

PHY5524 Problem Set 6: Solution

Problem 1

(a) The partition function for a single water molecule modeled by the given “rigid rotor” Hamiltonian is

$$Q_1(T, V) = \int \frac{d^3r d^3p}{h^3} \int \frac{d\theta d\phi dp_\theta dp_\phi}{h^2} e^{-\beta \left(\frac{\vec{p}^2}{2m} + \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \theta} + \mu E \cos \theta \right)} \quad (1)$$

$$= \left(\int \frac{d^3r d^3p}{h^3} e^{-\beta \vec{p}^2 / 2m} \right) \left(\int \frac{d\theta d\phi dp_\theta dp_\phi}{h^2} e^{-\beta \left(\frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \theta} + \mu E \cos \theta \right)} \right) \quad (2)$$

The first integral (over \vec{r} and \vec{p}) gives the familiar $V(2\pi m k_B T / h^2)^{3/2}$ factor. To do the integration over θ, ϕ, p_θ and p_ϕ we can make the change of variables $p'_\phi = p_\phi / \sin \theta$ to obtain

$$\int \frac{d\theta d\phi dp_\theta dp_\phi}{h^2} e^{-\beta \left(\frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \theta} \right) + \mu E \cos \theta} = \int \frac{\sin \theta d\theta d\phi dp_\theta dp'_\phi}{h^2} e^{-\beta \left(\frac{p_\theta^2}{2I} + \frac{p'^2_\phi}{2I} + \mu E \cos \theta \right)} \quad (3)$$

$$= \frac{4\pi}{h^2} \frac{2\pi I}{\beta} \int_0^{2\pi} d\phi \int_{-1}^1 d\cos \theta e^{-\beta \mu E \cos \theta} \quad (4)$$

$$= \frac{8\pi^2 I k_B T}{h^2} \frac{4\pi \cosh \beta \mu E}{\beta \mu E} \quad (5)$$

Thus we have

$$Q_1 = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \left(\frac{8\pi^2 I k_B T}{h^2} \right) \frac{4\pi \cosh \beta \mu E}{\beta \mu E} \quad (6)$$

For N water molecules the partition function is

$$Q_N = \frac{1}{N!} Q_1^N \quad (7)$$

And the Helmholtz free energy is

$$A = -k_B T \ln Q_N = -N k_B T \ln \left(V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \left(\frac{8\pi^2 I k_B T}{h^2} \right) \frac{4\pi \cosh \beta \mu E}{\beta \mu E} \right) + k_B T \ln N! \quad (8)$$

which, after applying Stirling's approximation, becomes

$$A = -k_B T \ln Q_N = -N k_B T \left(\ln \left(\frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \left(\frac{8\pi^2 I k_B T}{h^2} \right) \frac{4\pi \cosh \beta \mu E}{\beta \mu E} \right) + 1 \right) \quad (9)$$

The pressure is then

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

from which we see, with no surprise, that the ideal gas law is $PV = N k_B T$ is satisfied.

To find the dielectric constant of steam we first need to compute the electric polarization density P_0 (not to be confused with pressure!). By analogy with our study of the classical magnetic dipoles in a magnetic field, it is readily seen that

$$P_0 = \frac{N}{V} \langle \mu \cos \theta \rangle = \frac{1}{\beta} \frac{\partial}{\partial E} \ln Q_1 \quad (11)$$

$$= \frac{N}{V} \mu L(x) \quad (12)$$

where $x = \beta \mu E$ and $L(x) = \coth x - \frac{1}{x}$ is the Langevin function.

For $x \ll 1$ we showed in class that $L(x) \simeq x/3$. Thus, in this limit, the polarization is given by

$$P_0 = \frac{N}{V} \frac{\mu^2 E}{3k_B T} \quad (13)$$

The electric displacement is then (using cgs units)

$$D = E + 4\pi P_0 = \left(1 + 4\pi \frac{N}{V} \frac{\mu^2}{3k_B T}\right) E = \epsilon E \quad (14)$$

from which we see the dielectric constant ϵ is

$$\epsilon = 1 + 4\pi \frac{N}{V} \frac{\mu^2}{3k_B T} \quad (15)$$

Using the ideal gas law we can express the dielectric constant as a function of pressure and temperature only,

$$\epsilon = 1 + 4\pi \frac{P}{k_B T} \frac{\mu^2}{3k_B T} \quad (16)$$

$$= 1 + \frac{4\pi}{3} \frac{\mu^2 P}{k_B^2 T^2} \quad (17)$$

At 1 atm ($P \simeq 10^6 \text{ dynes/cm}^2$) and 100 C (=373 K) we find

$$\epsilon = 1 + \frac{4\pi}{3} \frac{(1.85 \times 10^{-18} \text{ esu-cm})^2 (10^6 \text{ dynes/cm}^2)}{(1.4 \times 10^{-16} \text{ erg/K})^2 (373 \text{ K})^2} \simeq 1.005 \quad (18)$$

which agrees well with the observed value.

Problem 2

(a) If $a(T)$ is the partition function for a single adsorbed molecule on a particular site, then the partition function for N molecules adsorbed on a surface with a total of N_0 adsorbent sites is simply $a(T)^N$ times the number of distinct configurations of the N adsorbed molecules on N_0 sites. Since the molecules are indistinguishable, this combinatoric factor is simply $\binom{N_0}{N}$ choose N and so Q_N is given by

$$Q_N(T) = \binom{N_0}{N} a(T)^N \quad (19)$$

(b) Given Q_N , the grand partition function is given by

$$\mathcal{Z} = \sum_{N=0}^{N_0} z^N Q_N = \sum_{N=0}^{N_0} \binom{N_0}{N} (za(T))^N = (1 + za(T))^{N_0} \quad (20)$$

where we have used the binomial theorem. Here $z = e^{\mu/k_B T}$ is the fugacity.

The grand potential of the surface is then

$$\Sigma = -k_B T \ln \mathcal{Z} = -N_0 k_B T \ln(1 + za(T)) \quad (21)$$

(c) Given Σ we can determine the number of adsorbed molecules N as follows

$$N = - \left(\frac{\partial \Sigma}{\partial \mu} \right)_T \quad (22)$$

$$= - \frac{\partial z}{\partial \mu} \frac{\partial \Sigma}{\partial z} \quad (23)$$

$$= \frac{z}{k_B T} N_0 k_B T \frac{a(T)}{1 + za(T)} \quad (24)$$

$$= N_0 \frac{za(T)}{1 + za(T)} \quad (25)$$

The covering fraction Θ is then

$$\Theta = \frac{N}{N_0} = \frac{za(T)}{1 + za(T)} \quad (26)$$

(d) As shown in class, the grand partition function for an ideal gas is

$$\mathcal{Z}_{gas} = \sum_{N=0}^{\infty} z^N \frac{1}{N!} Q_1^N = e^{zQ_1} \quad (27)$$

and the grand potential is

$$\Sigma = -k_B T \ln \mathcal{Z}_{gas} = -k_B T z V f(T) \quad (28)$$

where $Q_1 = V f(T)$.

(e) The number of particles in the gas is then

$$N = - \left(\frac{\partial \Sigma}{\partial \mu} \right)_{T,V} = z V f(T) \quad (29)$$

so the fugacity of the gas is

$$z = \frac{N}{V} \frac{1}{f(T)} = \frac{P}{k_B T} \frac{1}{f(T)} \quad (30)$$

where we have used the ideal gas law. Alternatively we can compute the pressure,

$$P = - \left(\frac{\partial \Sigma}{\partial V} \right)_{T,\mu} = k_B T z f(T) \quad (31)$$

and, solving for z , directly obtain the same result

$$z = \frac{P}{k_B T} \frac{1}{f(T)}. \quad (32)$$

(f) Setting the fugacities of the gas and surface equal we obtain the following general expression for the covering fraction as a function of pressure and temperature,

$$\Theta = \frac{Pa(T)}{k_B T f(T) + Pa(T)} \quad (33)$$

If we now consider the special case of having a single energy level with energy $-\epsilon$ associated with each adsorbed molecule so that $a(T) = e^{\epsilon/k_B T}$ and treat the gas as monatomic so that $f(T) = (2\pi m k_B T/h^2)^{3/2}$ we obtain the following expression for Θ ,

$$\Theta = \frac{P}{k_B T \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} e^{-\epsilon/k_B T} + P} \quad (34)$$

We see that in the limit of high pressure $\Theta \rightarrow 1$, as we would expect. Likewise in the limit of low pressure $\Theta \rightarrow 0$. The characteristic pressure which defines the crossover is

$$P_{crossover} = k_B T \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} e^{-\epsilon/k_B T} \quad (35)$$

Finally, if we fix P and take ϵ to be very large (so that the energy binding atoms to the adsorbent surface is large) we see that $\Theta \simeq 1$.

(g) If we model the adsorbed molecules assuming that, in addition to the binding energy ϵ , they act as quantized Harmonic oscillators then the only thing that changes is that $a(T)$ is given by the following expression

$$a(T) = e^{\epsilon/k_B T} \left(2 \sinh \frac{\hbar\omega}{2k_B T} \right)^{-1} \quad (36)$$

This will alter the “crossover pressure” at a given temperature, but it will still be the case that the covering fraction goes to 1 in the high pressure limit, and goes to 0 in the low pressure limit.

Problem 3

The partition function for a single particle in this gas is

$$Q_1 = \sum_{s=\pm 1} \int \frac{d^3r d^3p}{h^3} e^{-\beta p^2/2m} e^{+\beta s \mu_B H} \quad (37)$$

$$= V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} 2 \cosh \beta \mu_B H \quad (38)$$

and the partition function for N indistinguishable noninteracting particles is

$$Q_N = \frac{1}{N!} Q_1^N \quad (39)$$

The grand partition function is then

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N \frac{1}{N!} Q_1^N = e^{z Q_1} = e^{z V f(T)} \quad (40)$$

where

$$f(T) = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} 2 \cosh \frac{\mu_B H}{k_B T} = f_{gas}(T) f_{spin}(T) \quad (41)$$

with $f_{gas}(T) = (2\pi m k_B T/h^2)^{3/2}$ and $f_{spin}(T, H) = 2 \cosh \mu_B H/k_B T$. Note that all of the H dependence is in f_{spin} .

The grand potential is then

$$\Sigma = -k_B T \ln \mathcal{Z} = -k_B T z V f(T) \quad (42)$$

from which we can find that the number of particles is

$$N = - \left(\frac{\partial \Sigma}{\partial \mu} \right)_{T, V} = z V f(T) \quad (43)$$

The magnetization is

$$M = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial H} \quad (44)$$

and since

$$\ln \mathcal{Z} = z V f_{gas}(T) f_{spin}(T, H) \quad (45)$$

with all the H dependence appearing in f_{spin} , we have

$$M = k_B T z V f_{gas}(T) \frac{\partial f_{spin}(T, H)}{\partial H} \quad (46)$$

$$= k_B T z V f(T) \frac{1}{f_{spin}} \frac{\partial f_{spin}}{\partial H} \quad (47)$$

$$= k_B T N \frac{\partial \ln f_{spin}}{\partial H} \quad (48)$$

$$= k_B T N \frac{\mu_B}{k_B T} \tanh \frac{\mu_B H}{k_B T} \quad (49)$$

$$= N \mu_B \tanh \frac{\mu_B H}{k_B T} \quad (50)$$

This is the familiar result for the magnetization of spin-1/2 particles in a magnetic field.

There are several ways to compute the entropy. One way is to first obtain the Helmholtz free energy as a function of N , V and T ,

$$A = \Sigma + \mu N = -k_B T z V f(T) + k_B T \ln z N = k_B T \left(\ln \frac{N}{V f(T)} - 1 \right) \quad (51)$$

The entropy is then

$$S = - \left(\frac{\partial A}{\partial T} \right)_{V,N} = N k_B \left(1 + \ln \frac{V}{N} f(T) + T \frac{d \ln f(T)}{dT} \right) \quad (52)$$

Note that $f(T)$ enters the entropy only inside the \ln function. Since $f(T) = f_{ideal\ gas}(T) \times f_{spin-1/2}(T)$ we readily see that

$$S = S_{gas} + N k_B \left(\ln \left(2 \cosh \frac{\mu_B H}{k_B T} \right) - \frac{\mu_B H}{k_B T} \tanh \frac{\mu_B H}{k_B T} \right) \quad (53)$$

where the second term is S_{spin} the contribution to the entropy due to the spin-1/2 degrees of freedom of the atoms forming the gas. Since all of the H dependence of the entropy is in this second term, the change in entropy if H is reduced to zero while keeping N , T and V fixed is

$$\Delta S = S_{spin}(T, H = 0) - S_{spin}(T, H) = N k_B \left(\frac{\mu_B H}{k_B T} \tanh \frac{\mu_B H}{k_B T} - \ln \cosh \frac{\mu_B H}{k_B T} \right) \quad (54)$$

The heat absorbed by the gas is then

$$\Delta Q = T \Delta S = N k_B T \left(\frac{\mu_B H}{k_B T} \tanh \frac{\mu_B H}{k_B T} - \ln \cosh \frac{\mu_B H}{k_B T} \right) \quad (55)$$

which, for $\mu_B H \gg k_B T$ is

$$\Delta Q = N k_B T \ln 2 \quad (56)$$

Note that in doing this problem it is crucial to obtain the entropy S as a function of N , T and V . If one calculates the change in entropy keeping the chemical potential μ fixed, rather than the number of particles N , one gets the *wrong* answer. This is because the chemical potential depends on H .

Provided any explicit dependence of S on the chemical potential is eliminated (using $z = N/(V f(T))$), we would have obtained the same result (i.e. Eq. (52) for S) using

$$S = - \left(\frac{\partial \Sigma}{\partial T} \right)_{V,\mu} . \quad (57)$$