Statistical Mechanics 2012/2013   Problem Set 3

Submission date: 17.12.12

1.1   1-d gas with interactions (30 points)

Not many statistical mechanics models of interacting particles can be solved *exactly*. Such solutions are valuable as they allow to check the validity and reliability of different approximations.

One exactly solvable model, which will be studied in this problem, is a one-dimensional gas with short range interactions. Consider N (indistinguishable) particles of mass m confined to a line of length L, in which they are free to move. The positions of the particles $\{x_i\}$ will be labelled according to their *order*, i.e.,

$$0 \leq x_1 \leq x_2 \leq \ldots \leq x_N \leq L. \tag{1}$$

(a) First, consider a gas of hard impenetrable rods, each of length a. In the microcanonical ensemble, calculates the entropy of the gas as a function of the energy E, the number of particles N and the length L. Obtain the equation of state of the gas and compare the result to that of an ideal gas.

(b) Now consider point particles with a general interaction potential. We will assume that the particles screen the interactions, and therefore they only interact with their *nearest* neighbors. In this case he Hamiltonian can be written as

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

where $V(x)$ is the interaction potential. Write down the expression for the canonical partition function $Z(T, N, L)$. Change variables to $\delta_1 = x_1$, $\delta_2 = x_2 - x_1, \ldots, \delta_N = x_N - x_{N-1}$. Be careful with the allowed ranges of integration.

(c) The trick that allows a general calculation of the expression from (b) is to move to the constant-pressure ensemble. The partition function of the constant-pressure ensemble is obtained from the Laplace transformation

$$\mathcal{Z}(T, N, f) = \int_0^\infty dL \exp(-\beta f L) Z(T, N, L), \tag{3}$$

where f is the force (the pressure in one dimension). Find the standard formula for f in the canonical ensemble via a saddle point approximation of equation (3).

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

(e) At a fixed force f, find expressions for the mean length $L(T, N, f)$, and the density $n = N/L(T, N, f)$ (involving ratios of integrals that should be easy to interpret). Verify that you recover the known equation of state in the case of an ideal gas (i.e., when $V(x) = 0$ for all x).

(f) Calculate the Gibbs free energy and the entropy (as a function of T, N, f) for the interaction energy given by

$$V(x_i - x_{i-1}) = \left\{ \begin{array}{ll} \epsilon & |x_i - x_{i-1}| \leq a \\ 0 & |x_i - x_{i-1}| > a \end{array} \right. . \tag{4}$$

Verify that you recover the entropy calculated in (a) in the case of hard rods, i.e., when $\epsilon \to \infty$.

(g) **Optional (3 bonus points):** Can you find an interaction potential $V(x)$ for which the model will exhibit a phase transition? (As you will discuss later in the course, a phase transition occurs if the thermodynamic potential is non-analytic at some point).

1.2 Virial expansion of hard-core particle gas (25 points)

Consider a particle gas with hard core interparticle interaction

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma, \end{cases} \tag{5}$$

where r is the inter-particle distance.

In this question the definition of the virial coefficients is related to the one you had in class by $B_l(T) = a_l(T) \left(\lambda^3\right)^{l-1}$ where $a_l(T)$ are the virial coefficients as defined in class via eq. (116) in the lecture notes.

(a) Compute the second and third virial coefficients for a hard-core gas in $d = 1$ dimensions.

(b) Do the same in $d = 2$ dimensions.

(c) Compute the isothermal compressibility κ_T and the constant-pressure heat capacity c_p for the hard-core gas in $d = 1, 2, 3$ dimensions using the virial expansion to third order. The virial coefficients in $d = 3$ dimensions do not need to be calculated, they are given by $B_2^{(3d)}(T) = 2\pi\sigma^3/3$ and $B_3^{(3d)}(T) = 5\pi^2\sigma^6/18$. Discuss the effect of dimensionality on your results.

(d) In a exercise 2.2 you have found that the exact equation of state of a 1-dimensional gas of hard rods is given by $f(L - Na) = Nk_BT$ (where the force f is the 1-dimensional pressure, the length L is the 1-dimensional volume, and a is the size of the rods). From this expression obtain the general virial coefficient $B_\ell(T)$ of this gas. Compare with the results of (a).

2.3 Ionization in the grand-canonical ensemble (20 points)

Consider M ions A^+, and n_e electrons. The ionization energy of the A atom is denoted by ϵ. For simplicity, the Coulomb interactions shall be ignored. All experiments considered below are done in a container of volume V at temperature T.

(a) Assume first that the A^+ ions are fixed in space. The electrons are now divided into two components - a classical gas of free electrons, and a 'gas' of bounded electrons. Calculate the fraction of electrons in the free gas by equating the chemical potentials of the two gases.

(b) Now consider the case where the A^+, e^- and A particles are all moving freely in the container. Compare your result here to those of (a).

2.4 Van der Waals Equation of State (25 points)

Consider the Van der Waals equation of state

$$\left(P + \frac{a}{v^2}\right)(v - b) = T \tag{6}$$

where $v = \frac{V}{N}$. One can show that the critical point is given by $P_c = \frac{a}{27b^2}$, $v_c = 3b$ and $T_c = \frac{8a}{27b}$. Then the Van der Waals equation can be written in the following universal form

$$\left(P_r + \frac{3}{v_r^2}\right)\left(v_r - \frac{1}{3}\right) = \frac{8}{3}T_r \tag{7}$$

where we have used normalized variables defined by $P_r = \frac{P}{P_c}$, $v_r = \frac{v}{v_c}$ and $T_r = \frac{T}{T_c}$ so that $P_r = T_r = v_r = 1$ is the critical point. In the following we shall drop the subscript r and instead use the notation P, T, v for the normalized variables. In addition, we denote deviations from this critical point by $P = 1 + \delta P$, $T = 1 + \delta T$ and $v = 1 + \delta v$.

(a) Show that the coexistence curve (the curve that bounds the shaded region in the PV diagram on p.57 in the lecture notes) is given by

$$\delta P = 4\delta T + O(\delta T^{3/2}) \tag{8}$$

for small $\delta P, \delta T < 0$.

(b) Show that along the coexistence line and to leading order in δT

$$v_g - v_l = \sqrt{-16\delta T} \tag{9}$$

where v_g and v_l are the specific volumes of the gas and the liquid phases, respectively.

Later in the course you shall see that at second order phase transitions the scaling exponents of particular quantities with δT are given by universal numbers, meaning that the same values occur for different physical systems at a second order phase transition. These exponents are called critical exponents. The critical exponent in the case of the density given in this question is called β and one has $\beta = \frac{1}{2}$.

(c) Calculate the isothermal compressibility $\kappa_T = -\left(\frac{\partial v}{\partial P}\right)_T$ near the critical point along the line in the $P - T$ plane corresponding to the critical density $v = 1$. Show that for $\delta T > 0$ one has

$$\kappa_T = \frac{1}{6}\frac{1}{\delta T} \tag{10}$$

yielding $\gamma = 1$ for the critical exponent γ defined by $\kappa_T \sim (\delta T)^{-\gamma}$.