PH2C

Intro. to Statistical Physics and Thermodynamics

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Abstract

These notes are intended to be a summary of the lectures in the Caltech course ph2c: Introduction to Statistical Physics and Thermodynamics, from the Spring of 2021. For this course, we used the textbook "Thermal Physics", 2nd ed., by Kittel and Kroemer, so the topics follow the notation and logic presented therein. If you notice any mistakes, please contact me directly.

1 Probability Theory: March 31

2 Binary State Systems: April 2

3 Equilibrium: April 7

3.1 Review of Last Week

- **Fundamental Assumption of Statistical Mechanics:** "An isolated system in uqilibrium is equally likely to be found in any of the microstates available to it."

- g = "the multiplicity"; the number of accessible micro states for a given set of extensive parameters (e.g. U, N, V)

- If all such states are equally likely, then *the probability distribution is uniform*: $P_i = 1/g$

- The mean value or "Expectation value" of an observable $\mathcal{A}$ is defined $\langle \mathcal{A} \rangle = \sum_i \mathcal{A}_i P(i)$

- Fluctuations are ***tiny***: For N » 1, quantities like $\Delta U/U$ go as $1/\sqrt{N}$

- This is a consequence of the Central Limit Theorem. Ensembles of many varying distributions sum up to a Gaussian distribution.

Collection of N magnetic spins

$$g(N, s) = \frac{N!}{(N/2 + s)!(N/2 - s)!} \tag{3.1}$$

Using Stirling's Approximation (cf. [MathWorld](#)):

$$\log(N!) = N\log(N) - N + \frac{1}{2}\log(2\pi N) \tag{3.2}$$

after some substitutions, we find that

$$g(N, s) = 2^N \sqrt{\frac{2}{\pi N}} exp\left[-\frac{1}{2}\left(\frac{s}{\sigma_s}\right)^2 \right] \tag{3.3}$$

where $\sigma_s = \sqrt{N}/2$ is the standard deviation of the Gaussian probability distribution of s, the spin excess.

3.2 Thermal Equilibrium for Two Systems

Let us consider two non-interacting systems. Each system is a box with a collections of spins. Box 1 has N_1 total atoms and an initial spin excess of s_1. The combined multiplicity of these two systems (before we allow them to interact) is (using the same logic that we used to consider our binary model of coin flips) just the product of the individual multiplicities:

$$g_{tot} = g_1 \times g_2 \tag{3.4}$$

$$= \frac{2}{\pi} \frac{1}{\sqrt{N_1 N_2}} 2^{N_1 + N_2} exp\left[-2\left(\frac{s_1^2}{N_1} + \frac{s_2^2}{N_2}\right) \right] \tag{3.5}$$

Rather than consider some artificial magnetic spin exchange interaction, let us instead turn on an external magnetic field, such that the energy of each system becomes $U_i = -2mBs_i$, where m is the magnetic moment of each atom and B is the magnetic field. We then bring the boxes into contact, such that it is possible to interchange energy
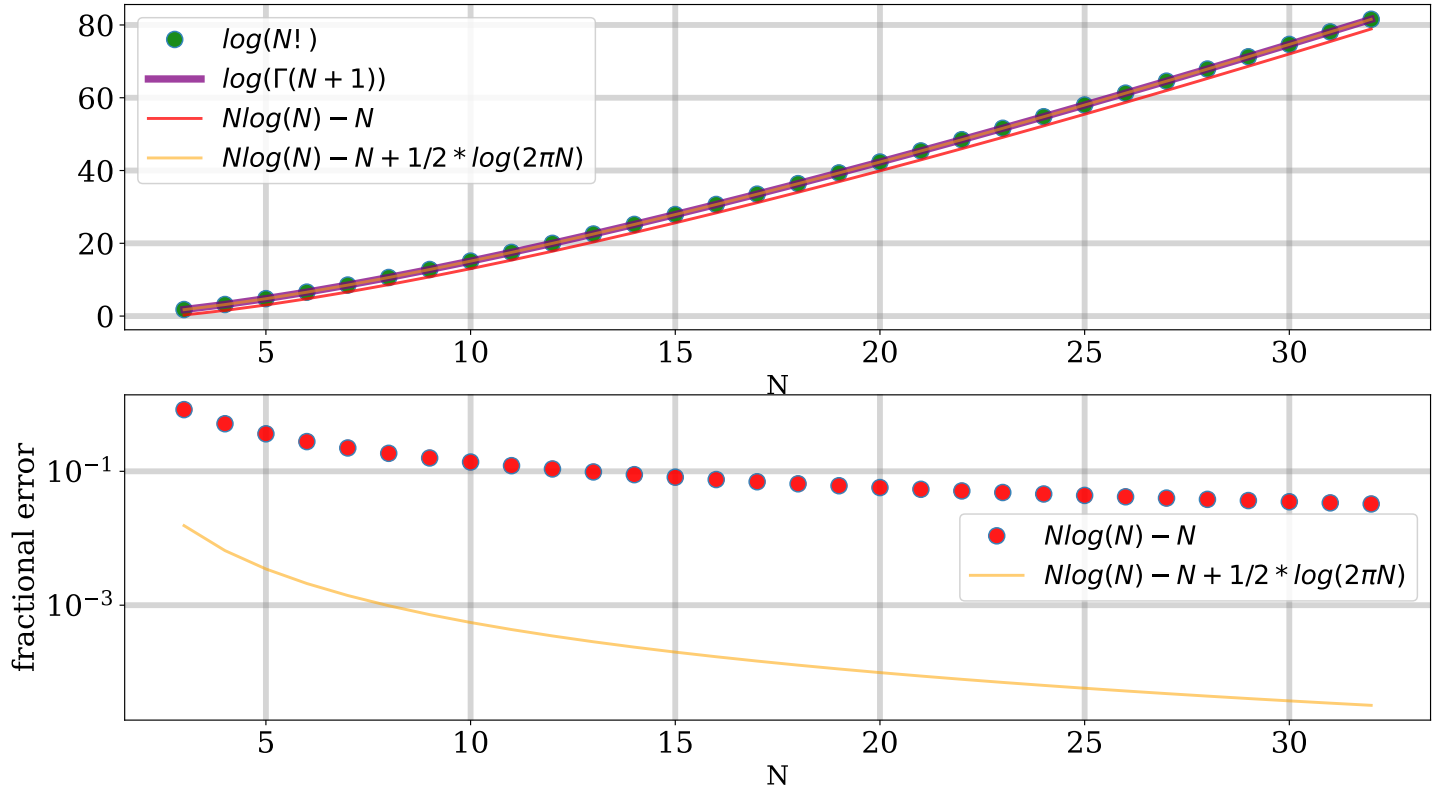
FIGURE 3.1: Comparison of various approximations to N!

between the two system. The total spin and the total energy will remain conserved (e.g. $U = U_1 + U_2$). For this two system example, we do not let the number of atoms in each box change: $N_1 = const, N_2 = const$.
After the energy exchange begins, the two systems move from their initial state (Eq. 3.5) into a new state

$$g_{tot} = g_1(U_1') \times g_2(U_2') \tag{3.6}$$

with more accessible microstates.
We would like to find what the new equilibrium state is. In other words, what is the most probable state after the two (sub)systems have been in contact long enough to come into equilibrium?
To find this, we would like to find the stationary point for the combined multiplicity function. To do this we set the $dg/dU = 0$:

$$dg = \left(\frac{\partial g_1}{\partial U_1}\right)_{N_1} g_2 \; dU_1 + \left(\frac{\partial g_2}{\partial U_2}\right)_{N_2} g_1 \; dU_2 = 0 \tag{3.7}$$

Since energy is conserved, any energy gained by one sub-system is equal to the amount lost by the other: $dU_1 = -dU_2$. Dividing through by $g_1 g_2$, we find the condition for *thermal equilibrium*:

$$\left(\frac{\partial \log(g_1)}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \log(g_2)}{\partial U_2}\right)_{N_2} \tag{3.8}$$

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FIGURE 3.2: The multiplicity functions for two systems before (Blue and Red) and after (Purple) being put into thermal contact.

4 Entropy: April 9

4.1 Entropy

The number of microstates is a huge number! Its much easier to work with the logarithm of such large numbers. The logarithm is also convenient since adding systems together requires just adding their logarithms, rather than multiplying the number of microstates.
So we define *entropy* as:

$$\sigma \equiv \log(g) \tag{4.1}$$

This is a dimensionless (unitless) quantity (its just the logarithm of a large number...).

As we saw in the previous lecture, the combined system moves from its initial configuration (where system 1 and 2 have the energies U_1 and U_2, respectively) into the one which is <u>overwhelmingly</u> likely. Recall that our conclusion from the discussion of thermal equilibrium is that for macroscopic systems (e.g. with $N \gtrsim 10^{15}$...actually the transition from micro to macro is a fuzzy concept, but this is an OK estimate for now), the chances of the energy being even 1 ppm different from the most probable value are astronomically unlikely (really? Yes - see the Shakespeare, monkeys, and typewriters problem in this week's problem set).

$$\left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2} \tag{4.2}$$

This tendency of the system to always move into a configuration which maximizes the number of accessible micro-states (g) is a just another way of stating the 2$^{\text{nd}}$ Law of Thermodynamics: The entropy of a closed system will always increase until the system reaches equilibrium.

> Turning and turning in the widening gyre
> The falcon cannot hear the falconer;
> Things fall apart; the centre cannot hold;
> Mere anarchy is loosed upon the world,...
>
> *William B. Yeats, 1919*

4.2 Temperature

Intuitively, we know that putting things in contact brings them to the same temperature (cf. the "Brain Freeze" available at the Red Door Cafe). So we want this to be implied by Eq. 4.2.
From Eq. 4.2, we could pick $\tau, 1/\tau, \text{or} -\tau, ...$, but we want temperature to correspond to our human definitions of it. Zero temperature should be very low energy and temperature should rise as we put more kinetic energy into the particles, so we define it like so:

$$\frac{1}{\tau} \equiv \left(\frac{\partial \sigma}{\partial U}\right)_N \tag{4.3}$$

4.3 The Laws of Thermodynamics

The 0ᵗʰ Law: Thermometers

[Wikipedia:Zeroth Law](#)
From our definitions of temperature and thermal equilibrium (cf. eqs. (4.2) and (4.3)), we see that if $\tau_1 = \tau_3$ and $\tau_2 = \tau_3$, then $\tau_1 = \tau_2$. In this example, τ_3 is the temperature of the thermometer we are using to establish the equivalence of the temperatures of our two example systems (1 and 2). Why is this seemingly trivial statement worthy of being a so-called "Law of Thermodynamics"?

The 1ˢᵗ Law: No Free Lunch
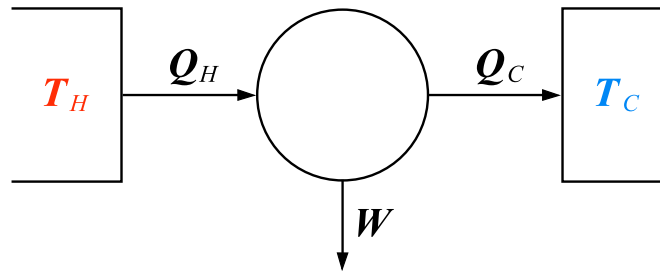
FIGURE 4.1: Schematic diagram of Carnot's Heat Engine
http://commons.wikimedia.org/wiki/File:Carnot_heat_engine_2.svg

A concise statement of the 1ˢᵗ Law is:

$$\Delta U = Q + W \tag{4.4}$$

where ΔU is the total internal energy of our system, W is the mechanical work done to the system[1], and Q is the *heat*. But what is heat? We all know what it is intuitively, but it is important to define it such that it can be used consistently in our studies of statistical mechanics. As defined in Ch. 8 of the textbook, heat is the energy transfer between two systems which are in thermal contact. It does not include work or any transfer of material. In the Carnot example above, $W = Q_H - Q_C$. Systems where $W > Q_H - Q_C$ are called perpetual motion machines of the first kind, and are known to be impossible to conservation of energy.

The 2ⁿᵈ Law: Everything Runs Down

As we saw above in Sec. 4.1, when a system begins in a non-equilibrium state (such as the one where we first bring the two sub-systems into contact), it always moves in the direction which increases the entropy:[2] pieces of a broken wine glass "never" reassemble into a whole glass. When we run the film backwards, we see this happen, but it seems that there is a preferred to direction to the flow of time. This is often referred to as the Arrow of TIme [3]
For the heat engine example above, $\Delta\sigma = Q_C/\tau_C - Q_H/\tau_H$. In order for $\Delta\sigma$ to be positive, we must have $\tau_H > \tau_C$, since $Q_H \geqslant Q_C$.

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[1]note the sign convention here; the work is done to the system and not by the system

[2]This is put to music in the song "Unsustainable", from the rock band Muse's album "The 2nd Law". Some Gaussian distributions and combinatorics are displayed for affect in their music video: [YouTube:Unsustainable](#)

[3][2004 Wired article](#) on how quantum correlations may be the underlying basis for the arrow of time

The 3rd Law: Nernst Theorem

The entropy of all systems approaches zero as the system goes towards absolute zero temperature: $\sigma \to 0$, and $\partial\sigma/\partial\tau \to 0$ as $\tau \to 0$.

This is simply a consequence of the ground state multiplicity. There is only one "lowest energy state", so in that state $g = 1$ and so $\log(g) = 0$.

There are some unusual systems for which this is not quite true. Some glassy systems or magnetic systems with geometric domains of different order can asymptote to a state of small, non zero entropy as the temperature goes to absolute zero.

> The law that entropy always increases, holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations — then so much the worse for Maxwell's equations. If it is found to be contradicted by observation — well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation.

Sir Arthur S. Eddington, 1928

5   Boltzmann Factor: April 14

5.1   The Boltzmann Factor

An important problem in Statistical Physics, is to find the probability of finding a system in a state s of energy ϵ_s. We already know how to do this for closed systems, but most systems are, in reality, open systems – that is, they are in contact with a large thermal bath or reservoir. This might be the rest of the room (in the case of a tiny experiment) or the rest of the city (in the case that the system is a building) or even the rest of the universe (in astrophysical or cosmological cases).

So lets take our little system $\mathcal{S}$ and put in contact with our large reservoir $\mathcal{R}$ with initial energy U_0 and temperature τ_R. Now we put our system in thermal (and later, mechanical) contact with the reservoir such that the new energy of the reservoir is $U_0 - \epsilon_s$. Now $\mathcal{R}$ can be in any of its $g_R(U_0 - \epsilon_s)$ microstates, just as we saw in last week's *microcanonical* picture.

For a given state s, there is no degeneracy; the multiplicity, $g_s = 1$. So the probability of finding the total system $(\mathcal{S} + \mathcal{R})$ in the state where $\mathcal{S}$ has energy ϵ_s, is just dependent on the multiplicity g_R: $P(s) \propto g_R(U_0 - \epsilon_s)$. Since $U_0 \gg \epsilon_s$, we can use the Taylor expansion to find a simplified form:

$$\log g_R = \sigma_R(U_0 - \epsilon_s) \simeq \sigma_R(U_0) - \epsilon_s \left(\frac{\partial \sigma_R}{\partial U_R} \right) + \mathcal{O}(\epsilon_s^2) \tag{5.1}$$

Since $(\partial \sigma_R / \partial U_R) = 1/\tau_R$, we can rewrite the proportionality for the probability as:

$$P(s) \propto exp(-\epsilon_s/\tau_R) \tag{5.2}$$

This is **one the most practically useful results in statistical physics**: it allows us to compute the relative probability of the system being in different energy states. This expression, $exp(-\epsilon_s/\tau_R)$, is called the <u>Boltzmann Factor</u>.

5.2   Partition Function

We would like to normalize the probability so that $\sum_s P(s) = 1$. To do this, we just sum over all possible energy states.

$$P(s) = \frac{exp(-\epsilon_s/\tau_R)}{\sum_s exp(-\epsilon_s/\tau_R)} \tag{5.3}$$

and where we will define the <u>Partition Function</u>[4] as

$$Z(\tau_R) \equiv \sum_s exp(-\epsilon_s/\tau_R) \tag{5.4}$$

There are many thermodynamic quantities which are easier to calculate using the partition function then going directly from the entropy or multiplicity alone. As an example, lets take a look at the average energy [5]:

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[4]an oddly named function for sure
[5]the last step is easier to verify going backwards than forwards – check it by doing the derivative

$$U = \langle \epsilon_s \rangle = \frac{\sum_s \epsilon_s \exp(-\epsilon_s/\tau_R)}{Z(\tau_R)} \tag{5.5}$$

$$= \tau_R^2 \left(\frac{\partial \log Z}{\partial \tau} \right) \tag{5.6}$$

which is a sensible way to go as long as the partition function itself is easier to compute than $g(\epsilon_s)$. In fact, this is true for a large number of cases.

5.3 Pressure

What is pressure? From our own experience we know that its simply related to the force exerted on the walls of a container by the system that it contains. Consider a system (like a gas) inside of a box where one of the walls is able to move (i.e. a piston). What happens if we slowly extert a force on that piston? We know that the gas will be compressed. What will be the energy delivered to the box? Recall (cf. 4.3) the discussion on the First Law of Thermodynamics: $\Delta U = Q + W$. In the case that we do not allow heat to flow through the walls of the box, the change in energy will just be the work done on the system.

$$dW = Fdx \tag{5.7}$$

$$= p(Adx) = pdV \tag{5.8}$$

here we have used the fact that pressure is defined as a force per unit area. So we have that the change in energy, for a small change in volume is just $dU = pdV$. If we make this change small enough and slowly enough, the change will be isentropic. The entropy is unchanged precisely the change in volume is made such that the microstate does not change (although the energy does). Therefore we can define the pressure as:

$$p = -\left(\frac{\partial U}{\partial V} \right)_\sigma \tag{5.9}$$

Why the minus sign? If we allow a balloon filled with gas to do work by expanding, we know that it is doing work and delivering energy to the environment. Therefore a positive change in volume of the system will *decrease* the system's energy. So there's a minus sign.

$\sigma, U, V,$ and N are all *extensive parameters* and σ depends on the other three. If we leave N fixed, there must be a clean relation between U and V for all isentropic changes. The expression for the differential of entropy will be:

$$d\sigma(U, V) = \left(\frac{\partial \sigma}{\partial U} \right)_V dU + \left(\frac{\partial \sigma}{\partial V} \right)_U dV \tag{5.10}$$

Setting the left hand side equal to zero, dividing through by dV, and then substituting in our previous expressions for pressure (eq. (5.9)) and temperature (eq. (4.3)), we get the following relationship:

$$\frac{p}{\tau} = \left(\frac{\partial \sigma}{\partial V} \right)_U \tag{5.11}$$

putting this together with the previous equation, we find that $dU = \tau d\sigma - pdV$, the expression for the total energy of the system.

5.4   Summary

- The probability of finding a system (in microstate s with energy ϵ_s, in thermal equilibrium with a reservoir at temperature τ_R) is proportional to the <u>Boltzmann factor</u> $P(s) \propto exp(-\epsilon_s/\tau_R)$.

- To normalize $P(s)$ properly ($\sum_s P(s) = 1$), we divide the Boltzmann factor by the sum over all energy states. $P(s) = exp(-\epsilon_s/\tau_R)/Z$, where $Z(\tau_R) \equiv \sum_s exp(-\epsilon_s/\tau_R)$. Z is called the partition function.

- For a compressible system, if we change the volume slowly and by a small amount, the entropy won't change (*isentropic*). This is defined as *pressure*: $p = -(\partial U/\partial V)_\sigma$

- The picture of closed system with an accessible number of microstates and associated entropy is the <u>microcanonical ensemble</u>. In this picture, the energy, volume, and number of the system is fixed.

- The <u>canonical ensemble</u> is the similar picture, but with the system now in thermal equilibrium with a heat bath. Consequently, the temperature is now fixed, but the energy of the system is not.

- Adiabatic vs. Isentropic vs. Isothermal: Isentropic and Isothermal are clearly defined ($d\sigma = 0$ or $d\tau = 0$). But adiabatic has confusing and contradictory definitions in quantum mechanics and thermodynamics...

6 Free Energy: April 16

Early on we dealt with isolated systems. An isolated system has a fixed energy, U. Once we bring this system into contact with a thermal reservoir, this is no longer true. So what will happen? Well, the fundamental assumption of statistical mechanics is still true, so the system still seeks to be in the most probable state.

Let's use the tools of our newly found canonical ensemble approach. Since the system is at a fixed temperature, we can rewrite the partition function as a sum over energies instead a sum over microstates, by including g, the multiplicity:

$$Z(\tau) \equiv \sum_s e^{-\epsilon_s/\tau} \tag{6.1}$$

$$= \sum_{\epsilon_s} g(\epsilon_s) e^{-\epsilon_s/\tau} \tag{6.2}$$

$$= \sum_{\epsilon_s} e^{\sigma(\epsilon_s)} e^{-\epsilon_s/\tau} \tag{6.3}$$

Then we can define a new quantity, the <u>free energy</u>, as $f \equiv \epsilon - \tau\sigma$. To find the most probable state, we can maximize the probability (eq. (5.3)), expressed in terms of energy (using the same swap as above):

$$P(\epsilon) = \frac{g(\epsilon)\exp(-\epsilon/\tau)}{Z} \tag{6.4}$$

So we find that the most probable state is the one for which the free energy is minimized (i.e. P is maximized when the argument of the exponential is minimized).
By averaging over the ensemble of microstates, we can write $F = \langle f(\epsilon) \rangle$ (just as we did for the energy, U). Using also the result (cf. K&K p. 71) that $F = -\tau \log Z$, we can see that the probability can be written simply as:

$$P(\epsilon) = \exp((F - \epsilon)/\tau) \tag{6.5}$$

We can also calculate a few useful **differential relations** with the free energy. Starting with the differential of F (and including the thermodynamic identity):

$$dF = dU - \tau d\sigma - \sigma d\tau \tag{6.6}$$

$$= -\sigma d\tau - p dV \tag{6.7}$$

we find the following two relations for the partial derivatives of F:

$$\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma \tag{6.8}$$

$$\left(\frac{\partial F}{\partial V}\right)_\tau = -p \tag{6.9}$$

7   Ideal Gas I: April 16

As a first look at the Ideal Gas model, we start by assuming that we have N identical point like particles in a box. These particles do not interact with each other and, by the virtue of being point-like, we can ignore the rotational and vibrational energies which real molecules have.

We can then procede to solve for the quantum wavefunctions and energies just as we do for the standard "particle-in-a-box" problem (cf. K&K, Ch. 1, pp. 9-10).

$$\hat{H} \langle \Psi \rangle = E \langle \Psi \rangle \tag{7.1}$$
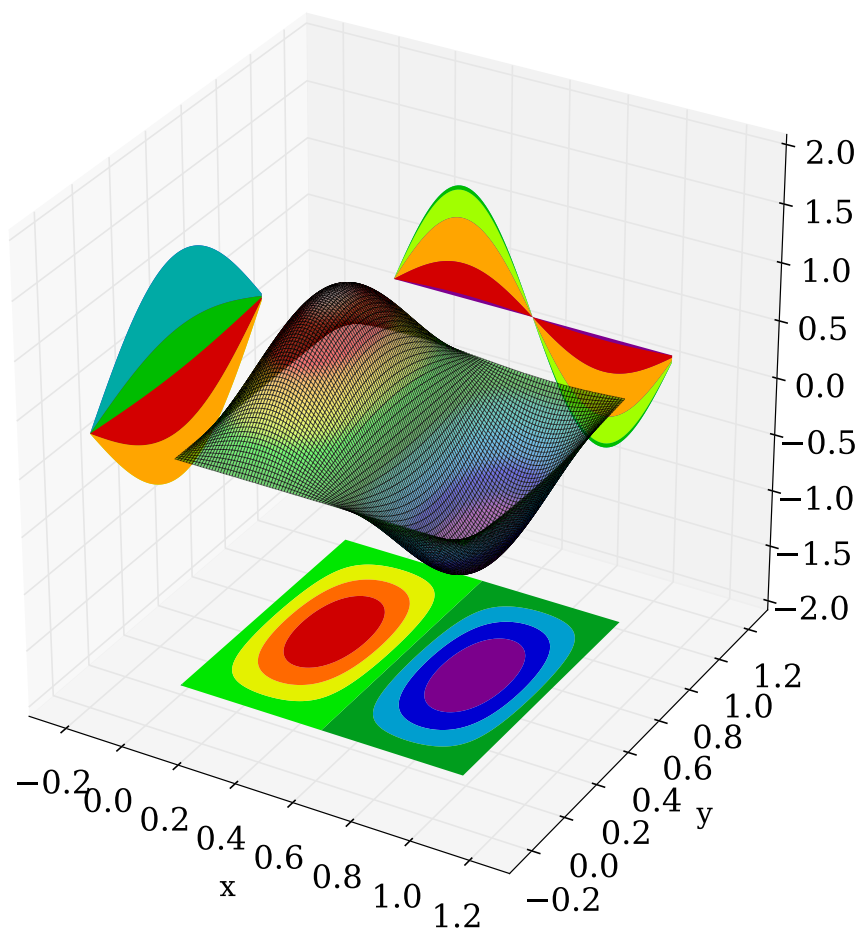
FIGURE 7.1: Example wavefunction for a particle in a square 2D box with sides of length L

For this potential (the box), the Hamiltonian is just that for a free particle:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 \tag{7.2}$$

This type of wave equation has solutions of the form $A \sin x + B \cos x$. By including the boundary conditions that

$\langle \Psi \rangle = 0$ when $(x, y, z) = 0$ or L, we can eliminate the cosine terms and we are left with:

$$\Psi(x, y, z) = \mathcal{C} \sin(n_x \frac{\pi}{L} x) \sin(n_y \frac{\pi}{L} y) \sin(n_z \frac{\pi}{L} z) \tag{7.3}$$

where $\mathcal{C}$ is the normalization constant. After normalization (to set the total probability equal to 1), we can get the quantized energies by plugging into the Schrödinger Equation above:

$$\epsilon_n = \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2) \tag{7.4}$$

7.1   Partition Function

We can now begin using our standard canonical ensemble 'toolbox' to derive relationships for the macroscopic observables of the system. The Boltzmann factor for a single particle is just $exp(-\epsilon_n / \tau)$ and the Partition function is

$$Z_1 = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-\epsilon_n / \tau} \tag{7.5}$$

Unsurprisingly, we would like to convert this summation into an integral in order to solve it, but is this really valid? It is, but only if the error between the sum and the series is small; i.e. true if $\epsilon_{n+1} - \epsilon_n \ll \tau$. At room temperature, $\tau = k_B T = (1.38 \times 10^{-23} \text{J/K})(300\text{K})$. To convert to eV, we divide by the electron charge (1.602×10^{-19}C), so $\tau \simeq \frac{1}{40}$eV. The prefactor in eq. (7.4) is $\sim 10^{-16}$eV for a 1 mm^3 box, so the approximation made by using an integral instead of an infinite series is extremely accurate even at the nano-Kelvin temperature now achievable through modern cryogenic methods.

We can then perform the integral by noting that its separable into three integrals (one for each n_i) and that each integral is of the form $\int exp(-\alpha^2 x^2)$, which we have done before and can look up in Appendix A of K&K or Wolfram Alpha.

$$Z_1 = L^3 \left(\frac{2\pi\hbar^2}{m\tau} \right)^{-3/2} \tag{7.6}$$

$$= n_Q V \tag{7.7}$$

where $V = L^3$ and

$$n_Q \equiv \left(\frac{2\pi\hbar^2}{m\tau} \right)^{-3/2} \tag{7.8}$$

which we define as the Quantum Concentration. Since for most gases at room temperature, the single particle density $(1/V)$ is much smaller than n_Q, $Z_1 \ll 1$, and the *classical approximation* is valid. Otherwise, we would have to consider the quantum entanglement between the molecules.

For distinguishable particles, the multi-particle partition function is just the product of the individual particle partition functions, just as the multi particle multiplicity is the product of the single particle multiplicities. Since the gas particles are identical, we weight it by the number of identical permutations:

$$Z_N = \frac{Z_1}{N!} = \frac{(n_Q V)^N}{N!} \tag{7.9}$$

7.2   The Ideal Gas Law

To understand the macroscopic properties of the N particle ideal gas, we can start with our expression for the Free Energy in terms of the Partition Function:

$$F = -\tau \, \log Z_N \tag{7.10}$$
$$= -\tau \, (N \log Z_1 - \log N!) \tag{7.11}$$
$$= -\tau \, (N \log n_Q V - \log N!) \tag{7.12}$$

From eq. (6.9), we have that

$$p = -\left(\frac{\partial F}{\partial V}\right)_\tau \tag{7.13}$$
$$= N\tau/V \tag{7.14}$$

and changing from our 'fundamental' units to SI units, we recover the Ideal Gas Law:

$$\boxed{pV = Nk_B T} \tag{7.15}$$

8 Planck Black Body: April 21 - 23

Let's consider now a system which is similar to the previous two (Ideal Gas and small System in a large Reservoir), but with a significant twist. Instead of a system where the constituents have a mass, we want to study what happens inside of a black [6] box in thermal equilibrium with a Reservoir. Instead of particles of a gas, we will be working with *photons*, the massless quanta of electromagnetic radiation. In the end we would like to end up with all the now usual concepts: total energy, entropy, pressure (yes, even light has a pressure [7]), and the energy distribution (i.e. can we predict what color something will be?).
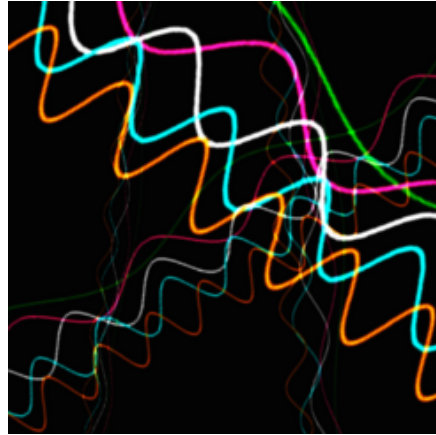

FIGURE 8.1: EM waves in a black box with sides of length L

We'll start off with the assumption [8] that the energy of each photon of angular frequency $\omega(= 2\pi\nu)$ will just be proportional to the frequency:

$$\epsilon = \hbar\omega \tag{8.1}$$

To an extremely good approximation, photons do not interact with each other (i.e. you cannot deflect a laser beam with another laser beam). So there can, in principle, be many photons with the same energy inside the box. We'll denote the occupancy of each mode as s, and so the energy per mode will be $\epsilon_s = s\hbar\omega$. The total energy will then just be an appropriately weighted sum over all the available modes.

At a temperature τ, the Boltzmann factor for a *single* mode is $e^{-s\hbar\omega/\tau}$. So the partition function for that mode is:

$$Z = \sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau} \tag{8.2}$$

$$= \frac{1}{1 - e^{-\hbar\omega/\tau}} \tag{8.3}$$

where we have used the relation $\sum_{s=0}^{\infty} x^s = 1/(1-x)$, valid when $x < 1$.

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[6] Here, by 'black', I mean that the walls of the box are a 'perfectly' absorbing conductor. This is a little counterintuitive; you know that very good conductors (e.g. aluminum, copper, silver) are very reflective and <u>not</u> perfectly absorbing. Nevertheless, this turns out to be a valid approximation for what we are looking into and, in fact, works well with boxes of almost any generic properties.

[7] cf. solar sails

[8] which will be qualified later

8.1　The Planck Distribution

At this point we can utilize all of the tools we have developed during the study of the canonical ensemble in Chapter 3. We know that the probability distribution can just be computed from the Boltzmann factor and the partition function (cf. eq. (5.3)):

$$P(s) = e^{-s\hbar\omega/\tau}\left[1 - e^{-\hbar\omega/\tau}\right] \tag{8.4}$$

and to find the average occupancy of each mode we just multiply by s and sum over all states:

$$\langle s \rangle = \sum_{s=0}^{\infty} s\, P(s) \tag{8.5}$$

$$= \frac{1}{Z} \sum_{s=0}^{\infty} s\, e^{-s\hbar\omega/\tau} \tag{8.6}$$

We can perform the sum here by transforming it into a more familiar form. To do this note that:

$$\sum s\, e^{-sx} = -\frac{d}{dx} \sum e^{-sx} \tag{8.7}$$

and the right hand side can be summed in the same way as eq. (8.3), above. So finally we arrive at the expression for the average occupancy:

$$\boxed{\langle s \rangle = \frac{1}{e^{\hbar\omega/\tau} - 1}} \tag{8.8}$$

which is the <u>Planck distribution</u> for the occupancy of a single mode in thermal equilibrium with a heat bath of temperature τ. The average energy in each mode is:

$$\boxed{\langle \epsilon \rangle = \langle s \rangle \hbar\omega = \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}} \tag{8.9}$$

Its interesting to look at the high and low temperature (or equivalently, the low and high frequency) limits of this expression.

At high temperatures, where $\tau \gg \hbar\omega$, we can expand the denominator ($e^x \simeq 1 + x$) and see that $\langle \epsilon \rangle \to \tau$. This is the 'classical limit'; the energy is just proportional to the temperature and there is no evidence of quantization.

At low temperatures, where $\tau \ll \hbar\omega$, the denominator becomes large and $\langle \epsilon \rangle \to 0$. So a black box will tend towards zero energy in the electromangetic field [9] as well as zero occupancy.

This highlights another interesting difference between a box of ideal gas molecules and a box of radiation: <u>the photon number is not a conserved quantity</u>. As we will see soon, the same is true for *phonons*, the acoustic excitations in a solid.

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[9]neglecting the ground state energy of $\frac{1}{2}\hbar\omega$ per mode

8.2   The Stefan-Boltzmann Law

We would like to now move on to the main goal, which is to find the total energy, entropy, etc. for the blackbody, summing over all the modes.

$$U = 2\sum_n \langle \epsilon_n \rangle = \sum_n \frac{\hbar \omega_n}{\exp(\hbar \omega_n / \tau) - 1} \tag{8.10}$$

where we have followed the convention from K & K pp. 92-93 which describes the accounting for the modes allowed in the box (similar reasoning as we use for waves on a string and particle in a box). The factor of 2 comes from accounting for the 2 polarizations of the radiation field and $\omega_n = n\pi c/L$.

We can replace the sum over the indices (n_x, n_y, n_z) with a triple integral to make the computation easier. This is valid as long as the box is not small with respect to the wavelength of the relavent radiation field ($L \gg c/\omega$).

To make the integral easier, we'll convert it from Cartesian coordinates to spherical coordinates and replace the volume element $dn_x dn_y dn_z$, with the spherical volume element $4\pi n^2 dn$.

$$U = 2 \times \frac{1}{8} \times 4\pi \int_0^\infty n^2 \frac{\hbar \omega_n}{\exp(\hbar \omega_n / \tau) - 1} dn \tag{8.11}$$

$$= \frac{L^3 \tau^4}{\pi^2 \hbar^3 c^3} \int_0^\infty \frac{x^3}{e^x - 1} dx \tag{8.12}$$

$$= \frac{\pi^2 L^3 \tau^4}{15 \hbar^3 c^3} \tag{8.13}$$

where the factor of 2 is for both polarizations, the 1/8 because we only want to consider one octant of the spherical volume (where the wavenumbers are positive), and the 4π covers the angular part of the volume integral. We then have made the substitution $x = \pi \hbar c n / L\tau$ to get the dimensionless integral. We can look up [10] the integral in a book or Mathematica to find that its $\pi^4/15$. The Stefan-Boltzmann constant (the above prefactor) is defined as:

$$\sigma_B = \frac{\pi^2}{15} \frac{k_B^4}{\hbar^3 c^3} \tag{8.14}$$

Its useful to also look at the spectral distribution of the energy. To get that we can rewrite the integrand above as:

$$\frac{U}{V} = \int_0^\infty u_\omega d\omega \tag{8.15}$$

$$u_\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar \omega / \tau} - 1} \tag{8.16}$$

where we've moved the volume ($V = L^3$) over to the left hand side and used our expression from above to replace n with ω. This *spectral density*, u_ω, is called the Planck Black Body Spectrum and the theoretical and experimental work which gave rise to it was the first evidence for $\hbar$ and was the birth of Quantum Mechanics.

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[10] you can do it for yourself in a few steps if you want: multiply top and bottom by e^{-x} and then recall our infinite sum for $1/(1-x)$
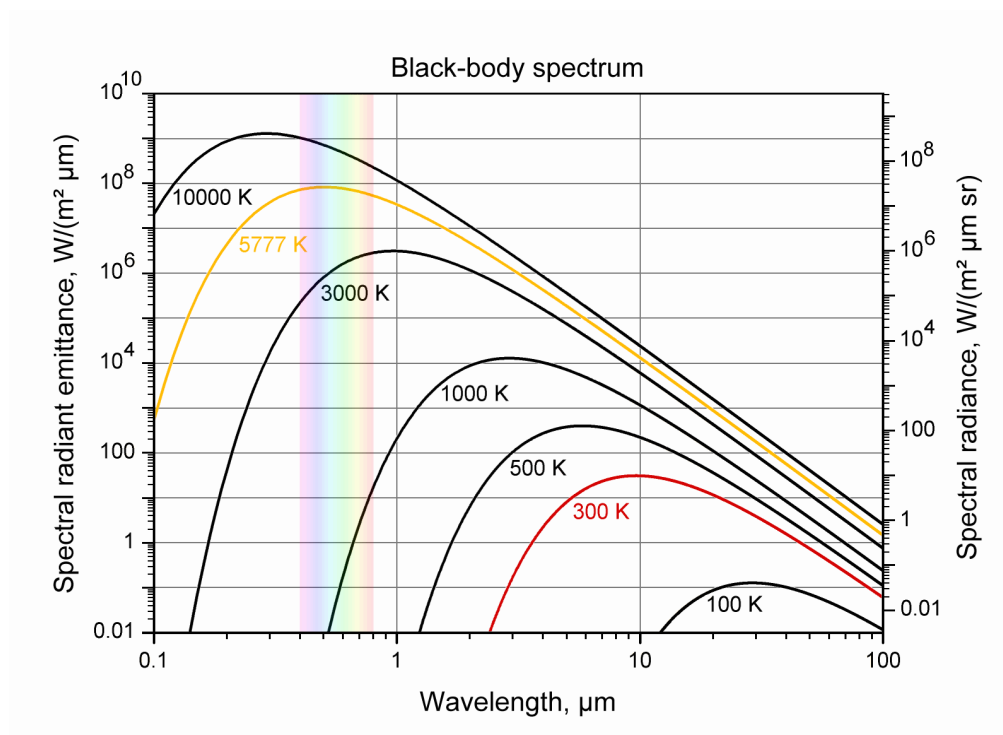
FIGURE 8.2: Blackbody Radiation Intensity Spectral density.
From https://commons.wikimedia.org/wiki/File:BlackbodySpectrum_loglog_150dpi_en.png

9 Chemical Potential: April 28

We have so far studied systems in which the volume and temperature are allowed to vary. In the microcanonical ensemble of chapters 1 & 2, we used the Fundamental Postulate of Statistical Mechanics:

> An isolated system in equilibrium is equally likely to be found in any of its available microstates.

to find the most probable state. In the canonical ensemble we were introduced to the concepts of the Helmholtz Free Energy, the Boltzmann Factor, and the Partition Function. This was useful in describing the behavior of a system in thermal equilibrium with another system (often a very large Reservoir or Heat Bath).

We could also imagine allowing the volume or the number of particles to change. We have already seen an example of this in the blackbody radiation case – there the number of particles was *not conserved*.

Here we would like to consider the case where the particle number is conserved, but where we allow the particles (as well as the thermal energy)to flow between the two systems, S_1 and S_2. This is called *diffusive contact*. We will use the tools developed for the canonical ensemble here again. Some examples where this will be a useful picture:

- Permeable membrane between two boxes of gas.

- Adsorption / contamination of a gas onto a surface, such as might occur in thin film deposition or contamination of a silicon wafer in a clean room environment.

- Flow of particles in a gravitational field: barometric pressure or relative gas concentration in the Earth's atmosphere.

- ...

Just as before, when we only had thermal contact, the free energy ($F = -\tau \log Z$) will be minimized when the two systems come to equilibrium; i.e. when the two non-equilibrium systems are allowed to diffuse into each other, they will change particle concentrations in the way that *minimizes the total free energy*: $F = F_1 + F_2$. To find the minimum, we set the differential equal to zero:

$$dF = \left(\frac{\partial F_1}{\partial N_1}\right) dN_1 - \left(\frac{\partial F_2}{\partial N_2}\right) dN_1 \tag{9.1}$$

$$= (\mu_1 - \mu_2) dN_1 = 0 \tag{9.2}$$

where we have used the total particle number conservation ($N = N_1 + N_2$) to set $dN_1 = -dN_2$. We can define the *chemical potential*:

$$\mu \equiv \left(\frac{\partial F}{\partial N}\right)_{\tau, V} \tag{9.3}$$

If we start off near equilibrium, and a small amount of particles, $dN_1 > 0$, is moved from S_2 to S_1 to bring the system closer to equilibrium, we know that F should get smaller:

$$dF = d(F_1 + F_2) < 0 \tag{9.4}$$

$$= (\mu_1 - \mu_2) dN_1 < 0 \tag{9.5}$$

so it must be that $\mu_1 < \mu_2$. The particle flow is from a region of higher to lower chemical potential. As long as we're treating the system as if the particles are non-interacting, we can also assert that the particles of one species do not effect the others and so a system with a collection of different kinds of particles will have a chemical potential for each kind:

$$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{\tau,V,N_{i\neq j}} \tag{9.6}$$

9.1 Ideal Gas

From section 7, we have the expression for the Ideal Gas Partition function (cf. eq. (7.9)) and the Quantum Concentration (cf. eq. (7.8)). Using Stirling's approximation (cf. FIXME) we can write the Free Energy as:

$$F = -\tau \log \frac{Z_1^N}{N!} \tag{9.7}$$

$$= -\tau \left[N \log n_Q V - N \log N + N \right] \tag{9.8}$$

and the chemical potential is then:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{\tau,V} \tag{9.9}$$

$$= -\tau \left(\log n_Q V - \log N \right) \tag{9.10}$$

$$= \tau \log \frac{n}{n_Q} \tag{9.11}$$

where $n \equiv N/V$ is the number density for the gas particles (molecules). Since, for the ideal gas, $n \ll n_q$, the chemical potential will always be very negative. An ideal gas with a higher number density will have a more positive potential and so the particles will flow from the system of high density into the system with low density, just as your intuition would tell you.

9.2 Barometric Pressure in the Earth's Atmosphere

As an example of the utility of the chemical potential, we can examine a simplified model of the atmosphere. Assume that the atmosphere is in thermal and chemical equilibrium. To simplify the problem, will assume that there is no significant temperature gradient for the regions that we are considering (in reality, of course, higher altitudes are much colder and there is often wind and turbulence).

In addition to the internal chemical potential, μ_{int}, there is an external potential, $\mu_{grav} = mgh$, due to gravity. If the lower and upper atmosphere are in equilibrium, we must set these to be equal.

$$\mu_{total} = \tau \log n(h)/n_Q = \tau \log n(0)/n_Q \tag{9.12}$$

Solving for $n(h)$, we find:

$$n(h) = n(0)e^{-mgh/\tau} \tag{9.13}$$

$$p(h) = p(0)e^{-mgh/\tau} \tag{9.14}$$

since, for an ideal gas, $p = n\tau$.

10   The Grand Canonical Ensemble: April 30

Microcanonical Ensemble: An isolated system. No thermal, mechanical, or diffusive contact with the outside world. For example, when we considered applying a magnetic field to the isolated system of spins, we did not take into account the effect this had on the thing producing the field.

Canonical Ensemble: The system is connected to a heat bath. The temperature of the heat bath is not effected by the connection - its assumed that the heat bath (reservoir) is large in comparison with the system so that its temperature is not changed by contact.

Grand Canonical Ensemble: In this model, we allow both thermal and diffusive contact. The reservoir determines the temperature of the combined system and the total number of particles is fixed, but the particles are allowed to flow between system and reservoir.

Given the added property of diffusion, we can now bring into action the techniques we used to arrive at the canonical ensemble picture. So we'd like to come up with formulae analagous to the Boltzmann factor (section 5.1) and the Partition Function (section 5.2).

10.1   The Gibbs Factor

For a given microstate $\mathcal{S}$ of our system, it will have N particles and an energy ϵ_S. The probability that our system is in this particular microstate is:

$$P(N, \epsilon_S) \propto g_{\mathcal{R}}(U_0 - \epsilon_S, N_0 - N) g_S(\epsilon_S, N) \tag{10.1}$$

where $g_S(\epsilon_S, N) = 1$ since this is for a precisely defned microstate (i.e. not an ensemble of microstates corresponding to a particular macrostate).
Since $N \ll N_0$ and $\epsilon_S \ll U_0$, it is reasonable to simplify our expression by taking the Taylor expansion of the entropy ($\sigma_{\mathcal{R}} = \log g_{\mathcal{R}}$), just as we did for the Boltzmann factor.

$$\sigma_{\mathcal{R}}(U_0 - \epsilon_S, N_0 - N) \simeq \sigma_{\mathcal{R}}(U_0, N_0) - \epsilon_S \left(\frac{\partial \sigma_{\mathcal{R}}}{\partial U} \right)_N - N \left(\frac{\partial \sigma_{\mathcal{R}}}{\partial N} \right)_U + \mathcal{O}(U^2) + \mathcal{O}(N^2) + \ldots \tag{10.2}$$

$$= \sigma_{\mathcal{R}}(U_0, N_0) - \frac{\epsilon_S}{\tau} + \frac{\mu N}{\tau} \tag{10.3}$$

where we have used our knowledge of partial derivatives of entropy to express the entropy in terms of the temperature and the chemical potential. So we can now rewrite eq. (10.1) as:

$$P(N, \epsilon_S) = \frac{e^{-\epsilon_S/\tau + \mu N/\tau}}{\mathcal{Z}} \tag{10.4}$$

where the factor $e^{\sigma_{\mathcal{R}}(U_0, N_0)}$ has been absorbed into the normalization factor in the denominator. The exponential in the numerator is called the <u>Gibbs factor</u>. It is the analog of the Boltzmann factor for a system in which the particle number is not fixed.

10.2 The Grand Partition Function

Since we want the above equation to be normalized such that $\sum P(N, \epsilon_S) = 1$, the normalization factor must be

$$\mathscr{Z} = \sum_{N=0}^{\infty} \sum_{s(N)} e^{-\epsilon_S/\tau + \mu N/\tau} \tag{10.5}$$

which is just the sum over all possible states and numbers of particles of the Gibbs factor. This normalization function is called the Grand Partition Function or sometimes the Gibbs sum.

10.3 Maxwell Relations

10.4 Fugacity

FIGURE 10.1: http://www.nzepc.auckland.ac.nz/features/fugacity/

FIGURE 10.2: The popularity of the word 'fugacity' over the years. Plot made using Google NGram Viewer. http://www.informationisbeautiful.net/visualizations/google-ngram-experiments/

11   Ideal Quantum Gases: May 5

A few weeks ago (cf. section 7), we did a first pass at examining the Ideal Gas:

- N identical particles in a box.

- the particles are do not interact with each other

- the particles are point-like; no rotational or vibrational modes

We then used the expression for the quantized energy levels based on the 'particle-in-a-box' Hamiltonian and found the Partition function (in the Canonical Ensemble representation) and expressions for the Quantum Concentration and the Free Energy of the Ideal Gas. Now we want to look at this in more detail, taking into account quantum mechanics and showing how we recover the classical ideal gas behavior in the limit of high temperatures or low concentration.

In K&K, the term 'orbital' denotes a particular state. It is motivated by the meaning of orbital in the case of an atom, where each set of quantum numbers refers to a unique quantum state. For the more general use in statistical physics, we'll use the term 'orbital' even when there are particles with no nucleus to orbit.

We use n_i to refer to the occupancy of the ith state with energy ϵ_i. The total quantum state of our system is fully specified by knowledge of n_i. With that information we can proceed to employ all of the statistical mechanics tools that we have developed over the term to calculate expressions for the behavior.

Our only constraints are that $\sum_i n_i = N$ (the total number of particles is fixed) and that the total energy of each microstate is given by:

$$\epsilon_s = \sum_i n_i \epsilon_i \tag{11.1}$$

We will examine the case for three different kinds of particles:

1. Distinguishable particles, i.e. "classical" particles

2. Fermions: $n_i = 0$ or 1

3. Bosons: $n_i = 0, 1, 2, 3, ...$

these yield, respectively, Maxwell-Boltzmann, Fermi-Dirac, and Bose-Einstein statistics.

11.1   Ideal Gas

With N particles in a box, we consider a single orbital to be our system and the rest of the orbitals to be the reservoir. Since particles can move between orbitals, we will consider the system to be in <u>diffusive and thermal</u> contact with the reservoir. This is where the use of the Grand Canonical ensemble comes into play. The Grand Canonical partition function is given by the sum over all possible states and numbers of particles of the Gibbs factor:

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{s(N)} e^{-\epsilon_s/\tau + \mu N/\tau} \tag{11.2}$$

$$= \sum_N \lambda^N \sum_s e^{-\epsilon_s/\tau} \tag{11.3}$$

In the case of N indistinguishable particles, we found that the sum over the states (which is just the N particle Partition function) is $Z_1^N/N!$. So for the ideal gas we can see that the Grand Canonical partition function is:

$$\mathscr{Z} = \sum_N \lambda^N \frac{Z_1^N}{N!} \tag{11.4}$$

$$= e^{\lambda Z_1} \tag{11.5}$$

using the expression $e^x = \sum x^N/N!$ to simplify the equation. As before, we can find the thermal average number of particles by 'integrating' our observable, N, by the distribution. This gives us (after some algebra):

$$\langle N \rangle = \tau \frac{\partial \log \mathscr{Z}}{\partial \mu} \tag{11.6}$$

$$= \lambda Z_1 \tag{11.7}$$

Using our expressions for the fugacity ($\lambda = n/n_Q$) and the single particle Partition function ($Z_1 = V n_Q$), we just recover the obvious result that $\langle N \rangle = N$. Which is a reassuring confirmation that this approach is valid.

11.2　Dilute Fermi Gas

According to the Pauli Exclusion Principle, two fermions cannot occupy the same state at the same time. The implication, for our analysis of particles in a box, is that the occupancy of each orbital can only be 0 or 1. The exclusion principle forbids having two electrons in a box with the same quantum numbers (n_x, n_y, n_z) unless they have opposite spin. So the Grand Canonical Partition function for Fermions just becomes:

$$\mathscr{Z} = 1 + e^{-(\epsilon - \mu)/\tau} \tag{11.8}$$

since there only two values (0 and 1) to sum over. Using eq. (11.7), we find that the average thermal occupancy of the single orbital we are considering is

$$\langle N \rangle = \frac{\lambda e^{-\epsilon/\tau}}{1 + \lambda e^{-\epsilon/\tau}} \tag{11.9}$$

$$= \frac{1}{e^{(\epsilon - \mu)/\tau} + 1} \tag{11.10}$$

which is the Fermi-Dirac Distribution Function.

11.3　Dilute Bose Gas

The procedure for deriving the Bose-Einstein distribution follows the same logic:

$$\mathscr{Z} = \sum_{N=0}^{\infty} \lambda^N e^{-N\epsilon/\tau} \tag{11.11}$$

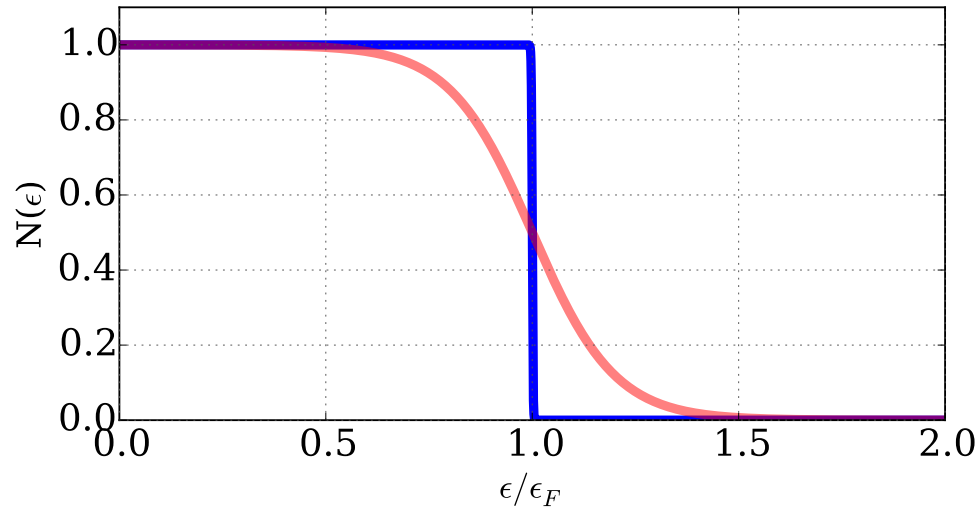$$= \frac{1}{1 - \lambda e^{-\epsilon/\tau}} \tag{11.12}$$

FIGURE 11.1: The Fermi-Dirac distribution for $\tau \simeq 0$ and $\tau = 0.1\epsilon_F$

where the infinite series summation is valid as long as $\exp((\mu - \epsilon)/\tau) < 1$ or equivalently that $\epsilon > \mu$. So similarly to the FD case above, we can find the occupancy by taking a derivative and performing some algebraic simplification:

$$\langle N \rangle = \frac{1}{e^{(\epsilon - \mu)/\tau} - 1} \tag{11.13}$$

which is the Bose-Einstein Distribution Function.

11.4 Density of States

11.5 White Dwarf Stars

11.6 Conduction Electronics in Metals

12 Fermi Dirac Statistics

13   Bose Einstein Statistics: May 14, 19

14   Heat and Work: May 21

This week, the objective is to study how heat and work behave in exchange between systems so that we can understand how practical devices work.

For a system with fixed number of particles N, the total internal energy can be expressed as a function of the entropy and volume:

$$dU = \tau d\sigma - p dV \tag{14.1}$$

where the negative sign in the second term indicates that this is work done *by* the system on the environment (it decreases the energy of the system). <u>Decreasing</u> the volume of the system <u>increases</u> its internal energy.
For a system with fixed N, there are a number of different ways to perform work on a system other than the obvious mechanical way of compression/expansion (such as changing the external magnetic field).

14.1   Heat Engines

Cycle/Process	Compression	Heat Injection	Expansion	Heat Extraction
Carnot (ideal)	adiabatic	isothermal	adiabatic	isothermal
Otto (gasoline)	adiabatic	isometric	adiabatic	isometric
Diesel	adiabatic	isobaric	adiabatic	isometric
Brayton	adiabatic	isobaric	adiabatic	isobaric
Ericsson	isothermal	isobaric	isothermal	isobaric
Stirling	isothermal	isometric	isothermal	isometric

FIGURE 14.1: Comparison of Heat Engine Properties

There are illuminating Flash animations of a few different heat engines from Don Ion at Santa Barbara: http://science.sbcc.edu/~physics/flash/index.html. The Carnot cycle is described in the textbook, the 4-stroke engine (Otto) is the basic model of today's internal combustion engine in many cars, and the Stirling cycle, which is very popular recenly due to its high efficiency and closed cycle operation.

The Carnot Cycle

The Carnot Cycle (named after Sadi Carnot) is an ideal version of a heat engine. A system (the engine) sits between a hot reservoir and a cold reservoir. Heat, Q_h, is extracted from hot reservoir at temperature τ_h and used to do some work. The system then ejects heat, Q_l, into a cold reservoir at temperature τ_l and then returns to its initial position. In the ideal Carnot picture, the engine is unchanged by this process and so the entropy remains constant:
$\sigma_h = \sigma_l$

The amount of work done by the engine can, at best, be the difference in the heat extracted and the heat which is dumped to the cold reservoir.

$$W = Q_h - Q_l = \frac{\tau_h - \tau_l}{\tau_h} Q_h \tag{14.2}$$

the *Carnot efficiency* is defined as the ratio of the work done to the heat extracted from the reservoir:

$$\eta \equiv \frac{W}{Q_h} = 1 - \tau_l/\tau_h \tag{14.3}$$

In principle, we could have $\tau_l \ll \tau_h$, such that $\eta \rightsquigarrow 1$, but, in practice, as Carnot realized, the limits of the material properties of common engine parts limits the upper working temperature to ~600 K, which is only a factor of 2 above room temperate (300 K) and so a more practical Carnot engine would only have an efficiency of $\eta \sim 1/2$. The P-V and T-S diagrams (from Thermopedia http://dx.doi.org/10.1615/AtoZ.c.carnot_cycle) give graphical representations

FIGURE 14.2: Carnot cycle in P-V and T-S planes

of the amount of work done.

1. The system begins at low temperature and low entropy. The system is compressed adiabatically (isentropically) and the temperature increases to τ_h.

2. At constant temperature τ_h, heat Q_h is injected into the system (increasing its entropy) and the system expands along the 2 to 3 isotherm of the figure above.

3. The system is allowed to expand isentropically, going from τ_h to τ_l

4. Heat, Q_l, is extracted from the system as it moves back into its initial position.

14.2   Refrigeration

Refrigeration is very nearly the opposite of the heat engine, when viewed in this diagramatic way. The equivalent efficiency is called the coefficient of refrigerator performance:

$$\gamma_c = \frac{\tau_l}{\tau_h - \tau_l} \tag{14.4}$$

which is not to be confused with our other symbol, γ, which is the adaibatic coefficient for an ideal gas.

14.3 Path Dependence

Using our knowledge of the ideal gas law, we can now compute the energy exchanges made during the isothermal and isentropic portions of the Carnot cycle.

14.4 Otto Cycle (gasoline)

The Otto cycle is interesting to us because it describes the behavior of the the 4-stroke internal combustion engine powering most of Los Angeles traffic.

14.5 Stirling Engine

The Stirling Engine is a closed cycle heat engine with the internal working fluid being manipulated through contact with a hot and cold surfaces. It is a very high efficiency engine which does not rely on combustion. It can use any heat source (such as renewables) and can be made to work very quietly.

14.6 Chemical Work

What about when we transform particles from one type to another?

14.7 Thermodynamic Impossibilities

One of the practical uses of a knowledge of thermodynamics is the ability to debunk scientific frauds in the form of impossible heat engines, perpetual motion machines, devices which produce 'free energy' from the 'energy of empty space', etc.

- The Incredible Hulk: where does he get his mass from?

- http://io9.com/new-test-suggests-nasas-impossible-em-drive-will-work-1701188933