

PHY5524 Problem Set 4: Solution

Problem 1

The partition function for this one-dimensional gas of N rods can be written

$$Q_N(L, T) = \frac{1}{h^N} \int' d^N x \int d^N p e^{-\beta p^2/2m} = \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} \int' d^N x \quad (1)$$

where the primed integration indicates an integral over all configurations consistent with the constraint that no two rods overlap. Because in 1D the rods cannot move through one another, we assume the ordering of the rods is fixed (i.e. $x_1 < x_2 < x_3 \dots$) and treat the rods as distinguishable.

Let R_N denote the spatial part of integration,

$$R_N = \int' d^N x \quad (2)$$

Now, if we have just one rod, this rod can be anywhere in the system of length L . Thus

$$R_1 = L \quad (3)$$

If we have two rods, and if we at first ignore the ordering of the rods, then there is an excluded volume of length $2a$ for the x integration for the second rod, where a is the length of the rod. By ignoring the ordering we are over counting by a factor of 2 ($=2!$). Thus we have

$$R_2 = \frac{1}{2} L(L - 2a) \quad (4)$$

Continuing this line of reasoning (and using the fact that we are working in the dilute limit, $Na \ll L$), we find for N rods

$$R_N \simeq \frac{1}{N!} L(L - 2a)(L - 4a) \dots (L - 2(N - 1)a) \simeq \frac{1}{N!} L^N \left(1 - \frac{1}{L} \sum_{n=1}^{N-1} 2na + O((Na/L)^2) \right) \quad (5)$$

$$\simeq \frac{1}{N!} L^N \left(1 - N(N - 1) \frac{a}{L} \right) \simeq \frac{1}{N!} (L - Na)^N \quad (6)$$

Thus we obtain the desired result

$$Q_N \simeq \frac{1}{N!} (L - Na)^N \left(\frac{2\pi m k_B T}{h^2} \right)^{N/2} \quad (7)$$

(b) The Helmholtz free energy is found in the usual way

$$A = -k_B T \ln Q_N = -k_B T N \ln \left((L - Na) \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} \right) + k_B T \ln N! \quad (8)$$

and, using Stirling's approximation $\ln N! = N \ln N - N$, we find

$$A = -k_B T N \left(\ln \left(\frac{(L - Na)}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} \right) + 1 \right). \quad (9)$$

(c) The pressure (which has units of force in 1D) is

$$P = - \left(\frac{\partial A}{\partial L} \right)_{T, N} = \frac{N k_B T}{L - Na} \quad (10)$$

and so the equation of state is

$$P(L - Na) = N k_B T \quad (11)$$

i.e., the ideal gas law is modified by removing Na from the volume.

(d) The entropy is

$$S = - \left(\frac{\partial A}{\partial T} \right)_{L,N} = k_B N \left(\ln \left(\frac{(L - Na)}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} \right) + \frac{3}{2} \right) \quad (12)$$

(e) The work done if the gas expands from ‘volume’ (really length) L_1 to ‘volume’ L_2 is

$$W = \int P dL = \int_{L_1}^{L_2} \frac{N k_B T}{L - Na} dL = N k_B T \ln \frac{L_2 - Na}{L_1 - Na} \quad (13)$$

For $L_1 = 2Na$ and $L_2 = 3Na$ we have

$$W = N k_B T \ln 2 \quad (14)$$

(f) From the expression for S obtained in Part (d) we know that for any process in which S is constant we must have

$$(L - Na) T^{1/2} = \text{Const.} \quad (15)$$

Thus, if the gas expands from $L_1 = 2Na$ to $L_2 = 3Na$ the temperature will decrease by a factor of 4.

Problem 2

(a) The classical partition function for a single molecule is

$$Q_1(T, V) = \int \frac{d^3 p_1 d^3 p_2 d^3 r_1 d^3 r_2}{h^6} e^{-\beta(\vec{p}_1^2 + \vec{p}_2^2 / 2m + K|\vec{r}_1 - \vec{r}_2|^2 / 2)} \quad (16)$$

The p integrations are straightforward Gaussian integrations which each yield the familiar ideal gas result. Thus

$$Q_1 = \left(\frac{2\pi m k_B T}{h^2} \right)^3 \int d^3 r_1 d^3 r_2 e^{-\beta K |\vec{r}_1 - \vec{r}_2|^2 / 2} \quad (17)$$

To do the \vec{r}_1, \vec{r}_2 integration it is convenient to change variables to relative and center of mass coordinates

$$\vec{r} = \vec{r}_1 - \vec{r}_2; \quad \vec{R} = (\vec{r}_1 + \vec{r}_2) / 2 \quad (18)$$

(one can readily check that the Jacobian of this transformation is 1). Thus we have

$$\int d^3 r_1 d^3 r_2 e^{-\beta K |\vec{r}_1 - \vec{r}_2|^2 / 2} = \int d^3 R d^3 r e^{-\beta K r^2 / 2} = V \left(\frac{2\pi k_B T}{K} \right)^{3/2} \quad (19)$$

and so

$$Q_1 = V \left(\frac{2\pi m k_B T}{h^2} \right)^3 \left(\frac{2\pi k_B T}{K} \right)^{3/2} \quad (20)$$

(b) For a gas of N such particles, assuming they are indistinguishable and do not interact with one another, the partition function is

$$Q_N = \frac{1}{N!} Q_1^N \quad (21)$$

The Helmholtz free energy is then

$$A = -k_B T \ln Q_N = -N k_B T \ln Q_1 + k_B T \ln N! \quad (22)$$

Once again using Stirling’s approximation $\ln N! = N \ln N - N$ and plugging in the above expression for Q_1 we find

$$A = N k_B T \left(\ln \left(\frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^3 \left(\frac{K}{2\pi k_B T} \right)^{3/2} \right) - 1 \right) \quad (23)$$

(c) The pressure of the gas is

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T,N} = \frac{Nk_B T}{V} \quad (24)$$

and we immediately see that the ideal gas law ($PV = Nk_B T$) is, of course, satisfied.

(d) The energy of the gas is

$$E = - \frac{\partial \ln Q_N}{\partial \beta} = \frac{9}{2} Nk_B T \quad (25)$$

This result is consistent with the equipartition theorem since we have 9 quadratic terms in the Hamiltonian.

(e) The specific heat at constant volume is simply the derivative of E w.r.t. T at constant V , and since $E = \frac{9}{2} Nk_B T$ we have

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{9}{2} Nk_B \quad (26)$$

The specific heat at constant pressure is the derivative of the *enthalpy* $H = E + PV$ w.r.t. T at constant P , and since $E = 9/2 Nk_B T$ and $PV = Nk_B T$ we have

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P = \left(\frac{\partial E + PV}{\partial T} \right)_P = \frac{11}{2} Nk_B \quad (27)$$

These values are higher than the more familiar result $C_V \simeq \frac{5}{2} Nk_B$ for a diatomic gas. One reason for this discrepancy is that in the model studied here the equilibrium length for the “spring” connecting the two atoms in the molecule is zero. In a real molecule there is a nonzero equilibrium length corresponding to the length of the chemical bond and, as a result, the rotational and vibrational degrees of freedom of the molecule are, to a good approximation, decoupled. As you will see in the next HW, if the translational and rotational degrees of freedom are treated classically one obtains the expected result $C_V = \frac{5}{2} Nk_B T$. The reason that at room temperature one does not observe the additional $Nk_B T$ contribution due to the two quadratic degrees of freedom associated with the radial oscillations of the molecule is that these vibrational modes are quantized, and at room temperature they are effectively “frozen out” leading to a violation of the equipartition theorem.

(f) The thermal expectation value of $|\vec{r}_1 - \vec{r}_2|^2$ is

$$\langle |\vec{r}_1 - \vec{r}_2|^2 \rangle = \frac{\int d^3r r^2 e^{-\beta K r^2/2}}{\int d^3r e^{-\beta K r^2/2}} = \frac{-\frac{2}{\beta} \frac{\partial}{\partial K} \int d^3r e^{-\beta K r^2/2}}{\int d^3r e^{-\beta K r^2/2}} = -\frac{2}{\beta} \frac{\partial}{\partial K} \ln \left(\frac{2\pi k_B T}{K} \right)^{3/2} = \frac{3k_B T}{K} \quad (28)$$

Problem 3 Bohr-van Leeuwen theorem.

The partition function for a classical gas is

$$Q_N = \frac{1}{N!} \int \frac{d^{3N} r d^{3N} p}{h^{3N}} e^{-\beta H(\vec{r}_i, \vec{p}_i)} \quad (29)$$

Let's assume the particles have charge q . If a magnetic field is applied to this gas then the Hamiltonian is modified via the usual “minimal coupling” prescription

$$\vec{p} \rightarrow \vec{p} - \frac{q}{c} \vec{A}(\vec{r}) \quad (30)$$

where \vec{A} is the vector potential corresponding to the applied field ($\vec{B} = \nabla \times \vec{A}$).

The new partition function is then

$$Q_N = \frac{1}{N!} \int \frac{d^{3N} r d^{3N} p}{h^{3N}} e^{-\beta H(\vec{r}_i, \vec{p}_i - (q/c)\vec{A}(\vec{r}_i))} \quad (31)$$

If we consider the momentum integrations while keeping the coordinates fixed then we can simply change variables, letting $\vec{p}'_i = \vec{p}_i - \frac{q}{c} \vec{A}(\vec{r}_i)$ and we see that the partition function is *unchanged* by adding a magnetic field.

It follows that, classically, the thermodynamic properties of a gas of charged particles does not depend on the magnetic field. One consequence of this is that the magnetic susceptibility of such a gas is zero.