# PHYS 427 - Discussion 07

March 11, 2025

Here is a quick review of the grand canonical ensemble. Suppose a system $\mathcal{S}$ can exchange energy and particles with a reservoir $\mathcal{R}$. Suppose $\mathcal{R}$ has temperature $T$ and chemical potential $\mu$. If the combined system $\mathcal{S} + \mathcal{R}$ is in thermal and diffusive equilibrium, then the probability that $\mathcal{S}$ is in the microstate "$i$" is given by

$$p_i = \frac{e^{-\beta(E_i - \mu N_i)}}{\mathcal{Z}}, \tag{1}$$

where $\beta = \frac{1}{k_B T}$. Here, $E_i$ and $N_i$ are respectively the energy and number of particles in $\mathcal{S}$ when $\mathcal{S}$ is in microstate "$i$", and $\mathcal{Z}$ is the grand partition function

$$\mathcal{Z} \equiv \sum_i e^{-\beta(E_i - \mu N_i)}. \tag{2}$$

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1. **Langmuir isotherms.** A reservoir of monatomic ideal gas is in contact with the surface of a catalyst. The catalyst's surface has $\mathcal{N}$ adsorption sites. A single gas particle can attach onto each site. The energy of an empty site is 0, and that of an occupied site is $\epsilon < 0$, i.e. it is energetically favorable to bind.

   (a) Calculate the grand partition function of the catalyst.

   (b) Show that the chemical potential of the gas is $\mu = k_B T \ln(n/n_Q)$.
   *Hint: $S = N k_B \left[\ln(n_Q/n) + 5/2\right]$ and $n_Q$ is the number of "thermal de Broglie boxes" that fit into a unit volume. A "thermal de Broglie box" is a cube whose side length is the de Broglie wavelength $\frac{h}{p}$ of a gas particle whose kinetic energy is $\frac{p^2}{2m} \approx k_B T$.*

   (c) In equilibrium, the $T$ and $\mu$ of the catalyst and the gas are the same. Show that the fraction of occupied surface sites is given by $f(T, p) = p/(p + p_0(T))$. Find $p_0(T)$, and fill in the blank: $p_0$ is the pressure at which ____________________________.

   (d) It is energetically favorable for every site to be occupied ($\epsilon < 0$). Then $f = 1$ minimizes the energy, so why are we finding $f < 1$? Give a physical explanation without any equations.

   (e) Qualitatively sketch the *Langmuir adsorption isotherms* (the curves of constant $T$ in the $(P, f)$-plane) for small, medium, and large $T$. If we want to increase the occupation at fixed pressure, should we increase or decrease $T$?

   (f) **(Optional)** Prove the general formula $\langle N \rangle = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu}$ for *any* system in the grand canonical ensemble, where $N$ denotes the number of particles in the system. Also prove the formula $\sigma_N^2 = \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu}$, where $\sigma_N^2 \equiv \langle (N - \langle N \rangle)^2 \rangle$. Note $\sigma_N$ is called the variance or *root-mean-square deviation* (see why?)

   (g) **(Optional)** Show that the relative variance in number of particles adsorbed to the surface, $\frac{\sigma_N}{\langle N \rangle}$, is $\sqrt{\frac{1-f}{\mathcal{N} f}}$.

2. **Blackbody radiation.** Consider a hot cube-shaped oven with volume $V = L^3$. The walls radiate electromagnetic energy into the oven, producing a photon gas that comes into equilibrium with the walls at some temperature $T$. We want to understand how various properties of the photon gas—energy, pressure, etc.—depend on $T$ and $V$.

   From classical E&M, standing electromagnetic waves in the oven can only have certain wavenumbers $\vec{k} = \frac{\pi}{L}\vec{n}$, where $n_x, n_y, n_z \in \{1, 2, 3, \dots\}$. A standing wave can have one of two independent polarizations $p = 1, 2$ (e.g. horiontal or vertical). These allowed waves are called the *normal modes*. The frequency of a mode is $\omega = |\vec{k}|c$, independent of $p$.

   From quantum mechanics, the amount of energy stored in the mode $(\vec{n}, p)$ is quantized:

$$\text{energy in the mode } (\vec{n}, p) = \hbar\omega_{\vec{n}} s_{\vec{n},p} \qquad\qquad s_{\vec{n},p} = 0, 1, 2, \dots. \tag{3}$$

   We say "there are $s_{\vec{n},p}$ photons in the mode $(\vec{n}, p)$".

   (a) Calculate the average number of photons $\langle s_{\vec{n},p}\rangle$ in the mode $(\vec{n}, p)$. *Hint: work in the canonical ensemble. Consider the single mode $(\vec{n}, p)$ to be the "system". The other modes and the walls act as the "reservoir". Start by writing down the partition function for this system.*

   (b) Write down an expression for $U(\omega)d\omega$, the average amount of energy contained in all modes whose frequencies lie between $\omega$ and $\omega + d\omega$. Your expression will contain $\mathcal{D}(\omega)$, the density of modes per unit frequency interval. You don't need to calculate $\mathcal{D}(\omega)$ yet.

   (c) Calculate $\mathcal{D}(\omega)$. Insert the result in your answer to part (b) to obtain

$$U(\omega)d\omega = \frac{V\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega} - 1}d\omega. \tag{4}$$

   More often, we work with $u(\omega) \equiv U(\omega)/V$, the so-called *spectral energy density*.

   (d) Cut a small hole in the wall. The photons fly out in all possible directions at speed $c$. We define $I(\omega)d\omega$ to be the *intensity* (power per unit area) of radiation leaving the hole with frequencies between $\omega$ and $\omega + d\omega$. Show that

$$I(\omega)d\omega = \frac{1}{4}cu(\omega)d\omega. \tag{5}$$

   This result, when combined with $u(\omega)$ found above, is known as *Planck's law*. You don't need to obtain the factor of $\frac{1}{4}$ exactly (you can if you want), but at least make sure you understand why this factor should be less than $\frac{1}{2}$. A sketch is helpful.

   (e) Integrate equation (5) to find the total intensity $I_{\text{tot}}$ emitted by a blackbody over all frequencies. Without evaluating the integral, show

$$I_{\text{tot}} = \sigma T^4, \tag{6}$$

   where $\sigma$ is some constant that we won't compute now. This is the *Stefan-Boltzmann law*.

   (f) Photons carry momentum $\vec{p}$ as well as energy $\varepsilon$, related by $\varepsilon = |\vec{p}|c$. By considering the momentum deposited into the walls by the photons, show that the pressure $P$ of the gas is

$$P = \frac{1}{3}u_{\text{tot}}, \tag{7}$$

   where $u_{\text{tot}} = \int_0^\infty u(\omega)d\omega$ is the total energy density[1].

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[1] Another way: the partition function for the whole gas is $Z = \prod_{\vec{n},p}\frac{1}{1-e^{-\beta\hbar\omega_{\vec{n}}}}$, so we have $F = -k_BT\ln Z = k_BT\sum_{\vec{n},p}\ln(1 - e^{-\beta\hbar\omega_{\vec{n}}}) \to k_BT\int_0^\infty d\omega\ \mathcal{D}(\omega)\ln(1 - e^{-\beta\hbar\omega}) = -\frac{1}{3}u_{\text{tot}}V$. To get the last equality, integrate by parts using $\int\mathcal{D}(\omega)d\omega = \frac{1}{3}\omega\mathcal{D}(\omega)$ and notice the resulting integrand is $u(\omega)$. Then use $P = -(\partial F/\partial V)_T$ to get equation (7).