Due May 30, Friday

Problem 1 (25 points) *BEC transition.*

Consider an ideal gas of bosonic atoms in d dimensions ($d = 1, 2, 3, ...$). Assume that the dispersion relation is given as $\varepsilon(\vec{k}) = a|\vec{k}|^{\alpha}$, where α is a positive real number and a is a positive constant. What condition must be met by d and α in order for a BEC transition to occur at a finite temperature?

Problem 2 (30 points) *BEC transition and finite size scaling.*

We have seen that Eq. 14.25 leads to two distinct regimes, Eqs. 14.28 and 14.29, separated by the phase boundary $n\lambda^3 = g_{3/2}(1)$. However, it is of importance to realize that this occurs only in the thermodynamic limit $N \to \infty$, with $n = N/V$ remaining finite. In this problem, we shall see how this transition occurs using numerical analysis. For this, our strategy is to **solve Eq. 14.25**, and it alone, and see how the results contained in Eqs. 14.28 and 14.29 will just follow.

(a) Eq. 14.25 contains three variables, $y = 1/(n\lambda^3)$, z, and N. Solving, numerically, for z, we get the function $z(y, N)$. Then, **the BEC condensate fraction**

$$f(y, N) \;=\; \frac{n(0)}{N} \;=\; \frac{1}{N} \cdot \frac{1}{z^{-1} - 1}$$

can be obtained. Fix the value of N at about 1000, and plot the function $f(y, N = 1000)$ as a function of y. For the y range, you can use $[0, 1]$. Repeat this for several values of N, increasing about 10 fold each time, up to say, $N = 10^9$ (for large N, you might need to reduce the y range to a narrow range around y_c). Plot all $f(y, N)$ functions for $N = 10^3, 10^4, ..., 10^9$ in one plot and compare them. Find the approximate position of y_c, the value of y at which the order parameter turns on in the $N \to \infty$ limit, from your analysis. Compare your value to the analytic solution, $1/\zeta(1.5)$ (Eq. 14.27). [Hint: $f(y, N) = 1$ at $y = 0$, and it starts out from that point as a line with a negative slope $= -\zeta(1.5)$ in the large N limit. If $y \gg y_c$, then $f(y, N) = 0$ to an exponential accuracy. Observe how the crossover behavior between these two regimes changes as N becomes large.]

(b) To infer the existence of a phase transition, or the value of the transition temperature, from a numerical work is a highly non-trivial task, since a numerical work cannot be done on an infinite system. An important technique in this regard is **the finite size scaling** analysis. The central assumption of the finite scaling analysis is the following scaling hypothesis: any finite size thermodynamic function, say ϕ, near the phase transition is given by

$$\phi_L(T, V) \;=\; L^{-\lambda}\, \psi\left(\frac{L}{\xi}\right), \qquad\qquad T \approx T_c$$

where ξ is the correlation length[1], and

$$\xi \to \infty \qquad \text{as} \quad T \to T_c.$$

L is the linear size of the system ($N \propto L^3$). The exponent λ is determined by "critical exponents" (like those that we will discuss in future lectures) of the problem. For the BEC condensate fraction, we take $\phi_L(T, V) \equiv f(y, N)$. Then, at $y = y_c$

$$f(y_c, N) \propto N^{-\lambda/3},$$

since, at $T = T_c$ (equivalently, at $y = y_c$), $L/\xi = 0$. Do one of the following two. (i) Estimate the exponent λ using this scaling hypothesis, from your data generated in part (a), and compare it with the analytic solution, 1. Or, (ii) assume $\lambda = 1$, and plot $f \cdot N^{1/3}$ for different values of N to identify the position of T_c (y_c) as the fixed point in the large N limit. [Note: For a challenging real-world problem, the latter is what typically happens in a numerical work for examining the presence of a phase transition, since the critical exponent is often known in advance.]

(c) Explain how these results confirm, and further quantify, the result that we proved in class (box in page 8 of LN 14).

Problem 3 (20 points) *Lattice gas theory.* In the lattice gas theory (Section 15.2.2), we assign an energy value ε_0 ($\equiv 0$ as energy reference), when a molecule occupies a small volume element, the size of which is on the order of the excluded volume Ω (LN 21). Consider Eqs. 15.15 and 15.16.

(a) Consider the case when $\varepsilon = 0$ in those equations. You might worry that we assumed no such thing as "the kinetic energy" in the Hamiltonian considered in Eq. 15.15. This is *not* the case, as we will show now. Prove that this model correctly predicts the classical limit of the grand potential, $\Phi = -Nk_BT$ (Eq. 8.13), thus giving the classical ideal gas equation of motion, $PV = Nk_BT$ (and everything else) in the limit of small fugacity $z \equiv e^{\beta\mu} \to 0$. This result shows that we must have introduced the kinetic energy in the above setup. Where did we do so?

(b) Now, consider the more general case $\varepsilon > 0$. Finish the program presented in page 8 of LN 15: i.e., upon the transformation $\sigma_i = 2n_i - 1$, what are the *effective field* H and the *effective exchange constant* J such that this problem maps to the Ising problem (Eqs. 15.13 and 15.14)? You can find $\varepsilon = \varepsilon(H, J)$ and $\mu = \mu(H, J)$ or, equivalently, $H = H(\varepsilon, \mu)$ and $J = J(\varepsilon, \mu)$.

[1] We have already encountered the correlation length in the polymer problem. In that case, it was the correlation of the directions of monomers that was quantified. For the BEC problem, it is the density correlation that ξ quantifies.

Problem 4 (35 points) *Van der Waals theory and phase transition.* Consider the van der Waals equation of state (for derivations, see LN 21).

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

The constants a and b (both positive) are explained in Eqs. 21.36, 37 and 21. We can re-write this equation in a dimensionless form as

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

where

$$P_r = \frac{P}{P_c}, \quad T_r = \frac{T}{T_c}, \quad v_r = \frac{v}{v_c}$$

(where $v \equiv \frac{1}{n} = \frac{V}{N}$) 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 left for your exercise. We will simply take this dimensionless form of the equation and explore it. Below, whenever P, V, or T is mentioned, it is recommended that you change the unit in your mind so that you work with P_r, V_r (or v_r), or T_r.

(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) Find the equation of state for $T_r = 1$ and small $P_r - 1$ and small $v_r - 1$. You will find that $(P_r - 1) \propto (v_r - 1)^\delta$. What is the exponent δ?

(c) 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 $v_r > 1/3$, since b is the minimum volume per particle.

(d) For $T < T_r$, your graph should show that there are three possible values for the volume at a given value of pressure, if the value of pressure falls

in a certain range. To prove that not all of these three volume values are physical, let us consider the Gibbs free energy, $\mathcal{G}(T,P,N;\mathcal{V}) = \mathcal{F}(T,\mathcal{V},N) + P\mathcal{V}$. Note that this Gibbs free energy is not the equilibrium ensemble average value yet. Instead, $\beta\mathcal{G}$ is precisely that of Eq. 7.3; when we make this connection, we take the temperature of the system as having already reached the equilibrium value (constrained by the reservoir), but take the volume as fluctuating. This is why $\mathcal{G}$ depends on *four independent* variables, and only after we minimize $\mathcal{G}$ with respect to $\mathcal{V}$, we get the equilibrium ensemble average value for $\mathcal{G}$ (and $\mathcal{V}$). From now on, we will call this *fluctuating* Gibbs free energy **Landau free energy**, for a reason that will become clear in the lecture (LN 16). Notice that one can obtain the $\mathcal{V}$-dependent part of the Landau free energy by simply integrating the van der Waals equation of state given above. Do this and obtain the $\mathcal{V}$-dependent part of $\mathcal{G}$.

(e) Note that $\mathcal{G}$, or any other thermodynamic quantity, can be obtained completely from the grand potential, which is equal to $-PV$. Do this and obtain the full solution of $\mathcal{G}(T,P,N;\mathcal{V})$ and check that your answer of the previous part is indeed correct. [Note: although you do not need them, Eqs. 21.23–21.27 may be helpful for cross-checking your calculations.]

(f) Minimize the free energy with respect to $\mathcal{V}$ and show that (i) there is a unique minimum if $T_r \geq 1$, and (ii) there is a unique global minimum ((for a certain pressure range) along with another local minimum (metastable state) and a maximum (unphysical state)) or there are two degenerate minima (V_l, V_g) and one maximum (V_{unphys}), if $T_r < 1$.

(g) Using the minimization of the Landau free energy, find the correct equation of state for $T_r < 1$. (i) Show that, according to this new equation of state, the volume is unique for all pressure values except that, for one value of pressure, P_t, V can assume a continuous value from V_l and V_g. This is an example[2] of a discontinuous "first-order phase transition" occurring at P_t. (ii) Show that the transition pressure P_t is determined by the so-called "Maxwell construction:"

$$\int_{V_l}^{V_{unphys}} dV\ (P_t - P_{vdW}(V)) = \int_{V_{unphys}}^{V_g} dV\ (P_{vdW}(V) - P_t)\,,$$

where $P_{vdW}(V)$ is the original uncorrected van der Waals equation of state and both integrands are non-negative.

[2]The transition at the critical point (T_c, P_c, v_c) is a continuous transition—a second-order transition.