

# Continuous phase transitions and critical points ①

- Curie temperature : example iron ( $T_c = 1043 \text{ K}$ )  
paramagnetic  $\leftrightarrow$  ferromagnetic

$$T > T_c \quad m \propto B$$

$T < T_c$  -  $m$  is ~~not~~ linearly related to  $B$

-  $m$  is finite even in the absence of field

- $m$  changes continuously - characteristic of ~~see~~ continuous phase transitions

- first-order change  $\Rightarrow$  abrupt change in  $\beta, c_v$ , etc.

- water-steam phase transition is continuous if

$$T = T_c \quad (\text{critical isotherm})$$

## Divergences and Critical Points Exponents

- vanishing of latent heat, does not mean  $c_v$  is ~~continuous~~ necessarily smooth or ~~see~~ even finite

$$l = \int_{T_c^-}^{T_c^+} c_v(T) dT \quad \Rightarrow \quad c_v(T) = |T - T_c|^{-\alpha} \quad \alpha > 0$$

$\alpha$  - critical exponent, describes singular behaviour of  $c$

$$\begin{aligned} l &= \int_{T_c^-}^{T_c} (T_c - T)^{-\alpha} dT + \int_{T_c}^{T_c^+} (T - T_c)^{-\alpha} dT \\ &= - \int_{\Delta}^0 T'^{-\alpha} dT' + \int_0^{\Delta} T'^{-\alpha} dT' = \underline{2 \int_0^{\Delta} T'^{-\alpha} dT'} \end{aligned}$$

$$\Delta = T_c - T_c^- \quad \Delta = T_c^+ - T_c$$

$$\text{integrate: } \Rightarrow 2 \frac{\Delta^{-\alpha+1}}{-\alpha+1}$$

consider limit  $\Delta \rightarrow 0$

if  $\alpha > 1$   $\ell \rightarrow \infty \Rightarrow \alpha < 1$

②

if  $\alpha > 0$  and  $\alpha < 1 \Rightarrow$  singular behaviour

if  $\alpha < 0 \Rightarrow C(T) = (T - T_c)^{-\alpha} \Rightarrow$  finite

other possibility: logarithmic divergence

$$\log\left(\frac{1}{x}\right) \approx \lim_{\alpha \rightarrow 0} \frac{1}{\alpha} (x^{-\alpha} - 1)$$

$\Downarrow$

$\Downarrow$

all three possibilities captured by functional form

$$C(T) \approx \frac{1}{\alpha} \left( \left| \frac{T - T_c}{T_c} \right|^{-\alpha} - 1 \right)$$

- in principle possible that as  $T \rightarrow T_c$  from below exponent  $\alpha$  is different from above  $(T \neq T_c)$

- for critical points associated with first order phase transitions  $\Rightarrow T \rightarrow T_c$  from below is not meaningful

# Superconductors

①

1911 Kamerlingh-Onnes

resistance of mercury drops to zero @  $T_c = 4.2\text{K}$

Ohm's law:  $\vec{J} = \sigma \vec{E}$

Faraday's law:  $\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$

if  $\sigma \rightarrow \infty \Rightarrow -\frac{\partial \vec{B}}{\partial t} \rightarrow 0$  inconsistent

$\frac{\partial \vec{B}}{\partial t} = 0$  implies that magnetization of sample

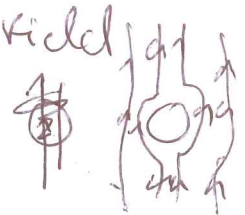
depends on its history

infinite conductivity would mean

sample



First cool, apply field



First apply field, then cool



→ not a valid thermodynamic state

Meissner / Ochsenfeld - cooled monocrystal of tin and

showed that superconductors are perfect diamagnets



$$\vec{B} = 0$$



- superconductivity is due to pairing of electrons into bound states (Cooper pairing)
- bound pairs can be thought of as bosons
  - $\Rightarrow$  they condense into state with lowest quantum number at  $T \rightarrow 0$
  - $\Rightarrow$  condensation leads to large scale coherence
  - when electric field is applied  $\Rightarrow$  condensed part moves all together
- large enough electric field can destroy superconductivity

$$B = \begin{cases} 0 & H < H_{\text{coex}}(T) \\ \mu_0 H & H > H_{\text{coex}}(T) \end{cases}$$



$$H_{\text{coex}}(T) = H_0 \left( 1 - \left( \frac{T}{T_c} \right)^2 \right)$$

~~analogous to liquid-vapour phase diagram~~

- along coexistence curve: chemical potentials of two phases are equal

$$-S_n dT$$

$$-S_n dT - B_n dH = -S_s dT - B_s dH$$

$\Downarrow$

$$S_n - S_s = (B_s - B_n) \frac{dH}{dT}$$

$$= -\mu_0 H_{\text{coex}}(T) \left( \frac{dH}{dT} \right)_{\text{coex}}$$

$\Rightarrow \Delta S$  is finite everywhere except  $H=0$

$\Rightarrow$  latent heat everywhere except  $H=0 \Rightarrow$  critical point

$\Rightarrow$  Gibbs free energy

$$dg = -s dT - BdH$$

$$g(T, H) - g(T, 0) = - \int_0^H BdH \quad (\text{constant temperature})$$

$$\Rightarrow g_s(T, H) - g_s(T, 0) = 0$$

$$g_n(T, H) - g_n(T, 0) = - \frac{\mu_0 H^2}{2}$$

$$g_s(T, H_{\text{max}}) = g_n(T, H_{\text{max}})$$

$$\Downarrow$$
$$g_s(T, 0) = g_n(T, 0) - \frac{\mu_0 H_{\text{max}}^2}{2}(T)$$

$\Rightarrow$  superconducting phase is stable

# Ginzburg-Landau Theory

- theory relates characteristics of phase transition to underlying symmetries
- phase transitions either break symmetries or not
  - for liquid-vapour transition, no symmetry is broken  $\Rightarrow$  both phases are invariant under all elements of the translation group  
(average density is independent of particle positions)
  - for solid-liquid transition
    - symmetry is broken
      - liquid phase: invariant under all elements of translation group
      - solid phase: invariant under only a specific set of elements of translation group (those which are periodic)
- first-order phase transition  $\Rightarrow$  <sup>slope of</sup> free energy changes discontinuously
  - $\Rightarrow$  symmetry is broken or not
- second-order phase transitions
  - $\Rightarrow$  slope of free energy changes continuously
  - $\Rightarrow$  symmetry is always broken
    - example: magnetic transition  
paramagnet  $\leftrightarrow$  ferromagnet  
breaks rotational symmetry  
below  $T_c$  spontaneous magnetisation appears
      - $\Rightarrow$  unique direction defined

assumption of GL theory:

- free-energy near a critical point is an analytic function of the order parameter

$\eta$  - order parameter

$$\Phi(T, Y, \delta) = \Phi_0(T, Y) + \alpha_2(T, Y)\eta^2 + \alpha_3(T, Y)\eta^3 + \alpha_4(T, Y)\eta^4 + \dots + f\eta$$

$Y$  - generalized thermodynamic force

$f$  - thermodynamic force conjugate to the order parameter

no first-order term in  $\eta$

$\Rightarrow$  so that above critical point  $\eta = 0$

- indeed minimum of function in  $\eta$

$$\frac{\partial \Phi}{\partial \eta} = 0 \Rightarrow 2\alpha_2(T, Y)\eta + \dots = 0$$

minimum @  $\eta = 0$

could also be maximum

$\Phi_0(T, Y)$  - includes variables not directly involved in transition

$\Rightarrow \eta$  realized in nature  $\Rightarrow$  one that minimizes free energy

essence of GL theory: for different values of coefficients  $\alpha_2, \alpha_3, \alpha_4, f \Rightarrow$  plot free energy profile and assess what types of phase transition occur

types of terms are related to symmetry

## Continuous phase transitions

- occurs if  $\alpha_3(T, Y) = 0$ ,  $f = 0$

↓

$$\Phi(T, Y, \eta) = \Phi_0(T, Y) + \alpha_2(T, Y)\eta^2 + \alpha_4(T, Y)\eta^4 + \dots$$

minimize:  $2\alpha_2(T, Y)\eta + 4\alpha_4(T, Y)\eta^3 + \dots = 0$

dependence of  $\alpha_2$  on  $T$  is such that if

if  $T > T_c \Rightarrow \eta = 0$  is the only minimum

~~but~~  
if  $T < T_c \Rightarrow \Phi(T, Y, \eta)$  minimized for  $|\eta| > 0$   
(both  $\pm \eta$ )

minimum condition:  $\left(\frac{\partial \Phi}{\partial \eta}\right)_{T, Y} = 0$        $\left(\frac{\partial^2 \Phi}{\partial \eta^2}\right)_{T, Y} \geq 0$

×  
stability condition

$$\frac{\partial^2 \Phi}{\partial \eta^2} = 12\alpha_4(T, Y)\eta^2 \geq 0$$

$$\Rightarrow \alpha_4(T, Y) \geq 0$$

$\Rightarrow$  ensures that free energy increases as  $\eta \rightarrow \pm \infty$

- critical point  $T_c$   $\alpha_2(T_c, Y) = 0 \Rightarrow @ T = T_c(Y)$

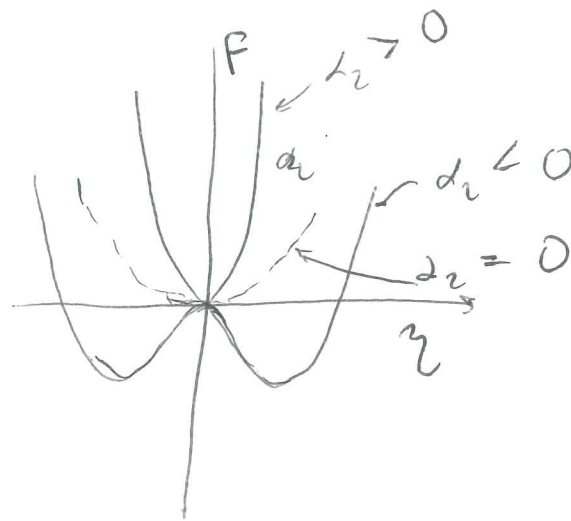
if  $\alpha_2(T, Y) > 0 \Rightarrow$  minimum of free energy  $\Rightarrow \eta = 0$

if  $\alpha_2(T, Y) < 0 \Rightarrow$  minimum of free energy  $\Rightarrow \eta = \pm \text{finite number}$

- these observations fix general behaviour of  $\alpha_2(T, Y)$   
as a fn. of temperature

can write:  $\alpha_2(T, \gamma) = \alpha_0(T - T_c)$  (around  $T_c$ )

Free energy curves:



Free energy minima extrema

$$\eta = 0, \pm \sqrt{\frac{-\alpha_2}{\alpha_4}} \approx \pm \sqrt{\frac{\alpha_0}{2\alpha_4}} (T_c - T)$$

$$T > T_c \text{ minimum } \eta = 0$$

$$T < T_c \text{ } \eta = \pm \sqrt{\frac{\alpha_0}{2\alpha_4}} (T_c - T) \text{ minimum}$$

order parameter varies as  $\propto \sqrt{(T_c - T)}$

$$\Rightarrow T > T_c \quad \phi(T, \gamma, \eta) = \phi_0(T, \gamma) \quad \text{for } T > T_c \quad \text{since } \eta = 0$$

$$T < T_c \quad \phi(T, \gamma, \eta) = \phi_0(T, \gamma) - \frac{\alpha_0^2 (T_c - T)^2}{4\alpha_4}$$

molar heat capacity

$$C_\gamma = -T \left( \frac{\partial^2 \phi}{\partial T^2} \right)_\gamma$$

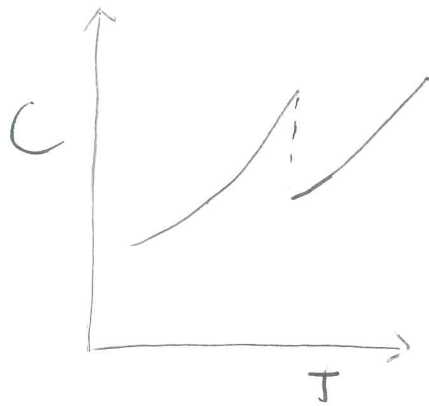
$$C_\gamma(T > T_c) = 0$$

(neglect derivatives  
of  $\phi_0, \alpha_0, \dots$  with  
respect to temperature)

$$C_\gamma(T < T_c) = + \frac{T_c \alpha_0^2}{2\alpha_4}$$

$\Rightarrow$  heat capacity jumps in a discontinuous manner  
 $\Rightarrow$  2nd point

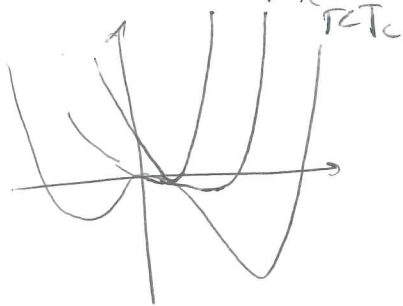
will do something like



Turn on external force  $f$

$$\tilde{\Phi}^*(T, \gamma, f) = \Phi(T, \gamma, \eta) - f\eta = \Phi_0(T, \gamma) + \alpha_2 \eta^2 + \alpha_4 \eta^4 - f\eta$$

~~$\frac{\partial \Phi}{\partial \eta}$~~  in this case minima are no longer equivalent



susceptibility:  $\eta \Rightarrow \frac{\partial \tilde{\Phi}}{\partial \eta} = 0$

$$\chi = - \frac{\partial^2 \tilde{\Phi}}{\partial f^2} = \frac{\partial \eta}{\partial f}$$

$$2\alpha_2 \eta + 4\alpha_4 \eta^3 - f = 0$$

$$\frac{\partial \eta}{\partial f} \Rightarrow 2\alpha_2 \frac{\partial \eta}{\partial f} + 12\alpha_4 \eta^2 \frac{\partial \eta}{\partial f} - 1 = 0$$

$$\chi = \frac{\partial \eta}{\partial f} = \frac{f}{2\alpha_2 + 12\alpha_4 \eta^2}$$

using  $\eta = \sqrt{\frac{-\alpha_2}{2\alpha_4}}$  for  $T < T_c$

$$\chi = - \frac{f}{4\alpha_4} = \frac{1}{4\alpha_4(T_c - T)}$$

using  $\eta = 0$  for  $T > T_c$   $\chi = \frac{f}{2\alpha_2} = \frac{1}{2\alpha_2(T - T_c)}$

susceptibility diverges @  $T_c$

## First-order transitions

third order term present in free energy  $\Phi$

$$\Phi(T, \gamma, \eta) = \Phi_0(T, \gamma) + \alpha_2 \eta^2 + \alpha_3 \eta^3 + \alpha_4 \eta^4$$

$$\frac{\partial \Phi}{\partial \eta} = 0 \Rightarrow 2\alpha_2 \eta + 3\alpha_3 \eta^2 + 4\alpha_4 \eta^3 = 0$$

extrema  $\eta = 0$

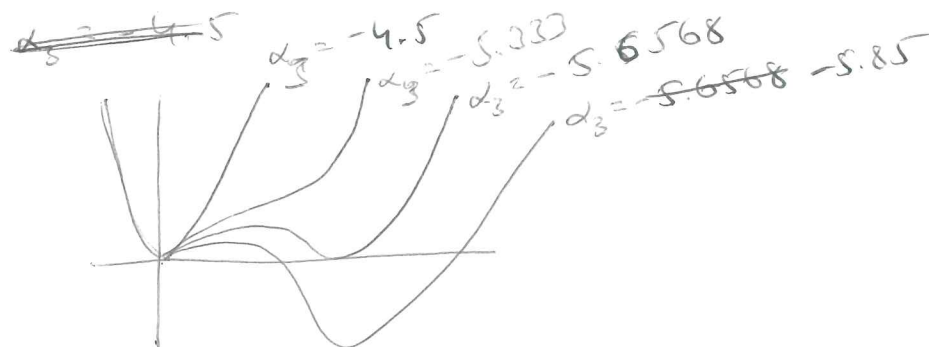
$$2\alpha_2 + 3\alpha_3 \eta + 4\alpha_4 \eta^2 = 0$$

$$\eta = \frac{-3\alpha_3 \pm \sqrt{9\alpha_3^2 - 32\alpha_2\alpha_4}}{8\alpha_4}$$

if  $9\alpha_3^2 - 32\alpha_2\alpha_4 > 0 \Rightarrow$  TWO minima

$$\alpha_2 = 2.0$$

$$\alpha_4 = 4.0$$



# Critical Exponents

- critical point: point at which order parameter begins to grow from zero
  - liquid vapor transition at critical point  
slope of free energy grows continuously
  - paramagnet  $\leftrightarrow$  ferromagnet  
 $T_c$  where magnetization  $m$  begins to "grow"
  - superconductor: temperature where condensate first appears
- approaching critical point
  - fluctuations begin to grow  $\Rightarrow$  drastic adjustments in behaviour of material

## Definition of critical exponents

- critical exponents describe approach to critical point

$$\Rightarrow \text{define } \varepsilon = \frac{T - T_c}{T_c}$$

near critical point, thermodynamic functions can be written

$$f(\varepsilon) = A \varepsilon^\lambda (1 + B \varepsilon^\gamma + \dots)$$

definition of critical exponent

$$\lambda = \lim_{\varepsilon \rightarrow 0} \frac{\ln f(\varepsilon)}{\ln \varepsilon}$$

$\lambda$  - negative  $f(\epsilon)$  diverges  
 $\lambda$  - positive  $f(\epsilon) \rightarrow 0$  at  $T_c$

$\lambda = 0$

two possibilities:

logarithmic divergence:  $f(\epsilon) = A \ln \epsilon + B$   
 $f(\epsilon) = A + B \sqrt{\epsilon}$

or

$\rightarrow$  for logarithmic divergence  
 modified exponent  $\Rightarrow \lambda' = j + \lim_{\epsilon \rightarrow 0} \frac{\ln |f^{(j)}(\epsilon)|}{\ln \epsilon}$

$j$  = smallest integer for which  
 $\frac{d^j f(\epsilon)}{d\epsilon^j} = f^{(j)}(\epsilon)$  diverges

## PVT critical exponents

describes variation of pressure as critical point  
 $\rightarrow$  approached for critical isotherm

$$\frac{p - p_c}{p_c^0} = A \sigma \left| \frac{\beta - \beta_c}{\beta_c} \right|^\sigma \text{sign}(\beta - \beta_c) \quad T = T_c$$

$\sigma \geq 4$

$p_c^{(0)} \Rightarrow$  pressure of an ideal gas @  $p_c, T_c, V_c$

$\beta$  - degree of critical isotherm

$$\frac{\beta_c - \beta_g}{\beta_c} = A_\beta (-\epsilon)^\beta \quad \epsilon = \frac{T - T_c}{T_c}$$

$T < T_c$   $\beta_c - \beta_g$  - order parameter

$\beta$  - degree of the coexistence curve

$$\beta \approx 0.34$$

## Heat capacity

as  $T \rightarrow T_c$

$$C_v = A_1' (-\varepsilon)^{-\alpha'}$$

$$C_v = A_2' (+\varepsilon)^{-\alpha}$$

$$T < T_c \quad \beta = \beta_c$$

$$T > T_c \quad \beta = \beta_c$$

$$\alpha \sim 0.1 \quad \alpha' \sim 0.1$$

## Isobaric compressibility

$$\frac{\kappa_T}{\kappa_T^0} = \begin{cases} A_1' (-\varepsilon)^{-\gamma'} \\ A_2' (\varepsilon)^{-\gamma} \end{cases}$$

$$T < T_c$$

$$T > T_c$$

$$\beta = \beta_c(T) \text{ or } \beta_g(T)$$

$$\beta = \beta_c$$

$$\gamma' \sim 1.2 \quad \gamma \sim 1.3$$