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Lecture 5: Thermodynamics

1 Introduction

Thermodynamics is the study of heat and temperature. One thing that makes thermodynamics hard (and generally unpopular) is all the damn variables. Everything is related and it's often tough to keep straight what is an independent and what is a dependent variable. We will do our best to write the dependent variables explicitly whenever possible. Another thing that makes thermodynamics hard is that we give new definitions to common words. Words like system, energy, work, heat, temperature, etc. have precise meanings in physics that do not always agree with their everyday meanings. For example, we defined temperature in terms of the number of states, not what you measure with a thermometer. So learning thermodynamics means unlearning some of your associations.

Let's start by defining some concepts we will use a lot. We define a **system** as the thing we are observing or calculating properties of. The system is separated from the **surroundings** by a barrier. The barrier could be **open**, so matter and energy can pass through, or **closed**.

For example, when we talk about doing work on a gas by moving a piston, the piston is usually part of the surroundings and the gas is the system. We could alternatively treat the whole gas/piston complex as the system, and our arm that pushes the piston as the surroundings. Or we could attach the piston to a weight, put a box around the whole thing and call the everything together the system. In such a case, where the surroundings have no influence on the system, we say the system is **isolated**.

Energy we take to mean the **internal energy** of the system, stored in chemical bonds, or kinetic motion of the atoms. Generally, we won't include in energy the gravitational energy from the earth or nuclear energy within the atoms. We use the symbol E for energy, although sometimes U is used for internal energy. Quantum mechanically, energy is the expectation value of the Hamiltonian; classically it is the value of the (classical) Hamiltonian. I like to use ε for energies for individual molecules (microscopic energy) and E for macroscopic energy. An important constraint on energy is

- **The first law of thermodynamics**: the total energy is conserved in time; energy is neither created nor destroyed.

This law follows from Noether's theorem: energy is conserved in any system whose Hamiltonian is independent of time (you would prove it in an advanced classical mechanics or field theory class).

One kind of energy is in the motion of molecules. This is called kinetic energy, $\frac{1}{2}m\vec{v}^2$. Another kind of energy is vibrational and rotational energy. When we have a large group of molecules all moving/vibrating/rotating incoherently we call the energy **thermal energy**. A kind of non-thermal energy is potential energy, such as from lifting a rock over your head (gravitational potential energy), or from separating two opposite charges, like in a battery (chemical potential energy). These types of potential energy are coherent and can be easily converted into other forms of energy. One goal of this lecture is to understand limits on how to convert thermal energy into other energy forms.

Work is an amount of energy we put in to change a system by organized motion. For example, lifting a weight up a height h against gravity requires work. The work required is $W = Fh = mgh$. In fact, we can define work as follows: a process that does work is one that could be used to lift a weight by some height. Of course we will rarely be using work for lifting weights, but we *could*. For example, the energy in your phone battery *could* have been used to lift a weight. The work done to spin a wheel underwater *could* have been used to lift a weight. One theme for this Lecture is how thermal energy can be turned into work, since it is not immediately clear how incoherent random motion can be coerced into coherent organized motion.

Heat is the transfer of energy from a temperature difference between two systems. Heat is a transfer of thermal energy. Energy transfer by heat involves incoherent chaotic molecular motion. Thus, one question we will try to answer in this lecture is how heat can be used to do work. A machine that does so is called a **heat engine**.

Importantly, the distinction between work and heat is about the surroundings, not the system itself. If we attach a weight to a pinwheel in a pot of water, as the weight falls, the pinwheel turns. This does work on the water, increasing its molecular motion and increasing its temperature. We did work on the water. We could have induced the same change on the system (the pot of water) by heating it over a fire. Thus these two processes leave the system the same. The distinction between work and heat is in the surroundings (the weight or the fire).

Another useful concept is a **quasistatic** process. This is one where things are changed slowly enough that equilibrium holds at all times. For example, if we allow a gas to expand by easing the pressure on the walls, that would be quasistatic. It doesn't even have to be that slow, just slower than the rate by which the molecules in the gas are hitting the walls (around the speed of sound), so that equilibrium is re-established continually as the gas is expanded. If we abruptly remove the wall of a gas, like popping a balloon, that would not be quasistatic. Or if we take two gases at different temperatures and put them in contact, as heat flows from one to another equilibrium does not hold, so this heat transfer is not quasistatic. If there is a time in the process when the system is clearly not in equilibrium, it's not quasistatic, otherwise it is.

Finally, we can talk about **reversibility**. A process is reversible if it can be brought back to a previous state exactly, with *no net change in the system or surroundings*. Compressing a gas quasi-statically with a piston is reversible: allow the gas to push back on the piston and it will end up exactly where it started (we have to check this of course, and we will). Letting a gas expand abruptly is not reversible – it takes work to compress it back to where it was, and the work takes energy from the surroundings. You can have situations that are quasistatic but not reversible. For example, slowly heating up a system by adding infinitesimal amounts of heat. Or, more simply, a ball rolling on the ground with friction is quasistatic but not reversible. Generally, any reversible thermodynamic process must be quasistatic.

The **thermodynamic limit** means taking N large and V large holding the number density $n = \frac{N}{V}$ fixed. More precisely, we Taylor expand in $\frac{1}{N}$ after setting $\frac{1}{V} = n\frac{1}{N}$ and keep only the leading terms. The thermodynamic limit lets us use the central limit theorem: systems in equilibrium are characterized by their mean values, which are the same as the most probable values, and fluctuations around these means scale like $\frac{1}{\sqrt{N}}$.

For completeness, we list the 4 laws of thermodynamics here:

0. If two systems are in equilibrium with a third system, they are in equilibrium with each other.

1. Energy is conserved in time. Energy is neither created nor destroyed.

2. The total entropy (system+surroundings) never decreases: $\Delta S_{\text{total}} \geqslant 0$.

3. Entropy is finite as $T \rightarrow 0$.

The first and second laws are sometimes summarized as "you can't win" and "you can't break even."

The 0th law we already proved by showing that $\beta = \frac{1}{k_B T} = \frac{\partial \ln \Omega}{\partial E}$ is the same for any two systems in equilibrium. The 1st law follows from classical mechanics (Noether's theorem, as mentioned above). The 2nd law is enormously important and will be discussed in this lecture and the next.

The 3rd law was orignally formulated (by Nerst around 1910) as that entropy of a crystal goes to zero as $T \rightarrow 0$. Having a crystal, rather than a gas, is necessary to fix the positions of the molecules beacuse otherwise there is the configurational entropy $\ln \Omega_q \sim N \ln V$, even at $T = 0$. However, even crystals can have nonzero entropy at $T = 0$ in quantum mechanics if they have degenerate ground states, since then at $T = 0$, $S = k_B \ln N_{\text{ground}}$. Thus the modern version of the third law is that entropy goes to a constant as $T \rightarrow 0$, which holds for crystals, gases, classical and quantum systems. The constant is not important physically, and in practice we are free to add an offset to the entropy (as we do with energy), using that only changes in entropy matter. There is

still content in the 3rd law when doing this, because the entropy is nonzero at finite temperature, so it should scale as a positive power of T as $T \to 0$. We'll come back to the 3rd law in Lectures 10 and onward, after we discuss quantum statistical mechanics, since at low temperature quantum effects become important.

2 Heat

Say we have two systems with different temperatures T_1 and T_2, energies E_1 and E_2 and numbers of particles N_1 and N_2. The number of microstates of each is $\Omega_1(N_1, E_1)$ and $\Omega_2(N_2, E_2)$ and their entropies are $S_1 = k_B \ln \Omega_1$ and $S_2 = k_B \ln \Omega_2$. When the systems are isolated, they are each in their own equilibrium. So each one separately has $\frac{1}{T_1} = \frac{\partial S_1}{\partial E_1}$ and $\frac{1}{T_2} = \frac{\partial S_1}{\partial E_2}$.

Let us then put these systems into thermal contact. Thermal contact means that the two can exchange energy, for example, by vibrating the molecules in a thermally-conducting barrier between them. We assume they cannot exchange particles. Thus E_1 and E_2 can change, as can T_1 and T_2 but N_1 and N_2 are fixed. At the moment when we put the two systems in contact, the total number of microstates is $\Omega_{\text{initial}} = \Omega_1(E_1)\Omega_2(E_2)$. The two systems will then exchange energy until equilibrium is reached, where $T_1 = T_2$. As equilibrium has the maximum value of Ω or equivalently maximal entropy $S = k_B \ln \Omega$ we must have $\Omega_{\text{final}} \geqslant \Omega_{\text{initial}}$. So entropy of the whole system increases. This is the second law of thermodynamics. Note that we only know the total entropy goes up

$$\Delta S_1 + \Delta S_2 \geqslant 0 \tag{1}$$

It is certainly possible for the entropy of one side to go down.

The heat Q is defined as the amount by which the energy changes through thermal contact

$$Q = -\Delta E_1 = \Delta E_2 \tag{2}$$

When a positive amount of heat $Q > 0$ leaves system 1, its energy goes down. When a negative amount of heat $Q < 0$ leaves system 1, a positive amount of heat $-Q > 0$ enters. So Q can take either sign and we just have to keep track of which sign we want by thinking about the physical situation.

Note that heat is *not* a property of a system in equilibrium. Heat is a non-equilibrium quantity related to how energy is transferred in the approach to equilibrium.

When energy enters a system, through heat or work, usually the temperature goes up too. But this is not guaranteed. Whether the temperature goes up is indicated by the heat capacity $C_V = \frac{\partial E}{\partial T}\big|_V$. Most systems have positive heat capacities, but some have negative heat capacities. For the total energy to go down when the temperature goes up, so $C_V < 0$, we generally need some kind of long-range interactions, like gravity. For example when stars get hotter, they expand and their gravitational potential energy goes down by more than their kinetic energy goes up. Thus their total energy goes down and $C_V < 0$. Stars, black holes, galaxies, etc, all have $C_V < 0$. We'll explore gravitational systems in more detail later on.

Now, suppose we have an infinitesimal heat transfer between two systems. We write dQ for such a small heat transfer (note that dQ just means a small amount of heat; it is not the difference between two heats). Then the change in entropy for a small dQ is

$$dS_{\text{heat transfer}} = \left(\frac{\partial S}{\partial E}\right)dE = \left(\frac{1}{T}\right)dQ = \frac{dQ}{T} \tag{3}$$

So to find the net change in entropy due to a heat transfer we can integrate over dQ, presuming we know the functional dependence of the temperature on the amount of heat transferred. Note that the entropy can increase in ways other than heat transfer, for example in the free expansion of a gas (see Eq (30) below).

2.1 Heat reservoirs

A heat reservoir is a system that does not change temperature or volume when heat is put in. For example, a bowl of soup acts like a heat reservoir for a fly that falls into it. Air in a room acts like a heat reservoir for a bowl of soup. Any system acts like a reservoir if the heat transferred is much less than the energy of the system $Q \ll E_{\text{res}}$.

Another way to define a reservoir is that $|\Delta T_{\text{res}}| \ll T_{\text{res}}$. Since ΔT_{res} is assumed small, we can write $\Delta T_{\text{res}} = \frac{\partial T}{\partial E}\Delta E = \frac{\partial T}{\partial E}Q$ where Q is the heat transferred as equilibrium is approached. So the condition for a heat reservoir can be written as

$$\left|\frac{\partial T}{\partial E}Q\right| \ll T \tag{4}$$

For a heat reservoir, the temperature and volume doesn't change throughout the heat transfer. So we can trivially integrate Eq. (3):

$$\Delta S_{\text{heat reservoir}} = \frac{Q}{T} \tag{5}$$

Because $S = S(E, V, N)$ and V and N are unchanging, this is the *total* change in entropy of the reservoir.

2.2 Heat + work

In general, we can transfer energy through heat and work at the same time. The net energy change is

$$\Delta E = Q + W \tag{6}$$

or, differentially,

$$dE = dQ + dW \tag{7}$$

Note that there is an implicit sign convention here: Q is the heat put *into* the system and W is the work done *on* the system. If we defined W as the work done *by* the system, then we would have $dE = dQ - dW$.

You can write the equation however you like as long as you are consistent with your definitions for W and Q. For example, say we compress a gas that is in thermal contact with a heat reservoir. As we push down on the gas, we do work on it, so its energy goes up. This will heat up the gas. As it heats up, it will go out of equilibrium with the reservoir so heat will start flowing out, lowering the internal energy of the gas. So we can write

$$\Delta E = W - Q \tag{8}$$

In this case we have defined W as the work done *on* the system, so $W > 0$, and Q as the heat flowing *out* of the system. It's always a good habit to write down explicitly what your sign convention is for W and Q. The energy change of the reservoir is $\Delta E_{\text{res}} = Q$, by energy conservation (1st law of thermodynamics).

2.3 Clausius entropy

Historically, the first definition of entropy was due to Rudolf Clausius in 1865. Clausius did not have a microscopic definition of entropy, and only specified a way to calculate entropy differences. His formula was that to compute the entropy change from a state A to a state B, find a reversible path connecting the two and then compute

$$\Delta S_{\text{system}} = S_A - S_B = \int_{\text{rev.}} \frac{dQ_{\text{in}}}{T} \tag{9}$$

Here, dQ_{in} is the infinitesimal heat absorbed along the path from A to B. Clausius was implicitly using that there are two sources of entropy increase: irreversibility and heat transfer. If you make the path reversible, then all you need to know is how much heat comes in as a function of temperature and you can compute the entropy change.

Note that entropy is a function of state: it doesn't matter how you get from A to B, the entropy change will be the same. For example, a gas could expand freely, doubling its volume. This is irreversible. However, we can find a reversible path to double the volume, by letting the gas expand slowly, doing work against a piston. To keep it from cooling as it does work, we can connect it to a heat bath. Then the entropy change in doubling the volume is given by $\Delta S_{\text{system}} = \frac{Q}{T}$, with Q the heat drawn in from the bath to do the expansion work. Although the surroundings change differently in the irreversible free expansion or the expansion with the heat bath, the *system* changes the same way, and so its entropy change is the same. More details of this example, and other examples of reversible and irreversible processes, are in Section 3.3.

The connection between reversibility and entropy was understood first by Clausius, as was the second law of thermodynamics, $\Delta S_{\text{tot}} \geqslant 0$. Clausius showed that the second law implies that $\Delta S_{\text{tot}} = 0$ for any reversible process. To see that, note that if states A and B (including system and surroundings) can be connected reversibly, then $S_B^{\text{tot}} - S_A^{\text{tot}} \geqslant 0$. For the reverse process $S_A^{\text{tot}} - S_B^{\text{tot}} \geqslant 0$. Thus $S_A^{\text{tot}} = S_B^{\text{tot}}$ and so $\Delta S_{\text{tot}} = 0$ for any reversible process.

Since $dS = \frac{1}{T} dE$ (at fixed V and N), it might seem like any change in energy, from heat or work would result in a change in entropy. Clausius argued that this is not true: only heat flow matters. To see this, consider doing work on a system, for example, by compressing it. This work can be done through a non-thermal mechanism, for example, a weight. Then $\Delta S_{\text{surroundings}} = 0$ in the compression. If the work is done reversibly, then since $\Delta S_{\text{tot}} = 0$ for any reversible process we must also have $\Delta S_{\text{system}} = 0$. Therefore, along a reversible path, work does not cause an entropy increase. This confirms Eq. (9) – entropy change is due to heat flow.

Eq. (9) is important because it lets us compute the entropy change without knowing anything about the microscopic composition of our system. We just need to find a reversible path between two states, and determine how much heat flows in. There is no counting of states involved. For example, we can apply Eq. (9) to a steam engine or an internal combustion engine without knowing anything about water or chemistry. In other words, Eq. (9) is useful in thermodynamics, as in the 19th century, regardless of whether there is a microscopic statistical mechanics description.a

3 Ideal gases

Much of thermodynamics will be about relations such as $\frac{1}{T} = \frac{\partial S}{\partial E}\big|_{N,V}$ that hold for any substance in equilibrium in the thermodynamic limit. Ideal gases, and monatomic ideal gases in particular, provide very useful systems for which we will be able to check many thermodynamic relations explicitly. Recall that the molecules of ideal gases are assumed to occupy no volume and have no long-range interactions.

3.1 Pressure

Pressure is the force per unit area on the walls of a container: $P = \frac{|\vec{F}_{\text{wall}}|}{A}$. This force depends on the average velocities of the molecules. Since the average velocity is the same in every direction, by the equipartition theorem, the force is the same in every direction. That's why pressure is a scalar, not a vector quantity: it is a number characterizing the force per unit area in any direction on any wall of any container.

For an ideal gas, we can work out a relation between pressure, volume and temperature using Maxwell's kinetic theory of gases. In a time Δt, a certain number N_{hit} of molecules will hit the wall. Then the net force is

$$\vec{F}_{\text{wall}} = N_{\text{hit}} m\, \vec{a} = N_{\text{hit}} \frac{\Delta \vec{p}}{\Delta t} \tag{10}$$

where $\Delta \vec{p}$ is the impulse (change in momentum). If a particle hits the wall in the x direction then only the x component of its velocity changes, by $\Delta v_x = -2 v_x$, so the impulse is $|\Delta \vec{p}| = 2m v_x$. Then the number of particles which hit the wall in time Δt are the ones within a distance $\Delta x = v_x \Delta t$ of the wall, within the area A, going $towards$ the wall:

$$N_{\text{hit}} = \frac{1}{2} n\, A \Delta x = \frac{1}{2} n\, A v_x \Delta t \tag{11}$$

where $n = \frac{N}{V}$ is the number density. The factor of $\frac{1}{2}$ is because the ones going away from the wall not hit in the time Δt. Thus,

$$|\vec{F}_{\text{wall}}| = \left(\frac{1}{2} n\, A v_x \Delta t \right) \frac{2m v_x}{\Delta t} = m n v_x^2 A \tag{12}$$

Taking the average, we then get

$$P = \frac{|\vec{F}_{\text{wall}}|}{A} = m n \langle v_x^2 \rangle \tag{13}$$

Recalling that $\langle \frac{1}{2}mv_x^2 \rangle = \frac{1}{2}k_B T$, as for any quadratic degree of freedom, we can then write

$$P = nm\langle v_x^2 \rangle = \frac{N}{V}k_B T \tag{14}$$

so that

$$\boxed{PV = Nk_B T} \tag{15}$$

This is the **ideal gas law**. It is very general and holds for any ideal gas, not just a monatomic one.

We also sometimes write the ideal gas law in terms of the gas constant $R = k_B N_A = 8.3\frac{J}{K \cdot \text{mol}}$ in the form

$$PV = nRT \tag{16}$$

where in this context n is the number of moles (not the number density; it's unfortunate that we use the same letter for n for number density and number of moles, but the notation is standard).

Note that for the force in Eq. (10) to be constant, we must average over time. If we don't time average, then as $\Delta t \to 0$ all the quantities N_{hit}, Δp, F_{wall} and P would be wildly fluctuating functions of time. On the other hand, $\langle v_x^2 \rangle$ refers to the average of v_x^2 over all the possible microstates (the ensemble average). Thus this derivation of the ideal gas law makes an implicit assumption of ergodicity, that the time average and the ensemble averarge are the same.

3.2 Heat capacity

Heat capacity characterizes how temperature changes when heat is put in. There are different types of heat capacity, depending on whether the volume is held fixed, in which case all the heat goes to raise the temperature, or whether the pressure is held fixed, in which case some of the heat goes into work in expanding the system. We give different symbols for the heat capacity in these different circumstances

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V, \quad C_P = \left(\frac{\partial Q}{\partial T}\right)_P \tag{17}$$

where the $|_V$ means volume is held fixed and $|_P$ means pressure is held fixed.

When the volume is held fixed, no work is done and all of the heat goes into internal energy of the gas. Then

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V \tag{18}$$

This was the heat capacity we computed in the previous lecture for ideal gases. Recall that for most comon gases, vibrational modes cannot be excited at room temperature. Then $C_V = \frac{3}{2}Nk_B$ for a monatomic gas, $C_V = \frac{5}{2}Nk_B$ for a diatomic gas like H_2 or N_2 (or air, which is mostly N_2), and $C_V = 3Nk_B$ for water or other non-linear molecules. If there are f excitable degrees of freedom then $C_V = \frac{f}{2}Nk_B$ for a general molecule.

The total internal energy of a gas can be determined by integrating the heat capacity:

$$E = \int_0^T C_V(T')dT' \tag{19}$$

If C_V is temperature-independent (as it is for a classical ideal gas), then we have the simple relation between the total internal energy of a gas and its temperature:

$$E = C_V T = \frac{C_V}{Nk_B}PV \qquad \text{(ideal gas)} \tag{20}$$

where the ideal gas law has been used in the second step. Note that Eq. (20) implies

- The internal energy of a classical ideal gas is linearly proportional to the temperature

- The internal energy of a classical ideal gas only depends on P and V through the combination PV.

To be clear, for a monatomic ideal gas, we know exactly the internal energy $E = \frac{3}{2}PV$ but for a general ideal gas, we know only that $E = \frac{C_V}{Nk_B}PV$ for some C_V.

What is the difference between heating a gas at constant volume and constant pressure? If we heat it at constant volume all of the heat goes into increasing the internal energy of the gas. For heating at constant pressure, imagine a syringe where you seal the end and put a 5 kg weight on top. The weight compresses it until equilibrium is reached. The pressure due to the weight is $P_{\text{weight}} = \frac{mg}{A}$, with A the area of the pistion in the syringe. The total pressure is $P = P_{\text{weight}} + P_0$ with P_0 atmostpheric pressure. Then you heat it up. As the gas expands, it does work on its weight, so some of the energy goes into this work. The work the gas does to psuh the weight by a small amount dx is

$$dW = Fdx = F\frac{dV}{A} = PdV \tag{21}$$

Note that the work done involves the total pressure, not just the pressure from the weight.

To separate out the weight, we often use the term **gauge pressure**: $P_{\text{gauge}} = P - P_0$, which just means pressure with atmopsheric pressure subtracted. For example, when you pump up a tire or a ball, the pressure listed on the pump is the gauge pressure: when a ball totally deflated the pressure inside is atmospheric pressure P_0, not $P = 0$. The gauge pressure when deflated is $P_{\text{gauge}} = 0$.

If pressure is constant, then the change in the energy of the gas is the heat we put in minus the work it does:

$$dE = dQ - PdV \tag{22}$$

To compute C_P we need to express the quantities in this equation entirely in terms of T and P, so that we can take $\left.\frac{\partial Q}{\partial T}\right|_P$. To do so, we will use that $E = C_V T$ for an ideal gas[1], so that $dE = C_V dT$ By the ideal gas law, $V = \frac{Nk_B T}{P}$ so at constant pressure $dV = \frac{Nk_B}{P}dT$. Putting these two relations into Eq. (22) gives

$$C_V dT = dQ - Nk_B dT \tag{23}$$

or equivalently,

$$(C_V + Nk_B)dT = dQ \tag{24}$$

and therefore

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_V + Nk_B \tag{25}$$

C_P is always larger than C_V since it takes more heat to increase the temperature at constant pressure than at constant volume: the extra heat goes into work on expanding the gas against the pressure.

Recall that for monatomic gas the number of microstates was $\Omega \sim V^N \left(\frac{mE}{N}\right)^{\frac{3}{2}N}$ and the entropy $S = k_B \ln \Omega$ was given by the classical Sackur-Tetrode equation

$$S = Nk_B \ln V + \frac{3}{2}Nk_B \ln \frac{E}{N} + \text{const} \tag{26}$$

Then the temperature is

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V = \frac{3}{2}Nk_B\frac{1}{E} \tag{27}$$

so that $E = \frac{3}{2}Nk_B T$. For a general ideal gas, $\Omega \sim V^N \left(\frac{mE}{N}\right)^{\frac{f}{2}N}$ with f the number of degrees of freedom. Then $E = C_V T$ with $C_V = \frac{Nf}{2}k_B$ (this follows from $\frac{1}{T} = k_B\frac{\partial \ln \Omega}{\partial E}$) and entropy has the form

$$S = Nk_B \ln V + C_V \ln \frac{E}{N} + \text{const} \tag{28}$$

Using Eq. (25) we can equivalently write

$$S = (C_P - C_V)\ln V + C_V \ln \frac{E}{N} + \text{const} \tag{29}$$

Eqs. (28) and (29) hold for any ideal gas (not just a monatomic one).

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1. "But wait!" you say, that calculation was for constant volume, and now we are discussing constant pressure. In fact the relation between energy and temperature, $E = C_V T$, is an exact statement about any ideal gas in equilibrium (constant V, P, T, N), independently of how it got there or what we're going to do to the gas.

3.3 Compressing/expanding an ideal gas

We want to know how V, P, T, E and S change as we compress or expand a gas. There are in fact many ways to compress or expand a gas: we can pressurize it and increase its volume so the temperature is fixed, we can pressurize it and heat it at fixed volume, or we can heat it and let it expand with fixed pressure. There are other ways too. The trick to understanding how things change as a gas is compressed or expanded is to always express the quantities in terms of dependent variables that involve the thing being held fixed.

Free expansion means letting a gas expand on its own. If a gas expands freely from V_1 to V_2, its energy doesn't change (energy is conserved). So its temperature doesn't change either ($E = C_V T$). Remember, temperature is the kinetic energy of the molecules. Just because they can move in a larger volume, it doesn't mean they are slowing down. Since temperature doesn't change, using the ideal gas law $PV = Nk_BT$, the pressure goes down by $P_2 = P_1 \frac{V_1}{V_2}$. Also, from the Sackur-Tetrode equation,

$$\Delta S = Nk_B \ln \frac{V_2}{V_1} \tag{30}$$

Since $V_2 > V_1$ this says that entropy increases upon free expansion.

Quasistatic isothermal expansion means letting a gas expand at fixed temperature. To use the ideal gas law, or any of the thermodynamic relations we've derived so far using statistical mechanics, the system has to be in equilibrium at all times. So the expansion should be done quasistatically. This means that the expansion has to be done more slowly than the molecules are moving. As mentioned in the introduction, quasistatic processes are pretty generic. Most natural processes, motion of clouds for example, are quasistatic. An example of a non-quasistatic process is abruptly moving a piston that had been compressing a gas. When the expansion is quasistatic, all the work done on moving the piston can be employed, say for lifting a weight. If the piston were abruptly moved, the gas would expand and its pressure would drop. We would then have to do work to compress it again.

A helpful visualization for quasistatic expansion is to picture the expansion being done against a pile of sand sitting on top of a piston. We slowly let sand slide off the piston. As each grain slides off, the pressure decreases and the piston rises. Equilibrium is maintained at all times:
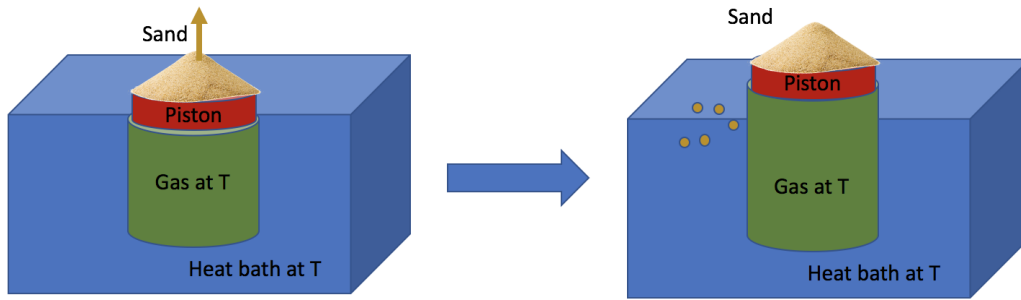

Figure 1. Isothermal expansion against a piston covered with sand

I like the sand picture too because there you see where the work is going – it's lifting the sand. We only take off a little bit to get the piston to go up and it doesn't cost any energy to let the sand fall off the piston. After the expansion, the rest of the sand is higher so work has clearly been done. If you have the piston without the sand it's a little confusing sometimes as to where the energy in the work has gone.

We already established in Eq. (21) that $dW = PdV$. In isothermal expansion $P = \frac{Nk_BT}{V}$ so

$$W = \int_{V_1}^{V_2} PdV = Nk_BT \int_{V_1}^{V_2} \frac{dV}{V} = Nk_BT \ln \frac{V_2}{V_1} \tag{31}$$

Where did the energy come from? Not from the gas, as we already established that its energy is unchanged if its temperature is unchanged. If we assume no friction, and there is no external source of energy, all the energy must have come from heat withdrawn from the reservoir. Thus

$$Q = Nk_B T \ln\frac{V_2}{V_1} \tag{32}$$

Using Eq. (5) the entropy change in the reservoir is therefore

$$\Delta S_{\text{res}} = -\frac{Q}{T} = -Nk_B \ln\frac{V_2}{V_1} \tag{33}$$

The entropy of the reservoir goes down, since heat is extracted.

Since T is fixed and the energy of the gas is fixed, the entropy change of the gas is the same as if it expanded freely

$$\Delta S_{\text{gas}} = Nk_B \ln\frac{V_2}{V_1} \tag{34}$$

So we see that the entropy of the gas goes up by exactly the same amount that the entropy of the reservoir goes down by. The net entropy change of the whole system and surroundings is zero. The process is reversible.

Quasistatic adiabatic expansion. Adiabatic means without transferring heat. To achieve adiabaticity, we can simply insulate a system. Let us consider the quasistatic adiabatic expansion of a gas. Then because $\Delta S = \int \frac{1}{T} dQ$, the system's entropy doesn't change.

We often colloquially say "adiabatic" to mean "slow". Usually, physicists mean a quasistatic adiabatic process when they say "adiabatic". Indeed, while a quaistatic process must be slow (slower than the average molecular speed), an adiabatic process does not have to be slow, it just has to be insulated. Free expansion of a gas is an adiabatic process that is not quasistatic. The expansion of a gas against an insulated piston is also adiabatic, and if done slow enough, can be quasistatic as well.

By adiabatic expansion, we usually mean an adiabatic quasistatic expansion, as the expansion against a piston:
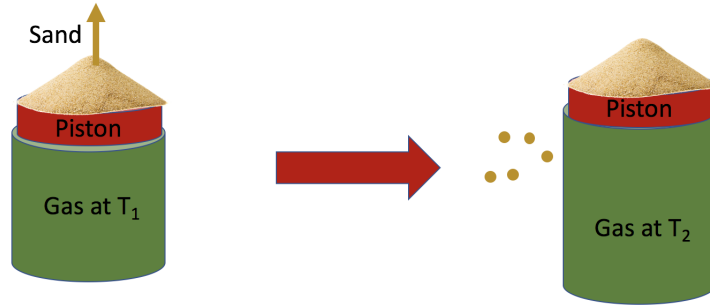

Figure 2. In adiabatic expansion there is no heat bath, so no heat transfer.

In adiabatic expansion, even though no heat flows, the temperature may still change. Consider quaistatic adiabatic expansion against a piston: the gas will do work on the piston as it expands, losing energy, so its temperature will go down. The work done by the gas is $dW = PdV$. To figure out by how much the energy of the gas changes, we use Eq. (20):

$$dE = \frac{C_V}{Nk_B} d(PV) = \frac{C_V}{Nk_B}(PdV + VdP) \tag{35}$$

By energy conservation $dE + dW = 0$ (since there is no heat involved), we then have

$$\frac{C_V}{Nk_B}(PdV + VdP) + PdV = 0 \tag{36}$$

Recalling Eq. (25), $C_P = C_V + Nk_B$, this simplifies to

$$C_P \frac{dV}{V} = -C_V \frac{dP}{P} \tag{37}$$

which integrates to $C_P \ln V = -C_V \ln P + \text{const}$. It is conventional to define the **adiabatic index** γ as

$$\gamma = \frac{C_P}{C_V} \tag{38}$$

so that $\ln PV^\gamma = \text{constant}$ and therefore

$$PV^\gamma = \text{constant} \tag{39}$$

So that

$$P_1 V_1^\gamma = P_2 V_2^\gamma \tag{40}$$

This equation tells us how pressure and volume are related as we compress a gas adiabatically.

Equivalently, since $P = \frac{nRT}{V}$ for an ideal gas, $TV^{\gamma-1}$ is constant, as is $VT^{\frac{1}{\gamma-1}}$, $TP^{\frac{1-\gamma}{\gamma}}$ and $PT^{\frac{\gamma}{1-\gamma}}$ in an adiabatic compression/expansion process. These alternative formulas are sometimes more useful for solving problems, depending on what you are trying to solve for.

As a check, we can conform Eq. (40) by using Eq. (29) and $E \propto PV$:

$$\Delta S = S_2 - S_1 = (C_P - C_V)\ln\frac{V_2}{V_1} + C_V \ln\frac{P_2 V_2}{P_1 V_1} = C_V \ln\frac{P_2}{P_1} + C_P \ln\frac{V_2}{V_1} = C_V \ln\left(\frac{P_2 V_2^{C_P/C_V}}{P_1 V_1^{C_P/C_V}}\right) \tag{41}$$

Setting $\Delta S = 0$ for adiabatic expansion gives Eq. (40).

By the way, you may have seen the adiabatic index before in 15c where you learned that the speed of sound in a gas is $c_\text{sound} = \sqrt{\gamma \frac{k_B T}{m}}$. A sound wave is adiabatic compression and rarefaction of a gas. We know it's adiabatic since there is no heat transfer involved.

Isobaric expansion. Isobaric means constant pressure. For a gas to expand and keep the same pressure it must heat up. Thus some heat must be absorbed into the system. We define the the **coefficient of thermal expansion** as

$$\alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{42}$$

We usually treat α_V as approximately constant over a small range of temperature, in which case

$$\Delta V = V\alpha_V \Delta T \tag{43}$$

Thus the bigger α_V is the more the volume changes for the same temperature change. You can get a more accurate formula for the change in volume by integrating Eq. (42), but most of the time Eq. (43) is sufficient.

For an ideal gas,

$$\alpha_V = \frac{1}{V}\frac{\partial}{\partial T}\left(\frac{Nk_B T}{P}\right) = \frac{Nk_B}{VP} = \frac{1}{T} \tag{44}$$

For example, at $298.2\,K$, the measured coefficient of thermal expansion for N_2 (i.e air) is $\alpha_{N_2} = 0.003365\,K^{-1} = \frac{1}{297.2\,K}$ in excellent agreement with this prediction. Comparing α_V to $\frac{1}{T}$ is an indication of how close to an ideal gas a substance is.

Liquids and solids generally do not act as ideal gases. They expand much less when heated. For example, liquid mercury at $T = 298.2\,K$ has $\alpha_\text{Hg} = 0.000181\,K^{-1} = \frac{1}{5524\,K}$, an expansion coefficient about 20 times smaller than for air.

Figure 3. Mercury thermometer.

A mercury thermometer has liquid mercury in a tiny capillary with vacuum above it. An important feature of mercury that makes it good for a thermometer is that essentially none of the liquid evaporates into the air. This prevents pressure from forming which would limit the expansion and make the volume/temperature relation nonlinear as the volume of the capillary fills up. Mercury thermometers were historically so important that a unit of pressure is defined with them: $1\,\mathrm{mm}\,\mathrm{Hg} = 1\,\mathrm{torr}$. Torr is related to bar as $1\,\mathrm{bar} = 750.06\,\mathrm{torr}$.

Now we can understand why the temperature measured by a thermometer is the same as the "T" we defined by $\frac{1}{k_B T} = \frac{\partial S}{\partial E}$. The explanation is almost tautological. All we need about the statistical-mechanics T is that it takes the same value for all systems in equilibrium with each other. So, let us put our mercury thermometer in equilibrium with a heat bath. As we make the bath hotter T changes and the mercury rises. We put little lines on the mercury and give them labels as "temperature". There is therefore a 1-to-1 correspondence with those labels and T. We just then need one system where we know both T and "temperature", such as the mercury thermometer, to determine the correspondence. Then since any two systems in equilibrium are at the same T, this correspondance between temperature and "T" holds for any system.

4 Carnot's engine

In the 1820's Sadi Carnot became interested in understanding how efficient steam engines could be. A steam engine is a type of heat engine that uses a temperature difference to do work. An example is the Watt engine, which looks like this
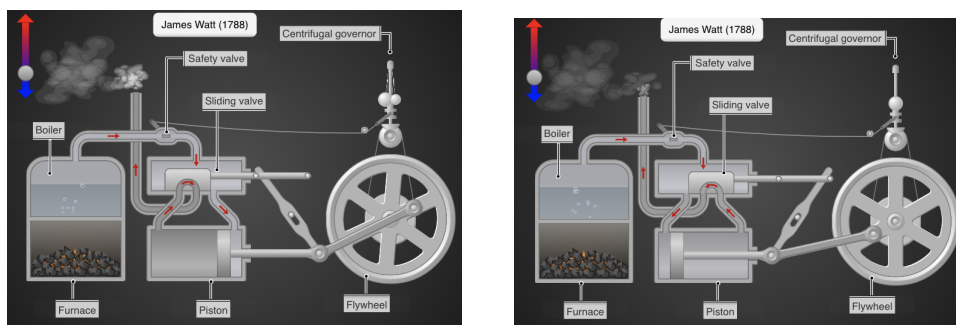

Figure 4. James Watt steam engine. Animation here https://www.youtube.com/watch?v=U-f9UqFiXXk

In the Watt engine, a furnace heats water which produces steam. The steam has high pressure which is used to move a piston, and then is vented out to the ambient air. Carnot wanted to know how much work W can be done *in principle* with the heat Q_1 drawn from the furnace. His important observation was that there is a maximal efficiency for such an engine, depending only on the temperatures of the steam and the air.

An idealized heat engine has two heat baths at temperatures T_H (furnace) and T_C (air) with $T_H > T_C$. Exploiting the temperature difference, we should be able to do some work W. How much work can we do? If we draw an amount of heat Q_{in} from the hot bath, then the efficiency by which the heat is turned into work is

$$\varepsilon = \frac{W}{Q_{\mathrm{in}}} \tag{45}$$

By energy conservation, the energy not used for work must be exhausted as heat $Q_{\mathrm{out}} = Q_{\mathrm{in}} - W$ into the cold bath.

One idea is that we could just put the two baths in contact with each other. Then the heat transfers are equal $Q_{\mathrm{in}} = Q_{\mathrm{out}}$ and no work is done. This has $\varepsilon = 0$.

Carnot realized that the most efficient conversion should involve only reversible processes. First we will describe Carnot's cycle and calculate its efficiency, then in the next section we will explore why reversibility is key to maximizing efficiency. We will use the convention that all the heats and work are positive.

Carnot's 4-stage process starts with a gas in volume V_1 at temperature T_H. The 4 stages are

1. Connect the gas to the T_H heat bath. Perform isothermal expansion at T_H to a volume V_2.

2. Remove the heat bath and insulate the gas. Cool the gas through adiabatic expansion to T_C and a volume V_3.

3. Put the gas in heat bath at T_C. Perform isothermal compression at T_C to some V_4.

4. Remove the heat bath and insulate the gas. Adiabatic compression to back up to T_H and back to V_1.

At the end of this cycle, we are back to where we started with a gas at T_H and V_1 and heat has been transferred from the bath at T_H to the bath at T_C.

Note that these volumes V_1, V_2, V_3 and V_4 are not independently selectable. In the adiabatic stages, the temperature change fixes the final volume. In these stages, PV^γ constant. Using the ideal gas law $PV \propto T$ we also have $TV^{\gamma-1}$ is constant which is more useful for current purposes. So V_2 is a free parameter, but V_4 is not free – it is fixed by what it needs to be for stage 4 to go back to V_1. So there is one free parameter V_2 which determines how big of a cycle we want.

Now let's calculate the efficiency.

Stage 1. Here heat is taken from the hot bath and some work is done. The heat removed is

$$Q_{\text{in}} = Nk_B T_H \ln\frac{V_2}{V_1} > 0 \tag{46}$$

As the gas does not heat up, its internal energy is unchanged, so all the heat goes into work. The work we get out is

$$W_{\text{out}}^1 = Nk_B T_H \ln\frac{V_2}{V_1} > 0 \tag{47}$$

Stage 2. In adiabatic expansion PV^γ is constant. Since no heat comes in, the energy change from doing work comes out of the internal energy of the gas, $E = C_V T$. Thus the work done this stage is

$$W_{\text{out}}^2 = C_V(T_H - T_C) > 0 \tag{48}$$

Using $TV^{\gamma-1}$ is constant we also find that

$$V_3 = V_2\left(\frac{T_H}{T_C}\right)^{\frac{1}{\gamma-1}} > V_2 \tag{49}$$

Stage 3. Like stage 1, but compressing to $V_4 < V_3$. Heat goes out and work needs to be done

$$Q_{\text{out}} = W_{\text{in}}^3 = Nk_B T_C \ln\frac{V_3}{V_4} > 0 \tag{50}$$

Stage 4 is like stage 2 but compressing

$$W_{\text{in}}^4 = C_V(T_H - T_C) > 0 \tag{51}$$

and

$$V_1 = V_4\left(\frac{T_C}{T_H}\right)^{\frac{1}{\gamma-1}} < V_4 \tag{52}$$

Note that

$$\frac{V_3}{V_4} = \frac{V_2}{V_1} \tag{53}$$

The net work is then

$$W = W_{\text{out}}^1 + W_{\text{out}}^2 - W_{\text{in}}^3 - W_{\text{in}}^4 = Nk_B T_H \ln\frac{V_2}{V_1} - Nk_B T_C \ln\frac{V_3}{V_4} = Nk_B(T_H - T_C)\ln\frac{V_2}{V_1} \tag{54}$$

So the efficiency is the net work divided by the heat extracted:

$$\boxed{\varepsilon = \frac{W}{Q_{\text{in}}} = \frac{T_H - T_C}{T_H}} \tag{55}$$

This is the Carnot efficiency.

It's sometimes helpful to think about the stages in the Carnot cycle as paths in the PV or ST plane:
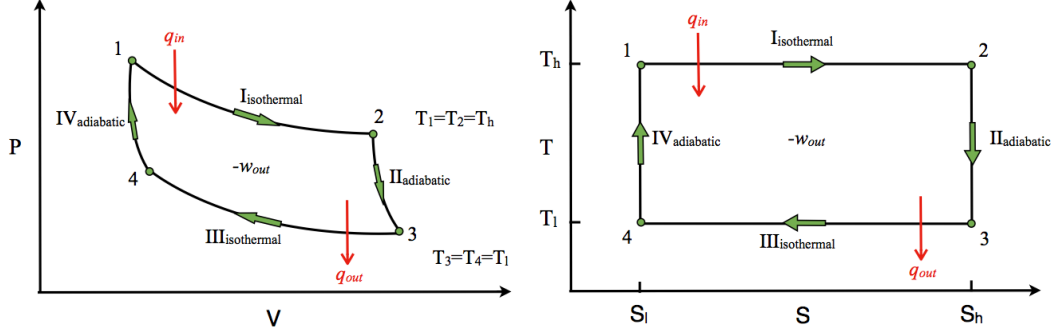

Figure 5. PV diagram and ST diagram for Carnot cycle. In the PV diagram, the isothermal curves have $PV = \text{const}$ i.e $P \sim \frac{1}{V}$ and the adiabatic curves have $PV^{\gamma} = \text{const}$ i.e. $P \sim V^{-\gamma}$.

The area under a curve in the PV diagram is $\int P dV$, which is the work done. So the area of the closed region of a reversible cycle is the net work done over a cycle, W. The area under a *reversible* curve in a TS diagram is the heat, $Q = \int T dS$, by Eq. (9), so the area in a closed region in a TS diagram with reversible paths is the net heat transferred, $Q_{\text{out}} - Q_{\text{in}}$. By energy conservation, we must have $Q_{\text{out}} - Q_{\text{in}} = W_{\text{net}}$ by conservation of energy. The efficiency is just $\frac{W}{Q_{\text{in}}}$ which is less than 1 if $Q_{\text{out}} \neq 0$.

5 Second law of thermodynamics

For the Carnot cycle

$$\frac{Q_{\text{in}}}{T_H} = Nk_B \ln\frac{V_2}{V_1} = Nk_B \ln\frac{V_3}{V_4} = \frac{Q_{\text{out}}}{T_C} \tag{56}$$

Recall that the entropy change of a heat bath is $\Delta S = \frac{Q}{T}$. So we see that the entropy decrease of the hot bath $\Delta S_{\text{hot}} = -\frac{Q_{\text{in}}}{T_H}$ is exactly compensated by an entropy increase in the cold bath $\Delta S_{\text{cold}} = \frac{Q_{\text{out}}}{T_C}$. There is no entropy change in the gas, $\Delta S_{\text{gas}} = 0$, since it comes back to its initial state after the cycle. Thus the net $\Delta S_{\text{total}} = \Delta S_{\text{hot}} + \Delta S_{\text{cold}} + \Delta S_{\text{gas}} = 0$.

In fact, if we were to use that $\Delta S_{\text{total}} = 0$ the efficiency would have been easy to calculate. $\Delta S_{\text{total}} = 0$ along with $\Delta S_{\text{gas}} = 0$ after a complete cycle, we then immediately have

$$\frac{Q_{\text{in}}}{T_H} = \frac{Q_{\text{out}}}{T_C} \tag{57}$$

So the efficiency is

$$\varepsilon = \frac{W}{Q_{\text{in}}} = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} = \frac{T_H - T_C}{T_H} \tag{58}$$

Any efficiency higher than this would *decrease* the entropy overall. (This calculation does not tell whether this efficiency can be achieved, which is why we needed the cycle.) Note that for $T_C = 0$ (which is not possible in any real system) the efficiency can be 1. The point is not that $\varepsilon < 1$ always, but rather that for a given T_H and T_C there *is* a maximum efficiency.

Another important observation about the Carnot cycle is that it's **reversible**. In fact, each step – adiabatic compression/expansion or isothermal compression/expansion – can be done in reverse, and each has $\Delta S = 0$. The result of reversing the whole cycle would be that we put work in and move heat from the cold bath to the hot bath. Thus the efficiency also tells us how efficient a refrigerator can be.

Can we make an engine more efficient than the Carnot engine? If we could, then this new energy would be able to do more work $W' = Q'_{in} - Q_{out} > W$ when depositing the same heat Q_{out} into the bath at T_C. We could then run the original Carnot engine in reverse, applying work W to pulling Q_{out} heat out of the T_C bath and putting Q_{in} heat into the hot bath. The net effect is that the difference in heat extracted $Q'_{in} - Q_{in}$ is turned *directly* into work $W' - W$. We could then use the work to power something, collect all the heat it produces, and put it back into the heat bath. Such a process is a type of **perpetual motion machine**: it converts heat directly into work (see Section 6).

Note also that the more efficient engine would decrease the entropy of the first bath by $\Delta S_1 = \frac{Q'_{in}}{T_H} > \frac{Q_{in}}{T_H} = \frac{Q_{out}}{T_C} = \Delta S_2$. Thus the net effect would be the overall total entropy decreases.

This leads us to the **second law of thermodynamics**. It has many forms

- Total entropy of system+surroundings never decreases: $\Delta S_{total} \geqslant 0$.

- The maximum amount of work extractible from heat Q_{in} removed from a heat bath at temperature T_H is $W = Q_{in}\frac{T_H - T_C}{T_H}$ where T_C is the temperature of the bath to which the energy not used as work is dumped.

- Maximally efficient heat engines are reversible, have $\Delta S_{total} = 0$, and have $\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$.

- All reversible heat engines have the same efficiency.

- No work can be extracted from heat using a system at a uniform temperature.

- Perpetual motion machines that convert thermal energy into mechanical work with no other consequence (no dumping of heat into a cold bath) are impossible.

- No machine can have the sole effect of transferring heat from a cold bath to a hot bath.

Any of these formulations imply the others.

Note that we used the ideal gas law in our calculation of the Carnot cycle efficiency. We could do this because all reversible engines have the same efficiency by the second law, so we can use any engine we can conceive of, such as an ideal gas one, to calculate that efficiency.

The second law does not say that we cannot convert thermal energy into work. There is no limitation on doing this, other than that imposed by the first law of thermodynamics (energy conservation). For example, we could have a hot gas expand against a piston, and expand and expand until the gas is infinitely large and at zero degrees. Then all the thermal energy would have been turned into work. This doesn't violate the second law, since a gas pushing against a piston really has a vacuum on the other side of the piston, which is at zero temperature, so this is like a heat engine with $T_C = 0$. The kind of perpetual motion machine that is forbidden by the second law is one that takes a single heat source and converts all the thermal energy into work, without dumping any heat anywhere, i.e. without heating anything up.

The second law is stronger than the first law. For example, if you have a hot bath and a cold bath, you can put them in contact and heat will spontaneously flow from hot to cold. You cannot however take heat out of the cold bath and dump it in the hot bath without doing work. Such a refrigerator would be consistent with the first law, since energy is conserved, but violate the second law. Two example constructions that attempt to violate the second law are the Brownian Ratchet, discussed below, and Maxwell's demon, discussed in Lecture 6.

6 Brownian Ratchet

The second law of thermodynamics is one of the most amazing results in all of physics. It seems to be true, has enormously important consequences (like not producing perpetual motion machines) but no one can prove it. All the "proofs" for it (like the Boltzmann H theorem) involve assumptions that are mostly true, but not true in every situation (such as the assumption of molecular chaos or ergodicity).

There are many great examples illustrating how a perpetual motion machine is foiled by a conspiracy of thermodynamics. One of the most famous is called the Brownian Ratchet. It was conceived of in 1912 by Marian Smoluchowski and popularized by Richard Feynman. There is a fantastic discussion of it in the Feynman Lectures on Physics.

A ratchet and pawl is a tool designed to turn only in one direction. The pawl is a little strip of metal held against a set of angular gears (the ratchet) by a spring. When a small force is applied in one direction, the ratchet will turn slowly lifting the pawl until it slips over a gear. But if the force is applied in the other direction, the ratchet will go nowhere - it pushes against the pawl in the wrong direction.

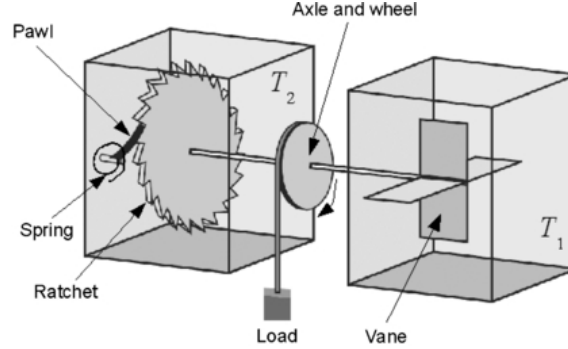The set up for the Brownian ratchet is shown in this Figure:

Figure 6. Brownian ratchet

A ratchet and pawl are placed in a box with a gas at temperature T_2. The ratchet is connected via an axle to a vane in another box, at a temperature T_1. The vane is symmetric and can rotate in either direction. Finally, a small weight (the load) is attached to a string tied to the axle.

The Brownian ratchet is meant to work as follows. There is thermal motion of the gas molecules on the vane side at temperature T_1. This motion jiggles the vane back and forth. Sometimes, perhaps rarely, a large enough displacement accumulates counterclockwise to push the pawl over the ratchet. This turns the axle lifting the load. The key point is that the ratchet can only turn in one direction because of the pawl. Thus over time, the wheel will spin in one direction and thermal energy is converted into work. This is called a Brownian ratchet because the ratchet undergoes a biased random walk and therefore Brownian motion.

Note that nothing in this explanation seems to require $T_1 \neq T_2$. If the Brownian ratchet works when $T_1 = T_2$ then it generates work from a system at constant temperature, producing perpetual motion and violating the second law of thermodynamics. What's the catch?

The catch is that thermal fluctuations can affect the pawl, just as they affect the vane. You can see this from the ratchet/pawl/vane system alone, without the weight. Say it takes energy ε for the pawl to be pushed far enough to slip over a gear. This energy is the same whether it accumulates by molecules pushing the vane that pushes the ratchet that pushes the pawl or by molecules that directly push the pawl. The probability for forward motion of the ratchet is then the probability of the energy ε accumulating through Brownian motion on the vane side $P_{\text{forward}} = \exp\left(-\frac{\varepsilon}{k_B T_1}\right)$. The probability of backwards motion, when energy ε accumulates through Brownian motion on the ratchet and pawl side, is $P_{\text{backward}} = \exp\left(-\frac{\varepsilon}{k_B T_2}\right)$. If $T_1 = T_2$ then these probabilities are the same, so it is no more likely for the ratchet to turn one way than the other, and no work gets done.

Now let's take $T_1 \neq T_2$ and see how much work we do. First of all, note that the pawl has to dissipate heat. If the pawl were elastic and completely frictionless, then after one click of the ratchet, it would just bounce up and down conserving energy, like an undamped harmonic oscillator. Such a pawl wouldn't do a very good job holding the ratchet in place – a clockwise force on the ratchet would let it easily slip under the pawl at the top of its bounce. So we already see the most important part of this whole thought experiment: doing work requires some dissipative element (this dissipation plays an important role in the second law of thermodynamics, as we'll see in Lecture 6).

We conclude that for this setup to work in any circumstance, the pawl must have some damping. Then, instead of bouncing forever, it dissipates the energy ε it took to bend back the pawl entirely into heat until the pawl is back to its rest position. Through this heat dissipation, the pawl, the ratchet, and the gas in volume T_2 will heat up. Thus, over time as the system is working T_2 will increase.

Say each time the pawl slips over a gear (one "click"), the ratchet turns by an angle θ. If the weight is exerting a torque L on the ratchet, then the work done in lifting the weight by one click is $\Delta = L\theta = mg\,\Delta h$, where m is the mass to be lifted by a height Δh. So it takes a total energy $\varepsilon + \Delta$ to lift the weight one click after which ε of the energy is dissipated as heat into the T_2 bath. The chance of this happening due to Brownian motion of the vane is

$$P_{\text{lift}} = \exp\left(-\frac{\varepsilon + \Delta}{k_B T_1}\right) \tag{59}$$

For Brownian motion on the ratchet side to cause the pawl to slip over the ratchet and drop the weight one click, only energy ε is required, so that

$$P_{\text{drop}} = \exp\left(-\frac{\varepsilon}{k_B T_2}\right) \tag{60}$$

If these probabilities are equal, then the weight doesn't move on average and no work is done. In such an equilibrium configuration $P_{\text{lift}} = P_{\text{drop}}$ so that

$$\frac{\varepsilon + \Delta}{T_1} = \frac{\varepsilon}{T_2} \tag{61}$$

Once we are in this equilibrium situation, say we then take a little bit of weight off, a grain-of-sand's worth. This will lower Δ and increase P_{lift} and the weight will start to slowly rise. Alternatively, by adding a grain of sand, the ratchet would turn the other way. So for a very small change in Δ we can make infinitesimal, quasistatic changes. Or we could make small changes in T_1 or T_2 with the same effect.

Now say we make a change so that the weight starts to rise, very very slowly. Each time it moves up it's because energy $\varepsilon + \Delta$ accumulated on the vane side of which Δ went to lifting the weight and ε is dissipated as heat into the T_2 bath. Thus this is an engine from which a heat $Q_1 = \varepsilon + \Delta$ is withdrawn from the T_1 bath, work $W = \Delta$ is done, and heat $Q_2 = \varepsilon$ is deposited into the T_2 bath. Thus

$$\frac{Q_1}{Q_2} = \frac{\varepsilon + \Delta}{\varepsilon} = \frac{T_1}{T_2} \tag{62}$$

So that $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$. This is exactly the condition satisfied by Carnot's engine! If we are farther from equilibrium, so T_2 is much hotter, then the efficiency goes down.

In other words, the Brownian Ratchet is maximum efficiency heat engine. As Feynman says, an advantage of this system over Carnot's is that you can see what is happening physically. Indeed, it gives you clues as to how to show perpetual motion machines cannot work.

7   Summary

This lecture introduced some of the basic concepts of thermodynamics. Thermodynamics concerns macroscopic quantities like heat, work, energy, temperature, volume etc. These quantities can be studied and measured and relations derived among them without recourse to a microscopic description (statistical mechanics). The main concepts are

- **Work**: energy transferred in an organized manner. Denoted by W

- **Heat**: energy transferred through thermal motion. Denoted by Q.

- **Reversibility**: A process $A \to B$ is reversible if the final state B can be brought back to the original state A exactly, i.e. both system and surroundings must be identical.

- Clausius defined entropy as a state variable (independent of history). To find the entropy change between systems A_{sys} and B_{sys} he said find suitable surroundings A_{surr} and B_{surr} such that the path $A \to B$ is reversible. Then $S_{A_{\text{sys}}} - S_{B_{\text{sys}}} = \int_{\text{rev.}} \frac{dQ_{\text{in}}}{T}$, where the integral is a path integral along the reversible path. That is, the source of entropy change is *heat flow*.

- Ideal gases have pointlike particles with pointlike interactions. These satisfy the ideal gas law $\text{PV} = Nk_B T$.

- **Adiabatic** means no heat flow. Adiabatic process do not have to be slow or reversible. The free expansion of a gas is adiabatic.

- **Quaistatic** means slow enough so equilibrium can be assumed to hold at all times. Reversible processes must be quasistatic, but quasistatic processes may not be reversible.

- A **heat engine** is a way to convert heat transfer into work.

- The maximum possible efficiency $\varepsilon = \frac{W}{Q_{\text{in}}}$ of a heat engine is $\varepsilon \leqslant \varepsilon_{\text{max}} = \frac{T_H - T_C}{T_H}$. **Carnot's** engine achieves this efficiency. Many other idealized engines do too. Any maximally efficient engine is reversible.

- The second law of thermodynamics says that $\Delta S_{\text{sys}} + \Delta_{\text{surr}} \geqslant 0$ in *any process*. If you violated this, you could make an engine with efficiency greater than ε_{max}. There are many other equivalent versions of the second law.

- The Brownian Ratchet is a "perpetual motion machine" that seems like it converts heat directly into work ($\varepsilon = 1$). A careful quantitative analysis shows that in fact, it does not convert heat to work, but has $\varepsilon \leqslant \varepsilon_{\text{max}}$.