Exercise Sheet No. 12

“Integrated Course II: Statistical Physics and Solid State Physics”

1 **Second virial correction - exchange contribution.**
   Consider a gas of non-interacting particles with spin $S$. The second virial coefficient is given by
   \[ b(T) = -\frac{V}{Z(1)^2} \left[ Z(2) - \frac{1}{2} Z(1)^2 \right], \]
   where
   \[ Z(2) = \sum_{\bar{p}_1, \bar{p}_2; s_1, s_2} \langle \bar{p}_1, s_1; \bar{p}_2, s_2 | e^{-(\bar{p}_1^2 + \bar{p}_2^2)/(2mkT)} | \bar{p}_1, s_1; \bar{p}_2, s_2 \rangle \]
   is the partition function of two particles. Note, that the exchange property of the wavefunction depends on the spin. Evaluate $b(T)$ and give the corresponding correction to the entropy and heat capacity.

2 **Liquid-vapor phase-transition and thermodynamic similarity.**
   Recall what has been said in the lecture about the critical point emerging from van-der-Waals theory. Then,
   a) calculate the critical values $n_c, T_c$ and $P_c$ from the equation of state of the van der Waals gas.
   b) express the equation of state in units of $P_c, T_c$ and $n_c$ ($P^* = P/P_c, V^* = V/V_c$ and $n^* = n/n_c$).
   Show, that
   \[ \left( P^* + \frac{3}{V^*^2} \right) \left( V^* - \frac{1}{3} \right) = \frac{8}{3} T^* \]
   and discuss this result.

3 **A Landau-Ginzburg-type theory of the van-der-Waals transition.** Discuss the liquid-gas transition within a framework analogous to the Landau-Ginzburg theory of magnetism. To this end, choose as an order parameter the deviation of the density from the critical value
   \[ \phi = \frac{n - n_c}{n_c} \]
   a) Consider the free energy density in van-der-Waals (vdW) approximation as given in the lecture,
   \[ f = -nkT \ln \left[ \frac{e(v - b_0)}{\lambda^3} \right] - an^2, \]
   and expand to order $\phi^4$. Show that
   \[ f = f_c + \mu_c n_c \phi + 3P_c \tau \phi^2 + \frac{3}{8} P_c \phi^4 + \mathcal{O}(\phi^5) \]
with $\tau = (T/T_c - 1)$ and

$$f_c = \frac{kT}{3b_0} \ln \left( \frac{\lambda^3}{2e b_0} \right) - \frac{a}{9b_0^2}$$

$$\mu_c = kT \left( \ln \frac{\lambda^3}{2b_0} + \frac{1}{2} \right) - \frac{2a}{3b_0}$$

How do the latter functions derive from $f(T,n)$ and $\mu(T,n)$?

b) Plot $f(\phi)$ at $T > T_c$ and $T < T_c$ and discuss. Illucidate, in particular, the way in which phase-separation manifests and what feature of the vdW-free-energy is not realistic.

c) Use

$$\mu = \frac{\partial F}{\partial N} \bigg|_{T,V}$$

and $\tau = T/T_c - 1$ to show that

$$\mu = \mu_c + 2an_c \tau \phi + \frac{9}{16} kT_c \phi^3 + \ldots$$

d) Plot $\mu(T,\phi)$ over $\phi$ at $T > T_c$ and $T < T_c$. Explain, how the Maxwell construction operates for $\mu$. (Hint: recall that $\partial P/\partial V$ and $\partial \mu/\partial n$ are related via a Maxwell relation.)

e) The density exhibits a step from $n_{\text{gas}}$ to $n_{\text{fluid}}$ at the transition. Show that

$$\frac{n_{\text{fluid}} - n_{\text{gas}}}{n_c} \propto |\tau|^{1/2}, \quad T < T_c.$$ 

f) Show that

$$\left. \frac{\partial n}{\partial \mu} \right|_T = \frac{1}{2a T - T_c}, \quad T > T_c$$

and discuss implications on the compressibility at $T \to T_c$. 