University of Illinois at Chicago
Department of Physics

Thermodynamics & Statistical Mechanics
PhD Qualifying Examination

January 10, 2013
9.00 am – 12:00 pm

Full credit can be achieved from completely correct answers to <u>4 questions</u>. If the student attempts all 5 questions, all of the answers will be graded, and the <u>top 4 scores</u> will be counted toward the exam's total score.

Problem 1

An ideal monatomic gas of N particles, each of mass m, is in thermal equilibrium at absolute temperature T. The gas is confined in a cubical box of side L. The velocities of the particles are distributed according to the Maxwellian distribution.

(a) What is the most probable speed v_{mp} of the particles?

(b) What is the most probable kinetic energy ϵ_{mp} of the particles?

(c) What is the average kinetic energy of the particles? No explicit derivation is required.

(d) Now consider the effect of the earth's gravitational field, assumed uniform over the height L of the container, with acceleration due to gravity being g. What is the average potential energy of a particle?

(e) Derive an expression for the chemical potential of the gas particles as a function of the concentration $c(z)$, where z is the height in the vertical direction, and other physical constants.

Solution

(a) $P(v_x)P(v_y)P(v_z)dv_x dv_y dv_z = C exp\left(-\frac{mv^2}{2k_B T}\right)dv_x dv_y dv_z$

$$P(v)dv = 4\pi C exp\left(-\frac{mv^2}{2k_B T}\right)v^2 dv$$

Set $\frac{dP}{dv} = 0$ to get $v_{mp} = \sqrt{\frac{2k_B T}{m}}$

(b) Make a change of variable to get $P(\epsilon)d\epsilon = C' exp\left(-\frac{\epsilon}{k_B T}\right)\sqrt{\epsilon}d\epsilon$

and set $\frac{dP}{d\epsilon} = 0$ to get $\epsilon_{mp} = \frac{k_B T}{2}$

(c) From the equipartition theorem: $\langle \epsilon \rangle = \frac{3}{2}k_B T$

(d) $< PE >= \dfrac{\int_0^L mgz \ exp\left(-\frac{mgz}{k_B T}\right)dz}{\int_0^L exp\left(-\frac{mgz}{k_B T}\right)dz} = \dfrac{I_N}{I_D}$

Evaluate $I_D = \int_0^L exp(-mgz/k_B T)\,dz = \int_0^L exp(-\alpha z)\,dz = \frac{1-exp(-\alpha L)}{\alpha}$

Evaluate $I_N = \int_0^L mgz \ exp(-mgz/k_B T)\,dz = mg\int_0^L z exp(-\alpha z)dz = -mg\frac{\partial I_D}{\partial \alpha}$

$$= \frac{mg}{\alpha}\left[\frac{1-exp(-\alpha L)}{\alpha} - L\ exp(-\alpha L)\right]$$

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Therefore, $< PE > = \dfrac{I_N}{I_D} = mg\left[\dfrac{1}{\alpha} - \dfrac{L}{\exp(\alpha L)-1}\right] = mg\left[\dfrac{k_B T}{mg} - \dfrac{L}{\exp\left(\frac{mgL}{k_B T}\right)-1}\right]$

(e) In the absence of a gravitational field, the particles are uniformly distributed over volume V, and the partition function for an ideal monatomic gas is

$$Z = \dfrac{Z_1^N}{N!} = \dfrac{1}{N!}\left(\dfrac{V}{v_q}\right)^N \quad \text{where } v_q = \left(\dfrac{h}{\sqrt{2\pi m k_B T}}\right)^3$$

Hence the free energy is $F = -k_B T\ln(Z) = -N k_B T\left[\ln(V) - \ln(N) - \ln(v_q) + 1\right]$
where we have used the Stirling approximation: $\ln(N!) \approx N\ln(N) - N$.

The chemical potential is given by $\mu = \left(\dfrac{\partial F}{\partial N}\right)_{T,V} = -k_B T\ln\left(\dfrac{V}{N v_q}\right) = k_B T\ln(c v_q)$

where c is the concentration of the molecules.

In the presence of a gravitational field, the concentration of molecules varies with the height z. Consider the number of molecules (δN) in each layer at height z and width dz (volume δV). The free energy of the molecules in this layer, including the potential energy of the molecules at height z, becomes:

$$F = -\delta N k_B T\left[\ln(\delta V) - \ln(\delta N) - \ln(v_q) + 1\right] + \delta N mgz$$

and the chemical potential can be expressed as:

$$\mu = \left(\dfrac{\partial F}{\partial(\delta N)}\right)_{T,V} = -k_B T\ln\left(\dfrac{\delta V}{\delta N v_q}\right) + mgz = k_B T\ln(c v_q) + mgz$$

Note that the concentration decreases and the potential energy increases with height z in such a way as to keep the chemical potential a constant, independent of z

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Problem 2

Consider a two-dimensional model of a solid at absolute temperature T that contains N negatively charged impurity ions per unit volume, such that these ions replace some of the ordinary atoms of the solid. The solid as a whole is electrically neutral. This is so because each negative ion (with charge $-e$) has in its vicinity one positive ion (with charge $+e$). The positive ion is small and thus free to move between four lattice sites surrounding the negative ion, as shown in the figure. The lattice spacing is a.
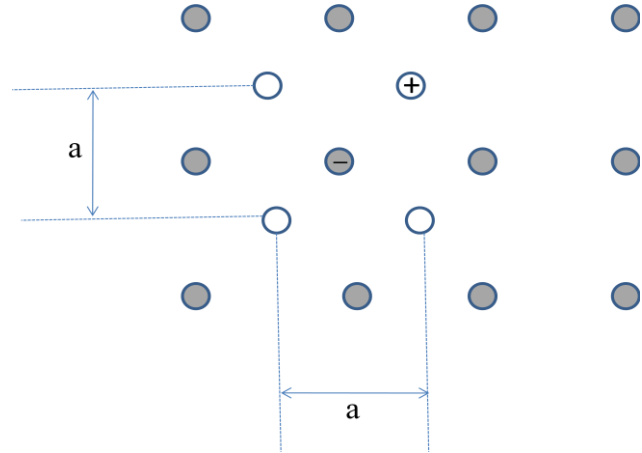
(a) What is the mean electric polarization, i.e. mean electric dipole moment per unit volume, in the presence of an electrical field $\mathcal{E}$ applied along the x direction?

(b) Without any explicit derivation, state the limiting values of the entropy per unit volume of this solid at (i) very low temperature ($k_BT \ll e\mathcal{E}$) and (ii) very high temperature ($k_BT \gg e\mathcal{E}$). Give your reasoning.

(c) Verify your results in part (b) by explicitly writing down an expression of the entropy per unit volume as a function of temperature, and taking the appropriate limits.

Solution

(a) $< p_x >= N \left[\frac{2pcos\theta \, \exp{(+\beta p\varepsilon cos\theta \,)}-2pcos\theta \, \exp{(-\beta p\varepsilon cos\theta \,)}}{2 \exp{(+\beta p\varepsilon cos\theta \,)}+2\exp{(-\beta p\varepsilon cos\theta \,)}} \right] = Npcos\theta tanh(\beta p\mathcal{E}cos\theta)$

$$< p_y >= 0$$

Here $pcos\theta = \left(ea/\sqrt{2}\right)\left(1/\sqrt{2}\right) = ea/2$

Therefore, $< p_x >= \frac{Nea}{2} tanh(\beta ea\mathcal{E}/2)$

(b) At low T, the positive ion is equally likely to be found at either of the two sites with the lower energy, and hence $S = k_B \ln(2^N) = Nk_B \ln(2)$. At high T, the positive ion is equally likely to be at any one of the four sites, therefore, $S = Nk_B\ln(4)$.

(c) $S = \frac{U-F}{T} = -\frac{Nea\mathcal{E}}{2T} tanh(\beta ea\mathcal{E}/2) + Nk_B\ln(4\cosh(\beta ea\mathcal{E}/2))$

since $U = -< p >\cdot \varepsilon = -\frac{Nea\mathcal{E}}{2} tanh(\beta ea\mathcal{E}/2)$

and $F = -k_BT \ln(Z) = -Nk_BT \ln(4\cosh(\beta ea\mathcal{E}/2))$

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As $T \to 0$ (or $\beta \to \infty$), $\tanh(\beta ea\varepsilon/2) \to 1$ and $\ln(2\cosh(\beta ea\varepsilon/2)) \to \beta ea\varepsilon/2$

$$S = -\frac{Nea\varepsilon}{2T} + Nk_B\ln 2 + Nk_B\left(\frac{\beta ea\varepsilon}{2}\right) = Nk_B\ln 2$$

As $T \to \infty$ (or $\beta \to 0$), $\tanh(\beta ea\varepsilon/2) \to 0$ and $\cosh(\beta ea\varepsilon/2) \to 1 \Longrightarrow S = Nk_B\ln(4)$

Problem 3

Consider a polymeric chain of N links, each of length a. In the absence of an applied force, each link is equally likely to be directed to the left or to the right. The polymer is extended to a length l under the influence of an external force f.

(a) Write down a thermodynamic identity for this polymer, analogous to the identity $dU = TdS - pdV$ for a hydrostatic system

(b) Show that $\frac{f}{T} = -\left(\frac{\partial S}{\partial l}\right)_U$

(c) Write an expression for the number of arrangements $\Omega(N, |m|)$ that give a head to tail length $l = 2|m|a$, where m is the number of links in excess of $N/2$ that point to the right or to the left.

(d) Assume that $\Omega(N, |m|)$ can be expressed as a Gaussian for $|m| \ll N$, and show that the entropy of the system is given by
$$S(l)/k_B = \ln[2\Omega(N, 0)] - l^2/2Na^2$$

(e) Show that for small extensions l, the polymer behaves like a Hookean spring.

Solution

(a) $dU = TdS + fdl$

(b) From (a) we have $\left(\frac{\partial U}{\partial l}\right)_S = f$ and $\left(\frac{\partial S}{\partial U}\right)_l = \frac{1}{T}$

Substitute into the following reciprocity relation:
$$\left(\frac{\partial S}{\partial U}\right)_l \left(\frac{\partial U}{\partial l}\right)_S \left(\frac{\partial l}{\partial S}\right)_U = -1$$

to get $\frac{f}{T} = -\left(\frac{\partial S}{\partial l}\right)_U$

(c) The total number of arrangements (or multiplicity) to get an end-to-end length $l = 2|m|a$ is given by
$$\Omega(N, -m) + \Omega(N, m) = \frac{2N!}{\left(\frac{1}{2}N + m\right)!\left(\frac{1}{2}N - m\right)!}$$

(d) Express $\Omega(N, m)$ as a gaussian function to get $\Omega(N, |m|) = 2\Omega(N, 0) \exp\left(-\frac{l^2}{2Na^2}\right)$

Therefore, $S(l) = k_B \ln\left[2\Omega(N, 0) \exp\left(-\frac{l^2}{2Na^2}\right)\right] = k_B[\ln(2\Omega(N, 0)) - l^2/2Na^2]$

(e) Use result from part (b) to get $\frac{f}{T} = \frac{k_B l}{Na^2} \Rightarrow f = (k_B T/Na^2)l$

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Problem 4

DNA can be modeled as two parallel polymer strands with links between the strands called *base pairs*. Each base pair can be in a closed state with energy 0 or in an open state with energy $\varepsilon > 0$.

Consider a DNA molecule with N base pairs in thermal equilibrium at temperature T, as shown. Thermal fluctuations can cause each base pair to open, leading to separation of the two strands. Assume that the two strands are tethered together at the right end such that the molecule can open only from the left end, and only in *sequential order* (i.e. base pair s can open only if 1, 2... s–1 to the left of it are already open).
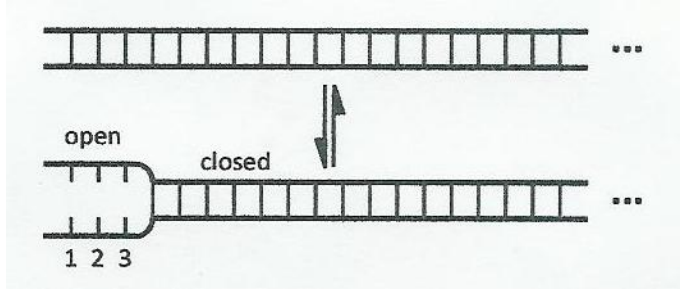

(a) Show that the partition function Z for this system is given by the following expression:

$$Z = \frac{1 - \exp\left(-\frac{(N+1)\varepsilon}{k_B T}\right)}{1 - \exp\left(-\frac{\varepsilon}{k_B T}\right)}$$

(b) In the limit that $N \to \infty$ determine the mean number $\langle n \rangle$ of open base pairs.

(c) Evaluate $\langle n \rangle$ from part (b) in the limit that (i) $T \to 0$ and (ii) $T \to \infty$

(d) Next, consider the same DNA molecule now surrounded by a protein p at concentration c. Protein p can bind to the DNA *only at a site that is open*, as shown.
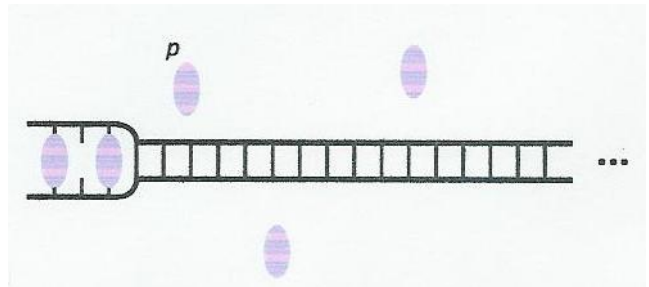
Assume each protein p can occupy no more than one base pair. The chemical potential for p is $\mu = \Delta + k_B T \ln\left(\frac{c}{c_0}\right)$, where c_0 and Δ are constants ($c_0 > 0$). Write down a closed form expression for the Grand canonical ensemble for this system, in the limit that $N \to \infty$

Solution

(a) $Z = 1 + \exp\left(-\frac{\varepsilon}{k_B T}\right) + \exp\left(-\frac{2\varepsilon}{k_B T}\right) + \cdots \cdots \exp\left(-\frac{N\varepsilon}{k_B T}\right) = \sum_{n=0}^{N} \left[\exp\left(-\frac{\varepsilon}{k_B T}\right)\right]^n$

Note that $\frac{1-x^{N+1}}{1-x} = 1 + x + x^2 + \cdots \cdots \cdots x^N = \sum_{n=0}^{N} x^n$

Identify x with $\exp\left(-\frac{\varepsilon}{k_B T}\right)$ to get

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$$Z = \frac{1 - \exp\left(-\frac{(N+1)\varepsilon}{k_B T}\right)}{1 - \exp\left(-\frac{\varepsilon}{k_B T}\right)}$$

(b) In the limit $N \rightarrow \infty$

$$Z = \frac{1}{1 - \exp\left(-\frac{\varepsilon}{k_B T}\right)} = (1 - \exp(-\beta\varepsilon))^{-1}$$

$$< n > = \frac{< E >}{\varepsilon} = -\frac{1}{\varepsilon}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) = \frac{(1 - \exp(-\beta\varepsilon))}{\varepsilon}\frac{\varepsilon\exp(-\beta\varepsilon)}{(1 - \exp(-\beta\varepsilon))^2}$$

$$= \frac{\exp(-\beta\varepsilon)}{1 - \exp(-\beta\varepsilon)}$$

(c) As $T \rightarrow 0$ $(\beta \rightarrow \infty)$, $< n > = 0$, and as $T \rightarrow \infty$ $(\beta \rightarrow 0)$, $< n > = \infty$

(d) Grand canonical partition function

$$\Xi = 1 + (1 + \lambda)\exp\left(-\frac{\varepsilon}{k_B T}\right) + (1 + \lambda)^2 \exp\left(-\frac{2\varepsilon}{k_B T}\right) + (1 + \lambda)^3 \exp\left(-\frac{3\varepsilon}{k_B T}\right) + \cdots..$$

$$= \sum_{p=0}^{\infty}\left[(1 + \lambda)\exp\left(-\frac{\varepsilon}{k_B T}\right)\right]^p = \frac{1}{1 - (1 + \lambda)\exp\left(-\frac{\varepsilon}{k_B T}\right)}$$

where $\lambda = exp\left(\frac{\mu}{k_B T}\right) = \frac{c}{c_0}\exp\left(\frac{\Delta}{k_B T}\right)$

Problem 5

Part I: Starting from the first and second law of thermodynamics, show that

(a) the maximum work that can be extracted from a system in a process at constant temperature is equal in magnitude to the change in its Helmholtz free energy

(b) the maximum <u>non-expansion</u> work that can be extracted from a system in a process at constant temperature and pressure is equal in magnitude to the change in its Gibbs free energy.

Part II: Consider a system consisting of <u>two particles</u>, each of which can be in any one of <u>three quantum states</u> of respective energies 0, $\mathcal{E}$, and $3\mathcal{E}$. The system is in contact with a heat reservoir at temperature T. Ignore the spin degrees of freedom.

(a) Write an expression for the partition function Z if the particles obey classical Boltzman statistics and are considered distinguishable.

(b) What is Z if the particles obey Bose-Einstein statistics?

(c) What is Z if the particles obey Fermi-Dirac statistics?

Solution

<u>Part I</u>

First law: $dU = dQ + dW$

Second law: $dS \geq \frac{dQ}{T}$

Therefore, $dU - dW \leq TdS \Rightarrow dU - TdS \leq dW$

(a) $F = U - TS \Rightarrow dF = dU - TdS - SdT$

For processes at constant temperature: $dF = dU - TdS \leq dW$

For work extracted from a system, $dW < 0 \Rightarrow |dW| \leq |dF|$

(b) $G = H - TS = U + PV - TS \Rightarrow dG = dU + PdV + VdP - TdS - SdT$

For processes at constant temperature and pressure: $dG = dU + PdV - TdS$

Also $dU - TdS \leq dW \Rightarrow dU - TdS \leq -PdV + dW_{other} \Rightarrow dU - TdS + PdV \leq dW_{other}$

Therefore, $dG \leq dW_{other}$

For other (non-expansion) work extracted from a system,

$$dW_{other} < 0 \Rightarrow |dW_{other}| \leq |dG|$$

Part II

(a) $Z = (1 + \exp(-\beta\varepsilon) + \exp(-3\beta\varepsilon))^2$

(b) $Z = 1 + \exp(-\beta\varepsilon) + \exp(-2\beta\varepsilon) + \exp(-3\beta\varepsilon) + exp(-4\beta\varepsilon) + \exp(-6\beta\varepsilon)$

(c) $Z = \exp(-\beta\varepsilon) + \exp(-3\beta\varepsilon) + \exp(-4\beta\varepsilon)$