Problem set for “Canonical ensemble”
Due April 27, 2020

Problem I: Thermal fluctuations of a string

Consider a string of constant mass density per unit length $\rho$ stretched between two fixed pins with constant tension $f$. Find the average fluctuation of the deviation of each point of the string, $\langle \xi^2(x) \rangle$, assuming that the deviation is small compared with the length of the string.

Figure 1:

(a) Ignore the quantum effects and consider the effect of thermal fluctuations only.

**Hint:** Expand the deviation $\xi(x)$ into a Fourier series, and regard the expansion coefficients $(Q_1, Q_2, \ldots)$ as the generalized coordinates describing the deviation.

Use the identity

$$\sum_{n=1}^{\infty} \frac{2 \sin^2(\pi n z)}{(\pi n)^2} = z(1 - z).$$

(b) Take into account the quantum fluctuations together with the thermal.

**Hint:** Use the identity (formula 16.30.1 from M.Abramowitz and I.Stegun):

$$\log \left( \frac{\vartheta_1(\alpha + \beta, q) \sin(\alpha - \beta)}{\vartheta_1(\alpha - \beta, q) \sin(\alpha + \beta)} \right) = 4 \sum_{n=1}^{\infty} \frac{1}{n} \frac{q^{2n}}{1 - q^{2n}} \sin(2n\alpha) \sin(2n\beta)$$  \hspace{1cm} (1)

for the Jacobi elliptic theta function $\vartheta_1(z, q)$

(http://mathworld.wolfram.com/JacobiThetaFunctions.html)

$$\vartheta_1(z, q) = 2 \sum_{n=0}^{\infty} q^{(n+\frac{1}{2})^2} \sin \left( (2n + 1) z \right) = \text{EllipticTheta}[1, z, q].$$

\[\text{1}^1\text{This part of the problem is optional.}\]
Problem II: Gibbs canonical ensemble

In the Gibbs canonical ensemble we consider the Hamiltonian with additional generalized forces added
\[ H(J) = H - \sum_i J_i \lambda_i . \]

Let’s illustrate this approach on the one-dimensional classical ideal gas with the Hamiltonian
\[ H = \sum_{a=1}^{N} \frac{p_a^2}{2m} . \]

However, instead of the gas being confined to a segment \( x_a \in (0, L) \), we consider a gas on the half-infinite line \( x_a \in (0, \infty) \). The left wall elastically reflects the particles, but instead of a wall on the right, we have a constant force \( F \) applied to the last particle, acting in the negative \( x \) direction (\( F < 0 \)) and preventing the gas from escaping to positive infinity. This mimics the system with the piston schematically shown below.

(a) Using the Gibbs canonical ensemble, find the Gibbs free energy for the system.

**Hint:** To get the correct result, it is important to keep in mind that the particles are indistinguishable.

(b) Performing the Legendre transform, find the Helmholtz free energy and check that the result coincides with the one obtained from the canonical ensemble.
Problem III: Langmuir’s isotherm $\theta = \theta(T, P)$

Consider an adsorbent surface having $N$ sites each of which can adsorb one gas molecule. Suppose that it is in contact with a classical ideal gas with the chemical potential $\mu$ (determined by the pressure $P$ and the temperature $T$).

(a) Assuming that an adsorbed molecule has energy $(-\varepsilon_0)$ compared to one in a free state, determine in this case the surface coverage $\theta = \theta(T, P)$ (the ratio of adsorbed molecules to adsorbing sites).

(b) Express the relative root-mean-square fluctuation in the number of adsorbed particles,

$$\sqrt{\langle (\Delta N_{ads})^2 \rangle}$$

in terms of the surface coverage $\theta$. 
Problem IV: Spherical top

The spherical top is a rigid body whose principal moments of inertia are equal, so that the Hamiltonian is given by

$$H_{\text{spt}} = \frac{\vec{L}^2}{2I}.$$  \hspace{1cm} (2)

(a) What is the energy spectrum in this case and what is the degeneracy of each level?

(b) Write an expression for the partition function of a single quantum mechanical spherical top. Express the result in terms of the Jacobi theta function

$$\vartheta_2(z, q) = 2 \sum_{n=0}^{\infty} q^{(n+\frac{1}{2})^2} \cos((2n+1)z) = \text{EllipticTheta}[2, z, q].$$  \hspace{1cm} (3)

(c) Using the Poisson summation formula (see Problem V, HW7), show that the partition function admits the following high-temperature expansion

$$Z = \sqrt{\pi} \Theta^3 e^{\frac{1}{4\Theta}} \left( 1 + 2 \sum_{n=1}^{\infty} (-1)^{n-1} \left( 2(\pi n)^2 \Theta - 1 \right) e^{-\left(\pi n\right)^2 \Theta} \right), \quad \text{where} \quad \Theta = \frac{T}{T_{\text{rot}}}.$$  \hspace{1cm} (4)

and we use the rotational temperature scale

$$T_{\text{rot}} = \frac{\hbar^2}{2Ik_B}.$$

(d) Using the results of (b) and (c), show that

$$c_{\text{rot}} = \begin{cases} \frac{3}{2} + 2\pi^2 \Theta \left( 2\pi^4 \Theta^2 - 9\pi^2 \Theta + 6 \right) e^{-\pi^2 \Theta} + \ldots & \text{as} \quad \Theta \to +\infty \\ 36 \Theta^{-2} e^{-\frac{1}{4\Theta}} + \ldots & \text{as} \quad \Theta \to 0 \end{cases}$$  \hspace{1cm} (5)

where $c_{\text{rot}}$ is the dimensionless specific heat capacity per spherical top:

$$c_{\text{rot}} = \frac{1}{k_B} \frac{d}{dT} \langle H_{\text{spt}} \rangle.$$

(d) Plot $c_{\text{rot}}$ as a function of the dimensionless temperature $\Theta$. 


Problem V: Debye model

Atoms in a solid vibrate about their respective equilibrium positions with small amplitudes. Debye approximated the normal vibrations with the elastic vibrations of an isotropic continuous body and assumed that the number of vibrational modes \( g(\omega) \) having angular frequencies between \( \omega \) and \( \omega + d\omega \) is given by

\[
g(\omega) = \begin{cases} \frac{V}{2\pi^2} \left( \frac{1}{v_\parallel^2} + \frac{2}{v_\perp^2} \right) \omega^2 & (0 < \omega < \omega_D) \\ 0 & (\omega > \omega_D) \end{cases} \equiv \frac{9N}{\omega_D^3} \omega^2.
\]  

Here \( v_\parallel \) and \( v_\perp \) denote the velocities of the longitudinal and transverse waves, respectively. The Debye frequency \( \omega_D \) is determined by

\[
\int_0^{\omega_D} d\omega \ g(\omega) = 3N,
\]

where \( N \) is the number of atoms and hence \( 3N \) is the number of degrees of freedom.

(a) Calculate the heat capacity \( C_V \) of a solid at constant volume using this model.

(b) Examine its temperature dependence at high as well as at low temperatures. Plot the dimensionless heat capacity per degree of freedom \( C_V/(3k_B N) \) as a function of the dimensionless temperature \( T/T_D \), where

\[
T_D = \frac{\hbar \omega_D}{k_B}
\]

is the so-called Debye’s characteristic temperature or the Debye temperature.

(c) Find the zero point energy \( E_0 \) and the leading large-\( N \) behaviour of the density of states \( \Omega(E, N) \) for the cases \( E - E_0 \ll N\hbar\omega_D \) and \( E - E_0 \gg N\hbar\omega_D \) in the Debye model.

(d) Consider a crystal with one atom per primitive lattice cell. Find the average squared displacement from the equilibrium position of a lattice atom in the Debye model. Analyze the low \( T \ll T_D \) and high \( T \gg T_D \) temperature limits.

**Hint:** Useful integrals

\[
\int_0^{+\infty} \frac{dx x^4 e^x}{(e^x - 1)^2} = 4 \int_0^{+\infty} \frac{dx x^3 e^x}{e^x - 1} = 4 \frac{\pi^4}{15},
\]

\[
\int_0^{\infty} \frac{dx x}{e^x - 1} = \frac{\pi^2}{6}.
\]
Problem VI: Cosmic microwave background

Consider a photon gas enclosed in a volume $V$ and in equilibrium at temperature $T$. The photon is a massless particle, so that $\epsilon(\vec{p}) = c|\vec{p}|$.

(a) What is the chemical potential of the gas? Explain.

(b) Determine how the average number of photons $\langle N \rangle$ in the volume depends upon the temperature.

**Hint:** Useful integral

$$\int_0^\infty \frac{dx x^2 e^x}{e^x - 1} = 2 \zeta(3) = 2.40411 \ldots .$$

Here we used the so-called Riemann $\zeta$-function which is defined by the convergent series

$$\zeta(s) = \sum_{n=1}^{\infty} \frac{1}{n^s} \quad \text{for} \quad \Re(s) > 1 .$$

(c) Our universe is filled with black body radiation (photons) at a temperature of $T = 2.73\,\text{K}$ which is usually referred to as the Cosmic Microwave Background (CMB). This is thought to be a relic of the early developments following the “big bang”. Estimate the photon number density for the CMB.
Problem VII: One-dimensional plasma\textsuperscript{2}

(a) Read any textbook on the path-integral representation of the thermal density matrix. I would recommend chapter 3 in the classic book \textit{Statistical Mechanics: A Set of Lectures} by R. Feynman.

(b) Consider a quantum rotator in two dimensions (see Problem V, HW10) in the presence of a constant external electric field \( \vec{E} \). Assuming that the rotator has a dipole moment \( \vec{d} \), the Hamiltonian of the system is given by

\[
H_{\text{rot}} = -\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2} - \mathcal{E} d \cos(\phi) .
\]

(The corresponding stationary Schrödinger equation is known in the mathematics literature as the Mathieu equation.) Using the path integral representation, develop a weak field perturbative expansion for the partition function

\[
Z = \text{Tr}(e^{-\beta H_{\text{rot}}}) .
\]

(c) Recall that the Coulomb potential of a particle of charge \( e \) in \( d \)-dimensions is defined as the solution of the Laplace equation

\[
\triangle \Phi(\vec{x}) = -e S_d \delta^{(d)}(\vec{x}) , \quad \text{where} \quad S_d = \frac{2\pi^{\frac{d}{2}}}{\Gamma\left(\frac{d}{2}\right)} .
\]

Show, that in the case of \( d = 1 \), the Coulomb potential energy between two particles of charge \( e_1 \) and \( e_2 \), is given by

\[
\Phi(x) = -e_1 e_2 |x| .
\]

(d) Consider the one-dimensional \textbf{classical} plasma consisting of a mixture of particles of charge \( \pm e \) (note that the Coulomb interaction between the ions is long distance, and not like the nearest neighbor interactions discussed in Problem II from HW8). Write down the formula for the partition function in the grand canonical ensemble for this system. Using the solution to part (b), derive the equation of state for the one-dimensional classical plasma.

(e) Investigate the low and high temperature limits. In particular, show that at high temperatures, the system is in a plasma phase, and that at low temperatures, it can be interpreted as a gas of neutral molecules. It is important to note that there is no phase transition between these two phases.

\textsuperscript{2}This problem is optional and will not be graded