School of Physics and Astronomy

Junior Honours **Thermodynamics**   GJA 2019-2020

Lecture TOPIC 16 (Finn: 9.8, 9.9, 9.10)

Synopsis: Gibbs Rule. First and Second order phase changes. The Ehrenfest equations and illustrative examples (the lambda transition in liquid He^4 and superconductivity).

Gibbs Phase Rule for multicomponent systems

The number of independent variables which must be specified to fully describe thermodynamic equilibrium is equal to $C + 2 - N_P$ where C is the number of components (different chemical species, minus constraints from reactions or charge balance) and N_P is the number of phases. For example

- in liquid water $N_P = 1$, C=1, so there are two independent variables (P,T).
- At the freezing line P and T are related via Clausius-Clapeyron: $N_P = 2$;
- At the triple point P_t, v_t and T_t are uniquely defined: $N_P = 3$,
- A gas mixture of O_2 and H_2 molecules and H_2O vapour, C=3, $N_P = 1$ four independent variables (e.g. T, P, N_{O_2} N_{H_2})
- Allowing a reaction in the gas mixture, $\frac{1}{2}O_2 + H_2 \Leftrightarrow H_2O$ introduces another constraint from the reaction equilibrium. So C=2 and there are only three independent degrees of freedom.

Ehrenfest classification of the "order" of a Phase Transition.

First order transitions have a discontinuous change of first derivative of the free energy (e.g. entropy or volume, magnetic moment).
Second order phase transitions have discontinuous derivatives of second derivative of the free energy (e.g. heat capacity, thermal expansion, compressibility, Magnetic susceptibility).

The discontinuities at 1st order transitions

First order phase changes can be specified in terms of changes in the properties across the phase boundary:

First Order Transitions	
$g_1 = g_2$ and . . .	
$s_1 \neq s_2$	$v_1 \neq v_2$
$-\left(\frac{\partial g_1}{\partial T}\right)_P \neq -\left(\frac{\partial g_2}{\partial T}\right)_P$	$\left(\frac{\partial g_1}{\partial P}\right)_T \neq \left(\frac{\partial g_2}{\partial P}\right)_T$

The 'discontinuities' at continuous phase changes (2nd order or higher)

For continuous transitions, The entropy is continuous crossing the phase boundary and so there is no latent heat. In the region very close to the transition, called the critical region very general scaling laws can be derived that describe the behaviour. Typically, the disordered phase contains many mesoscopic "ordered" regions, of varied orientation which fluctuate in size. As one gets closer to the transition, this regions approach the macroscopic size of the sample. Once a single ordered region spans the entire sample, the transition occurs.

For an ordering transition, we define a parameter which specifies the long-range order. e.g. the magnetisation[1] of a ferromagnet is:

$$M = M_0 \left(\frac{T_c - T}{T_c}\right)^{\beta}, \qquad (T < T_c)$$
$$= 0 , \qquad (T > T_c)$$

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[1]For MP students: magnetisation is the ratio of induced to applied magnetic field

For the idealised Curie ferromagnet, the *critical exponent* $\beta = \frac{1}{2}$. Just above the transition, the spontaneous magnetisation is zero, susceptibility is:

$$\chi = \chi_0 \left(\frac{T_c}{T_c - T} \right)^{\gamma}, \quad (T > T_c)$$

with $\gamma = 1$ for the idealised Curie Weiss Law. Phase transitions can be assigned to *Universality Classes* according to these exponents.

Second Order Transitions			
$g_1 = g_2$			
$s_1 = s_2$		$v_1 = v_2$	
Heat capacity		Expansivity	Compressibility
$\left(\frac{\partial s_1}{\partial T}\right)_P \neq \left(\frac{\partial s_2}{\partial T}\right)_P$ $T\left(\frac{\partial s_1}{\partial T}\right)_P \neq T\left(\frac{\partial s_2}{\partial T}\right)_P$ $c_{P,1} \neq c_{P,2}$	$\left(\frac{\partial s_1}{\partial P}\right)_T \neq \left(\frac{\partial s_2}{\partial P}\right)_T$	$\left(\frac{\partial v_1}{\partial T}\right)_P \neq \left(\frac{\partial v_2}{\partial T}\right)_P$ $\frac{1}{v_1}\left(\frac{\partial v_1}{\partial T}\right)_P \neq \frac{1}{v_2}\left(\frac{\partial v_2}{\partial T}\right)_P$ $\beta_1 \neq \beta_2$	$\left(\frac{\partial v_1}{\partial P}\right)_T \neq \left(\frac{\partial v_2}{\partial P}\right)_T$ $\frac{-1}{v_1}\left(\frac{\partial v_1}{\partial P}\right)_T \neq \frac{-1}{v_2}\left(\frac{\partial v_2}{\partial P}\right)_T$ $\kappa_1 \neq \kappa_2$

$$\searrow \left(\frac{\partial s}{\partial P}\right)_T \overset{Maxwell}{\equiv} -\left(\frac{\partial v}{\partial T}\right)_P \nearrow$$

The relations are useful for identifying many phase changes experimentally. Even if there is no latent heat, and no visible separation of the phases, second-order transitions can be identified by discontinuous changes in other state variables: heat capacity, expansivity and compressibility. These changes frequently occur under extreme conditions of T and P, and can be correlated with changes in behaviour of substances such as ferromagnetism, piezoelecticity, superfluidity, superconductivity, Bose condensation etc. Detailed study of these latter properties is beyond the scope of this course.

The Ehrenfest equations for second order phase changes

The Ehrenfest equations are the equivalent of the Clausius Clapeyron equation for second order transitions. Consider entropy across the phase boundary. For a second order transition $s_1(T,P) = s_2(T,P)$, but

$$\left(\frac{\partial s_1}{\partial T}\right)_P \neq \left(\frac{\partial s_2}{\partial T}\right)_P \quad \text{which is} \quad \left(\frac{\partial}{\partial T}\left(-\left(\frac{\partial g_1}{\partial T}\right)_P\right)\right)_P \neq \left(\frac{\partial}{\partial T}\left(-\left(\frac{\partial g_2}{\partial T}\right)_P\right)\right)_P$$

Because $c_P = T(\partial s/\partial T)_P$, the discontinuous **second** partial derivative of g implies different values of the heat capacity for the two phases (labelled 1 and 2): $c_{P,1} \neq c_{P,2}$.

The variation of s with changing pressure at constant temperature can be used via a Maxwell relation, to bring in the variation of v:

$$\left(\frac{\partial s_1}{\partial P}\right)_T \neq \left(\frac{\partial s_2}{\partial P}\right)_T \quad \text{which is} \quad \left(\frac{\partial v_1}{\partial T}\right)_P \neq \left(\frac{\partial v_2}{\partial T}\right)_P \quad \text{or} \quad \left(\frac{\partial}{\partial T}\left(\frac{\partial g_1}{\partial P}\right)_T\right)_P \neq \left(\frac{\partial}{\partial T}\left(\frac{\partial g_2}{\partial P}\right)_T\right)_P$$

So this discontinuous **second** partial derivative of g implies different values of thermal expansivity β_P for the two phases: $\beta_1 \neq \beta_2$.

Finally, from $(\partial v_1/\partial P)_T \neq (\partial v_2/\partial P)_T$, we see that the compressibilities are different.

To use this in generating a phase diagram, we use a similar approach to the Clausius-Clapeyron derivation. Let A and B be neighbouring points on the phase boundary, at (T,P) and $(T+dT,P+dP)$, respectively. For *second order* transitions there is no change in s and no change in v in going from one phase to the other. So:

$$\text{at A} \quad s_1(T,P) = s_2(T,P)$$

$$\text{at B} \quad s_1(T+dT,P+dP) = s_2(T+dT,P+dP)$$

Use the first of these together with the second expanded to first order using Taylor's theorem to get:

$$\left(\frac{\partial s_1}{\partial T}\right)_P dT + \left(\frac{\partial s_1}{\partial P}\right)_T dP = \left(\frac{\partial s_2}{\partial T}\right)_P dT + \left(\frac{\partial s_2}{\partial P}\right)_T dP$$

Multiply through by T and make replacements according to the definitions of c_P, β. This leads to "the first Ehrenfest equation":

$$\frac{dP}{dT} = \frac{c_{P,1} - c_{P,2}}{Tv(\beta_1 - \beta_2)} = \frac{C_{P,1} - C_{P,2}}{TV(\beta_1 - \beta_2)}$$

"The second Ehrenfest equation" follows from a parallel treatment of the continuity of specific volume v across the phase boundary. It is:

$$\frac{dP}{dT} = \frac{\beta_2 - \beta_1}{\kappa_2 - \kappa_1}$$

Equating the two gives a relationship between the properties of the two phases

$$C_{P,1} - C_{P,2}\kappa_1 - \kappa_2 = TV(\beta_1 - \beta_2)^2$$

Discontinuity in the equation of state, and metastability

For any particular material, the equation of state for a given single *phase* (e.g water) is a continuous function, represented by a surface in PVT space. A different *phase* of the same material (e.g. ice) is represented by a different surface in PVT space. The equation of state for the *material* comprises the EoS for the phase with lowest Gibbs free energy. Thus it can jump discontinuously from the surface representing one phase to another.

In practice, a material may stay in the "wrong" phase even for (T,P) conditions beyond the phase boundary (e.g. supercooled water). This is called "metastability" and the delayed onset of the transition is called "hysteresis". Hysteresis is normal in any first order transition between condensed phases.

Second order transition: Ising ferromagnet

The Ising Model is a simple example of a magnetic transition based on an energy relation $U = \sum_{i,j} \varepsilon \sigma_i \sigma_j$. The spins are $\sigma_i = \pm 1$, located on a square lattice, and ε is the ratio of interaction energy to temperature. A ferromagnetic transition involves long range order in the alignment of the spins. In fact, the ordering depends on length scale, paramagnets have short range order. Fig. 1 shows the change of magnetisation (M), heat capacity (C) and susceptibility (χ) through the phase transition. There is a continuous change in the magnetisation, with discontinuous slope at T_C. The exceptionally high values of $\frac{dM}{dT}$ close to the transition mean that small fluctuations in T give rise to massive fluctuations in M (above T_C these are short ranged). The critical exponent for the 2D Ising model is $\beta = 0.125$.


Fig.1
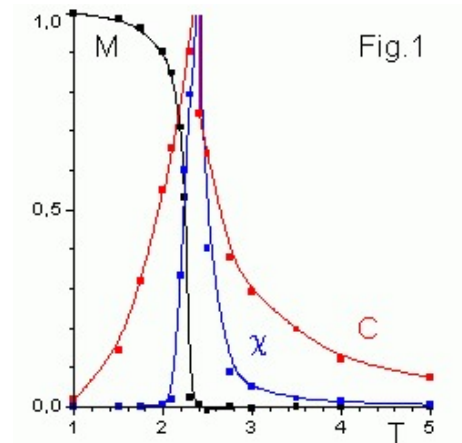
Examples of continuous phase transitions

Typically, a "continuous" phase transition can be viewed as coexistence of two intermingled phases which, for some reason, cannot form an interface or boundary.

Superfluid transition (Bose Condensate)

The superfluid transition occurs when a finite fraction of the atoms "condense" into a single many-body quantum state. This fraction of atoms has ZERO entropy. Superfluid liquid helium (^{4}He) occurs at $T_\lambda = 2.2$ K, on cooling – from normal liquid helium (He I) to "superfluid" (He II). The He II phase may be thought of as two interpenetrating fluids, although atoms are continually transferring between the normal fluid and Bose condensate. The condensate has no viscosity, and the viscosity of He II is a harmonic average of the components ($\eta^{-1} = \eta_{cond}^{-1} + \eta_{normal}^{-1}$) – hence He II is a "superfluid".

There is a marked feature in the otherwise slowly decreasing value of specific heat at temperature T_λ. The plotted data (figure) has the shape of the Greek letter lambda – hence the name. Liquid He II low-pressure/low-temperature corner of the phase diagram. Despite the peak, $C_P(T)$ is continuous: the fraction of superfluid in He II increases from zero at the transition to 100% at T=0.

In more detail: Experimentally, the phase transition is clear since the two phases of liquid He^4 have very different properties. Liquid helium can be very pure because any contaminants (except ^{3}He) freeze out, and the heat capacity can be measured with exceptional precision. For temperatures above 2.5 K, the heat capacity of He I behaves normally: decreasing as temperature decreases, apparently towards $c_P(T = 0) = 0$. Then the heat capacity increases and goes through a maximum at T_λ (with a cusp at T_λ itself) and then decreases towards zero at T=0. The most accurate measurements with a resolution of 10^{-8} K show, that the heat capacity is continuous at T_λ!
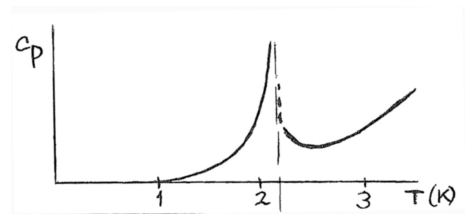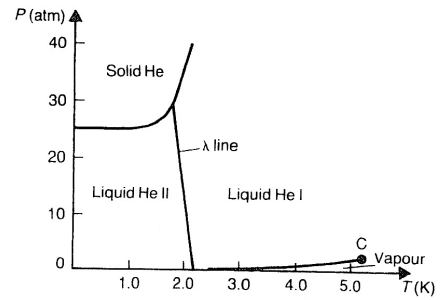
Superconducting transition

The superconducting transition occurs when a finite fraction of the electrons are in a single many-body quantum state. The figure shows the measured heat capacity of pure indium in zero field as the temperature is changed crossing the superconducting critical temperature $T_c = 3.4$ K. Below this temperature the electrical resistance drops sharply to zero. Although in detail, very close to T_c the transition must again be continuous with a sharp λ peak, the width of the critical region is very very small and it makes a negligible contribution to the heat transfer required to change the state of the sample, and is not visible in the data.
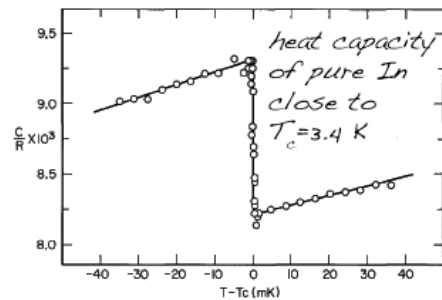
Statistics, the thermodynamic limit and fluctuations at phase transitions

The *thermodynamic limit* refers to infinite numbers of particles, where statistical probabilities become exact. In this context Avogadro's number is reassuringly large. Although the details are beyond the scope of the course, its good to know about fluctuations.

We know that any quantity measured as an average of N readings has an uncertainty (error in the mean) of $N^{-1/2}$. Thermodynamic quantities are no different, e.g. the *instantaneous* value of the kinetic energy varies, and so does the "Ideal gas temperature". At the "thermodynamic limit" of Avogadro's number of independent particles, the error for an intensive quantity is proportional to $N_A^{-1/2}$ (effectively nothing). But for small systems, or for correlated fluctuations, e.g. near a phase transition, these can become noticable. The size and correlation of these fluctuations is also related to thermodynamic quantities. If we measure correlation functions of fluctuations in a small piece of material, then e.g.

$$< \Delta T^2 > \sim T^2/C_V; \quad < \Delta V^2 > \sim -T \left(\frac{\partial V}{\partial T}\right)_T; \quad < \Delta S^2 > \sim C_p; \quad < \Delta P^2 > \sim -k_B T \left(\frac{\partial P}{\partial V}\right)_S; \quad < \Delta T \Delta S > \sim k_B T;$$

$$< \Delta T \Delta P > \sim \frac{k_B T^2}{C_V} \left(\frac{\partial P}{\partial T}\right)_V; \quad < \Delta V \Delta S > \sim k_B T \left(\frac{\partial V}{\partial T}\right)_P.$$