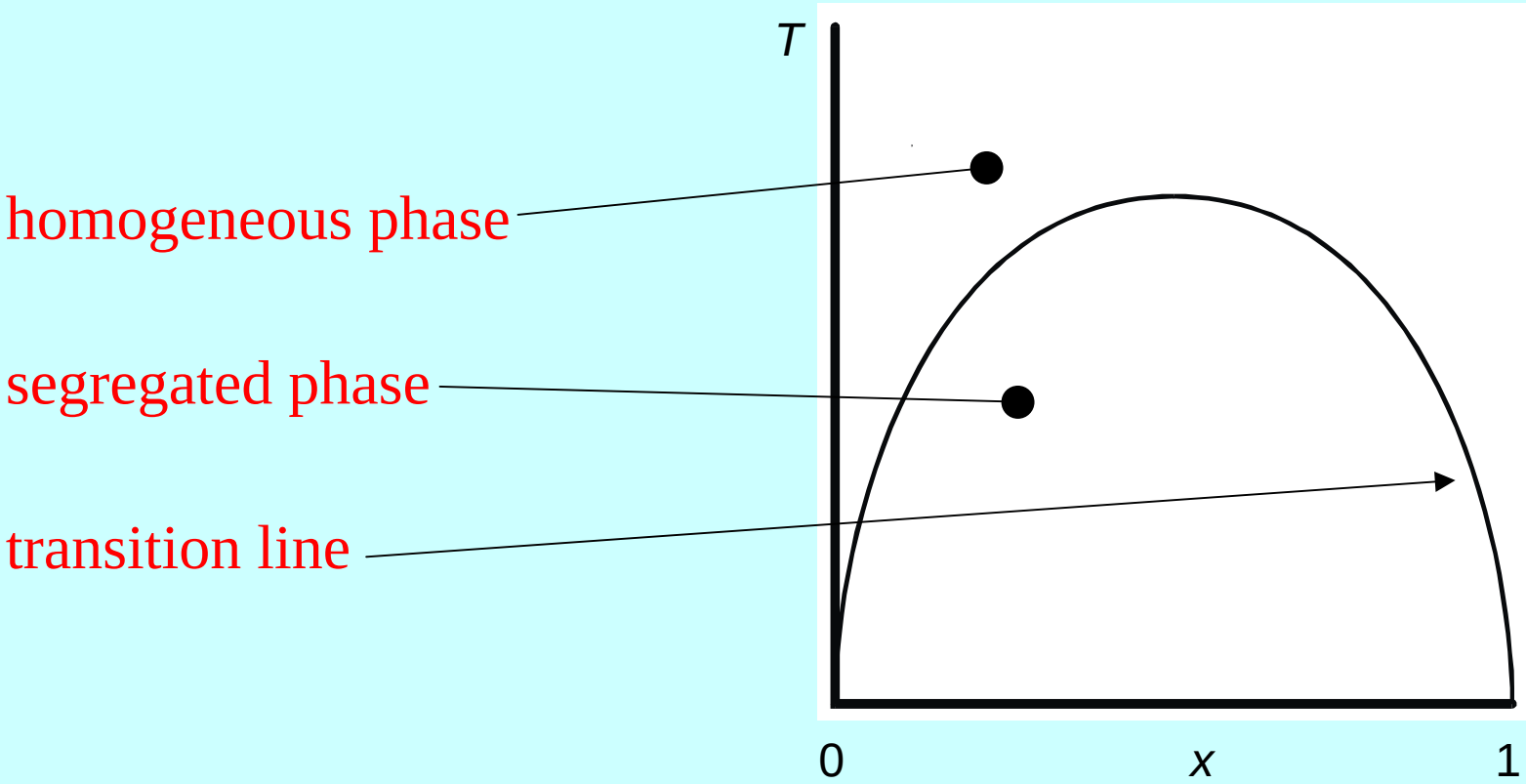
Low T – energy wins: phase separation

High T – entropy wins: homogeneous phase

Phase diagram – binary alloy

- Simple mean field / regular solution model

Regular solution $\rightarrow$ symmetry

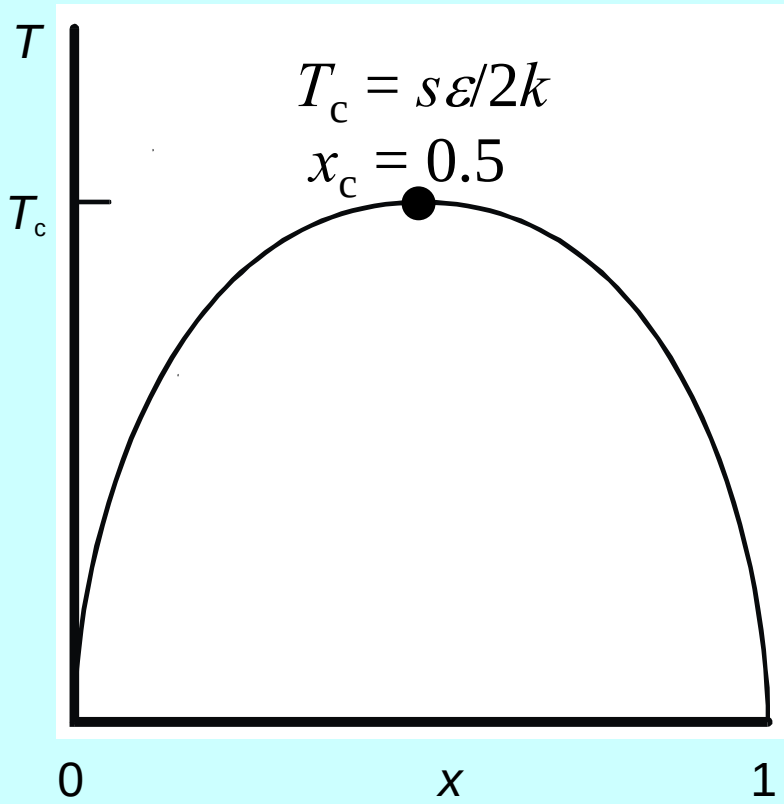


Phase diagram – binary alloy

- Simple mean field / regular solution model

Critical point

$T_c \sim 400\text{mK}$,
depends on pressure.



Phase diagram – binary alloy

- Regular solution model

Free energy density

For future reference

$$f(x) = f_0(x) + \kappa(\nabla x)^2$$

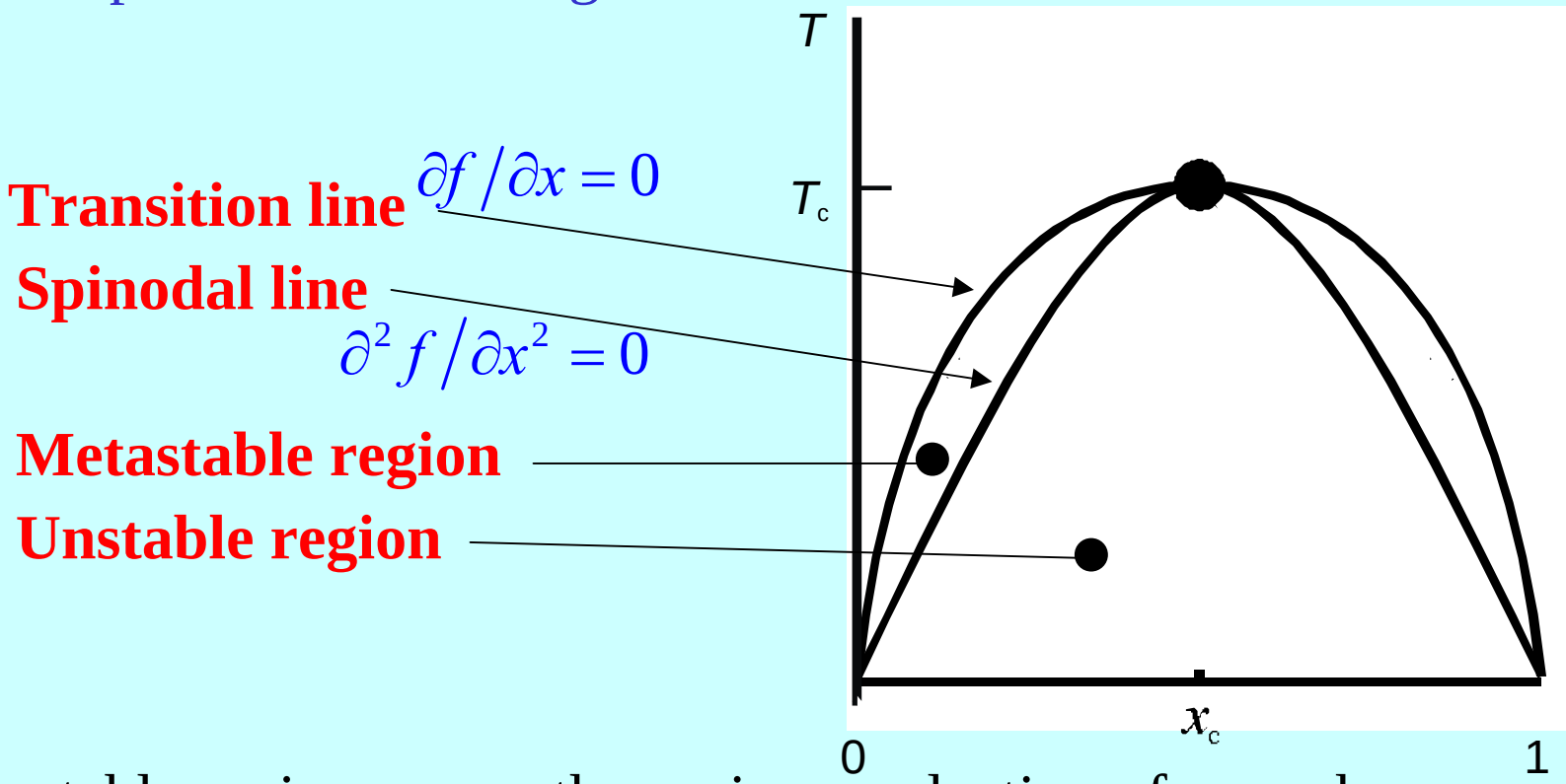
stiffness

$$f_0(x) = nkT_c\, 2x(1-x) + nkT\left\{x\ln x + (1-x)\ln(1-x)\right\}$$

$$\kappa = nkT_c a^2 \times \text{const} \quad \text{in mean field}$$

Phase diagram – binary alloy

- Simple mean field / regular solution model



Metastable region – growth requires nucleation of new phase
– must wait for thermodynamic fluctuation

Unstable region – growth proceeds through spinodal decomp.

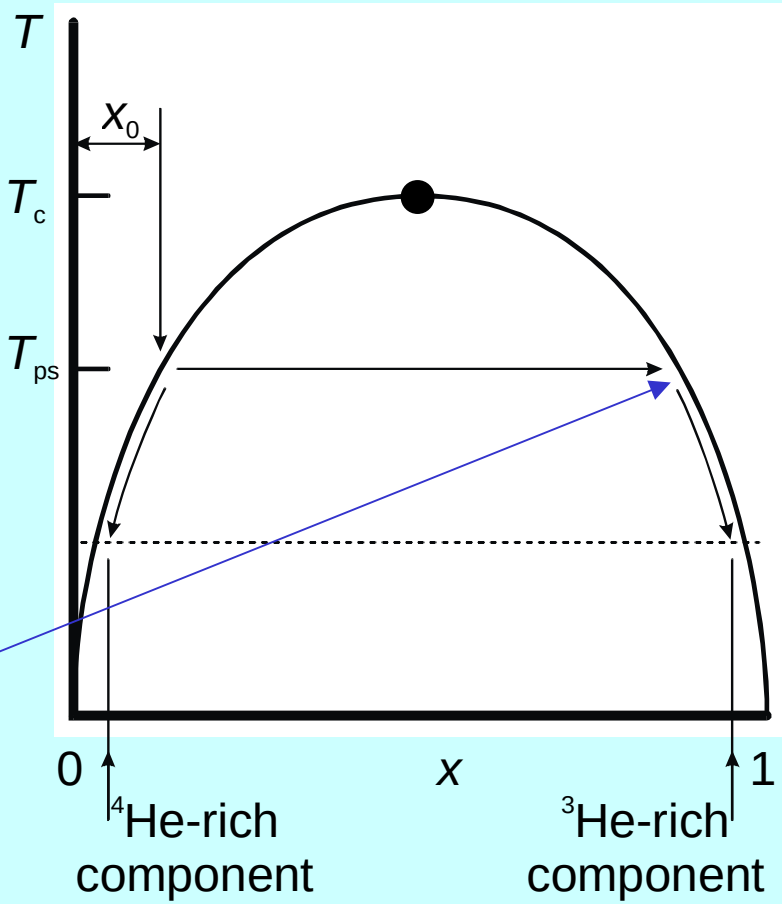
Phase diagram – binary alloy

- Simple mean field / regular solution model

Phase separation

First measurements were heat capacity – made by Edwards *et al*. (1962).

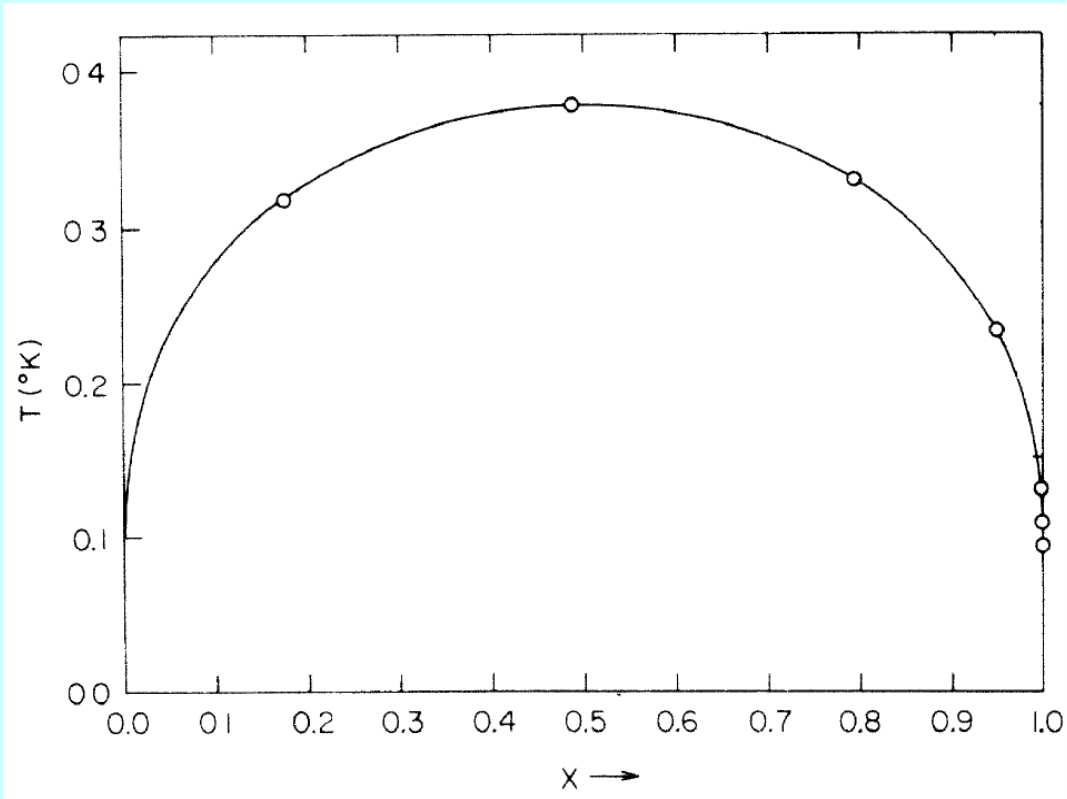
The new phase forms as ^{3}He-rich droplets – solid or liquid

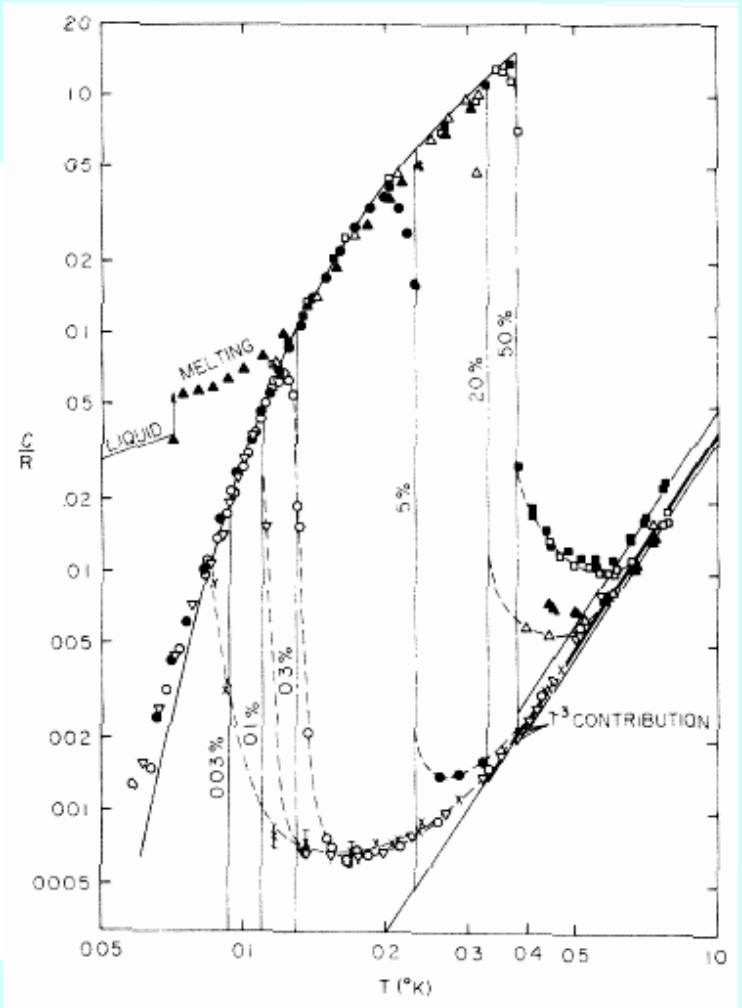


Phase diagram – binary alloy

- Experimental data of Edwards, McWilliams and Daunt
  Phys. Rev. Lett. **9**, 195 (1962)

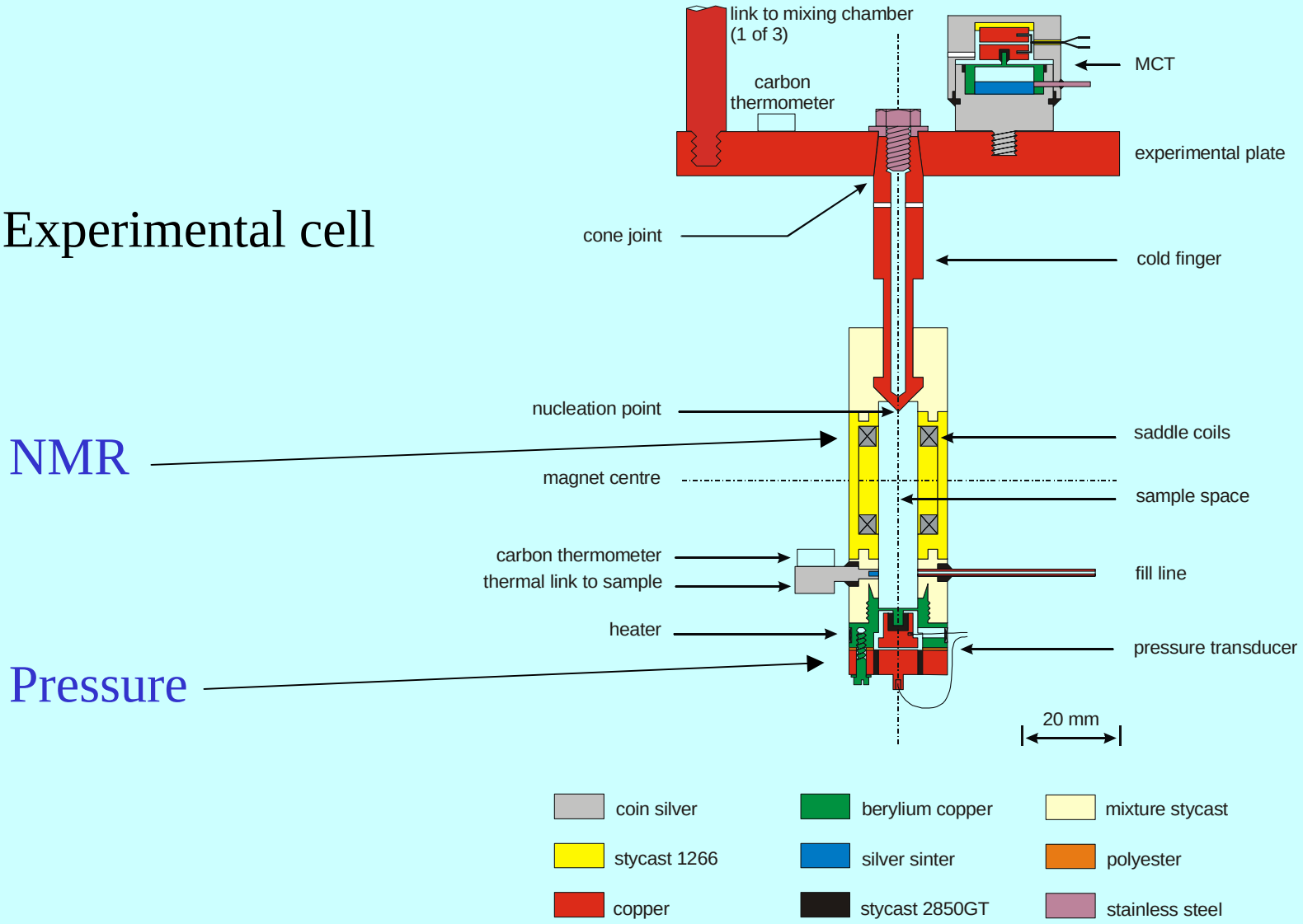
equillibration times !!





Experimental

- Experimental cell



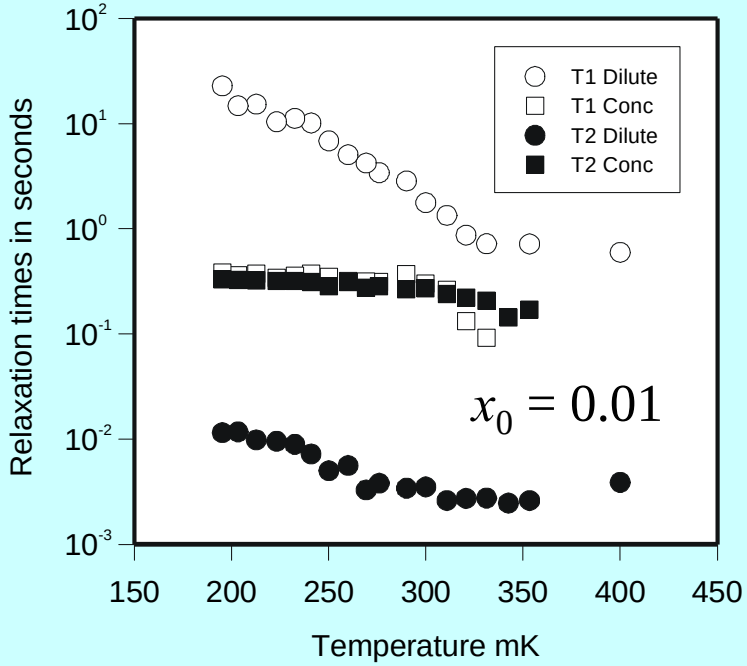
Experimental

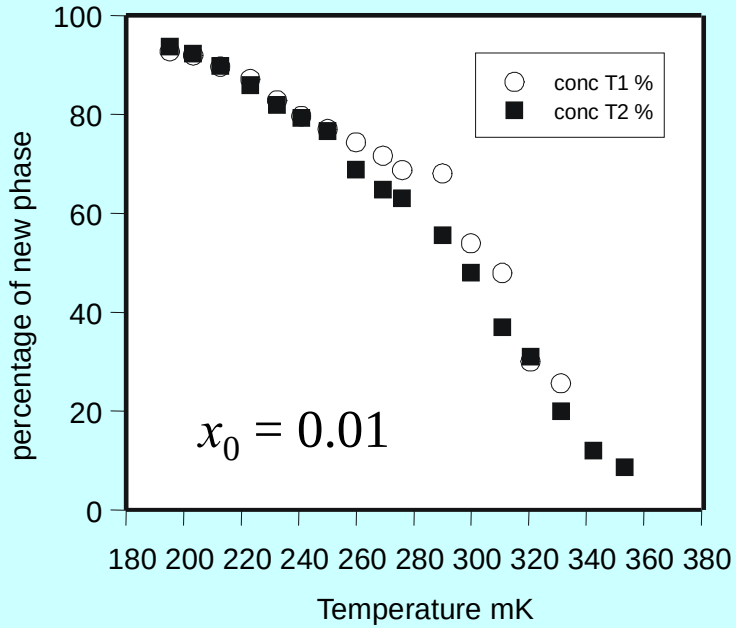
- NMR measurements

NMR sees only ^{3}He.

Relaxation times T_1 and T_2 depend on ^{3}He concentration – dipole interaction of ^{3}He modulated by exchange motion.

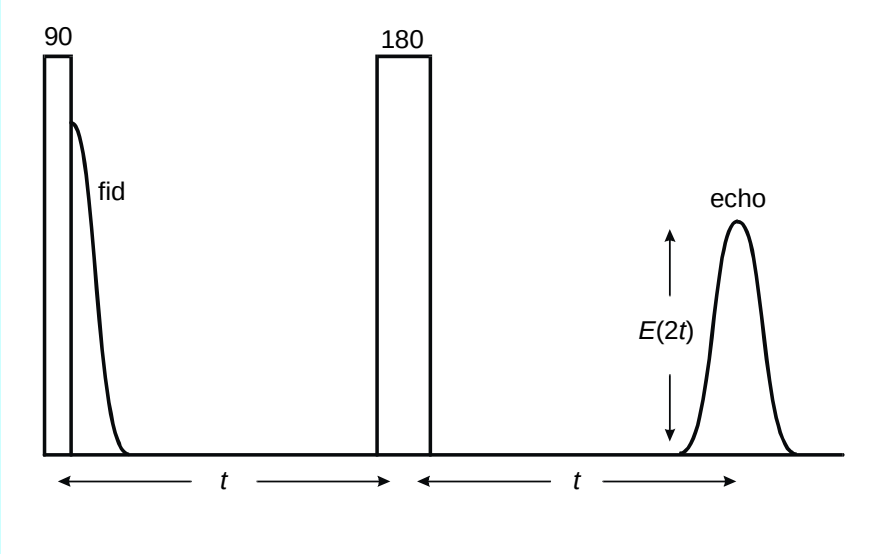
- Single component signal
  → single (homogeneous) phase
- Double component signal
  → two phases





Experimental

Carr-purcell sequence – apply field gradient



- NMR measurements

NMR also allows the measurement of ^{3}He (spin) diffusion coefficient and the size of the ^{3}He-rich droplets.

$$\frac{E(2t)}{E(0)} = \exp - \left(\frac{2}{3} \gamma^2 G^2 D t^3 \right)$$

conventional (unbounded) diffusion

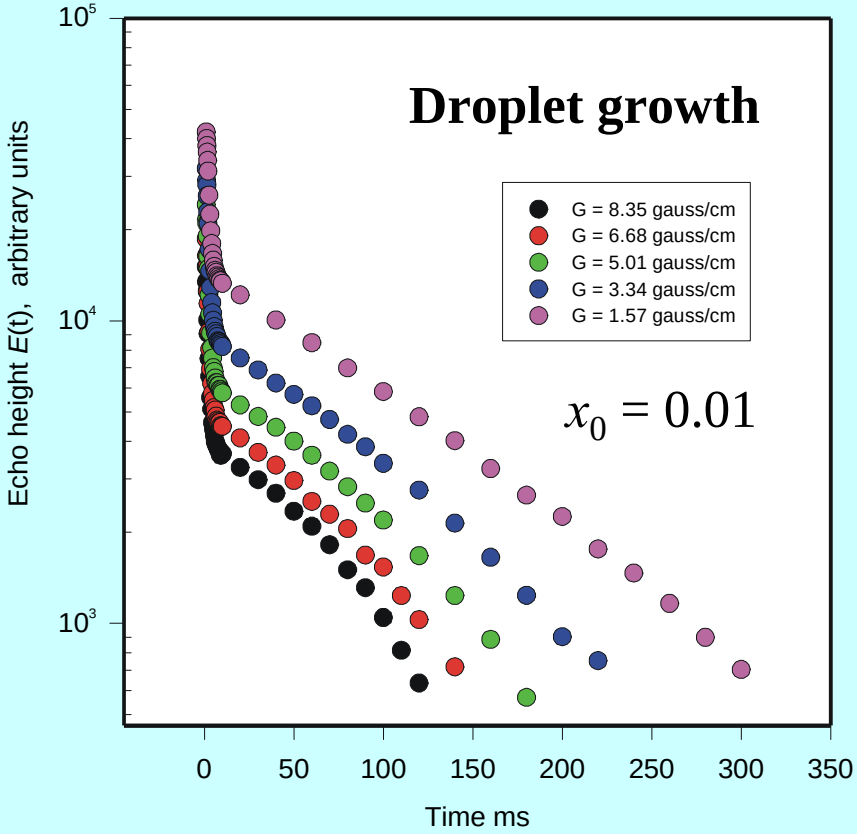
$$\frac{E(2t)}{E(0)} = \exp - \frac{a^6 \gamma^2 G^2}{\pi^6 D^2} \left\{ \frac{2t}{\tau_c} + 4\exp\left(\frac{-t}{\tau_c} \right) - \exp\left(\frac{-2t}{\tau_c} \right) - 3 \right\}$$

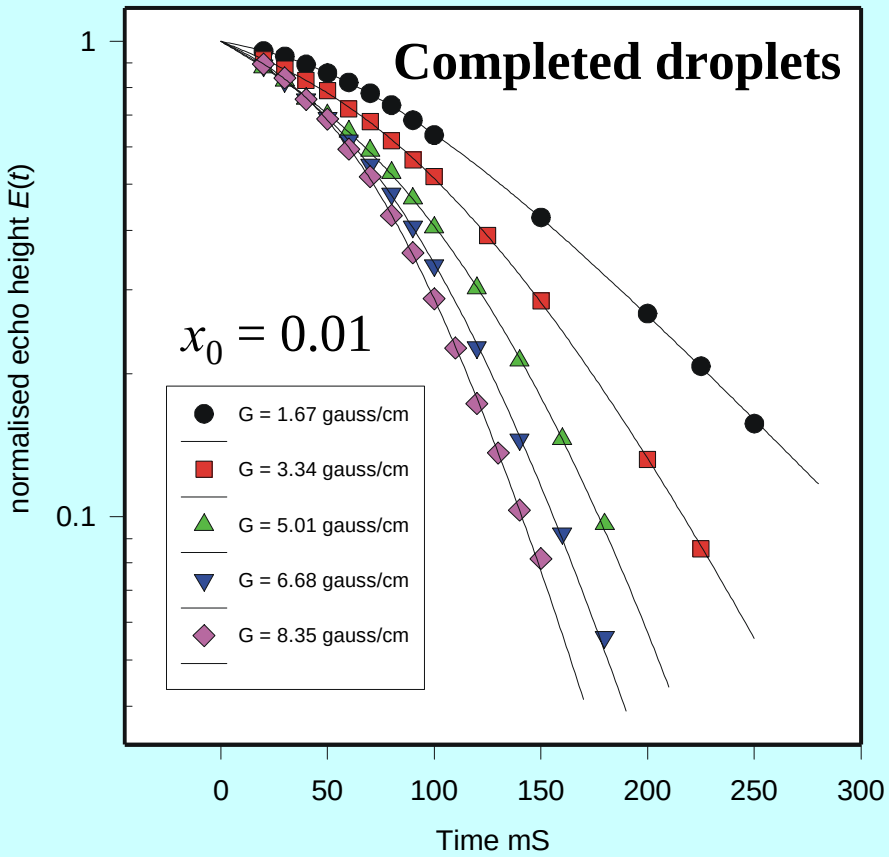
bounded diffusion

where , $\tau_c = a^2/\pi^2 D$, essentially the time for a spin to diffuse across a droplet.

Experimental

- NMR measurements





$D = 4.9 \pm 0.3 \times 10^{-8}$ cm^{2}s^{-1}

$a = 4.5 \pm 0.5$ micron

Short component: ^{4}He-rich background

Long component: ^{3}He droplets

Experimental

- Pressure measurements

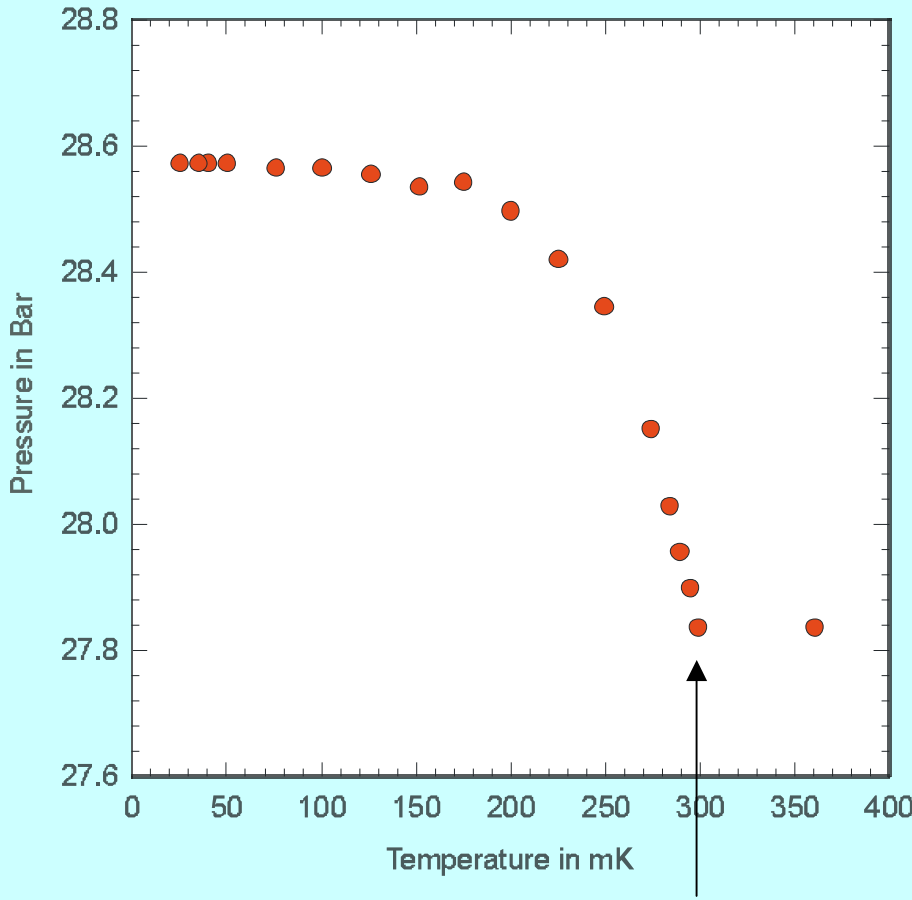
Early measurements by Adams *et al*. PRL, 9, 594 (1968)

and extensively by Rudavskii and Kharkov group

Molar volume of homogeneous mixture is less than weighted mean of that of pure ^{3}He and ^{4}He.

$v(x, p) = xv_3 + (1 - x)v_4 - v_x$.

So volume (pressure) increases on separation.



Start of phase separation

Mullin (1968) calculated excess volume v_x for some p. Observed pressure increases are in agreement with his values: $\Delta p \sim 0.7$ bar for $x_0 = 0.01$, $p_0 = 27.9$ bar.

Experimental

- Pressure and NMR measurements

NMR allows measurement of size of droplets.

This gives number of droplets.

Pressure also permits following size of droplets.

Joint work between RHUL group and Kharkov group analysed data to infer that new phase grew through homogeneous nucleation and inferred droplet surface tension coefficient of 1.27×10^{-5} Jm^{-2}.

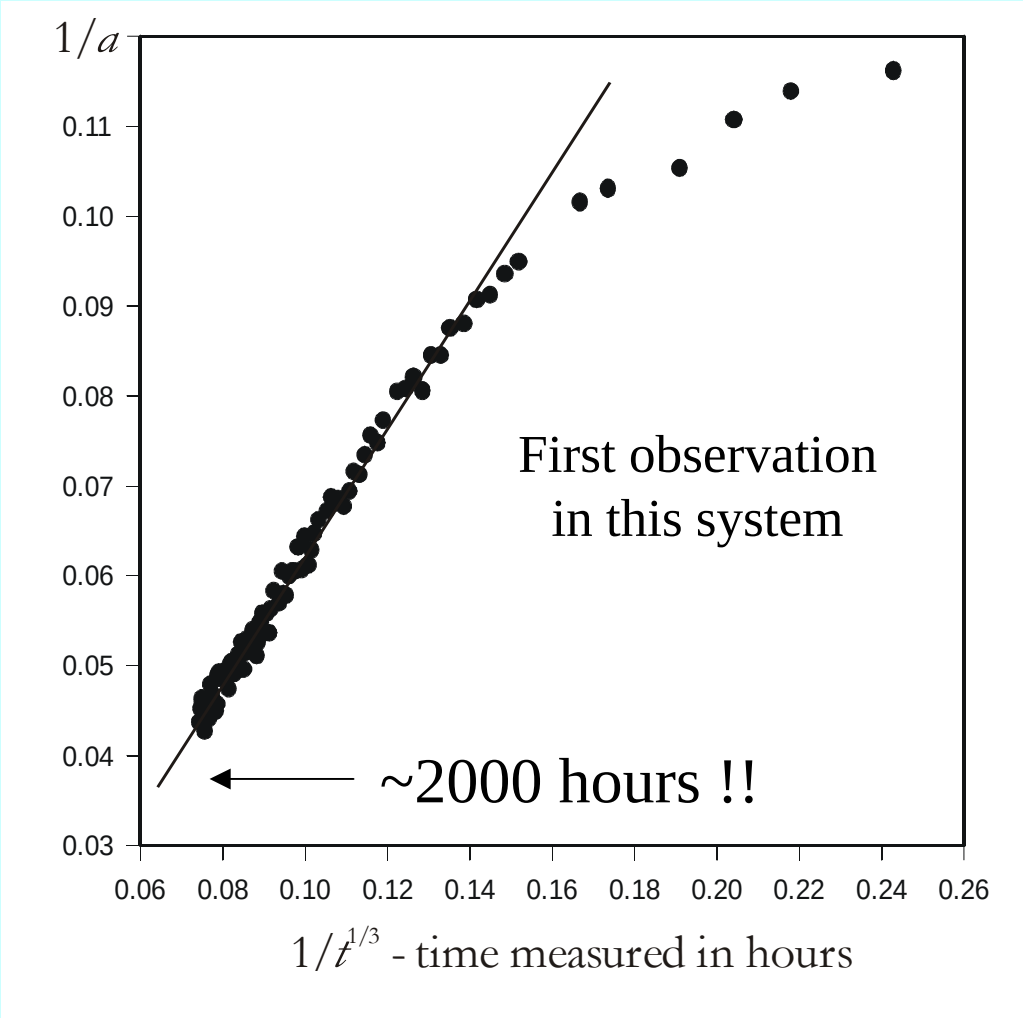
A.Smith, S.Kingsley, V.A.Maidanov, E.Ya.Rudavskii, V.N.Grigorev, V.V.Slezov, M.Poole, J.Saunders and B.Cowan

Phys. Rev. B. 67, 245314-245317 (2003)

Stages of Nucleation / Growth Process

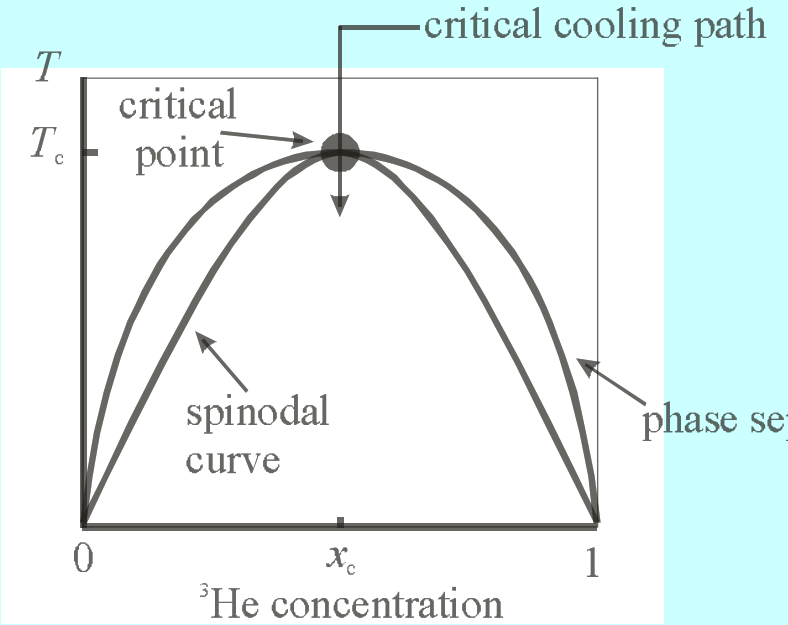
- Nucleation – new phase appears
- Growth – droplets grow but n^o remains constant
- Ripening – sub-critical droplets evaporate and super-critical droplets grow – $a \sim t^3$

We have observed them all



Spinodal Decomposition

- Phase separation curve and spinodal curve meet at the critical point ($x = 0.5$, $T = T_c$).
- Then phase separation proceeds through spinodal decomposition. – enter the **unstable** region directly.



- the new phase evolves through spatial modulation of the ^{3}He density.

Spinodal Decomposition

- Particle flow is driven by gradient in chemical potential

$$\mathbf{J} = -A\nabla\mu$$

- Now μ is obtained from the free energy density f, so that the spatial variation of x is

$$\frac{\partial x}{\partial t} = A\frac{\partial^2 f}{\partial x^2}\nabla^2 x + 2A\kappa\nabla^4 x$$ Cahn-Hilliard eqn

  where κ is the 'stiffness' coefficient.

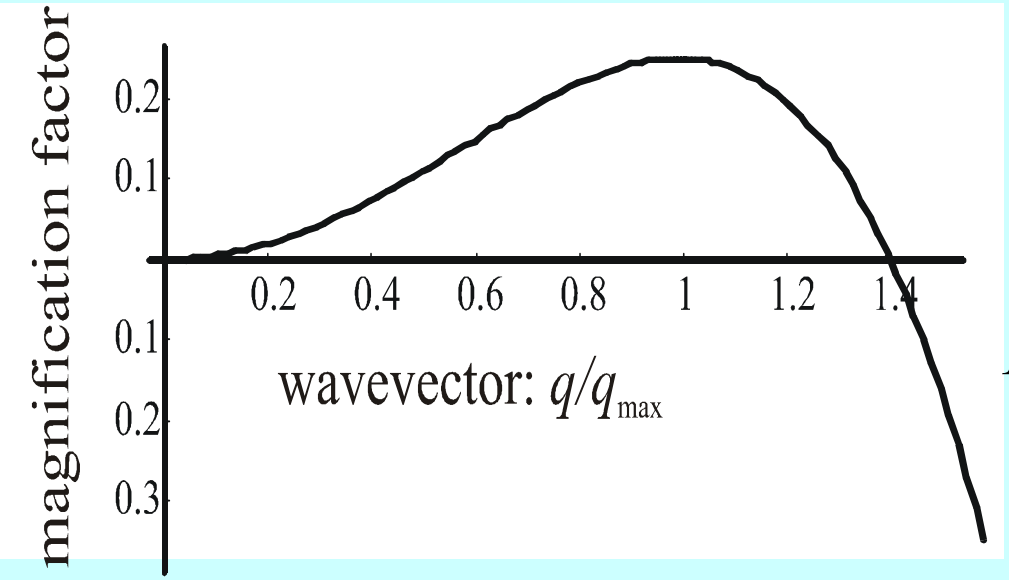
- $D_{\text{eff}} = A\partial^2 f / \partial x^2$ is an effective diffusion coefficient
- In the unstable region $\partial^2 f / \partial x^2$ is negative so get reverse diffusion.

Spinodal Decomposition

- Below the spinodal curve fluctuations will *lower* the free energy → instability
- Atoms flow from regions of low concentration to regions of high concentration – reverse diffusion
- Concentration fluctuations *grow*. But different wavelengths grow at different rates.
- Long wavelength fluctuations grow slowly because atoms have to travel large distances.
- Short wavelength fluctuations grow slowly because of the cost in interfacial energy is too great.

Spinodal Decomposition

- Intermediate fluctuations grow fastest – characterised by a ‘magnification factor’ $M(q)$ – magnification of the effective diffusion coefficient.



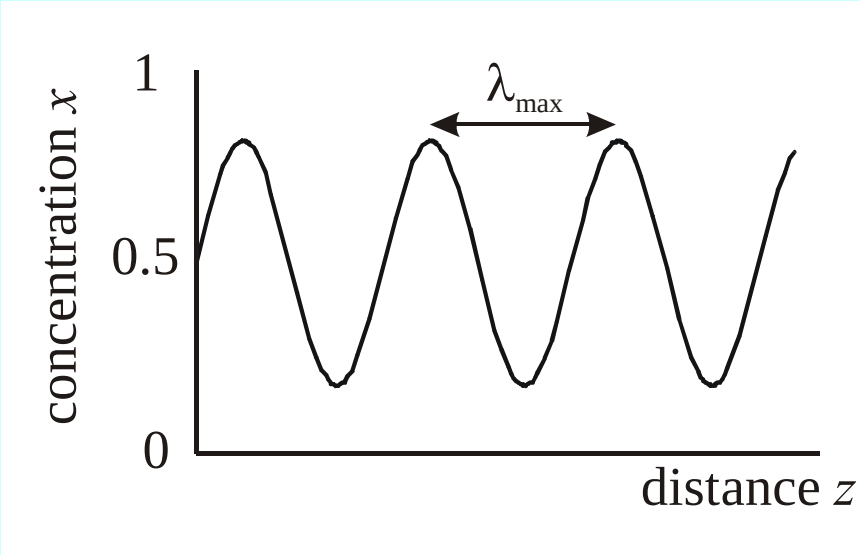
Linearised Cahn-Hilliard equation gives

$$M(q) = q^2\left(1 + 2\kappa q^2\left(\frac{\partial^2 f}{\partial x^2}\right)^{-1}\right)$$

mean-field stiffness κ gives $q_{\max} = \frac{1}{a\sqrt{3}}\sqrt{\frac{T_c - T}{T_c}}$

Full equations have a time dependence – then $q_{\max}$ depends on time.

NMR Study of Spinodal decomposition



- In spinodal region there is a concentration distribution.
- NMR relaxation times depend on ^{3}He concentration.

$\rightarrow$ There will be a distribution of relaxation times

$\rightarrow$ Non-exponential relaxation.

NMR Study of Spinodal decomposition

- Non-exponential relaxation profiles follow well the *stretched exponential* form:

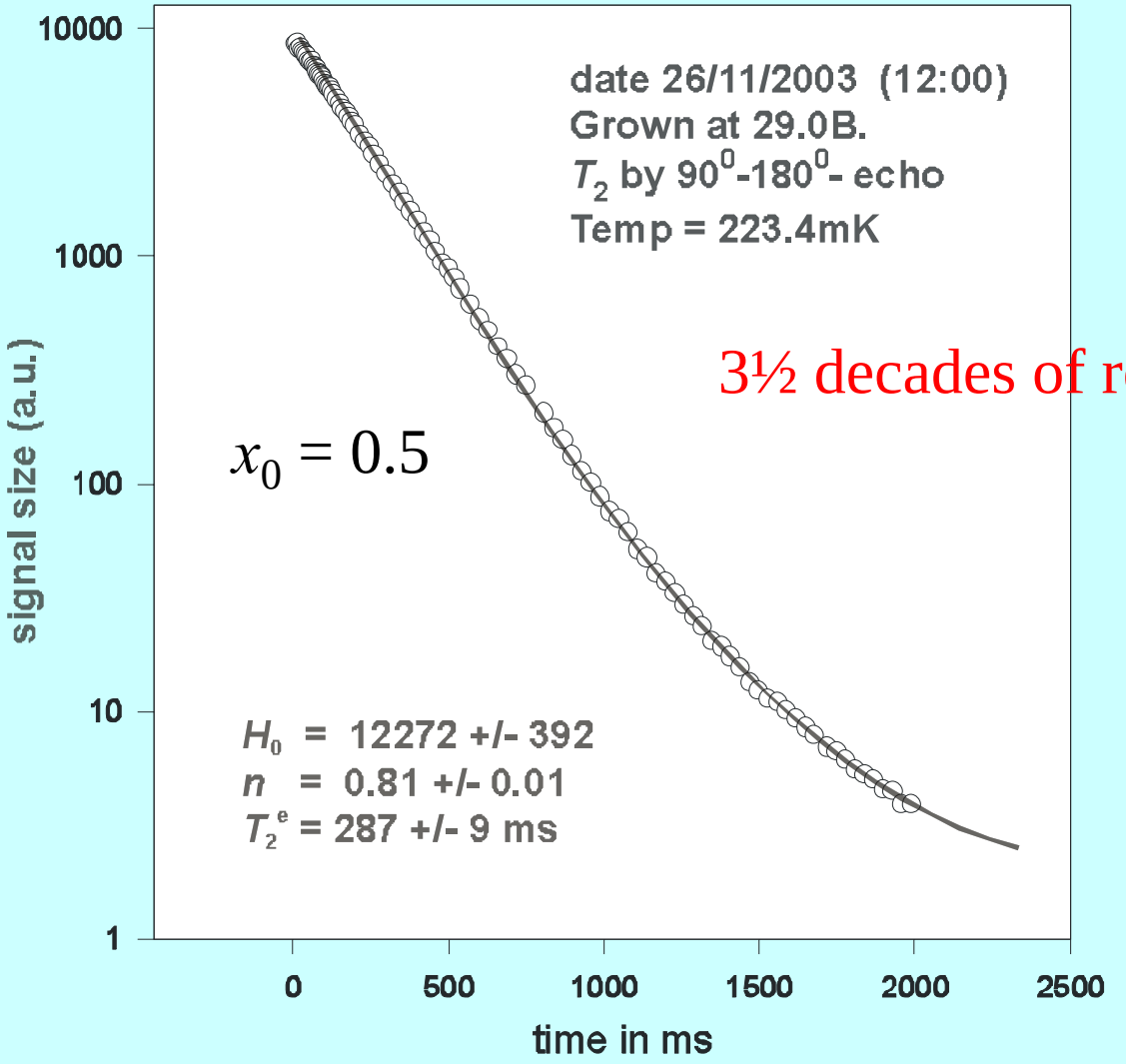
$$F(t) = e^{-\left(t/T_2^{\mathrm{e}}\right)^n}$$

Where T_2^{e} is the effective relaxation time and n is an index (between 0 and 1).

Here n is a measure of the *breadth* of the distribution.

So use n and T_2^{e} to parameterise the relaxation.

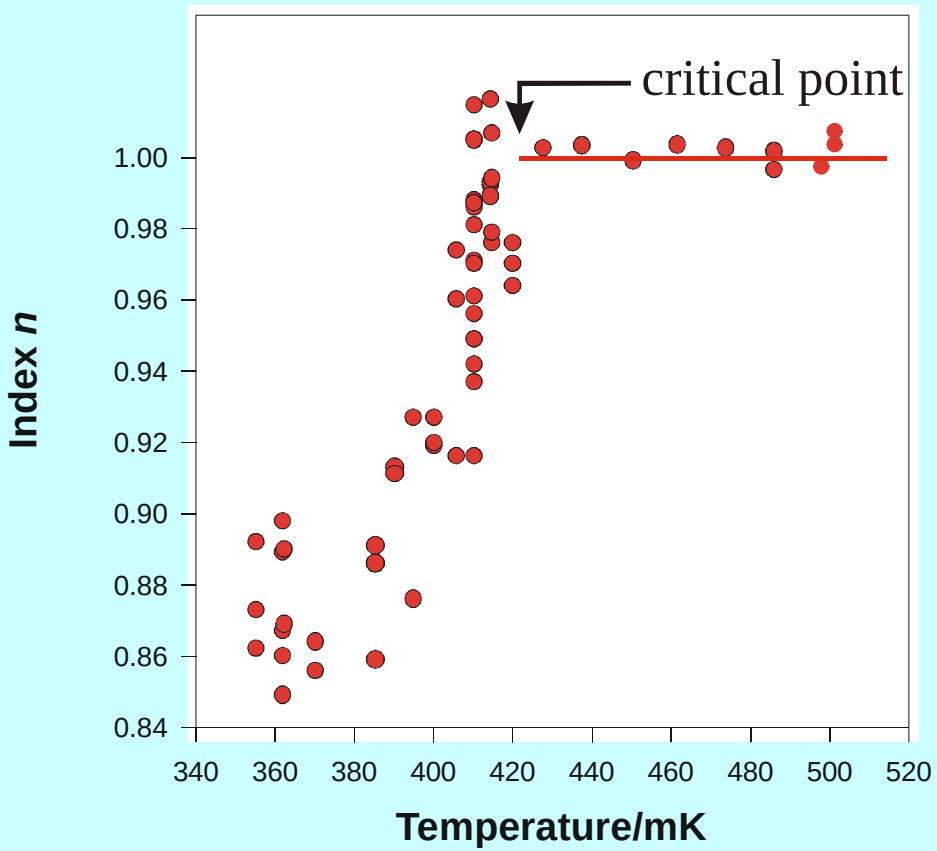
NMR Study of Spinodal decomposition

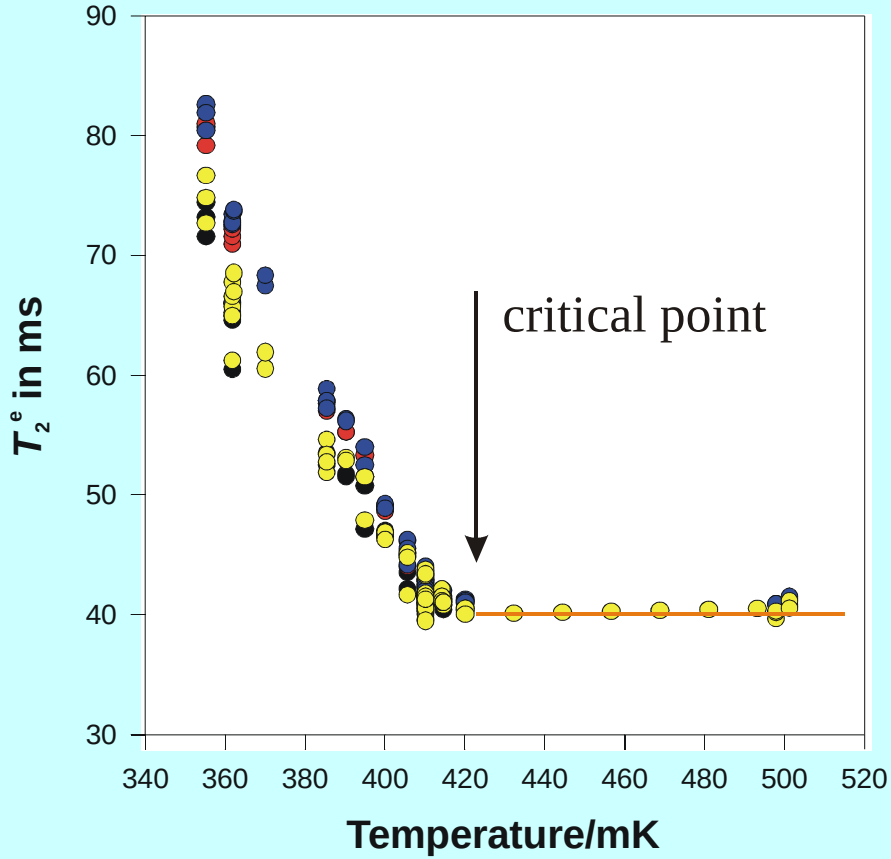


3½ decades of relaxation!!

NMR Study of Spinodal decomposition

- Experimental data show clearly the onset of spinodal decomposition.





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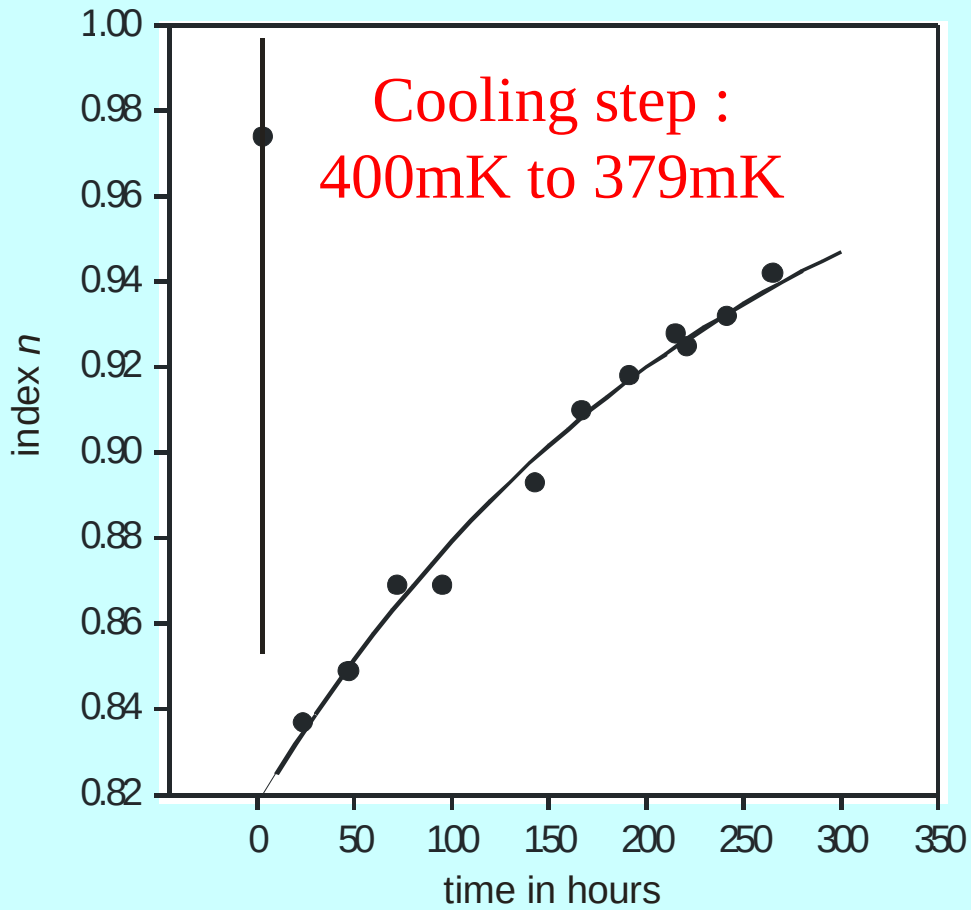
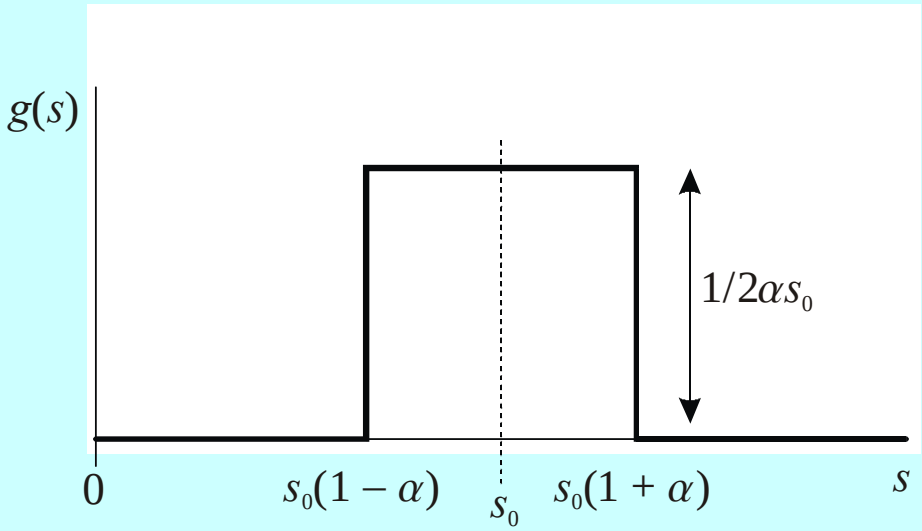


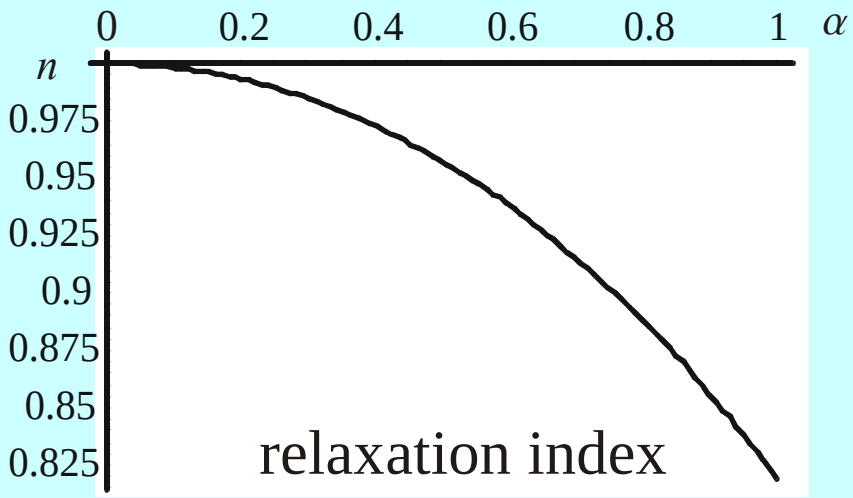
- Initial drop of *n* from 1 to 0.83 over ~20 hours indicates growing spread of relaxation rates (concentrations).
- Subsequent increase of *n* over ~300 hours indicates evolution to regions of two distinct concentrations.

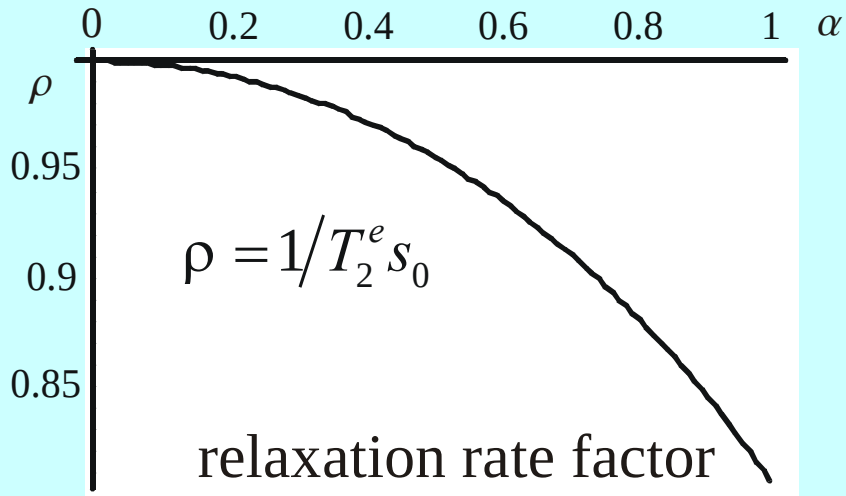
NMR Study of Spinodal decomposition

- Stretched exponential analysis – dependence of n and T^e upon spread of the distribution.



Drop in n indicates increasing spread of concentrations.

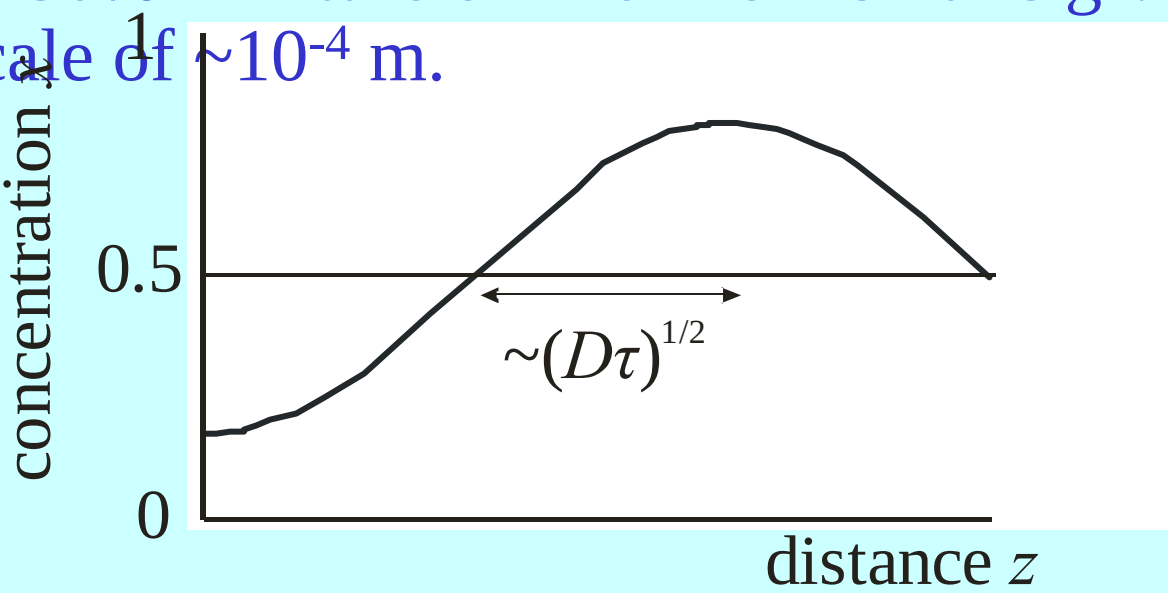




NMR Study of Spinodal decomposition

Estimation of dominant length scale $\lambda_{max} = 2\pi/q_{max}$.

- Time constant τ of n evolution (~250 hours) gives time atoms take to travel $\sim(D\tau)^{1/2}$. Then with known value for D for 50% mixture of $\sim 10^{-10}$ cm^{2}s^{-1} this gives a length scale of $\sim 10^{-4}$ m.

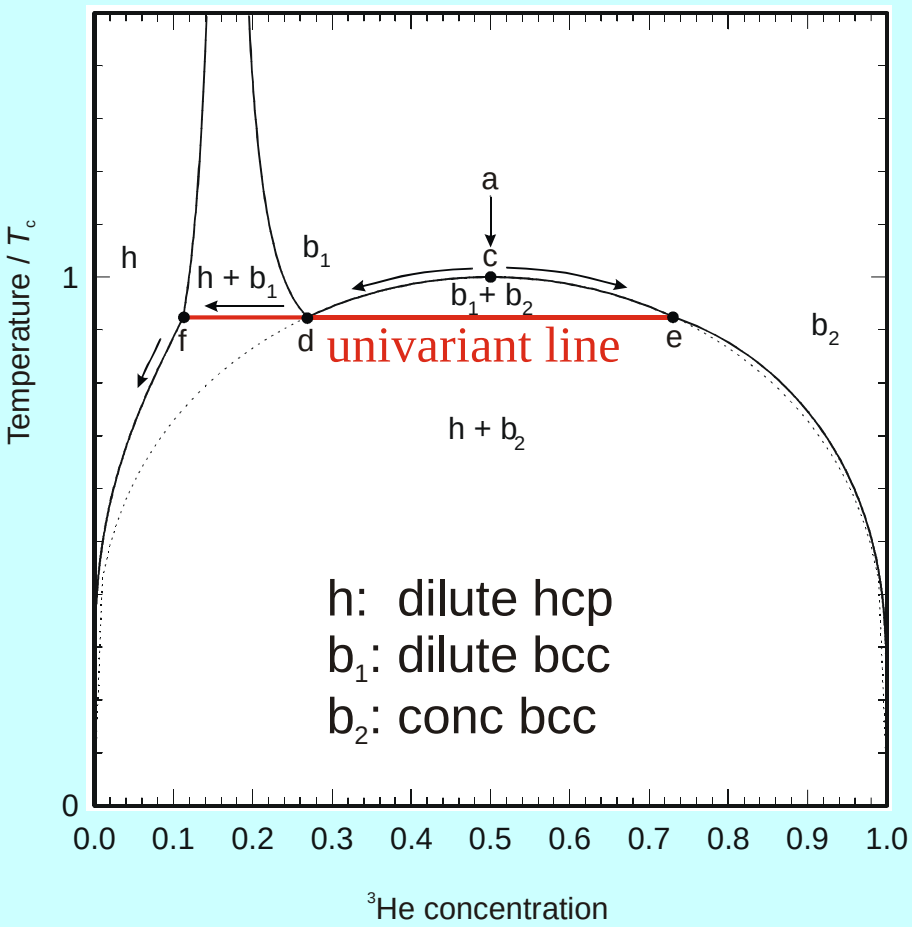


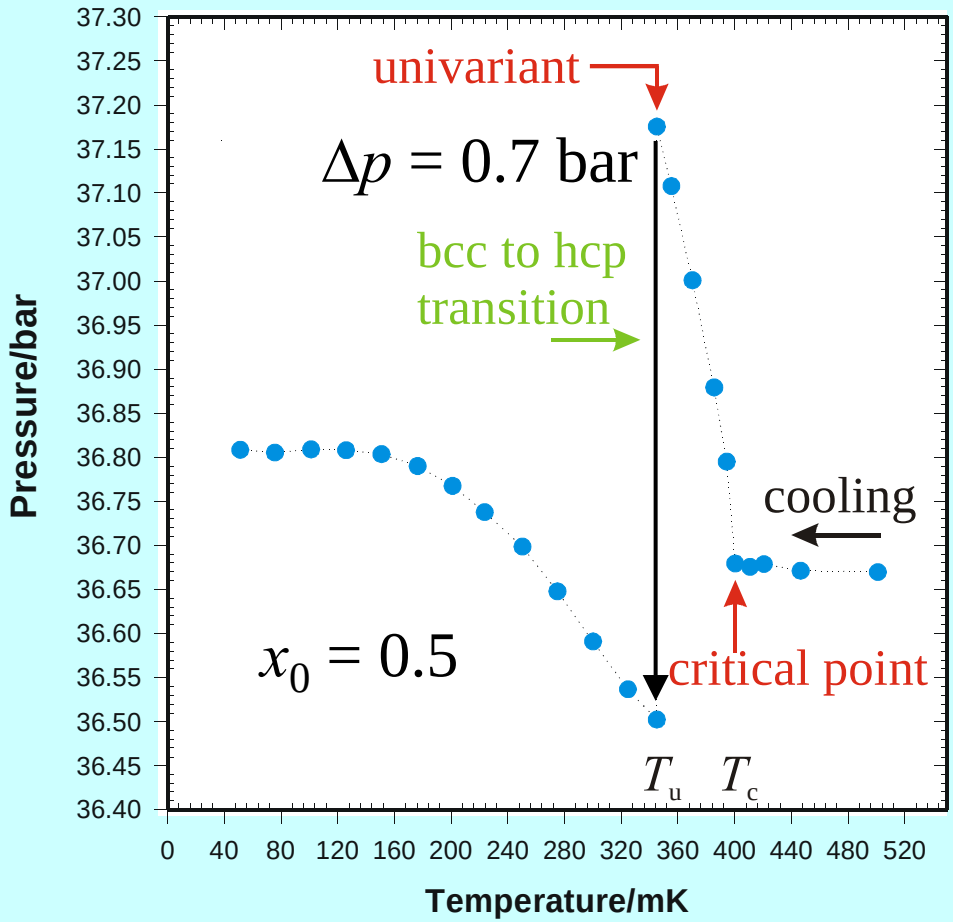
- Compare with $\sim 10^{-5}$ m for afm measurements in

Pressure Studies of Critical Phase Separation

- Pressure measurements show dramatic indication of the bcc → hcp transition of dilute phase

equillibration times !!





Conclusions

- NMR and pressure are ideal tools to study phase separation in this system.
- In the metastable region we have observed homogeneous nucleation and all three stages of the nucleation – growth process.
- In the unstable/critical region we have observed spinodal decomposition and the evolution of the density modulation of the mixture.
- Have estimated the dominant length scale of the spinodal decomposed mixture.