**The Laws of Thermodynamics**

So far the balance equations have not imparted any intrinsically new concepts, just wrapped old concepts in a perhaps unfamiliar package. But now we’ll discuss the last, most concept, and associated balance equation – entropy. This is how Thermodynamics distinguishes itself all the previous topics.

**Entropy balance for closed systems**

To make progress calculating entropy changes we first need to discuss the distinction between reversible and irreversible processes. Reversible processes are those whose reverse can naturally occur in nature (or are probable to occur in nature). Such processes do not convert ordered energy into disordered energy. As such they would be characterized by no net entropy change. An irreversible process is one whose reverse cannot naturally occur, and would be naturally characterized by a transformation of ordered energy into a more dispersed, disordered form. And so irreversible processes increase entropy. So…



Let’s elaborate.

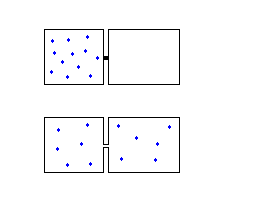
***Irreversible processes***

A prototypical one would be this. We’ve seen a block slide across the floor and gradually come to rest via friction transferring its kinetic energy into thermal energy of both the block’s and floor’s atoms (as well as transferring some of this energy to thermal energy of the air, and sound waves). But we’ve never seen the reverse process, i.e., random thermal energy in the floor, air, and block itself coalescing into ordered energy in the block, starting it to move backwards faster and faster, and in the process leaving themselves a little colder. In other words, we readily see a transformation of mechanical energy into thermal energy. But we do not see a spontaneous transformation of thermal energy into mechanical energy. So this is considered an irreversible process. A key feature of this process is that energy initially confined to the block got dispersed into the floor as well. In addition, the energy that was initially present in the block was highly ordered, but by the end of the process it became quite disordered.

Consider a similar example: a block falling from the top of a building to the ground. The block will transfer most of its initial potential energy to kinetic energy as it falls, but some will be dissipated in the air and the block itself as thermal energy. Whatever kinetic energy it has left by the time it hits the ground will be transferred to thermal energy in both itself and the ground upon impact. This is an irreversible processes because you’ll never see a block sitting on the floor get cooler and jump into the air. So again this is an irreversible process. And again it is characterized by energy going from an ordered to a disordered state.

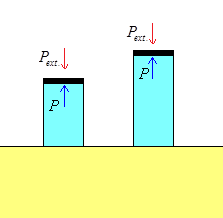
Suppose we have two blocks in contact with each other, block 1 at temperature T1 = 50˚C and block 2 at temperature T2 = 100˚C. As we know, a certain amount of heat, Q, will flow from block 2 to block 1. But we will never see heat flow from the colder one to the hotter one. So this too is an irreversible process. It would be hard to gauge intuitively in this case whether the energy is now more disordered than before, but by analogy with the other examples we would imagine so.

Consider the example of a free expansion of gas. In picture 1, a valve prevents the gas from expanding into the second container, and in picture 2 we’ve opened the valve allowing the expansion to occur.



This is an irreversible process because you will never see a free compression of a gas, whereby the gas particles all spontaneously transfer themselves to the left container. And clearly the energy has become more disordered as it now occupies twice the volume.

Another example is the compression of a gas by a piston, illustrated below. Suppose that Pext. > P (should’ve written Π, instead of P, perhaps, but we are assuming we’re very close to equilibrium). Then the piston will go down obviously, accelerating as it goes. This will create turbulences (basically compression waves) inside the gas (or liquid or solid) which will die out eventually when the piston is stopped. But you would never see the reverse: an equilibrium compressed gas suddenly develop turbulences and shoot upwards. Again energy has become more disordered because turbulences, i.e. compression waves, which are an ordered form of energy get transformed into random thermal energy.



Finally, pushing a current through a wire would be an irreversible process. As the field pushes the charges along the wire, the charges will accelerate until they hit an impurity, basically come to rest delivering all their kinetic energy to the impurity. Then they will start accelerating again through the wire until it hits another impurity and the process repeats itself. In this fashion, relatively ordered kinetic energy of the charges (ordered because all the electrons would be going in the same direction) gets transformed into disordered kinetic energy in the impurities (disordered b/c the impurities are moving in random directions). Now certainly you would not see impurities give up their random kinetic energy to an electron during a collision, explosively accelerating backwards against the ambient electric field, and then watch as the electric field decelerates the electron until it hits another impurity which explosively transfers its kinetic energy into the electron accelerating it backwards against the field again? As a consequence of this reverse process we would also observe the wire getting colder and colder as its random thermal energy gets converted into order electron kinetic energy. So this is definitely an irreversible process.

***Reversible processes***

Not all processes are irreversible however. Consider the case of a block falling (in a vacuum technically) from a building onto a spring, which then compresses a certain distance bringing the block to rest. This process is reversible because we can easily have the reverse happen – we can start with a block on a compressed spring, let it go, and watch it get catapulted into the air back to the top of the building. And we do not observe any energy dispersal.

Let’s consider a hypothetical example of two blocks one at temperature T1 = 99.9˚C, and another at T2 = 100˚C. When we place them in thermal contact, heat Q will flow from object 2 to object 1. Heat would never flow the other way, and so this process is irreversible. But it is *almost* reversible because the temperatures are so close. In the limit that T1 → T2, the process would approach reversibility. A similar example would be a substance undergoing a phase change by application of heat coming from a *slightly* higher T reservoir. In that case the temperature of both substance and reservoir would not change. And it could be reversed by making an infinitesimal change, i.e., changing the reservoir temperature to slightly below the phase change temperature.

Now consider the compression of a substance via an external pressure which is infinitesimally greater than the internal pressure. In this case the compression will happen exceedingly slowly. So barely any turbulences will develop and die out when the piston is stopped. So the compression will be exceedingly close to reversible. In the limit that Pext. → P the compression would be reversible.

Consider battery with potential difference approaching zero. Then it barely drives charges through the wire and there is vanishingly small energy dispersal into the impurities. Then this process would be almost reversible, and would become reversible in the limit that ΔV → 0.

Or we might consider a chemical reaction: aA + bB ↔ cC. If this reaction barely proceeds and is nearly balanced, then the reaction would be considered reversible.

So the upshot is this: irreversible processes are those which do not occur in reverse in nature. Another way to frame it is this. If after performing the process, you reverse the forces causing the motion and this causes everything to proceed back to the initial state, then it is reversible. Otherwise it is irreversible. Another takeaway could be that as the forces driving the irreversible process go to zero, the process becomes reversible. Also, as the forces go to zero, the currents that the forces drive go to zero. We could hypothesize that ΔSirr. is proportional to these forces and currents, and this idea will be taken up when we talk about NETD.

***2nd law of thermodynamics***

You’ll notice that for reversible processes, the total entropy of the system + environment remains the same, whereas for irreversible ones, the total entropy increases. So this brings us to our second law of thermodynamics. It simply states that for a *closed* and *isolated* system undergoing any change, its entropy will always either increase or remain the same.



It will remain the same for reversible processes, but will increase for irreversible ones. With an eye towards non-equilibrium thermodynamics, we can say that a system has reached thermal equilibrium, when it’s no longer producing entropy [this definition seems to work better than to say it is when system properties are time-independent as the latter criterion would allow electrons in a current to be in equilibrium whereas the former criterion (and correct one) would not]. It’s conceptually important to realize that this is only a probabilistic statement. It is not theoretically impossible for a system of particles that presently occupies both halves of the container to shrink into one half. It is just fantastically improbable. And so entropy is *almost* guaranteed to increase at all times (or remain the same). So the entropy will for all intents and purposes increase at all times (or remain the same) if the system is closed. Of course the entropy cannot continue to increase forever; eventually it will reach a maximum value, and at this point we would consider the system to be in equilibrium. So we can say that the processes in a closed system will always drive it towards equilibrium. So this is the equation that describes the statistical behavior of the system. This is the equation which says that if you lift the lid off of a gas, it will expand to fill its new container. This is the equation that will eventually stipulate the temperatures, pressures, and chemical potentials equilibrate with their environment, under suitable conditions.

We can loosen up the *isolated* condition. Suppose we had a system in the presence of external conservative force fields. If we took the force fields out of the description of the energy of the system, then as it came to equilibrium, upon some non-equilibrium initial condition, it’s energy would not be constant, since we’d be considering its energy to consist entirely of its *internal* energy. So then we could say that the system will maximize its entropy subject to the first law of thermodynamics, meaning that in this case it would be allowed to alter its energy too. But with a conservative field, the net work done on the system would only depend on initial and final state of the system, not how it evolved between the two states, and so we could just as rigorously ascertain the max entropy state in this case too.

While internal fluctuations will almost always drive the system towards the maximum entropy equilibrium state, as aforementioned, there is a probability, however small, that the system will reduce its entropy. Interestingly, Einstein proposed a formula for this probability:



where ΔS is the difference in entropy between the equilibrium state and the lesser entropy state α, k is a constant we’ll run into later k = 1.38×10-23 J/K, and C is some normalization constant. We’ll find support for this statement when we consider statistical mechanics.

**Entropy balance for open systems**

Now we are in position to write an entropy balance equation. We’ve discussed the fact that processes internal to the system will irreversibly increase its entropy (or potentially keep it same). Now we would like to consider the effect of processes external to the system, whereby it interacts with its environment. To distinguish these external effects from internal ones we will consider the part of the process for which the system remains in quasi-equilibrium, and relegate to δSint. the part that comprises internal changes with the system.

*Equilibrium/Quasi-Equilibrium & Reversible/Quasi-Reversible Processes*

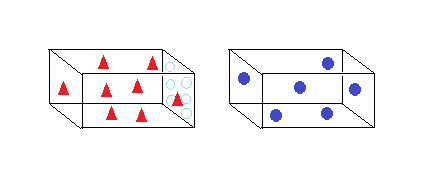
Since we’re discussing *open* systems, it’s prudent at this point to differentiate reversible/irreversible processes and equilibrium/non-equilibrium processes. Suppose we have a system undergoing some process. If the section undergoing the process (i.e. exchanging energy, work, particles) is always in a state of instantaneous maximum entropy within its (perhaps imaginary) volume, then it can be described as always being in instantaneous equilibrium. If it is close, but not entirely in equilibrium, i.e. ΔS/S << 1 (where ΔS = Smax – S), then we might say it is in quasi-equilibrium. Quasi-equilibrium would be characterized by (as we’ll discuss later) small gradients of pressure, temperature, and chemical potential. And this doesn’t mean we necessarily need to ignore internal entropy generation occuring as a result of ΔS not being zero. I think it would rather invite us to say that instantaneous S is just about always given (see Equilibrium Systems file) by the equilibrium formula for S(U,X,N), even if formulas for changes in U, X, N – the balances above – involve non-equilibrium values of pressure, etc., and so entropy balance – see balance below – requires non-zero internal entropy generation (but should be smallish, right). On the other hand, if it can be delineated into sections which have their entropy maximized, but not necessarily w/r to each other (meaning there are definite temperature, pressure, chemical potential, etc., differences between adjacent sections), then we would say it’s in local equilibrium. If they are close, but not entirely in equilibrium, i.e. ΔS/S << 1 (where ΔS = Smax – S), then we might say it is in quasi local-equilibrium. And we would propose that each given piece’s entropy is given by the S(U,X,N) formula, even if the balances for that piece’s U, X, N, involve non-equilibrium processes. Otherwise, it’s just completely non-equilibrium. This would be like a gas whose lid has suddenly been released.

Suppose have closed system with the two subsections interacting with each other. If they are both in equilibrium the entire time (so that dSint. = 0), *and in equilibrium with each other* – i.e. the conjugates to their modes of interaction are equal, then this interaction would be reversible. If they are in quasi-equilibrium within themselves and with each other, then the interaction could be said to be *quasi-reversible* (but might still want to calculate the entropy generation). Otherwise, it simply isn’t close to reversible. For example the two systems could be in quasi-equilibrium with a finite temperature difference and exchanging heat. And in this case, the interaction certainly would not be close to reversible. However, perhaps there could be a finite pressure difference between them. Then maybe one could make the case that their interaction is still quasi-reversible since perhaps not much entropy would accrue from the fluctuations internal to the system due to the finite pressure difference (and hence acceleration of boundary of the system).

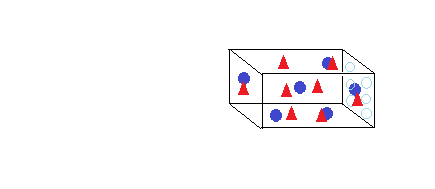
***entropy change due to particle transfer***

Finally, let’s consider entropy change due to adding particles to the system. When one adds particles, typically of different pressure/temperature, etc. there will be an entropy change associated with the entrance of these particles into the system and also an irreversible internal entropy change due to the new particles spreading out within the system, making collisions with the other particles and so distributing their energy to these particles, etc. We want to isolate the mere addition of the particles from the irreversible internal equilibration of the new particles with the rest of the system.

So to that end, consider a container of NT triangle particles, and a separate container of NC circle particles. Let box T have a semi-permeable membrane so that circles can pass through, but triangles cannot.



Further now assume that the triangles and circles are of the same volume per particle and temperature (this is so the triangles don’t expand upon entering the box or transfer energy to the circles, or vice versa – which would be non-equilibrium processes). Now we will slide the triangle box forward into the circle box. We would have to do this slowly so as not to exert any appreciable force on the circles, thereby inadvertently changing their state.



Observe that if we reverse the process and pull the triangle box back out, we will have separated the two substances, returning everything to its original state. So this is a reversible process. This is how you can reversibly mix or separate two species. So what is the entropy increase to the circle box by adding the triangle particles to it? Suppose that the entropy of the triangles by themselves were ST and the entropy of the circles were SC. Since mixing them was a reversible process, the entropy of the combined state must be the same. And so the entropy is merely ST + SC. So then the reversible entropy increase is just the entropy of the additional particles: dS = S(k) ­­I(k)dt., where S(k) is the entropy per particle of the added species. I’m writing like this, rather than as just an arbitrary particle *current*, to emphasize that the particle transfer must be reversible, and so the current must be convective basically.

Only way identical particles can be added reversibly is if none such are there in the first place, or if they’re entering at same rate which others are leaving. But perhaps could define this as the entropy flux anyway, and then shuffle the rest into Sint. Think this is what is done.

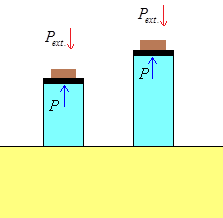
***entropy change due to translational and angular momentum transfer***

These should be zero because of science. Certainly the first would be zero as all we’d be doing by adding momentum, uniformly distributed throughout the system, is basically changing our inertial reference frame. And can reason that system progresses through states at the same rate regardless of inertial frame. As far as angular momentum, seems a little harder to justify from a ‘rate at which it passes through states’ basis, but it seems necessary that this too must not affect the entropy.

***entropy change due to work, or changing field***

Now let’s consider the entropy change due to work. When one does work on an object, for instance pressure work, there might be a change in entropy due to change in volume. If the work is done quickly, faster than the system can adjust, then this will induce various gradients of pressure, density, temperature, etc. And as the system works to come back to equilibrium there will be an irreversible internal entropy change associated with this. But we want to simply get the external entropy change associated with the work alone. So we will do the work very slowly so system remains in quasi-equilibrium and internal changes are non-existent/negligible. And this will require that the external pressure driving the work is basically equal to the internal pressure of the gas (which we’ll be using as our example).

So let a gas be adiabatically insulated (so that no heat can enter/leave and thus we won’t incur entropy changes due to heat as well). Now consider a brick on top of the piston exerting a force only slightly greater than the internal pressure (this is to keep the substance in equilibrium so that). Further we imagine that the gravitational field is tuned so that as the brick gets closer to the ground, the gravitational force on it increases so that it is always *just* greater than the internal pressure. Note we could do this in principle because we can create any gravitational field we want by judicious placement of mass. Or if you prefer we could use a charge instead of a brick, and an electric instead of gravitational field, which would be a bit easier to manipulate. In any event this would compress the piston slowly without turbulence.



But now consider this process in reverse. If we infinitesimally lighten the brick, the gas will expand back to its original height. So this process is infinitesimally close to being reversible. And as such, the net entropy change at all points must be 0. But what is the entropy change of the *gas* during the initial compression, or expansion? We can figure this out as follows. Consider the compression. The initial entropy must be equal to the final entropy. So Sbrick(i) + Sgas(i) = Sbrick(f) + Sgas(f). Now the brick’s entropy does not change during the process because it has not become more disordered, its energy has not become dispersed. So Sbrick(i) = Sbrick(f) and these terms cancel out of the equation. Therefore Sgas(i) = Sgas(f). And so we see that entropy does not change for an equilibrium compression. It is generally true that equilibrium work of all kinds does not change the entropy of the system. This result is not necessarily obvious because work does reduce the volume of the substance, thereby confining the disordered energy to a smaller volume. It might be thought that this decreases entropy. But work also increases disordered energy as well since the change in gravitational potential energy (work done by brick) is going into disordered thermal energy of the substance. So these two effects apparently cancel.

Sometimes it might be problematic to distinguish work as ‘work’ and work as ‘heat’, since they’re both fundamentally the same thing. And I guess I would say, anticipating future comments, that ‘work’ is the work done which is coupled to an internal parameter change of the system, like volume, density distribution, magnetization, dipole moment, etc., whereas ‘heat’ is not coupled to any such change. But we should be careful to note the relationship doesn’t precisely go backwards; friction for example, doesn’t do any ‘work’ at all, even though the force is coupled to a change in momentum. So not all couplings are work or ‘work’, but all ‘work’ is couplings I think. This will be elucidated when we do the continuum description too.

***entropy change due to heat transfer***

Now let’s consider equilibrium heat transfer. When we add heat to a system (in such a way as to keep the other system parameters X the same so that there is no work associated with the heat transfer) there will possibly be an entropy change to the system associated with the mere fact. But there will also be an entropy increase due to internal changes as well as the heat distributes itself throughout the system. We want to isolate the entropy change associated with the external heat transfer process from the internal changes associated with the heat dispersal.

So to that end will consider quasi-equilibrium heat transfer so that the internal changes are negligible to non-existent. Quasi-equilibrium heat transfer would happen when no temperature gradients and concomitant density or pressure fluctuations are induced in the gas. And this could be effected by having the temperatures of the two substances the same (or nearly the same). So let an amount of heat Q be transferred from one substance to another in this fashion. Then this is a reversible process. And so the initial entropy must be equal to the final entropy. And so the changes in entropy must be equal and opposite. Now one substance gains heat Q and the other loses heat Q. So we can say that S(Q) + S(-Q) = 0. This means that the function S(Q) must be odd. We will not propose what this function might be per se´. But all we really need is to know what S(δQ) is. Then we can then integrate to get S for finite Q’s. Since then we’re only looking for S at infinitesimally small values of δQ, it is appropriate to expand this unknown function in a Taylor series. So we can say S(δQ) = S(0) + S´(0)δQ + (1/2)S´´(0)(δQ)2 + … Oddness requires that S(0) = 0, and we can simply keep the first term so we get S(δQ) = S´(0)δQ. We don’t know what this coefficient S´(0) is, but let’s call it 1/T. And so then we can say that the entropy increase dS = δQ/T. Now we are not saying what this parameter T is, though it will later turn out to be the temperature of course (or more precisely the temperature of the boundary of the system if it is not at equilibrium). Note that we can say this parameter must be an intensive parameter because our argument above applies regardless of the size of the two systems – we would have to get the same parameter.

***Adding it all up***

Putting everything together we have:



where I(k) is the particle current, T(k) is the temperature of our species of course, and δQ(k) is the heat absorbed (or given off) by our species. Dividing by dt, we have:



Really we should put (k)int in the energy balance with the (k) guy too as it’s like a heat term.



If we add chemical reactions, then we’d say:



And then including irreversible processes internal to species k,



Note int. would account for the non-equilibrium processes that take place inside the system of species (k) particles. The second law requires that this term is ≥ 0. And moreover, it is always increasing towards its maximum possible value consistent with external constraints – like total volume, energy, particle #, etc. And this is our entropy balance equation. If did balance on all species, by basically adding up the entropy balance S(k) for all species, then we’d have:



But then we’ll just note that the chemical reaction term and Sint(k) term would both be internal to the system now. And so really they could be combined into one Sint, and we’d write:

