Theory of Phase Transitions – 1st Order

Physics 210B
Special Topic

I.) Review of Fundamentals

→ Examples of Phases and Transitions
- liquid, gas → vaporization, boiling
- magnetized, unmagnetized ferromagnet → magnetization transition

→ For phase equilibria: (2 phases "1, 2")

$$\left.\begin{aligned} T_1 &= T_2 \\ P_1 &= P_2 \\ \mu_1 &= \mu_2 \end{aligned}\right\} \underline{\text{conditions}}$$

$$\left\{\begin{aligned} &\mu \equiv \text{chemical potential} \\ &\mu = (\partial F/\partial N)_{T,V} \\ &\quad = (\partial \Phi/\partial N)_{P,T} \end{aligned}\right.$$

F = Helmholtz free energy

Φ = Thermodyn. potential

are additive: i.e. $F = N f(V/N, T)$

$\Phi = N f(P,T)$

For convenience, express chemical potential as function of pressure, temperature ⇒

$$\mu_1(P,T) = \mu_2(P,T)$$

so can immediately write Clausius-Clapeyron equation:

$$d\mu_1 = d\mu_2 \Rightarrow \left(\frac{\partial \mu_1}{\partial T}\right) dT + \left(\frac{\partial \mu_1}{\partial P}\right) dP = \left(\frac{\partial \mu_2}{\partial T}\right) dT + (\partial \mu_2/\partial P)\, dP$$

i.e. $$\left(\frac{\partial \mu_1}{\partial T}\right) + \left(\frac{\partial \mu_1}{\partial P}\right)\left(\frac{dP}{dT}\right) = \left(\frac{\partial \mu_2}{\partial T}\right) + \left(\frac{\partial \mu_2}{\partial P}\right)\frac{dP}{dT}$$

but: chemical potential additive, so

$$\Phi = N f(P,T) \qquad \text{but} \quad \frac{\partial \Phi}{\partial N} \equiv \mu$$

$$\Rightarrow \quad \Phi = N \mu(P,T)$$

$$\therefore \quad d\left(\frac{\Phi}{N}\right) = d\mu = \frac{1}{N}\left(-S\,dT + V\,dP\right)$$

$$= -\underbrace{s}_{\text{entropy per particle}}\,dT + \underbrace{v}_{\text{volume per particle}}\,dP$$

$$\therefore \Rightarrow \quad \partial\mu/\partial T = -s, \qquad \partial\mu/\partial P = v$$

$$\Rightarrow \quad \boxed{\frac{dP}{dT} = \frac{s_1 - s_2}{v_1 - v_2}}$$

Clausius-Clapeyron Eqn.

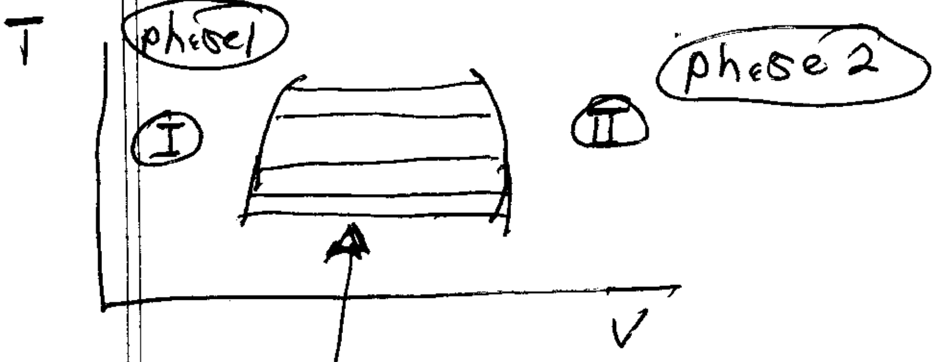
As $T(s_2 - s_1) = q \equiv$ heat of transition,

$$\frac{dP}{dT} = \frac{q}{T(v_2 - v_1)}$$

(alternate form).

→ phase Equilibria and Coexistence : Properties

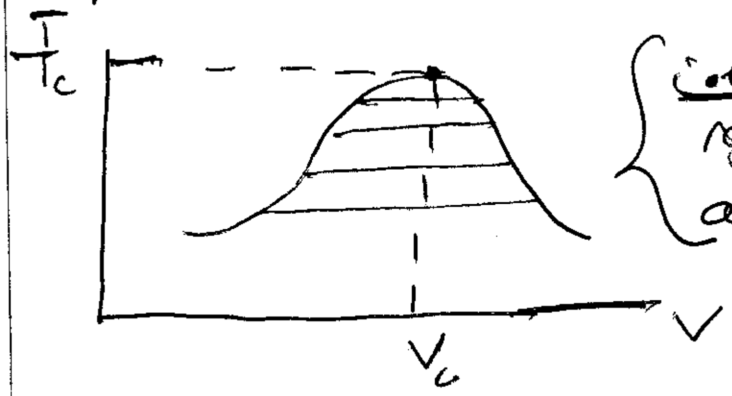
- if plot phase equilibrium in V, T space:



I, II } homogeneous single phase regions.

→ co-existence region → phases can exist in equilibrium
(i.e. since V not same for 2 phases)

→ peak of coexistence region ⇒ critical pt.



{ i.e. at peak of coexistence regions V_1 → V_2, coincide at critical point

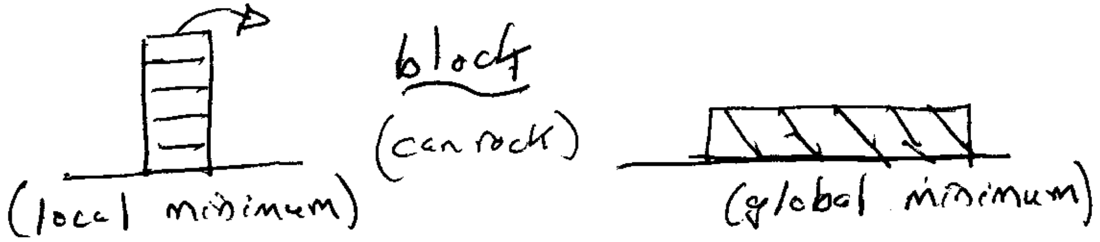
note:

i.) with critical point, can transition I → II without separating into two phases by skirting T_c

Key pt.

(*) ii.) phase I or II can be slowly brought into { transition / coexistence } region, but are metastable (e.g. super-heated liquid, super-cooled air), not stable.

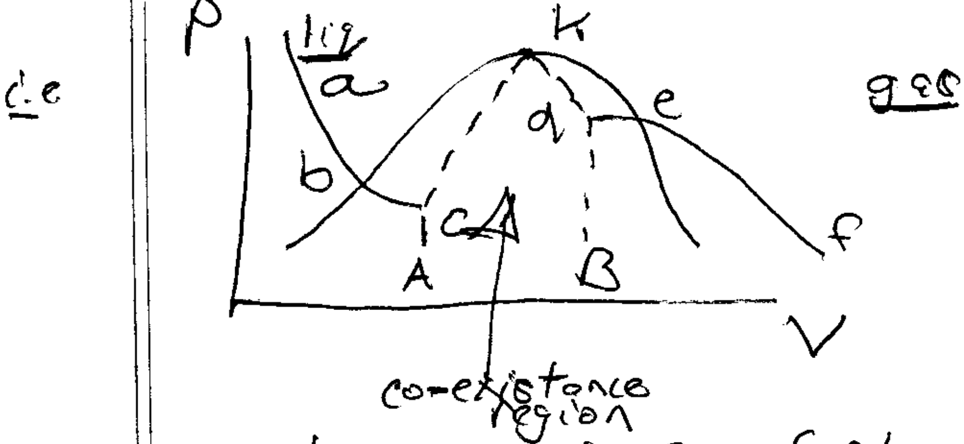
aside: metastability vs. stability



⇒ Questions suggested:

- nature of dynamics in coexistance region? (i.e. after quench) rapid transition
- dynamics near critical point?

→ for dynamics in co-existance region, consider isotherms abc, def



N.B. Dynamics in co-existance region is key question

- isotherms satisfy $(\partial P/\partial V)_T < 0$ (thermodynamic stability criterion)
- bc, ed } metastable { superheated liquid, supercooled vapor
- isotherms terminate at $\partial P/\partial V = 0$

- for Van-der-Waals gas, will encounter regions with $\partial P/\partial V > 0$ $\Rightarrow$ instability $\Rightarrow$ interpolate transition route via Maxwell's rule $\left\{ \begin{array}{l} A_1 = A_2 \\ d\mu = 0 \Rightarrow \\ \int V dP = 0 \end{array} \right.$

i.e.

{ equal area construction

$\Rightarrow$ Now, could just as well consider binary alloy, with constituents A, B

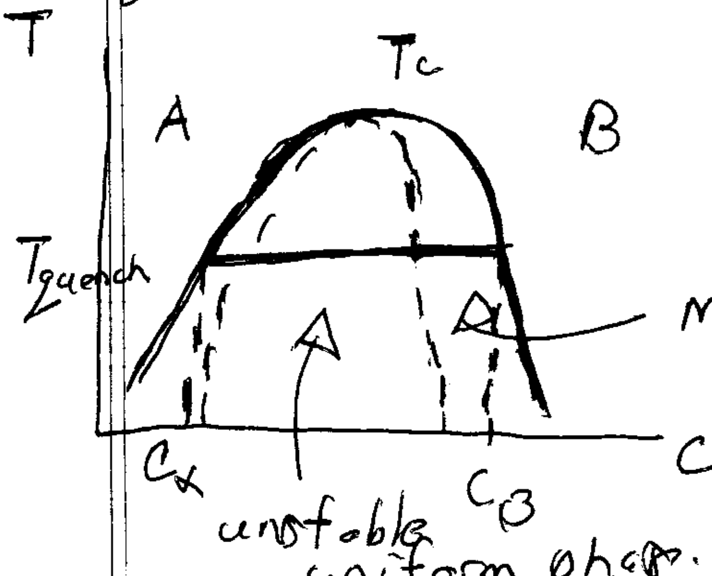
- consider rapid quench of mixture/binary alloy from $T > T_c$ to $T < T_c$

$\downarrow$

- phase separation occurs $\Rightarrow$ domains of A and B, with differing routes. $\rightarrow$ decomposition

Key problem

i.e.



Stable uniform phase

metastable uniform phase

unstable uniform phase.

$\rightarrow$ spinodal region corresponds loosely to $\partial P/\partial V > 0$ region $\rightarrow$ unstable i.e.

a) if quench to metastable region, ⇒ separation by homogeneous nucleation

→ large thermal fluctuation occurs,

→ making a droplet of one of two phases

$$\underset{\text{change in free energy}}{\Delta F} = \underset{\text{penalty for surface}}{4\pi \overset{\text{surface energy/area}}{\sigma} R^2} - \frac{4\pi}{3} R^3 \underset{\text{energy/volume}}{G}$$

$\therefore \begin{cases} R > R_c = 2\sigma/G & \text{survive, grow, coalesce} \\ R < R_c & \text{shrink} \end{cases}$

Key Problem ① } ⇒ nucleation: birth, coalescence of homogeneous phase droplets

b) if quench to $\sigma \to 0$ region ⇒ homogeneous state unstable to arbitrarily small perturbations ⇒ phase separation by growth of long wavelength perturbations ⇒ spinodal decomposition

Key problem ② { ⇒ during spinodal decomposition, small scale fluctations

"Coarsening" in action ...

Nucleation Spinodal Decomp.

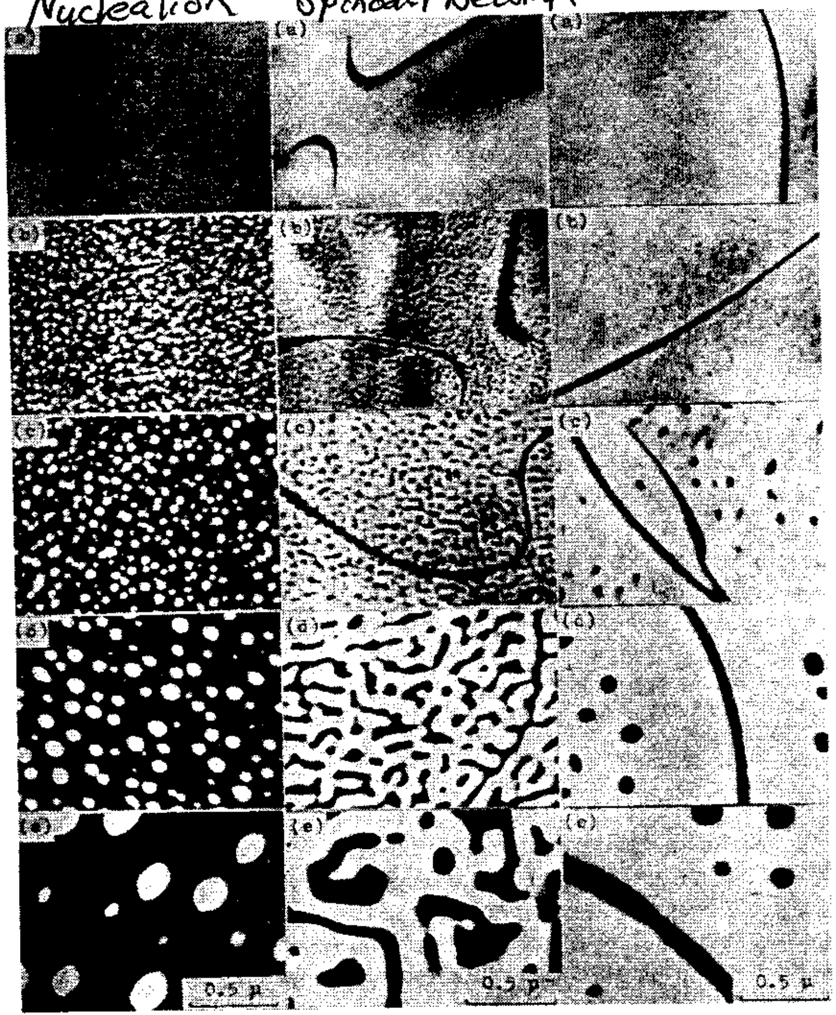


FIG. 3. Domain structures imaged with B_2 superlattice reflection in 23.0, 24.7 and 24.9 at% Al alloys, from left to right. The samples are quenched from 630°C and annealed at 570°C in the case of 23.0 and 24.7 at% Al alloys and at 568°C in the case of 24.9 at% Al alloy. (a) As quenched; (b) annealed for 15 min in 23.0 and 24.9 at% Al and for 10 min in 24.7 at% Al alloy; (c) 100 min; (d) 1000 min; (e) 10000 min. (From Oki *et al.*, 1977.)

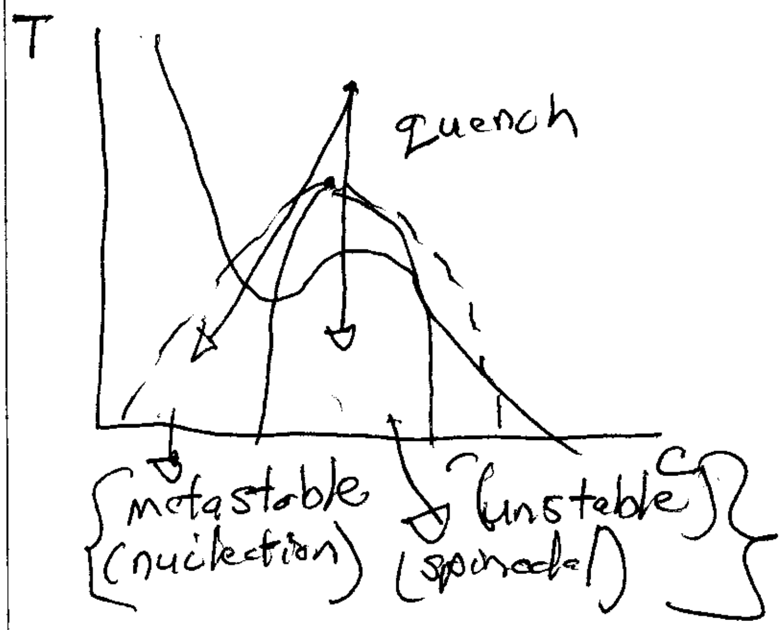
a quench into an unstable region of the Fe–Al phase diagram. This shows the characteristic interconnectivity of phases which is often used as a mark of spinodal decomposition. The reaction following a quench into the region of instability starts with the appearance of a fine, uniformly dispersed precipitate. This shows the long wavelength instability mentioned above.

in composition grow into domains on larger scale → i.e. coarsening

e.g. Gunton Article Picture:

a, c → droplet nucleation and coalescence
b → spinodal decomposition

⇒ will focus on dynamics of
- droplet coalescence
- spinodal decomposition.



i.) Droplet Nucleation and Coalescence

→ Seek model of:
- probability of individual bubble growth, evaporation (due thermal flctns).
- growth and coalescence dynamics

in order to describe nucleation process of phase separation:

∴ pragmatically, need $f(R,t) \equiv$ bubble size distribution function (pdf)

⇒ need
- equilibrium distribution $f_0(R)$ derived from energetics fluctuation probability for single bubble
- kinetic equation, for bubble growth from molecular aggregation i.e. $f(R,t)$ (i.e. Lifshitz, Slyozov theory)

a.) Single Bubble (Nucleation Probability)

- interface (i.e. A, B; liquid-gas) ⇒ surface tension, which contributes to thermodynamic work

$$dW = \underset{\substack{\uparrow\\\text{surface tension}\\\text{coefficient}}}{\sigma}\, \overset{\substack{\text{change in}\\\text{surface area}}}{dS_A} \quad \longleftrightarrow \text{ analogue to } -PdV$$

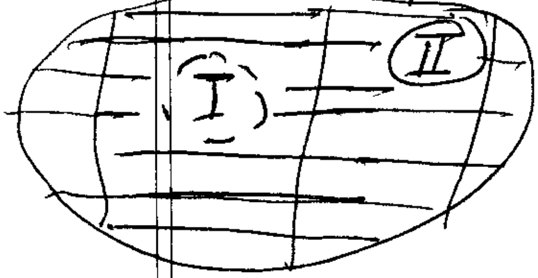
$\sigma > 0$

we have: $dE = TdS + \mu dN + \sigma dS_A$

$\Omega = \Phi - \mu N$

$$d\Omega = -SdT - Nd\mu + \sigma dS_A$$

- Now, consider spherical drop of phase I immersed in phase II



$\Rightarrow \Omega = -P_1 V_1 - P_2 V_2 + \sigma S_A$

$V_1 + V_2 = V_{sys} \rightarrow$ constant

equilibrium: $\frac{\partial \Omega}{\partial r} = -P_1 \frac{\partial V_1}{\partial r} - P_2 \frac{\partial V_2}{\partial r} + \sigma \frac{\partial S_A}{\partial r} = 0$

(also maximum)

$$= \underset{\text{pressure diffnce across interface}}{\underbrace{-(P_1 - P_2)}} \frac{\partial V_1}{\partial r} + \sigma \frac{\partial S_A}{\partial r}$$

droplet radius

but $V_1 = \frac{4\pi}{3} \overset{\downarrow}{r}^3$

$S = 4\pi r^2$

$$\frac{\partial \Omega}{\partial r} = -(P_1 - P_2)\, 4\pi r^2 + \sigma\, 8\pi r = 0$$

$$\Rightarrow \boxed{(P_1 - P_2) = \frac{2\sigma}{r}}$$

Laplace's Law

→ equilibrium condition

- now, for nucleation probability, realize

1) probability of bubble/nucleus formation simply:

$$P_N = P_{\text{nucleation}} = c \exp\left[-\overbrace{W_N}^{\text{work of nucleation}} / k_B T\right]$$

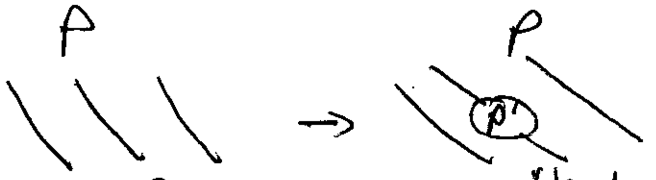
1 ... eqbm.

$W_N \equiv$ minimum work done to form bubble

$W_N = W_N(r)$

2) W_N obviously competition between energy gain for bubble, energy penalty due surface area.

Thus if



uniform → with bubble fluctuation

{prime → bubble rgn

T } const. throughout
μ }

$$\Omega = -P(V+V') \qquad \Omega = -pV - p'V' + \sigma S_A$$

difference

∴

work of nucleation

$$W_N = -(p'-p)V' + \sigma S_A$$

$$= -(p'-p)\frac{4\pi r^3}{3} + \sigma 4\pi r^2$$

and for nucleus equilibrium

$$\frac{2\sigma}{r} = p' - p \Rightarrow r = \left(\frac{2\sigma}{p'-p}\right)$$

$$\Rightarrow \boxed{W_N = 16\pi\sigma^3/3(p'-p)^2}$$

' → nucleus

so $W_N = 16\pi\sigma^3/3(p'-p)^2$

$\downarrow$
work of nucleation

Now, $p_0 \equiv$ pressure for which T is transition point

i.e. $\left.\begin{array}{l}\delta p = p - p_0 \\ \delta p' = p' - p_0\end{array}\right\}$ degree of superheating, supercooling

and $v'\delta p' = v\delta p \quad \leftrightarrow \quad d\mu' = \boxed{d\mu}$

so $p' - p \approx \delta p' - \delta p = \left(\frac{v}{v'} - 1\right)\delta p$

$\delta p' = \frac{v}{v'}\delta p$

$\Rightarrow$

$P_N = C\exp\left[-W_N/T\right]$ (usual fluctuation theory formula)

$$\boxed{P_N = C\exp\left[-\frac{16\pi\sigma^3 v'^2}{3T(v-v')^2\delta p^2}\right]}$$ } nucleation probability

If consider vapor bubbles in superheated liquid

$\underset{\text{liquid}}{v} \ll \underset{\text{gas}}{v'} \Rightarrow$

$$P_N = \exp\left\{-\left[\frac{16\pi\sigma^3}{3T\delta p^2}\right]\right\}$$

re-write:

$$\boxed{P_N = C\exp\left[-\frac{16\pi\sigma^3}{3T\delta p^2}\right]}$$

vapor bubble nucleation probability in superheated liquid correspondingly,

If consider liquid droplets in super-cooled vapor,

$$P_N = c \exp\left[-\frac{16\pi\sigma^3 v'^2}{3T v^2 \delta p^2}\right]$$

but $v = T/p \cong T/p_0$

$$\Rightarrow \boxed{P_N = c \exp\left[-\frac{16\pi\sigma^3 v'^2 p_0^2}{3T^3(\delta p)^2}\right]}$$

liquid drop nucleation probability in super-cooled vapor

It's clearly useful to define nucleation probability as function of degree of meta-stability, i.e. how far into coexistance.

$$P_N = P_N(\delta T) \qquad \delta T = \underset{\substack{\downarrow \\ \text{temp of meta-stable phase}}}{T} - \overset{\substack{\text{temp. of phase eqbrm.} \\ \uparrow}}{T_0}$$

Now, Clausius-Clapeyron $\Rightarrow$

$$\frac{dP}{dT} = \frac{s-s'}{v-v'} = \frac{\overset{\text{transition heat}}{q}}{T_0(v-v')}$$

$$\delta p = \frac{q}{T_0(v-v')}\delta T$$

$\Rightarrow$

$$\boxed{P_N = c \exp\left[-\frac{16\pi\sigma^3 v'^2 T_0}{3 q^3 (\delta T)^2}\right]}$$

alternate form → drop nucleation probability

↱ ~ σ^3 of surface tension

Note: $P_N \sim \exp\left[-\frac{\sigma^3 v'^2}{(\delta T)^2}\right]$

↳ ~ $\exp\left[-1/(\delta T)^2\right]$ in metastability margin

i.e. extreme dependence on $\delta T, \sigma$

Now, observe:

→ evolution metastable → stable phase occurs via nucleation upon fluctuation

nucleus → droplet → favorable
+ interface → unfavorable ⇒ critical radius for nucleation

formation energy ↓

→ $$E = -(p'-p)v' + \sigma S$$
$$= -(p'-p)\frac{4\pi}{3}r^3 + \sigma 4\pi r^2$$

$$\frac{dp}{dT} = \frac{q}{T_0(v-v')}$$

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

$$\frac{dE}{dr} = \frac{d\Omega}{dr} = 0$$ → radial eqbrm condition is also maximum in formation energy

$$\Rightarrow \boxed{r_{crit} = \frac{2\sigma}{\Delta p}}$$

$$\Rightarrow \Delta p = \frac{2\sigma}{r_{crit}},$$ and

$$E_{Form} = -\frac{8\pi\sigma}{3}\frac{r^3}{r_{crit}} + 4\pi\sigma r^2$$

and expanding about r_{crit} ⇒

$$\boxed{E_{form} = \frac{4\pi}{3}\sigma r_{crit}^2 - 4\pi\sigma (r - r_{crit})^2}$$

→ now can generalize probability of nucleation to notion of $f_0(r)$ → droplet distribution (equilibrium)

$f_0(r)\,dr \equiv$ # nuclei-per-volume with size in range dr

↓

size distribution function

$$f_0(r) = c\exp\left[-E_{form}(r)/T\right]$$

$$\left\{ \begin{array}{l} f_0(r) = f_0(r_{crit}) \exp\left[4\pi\sigma (r-r_{crit})^2/T\right] \\ f_0(r_{crit}) = c \exp\left[-4\pi\sigma r_{crit}^2/3T\right] \end{array} \right.$$

Note:

→ $r > r_{crit}$ ⇒ demarks range of significant droplet formation

→ with fluctuations, really a range

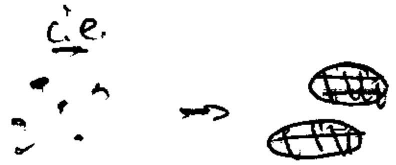
$$r = r_{crit} \pm \Delta r$$

$$\Delta r \sim (T/4\pi\sigma)^{1/2}$$

of nuclei separates $\left\{ \begin{array}{l} \text{evaporation} \\ \text{coalescence} \end{array} \right.$ fate;

Now, proceed to nuclei kinetics.

D.) Kinetics of Droplets and Nuclei



→ seek $f(R, t)$: time-evolving distribution function of grains and droplets' sizes

Can delineate two stages in droplet evolution

i.) fluctuation dominated stage (early stage of droplet creation and initial growth)

- fluctuations induce birth of nuclei
- subcritical ($r < r_{cr}$) nuclei evaporate, supercritical nuclei ($r > r_{cr}$) grow

→ mechanism of growth is fluctuation-induced molecular accretion (i.e. small "kicks" in size)

- no accnting for depletion super-sat.

ii.) droplet competition stage (later stage of droplet growth) deteministic

- viable nuclei established, unviable have evaporated; growth rate increases with size
- larger droplets tend to squeeze out smaller droplets (a la' R-T bubble competition)

i.e.

- mechanism is determined by physics of droplet growth dynamics

~ steady
- super-sat. reservoir finite

.. natural to suggest approaches via:

i.) statistical ⇒ Fokker-Planck theory of transport in R-space via small accretion events due fluctuations

ii.) dynamical ⇒ bubble growth

i.) Fluctuation-Dominated Phase

Now, have:

$$f_0(R) = \exp\left[-W_N(R)/T\right]$$

$$= f_0(R_{cr})\exp\left[4\pi\sigma(R-R_{cr})^2/T\right]$$

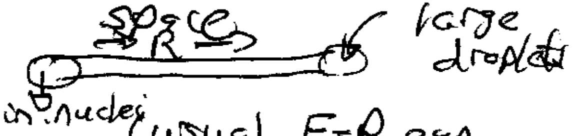
$$f_0(R_{cr}) = c\exp\left[-4\pi\sigma R_{cr}^2/3T\right]$$

and seek construct F-P. Eqn., i.e.

$$\frac{\partial f(R,t)}{\partial t} = -\frac{\partial \Gamma_R}{\partial R}$$

Γ ≡ flux, in radius space

i.e.



where

$$\Gamma_R = \underbrace{-B\frac{\partial f}{\partial R}}_{\text{diffusion}} + \underbrace{Af}_{\text{drag/drift term}},$$

(usual F-P eqn. structure)

To relate A, B, note must have $\partial f_0/\partial t = 0$, as equilibrium. Thus,

$$0 = -B\,\partial f_0/\partial R + A f_0$$

$$\Rightarrow \quad A f_0 = B\, f_0(R_{cr}) \left(\frac{8\pi\sigma(R-R_{cr})}{T}\right) \exp\left[-W_N(R)/T\right]$$

$$= -f_0 \frac{B}{T} \frac{\partial W_N}{\partial R}$$

$$\therefore \quad \boxed{A = -\frac{B}{T} \frac{\partial W_N}{\partial R}}$$

$$\Rightarrow \quad \Gamma_R = -B \frac{\partial f}{\partial R} - \frac{B}{T} \frac{\partial W_N}{\partial R} f$$

$$= -B\left(\frac{\partial f}{\partial R} + \frac{1}{f_0} \frac{\partial f_0}{\partial R} f\right)$$

$$\boxed{\Gamma_R = -B f_0 \frac{\partial}{\partial R} (f/f_0)} \qquad \frac{\partial f}{\partial t} + \frac{\partial}{\partial R} \Gamma = 0$$

Now,

- continuous phase transition process $\Leftrightarrow$ stationary state
  $\Rightarrow \Gamma = \text{const}$
- $\partial(f/f_0)/\partial R = -\Gamma/B f_0$

$$f/f_0 = -\Gamma \int dR/B f_0 + \text{const.}$$

- to determine const, note boundary conditions on 'flux' in radius space $\Rightarrow$

1) at $R \sim R_{cr}$, fluctuations most probable (i.e., recall $\delta R \sim (T/\sigma)^{1/2}$), so reasonable to assume "reservoir" of small nuclei maintained to initialize cascade

$\Leftrightarrow$ T reservoir $\Leftrightarrow$ small nuclei reservoir

$\Rightarrow$ $f/f_0 \to 1$ as $R \to 0$

2) at $R \gg R_{cr}$, f_0 diverges while f finite ∴ can take $f/f_0 \to 0$ as $R \to \infty$

$$\Rightarrow \boxed{f/f_0 = \Gamma \int_R^{\infty} dR/Bf_0}$$

"steady flow" solution

a, normalizability $\Rightarrow$

$$\boxed{1/\Gamma_R = \int_0^{\infty} dR/Bf_0}$$

flux value

but have $f_0\big|_{R\sim R_{cr}} = f_0(R_{cr})\exp\left[4\pi\sigma(R-R_{cr})^2/T\right]$

$$\Rightarrow \Gamma_R = 2\sqrt{\sigma/T}\; B(R)\, f_0(R_{cr})$$

} # of viable nuclei (i.e. # passing/growing thru critical stage) per time per volume

relates flux thru critical stage to equilibrium distribution (thermodynamic) and diffusion coefficient

(i.e. $\frac{\partial f(R,t)}{\partial t} + \frac{\partial}{\partial R}\Gamma = 0$

$\Rightarrow \frac{\partial}{\partial t}\int_{R_V}^{\infty} f\,dR = -\Gamma\Big|_{R_V}^{\infty} = \Gamma_{R_V}$)

→ Now, can simplify evolution equation for $f(R,t)$ and relate A, B to macroscopic quantities by noting:

- for $R >> R_{cr}$, $f << f_0$ is only information from F-P Eqn.
- once $R >> R_{cr}$, fluctuations insufficient to cause reversion of nuclei to subcritical scales ∴ nuclei just keep growing

⇒ evolution is not really random walk for $R >> R_{cr}$.
∴ can neglect diffusion ⇒

$$\Gamma = Af \Rightarrow A = \frac{dR}{dt} \Big\} \text{ velocity in size space}$$

$$\boxed{a \to R}$$

so

$$A = (da/dt)_{macro}$$

$$B(a) = \frac{-T}{(\partial W_N/\partial R)}\left(\frac{dR}{dt}\right)_{macro}$$

$$= \frac{+T}{8\pi\sigma(R-R_{crit})}\left(\frac{dR}{dt}\right)$$

consistency? i.e. B from extrapolation A to $R \sim R_{crit}$

(→ no singularity, as $\frac{dR}{dt} \sim R-R_{crit}$)

⇒ suggests can determine A, B from macroscopic arguments underlying dR/dt!

→ Now;

⇒ seek determine A, B from macroscopic (continuum) consideration

∴ - for clarity, consider precipitation of solute out of super-saturated solution

- ∴ proceed via determination of stationary diffusive flux to nucleus surface (of radius R)

[Notation: R → location in size space
r → radial position]

diffusive accretion flux rate

→ solution concentration

$$I = 4\pi r^2 D \frac{\partial c}{\partial r} \qquad \left(R^2 4\pi \frac{dR}{dt} = I v\right)$$

rate of accretion thru r-sphere (#/time)

$$= A D \frac{\partial c}{\partial r}$$ → need c(r) to calculate

For concentration profile:

$$\cancel{\frac{\partial c}{\partial t}} = D\nabla^2 c = 0 \text{, stationary state}$$

$$\Rightarrow \frac{D}{r}\frac{\partial^2}{\partial r^2}\left(r\, c(r)\right) = 0$$

$$c(r) = a + \frac{b}{r}$$

imposing boundary conditions : $C(\infty) = C$ (given bckgnd concen.)
$C(R) = C_{0R}$

C_{0R} → concentration of solution about nucleus of radius R

$$\Rightarrow \; C(r) = C - (C - C_{0R})\frac{R}{r}$$

$$\therefore \; I\Big|_R = 4\pi r^2 D\,(C - C_{0R})\frac{R}{r^2}\Big|_R \qquad \text{(inward)}$$

$$= 4\pi R D\,(C - C_{0R})$$

$$\Rightarrow \; \boxed{I(R) = 4\pi R D\,(C - C_{0R})} \rightarrow \text{diffusive flux rate}$$

d

$$\frac{dR}{dt}(4\pi R^3) = I(R)\,V' \qquad (V' \equiv \text{nucleus specific volume (thermo. flctn.)})$$

↳ rate of nucleus volume growth

$$\Rightarrow \; \boxed{\frac{dR}{dt} = \frac{I(R)V'}{4\pi R^2}} \rightarrow \text{rate of growth of nucleus/droplet}$$

$$\therefore \; \frac{dR}{dt} = V'\cancel{4\pi} R D\,(C - C_{0R}) \Big/ \cancel{4\pi} R^2$$

$$= \frac{V'D}{R}\,(C - C_{0R})$$

To determine C_{0R}, consider relation between chemical potential and critical radius :

recall : $W_N \equiv$ Work done to form droplet

$$= \Delta(\underset{\text{Free energy}}{F} + P_0 V)$$

$$\Rightarrow W_N = (\underset{\text{Thermo potential}}{F'(P')} + PV') - (F(P) + PV) + \sigma A$$

$$= \Phi'(P') - \Phi(P) + \sigma A$$

$$\Phi'(P') = \Phi'(P) + (P'-P)V'$$

$$\Rightarrow W_N = \Phi'(P) - \Phi(P) + (P'-P)V' + \sigma A$$

$$= (\Phi'(P) + P'V) - (\Phi(P) + PV') + \sigma A$$

$$= n\,[\mu'(P) - \mu(P)] + \sigma A$$

particles in nucleus

$$\Rightarrow W_N = -\frac{4\pi R^3}{3V'}[\mu(P) - \mu'(P)] + 4\pi R^2\sigma$$

volume-per-particle

(for spherical nucleus)

$\partial W_N / \partial R = 0$ gives

$$R_{crit} = 2\sigma V' / [\mu(P) - \mu(P')] \Big\}$$

critical radius in terms potential

Now, for concentration of saturated solution above plane surface of solute $c_{0,\infty}$,

$$T \ln C_{0,\infty} + \psi = \mu_0 \quad \Rightarrow \quad C_{0,\infty} = \exp\left[\frac{\mu_0}{T} + \frac{\psi}{T}\right]$$

$$\Rightarrow \quad \mu - \mu_0 = T \ln (C/C_{0,\infty}) \cong T \frac{(C - C_{0,\infty})}{C_{0,\infty}}$$

$$\Rightarrow \quad \boxed{R_{crit} = 2\sigma v' C_{0\infty} / T\,\underbrace{(C - C_{0,\infty})}_{\text{degree supersatn.}}}$$

$$\therefore \quad C\Big|_{R_c} = C_{0\infty}\left(1 + \frac{2\sigma v'}{T R_{crit}}\right) \quad \rightarrow \text{specifies } C \text{ at } R_{crit}.$$

$$\Rightarrow \quad \left.\begin{aligned} C_{0R} &= C_{0,\infty}\left(1 + \frac{2\sigma v'}{TR}\right) \\ &= C_{0\infty} + \frac{R_c}{R}(C - C_{0,\infty}) \end{aligned}\right\}$$

$$\therefore \quad (C_{0R} - C_{0,\infty})R = R_c(C - C_{0,\infty})$$

$$C_{0R} R - C R_c = C_{0,\infty}(R - R_c)$$

$$C_{0R} R - C R_c + CR - CR = C_{0,\infty}(R - R_c)$$

$$(C_{0R} - C)R + C(R - R_c) = C_{0,\infty}(R - R_c)$$

$$\Rightarrow \quad (c - c_{0R})\, R = (c - c_{0,\infty})\,(R - R_0)$$

Thus finally,

$$\boxed{\left.\frac{dR}{dt}\right|_{macro} = \frac{v' D}{R^2}\,(R - R_0)\,(c - c_{0,\infty})}$$

accretion vanishes with supersatn.

$$\Rightarrow \left\{ \begin{aligned} &B(R_{cr}) = D\, v'^3 c_{0,\infty} / 4\pi R_{cr}^3 \\ &A = dR/dt \end{aligned} \right.$$

i(c.)

Co-alescence Phase - Nuclei Growth

Recall can separate phase separation dynamics into two stages:

a.) fluctuation dominated

- strongly supersaturated state
- critical radius small, i.e.

{statistical model

$$R_{crit} = 2\sigma\dot{v}c_{0,\infty} / T(c - c_{0,\infty})$$

→ degree of super-saturation

↳ {concentration of solution above precipitate formed on flat surface

$(R_c \sim 1/\Delta SS)$

- numerous small nuclei

b.) coalescence

{dynamical model

- weak supersaturation
- large critical radius
- little formation, rather (due fluctuations → energy penalty too large)

⇒

- nuclei grow by competition (i.e. big droplets squeeze out little droplets)
- critical radius large and growing

Here, seek describe <u>coalescence</u> phase.

Now, in coalescence phase, nuclei grow by diffusive accretion, i.e.

$$\frac{dR}{dt} = D\frac{\partial c}{\partial r}\Big|_R$$

→ c dimless (i.e. volume solute per unit volume solvent)

(contrast previous → not single particle i.e. large grain)

↳ diffusive flux thru sphere, radius R

Now, $\nabla^2 C = 0$ with $C(r)\big|_R = C_{0R}$

$C(\infty) = C$

$\Rightarrow C(r) = C - (C - C_{0R})\, R/r$

Then,

$$\frac{dR}{dt} = D\,(C - C_{0R})\frac{R}{R^2} = \frac{D}{R}\,(C - C_{0R})$$

but $C_{0R} = C_\infty(1 + 2\sigma V'/TR) \rightarrow$ concentration above nucleus of radius R

$$\Rightarrow \left\{ \begin{aligned} \frac{dR}{dt} &= \frac{D}{R}\left(C - C_\infty - C_\infty\frac{2\sigma V'}{TR}\right) \\ &= \frac{D}{R}\left(\Delta - \frac{\alpha}{R}\right) \end{aligned} \right.$$

→ defines dynamical R_{crit}

→ degree supersatn.

$$\left\{ \begin{aligned} \Delta &= C - C_\infty \\ \alpha &= 2\frac{C_\infty \sigma V'}{T} \end{aligned} \right.$$

effectively defs $\Rightarrow R_{crit} = \alpha/\Delta = \alpha/\Delta(t)$ } dynamical (as opposed statistical) definition of R_{crit}.

so $R > R_{crit} \Rightarrow dR/dt > 0$ grain grows

$R < R_{crit} \Rightarrow dR/dt < 0$ " " dissolves.

Now, $t \to t/\left(R_{cr}(0)^3/D\alpha\right)$

$\left\{ R_{cr}(0) \equiv \right.$ crit. radius at time coalescence begins

$$\frac{dR}{dt} = \frac{R_{cr}(0)^3}{R(t)}\left(\frac{1}{R_{cr}(t)} - \frac{1}{R(t)}\right)$$

$\left(\Rightarrow \text{dimensionally, } R \sim t^{1/3}\right)$

↓ Lifshitz-Slyozov scaling

i.e., in coalescence phase:

$$(1)\qquad \frac{dR}{dt} = \frac{R_{cr}(0)^3}{R}\left(\frac{1}{R_{crit}(t)} - \frac{1}{R}\right), \qquad R_{crit} = \alpha / \Delta(t)$$

and $V_R \equiv dR/dt$ $\Rightarrow$ $f(R,t)$ evolves according:

(i.e. continuity)

$$(2)\qquad \frac{\partial f}{\partial t} + \frac{\partial}{\partial R}\left(V_R f\right) = 0$$

where # grains $N(t) = \int_0^\infty f(t,R)\, dR$ is normalization for f.

Finally, conservation of solute $\Rightarrow$

[Total initial concentration] =

(initial)

[Concentration Precipitated Grains] + [Concentration in Supersaturation]

i.e.

$$(3)\qquad Q = q(t) + \Delta(t) \qquad \begin{cases} \Delta(t) = C - C_{0,\infty} \\ q(t) = \frac{4\pi}{3}\int R^3 f(t,R)\, dR \end{cases}$$

$\Delta(t)$ → degree supersaturation

Eqns. (1), (2), (3) describe coalescence phase.

⇒ if: $\rho = R(t)/R_{cr}(0)$, $X = R_{cr}(t)/R_{cr}(0)$ $\Rightarrow \frac{d\rho^3}{dt} = 3\left(\frac{\rho}{X} - 1\right)$

Key Point:

→ both $R(t)$ and $R_{crit}(t)$ evolve in time!

→ nuclei growth depletes reservoir of super-saturation $R_{crit}(t) = \alpha/\Delta(t)$
(akin perturbation theory about time-evolving background).

∴ → useful to define new variables:

$$\left.\begin{aligned} X(t) &= R_{crit}(t)/R_{cr}(0) \\ u(t) &= R/R_{crit}(t) \end{aligned}\right\}$$

and

$\tau = 3\ln X(t)$ → new time variable (appr. exp grain bndry).

upon crank,

$$\Rightarrow \boxed{\frac{du^3}{d\tau} = \gamma(u-1) - u^3}$$ → NL equation for $R(t)$ evolution.

$$\gamma = \gamma(t) = (dt/dx)(1/X^2)$$

Now:

$$\frac{du^3}{d\tau} = \gamma(u-1) - u^3 = F(u)$$

→ view as dynamical system

observe: $F(u) \to -\infty, \quad u \to \infty$

$\to -\gamma, \quad u \to 0$

(i.e. both ⊖ not S-curve.

$$\frac{dF}{du} = 0 \Rightarrow \gamma = 3u^2 \Rightarrow u_{max} = (\gamma/3)^{1/2}$$

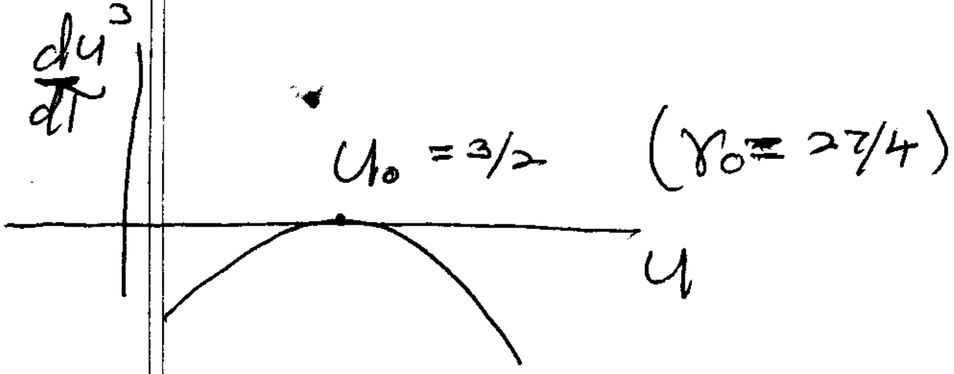
$$F(u_{max}) = \gamma\left[\frac{2}{3}\left(\frac{\gamma}{3}\right)^{1/2} - 1\right]$$

so can have: (depending on γ!)

a)

or

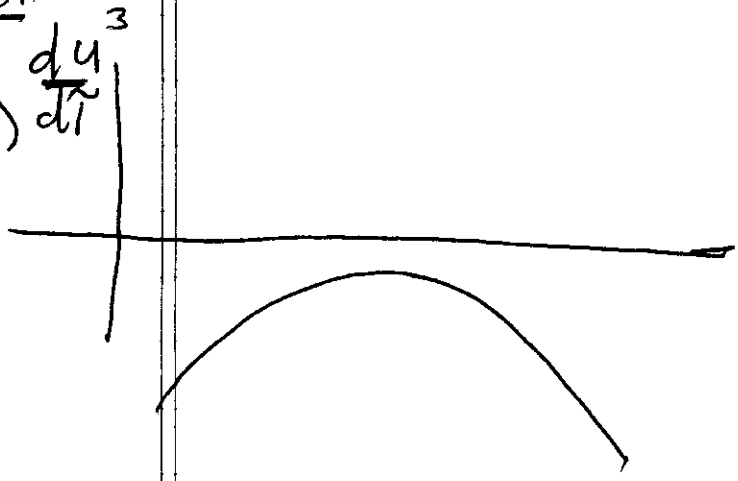
b)



note:
→ seek motion to left ⇒ "swept up"
as motion rt. violates cons.

or

c)



considering the possibilities: → no distribution.

c) → $du^3/d\tau < 0$ everywhere ⇒ all nuclei disappear (squeezed out)

a) → $u < u_1$ have $du^3/d\tau < 0$ ⇒ disappear (squeezed out for $\dot{u}^3 < 0$)
$u > u_1$ move to u_2

i.e. all $u > u_1 \Rightarrow R > R_{crit}(t)\, u_1$ asymptotically reach $R = R_{crit}\, u_2$.

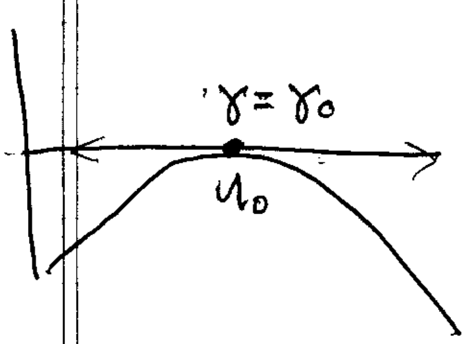
But $R_{crit}(t) \to \infty$, so conservation of concentration violated!

so must have case (b), with $\gamma \to \gamma_0$ from below

b) $\gamma(\tau) = \gamma_0[1 - \epsilon^2(\tau)]$ (swept up)

prevents points moving to left from getting "stuck" at u_0, i.e. would result in
∴ $R = R_{crit}\, u_0 \to$ blows up!
⇒ ϵ^2 from conservation of matter!

i.e.



i.e. want $\frac{dt}{dx} < 0$, slightly.

I.M. Lifshitz + V.V. Slyozov
J. Chem. Phys. Solids
19 35 (1961).

Then;

- grain dynamics and conservation of matter constrain $X(t) \Rightarrow \gamma(T)$
- $\gamma(T) = \gamma_0(1 - \epsilon^2(T))$
- Lengthy calculation ⇒ grain distribution function $f(R,t)$ (Lifshitz-Slyozov Theory)

1) mean grain radius

$$\bar{R} = (4\alpha D t/9)^{1/3}$$

(✓ dim. analysis)

2) number of grains-per-volume

$$N(t) = .5\, Q/D\alpha t$$

($N\bar{R}^3 \sim$ const)

3) degree supersaturation

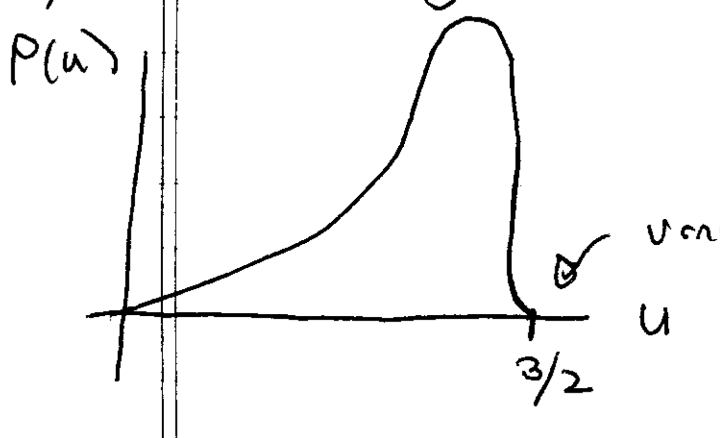
$\Delta \sim \bar{R}^{-1}$

$$\Delta(t) = (9\alpha^2/Dt)^{1/3}$$

(should drop to conserve concen.)

4) Pdf of grain size

(universal → indep. i.c.'s).



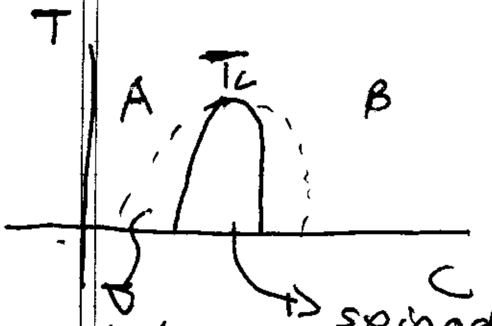
vanishes at u_0

($u > u_0$ swept to u_0 from right).

II.) Spinodal Decomposition.

Recall phase co-existance region < meta-stable (nucleation)
unstable (spinodal decomposition)

i.e.



→ nucleation (metastable: corresponds $\partial P/\partial V|_T < 0$)

→ spinodal (i.e. corresponds $\partial P/\partial V|_T > 0$, unstable)

{ nucleation → droplet coalescence
spinodal → domain decomposition.
→ phase separation mechanisms

Here: discuss spinodal decomposition

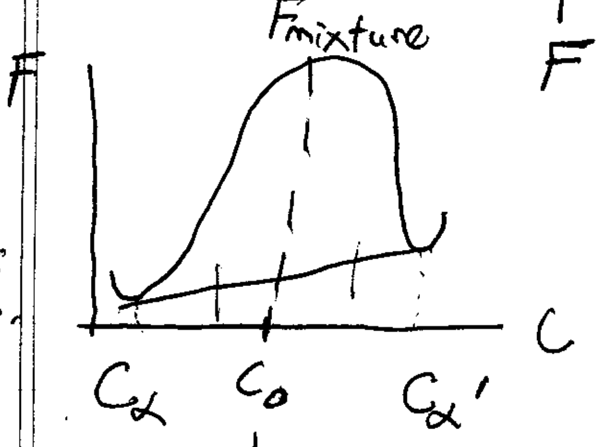
a.) Basics of spinodal

→ what?

- consider binary fluid (homogeneous mixture) of C_0
- allow?: $C_0 \to C_\alpha, C_{\alpha'}$ ⇒ change in free energy?

↓ two regions of differing composition

then!



Gibbs constr.

↓ avg. concentration

molar free energy
↑
F vs c curve.
↓
composition / concentration

spinodal ~ region $F'' < 0$

$\left.\begin{matrix} C_\alpha \\ C_{\alpha'} \end{matrix}\right\}$ constant concen.

$F(C_0)$ ⇒ determines free energy of mixture

⇒ $F'' < 0$ ⇒ homogeneous (uniform) state unstable!

- separation phases lower free energy
- separation should occur spontaneously (i.e. from fluctuations)
- but spontaneous separation implies diffusive flux against concentration gradient

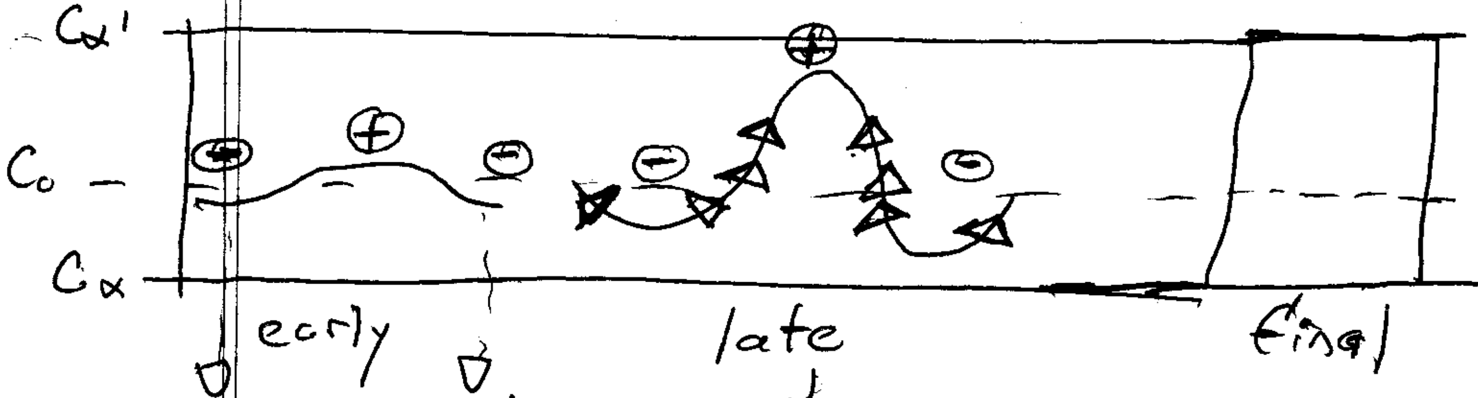
⇒ clustering, aggregation process described via backward or negative diffusion

→ How? – Clustering / Negative Diffusion.

→ Consider: "negative diffusion", i.e. flux up local concentration gradient

Then:

When: $T < T_c$ ⇒ quench to unstable part of phase co-existance region



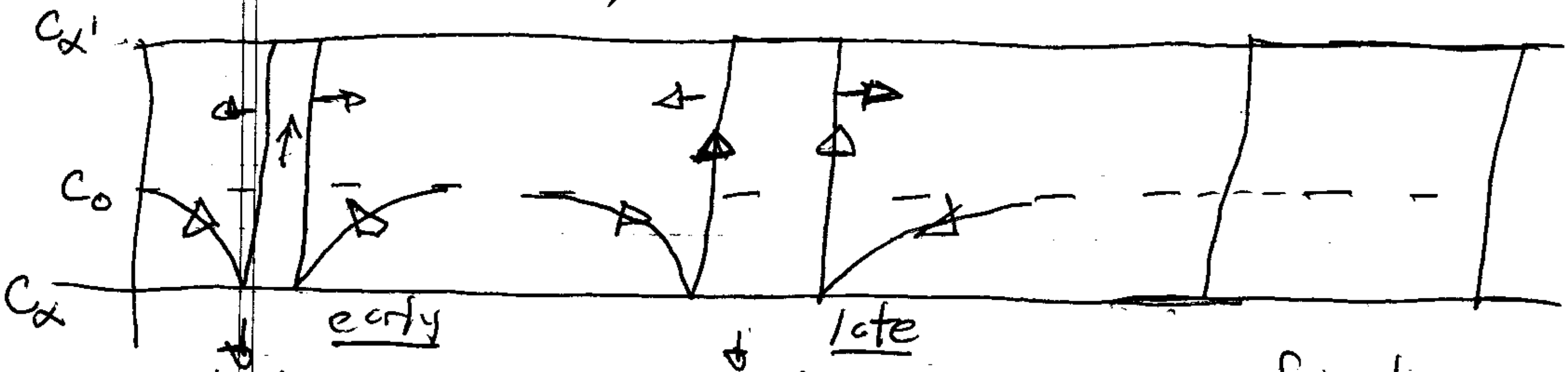
note ⊕ aggregation necessarily implies depletion of neighbors.

→ {suggests periodic arrangement of clusters

separated state of spinodal decomposition

i.e. spinodal decomposition is consistent with (~) periodic clustering due negative diffusion

→ contrast: nuclei growth (driven by diffusive flux)



final

cluster grows by
- diffusion <u>down</u> local gradient
- particles stick to cluster

∇c decreases

{all diffusion down gradient, here
⇒ no periodicity, etc.

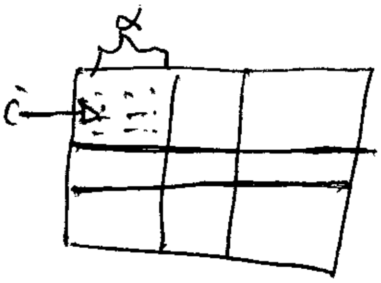
hen $\{C_i\} \rightarrow$ particular configuration C_i

so $$\underset{\substack{\downarrow \\ \text{probability} \\ \text{(Boltzman factor)}}}{P(\{C_i\})} = \exp[-H\{C_i\}/T] \,/\, \underset{\substack{\downarrow \\ \text{partition fctn.}}}{Z}$$

$$Z = \sum_{\{C_i\}} e^{-H\{C_i\}/T}$$

- to coarse grain ("block spin")
  - divide lattice into (hyper)cubes of size L
  - introduce average concentration variable for α^{th} cell

$$C_\alpha \equiv \frac{1}{(N/L^m)} \sum_{\underset{\substack{\downarrow \\ \alpha\text{th cell}}}{\{C\}_i}} C_i$$



and coarse grained Helmholtz free energy:

$$\exp[-F(\{C_\alpha\})/T] = \sum_{\{C_i\}}{}' \exp[-H(\{C_i\})/T]$$

where $\sum'_{\{C_i\}} \equiv$ sum over all microstates $\{C_i\}$ s/t cell configuration $\{C_\alpha\}$ and avg. C_α

- generally, $\sum'_{\{C_i\}}$ not calculated, and one uses symmetry to argue for Ginzburg-Landau form!

$$F\{C_\alpha\} = \sum_\alpha f(C_\alpha) + \sum_{\langle\alpha\beta\rangle} \underbrace{\frac{1}{2} K_L (C_\alpha - C_\beta)^2}$$

nearest neighbor interaction (a la' harmonic oscillator ⇒ symm.)

$$\underbrace{f(C_\alpha)} = \frac{1}{2} \underbrace{a}(T-T_c)\, C_\alpha^2 + \frac{1}{4} b\, C_\alpha^4$$

local free energy

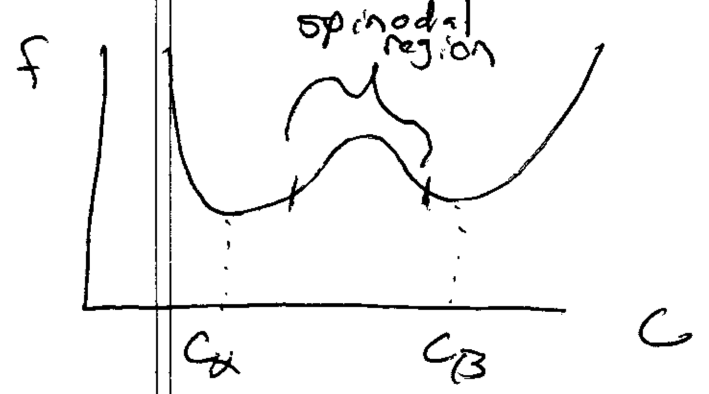
$\ominus$ for $T<T_c$

AB symmetry ⇒ even powers <u>only</u>

Note:

- sum $\langle\alpha\beta\rangle$ is over nearest neighbors. Coupling coeffs a, b, K_L etc. depend on L, T etc.
- valid scheme <u>only</u> if $L \ll L_{corr}$.
- for T near T_c, $L_{corr} \to \infty$, so $L \gg L_0$ (lattice spacing) and can apply continuum approximation.

- shape of coarse-grained potential is double well:



$c_\alpha, c_\beta \Rightarrow$
correspond to A, B
domains formed

- catch: difficult to relate parameters of (quasi-phenomenological) coarse-grained free energy to parameters of actual free energy
i.e. $\langle F \rangle \neq F(\langle c \rangle)$

⇒ Now, having coarse-grained:

c conserved $\Rightarrow \frac{dc}{dt} + \underline{\nabla}\cdot\underline{J} = 0$

$$\underset{\substack{\downarrow \\ \text{imbalance} \\ \text{current}}}{\underline{J}} = -\underset{\substack{\downarrow \\ \text{mobility}}}{M}\,\underline{\nabla}\mu$$

and: $\frac{\partial c}{\partial t} - M\nabla^2\frac{\delta F}{\delta c} = 0$

continuum

$$F = \int d^3x \left(\frac{K(\nabla c)^2}{2} - \frac{\alpha}{2} c^2 + \frac{\beta c^4}{4} \right)$$

$$\equiv \int d^3x \left(f_0 + K(\nabla c)^2/2 \right)$$

Note: Coarse graining obsc. reln. K, α, β to any micro. model → @ phenom.

⟹ $-\alpha$ as $f_0'' < 0$ in spinodal region

→ odd excluded as A, B labels arbitrary

$$\therefore \quad \frac{\delta F}{\delta c} = -\alpha c + \beta c^3 - K\nabla^2 c$$

$$\underline{J} = -M\left(-\alpha \underline{\nabla} c + \beta \underline{\nabla} c^3 - K\underline{\nabla}\,\nabla^2 c\right)$$

⟹ Cahn-Hilliard Equation:

$$\boxed{\frac{\partial c}{\partial t} = -M\alpha\nabla^2 c - MK\nabla^4 c + N.L.T.}$$

negative diffusion → clustering

cut-off due local interaction (i.e. bending)

can re-write:

$$\frac{\partial c}{\partial t} = M \underbrace{\frac{\partial^2 F_0}{\partial c^2}}_{<0} \nabla^2 c - MK\nabla^4 c + N.L.T.$$

if $c = \sum_{\underline{k}} c_{\underline{k}} e^{i(\underline{k}\cdot x - \omega t)}$

$$-i\omega = -M \frac{\partial^2 f_0}{\partial c^2} k^2 - 2M\kappa k^4$$

$$\omega = i k^2 M \left[\frac{\partial^2 f_0}{\partial c^2} - 2\kappa k^2 \right] \rightarrow$$ negative diffusion mode

defines length-scale

$\Rightarrow$ $k^2 < \frac{1}{2\kappa} \frac{\partial^2 f_0}{\partial c^2}$ $\rightarrow$ clustering unstable

$k^2 > \frac{1}{2\kappa} \frac{\partial^2 f_0}{\partial c^2}$ $\rightarrow$ clustering stable

$\hookrightarrow$ $l_{cluster} \gtrsim \left(2\kappa / \partial^2 f / \partial c^2 \right)^{1/2}$.

Note:

- in spinodal region, no uniform state possible, i.e. must have curvature to balance $-\alpha$

$\therefore$

- system must "coarsen", forming blobs
- observe in 1D,

$$\frac{\delta f}{\delta \eta} = 0 \Rightarrow -\kappa \frac{\partial^2 \eta}{\partial x^2} - \alpha \eta + \eta^3 = 0$$

$\Rightarrow$ $$\eta = \alpha^{1/2} \tanh\left[\pm \left(\alpha/2R\right)^{1/2}(x-x_0)\right]$$

- not blob (i.e. 3D)
- as drop blobs grow, 1D is better approx. to interface of blobs

$\Rightarrow$ coarsening!?

→ Coarsening : The Key Question

- Coarsened system exhibit ~~b~~lobs of visible characteristic scale, pattern (see Cahn article pictures)

∴ motivates obvious question:

- what set blob scale, amplitude

$\Rightarrow$

- What is nature of / how describe saturated state of coarsening / spinodal decomposition instability?

∴ consider quasilinear theory of Cahn-Hilliard equation.