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 μ. 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.

   Solution. If $\mathcal{N} = 2$, then

   $$\mathcal{Z} = 1 + 2e^{-\beta(\epsilon - \mu)} + e^{-\beta(2\epsilon - 2\mu)} = (1 + e^{-\beta(\epsilon - \mu)})^2. \tag{3}$$

   For general $\mathcal{N}$, the answer is $\mathcal{Z} = (1 + e^{-\beta(\epsilon - \mu)})^{\mathcal{N}}$. You can prove this using the binomial theorem.

   To see how it works, let's do it for $\mathcal{N} = 3$ taking care to write things a certain way. The number of states with $N = 0$ particles is $\binom{3}{0}$, the number of ways to choose zero of the sites to be occupied. The number of states with $N = 1$ particles is $\binom{3}{1}$, the number of ways to choose one of the sites to be occupied. And so on. So

   $$\mathcal{Z} = \binom{3}{0} + \binom{3}{1}e^{-\beta(\epsilon - \mu)} + \binom{3}{2}e^{-\beta(2\epsilon - 2\mu)} + \binom{3}{3}e^{-\beta(3\epsilon - 3\mu)} \tag{4}$$

   $$= \sum_{k=0}^{\mathcal{N}} \binom{\mathcal{N}}{k} \left[e^{-\beta(\epsilon - \mu)}\right]^k \tag{5}$$

   $$= \left(1 + e^{-\beta(\epsilon - \mu)}\right)^3 \tag{6}$$

   (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 $\frac{p^2}{2m} \approx k_B T$.

Solution. The hint is just to establish that $n_Q \sim T^{3/2}$, and remind you of the physical meaning of n_Q along the way. It's fine to just recall $n_Q \sim T^{3/2}$ from the formula sheet. But as an aside, let's invert the logic of the hint, because it's instructive.

Aside: Consider an isolated ideal monatomic gas. Suppose we wanted to count the multiplicity of a single particle in position space rather than momentum space as in the first part of the course. And let's be sloppy about it. The typical momentum of a particle is going to be found from $p^2/2m \approx k_B T$, which gives $p = \sqrt{2mk_B T}$. By the Heisenberg relation $\Delta x \Delta p \sim \hbar$, I conclude $\Delta x \approx \frac{\hbar}{\sqrt{2mk_B T}}$. So the volume occupied by the particle is $(\Delta x)^3 \approx \left(\frac{\hbar^2}{2mk_B T}\right)$. The number of spatially localized quantum states that can be fit in a unit volume, aka the "quantum density" (that's where it gets its name), is therefore $n_Q \approx (\Delta x)^{-3}$. So the number of quantum states that can be fit in the container, i.e. the multiplicity of a single particle, is $\Omega_1 = n_Q V$, and the multiplicity of N particles is $\Omega_N = \Omega_1^N/N!$. Then using Stirling's approximation you can find $S = k_B \ln \Omega_N = N k_B \left[\ln \frac{n_Q}{n} + 1\right]$. That's not quite right, but it's remarkably close given how sloppy we were.

From $dU = TdS - pdV + \mu dN$, we find $\mu = -T(\partial S/\partial N)_{U,V}$. So we need to express S in terms of N, U, and V. We recall $n = N/V$. What do we do about n_Q? Well we know $n_Q \sim T^{3/2}$, and $U \sim NT$ by equipartition, so $n_Q \sim U^{3/2}N^{-3/2}$. Then

$$S = N k_B \left[\ln\left(cN^{-5/2}\right) + \frac{5}{2}\right], \tag{7}$$

where c is something that only depends on U, V, and constants. Now we compute

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = \frac{S}{N} + N k_B \left[-\frac{5}{2}\frac{1}{N}\right] = k_B \ln\left(cN^{-5/2}\right) = k_B \ln(n_Q/n). \tag{8}$$

Multiplying by $-T$ gives the desired result.

(c) In equilibrium, the T and μ 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 _____.

Solution. One way to do this is to notice $f = \frac{\langle N \rangle}{\mathcal{N}}$, and compute $\langle N \rangle = \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \mu}$ (the average number of particles on the catalyst).

A simpler way is to take the "system" to be a single site, rather than the entire $\mathcal{N}$-site catalyst. Then, for this system, $\mathcal{Z} = 1 + e^{-\beta(\epsilon-\mu)}$. Also, f is the average number of particles in this one-site system, which is by definition given by $\sum_i N_i p_i$ (here p_i is a probability, not pressure, sorry for the notation). We have

$$f = 0 \cdot p_0 + 1 \cdot p_1, \tag{9}$$

where $p_1 = e^{-\beta(\epsilon-\mu)}/\mathcal{Z}$ is the probability of a single particle being in the one-site system. So

$$f = \frac{e^{-\beta(\epsilon-\mu)}}{1 + e^{-\beta(\epsilon-\mu)}} = \frac{1}{1 + e^{\beta(\epsilon-\mu)}}. \tag{10}$$

Now we use the fact that the μ and T of the catalyst in this equation are the same as those of the gas, when the two are in equilibrium. Therefore $\mu = k_B T \ln(n/n_Q)$, or $e^{-\beta\mu} = n_Q/n$. Also from the ideal gas law, $p = nk_B T$ so $\mu = k_B T n_Q/p$. Then

$$f = \frac{1}{1 + \frac{k_B T n_Q}{p}e^{\beta\epsilon}} = \frac{p}{p + p_0(T)}, \tag{11}$$

where $p_0(T) = k_B T n_Q e^{\beta\epsilon}$.

(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.

Solution. A thermal system in equilibrium doesn't minimize the energy. For an isolated system, the principle is that the entropy is maximal in equilibrium (likeliest macrostate is the one with the most microstates). In the grand canonical ensemble, "system plus reservoir" is isolated. By applying the principle of maximum entropy to "system plus reservoir", we concluded in lecture that the grand potential $\Phi = U - TS - \mu N$ is minimized in equilibrium. Hence there is a tradeoff. If we tried to minimize the energy, then S would get small (actually zero), so Φ would be big compared to its minimum possible value. In equilibrium, the system hits a sweet spot where any benefit of lowering the energy is balanced by the accompanying cost of its entropy decreasing.

(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?

Solution. At constant T, $p_0(T)$ is constant. The isotherms are just the graphs of $f(p) = p/(p + p_0)$ with different values of p_0. Note that $p_0(T) \propto T^{5/2}e^{\epsilon/k_BT}$, which increases with increasing T because $\epsilon < 0$. If we want to increase f at a fixed p, we must decrease p_0, hence we must decrease T. It makes sense that f should increase as T decreases, because all the way at $T = 0$ we expect the catalyst to be in its ground state where $f = 1$ (as large as it can be).

(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 σ_N is called the variance or *root-mean-square deviation* (see why?)

Solution.

$$\frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \mu} = \frac{1}{\beta}\frac{1}{\mathcal{Z}}\sum_i \frac{\partial}{\partial \mu}e^{-\beta(E_i - \mu N_i)} = \frac{1}{\beta}\frac{1}{\mathcal{Z}}\sum_i \beta N_i e^{-\beta(E_i - \mu N_I)} = \sum_i N_i p_i \equiv \langle N \rangle. \tag{12}$$

To prove the other formula, use the above result for $\langle N \rangle$, compute $\frac{1}{\beta}\frac{\partial \langle N \rangle}{\partial \mu}$, and show that it equals $\langle N^2 \rangle - \langle N \rangle^2$, which is equal to σ_N^2. Note that $\langle N^2 \rangle \equiv \sum_i N_i^2 p_i$.

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

Solution. By definition of f, we have $\langle N \rangle = \mathcal{N}f$. From the formula in the previous part, and the fact that $f = 1/(1 + e^{\beta(\epsilon - \mu)})$.

$$\sigma_N^2 = \mathcal{N}\frac{1}{\beta}\frac{\partial f}{\partial \mu} = \mathcal{N}\frac{e^{\beta(\epsilon - \mu)}}{(1 + e^{\beta(\epsilon - \mu)})^2} = \mathcal{N}f(1 - f). \tag{13}$$

Then $\sigma_N^2/\langle N \rangle^2 = (1 - f)/\mathcal{N}f$. The main thing to notice is that this goes to zero as $\mathcal{N} \to \infty$. So the thermal fluctuations in the number of adsorbed particles becomes negligible when there are many sites.

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:

$$\text{energy in the mode } (\vec{n}, p) = \hbar\omega_{\vec{n}}s_{\vec{n},p} \qquad s_{\vec{n},p} = 0, 1, 2, \dots. \tag{14}$$

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.*

Solution. The canonical partition function for the mode $(\vec{n}, p)$ is

$$Z = \sum_{s_{\vec{n},p}=0}^{\infty} e^{-\beta s_{\vec{n},p}\hbar\omega_{\vec{n}}} = \sum_{s_{\vec{n},p}=0}^{\infty} [e^{-\beta\hbar\omega_{\vec{n}}}]^{s_{\vec{n},p}} = \frac{1}{1 - e^{-\beta\hbar\omega_{\vec{n}}}}, \tag{15}$$

where I used the geometric series. The average energy in the mode $(\vec{n}, p)$ is

$$\frac{\hbar\omega_{\vec{n}}}{\beta}\frac{\partial \ln Z}{\partial \beta} = \frac{1}{e^{\beta\hbar\omega_{\vec{n}}} - 1}. \tag{16}$$

The number of photons is the number of packets of energy $\hbar\omega_{\vec{n}}$ contained in the mode, i.e. the average energy in the mode divided by $\hbar\omega_{\vec{n}}$, i.e.

$$\langle s_{\vec{n},p} \rangle = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \beta} = \frac{1}{e^{\beta\hbar\omega_{\vec{n}}} - 1}. \tag{17}$$

(b) Write down an expression for $U(\omega)d\omega$, the average amount of energy contained in all modes whose frequencies lie between ω 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.

Solution. The number of modes between ω and $\omega + d\omega$ is $\mathcal{D}(\omega)d\omega$ by definition. From the previous part, each of those modes contiains energy $\hbar\omega_{\vec{n}}/(e^{\beta\hbar\omega_{\vec{n}}} - 1)$ on average. So we just multiply the two:

$$U(\omega)d\omega = \frac{\hbar\omega_{\vec{n}}}{e^{\beta\hbar\omega_{\vec{n}}} - 1}\mathcal{D}(\omega)d\omega. \tag{18}$$

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

$$U(\omega)d\omega = \frac{V\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega} - 1}d\omega. \tag{19}$$

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

Solution. We have $\omega = ck$, so $d\omega = cdk$. To count the number of modes with frequencies between ω and $\omega + d\omega$, which is the definition of $\mathcal{D}(\omega)d\omega$, we need to calculate the number of allowed wavevectors contained in the $\vec{k}$-space region between radii k and $k + dk$ within the first octant. Only the first octant, because the allowed wavevectors are only in the first octant (see problem statement). The volume in $\vec{k}$-space is therefore $\frac{1}{8}4\pi k^2 dk$. The $\vec{k}$-space volume per allowed wavevector is $(\pi/L)^3$. So

$$\mathcal{D}(\omega)d\omega = 2\frac{\frac{1}{8}4\pi k^2 dk}{(\pi/L)^3}. \tag{20}$$

The factor of 2 out front is because there are two photon polarizations for every allowed wavevector. After simplifying, and putting $k = \omega/c$ and $dk = d\omega/c$, we find

$$\mathcal{D}(\omega)d\omega = \frac{V\omega^2}{\pi^2 c^3}d\omega. \tag{21}$$

Inserting this into the answer to the previous part gives the desired result.

(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 ω and $\omega + d\omega$. Show that

$$I(\omega)d\omega = \frac{1}{4}cu(\omega)d\omega. \tag{22}$$

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.

Solution. Suppose the wall is perpendicular to the z-direction. Suppose for some reason that all of the photons are moving in the positive z-direction (even though they're not). In that case, how much energy leaves the hole in a time Δt? Well, the volume of photon gas that leaves the hole will be $Ac\Delta t$, where A is the area of the hole and $c\Delta t$ is the distance photons travel in time Δt. The energy of the photons with frequencies between ω and $\omega + d\omega$ that passed through the hole is therefore $u(\omega)d\omega \, Ac\Delta t$. The intensity contributed by photons with frequencies between ω and $\omega + d\omega$ is this divided by Δt and by A, i.e. $cu(\omega)d\omega$. But we assumed all the photon were moving along the $+z$-direction, which is obviously wrong. It's a little better to assume half of the particles are moving along $+z$ and half along $-z$. Then the intensity we find would be $\frac{1}{2}cu(\omega)d\omega$. But in reality, the photons can be moving at an angle, not just along the z-axis. Taking this into account gives the $1/4$. It requires evaluating a geometrical integral and will be done in the lecture notes later on.

(e) Integrate equation (22) to find the total intensity I_{tot} emitted by a blackbody over all frequencies. Without evaluating the integral, show

$$I_{\text{tot}} = \sigma T^4, \tag{23}$$

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

Solution. From the previous parts,

$$I_{\text{tot}} = \int_0^\infty I(\omega)d\omega \propto \int_0^\infty u(\omega)d\omega \propto \int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1}d\omega, \tag{24}$$

where the proportionality constants are things independent of T, like the speed of light and volume and $\hbar$ and so on. Now multiply the right-hand side by $\frac{(\beta\hbar)^4}{(\beta\hbar)^4} = 1$. We find

$$I_{\text{tot}} \propto \frac{1}{\beta^4}\int_0^\infty \frac{(\beta\hbar\omega)^3}{e^{\beta\hbar\omega} - 1}d(\beta\hbar\omega) = \frac{1}{\beta^4}\int_0^\infty \frac{x^3}{e^x - 1}dx \tag{25}$$

The integral is now some pure number that you can look up in a table of integrals, or compute with some tricks discussed in the lecture notes. But the main point is that the T-dependence is $\beta^{-4} \sim T^4$, i.e. $I_{\text{tot}} = \sigma T^4$ where σ is something that doesn't depend on T.

(f) Photons carry momentum $\vec{p}$ as well as energy ε, 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

$$P = \frac{1}{3}u_{\text{tot}}, \tag{26}$$

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

Solution. The reasoning is similar to part (d). Suppose the wall is perpendicular to $\hat{z}$. Suppose for some reason all of the photons are moving in the positive z-direction. Then the total amount of energy that hits the an area A on the wall during time Δt is $u_{\text{tot}} Ac\Delta t$. The momentum that hits the wall is obtained by dividing by c, i.e. $u_{\text{tot}} A\Delta t$, and all of that momentum is reflected back, so the total change in momentum is $\Delta p = 2u_{\text{tot}} A\Delta t$. The force experienced by that piece of the wall is $\Delta p/\Delta t = 2u_{\text{tot}} A$, and the pressure is that divided by A, i.e. $P = 2u_{\text{tot}}$. But we assumed all the photons were going in the positive z direction. If we assumed half were going in the positive z direction and half in the negative z direction, we would have found $P = u_{\text{tot}}$. But we still haven't taken into account that the photons are flying in all possible directions. This ends up reducing it to $P = \frac{1}{3}u_{\text{tot}}$. To see this exactly requires doing a geometric integral, and it'll be done later in the course. But see the footnote for a nice method that doesn't involve a geometric integral.

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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 $F = -k_B T \ln Z = k_B T \sum_{\vec{n},p} \ln\left(1 - e^{-\beta\hbar\omega_{\vec{n}}}\right) \to k_B T \int_0^\infty d\omega \; \mathcal{D}(\omega) \ln\left(1 - e^{-\beta\hbar\omega}\right) = -\frac{1}{3}u_{\text{tot}}V$. 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 (26).