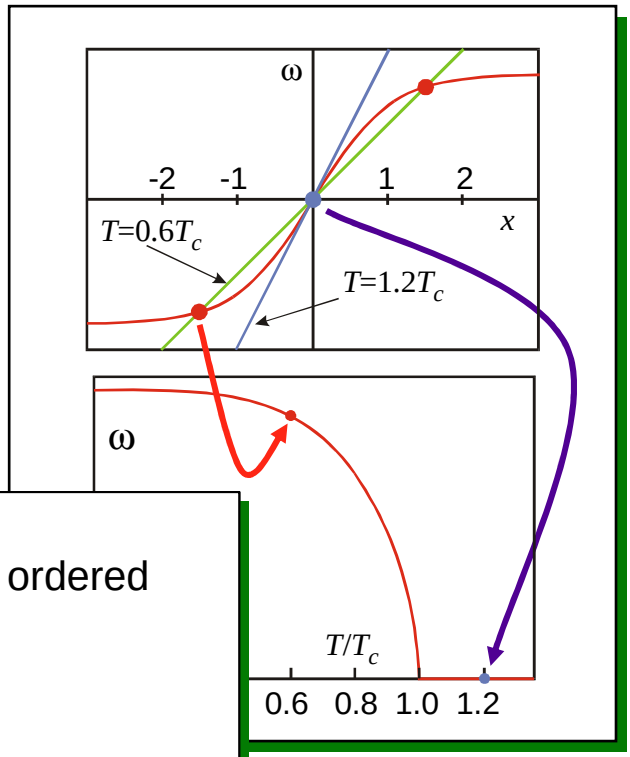
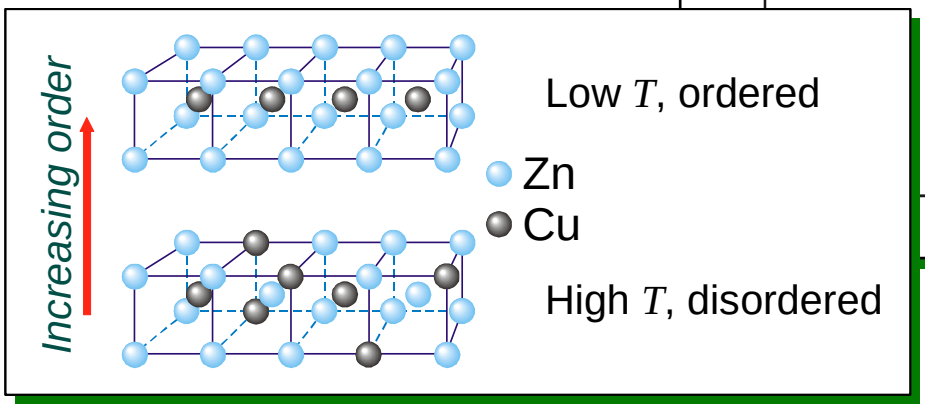
Lectures 16: Phase Transitions

Continuous Phase transitions

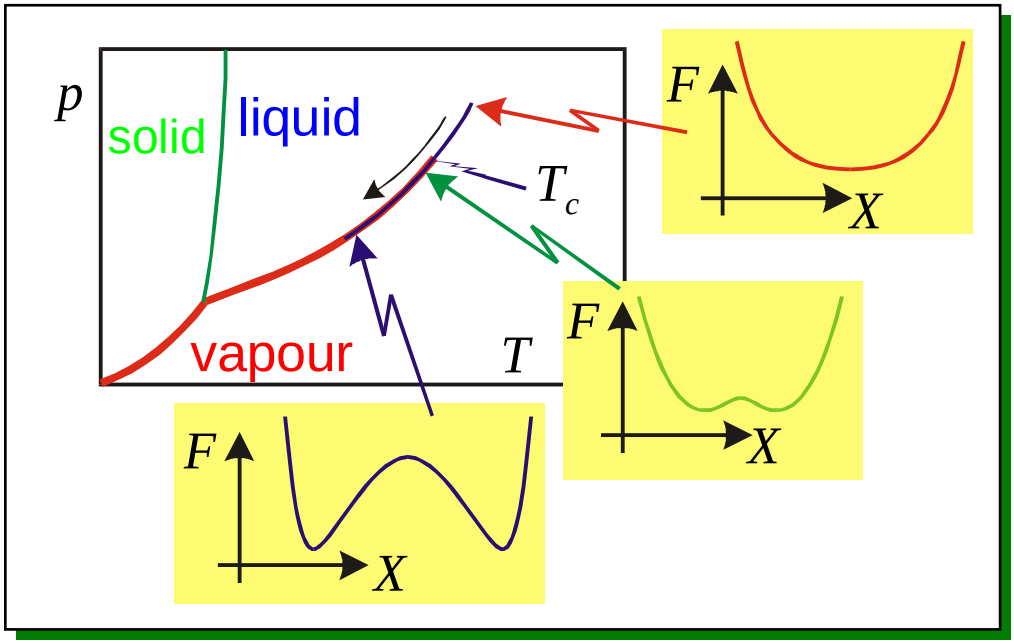
- Aims:
  - Mean-field theory:
    - Order parameter.
  - Order-disorder transitions. Examples:
    - β-brass (CuZn),
    - Ferromagnetic transition in zero field.
  - Universality.





Phase transitions

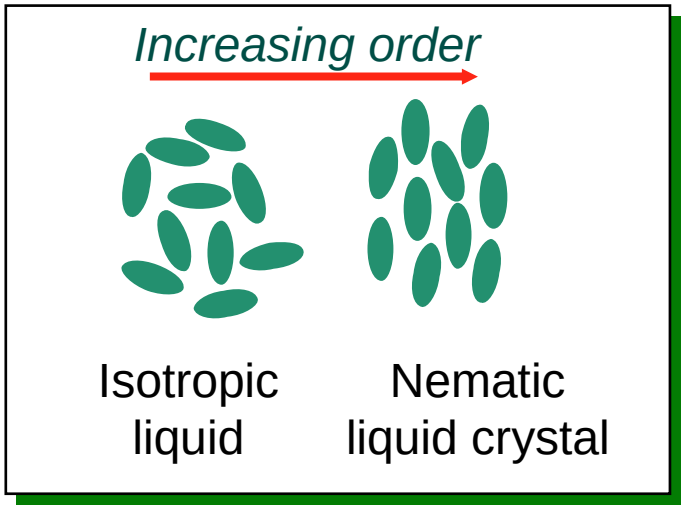
- Continuous phase transitions:
  - occur when the minimum in the thermodynamic potential evolves smoothly into two *equal* minima.
  - An example is seen in the model of phase separation, along the co-existence line (last lecture).



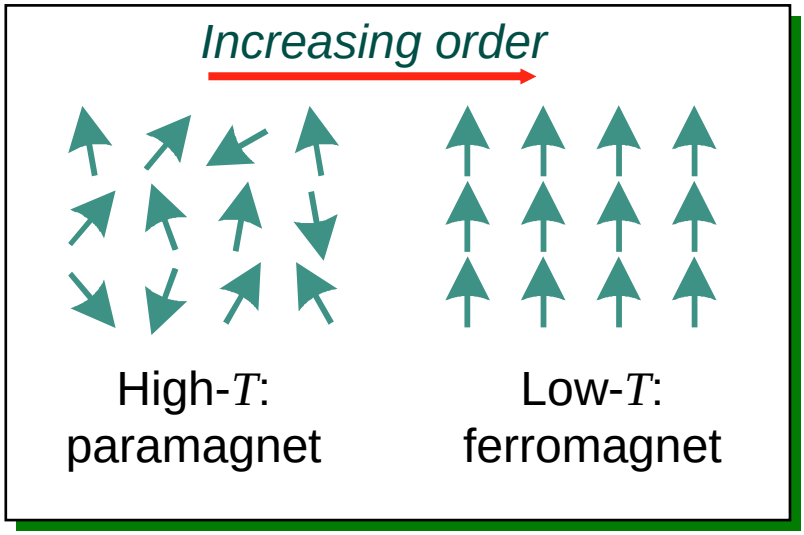
  - Aside: the phase transition as one moves across the co-existence line (from liquid to vapour) is fundamentally different. That transition is known as "1st order" and there are 2 minima in the potential throughout. In the transition the lowest minimum changes from liquid to vapour (and vice-versa).

Order-disorder transitions

- Other examples (there are many):
  - Isotropic – nematic transition in liquid crystals: appearance of orientational order (liquid crystals have no long-range, positional order).

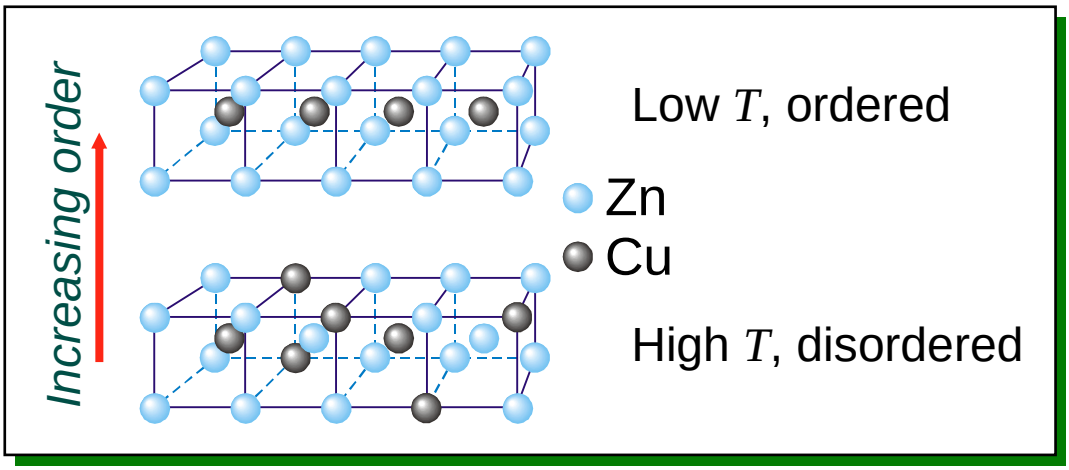


  - Ferromagnetic - paramagnetic transition: manifests itself as a spontaneous polarisation, in zero external field.



Mean-field theory

- Order-disorder transition in β-brass.
  - a further example, which we will follow in detail.
  - Brass is a 50:50, Cu:Zn alloy with a b.c.c. structure. At low temperatures, T<460K, the Zn and Cu atoms for an ordered structure (eg. Cu atoms in the body-centre sites in top diag.)



  - Two types of site call them: A-sites and B-sites.
  - At high T, equal probability for any site to be occupied by Cu or Zn.
- Mean-field theory
  - Describe the state of the system by its average state. Look for a variable behaving like:

Order parameter

$$\omega = \begin{cases} 0 & \text{no order} \\ 1 & \text{full order} \end{cases}$$

Thermodynamic potential, F

- Order parameter (continued…)
  - with n_A as the number of Cu atoms on A sites
    n_B as the number of Cu atoms on B sites
    $n_A + n_B = N$. ($2N$ sites in all)
  - An order parameter with the desired property is

$$\omega = \frac{n_A - n_B}{n_A + n_B} \Rightarrow n_A = \frac{1+\omega}{2} \quad ; \quad n_B = \frac{1-\omega}{2}$$

- Internal energy, U, in the mean-field approx.
  - Replace the true, local ordering field with an average over the whole crystal.
  - Bond energies
    Cu-Cu u_{cc}
    Zn-Zn u_{zz}
    Cu-Zn u_{cz}

site	Cu		Zn	
	No.	Prob.	No.	Prob.
A	n_A	$(1+\omega)/2$	n_B	$(1-\omega)/2$
B	n_B	$(1-\omega)/2$	n_A	$(1+\omega)/2$

  - Average energy at each site

$$u = ((1+\omega)/2)^2 u_{cz} + ((1-\omega)/2)^2 u_{cz} + ((1+\omega)/2)((1-\omega)/2)(u_{cc} + u_{zz})$$

$$u = \left(\omega^2 (2u_{cz} - u_{cc} - u_{zz}) + (2u_{cz} + u_{cc} + u_{zz})\right)/4$$

$$= const. - \omega^2 \Delta$$

an ordering energy, per bond

F, continued …

- Note on signs:
  - attractive interactions correspond to negative energies, u. The system will order if Cu-Zn bonds are preferred i.e. $|u_{cz}|>|u_{cc}|,|u_{zz}|$. In which case $\Delta > 0$.

Entropy, S.

- Number of arrangements of the atoms is

$$g = \left(\frac{N!}{n_A! n_B!} \right)^2$$

Cu and Zn atoms

$$S = k \ln g \approx 2k\left(N \ln N - n_A \ln n_A - n_B \ln n_B\right)$$
$$= 2Nk\left[\ln 2 - (1+\omega)\ln(1+\omega) - (1-\omega)\ln(1-\omega)\right]$$

Free energy, $F = U - TS$.

$$F = const. - N\Delta\omega^2$$
$$- 2NkT\left[(1+\omega)\ln(1+\omega) + (1-\omega)\ln(1-\omega) - \ln 2\right]$$

  - (Note: the form is similar to the phase separation example in the last lecture.)
- Equilibrium occurs when F is a minimum.

$$\left(\partial F / \partial \omega\right)_T = 0$$

Equilibrium value of the order parameter

- differentiating gives

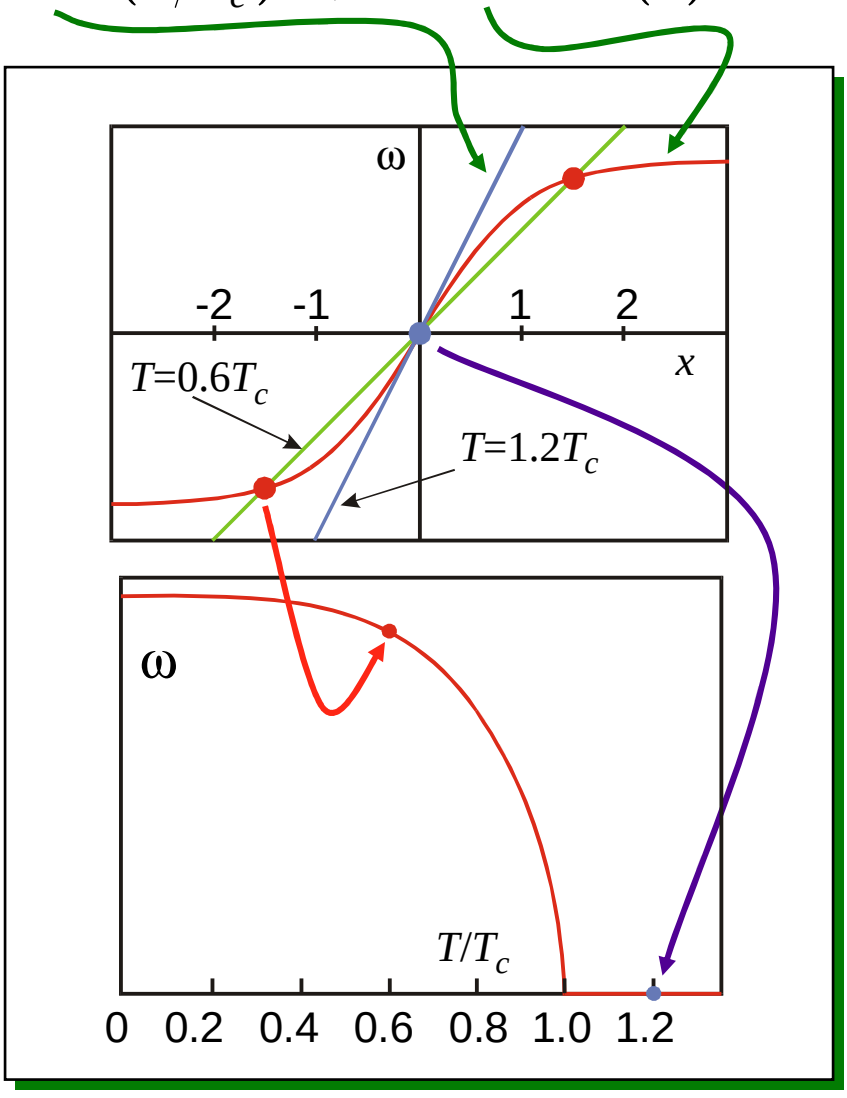
$$\left(\partial F/\partial\omega\right)_T = 0 = -2N\Delta\omega - 2NkT\ln\left(\frac{1+\omega}{1-\omega}\right)$$

- after some algebra, we get

$$\omega = \tanh\left(\Delta\omega/2kT\right) = \tanh\left(T_c\omega/T\right)$$

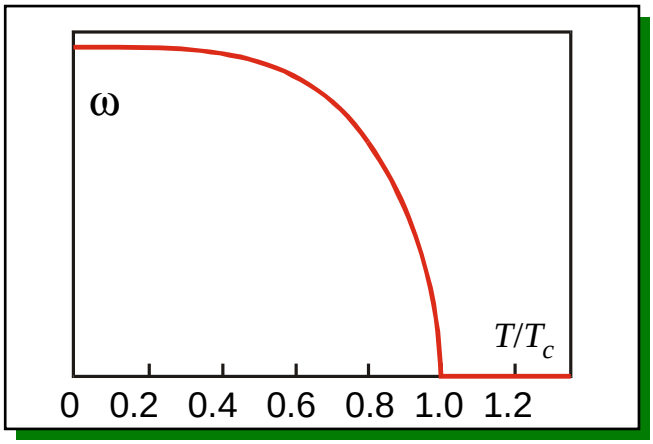
- Graphical solution

$$\omega = x\left(T/T_c\right) \quad ; \quad \omega = \tanh\left(x\right)$$

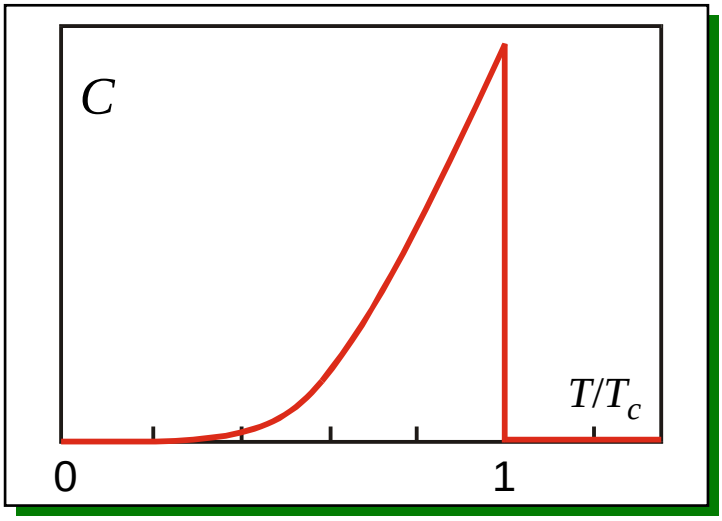


Transition in β-brass

- State of order:
  - Above T_c, the order parameter, ω, is zero
    - Cu and Zn atoms have random lattice sites.
  - Below T_c, the order parameter increases rapidly and approaches full order as $T \rightarrow 0$.

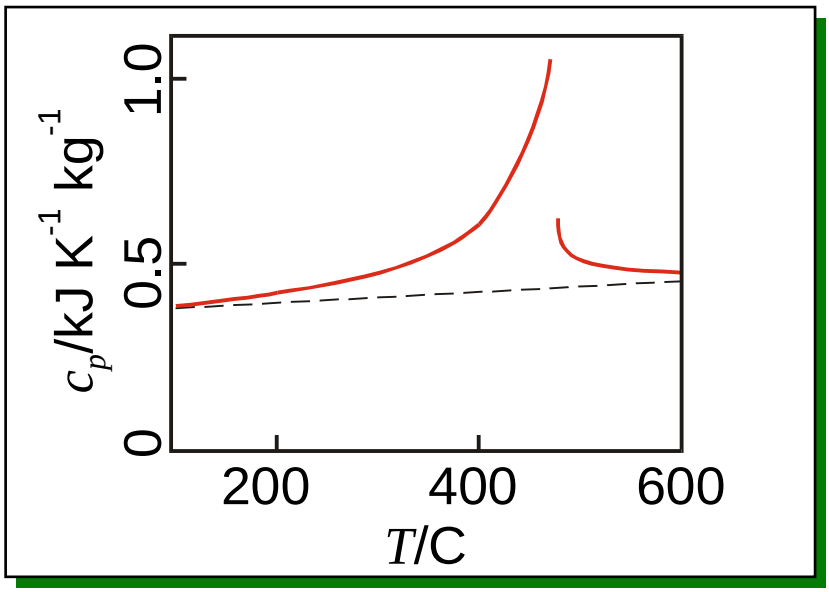


- Heat capacity
  - Once ω is known, other thermal properties can be calculated. e.g. thermal capacity $C = \partial U / \partial T$



Mean-field theory: comparison with experiment

- Heat capacity:
  - A heat capacity “anomaly” is observed. Mean field theory predicts such behaviour and describes the shape correctly at a qualitative level.



    - Note: Calorimetry measurements are often used to show the presence of phase transitions.

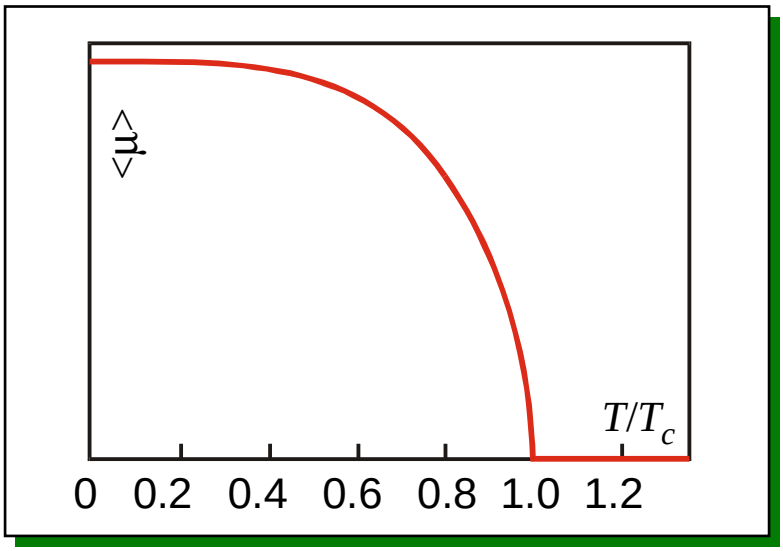
- Order parameter:
  - The order parameter agrees qualitatively with experiment.
  - In all cases, the theory is least good close to T_c, where the effects of fluctuations are most important (yet are ignored by the model).

Ferromagnetism

- Weiss theory of ferromagnetism
  - The spontaneous polarisation, in zero external field, arises as a result of interactions between spins.
  - The Weiss theory represents the interaction a mean, "internal field". $B_{int} = \lambda<\mu>$.
  - $$B = B_{int} + B_{ext} = \lambda\langle\mu\rangle + B_{ext}$$ A
  - We have, from our previous analysis of paramagnetism (lecture 7/8), a relationship between $<\mu>$ and B, which must be satisfied.
    $$\langle\mu\rangle = \mu \tanh(\mu B/kT)$$ B
  - We get the behaviour at B_{ext}=0 from a second equation (from *A*, above, with B_{ext}=0):
    $$\langle\mu\rangle = \frac{B_{int}}{\lambda} = \frac{B}{\lambda} = \left(\frac{kT}{\lambda\mu}\right)\frac{\mu B}{kT}$$ C
  - Equations B and C are the same as we obtained for β-brass! The solution is the same…

Ferromagnetic-paramagnetic transition

- Temperature dependence of the magnetic moment
  - Above T_c there is no magnetic order
  - Below T_c ferromagnetism



- Above T_c
  - System behaves like a paramagnet
  - Curie-Weiss Law

$$\chi = \frac{\mu^2}{k(T - T_c)}$$

Universality

- Beyond the mean-field theory:
  - Mean-field theory is relatively simple. It is best used to describe systems where fluctuations are unimportant and/or where there are long range interactions. A good example is the transition in type-1 superconductors.
  - In practice, interactions are often short range and fluctuations near T_c occur on all length scales. Here, the mean-field approach breaks down.
- Universality:
  - Very different systems exhibit similar behaviour indicating an underlying universality.
  - This is the subject of Landau theory (and, when fluctuations are included, Ginzburg-Landau theory). Both covered in Part II/III Physics.
  - The phenomenon arises from the limited number of ways in which functions (Thermodynamic potentials) can be modified to create/destroy the minima associated with different phases. See final question on examples sheet 2.