Phase Transitions

1. *Dieterici's equation:* A gas obeys Dieterici's equation of state:

$$P(v-b)=k_BT\exp\left(-\frac{a}{k_BTv}\right),$$

where $v=V/N$.

(a) Find the ratio Pv/k_BT at the critical point.

(b) Calculate the isothermal compressibility κ_T for $v=v_c$ as a function of $T-T_c$.

(c) On the critical isotherm expand the pressure to the lowest non-zero order in $(v-v_c)$.

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2. *2d Coulomb Gas:* Consider a classical mixture of N positive, and N negative charged particles in a *two dimensional* box of area $A=L\times L$. The Hamiltonian is

$$\mathcal{H}=\sum_{i=1}^{2N}\frac{\vec{p_i}^{\,2}}{2m}-\sum_{i<j}^{2N}c_ic_j\ln|\vec{q_i}-\vec{q_j}|\quad,$$

where $c_i=+c_0$ for $i=1,\cdots N$, and $c_i=-c_0$ for $i=N+1,\cdots 2N$, denote the charges of the particles; $\{\vec{q_i}\}$ and $\{\vec{p_i}\}$ their coordinates and momenta respectively.

(a) Note that in the interaction term each pair appears only once, and that there is no self interaction $i=j$. How many pairs have repulsive interactions, and how many have attractive interactions?

(b) Write down the expression for the partition function $Z(N,T,A)$ in terms of integrals over $\{\vec{q_i}\}$ and $\{\vec{p_i}\}$. Perform the integrals over the momenta, and rewrite the contribution of the coordinates as a product involving powers of $\{\vec{q_i}\}$, using the identity $e^{\ln x}=x$.

(c) Although it is not possible to perform the integrals over $\{\vec{q_i}\}$ exactly, the dependence of Z on A can be obtained by the simple rescaling of coordinates, $\vec{q_i}\,'=\vec{q_i}/L$. Use the results in parts (a) and (b) to show that $Z\propto A^{2N-\beta c_0^2N/2}$.

(d) Calculate the two dimensional pressure of this gas, and comment on its behavior at high and low temperatures.

(e) The unphysical behavior at low temperatures is avoided by adding a hard–core which prevents the coordinates of any two particles from coming closer than a distance a. The appearance of two length scales a and L, makes the scaling analysis of part (c) questionable.

By examining the partition function for $N = 1$, obtain an estimate for the temperature T_c at which the short distance scale a becomes important in calculating the partition function, invalidating the result of part (c). What are the phases of this system at low and high temperatures?

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3. *One dimensional gas:* In statistical mechanics, there are very few systems of interacting particles that can be solved *exactly.* Such exact solutions are very important as they provide a check for the reliability of various approximations. A one dimensional gas with short-range interactions is one such solvable case.

(a) Show that for a potential with a hard core that screens the interactions from further neighbors, the Hamiltonian for N particles can be written as

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=2}^{N} \mathcal{V}(x_i - x_{i-1}).$$

The (indistinguishable) particles are labelled with coordinates $\{x_i\}$ such that

$$0 \leq x_1 \leq x_2 \leq \cdots \leq x_N \leq L,$$

where L is the length of the box confining the particles.

(b) Write the expression for the partition function $Z(T, N, L)$. Change variables to $\delta_1 = x_1$, $\delta_2 = x_2 - x_1$, $\cdots$, $\delta_N = x_N - x_{N-1}$, and carefully indicate the allowed ranges of integration and the constraints.

(c) Consider the Gibbs partition function obtained from the Laplace transformation

$$\mathcal{Z}(T, N, P) = \int_0^\infty dL \exp(-\beta PL) Z(T, N, L),$$

and by extremizing the integrand find the standard formula for P in the canonical ensemble.

(d) Change variables from L to $\delta_{N+1} = L - \sum_{i=1}^{N} \delta_i$, and find the expression for $\mathcal{Z}(T, N, P)$ as a product over one-dimensional integrals over each δ_i.

(e) At a fixed pressure P, find expressions for the mean length $L(T, N, P)$, and the density $n = N/L(T, N, P)$ (involving ratios of integrals which should be easy to interpret).

Since the expression for $n(T, P)$ in part (e) is continuous and non-singular for any choice of potential, there is in fact no condensation transition for the one-dimensional gas. By contrast, the approximate van der Waals equation (or the mean-field treatment) incorrectly predicts such a transition.

(f) **(Optional)** For a hard sphere gas (as in PS#6, problem 3, or PS# 8, problem 2, part (d)) calculate the equation of state $P(T, n)$. Compare the excluded volume factor with the approximate result obtained in PS#3, and also obtain the general virial coefficient $B_\ell(T)$.

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Suggested reading: Feynman, Chapter 4; Ma, Chapter 8.