Statistical Mechanics and Thermodynamics Lecture Notes

Physics 245, Spring 2025

Prof. Emily Nardoni

Department of Physics and Astronomy, Vassar College, 124 Raymond Avenue,
Poughkeepsie, NY 12604 USA

Contents

1 States, Ensembles and the Basic Tools of Thermodynamics

Textbook readings: (a first reading is due before Lecture 2; most pertinent to Lectures 1-3)

- Ch. 1, all (this should mostly be review / introductory material)
- Ch. 2, all
- Ch. 3 sections 3.1-3.4
- Ch. 4 sections 4.1-4.5

Learning Objectives:

- Combinatorial Problems: 2-state systems, collections of harmonic oscillators
- Probability Basics: mean, probability
- Statistical definitions of temperature and entropy: $S = k \ln \Omega$, 2 oscillator solids sharing energy
- Heat Capacity
- Ideal Gas Law: know how to use the formulas $pV = NkT$, $U = (3/2)NkT$

1.1 Preliminaries of Thermodynamics and Probability

This course is concerned with thermodynamics. We will study the fundamentals of classical thermodynamics (concerned with the conversion of heat into work), and statistical mechanics (concerned with the statistical behavior of the underlying microstates of the system). We'll begin with some introductory remarks on the basic concepts of thermodynamics and statistical mechanics.

To introduce some of the main concepts of thermodynamics, we can have in mind the vague example of two systems: these could be gas, liquid, or solid.

- Intuitively we all have a notion of what heat is: we can *feel* it when heat warms us up, or when heat leaves us making us feel cold. More precisely, when two systems are in **thermal contact** (able to exchange energy), there can be a transfer of heat from one to the other. **Heat** is a form of energy, but we only use this term when talking about *transfer*.

  As a form of energy, heat is measured in Joules (J); while the rate of heating has units of watts $1W = 1J \cdot s^{-1}$. If a $60W$ lightbulb is switched on for 10 minutes, then it produces $Q = 60W \cdot 600\,s = 36kJ$ of heat.

- The **first law of thermodynamics** essentially states that energy is conserved in any process. The heat lost by the hot system is equal to the heat gained by the cold system.
- **Temperature** is the measurable characteristic of a system that tells us how likely it is to give off some heat. Heat will always flow from an object with a *larger* temperature to one with a *smaller* temperature.

- After some amount of time, known as a *relaxation time* or **thermalization** time, both systems in contact will have the same temperature. We say that the two systems are in **thermal equilibrium**, with their energy content and temperatures no longer changing with time.

  If various bodies (more than two) are all in thermal equilibrium with one another, then their temperatures are all the same. (This is also known as the *zeroth law of thermodynamics*—essentially it says that thermal equilibrium is transitive.)

But what MOTIVATES this transfer of energy? What makes that process a one-way, or **irreversible**, one? The first law tells us nothing about that. For that we need the idea of entropy, the 2nd Law, and statistical mechanics.

In thermodynamics, we accept as a fact of life that heat transfer is due to thermal contact between two systems of different temperatures. In statistical mechanics, however, we look inside the box: all possible states of the system (with an absurd number of velocities, positions, etc) must be considered...even the ones where the hot side gets hotter and the cold side gets colder. But, of all things, it turns out we get saved by probability! It is not *technically* impossible for such weird states to occur, just absurdly improbable.

The subject of thermal physics naturally involves studying very large numbers of atoms, and all of these different possibilities for their possible states. This is the *problem of counting*: the universe contains many many things! A small cup of water contains about 3×10^{24} molecules of water. This lecture room contains on the order of 10^{27} molecules of air. A magnet on your refrigerator contains 10^{18} little magnetic dipoles that arrange themselves to yield the collective magnetic property. Each of these individual things obey some equation of motion... and perhaps we can solve the system when there are 2 or 3 things. But how are we supposed to solve a system of 10^{24} things?

Despite this complexity, we mostly understand how the **macroscopic** world around us works. We don't care about how each molecule in the cup of water behaves, all we need is its temperature. The laws of thermodynamics are examples of such macroscopic laws. Nonetheless...sometimes the microphysics actually matters. *Why* and *How* does water boil? This is where statistical mechanics comes in: where we try to explain the macrophysics of a system from its fundamental microphysics, without actually trying to solve the entire system of equations describing all the particles. In statistical mechanics, we some of the most important buzzwords are:

- **Ensemble**: a collection of a very large number of similar systems.
- **Microstate**: a specific arrangement of a system (one member of an ensemble).
- **Macrostate**: An experimentally observable state of a system.
- **Multiplicity**: The number of microstates in a particular macrostate
- **Probability**: The likelihood of a particular macrostate being realized (ranges from 0 (0% chance of being realized) to 1 (100% chance of being realized)

Probability basics and combinatorial problems

For example, suppose you set a penny, a nickel, and a dime on the table. Each coin can be either heads or tails. This *ensemble* has 8 possible *microstates*:

penny	nickel	dime
H	H	H
H	H	T
H	T	H
T	H	H
T	T	H
T	H	T
H	T	T
T	T	T

There are 4 possible *macrostates*: 1 microstate yields all three heads; 3 microstates yield 2 heads, 1 tails; 3 microstates yield 1 head, 2 tails; 1 microstate yields all three tails. The macrostates have a *multiplicity* Ω of either 1 or 3. Then, the probabilities of these macrostates being realized are given in general by:

$$P(n \text{ Heads}) = \frac{\Omega(n \text{ Heads})}{\Omega(\text{total})}$$

Specifically, these probabilities for the 4 possible macrostates of $n = 0, 1, 2$, or 3 Heads are:

$$P(0) = \frac{1}{8}\,, \quad P(1) = P(2) = \frac{3}{8}\,, \quad P(3) = \frac{1}{8}$$

Of course, the probability of *some* configuration being realized, which is the sum of these individual probabilities, is equal to 1 (or, 100%):

$$\boxed{\sum_i P_i = 1\,.}$$

Given a distribution of possible microstates that yield a set of macrostates, we can compute statistical information about this ensemble. For example, the **mean**, or average, of outputting a value x of a distribution is defined,

$$\boxed{\text{mean} = \langle x\rangle = \bar{x} = \sum_i x_i P_i}$$

In this example, the average number of heads is given by

$$\langle n\rangle = 0\cdot P(0) + 1\cdot P(1) + 2\cdot P(2) + 3\cdot P(3) = 0 + \frac{3}{8} + \frac{6}{8} + \frac{3}{8} = 1.5$$

This makes sense; there can be between 0 and 3 heads, and the possible macrostates (0,1,2,3) are evenly distributed, so the average is the middle of these numbers, which equals to 1.5.

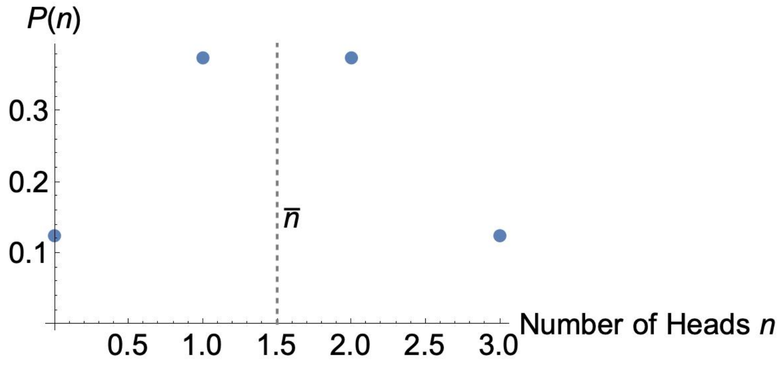
More generally, if we wish to calculate the average of a function of x, then we compute the weighted sum,

$$\langle f(x)\rangle = \begin{cases} \sum_i f(x_i) P_i & \text{discrete} \\ \int f(x) P(x)\, dx & \text{continuous} \end{cases}$$

where whether we are doing a discrete sum or an integral depends on whether the probability distribution is discrete (as in the case of the coins) or continuous.

Furthermore, we can quantify how spread out the values are. The *deviation* from the mean for a particular value of x is defined by

$$\text{deviation from } x = x - \langle x\rangle$$



The standard deviation σ_x of the distribution is the square root of the variance,

$$\boxed{\text{standard deviation } \sigma_x = \sqrt{\langle(x - \langle x\rangle)^2} = \sqrt{\langle x^2\rangle - \langle x\rangle^2}}$$

For instance, the standard deviation in our coin example is computed using $\langle n\rangle^2 = 1.5^2 = 2.25$, and

$$\begin{aligned}\langle n^2\rangle = 0^2P(0) + 1^2P(1) + 2^2P(2) + 3^2P(3) = 3 \\ \Rightarrow \quad \sigma_n = \sqrt{3 - 2.25} = 0.866\end{aligned}$$

This sort of statistical information will be very useful throughout this course!

Example Problem: The Random Drunken Walk

An example application is the theory of **random walks**. Imagine a drunken person staggering attempting to walk home along a narrow street, so that their motion is confined along one dimension. Let's pretend that with each step, the drunken person is equally likely to travel one step forwards or one step backwards, where subsequent steps are completely uncorrelated with any previous one.

1. Suppose that the person starts at position 0. On average, where will they end up after N steps?
2. What is the probability that he will be 2 steps closer to his destination after having taken 4 steps?

Solution: At each step i, there are two possibilities, the drunk taking a step forward or backward, each with equal probability 1/2 of being realized. So after N steps, there are 2^N possible microstates, each being realized with equal probability. However, some of these microstates lead to the same macrostate, with n_{tot} total steps forward being taken. The actual probability of a macrostate will be equal to the multiplicity of that macrostate divided by the total number of possible microstates at that step,

$$P(n_{\text{tot}}) = \frac{\Omega(n_{\text{tot}})}{2^N}$$

Because there is always equal probability of moving forward and backward, *on average* we expect that the drunk will end up back at 0 after N steps.

Let's do the counting up to 4 steps. We can label each possible microstate by whether n_+ at that step equals +1 (so the drunk steps forward) or -1 (so the drunk steps backwards).

So, at the N'th step, there will be N labels, each of which is $+1$ or -1. Then, the total number of steps forward (labeling the macrostate) after N steps is equal to

$$n_{\text{tot}} = \sum_{i=1}^{N} n_{+}(i)$$

For example: after 1 step, the possible states are

$$\begin{aligned} \{+\} &\ \to n_{\text{tot}} = 1 \\ \{-\} &\ \to n_{\text{tot}} = -1 \end{aligned}$$

At this step, the probability of achieving these different macrostates is $P(1) = \frac{1}{2}$ and $P(-1) = \frac{1}{2}$, so the person is equally likely to be found at either of these positions. The average macrostate is

$$N = 1: \qquad \langle n_{\text{tot}} \rangle = 1\frac{1}{2} - 1\frac{1}{2} = 0\,.$$

After two steps, there are four possible microstates, but only three possible macrostates:

$$\begin{aligned} \{+,+\} &\ \to n_{\text{tot}} = 2 \\ \{+,-\} \text{ or } \{-,+\} &\ \to n_{\text{tot}} = 0 \\ \{-,-\} &\ \to n_{\text{tot}} = -2 \end{aligned}$$

At this step, $P(2) = \frac{1}{4}$, $P(0) = \frac{2}{4} = \frac{1}{2}$, and $P(-2) = \frac{1}{4}$, so they are most likely to be found back where they started. The average macrostate is

$$N = 2: \qquad \langle n_{\text{tot}} \rangle = 2\frac{1}{4} + 0 - 2\frac{1}{4} = 0\,.$$

After three steps, there are eight possible microstates, which result in only four possible macrostates:

$$\begin{aligned} \{+,+,+\} &\ \to n_{\text{tot}} = 3 \\ \{+,+,-\} \text{ or } \{+,-,+\} \text{ or } \{-,+,+\} &\ \to n_{\text{tot}} = 1 \\ \{+,-,-\} \text{ or } \{-,+,-\} \text{ or } \{-,-,+\} &\ \to n_{\text{tot}} = -1 \\ \{-,-,-\} &\ \to n_{\text{tot}} = -3 \end{aligned}$$

so that $P(3) = \frac{1}{8}$, $P(1) = \frac{3}{8}$, $P(-1) = \frac{3}{8}$, and $P(-3) = \frac{1}{8}$. The average macrostate is again,

$$N = 3: \qquad \langle n_{\text{tot}} \rangle = 3\frac{1}{8} + 1\frac{3}{8} - 1\frac{3}{8} - 3\frac{1}{8} = 0\,.$$

Finally, after four steps, there are 16 possible microstates,

$$\begin{aligned} \{+,+,+,+\} &\ \to n_{\text{tot}} = 4 \\ \{+,+,+,-\} \text{ or } \{+,+,-,+\} \text{ or } \{+,-,+,+\} \text{ or } \{-,+,+,+\} &\ \to n_{\text{tot}} = 2 \\ \{+,+,-,-\} \text{ or } \{+,-,+,-\} \text{ or } \{-,+,+,-\} & \\ \text{or } \{+,-,-,+\} \text{ or } \{-,+,-,+\} \text{ or } \{-,-,+,+\} &\ \to n_{\text{tot}} = 0 \\ \{-,-,-,+\} \text{ or } \{-,-,+,-\} \text{ or } \{-,+,-,-\} \text{ or } \{+,-,-,-\} &\ \to n_{\text{tot}} = -2 \\ \{-,-,-,-\} &\ \to n_{\text{tot}} = -4 \end{aligned}$$

so that $P(4) = \frac{1}{16}$, $P(2) = \frac{4}{16} = \frac{1}{4}$, $P(0) = \frac{6}{16} = \frac{3}{8}$, $P(-2) = \frac{4}{16} = \frac{1}{4}$, and $P(-4) = \frac{1}{16}$. So, the answer to the original question is $P(2) = \frac{1}{4} = 0.25$. Again, the average is zero:

$$N = 4: \qquad \langle n_{\text{tot}} \rangle = 4\frac{1}{16} + 2\frac{1}{4} + 0\frac{3}{8} - 2\frac{1}{4} - 4\frac{1}{16} = 0\,.$$

——— End Lecture 1.

Do you see the pattern? At the N'th step, the possible macrostate values n_{tot} that can be achieved are labeled by partitions of N into two parts. Let n_1 represent the number of times $+1$ appears in the partition of N, and n_2 represent the number of times that -1 appears in the partition of N:

$$N = n_1 + n_2\,, \qquad n_{\text{tot}} = (+1)n_1 + (-1)n_2 = n_1 - n_2$$

Since n_1 runs from 0 to N, $-N \leq n_{\text{tot}} \leq N$, in increments of 2, so that if N is even then n_{tot} is always even, and if N is odd then n_{tot} is always odd.

The multiplicity $\Omega(n_{\text{tot}})$ of each partition is equal to the number of ways that n_1 $(+1)$'s and n_2 (-1)'s can be arranged in the partition. The number of ways to arrange these two choices is given by the **binomial coefficient**. The binomial coefficient is defined as follows: whenever each element corresponds to making a binary choice (in this case, ±1 at each step), and you have N elements (total steps), then the number of ways to arrange those choices is

$$\boxed{\begin{pmatrix} N \\ n_1 \end{pmatrix} = \text{“}N \text{ choose } n_1\text{”} = \frac{N!}{n_1!n_2!} = \frac{N!}{n_1!(N-n_1)!}} \tag{1.1}$$

This is the number of ways to choose n_1 elements from the N-element set of $N = n_1 + n_2$, said “N choose n_1”. In our case, then, the multiplicity of a macrostate n_{tot} is computed as

$$\Omega(n_{\text{tot}}) = \begin{pmatrix} N \\ n_1 \end{pmatrix}$$

Of course, if we wish we can write this expression in terms of the macrostate variable n_{tot} by substituting

$$n_{\text{tot}} = n_1 - n_2 = n_1 - (N - n_1) \quad \Rightarrow \quad n_1 = \frac{1}{2}(n_{\text{tot}} + N)$$

Fixing the total number of steps N, the partition is equally well labeled by n_1 running from $0, 1, \ldots, N$, or n_2 running from $0, 1, \ldots, N$, or n_{tot} running from $-N, -N+2, \ldots, N-2, N$.

Then, for a given number of steps N we can compute the probability of the macrostate being realized:

$$P(n_{\text{tot}}) = \frac{\Omega(n_{\text{tot}})}{2^N} = \frac{N!}{\left[\frac{1}{2}(N + n_{\text{tot}})\right]!\,\left[\frac{1}{2}(N - n_{\text{tot}})\right]!\,2^N}$$

You can verify that this formula gives the expected results, for example, for $N = 4$ and $n_{\text{tot}} = -2$:

$$N = 4: \qquad P(-2) = \frac{4!}{\left[\frac{1}{2}(4-2)\right]!\,\left[\frac{1}{2}(4+2)\right]!\,2^4} = \frac{1}{4} \quad \checkmark$$

Another check on this formula is that it is invariant under $n_{\text{tot}} \to -n_{\text{tot}}$, as it should be!

$$P(n_{\text{tot}}) = P(-n_{\text{tot}})$$

This symmetry immediately implies that the average is always zero: the average is taken by summing all the possible values of n_{tot} weighted by their probabilities, where recall n_{tot} runs from $-N$ to N in increments of 2:

$$\begin{aligned}\langle n_{\text{tot}}\rangle &= \sum_{n_{\text{tot}}=-N}^{N} n_{\text{tot}} P(n_{\text{tot}}) \\ &= \sum_{n_{\text{tot}}=-N}^{0} n_{\text{tot}} P(n_{\text{tot}}) + \sum_{n_{\text{tot}}=0}^{N} n_{\text{tot}} P(n_{\text{tot}}) \\ &= \sum_{0}^{N}(-n_{\text{tot}})P(-n_{\text{tot}}) + \sum_{0}^{N} n_{\text{tot}} P(n_{\text{tot}}) = 0 \quad \checkmark\end{aligned}$$

This binomial formula (1.1) is quite useful in counting microstates of 2-state systems. For example, consider a 2-state paramagnet in a magnetic field. This is a system of N particles of intrinsic spin 1/2, which can be thought of as N magnetic dipoles of moment μ. (We assume the dipoles do not interact with each other.) Quantum mechanics dictates that all the spins must be either "up" (+1/2) or "down" (−1/2), so that the energy of each dipole is either μB or $-\mu B$, respectively. What are the total number of microstates possible for this system? In other words, what is the multiplicity of a given total energy state?

This is another example where the number of microstates is labeled by a partition of N into two: this time into $N_\uparrow$ up-spins and $N_\downarrow$ down-spins, so that the total number of spins is $N = N_\uparrow + N_\downarrow$. A total energy state with $N_\uparrow$ up-spins will have multiplicity

$$\boxed{\text{multiplicity for a partition of } N = N_\uparrow + N_\downarrow : \qquad \Omega(N_\uparrow) = \frac{N!}{N_\uparrow! N_\downarrow!}}$$

In-Class Exercise: Rolling the die

You have a regular 6-sided die. You roll the die until you get a 6, and then stop.

(a) What is the probability of not having rolled a 6 after N rolls?

Solution: Each roll is independent of the previous roll. After 1 roll, there is 1/6 chance of rolling a 6 (success) and 5/6 chance of not rolling a 6 (failure). If I didn't roll the 6 then I roll again: at this roll there is 1/6 chance of rolling a 6, and 5/6 chance of not rolling a 6.

Let p denote the probability of success on each trial, $p = \frac{1}{6}$, and q denote the probability of failure on each trial, $q = 1 - p = \frac{5}{6}$. After N rolls, I still haven't rolled a 6 with probability

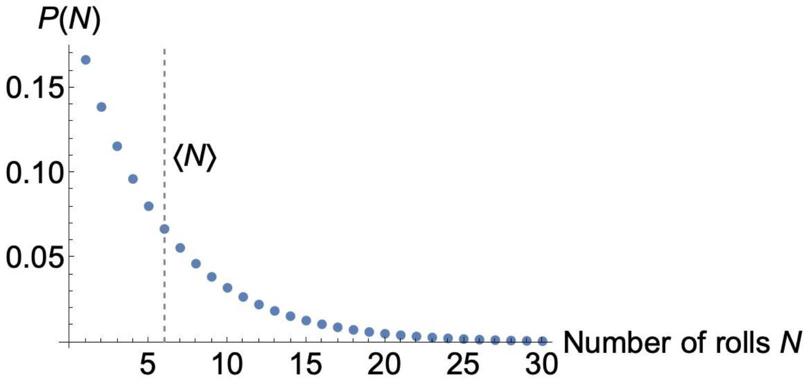
$$q^N = \boxed{\left(\frac{5}{6}\right)^N}$$

(b) What is the probability of rolling a 6 on the N'th roll?

Solution: We have determined that after $N-1$ rolls, there is a probability of $\left(\frac{5}{6}\right)^{N-1}$ of still having not rolled a 6. On the N'th roll, there is a probability of 1/6 that I roll the 6. So, the probability of "success on the N'th try" $P(N)$ is

$$P(N) = q^{N-1}p = \boxed{\left(\frac{5}{6}\right)^{N-1}\frac{1}{6}}$$

This is called a *geometric distribution*, and it's plotted in the figure.



Note that there is 100% probability that I have success after *some* number of tries; that is to say, that if I add up $P(N)$ for $N = 1, \ldots, \infty$, I should get 1. We can show that this is the case using the infinite sum (1.2):

$$\sum_{N=1}^{\infty} P(N) = \sum_{N=1}^{\infty} q^{N-1}p = p\sum_{N=1}^{\infty} q^{N-1} = p\left[q^0 + \sum_{N=2}^{\infty} q^{N-1}\right]$$

Evaluating $q^0 = 1$, and changing variables to $k = N - 1$, which runs in the leftover sum from $(N = 2 \leftrightarrow k = 1)$ up to $k = \infty$, allows us to simplify this expression as

$$\begin{aligned}\sum_{N=1}^{\infty} P(N) &= p\left[1 + \sum_{k=1}^{\infty} q^k\right] = p\left[1 + \frac{q}{1-q}\right] \\ &= p\left[\frac{1}{1-q}\right] = 1 \quad \checkmark\end{aligned}$$

In the first line we used the equation (1.2) to evaluate the infinite sum, and then in the second line we simplified using $p + q = 1$.

(c) Intuitively, what is the mean number of times you would roll the die, each time you played this (admittedly rather dull) game? Now try to derive the answer using the definition of a mean value.

The following two infinite sums valid for $q < 1$ are useful:

$$\sum_{k=1}^{\infty} q^k = \frac{q}{1-q}, \tag{1.2}$$

$$\sum_{k=1}^{\infty} kq^k = \frac{q}{(1-q)^2} \tag{1.3}$$

Solution: Intuitively, since on each turn there's 1/6 chance of success, you expect to need to play approximately 6 times in order to roll a 6.

We can derive this result as follows. The probability of success on the N'th roll is $P(N)$ given above. In general, N can run from 1 (if you are lucky) to infinity (if you are very very unlucky). The average value of N is then computed by the weighted sum,

$$\langle N \rangle = \sum_{N=1}^{\infty} N P(N) = \sum_{N=1}^{\infty} N q^{N-1} p$$

We can evaluate the sum as follows:

$$\langle N \rangle = p \sum_{N=1}^{\infty} N q^{N-1} = p \left[(1) q^0 + \sum_{N=2}^{\infty} N q^{N-1} \right]$$

Evaluating $q^0 = 1$, and changing variables to $k = N - 1 \leftrightarrow N = k + 1$ so that the remaining sum runs from $k = 1$ to ∞, we can rewrite the expression in terms of the given sums (1.2) and (1.3):

$$\begin{aligned} \langle N \rangle &= p \left[1 + \sum_{k=1}^{\infty} (k+1) q^k \right] = p \left[1 + \sum_{k=1}^{\infty} k q^k + \sum_{k=1}^{\infty} q^k \right] = p \left[1 + \frac{q}{(1-q)^2} + \frac{q}{(1-q)} \right] \\ &= p \left[\frac{(1-q)^2 + q + q(1-q)}{(1-q)^2} \right] = \frac{1}{p} = 6 \end{aligned}$$

In the second line we simplified using $1 - q = p$, and $p = 1/6$.

1.2 Statistical Definitions of Temperature and Entropy

Example: Interacting Einstein solids with oscillators A useful step in understanding the specific heats of solids and statistical definitions of temperature and entropy was Einstein's 1907 proposal that a solid could be considered to be a large number of identical quantum harmonic oscillators, each oscillating with the same frequency ω. This was a first attempt at including quantum mechanical effects in the model of a solid. To get a feel for this model of heat transfer, we will first do an example.

In-Class Exercise: Probability and Heat Transfer

You will need 4 chips and 2 index cards. Take two index cards and draw two circles about the size of the chips on each card. Label the cards "A" and "B". A and B will be your two objects.

Now take 4 chips, which will represent thermal energy. For example, if Object A has 3 chips and Object B has 1 chip, then Object A is hotter than Object B. The circles on the cards represent places in the object where thermal energy can be stored. *It is ok to store more than one chip on the same circle.*

1. Let's say A has 3 chips, and B has 1 chip. The two objects are far away from each other, so heat cannot flow from one to the other. Count up the number of ways you can arrange the chips for each object (each arrangement is called a "macrostate").

   Which macrostate has the most microstates (multiplicity Ω), and thus the largest entropy, defined as $S = k_B \ln \Omega$?

Solution: There are two ways to arrange the single chip in B: the chip can be in the first circle, or the second circle.

The possibilities for Object A are the number of ways to partition 3 chips into 2 distinct spaces. There are 4 such possibilities: 3 chips in the first circle $(3+0)$; 2 chips in the first circle, 1 in the second circle $(2+1)$; 1 chip in the first circle, 2 in the second circle $(1+2)$; 0 chips in the first circle, 3 chips in the second circle $(0+3)$.

As we will discuss below, applying the general formula yields

$$\Omega_A = \frac{(3+2-1)!}{3!(2-1)!} = 4\,, \qquad \Omega_B = \frac{(1+2-1)!}{1!(2-1)!} = 2 \quad \checkmark$$

2. Now bring the two cards together, allowing for the possibility of chips to jump from one to the other. Boltzmann's theory says that all states are possible: 4 in A and 0 in B, 3 in A and 1 in B, *etc.* For each state, count all the arrangements of the chips that are possible, and remember, you always have to have 4 chips on the cards—we're not counting cases where some chips have fallen on the floor (conservation of chips/energy!)

   Which state is most likely? Which state has the highest entropy? Which way should heat (chips) flow?

Description of Macrostate	# of Arrangements (Microstates)	$S = k_B \ln \Omega$
4 in A, 0 in B		
3 in A, 1 in B		
2 in A, 2 in B		
1 in A, 3 in B		
0 in A, 4 in B		

Solution:

Description of Macrostate	# of Arrangements (Microstates)	$S = k_B \ln \Omega$
4 in A, 0 in B	$5 \times 1 = 5$	$k_B(1.6)$
3 in A, 1 in B	$4 \times 2 = 8$	$k_B(2.1)$
2 in A, 2 in B	$3 \times 3 = 9$	$k_B(2.2)$
1 in A, 3 in B	$2 \times 4 = 8$	$k_B(2.1)$
0 in A, 4 in B	$1 \times 5 = 5$	$k_B(1.6)$

The macrostate with the highest entropy is the one with the highest multiplicity of microstates, which is the one with 2 in A and 2 in B, so that the thermal energy is evenly spread out and the system is in equilibrium. We expect that if we start in one of the other states, we should flow to thermal equilibrium, so we should flow to the state with the maximum entropy.

The above problem represents a simple model of two Einstein solids, A and B, each with $N_A = N_B = 2$ oscillators, exchanging $q = 4$ units of thermal energy between them. Recall that the quantum harmonic oscillator is the quantum treatment of a particle in the harmonic potential $U(x) = \frac{1}{2}kx^2$, where k is the spring constant related to the classical angular frequency ω of the simple harmonic motion as $k = m\omega^2$. Classically, the particle oscillates back and forth. Quantum mechanically, the probability of finding the particle at some location is given by the wavefunction. The possible wavefunctions describe a series of equally spaced quantized states, with energies

$$E_n = \hbar\omega(\frac{1}{2} + n)\,, \qquad n = 0, 1, \ldots, \infty$$

Consider the solid to be composed of N oscillators. Given a total amount of q units of energy in the solid, what is the multiplicity of the distribution of energy among the available energy states of the system? We assume that all of the quantum harmonic oscillator levels are considered equally probable, within the constraint of having a total of q units of energy and N oscillators. (So, in particular, the total internal energy is $U = q\hbar\omega + \frac{N\hbar\omega}{2}$, since there are q total energy quanta in the system plus the ground state energy of each oscillator.)

In the in-class exercise, you considered the case of two solids that each had 2 oscillators. Just focusing on a single solid for the moment, consider a solid with 3 oscillators, and assume the total energy is fixed at 3 units (the macrostate). The possible microstates are:

Oscillator:	1	2	3	
Energy in each oscillator:	3	0	0	● ● ● | |
	0	3	0	| ● ● ● |
	0	0	3	| | ● ● ●
	2	1	0	● ● | ● |
	2	0	1	● ● | | ●
	1	2	0	● | ● ● |
	0	2	1	| ● ● | ●
	1	0	2	● | | ● ●
	0	1	2	| ● | ● ●
	1	1	1	● | ● | ●

This macrostate ($q = 3$ units of energy amongst $N = 3$ oscillators) has multiplicity 10.

——— *End Lecture 2.*

To obtain the general formula for the multiplicity, it is nice to think about this problem as follows. We have q units of energy (denote these by dots ●), which must be distributed amongst N slots, which can be represented by placing $N - 1$ boundaries amongst the circles. See the table above for an example.

The possible microstates thus consist of the distribution of two types of items: q circles and $N - 1$ boundaries. Therefore, there are $q + (N - 1)$ total slots in which to place a symbol, where each slot has a binary choice: either circle or boundary. This rephrases the problem in terms of our binomial coefficient! For N oscillators, the multiplicity of the macrostate with q units of energy is equal to the number of ways to arrange these $q + (N - 1)$ binary choices is

$$\Omega(q; N) = \left(\begin{array}{c} q + (N-1) \\ q \end{array} \right) = \frac{(q + N - 1)!}{q!(N-1)!}$$

Indeed, we may verify that for $N = 3$, $\Omega(3; 3) = \frac{(3+2)!}{3!2!} = 10$. You may also verify that applying this formula to the in-class exercise gives the correct multiplicities in that example.

Now, we wish to use this model to model a system of two interacting solids A and B. Suppose we have two interacting Einstein solids that each have 3 oscillators. Assume the total energy is fixed at $q = 6$ units. (Also, assume that the transfer of energy between the solids is slow compared with the transfer between oscillators within one solid.) There are 7 possible macrostates of the combined system: $q_A = 0$ units of energy in solid A and $q_B = 6$ untis of energy in solid B; $q_A = 1$ units of energy in solid A and $q_B = 5$ units of energy in solid B, and so on. For each macrostate, we have already calculated the multiplicity of microstates for each individual solid (which each have $N_A = N_B = 3$ oscillators):

$$\Omega_A(q_A; N_A) = \frac{(q_A + N_A - 1)!}{q_A!(N_A - 1)!}\,, \qquad \Omega_B(q_B; N_B) = \frac{((q - q_A) + N_B - 1)!}{(q - q_A)!(N_B - 1)!}\,, \quad N_A = 3\,, \; N_B = 3$$

where we used $q = q_A + q_B$ to write the multiplicity Ω_B in terms of the variable q_A, which is sufficient to label the macrostate. Then, the *total* multiplicity for each macrostate labeled by q_A is the product of these two, $\Omega_{\text{tot}}(q_A) = \Omega_A \Omega_B$. In particular, for this example the 7 different macrostates have the following number of microstates:

q_A	$\Omega_A(q_A; N_A)$	q_B	$\Omega_B(q_B; N_B)$	$\Omega_{\text{tot}} = \Omega_A\Omega_B$
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28

There are a total of $28 + 63 + 90 + 100 + 90 + 63 + 28 = 462$ possible microstates amongst all the possible macrostates. *Note:* this total number of 462 microstates is the same as what you would get from 6 oscillators with 6 energy units regardless of whether you split them up into two solids: $\Omega(6; 6) = \frac{(6+6-1)!}{6!(6-1)!} = 462$. This makes physical sense, but also follows from the following mathematical identity of binomial coefficients (called the Chu-Vandermonde identity):

$$\begin{pmatrix} \alpha \\ q \end{pmatrix} = \sum_{q_A=0}^{q} \begin{pmatrix} \beta \\ q_A \end{pmatrix} \begin{pmatrix} \alpha - \beta \\ q - q_A \end{pmatrix}$$

which holds for any nonnegative integer q.

The probability distribution for a given macrostate labeled by $q_A = 0, 1, 2, 3, 4, 5, 6$ is,

$$P(q_A) = \frac{\Omega_{\text{tot}}(q_A)}{462}$$

and is plotted in Figure 1. Clearly, the number of multiplicities gets huge as I consider even slightly more realistic solids. For example, the system of two interacting Einstein solids with 300 oscillators in A, 200 oscillators in B, and a total of 100 units of energy has a total of 9.3×10^{115} microstates, with probabilities of each of the 101 macrostates being realized ranging from $\sim 3 \times 10^{-35}$ to $\sim 7 \times 10^{-2}$. This huge number of microstates is pictured in Figure 2. Notice that the plot of the multiplicity as a function of q_A is highly peaked around $q_A = 60$ (so, $q_B = 40$); this is precisely the point where energy is shared equally amongst all the oscillators. Since solid A has 300 oscillators sharing 60 units of energy and solid B has 200 oscillators sharing 40 units of energy, on average, every oscillator has 1/5 a unit of energy. (Not actually possible, but you get the idea!) This is precisely when the two systems are at thermal equilibrium.

As a simpler example where the two solids have equal sizes, consider this plot for $N_A = N_B = N$, so that there are $2N$ total oscillators with $q = q_A + q_B$ total units of energy. We're interested in the thermodynamic limit, where N is large. The average value of q_A is $q/2$, and the plot of the multiplicity as a function of q_A is highly peaked around this average value, while the width of the peak is relatively small — much much smaller than the total energy (ignoring the ground state energy contribution, the total energy goes like $U = q\hbar\omega$, and the standard deviation is smaller by a factor of $\sim 1/\sqrt{N}$). This means that for large N, we can

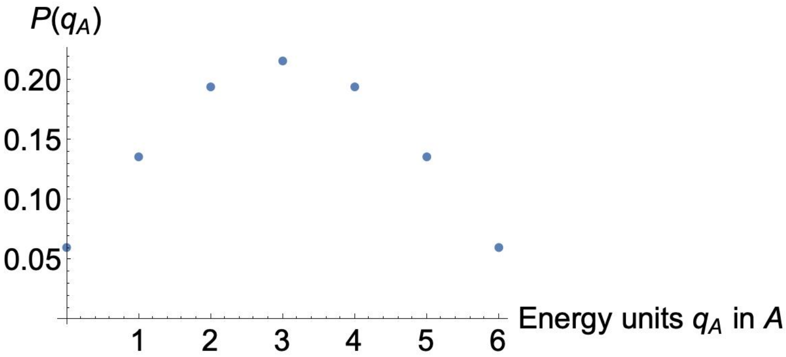


Figure 1: Probabilities of realizing the 7 different macrostates for the two-Einstein solid system with 6 total oscillators and 6 total units of energy.

pretty confidently say that the energy units will be split evenly between the two sides, with $q_A = q_B = q/2$. This *most likely* macrostate corresponds to the equilibrium state of the system: the state where the internal energy is evenly distributed between the two solids in contact. This is an example of how things simplify in the **thermodynamic limit**: here, N is so large that deviations from the most common macrostate are undetectable. There is a small chance that the energy will be distributed unevenly amongst the two solids, but the probability of actually realizing the most unlikely configurations becomes vanishingly small.

This is a nice model for exploring the statistical connection between thermodynamic entropy, the number of microstates, and the temperature, as understood by Boltzmann. The second law of thermodynamics establishes the concept of entropy as a property of a thermodynamic system, and can be understood essentially as the following statements:

- Systems will spontaneously shift towards states of larger multiplicity.
- Multiplicity tends to increaes.
- Any large system in equilibrium will be found in the macrostate with the greatest multiplicity.
- If a system composed of a large number of molecules is allowed to evolve in isolation, then with overwhelming probability, the system will evolve into the macrostate of largest multiplicity and will subsequently remain in that state.

These statements are formalized by introducing the concept of **entropy**: the entropy S of a system at fixed energy that is in a particular macrostate, with multiplicity Ω number of macrostates associated to that macrostate, is given by,

$$\boxed{S = k_B \ln \Omega}$$

where k_B is Boltzmann's constant, $k_B = 1.3807 \times 10^{-23} J \cdot K^{-1}$. (This famous equation of Boltzmann's is engraved on his tombstone in Vienna!) Then, the 2nd law of thermodynamics can be phrased as the statement that:

- The total entropy of an isolated system either increases or remains constant in any spontaneous (irreversible) process; it never decreases:

$$\boxed{\Delta S \geq 0}$$

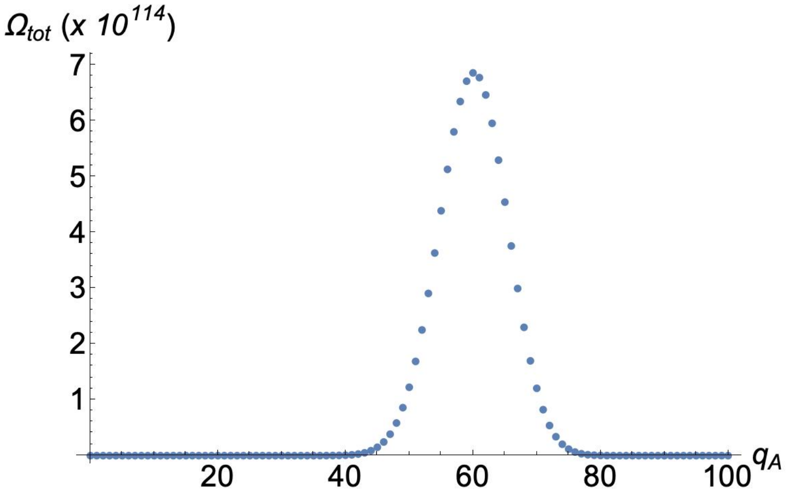


Figure 2: Number of microstates realizing each of the 101 different macrostates for the two-Einstein solid system with 300 + 200 total oscillators and 100 total units of energy.

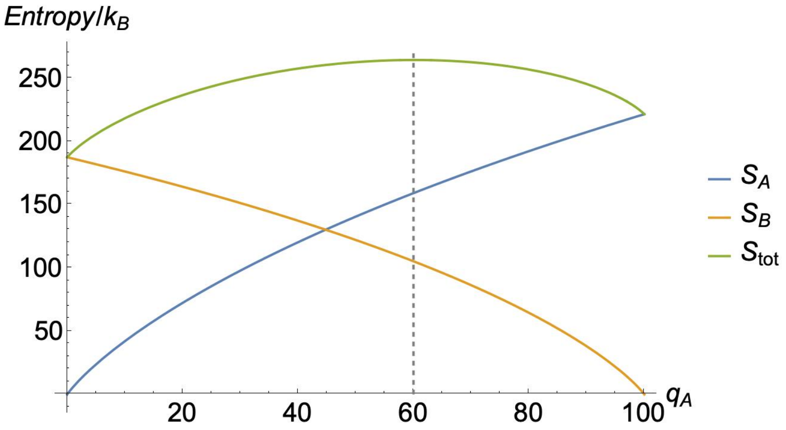


Figure 3: Entropy as a function of q_A for the example in Figure 2.

For instance, consider again our example system of the Einstein solids, with $N_A = 300$ and $N_B = 200$ total oscillators in each solid, so that there are 500 total oscillators, and total energy units $q = 100 = q_A + q_B$. The entropy associated to each of the solids in a given macrostate is

$$S_A = k_B \ln \Omega_A \,, \qquad S_B = k_B \ln \Omega_B$$

and the total entropy is the sum of the two:

$$S_{\text{tot}} = k_B \ln \Omega_A \Omega_B = k_B \left(\ln \Omega_A + \ln \Omega_B \right) = S_A + S_B$$

(We can also rewrite these in terms of the total internal energies of the solids, $U_A = q_A(\hbar\omega)$, and $U_B = q_B(\hbar\omega)$.) Figure 3 plots these entropies as a function of the units of energy q_A in solid A. The total entropy has a maximum precisely at the most likely macrostate, with $q_A = 60$. This system therefore nicely realizes the expectation of the 2nd law of thermodynamics.

We have discussed that heat flows from objects with larger temperature to ones with smaller temperature. Intuitively, the solid with more energy per oscillator is at a larger temperature (the atoms oscillating "faster"), so that as thermal energy is exchanged the system evolves to the state where the temperature of the two solids is the same. The statistical definition of the temperature defines it in terms of the change of entropy as a function of internal energy: for a system at constant volume (as is the case for our Einstein solids),

$$\frac{1}{T} = \frac{\partial S}{\partial U} \tag{1.4}$$

You can check from this definition that precisely at the maximum entropy, the two solids A and B have the same temperature, $T_A = T_B$ precisely at $q_A = 60$, which is where $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$. We'll come back to the definition of temperature later.

1.3 Heat Capacity

As we have discussed, *heat* denoted by the symbol (Q) is the spontaneous transfer of energy between two objects in thermal contact that have different temperatures. **Heat capacity** is defined as a property of a particular object, that tells us how much energy it would take to raise the temperature of that object by $1K$. It answers the question: how much heat needs to be supplied to an object to raise its temperature by a small amount dT? We use the symbol C, and it is given in units of energy per Kelvin, $[C] = J \cdot K^{-1}$,

$$\boxed{\text{Heat capacity:} \qquad C = \frac{dQ}{dT}}$$

This is a useful, measurable characteristic of an object.

Specific heat is the property of a particular substance that tells us how much energy it would take to raise the temperature of a known amount of the substance (in principle could be by volume, mass, or number of moles) by an amount $1K$. So, this is given as heat per unit mass (or per unit volume) per unit temperature. Typically when we discuss **specific heat capacity** we mean heat capacity C per unit mass kg, and use the letter c.

For example, the heat required to raise the temperature of 1 kg of liquid water by 1 K is 4184 J, so we would say that the specific heat capacity of water is $c = 4184\, J\, K^{-1}\, kg^{-1}$.

For our Einstein solids, their heat capacity can be found by expressing the internal energy U as a function of their temperature T, so that

$$C = \frac{\partial U}{\partial T}$$

We'll see later that this is the general definition of the heat capacity of an object at constant volume V, as is the case for our Einstein solids with constant number of oscillators N.

In-Class Exercise: Measuring Heat Capacity

To measure the heat capacity of an object, all you usually need to do is put it in thermal contact with another object whose heat capacity you know.

Suppose that a chunk of metal (Unobtainium perhaps?) is immersed in boiling water at $100^\circ\, C$ then is quickly transferred to a Styrofoam cup containing $250g$ of water at $20^\circ\, C$. Water has a specific heat capacity of $4.184 \times 10^3\, J \cdot kg^{-1} \cdot K^{-1}$. After a minute or so, the contents of the cup are $24^\circ\, C$. Assume that during this time no significant energy is transferred between the contents of the cup and the surroundings, and that the heat capacity of the cup itself is negligible.

1. How much heat was gained by the water?

Solution: Denote the specific heat capacity of water as $c = 4.184 \times 10^3\, J \cdot kg^{-1} \cdot K^{-1}$, which is the heat capacity per unit mass. $250\, g$ of water undergoes a temperature change of $\Delta T = (24+273.15)K - (20+273.15)K = 4\, K$. We can compute the change in heat ΔQ as

$$C = c \cdot \text{mass} = \frac{\Delta Q}{\Delta T}$$
$$\Rightarrow \ \Delta Q = c(\text{mass})\Delta T = (4.184 \times 10^3\, J \cdot kg^{-1} \cdot K^{-1})(4\, K)(0.250\, kg) = 4184\, J$$

2. How much heat was lost by the metal?

   Solution: By the first law (again, basically energy conservation!) the heat lost must equal to the heat gained, since we assume no energy transfer to the environment. $\Delta Q = 4184\, J$.

3. What is the heat capacity of the metal?

   Solution: Since the contents of the cup came to $24°C$, we know the temperature change of the metal, $\Delta T = (100 + 273.15)K - (24 + 273.15)K = 76\, K$, so we can compute

$$C = \frac{\Delta Q}{\Delta T} = \frac{4184\, J}{76\, K} = 55\, J \cdot K^{-1}$$

4. If the mass of the metal is $100\, g$, what is the specific heat capacity of the metal?

   Solution: Specific heat capacity is C per unit mass, so we can just divide:

$$c = \frac{C}{\text{mass}} = \frac{55\, J \cdot K^{-1}}{0.100\, kg} = 550 J \cdot K^{-1} \cdot kg^{-1}$$

——— End Lecture 3.

1.4 The Microscopic View of an Ideal Gas

Experiments on gases led to the following *ideal gas law*:

$$\boxed{\text{Ideal gas law:} \qquad PV = Nk_BT} \tag{1.5}$$

where N is the number of molecules in the gas, P is pressure, V is volume, T is temperature, and k_B is Boltzmann's constant, $k_B = 1.3807 \times 10^{-23}\, J \cdot K^{-1}$. This law says:

- For a fixed amount of gas at a constant temperature (fixed N, T), its pressure is inversely proportional to its volume.
- For a fixed amount of gas at constant pressure (fixed N, P), its volume is proportional to its temperature.
- For a fixed amount of gas at fixed volume (fixed N, V), its pressure is proportional to its temperature.

While this is an empirical law, it can be derived from the microscopic view of the gas under the following ideal gas assumptions: (1) that there are no forces between the molecules; (2) the molecules are point-like so we can neglect their size. This law describes a wide variety of gases for which these assumptions are pretty good.

To gain some intuition for this law, it is helpful to relate a microscopic kinetic model with the empirical ideal gas law. Consider the following setup: a piston of area A and length L has 1 single molecule of mass m in it. The molecule bounces around with some velocity, $\vec{v} = \vec{v}_x\hat{x} + \vec{v}_y\hat{y} + \vec{v}_z\hat{z}$. We assume that the collisions with the walls are elastic (preserve kinetic energy), so the velocity and therefore kinetic energy K will remain constant,

$$K = \frac{1}{2}mv^2 \, .$$

This is going to be a model for an ideal gas with $N = 1$ molecule. (We are assuming that the gas particle is a "point" particle, so it cannot vibrate or rotate, so its energy is entirely given by this kinetic energy.)

The pressure exerted by the piston on the gas (or equivalently, the pressure felt by the piston) is equal to the time averaged force applied by the piston per unit area,

$$P = \frac{\langle F \rangle}{A}$$

The force is due to the particle colliding with the piston, which causes an acceleration to the particle and changes its velocity. Let's focus on just one dimension for the moment. If the piston is applying force in the x direction, then this reverses the x-component of the velocity from $+v_x \to -v_x$, so that $\Delta v_x = 2v_x$. The instantaneous force due to a collision is then

$$F_x = ma_x = m\frac{\Delta v_x}{\Delta t} = m\frac{2v_x}{\Delta t}$$

The time-averaged force is given by assuming that the velocity change happens over an interval of time that it takes the particle to make a round trip inside the chamber, $\Delta t = 2L/v_x$,

$$\langle F_x \rangle = m\frac{2v_x}{\Delta t} = m\frac{2v_x}{2L/v_x} = m\frac{v_x^2}{L}$$

so the pressure is equal to

$$P = \frac{\langle F \rangle}{A} = \frac{mv_x^2}{LA} = \frac{mv_x^2}{V}$$

for V the volume of the chamber. Evidently, we see that this pressure is a kind of *kinetic energy per volume*, $P = 2K_x/V$. If we had many particles N, then there would be N times as much pressure due to their individual kinetic energies,

$$P = \frac{Nmv_x^2}{V} \quad \Rightarrow \quad PV = 2NK_x$$

This expression is from our kinetic model of the gas. This can be compared to the ideal gas law (1.5), $PV = Nk_BT$, which is from years of experiments on gases. If *both* are true, then we have derived the nice relationship between the (x-component of the) kinetic energy of each gas molecule, and the temperature:

$$K_x = \frac{1}{2}k_BT$$

We have identified the *energy per degree of freedom* of a particle as equal to $\frac{1}{2}k_BT$. Taking into account all three components of the kinetic energy in three dimensions (*i.e.* the three degrees of freedom) this expression is modified

$$K = K_x + K_y + K_z = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \frac{3}{2}k_BT \quad \text{per particle}$$

(There is a more rigorous way to derive this relationship between the average energy per degree of freedom of each particle and the temperature, known as the *equipartition theorem*, but this provides the intuition for where it comes from!)

We have learned that the ideal gas law $PV = Nk_BT$ microscopically comes from interpreting the kinetic energy of the gas molecules as the thermal energy of the gas, related to the gas's pressure and volume as

$$\boxed{U = \frac{3}{2}Nk_BT = \frac{3}{2}PV \quad \text{for an ideal monatomic gas.}} \tag{1.6}$$

2 The First Law of Thermodynamics

Textbook readings: (a first reading is due before Lecture 4; most pertinent to Lecture 4)

- Ch. 11, all

Learning Objectives:

- Energy, Heat, Work and the 1st Law: know the various statements of the 1st law, be comfortable with the partial derivatives

2.1 The First Law and Equations of State

We return to the first law of thermodynamics, which essentially states that energy is conserved, and heat and work are both forms of energy. First some terminology:

- As we have already seen, **heat** Q is thermal energy in transit. We'll denote the change in thermal energy by ΔQ, so that ΔQ is the heat supplied to a system (positive for heat supplied, negative for heat subtracted).

  Heat transfer can take place by three methods:

  - **Conduction** is heat transfer through physical contact; for instance, heat transferred between the burner on a stove and the bottom of a pan.
  - **Convection** is the transfer of heat by the motion of or within a fluid, for instance due to the expansion and rising of a warmer fluid versus a colder fluid, causing currents that transfer heat.
  - **Radiation** is heat transfer from the emission or absorption of electromagnetic radiation (photons), for instance by the warming of the Earth by the Sun.

- **Work** is a second form of energy transfer between two systems that is distinct from heat in the following way: while heat transfer occurs spontaneously once thermal contact is established, *work* is done by one system on another when it directly alters some parameter of the system *other than temperature*. Basically, any energy transfer that is not heat is work. We'll denote by ΔW the work done on a system, so that ΔW is positive for work done on the system and negative when the system does work on its surroundings.

  Work can take many forms; a common example of which is expansion or compression (volume change). The work done by compressing a gas (of pressure P and volume V) by a piston of surface area A is related to the force $F = PA$ applied by the piston, as[1]

$$đW = F\,dx = PA\,dx = P(-dV) \quad \Rightarrow \quad đW = -PdV$$

In this equation, the negative sign is so that the work $đW$ done *on* the system is positive when dV is negative, so when the gas is being compressed. We will explain the notation $đ$ rather than d in a moment.

In equations, the first law states that the total change in the internal energy U of a system is equal to the heat supplied to the system plus the work done on the system,

$$\boxed{\Delta U = \Delta Q + \Delta W} \tag{2.1}$$

The differential version of this equation is

$$\boxed{dU = đQ + đW} \tag{2.2}$$

For instance, consider the work done to go from some initial state to some final state through compression/expansion of the gas, $đW = -PdV$. The PV diagram gives a visual representation of the work done on the gas as the volume changes. If we know how the pressure changes as a function of volume, we can integrate this function, *i.e.* calculate the area under the PV curve in a plot of P versus V:

$$\Delta W \text{ done on the gas} = -(\text{area under } PV \text{ curve})$$

Some special cases:

- If P is constant as a function of V, then this is indeed equal to just $-P(V_f - V_i) = -P\Delta V$. This is an **isobaric** (constant pressure) process.
- More generally, if P is a nontrivial function of V, we need to compute the integral. For instance, suppose we have an ideal gas that undergoes **isothermal** process, *i.e.* a process that occurs at constant temperature. The pressure as a function of the constant temperature and changing volume is,

  $$PV = Nk_BT = \text{constant} \quad \Rightarrow \quad P = \frac{Nk_BT}{V}$$

  so that the work done is

  $$đW = -P\,dV = -\frac{Nk_BT}{V}\,dV \quad \Rightarrow \quad \Delta W = -Nk_BT\int_{V_1}^{V_2}\frac{dV}{V} \tag{2.3}$$

  This graph is hyperbolic, and we can compute

  $$\Delta W = -Nk_BT\,(\ln V_2 - \ln V_1) = Nk_BT\ln\frac{V_1}{V_2}$$

---

[1] In this equation, we are assuming that the piston is frictionless, so that extra heat is not dissipated in the process of applying force to the gas. In this case, the change process is *reversible.*

Exact versus inexact differentials Here we need to be careful, since $đQ$ and $đW$ are *inexact differentials*, rather than *exact differentials.* The difference is illustrated by the following example: If a system is described by only two parameters, x and y, and $f = f(x, y)$ is a function of x and y, then

$$df = \frac{\partial f}{\partial x}\, dx + \frac{\partial f}{\partial y}\, dy$$

If (x, y) change from (x_0, y_0) to (x_1, y_1), then the total change in the function f can be given by integrating the differential, which is completely independent of the exact path taken since df is an exact differential; it only depends on the values of f at the endpoints.

$$\Delta f = \int_{(x_0,y_0)}^{(x_1,y_1)} df = f\big|_{(x_0,y_0)}^{(x_1,y_1)} = f(x_1, y_1) - (x_0, y_0)$$

In particular, this implies that the integral of an exact differential over a closed loop is always zero,

$$\oint df = 0 \quad \text{since} \quad f(x_0, y_0) - (x_0, y_0) = 0$$

We would call $f(x, y)$ a *function of state*, where the state of the system is described by the parameters x, y, since it depends only on the initial and final states, and not the path taken between those intermediate and final states.

However, consider a differential of the form

$$đg = a(x, y)dx + b(x, y)dy$$

where $g = g(x, y)$, and where a and b are two general functions of x and y. If $a = \partial g/\partial x$ and $b = \partial g/\partial y$, then this would be an exact differential, since it would correspond to the total derivative dg. But if this is not the case, then when we try to integrate $đg$ to get the total change in the function g, the result is going to depend on the specifics of the path taken — on the specific functions a and b.

In general, whenever there is some amount of heat exchange involved, the amount of work done on a system depends on external factors such as the means of applying work, and not only on the initial final states. So, in general we should write $đW$ as an inexact differential, to remind ourselves that we will need to take into account the process by which the work was done and not just the endpoints. Of course, this also means that in general heat is not a function of state, so we need to write $đQ$ rather than dQ and specify the path that heat is exchanged. Put together, however, in general the internal energy U *is* a function of state; in general, the internal energy is a function of temperature and volume, $U = U(T, V)$, and we can write the exact differential as

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{2.4}$$

So, when no heat is exchanged ($\Delta Q = 0$) and the process is **adiabatic**, the work done equals the change in internal energy $\Delta U = \Delta W$, and we can replace the inexact differential $đW$ with an exact differential dW. Similarly, if no work is done in a process ($\Delta W = 0$), the heat transfar is equal to the change in internal energy $\Delta U = \Delta Q$, and we can replace $đQ \to dQ$.

2.2 Heat Capacity and the 1st Law

Next we would like to understand in greater detail how adding heat can change the internal energy of a gas. Recall that we have defined heat capacity as the property of an object that tells us how much energy it would take to increase the temperature of that object by 1 K. Since heat exchange in general depends on the path by which it is supplied (as we have said, heat is in general not a function of state), in applying the general definition "$C = dQ/dT$" we need to specify the details of the process: for a gas, for example, we can calculate the heat capacity at either constant volume or constant pressure, defined as

$$C_V = \left(\frac{đQ}{dT}\right)_V , \qquad C_P = \left(\frac{đQ}{dT}\right)_P \tag{2.5}$$

Using the second law, we can understand how these definitions are related to the change of the gas's internal energy. Starting with (8.1) and using the first law with $đW = -PdV$, we can rewrite

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = đQ - PdV \tag{2.6}$$

$$\Rightarrow đQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right) dV$$

$$\Rightarrow \frac{đQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right) \frac{dV}{dT} \tag{2.7}$$

This is an expression valid for any change in T or V. When V is held constant, however, we can drop the second term proportional to dV/dT, so that we identify the heat capacity at constant volume with

$$\boxed{C_V = \left(\frac{đQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V}$$

On the other hand, the heat capacity at constant pressure is in general *larger*, since some of the heat is used up in work done in changes of volume. In this case, it is simplest to start with the expression $đQ = dU + PdV$ to identify

$$\boxed{C_P = \left(\frac{đQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P} \tag{2.8}$$

——— *End Lecture 4.*

Note, another useful way to write these formulas is to express the difference as,

$$C_P - C_V = \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)\left(\frac{\partial V}{\partial T}\right)_P \tag{2.9}$$

Example: Heat capacities of an ideal monatomic gas. What are the heat capacities C_V, C_P for an ideal monatomic gas?

Solution: As we have seen, the internal energy U of an ideal, monatomic gas is due to kinetic energy, and can be written as a function only of temperature as (see (1.6))

$$U = \frac{3}{2} N k_B T \tag{2.10}$$

Therefore, even though in general we would expect $U = U(T, V)$, in this case it depends only on T, so

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad \text{for an ideal monatomic gas}$$

and the change in internal energy is given by

$$dU = C_V dT$$

since we can drop the second term in (2.6). This means that we can easily find the specific heat C_V of the ideal gas by differentiating (2.10) with respect to T, as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}Nk_B\,. \tag{2.11}$$

On the other hand, to compute C_P using (2.8), we can use the equation of state $PV = Nk_BT$ to differentiate V with respect to T at constant P:

$$\begin{aligned} C_P &= \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \\ &= \frac{3}{2}Nk_B + P\frac{\partial}{\partial T}\left(\frac{Nk_BT}{P}\right)_P \\ &= \frac{3}{2}Nk_B + P\frac{Nk_B}{P} = \frac{5}{2}Nk_B \end{aligned}$$

So, we see that $C_P > C_V$. (We could have equivalently used (2.9) to find $C_P - C_V = Nk_B$, yielding the same result.)

The ratio of C_P to C_V is called the **adiabatic index** γ, defined by

$$\boxed{\text{adiabatic index:} \quad \gamma = \frac{C_P}{C_V}} \tag{2.12}$$

Therefore, we see that the adiabatic index of an ideal monatomic gas is

$$\gamma = \frac{C_P}{C_V} = \frac{5/2\,Nk_BT}{3/2\,NK_BT} = \frac{5}{3} \quad \text{for an ideal gas}\,.$$

More generally, for a non-monatomic ideal gas where $U = \alpha Nk_BT$, you can follow through this derivation to find that $\gamma = 1 + \frac{1}{\alpha}$, so it's useful to write things in terms of γ in case we are dealing with a non-monatomic gas.

Aside: Ideal gas law per mole. The ideal gas law $PV = Nk_BT$ holds for a gas of N molecules. Another useful way to write this equation is to rewrite it per **mole**, where 1 mole of the gas is equal to Avogadro's number $N_A = 6.022 \times 10^{23}$ molecules of the gas. We can rewrite the number of molecules N as the number of moles n_m times N_A molecules per mole,

$$N = n_m N_A$$

Defining the **gas constant** $R = N_Ak_B = 8.31447\,J \cdot K^{-1} \cdot \text{mol}^{-1}$, the ideal gas law becomes

$$PV = n_m RT\,.$$

So, one mole of an ideal gas obeys the equation $PV = RT$.

In-Class Exercise: Expanding a Balloon

You are given an expandable balloon of Helium (a pretty good ideal, monatomic gas) with initial volume of $1L$, and an initial pressure of 1 atm. For some strange reason, you decide to expand the volume to $3L$ while simultaneously raising the pressure in direct proportion to the volume.

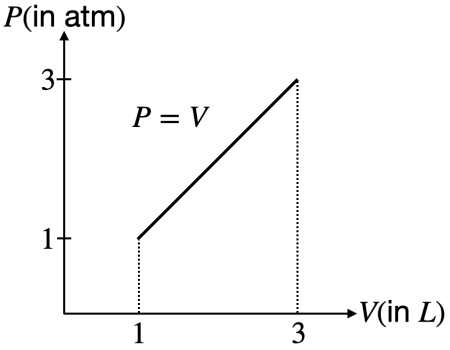
(a) Sketch P vs V.

Solution: We are raising the pressure in direct proportion to the volume, so the plot will take the form $P = V + b$ where b is the y-intercept. Since the slope of the curve is 1, and $P_i = 1$ we can compute

$$\text{slope} = 1\frac{\text{atm}}{L} = \frac{(P_f - 1)\text{atm}}{(3-1)L} \quad \Rightarrow \quad P_f = 3 \text{ atm}$$

Since $P_i = 1$ at $V_i = 1$, b is just zero, so the curve is

$$P = V.$$



(b) Calculate the work done **on** the gas.

Solution: The work done on the gas is minus the area under the curve, which is $(2L) \times (1\text{atm}) + \frac{1}{2}(2L) \times (2\text{atm}) = 4L \cdot \text{atm}$, or equivalently,

$$\Delta W = -\int_1^3 V\,dV = -\frac{V^2}{2}\bigg|_1^3 = -(3^2/2 - 1/2) = -4 \text{ atm} \cdot L$$

Since 1 atm $= 101,325$ Pa, 1 Pa $= 1\,J/m^3$, and $1L = 0.1 \times 10^{-3}\,m^3$, we can convert

$$\Delta W = -4 \text{ atm} \cdot L = 4 \times 101,325 \times 10^{-3}\,J/m^3 \cdot m^3 = -405\,J$$

Since the gas has expanded, the work done on the system is negative — this makes sense, since this corresponds to the case that the gas has actually done work to expand.

(c) Calculate the change in internal energy of the gas.

Solution: We know that the total change in internal energy is related to the heat supplied plus the work done, $\Delta U = \Delta Q + \Delta W$. However, we have not yet figured out the heat supplied. Intuitively we expect that there must be *some* heat supplied, since according to the equation of state,

$$PV = Nk_BT$$

as we change the pressure and the volume on the left-hand-side from $P_iV_i = 1$ to $P_fV_f = 3 \cdot 3 = 9$ atm$\cdot L$ (while keeping N the number of molecules the same), the temperature T on the right-hand-side must also be changing. Since the temperature is changing, the internal energy is changing, since recall that for an ideal gas we have that,

$$dU = C_V\, dT\,, \qquad C_V = \frac{3}{2}Nk_B$$

Using the equation of stat $PV = Nk_BT$ and substituting $P = V$ as we found in part (a):

$$T = \frac{PV}{Nk_B} = \frac{V^2}{Nk_B} \quad \Rightarrow \quad dT = \frac{2V\,dV}{Nk_B}$$

and we can integrate:

$$\begin{aligned}\Delta U = C_V \int_{V_i=1\,L}^{V_f=3\,L} \frac{2V\,dV}{Nk_B} &= \frac{3}{2}V^2\Big|_{V_i=1}^{V_f=3} = \frac{3}{2}(9-1)\,\text{atm}\cdot L \\ &= 12\,\text{atm}\cdot L = 12(101,325)(10^{-3})\,J = 1216\,J\end{aligned}$$

Of course, since dU is an exact differential, this only depends on the endpoints, and we could have equivalently evaluated:

$$\begin{aligned}\Delta U &= C_V\,(T_f - T_i) = \frac{3}{2}Nk_b\left(\frac{P_fV_f}{Nk_B} - \frac{P_iV_i}{Nk_B}\right) \\ &= \frac{3}{2}\,(9-1)\,\text{atm}\cdot L = 12\,\text{atm}\cdot L = 12(101,325)(10^{-3})\,J = 1216\,J\end{aligned}$$

In either case, we compute the total change in internal energy $\Delta U = 1216\,J$.

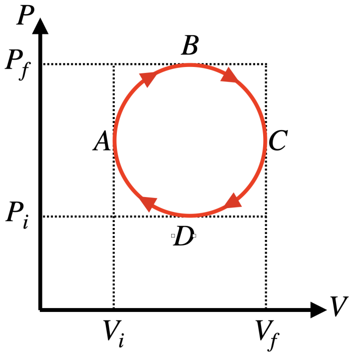
(d) Calculate the heat added or removed during this mysterious and wonderful process.

Solution: Finally, we can use

$$\Delta U = \Delta Q + \Delta W \quad \Rightarrow \quad \Delta Q = \Delta U - \Delta W = 1216\,J - (-405)J = 1621\,J$$

Note: 1 atm = $101,325$ Pa, and 1 Pa = $1\,J/m^3$, and $1\,L = 10^{-3}\,m^3$.

Another nice example of a problem like this is as follows.



Example: A cyclic process Consider the above example of a cyclic process for an ideal gas: the gas first expands from V_i to V_f from $A \to B \to C$, and then contracts from V_f back to V_i from $C \to D \to A$. What is the net work done during this cycle?

We can break this up into two pieces: first the work done from $A \to B \to C$, and then the work done from $C \to D \to A$. In each case, the work done is equal to minus the area under the curve:

$$\begin{aligned} -\Delta W_{A\to B\to C} &= \frac{1}{2}(\text{area of circle}) + (\text{area of rectangle } ACV_fV_i) \\ -\Delta W_{C\to D\to A} &= -\left[(\text{area of rectangle } ACV_fV_i) - \frac{1}{2}(\text{area of circle})\right] \end{aligned}$$

where there is an overall extra minus sign in the latter expression since we are integrating in the opposite direction, from $V_f \to V_i$ rather than $V_i \to V_f$. Adding these two contributions together,

$$-\Delta W_{\text{full cycle}} = -\Delta W_{A\to B\to C} - \Delta W_{C\to D\to A} = (\text{area of circle})$$

The total work done is (minus) the area enclosed by the curve, since the other pieces cancel out. This is equal to π times the radius in the P-direction, $\frac{1}{2}(P_f - P_i)$, times the radius in the V-direction, $\frac{1}{2}(V_f - V_i)$:

$$-\Delta W_{\text{full cycle}} = \frac{\pi}{4}(P_f - P_i)(V_f - V_i)$$

This is a general result: **for a cyclic process, the net work done is (minus) the area bounded by the loop.**

Follow up question: what is the total change in the internal energy of the gas in this process?

The internal energy of an ideal gas depends only on its temperature, $dU = \frac{3}{2}Nk_B\,dT$. So, the change in internal energy as the gas goes between T_1 and T_2 is proportional to the change in temperature:

$$\Delta U = \frac{3}{2}Nk_B(T_2 - T_1) = \frac{3}{2}(P_2V_2 - P_1V_1)$$

This means that for the cyclic process where we start and end at the same values of P and V, $\Delta U = 0$!

$$\boxed{\Delta U_{\text{full cycle}} = 0}$$

3 Isothermal and Adiabatic Processes

Textbook readings: (a first reading is due before Lecture 5; most pertinent to Lecture 5):

- Ch. 12, all

Learning Objectives:

- Processes: Isothermal and Adiabatic: be able to calculate W, Q, ΔU for constant P and V processes

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Throughout this section we will assume that processes are reversible; so for instance there is no friction.

An **isothermal** process is a process that occurs at constant temperature, $\Delta T = 0$. Recall that for an ideal gas, $dU = C_V dT$, so an isothermal expansion of an ideal gas has no change in U, and we can set

$$đW = -đQ = -PdV$$

To compute ΔW and ΔQ we need to integrate, which we did above in (2.3); substituting for $P = Nk_BT/V$ and integrating $\int dV/V = \ln V$, we can calculate the change in heat as,

$$\Delta Q = Nk_BT \int_{V_1}^{V_2} \frac{dV}{V} = Nk_BT \ln \frac{V_2}{V_1} \tag{3.1}$$

On the other hand, an **adiabatic** process is one in which there is no flow of heat; the system is thermally isolated, so $đQ = 0$, and the first law implies that $dU = đW$. Since for an ideal gas $dU = C_V dT$, and using $đW = -PdV$, this allows us to obtain a relationship between the temperature and volume as:

$$C_V dT = -PdV = -\frac{Nk_BT}{V} dV \quad \Rightarrow \quad \frac{dT}{T} = -\frac{Nk_B}{C_V}\frac{dV}{V}$$

Recall that for an ideal gas, $C_V = \frac{3}{2}Nk_B$ (see (2.11)). Now that we've isolated a function of T on the left-hand-side and a function of V on the right-hand-side, we can integrate

$$\int_{T_1}^{T_2} \frac{dT}{T} = -\frac{Nk_B}{C_V} \int_{V_1}^{V_2} \frac{dV}{V}$$
$$\ln \frac{T_2}{T_1} = -\frac{Nk_B}{C_V} \ln \frac{V_2}{V_1}$$

Exponentiating both sides,

$$\Delta T = (\Delta V)^{-\frac{2}{3}} \quad \Rightarrow \quad \Delta T (\Delta V)^{\frac{2}{3}} = 1$$

——— *End Lecture 5.*

This is related to the coefficient we called the *adiabatic index* as,

$$\gamma = \frac{C_P}{C_V} = \frac{5}{3} \quad \Rightarrow \quad \frac{2}{3} = \gamma - 1$$

so a nice way to write this expression is as

$$TV^{\gamma-1} = 1$$

or equivalently, using $T = \frac{PV}{Nk_B}$,

$$PV^{\gamma} = Nk_B = \text{constant}$$

It's useful to leave these relations in terms of γ, since ideal gases that are not monatomic will have different values of γ.

To summarize, we have discussed the following processes for an ideal gas:

$$\boxed{\begin{aligned} \text{Isobaric expansion of ideal gas: } & P = \text{const} \\ \text{Isothermal expansion of ideal gas: } & P = Nk_BTV^{-1} \\ \text{Adiabatic expansion of ideal gas: } & P = Nk_BV^{-\gamma} \end{aligned}}$$

4 The Second Law, Entropy, and Heat Engines

Textbook readings: (a first reading is due before Lecture 6; most pertinent to Lectures 6-8):

- Ch. 13, all
- Ch. 14 sections 14.1-14.3

Supplementary references:

- This is a nice video on heat engines, with some worked problems on efficiency at the end `https://www.youtube.com/watch?v=X3cuxQEc2gs`.

Learning Objectives:

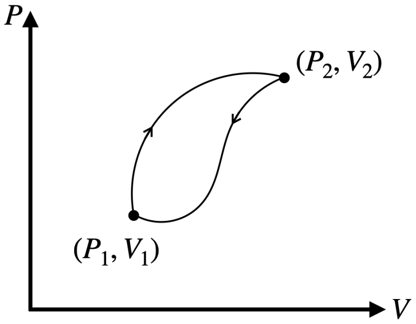
- Heat engines: Carnot, Otto, Diesel
- For a cycle: $\Delta S_{\text{system}} = 0$, $\Delta S_{\text{universe}} \geq 0$
- The thermodynamic definition of entropy and the 2nd law: $dS = dQ/T$ and its use, for systems at constant T versus systems undergoing a change in T

4.1 The 2nd law and Cyclic Processes

The essence of the second law of thermodynamics is that there is a preferred arrow of time in the macroscopic world. Hot coffee cools down, a ball on top of a hill falls down the hill, *etc.*

Before we state the thermodynamic version second law, it will be useful to again emphasize our focus so far on processes which are *reversible*: that can work in both directions of time, or in other words, can be run backwards. This is the thermodynamic equivalent of frictionless motion in mechanics.

For example, we've been considering a closed loop on a PV-diagram, where we start at some (P_1, V_1), take one path to (P_2, V_2), and then take another path back to (P_1, V_1). As we have



discussed ,the first law states that $\Delta U = 0$ along this whole cycle (this is the statement of energy conservation!). Going one way around the loop, work is performed *by* the system, by absorbing heat from its surroundings: it converts heat into work. Going the other way around the loop, work is done *on* the system, and the system emits energy as heat. It is useful to think about these cyclic processes; run the right way, they convert heat into work.

The second law is usually expressed in one of two forms:

- á la Lord Kelvin: *No process is possible whose sole result is the complete conversion of heat into work.* In other words, it is easy to convert work to heat, but much harder to go the other way around!
- á la Clausius: *No process is possible whose sole result is transfer of heat from a colder body to a hotter body.* In other words, heat flows from hot to cold. This views the second law as a statement about the direction of heat flow as a system approaches equilibrium: heat flows from hot to cold.

Historically, the practical impetus for the development of the science of thermodynamics in the 19th century was the advent of heat engines, which led to these scientists' important works. As we will see, these statements will allows us to define a quantity called *entropy*.

We call an **engine** is a cyclic process that converts heat to work. A heat engine takes some heat from a hot reservoir (for instance, a coal fire), does some work, and dumps the rest of the heat into a cold reservoir (for instance, the atmosphere). The cost of running the engine is heat, and the benefit is work.

Kelvin's statement is that we can't extract heat from a hot reservoir and turn it *entirely* into work: it also deposits some heat elsewhere (gives some back). There is no such thing as a perfect engine. The energy available for work is the difference between the heat extracted and the heat lost,

$$-\Delta W = \Delta Q = Q_H - Q_C$$

A **refrigerator** does the opposite: it takes heat from a cold reservoir and some external work, and dumps the rest of the heat into a hot reservoir. In this case we supply work in order to transfer heat from a cold environment (inside the fridge) to a hot one (outside the fridge).

Because we are supplying work, we get around Clausius' statement that heat normally flows from hot to cold; this is why your electricity meter goes up! Clausius' statement is the statement that there is no such thing as a perfect refrigerator. The cost of running the refrigerator is work (done by expending electricity), and the benefit is heat.

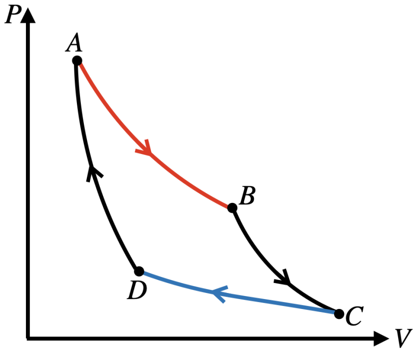


Figure 4: A Carnot cycle.

Denote by $đQ$ the heat supplied to the system at each point of the closed cycle. (So, if the system releases heat, this quantity is negative, and if it absorbs heat it is positive.) It is a fact about *reversible* cycles that the total heat absorbed must obey:

$$\sum_{\text{cycle}} \frac{\Delta Q}{T} = \oint \frac{đQ}{T} = 0 \quad \text{reversible cycle} \tag{4.1}$$

To get some intuition as to why this is true, let us consider the *Carnot engine*. A Carnot engine is an idealized version of a heat engine that is reversible, run in a cycle, and where all of its heat exchanges take place at a source temperature T_H and a sink temperature T_C. Then, the distinguishing characteristic of the Carnot engine is that heat exchanges with the surroundings are carried out at only two temperatures. Basically, the two reservoirs are assumed to be so large as to have an infinite heat capacity, so that their temperatures remain constant cycle after cycle.

The way that the Carnot engine can operate between only the two temperatures T_H and T_C is by undergoing a series of isothermal and adiabatic processes. Again, the net heat absorbed by the system is $\Delta Q = Q_H - Q_C$, which is equal to minus the area inside the PV curve. Consider the pictured Carnot cycle going from $A \to B \to C \to D \to A$.

1. On $(A \to B)$, the system undergoes an isothermal expansion at a constant hot temperature T_H. The gas is doing work on its surroundings to expand, and absorbing some heat Q_H from its surroundings.
2. On $(B \to C)$, the system undergoes an adiabatic expansion with no heat exchange. Since no heat is exchanged but the gas is still allowed to expand, the temperature decreases from $T_H \to T_C$.
3. On $(C \to D)$, the system undergoes an isothermal contraction at the constant cooler temperature T_C. The surroundings do work on the gas to compress it, and some heat Q_C is dumped into the surroundings.
4. Finally, from $(D \to A)$ the system undergoes an adiabatic contraction with no heat exchange. Since no heat is exchanged by the gas is squeezed, the temperature rises back from $T_C \to T_H$.

We can add up the total $đQ/T$ around the cycle as follows:

$$\sum_{\text{cycle}} \frac{đQ}{T} = \frac{Q_H}{T_H} + 0 - \frac{Q_C}{T_C} + 0 = \frac{Q_H}{T_H} - \frac{Q_C}{T_C}\,.$$

There is no heat change on the adiabats, but on the isotherms there is. Recall that we have already shown in (3.1) that the heat transfer of an ideal gas on an isotherm is related to the gas' temperature and change in volume $V_1 \to V_2$ as:

$$Q = Nk_BT \ln \frac{V_2}{V_1}$$

Therefore, actually Q_H and Q_C are simply related to each other:

$$\begin{aligned} Q_H &= Nk_BT_H \ln \frac{V_2}{V_1}\,, \qquad Q_C = -Nk_BT_C \ln \frac{V_1}{V_2} \\ \Rightarrow \quad \frac{Q_H}{T_H} - \frac{Q_C}{T_C} &= Nk_BT\left(\ln \frac{V_1}{V_2} - \ln \frac{V_1}{V_2}\right) = 0 \end{aligned} \tag{4.2}$$

Thus, we see explicitly that the heat absorbed on a Carnot cycle of an ideal gas satisfies (4.1). It turns out that this statement will actually hold true for any *reversible* process; the total heat exchanged obeys $\oint đQ/T = 0$.

What this means is that if we reversibly change our system from say $A \to B$, the quantity $\int_A^B đQ/T$ is independent of the path taken from A to B. This quantity is a function of state! We call this function of state the **entropy**, S:

$$\boxed{\Delta S = S(B) - S(A) = \int_A^B \frac{đQ}{T} \qquad \text{for reversible changes}}$$

or in differential form,

$$\boxed{dS = \frac{đQ}{T} \qquad \text{for reversible changes}}$$

Then, $\Delta S = 0$ for a closed cycle, for instance for the Carnot cycle. Amazingly, this thermodynamic definition of entropy is the same as the statistical one we saw earlier, $S = k_B \ln \Omega$. We will see this later in the course.

A more general statement applies to any path, reversible or irreversible, using *Clausius' inequality* for any cyclic process:

$$\boxed{\text{Clausius' inequality:} \qquad \oint \frac{đQ}{T} \leq 0} \tag{4.3}$$

(We will derive this inequality a bit later in this section.) For example, suppose we have two possible paths between A and B: irreversible path (1), and reversible path (2). We can compute:

$$\begin{aligned} \oint \frac{đQ}{T} = \int_{(1)} \frac{đQ}{T} - \int_{(2)} \frac{đQ}{T} &= \int_{(1)} \frac{đQ}{T} - (S(B) - S(A)) \leq 0 \\ \Rightarrow \int_{(1)} \frac{đQ}{T} &\leq (\Delta S = S(B) - S(A)) \end{aligned}$$

Now, suppose our system is thermally isolated, so that $đQ = 0$. Then the left-hand-side is actually zero, and

$$\boxed{\Delta S \geq 0 \quad \text{for any thermally isolated system}}$$

For an isolated system where heat is not being exchanged, entropy either stays the same (for a reversible change) or increases (for an irreversible change). Considering the universe to be an isolated system, this means in particular that the entropy of the universe never decreases!

For instance, you might consider your isolated system to be a hot cup off coffee, and the surrounding environment. The hot cup of coffee releases heat, which leads to $\Delta S_{\text{system}} > 0$. The surroundings absorb heat from the system, leading to $\Delta S_{\text{surroundings}} < 0$. However, you will find that when you add up the contributions, you will get

$$\Delta S_{\text{universe}} = S_{\text{system}} + S_{\text{surroundings}} \geq 0\,.$$

——— End Lecture 6.

In-Class Exercise: The entropy of the universe increases

A system at temperature T_S is placed in contact with a large reservoir at temperature T_R. They both end up at temperature T_R since the heat capacity, C, of the system is so small compared with that of the reservoir. Calculate an expression for $\Delta S_{\text{universe}}$.

Now, suppose the system is a cup of hot coffee at $100°C$, and the reservoir is the environment at room temperature, $20°C$. Suppose there are 250 grams in the cup, and that the specific heat capacity of the coffee is the same as water, $c = 4190\,J \cdot kg^{-1} \cdot K^{-1}$. What is $\Delta S_{\text{universe}}$?

Hint: Remember, $C = đQ/dT$.

Solution:

The heat transferred from the reservoir into the system is ΔQ, which is minus the heat transferred from the system into the reservoir. To compute the change in entropy of the reservoir (which remains at a constant temperature T_R), we compute

$$\Delta S_{\text{reservoir}} = \int \frac{đQ}{T_R} = \frac{1}{T_R}\int đQ = \frac{-\Delta Q}{T_R} = \frac{C(T_S - T_R)}{T_R}$$

To compute the change in entropy of the system (which changes from $T_S \to T_R$), we need to actually do an integral:

$$\Delta S_{\text{system}} = \int \frac{đQ}{T} = \int_{T_S}^{T_R} \frac{C\,dT}{T} = C \ln \frac{T_R}{T_S}$$

Then, we can add up

$$\Delta S_{\text{universe}} = C\left(\ln \frac{T_R}{T_S} + \frac{T_S}{T_R} - 1\right)$$

Now let's put in the numbers. Supposing the cup of $m = 250g = 0.25kg$ of coffee cools from 100° to room temperature, 20°, and the specific heat capacity of the coffee is equal to that of water, $c = 4190\,J \cdot kg^{-1} \cdot K^{-1}$,

$$C = mc = 4190\,J \cdot kg^{-1} \cdot K^{-1} \cdot 0.25kg = 1047.5\,J/K\,.$$

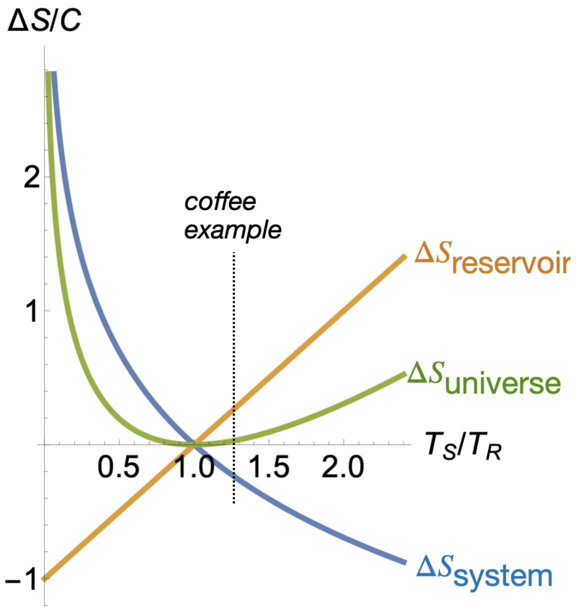
Then,

$$\Delta S_{\text{system}} = C \ln \frac{T_R}{T_S} = (1047.5\,J/K) \ln \frac{20 + 273\,K}{100 + 273\,K} = -252.9\,J/K$$
$$\Delta S_{\text{reservoir}} = \frac{C(T_S - T_R)}{T_R} = (1047.5\,J/K)\frac{(373 - 293)K}{293\,K} = 286\,J/K$$

As expected, the entropy of the coffee decreased as it cooled, since heat was flowing out, while the entropy of the surroundings increased as it absorbed the heat coming off the coffee. In total, the entropy of the universe increased in this irreversible process:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{reservoir}} = +33.1\, J/K$$

The below figure plots these different entropies as a function of T_S/T_R. $\Delta S_{\text{universe}}$ is always greater than or equal to zero. The region to the right of $T_S/T_R = 1$ corresponds to the case that the system is cooling down (so $\Delta S_{\text{system}} < 0$); the region to the left is when the system is heating up (so $\Delta S_{\text{system}} > 0$). This coffee example has $T_S/T_R = 373/293 = 1.27$.



4.2 The 1st Law Revisited

Let us put our definition of entropy to good use. Since $đQ = TdS$ (for reversible changes), and $đW = -PdV$ (for reversible changes), we can rewrite the first law as

$$dU = TdS - PdV \tag{4.4}$$

This is a very useful version of the first law, especially because *it holds even for irreversible paths*. This is a bit of a confusing point: we wrote this equation by using equations that were true only for reversible paths, but once we wrote it down in this form we got rid of all the inexact differentials; the left-hand-side is an exact differential, and the right-hand-side only contains exact differentials, dS and dV (because S and V are functions of state). So actually, this is a version of the equation

$$dU(S,V) = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

which is to say that $U(S,V)$ is a function of state. By comparing with (4.4), what we have achieved is identifying these partial derivatives with T and $-P$, respectively.

We will deal more with equations like this later.. but for now it is useful to try an example. Let's see that two systems at different temperatures that are able to exchange energy will reach equal temperature only when the total entropy is maximized.

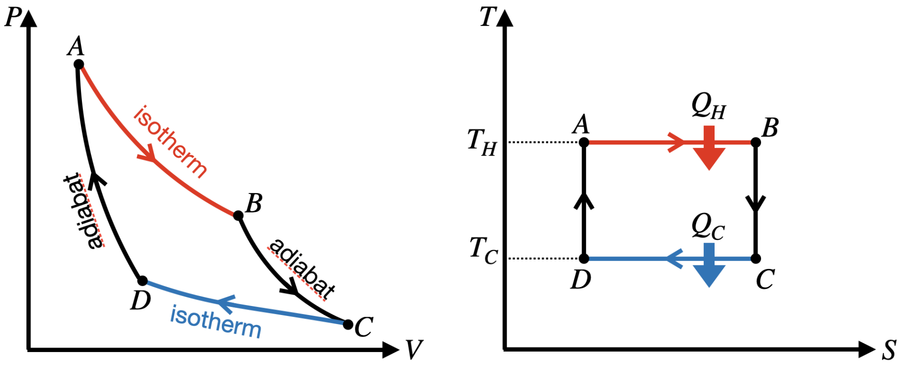


Figure 5: A Carnot cycle in two diagrams.

Example: Consider two systems with pressures P_1 and P_2, and temperatures T_1 and T_2, that exchange some internal energy ΔU and some volume ΔV. What is the total change in entropy of the combined systems?

Using the first law, we can write for each system that,

$$dS = \frac{P}{T}dV + \frac{1}{T}dU$$

This holds for each system, system (1) and system (2). One system loses volume $(-\Delta V)$ and energy $(-\Delta U)$, while the other gains volume $(+\Delta V)$ and energy $(+\Delta U)$. The change in entropy for each system is,

$$\begin{aligned} dS_1 &= \frac{P_1}{T_1}(+\Delta V) + \frac{1}{T_1}(+\Delta U) \\ dS_2 &= \frac{P_2}{T_2}(-\Delta V) + \frac{1}{T_2}(-\Delta U) \end{aligned}$$

so that together,

$$\Delta S = dS_1 + dS_2 = \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right)\Delta V + \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta U$$

We know that entropy always increases in any physical process. Thus when equilibrium is achieved, the entropy will have achieved a maximum, so $\Delta S = 0$ for the combined system, so that the joint system can't increase its entropy any more. This is only achieved when $T_1 = T_2$ and $P_1 = P_2$, which is the equilibrium state of this joint system.

4.3 Efficiencies

Let us return to the Carnot engine, which is described equally well on a PV and TS diagram as in Figure 5. The total work done on the system over one cycle is

$$\Delta W = -(Q_H - Q_C)$$

so the total work output by the engine W_{output} has the opposite sign,

$$W_{\text{output}} = Q_H - Q_C$$

It will be useful to relate Q_H and Q_C to the temperatures of the reservoirs, T_H and T_C. We can do this by noting that along the isotherms, we know that $\Delta Q = Nk_BT \ln V_f/V_i$, and along the adiabats $TV^{\gamma-1}$ is a constant. In particular:

$$\begin{aligned} A \to B: &\qquad Q_H = Nk_BT_H \ln \frac{V_B}{V_A} \\ B \to C: &\qquad T_H V_B^{\gamma-1} = T_C V_C^{\gamma-1} \\ C \to D: &\qquad Q_C = -Nk_BT_C \ln \frac{V_D}{V_C} \\ D \to A: &\qquad T_C V_D^{\gamma-1} = T_H V_A^{\gamma-1} \end{aligned}$$

Dividing the two adiabatic equations by each other leads to:

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}$$

Dividing the two isothermal equations by each other and substituting this previous result leads to:

$$\frac{Q_H}{Q_C} = -\frac{T_H}{T_C}\frac{\ln \frac{V_B}{V_A}}{\ln \frac{V_D}{V_C}} = -\frac{T_H}{T_C}\frac{\ln \frac{V_B}{V_A}}{\ln \frac{V_A}{V_B}} = \frac{T_H}{T_C}$$

This equation, that for a Carnot engine $\boxed{Q_H/Q_C = T_H/T_C}$, is something we previously found in (4.2) when we were adding up dS around the whole Carnot cycle, and turns out to be a very useful equation.

The concept of efficiency is important to characterize engines. We want to ask, what is the best you can do to convert heat to work? In other words, what is the ratio of the benefit to the cost? We define the efficiency η as this ratio,

$$\text{efficiency} \quad \eta = \frac{\text{benefit}}{\text{cost}}$$

For a heat engine, the benefit is the work you get out W_{output}, and the cost is the heat you put in, while for a refrigerator the opposite is true,since the benefit is “heat sucked out of the refrigerator” and the cost is the electrical work, so we define

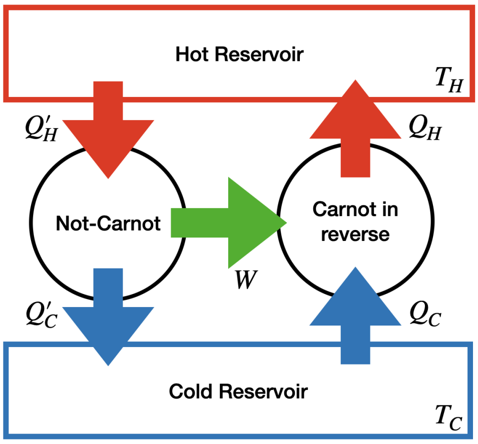
$$\boxed{\eta_{\text{heat engine}} = \frac{W_{\text{output}}}{Q_H}, \qquad \eta_{\text{refrigerator}} = \frac{Q_C}{W_{\text{input}}}}$$

This ratio for a heat engine always must be less than 1: the work output cannot be greater than the heat input. So, the efficiency of a heat engine is always a number between 0 and 1, where 1 corresponds to 100% efficiency (not possible, though desirable!).

We immediately see that the efficiency of a Carnot engine is,

$$\boxed{\eta_{\text{Carnot}} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}}$$

Since $T_C < T_H$, the efficiency of even this idealized engine is always less than 100%. Actually, it turns out that this is the efficiency of *any* reversible engines operating between two temperatures: the ratio Q_H/Q_C is the same for all reversible engines.



Why is Carnot the best? A Carnot engine is the best engine. Or more precisely, of all engines operating between two heat reservoirs, a reversible engine is the most efficient. To prove this statement, let us consider a second engine (call it engine Not-Carnot) to our original Carnot engine set to reverse. The Not-Carnot engine also operates between the same two temperatures T_H and T_C, performing some work W_{output}, but in contrast to the Carnot engine is not reversible. We suppose that the Not-Carnot engine absorbs some amount of heat Q'_H from the hot reservoir, and deposits Q'_C into the cold reservoir. We use its work output as work input that powers the Carnot engine.

The net effect of the two engines is to extract $Q'_H - Q_H$ from the hot reservoir, and by conservation of energy, deposit the same amount $Q'_H - Q_H = Q'_C - Q_C$ into the cold reservoir. But, Clausius' statement tells us that we must have $Q'_H \geq Q_H$; if this were not true, then energy would have been moved from the colder body to the hotter body. The efficiency of the Not-Carnot engine is, by definition,

$$\eta_{\text{Not-Carnot}} = \frac{Q'_H - Q'_C}{Q'_H}$$

With a bit of algebra, we find

$$Q'_H - Q_H = Q'_C - Q_C \quad \Rightarrow \quad \eta_{\text{Not-Carnot}} = \frac{Q'_H - Q'_C}{Q'_H} = \frac{Q_H - Q_C}{Q'_H}$$

But, since $Q'_H \geq Q_H$, this is always smaller than the efficiency of the Carnot engine:

$$\eta_{\text{Not-Carnot}} = \frac{Q_H - Q_C}{Q'_H} \leq \frac{Q_H - Q_C}{Q_H} = \eta_{\text{Carnot}}$$

Therefore, **the efficiency of the Carnot engine is always the largest possible**.

The proof that **all reversible engines working between two temperatures have the same efficiency** η_{Carnot} is a corollary of this argument: if we suppose that the Not-Carnot engine was actually reversible, we could run the argument in reverse (reversing the Not-Carnot engine and on the left, and going back to a normal Carnot engine on the right), and we would find that $\eta_{\text{Not-Carnot}} \geq \eta_{\text{Carnot}}$, which with our previous inequality implies that $\eta_{\text{Carnot}} = \eta_{\text{Not-Carnot}}$ if the Not-Carnot engine is reversible.

4.4 Clausius' Theorem

We can now return to a point we assumed last lecture, that for any closed cycle,

$$\oint \frac{đQ}{T} \leq 0 \quad \text{for any cycle}$$

with the equality for a reversible cycle. We already proved that the equality held true for a Carnot cycle, but now we can make the argument in general. Remember that this inequality was important because it allowed us to define a function of state, the entropy.

The idea of the proof is that by Carnot's theorem, we know that an irreversible engine that operates between two temperature T_H and T_C is less efficient than the Carnot engine. We can use the same notation as we did above: assume the Carnot engine extracts heat Q_H and dumps heat Q_C, and the Not-Carnot engine extracts heat Q'_H and dumps heat Q'_C (but we will not hook up the two engines to each other). Both engines do the same amount of work; the work output is $W_{\text{output}} = Q_H - Q_C = Q_{H'} - Q_{C'}$. We wish to find an inequality involving

$$\oint \frac{đQ}{T} = \frac{Q'_H}{T_H} - \frac{Q'_C}{T_C}$$

for this cycle. So, we can write

$$\begin{aligned}
Q_H - Q_C &= Q'_H - Q'_C \\
\frac{Q'_H}{T_H} - \frac{Q'_C}{T_C} &= \frac{Q_H - Q_C}{T_H} + \frac{Q'_C}{T_H} + \frac{Q_H - Q_C}{T_C} - \frac{Q'_H}{T_C} \\
&= \frac{Q'_C - Q_C}{T_H} + \frac{Q_H - Q'_H}{T_C} \\
&= (Q'_H - Q_H)\left(\frac{1}{T_H} - \frac{1}{T_C}\right)
\end{aligned}$$

We used that $Q_H/T_H = Q_C/T_C$ to derive the last line. Now using Carnot's theorem, $Q'_H \geq Q_H$, and since $T_H > T_C$, $1/T_H < 1/T_C$, so the total expression is negative:

$$Q_H - Q_C = (Q'_H - Q_H)\left(\frac{1}{T_H} - \frac{1}{T_C}\right) \leq 0$$

Therefore, we have found Clausius' inequality,

$$\oint \frac{đQ}{T} \leq 0$$

We showed this for an irreversible cycle operating between two temperatures, but you can break up a general cycle into bits where the temperatures change a little bit each time, and this result will continue to hold true.

——— *End Lecture 7.*

4.5 Equivalence of Clausius' and Kelvin's Statements

Kelvin's statement rules out perfect heat engines, and concerns the conversion of heat into work: we cannot have $W_{\text{output}} = Q_H$, so no heat engine can have perfect efficiency. Clausius' statement rules out perfect refrigerators, and concerns the transfer of heat from a colder to hotter body: We cannot have a process that only takes Q_C without work input, which would yield a refrigerator with 100% efficiency. (Note, refrigerators can have efficiencies greater than 1!) These statements are actually equivalent; if one is violated, then so is the other. Why?

Suppose there is a machine that violates Clausius's statement by taking heat Q_C from a cooler to hotter region without requiring work, *i.e.* a perfect refrigerator. Conservation of energy would say that such a Clausius-violating-machine would take Q_C out of the cold reservoir and deposit the same amount Q_C in the hot reservoir.

Hook up a Carnot operating between these two reservoirs, taking heat Q_H from the hotter one and dumping Q_C into the colder one, producing work $Q_H - Q_C$. Then, the combined system takes $Q_H - Q_C$ from the hot source, and produces work equal to $Q_H - Q_C$, dumping net 0 heat into the cold sink. This net result is an engine with 100% efficiency. So, the existence of a perfect refrigerator implies a perfect heat engine. The opposite is also true: the existence of a perfect heat engine implies a perfect refrigerator. So, the statements are equivalent.

4.6 Efficiency of Heat Pumps

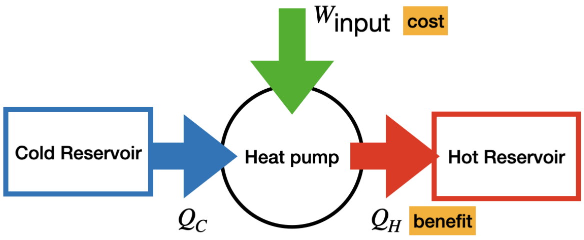
Refrigerators and heat pumps are like heat engines running in reverse. In the following problem, we'll explore how to define the efficiency of a heat pump.

In-Class Exercise: Heat pumps

A *heat pump* is a kind of 'inverted refrigerator' that can be used to heat your house. The way it works is that you have an engine that does work on some substance in order that it may extract some heat from the outdoors and dump it into your house.

Draw a schematic diagram of a heat pump. Keeping in mind that you would only do this when it is *colder* outdoors than indoors, calculate a coefficient of performance (the ratio of benefit to cost) for such a device for a typical wintertime situation. Would a heat pump work better in Florida or New York?

Hint: Coefficients of performance are usually larger than 1, unlike efficiencies.



Solution: For a heat pump, the *benefit* is Q_H, the heat added to the house. The cost is W_{input}, the work we must apply (typically in the form of electrical work) to accomplish this. So, a coefficient of performance or efficiency would be defined as,

$$\eta = \frac{Q_H}{W_{\text{input}}}$$

From the first law, since $W_{\text{input}} = \Delta Q = Q_H - Q_C$, $Q_H > W_{\text{input}}$, so this coefficient is always larger than 1.

For a heat pump fitted with a Carnot engine, since $Q_H/Q_C = T_H/T_C$, we can rewrite

$$\eta = \frac{Q_H}{Q_H - Q_C} = \frac{Q_H/Q_C}{Q_H/T_C - 1} = \frac{T_H/T_C}{T_H/T_C - 1} = \frac{T_H}{T_H - T_C}$$

The efficiency η is *larger* when $T_H - T_C$ is smaller. So, say that you want to keep your house a nice 72° Fahrenheit, or about $22°\,C = 273+22 = 295\,K$, so we set $T_H = 295\,K$. In Miami Florida, the outside temperature right now is probably *larger* than this, so we wouldn't even be able to use the heat pump. But let's say that the outside temperature in Miami was $20°C$, and let's compare with our outside temperature of $0°C$ here in Poughkeepsie. We would compute:

$$\eta_{\text{Miami}} = \frac{295}{295 - 293} = 147.5$$
$$\eta_{\text{Poughkeepsie}} = \frac{295}{295 - 273} = 13.4$$

The smaller the temperature gap, the better the efficiency out of the heat pump, so a heat pump operating in Miami

What's actually happening with a real world heat pump? The pump consists of two sets of coils (an evaporator and a condenser), with a motor that moves refrigerant (the working fluid) from one side to the other and back.

1. The working fluid moves through the heat pump. As it goes through the expansion valve, it goes from being a warm, high-pressure liquid to a cold, low-pressure fluid. So in an actual heat pump, T_C is the temperature of the heat pump's refrigerant, which is able to be colder than the outside air temperature, allowing heat transfer to the working fluid.
2. As the refrigerant passes through the evaporator, it absorbs heat from the outside air – even though the outside air is cold, the refrigerant is even colder! Since refrigerants with very low boiling temperatures are chosen, even on a cold day, the outdoor temperatures will be warm enough to boil the refrigerant into vapor.
3. The refrigerant gas reaches a compressor, which increases the pressure on the gas, raising its temperature.
4. Finally, the high pressure, high temperature gas goes through the condenser, which condenses it to a warm liquid, releasing heat – including the heat that the gas absorbed from the outside heat exchanger. This heat warms the inside air, and the high pressure, high temperature refrigerant is ready to go through the cycle again.

Test results of the best heat pump systems are around $\eta \approx 4.5$.

4.7 More Examples of Heat Engines

One of the most popular engines is the internal combustion engine used in cars. Useful work is produced from burning fuel inside the engine's combustion chamber at a high temperature and pressure.

An Otto cycle models the combustion engine, a typic of internal combustion engine. It is named after German engineer Nicolaus Otto, the first person to build a working four-stroke

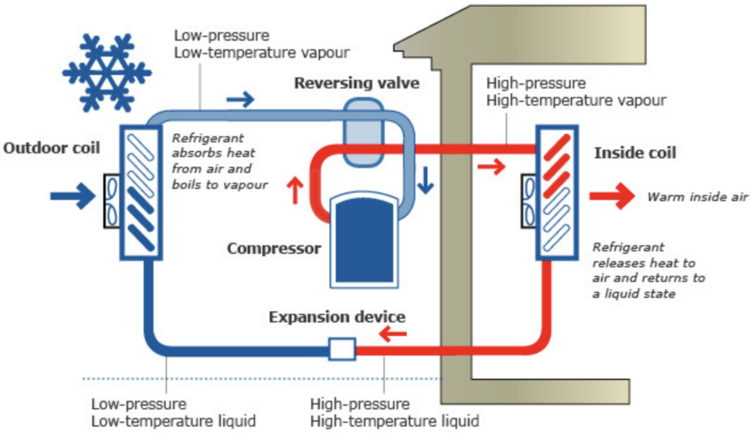


Figure 6: A diagram of an electric heat pump, from www.sciencelearn.org.nz.

engine in 1876. The Wright brothers used a gasoline-powered four-stroke internal combustion engine to power their aircraft that was based on early automobile engine designs using the Otto cycle.

The Otto cycle consists of:

(0) First there's an *intake stroke*, where gasoline vapor and air are drawn into the engine.

(1) Then there's a compression stroke, where the gasses compress adiabatically, and both pressure and temperature increase.

(2) Combustion (spark), where the fuel-air mixture ignites, with rapid heating at essentially at constant volume.

(3) Then there's the power stroke, where the gas expands adiabatically.

(4) The valve opens, gas escapes to the exhaust pipe with heat rejected from the air, which we can model as rapid cooling.

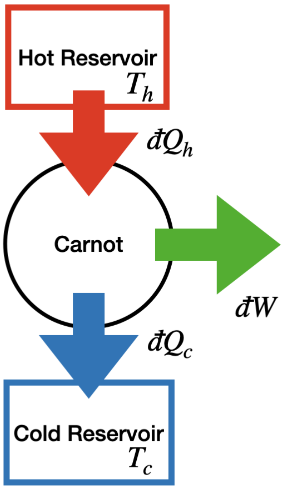
The Diesel cycle is similar to the Otto cycle, except fuel is ignited by heat that is generated during the compression of air in the combustion chamber at constant pressure, in contrast to igniting the fuel-air mixture with a spark-plug.

4.8 Worked Example: A Non-Idealized Heat Engine

Real engines can be much more complicated than idealized engines; they do not behave perfectly reversibly, and whatever is being used to power the engines changes temperature in a much more complicated way.

In an idealized model of a heat engine, the two reservoirs are assumed to be so large as to have an infinite heat capacity, so that their temperatures remain constant cycle after cycle. Suppose, however, that you have a Carnot engine that uses two somewhat smaller bodies as its hot and cold reservoirs. Initially the two bodies with equal heat capacities, C, are at T_H and T_C. As a result of the engine moving heat from the hot reservoir to the cold reservoir, however, the two systems will eventually come to the same temperature T_f after some amount of time.

(a) Use the first law to find an expression for the total work done by this engine during this time. Your answer should be in terms of C, T_H, T_C, and T_f.



Solution: At one step in the cycle: an amount of heat $đQ_h$ is extracted from the hot reservoir, an amount of work $đW$ is produced, and some heat $đQ_c$ is dumped into the cold reservoir. (We'll use lowercase h, c to denote heat extracted / dumped in one step, and similarly for the temperature changes at each step.) Because the heat capacities C of the reservoirs are finite, their temperatures will change as heat is extracted from / added to them. In the infinitesimal change, the changes in temperature of the reservoirs are related to the heat capacities as,

$$đQ_h = -C dT_h \,, \qquad đQ_c = C dT_c$$

The negative sign in the first equation is because heat is flowing out of the hot reservoir, so that C has a positive sign as dT_h is negative.

By the first law, the work performed in this step is

$$đW_{\text{output}} = đQ_h - đQ_c = -C dT_h - C dT_c$$

These steps are done incrementally between starting temperatures T_H, T_C, until they both reach a final temperature T_f. The total work done by the engine in this time is:

$$\begin{aligned} \Delta W_{\text{output}} &= -C \int_{T_H}^{T_f} dT_h - C \int_{T_C}^{T_f} dT_c = -C\left(T_f - T_H + T_f - T_C\right) \\ &= C(T_H + T_C) - 2CT_f \end{aligned}$$

(b) Use the second law and the unique characteristic of the Carnot engine to determine a value for T_f in terms of T_H and T_C.

Solution: For a Carnot engine in particular, we know that at each step of the process,

$$\frac{đQ_h}{T_h} = \frac{đQ_c}{T_c}$$

This is just the version of $Q_H/T_H = Q_C/T_C$ that holds at each step in a Carnot cycle: that the ratios of the heat extracted / dumped to the temperatures of the reservoirs are fixed.

We can integrate this relation over the process from the starting temperatures to the final temperature,

$$\begin{aligned}\frac{đQ_h}{T_h} = \frac{đQ_c}{T_c} \quad \Rightarrow \quad \frac{-CdT_h}{T_h} &= \frac{CdT_c}{T_c} \\ C\int_{T_f}^{T_H} \frac{dT_h}{T_h} &= C\int_{T_C}^{T_f} \frac{CdT_c}{T_c} \\ \ln\frac{T_H}{T_f} &= \ln\frac{T_f}{T_C}\end{aligned}$$

Since C is the same for both the hot and cold reservoir in this problem, it canceled from either side of the integral, and we are left with the simple relation:

$$T_H T_C = T_f^2$$

This determines the final temperature in terms of the initial ones.

How is this related to the second law of thermodynamics? At each step, the magnitude of the change in entropy of the hot reservoir equals the magnitude of the change in entropy of the cold reservoir (since this is a Carnot engine with $đQ_h/T_h = đQ_c/T_c$), where the entropy of the hot reservoir decreases as it releases heat (cools), and the entropy of the cold reservoir increases as it absorbs heat. The total change in entropy for the combined system is zero:

$$\begin{aligned}\Delta S_{\text{hot reservoir}} &= \int_{T_H}^{T_f} \frac{-đQ_h}{T_h} = C\ln\frac{T_f}{T_H} < 0 \\ \Delta S_{\text{cold reservoir}} &= \int_{T_C}^{T_f} \frac{đQ_c}{T_c} = C\ln\frac{T_f}{T_C} > 0 \\ \Delta S_{\text{hot reservoir}} + \Delta S_{\text{cold reservoir}} &= 0\end{aligned}$$

since $T_H/T_f = T_f/T_C$. This makes sense – this is a cyclic process and the total change in the entropy of the cyclic process should be zero!

Substituting into the result of part (a) yields,

$$\Delta W_{\text{output}} = C(T_H + T_C - 2\sqrt{T_H T_C}) = C(\sqrt{T_H} - \sqrt{T_C})^2$$

(c) Is your answer greater than or less than the temperature that the two bodies would attain if they were in simple thermal contact, rather than connected by an engine?

——— End Lecture 8.

Solution: How does this compare with putting the two bodies in simple thermal contact? If we put the two bodies in thermal contact, assuming no loss of energy to the environment the heat gained by one is equal to the heat lost by the other. (Recall we did an in class problem like this!) Since $C = \Delta Q/\Delta T$ and both bodies have the same magnitude of ΔQ and same heat capacity C, their temperatures are related as

$$C(T_f - T_C) = C(T_H - T_f) \quad \Rightarrow \quad T_f = \frac{T_H + T_C}{2}$$

Since the bodies have the same heat capacity, their final temperature will just be the average of their starting temperatures. Note, this is the same result we get by setting the work output to zero in our problem: $\Delta W_{\text{output}} = 0$ in part (a) implies $\frac{T_H+T_C}{2} = T_f$.

This is quite different from the relation $T_f = \sqrt{T_H T_C}$ derived for our engine. We can compare the ratios of T_f to T_C in each case, which are always larger than 1 (since the colder body heats up by some amount):

$$\left(\frac{T_f}{T_C}\right)_{\text{thermal contact}} = \frac{1}{2} + \frac{1}{2}\frac{T_H}{T_C}, \qquad \left(\frac{T_f}{T_C}\right)_{\text{engine}} = \sqrt{\frac{T_H}{T_C}}$$

Since $T_H/T_C > 1$, we find that the final equilibrium temperature from simple thermal contact is *larger* than in the case where we do work with the engine. This makes sense; since heat was converted to work with the engine, the hot reservoir cooled down more in that case.

5 The Four Thermodynamic Potentials

Textbook readings: (a first reading is due before Lecture 9; most pertinent to Lectures 9-10):

- Ch. 16, all

Learning Objectives:

- The thermodynamic potentials: U, H, F, G; obtaining differential expressions dU, dH, dG, dF; obtaining partial derivative definitions; obtaining and using Maxwell's relations; Gibbs as available energy

5.1 The Four Potentials

We have developed quite the collection of thermodynamic variables for describing the state of a system: volume V, pressure P, temperature T, internal energy U, entropy S. We've seen that certain quantities are naturally expressed in terms of some variables instead of others; for example, we have seen that labeling the energy as $U(S,V)$ is nice because then everything is a function of state (recall (4.4)):

$$dU = TdS - PdV$$

This equation tells us that changes in U are due to changes in S or V, so we can write $U = U(S,V)$ to show that U is a function of S and V. This equation implies that if S and V are held constant for the system, then U is also a constant, since $dU = 0$. This equation also implies that we can identify T and P with partial derivatives of U:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\Rightarrow \quad \boxed{T = \left(\frac{\partial U}{\partial S}\right)_V, \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S}$$

These equations hold for any reversible or irreversible process, although we've also seen that some relations will only hold for reversible processes. For example, in an **isochoric** (constant V) reversible process, $dV = 0$ and we can replace $đQ = TdS$, so that

$$\text{reversible with } dV = 0: \qquad dU = đQ = C_V dT$$

On the other hand, in an **isentropic** (constant entropy) reversible process, $dS = 0$ and we can replace $đW = -PdV$ so that

$$\text{reversible with } dS = 0: \qquad dU = đW$$

and the total work done by the system is equal to the change in internal energy of the system. Of course, since for reversible processes $dS = đQ/T$, so a reversible process at constant entropy is an adiabatic process with no exchange of heat. So far in this course we've had practice using all of these relations in different contexts.

Enthalpy What if we have a system held at constant pressure – what is the natural thermodynamic quantity to consider? The answer, it turns out, is the thermodynamic potential called the **enthalpy**, H. We define enthalpy as,

$$H = U + PV$$

so that its differential satisfies:

$$dH = dU + dPV + PdV = TdS - PdV + dPV + PdV = TdS + VdP$$

So, we see that the natural variables for enthalpy H are S and P,

$$\boxed{H = H(S, P); , \qquad dH = TdS + VdP} \tag{5.1}$$

and the partial derivatives of H with respect to S and P are identified with the coefficients of (5.1),

$$\left(\frac{\partial H}{\partial S}\right)_P = T\,, \qquad \left(\frac{\partial H}{\partial P}\right)_S = V$$

What's a situation where enthalpy might be useful? Consider a constant pressure (**isobaric**) process. Then the dP term cancels, and

$$dH = TdS \quad \text{(isobaric)}$$

If the process is reversible, we can use $TdS = đQ$. This equation then says that *if you add heat to the system at constant pressure, the enthalpy goes up.* Substituting $đQ = C_P dT$, the change in the enthalpy is

$$\Delta H = C_P \int_{T_1}^{T_2} dT = C_P(T_2 - T_1)$$

The change in enthalpy is exactly equal to the heat transfer. The enthalpy roughly measures the total internal energy plus work required to make space for it, and is an extremely useful quantity for engineers.

Helmholtz free energy Next up: what is the natural object to consider at constant temperature T? The answer is the **Helmholtz free energy function**, F. We define the Helmholtz function using

$$F = U - TS$$

so that taking the differential,

$$dF = dU - SdT - TdS = (TdS - PdV) - SdT - TdS = -SdT - PdV$$

so that the natural variables for F are V and T:

$$F = F(V,T); \, , \qquad dF = -SdT - PdV$$

Again, we can take the total derivative to relate the partial derivatives of F at constant temperature and volume to the coefficients:

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

so that we identify

$$\boxed{\left(\frac{\partial F}{\partial T}\right)_V = -S\,, \qquad \left(\frac{\partial F}{\partial V}\right)_T = -P}$$

For example, suppose we have a reversible isothermal process. Then, F *represents the amount of reversible work done by the system in an isothermal process*:

$$\text{reversible isothermal:} \quad dF = -PdV \quad \Rightarrow \quad \Delta F = \Delta W$$

The Helmholtz free energy is a measure of the amount of energy that is free to do work at fixed temperature.

Gibbs free energy Finally, we can define the **Gibbs free energy function** G as,

$$G = H - TS$$

so that

$$dG = dH - SdT - TdS = (TdS + VdP) - SdT - TdS = -SdT + VdP$$

We see that the natural variables of G are T and P, so that

$$G = G(T,P)\,, \qquad dG = -SdT + VdP$$

Yet again, we can go through the same exercise to identify the partial derivatives:

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_P = -S\,, \qquad \left(\frac{\partial G}{\partial P}\right)_T = V}$$

Let us summarize:

- The internal energy $U = U(S,V)$ is conserved in any isentropic isochoric process, and satisfies

$$\boxed{dU = TdS - PdV}$$

- The enthalpy $H = H(S,P)$ is conserved in any isentropic isobaric process, and satisfies

$$\boxed{dH = TdS + VdP}$$

- The Helmholtz free energy $F = F(T,V)$ is conserved in any isothermal isochoric process, and satisfies

$$\boxed{dF = -SdT - PdV}$$

- The Gibbs free energy $G = G(T,P)$ is conserved in any isothermal isobaric process, and satisfies

$$\boxed{dG = -SdT + VdP}$$

5.2 Conceptual Meaning of Free Energy

These different thermodynamic potentials are useful precisely because they describe how much energy is available ("free") to do useful work, depending on what constraints we apply to the system.

Suppose a system is able to exchange heat with its surroundings, and if the volume changes, do work on its surroundings. Suppose this system is in contact with surroundings that are at some ambient temperature T_0 and pressure P_0. If some amount of heat $đQ$ enters the system from the surroundings, the entropy change of the surroundings S_0 and system S satisfy

$$dS_0 = -\frac{đQ}{T_0}, \qquad dS_0 + dS \geq 0 \quad \Rightarrow \quad dS \geq \frac{đQ}{T_0}$$

where the second equation is the second law of thermodynamics, which implies the inequality in the last equation.

Now, we want to use this inequality in the first law of thermodynamics to ask about the energy available for the system to do thermodynamics work. To do this we're going to separate out the work done by the surroundings on the system automatically due to the volume change of the system, $-P_0 dV$, from the mechanical work added to the system, $đW$.

We can write the first law as follows:

$$dU = đQ + đW - P_0 dV \quad \Rightarrow \quad đW = dU + P_0 dV - đQ$$

Using the inequality $đQ \leq T_0 dS$ from earlier, this is

$$đW \geq dU + P_0 dV - T_0 dS$$

The right-hand-side of this equation is a total derivative; we can define

$$A = U + P_0 V - T_0 S \quad \Rightarrow \quad dA = dU + P_0 dV - T_0 dS$$

so we can write this inequality as

$$đW \geq dA$$

We call A the "availability": changing A changes the free energy available for doing work. If the system is mechanically isolated, then $dA \leq 0$, which says that changes in A are always negative: all processes will tend to force A down to a minimum value. **Equilibrium is achieved by minimizing A.**

Specifically, we have the following different types of scenarios:

- If a system is thermally isolated with fixed volume, then no heat can enter the system and the system can do no work on its surroundings, $dU = 0$. Then, $dA = -T_0 dS$, so that the inequality $dA \leq 0$ implies $dS \geq 0$. In other words, the equilibrium state is found by maximizing S.
- If a system is held at fixed volume and temperature, then dA is precisely identified with the Helmholtz free energy F, so the equilibrium state is found by minimizing F.
- If a system is at constant pressure and temperature, we can identify dA with dG, so that we must minimize the Gibbs free energy G to find the equilibrium state.

So, depending on what's held fixed, these different quantities are the quantities that are extremized in the equilibrium state.

——— *End Lecture 9.*

5.3 Maxwell's Relations

So far, to identify partial derivatives of the thermodynamic potentials with other thermodynamic quantities, we have used the fact that if f is a function of x and y, $f(x,y)$, then

$$\boxed{f = f(x,y) \quad \Rightarrow \quad df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy}$$

We can also take a second derivative to get useful relations: since *df* is an exact differential, the order in which we take the partial derivatives of its variables does not matter:

$$\boxed{\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}}$$

We can readily apply these relations to the potentials and their thermodynamic variables. For instance, consider the energy, whose partial derivatives we previously identified as:

$$T = \left(\frac{\partial U}{\partial S}\right)_V , \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

Taking another derivative would let us write

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$$

so that:

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

Similarly, we can consider the derivatives of the Gibbs free energy,

$$\left(\frac{\partial G}{\partial T}\right)_P = -S\,, \qquad \left(\frac{\partial G}{\partial P}\right)_T = V$$

Taking another derivative and setting,

$$\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T}$$

allows us to relate:

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P}$$

and so on. These are called **Maxwell's relations**, and they relate a partial derivative of something that can be easily measured (like the change in volume with temperature at fixed pressure, which can be easily measured in a laboratory), to something that is hard to measure (like, the change in entropy with pressure at constant temperature). These are *not* equations that should be memorized: they are equations that should be derived if you need them.

One example of where this is useful is finding useful expressions for heat capacities in terms of various partial derivatives. For example, consider the definition of C_V,

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

where we used $dQ = TdS$ in the second equality. Taking a derivative with respect to V,

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 S}{\partial V \partial T}\right)$$

since a Maxwell relation relates

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V ,$$

this allows us to express

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial T}\right)_V = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

Of course, for an ideal gas C_V was a constant, and the pressure depends only linearly on the temperature, so both the left-hand-side and right-hand-side of this expression would be zero; but for a more general substance this is a nontrivial relation. You will do some examples like this on your homework.

Another useful trick for manipulating partial derivatives is the **reciprocal theorem**,

$$\boxed{\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}}$$

This allows me to change exchange the variables being differentiated, up to an inverse.

Expansivities and Compressibilities A **generalized susceptibility** quantifies how much a particular variable changes when a generalized force is applied. An example of a generalized susceptibility is $\left(\frac{\partial V}{\partial T}\right)_x$, which answers the question: keeping x constant, how much does the volume change when you change the temperature? For example, the fractional generalized susceptibility $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S$, known as the adiabatic expansivity β_S, measures the fractional volume change when you change the temperature at constant S. In the following exercise, you will derive a formula for β_S in terms of easily measurable quantities.

In-Class Exercise: Adiabatic Expansivity

The goal of this problem is to obtain a formula for the *adiabatic coefficient of volume expansion* β_S, also known as the *adiabatic expansivity*, of a material as a function of T, V, the heat capacity C_V, and one known partial derivative: $\left(\frac{\partial T}{\partial P}\right)_V$.

Key definitions:

$$\beta_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S , \qquad C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Suggested Steps:

1. Begin with the Helmholtz function $F = U - TS$. Find a differential formula for dF containing only 2 terms on the right-hand-side.

   Solution:

$$F = U - TS \quad \Rightarrow \quad \begin{aligned} dF &= dU - TdS - SdT = (TdS - PdV) - TdS - SdT \\ &= -PdV - SdT \end{aligned}$$

2. Establish 2 partial derivative definitions based on dF.

   Solution: Since F is naturally a function of V and T, we can relate

$$dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT \quad \Rightarrow \quad \left(\frac{\partial F}{\partial V}\right)_T = -P\,, \quad \left(\frac{\partial F}{\partial T}\right)_V = -S$$

3. Establish a Maxwell relationship based on the 2nd derivatives of dF.

   Solution: Taking another derivative, we need to have

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V}$$

   which allows us to relate:

$$\left.\frac{\partial}{\partial V}\right|_T \left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T\,, \qquad \left.\frac{\partial}{\partial T}\right|_V \left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$$
$$\Rightarrow \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

   This is one of the Maxwell relations.

4. One of the terms in the Maxwell relation should give the inverse of one of the partial derivatives that we need. Use the reciprocal theorem,

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

   to relate it to the term we need.

   Solution: We have managed to relate the inverse of one of the quantities we need, $\left(\frac{\partial T}{\partial P}\right)_V$, to another partial derivative. We can invert it using the reciprocal theorem:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{\left(\frac{\partial T}{\partial P}\right)_V}$$

   which allows us to relate:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{\left(\frac{\partial T}{\partial P}\right)_V} \quad \Rightarrow \quad \left(\frac{\partial T}{\partial P}\right)_V = \frac{1}{\left(\frac{\partial S}{\partial V}\right)_T}$$

5. Now mess with the other term from the Maxwell relation using the reciprocity theorem to get something with the heat capacity in it. *Hint:* Use $S = S(T, V)$, and consider dS.

   Solution: Since $S = S(T, V)$, we can write

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\ &= \frac{C_V}{T} dT + \frac{1}{\left(\frac{\partial T}{\partial P}\right)_V} dV \end{aligned}$$

where we replaced the partials with the quantities we wish to solve for β_S in terms of. When $dS = 0$ so that S is a constant, we can set the left-hand-side to zero and differentiate with respect to T at constant S:

$$0 = \frac{C_V}{T} + \frac{1}{\left(\frac{\partial T}{\partial P}\right)_V} \left(\frac{\partial V}{\partial T}\right)_S$$

Using the definition of β_S, we finally have a relation for β_S in terms of the desired quantities:

$$0 = \frac{C_V}{T} + \frac{1}{\left(\frac{\partial T}{\partial P}\right)_V} V\beta_S \quad \Rightarrow \quad \beta_S = -\frac{C_V}{VT}\left(\frac{\partial T}{\partial P}\right)_V$$

This is one of the relations you are asked to prove on your homework, in Exercise (16.2).

There are four main types of general susceptibility:

- As we just discussed, the *adiabatic expansivity* β_S quantifies how much the volume of a system changes with temperature in an adiabatic process:

$$\boxed{\beta_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S}$$

- Similarly, the *isobaric expansivity* β_P quantifies how much the volume of a system changes with temperature at constant pressure:

$$\boxed{\beta_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}$$

- The *isothermal compressibility* quantifies how much the volume of a system changes with pressure, at constant temperature:

$$\boxed{\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}$$

  This is defined with the minus sign in order to keep κ_T positive, since increase in pressure leads to a decrease in volume.

- The *adiabatic compressibility* quantifies how much the volume changes with pressure in an adiabatic process:

$$\boxed{\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S}$$

Example: heat capacities of a non-ideal gas With these definitions, we can answer: what is the general relation between C_P and C_V? We learned that for an ideal monatomic gas, $C_P - C_V = Nk_B$. What about for a general substance?

The simplest path forward is to start with the last step of the in class exercise: consider $S = S(T, V)$, so that

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

where recall that the heat capacities can be related to derivatives of the entropy (using $đQ = TdS$) as,

$$\boxed{C_V = T\left(\frac{\partial S}{\partial T}\right)_V , \qquad C_P = T\left(\frac{\partial S}{\partial T}\right)_P}$$

Therefore, if we divide out by dT at constant pressure,

$$\begin{aligned}\left(\frac{\partial S}{\partial T}\right)_P &= \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \\ \frac{C_P}{T} &= \frac{C_V}{T} + \left(\frac{\partial S}{\partial V}\right)_T (V\beta_P)\end{aligned}$$

We can use the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ and a partial derivative identity,

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

to simplify the remaining derivative term as follows:

$$\begin{aligned}\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V \\ &= -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \\ &= -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = +\frac{\beta_P V}{\kappa_T V}\end{aligned}$$

which finally allows us to express:

$$\frac{C_P}{T} = \frac{C_V}{T} + \left(\frac{\partial S}{\partial V}\right)_T (V\beta_P) = \frac{C_V}{T} + \frac{V\beta_P^2}{\kappa_T} \quad \Rightarrow \quad C_P - C_V = \frac{VT\beta_P^2}{\kappa_T}$$

This equation is the generalization of $C_P - C_V = Nk_B$ for an ideal monatomic gas.

What does this equation mean?

- $C_P - C_V$ is proportional to the volume V, so it is an *extensive* quantity.
- Since β_P^2 is positive, and κ is positive for all known substances, $C_P > C_V$ always.
- For solids and liquids, β_P is small, so we often "lazily" just talk generically about "heat capacity" and don't specify C_P versus C_V. But for gases, β_P can be large. For example, see this site `https://www.engineeringtoolbox.com/specific-heat-capacity-gases-d_159.html` for a list of heat capacities of various gases.

——— *End Lecture 10.*

6 Expansions of Gases

Textbook readings: (a first reading is due before Lecture 10; most pertinent to Lectures 10-12):

- Ch. 14 sections 14.4-7 (a first reading is due before Lecture 10; most pertinent to Lectures 10-12)
- Ch. 26 section 26.1 and Ch. 27, all (a first reading is due before Lecture 12; most pertinent to Lectures 12-13)

Learning Objectives:

- The free expansion (joule expansion) of the ideal gas; the statistical basis for entropy; the entropy of mixing
- The difference between real and ideal gases: The van der Waal's gas; the free expansion (Joule expansion) of the non-ideal gas; Joule-Kelvin expansion (throttling)

6.1 The Free Joule Expansion

A nice example which illustrates some subtleties with how to compute changes of entropy of a system is the *joule expansion*. We consider the following situation: one mole of an ideal gas is confined in a thermally isolated container. After opening a tap to another equally sized container (also thermally isolated), the gas fills the entire container so that the volume is doubled. What is the change in entropy of the gas, the surroundings, and the universe?

This entire process is thermally isolated ($\Delta Q = 0$), and no work is being done on the gas ($\Delta W = 0$), and so naturally $\Delta U = 0$. Since U for an ideal gas only depends on the temperature, this means that T of the gas does not change in this process. Both P and V do change, however; since the volume is doubled from $V_i \to V_f = 2V_i$, the pressure is halved:

$$P_i V_i = RT = P_f(2V_i) \quad \Rightarrow \quad P_f = P_i/2\,.$$

What is the change in entropy of the gas?

You might first be worried that since $\Delta Q = 0$, we should also have $\Delta S_{\text{gas}} = 0$. However, we stress that this is an *irreversible* process, since the gas is in a non-equilibrium state after the partition is suddenly removed – we cannot use $đQ = TdS$ valid for reversible changes to conclude that the entropy change should be zero. Instead, in general $đQ \leq TdS$ with equality only for reversible changes, so since $\Delta Q = 0$ in this process, we should have $0 \leq T\Delta S$, or in other words that $\Delta S_{\text{gas}} > 0$ for this irreversible process.

So, we know the gas should gain entropy, but how do we compute this gain? Now we can use the fact that entropy is a function of state: the change in entropy between two endpoints can be computed along any path separating the endpoints... including along a reversible path! We might as well compute the change in entropy for a reversible isothermal expansion of the gas from the initial state V_i to final state $2V_f$ (during which the gas actually does work on the environment), since this is something we know how to compute and will give us the right answer. Therefore, we compute:

$$\Delta U = 0 \quad \Rightarrow \quad TdS = PdV \qquad \text{for isothermal expansion}$$
$$\int_i^f dS = \int_{V_i}^{2V_i} \frac{P\,dV}{T} = \int_{V_i}^{2V_i} \frac{R\,dV}{V} = R\ln 2$$

We conclude that $\Delta S_{\text{gas}} = R\ln 2 > 0$.

What about the change of entropy of the universe? If we were actually computing the change in entropy of the universe for the reversible isothermal expansion, we should have $\Delta S_{\text{universe}} = 0$ (true for a reversible adiabatic process), so we would need to have that $\Delta S_{\text{surroundings}} = -\Delta S_{\text{gas}}$. In other words, the isothermal expansion is *not* thermally isolated in itself, so we need to also include the negative entropy change of the environment.

However, the free joule expansion is by assumption a thermally isolated process in itself, so there is no entropy change of the environment. For the irreversible free joule expansion we expect that $\Delta S_{\text{universe}} > 0$, and indeed since the gas is thermally isolated, it constitutes the whole entropy change of the universe: $\Delta S_{\text{gas}} = \Delta S_{\text{universe}} = R\ln 2$.

To summarize, this example demonstrates all of the following facts:

- Entropy is a function of state, and so entropy change between two endpoints can be computed along any path, whether reversible or irreversible. We can use this to our benefit to take advantage of the reversible formula $đQ = TdS$, even for a process which is adiabatic.
- The entropy of a thermally isolated system always increases (for irreversible processes) or doesn't change (for reversible processes). In general, $\Delta S \geq \Delta Q/T$ so is always ≥ 0 for a thermally isolated system.
- The entropy of non-thermally isolated systems can decrease (like it does for the surroundings in the case of isothermal expansion of the gas), as long as the entropy of the universe satisfies $\Delta S_{\text{universe}} \geq 0$. We have of course at this point seen many examples of the entropy of individual systems decreasing consistent with the entropy of the universe continuing to increase.

This example also provides a nice way to make contact with the statistical definition of entropy, that the entropy of a system in a particular macrostate is computed from the multiplicity of microstates Ω as $S = k_B \ln\Omega$. To count the microstates in the Joule expansion, we note that after the valve is opened each gas molecule can be either on the left-hand-side or right-hand-side of the container. Since each molecule has 2 choices, and there are Avogadro's number N_A of molecules in a mole of gas, there are 2^{N_A} ways of arranging the gas molecules. Thus, the number of microstates associated with the gas being in a container twice as big as the initial volume is larger by a factor of 2^{N_A}, so that the additional entropy is

$$\Delta S = k_B \ln 2^{N_A} = N_A k_B \ln 2 = R\ln 2$$

precisely as computed from the thermodynamic definition of the entropy.

6.2 The Entropy of Mixing

We can generalize the example from the last subsection to two different ideal gases (1 and 2) in separate vessels with volumes V_1 and V_2, with total volume $V_1 + V_2 = V$. Suppose the gases start at the same pressure and temperature P and T, and then we open the valve between the vessels, allowing the vessels to spontaneously mix. The number of particles N_1 and N_2 of each gas satisfies,

$$PV_1 = N_1 k_B T\,, \qquad PV_2 = N_2 k_B T\,, \qquad PV = Nk_B T \quad \Rightarrow \quad N_1 = \frac{V_1}{V}N\,, \;\; N_2 = \frac{V_2}{V}N$$

where $N = N_1 + N_2$ is the total number of particles.

Even though this is an irreversible process, just as for the Joule expansion we can imagine going from the starting state to the final state via a reversible route via an isothermal expansion of gas 1 from V_1 to V and of gas 2 from V_2 to V. The total change in the entropy of the gases is computed as,

$$\Delta S = \int_{V_1}^{V} \frac{P\,dV}{T} + \int_{V_2}^{V} \frac{P\,dV}{T} = k_B \left(N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \right)$$

Suppose V_1 is some fraction xV of the total volume, for x a number between 0 and 1, so that V_2 is equal to $(1-x)V$. This entropy of mixing is then given by,

$$\Delta S = -Nk_B \left(x \ln x + (1-x)\ln(1-x) \right)$$

where we substituted $V_1 = xV$, $V_2 = (1-x)V$, and $N_1 = xN$, $N_2 = (1-x)N$. As a function of the fraction x, this expression looks like an upside down parabola centered around $x = 1/2$. There is a positive entropy change whenever some mixing is involved (with $0 < x < 1$), and the entropy change is maximum at $x = 1/2$, when the initial volumes are equal and doubled by opening the valve. This additional entropy comes from the fact that each molecule can exist in additional microstates: for every microstate with a molecule of gas 1 on the left there is now an additional one with a molecule of gas 1 on the right.

However, we have made a crucial assumption that the gases are distinguishable. If the gases are not distinguishable from one another, physically we would expect that mixing them would have no observable consequence, so that there is no increase in the entropy. The mixing should only increase if the gases are distinguishable.

6.3 Real Gases: Van der Waals Forces

So far in all our discussion involving gases, we have assumed an ideal gas that satisfies the equation of state

$$PV = Nk_B T \quad \leftrightarrow \quad PV = n_{\text{moles}} RT \tag{6.1}$$

Of course, real gases don't behave quite like this – for one thing, at cold enough temperatures real gases were liquefy, at which point the system is no longer described by the equation of state (6.1). For another, the ideal gas law ignores intermolecular interactions – the fact that the gas molecules actually (weakly) attract each other.

A common model of real gas behavior is the **van der Waals gas**, which makes the following two modifications to the ideal gas law. First, it accounts for the particles interacting with each other, so that the internal energy of the gas needs to account for these interactions in addition to the kinetic energy of the gas molecules. In particular, it accounts for van der Waals forces between the molecules, which are weak, distance-dependent, short-ranged attractive interactions.

Second, it accounts for the finite size of gas molecules, so that there is less overall free volume for the molecules to move around in. The equation of state for a van der Waals gas is,

$$\boxed{\left(P + \frac{an_{\text{moles}}^2}{V^2}\right)(V - n_{\text{moles}}b) = n_{\text{moles}}RT \quad \leftrightarrow \quad \left(P + \frac{aN^2}{V^2}\right)(V - bN) = Nk_BT} \tag{6.2}$$

where again, n_{moles} is the number of moles in the gas, and a and b are parameters that when set to zero, yield the ideal gas equation. (We've also written the version of this equation valid for N molecules.) We can schematically understand this equation as follows:

- The constant b accounts for the volume excluded due to the finite size of the molecules, since the molecules are only free to explore a volume not already taken up by other molecules. If there are N molecules in the gas, and each has some finite volume, then there will be some reduction in the volume V available for the molecules to roam around in, so that the effective available volume is reduced to $V - bN$ for some constant b.
- The constant a parameterizes the strength of the intermolecular interactions. Its origin can be explained as follows: suppose N molecules of gas in a volume V. The number of nearest neighbors is then proportional to N/V. Attractive intermolecular interactions between molecules lower the total potential energy by an amount proportional to the number of molecules times the number of nearest neighbors,

  $$U_{\text{pot}} = a\frac{N^2}{V}$$

  so that if you change V, the energy changes by,

  $$dU_{\text{pot}} = \frac{U_{\text{pot}}(V)}{dV} = -a\frac{N^2 dV}{V^2}$$

  This change in the energy due to the interactions can be thought of as being due to an effective change in the pressure of the gas,

  $$dU_{\text{pot}} = -P_{\text{eff}}dV \quad \Rightarrow \quad P_{\text{eff}} = a\frac{N^2}{V^2}$$

  The pressure P that you measure for the gas is equal to the pressure neglecting the interactions, plus this effective pressure.

——— *End Lecture 12.*

Isotherms for a van der Waals gas have a richer behavior than those of ideal gases. Multiplying out the equation of state to get P as a function of V at fixed temperature and N, we find:

$$P = \frac{Nk_BT}{V - bN} - \frac{aN^2}{V^2}$$

Plotting this equation of state on a P-V diagram for various isotherms leads to the following behavior:

- For larger temperatures, the isotherms look somewhat ideal-gas like, like $P \sim 1/V$ (so that we can ignore the a/V^2 term). At high enough temperatures, the attractive forces between the molecules play no role.

- As the temperature is lowered, they change shape to have a wiggle with both a minimum and a maximum. In this case the attractive forces take effect, so that at small volumes there is a region where it looks like compressing the gas can actually *reduce* the pressure (the compressibility κ_T is negative!), or increasing the pressure can increase rather than decrease the volume. This is a highly unstable situation – if we were able to create such a state, it wouldn't be around for long since a tiny perturbation would lead to a rapid change in its density.

This shift happens below a critical temperature T_*, which occurs precisely when is an inflection point in the curve so that both the first and second derivative of the pressure with respect to the volume is zero:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 = -\frac{Nk_BT_*}{(V_* - bN)^2} + \frac{2aN^2}{V_*^3}$$

and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 = \frac{2Nk_BT_*}{(V_* - bN)^3} - \frac{6aN^2}{V_*^4}$$

Solving these two equations allows us to solve for the inflection point, which occurs at

$$k_BT_* = \frac{8a}{27b}$$

What's going for $T < T_*$ is that we see a phase transition. In the high density part (low volume) of the diagram before the minimum, the state of the system is actually a liquid. The large negative slope means that it is difficult to compress the state; we need to add a lot of pressure to change the volume only slightly. This is characteristic of a liquid phase of matter. On the other hand, in the low-density high volume region after the maximum, the system is in a gas state. The naive middle solution with negative compressibility κ_T is unstable, and represents a region in which gas and liquid coexist at once. So, the van der Waals model predicts the existence of liquids as the gas is compressed for low enough temperatures!

It be useful to plot the liquid-phase diagram on the P-T plane. Here, the co-existence liquid-gas region that exists for small enough T is squeezed onto a line. If we're sitting in the gas phase and increase the pressure a little bit at fixed $T < T_*$, we undergo a phase transition and jump to the liquid phase. Above the critical point, there isn't actually a sharp phase transition / distinction between the liquid and gas phases. At fixed pressure, the stable low-temperature state is the liquid, and the stable high-temperature state is the gas, without a sharp transition. Right at P_*, T_* there is what's called a second-order phase transition, where the susceptibility becomes infinite.

6.4 Cooling Real Gases

The Joule expansion for non-ideal gases Consider the free Joule expansion of a general non-ideal gas: we allow the gas to expand to a larger volume, with no work done and no change in internal energy, with the entire system isolated from its surroundings so there is also no heat exchange. For an ideal gas, U only depends on the temperature, so the temperature of the gas does not change in this process. But for a non-ideal gas, we expect that the temperature might change – how do we calculate it?

To do so, it is useful to define the **Joule coefficient** μ_J, which expresses the change in temperature with volume at constant energy,

$$\boxed{\text{Joule coefficient:} \qquad \mu_J = \left(\frac{\partial T}{\partial V}\right)_U}$$

Knowing the Joule coefficient, we can integrate it with respect to the volume to figure out the change in temperature in the Joule expansion:

$$\Delta T = \int_{V_i}^{V_f} \mu_J \, dV$$

A useful way to evaluate this coefficient is to use our partial derivative rules to relate:

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T$$

where we used the definition of $C_V = (\partial U/\partial T)_V$ to invert $1/C_V = (\partial T/\partial U)_V$. Using the first law $dU = TdS - PdV$ and dividing out by dV at constant temperature, we can evaluate the partial derivative of U as:

$$dU = TdS - PdV \quad \Rightarrow \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

This is useful because we can now use a Maxwell relation $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ to express this as:

$$\mu_J = -\frac{1}{C_V}\left(T\left(\frac{\partial S}{\partial V}\right)_T - P\right) = -\frac{1}{C_V}\left(T\left(\frac{\partial P}{\partial T}\right)_V - P\right)$$

Now we can use our equation of state for the gas to evaluate this formula, since we know P as a function of T. For an ideal gas, we can simply use that $P = RT/V$, so that $(\partial P/\partial T)_V = R/V$, and $\mu_J = 0$, so that as expected the temperature of the ideal gas does not change in this expression. For real gases, however, the attractive effect of interactions between the gas molecules means that when the molecules are more spread out in the final state the gas will cool down, so that $\mu_J < 0$. In the following exercise you will use this coefficient and the van der Waals equation of state to derive the temperature change of a van der Waals gas.

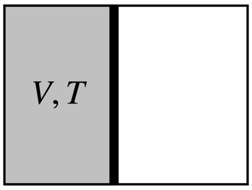
In-Class Exercise: Van der Waal's Expansion

n moles of a Van der Waal's gas initially are contained in a vessel of volume V at temperature T. The gas is isolated from the world around it. The partition is then removed, and the gas freely expands to a total volume of αV, where α is a constant. Find a formula for the change in temperature of the Van der Waal's gas during this process. Is this an increase or a decrease?

Note: the molar form of the Van der Waals equation is

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

for n the number of moles. Begin with the definition of the Joule coefficient $\mu_J = \left(\frac{\partial T}{\partial V}\right)_U$ and the formula we derived today for this coefficient.



Solution: In a Joule expansion U is constant, so the strategy is integrate up to get the change in temperature:

$$\Delta T = \int_{V_1}^{V_2} \left(\frac{\partial T}{\partial V}\right)_U dV = \int_{V_1}^{V_2} \mu_J \, dV$$

We derived

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]$$

For a van der Waals gas, we can evaluate

$$P = \frac{nRT}{V-nb} - \frac{an^2}{V^2} \quad \Rightarrow \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb}$$

so that the Joule coefficient evaluates to

$$\mu_J = -\frac{1}{C_V}\left[\frac{nRT}{V-nb} - \left(\frac{nRT}{V-nb} - \frac{an^2}{V^2}\right)\right] = -\frac{an^2}{C_V V^2}$$

Integrating up to get the change in temperature yields

$$\Delta T = \int_{V_1}^{V_2} \mu_J \, dV = -\frac{an^2}{C_V}\int_V^{\alpha V} \frac{dV}{V^2} = \frac{an^2}{C_V}\left(\frac{1}{\alpha V} - \frac{1}{V}\right) = -\frac{an^2}{C_V V}\left(1 - \frac{1}{\alpha}\right)$$

Since $\alpha > 1$ this is a negative quantity, and the temperature decreases.

ΔS in the Joule expansion In the free Joule expansion of an ideal gas we calculated the entropy change of the gas using the isothermal expansion with the same endpoints. For the van der Waals gas we can't do this, since the temperature changes between the endpoints. Instead, a useful way to compute the entropy is to write the entropy as a function of T and V, so that

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\ &= \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV \end{aligned}$$

where we used the relation $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ that we used previously in deriving the form of the Joule coefficient, and also the relation between the heat capacity and derivatives of the entropy with respect to the temperature. Using the equation of state for the van der Waals gas, we can evaluate

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{Nk_BT}{V-bN} - \frac{aN^2}{V^2}\right) = \frac{Nk_B}{V-bN}$$

and therefore write dS as,

$$dS = \frac{C_V}{T}dT + \frac{Nk_B}{V - bN}dV$$

Integrating, we see that:

$$\Delta S = C_V \ln\left(\frac{T_f}{T_i}\right) + Nk_B \ln\left(\frac{V_f - bN}{V_i - bN}\right)$$

For an ideal gas, $b = 0$ and $T_f = T_i$, so this would just derive the expression we previously found for $\Delta S_{\text{gas}} = Nk_B \ln \frac{V_f}{V_i}$. For the van der Waals gas the expression is a bit more complicated: it depends on the temperature of the gas, C_V of the gas, as well as the constant b that indicates how much volume is occupied by the molecules in the gas.

Joule-Kelvin expansion For practical purposes it is useful to replace the free-expansion process of lifting the valve with a continuous steady-flow process, as suggested by Joule and Thompson. The following Joule-Kelvin / Joule-Thompson throttling process can be used to cool down gases to very low temperatures.

In a Joule-Kelvin expansion, a gas at a high pressure P_1 is forced by a steady flow through a throttle valve (a porous plug) to a lower pressure P_2 in an adiabatic process. The pressure P_1 is maintained on the high-pressure side of the constriction. To push the gas through the valve, the high pressure gas behind it has to do work on it, equal to P_1V_1. As it passes through to the low pressure region, the gas expands into a larger volume on the other side of the valve, doing work on the low-pressure gas in front of it equal to P_2V_2. In the process of adiabatically expanding the gas from P_1 to P_2 by a steady flow through a throttle valve, we have that

$$\Delta U = \Delta W = P_1V_1 - P_2V_2$$

since $\Delta Q = 0$. In this case, the energy changes in an amount equal to the work being done, but actually the enthalpy is conserved: using the definition $H = U + PV$, we have that:

$$\Delta H = \Delta U + P_2V_2 - P_1V_1 = 0$$

so that this is an *isenthalpic process.*

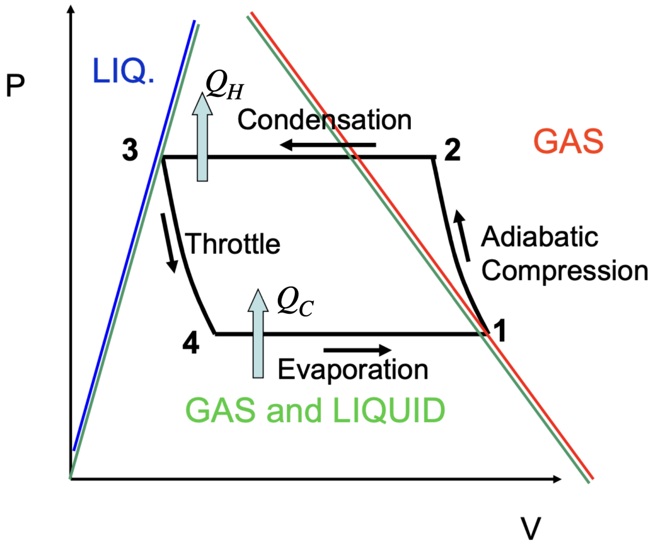
To compute the temperature change in this process, we should define a *Joule-Kelvin coefficient* that measures how the temperature changes with respect to the pressure at constant enthalpy:

$$\boxed{\text{Joule-Kelvin coefficient:} \qquad \mu_{JK} = \left(\frac{\partial T}{\partial P}\right)_H}$$

By integrating this coefficient with respect to the pressure, we can therefore compute the temperature change of the gas. (See your book p. 316-317 for the manipulations – they are identical to the sort of manipulations we underwent for the Joule coefficient μ_J). It turns out that this process can actually actually result in either heating or cooling, since μ_{JK} can take either sign. When the sign is negative so that the gas cools, this process is extremely useful for cooling gases down to low enough temperatures to liquefy them.

Refrigeration cycle A standard refrigeration cycle consists of cycling a fluid with a low boiling temperature through its gas/liquid phases.

- The gas condenses to a liquid at constant pressure, giving up heat while in thermal contact with the reservoir at T_H.
- An adiabatic throttling process then cools the refrigerant below T_C.
- The liquid evaporates to a gas at constant pressure while in contact with the cold reservoir, taking in Q_C from the cold reservoir.
- Finally, the gas is adiabatically compressed.



——— End Lecture 13.

7 The 3rd Law, the Canonical Ensemble and the Equipartition Theorem

Textbook readings: (a first reading is due before Lecture 14; most pertinent to Lecture 14):

- Ch. 18, all
- Ch. 19, all
- Ch. 4 sections 4.6-4.7

Learning Objectives:

- The third law, basic concepts
- Classical systems and the equipartition theorem
- The canonical ensemble

7.1 The Third Law

The third law is concerned with the limiting behavior of systems as the temperature approaches absolute zero. Absolute zero is the coldest possible temperature on the thermodynamic temperature scale, where particles exhibit their minimum vibrational motion (as you learn in quantum mechanics there is always some zero-point energy associated with the ground state of the system; at absolute zero this is the only contribution to the particle's motion). Absolute zero is set as $T = 0$ Kelvin by definition, or $T = -273.15^\circ$ Celsius.

The third law can be stated in the following three ways:

- Nernst's statement of the third law (1906): Near absolute zero, all reactions in a system in internal equilibrium take place with no change in entropy.
- Planck's statement of the third law (1911): the entropy of all systems in internal equilibrium is the same at absolute zero, and may be taken to zero.
- Simon's statement of the third law: the contribution to the entropy of a system by each aspect of the system in internal thermodynamic equilibrium tends to zero as the temperature tends to zero. By *aspect* we mean some part of the system which essentially independently contributes to the properties of the whole.

So, the third law concerns entropy, and the minimum possible value of the entropy of a system. The essential point is that experiments can only determine *differences* in entropy. In particular, recall that you've learned one useful way to measure the entropy is to measure the heat capacity. For example, in a constant pressure process,

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P \quad \Rightarrow \quad S = \int \frac{C_P}{T} dT$$

This allows us to find changes of entropy between changes of temperature T_i and T_f; written as a definite integral

$$\Delta S = S(T_f) - S(T_i) = \int_{T_i}^{T_f} \frac{C_P}{T} dT = C_P \ln \frac{T_f}{T_i}$$

where in the last equation we assumed C_P was independent of temperature (not always a good approximation!)

The question is, is there a good definition of the absolute value of the entropy of a system, not just changes in entropy? Since you have also learned the statistical definition of entropy $S = k_B \ln \Omega$, you should expect that the answer is yes: when there is no multiplicity of the possible microstates of the system for a given macrostate (*i.e.*, only one available microstate), $\Omega = 1$ and so by the statistical defininition $S = 0$. The question is, what is the thermodynamic definition of entropy consistent with this?

The third law provides a value of entropy at absolute zero, so allows us to determine an absolute definition of entropy and not just differences of entropy. It essentially states that the entropy of all systems at absolute zero temperature is a universal constant – this constant is the same for all systems, and we can take it to be zero. This implies that the ground state of the system at zero absolute temperature is non-degenerate ($\Omega = 1$), consistent with the statistical definition $S = 0$. To put it simply,

$$S \to 0 \quad \text{as} \quad T \to 0$$

Some physical consequences of the third law are as follows:

- *Heat capacities tend to zero as $T \to 0$.* We can see this from considering the total change of entropy upon cooling from a temperature T down to absolute zero:

  $$\Delta S = S(0) - S(T) = \int_T^0 \frac{C}{T'} dT'$$

  The integral will diverge as $T \to 0$ (because $\ln 0 \to -\infty$); it is only finite if $C \to 0$ as $T \to 0$. Of course, classically heat capacities do not vary with temperature, so this is the statement that quantum considerations show that all heat capacities must eventually vanish exponentially.

- Since derivatives of entropy are related by Maxwell relations to derivatives of other system parameters, the third law tells us about the limiting behavior of other common thermodynamic quantities. In particular, *thermal expansion stops.* The thermal expansivity β_P can be expressed using a Maxwell relation as

  $$\beta_P = \frac{1}{V} \frac{\partial V}{\partial T}\bigg|_P = -\frac{1}{V} \frac{\partial S}{\partial P}\bigg|_T$$

  The third law implies that in the limit of $T \to 0$, the derivative of S with respect to some thermodynamic variable x also tends to 0:

  $$\text{lim}_{T\to 0} \left(\frac{\partial S}{\partial x}\right)_T = 0$$

  So, $\beta_P \to 0$ at absolute 0.

- *The ideal gas law breaks down at $T \to 0$.* One easy way to see this is that for an ideal gas, $C_P - C_V = R$ per mole, but both C_P and C_V tend to 0 as T goes to zero, so that this equation cannot be satisfied. In particular, this is because weak interactions between gas molecules become more important as temperature is reduced.

- *Unattainability of absolute zero.* It follows from the third law (in particular, Simon's statement) that it is impossible to cool a system to absolute zero. Formally, it is impossible to reduce the temperature of any system or part of a system to absolute zero in a finite number of steps and within a finite time.

  The lowest temperature that matter has been cooled to is 38 picoKelvin ($38 \times 10^{-12}\, K$), achieved (and maintained for 2 seconds!) by a team in Germany with a Bose-Einstein condensate (to be discussed later). You can read more about this result at this link.

This discussion motivates the need to consider the microscopic properties of the system – statistical mechanics! We need to be able to take into account the microscopic properties of individual atoms or molecules, analyzed statistically. This is where we're heading with the rest of the course.

7.2 The Boltzmann (Canonical) Distribution

General Definitions Statistical mechanics is a probabilistic approach to finding the equilibrium macroscopic properties of systems with large numbers of degrees of freedom. So far we've been mostly discussing phenomenological properties of macroscopic bodies, which are well described by thermodynamics. Statistical mechanics examines an ensemble of microstates corresponding to a given macrostate, and aims to provide the probabilities for realizing the equilibrium ensemble. First, some definitions:

- **The microcanonical ensemble:** Often we are interested in a mechanically and adiabatically isolated system, so that the internal energy U is constant. (Note that in this section and beyond we might often use E for U since this is conventional in stat mech – apologies for the change in notation!) The macrostate is specified by U and other thermodynamic variables. The basic assumption is that all available microstates are equally likely to be realized, and that macroscopic variables are completely determined by the multiplicity of microstates.

- **The canonical ensemble:** We consider a system maintained in thermal equilibrium with a large reservoir / heat bath. The system is maintained at a constant equilibrium temperature T through contact with a reservoir, so that the macrostate is heavily dependent on the ambient temperature T. Energy can be exchanged between the system and reservoir, with the total energy of the reservoir plus system fixed (so that the total system plus reservoir as a whole can be considered as being in the microcanonical ensemble). We are interested in predicting the probability that the system at fixed temperature is in a particular microstate.

We will have in mind the latter setup: two systems are in thermal contact. The total energy of these two systems is fixed, but they can exchange energy and come to thermal equilibrium. First let's recall the statistical definitions of entropy and temperature. As in our discussion of the Einstein solids (recall (1.4)), for a system with some number of microstates Ω,

$$\boxed{S = k_B \ln \Omega\,, \qquad \frac{1}{T} = \frac{\partial S}{\partial U}}$$

The latter equation can be rewritten in a useful way in terms of the microstates as

$$\frac{1}{T} = \frac{\partial S}{\partial U} \quad \Rightarrow \quad \frac{1}{k_B T} = \frac{\partial \ln \Omega}{\partial U}$$

When two systems are brought into thermal contact, thermal equilibrium maximizes their entropy, which we've motivated is precisely the same as requiring that the temperatures of the two systems are equal: $T_1 = T_2$. This is not too hard to show: the total energy is $E_{\text{tot}} = E_1 + E_2$ (below we'll follow the book's convention and use the symbol E rather than U for energy) which remains constant, and the combined entropy is $S = S_1 + S_2$,

$$S = S_1(E_1) + S_2(E_2) = S_1(E_1) + S_2(E_{\text{tot}} - E_1)$$

Maximizing the total entropy means that we can set the following to zero:

$$\frac{\partial S}{\partial E_1}\Big|_{E_{\text{tot}}} = \frac{\partial S_1}{\partial E_1}\Big|_{E_{\text{tot}}} + \frac{\partial S_2}{\partial E_1}\Big|_{E_{\text{tot}}} = \frac{\partial S_1}{\partial E_1}\Big|_{E_{\text{tot}}} + \left(\frac{\partial E_2}{\partial E_1}\right)\frac{\partial S_2}{\partial E_2}\Big|_{E_{\text{tot}}} = \frac{\partial S_1}{\partial E_1}\Big|_{E_{\text{tot}}} - \frac{\partial S_2}{\partial E_2}\Big|_{E_{\text{tot}}}$$

since $E_2 = E_{\text{tot}} - E_1$ implies $\frac{\partial E_2}{\partial E_1} = -1$. Setting this to zero at equilibrium is equivalent to setting

$$\frac{1}{T_1} = \frac{1}{T_2} \qquad \text{at equilibrium}\,.$$

We will actually consider the even simpler scenario of the *canonical ensemble*: let one of the systems be huge (the reservoir, or heat bath, or environment) and one of them relatively smaller (the "system"). The energy of the reservoir is much larger than the energy of the system, with their total energy a constant:

$$E_{\text{tot}} = E_S + E_R\,, \qquad E_S \ll E_R\,.$$

The system exchanges energy with the reservoir, but in doing so the temperature of the heat bath remains constant since it's so large and has approximately infinite heat capacity. At a given allowed energy of the heat bath, the number of microstates of the heat bath is ginormous, but we assume that for each allowed energy of the system there is only a single microstate. The macrostates are labeled by the possible energies of the system, E_S.

What is the probability of finding the system in a particular macrostate $P(E_S)$ labeled by its energy? It is proportional to the number of microstates $\Omega_R(E_R)$ that are accessible to the reservoir (which is large), multiplied by the number of microstates accessible to the system, which we have assumed to be 1 ($\Omega_S(E_S) = 1$). Then this probability is proportional to

$$P(E_S) \;\propto\; \Omega_R(E_R)\Omega_S(E_S) = \Omega_R(E_{\text{tot}} - E_S)\Omega_S(E_S) = \Omega_R(E_{\text{tot}} - E_S)$$

Note that since the system is small, we can still consider all the microstates of the reservoir to be equally likely. The "$\propto$" is because of course we would have to normalize by dividing by the total number of possible microstates of the system at a given E_{tot}, though we will neglect this constant denominator for the moment. Since we assume the energy of the system is much smaller than the energy of the system plus reservoir, we can Taylor expand for small $E_S \ll E_{\text{tot}}$, and express the result in terms of the temperature. To do this it is easiest to expand $\ln \Omega_R(E_{\text{tot}} - E_S)$ since the temperature is related to the log of the number of microstates:

$$\begin{aligned}\ln \Omega_R(E_{\text{tot}} - E_S) &= \ln \Omega_R(E_{\text{tot}}) - E_S \frac{d \ln \Omega_R(E)}{dE}\Big|_{E_{\text{tot}}} + \ldots \\ &= \ln \Omega_R(E_{\text{tot}}) - E_S \frac{1}{k_B T} + \ldots \end{aligned} \tag{7.1}$$

where T is the temperature of the reservoir – of course at equilibrium, both the system and reservoir are at the same temperature T. Exponentiating to get the probability, we find

$$P(E_S) \propto \Omega_R(E_{\text{tot}}) e^{-\frac{E_S}{k_B T}} \tag{7.2}$$

This is known as the Boltzmann distribution, or canonical distribution, and the exponential factor $e^{-E_S/(k_BT)}$ is known as the *Boltzmann factor*. It says that when we consider a system in thermal contact with a heat bath, at fixed equilibrium temperature T, its energy is *not* a constant but is governed by this exponentially decaying probability distribution: systems tend to be found in lower energy states.

——— End Lecture 14.

Of course, we should properly normalize by dividing by the total number of possible microstates, which is obtained by summing over all possible values of the system's energy E_S for a given E_{tot}:

$$\begin{aligned}\Omega(E_{\text{tot}}) &= \sum_n \Omega_R(E_{\text{tot}} - E_n)\\ &= \Omega_R(E_{\text{tot}}) \sum_n e^{-\frac{E_n}{k_BT}}\end{aligned}$$

where in the second line we used the result (7.1). Thus, in the properly normalized Boltzmann distribution the constant prefactor $\Omega_R(E_{\text{tot}})$ cancels out, and we have that the probability of finding the system in a canonical ensemble with energy E_S is given as,

$$\boxed{P(E_S) = \frac{e^{-\frac{E_S}{k_BT}}}{\sum_n e^{-\frac{E_n}{k_BT}}}} \tag{7.3}$$

This sum in the denominator is called the *partition function* – it is extremely important and we will study it in some detail later.

Let's consider the following examples that explore this Boltzmann distribution.

Example Problem: A 2-state system

Consider a 2-state system in thermal equilibrium at temperature T with a reservoir, whose energy can take two possible values: with with energy $E = 0$ and the other with energy $\epsilon > 0$. What are the probabilities of the system being in each state, and what is the average energy of the system?

Solution:

$$\begin{aligned}P(0) &= \frac{e^{-\frac{0}{k_BT}}}{e^{-\frac{0}{k_BT}} + e^{-\frac{\epsilon}{k_BT}}} = \frac{1}{1 + e^{-\epsilon/(k_BT)}}\\ P(\epsilon) &= \frac{e^{-\frac{\epsilon}{k_BT}}}{1 + e^{-\epsilon/(k_BT)}}\end{aligned}$$

Of course, $P(0) + P(\epsilon) = 1$ since we've properly normalized. What is the average energy of the system?

$$\begin{aligned}\langle E\rangle &= \sum_i E_i P(E_i) = 0 \cdot P(0) + \epsilon \cdot P(\epsilon)\\ &= \frac{\epsilon e^{-\frac{\epsilon}{k_BT}}}{1 + e^{-\epsilon/(k_BT)}} = \frac{\epsilon}{e^{\epsilon/(k_BT)} + 1}\end{aligned}$$

What does this look like? At high temperatures $T \to \infty$ (or more properly, $k_BT \gg \epsilon$), the $e^{\epsilon/(k_BT)}$ factor tends to $e^0 = 1$, so the average energy tends to $\epsilon/2$. That is to say, when T is high both levels are equally occupied on average: $P(0) \to 1/2$ and $P(\epsilon) \to 1/2$. However when T is small, $k_B T \ll \epsilon$, $e^{\epsilon/(k_B T)} \to \infty$, so the average energy tends to a constant/$\infty \to 0$, so that the system tends to be in its ground state.

$$\langle E \rangle = \frac{\epsilon}{e^{\epsilon/(k_B T)} + 1} = \begin{cases} \epsilon/2 & T \to \infty \\ 0 & T \to 0 \end{cases}$$

In-Class Exercise: The state of the sun

The temperature of the sun is 5800 K and is 71% Hydrogen by mass. Hydrogen has energy levels that are given by the formula $E = (-13.6/n^2)eV$ for $n = 1, 2, 3, \ldots$.

(a) Calculate the ratio of the number of atoms in state 2 to the number of atoms in the ground state $n = 1$. (Note that the value of Boltzmann's constant is $k_B = 8.62 \times 10^{-5}\, eV/K$.)

Solution: Any given Hydrogen atom is an infinite-state system, with possible energy levels E_n. We can consider a given atom in thermal equilibrium with the rest of the sun, at equilibrium temperature of $T = 5800$ K. The probability of the atom being in the n'th state is proportional to the Boltzmann factor,

$$P(E_n) \propto e^{-E_n/(k_B T)}$$

If this is the probability of a given atom being in the n'th state, then the ratio of the number of atoms in the n'th state to the number of atoms in the ground state is the ratio,

$$\frac{N_n}{N_1} = \frac{\deg(E_n) P(E_n)}{\deg(E_1) P(E_1)} = \frac{n^2 e^{-E_n/(k_B T)}}{e^{-E_1/(k_B T)}}$$

where we shouldn't forget that since the n'th state has degeneracy $2n^2$, we should multiply our Boltzmann factors by the degeneracies of the energy levels. Evaluating $k_B T = (8.62 \times 10^{-5}\, eV/K)(5800\, K) = 0.50\, eV$, and $E_1 = -13.6\, eV$, $E_2 = -3.4\, eV$, we have:

$$\frac{N_2}{N_1} = \frac{4P(E_2)}{P(E_1)} = \frac{4e^{-(-3.4\, eV)/(0.50\, eV)}}{e^{-(-13.6\, eV)/(0.50\, eV)}} = 5.53 \times 10^{-9}$$

Note that we didn't need the denominator factor at all in evaluating this expression. We expect that we are more likely to be in the state of smaller energy, and this ratio is indeed less than 1 as expected. In fact, this is a tiny number – the vast majority of the atoms will be in the ground state! This result says that for every approximately 1 billion ground state atoms, there is one excited atom in the first excited state.

(b) If we were to assume naively that all of the Hydrogen in the sun were either in the ground state or first excited state ($n = 2$), how many atoms would be in the 1st excited state? Note that the total mass of the sun is $2 \times 10^{30}\, kg$, and the molar mass of Hydrogen is $1.008 g$/mol.

Solution: We need to calculate the number of Hydrogen atoms in 71% of $2 \times 10^{30}\, kg$ $= 1.42 \times 10^{30}\, kg$ of Hydrogen. The molar mass of Hydrogen is $1.008 g$/mol, and 1 mole is equal to $N_A = 6.022 \times 10^{23}$ atoms, so:

$$\frac{1.42 \times 10^{30}\, kg}{1.008\, g/\text{mol} \times \frac{1\,\text{mol}}{6.022\times 10^{23}\,\text{atoms}}} \times \frac{1000\, g}{1\, kg} = 8.48 \times 10^{10}\text{atoms}$$

Since we found in part (a) the ratio of the number of atoms in the $n = 2$ state to the number of atoms in the $n = 1$ state, if we naively assume that all of the atoms are in one of these states then we can solve for N_2 as:

$$N_{\text{tot}} = N_1 + N_2 = N_1 + N_1(5.53 \times 10^{-9}) = 8.48 \times 10^{10}\text{atoms}$$
$$\Rightarrow \quad N_2 = (8.48 \times 10^{10}) - \frac{8.48 \times 10^{10}}{1 + 5.53 \times 10^{-9}} = 469 \text{ atoms}$$

The vast majority of the atoms are in the ground state, with only a tiny fraction in the first excited state. It would be an excellent approximation to approximate most of the Hydrogen atoms in the sun as in their ground state.

(c) Re-answer (a) if the sun were only at room temperature, $T = 300\, K$.

Solution: First let's answer what we would expect. At smaller temperatures, we know from the previous example that the system will be even more likely to be in its ground state, so we expect an even smaller ratio of atoms in the first excited state to ground state.

If the sun were room temperature, we would have $k_B T = (8.62\times 10^{-5}\, eV/K)(300\, K) = 0.026$, so that

$$\frac{N_2}{N_1} = \frac{4e^{-(-3.4\, eV)/(0.026\, eV)}}{e^{-(-13.6\, eV)/(0.026\, eV)}} = 1.7 \times 10^{-170}$$

which indeed is an unbelievably tiny number.

We should emphasize the result of this exercise: as the temperature of the reservoir (the sun) goes up, the likelihood of finding the hydrogen atom in an excited state also goes up, whereas if the temperature of the reservoir goes down, the likelihood of finding the atom in an excited state also goes down.

7.3 Application: Classical Systems and the Equipartition Theorem

Before we move on to our study of the partition function, we will first have a discussion of the equipartition theorem, which provides a simple classical theory of thermal systems valid at high temperatures. The basic idea is that the internal energy of a classical system composed of a large number of particles in thermal equilibrium will distribute itself evenly among each of the quadratic degrees of freedom.

Suppose we have a system whose energy is given by

$$E(x) = \alpha x^2$$

so that it depends quadratically on some variable x. This is very common; for example, a free particle with just kinetic energy has energy $E = \frac{1}{2}mv^2$, so $x = v$. Or, the potential energy of a mass attached to a spring is $E = \frac{1}{2}k\Delta x^2$ where Δx is the displacement of the mass from equilibrium. In fact, If I consider a system in some general potential $V(x)$ that is a function of the position x of some system, and expand for small displacements Δx around an equilibrium state corresponding to a minimum of the potential at $x = x_0$, then

$$V(\Delta x) = V(x_0) + \Delta x \frac{dV(x)}{dx}\Big|_{x=x_0} + \frac{1}{2}(\Delta x)^2 \frac{d^2V(x)}{dx^2}\Big|_{x=x_0} + \dots$$

where we drop small corrections to the first terms that are higher order in small Δx. The first term is just a constant. The linear term in Δx vanishes, since at the minimum the derivative of the potential vanishes, $U'(x_0) = 0$. Then, the potential energy of *any* system near equilibrium is described at leading order by a quadratic function in the displacement from equilibrium,

$$E = \text{constant} + \frac{1}{2}V''(x_0)(\Delta x)^2 \dots \qquad \text{near equilibrium}$$

This is known as the *harmonic approximation.*

Now, suppose the system is allowed to interact with a heat bath, so that it can exchange energy with the environment. The heat bath is large so you can take a lot of energy out of it and it can remain at essentially the same temperature. What is the system's average thermal energy?

We've learned that the probability $P(x)$ of the system having a particular energy $E = \alpha x^2$ is proportional to the Boltzmann factor $e^{-\alpha x^2/(k_BT)}$. Normalizing means dividing by the sum of the probabilities for all possible states, which in this case is an integral since x is a continuous variable. Let us assume that x could in principle take any value with equal probability; then,

$$P(x) = \frac{e^{-\alpha x^2/(k_BT)}}{\int_{-\infty}^{\infty} e^{-\alpha x^2/(k_BT)}\, dx}$$

Recall that for a continuous variable that can vary over the range $-\infty$ to ∞, the average is computed by

$$\langle x \rangle = \int_{-\infty}^{\infty} xP(x)\, dx$$

where $P(x)$ is the probability distribution. Then the average energy is given by

$$\begin{aligned}\langle E \rangle &= \int_{-\infty}^{\infty} EP(x)\, dx = \int_{-\infty}^{\infty} \alpha x^2 P(x)\, dx \\ &= \frac{\int_{-\infty}^{\infty} \alpha x^2 e^{-\alpha x^2/(k_BT)}\, dx}{\int_{-\infty}^{\infty} e^{-\alpha x^2/(k_BT)}\, dx}\end{aligned}$$

These are both Gaussian integrals, given by

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \qquad \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \sqrt{\frac{\pi}{4a^3}}$$

so this evaluates to

$$\langle E \rangle = \frac{\alpha \sqrt{\frac{\pi}{4\alpha^3/(k_BT)^3}}}{\sqrt{\frac{\pi}{\alpha/(k_BT)}}} = \frac{1}{2}k_BT$$

This is a remarkable result: it says that the mean energy for any system with a quadratic energy dependence is proportional to the temperature, and completely independent of the constant α.

This theorem can be extended straightforwardly to the case when the energy is a sum of n quadratic terms. In particular, if the total energy of my system is a sum of n independent quadratic terms,

$$E = \sum_{i=1}^{n} \alpha_i x_i^2$$

Then we could perform exactly the same computation, except now the probability distribution depends on n variables that can vary from $-\infty$ to ∞: the probability of the system having total energy E is

$$P(E) = P(x_1, x_2, \ldots, x_n) = \frac{\exp\left(-\frac{1}{k_B T}\sum_{i=1}^{n} \alpha_i x_i^2\right)}{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\left(-\frac{1}{k_B T}\sum_{i=1}^{n} \alpha_i x_i^2\right) dx_1\, dx_2 \ldots dx_n}$$

The integral in the denominator is now a product of n Gaussian integrals. To compute the average energy we would need to compute $\int_{-\infty}^{\infty} E P(x)\, dx$ as before, just now there is a sum of n integrals to do. (I encourage you to go through the steps in Example 19.1 in Blundell and Blundell; there is also a homework problem on HW 6 that revisits this system!) The result is simple: the expression simplifies into a sum of n copies of the previous result,

$$\boxed{\text{Equipartition theorem:} \qquad \langle E \rangle = \sum_{i=1}^{n} \frac{1}{2} k_B T = \frac{n}{2} k_B T}$$

——— *End Lecture 15.*

This means that every separate quadratic energy dependence of my system contributes $\frac{1}{2}k_B T$ to the average energy of the system, regardless of the constant multiplying the x_i^2! We refer to each quadratic energy dependence as a **degree of freedom**, or **mode** of the system. This result is summarized in the *Equipartition theorem:* If the energy of a classical system is the sum of n degrees of freedom and that system is in contact with a heat reservoir at temperature T, the mean energy of the system is given by $n \times \frac{1}{2}k_B T$.

This is precisely the result that we motivated in our discussion of the internal energy of an ideal gas. Recall that there we claimed that if we have N gas molecules in d dimensions, then the system has dN degrees of freedom, with total internal energy $U = \frac{d}{2} N k_B T$. Here we have derived this result: we interpret the thermodynamic internal energy U of the ideal gas as the *average* measured energy. The monoatomic gas in 3 dimensions, for example, has 3 quadratic components to the kinetic energy of each gas molecule, times N molecules, so that by the equipartition theorem a monoatomic ideal gas in three dimensions has internal energy $U = 3N \times \frac{1}{2}k_B T = \frac{3}{2} N k_B T$.

The molecules in a diatomic ideal gas, by contrast, can additionally have rotational kinetic energy and vibrational kinetic energy. The rotational kinetic energy adds 2 degrees of freedom associated to each molecule of the gas, while the vibrational motion adds another 2 degrees of freedom, so that the average energy of a diatomic ideal gas that accounts for the translational, rotational, and vibrational motion of the molecules is $U = (3+2+2)N \times \frac{1}{2}k_B T = \frac{7}{2} N k_B T$. This explains the different internal energies and heat capacities of monoatomic versus diatomic ideal gases: for instance, since

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \Rightarrow \quad C_V = (\#\text{ of degrees of freedom}) \times \frac{1}{2} k_B\,.$$

Another example is a mass on a spring in one dimension; the mass has kinetic energy $\propto v^2$ and potential energy $\propto x^2$, so there are two degrees of freedom that contribute to its average energy: $\langle E\rangle = 2 \times \frac{1}{2}k_BT = k_BT$. This means that we can assign an average energy of k_BT to a harmonic oscillator in one dimension.

It is important to note that the equipartition theorem is generally valid only at high temperatures, when the thermal energy is much larger than the energy gap between quantized energy levels so that we can ignore quantum effects and approximate the variables x_i as continuous. However, if you are modeling your system by expanding around some minimum of a potential, you also have to be careful not to take T too high so as the harmonic approximation is no longer valid, and we need to include higher order terms in the potential energy that are cubic, quartic, *etc.* As your book points out, fortunately there is plenty of room between these two extremes.

8 Boltzmann and the Partition Function

Textbook readings: (a first reading is due before Lecture 15; most pertinent to Lecture 15-17)

- Ch. 4 sections 4.6-7
- Ch. 20, all

Learning Objectives:

- The partition function: calculation of Z for simple quantum systems
- Obtaining functions of state from Z

8.1 Partition Function Basics and Computing U

The ratio of two Boltzmann factors is just a ratio of two probabilities,

$$\frac{P_2}{P_1} = \frac{e^{-E_2/(k_BT)}}{e^{-E_1/(k_BT)}}$$

We've learned that to compute absolute probability, we need to properly normalize by dividing out by the sum of all possible probabilities, the **partition function**. If there are N terms in the sum, then this sum is given by

$$\boxed{Z = \sum_{n=1}^{N} e^{-E_n/(k_BT)} = \sum_{n=1}^{N} e^{-\beta E_n} \qquad \beta \equiv 1/(k_BT)}$$

We will often use the symbol β to denote the inverse temperature (times Boltzmann's constant). The origin of the symbol Z for the partition function is its German name, *Zustandsumme*, or "sum over states".

What is this sum? At low temperatures compared to the energies of the states, so that $k_BT \ll E_n$, $Z \sim 1$ since $e^{-\infty} \to 0$. Why? This is the limit in which only the ground state term contributes to Z; the resulting probability will be ~ 1 for the ground state and ~ 0 for the other excited states. But for high temperatures, Z can get quite large as excited states become more and more possible.

Despite being introduced as a seemingly innocuous normalization factor, the partition function contains all the information about the energies of the states of the system. As we will see in this section, all thermodynamic quantities can be obtained from it.

Some basic properties of the partition function are the following:

- The zero energy is arbitrary: only energy differences are important. Imagine we shifted all the energy states by a constant c, $E_n \to E_n + c$. The partition function would change by an overall multiplicative factor,

  $$Z \to Z' = \sum_{n=1}^{N} e^{-\beta(E_n+c)} = e^{-\beta c} Z$$

  However, any probability that I compute will have the *same* multiplicative factor in the numerator,

  $$P(E_n) = \frac{e^{-\beta E_n}}{Z} \quad \to \quad \frac{e^{-\beta c} e^{-\beta E_n}}{e^{-\beta c} Z} = P(E_n)$$

  So, the probabilities of macrostates that I compute for a system described by partition function Z don't care about the zero of energy. Of course, if I want to compute the average energy, the whole average will shift by this constant:

  $$\langle E \rangle = \sum_n E_n P(E_n) \quad \to \quad \sum_n (E_n + c) P(E_n) = \langle E \rangle + c$$

- For independent systems, Z's multiply. This is easy to prove. Suppose that we have two systems which don't interact with one another, so that the energy of the combined system is the sum of the individual energies, $E_{\text{tot}} = E^{(1)} + E^{(2)} = \sum_n E_n^{(1)} + \sum_m E_m^{(2)}$. The partition function for the combined system takes the form,

  $$Z = \sum_{n,m} e^{-\beta(E_n^{(1)} + E_m^{(2)})} = \sum_{n,m} e^{-\beta E_n^{(1)}} e^{-\beta E_m^{(2)}} = \sum_n e^{-\beta E_n^{(1)}} \sum_m e^{-\beta E_m^{(2)}} = Z_1 Z_2$$

  Of course if the systems are not independent so that there is some interaction term that depends on both systems, this property will not hold.

Let's examine what information is contained in the partition function. We will start by thinking about the system energy, which we should recall is not fixed in the canonical ensemble. We've already gone through some examples computing the average energy of a system using the formula,

$$\boxed{\langle E \rangle = \sum_n E_n P(n) = \sum_n \frac{E_n e^{-\beta E_n}}{Z}}$$

or the integral version of this formula if the distribution is continuous. (We are interchangeably using the notation $P(E_n)$ and $P(n)$ to label the macrostate whose energy is given by E_n – hopefully the meaning of this notation is clear.) However, evaluating these sums can get a bit tedious. Observe that there is a way to nicely express the average energy solely in terms of Z, without reference to the probabilites: by differentiating with respect to β, we pull down a factor of the energy E_n in each term of the sum, so that

$$-\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \sum_n e^{-\beta E_n} = \sum_n E_n e^{-\beta E_n} = Z \cdot \langle E \rangle$$

In other words, this derivative just computes the unnormalized average energy (before we've divided out by the normalization factor Z.) The average energy can therefore be written as

$$\boxed{\langle E\rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}}$$

where in the second equality we used the fact that $d\ln f(x)/dx = (1/x)df/dx$ to write the derivative in terms of $\ln Z$ rather than just Z. (Feel free to use whichever version of this formula you like, it's a matter of preference! Also if you prefer to express everything in terms of T rather than β, don't forget to chain rule the derivatives: $\frac{d}{d\beta} = \frac{dT}{d\beta}\frac{d}{dT} = -k_B T^2 \frac{d}{dT}$.)

Now, statistically speaking, the variable E refers to the total internal energy of the system upon measurement, where repeated measurements will roughly follow the probability distribution $P(n)$ whose average is $\langle E\rangle$. We identify $\langle E\rangle$ with the *thermodynamic* quantity U – the function of state which describes the internal energy of the thermodynamic system consisting of a large number of degrees of freedom. So this equation tells us that by simply differentiating the partition function, we can compute the system's internal energy U – a function of state!

$$U = \langle E\rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \tag{8.1}$$

This is a very powerful formula! Let's check (8.1) by revisiting the 2-state system example from earlier. We consider again the example of a 2 state system in thermal equilibrium at temperature T with a reservoir. In the previous example problem, we solved this for the case that the two possible energy levels are $E = 0$ and $E = \epsilon > 0$, where we explicitly computed

$$\langle E\rangle = \frac{\epsilon}{e^{\epsilon/(k_B T)} + 1}$$

Now let's do the same exercise, but only using our partition function formula (8.1). Z for this system is given by $Z = 1 + e^{-\beta\epsilon}$. We can compute

$$\begin{aligned}\langle E\rangle &= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial}{\partial \beta}\left(1 + e^{-\beta\epsilon}\right)\\ &= -\frac{-\epsilon e^{-\beta\epsilon}}{Z} = \frac{\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} = \frac{\epsilon}{e^{\beta\epsilon} + 1}\end{aligned}$$

This is the same result we found before. No need to compute probabilities, just take a derivative of the partition function!

As an explicit example of a 2-state system, let's revisit the 2-state paramagnet that we discussed at the very beginning of this class.

Example Problem: The 2-state Paramagnet

This system consists of N particles of spin-1/2 in a uniform magnetic field of magnitude B. The particles can be thought of as N magnetic dipoles of magnet moment μ. Their spins must be either up or down (thank you quantum mechanics), and when the spin is down the i'th dipole contributes positively to the energy as $E_\downarrow = +\mu B$, while when the spin is up it contributes negatively as $E_\uparrow = -\mu B$. We put the whole system in thermal equilibrium with a heat bath of temperature T. This is therefore a set of N 2-state systems, each with possible energies $E_\uparrow$ or $E_\downarrow$, all in thermal equilibrium at temperature T. (*Caution:* in this problem N denotes the number of dipoles, not the number of states of the system!! This is a collection of N 2-state systems.)

First consider only one of the dipoles at a time, say the i'th dipole. Find (1) the partition function for this system, (2) the probability of measuring the i'th particle in the spin up state, and (3) the average energy of the dipole.

Then, consider the whole collection of N dipoles. Find (1) the partition function for this system, (2) the probability of measuring $N_\uparrow$ dipoles in the spin up state and $N_\downarrow$ dipoles in the spin down state, with $N_\uparrow + N_\downarrow = N$, and (3) find the average energy of the paramagnet.

Solution: Let's first answer these questions considering only one of these dipoles at a time (say, the i'th dipole, where i runs from 1 to N). The partition function of that single dipole is

$$Z_i = \sum_{n=\uparrow,\downarrow} e^{-\beta E_n} = e^{-\beta E_\uparrow} + e^{-\beta E_\downarrow} = e^{\mu B\beta} + e^{-\mu B\beta}$$

A nice way to write this expression is in terms of hyperbolic cosine cosh,

$$Z_i = e^{\mu B\beta} + e^{-\mu B\beta} = 2\cosh\left(\mu B\beta\right)$$

The probability of measuring that dipole in the ↑ state is given by the Boltzmann distribution,

$$P(\uparrow) = \frac{e^{-\beta E_\uparrow}}{Z_i} = \frac{e^{\beta\mu B}}{2\cosh\left(\mu B\beta\right)}$$

and similarly,

$$P(\downarrow) = \frac{e^{-\beta E_\downarrow}}{Z_i} = \frac{e^{-\beta\mu B}}{2\cosh\left(\mu B\beta\right)}$$

Finally, we can compute the average energy of the dipole in one of two ways: we can either explicitly compute

$$\langle E_i\rangle = E_\uparrow P(\uparrow) + E_\downarrow P(\downarrow) = \mu B\frac{\beta\left(-e^{\beta\mu B} + e^{-\beta\mu B}\right)}{2\cosh(\mu B\beta)} = -\mu B\tanh\left(\mu B\beta\right)$$

Or, we can use our handy formula (8.1):

$$\langle E_i\rangle = -\frac{1}{Z_i}\frac{\partial}{\partial\beta}2\cosh\left(\mu B\beta\right) = -\frac{2\mu B\sinh(\mu B\beta)}{2\cosh(\mu B\beta)} = -\mu B\tanh(\mu B\beta)$$

As expected, we got the same answer.

So far we have answered these questions for a single dipole; what about the system of N dipoles? In this case, since the dipoles don't interact with each other, the total energy is the sum of the energies of all the individual dipoles,

$$E = \sum_{i=1}^{N} E_i$$

where E_i can be either $E_\uparrow$ or $E_\downarrow$ depending on whether that dipole is spin up or spin down. Then, the partition function is simply the product of all the individual partition functions; as these are all identical, the partition function of a single dipole to the N'th power:

$$Z = Z_1 Z_2 \ldots Z_N = Z_i^N = 2^N\left[\cosh(\mu B\beta)\right]^N$$

Now we can ask about the probability of measuring $N_\uparrow$ total dipoles in the spin up state, with $N_\uparrow + N_\downarrow = N$. Since we know the probabilities for each single dipole, the probability of measuring $N_\uparrow$ dipoles in the up state and $N_\downarrow$ in the down state is given by multiplying all the individual probabilities for $N_\uparrow$ dipoles and $N_\downarrow$ dipoles, times the combinatorial factor to account for the fact that there are N *choose* $N_\uparrow$ possible ways of arranging the $N_\uparrow$ up states amongst the N dipoles (remember, this is the binomial coefficient factor $\Omega(N_\uparrow) = N!/(N_\uparrow!N_\downarrow!)$ that we computed in an early lecture!):

$$\begin{aligned}
P(N_\uparrow) &= \left(\begin{array}{c} N \\ N_\uparrow \end{array}\right) (P(\uparrow))^{N_\uparrow} (P(\downarrow))^{N_\downarrow} \\
&= \frac{N!}{N_\uparrow! N_\downarrow!} \left(\frac{e^{\beta\mu B}}{2\cosh(\mu B\beta)}\right)^{N_\uparrow} \left(\frac{e^{-\beta\mu B}}{2\cosh(\mu B\beta)}\right)^{N_\downarrow} \\
&= \frac{N!}{N_\uparrow! N_\downarrow!} \frac{e^{\beta\mu B N_\uparrow} e^{-\beta\mu B N_\downarrow}}{2^{N_\uparrow + N_\downarrow} [\cosh(\mu B\beta)]^{N_\uparrow + N_\downarrow}} \\
&= \frac{N!}{N_\uparrow! N_\downarrow!} \frac{e^{\beta\mu B N_\uparrow} e^{-\beta\mu B N_\downarrow}}{Z}
\end{aligned}$$

where we used $N_\downarrow = N - N_\uparrow$ to simplify the denominator.

The average energy of the whole system is computed as,

$$\begin{aligned}
\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} &= -\frac{1}{2^N [\cosh(\mu B\beta)]^N} \frac{\partial}{\partial \beta} 2^N [\cosh(\mu B\beta)]^N \\
&= -\frac{1}{[\cosh(\mu B\beta)]^N} \cdot N\mu B [\cosh(\mu B\beta)]^{N-1} \sinh(\mu B\beta) \\
&= -N\mu B \tanh(\mu B\beta) = N\langle E_i \rangle
\end{aligned}$$

The average energy of the whole system is the sum of the average energies of each of the individual dipoles. This is completely as expected, because the dipoles don't interact with each other! The average energy is simply given by

$$\langle E \rangle = \sum_{i=1}^{N} \langle E_i \rangle = N\langle E_i \rangle \,.$$

——— End Lecture 16.

After we discuss how to compute more thermodynamic properties from Z, we will return to the 2-state paramagnet and better understand its physics. Another very nice example is the simple harmonic oscillator – you will compute U for the simple harmonic oscillator system in your homework.

8.2 Functions of State from Z

Heat capacity Besides U, other familiar functions of state can be computed from Z. One example is the heat capacity at constant volume. Recall that C_V is given by the derivative of U with respect to temperature at constant volume. Using (8.1), we can therefore find C_V just by differentiation the partition function:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = -\frac{\beta}{T}\left(\frac{\partial U}{\partial \beta}\right)_V = \frac{\beta}{T}\frac{\partial^2 \ln Z}{\partial \beta^2} \tag{8.2}$$

(Your book changes variables from β to T to rewrite this formula entirely in terms of derivatives with respect to T: I recommend checking for yourself that you can reproduce equation (20.19) in your book directly from (8.2) above using $\frac{d}{d\beta} = -k_B T^2 \frac{d}{dT}$!) If you prefer to write this without the log, we can do out the chain rule:

$$\begin{aligned} C_V &= \frac{\beta}{T}\left(\left(\frac{\partial}{\partial\beta}\frac{1}{Z}\right)\frac{\partial Z}{\partial\beta} + \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2}\right) \\ &= \frac{\beta}{T}\left(-\frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2 + \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2}\right) \end{aligned}$$

Actually, this expression is proportional to the variance in the energy $(\Delta E)^2$ (the *mean squared deviation*, or the standard deviation squared): it is not too hard to show that

$$C_V = \frac{\beta}{T}\left(\langle E\rangle^2 - \langle E^2\rangle\right) = \frac{\beta}{T}(\Delta E)^2$$

Remember, the variance $(\Delta E)^2$ measures the size of the probabilistic fluctuations in the energy of the system. This is an interesting result: it says that statistically speaking, the heat capacity C_V of a system is a measure of the systems thermal energy fluctuations. How important are these fluctuations? For systems with many particles (say, N degrees of freedom), we've learned from the equipartition theorem that typically $\langle E\rangle \sim N k_B T$, so that $C_V \sim N k_B$ (here just tracking the factors of N and $k_B T$, not so much the order 1 constants like 3 or 1/2). Then,

$$\frac{\Delta E}{\langle E\rangle} = \frac{\sqrt{C_V T/\beta}}{\langle E\rangle} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$$

This says the relative size of the fluctuations to the typical energy in the system decreases with the number of particles, going to zero in the thermodynamic limit that $N \to \infty$. So, in the thermodynamic limit the energy becomes peaked closer and closer to the mean value $\langle E\rangle$ and can be treated essentially as fixed.

Entropy S We've previously statistically defined the entropy of a configuration with some energy E as due to the number of different states in which the system can exist, $S = k_B \ln\Omega$. This is an expression useful for the microcanonical ensemble, where the energy E of the system is taken to be fixed, and there is no mention of a thermal equilibrium temperature T.

It turns out that the entropy can also be expressed more generally in terms of the probabilities P_i of realizing a particular macrostate labeled by i,

$$S = -k_B \sum_i P_i \ln P_i$$

(We won't actually prove this expression; if you're interested this is discussed in some detail at the end of Chapter 14 of the textbook.) In the microcanonical ensemble, where Ω is the total number of macrostates possible for the system and where each has macrostate equal probability $P_i = \frac{1}{\Omega}$ of being realized, this readily gives the same definition we were using before:

$$S = -k_B \sum_i P_i \ln P_i = -k_B \sum_{i=1}^{\Omega} \frac{1}{\Omega} \ln\frac{1}{\Omega} = k_B \ln\Omega \quad \checkmark$$

In the canonical ensemble, the macrostates are labeled by their energies E_n, and the probability P_n is given by the Boltzmann distribution:

$$P_n = \frac{e^{-\beta E_n}}{Z} \qquad \Rightarrow \qquad S = -k_B \sum_n P_n \ln P_n = -k_B \sum_n \frac{e^{-\beta E_n}}{Z} \left(-\beta E_n - \ln Z\right)$$
$$= k_B \left(\beta U + \ln Z\right)$$

where we used that $\sum_n e^{-\beta E_n} = Z$, and $U = \langle E \rangle = \sum_n E_n e^{-\beta E_n}/Z$. Since U can itself be written as a derivative of Z, this expresses the entropy of the system entirely in terms of the partition function Z.

Helmholtz function F Recall that the Helmholtz function is defined as $F = U - TS$. Therefore, combining the equations for S and U and using $T = 1/(\beta k_B)$ allows us to write

$$F = U - \frac{1}{\beta}\left(\beta U + \ln Z\right) = -\frac{1}{\beta} \ln Z$$

or in other words,

$$\boxed{Z = e^{-\beta F}}$$

No more sum! That is to say, the Helmholtz function F contains information about the sum over all the energy states.

From the expression for F we can find an expression for the pressure P; we can use

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial V}\right)_T$$

... And so on. At this point we can use the many relations we've learned between the various thermodynamic variables to generate the relevant thermodynamic properties from Z. For instance, since $H = U + PV$ and $G = F + PV$ we can use the above definitions to write the other thermodynamic potentials in terms of Z, and then use all the partial derivative expressions we've learned involving the thermodynamic potentials to find anything else we like. It all follows from Z! Etcetera.

With all these expressions in hand, let's revisit several different systems we have discussed to this point to discuss their physics.

- **The 2-state system:** Consider a 2-state system whose energies are given by $\pm\Delta$. (For instance, if the 2-state system is a dipole in a magnetic field we would have $\Delta = \mu B$; or we could shift everything by a constant Δ so that the energies are 0 and 2Δ, in which case we would identify $\epsilon = 2\Delta$ in the previous example problem we did.) In any case, we can write down the partition function as

  $$Z = 2\cosh(\beta\Delta)$$

  Let's plot U and S for this system as a function of β, as computed from Z using the formulas $U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$ and $S = k_B\left(\beta U + \ln Z\right)$.

  At low temperatures (large β), the system is in the ground state and so the internal energy is $U = -\Delta$. Since the ground state has degeneracy 1, we expect the entropy should match $S = k_B \ln \Omega = k_B \ln 1 = 0$, and indeed the entropy in the low temperature limit is 0. This also makes sense with the third law of thermodynamics: $S \to 0$ as $T \to 0$.

At high temperatures (small β), both levels are occupied with equal probability $1/2$, and so U tends to the average of the two levels, which in this case is 0. Since there are two possible states, we expect the entropy to go to $S = k_B \ln 2$, which indeed is born out in the plot of S. Generally speaking, higher temperatures correspond to more possible states the system could be in so correspond to increased entropy, whereas cooling gives rise to a reduction in the entropy.

It is also interesting to plot the heat capacity C_V as a function of β, using $C_V = (\partial U/\partial T)_V$. The heat capacity is very small both at low temperatures, and at high temperatures. Basically, this is because in either case changes in temperature have only a very small effect on the internal energy; in the low temperature limit the system is stuck in the ground state and small temperature changes don't alter that conclusion (and of course, we expect from the third law that $C_V \to 0$ as $T \to 0$), whereas in the high temperature limit the system has equal probability of being in either of the states and small temperature changes don't alter that conclusion. However in the middle there is an interesting peak, at roughly $\beta \sim 1/\Delta$, or when the temperature approaches the difference between the energy levels. At this temperature it is possible to thermally excite transitions between the two states of the system. This is known as the *Schottky anomaly*.

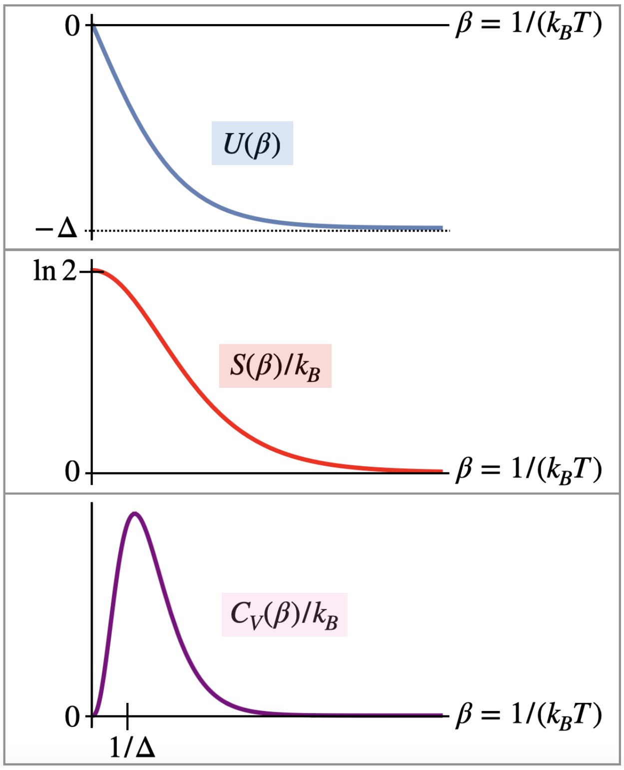


Figure 7: Plots of energy, entropy, and heat capacity as a function of β for the two-state system with energies $E = \pm\Delta$.

- **The paramagnet:** We've also considered the paramagnet consisting of N spin-1/2 particles in a constant magnetic field, each with energy $\pm\mu B$ depending on whether their spin is up or down. Recall that the partition function is equal to the product of the partition function of each individual dipole, which is just the 2-state system partition function $Z_i = 2\cosh\beta\Delta$ taken to the N'th power for $\Delta = \mu B$:

$$Z = [2\cosh(\beta\mu B)]^N$$

The behaviors for the set of N 2-state systems are similar to those of the 2-state system: as $T \to 0$ the spins want to be in their lowest energy state (pointed up), and so are aligned up along the magnetic field, while at high temperatures approximately half of the spins will be pointed up and half will be pointed down. There are many possible microstates possible at high temperatures, so the entropy gets huge as the temperature gets large.

A useful physical quantity to compute is the *magnetization* M, defined as the magnetic moment per unit volume. When all the individual magnetic moments are pointed up, the magnetization will tend to be like $M \sim N\mu$, while if the spins are not aligned along a particular direction and instead randomly distributed between up and down, the magnetization will tend to 0. The magnetization is computed from the Helmholtz function F as

$$M = -\frac{1}{V}\left(\frac{\partial F}{\partial B}\right)_T$$

which means we can compute it from the partition function using $F = -(1/\beta)\ln Z$, with result

$$M = \frac{N\mu}{V}\tanh(\beta\mu_B B)$$

At low temperatures, $\beta \to \infty$ and $\tanh(\infty) \to 1$, while at high temperatures $\beta \to 0$ and $\tanh(0) \to 0$, so that

$$M \longrightarrow \begin{cases} \frac{N\mu}{V} & T \to 0 \\ 0 & T \to \infty \end{cases}$$

So indeed: at low temperatures the material is magnetized, with net magnetic moment per unit volume equal $N\mu/V$, while at high temperatures the material is not magnetized. This is the defining behavior of a paramagnet.

——— *End Lecture 17.*

In-Class Exercise: Partition *fun*ction *fun* with a simple harmonic oscillator

A simple harmonic oscillator is known to have energy levels given by

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega\,, \qquad n = 0, 1, 2, 3, \ldots$$

(a) Write down the formula for Z, then simplify it using the following infinite sum:

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \qquad \text{for } x < 1\,.$$

Solution: Z is given by the sum over all the Boltzmann factors for the energy levels,

$$Z = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega}$$

We can evaluate the sum by repackaging things in a nice way:

$$Z = e^{-\beta\hbar\omega/2}\sum_{n=0}^{\infty}\left(e^{-\beta\hbar\omega}\right)^n$$

so that we can identify $x = e^{-\beta\hbar\omega}$ and use the infinite sum formula,

$$\begin{aligned} Z &= e^{-\beta\hbar\omega/2}\sum_{n=0}^{\infty}\left(e^{-\beta\hbar\omega}\right)^n \\ &= \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} \end{aligned}$$

(b) Calculate U and C_V from Z.

Solution: We compute the average energy as

$$\begin{aligned} U &= -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{1-e^{-\beta\hbar\omega}}{e^{-\beta\hbar\omega/2}}\left(\frac{-(\hbar\omega/2)e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} - \frac{e^{-\beta\hbar\omega/2}\cdot\left(\hbar\omega e^{-\beta\hbar\omega}\right)}{(1-e^{-\beta\hbar\omega})^2}\right) \\ &= \frac{\hbar\omega}{2}\left(1+\frac{2}{e^{\beta\hbar\omega}-1}\right) = \frac{\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right) \end{aligned}$$

(You showed how to simplify this expression in Homework 6! But writing either in terms of exponentials or hyperbolic trig functions is fine.) We can compute C_V by differentiating with respect to temperature:

$$\begin{aligned} C_V &= \frac{\partial}{\partial T}\left(\frac{\hbar\omega}{e^{\hbar\omega/(k_BT)}-1}\right) = -\frac{\hbar\omega}{(e^{\hbar\omega/(k_BT)}-1)^2}\left(-\frac{\hbar\omega e^{\hbar\omega/(k_BT)}}{k_BT^2}\right) \\ &= \frac{k_B\beta^2(\hbar\omega)^2e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} = \frac{k_B\beta^2(\hbar\omega)^2}{4\left[\sinh(\beta\hbar\omega/2)\right]^2}\,. \end{aligned}$$

(c) What do you expect U and C_V to reduce to at very low temperatures? What about at high temperatures?

Solution: We expect that at low temperatures, the average energy is just the ground state energy, and $C_V \to 0$ according to the third law. Indeed, at low temperatures $\beta\to\infty$ so the second term in U goes to zero, and if you're careful about taking limits you can also show that $C_V\to 0$ as $\beta\to\infty$:

$$T\to 0: \qquad U\approx\frac{\hbar\omega}{2}\,, \qquad C_V\approx 0 \qquad \checkmark$$

At high temperatures we expect to recover $U = k_BT$ and $C_V = k_B$, since this is the limit in which the equipartition theorem is valid. Indeed, in this limit $\beta\to 0$, and we can expand $\coth(\beta x) = 1/(\beta x)+\dots$ in U, where the $\dots$ denote terms subleading for small β. This reproduces $U\approx k_BT$. One can similarly do series expansions for C_V using $\sinh(\beta x) = \beta x+\dots$ for small β to show that $C_V\approx k_B$ in this limit:

$$T\to\infty: \qquad U\approx k_BT\,, \qquad C_V\approx k_B \qquad \checkmark$$

The results of this exercise (as well as a plot of the entropy) are shown in the figure below. At low temperatures (large β), only the lowest level is occupied, so the internal energy is $U = \frac{1}{2}\hbar\omega$, and as expected $S\to 0$ and $C_V\to 0$. At high temperatures (small β), more and more energy levels can be occupied, so that U rises without limit (linearly with temperature as $U\sim k_BT$, or equivalently as $\sim 1/\beta$) since there are in principle an infinite number of energy levels. The entropy also rises accordingly. Meanwhile, the heat capacity rises to a plateau of $C_V = k_B$, in accordance with the result of the equipartition theorem.

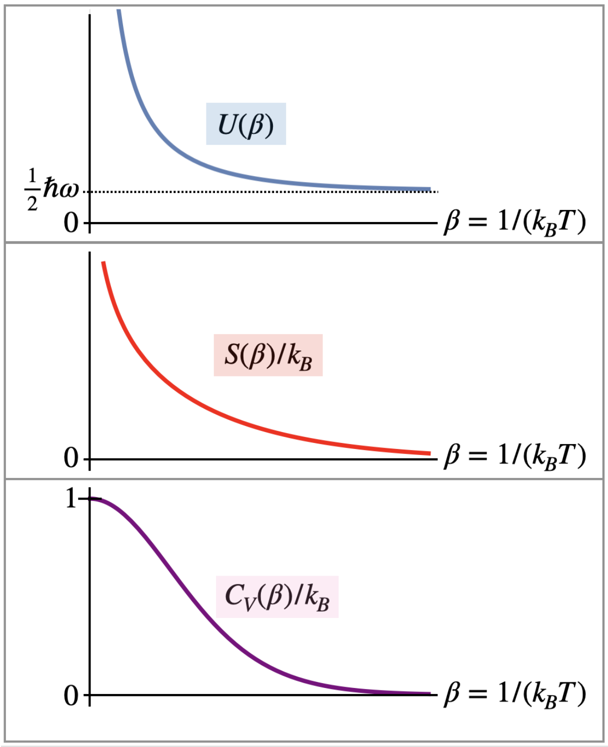


Figure 8: Plots of energy, entropy, and heat capacity as a function of β for the quantum simple harmonic oscillator.

——— End Lecture 18.

9 Statistical Mechanics of an Ideal Gas

Textbook readings: (a first reading is due before Lecture 18; most pertinent to Lecture 18)

- Ch. 21, all

Learning Objectives:

- Statistical mechanics of the ideal gas: density of states; what is Z for 1 particle? distinguishability and Gibbs paradox

9.1 Single Particle Partition Function of an Ideal Gas

As we've seen, the partition function is an extremely useful quantity. We can compute it once we know the energy levels of my system, and at this point we've computed it for a number of quantum systems of interest. But we haven't computed it for our most basic system we've been discussing in this course: the ideal gas. What is the partition function of an ideal gas?

In our classical model of the ideal gas, the gas' energy is due to the kinetic energy of each of the molecules. We expect the single molecule partition function to look something like this:

$$Z_1 \;\propto\; \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta\left(\frac{p_x^2}{2m}+\frac{p_y^2}{2m}+\frac{p_z^2}{2m}\right)}\, dp_x dp_y dp_z = \left(\frac{2\pi m}{\beta}\right)^{3/2} = (2\pi m k_B T)^{3/2}$$

where we performed the 3 Gaussian integrals, and the N-particle version to go like $Z \sim Z_1^N$. However, there is something not quite right with this formula as I wrote it: it has the wrong units! The partition function should be *dimensionless*, which is obvious in the discrete version as a sum over discrete energy levels:

$$Z = \sum_n e^{-\beta E_n} \quad \text{is dimensionless}$$

The problem is the dimensionful measure d^3p in passing from the discrete sum to a continuous, classical integral. We are missing a dimensionful constant, which turns out to be equal to the volume of space divided by Planck's constant h cubed:

$$Z_1 = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2} \tag{9.1}$$

Why does Planck's constant appear, when we are trying to talk about a classical system?? This is a hint that we really need quantum mechanics to derive the correct partition function of the ideal gas. (This is a rare case where understanding the quantum version is easier than understanding the classical one!) We'll see that with a quantum (really, semi-classical) treatment of the ideal gas molecules as particles trapped in a box of volume V, we will be able to reproduce this formula on the nose. To do this problem correctly, we'll have to compute a partition function that looks like

$$Z \sim \int e^{-\beta E(p)} g(p)\, dp$$

where the measure $g(p)\, dp$ is what we call the *density of states*: it is the function that tells you how many states are possible between momenta p and $p + dp$, or in other words, how many energy states lie in a certain momentum interval.

The steps go as follows:

0. We consider a cubical box of volume $V = L^3$ filled with gas molecules. We label each molecule by its momentum, $\vec{p}$, with its energy given by the kinetic energy $E = \frac{\vec{p}^2}{2m}$. Let's focus our discussion first on the possible states for *one* of these gas molecules.
1. Recall from Modern Physics: particles are waves! We can model each gas molecule as a free particle trapped in a box. Quantum mechanically, the free particle with mass m trapped in a 1d box with sides at $x = 0$ and $x = L$ is described by the wavefunction

   $$\psi(x) = \sqrt{\frac{2}{L}} \sin(k_x x)$$

   where k_x is the wavenumber inversely related to the wavelength as $\lambda = 2\pi/k_x$, related to the particle's momentum as

   $$p_x = \hbar k_x \quad \leftrightarrow \quad E = \frac{p_x^2}{2m} = \frac{\hbar^2 k_x^2}{2m}$$

   The particle in a 3d box has a total wavefunction which is just 3 copies of the 1d wavefunction (1 for each direction):

   $$\psi(x) = \left(\sqrt{\frac{2}{L}}\right)^3 \sin(k_x x)\sin(k_y y)\sin(k_z z)\,, \qquad \vec{p} = \hbar\vec{k}\,, \qquad E = \frac{\vec{p}^2}{2m} = \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m}$$

   We can label the momenta / energy of the particles equivalently by their possible $\vec{k}$-values, or wave vectors. Note that short wavelength (large k) waves have *more* energy than long wavelength (small k) waves.

2. Waves trapped in a box have a *discrete* set of possible states forced by the boundary conditions. In particular, since the wavefunction for the particle has to vanish at the boundaries of the box $(x, y, z) = 0$ and L), a half-integer number of wavelengths $\lambda = 2\pi/k$ have to fit inside the box in each direction:

$$n_x \cdot \frac{\lambda}{2} = L \quad \Rightarrow \quad k_x = \frac{n_x \pi}{L}$$

and similarly for the y and z directions. This imposes that the energy/momentum is quantized:

$$k_x = \frac{n_x \pi}{L}, \quad k_y = \frac{n_y \pi}{L} \quad k_z = \frac{n_z \pi}{L} \quad \Rightarrow \quad E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

The energies are labeled by the three integers n_x, n_y, n_z which each independently run from 1 up to infinity.

3. Each allowed state is represented by the three integers n_x, n_y, n_z, which determine the wave vector $\vec{k}$. We can represent an allowed state in three-dimensional $\vec{k}$-space, where these points are equally spaced, separated by distance π/L in each direction. A single point (corresponding to an allowed state) occupies a volume in k-space of

$$\text{vol. in } k\text{-space occupied per allowed state:} \quad \frac{\pi}{L} \times \frac{\pi}{L} \times \frac{\pi}{L}$$

4. The "density of states" function tells you how many more possible states are accessible when your momentum increases by a small amount. Allowed states with a wave vector whose (positive) magnitude lies between k and $k + dk$ lie on one octant of a spherical shell of radius k and thickness dk. The volume of this shell is thus

$$\text{vol. in } k\text{-space of one octant of shell } (k, k + dk) \ = \frac{1}{8} \times 4\pi k^2 \, dk$$

The **density of states** in k-space is the number of allowed states with a wave vector whose magnitude lies between k and $k + dk$:

$$\boxed{\text{density of states} = g(k)\, dk = \frac{\text{vol. in } k\text{-space of one octant of shell } (k, k + dk)}{\text{vol. in } k\text{-space occupied per allowed state}}}$$

which when substituting for our previous formulas, yields

$$g(k)\, dk = \frac{V}{2\pi^2} k^2 \, dk$$

This result says that there are *more* states at larger wavevectors / shorter wavelengths / higher energies, as you would expect when counting waves in a box.

Having derived our density of states, we can finally write the partition function for the single gas molecule, which we will call Z_1. It's given by adding up the Boltzmann factors $e^{-\beta E(k)}$ with measure $g(k)\, dk$, over all values of the magnitude k from 0 to infinity:

$$Z_1 = \int_0^\infty e^{-\beta E(k)} g(k)\, dk = \frac{V}{2\pi^2} \int_0^\infty e^{-\frac{\beta \hbar^2 k^2}{2m}} k^2 \, dk \tag{9.2}$$

Note that the Boltzmann factors $e^{-\beta E(k)} = e^{-\beta \hbar^2 k^2/(2m)}$ imply as usual that lower energy states are more likely – so we are *more* likely to find particles in smaller energy = smaller k = larger wavelength states.

The partition function (9.2) is simply a Gaussian integral, whose result is:

$$Z_1 = \frac{V}{\hbar^3}\left(\frac{m}{2\pi\beta}\right)^{3/2}$$

Recalling that $\hbar = h/2\pi$, this exactly reproduces (9.1), deriving from first principles the constants that we stuck ad-hoc into that formula to make the dimensions work out.

Thermal wavelength We define the **thermal wavelength** λ_{th}, also called the thermal de Broglie wavelength, as the following combination of constants:

$$\boxed{\lambda_{\text{th}} = \frac{h}{\sqrt{2\pi m k_B T}}}$$

in terms of which we can also write the single particle partition function as

$$Z_1 = \frac{V}{\lambda_{\text{th}}^3} \tag{9.3}$$

You can think of λ_{th} as something like the average de Broglie wavelength of a particle at temperature T. Since the average energy per particle is $\frac{1}{2}k_BT$ (due to the equipartition theorem), and this is due to the kinetic energy of the particle, we have

$$\frac{p^2}{2m} = \frac{1}{2}k_BT \quad \Rightarrow \quad p^2 = mk_BT$$

The quantum mechanical de Broglie wavelength is related to the momentum as $p = \frac{2\pi\hbar}{\lambda_{dB}}$, which allows us to relate

$$\lambda_{dB} = \frac{2\pi\hbar}{\sqrt{mk_BT}} = \frac{1}{\sqrt{2\pi}}\lambda_{\text{th}}$$

So up to a factor of $\sqrt{2\pi}$, the thermal de Broglie wavelength is the *average* de Broglie wavelength of each particle.

9.2 Distinguishable vs. Indistinguishable

In order to understand the partition function for our gas of N particles, we need to understand the following somewhat subtle idea of distinguishability of the particles.

Suppose I have two *distinguishable* non-interacting two-state systems (dipoles), each of which can either be in the up state or down state. The particles are distinguished by their physical location: left versus right. The possible states of my system are:

$$\uparrow\uparrow, \qquad \uparrow\downarrow, \qquad \downarrow\uparrow, \qquad \downarrow\downarrow$$

Even though the middle two possibilities have the same total energy, $E_\uparrow + E_\downarrow = E_\downarrow + E_\uparrow$, we distinguish them as two separate states, since we distinguish the left and right dipoles from one another. The total partition function of this two-particle system is equal to the product of the two single particle partition functions, since I sum over all the possible states: $Z_2 = Z_1^2$.

$$\begin{aligned} Z_2 &= e^{-\beta(E_\downarrow + E_\downarrow)} + e^{-\beta(E_\downarrow + E_\uparrow)} + e^{-\beta(E_\uparrow + E_\downarrow)} + e^{-\beta(E_\uparrow + E_\uparrow)} \\ &= \left(e^{-\beta E_\downarrow} + e^{-\beta E_\uparrow}\right)^2 \end{aligned}$$

Suppose, however, that my two particles were *indistinguishable* – I couldn't tell which one was on the left and which one was on the right. Then, the middle two states are not distinguishable from one another; they count as just one possible state of the system with one particle up and one particle down. The partition function would be

$$Z_2 = e^{-\beta(E_\downarrow + E_\downarrow)} + e^{-\beta(E_\downarrow + E_\uparrow)} + e^{-\beta(E_\uparrow + E_\uparrow)} \neq Z_1^2$$

Z_1^2 overcounts states. In general if we have N particles all in different states, then this overcounting factor is $N!$ for the terms with the N all in different states. In this example, there is a factor of 2! difference between the middle terms in the two expressions.

Particles in a gas would be considered as indistinguishable – we don't *actually* have a means of labeling which is which. So the partition function for the N particle system should not be equal to $(Z_1)^N$ – that would overcount states. We will instead approximate that the N-particle partition function for indistinguishable particles is

$$\boxed{Z_N = \frac{(Z_1)^N}{N!}, \qquad \text{indistinguishable}}$$

This is an approximation because it assumes it is possible to ignore those states in which two or more particles occupy the same energy level, in which case the $N!$ factor is not quite right. When is this approximation possible? It is possible when there is a huge number of available states for the system to be in, much larger than the number of particles. For the ideal gas, if we require that the number of thermally accessible energy levels is much larger than the number of molecules in the gas, then it's reasonable to assume that all the gas molecules will be in different states, and so the $N!$ factor is correct. When this approximation holds, we have that the ideal gas partition function is

$$Z = \frac{Z_1^N}{N!} = \frac{1}{N!}\left(\frac{V}{\hbar^3}\right)^N \left(\frac{m}{2\pi\beta}\right)^{3N/2}$$

As a historical aside, the necessity of adding the extra factor of $N!$ was noticed before the advent of quantum mechanics by Gibbs, who was studying the entropy of mixing gases. Including this factor in the partition function ensures that the entropy of mixing indistinguishable gases does *not* increase, resolving what was known as Gibb's paradox.

9.3 Functions of State

Let's check that we get the expected functions of state for the ideal gas from our partition function. Firstly, we compute

$$F = -k_B T \ln Z = -k_B T \left(N \ln V + \frac{3N}{2}\ln m - \ln N! - 3N \ln \hbar - \frac{3N}{2}\ln 2\pi\beta\right)$$

so that

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{N k_B T}{V} \quad \Rightarrow \quad PV = N k_B T$$

The ideal gas equation of state pops out as expected! Furthermore, we can compute the average energy,

$$U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\beta^{3N/2}\left(-\frac{3N}{2}\right)\beta^{-3N/2-1} = \frac{3}{2}N k_B T$$

precisely in agreement with our previous results (and, the equipartition theorem.)

——— *End Lecture 19.*

In-Class Exercise: 2D Density of states

Calculate the density of states $g(k)$ for an ideal gas confined to two dimensions.

Note: while this may sound like a theoretical exercise, a number of micro and electronic devices operate using electrons that are confined to an extremely narrow region that is sandwiched between two different semiconductor layers. These electrons are said to form a 2DEG (2-D electron gas). Furthermore, note that this is a homework problem!

Follow the following steps:

- First find the possible values of the wavevector k based on the "particle in a box" problem.

  Solution: For a particle in a 2d box with sides of length L, we have that energies are labeled by two integers n_x and n_y, with

  $$k_x = \frac{n_x \pi}{L}\,, \qquad k_y = \frac{n_y \pi}{L}\,, \qquad n_x = 1, 2, \ldots;\ n_y = 1, 2, \ldots$$

  and total magnitude

  $$k^2 = \left(\frac{n_x \pi}{L}\right)^2 + \left(\frac{n_y \pi}{L}\right)^2 = \frac{\pi^2}{L^2}\left(n_x^2 + n_y^2\right)$$

- Then, consider how many such points exist per area in 2D "k-space".

  Solution: In 2d k-space, each allowed state is represented by a point (n_x, n_y), each separated by a distance of π/L in each direction. A single point occupies a volume of $(\pi/L)^2$.

- Then, consider how many values are confined to a circular region of a given magnitude of k.

  Solution: Allowed states with a wave vector whose positive magnitude lies between k and $k + dk$ lie on one quadrant of a circle of radius k, whose volume is $1/4$ times the circumference of the circle: $\frac{1}{4} \times 2\pi k\, dk$.

- Finally, consider how the total number of possible k-values in this region will increase as k is increased.

  Solution: The density of states is the number of allowed states with a wave vector whose magnitude lies between k and $k + dk$:

  $$\begin{aligned} \text{density of states} = g(k)\, dk &= \frac{\text{vol. in } k\text{-space of one quadrant of shell } (k, k+dk)}{\text{vol. in } k\text{-space occupied per allowed state}} \\ &= \frac{\frac{1}{2}\pi k\, dk}{\frac{\pi^2}{L^2}} = \frac{L^2}{2\pi} k\, dk \end{aligned}$$

We can check that the result of the exercise makes sense by applying it to a two-dimensional ideal gas. The partition function for a single gas molecule in 2 dimensions is given by

$$Z_1 = \int_0^\infty e^{-\beta E(k)} g(k)\, dk = \frac{L^2}{2\pi} \int_0^\infty e^{-\beta \hbar^2 k^2/(2m)} k\, dk = \frac{m L^2}{2\pi \beta \hbar^2}$$

In particular, this can be written as the area A divided by λ_{th}^2,

$$Z_1 = \frac{A}{\lambda_{\text{th}}^2}\,, \qquad \lambda_{\text{th}} = \frac{h}{\sqrt{2\pi m k_B T}} = \hbar\sqrt{\frac{2\pi\beta}{m}}$$

Comparing to (9.3), the general formula in d-dimensions will be expressed as $V_d/\lambda_{\text{th}}^2$. Then, the average internal energy of a single gas molecule in d-dimensions would be computed as, $U = -\frac{1}{Z_1}\frac{\partial Z_1}{\partial \beta} = d \times \frac{1}{2}k_B T$, in agreement with the equipartition theorem.

10 Chemical Potential and the Grand Partition Function

Textbook readings: (a first reading is due before Lecture 21; most pertinent to Lecture 21)

- Ch. 22 sections 22.1-7

Learning Objectives:

- Statistical mechanics of systems that can exchange particles: the chemical potential, grand partition function, chemical potential and Gibbs function

10.1 Meaning of the Chemical Potential

So far, we have focused on systems for which the number of particles N is constant. We now want to consider systems that can exchange particles with their surroundings. In much the same way that temperature differences drive the flow of heat, it turns out that differences in a quantity called the *chemical potential* drive the the flow of particles from one place to another.

What happens if I add a particle to a system? Our combined formula for the 1st and 2nd law now becomes:

$$\boxed{dU = TdS - PdV + \mu dN} \tag{10.1}$$

where μ is the **chemical potential**. You should think of μ as something like an "energy per particle": if the number of particles goes up by some amount dN, the internal energy of the system goes up by $\mu\, dN$.

In particular, this means that when S and V are held constant, differentiating the internal energy with respect to N yields the chemical potential:

$$\boxed{\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}} \tag{10.2}$$

How can we understand this formula? Let's go back to our Einstein solids. Suppose we have an Einstein solid with $N = 3$ oscillators. The multiplicity of the macrostate with $q = 3$ units of energy, so $U = \hbar\omega q$, leads to an entropy of,

$$\Omega(q = 3; N = 3) = \frac{(3+3-1)!}{3!(3-1)!} = \frac{5\cdot 4}{2} = 10 \quad \Rightarrow \quad S = k_B \ln 10$$

Now to find μ, we would need to see what happens when N goes up, let's say by 1 oscillator: we would compute

$$\Omega(q = 3; N = 4) = \frac{(3 + 4 - 1)!}{3!(4 - 1)!} = \frac{6 \cdot 5 \cdot 4}{3 \cdot 2} = 20 \quad \Rightarrow \quad S = k_B \ln 20$$

But this violates that we want to compute μ when N changes with S held constant; so, apparently q must get lower. If we insist on keeping the entropy fixed while adding an oscillator, then we will need to reduce the energy at the same time. In particular, we keep the entropy the same by lowering q to 2:

$$\Omega(q = 2; N = 4) = \frac{(2 + 4 - 1)!}{2!(4 - 1)!} = \frac{5 \cdot 4}{2} = 10 \quad \Rightarrow \quad S = k_B \ln 10$$

So, the result is that U went down as N went up, so the chemical potential μ is *negative* for this system. This is a general rule of thumb: the chemical potential is typically negative, for most classically behaving systems. You have to pay some energy cost in order to add an extra particle to the system while somehow keeping the entropy the same.

From (10.1) we can run through the usual manipulations to find how the other thermodynamic potentials change as N changes. In particular, using $G = U + PV - TS$, the Gibbs free energy satisfies,

$$dG = V\,dP - S\,dT + \mu\,dN$$

from which we have another useful definition of μ:

$$\boxed{\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}}$$

This result says that μ is the slope of G versus N for a given P, T. This is an especially useful relation because the constraints of constant P and T are experimentally convenient for chemical systems. We will use this to study phase transitions in the next section.

Some other useful relations can be obtained from the other thermodynamic potentials; for example, using $dF = -PdV - SdT + \mu dN$, we would obtain

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}.$$

See the example problem in your book + homework problem for more discussion.

What drives a system that can exchange particles to form a particular equilibrium state? Let's go back to our Einstein solids. We considered the case where we have 2 Einstein solids which can exchange heat with each other while remaining thermally isolated from their surroundings. We found that the equilibrium of this system (when there is no more exchange of thermal energy) is found when their temperatures are equal; this was the configuration that maximized the total entropy of the two solids.

Now instead, consider two systems that are able to exchange particles with one another. Equilibrium (no more exchange of particles) will occur when $\mu_1 = \mu_2$: when the chemical potentials are the same for each system. So, the chemical potential plays a similar role in particle exchange as temperature does in heat exchange.

10.2 The Grand Partition Function

We would now like to generalize the partition function to include the effect of changing numbers of particles. To do this, we need to generalize the canonical ensemble to the case where both energy and particles can be exchanged between the system and the large reservoir. This is called the **grand canonical ensemble.**

The determination of the probability distribution and partition function proceeds in much the same was as for the regular canonical ensemble. We will consider a system with energy E and number of particles N, which can exchange both E and N with a reservoir at temperature T and chemical potential μ, where the total energy and number of particles of the system plus reservoir is fixed, $E_{\text{tot}} = E_R + E$, $N_{\text{tot}} = N_R + N$. The reservoir is much larger than the system, so $E_R \gg E$ and $N_{\text{tot}} \gg N$.

To proceed, recall that we expect the probability of finding the system in a state labeled by E and N is proportional to the number of microstates, where the difference is that now the number of microstates will depend both on how much energy and how many particles are partitioned into the reservoir versus the system:

$$P(E,N) \propto \Omega_R(E_R,N_R)\Omega_S(E,N) = \Omega_R(E_{\text{tot}} - E, N_{\text{tot}} - N)$$

where again we have taken $\Omega_S = 1$. In other words, the probability is due to the large number of possible microstates of the reservoir, which is related to the entropy as

$$S = k_B \ln \Omega_R$$

The next step in our derivation of the Boltzmann distribution was to expand $S \sim \ln \Omega_R$ in a Taylor series for small E. We will need to do the same thing here, this time for small E and small N. The key is that now the entropy of the system can be considered to be a function of U, V, *and* N, $S(U,V,N)$, so that

$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{N,U} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

Then, we see that $dU = TdS - PdV + \mu dN$ implies

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T}, \qquad \left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}$$

We've already used the first relation many times to relate the temperature and the entropy (where we were assuming constant particle number anyway), but we've gained a new equation that relates the change in entropy with respect to number of particles to the chemical potential. (As an aside: the relations $\mu = -T(\partial S/\partial N)|_{U,V}$ and $\mu = (\partial U/\partial N)|_{S,V}$ also can be seen to be related by one of our partial derivative formulas:

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \quad \Rightarrow \quad \left(\frac{\partial U}{\partial N}\right)_S = -\left(\frac{\partial U}{\partial S}\right)_N \left(\frac{\partial S}{\partial N}\right)_U$$

$$\mu = -T\left(-\frac{\mu}{T}\right) \quad \checkmark$$

End aside.)

Now, expanding $S = k_B \ln \Omega_R$, we find:

$$\begin{aligned} S(E_{\text{tot}} - E, N_{\text{tot}} - N) &= S(E_{\text{tot}}, N_{\text{tot}}) - E\frac{dS}{dE'}\Big|_{E_{\text{tot}}} - N\frac{dS}{dN'}\Big|_{N_{\text{tot}}} + \dots \\ &= k_B \ln \Omega_R(E_{\text{tot}}, N_{\text{tot}}) - \frac{E}{T} + \frac{N\mu}{T} + \dots \end{aligned}$$

Taking the exponential, we see that

$$P(E, N) \propto \Omega_R(E_{\text{tot}}, N_{\text{tot}}) e^{-\beta E + \beta N \mu}$$

This is known as the **Gibbs distribution**; it's proportional to the Boltzmann distribution, with an exponential factor $e^{\beta \mu N}$ to account for the effect of the changing number of particles, so that it explicitly depends on E, N, μ and the equilibrium temperature T.

As usual, to normalize this probability distribution we need to divide by the sum over all possible states of the system, where now the possible states are labeled both the values of E and N. Supposing a discrete set of possible values labeled by some integer n as (E_n, N_n), the result is the **grand partition function**:

$$\boxed{Z = \sum_n e^{\beta(\mu N_n - E_n)}}$$

Then, the normalized Gibbs distribution is

$$\boxed{P(E_n, N_n) = \frac{e^{\beta(\mu N_n - E_n)}}{Z}}$$

Much as all the information about the canonical ensemble is contained in the partition function, all the information about the grand canonical ensemble is contained in the grand partition function. From Z we can derive all the various functions of state that we wish, where now the answers that were valid for the canonical ensemble will be modified to account for the nonzero chemical potential. For example, we can compute (you will show these relations on your homework!) that the average number of particles is,

$$N = \sum_n N_n P_n = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial \mu} \right)_\beta$$

while the average internal energy is modified by a μ dependent term,

$$U = \sum_n E_n P_n = -\left(\frac{\partial \ln Z}{\partial \beta} \right)_\mu + \mu N$$

——— *End Lecture 21.*

Particle number conservation laws An important aside on particle number conservation. The chemical potential μ is associated with the conservation of particle number: it is nonzero and able to change only when the system exchanges particles with an external reservoir, where total particle number of the reservoir plus system is conserved.

This idea is *not* applicable to particles that have no such conservation law concerning particle number, such as photons in vacuum. In vacuum, photons can be created/destroyed willy-nilly; there is no sense in which some total number of photons is conserved. In such cases, $\mu = 0$.

11 Phase Transitions

Textbook readings: (a first reading is due before Lecture 22; most pertinent to Lectures 22-23)

- Ch. 28, all

Learning Objectives:

- Phase transitions! Focus on Ch. 28.1-28.3.

A phase transition is an abrupt, discontinuous change in the properties of a system. Examples include steam condensing to water, and water freezing to ice. In this section, we'll explore some properties of phase transitions in detail.

11.1 Latent Heat

Recall we've defined heat capacities as

$$C_x = T\left(\frac{\partial S}{\partial T}\right)_x$$

for x the constraint of either P, V. The heat capacity tells us how much heat we need to apply to change the temperature of a substance.

Consider two phases in thermodynamic equilibrium at some critical temperature T_*. Often to change from 1 phase to another at a constant temperature T_*, you need to supply some extra heat to the system, known as the **latent heat** L,

$$\boxed{L = T_*(S_2 - S_1)}$$

where S_1 is the entropy of phase 1, and S_2 the entropy of phase 2. This implies that there will be a spike in the heat capacity as a function of temperature at the phase transition.

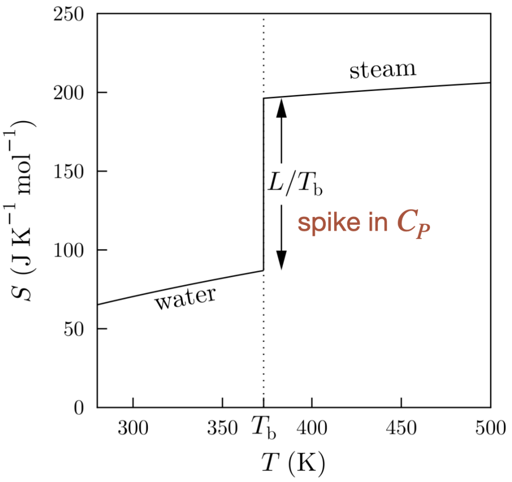


Figure 9: Plot of the entropy as a function of temperature near the boiling point phase transition of water (from Blundell).

For instance, consider the liquid-gas phase transition. Recall when we first discussed the van der Waals equation, we argued that as the temperature is lowered, there is a critical temperature T_* where a phase transition occurs and the system transitions from a gas to a liquid (the gas condenses), or equivalently as the temperature is raised past T_* the liquid boils. We can plot the entropy as a function of the temperature near this transition. There is a *discontinuous* change in the entropy at the phase transition, which is indicative of the fact that this is what we call a *first order* phase transition. Below the phase transition, C_P of liquid water is about $75\,J/(K \cdot \text{mol})$, and as T changes by an amount ΔT, S changes by an amount

$$\Delta S = C_P \int_{T_i}^{T_f} \frac{dT}{T} = C_P \ln\left(\frac{T_f}{T_i}\right)$$

Similarly, above the phase transition the slope of the line is determined by the C_P of steam, which is about $34\,J/(K \cdot \text{mol})$. At the boiling point T_b, there is a jump in the entropy where the slope of the line is infinite. This jump ΔS has magnitude L/T_b, where L is the latent heat, equal to about $40.7\,kJ/\text{mol}$.

11.2 Chemical Potential and Phase Changes

Since there are two possible states involved in the liquid-gas phase transition – the gas and the liquid state – we could consider more general configurations where part of the system could be a liquid, and part of the system could be a gas. This situation is called **phase equilibrium**. For instance, when you boil water to make a cup of tea, you see the liquid/gas states co-exist as a mixture once water hits the boiling point. In general, how do we figure out if/when this can happen?

Recall that when systems are held at constant pressure and temperature, the quantity that must be minimized is the Gibbs function G. We wrote last time that for a system that is allowed to also have changing particle number, the Gibbs function changes with P, T, and N as,

$$dG = VdP - SdT + \mu dN$$

More generally, if there is more than one type of particle, we would introduce a chemical potential μ_i for each species of particle i, with number N_i. Then, at constant pressure and temperature,

$$dG\big|_{P,T} = \sum_i \mu_i dN_i$$

So, consider the situation where we have N_1 particles in phase 1 in mechanical and thermal equilibrium with N_2 particles with phase 2, at constant pressure and temperature, where the two systems can exchange particles. Since we are in equilibrium,

$$G_{\text{tot}} = N_1\mu_1 + N_2\mu_2 = \text{fixed}$$

To remain in equilibrium while changing the number of particles in phase 1 (say by Δ), the number of particles in phase 2 must decrease by the same amount, this means that we must have

$$(N_1 + \Delta)\mu_1 + (N_2 - \Delta)\mu_2 = N_1\mu_1 + N_2\mu_2 \quad \Rightarrow \quad \mu_1 = \mu_2$$

So in phase equilibrium where two phases coexist, $\mu_1 = \mu_2$.

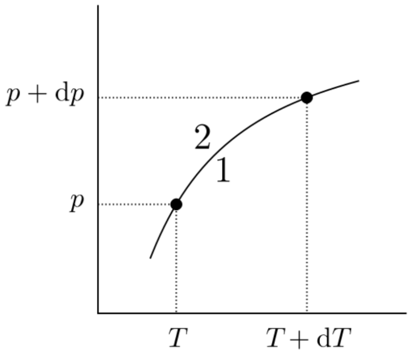


Figure 10: The coexistence line of two phases in the P-T plane.

11.3 Phase Boundaries

Now, suppose we wish to plot the liquid-gas phase diagram in the P-T plane. The *co-existence region* of the phases is a line on which the condition $\mu_1 = \mu_2$ is satisfied, which is determined by the equation

$$\mu_{\text{liquid}}(P,T) = \mu_{\text{gas}}(P,T)$$

so (call the liquid phase the 1st phase and the gas phase the 2nd phase), as P and T change, we require

$$\mu_1(P+dP, T+dT) = d\mu_2(P+dP, T+dT)$$
$$\mu_1(P,T) + \left(\frac{\partial \mu_1}{\partial P}\right)_T dP + \left(\frac{\partial \mu_1}{\partial T}\right)_P dT = \mu_2(P,T) + \left(\frac{\partial \mu_2}{\partial P}\right)_T dP + \left(\frac{\partial \mu_2}{\partial T}\right)_P dT$$

The first terms cancel, since $\mu_1 = \mu_2$ on this line. Recall that we can think of the chemical potential μ as the Gibbs function per particle,

$$\mu = \frac{G}{N}$$

so that we can identify these partials with partials of G:

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \frac{1}{N}\left(\frac{\partial G}{\partial P}\right)_T = \frac{V}{N} = \text{volume density } v$$
$$\left(\frac{\partial \mu}{\partial T}\right)_P = \frac{1}{N}\left(\frac{\partial G}{\partial T}\right)_P = -\frac{S}{N} = -\text{entropy density } s$$

so that the condition becomes

$$v_1 dP - s_1 dT = v_2 dP - s_2 dT$$

which allows us to solve for

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1}$$

where again, s_i is the entropy per particle in phase i, and v_i is the volume per particle in phase i. Equivalently, we can consider s and v to be entropy and volume per mole, so that everything on the right-hand-side is a molar quantity. (This is the easier way to think about this – think of $\mu =$ the Gibbs function per mole g, so that we are really just equating $dg_1 = dg_2$.)

This expression can be re-written in terms of the latent heat $L = T\Delta S$, in which form it is known as the **Clausius-Clapeyron equation**,

$$\boxed{\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}}$$

This expression allows us to determine the *coexistence curve* in the P-T plane.

Approximation for a liquid-gas transition: We can solve the Clausius-Clapeyron equation for $P(T)$ if we make the following assumptions: (1) that the latent heat L is constant, (2) that the vapour (the 2nd phase) can be treated as an ideal gas satisfying $PV = Nk_BT$, and (3) that $V_2 \gg V_1$. For example, for water it is true that $V_{\text{gas}} \gg V_{\text{liquid}}$, and this would be an error of less than 0.1%. With these assumptions, we can solve

$$\begin{aligned} \frac{dP}{dT} = \frac{L}{TV_2} = \frac{LP}{T^2Nk_B} \quad &\Rightarrow \quad \int \frac{dP}{P} = \frac{L}{Nk_B}\int\frac{dT}{T^2} \\ &\ln\frac{P}{P_i} = -\frac{L}{Nk_B}\left(\frac{1}{T} - \frac{1}{T_i}\right) \qquad (11.1) \\ &P(T) = P_i e^{-\frac{L}{Nk_BT} + \text{const}} \end{aligned}$$

This equation describes the phase boundary of the liquid and gas phases, under the above assumptions.

Approximation for a liquid-solid transition: For a solid to liquid transition (melting), it is not a good approximation to assume that $V_2 \gg V_1$; instead we should account for some finite ΔV, where actually typically ΔV is usually quite small ($V_2 \approx V_1$). In this case, if we can approximate that (1) the latent L is approximately constant, and (2) the volume change ΔV is approximately constant, then we would find

$$\begin{aligned} \frac{dP}{dT} = \frac{L}{T\Delta V} \quad &\Rightarrow \quad \int dP = \frac{L}{\Delta V}\int\frac{dT}{T} \\ &P - P_i = \frac{L}{\Delta V}\ln\frac{T}{T_i} \end{aligned}$$

For example, consider the phase diagram of water. The coexistence line of the liquid-gas phases (boiling) is described by $P(T) \approx \text{const} \times e^{-L/(RT)}$ where $L \approx 40.7\,kJ/\text{mol}$, and the coexistence line of the liquid-solid phases (melting) is described by $P(T) \approx \frac{L}{\Delta V}\ln T + \text{const}$ where $L \approx 6.01 \times 10^3\,J/\text{mol}$. The actual plot is shown in the figure.

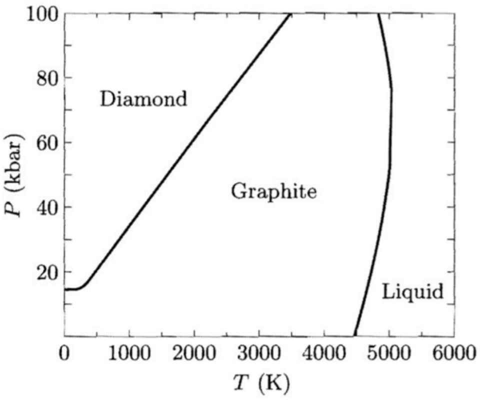
For example, at fixed pressure $P < 217\,atm$, as we increase the temperature there is a first order phase transition first when the solid ice melts to liquid water, and then when the liquid water evaporates to gaseous water vapor. At high enough pressures, however, when the water is heated above the critical temperature T_c there is no sharp distinction between the liquid/gas phases. This critical point at the end of the phase equilibrium line is the point we discussed when considering the isotherms on a P-V diagram of the van der Waals gas; it's the point where the isotherms have an inflection point $\partial P/\partial V = \partial^2 V/\partial V^2 = 0$ at constant T). Note that this diagram also has a **triple point**, where there is a certain temperature where all three phases (solid, liquid, gas) can coexist.

——— End Lecture 22.

Example Problem: The graphite-diamond phase boundary

Consider the linear phase boundary on a P-T diagram for carbon. The table below lists the Gibbs energy of formation, the entropy, and the volume for 1 mole of graphite and carbon at 300K and pressure $P = 1\,atm = 1.01 \times 10^5\,J/m^3$.

	$G\ (kJ)$	$S\ (J/K)$	$V\ (cm^3)$
Carbon (Graphite)	0	5.74	5.30
Carbon (Diamond)	2.90	2.38	3.42



(a) Calculate the slope of the phase boundary at $T = 300K$. How does your answer compare to the figure?

Solution: First we should recall that the latent heat of the transition is given in terms of ΔS at a fixe temperature as,

$$L = T(S_2 - S_1)$$

We know from the Clausius-Clapeyron equation that the slope in the P-T plane is given by

$$\text{slope at temperature } T = \frac{dP}{dT} = \frac{L}{T\Delta V} = \frac{\Delta S}{\Delta V}$$

substituting for the values in the table,

$$\text{slope} = \frac{\Delta S}{\Delta V} = \frac{(5.74 - 2.38) J/K}{(5.30 - 3.42)\,cm^3} \times \frac{10^6 cm^3}{m^3} = 1.79 \times 10^6\,\frac{J}{K \cdot m^3}$$

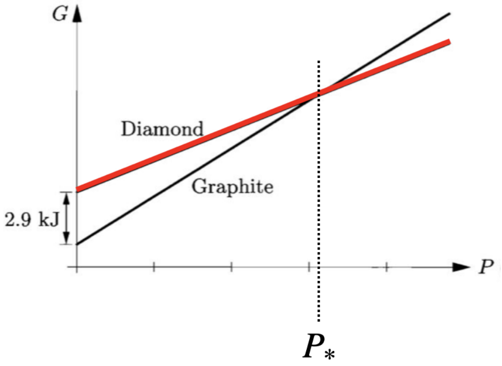
Comparing to the figure, I would estimate the slope as $\frac{(34-20)10^3\text{bar}}{(1000-500)K} \times \frac{10^5 J/m^3}{1\text{bar}} = 2.8 \times 10^6\,J/K \cdot m^3$. Not too bad, right order of magnitude!

(b) If graphite is compressed while being held at $300K$ it will eventually turn into diamond. This should occur when the Gibbs energy of diamond is equal to that of graphite. Find this transition pressure by determining an equation for G as a function of P of both graphite and diamond.

Solution: At fixed temperature and increasing the pressure from $P = P_i$ to the transition point P_*, we will cross the phase boundary and undergo the phase transition when $G_1(P_*) = G_2(P_*)$. At fixed temperature, assuming the volume doesn't change much with the pressure, we have that $G(P)$ is given as,

$$dG_1\Big|_T = V_1 dP \quad \Rightarrow \quad G_1(P) = V_1(P - P_i) + G_1(P_i)$$
$$dG_2\Big|_T = V_2 dP \quad \Rightarrow \quad G_2(P) = V_2(P - P_i) + G_2(P_i)$$

In other words, $\Delta G = V \Delta P$ in each phase.



So, at the phase transition, we set the Gibbs energies equal to one another,

$$G_1(P_*) = G_2(P_*) \quad \Rightarrow \quad V_1(P_* - P_i) + G_1(P_i) = V_2(P_* - P_i) + G_2(P_i)$$

which allows us to solve for P_* as,

$$\begin{aligned} P_* &= \frac{G_1(P_i) - G_2(P_i)}{(V_2 - V_1)} + P_i \\ &= \frac{(0 - 2.90)\ \times 10^3\, J}{(3.42 - 5.30)\, cm^3} \cdot \frac{10^6\, cm^3}{1\, m^3} + 1.013 \times 10^5\ J/m^3 = 1.54\, kJ/cm^3 \\ &= 1.54 \times 10^9\ J/m^3 \end{aligned}$$

In this last problem, we saw that the stable phase as a function of P is the one with *smaller* Gibbs free energy. So, at fixed temperature, when the pressure is greater than P_*, diamond is more stable, while at fixed temperature when the pressure is less than P_*, graphite is more stable. This is why the transition goes from graphite to diamond as the pressure is increased.

In-Class Exercise: The pressure melting of ice

The density of ice is $917\,kg/m^3$. The density of water is $1000\,kg/m^3$. The latent heat of transformation for ice/water is $333\,J/g$. How much pressure would you have to put on an ice cube (say $1\,g$ of ice) to make it melt at $-1°$ C instead of $0°$ C?

Solution: This problem explores the fact that when you apply extra pressure to ice, you lower its melting point! Clausius-Clapeyron tells us that,

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

We know that ice usually melts at $0°C$, at normal pressures of $P = 1atm$. Assuming that the densities of water/ice and the latent heat do not change much with the temperature or temperature, we can solve for the pressure difference in making the transition happen at $T = -1°C$ versus $T = 0°C$ by integrating,

$$\Delta P = \frac{L}{\Delta V}\int \frac{dT}{T} = \frac{L}{\Delta V}\ln\frac{272.15\,K}{273.15\,K}$$

We can convert the densities we're given to volumes per kg by inverting

$$\begin{aligned} \rho_{\text{water}} = 1000\,kg/m^3\,, \qquad \rho_{\text{ice}} = 917\,kg/m^3 \\ \Rightarrow \quad \Delta V/kg = 1/\rho_{\text{water}} - 1/\rho_{\text{ice}} = -9.05\times 10^{-5}\,m^3/kg \end{aligned}$$

so that,

$$\begin{aligned} \Delta P &= -\frac{333\,J/g \times (10^3 g/kg)}{9.05\times 10^{-5}\,m^3/kg}\ln\frac{272.15}{273.15} \\ &= 1.35\times 10^7\,J/m^3 \times \frac{1\,atm}{1.013\times 10^5\,J/m^3} = 133.3\,atm \end{aligned}$$

So, we expect to have to apply an additional $1.35\times 10^7\,Pa = 133.3\,atm$ of pressure to melt ice at one lower degree. (That's a lot...)

Note, that it is actually a very good approximation to not do out the integral, and instead use

$$\Delta P \approx \frac{L\Delta T}{\Delta V T} = \frac{333\,J/g\times 10^3\,g/kg}{9.05\times 10^{-5}\,m^3/kg}\frac{1\,K}{273.15\,K} = 1.35\times 10^7\,J/m^3\,.$$

Similarly, this is why the boiling temperature of water on Mount Everest is lower! The pressure at the top of Everest is about 1/3 the sea-level pressure. To get a rough estimate of the change in the boiling point, we can use that $\Delta P \approx -0.7$ atm; $\Delta V \approx V_{\text{gas}}$ which we can obtain from the density of water vapor $\rho_{\text{gas}} = 0.6\,kg/m^3$ at $T = 100°C$; look up $L \approx 2.3\times 10^3\,J/g$; and approximate $dP/dT \approx \Delta P/\Delta T$. This yields the estimate,

$$\frac{\Delta P}{\Delta T} = \frac{L}{T\Delta V} = \frac{L\rho_g}{T} \quad \Rightarrow \quad \Delta T \approx \frac{T\Delta P}{L\rho_g} = \frac{(373\,K)(-0.7\times 10^5\,J/m^3)}{(2.3\times 10^3\,J/g)(0.6\times 10^3\,g/m^3)} = -19\,K$$

(Of course, the more correct thing is to repeat the derivation of (11.1)... this is the faster back-of-the-envelope calculation.)

12 Blackbody Radiation

Textbook readings: (a first reading is due before Lecture 24; most pertinent to Lectures 24)

- Ch. 23.5-23.7

Before moving on to the fully quantum treatment of gases of massive particles, we turn briefly to the quantum treatment of *light.* We will consider essentially a gas of photons – the quanta of the electromagnetic field – and understand some of its properties, including the distribution of wavelengths. (Or, in other words, its color!)

Blackbodies are an idealized system for understanding absorption and emission of thermal radiation. As you likely know, any real object when heated emits radiation (in the form of photons). It is useful to talk about an idealized body that absorbs photons of of any wavelength – absorbs all light incident on it – and reflects none back. At zero temperature, such an object would appear black. But to maintain its temperature in thermal equilibrium with its surroundings, it radiates an amount of energy equal to what it has absorbed. We would like to understand the spectrum of radiation as we turn up the heat.

Model: We can model the blackbody as a cavity with a small hole out of which radiation can leak. The blackbody absorbs all radiation incident on it, and re-radiates out energy which is characteristic of the blackbody and *not* of the light incident upon it.

What we can measure is the *spectral energy density* of the electromagnetic radiation, u, as a function of the frequency or wavelength of the light and at a given temperature. (Recall that these things are related as $\lambda = 2\pi c/\omega$). You can think of this as the intensity of the emitted light per unit wavelength, since the intensity is just proportional to the spectral energy density up to some constants. The total intensity of the emitted light integrated over all wavelengths is equal to the area under this curve, which experimentally was found to obey the *Stefan-Boltzmann law:* that the radiative flux from a blackbody is $\sigma_B T^4$, with $\sigma_B = 5.67 \times 10^{-8}\, W/(m^2 \cdot K^4)$.

So, how do we compute the spectral energy density? (We will n̲ot actually do the computation here, but just conceptually talk through the main ideas.) Choosing to work with the angular frequency ω rather than wavelength, the spectral energy density $u(\omega, T)d\omega$ is the electromagnetic energy per unit volume at temperature T, in a frequency range of $(\omega, \omega + d\omega)$. It is equal to the density of states – the number of modes in the cavity per unit volume with frequencies between ω and $\omega + d\omega$ – times the average energy per mode,

$$u(\omega, T)d\omega = \langle E(\omega)\rangle\, g(\omega)d\omega$$

So, there are 2 ingredients to the calculation. (1) We need the density of states $g(\omega)d\omega$. Photons are massless particles traveling at the speed of light, and their energy is determined by their wavelength λ or equivalently frequency $\omega = 2\pi c/\lambda$, as $E = hc/\lambda = \hbar\omega = \hbar kc$. We thus need to re-do the particle-in-a-box computation of the density of states from earlier, but now asking how many standing waves can fit in the cavity of volume V with the dispersion relation $E = \hbar\omega$ in a given frequency range. The result of this computation is,

$$g(\omega)d\omega = \frac{V\omega^2}{\pi^2 c^3} d\omega$$

(2) We also need the average energy per mode, $\langle E(\omega)\rangle$. In the 1800s, people figured that the origin of the radiation was thermally excited, harmonically oscillating electrons in the walls of the cavity, whose average energy per mode would follow the equipartition theorem, $\langle E\rangle = k_B T$.

Back in 1895 nobody had any reason to think that energy was related to frequency or wavelength, so even though people knew about Boltzmann's factors, it did not seem relevant.

However, this idea had a problem: if $\langle E(\omega)\rangle$ = a constant, then one would predict that at high frequencies (small wavelengths) the measured intensity of the radiation should have increased without bound, as $u(\omega, T) \sim \text{const} \times T\omega^2$. This didn't at all match the data, and was dubbed the *ultraviolet catastrophe*.

Enter Max Planck: Planck's fix was that the density of states is fine, but that the average per mode is not... we need statistical mechanics! What we should really do is derive the partition function for a gas of photons in a box of volume V, and then calculate the average energy from the partition function. While we're not actually going to do that computation, we'll note the main ideas. Since the number of photons is *not* conserved (there is no reason the walls of the box can't absorb one photon and emit 2!), we cannot define a chemical potential for photons, and so we need to consider states with any number N of photons. A state with N photons of definite frequency ω has energy $E = N\hbar\omega$. The partition function for fixed frequency, summing over N, is

$$Z_\omega = \sum_N e^{-\beta(N\hbar\omega)} = \frac{1}{1 - e^{-\beta\hbar\omega}}$$

The final form of the partition function is derived from Z_ω by taking into account the sum over all possible frequencies (which will of course again require the density of states!) Once we have Z, we can compute $\langle E\rangle$ with the usual formula that involves differentiating with respect to β, with result:

$$\langle E(\omega)\rangle = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

Note that expanding this expression at high temperatures matches on to the classical expectation: as $\beta \to 0$, $\langle E\rangle \to k_B T$. However, now this is a function of ω, and plugging into the spectral energy density now yields,

$$\boxed{u(\omega, T)d\omega = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega} - 1}d\omega}$$

This result is a good match to the experimental data, fixing both the UV catastrophe, and reproduces the Stefan-Boltzmann law.

Planck's achievement of the blackbody spectrum by applying Boltzmann's statistical methods to photos provided the first hints of quantum mechanics. Key to the derivation is the fact that light comes in quanta – photons. This insight helped kick off the quantum revolution in the early 1900s.

——— *End Lecture 23.*

13 Quantum Statistical Mechanics

Textbook readings: (a first reading is due before Lecture 24; most pertinent to Lectures 24-26)

- Ch. 29, all

Learning Objectives:

- Quantum statistical mechanics for simple systems
- Fermi-Dirac statistics, Bose-Einstein statistics, Distribution functions

13.1 The Need for More Quantum

We are now going to consider the way in which quantum mechanics changes the statistical properties of gases. Let's first review where we had gotten with our semi-classical/semi-quantum ideal gas.

- We said particles were waves, with momentum $p = h/\lambda = \hbar k$ (Quantum).
- We said that short wavelength waves had more energy than long wavelength waves, $E = p^2/(2m) = \hbar^2 k^2/(2m)$ (Quantum), and therefore we are less likely to find particles in short wavelength states, $P \sim e^{-\beta\hbar^2 k^2/(2m)}$ (Classical Boltzmann).
- We said that there is a density of states as a function of wavevector that says there are more states at higher wavevectors / shorter wavelengths, $g(k)_{3d} = Vk^2/(2\pi^2)$ (Classical waves-in-a-box).
- We integrated a product of those states and their probabilities to get Z_1 for a single particle (Classical Boltzmann).
- For N particles we raised Z_1 to the N but then we divided by $N!$ so we would not double-count arrangements, $Z_{\text{indistinguishable}} = \frac{Z_1^N}{N!}$ (Classical Boltzmann-Gibbs).

When do we need to go beyond this treatment to a full quantum mechanical treatment?

Boltzmann statistics accounts for the wavefunction interpretation of particles and states that if any two indistinguishable particles are switched, the state of the system is unchanged (the last bullet point above). But there is an implicit assumption that there are many more states than there are particles. When this assumption fails, we find that we have two types of particles: those that do not mind sharing a state (bosons), and those that do mind (fermions). Bosons include photons, phonons, pi-mesons, helium-4 atoms, gluons, the Higgs particle *etc.*. Fermions include electrons, protons, neutrons, helium-3 atoms, quarks, neutrinos, *etc.* The *spin-statistics* theorem states that bosons have integer spin $(0, 1, 2, \dots)$, while fermions have half-integer spin $(1/2, 3/2, 5/2, \dots)$.

Furthermore, the size of the thermal wavelength of the ideal gas particles gives us an indication of when the semi-classical treatment of the ideal gas from Boltzmann statistics tends to fail; we will need a *full* quantum treatment when the wavelengths λ_{th} start to overlap, so when λ_{th} becomes comparable to the inter-particle separation. Since the average volume taken up by each particle V/N, we trust our semi-classical computation when $\lambda_{\text{th}}^3 \ll V/N$. This occurs when density and temperature are low, or when wavefunctions happen to be very spread out (as is the case of electrons in a metal).

13.2 Wavefunctions for Identical Particles

The indistinguishability of the fundamental particles has implications for the types of wavefunctions that can describe them.

In particular: suppose we wish to write the multi-particle wavefunction $\psi(x_A, x_B)$ that describes two particles, say an electron who might be found at x_A and an electron who might be found at x_B. The wavefunction yields the probability density for the state, $P(x_A, x_B) = |\psi(x_A, x_B)|^2$. The fact that the two electrons are *indistinguishable* implies that the probability of finding electron 1 at x_A and electron 2 at x_B must be **equal** to the probability of finding electron 2 at x_A and electron 1 at x_B; in other words,

$$P(x_A, x_B) = P(x_B, x_A)\,. \tag{13.1}$$

(This of course would not have to be true if the particles were not identical!)

Since $P(x_A, x_B) = |\psi(x_A, x_B)|^2$, this condition (13.1) says that $|\psi(x_A, x_B)|^2 = |\psi(x_B, x_A)|^2$, or in other words,[2]

$$\text{For any identical 2-particle wavefunction:} \quad \psi(x_A, x_B) = \pm\psi(x_B, x_A) \tag{13.2}$$

We conclude that indistinguishable particles come in one of two types: particles whose wavefunctions are symmetric under exchange, *i.e.* satisfying $\psi(x_A, x_B) = +\psi(x_B, x_A)$, and those that are antisymmetric under exchange, satisfying $\psi(x_A, x_B) = -\psi(x_B, x_A)$. We call the former types of particles *bosons*, and the latter *fermions*. It is an experimental fact that electrons are fermions; their wavefunctions are antisymmetric under exchange of two particles, while photons (for instance) are bosons. In fact, there is a theorem called the *spin-statistics theorem* which proves that all particles with half-integer spin (like the electron, with spin 1/2) are fermions, and all particles with integer spin (like photons, with spin 0) are bosons.

An immediate consequence of the fact that fermions have antisymmetric wavefunctions is that if a system includes two identical fermions, they cannot be in the same place: since $\psi_f(x_A, x_B) = -\psi_f(x_B, x_A)$, setting $x_A = x_B$ implies that $\psi_f(x_A, x_A) = -\psi_f(x_A, x_A)$, which is only possible if the wavefunction is equal to 0 so that there is zero probability of finding the two identical fermions in the same location. Fermions are antisocial particles (they need their space!) while bosons are social (as many as they like can occupy the same space at the same time). This fact that we can't find two identical fermions in the same location is called the *Pauli exclusion principle*. More generally stated, the Pauli exclusion principle states that no two identical fermions can simultaneously occupy the same quantum state.

This of course has implications for configurations of particles. Imagine a particle can exist in one of two states, states + and −. If there are two such particles, what are the possible states for this system to be in? The answer depends on the particles' statistics.

(a) If the particles are *distinguishable*, say labeled by A and B then there are four possible

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[2] You might complain that actually this only requires $\psi(x_A, x_B) = e^{i\theta}\psi(x_B, x_A)$, where the phase could be something other than ±1. It turns out that this possibility is not possible in 3 dimensions, but *is* possible in 2 dimensions, where particles called *anyons* with non-integer / half-integer statistics are possible.

states:

$$(+,+)\,, \quad (+,-)\,, \quad (-,+)\,, \quad (-,-)$$

where here the first position specifies A's state, and the second B's state.

(b) If the particles are *indistinguishable* but classical, then there are only three possible states:

$$(+,+)\,, \quad (+,-)\,, \quad (-,-)$$

Since we can't tell the difference between A and B, so all we can measure is that one particle is $+$ and the other $-$, so $(+,-) = (-,+)$ count as the same state. This is the case we considered in our treatment of the ideal gas.

(c) If the particles are *indistinguishable bosons*, there are also only 3 states. However, bosons need to have wavefunctions that are *symmetric* under particle exchange, so the 2-particle wavefunction corresponding to the case where one particle is $+$ and the other $-$ needs to be a linear combination,

$$\psi(+,+)\,, \quad \psi(+,-) + \psi(-,+)\,, \quad \psi(-,-)$$

since under particle exchange, $\psi(+,-)+\psi(-,+) \to \psi(-,+)+\psi(+,-)$ goes back to itself.

(c) If the particles are *indistinguishable fermions*, then there is only one state – no two fermions can be in the same quantum state, so the $(+,+)$ and $(-,-)$ options are not allowed, The wavefunction needs to be antisymmetric under particle exchange, so the only possible 2-particle wavefunction is of the form

$$\psi(+,-) - \psi(-,+)$$

This is so that under particle exchange, the wavefunction gets a minus sign: $\psi(+,-) - \psi(-,+) \to \psi(-,+) - \psi(+,-)$ is minus itself.

13.3 The Statistics of Identical Particles (fixed N)

Let's start easy with some counting problems for fixed number of particles (so, no worrying about the chemical potential). For example, let's say we have a system with 3 possible states, all of which have the *same* energy E. We want to compute the 2-particle partition function, which will be different depending on the statistics of the particles.

- What is the 1-particle partition function? We need to sum over the possible states. The particle could be in one of the three states, all of which have energy E, so

$$Z_1 = e^{-\beta E} + e^{-\beta E} + e^{-\beta E} = 3e^{-\beta E}$$

- What is the partition function if the system has 2 distinguishable particles? As we learned, for distinguishable particles that can independently be in different configurations, we should take

$$Z_{N \text{ dist}} = Z_1^N \quad \Rightarrow \quad Z_2 = Z_1^2 = 9e^{-2\beta E}$$

  (If you want to verify this for yourself, count the states! There are 6 configurations where the 2 particles are in separate states, and 3 configurations where the particles are in the same state. The total energy of each of these configurations is $2E$. So, the partition function is $9 \times e^{-2\beta E}$.)

- What is the partition function if the system has 2 identical bosons?

  Now we want to be careful about not overcounting. There are only 3 configurations where the 2 particles are in separate states (this is 3 choose 2 = 3), plus 3 configurations where the particles are in the same state, which adding everything up gives

  $$Z_{2\text{ bosons}} = 6e^{-2\beta E}$$

- What is the partition function if the system has 2 identical fermions?

  Fermions can't share, so now there are only 3 configurations where the 2 particles are in separate states; adding everything up we get

  $$Z_{2\text{ fermions}} = 3e^{-2\beta E}$$

- What is the partition function if the system has 2 identical particles obeying Gibbs' corrected classical statistics? Gibbs told us to approximate the 2-identical particle partition function with a $1/N!$, so

  $$Z_{N\text{ ind.}} = \frac{Z_1^N}{N!} \quad \Rightarrow \quad Z_2 = \frac{Z_1^2}{2!} = 4.5\, e^{-2\beta E}$$

  We see that this is actually the average of the answer for the fermions and bosons. So, this approximates quantum statistics, but doesn't get it quite right!

We now want to apply the logic of the last subsection to the statistics of many more than two identical particles. This means we need to figure out how many particles are allowed in each state, which as we've discussed we expect to be different depending on whether the particles are distinguishable, classically indistinguishable, or treated as bosons or fermions. Let's denote this number of particles in the i'th state with energy E_i as n_i. We call n_i the **occupation number** of the state. We'll demonstrate this idea through the following example.

In-Class Exercise: A pictorial method for quantum statistics

We have a collection of N fermions in a system where the energy levels are non-degenerate and evenly spaced. The lowest energy level has energy E_1, the second lowest energy level has energy $E_2 = 2E_1$, and so on, so the i'th energy level has energy $E_i = iE_1$.

Assume that the fermions all have the same spin, so each energy level can only be occupied by either 1 or 0 particles. We can represent the possible states of the system with increasing total energy units q by a simple column of white and filled dots, where filled dots represent occupied levels, and white dots represent empty levels.

For an $N = 4$ fermion system, what is the degeneracy/multiplicity of the $q = 5$ level (total energy $= E_{\text{ground-state}} + 5E_1$)? For the $q = 5$ level, calculate and plot the average occupation number versus energy level.

——— *End Lecture 24.*

Solution:

We have $N = 4$ fermions. Each level can only be occupied by at most 1 fermion, so the occupation number of the i'th level can be $n_i = \{0, 1\}$. The ground state of the 4-fermion system (which we label by $q = 0$) consists of the 4 fermions each occupying one of the four lowest energy states, and has total energy

$$E_{\text{ground-state}} = E^{(q=0)} = E_1 + E_2 + E_3 + E_4 = 10E_1\,.$$

The occupation number of the i'th energy level in this ground state, n_i, is equal to: $n_i = 1$ for $i = 1, 2, 3, 4$, and $n_i = 0$ for $i > 4$.

Now increase the total energy units q by 1 to consider the first excited state of the 4-fermion system. The total energy of this state is now $E^{(q=1)} = E^{(q=0)} + E_1$. This state consists of 3 fermions each occupying the first 3 levels, and one fermion occupying the 5th level, since this configuration has total energy increased by 1 unit from the ground state, $E^{(q=1)} = E_1 + E_2 + E_3 + E_5 = 11E_1 = E^{(q=0)} + E_1$. So for this state, $n_i = 1$ for $i = 1, 2, 3, 5$, and $n_i = 0$ otherwise.

Increasing the total energy units by 2, we find a degeneracy: there are two microstates that add up to the total energy $E^{(q=2)} = E^{(0)} + 2E_1$; one with $n_i = 1$ for $i = 1, 2, 3, 6$, and one with $n_i = 1$ for $i = 1, 2, 4, 5$.

At this point the pattern is clear: if we increase the total energy units by q, the total energy of the state is $E^{(q)} = E^{(0)} + qE_1$. This total energy has to be equal to the sum over the energies E_i of the individual energy levels times their occupation numbers,

$$E^{(q)} = E^{(0)} + qE_1 = \sum_{i=1}^{\infty} n_i E_i = E_1 \sum_{i=1}^{\infty} n_i i\,, \qquad n_i = \{0, 1\}$$

where the occupation number is restricted to be $n_i = \{0, 1\}$ since identical fermions can't share the same quantum state. Since for this 4-fermion system we had that the ground state has $E^{(0)} = 10E_1$, for this particular system the state with q total energy units satisfies,

$$10 + q = \sum_{i=1}^{\infty} n_i i\,, \qquad n_i = \{0, 1\}\,.$$

For a given value of q, there will be degeneracies if there are multiple different choices of the occupation numbers that give the same value of this sum on the right-hand-side.

We can now answer: for this 4-fermion system, what is the degeneracy/multiplicity of the $q = 5$ level (total energy $E^{(0)} + 5E_1$)? The answer is 6, where

$$n_i = 1 \quad \text{for} \quad i = \{1, 2, 3, 9\};\ \{1, 2, 4, 8\};\ \{1, 2, 5, 7\};\ \{1, 3, 4, 7\};\ \{1, 3, 5, 6\};\ \{2, 3, 4, 6\}$$

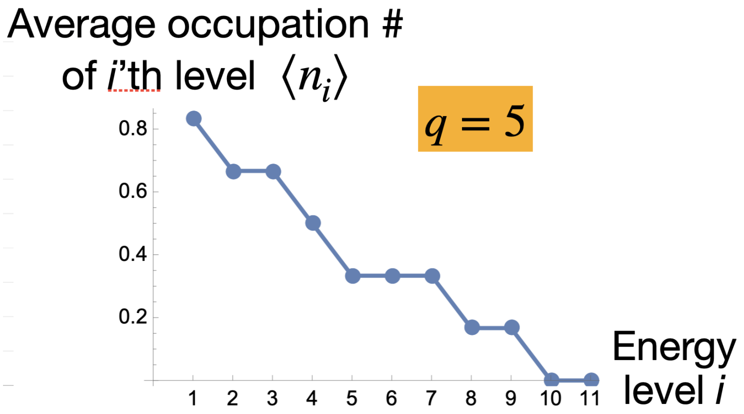
and $n_i = 0$ otherwise.

We now wish to calculate and plot the *average* occupation number versus energy level for $q = 5$. For $q = 5$, there are 6 microstates as described above. In each of the microstates,

n_i can be 0 or 1.

$$\begin{aligned}
\langle n_1\rangle &= \frac{1+1+1+1+1+0}{6} = \frac{5}{6}\\
\langle n_2\rangle &= \frac{1+1+1+1+0+0}{6} = \frac{4}{6}\\
\langle n_3\rangle &= \frac{1+1+1+1+0+0}{6} = \frac{4}{6}\\
\langle n_4\rangle &= \frac{1+1+1+0+0+0}{6} = \frac{3}{6}\\
\langle n_5\rangle &= \frac{1+1+0+0+0+0}{6} = \frac{2}{6}\\
\langle n_6\rangle &= \frac{1+1+0+0+0+0}{6} = \frac{2}{6}\\
\langle n_7\rangle &= \frac{1+1+0+0+0+0}{6} = \frac{2}{6}\\
\langle n_8\rangle &= \frac{1+0+0+0+0+0}{6} = \frac{1}{6}\\
\langle n_9\rangle &= \frac{1+0+0+0+0+0}{6} = \frac{1}{6}\\
\langle n_{i>9}\rangle &= 0
\end{aligned}$$

Two notes about these results: firstly, the average is always less than (or in principle equal to) 1; this must be the case, since there can't be more than one fermion occupying any given level. Also, note that that $\sum_i \langle n_i\rangle = N = 4$, so that the sum of the occupation numbers over all the energy levels equals the total number of particles.

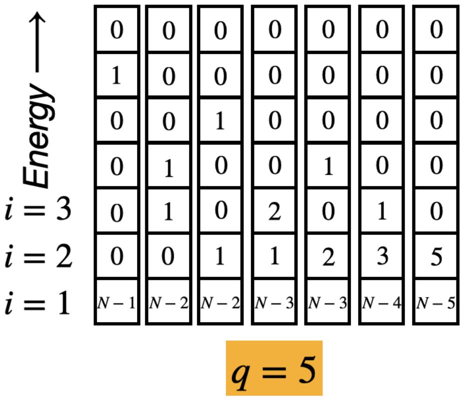


Example continued: bosons Now consider the same set of evenly-spaced, non-degenerate energy levels $E_1, E_2 = 2E_1, E_3 = 3E_1, \ldots$, with a collection of N bosons. Each energy level can be occupied by any number of particles, and we can represent the possible system states with increasing total energy units q by a simple row of boxes with numbers in them. Plot a graph of the average occupation number of the levels versus the energy level for the total energy units $q = 5$ (total energy $E = E_{\text{ground-state}} + 5E_1$).

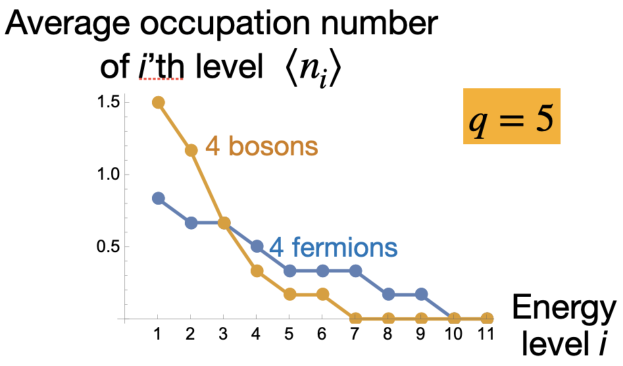
In this case, the ground state has all N bosons in the first energy level E_1, so

$$E_{\text{ground-state}} = E^{(q=0)} = NE_1\,.$$

The first excited state has $N-1$ bosons in the first energy level and one boson elevated to the



	0	0	0	0	0	0	0
	1	0	0	0	0	0	0
	0	0	1	0	0	0	0
	0	1	0	0	1	0	0
$i = 3$	0	1	0	2	0	1	0
$i = 2$	0	0	1	1	2	3	5
$i = 1$	$N-1$	$N-2$	$N-2$	$N-3$	$N-3$	$N-4$	$N-5$



second energy level, so that

$$E^{(q=1)} = (N-1)E_1 + E_2 = (N-1)E_1 + 2E_1 = E_{\text{ground-state}} + E_1$$

where recall that $E_2 = 2E_1$. We can continue counting up, so that the energy level with q energy units above the ground state has energy $E^{(q)} = E_{\text{ground-state}} + qE_1$.

For $N \geq 5$ there are 7 microstates with $q = 5$ total energy units above the ground state. These microstates have the following nonzero occupation numbers:

$$\{n_1 = N-1,\, n_6 = 1\}\,, \quad \{n_1 = N-2,\, n_3 = 1,\, n_4 = 1\}\,, \quad \{n_1 = N-2,\, n_2 = 1,\, n_5 = 1\}$$
$$\{n_1 = N-3,\, n_2 = 1\; n_3 = 2\}\,, \quad \{n_1 = N-3,\, n_2 = 2,\, n_4 = 1\}\,, \quad \{n_1 = N-4,\, n_2 = 3,\, n_3 = 1\}\,,$$
$$\{n_1 = N-5,\, n_1 = 5\}$$

These all satisfy in each microstate,

$$\sum_i E_i n_i = E_1 \sum_i i n_i = E_{\text{ground-state}} + 5E_1 \quad \checkmark$$

We can compute the average occupation number in the i'th level as,

$$\begin{aligned}
\langle n_1 \rangle &= \frac{(N-1) + 2(N-2) + 2(N-3) + (N-4) + (N-5)}{7} = \frac{7N-20}{7} \\
\langle n_2 \rangle &= \frac{1+1+2+3+5}{7} = \frac{12}{7} \\
\langle n_3 \rangle &= \frac{1+2+1}{7} = \frac{4}{7} \\
\langle n_4 \rangle &= \frac{1+1}{7} = \frac{2}{7} \\
\langle n_5 \rangle &= \frac{1}{7} \\
\langle n_6 \rangle &= \frac{1}{7} \\
\langle n_{i>6} \rangle &= 0
\end{aligned}$$

As a check that we got these numbers correct, the sum over all the average occupation numbers yields the total number of bosons, $\sum_i \langle n_i \rangle = N$. Now the average occupation number can certainly be larger than 1, since bosons can crowd states!

Note, however, that for $N = 4$, the last microstate listed above is not possible and there are only 6 microstates, which changes the averages as follows,

$$\begin{aligned}
\langle n_1 \rangle &= \frac{(N-1) + 2(N-2) + 2(N-3) + (N-4)}{6} = \frac{9}{6} \\
\langle n_2 \rangle &= \frac{1+1+2+3}{6} = \frac{7}{6} \\
\langle n_3 \rangle &= \frac{1+2+1}{6} = \frac{4}{6} \\
\langle n_4 \rangle &= \frac{1+1}{6} = \frac{2}{6} \\
\langle n_5 \rangle &= \frac{1}{6} \\
\langle n_6 \rangle &= \frac{1}{6} \\
\langle n_{i>6} \rangle &= 0
\end{aligned}$$

Again, we can check that $\sum_i \langle n_i \rangle = N = 4$.

13.4 The Grand Partition Function for Identical Particles

In these previous examples we fixed the number of particles, $\sum_i n_i = N$. Generally, however, we are interested in cases where the number of particles is not fixed. **WARNING:** The formulas in section 29.3 of the book can be somewhat confusing, so I recommend sticking to the formulas as written below!

Before when we built the partition function for a set of (classical) non-interacting particles, we used that the N-particle partition function is the product of all the 1-particle partition functions,

$$Z = \prod Z_1 \qquad N\text{-particle partition function} \tag{13.3}$$

Then we considered the grand partition function where N could vary, so that if our states were labeled by an integer n with energy E_n and particle number N_n, the sum over states is given by

$$\mathcal{Z} = \sum_n e^{-\beta(E_n - \mu N_n)} \qquad \text{grand partition function} \tag{13.4}$$

We now wish to determine the grand partition function for bosons and fermions. However, we just did a number of counting exercises in determining the energies for various particle numbers N_n, from which you might conclude that it is quite complicated for a given particle number to count how many states are possible for the system. Working in the grand canonical ensemble where N can vary, it is actually simplest to choose a different way of adding up all the different possible microstates of the system, as follows.

Our system has some available states labeled by i, with energies E_i and occupation numbers n_i. Rather than considering a single particle as a subsystem and taking the product of all single particle subsystems, we will partition up the system into subsystems of the available states labeled by i. For a state with occupation number n_i, the energy is $n_i E_i$ (the total number of particles in that state times the energy of that state), so the corresponding Boltzmann-Gibbs factor is $e^{-n_i\beta(E_i-\mu)}$. But n_i can vary, so the partition function $\mathcal{Z}_i$ corresponding to the state

i is the sum over all possible microstates corresponding to a state i, which is the sum over the occupation numbers possible for that state:

$$Z_i = \sum_{n_i} e^{-n_i\beta(E_i-\mu)}$$

This is the grand canonical partition function for a subsystem in the quantum state i. Then, the partition function for the *entire* system is the product over all possible subsystems of quantum states,

$$Z = \prod_i Z_i \qquad \text{grand partition function, take 2}$$

In this way we capture all the possible configurations of all possible particle numbers of the system, but in a much more useful way than in (13.4).

To summarize: the grand partition function is the sum over all the possible microstates. We get to choose how to execute this sum. Since we want to do this for case of varying particle number, it is easiest to view this as a sum over all possible occupation numbers for the i'th state, considering that as a subsystem, so that the total partition function is a product over all possible quantum states i.

Bosons Now we need to perform the sums/products! For bosons, there are no restrictions on the occupation numbers n_i; in a system where particle number can vary, any state might have any number of particles in it. So, we need to perform the sum,

$$Z_i^{(\text{bosons})} = \sum_{n_i=0}^{\infty} e^{-n_i\beta(E_i-\mu)} = \sum_{n_i=0}^{\infty} \left(e^{-\beta(E_i-\mu)}\right)^{n_i}$$

This takes the form of a geometric series,

$$\sum_{k=0}^{\infty} x^k = \frac{1}{1-x}\,, \qquad x = e^{-\beta(E_i-\mu)}$$

so that[3]

$$Z_i^{(\text{bosons})} = \frac{1}{1-e^{-\beta(E_i-\mu)}}$$

The grand partition function for bosons is then the product,

$$\boxed{Z^{(\text{bosons})} = \prod_i \frac{1}{1-e^{-\beta(E_i-\mu)}} \qquad \text{grand partition function for bosons}} \tag{13.5}$$

To compute some physical quantities, it is often useful to take the log, and remember that $\ln(abc\dots) = \ln a + \ln b + \ln c + \dots$, so that the product becomes a sum:

$$\ln Z^{\text{bosons}} = -\sum_i \ln\left(1 - e^{-\beta(E_i-\mu)}\right)$$

---

[3] The convergence of this sum requires that $x < 1$, which means $\mu < E_i$ for all states, or in particular $\mu < E_{\text{ground-state}}$.

For instance, from (13.5) we can compute the average number of particles as,

$$\langle N\rangle = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \mu} = -\frac{1}{\beta}\sum_i \frac{\partial}{\partial \mu}\ln\left(1-e^{-\beta(E_i-\mu)}\right) = \sum_i \frac{1}{\beta}\frac{\beta e^{-\beta(E_i-\mu)}}{1-e^{-\beta(E_i-\mu)}} = \sum_i \frac{1}{e^{\beta(E_i-\mu)}-1}$$

What is this quantity? Compare it to the average particle number in the state i, which is given by the occupation number $\langle n_i\rangle$,

$$\langle n_i\rangle = \frac{1}{\beta}\frac{\partial \ln Z_i}{\partial \mu} = \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln\left(\frac{1}{1-e^{-\beta(E_i-\mu)}}\right) = \frac{1}{\beta}\frac{\beta e^{-\beta(E_i-\mu)}}{1-e^{-\beta(E_i-\mu)}} = \frac{1}{e^{\beta(E_i-\mu)}-1}$$

This average occupation number for bosons is known as the **Bose-Einstein distribution**. We see that the average number of particles is precisely equal to the sum over all the states of the average occupation number per state,

$$\langle N\rangle = \sum_i \langle n_i\rangle$$

as expected!

——— *End Lecture 25.*

Fermions Alternatively we can consider a gas of fermions. For fermions, the occupation number n_i can only ever be 0 or 1 from the Pauli exclusion principle, so the sum truncates:

$$\boxed{Z_i^{(\text{fermions})} = \sum_{n_i=0,1} e^{-n_i\beta(E_i-\mu)} = 1+e^{-\beta(E_i-\mu)}}$$

and the grand partition function evaluates to

$$Z^{(\text{fermions})} = \prod_i Z_i^{(\text{fermions})} = \prod_i \left(1+e^{-\beta(E_i-\mu)}\right) \qquad \text{grand partition function for fermions}$$

Again, it is often useful to consider the log of this quantity, where the product is converted to a sum,

$$\ln Z^{(\text{fermions})} = \sum_i \ln\left(1+e^{-\beta(E_i-\mu)}\right)$$

We can now compute both the average number of particles, and the average occupation number in each state. The average occupation number in the state i is given by,

$$\langle n_i\rangle = \frac{1}{\beta}\frac{\partial \ln Z_i}{\partial \mu} = \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln\left(1+e^{-\beta(E_i-\mu)}\right) = \frac{1}{\beta}\frac{\beta e^{-\beta(E_i-\mu)}}{1+e^{-\beta(E_i-\mu)}} = \frac{1}{e^{\beta(E_i-\mu)}+1}$$

known as the **Fermi-Dirac distribution**. This differs from the answer for the bosons by a + sign rather than a − sign in the denominator. Then, the average particle number of the fermion gas is,

$$\langle N\rangle = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \mu} = \frac{1}{\beta}\sum_i \frac{\partial}{\partial \mu}\ln\left(1+e^{-\beta(E_i-\mu)}\right) = \sum_i \langle n_i\rangle$$

Let us summarize: the grand partition function for a gas of fermions (+) versus bosons (−) can be expressed as the following sum over the possible quantum states i,

$$\boxed{\ln Z^{(\pm)} = \pm\sum_i \ln\left(1\pm e^{-\beta(E_i-\mu)}\right)}$$

which yields the following average occupation number in the state i:

$$\boxed{\langle n_i \rangle^{(\pm)} = \frac{1}{e^{\beta(E_i-\mu)} \pm 1}}$$

These are known as the Fermi-Dirac versus Bose-Einstein distributions.

The classical limit In the limit that $\beta(E_i - \mu) \gg 1$, both of these distributions tend to the Boltzmann-Gibbs distribution $e^{-\beta(E-\mu)}$:

$$\beta(E_i - \mu) \gg 1 \quad \Rightarrow \quad \langle n_i \rangle^{(\pm)} \to e^{-\beta(E_i-\mu)} \tag{13.6}$$

This is the low density limit, where μ is small, and there are many more states accessible to the particles than there are number of particles. In this limit, you never need to worry about multiple particles occupying the same state, and both fermions and bosons behave like classical particles, whose probability of being found in that state is given by the Boltzmann-Gibbs distribution. This is also the right limit to take in the high-temperature limit (even though you are tempted in the high-T / small-β limit to consider $\beta \to 0$!) This is because as $\beta \to 0$, there is greater accessibility of higher energy states, so large-E_i competes with small β such that $\beta(E_i - \mu) \gg 1$ so that the occupation number remains small. (In particular, we need that $\sum_i \langle n_i \rangle = N$ is fixed and small compared to the number of states, which implies the constraint $\beta(E_i - \mu) \gg 1$.)

So really, we should think of the limit (13.6) as the classical limit of the quantum gas. Physically, this is the criterion that the mean separation between the particles is much greater than their mean de Broglie wavelengths.

Gibbs paradox revisited In deriving the Bose-Einstein and Fermi-Dirac distributions, we used the grand canonical partition function. To excellent approximation, the canonical partition function Z_c for N-particles is related to the grand canonical partition function Z_{gc} as

$$\ln Z_c = \ln Z_{gc} - \beta\mu N$$

(We won't prove this expression, apologies!) Then for the quantum gases, this expression takes the form,

$$\ln Z_c = \pm \sum_i \ln\left(1 \pm e^{-\beta(E_i-\mu)}\right) - \beta\mu N$$

How does this expression look in this classical limit? Expanding the logarithm for large $\beta(E_i-\mu)$ means expanding for small $e^{-\beta(E_i-\mu)}$, so that $\ln\left(1 \pm e^{-\beta(E_i-\mu)}\right) \approx \pm e^{-\beta(E_i-\mu)}$ and

$$\ln Z_c \approx \sum_i e^{-\beta(E_i-\mu)} - \beta\mu N$$

From the expression for $N = \sum_i \langle n_i \rangle$, we can expand in the classical limit and take the logarithm,

$$N = \sum_i \langle n_i \rangle \approx \sum_i e^{-\beta(E_i-\mu)} \quad \Rightarrow \quad \ln N = \beta\mu + \ln\left(\sum_i e^{-\beta E_i}\right)$$

Taking everything together,

$$\ln Z_c \approx N - \beta\mu N = N - N\left(\ln N - \ln\left(\sum_i e^{-\beta E_i}\right)\right) \approx N \ln\left(\sum_i e^{-\beta E_i}\right) - \ln N!$$

where we used Stirling's approximation, $\ln N! \approx N \ln N - N$. Putting everything together, we have found that in the classical approximation, the N-particle partition function takes the form

$$Z_c \approx \frac{\left(\sum_i e^{-\beta E_i}\right)^N}{N!}$$

which is precisely the single particle partition function raised to the power of N and divided by $N!$, as was necessary to resolve the Gibbs paradox. Without quantum mechanics we had to put in the factor of $N!$ by hand, knowing that we were overcounting if the particles were identical. But now we see that by imposing the classical limit from the statistics of identical bosons / fermions, the $N!$ comes out naturally!

13.5 Bose-Einstein Condensation

What happens to bosons away from the classical limit?

If given N bosons at $T = 0$, they should all share the exact same state (wavefunction). But, they have a nonzero chemical potential which should be causing them to repel. These two effects compete, but at some low enough temperature the system does in fact collapse into its ground state in a phase transition to a *Bose-Einstein condensate.*

To argue for this transition, we can look again at a gas of non-relativistic particles, now through the eyes of quantum mechanics, assuming the particles are (spin 0) bosons. We start with the non-interacting Bose-Einstein distribution,

$$\langle n_i \rangle = \frac{1}{e^{\beta(E_i - \mu)} - 1}$$

with total particle number $\langle N \rangle = \sum_i \langle n_i \rangle$. We can compute the total number of particles in the gas N by converting the sum to an integral using the density of states,

$$\langle N \rangle = \sum_i \langle n_i \rangle \to \int_0^\infty \langle n(E) \rangle g(E)\, dE$$

Assuming that the gas particles have a dispersion relation like $E = \hbar^2 k^2/(2m)$ (*i.e.* they are non-relativistic massive particles), we can convert to a function of the energy $E = \hbar^2 k^2/(2m)$:

$$g(k)\, dk = \frac{V}{2\pi^2} k^2\, dk \quad \Rightarrow \quad g(E)\, dE = \frac{V m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \sqrt{E}\, dE$$

and integrate

$$\langle N \rangle = \sum_i \langle n_i \rangle \to \frac{V m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\sqrt{E}}{e^{\beta(E-\mu)} - 1}\, dE \tag{13.7}$$

This integral gives an expression for the number of particles in the gas as a function of the chemical potential and temperature: $N = N(\mu, T)$.

While we will not show this explicitly in these lectures, in the classical limit of high temperature and low density, turning the crank on these equations yields the ideal gas las $PV = Nk_BT$, plus corrections that you can compute due to taking into account the quantum statistics. We wish to explore what happens away from this limit. We can do this by taking the high-density limit: fixing V and T, and slowly increasing N to increase the density N/V. Correspondingly, μ also increases (if the left-hand-side of (13.7) increases, then the right-hand-side must also increase, which at fixed V and T implies μ must increase!). But since $\mu < 0$ for bosons (recall for the convergence of the grand partition function we needed $\mu < 0$ so that $0 < e^{\beta\mu} < 1$), this means that we can increase $\mu \to 0$ and can't go beyond that. At the critical value of $\mu = 0$, the number of bosons N_{crit}, given by

$$\langle N_{\text{crit}} \rangle = \frac{V m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\sqrt{E}}{e^{\beta E} - 1} dE$$

This is an integral that can be done, with result

$$\frac{N_{\text{crit}}}{V} = \frac{2.612}{\lambda_{\text{th}}^3}$$

So, we reach $\mu = 0$ when the number density is very close to the thermal de Broglie density, which is precisely when quantum mechanics plays an important role. Equivalently, this can be expressed as occurring at a critical temperature T_{crit} as a function of the number density,

$$T_{\text{crit}} = \frac{2\pi\hbar^2}{k_B m} \left(\frac{N}{2.612 V} \right)^{2/3}$$

If we try to increase the density past N_{crit} or decrease the temperature past T_{crit}, we would arrive at a contradiction that μ should become larger than 0. This contradiction is occurring because our approximation in going from a sum to an integral is no longer valid! The problem is that the non-relativistic density of states,

$$g(E)\, dE \propto \sqrt{E}\, dE$$

implies that $g(E = 0) = 0$, or in other words that there are no bosons with ground state energy $E = 0$ (the ground state with $E = 0$ apparently doesn't contribute to the integral (13.7) at all). But of course, this simply cannot be true. We expect that actually as temperature is lowered, *all* the bosons want to go to the ground state!

What's happening? For most values of $e^{\beta\mu}$, there are just a handful of particles sitting in the lowest state, and it doesn't matter if we miss them in the formula (13.7). But as $e^{\beta\mu} \to 1$ (meaning $\mu \to 0$), then we actually get a macroscopic number of particles occupying the ground state, and at $T = 0$ we expect *all* the particles to be in the ground state. So, the calculation needs to be corrected to account for these particles. Without going into the details, we can summarize the results: For $T = 0$, all the bosons are in the ground state. For $0 < T < T_{\text{crit}}$, the ground state has a large fraction of the total number of bosons, so that there is macroscopic occupation of the ground state. This is known as *Bose-Einstein condensation*: we call the condensate of bosons in the ground state the Bose-Einsten condensate (BEC for short). Above T_{crit} there is a phase transition, where the vast majority of the bosons are in excited states. The BEC is a funny state: a macroscopic number of particles have merged into a single quantum state so large that it can be seen with the naked eye!

BEC was predicted by Bose and Einstein back in 1924, and was finally created in the lab by Eric Cornell and Carl Wieman in 1995. They cooled off a gas of Rubidium atoms to a temperature of 170 nano-Kelvin, showing that a BEC could be formed with ultra-cold atoms. Wolfgang Ketterle performed similar experiments with Sodium atoms shortly afterwards. These three scientists won the 2001 Nobel Prize in physics for their achievement.

——— *End Lecture 26.*