

Exercise Problems - Week 11

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

Consider a solid with N , atoms each having a mass m . Assume that each atom has three independent modes of oscillation, each at the same frequency ω_0 . This is known as the Einstein model. Let the solid be in equilibrium with a vapor of the same type of atom, and let $\epsilon_0 > 0$ be the sublimation energy per atom, i.e. the energy which is necessary to remove an atom from the solid to the vapor with zero final kinetic energy.

The vapor can be treated as an ideal gas. Its free energy is

$$F_g = -k_B T N_g \left[\log \left(\frac{V_g}{N_g \Lambda_T^3} \right) + 1 \right], \quad \Lambda_T = \frac{\sqrt{2\pi\hbar}}{\sqrt{mT}}$$

where we have assumed that the vapor contains N_g particles occupying a volume V_g .

1. Find the free energy F_s of the solid.
2. Find the equilibrium vapor pressure as a function of temperature if the volume V_g is maintained constant. Neglect any volume changes in the solid, due to evaporation.

Problem 2

1. If l_S is is latent heat of sublimation per mole, and the vapor phase can be considered to be an ideal gas, show by using Clausius-Clapeyron equation that

$$\frac{dP}{P} = \frac{l_S}{RT^2} dT, \quad \text{and} \quad l_S = -R \frac{d(\log P)}{d(1/T)}$$

where the volume occupied by the solid can be neglected compared to that occupied by the vapor.

2. Iodine vapor can be assumed to be an ideal diatomic gas with constant C_P . At $301K$, the vapor pressure is $51.5N/m^2$ and at $299K$ it is $43.5N/m^2$. Compute the latent heat of sublimation at $300K$.
3. Assuming constant latent heat, calculate the vapor pressure at $305K$, assuming no phase transition exist in the intervening temperature range.

Problem 3

Remembering that the free energy F will be minimized in a given phase, and that the “order parameter” is defined to be zero above a phase transition, consider a system whose free energy F depends on an order parameter ϕ according to

$$F(\phi, T) = F_0 + a(T - T_c) \phi^2 + b\phi^4 - H\phi$$

where F_0 , a , and b are all positive constants, H is the external field.

1. Assuming that $H = 0$ show that there is a phase transition at a temperature T_c and deduce the temperature dependence of the order parameter.
2. Calculate the jump in the heat capacity at $T = T_c$, $H = 0$.
[Hint: $C = -T(\partial^2 F / \partial T^2)$.]
3. For $H \neq 0$ calculate $\phi(T, H)$ above and below the critical temperature.

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4. Calculate temperature dependence of susceptibility $\chi_T = (\partial\phi/\partial H)_T$
 5. Find the critical indices in the vicinity of the critical temperature. Critical indices $\alpha, \beta, \gamma, \delta$ are defined as follows: $C \propto |T - T_c|^{-\alpha}$, $\phi \propto |T - T_c|^\beta$, $\chi_T \propto |T - T_c|^{-\gamma}$, $H \propto |\phi|^\delta$. Do these indices satisfy the scaling hypothesis $\alpha + 2\beta + \gamma = 2$?
[Hint: In the case when the temperature dependence $C(T)$ differs from the power law (e.g., logarithmic or has a step in the transition point) $\alpha = 0$.]

Problem 4

The van der Waals equation of state for a nonideal gas is given by $(P + aN^2/V^2)(V - Nb) = Nk_B T$. The critical point is defined as $k_B T_c = 8a/27b$, $V_c = 3Nb$ and $P_c = a/27b^2$.

1. Find dependence of the dimensionless pressure $\pi = P/P_c$ as a function of small variations of the temperature, $\tau = (T - T_c)/T_c$, and volume, $\eta = (V - V_c)/V_c$, in the vicinity of the critical point. Cut your series at the terms $O(\eta^4, \tau\eta^2)$.
2. From the Maxwell constriction for the gas below T_c , $\oint PdV = 0$ (or, equivalently, $\oint \phi d\eta = 0$) find equation for coexisting volumes η_1 and η_2 .
3. Calculate the temperature dependence of the order parameter $\eta(\tau)$, $\pi(\eta)$, temperature dependence of the compressibility $\kappa_T = -(\partial\eta/\partial\pi)_T$ and find the critical indices β, γ and δ . What can you say about the temperature dependence of heat capacity at constant pressure in the vicinity of the critical point? Critical indices $\alpha, \beta, \gamma, \delta$ are defined as follows: $C_V \propto |T - T_c|^{-\alpha}$, $\eta \propto |T - T_c|^\beta$, $\kappa_T \propto |T - T_c|^{-\gamma}$, $\pi \propto |\eta|^\delta$.
[Hint: You may want to use scaling relations $\alpha + 2\beta + \gamma = 2$.]

Problem 5

The van der Waals equation of state for a nonideal gas is given by $(P + aN^2/V^2)(V - Nb) = Nk_B T$.

1. Calculate the difference $F_{\text{vdW}}(V, T) - F_{\text{ideal}}(V, T)$ between the free energies of the nonideal and ideal gas.
2. Calculate the difference $G_{\text{vdW}}(P, T) - G_{\text{ideal}}(P, T)$ between the nonideal and ideal gas.
3. Using approximate equation in the vicinity of the critical point T_c can be presented as

$$\pi = 1 + 4\tau + 6\tau\eta + \frac{3}{2}\eta^3 + O(\eta^4, \tau\eta^2) \quad (0.1)$$

where $\pi = P/P_c$, $\tau = (T - T_c)/T_c$, and $\eta = (V - V_c)/V_c$, construct the Landau potential $L(P, T, \eta)$, minimization of which with respect to independent variable η gives Eq. (0.1). Explain the difference between $G_{\text{vdW}}(P, T)$ and $L(P, T, \eta)$.

4. Compare the obtained Landau potential $L(\eta)$, for the nonideal gas with the Landau potential for ferromagnet:

$$F(M, T, H) = F_0 + a(T - T_c)M^2 + bM^4 - \mathbf{H}\mathbf{M}$$

where \mathbf{M} is the magnetization and \mathbf{H} is the magnetic field. Which parameter plays a role of the magnetic field in the case of the nonideal gas?

5. Analyse and sketch $L(\eta)$ dependence for the nonideal gas below and above T_c , for different values of π . What can you tell about the phases and transitions between them from these sketches?

Problem 6

Consider a ferromagnet with magnetization M whose Landau potential is modeled as

$$\mathcal{L} = \int_0^L dx \left[a(T - T_c)M^2 + \frac{1}{2}bM^4 + \frac{\gamma}{2} \left(\frac{dM}{dx} \right)^2 + \frac{\sigma}{2} \left(\frac{d^2M}{dx^2} \right)^2 \right],$$

where $a, b, \sigma > 0$, and γ can be of either sign.

1. Define the Fourier transform

$$M(x) = \frac{1}{L} \sum_{n=-\infty}^{\infty} M_n e^{iq_n x}, \quad q_n = \frac{2\pi n}{L}.$$

Write the inverse Fourier transform for M_n and write the Landau potential in terms of the Fourier components M_n .

2. By minimising both with respect to M_n and q_n show that the system exhibits three possible phases: paramagnetic ($M = 0$), ferromagnetic ($M \neq 0$) and spatially modulated phase ($M_q \neq 0, q \neq 0$). Assume that in the modulated phase you need to consider only one Fourier component.
3. Calculate the wavelength of the modulation, phase boundaries and draw the phase diagram. What is the order of the different phase boundaries?