Due ~~May. 18, Friday~~ May. 22, Tuesday

Problem 1 (30 points) *Variational principle, Virial theorem, Pair distribution function.*

(a) *Variational principle.* While we did not have time to cover this in class, the variational principle as expressed in Eq. 9.29 is well worth your attention. Show that this *Gibbs inequality* can be re-expressed, in terms of the Helmholtz free energy, as

$$F \le F_0 + \langle H - H_0 \rangle^0$$

where H is the Hamiltonian to solve and H_0 is the Hamiltonian, which is based on the same dynamical degrees of freedom and is already solved for the free energy F_0. The superscript 0 means the ensemble average in the H_0 system.

(b) Following the proof of this inequality (Sections 9.4, T5.6), show that

$$F(\epsilon) \;\approx\; F_0 + \langle H(\epsilon) - H_0 \rangle^0$$

if $H(\epsilon)$ is only slightly different ($|\epsilon| \ll 1$) from H_0.
~~(Notation: ϵ replaces λ of the LN and the book.)~~

(c) *Virial theorem.* Taking $H(\epsilon)$ as the Hamiltonian for which the volume of the system is slightly increased $V \to V(1+3\epsilon)$, while $H_0 = T + \sum_{i<j} U_{ij}$, show that the above implies that

$$3PV \;=\; 2\,\langle T \rangle - \left\langle \sum_{i<j} \vec{q}_{ij} \cdot \frac{\partial U_{ij}}{\partial \vec{q}_{ij}} \right\rangle$$

where T is the total kinetic energy, $U_{ij} = U(\vec{q}_i - \vec{q}_j)$ (cf. Eq. 8.1) is the pair potential energy, and

$$\vec{q}_{ij} \;\equiv\; \vec{q}_i - \vec{q}_j$$

Here, the quantity $\vec{q}_{ij} \cdot \frac{\partial U_{ij}}{\partial \vec{q}_{ij}}$ is the so-called "virial." The above is the generalization of the *virial theorem*, well-known from (both classical and quantum) mechanics.

(d) *Virial theorem.* Assuming that $U(\vec{q}_i - \vec{q}_j) \propto |\vec{q}_i - \vec{q}_j|^l$, show that this result means

$$3PV = 2\,\langle T \rangle - l\,\langle H_{int} \rangle$$

This is the generalization of the *virial theorem* for power law forces, well known from (both classical and quantum) mechanics (cf. footnote 4 of page 4 of LN 6), now applicable to a thermodynamic system.

(e) *Pair distribution function.* Show from part (c) that

$$PV \;=\; Nk_BT - \frac{1}{6}\int d^3\vec{q}_1\, d^3\vec{q}_2\, \vec{q}_{12}\cdot\nabla_{\vec{q}_{12}}U(\vec{q}_{12})\, n_2(\vec{q}_1,\vec{q}_2)$$

where n_2 is the pair distribution function (Eqs. 10.7,10.9 with $\vec{x}\to\vec{q}_1$ and $\vec{x}'\to\vec{q}_2$). This is the sense in which the knowledge of the pair distribution function will lead to the knowledge of PV, the negative of the grand potential, within the semi-classical statistical mechanics.

(f) *Equation of state.* Now assume a power law force like that in part (d). Combining the result of the previous part and Eq. 10.17, show that

$$PV \;=\; Nk_BT\left(1+\frac{l}{2}\right) - \frac{l}{3}E$$

Problem 2 (30 points) *Van der Waals theory and phase transition.* Consider the van der Waals equation of state (Eq. 8.27 or 9.20)

$$(P+an^2)(V-bN) = Nk_BT$$

We can re-write this equation as (cf. Eq. T5.80)

$$P_r = \frac{8T_r}{3v_r-1} - \frac{3}{v_r^2}$$

where $P_r = P/P_c, T_r = T/T_c, v_r = v/v_c$ (where $v = 1/n$) are reduced dimensionless thermodynamic variables and

$$P_c = \frac{a}{27b^2},\quad v_c = 3b,\quad T_c = \frac{8a}{27bk_B}$$

are the critical pressure, the critical molecular volume, and the critical temperature, respectively, within this theory. In this problem, we are *not* interested in the derivation of the above dimensionless form of the van der Waals equation from the first form. This is done in the textbook, Section T5.7. We will simply take this dimensionless form of the equation and explore it.

(a) Verify explicitly that $P_r(T_r, V_r)$ satisfies

$$\begin{aligned} P_r(T_r=1, v_r=1) &= 1 \\ \left.\frac{\partial P_r}{\partial v_r}\right|_{v_r=1,\,T_r=1} &= 0 \\ \left.\frac{\partial^2 P_r}{\partial v_r^2}\right|_{v_r=1,\,T_r=1} &= 0 \end{aligned}$$

(b) Using a computer program, plot three isotherms $P_r(T_r = \text{fixed}, v_r)$ for three values of T_r: one just above T_c, one at T_c, and the third just below T_c. Choose the last one so that P_r does not become unphysical. Keep in mind that $v_r > 1/3$. Your plot should demonstrate clearly the behaviors summarized in Fig. T5.3.

(c) Study the diagrams in Fig. T5.4 and the accompanying text. In the diagram on the right, is the curve near point C smooth or not? How about near point D?

(d) Below T_c, the physical isotherm is given by A-B-O-E-F, not the van der Waals isotherm, since states along the segments B-C-O and O-D-E are meta-stable. Imagine that this system of gas+liquid is contained in a cylinder, with a piston that defines the total volume. The system is kept at a constant temperature below T_c, while you slide piston in or out to change the total volume. Let us suppose that the initial total volume is very large (point A). The cylinder wall is transparent so that you can see what is going on. Describe what you will see as you press on the lid so as to decrease the volume all the way to point F. Describe what happens to the *total* Gibbs free energy, as you do so.

(e) Now, consider two isotherms at T and $T + dT$, both below T_c. We are interested in the phase coexistence regime B-O-E only. By considering the Gibbs free energy change between these two coexistence regimes, show that

$$\left.\frac{dP}{dT}\right|_{coexistence} = \frac{\Delta S}{\Delta V}$$

where $\Delta V = V_B - V_E$ and $\Delta S = S_B - S_E = L/T$, where L is the latent heat. This is the Clausius-Clapeyron equation for the vapor pressure curve.

(f) Note that from the grand canonical ensemble point of view, the "would-be grand potential" becomes minimized at the physical value of density. Take Eq. 9.24, and plot it, using a computer, as a function of x at three different temperatures $T > T_c$, $T = T_c$ and $T < T_c$, while $\mu = \mu_c$ or, better, $\beta\mu = \beta_c\mu_c$, is fixed. The goal is to demonstrate that the expression in Eq. 9.24 has two maxima below $T < T_c$ with the liquid density corresponding to the lower grand potential. [Hint: you would need to use ~~Eq. 9.5, with b_1 and b_2 as obtained in LN 8~~ Eq. 9.22 to get $\beta(_c)\mu_c$.]

Problem 3 (10 points) *Meyer cluster expansion.* *Assuming* that the virial coefficients B_k involve only one particle irreducible diagrams (đ_k), prove Eq. 9.7 from Eqs. 9.4 and 9.5.

Problem 4 (10 points) *Virial coefficients.* Estimate the magnitude of the second virial coefficient when temperature is not too high (say, $\beta u_0 \sim 1$). (cf. Section T5.3.) What does it say about the theory as the perturbation expansion?

Problem 5 (20 points) Kardar problem 6.6

Problem 6 (20 points) Kardar problem 6.9

Problem 7 (10 points) Kardar problem 6.10