

Some preliminary intensive - extensive pair knowledge

Overview of StatMech (I)

$$ds = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dM - \frac{u}{T} dW$$

$dU = T ds - P dV + H dM + u dW$ usually:

Legendre transformation $A = U - TS$ (T, V, M, N) $\psi = \left(S - \frac{U}{T} \right)$ (F) $A = U - TS + \frac{H^2}{2\pi} V$

transformation $dA = -S dT - P dV + H dM + u dW \Rightarrow dA = -S dT - P dV + H dB$

$F = A - MH$ $B = \frac{M}{V} + \frac{H}{2\pi}$

$dF = -S dT - P dV - M dH + u dW$ $G = A - F + B \cdot H$

$dG = -S dT - P dV - B dH$

$G = F + PV$

$dG = -S dT + V dP - M dH + u dN \Rightarrow G = G(T, P, H, N)$ is V

from $G(T, P, H, \lambda N)$ partition function $\Omega = \lambda G(T, P, H, N)$ $\Omega = PV$ (intensive) \rightarrow Similarly, Ω 's extensive variable $(U = U(S, V, M, N))$

Canonical $\frac{\partial}{\partial \lambda} \Big|_{\lambda=1} \Rightarrow G = \sum \frac{\partial G}{\partial N_i} N_i = \sum \mu_i N_i = TS - PV + HM + uW$

$$\begin{aligned} \Omega_N &= \frac{1}{N! h^{3N}} \int d^3N_p \int d^3N_q e^{-\frac{H(p,q)}{k_B T}} \\ &= \int_0^\infty dE e^{-\frac{E}{k_B T}} \int \frac{dp dq}{N! h^{3N}} \delta(E - H(p,q)) \\ &= \int_0^\infty dE \Omega(E) e^{-\frac{E}{k_B T}} \\ &= \int_0^\infty dE e^{-\frac{1}{k_B T} (E - TS(E))} \end{aligned} \quad \left. \begin{array}{l} \Omega_N = e^{-\frac{A}{k_B T}} \\ \downarrow \text{entropy effect!} \end{array} \right\}$$

D.M. $\Omega_N = \sum_E \Omega(E) e^{-\frac{E}{k_B T}} = \sum_E e^{-\frac{1}{k_B T} A(E)}$

Grand-canonical $Z = \text{Tr} e^{-\beta(\hat{H} - \mu \hat{N})} = e^{-\frac{\Omega}{k_B T}} = e^{-\frac{PV}{k_B T}}$

Introduction to phenomena of phase transitions

6-1

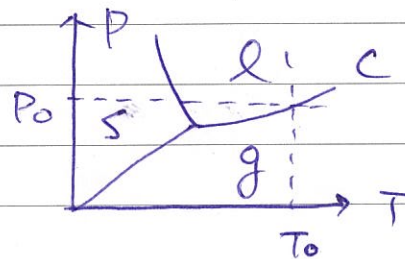
As we have seen, for 3D crystals, $\langle u^2 \rangle \propto T$.

It seems to imply that $\langle u^2 \rangle$ can increase

indefinitely. In reality, this is not so. — phase transition happens. Empirically, crystals melt

at T_m with T_m roughly given by the Lindemann criterion: $\langle u^2 \rangle = C_L a^2$ ($C_L =$ Lindemann's const. ($C_L \sim \frac{1}{100}$ roughly))

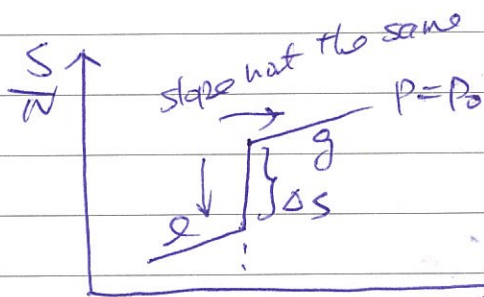
As we have indicated at the beginning of this course, the simplest & the most common (roughly universal) phase transitions can be illustrated by the water, ice and vapor system.



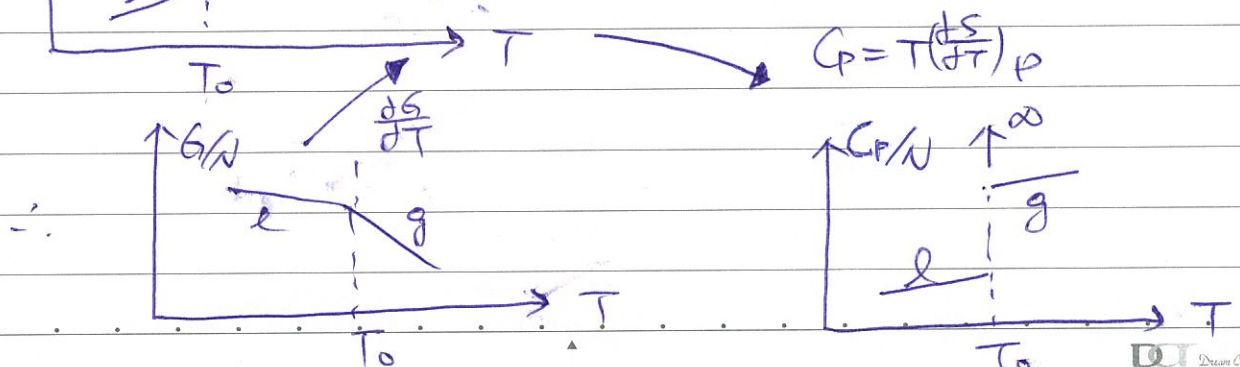
Discontinuities are often encountered with phase transitions.

For instance, as we go across $l-g$ boundary, one experiences $\Delta S = S_g - S_l > 0$

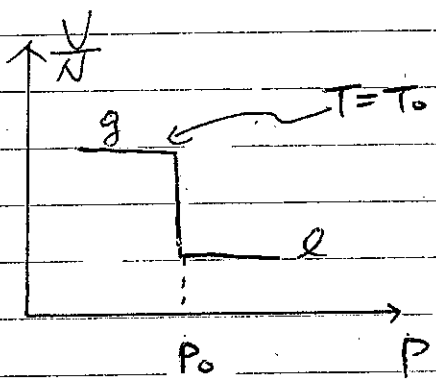
The latent heat $\Delta Q = T_0 \Delta S$



$$\therefore \left(\frac{dS}{dT} \right)_{P,S} = -S$$

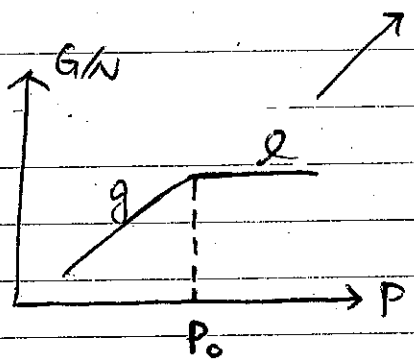


Q Similarly, $\Delta U = U_g - U_l \neq 0$ (> 0)

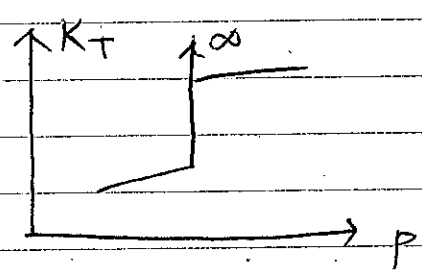


Corresponding thermodynamic potential:

$$\left(\frac{dG}{dP}\right)_T = V$$



$$K_T = -\frac{1}{V} \left(\frac{dV}{dP}\right)_T = \infty \quad \text{(isothermal Compressibility)}$$



Q Because the free energy's (or other potential) first derivative is not continuous, these are called 1st order phase transitions or fields discontinuous phase transitions. They are often connected with an entropy discontinuity.

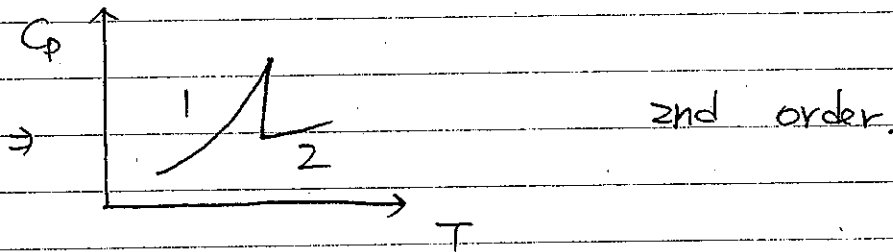
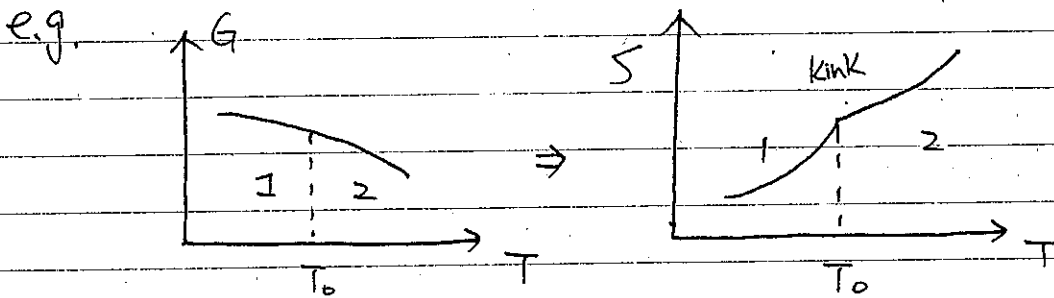
$$S = -\frac{dG}{dT}$$

$$V = \left(\frac{dG}{dP}\right)_T$$

external

Q There exist phase transitions in which $\Delta S = 0$, i.e. S is continuous. Then discontinuity can only start from the derivative of S , which is the 2nd derivation of G (or other potentials)

Such phase transitions are termed as the 2nd order phase transitions or continuous phase transitions or higher order.

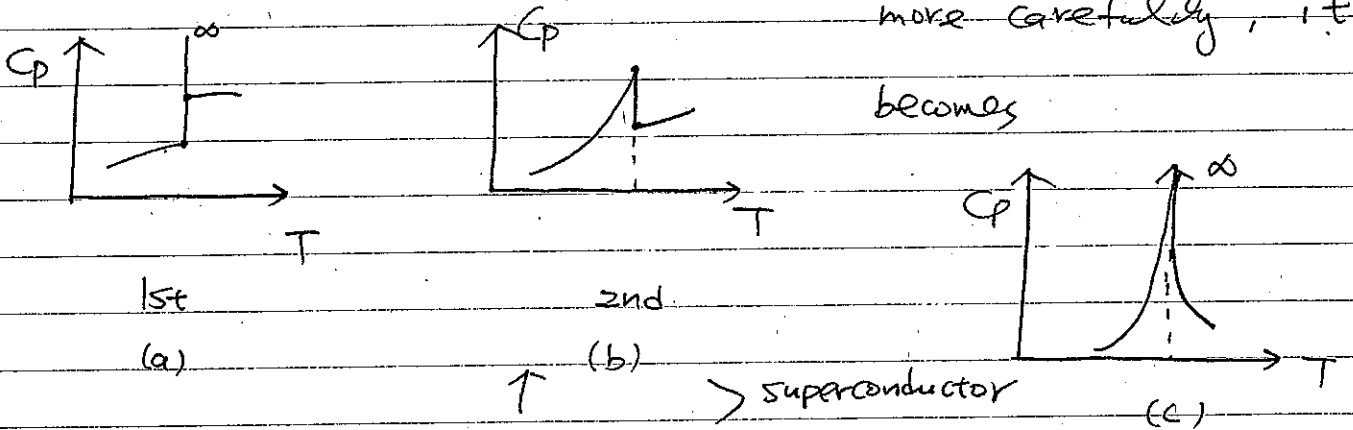


(Ehrenfest)
In old classification, one defines the 3rd order phase transitions, the 4th ... according to the largest ^{# of} derivatives of G (or other equivalent potentials) that becomes discontinuous. This turns out not to be useful. In

modern phase transitions, we only distinguish theory of

discontinuous (1st) & continuous phase transitions.

Q This is because for many experiments, at first the results look like (b), but when we look more carefully, it becomes

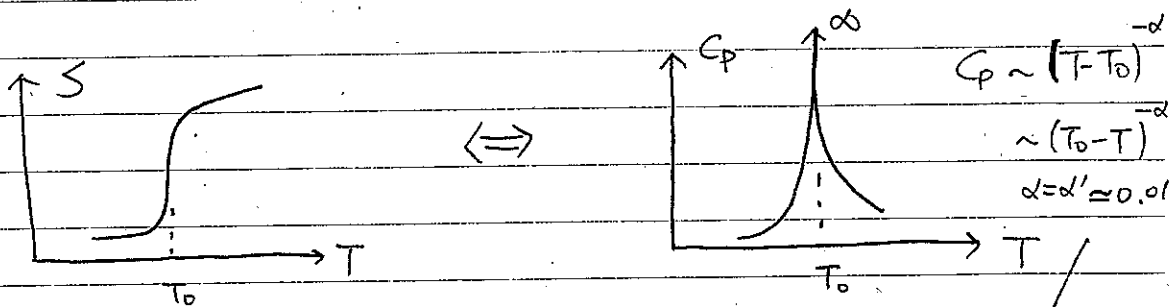


but S.V. ... continuous

Q ∴ Cp does not behave as what 2nd order was meant to be (b)!

As a result, distinguishing between continuous of S.V. or not is enough!

most cases ⇒

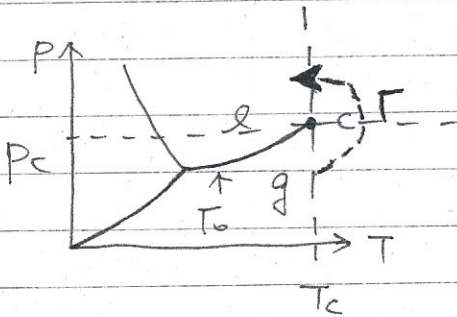


not discontinuous but has a vertical tangent at $T=T_0$.

example: He^4 λ transition

$\Delta S \sim (T-T_0)^{1-\alpha}$
 $S - S(T_0) \sim -(T_0-T)^{1-\alpha}$

9 An important example for continuous phase transition is the critical point in the water-ice-vapor system

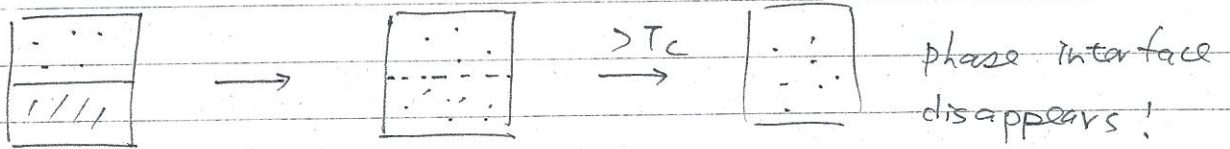


the l-g coexist line Γ_0 ends up with the critical point beyond which there is no distinction between l & gas!

\therefore if we go from g to l along Γ , the gas simply is converted in the liquid continuously without crossing the phase transition line.

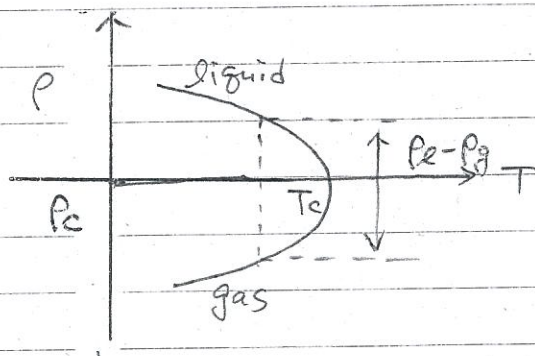
9

If we go along Γ_0 , we shall see



i.e. both gas & liquid have the same density.

If we plot out ρ v.s. T , we get



9

9 $p_c - p_g \propto (1 - \frac{T}{T_c})^\beta$ (e.g. $\beta = 0.362$ for Ar. ...)

$\therefore p \propto \frac{1}{V}$ $(\frac{\partial G}{\partial p})_T = V$

\therefore For fixed T but approaching T_c^- , we have

$\Delta(\frac{\partial G}{\partial p})_T \rightarrow 0$ \therefore it becomes continuous phase

transition. \therefore critical point \Rightarrow continuous phase transition

(Similarly, for fixed p but approaching p_c^- ,

$\Delta(\frac{\partial G}{\partial T})_p \rightarrow 0$ no $\Delta S!$)

Other quantities have similar behaviors:

9 e.g. $C_V - \tilde{C}_V \sim (T/T_c - 1)^{-\alpha}$ $T|_{p=p_c} \geq T_c$
 $\sim (1 - \frac{T}{T_c})^{-\alpha'}$ $T|_{p=p_c} \leq T_c$

$T = T_c$ $p - p_c \propto (p - p_c)^\delta$

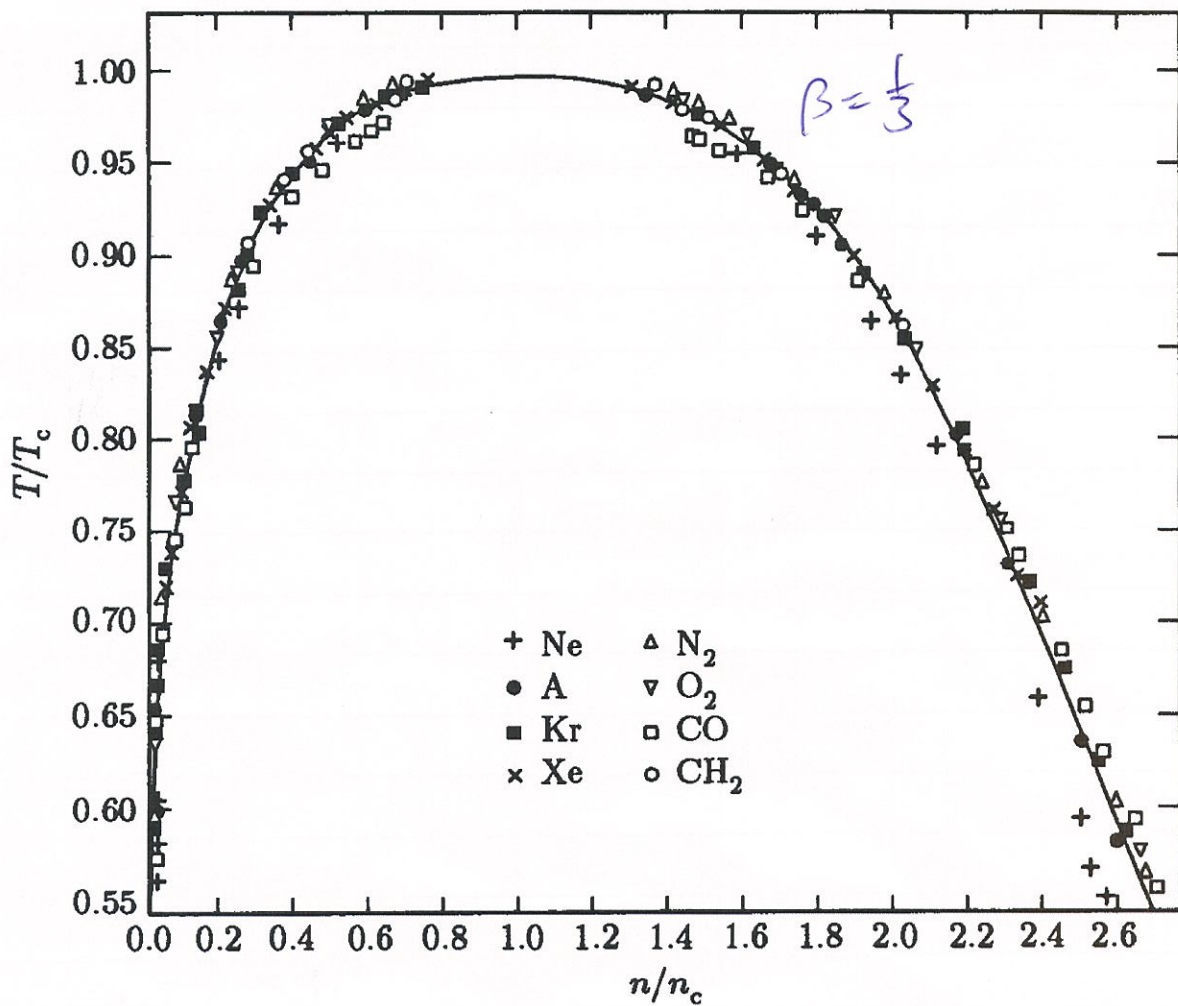
$\alpha, \alpha', \delta, \dots, \beta \dots \Rightarrow$ critical indices (exponents)

different systems ^{may} have different indices but
 surprisingly, many apparent-different-looking systems
 have the same indices \Rightarrow universality class.

9 $(\alpha, \alpha', \delta, \dots)$ serves to classify all
 the continuous phase transitions!

Calculating $(\alpha, \alpha', \delta, \dots)$ from the micro-model \Rightarrow theory
 of critical phenomena!

Universal behavior in gases



Phase boundary in units of reduced temperature and density for eight different molecular fluids near their liquid-gas transitions. Note the universal behavior and the fact that the solid line is $\Delta\phi \propto (T_c - T)^\beta$ with $\beta = 1/3$ rather than the mean-field result $\beta = 1/2$. [E.A. Guggenheim, *J. Chem. Phys.* 13, 253 (1945).]

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6-7

Many phase transitions are continuous types in

which the second derivatives of free energies diverges at T_c . \Rightarrow such points are called critical points.

The ways they diverge are power law types

characterized by critical exponents $\alpha, \alpha', \delta, \beta, \dots$

The formal definition of these exponents is

$$\epsilon \equiv \frac{T - T_c}{T_c}$$

$$\lambda \equiv \lim_{\epsilon \rightarrow 0} \frac{\ln f(\epsilon)}{\ln \epsilon}$$

$\lambda =$ critical-point exponent

\therefore near T_c $f(\epsilon) \sim \epsilon^\lambda$

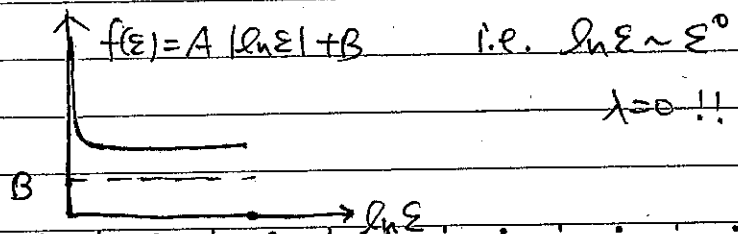
Note that it does not imply

$$f(\epsilon) \equiv A \epsilon^\lambda$$

but $f(\epsilon) = A \epsilon^\lambda (1 + B \epsilon^\gamma + \dots)$ $\gamma > 0$

for $\epsilon \rightarrow 0$, ϵ^λ dominates!

A couple of interesting plots



An important difference ^{between} continuous phase transition

& discontinuous phase transition is in the behavior of correlation length $\xi(T)$. $\xi(T=T_c) = \infty$ for continuous phase transitions, while $\xi(T)$ is always finite for discontinuous phase transitions.

The associated phenomenon is the critical opalescence.

Critical opalescence

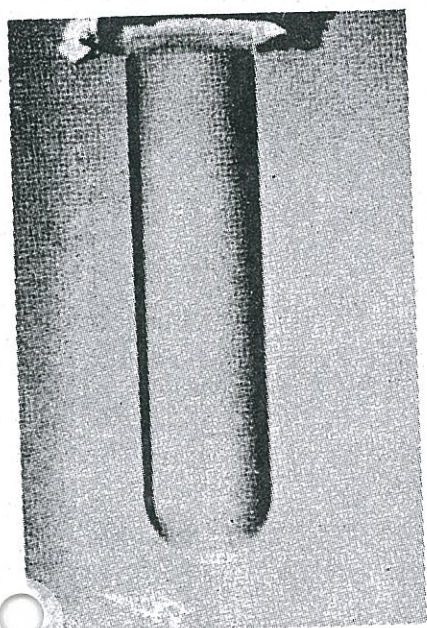
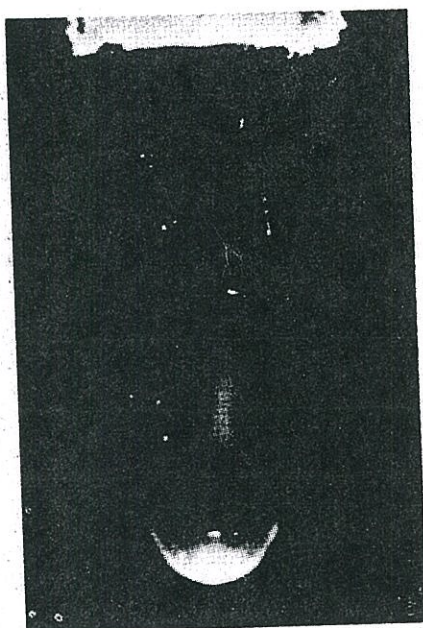
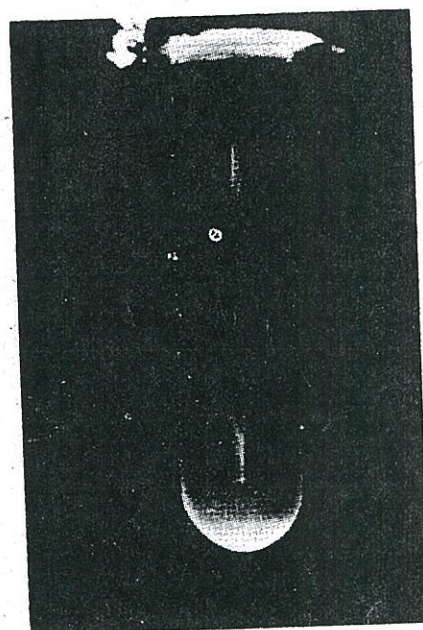
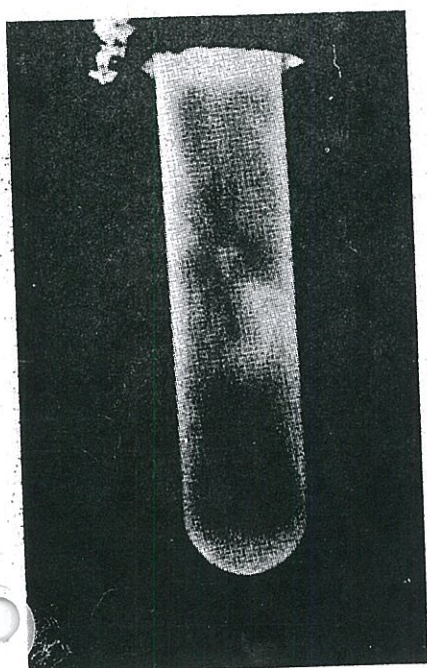
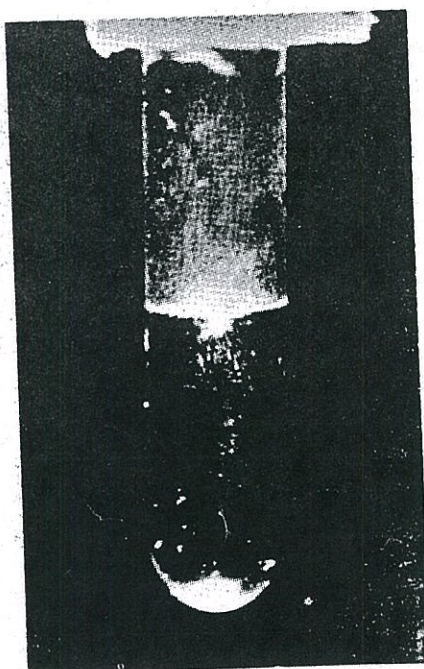
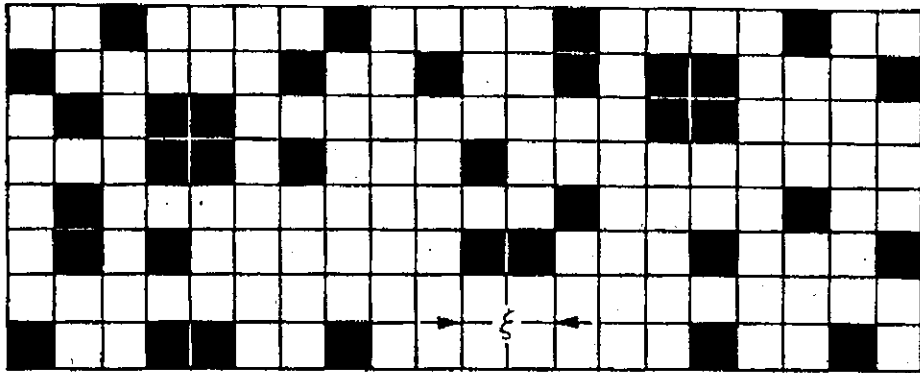
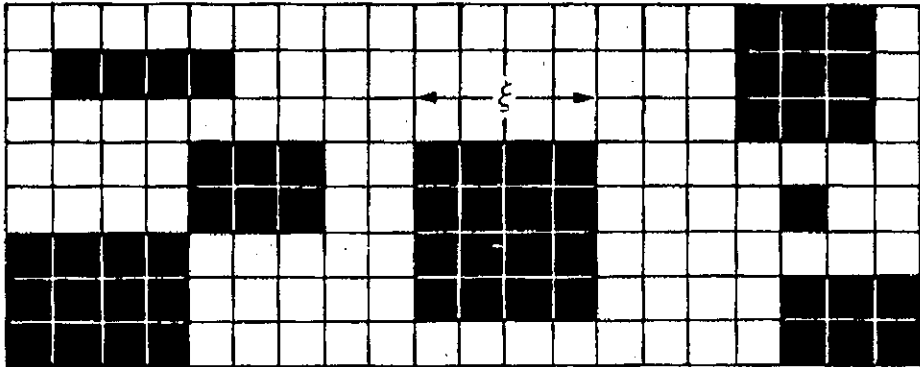
*a**b**c**d**e**f*

FIG. 1.6. Behaviour of a fluid as the temperature is lowered past the critical temperature: (a), $T \gg T_c$; (b), $T \gtrsim T_c$; (c), $T \approx T_c$; (d), $T \lesssim T_c$; (e), $T < T_c$; and (f), $T \ll T_c$. The fluid shown is the binary mixture cyclohexane-aniline. After Ferrell (1968).

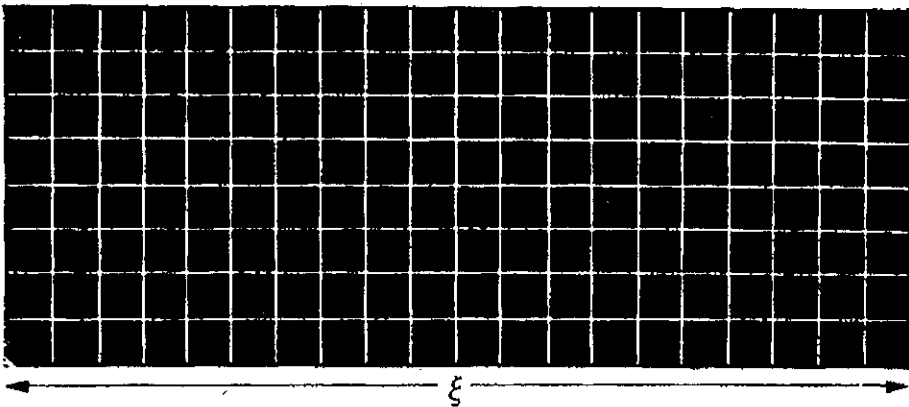
$T \gg T_c$



$T \gtrsim T_c$



$T = T_c$



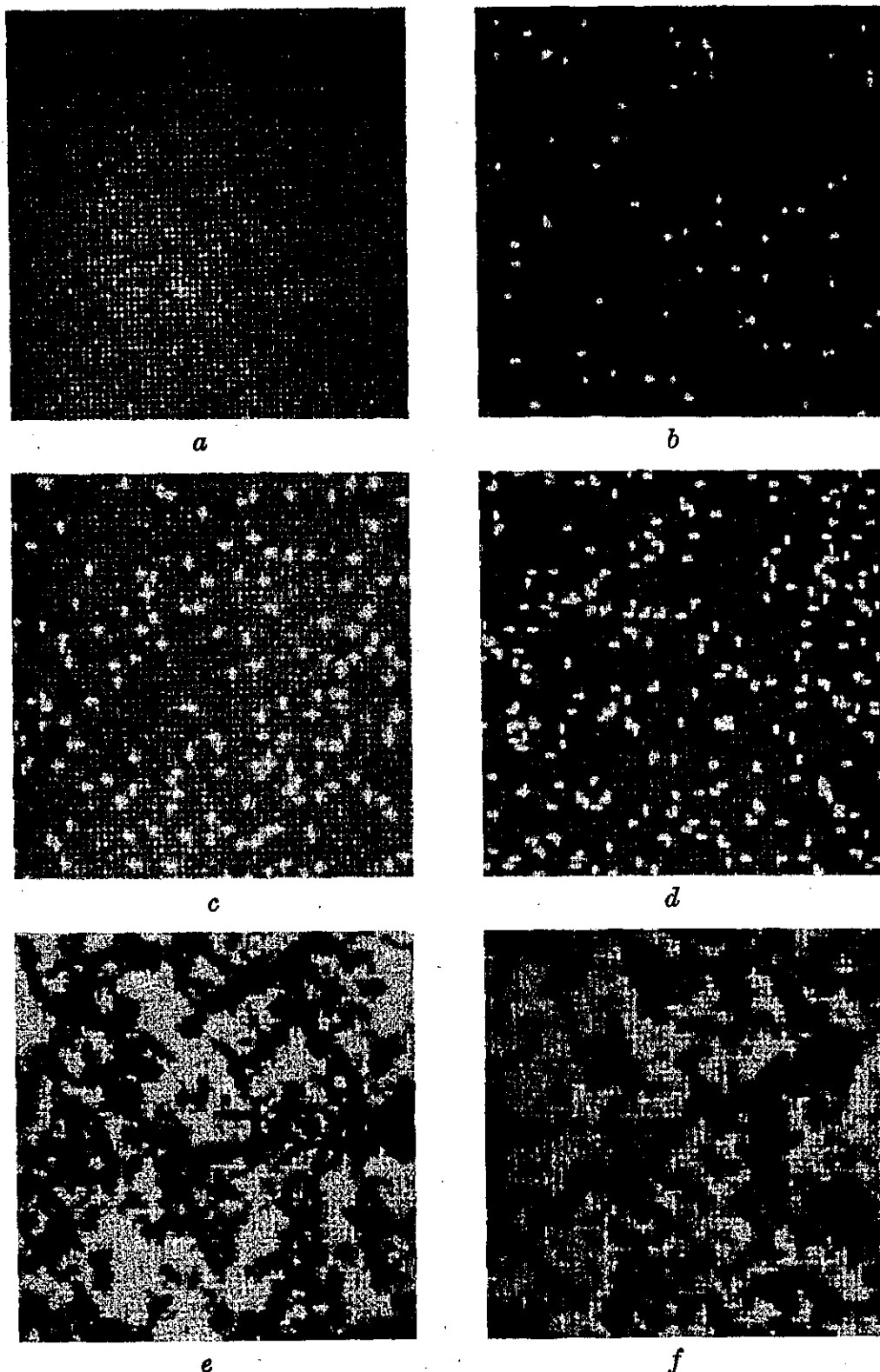
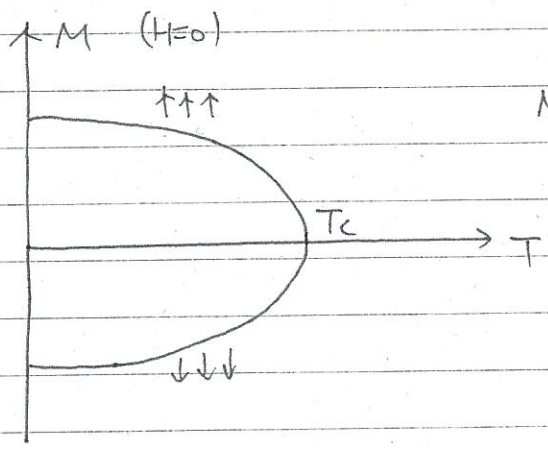


FIG. 1.5. Schematic indication of the lattice-gas model of a fluid system. Fig. 1.4 (which contains 8×20 cells) should be interpreted as representing a relatively small portion of this lattice (which contains 64×64 cells). (a) is the completely ordered state (which exists only at $T = 0$); (b), $T \simeq \frac{1}{2}T_0$; (c), $T \simeq \frac{1}{2}T_0$; (d), $T \simeq \frac{1}{2}T_0$; (e), $T \simeq T_0$; (f), $T \gtrsim T_0$. This illustration and the associated temperatures are to be regarded as purely schematic. In fact, the figure was constructed from a computer simulation of the time-dependent aspects of the two-dimensional Ising model and actually represents rather different phenomena (cf. Appendix E). After Ogita *et al.* (1969).

Another example of continuous phase transition:
* Ferromagnetism (nickel, iron, cobalt)



$$M(T) = \frac{-1}{V} \left(\frac{\partial F}{\partial H} \right)_{T, V, N}$$

$$= (T_c - T)^\beta$$

Fe : $\beta = 0.34 \pm 0.02$

Ni : $\beta = 0.33 \pm 0.03$

YFeO_3 : $\beta = 0.354 \pm 0.005$

Other quantities such as

χ also diverges ($\sim (T_c - T)^{-\gamma}$)
 $\sim (T - T_c)^{-\gamma'}$

$\delta \approx \gamma' \approx 1.33$

\Rightarrow rec over for thermodynamic exponents

Two important features:

* phase transitions are associated with non-analyticity of "free energies"

* ordering of the material changes

e.g. 1st order $\Rightarrow \Delta S$ measures the change of order.

2nd order $\Rightarrow \Delta p = p_2 - p_1 \cdot M$

(i) non-analyticity of the grand potential

- Scenario of Lee & Yang (phase transition at $T \neq 0$)

$$\Phi = -k_B T \ln Z = -P V$$

$$Z = Z(z; V, T) = \sum_{N=0}^{\infty} z^N Q_N(V, T) \quad z = e^{\mu/k_B T}$$

$$\lim_{V \rightarrow \infty} \frac{-\Phi}{k_B T V} = \lim_{V \rightarrow \infty} \frac{1}{V} \ln Z \text{ exists } (\because P \text{ exists})$$

(for certain given models, Yang-Lee theorem)

⇒ Thermodynamic limit

Finite system, $\sum_{N=0}^{\infty} \rightarrow \sum_{N=0}^{N_{\max}}$

$$Z = \sum_{N=0}^{N_{\max}} z^N Q_N = \prod_{k=1}^{N_{\max}} \left(1 - \frac{z}{z_k}\right)$$

↑
pairwise z_k, z_k^* must exist in pair
 $\because Q_N = \text{real}$

$\because Q_N > 0$ all z_k can't be real!
positive

For real z (which is the physical value of μ)
& positive

$$\left\{ \begin{aligned} P_V = \frac{k_B T}{V} \ln Z &= \frac{k_B T}{V} \sum_{k=1}^{N_{\max}} \ln \left(1 - \frac{z}{z_k}\right) \text{ is analytical!} \\ P_V = \left(\frac{\partial P}{\partial \mu}\right)_{V, T} &= \left[\frac{\partial}{\partial \ln z} (\beta P)\right]_{V, T} \\ &= \left[\frac{\partial}{\partial \ln z} \frac{1}{V} \ln Z\right]_{V, T} \\ &= \frac{1}{V} z \sum_{k=1}^{N_{\max}} \frac{\partial}{\partial z} \ln \left(1 - \frac{z}{z_k}\right) \\ &= \frac{z}{V} \sum_{k=1}^{N_{\max}} \frac{1}{z - z_k} \end{aligned} \right.$$

$$dR = -SdT - PdV - M dH - N d\mu = -PdV - V dP$$

$$dR = -SdT + M dH + \frac{S}{T} dT$$

Universality between liquid/gas system & magnetic system 6-11

$$-pdV \Leftrightarrow +H dM \quad M \leftrightarrow V \quad P \leftrightarrow H$$

$$\rho_l - \rho_g \sim \left(1 - \frac{T}{T_c}\right)^\beta \Leftrightarrow M \sim \left(1 - \frac{T}{T_c}\right)^\beta$$

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right) \sim \begin{cases} \left(1 - \frac{T}{T_c}\right)^{-\gamma'} & T < T_c \\ \left(1 + \frac{T}{T_c}\right)^{-\gamma} & T > T_c \end{cases} \Leftrightarrow \chi_T = \left(\frac{\partial M}{\partial H}\right)_T \sim \begin{cases} \left(1 - \frac{T}{T_c}\right)^{-\gamma'} \\ \left(\frac{T}{T_c} - 1\right)^{-\gamma} \end{cases}$$

$$P - P_c \sim |P - P_c|^\delta \operatorname{sgn}(P - P_c) \Leftrightarrow H \sim M^\delta \quad (T = T_c)$$

$$C_V \sim \begin{cases} \left(1 - \frac{T}{T_c}\right)^{-\alpha'} & T < T_c \\ \left(\frac{T}{T_c} - 1\right)^{-\alpha} & T > T_c \end{cases} \Leftrightarrow C_H \cong \begin{cases} \left(1 - \frac{T}{T_c}\right)^{-\alpha'} \\ \left(\frac{T}{T_c} - 1\right)^{-\alpha} \end{cases}$$

$C_H = T \left(\frac{\partial S}{\partial T}\right)_H$

		δ ($T = T_c$)	β	γ ($T > T_c$)
Fluid	CO ₂ :	4.2	0.34	1.35
	Xe :	4.4	0.35	1.3
Magnets	Ni :	4.22	0.62	1.35
	CrBr ₃ :	4.3	0.368	1.25

Other exponents

$$\xi \sim \left(1 - \frac{T}{T_c}\right)^{-\nu} \quad \nu'$$

$$\langle r(r) \rho(r) \rangle = G(r) \sim \frac{1}{r^{d-2+\eta}} \quad \text{Scale invariance at } T = T_c!$$

not all exponents are independent!

Landau's theory of phase transitions - mean field

To describe phase transitions, Landau argued

that one must include the order parameter ψ in the thermodynamic description so that $T < T_c$

$$\underline{\psi \neq 0, \quad T > T_c \quad \psi = 0}$$

examples:

* liquid-gas transition $\psi = P/P_c - 1$

* magnet $\psi = M$ (magnetization)

* crystal $\{P_G\}_G$

* Ferroelectricity $\psi = P$ (electric dipole moment)

* Superfluid $\psi = \langle \hat{\psi}(x) \rangle$

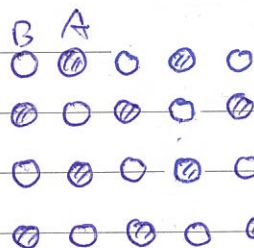
↑

Boson annihilation operator

* Superconductor $\psi \propto \langle C_{i\uparrow} C_{i\downarrow} \rangle$

* disorder-order alloy transition ($\text{CuZn}, T_c = 743 \text{ K}$
 $\text{Cu}_3\text{Au}, T_c = 665 \text{ K} \dots$)

example:

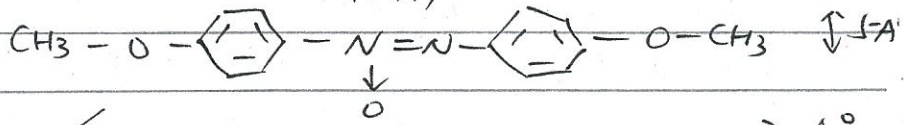


ordered

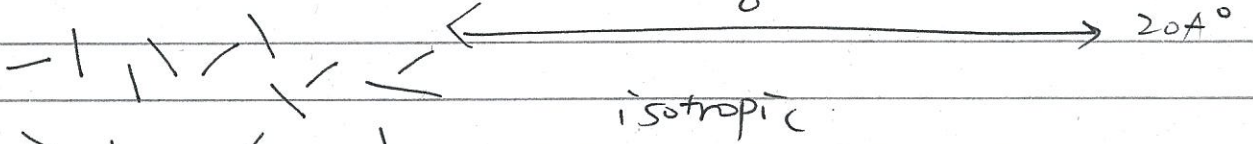
$P_A =$ probability of
finding A at a given
Site

$$\psi = \frac{P_A - P_B}{P_A + P_B}$$

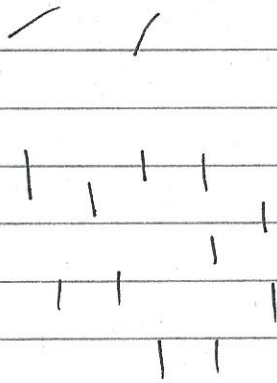
classical example: P-azoxyanisole (PAA)



* Liquid crystal



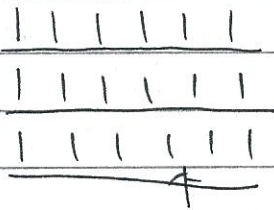
↓ lowering T



↑ \hat{n} (director) (uniaxial)

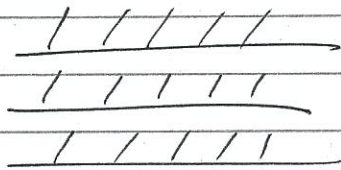
nematic (orientational ordering!)

↑ position order
↓ order
along this direction



smectic-A

no position order in each layer



smectic-C

isotropic \Leftrightarrow nematic transition 1st order

∴ $\hat{n}, -\hat{n}$ equivalent
can't use vector as order parameter

order parameter

$$Q_{\alpha\beta} \equiv \lambda \left(\hat{n}^\alpha \hat{n}^\beta - \frac{1}{3} \delta_{\alpha\beta} \right) \quad (\text{uniaxial})$$

(\sim quadrupole moment $\equiv \int (3x_i'x_j' - r^2\delta_{ij}) \rho(x')$)

isotropic $\langle Q_{\alpha\beta} \rangle = 0$
nematic $\neq 0$

↑ measure deviation from sphere
 $\rightarrow \text{Tr } Q = 0$

In addition to the introduction of ψ ,

Landau further postulated that a function F (\equiv Landau Free energy) exists and is a function of ψ . Such that

(i) F is consistent with the symmetry of the system

(ii) Near T_c , F is analytic ψ and can be expanded

$$f = \frac{F}{V} = \sum_{n=0}^{\infty} \frac{g_n(T)}{n} \psi^n \quad \text{for homogeneous cases}$$

(iii) F/V is constructed in the way

that $T > T_c$, solution to $\frac{\partial F}{\partial \psi} = 0$ is $\psi = 0$

$T < T_c$, \dots , $\psi \neq 0$

$\therefore \psi$ is a fixed quantity without fluctuation, Landau's theory is also a mean-field theory.

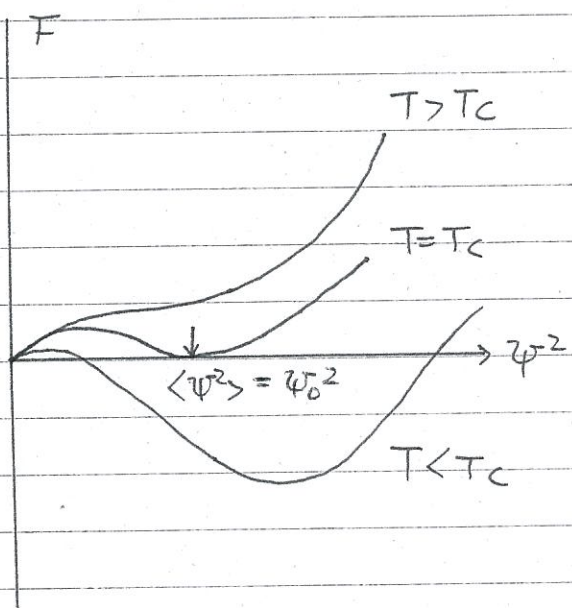
To construct F , we first note that

there are obviously only two possible ways that ψ goes

from $\psi = 0$ to $\psi \neq 0$. This is the

difference between discontinuous & continuous phase transitions.

* First order phase transition vs. 2nd order (continuous) phase transition(s)

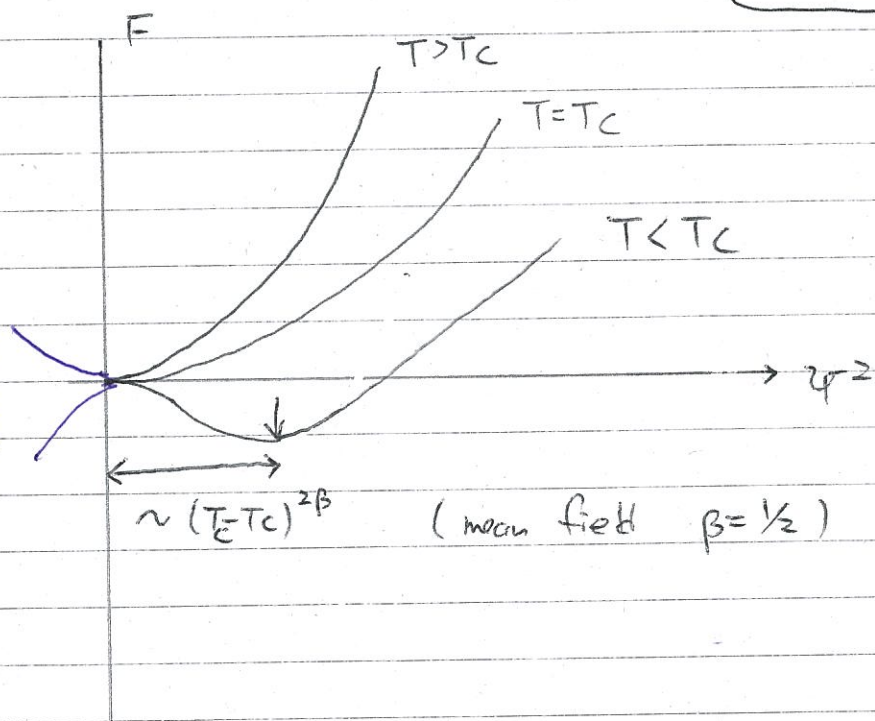


1st order

$\langle \psi^2 \rangle (T_c) \neq 0$

$T = T_c, \psi_0 = 0 \text{ \& } \psi_0 \neq 0$
Coexist.

Rigorously speaking, \because We expand free energy w.r.t. ψ
 ψ has to be small in order to be able to expand
 \therefore This is only correct for weakly
 2nd order 1st order



$\langle \psi^2 \rangle (T_c) = 0$

$\psi_0 \neq 0$ wins over $\psi_0 = 0$ gradually!

This picture suggests the curvature of F changes sign when going from $T > T_c$ to $T < T_c$!

* First order phase transition (lack of justification for truncation!)

$$g_2(T) = \alpha (T - T_c^0) \quad (\text{curvature})$$

$$g_4(T) < 0, \quad g_4 \equiv -\beta(T), \quad \beta > 0$$

$$\text{other } g_i > 0$$

$$\left. \frac{\partial F}{\partial \psi} \right|_{\psi_0} = 0 \Rightarrow \alpha (T - T_c^0) \psi_0 - \beta \psi_0^3 + g_6 \psi_0^5 + \dots = 0$$

$$\therefore \psi_0 = 0 \quad \text{or} \quad \alpha (T - T_c^0) - \beta(T) \psi_0^2 + g_6(T) \psi_0^4 + \dots = 0 \quad \text{①}$$

$$T = T_c, \quad F(\psi_0 = 0, T_c) = F(\psi_0, T_c)$$

$$\therefore \frac{\alpha}{2} (T_c - T_c^0) \cancel{\psi_0^2(T_c)} - \frac{1}{4} \beta(T_c) \psi_0^4(T_c) + \frac{1}{8} g_6(T_c) \psi_0^6(T_c) + \dots = 0 \quad \text{②}$$

$$\text{Set } T = T_c \text{ in ①,} \quad \text{①} \times \frac{1}{2} - \text{②}$$

$$\Rightarrow \frac{1}{4} \beta(T_c) \psi_0^2(T_c) - \frac{1}{3} g_6(T_c) \psi_0^4(T_c) + \dots = 0$$

$$\therefore \psi_0^2(T_c) \approx \frac{3}{4} \frac{\beta(T_c)}{g_6(T_c)} > 0 \quad \text{only if } \beta(T_c) > 0 \\ \text{i.e. } g_4(T_c) < 0!$$

Substituting $\psi_0^2(T_c)$ back to ②, we get

$$\frac{\alpha}{2} (T_c - T_c^0) - \frac{3}{16} \frac{\beta^2(T_c)}{g_6(T_c)} + \frac{1}{8} g_6(T_c) \frac{9}{16} \frac{\beta^2(T_c)}{g_6^2(T_c)} + \dots = 0$$

$$\therefore T_c = T_c^0 + \frac{3}{8\alpha} \frac{\beta^2(T_c)}{g_6(T_c)} \approx T_c^0 + \frac{3}{8\alpha} \frac{\beta^2(T_c^0)}{g_6(T_c^0)}$$

Latent heat:

$$f \cong \frac{\alpha}{2} (T - T_c^0) \psi_0^2$$

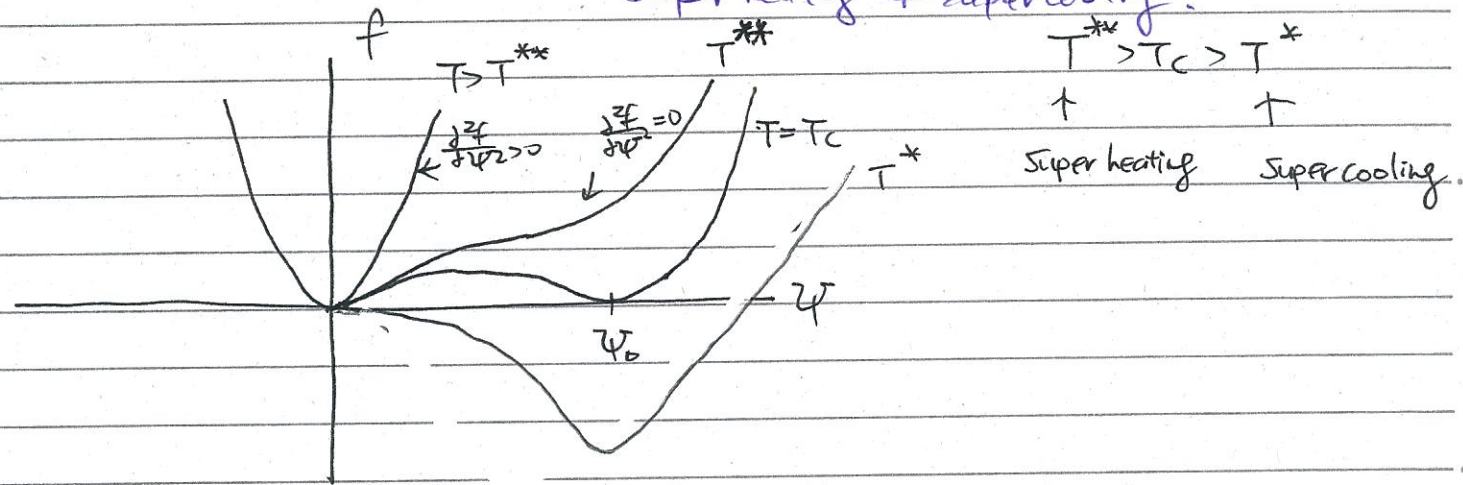
$$= \frac{\alpha}{2} (T - T_c^0) \frac{3}{4} \frac{\beta}{g_6}$$

$$= \frac{3\alpha}{8} (T - T_c^0) \frac{\beta}{g_6}$$

$$\therefore S = - \frac{\partial f}{\partial T} = - \frac{3\alpha}{8} \frac{\beta}{g_6}$$

$$\text{Latent heat} = -T_c S = \frac{3\alpha}{8} T_c \frac{\beta}{g_6}$$

Superheating & supercooling: 1st order implies the phenomena of superheating & supercooling:



T^* : $\frac{\partial^2 f}{\partial \psi^2} = 0$ at $\psi = 0$ i.e. $\psi = 0$ becomes local min! give way to ψ_0

Supercooling: lowering T the $\psi = 0$ phase can still be stable against small fluctuations until T^* !

T^{**}

When $\frac{df}{d\psi} = 0$ & $\frac{d^2f}{d\psi^2} = 0$
 ($f = F/N$)



, a min is emerging.

$$\alpha(T^{**} - T_C^0) - \beta\psi^2 + g_6\psi^4 = 0 \quad \left(\frac{df}{d\psi} = 0\right)$$

$$\alpha(T^{**} - T_C^0) - 3\beta\psi^2 + 4g_6\psi^4 = 0$$

$$\therefore 2\beta\psi^2 = 4g_6\psi^4, \quad \psi^2 = \frac{\beta}{2g_6}$$

$$\alpha(T^{**} - T_C^0) = \beta\psi^2 - g_6\psi^4$$

$$= \frac{\beta^2}{2g_6} - \frac{\beta^2}{4g_6} = \frac{\beta^2}{4g_6}$$

$$T^{**} \approx T_C^0 + \frac{\beta^2}{4\alpha g_6}$$

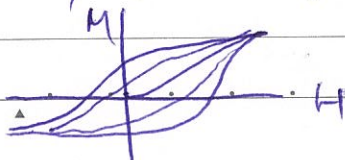
Superheating: increasing T , the ψ_0 phase

can be stable until T^{**} . Transition

In addition to supercooling & superheating, ^{for 1st order} it also implies that the system tends to have memory.

It results in so-called hysteresis phenomena.

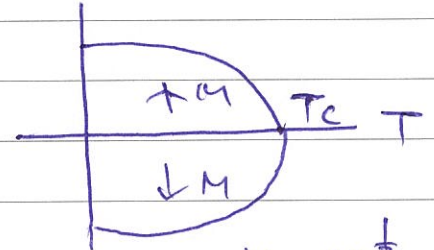
example



Other forms ^{of f} that also exhibit 1st order transition.

$$* \quad \frac{F}{V} = -H\psi + \frac{\alpha}{2}(T-T_c)\psi^2 + \frac{1}{4}\beta\psi^4$$

e.g. $\psi = M$, $H = \text{magnetic field}$

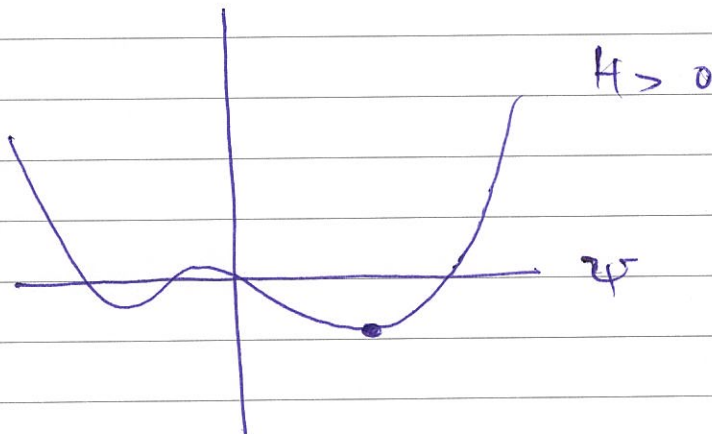


$$M \sim H^{\frac{1}{3}} \text{ at } T = T_c$$

$$\frac{df}{d\psi} = 0 \text{ at } T_c \quad -H + \beta\psi^3 = 0$$

$$\psi \sim H^{\frac{1}{3}}$$

$T < T_c$

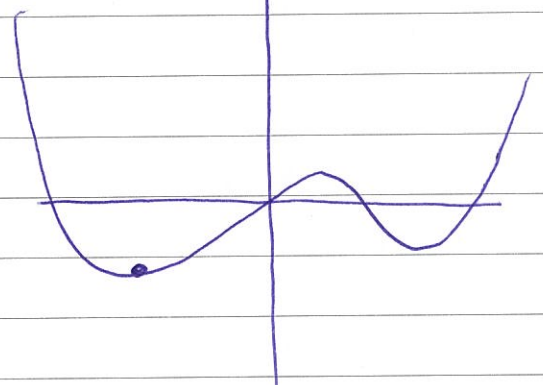


discontinuous
change of ψ (1st
order)

$H = 0$



$H < 0$

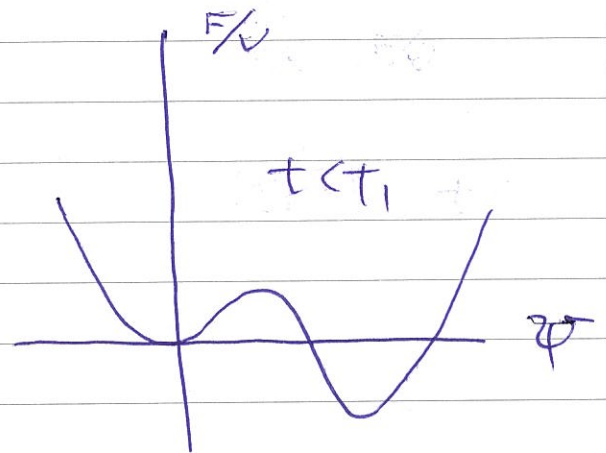
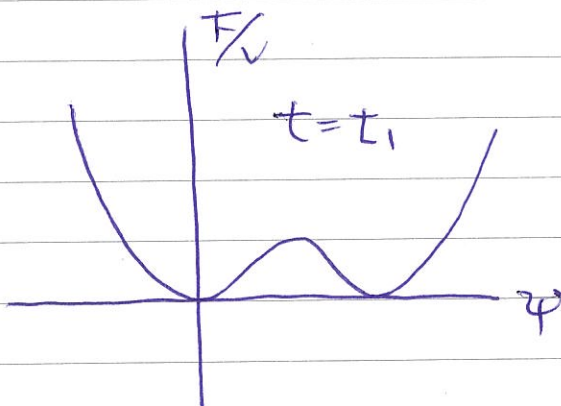
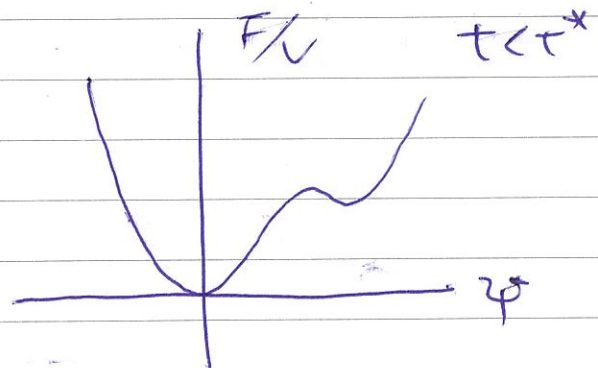
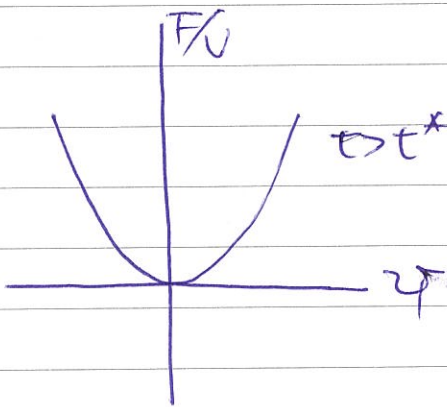


$$* \quad F/\nu = \frac{1}{2} a t \psi^2 + \frac{1}{4} b \psi^4 + c \psi^3 \quad t = \frac{T}{T_c} - 1$$

$$b > 0 \quad \underline{c < 0}$$

$$\underline{F(-\psi) \neq F(\psi)} !$$

(Maier-Saupe model of ^{nematic phase} LCD)



$$a t^* + 6c\psi + 3b\psi^2 = 0$$

$$a t^* \psi + 3c\psi^2 + b\psi^3 = 0$$

$$t^* = \frac{b\psi^2}{a} \quad \text{with} \quad \tilde{c} = \frac{3c}{3b}$$

* Second order (continuous) phase transition

$$g_0, g_4, g_6 \dots > 0$$

only g_2 changes sign at T_c^0

$$\therefore g_2 = \alpha (T - T_c^0)$$

$$\left. \frac{\delta F}{\delta \psi} \right|_{\psi_0} = 0 \Rightarrow \alpha (T - T_c^0) \psi_0 + g_4(T) \psi_0^3 + \dots = 0$$

$$\therefore \psi_0 = 0 \quad \text{if } T > T_c^0$$

$$\psi_0 \cong \pm \sqrt{\frac{\alpha}{g_4(T_c^0)}} \sqrt{T_c^0 - T} \quad T < T_c^0, \quad T \rightarrow T_c^0^-$$

\therefore if $\psi_0 = M$, $\beta = \frac{1}{2}$ (mean field, ψ is treated in averaged fashion)
or no fluctuation of ψ !

$$\psi_0 = \rho_e - \rho_g, \quad \beta = \frac{1}{2}$$

Substituting ψ_0 back to F , one can

$$\text{get } F[T] = -\frac{1}{4} \frac{\alpha^2 (T - T_c^0)^2}{g_4}$$

$$\therefore \left(\frac{\delta F}{\delta T} \right) \Big|_A = -S$$

$A = V, N$ for Helmholtz free energy

$A = P, N$ for Gibbs free energy

$$\text{one get } \underline{S} \Rightarrow C = T \left(\frac{\delta S}{\delta T} \right) = -T \frac{\delta^2 F}{\delta T^2}$$

$$= \begin{cases} 0 & T > T_c^+ \\ -\frac{1}{2} \frac{\alpha^2 T_c^-}{g_4} & T < T_c^- \end{cases} \quad \underline{\alpha = 0}$$

One can also calculate δ . For this

purpose, one introduces an external field H .

$$\therefore \mathcal{F}[\psi] = g_0 + \frac{1}{2}g_2\psi^2 + \frac{1}{4}g_4\psi^4 + \dots - H\psi$$

$$\frac{d}{d\psi}(\mathcal{F}[\psi]) = 0 \Rightarrow g_2\tilde{\psi}_0 + g_4\tilde{\psi}_0^3 = H$$

$$\text{At } T_c, g_2 = 0, \therefore H \sim \tilde{\psi}_0^3, \therefore \delta = 3$$

$$\chi(H) \equiv \left. \frac{d\tilde{\psi}_0}{dH} \right|_T \Rightarrow g_2\chi + 3g_4\tilde{\psi}_0^2\chi = 1$$

$$\therefore \chi = \frac{1}{g_2 + 3g_4\tilde{\psi}_0^2}$$

$$\therefore \chi(H=0) = \frac{1}{g_2 + 3g_4\tilde{\psi}_0^2} = \begin{cases} -\frac{1}{2g_2} = \frac{1}{2\alpha(T_c - T)} & T < T_c \\ = \frac{1}{g_2} = \frac{1}{\alpha(T_c)} & T > T_c \end{cases}$$

$$\therefore \delta = \delta' = 1$$

Ginzburg-Landau theory & Goldstone theorem

Landau's theory doesn't consider spatial variation

of ψ . In real systems, there is no reason

that ψ does not fluctuate and ^{does not} depend on positions \vec{r} .

Clearly, for length scale in the region

$$a \ll \ell \leq \xi(T),$$

$\psi \sim \text{constant}$.

\therefore If we divide the system into blocks of ℓ^d ,

each labelled by \vec{r}_i

$$F = \sum_i F[\psi(\vec{r}_i)]?$$

Apparently, this is correct only when each block is independent of each other.

Energetically, one expects that the system

tries lock each block into the same ψ , hence one expects deviation from

uniform state gets penalty:

$$\frac{\delta}{2} \sum_i \sum_{\delta} \left(\frac{\psi(\vec{r}_i) - \psi(\vec{r}_i + \delta)}{\delta} \right)^2 \quad \delta \sim \ell$$

↑
neighbours of i

$$\rightarrow \int d^d r \frac{M}{2} (\nabla \psi)^2$$

Hence, one expects

$$F = \int d^d r \left[\frac{1}{2} \alpha(T) \psi^2 + \frac{\beta}{2} \psi^4 + \frac{1}{2} M (\nabla \psi)^2 \right]$$

$\alpha(T - T_c^0)$

If ψ couples to magnetic fields, one

replaces $(\nabla\psi)^2 \rightarrow |(\vec{\nabla} - \frac{i\vec{e}\times\vec{A}}{c})\psi|^2$

In this case, one replaces $\frac{\delta}{\delta\psi}(F\psi)$ by

$\frac{\delta F}{\delta\psi(\vec{r})} = 0$. One finds

$$\lambda(\vec{r})\psi(\vec{r}) + \beta\psi^3(\vec{r}) - M\psi^2 = 0$$

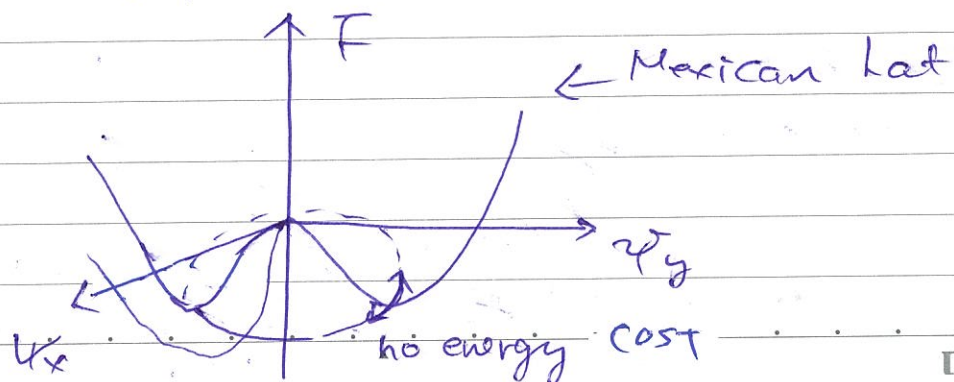
This is the Ginzburg-Landau equation.

for describing non-uniform $\psi(\vec{r})$.

Multi-component & Goldstone theorem

The above is the case when the order parameter is a scalar. In that case, it causes extra energy for ψ to change magnitudes.

However, if ψ is a vector, $\psi = \vec{\psi}$, there would be no cost for $\vec{\psi}$ to vary along the direction perpendicular directions:



In other words, one expects

$$F = \int d^d r \left[\frac{1}{2} \alpha(r) |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2} M (\nabla |\psi|)^2 \right] \quad \text{--- (3)}$$

↑ magnitude of $\vec{\psi}$

$$+ \int d^d r \frac{1}{2} M (\nabla \psi_{\perp})^2$$

Indeed, if we start from the multi-component Ginzburg-Landau Free energy:

$$F = \int d^d r \left[\frac{1}{2} \alpha(r) |\vec{\psi}|^2 + \frac{\beta}{2} |\vec{\psi}|^4 + \frac{1}{2} M \sum_{\alpha} (\nabla_{\alpha} \vec{\psi})^2 \right] \quad \text{--- (4)}$$

we find that for $T < T_c$, one can write

$$\vec{\psi} = \psi_{\parallel} \hat{e}_{\parallel} + \vec{\psi}_{\perp} \quad \psi_{\parallel} \cdot \vec{\psi}_{\perp} = 0$$

(4) reduces to (3).

In the Fourier space, one finds

$$F = \int d^d k \left[\frac{1}{2} \alpha(r) |\psi_{\parallel}(k)|^2 + \frac{\beta}{4} |\psi_{\parallel}(k)|^4 + \frac{M}{2} k^2 |\psi_{\parallel}(k)|^2 \right. \\ \left. + \int d^d k \frac{1}{2} M k^2 |\psi_{\perp}(k)|^2 \right]$$

One sees that excitation of ψ_{\perp} away

from the uniform case ($k=0$) has the cost

$\sim k^2$. Hence, as $k \rightarrow 0$, the cost (energy)

$\rightarrow 0$. This is the classical Goldstone theorem.

