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## 06. Thermodynamics of Phase Transitions II

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### Abstract

Part six of course materials for Statistical Physics I: PHYS25, taught by Gerhard Müller at the University of Rhode Island. Documents will be updated periodically as more entries become presentable.

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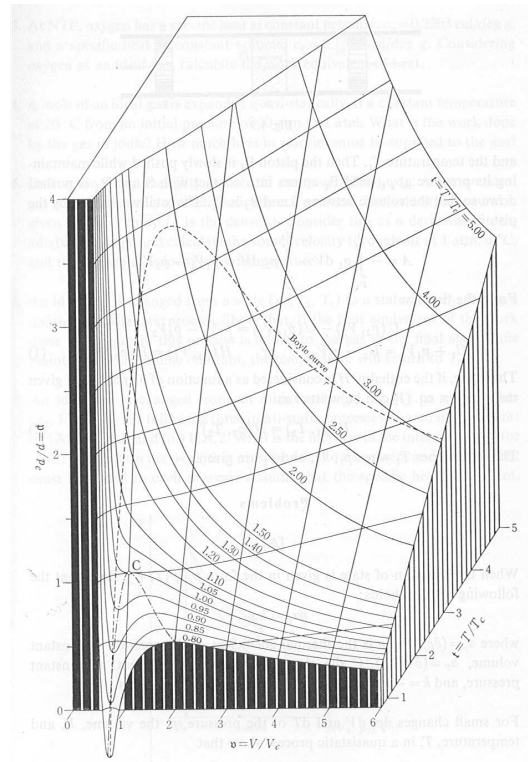
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## 6. Thermodynamics of Phase Transitions II

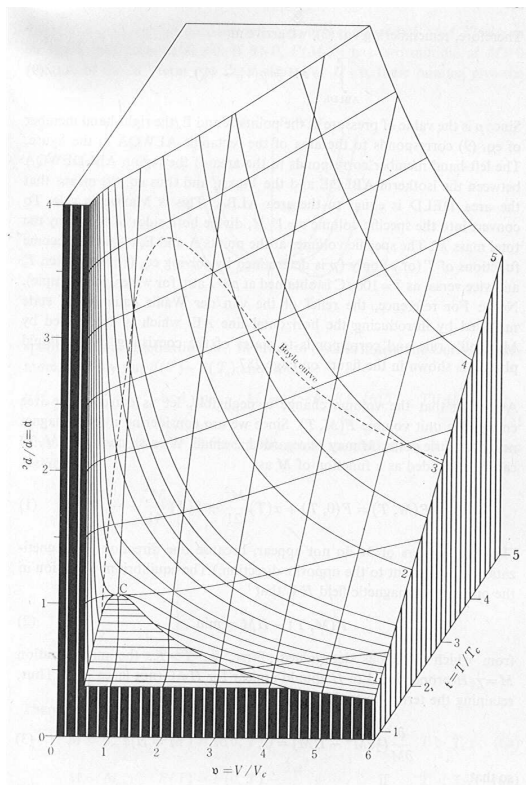
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# Van der Waals equation of state [ts110]

with spinodal curve



with coexistence curve



## Law of corresponding states [tln30]

Use the critical-point values,  $p_c, V_c, T_c, \rho_c$ , for the thermodynamic variables and introduce reduced quantities:

$$\bar{p} \equiv \frac{p}{p_c}, \quad \bar{V} \equiv \frac{V}{V_c}, \quad \bar{T} \equiv \frac{T}{T_c}, \quad \bar{\rho}_l \equiv \frac{\rho_l}{\rho_c}, \quad \bar{\rho}_g \equiv \frac{\rho_g}{\rho_c}.$$

Empirical fact: Near the critical point, the relations between (reduced) thermodynamic quantities are *universal*.

### Experimentally:

*Guggenheim plot* of liquid-vapor coexistence curves:

$$\frac{1}{2}(\bar{\rho}_l + \bar{\rho}_g) \simeq 1 + \frac{3}{4}(1 - \bar{T}), \quad \bar{\rho}_l - \bar{\rho}_g \simeq \frac{7}{2}(1 - \bar{T})^{1/3}.$$

### Theoretically:

Van der Waals equation:  $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$ .

Critical point condition:  $\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial^2 p}{\partial^2 V}\right)_T = 0$ .

Critical-point values:  $p_c = \frac{a}{27b^2}$ ,  $V_c = 3nb$ ,  $T_c = \frac{8a}{27bR}$ .

VdW equation in reduced units:  $\left(\bar{p} + \frac{3}{\bar{V}^2}\right)(3\bar{V} - 1) = 8\bar{T}$ .

# Maxwell construction [tln31]

Goal: Study the liquid-gas transition for a fluid system described by the van der Waals equation of state.

Consider an isotherm at  $T < T_c$  with roadmarks A–I as shown in [tsl11]. Determine the variation of the Gibbs potential along the subcritical isotherm:

$$dG = -SdT + Vdp = Vdp \Rightarrow G(T, p) = G(T, p_A) + \int_{p_A}^p dp V(p).$$

Consider the self-intersecting curve in the plot  $G$  versus  $p$ .  $G(T, p_C) = G(T, p_G)$  implies that area 1 = area 2.

Discuss stability of thermodynamic state along all segments of the curve A–I:

- Segments ABC, GHI:  $\left(\frac{\partial p}{\partial V}\right)_T < 0$ ,  $G(T, p)$  is either the only branch or the lowest branch of a multi-valued function. The state is *stable*.
- Segments CD, FG:  $\left(\frac{\partial p}{\partial V}\right)_T < 0$ ,  $G(T, p)$  is not the lowest branch of a multi-valued function. The state is *metastable*.
- Segment DEF:  $\left(\frac{\partial p}{\partial V}\right)_T > 0$ . This implies that the state is *unstable*.

The physical isotherm includes only stable states. It is described by the curve ABCGHI in the plot  $G$  versus  $p$ .

Stability requires that the Gibbs potential  $G(T, p)$  is a concave function  $p$  and that the Helmholtz potential  $A(T, V)$  is a convex function of  $V$ :

$$\left(\frac{\partial p}{\partial V}\right)_T < 0 \Rightarrow \left(\frac{\partial^2 G}{\partial p^2}\right)_T < 0, \quad \left(\frac{\partial^2 A}{\partial V^2}\right)_T > 0.$$

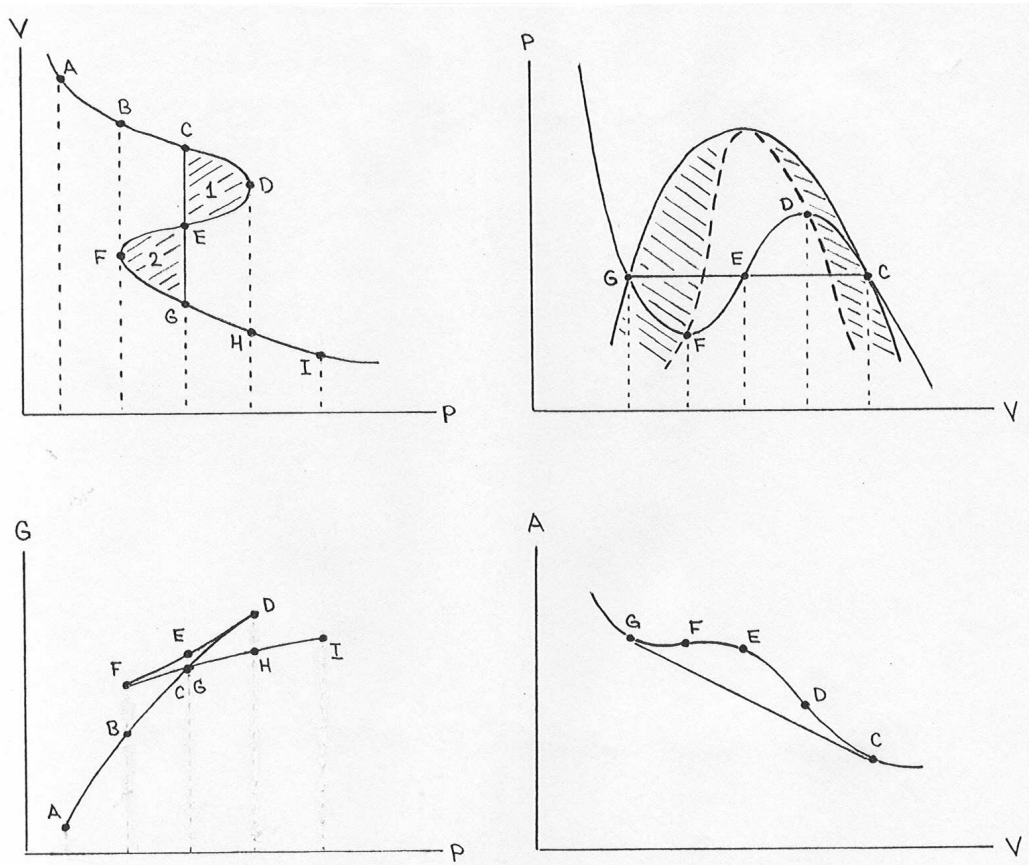
Variation of the Helmholtz potential along the subcritical isotherm:

$$dA = -SdT - pdV = -pdV \Rightarrow A(T, V) = A(T, V_A) - \int_{V_A}^V dv p(V).$$

In the unstable and metastable regions,  $A(T, V)$  can be made smaller if we replace the homogeneous system by a system with two coexisting phases.

Note: the (shaded) metastable region is bounded by the *coexistence* curve (solid line) and the *spinodal* curve (dashed line).

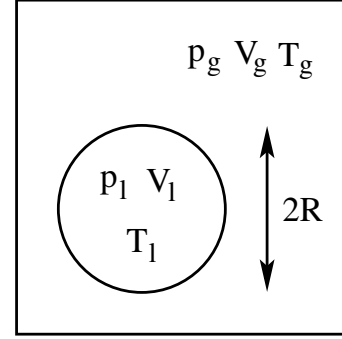
# Gibbs and Helmholtz free energies of the van der Waals fluid at $T < T_c$ [tsl11]



## Condensation and evaporation [tln32]

*Supersaturated* gases and *superheated* liquids owe their metastable existence to the surface tension  $\sigma$ . Consider a liquid droplet in equilibrium with the surrounding vapor, implying  $T_l = T_g$ ,  $\mu_l = \mu_g$ , and  $p_l > p_g$  because of surface tension.

For a vapor bubble surrounded by liquid, the argument proceeds along analogous lines.



Work done if droplet expands or contracts:  $\delta W = -p_l dV_l - p_g dV_g + \sigma dA$ .

Grand potential:  $\Omega(T, V, \mu) = -p_l V_l - p_g V_g + \sigma A$ .

$$\Rightarrow \Omega(T, V, \mu) = -\frac{4\pi}{3} R^3 p_l - \left( V_{tot} - \frac{4\pi}{3} R^3 \right) p_g + 4\pi R^2 \sigma.$$

Mechanical equilibrium:  $(\partial\Omega/\partial R)_{T,V,\mu} = 0 \Rightarrow 4\pi R^2(p_g - p_l) + 8\pi R\sigma = 0$ .

Excess pressure in droplet:  $p_l - p_g = 2\sigma/R$ .

Gibbs-Duhem equations (with  $dT = 0$ ),  $N_l d\mu_l = V_l dp_l$ ,  $N_g d\mu_g = V_g dp_g$ .

Chemical equilibrium:  $d\mu_l = d\mu_g \Rightarrow (V_l/N_l) dp_l = (V_g/N_g) dp_g$ .

Differential excess pressure:  $d(p_l - p_g) = \frac{V_g/N_g - V_l/N_l}{V_l/N_l} dp_g = d\left(\frac{2\sigma}{R}\right)$ .

Use  $\frac{V_g}{N_g} \gg \frac{N_l}{V_l}$ ,  $\frac{V_g}{N_g} \simeq \frac{k_B T}{p_g} \Rightarrow \frac{k_B T/p_g}{V_l/N_l} dp_g = d\left(\frac{2\sigma}{R}\right)$ .

Integrate  $\frac{dp_g}{p_g} = \frac{V_l}{N_l k_B T} d\left(\frac{2\sigma}{R}\right)$  from  $\infty$  to  $R$ .

$$\Rightarrow \ln \frac{p_g(R)}{p_g(\infty)} = \frac{2\sigma V_l}{R N_l k_B T} = \frac{2\sigma m}{R \rho_l k_B T} \Rightarrow p_g(R) = p_g(\infty) \exp\left(\frac{2\sigma m}{R \rho_l k_B T}\right).$$

Only liquid droplets of a particular radius  $R_c$  coexist with the supersaturated gas phase. Droplets with  $R < R_c$  will shrink. Droplets with  $R > R_c$  will grow. Hence the condensation process at pressure  $p = p_g(R_c)$  can be initiated by the presence of droplets with radius  $R > R_c$ .

Metastability depends on the absence of droplets with radius  $R > R_c$ . The boundary of the metastable region (spinodal line) corresponds to a value of  $R_c$  comparable to the molecular radius. Supersaturation cannot be pushed beyond that point.

### [tex34] Dieterici equation of state

The Dieterici equation of state of a fluid system reads

$$p = \frac{nRT}{V - nb} \exp\left(-\frac{an}{RTV}\right),$$

where  $a, b$  are phenomenological constants.

(a) Show that the pressure, volume, and temperature at the critical point are

$$p_c = \frac{a}{4b^2e^2}, \quad V_c = 2nb, \quad T_c = \frac{a}{4Rb}.$$

(b) Rewrite the Dieterici equation of state as a relation between the dimensionless quantities  $\bar{p} \equiv p/p_c$ ,  $\bar{V} \equiv V/V_c$ ,  $\bar{T} \equiv T/T_c$  (law of corresponding states).

**Solution:**



# Helium liquids [tln33]

Helium has a small atomic mass and a weak interatomic interaction. This enhances quantum effects. Solid helium exists only at high pressure. Helium at low  $T$  and moderate  $p$  is a quantum liquid with peculiar features.

The two helium isotopes,  $^3\text{He}$  and  $^4\text{He}$ , are chemically similar but physically very different. The physical difference is governed by the difference in nuclear spin ( $\frac{1}{2}$  versus zero).

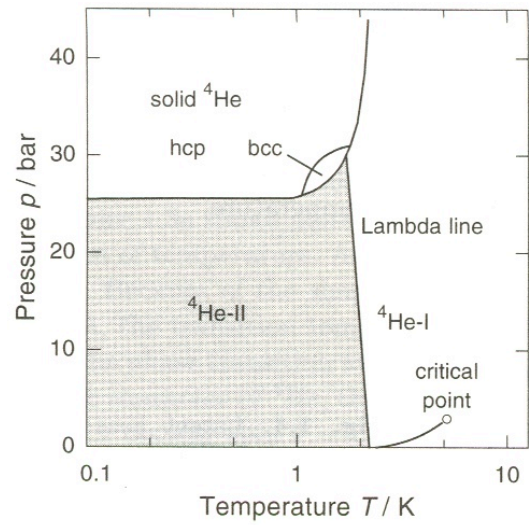
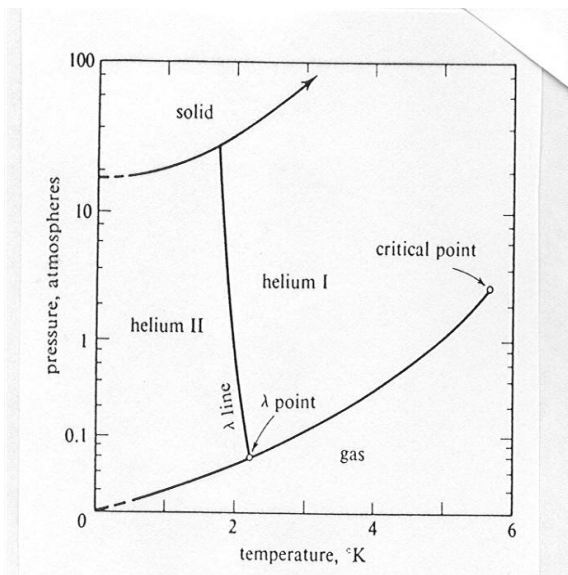
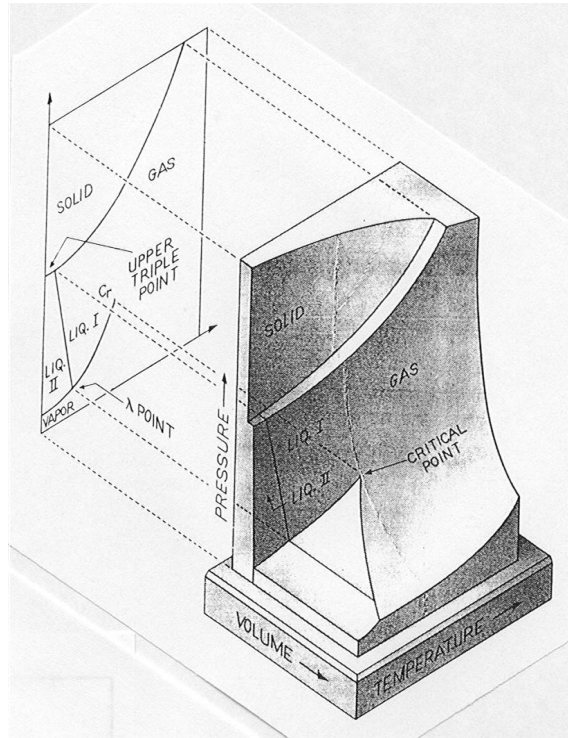
## $^4\text{He}$ Features

- The liquid-vapor coexistence line terminates in a critical point.
- The solid-liquid transition line is monotonic and ends at  $T = 0$  and  $p \simeq 25\text{atm}$  with zero slope ( $dp/dt = \Delta S/\Delta V = 0$ ).
- The  $\lambda$ -line separates the normal fluid (He I) from the superfluid (He II) via a continuous transition.
- Each end of the  $\lambda$ -line is a triple point.
- $^4\text{He}$  was first liquefied in 1908 by Kamerlingh Onnes (at 4.2K, 1atm).
- The  $\lambda$ -transition has been interpreted microscopically as the condensation of interacting bosons.

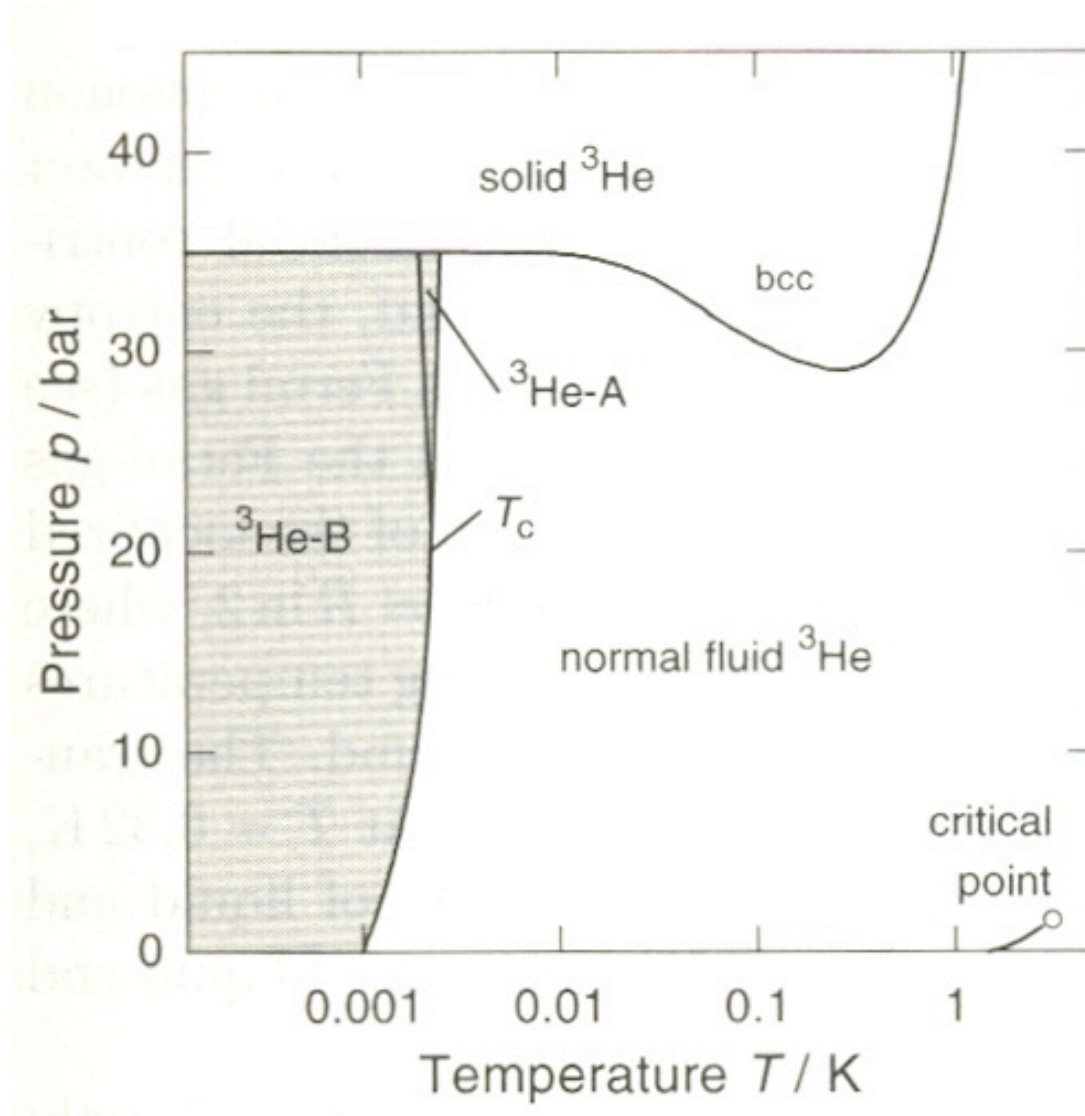
## $^3\text{He}$ Features

- The relative abundance of  $^3\text{He}$  in natural helium is  $10^{-6}$ .
- $^3\text{He}$  can be produced artificially from tritium ( $^3\text{H}$ ) via  $\beta$ -decay.
- $^3\text{He}$  has not been available in large quantities until 1940 (Manhattan project).
- $^3\text{He}$  was first liquefied in 1948.
- A superfluid transition in  $^3\text{He}$  was first observed in 1971.
- The superfluid phase in  $^3\text{He}$  is akin to the superconducting phase. It is described by bound pairs of quasi-particles with spin  $\frac{1}{2}$ .
- The A-phase and the B-phase differ by the orientation of the bound pairs.
- The negative slope in the solid-liquid coexistence curve is attributable to an entropy effect of nuclear spins ( $dp/dt = \Delta S/\Delta V < 0$ ).

# Phase diagram of $^4\text{He}$ [ts113]



# Phase diagram of $^3\text{He}$ [tsl14]



[from Enss and Hunklinger 2005]

## Exotic Properties of helium II [tln34]

Helium II behaves like a mixture of normal fluid and superfluid. The superfluid portion increases with decreasing temperature at the expense of the normal fluid portion. The superfluid has no viscosity and no entropy.

Consider two vessels A and B with rigid insulating walls, connected by a capillary that allows unimpeded superfluid flow but prevents any normal fluid flow.

In general, the thermal equilibrium of that system is characterized by the following relations between intensive variables:

$$T_A \neq T_B, \quad p_A \neq p_B, \quad \mu_A(T_A, p_A) = \mu_B(T_B, p_B).$$

Consider situations in which system B is very large compared to system A. Any process in which a change of  $p_A$  or  $T_A$  is forced in the smaller system must then satisfy  $\mu_A(T_A, p_A) = \mu_B(T_B, p_B) = \text{const}$  i.e.  $d\mu_A = 0$ .

$$\Rightarrow \left( \frac{\partial \mu_A}{\partial T_A} \right)_{p_A} dT_A + \left( \frac{\partial \mu_A}{\partial p_A} \right)_{T_A} dp_A = -\frac{S_A}{N_A} dT_A + \frac{V_A}{N_A} dp_A = 0.$$

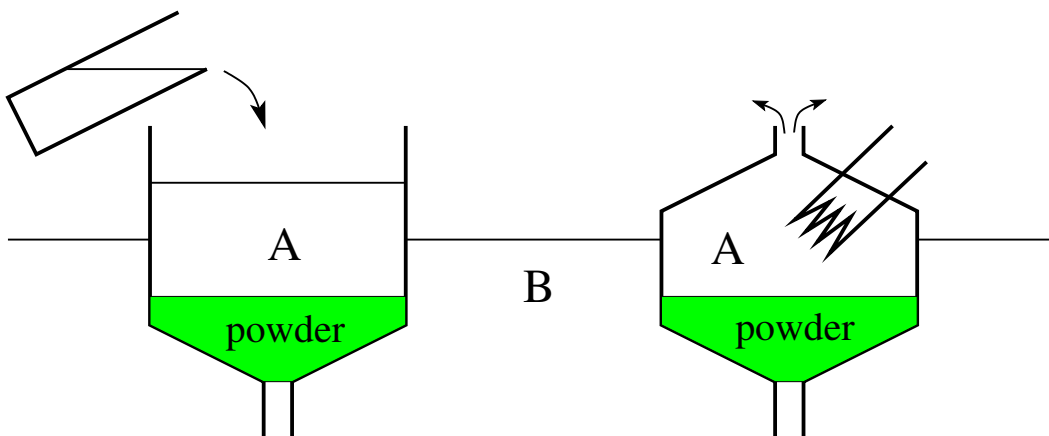
$$\Rightarrow dp_A = \frac{S_A}{V_A} dT_A.$$

**Mechanocaloric effect:**

Pressure increase  
causes temperature increase.

**Thermomechanical effect:**

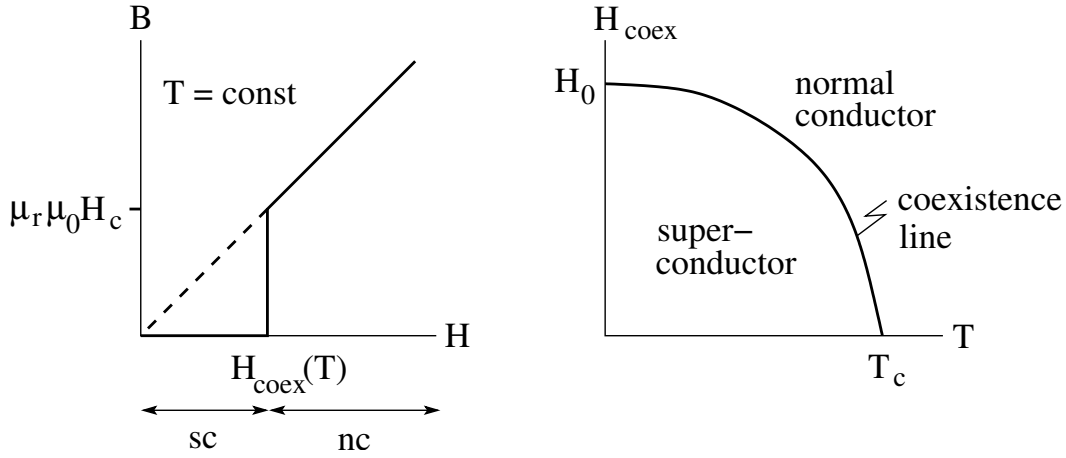
Temperature increase  
causes pressure increase.



# Superconducting transition [tln35]

## Meissner-Ochsenfeld effect:

Observation that the magnetic induction  $B = \mu_r \mu_0 H$  vanishes inside a superconductor (of type I).  $B$  is expelled by surface supercurrents. However, a sufficiently strong external magnetic field  $H$  destroys superconductivity.



Coexistence between the superconducting and the normal conducting phases requires  $G^{(sc)}(T, H) = G^{(nc)}(T, H)$  (Gibbs free energy per unit volume).

Along the coexistence line:  $dG^{(sc)} = dG^{(nc)}$ .

$$\Rightarrow -S^{(nc)}dT - B^{(nc)}dH = -S^{(sc)}dT - B^{(sc)}dH$$

with  $B^{(nc)} = \mu_r \mu_0 H_{coex}(T)$  and  $B^{(sc)} = 0$ .

Clausius-Clapeyron equation:  $S^{(nc)} - S^{(sc)} = -\mu_r \mu_0 H_{coex}(T) \left( \frac{dH}{dT} \right)_{coex}$ .

Latent heat:  $L = T (S^{(nc)} - S^{(sc)})$ .

As  $H$  increases,  $G^{(sc)}$  stays constant but  $G^{(nc)}$  decreases:

$$G^{(nc)}(T, H) - G^{(nc)}(T, 0) = - \int_0^H B^{(nc)} dH = -\frac{1}{2} \mu_r \mu_0 H^2.$$

On the coexistence line:  $G^{(nc)}(T, H_{coex}) = G^{(sc)}(T, H_{coex})$ .

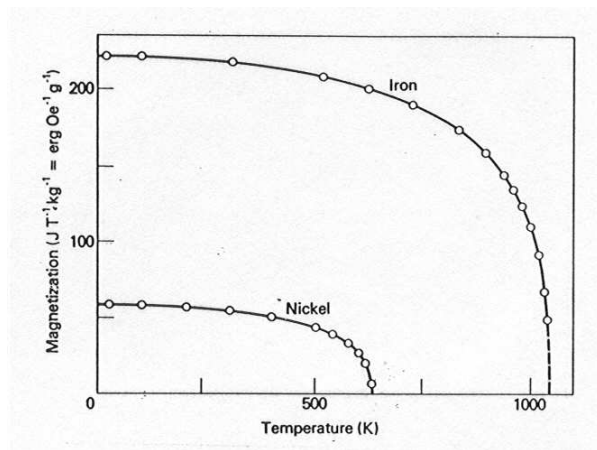
$$\Rightarrow G^{(sc)}(T, 0) - G^{(nc)}(T, 0) = -\frac{1}{2} \mu_r \mu_0 H_{coex}^2(T).$$

## Thermodynamics of a Ferromagnet [ts15]

Materials with ions that have permanent electronic magnetic moments may be paramagnetic, ferromagnetic, antiferromagnetic, or exhibit some other kind of magnetic ordering.

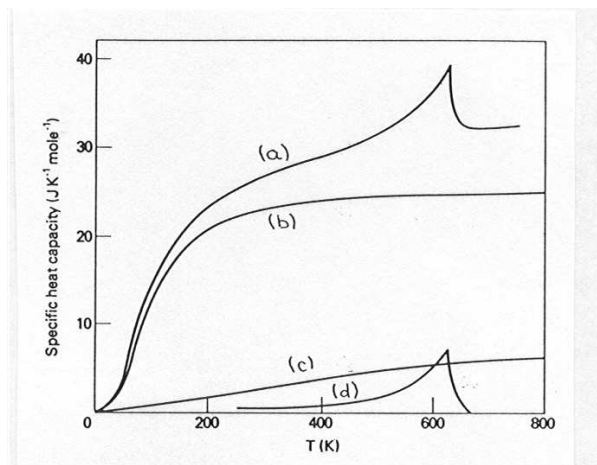
In ferromagnetic materials there exists a continuous transition from the paramagnetic phase to the ferromagnetic phase when the system is cooled through the Curie temperature  $T_c$ .

### Spontaneous magnetization of nickel and iron:



### Heat capacity of nickel:

- (a) total heat capacity,      (b) contribution of lattice vibrations  
(c) electronic contribution,      (d) magnetic contribution.



### [tex53] Structural transitions of iron

At constant atmospheric pressure, the stable phase of Fe below  $900^{\circ}\text{C}$  and above  $1400^{\circ}\text{C}$  is  $\alpha$ -iron. Between these temperatures, the stable phase is  $\gamma$ -iron. The specific heat of each phase can be taken as constant:  $c_{\alpha} = 0.775\text{J/gK}$ ,  $c_{\gamma} = 0.690\text{J/gK}$ . Find the latent heat (per gram) at each of the two phase transitions.

**Solution:**

## [tex44] Latent heat and heat capacities at superconducting transition

The coexistence line between the normal and superconducting phases of some metallic material is observed to be well approximated by the empirical formula,

$$H_{coex}(T) = H_0(1 - T^2/T_c^2), \quad 0 \leq T \leq T_c,$$

where  $H_0, T_c$  are constants.

(a) Use the Clausius-Clapeyron equation adapted to this situation (see [tln35]) to calculate the latent heat  $L$  (per unit volume) at the transition. Plot  $L$  versus  $T$  for  $0 \leq T \leq T_c$ .

(b) When the material is heated up along the coexistence line, different specific heats obtain for the two phases. Use the results of (a) to calculate the discontinuity  $\Delta C = C^{(nc)} - C^{(sc)}$  (per unit volume) across the coexistence line. Plot  $\Delta C$  versus  $T$  for  $0 \leq T \leq T_c$ .

**Solution:**



## [tex45] Thermodynamics of the mean–field ferromagnet I

The mean-field ferromagnet is specified by the heat capacity  $C_M = 0$  and by the equation of state  $M = \tanh([H + \lambda M]/T)$ , where  $\lambda$  is a constant. In zero magnetic field ( $H = 0$ ), this system undergoes a continuous transition at temperature  $T_c = \lambda$  between a paramagnetic phase ( $M = 0$ ) and a ferromagnetic phase ( $M \neq 0$ ).

(a) Determine the spontaneous magnetization  $M(T, H = 0)$  in the ferromagnetic phase by numerically solving the equation of state at  $H = 0$ . Plot  $M$  versus  $T$  for  $0 \leq T \leq T_c$ .

(b) Show that the entropy depends only on  $M$ :

$$S(M) = -\frac{1+M}{2} \ln \frac{1+M}{2} - \frac{1-M}{2} \ln \frac{1-M}{2}.$$

Plot  $S$  versus  $T$  at  $H = 0$  for  $0 \leq T \leq 2T_c$ .

(c) Calculate an analytic expression for the Helmholtz free energy  $A(T, M)$ .

**Solution:**

## [tex46] Thermodynamics of the mean–field ferromagnet II

The mean-field ferromagnet is specified by the heat capacity  $C_M = 0$  and by the equation of state  $M = \tanh([H + \lambda M]/T)$ , where  $\lambda$  is a constant. In zero magnetic field ( $H = 0$ ), this system undergoes a continuous transition at temperature  $T_c = \lambda$  between a paramagnetic phase ( $M = 0$ ) and a ferromagnetic phase ( $M \neq 0$ ).

(a) Calculate an analytic expression for the isothermal susceptibility  $\chi_T(T, M)$  from the equation of state. Use the numerically determined  $M(T, H = 0)$  from [tex45] to plot  $\chi_T(T, H = 0)$  versus  $T$  for  $0 \leq T \leq 2T_c$ .

(b) Determine the heat capacity  $C_H(T, M) = T\alpha_H^2/(\chi_T - \chi_S)$  from  $\alpha_H = (\partial M/\partial T)_H$ ,  $\chi_T = (\partial M/\partial H)_T$ ,  $\chi_S = (\partial M/\partial H)_S$ , and plot  $C_H$  versus  $T$  for  $0 \leq T \leq 2T_c$ .

(c) Plot in the same diagram (with different symbols) the function  $T(\partial S/\partial T)_{H=0}$  by using the data of  $S(T, H = 0)$  from [tex45].

**Solution:**