**The Laws of Thermodynamics**

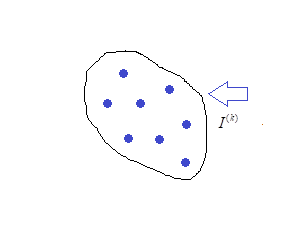
In classical and quantum mechanics one studies the laws of motion for particles, or systems of particles, though typically small in number (or at T = 0). One can attempt to apply these theories to the particles comprising a system of a large number of particles, say on the order of 1023 or so. But you would be quickly overwhelmed by the complexity of the task. So certain simplifying assumptions would have to be made, and much thought given to how to proceed, and what constitutes useful knowledge. This is the realm of statistical mechanics, which will be covered in the second half.

For now however, we will content ourselves with a less ambitious, though fruitful approach: thermodynamics. This approach was historically prior to statistical mechanics and is more broadly applicable. Plus it is the field from which statistical mechanics gets many of its ideas. Thermodynamics proceeds by examining the behavior of a system of particles from the outside in, instead of the inside out. That is, it examines the outside forces acting on the system and attempts to say something about its subsequent behavior, without presuming very much, theoretically at least, about what is going on inside the system. Actually, it generalizes the scope of interactions between systems from just forces, to forces, heat, and particle transfer. The basic tools at its disposal are a couple quasi-conservation laws.

So let’s consider a set of particles, with species enumerated by index k and masses mk, charges qk, moments of inertia Ik, etc. We’ll say that they have a position **r**k, and velocities **v**k and **ω**k. And we’ll suppose that these experience external conservative and non-conservative force fields. The former may be some electromagnetic or gravitational field, while the latter could be the walls of a container perhaps, either in the form of a normal force, or frictional force. We’ll also suppose that there are interaction forces acting between these particles.

**Particle balance equation**

Let’s consider the number of particles of species k in a volume. The particle number may change via particle flux into or out of the volume, or additionally via any chemical reactions that create such particles in the interior of the volume.



Basically we can say,



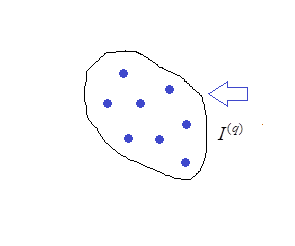
where I(k) is the net particle current of species k into the volume. What if we have chemical reactions going on? Suppose we have a chemical reaction like this:



In that case the particle numbers can change even if there is no flux from the outside. To handle this scenario it is useful to introduce the concept of *extent of reaction*. The extent of reaction, ξ, is simply the number of reactions that have taken place. If ξ reactions take place, then *aξ* particles of A will disappear, *bξ* particles of B will disappear, *cξ* particles of C will appear, and *dξ* particles of D will appear. So then if the rate of reaction is R = dξ/dt, then the rate of particle creation for the four species respectively will be -aR, -bR, cR, dR. –a, -b, c, and d are called the stoichiometric coefficients of the respective species. These coefficients are generically symbolized as νk. So then if we have perhaps multiple chemical reactions taking place, we may write our conservation equation as



A related balance equation is the charge balance equation. Sometimes, there are conserved quantities, like mass, or electrical charge, or baryon number, etc. Usually it is also the quantity which couples the particle to the field and results in the force the field exerts on it. I’ll call the charge q. Basic idea of this equation is that there is no ‘source’ term for conserved quantities.



Basically we can say,



**Volume balance equation**

It would seem a little strange to have such an equation, I suppose because we usually consider the volume of our system to be fixed. But nonetheless it could change, and there are examples I’ve done (later) where it does change. In any event, I’ll just say:

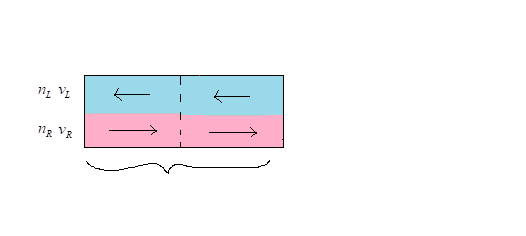


**Momentum balance equation**

Now let’s consider a momentum balance on the system. There are three ways that momentum can be transferred to a group of particles. It can flow in from the boundaries, be generated or attenuated by a force, or be created/dissipated by interactions with another set of particles (we’re not writing a balance for) inside the control volume. Or could have some sort of chemical reactions occuring which change identity of particles and perhaps impart momentum to certain species in the reaction. So basically we can say:



**P**I is the momentum current across the surface, i.e., the average momentum of the particles crossing the surface × rate at which particles cross the surface. **Π** is the pressure (might call this **π** when I feel like it), which is either an actual force exerted on the system’s surface boundary or a diffusive momentum flux if surface is not present/is imaginary. The microscopic definition of **Π** is given in next file. But basically it is the momentum passing across the system’s boundary surface, in the frame of reference in which there is no particle current crossing that system’s boundary. Delving a little deeper, Π will only exist if there is some spread of particle velocities about the mean particle velocity – i.e., some going right and some going left w/r to the mean. For instance, consider a section of gas below. We could have 10 particles, all with mass m = 1, and speed 5m/s going right, and 10 particles, all with mass m = 1, and with speed 5m/s, going left (these particles are displaced vertically from one another for clarity, but not in actuality). Then the net current at any given point would be zero. But at any given point within our compartment – say at the dotted line, the momentum flux would be non-zero: (10)(5)(5) + (10)(-5)(-5) = 500.



And can see we get the same momentum flux across the dotted line regardless of whether the pink particles reflect off of it and reverse left (then we’d have physical pressure force), or whether they go straight through, and leftward ones on the other side of the dotted line also go straight through (then more like diffusive momentum flux). Should keep Π distinct from the *equilibrium* pressure p, which only equals Π when the substance is in equilibrium, obviously. **F** is some bulk force coming from whatever fields are present. Note the force may come from external fields, the neighboring bulk, or surface forces. ­­int(k) is a source term that accounts for momentum transfer to other particles within the volume (while total momentum within the volume must be conserved if the system is closed – i.e. no I or F – the momentum of an individual species of particle need not be). And the last term accounts for chemical reactions: i is the rate of the ith reaction (# per second), νi(k) is the number of (k) particles which are created for each reaction, and **P**i(k) the momentum carried by the particle in the reaction.

**Angular momentum balance equation**

An angular momentum balance equation is also sometimes a useful thing to have. So basically we can say:



**L**I is the angular momentum current crossing into the system, i.e., the average angular momentum of the particles crossing the surface × rate at which the particles cross the surface. **Λ** (sometimes called **λ**) is the torque pressure (for lack of a better word) exerted on the system boundary, or a diffusive angular momentum flux if surface not present/is imaginary. Again, a microscopic definition of Λ is given in the next file, but basically it is the angular momentum passing across the system’s boundary surface, in the frame of reference in which there is no particle current crossing that system’s boundary. And this will only exist if on average the particle going faster than the mean velocity have a different angular momentum than the ones going slower. **Τ** is the net torque acting on the system coming from external fields. int(k) accounts for interior angular momentum transfers between particles in the system and other particles not in the system, but in the same volume. Should include the torque, if any, that we exert on the system to add new particles. And the last term accounts for chemical reactions: i is the rate of reaction (# per second), νi(k) is the number of (k) particles which are created for each reaction, and **L**i(k) the angular momentum carried by the particle in the reaction.

**Energy balance equation (1st law)**

Now let’s look at the energy conservation equation. This also known as the first law of thermodynamics We can say something like:



EI is the energy current – energy brought in from particles entering or leaving our volume of interest – E is the energy per particle entering, and I is the particle current. But it is not the *total* energy flux into our volume through the surface.

dWS/dt is the rate of work done on the system surface from forces like ΠS, or, if the surface is imaginary, from the rate of energy flux across the surface due to diffusive momentum flux across the surface. If there is an actual surface, it can be written as WS = Π + Λω where Π is the pressure exerted on the surface, the rate of change of volume enclosed by the surface, and Λ is the torque exerted on surface and ω the rate of rotation. Or if the surface is imaginary, could write this as S = ΠVI + Λω, where V is the volume per particle crossing the surface, and I the current crossing the surface (need this alternative definition to accord with what we get from continuum analysis). This could be interpreted as the work required to push the particle(s) through the surface and into substance. Can think of it like that example where we have a container of gas that is inserted into another larger container of gas. The energy added is not merely the energy of the particles, but also the work required to insert them into the larger container. Note again, Π need not be the equilibrium pressure of the gas, rather Π is the *actual* pressure of the gas exerted on that surface. Nor must Λ be the equilibrium torque, if there can be such a thing.

Next we have dQS/dt. This is the energy flux through the system surface which cannot be accounted for via mechanical work or particle influx. Say we have an actual surface, then we can go the frame of reference (i.e., adjust our velocity) so that we’re moving at the same speed as that surface. Then first of all, there would be no particle influx since we have a surface, so EI = 0, and second of all Ws = Π = 0 because V is constant. Or say we only have an imaginary surface. Then adjust the velocity of our frame of reference so that it matches the rate of particle flux, I. Then we will eliminate the EI term (because I = 0), and the Ws = ΠVI term would likewise be zero. And so in either case, any residual heat transfer will be from heat (well, if we also eliminate the angular mechanical energy transfer too). How can we be in a frame of reference where particle current is zero, but still have net heat transfer, say to the right? Well in our frame of reference, we’d have equal number of particles going right vs. left. But apropos translational kinetic energy (heat) transfer, the ones, say, going right, would be faster with lower density than the ones going left. So we’d have nRR = nLL, but R > L. And so the kinetic energy (heat) transfer rightward would be nRR3 which would be greater than that going leftward nLL3. If we’re dealing with energy transfer via angular momentum transfer, then we don’t need different speeds, just that ωR is different than ωL, say.

Apropos WB, this is just the work done on the system via some external force (field) that manifests itself through a *net* macroscopic force (or torque). Bulk heat would be work done on the system via some external force (field) that doesn’t manifest itself through a net macroscopic force or torque. The latter could be caused by external fields which produce *random* or extremely quickly spatially or temporally fluctuating forces that don’t therefore manifest themselves as a *net* force or torque on any appreciable macroscopic time interval (which would then manifest as a net change in V, or **P** or **L**), but do result in net work being done nonetheless. At a microscopic level, this could play out as follows. Let’s say we have a macroscopic object composed of a bunch of smaller constituents. And say that each of these constituents is moving with velocity vi(t). And each experiences a force Fi(t). Then the power delivered to these guys would be:



and moreover, the time averaged power (averaged between say t and t + τ, where τ is a macroscopically small time, but microscopically large, say around a microsecond or something) would be:



Now let’s split the force and velocity up into two parts, an average and a fluctuation about the average.



Now then we’d expect to be smoothly varying with time and basically constant on the timescale (t, t+τ), wheras i(t) we’d expect to be rapidly fluctuating, presumably, within that time-scale. And same with **v**(t). Then let’s revisit the time-averaged power,



So then basically the first term we’d identify as dWB/dt, and the second as dQB/dt. Penultimately, the int term accounts for energy transfer to other particles within the volume – perhaps one should consider this a heat term rather, but whatever. And then we have the chemical reaction term thing too. FWIW, the two W terms are usually combined into a single ‘W’, and the two Q terms and Eint term are usually combined too into a single ‘Q’. So that makes the equation a little more succint. Last, the chemical reaction term is a follows: i is the rate of reaction (# per second), νi(k) is the number of (k) particles which are created for each reaction, and Ei(k) the energy carried by the particle in the reaction.

What is energy? Energy is a somewhat ambiguous object. But we should consider E to be the energy inherent within object/system itself. This will be just the sum of its constituents kinetic and potential energies. Regarding potential energy and fields, if we want to include fields within the description of our system/object, and the fields are *constant* throughout the considered motion of the system/object, then we need not include the field source within the system. We just consider the fields to provide a source of potential energy for the object. But if the fields are changing with time, being turned on/off, then certainly we must encompass the field and its source within the system. Otherwise, we can jettison the field from the description of our system entirely and just consider it to be a means of external work, but not a source of ‘energy’ per se´.

**How to calculate work**

We can elaborate on the work term a little bit. The work accomplished by a force can be calculated via the familiar formula:



There are many ways that work can be done on a substance. Work can be performed by someone pushing or pulling on the object, or by gravitational or atmospheric forces. Work can also be done via electric forces. When we immerse a substance in an electric field, it can cause charges in the substance to move, and so work will be done. It can cause the charges inside an otherwise neutral molecule to separate, and so work can be done creating or changing a net dipole moment in the substance. Work can also be accomplished indirectly by a magnetic field, via the electric field it induces upon change (Faraday’s law). It is not worthwhile to develop a general all-encompassing formula for these different kinds of work. So we will mostly analyze it on a case by case basis, increasing our complexity as necessary. But here are a few cases that generally span the breadth, if not depth of the work possibilities. You will notice that work can be written in general as the product between an external ‘force’ term and an internal ‘structure’ term.

***Normal work***

Can’t really think of term for this. But if you exert a force **F** on an object and it moves a distance d**r**, then the work done is:

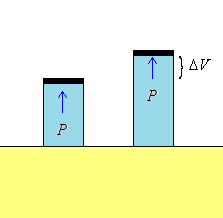


or if rotating an object, then we could alternately write:



***Pressure work***

An important special case is the work done on a gas by a pressure.



Suppose we have a gas in a piston of cross section area A, and that it forces the piston to rise a distance h, at constant pressure. Then the work done by the gas is



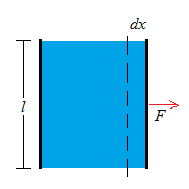
More generally, if the pressure changes as the volume changes, then our formula would only apply infinitesimally:



It is important to note that this pressure P is the pressure of the *gas*, not the pressure (necessarily) that we exert on the lid. These will not be the same if the piston is accelerating, or even if it is moving with constant speed (because of extra force of gravity). One possibility that we needn't generally consider is if the pressure on the surface of the substance isn't uniform. This introduces a simple modification of our formula. Finally pressure could be uneven of the surface of the piston, especially if the system is not in equilibrium. In that case we’d have to modify the formula a bit to take that into account.

***Surface work***

Another mode of work is surface work - the work required to expand a surface by some amount dA. This is relevant when analyzing drops, etc. The work required to expand a surface by dA is,



δW = Fdx = (F/Ɩ)Ɩdx = γdA. Note γ = F/Ɩ is defined to be the tension in the film. So altogether we have:



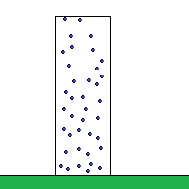
Again, the tension may be uneven over the boundary of the film, but this could be accounted for by modifying the formula.

***Gravitational Work***

Not like this happens a lot, but we could somewhat change the gravitational field in the vicinity of particles. As we do, their mass density distribution would change. And over an infinitesimal time interval δt, the work done by the field would be:



(can see the Random file at end of CM folder for this)

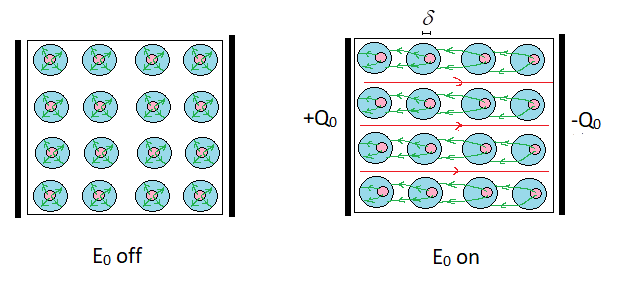


***Electrical work***

Another important case is electrical work. Suppose our substance has some free charges and is immersed in an electric field E, with resulting potential Φ. Then the work required to move an amount of charge dq through that potential would be:



We could have more complicated situations where not all the charges travel the same distance, and through different potential differences, but we'll deal with that when necessary. Here's another case. Suppose we have a polarizable sample, with some free charges available for distribution as well. And we are interested in calculating the external work done on the bound charges as we move the free charges into some arrangement. The typical application would be to a capacitor or something, as illustrated below.



The material will have some internal energy partly manifesting as a net electric field within the molecule itself, at least if we model it as a positive nucleus surrounded by a uniform electron cloud. Then when we arrange some free charge on the plates, a free electric field will be set up, which will polarize the molecules and alter their internal potential energy – can either think of it as by altering the electric field these molecules possess, or as by ‘stretching’ a spring like bond. Either way works. The bound charges will also interact with each other, to set up a mutual repulsion. Anyway, as elaborated on in the EM folder, the work the free charges perform on the bound charges in the dielectric would be (and this presumes a geometry where we can say that the field produced by the free charges is **E**f = **D**/ε0):



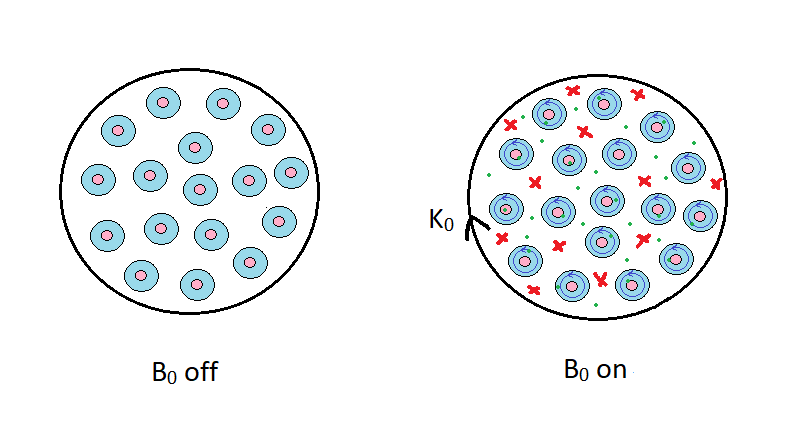
where P is the polarization density. And we can use **D** = ε0**E** + **P** to put this in terms of E and P or whatever, like we have in EM file. If we’re interested, rather, in treating the whole system as system as constituting the *free* and bound charges, then the work required to polarize everything, create the bound field, and create the free field would be (see EM folder again):



This formula is true regardless of whether **E**f = **D**/ε0.

***Magnetic work***

And suppose we have a magnetic material in an ambient magnetic field, supplied by a current (K0) maintained by an emf I suppose. In picture below I’m intending to convey a dimagnetic material inside a solenoid (top-down view). When we start up the current to set up the free magnetic field, it will magnetize the dimagnetic.



And the work done on the dimagnet, as covered in the EM folder/Insulating Energy, is:



where **H** = **B**/μ0 – **M**, and **M** is magnetization density (this formula presumes a highly symmetric situation, like solenoidal geometry, where can say that **B**f = μ0**H**, and **B**f is field produced by the free charges). Either way, note this work term does *not* include the work required to set up the free magnetic field itself, i.e., (1/2μ0)∫B2dτ. If we wanted to include such work, which we’d have to do if we wanted to consider the field as part of our system, then we’d get (see same file):



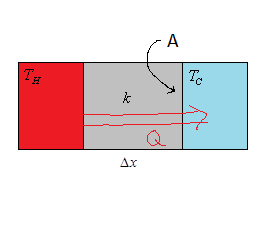
And we could insert **H** = **B**/μ0 – **M** to put in terms of the field and magnetization if desired. This formula is true regardless of relationship between H and Bf.

**How to Calculate Heat Transfer**

So apropos surface heat transfer, there’s a variety of formulas pertitent to different situations. Non-equilibrium Thermodynamics can be used to guess their form somewhat, and non-equilibrium Statistical Mechanics can derive them, but for us right now, I’d say these must be calculated experimentally. There are five general cases associated with this sort of microscopic work, aka, heat.

***Conduction***

The first is conduction. Suppose you have a hot object at temperature TH and a cold object at temperature TC separated by a thermal insulator with thermal conductivity k, cross section area A, and length Δx. Then the hot object atoms will collide with the insulator atoms, thereby doing work and transfering energy to them. And then the insulator atoms will collide with the cold atoms, doing work and transfering that energy to them.



The rate of energy transfer is roughly proportional to cross sectional area A, which would be proportional to the number of atoms in the cross section of the insulator, which is the number of atoms in the insulator able to absorb heat from the hot object. The rate of energy transfer is also proportional to the density of the material, the mobility of its atoms, etc., a factor encapsulated by *k*. And finally it would be proportional to the difference in temperature of the nearby layers of the insulator (if the nearby layers were at the same temperature, then no energy would be imparted during collisions). This is captured by the temperature gradient ΔT/Δx = (Tenvironment – T)/Δx. Altogether then, we have the rate at which heat will be transferred to the cold object is:

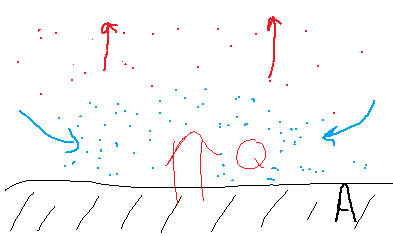


Some typical thermal conductivities are:



***Convection***

This process occurs when a colder fluid is in contact with a hotter object. The hotter object will make the fluid in contact with it hotter, causing it to expand, and then by Archimedes principle, rise upwards. Then as a consequence, colder fluid will take up the partial vacuum creating by the rising hotter fluid. And then the process will continue.



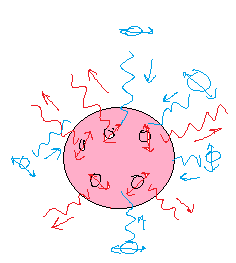
Thus we get a situation of rising thermal fluid currents. This happens in the Sun, and in the air. Birds will often seek these thermal currents which will help keep them aloft. The rate of heat flow via convection is given by the following *approximate* formula:



Again, A measures in some sense the number of fluid molecules in contact with the hot object. *h* is the convection heat coefficient, which typically depends on the density (water is a better convector than air) and mobility of the fluid molecules. And ΔT = Tenvironment­ – T is sort of again a measure of how much energy is being transferred per collision between hot object molecule and fluid molecule. Convection is often a faster method of heat because of the greater mobility of the atoms.

***Thermal radiation***

Another form of heat transfer is via EM radiation. These types of waves occur when charged particles oscillate back and forth, and the waves that they create are called electromagnetic waves – you’ll learn about them in PHY 133. These waves carry off energy. And the amount of energy they carry off is, for quantum mechanical reasons, proportional to T4. For instance consider the air molecules at temperature Tenv., vibrating back and forth and radiating EM energy, proportional to Tenv.4. An object in the vicinity (depicted below) will intercept this radiation and aborb some of the energy. The energy it would absorb would be proportional to its surface area A, as well as its emissivity (basically the amount of this radiation that it absorbs rather than reflects: for instance a black shirt has emissivity ε = 1, whereas a mirror would have ε = 0 at least for EM radiation in the visible spectrum). And so the energy it absorbs would be proportional to εATenv.4. On the other hand, the object is at its own temperature T and will thereby be radiating energy away from itself at rate εAT4. And so the total energy coming into the object will be proportional to the difference of these two terms:

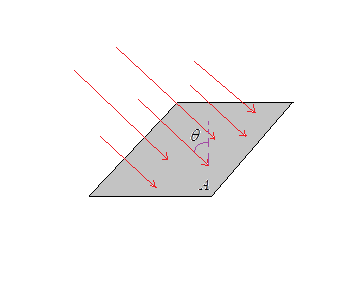




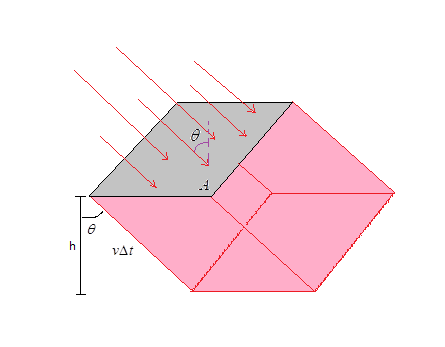
where σ is the Stefan-Boltzman constant.

***Solar radiation***

Not all radiant energy intercepted by the object must come from its immediate environment. For instance, if you stand outside, you will absorb radiant energy from the surrounding air molecules (the immediate environment), and you will also absorb radiant energy directly from the Sun’s rays as well. We can conjur a formula for the energy (heat) absorbed by a surface with area A, intercepting radiation incident upon it at angle θ w/r to its normal.



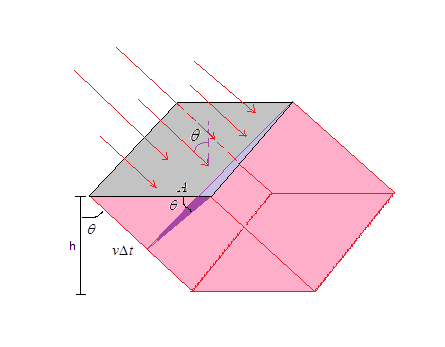
And we do it like this. Consider the radiation to have energy density u (that is, energy per unit volume), and to be traveling at some speed v (if it’s EM radiation, then v = c = 3×108m/s). Then if the surface were a perfect absorber, the amount of energy, ΔQ, that it would absorb would just be equal to u × volume of radiation absorbed. The volume absorbed would be



V = Ah = A(vΔtcosθ). And so the energy absorbed would be uA(vΔtcosθ). And so the rate at which energy (heat) would be absorbed would be ΔQ/Δt = uA(vΔtcosθ)/Δt = uv∙A∙cosθ. The product uv is called the ‘intensity’, I, of the radiation, and has units (J/m3)(m/s) = W/m2. Given that definition, we can write:



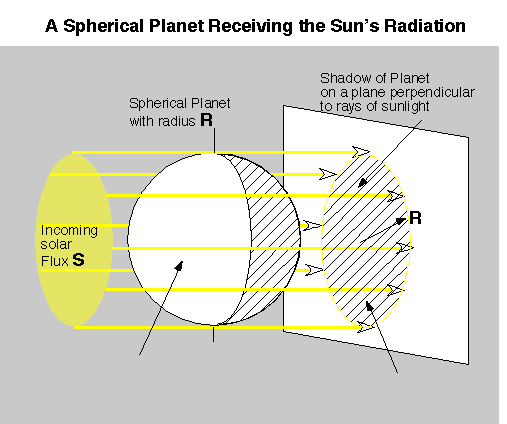
Another way to think of this formula is to consider the term Acosθ. This represents the portion of the area that is perpendicular to the radiation, feebly represented by the purple rectangle.



and so we could write:



The utility of thinking of it this way is that sometimes, our object is not flat, but rather has a curved surface, like for instance the case of the Earth intercepting the Sun’s radiation. In this case, to get the rate of energy intercepted, we will realize, without having to do 2 dimensional integrals, that it is given by the product of I and the area of the surface which is perpendicular to the rays, i.e., the cross sectional area.



So that in this case:

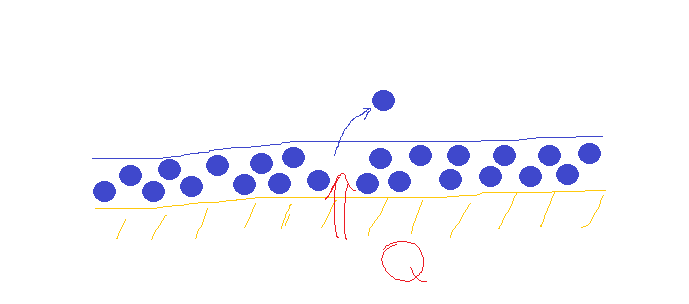


Finally, it may (usually does) happen that some of the energy intercepted is not necessarily absorbed, but may be reflected back. So let ε denote the fraction of energy absorbed (note this ε is usually a different value than the thermal radiation ε), and then we can write:



***Evaporation***

Another way that heat may be lost, similar to conduction, is evaportion. This is one of the main mechanism by which humans lose heat. Basically what happens is this. The water molecules on your skin will be at the same temperature as your skin. But not all water molecules are moving with the same speed. Some will be moving faster than average and will be able to break free of the surface tension holding the liquid water together. When this happens, then the water will consequently drop to a slightly lower temperature than the skin below it. And so then heat will conduct from your skin to the water, raising its temperature back up to the skin temperature.



Then this process repeats until basically all the water is gone. We can estimate the amount of heat lost given the mass of water evaporated. Since basically evaporation is boiling water, one molecule at a time, we can say:



where dm/dt is the rate (in kg/s) at which water is being evaporated, and Lv is the latent heat of vaporization, i.e., Lv = 2256 kJ/kg.