

Exercise Problems - Week 10

Statistical Mechanics and Thermodynamics

SoSe 2018

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JGU Mainz - Institut für Physik

Choose 4 of the 6 problems below. Each problem is worth 12 points.

Problem 1

The van der Waals equation of state for a mole of gas is given by $(P + a/V^2)(V - b) = RT$, where V is the molar volume of the gas.

1. Define the critical point T_c , V_c and P_c in terms of $(\partial p/\partial v)_T$ and $(\partial^2 P/\partial V^2)_T$.
2. Express a and b in terms of T_c and V_c .
3. Express P_c in terms of T_c and V_c .
4. Calculate the compressibility $\kappa_T = -V^{-1}(\partial V/\partial P)_T$ and the thermal expansion coefficient $\beta = V^{-1}(\partial V/\partial T)_P$ for the van der Waals gas. What do these quantities do at the critical point?

Problem 2

The work done by a long solenoid in magnetizing a thin rod shaped magnetic sample inside it is

$$\delta W_{\text{sol}} = \mu_0 V H_a dM$$

here μ_0 is the permeability of free space, V the sample volume, H_a , the applied field and M the magnetization of the sample (magnetic moment per unit volume), The magnetic induction inside the sample is given by

$$B = \mu_0 (H_a + M) = \mu_0 (1 + \chi) H_a$$

where χ is the magnetic susceptibility of the material. For most ordinary metals in the normal state, χ is rather small. (For this problem it can be set equal to zero.) If the metal goes into the superconducting state, however, it would usually exhibit a Meissner effect which means that $B = 0$ inside the superconductor, i.e. $\chi = -1$. At temperatures below the superconducting transition temperature, $T < T_c$, an applied field $H_a = H_c$, (the critical field) is sufficient to destroy superconductivity. The phase boundary between the superconducting state and the normal state can be approximated by

$$H_c = H_0 \left[1 - (T/T_c)^2 \right]$$

1. For this phase boundary in the H_a, T plane. Write the defining expression for the magnetic Gibbs free energy $G(T, P, H_a)$ and its differential.
2. What is the relationship between $G_N(T, P_0, H_c)$ and $G_S(T, P_0, H_c)$, the Gibbs free energies for the normal and superconducting phases along this phase boundary. P_0 is an arbitrary, fixed pressure at which the relation for H_c , given above was determined. Find the relationship between $G_N(T, P_0, H_a)$ and $G_N(T, P_0, 0)$ and between $G_S(T, P_0, H_a)$ and $G_S(T, P_0, 0)$.
3. Use the results of the previous parts to show that
 - (a) there must be a jump discontinuity in the heat capacity of a metal when it undergoes the superconducting transition at $T = T_c$. (Relate this jump to dH_c/dT at $T = T_c, H_a = 0$);
 - (b) there must be a latent heat of transformation when the superconductor is driven from the superconducting state to the normal state by a magnetic field applied at a constant temperature T . (Relate this latent heat to the slope of the phase boundary as a function of temperature.)

Problem 3

Consider a single component system with two phases 1 and 2

1. Starting from the condition of equilibrium for the two phases that the Gibbs free energies g_1 and g_2 are the same, i.e. $g_1 = g_2$, derive the Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{l_{1,2}}{T\Delta v}$$

where $l_{1,2}$ is the heat absorbed when one mole of phase 1 is transformed to phase 2, $\Delta v = v_2 - v_1$ is the corresponding volume change, and P and T are, respectively, the pressure and temperature of the system.

2. Using the above equation show that the slope of any vapor pressure curve (liquid or solid) is positive.
3. Show that the melting curve for water has a negative slope.
4. The slope of a vapor pressure curve near the critical point is finite. Using the above equation find the expected numerical value for $l_{1,2}$ at the critical point.

Problem 4

A substance is found to have two phases N and S . In the normal state, the N phase, the magnetization M is negligible. At a fixed temperature $T < T_c$, as the external magnetic field H is lowered below the critical field

$$H_c(T) = H_0 \left[1 - \left(\frac{T}{T_c} \right)^2 \right]$$

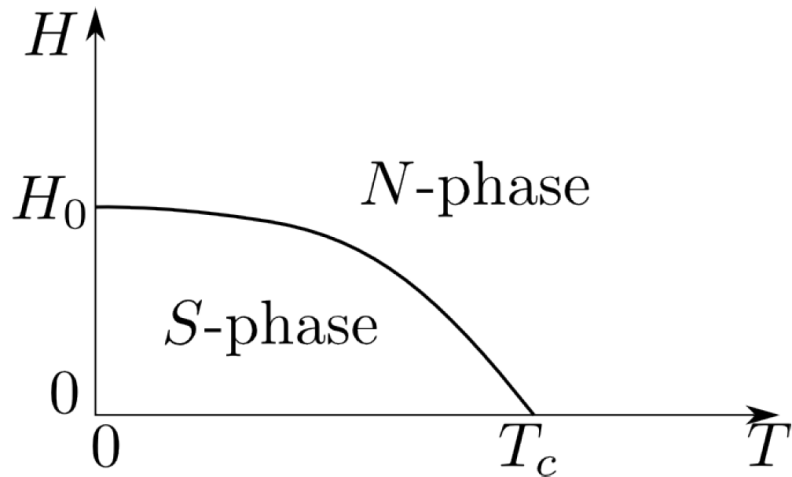
the normal state undergoes a phase transition to a new state, the S phase. In the S state, it is found that $B = 0$ inside the material. The phase diagram is shown below.

1. Show that the difference in Gibbs free energies (in cgs units) between the two phases at temperature $T \leq T_c$, is given by

$$G_S(T, H) - G_N(T, H) = \frac{1}{8\pi} [H^2 - H_c^2(T)].$$

(You may express your answer in another system of units. The Gibbs free energy in a magnetic field is given by $G = U - TS - HM$.)

2. Compute the latent heat of transition L from the N to the S phase.
[Hint: one approach is to consider a "Clausius-Clapeyron" type of analysis.]
3. At $H = 0$, compute the discontinuity in the specific heat as the material transforms from the N to the S phase.
4. Is the phase transition first or second order at $H = 0$? What is the basis of your conclusion?

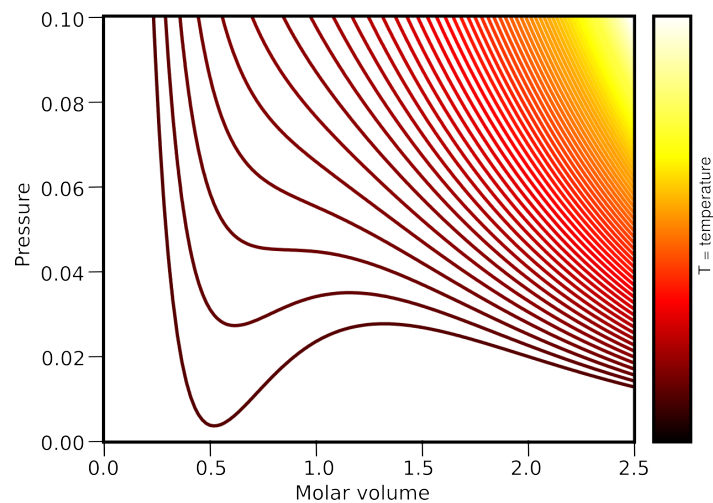


Problem 5

The figure shows the pressure versus molar volume isotherms for the Van der Waals gas

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

1. Which of the isotherms in the figure contains regions that do not satisfy the thermodynamic stability conditions?
2. Which isotherm represents the critical temperature?
3. Sketch on the graph the region in which the system is unstable to local perturbations (spinodal line).
4. Sketch on the graph the region in which the system is globally unstable.
5. What is physically occurring within this region of global instabilities?
6. Sketch the qualitative behavior of the molar volume against temperature for an isobar at $P = 0.02$ and $P = 0.06$.



Problem 6

The intersection of two Gibbs free energy surfaces is a line where $G_\alpha = G_\beta$, along which two phases α and β coexist. Let the phases α and β be the liquid phase and the gas phase, respectively. Along the liquid-gas coexistence line in the $P - T$ plane, show that, to a very good approximation,

$$\log\left(\frac{P}{P_0}\right) = \frac{L_{vap}}{R} \left(\frac{1}{T_b} - \frac{1}{T}\right)$$

where P is the vapor pressure of the liquid present, P_0 is the atmospheric pressure (1atm), R is the ideal gas constant, T is the absolute temperature, T_b is the boiling point of the system (at atmospheric pressure), and L_{vap} is the heat of vaporization per mole (whose dependence on T and P may be neglected). You may assume that the gas phase obeys the ideal gas law.