11. (Statistical Mechanics)

When a certain molecule A absorbs a photon it decays into molecules B and C according to the reaction $\gamma + A \to B + 3C$. The time reversed process is also possible. The masses of the molecules are m_A, m_B, and m_C. Let E_b be the binding energy (i.e. E_b is the minimum photon energy needed to produce the reaction).

Assume the validity of non-relativistic statistical mechanics and Maxwell-Boltzmann statistics for the molecules. Further, ignore the internal degrees of freedom of the molecules.

(a) Now suppose some A, B, and C molecules are placed in a box, whose walls can absorb and emit photons, and allowed to come to thermal equilibrium at temperature T. What is the density per unit volume, n_A of A molecules in terms of the densities $n_{B,C}$ of B and C molecules? Your answer should involve (n_B, n_C, m_A, m_B, m_C, E_b) as well as fundamental constants.

(b) Now suppose that the photon γ is replaced by another particle γ^* which has mass m^* (and is relativistic), spin-1 (and so obeys Bose-Einstein statistics), and which is not emitted/absorbed by the walls of the box. We start with some number of γ^* particles and molecules in the box and let the system come to thermal equilibrium at temperature T. Derive an expression for the density n_{γ^*} in the box in terms of the densities of molecules n_A, n_B, n_C. Your answer can be given in the form of an unevaluated integral.

Solution: *Solution by Jonah Hyman (jthyman@g.ucla.edu)*

This problem asks for the relative number density of two different types of particles, which places it into a common category of comp problem:

Chemical potential matching:
When a statistical mechanics problem asks you to compare the number of noninteracting classical particles of two different types, you should set the chemical potentials of each type of particle equal to one another.
The chemical potential is the free energy needed to add a particle of a certain type, i.e, the partial derivative of F with respect to N: $\mu = \frac{\partial F}{\partial N}\big|_{T,V}$. For that reason, the following statements are all equivalent for a system of noninteracting particles of types 1 and 2, where a particle of one type can become a particle of the other type:
A. The system is in thermodynamic equilibrium.
B. The free energy of the system is minimized.
C. The change in free energy when a particle of type 1 becomes a particle of type 2 is zero.
D. The free energy needed to subtract a particle of type 1, plus the free energy needed to add a particle of type 2, is zero.
E. The chemical potential of type 1 particles is equal to the chemical potential of type 2 particles: $-\mu_1 + \mu_2 = 0$, or $\mu_1 = \mu_2$.
To find the chemical potential of a system of noninteracting classical particles of a certain type:
1. Calculate the partition function for that type of particle. For noninteracting, indistinguishable classical particles, the partition function for all the particles Z can be written in terms of the partition function for one particle Z_1 using $Z = Z_1^N/N!$.
2. Calculate the free energy for that type of particle using $F = -kT \ln Z$.
3. The chemical potential is the free energy needed to add a particle of a certain type, i.e, the partial derivative of F with respect to N: $\mu = \frac{\partial F}{\partial N}\big|_{T,V}$.
If there is a constant energy shift between the types of particles (i.e. each particle of type 1 has an energy ϵ greater than a particle of type 2), then the chemical potentials of the types of particles should have the same energy shift (the chemical potential for particles of type 1 is ϵ greater than the chemical potential for particles of type 2).
In chemical reactions, there are cases in which one particle of type 1 becomes multiple particles of type 2. In that case, the chemical potential of each type of particle must be multiplied by the multiplicity of the particle.

To find the partition function in the classical limit, we also need to know about the phase-space formalism:

Phase space:
Consider a particle in d-dimensional space. The particle's state can be defined by its position $\mathbf{x} = (x_1, \ldots, x_d)$, its momentum $\mathbf{p} = (p_1, \ldots, p_d)$, and any internal degrees of freedom (e.g. spin). Assume that there are g possible internal states for the particle.
The position and momentum of the particle constitute a point in $2d$-dimensional phase space: $(x_1, \ldots, x_d, p_1, \ldots, p_d)$.
To solve problems, discretize phase space by dividing it into $2d$-dimensional boxes. The volume of each box is h^d, where h is Planck's constant (which has units of position times momentum). The number of boxes in a phase-space volume $d^d p\, d^d x$ is the total volume divided by the volume of each box, or $\frac{d^d p\, d^d x}{h^d}$. Each box has g possible states, corresponding to the internal degrees of freedom of the particle. Therefore, the number of possible states in a phase-space volume $d^d p\, d^d x$ is

$$\text{Number of possible states in a phase-space volume } d^d p\, d^d x = g\frac{d^d p\, d^d x}{h^d} \tag{399}$$

In this problem, we need to match the chemical potential of the reactants (one photon and one A molecule) with the chemical potential of the products (one B and three C molecules).

(a) Since the problem specifies that the walls can absorb and emit photons, the chemical potential of the photon is zero. Therefore, the chemical potential of the reactants is solely due to the A molecules.

We will set the zero point for energy to be a product state $B + 3C$ with zero kinetic energy. Since the binding energy of the reaction is E_b, the product state $B + 3C$ has energy E_b greater than the A molecule. To account for this, we apply a negative energy shift $-E_b$ to each A molecule.

Using the phase-space formalism for classical noninteracting point particles, the partition function for a single A molecule is

$$Z_{1,A} = \int \frac{d^3p\, d^3x}{h^3} e^{-\beta E_A} \quad \text{where } \beta \equiv \frac{1}{kT} \tag{400}$$

The energy of a single A molecule is its nonrelativistic kinetic energy, minus the energy shift:

$$E_A = \frac{p^2}{2m_A} - E_b \tag{401}$$

Plugging this in and carrying out the spatial integral for the partition function, we get

$$\begin{aligned} Z_{1,A} &= \int \frac{d^3p\, d^3x}{h^3} e^{-\beta\left(\frac{p^2}{2m_A} - E_b\right)} \\ &= e^{\beta E_b} \int \frac{d^3p\, d^3x}{h^3} e^{-\beta p^2/(2m_A)} \\ &= e^{\beta E_b} \frac{V}{h^3} \int d^3p\, e^{-\beta p^2/(2m_A)} \quad \text{since } \int d^3x = V \\ &= e^{\beta E_b} \frac{V}{h^3} \left[\int_{-\infty}^{\infty} dp_x\, e^{-\beta p_x^2/(2m_A)}\right] \left[\int_{-\infty}^{\infty} dp_y\, e^{-\beta p_y^2/(2m_A)}\right] \left[\int_{-\infty}^{\infty} dp_z\, e^{-\beta p_z^2/(2m_A)}\right] \end{aligned} \tag{402}$$

Each of these three integrals is the same Gaussian integral, which can be calculated by a change of coordinates $u \equiv (\beta/(2m_A))^{1/2}\, p = (2m_A kT)^{-1/2}\, p$:

$$\begin{aligned} \int_{-\infty}^{\infty} dp\, e^{-\beta p^2/(2m_A)} &= (2m_A kT)^{1/2} \int_{-\infty}^{\infty} du\, e^{-u^2} \\ &= (2\pi m_A kT)^{1/2} \quad \text{using the result } \int_{-\infty}^{\infty} du\, e^{-u^2} = \pi^{1/2} \end{aligned} \tag{403}$$

Plugging this back into (402), we get

$$\begin{aligned} Z_{1,A} &= e^{\beta E_b} \frac{V}{h^3} (2\pi m_A kT)^{3/2} \\ &= e^{\beta E_b} V \left(\frac{2\pi m_A kT}{h^2}\right)^{3/2} \\ Z_{1,A} &= e^{\beta E_b} \frac{V}{\lambda_A^3} \quad \text{for} \quad \lambda_A \equiv \left(\frac{h^2}{2\pi m_A kT}\right)^{1/2} \end{aligned} \tag{404}$$

The quantity λ_A is called the thermal wavelength.

Assuming the A molecules are indistinguishable and noninteracting classical particles, the partition function for all A molecules is related to the partition function for one A molecule. For simplicity, in this part of the solution, N refers to the number of A molecules.

$$Z_A = \frac{Z_{1,A}^N}{N!} = \frac{1}{N!}\frac{V^N}{\lambda_A^{3N}} \quad \text{for} \quad \lambda_A \equiv \left(\frac{h^2}{2\pi m_A kT}\right)^{1/2} \tag{405}$$

To find the free energy for the A molecules, use the definition of F in terms of Z:

$$\begin{aligned}
F_A &= -kT \ln Z_A \\
&= -kT \ln\left(\frac{1}{N!} e^{N\beta E_b} \frac{V^N}{\lambda_A^{3N}}\right) \\
&= -kT \left(\ln e^{N\beta E_b} + \ln V^N - \ln \lambda_A^{3N} - \ln N!\right) \quad \text{using } \ln(AB) = \ln A + \ln B \\
&= -kT \left(N\beta E_b + N \ln V - 3N \ln \lambda_A - \ln N!\right) \quad \text{using } \ln x^n = n \ln x \\
&= -NE_b - NkT \ln V + 3NkT \ln \lambda_A + kT \ln N! \quad \text{using } \beta = \frac{1}{kT} \\
&\approx -NE_b - NkT \ln V + 3NkT \ln \lambda_A + kT \left(N \ln N - N\right) \\
&\quad \text{by Stirling's formula } \ln N! \approx N \ln N - N
\end{aligned} \tag{406}$$

To get from the free energy to the chemical potential for the A molecules, take the partial derivative of the free energy with respect to N:

$$\begin{aligned}
\mu_A &= \left.\frac{\partial F_A}{\partial N}\right|_{T,V} \\
&= -E_b - kT \ln V + 3kT \ln \lambda_A + kT \left(\ln N + N\left(\frac{1}{N}\right) - 1\right) \\
&= -E_b - kT \ln V + 3kT \ln \lambda_A + kT \ln N \\
&= -E_b + kT \left(-\ln V + 3 \ln \lambda_A + \ln N\right) \\
&= -E_b + kT \ln\left(\frac{N}{V}\lambda_A^3\right)
\end{aligned}$$

Since N is the number of A molecules, N/V is the number density of A molecules, which we will call n_A:

$$\mu_A = -E_b + kT \ln\left(n_A \lambda_A^3\right) \quad \text{for} \quad \lambda_A \equiv \left(\frac{h^2}{2\pi m_A kT}\right)^{1/2} \tag{407}$$

The partition functions for the B and C particles are essentially the same as for the A molecules, except for the lack of an energy shift $-E_b$:

$$Z_{1,B} = \int \frac{d^3p\, d^3x}{h^3} e^{-\beta p^2/(2m_B)} \quad \text{and} \quad Z_{1,C} = \int \frac{d^3p\, d^3x}{h^3} e^{-\beta p^2/(2m_C)} \tag{408}$$

We can therefore follow the same process as for the A molecules to get the chemical potentials for the B and C particles:

$$\mu_B = kT \ln\left(n_B \lambda_B^3\right) \quad \text{and} \quad \mu_C = kT \ln\left(n_C \lambda_C^3\right) \quad \text{for} \quad \lambda_i \equiv \left(\frac{h^2}{2\pi m_i kT}\right)^{1/2} \tag{409}$$

Note that in the classical limit, where $n_i \ll \frac{1}{\lambda_i^3}$ (when the gas is very diffuse), the chemical potential is negative. This is a general fact for a classical ideal gas.

To complete this part of the problem, we need to match the chemical potentials. At thermodynamic equilibrium, the free energy of the system is minimized. Therefore, the change in free energy when an A molecule and a photon become a B molecules and three C molecules is zero. Since the chemical potential is the free energy to add a particle, this condition means that

$$\begin{aligned} -\mu_A + \mu_B + 3\mu_C &= 0 \\ \implies \mu_A &= \mu_B + 3\mu_C \end{aligned} \tag{410}$$

Note the extra factor of 3, which comes from the fact that one A molecule produces three C molecules, instead of just one.

We now plug in the earlier expressions for the chemical potentials (407) and (409):

$$-E_b + kT \ln\left(n_A \lambda_A^3\right) = kT \ln\left(n_B \lambda_B^3\right) + 3kT \ln\left(n_C \lambda_C^3\right) \tag{411}$$

The last step is to solve for n_A:

$$\begin{aligned} kT \ln\left(n_A \lambda_A^3\right) &= E_b + kT \ln\left(n_B \lambda_B^3\right) + 3kT \ln\left(n_C \lambda_C^3\right) \\ \ln\left(n_A \lambda_A^3\right) &= \frac{E_b}{kT} + \ln\left(n_B \lambda_B^3\right) + 3\ln\left(n_C \lambda_C^3\right) \\ \ln\left(n_A \lambda_A^3\right) &= \frac{E_b}{kT} + \ln\left[\left(n_B \lambda_B^3\right)\left(n_C \lambda_C^3\right)^3\right] \quad \text{using logarithm rules} \\ n_A \lambda_A^3 &= \exp\left(-\frac{E_b}{kT} + \ln\left[\left(n_B \lambda_B^3\right)\left(n_C \lambda_C^3\right)^3\right]\right) \\ n_A \lambda_A^3 &= e^{E_b/(kT)}\left(n_B \lambda_B^3\right)\left(n_C \lambda_C^3\right)^3 \\ n_A &= e^{E_b/(kT)}\, n_B n_C^3 \left(\frac{\lambda_B \lambda_C^3}{\lambda_A}\right)^3 \end{aligned} \tag{412}$$

Using the definition of the thermal wavelength, $\lambda_i \equiv \left(\frac{h^2}{2\pi m_i kT}\right)^{1/2}$, we can simplify the last factor:

$$\begin{aligned} \frac{\lambda_B \lambda_C^3}{\lambda_A} &= \frac{\left(\frac{h^2}{2\pi m_B kT}\right)^{1/2}\left(\frac{h^2}{2\pi m_C kT}\right)^{3/2}}{\left(\frac{h^2}{2\pi m_A kT}\right)^{1/2}} \\ &= \left(\frac{h^2}{2\pi kT}\right)^{3/2}\left(\frac{m_A}{m_B m_C^3}\right)^{1/2} \end{aligned} \tag{413}$$

Plugging this into (412), we get the final answer:

$$n_A = e^{E_b/(kT)}\, n_B^3 n_C \left(\left(\frac{h^2}{2\pi kT}\right)^{3/2}\left(\frac{m_A}{m_B m_C^3}\right)^{1/2}\right)^3$$

$$\boxed{n_A = e^{E_b/(kT)}\, n_B^3 n_C \left(\frac{h^2}{2\pi kT}\right)^{9/2}\left(\frac{m_A}{m_B m_C^3}\right)^{3/2}} \tag{414}$$

Note the Boltzmann factor $e^{E_b/(kT)}$. This factor means that since the A molecules have lower energy than the B and C molecules, the number density of the A molecules is correspondingly greater.

(b) As in part (a), our starting point involves matching the chemical potentials for the reactants and products in the process

$$\gamma^* + A \longrightarrow B + 3C \tag{415}$$

Only a slight modification of our part (a) chemical-potential matching equation (410) is needed here. In part (a), the chemical potential of the photon is zero; here, the chemical potential of the γ^* particle is nonzero and must be accounted for. The change in free energy when an A molecule and a photon γ^* become a B molecule and three C molecules is zero, meaning that

$$-\mu_A - \mu_{\gamma^*} + \mu_B + 3\mu_C = 0 \tag{416}$$

We can solve this equation for μ_{γ^*}, which we don't know. This gives us

$$\mu_{\gamma^*} = -\mu_A + \mu_B + 3\mu_C \tag{417}$$

Plugging in the expressions for the chemical potentials of the A, B, and C molecules, (407) and (409), we get

$$\begin{aligned}\mu_{\gamma^*} &= E_b - kT\ln\left(n_A\lambda_A^3\right) + kT\ln\left(n_B\lambda_B^3\right) + 3kT\ln\left(n_C\lambda_C^3\right) \\ &= E_b + kT\ln\left(\frac{n_B n_C^3}{n_A}\right) + kT\ln\left(\frac{\lambda_B\lambda_C^3}{\lambda_A}\right)^3\end{aligned} \tag{418}$$

Now that we have the chemical potential for the γ^* particle, how do we find the number density of γ^* particles? The key is the occuptation number formalism:

Occupation numbers:
When a statistical mechanics problem describes a system of bosons or fermions, you should consider using occupation numbers.
Occupation numbers describe the average number of particles in each state.

$$\text{For fermions (Fermi-Dirac statistics):} \quad n^{FD}(\epsilon_k,\mu) = \frac{1}{e^{\beta(\epsilon_k-\mu)}+1} \tag{419}$$

$$\text{For bosons (Bose-Einstein statistics):} \quad n^{BE}(\epsilon_k,\mu) = \frac{1}{e^{\beta(\epsilon_k-\mu)}-1} \tag{420}$$

$$\text{For classical particles (Maxwell-Boltzmann statistics):} \quad n^{MB}(\epsilon_k,\mu) = e^{-\beta(\epsilon_k-\mu)} \tag{421}$$

Here, ϵ_k is the energy of the state k, μ is the chemical potential, and $\beta = 1/(kT)$.

In this case, the γ^* particles are spin-1 particles, so Bose-Einstein statistics apply. They are relativistic particles, so the energy of a single particle γ^* state with momentum $\mathbf{p}$ is given by the standard energy-momentum relationship in special relativity:

$$\epsilon_*(\mathbf{p}) = \sqrt{(pc)^2 + (m_*c^2)^2} \tag{422}$$

Therefore, the average number of γ^* particles per state of momentum $\mathbf{p}$ is given by

$$\begin{aligned}n_*^{BE}(\mathbf{p}) &= \frac{1}{e^{\beta\epsilon_*(\mathbf{p}-\mu_{\gamma^*})}-1} \\ &= \left[\exp\left[\beta\left(\sqrt{(pc)^2+(m_*c^2)^2}-\mu_{\gamma^*}\right)\right]-1\right]^{-1}\end{aligned} \tag{423}$$

To get the total number of γ^* particles, use the following relation:

Number of particles in a phase-space volume $d^3p\,d^3x$

$= \big($Number of states in the phase-space volume $d^3p\,d^3x\big) \cdot$ (Average number of particles per state)

(399) tells us that the number of states in the phase-space volume $d^3p\,d^3x$ is $g\frac{d^3p\,d^3x}{h^d}$. Here, g is the number of internal states for each γ^* particle. Since the electron is a spin-1 particle, there are three internal states and so $g = 3$. The average number of particles per state is just the occupation number $n_c^{BE}(\mathbf{p})$ found in (423). With that in mind, we get

$$\begin{aligned}&\text{Number of } \gamma^* \text{ particles in a phase-space volume } d^3p\,d^3x\\ &\quad= 3\frac{d^3p\,d^3x}{h^3}\,\left[\exp\left[\beta\left(\sqrt{(pc)^2+(m_*c^2)^2}-\mu_{\gamma^*}\right)\right]-1\right]^{-1}\end{aligned} \tag{424}$$

To find the total number of γ^* particles, integrate over phase space:

$$N_{\gamma^*} = 3\int \frac{d^3p\,d^3x}{h^3}\,\left[\exp\left[\beta\left(\sqrt{(pc)^2+(m_*c^2)^2}-\mu_{\gamma^*}\right)\right]-1\right]^{-1}$$

The integral over d^3x yields the volume of space:

$$N_{\gamma^*} = 3V\int \frac{d^3p}{h^3}\,\left[\exp\left[\beta\left(\sqrt{(pc)^2+(m_*c^2)^2}-\mu_{\gamma^*}\right)\right]-1\right]^{-1}$$

To find the number density of γ^* particles, divide both sides by V:

$$n_{\gamma^*} \equiv \frac{N_{\gamma^*}}{V} = 3\int \frac{d^3p}{h^3}\,\left[\exp\left[\beta\left(\sqrt{(pc)^2+(m_*c^2)^2}-\mu_{\gamma^*}\right)\right]-1\right]^{-1} \tag{425}$$

We can simplify this using our expression for μ_{γ^*} (418):

$$\begin{aligned}\exp\left(-\beta\mu_{\gamma^*}\right) &= \exp\left[-\beta\left(E_b + kT\ln\left(\frac{n_Bn_C^3}{n_A}\right) + kT\ln\left(\frac{\lambda_B\lambda_C^3}{\lambda_A}\right)^3\right)\right]\\ &= e^{-E_b/(kT)}\exp\left[-\ln\left(\frac{n_Bn_C^3}{n_A}\right) - \ln\left(\frac{\lambda_B\lambda_C^3}{\lambda_A}\right)^3\right]\\ &= e^{-E_b/(kT)}\left(\frac{n_A}{n_Bn_C^3}\right)\left(\frac{\lambda_B\lambda_C^3}{\lambda_A}\right)^{-3}\\ \implies \exp\left[\beta\left(\sqrt{(pc)^2+(m_*c^2)^2}-\mu_{\gamma^*}\right)\right] &= e^{\left(\sqrt{(pc)^2+(m_*c^2)^2}-E_b\right)/(kT)}\left(\frac{n_A}{n_Bn_C^3}\right)\left(\frac{\lambda_B\lambda_C^3}{\lambda_A}\right)^{-3}\end{aligned} \tag{426}$$

Therefore, plugging into (425), we get

$$n_{\gamma^*} = 3\int \frac{d^3p}{h^3}\left[e^{\left(\sqrt{(pc)^2+(m_*c^2)^2}-E_b\right)/(kT)}\left(\frac{n_A}{n_Bn_C^3}\right)\left(\frac{\lambda_B\lambda_C^3}{\lambda_A}\right)^{-3} - 1\right]^{-1} \tag{427}$$

Using (413) to simplify the factor $\left(\frac{\lambda_B\lambda_C^3}{\lambda_A}\right)$, we get

$$\boxed{n_{\gamma^*} = 3\int \frac{d^3p}{h^3}\left[e^{\left(\sqrt{(pc)^2+(m_*c^2)^2}-E_b\right)/(kT)}\left(\frac{n_A}{n_Bn_C^3}\right)\left(\frac{h^2}{2\pi kT}\right)^{-9/2}\left(\frac{m_A}{m_Bm_C^3}\right)^{-3/2} - 1\right]^{-1}} \tag{428}$$