6CCP3212 Statistical Mechanics Homework 3

Lecturer: Prof. Eugene A. Lim
https://nms.kcl.ac.uk/eugene.lim/teach/statmech/sm.html

1) (**Diatomic Gas**) Consider a diatomic gas (see Figure 1), with equal mass atoms $m/2 = m_1 = m_2$ such that the total mass is m. In class, we showed that according to classical theory, the heat capacity of the ideal diatomic gas with N diatoms with N diatoms is given by

$$C_V = \frac{7}{2}Nk_b \ , \tag{1}$$

which we derived by dividing the d.o.f. of the diatom into 2 pairs of 3 translational d.o.f. (for each atom) and a single d.o.f. for the energy in the tension between the atoms. We will now rederive this formula, by instead decomposing the d.o.f. into bulk translation (i.e. the joint motion of both atoms), rotation, and vibration. Let's consider each d.o.f. independently.

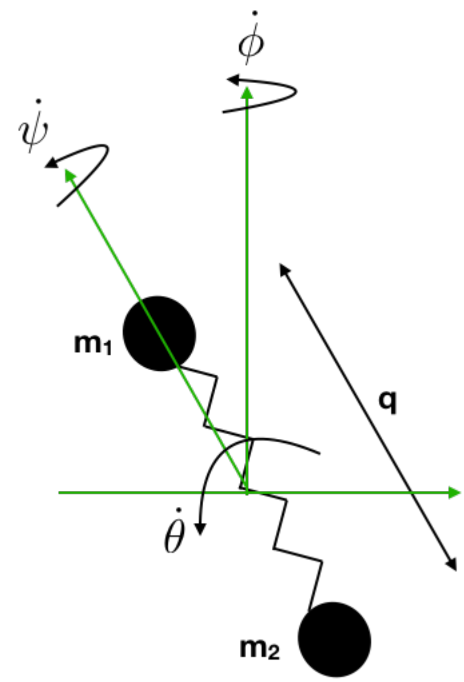

Figure 1: (Problem 1) A di-atomic molecule.

(i) *Bulk translation*: This is the motion of the location of the center of mass $\mathbf{x}$ of the molecule. The Hamiltonian of such a motion is given by

$$H_{\rm tr}(\mathbf{p}) = \frac{\mathbf{p}^2}{2m} \tag{2}$$

where $\mathbf{p} = m(d\mathbf{x}/dt)$. Show that the partition function for this d.o.f. is given by

$$Z_{\rm tr} = V\left(\frac{mk_bT}{2\pi\hbar^2}\right)^{3/2} \ . \tag{3}$$

(ii) *Rotation*: In general, there are three possible axes for the diatom to rotate, $\dot{\psi}$, $\dot{\phi}$ and $\dot{\theta}$, where (ψ, ϕ, θ) are the Euler angles. The moment of inertias associated with these angles are I_ψ, I_ϕ and I_θ respectively.

Symmetry implies that $I_\phi = I_\theta \equiv I$ and since the length of the atomic bond is much longer than the atomic radii, $I_\psi \ll I$, and hence we can ignore the rotation energy of the ψ angle. The Hamiltonian of the system is given by

$$H_{\rm rot} = \frac{1}{2}I(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2)\ . \tag{4}$$

The canonical momenta for rotation along these Euler angles are given by[1]

$$p_\theta = I\dot{\theta}\ ,\ p_\phi = I\sin^2\theta\dot{\phi}, \tag{5}$$

and hence show that

$$H_{\rm rot} = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right)\ . \tag{6}$$

The partition function for rotation d.o.f. is the integral over all possible angles and momenta

$$Z_{\rm rot} = \frac{1}{(2\pi\hbar)^2}\int_0^\pi d\theta \int_0^{2\pi} d\phi \int dp_\phi dp_\theta\ e^{-\beta H_{\rm rot}(p_\phi, p_\theta)}\ . \tag{7}$$

Show that this has the result

$$Z_{\rm rot} = \frac{2Ik_bT}{\hbar^2}\ . \tag{8}$$

(iii) *Vibration*: The vibration motion of the diatoms with respect to each other is a simple harmonic oscillator with natural frequency ω (which is determined by the strength of the atomic bond). Suppose the equilibrium position of the diatom is z, then the energy of the vibration is given by

$$H_{\rm vib} = \frac{1}{2}m\dot{z}^2 + \frac{1}{2}m\omega^2 z^2\ . \tag{9}$$

Using the canonical momentum $p_z = m\dot{z}$, show that the partition function for the vibration motion is

$$Z_{\rm vib} = \frac{k_bT}{\hbar\omega}\ . \tag{10}$$

(iv) Using the results of the derived Hamiltonians in (i), (ii) and (iii), show that the mean energies for the bulk translation, rotation and vibration modes are given by

$$E_{\rm trans} = \frac{3}{2}k_bT\ ,\ E_{\rm rot} = k_bT\ , E_{\rm vib} = k_bT \tag{11}$$

and hence $C_V = (7/2)Nk_b$ as expected. You can use the equipartition theorem to derive these equations, or directly compute it from the partition functions.

2) In class, we showed that if a gas is made out of indistinguishable particles, the entropy is given by

$$S = k_b(\ln Z + \beta\bar{E})\ , \tag{12}$$

where the partition function is

$$Z = \frac{V^N}{N!\lambda^{3N}}\ , \tag{13}$$

and the thermal de Broglie wavelength

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_bT}}\ . \tag{14}$$

Calculate $\bar{E}$ and derive the **Sackur-Tetrode formula**

$$S = Nk_b\left[\ln\left(\frac{V}{N\lambda^3}\right) + \frac{5}{2}\right]\ . \tag{15}$$

[1]They can be derived from the Lagrangian $L = (1/2)I(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2)$ and $p_x = \partial L/\partial\dot{x}$ for $x = \{\theta, \phi\}$. Hopefully you have learned this in your classical dynamics class, but don't worry if you haven't.

(*Hint*: You might need to use Stirling's approximation.)

3) The Maxwell-Boltzmann distribution of a gas at temperature T is given by

$$f(v)e^{-mv^2/2k_bT} = \sqrt{\frac{2}{\pi}}\left(\frac{m}{k_bT}\right)^{3/2} v^2 e^{-mv^2/2k_bT} \ , \tag{16}$$

where the absolute velocity is

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2} \ , \tag{17}$$

and v_x , v_y , v_z are the velocities in the 3 Cartesian directions.
(i) Show that this distribution has a peak at $v_{max} = \sqrt{2k_bT/m}$.
(i) The ensemble average of any quantity X is given by

$$\langle X \rangle = \int_0^\infty X f(v) e^{-mv^2/2k_bT} dv \ . \tag{18}$$

Calculate $\langle v \rangle$ and $\langle 1/v \rangle$, and hence show that

$$\frac{\langle v^{-1} \rangle}{(\langle v \rangle)^{-1}} = \frac{4}{\pi} \ . \tag{19}$$

(iii) Calculate the following ensemble averages
(a) $\langle v_x \rangle$
(b) $\langle v_y^2 \rangle$
(c) $\langle v^2 v_x \rangle$
(d) $\langle (v_x + bv_y)^2 \rangle$, $b = \text{const}$
(e) $\langle (v_x^3 v_y^2) \rangle$
(f) $\langle (v_x^2 v_y^2) \rangle$
(*Hint*: You may not have to do any integrals.)

4) In chemistry, a model for a non-ideal interacting gas is given by the **Lennard-Jones** potential

$$U = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \ , \tag{20}$$

where ϵ and σ are measured empirical values.
(i) Find the minimum of the potential, and plot the potential as a function of r.
(ii) In class, we showed that the Helmholtz free energy for an interacting gas is given by

$$F = F_{\text{id}} - k_bT \times I \tag{21}$$

where

$$I = \frac{N^2}{2V}\int d^3r f(r) \tag{22}$$

and

$$f(r) = e^{-\beta U(r)} - 1 \ . \tag{23}$$

By splitting the integral into $\int_0^\infty \to \int_0^\sigma + \int_\sigma^\infty$, argue that

$$\int_0^\sigma f(r) d^3r \approx -\frac{4\pi\sigma^3}{3} \ . \tag{24}$$

(*Note* : In fact, you don't have to split the integral into 2 parts – the integral can be exactly integrated from 0 to ∞ to yield an analytic closed form as hypergeometric functions, but it is unnecessarily complicated.)

(iii) Using the results of (ii), derive the Van der Waals equation of state

$$k_bT = \left(P + \frac{N^2}{V^2}a\right)\left(\frac{V}{N} - b\right) \ , \tag{25}$$

and find a and b in terms of ϵ and σ.

5) Consider a gas of non-interacting particles in 2D contained in an area A, in thermal equilibrium with temperature T. The particles obey the Hamiltonian

$$E = \frac{\mathbf{p}^2}{2m} \ , \ \mathbf{p} = (p_x, p_y) \ , \tag{26}$$

which gives its energy.
(i) Show that the partition function is give by

$$Z = \frac{1}{N!}\left(\frac{A}{\lambda^2}\right)^N \tag{27}$$

where λ is the thermal de Broglie wavelength

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_bT}} \ . \tag{28}$$

(ii) The "Pressure" P for a 2D gas can be defined as the force per unit length. Show that 2D ideal gas has the the equation of state $PA = Nk_bT$.

6) (**Ultra-relativistic Classical Ideal Gas**). Einstein's theory of special relativity tells us that the energy of a particle with mass m and absolute momentum p is given by

$$E^2 = m^2c^4 + p^2c^2 \ . \tag{29}$$

(i) Show that in the ultra-relativistic limit $pc \gg mc^2$, the energy is approximately

$$E = pc \ . \tag{30}$$

(Think of why we cannot assume $p = mv$ and taking $v \to c$ as the ultrarelavistic limit.)
(ii) Consider N ultra-relativistic non-interacting particles in a box of volume V, in 3 spatial dimemnsions. Show that the canonical partition function is given by

$$Z = \frac{1}{N!}\left[\frac{V}{\pi^2}\left(\frac{k_bT}{\hbar c}\right)^3\right]^N \ . \tag{31}$$

(iii) Show that the equation of state for an ultra-relativistic non-interacting gas is also given by the ideal gas law $PV = Nk_bT$.

7) Consider a gas of non-interacting particles which possess a hard core with radius r_0 (i.e. they cannot occupy each other's space). Such a particle can be modeled by a hardcore potential

$$U(r) = \begin{cases} \infty & , \quad r < r_0 \\ 0 & , \quad r > r_0 \end{cases} \ . \tag{32}$$

The gas is in thermal equilibrium inside a container at temperature T.

(*For this question, you may use any results from the lecture notes without proof.*)
(i) Calculate the equation of state for this gas in *three* dimensions, up to the virial coefficients to 2nd order. The volume of the container is V.

(ii) Suppose the particles are constrained to move only on a 2 dimensional plane, so instead of a hard core, they are *hard discs* with radius r_0. Calculate the equation of state for this gas in *two* dimensions, up to the virial coefficients to 2nd order. The area of the container is A. You may find the results from Q5 useful.

8) (**Statistical mechanics of a classical**[2] **piano string**). A piano string of length L is fixed at both ends. Its tension is tuned to τ, with a density per unit length of ρ (i.e. ρ has units of mass/length). Let $y(x,t)$ be the displacement of the string from its position at rest. It can be shown (can you show it?) that $y(x,t)$ obeys the wave equation

$$\frac{\partial^2 y}{\partial x^2} = \frac{\rho}{\tau}\frac{\partial^2 y}{\partial t^2} \ . \tag{33}$$

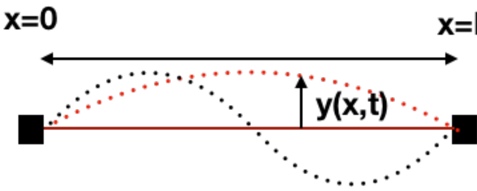

Figure 2: (Problem 8) Standing waves on a piano string.

(i) Show that the following *standing wave* is a solution to the above wave equation (for constant amplitiude $\zeta > 0$)

$$y(x,t) = \zeta \sin(k_n x)\cos(\omega_n t) \tag{34}$$

as long as the *dispersion relation* $\sqrt{\tau/\rho}k_n^2 = \omega_n^2$ is obeyed. Hence show that, given the fixed ends, the frequencies ω_n are given by

$$\omega_n = n\frac{\pi}{L}\sqrt{\frac{\tau}{\rho}} \ , \ n = 1, 2, 3, \ldots \tag{35}$$

These modes are called *harmonics* of the string.
(ii) The kinetic K and potential energy densities V of the string are given by (again, can you show it?)

$$K(x,t) = \frac{1}{2}\rho\left(\frac{\partial y}{\partial t}\right)^2 \ , \ V(x,t) = \frac{1}{2}\tau\left(\frac{\partial y}{\partial x}\right)^2 \ . \tag{36}$$

Show that the *total* energy carried by a mode n is given by

$$E_n = \frac{1}{4}\frac{\tau}{L}n^2\pi^2\zeta^2 \ . \tag{37}$$

(*Hint* : You might need to integrate over the length of the string to obtain the total energy from the energy densites.)
(iii) If we assume ζ to be a constant, we can model the string as a canonical ensemble with partition function

$$Z = \sum_n e^{-\beta E_n} \ . \tag{38}$$

One can think of this system as immersing the piano string in a large cloud of external particles with temperature T, which will periodically collide with the string to excite some of the harmonics. Argue that, the hotter the cloud, the more likely the higher harmonics are excited.
(iv) Suppose now we apply an infinitisimal force to *stretch* the string from $L \to L + dL$. Show that the work done on the string is given by

$$đW = \left(\tau - \frac{\langle E\rangle}{L}\right) dL \ . \tag{39}$$

[2] Classical as in classical physics, not classical music.

(*Hint:* You have to consider the work required to extend the length of the string itself, and also the effects of extending the string on the energies of the harmonics E_n.)

9) The atmosphere of the Earth is kept from escaping into deep space by Earth's gravity, which we can approximate by a constant acceleration coefficient g. We can model the Earth's atmosphere as an ideal gas at thermal equilibrium with temperature T. Choosing coordinates such that $z = 0$ is the surface of the Earth, and $z > 0$ is the atmosphere, the energy of each particle is then given by

$$E = \frac{\mathbf{p}^2}{2m} + mgz \tag{40}$$

where m is the mass of each particle.
(i) Show that the partition function for a single particle is given by

$$Z_1 = \frac{Ak_bT}{mg\lambda^3} \ , \tag{41}$$

where A is the area of the surface in consideration.
(ii) Show that the probability of finding a particle depends on the height z given by

$$P(z)dz = C \times e^{-mgz/k_bT}dz \tag{42}$$

where C is some constant of proportionality. Argue that this implies that the *density* of Earth's atmosphere is given by

$$\rho(z) = \rho(0)e^{-mgz/k_bT} \tag{43}$$

where $\rho(0)$ is the density at ground level. This is known as the "Law of atmospheres" which describes the density variations of the air near the surface of Earth at constant T.
(iii) The density of the atmosphere at ground level is $\rho(0) = 0.0012$ g/cm^3, the mean molar mass of air is 28.9 g/mol, with temperature $T = 300K$. Calculate the density of the atmosphere at a height of $z = 100$ km, which is the so-called Kármán Line that defines the beginning of outer space.

10) Consider a particle of mass m moving in 1 dimension, which obeys the following Hamiltonian

$$H(p,q) = \frac{p^2}{2m} + \lambda q^4 \ , \tag{44}$$

where p and q are the canonical momentum and canonical position respectively. Show that the heat capacity for a gas of N such particles is given by

$$C_V = \frac{3}{4}Nk_b \ . \tag{45}$$

You may use any appropriate theorems.