**Laws of Thermodynamics: Continuum Description**

So the balance equations were presented in a sort of ad hoc manner in the first two files. And it’d be nice to put them on a firmer mathematical ground (at least somewhat). Might want to check out the the statistical mechanics folder’s distribution function file for some complementary insight on the statistical description of a system of particles. What we do below parallels it, but also stands alone.

**Defining Thermodynamic Average as Running Time Average**

Now let’s move to a continuum description. I’d like to derive a continuum version of the balance equations starting from a statistical description of Newton’s laws, basically. We’ll have to think more carefully about what exactly N, V, P, L, E, S, etc. mean. These values will fluctuate, in general, due to external forces, and/or external flows. And yet we will, when considering equilibrium systems for instance, propose to characterize the system’s N, P, L, E, S, by a single number. I would argue that this number is the time average of these variables, over an appropriate time interval τ. Time average is defined as:



for instance, a density function, and momentum density function would be defined as:



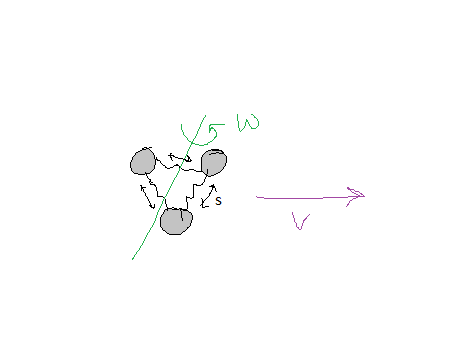
where **r**i(t´) and **v**i(t´) are the position and velocity of the ith particle in the system. We’ll be interested in temporal and spatial derivatives of these quantities. As for time, I think we can say:



Just to illustrate, if we let f(t) = fθ(t), where θ(t) is the step function, then have:



When are these operations okay? I think our functions have to be probably piece-wise continuous? However I don’t think there is any requirement that τ be small in any sense. So let’s consider an aggregate of particles. I’ll say that each particle can be characterized by its species k, a mass mi, generalized charge ci, moment of inertia **I**i. I’ll say that they have position **r**i, and orientation **θ**i, as well as velocity **v**i, and angular velocity **ω**i. And finally also some internal states I’ll label as *s­i*. And finally they may interact with each other or with external fields. Obviously, by the drawing I mean to indicate that a ‘particle’ may be a composite of more fundamental elements.



**Particle balance**

So then let’s consider the time-averaged density of particles of species k at time t and position **r**. Let the positions of all particles of species k be **r**i(t). Then we can write this as:



Taking the derivative, we would have:



We’ll define the current density **j**(k)(**r**,t) as:



Now it’s customary to define the ‘entropic’ velocity, **v**(r,t), as the velocity about which velocity fluctuations, averaged against the density (delta function thingy), are zero, so that one can say:



And so it obviously follows from this definition that:



And either way, we come to,



If we have multiple chemical reactions taking place, defining = R/V as the # of reactions per unit volume per unit time, we would write:



So we see the particle density, current density, and particle balance equation emerge naturally, which is nice. Now let’s consider a charge balance equation. This wouldn’t be an equation pertaining to an extra d.o.f. per seˊ, so I won’t give it a separate heading, but it would serve as a constraint on the particle equation. And basically, it should find itself embedded in the chemical reaction term in the particle balance. Charge density would be defined as:



where ci is the ‘charge’ of the ith particle, and c(k) is the charge of the species k. Taking the derivative, we would have:



So then defining the last term as the charge current, **j**c(**r**,t),



and so altogether,



I think that typically, this equation will reduce to a linear combination of particle balance equations, perhaps with the restriction that the chemical reaction terms must conserve charge, which of course they would. So we may think of this equation as more like a constraint on the general particle balance equations.

**Momentum balance**

Now let’s work out a momentum balance equation. The time-averaged momentum density for species k would be defined as:



So we have:



where the index i runs over all particles in the system of species k and m(k) is the mass of particles of species k. And so momentum density can be thought of as a mass current, interestingly. Note that with this result, we have the entropic velocity satisfies: **v** = <**P**>/<M> = <**P**>/m<N>, which we ascertained from the Thermodynamic Potentials file. Now differentiating (the first expression for **℘**),



The first term is the momentum transfer out of the system, **j**k**p**.



We can split this up into a convective and diffusive part,



and that middle term is zero because velocity fluctuations about the entropic velocity, modulated against the density, are zero, as stated above. The first term is the convective momentum transfer. The second is the diffusive momentum transfer. Alternatively, if we’re dealing with a scenario where the particles are not freely diffusing into the next differential segment, but are rather uniformly repelled by it back into their original segment, then the second quantity is called the pressure tensor (well it’s usually called the pressure tensor either way). And it would give the momentum transferred to the next segment via the force it exerts on it. Either way, whether by particle flux or force or a mixture of both, this last term captures the concomittant momentum transfer. And so we could write:



As for the force term, I think we can distinguish two sources. One would be field forces coming from the bulk external to our system (i.e. our differential control volume). An example we’ll cover later would be that of electric field forces originating from one part of the plasma being exerted on another part of the plasma. Another example would be an external field force like gravity. Another source would be internal forces coming *other* species of particles inside the control volume (don’t include forces from same species because we know these cancel overall). Another possibility that might occur to one is nearby contact forces from particles immediately outside our system. But net momentum transfer via collisions is zero (see statistical mechanics folder for this – conservation laws) and in any event, this is captured by the pressure tensor. So,



Note these forces could in principle depend on all the parameters of the particle, not just it’s position **r**i(t), but also its orientation **θ**i(t), velocity **v**i­(t), angular velocity **ω**i(t), and even internal state si. But I will suppress these parameters in the notation since we will be taking no time-derivatives with respect to them. Also, going to change notation of Ffield to just F, so as not to exclude possible non-conservative, but field-like, forces acting on our particles. The internal force would be some sort of force coming from other particles (often impurities) within the differential volume we’re averaging over. I’ll do each of these in turn. So for the field force, let’s split it up into an ‘entropic’ force average and a fluctuation about it, defined to be zero, when averaged against density. Then we can say:



And then for the last term, the internal force, I’ll just call it a momentum sink. We cannot be any more specific because we cannot grid up what is already our smallest differential grid piece.



So then altogether, we have:



and so more concisely, adding some chemical reaction stuff – **p**i is the momentum imparted to (k) species particle from i reaction.



Note the contraction ∇·(**℘v**) is against the v, so in components, ∇j℘ivj.

**Angular momentum balance**

Now let’s consider angular momentum. Angular momentum density would be defined as:



where the index i runs over all particles in the system of species k, and I’m imagining the angular momentum as a bunch of local spinning molecules or something, whereby we can represent **ℓ**i as **I**i∙**ω**i, where **I** is the molecule’s moment of inertia and **ω** its angular velocity. We can define an ‘entropic’ angular velocity perhaps, the same way we did translational velocity.



similar to the definition of the entropic velocity. With this, we may then write:



The middle line serves as a definition for **I**(k)(**r**,t). So we have:



Anyway, differentiating, we’d have:



The first term is basically the angular momentum transfer out of the system, **j**k**ℓ**.



As usual we can bother to separate the current into a convective and diffusive part by separating the velocity into an entropic part and fluctuations about, if we wish, though nothing special seems to come of it:



The last term would alternately function as a sort of surface torque, analogous to the pressure guy, if there is no diffussive angular momentum flux from our differential segment due to some sort of ‘repulsion’ at the boundary. Either way, via diffusive flux or force/torque, we have the surface torque tensor:



I suppose this could be non-zero. Would have to be to exert surface torque. But can see that it would be equivalent to such as one way it’d be non-zero is if ℓ were + for going in towards surface (+) and ℓ were (-) for going back out away from surface (-). So we can write:



As for torques, I think we can just do it like we did for forces.



and of course I’ll do each of these in turn. So for the field torque, which I’ll redesignate as simply τ, can do similarly as above and *define* an ‘entropic’ torque according to **τ**field(i) = **τ**(**r**,t) + i(**r**,t)

so that:



Could further say **τ**(**r**,t) = **r**×**F**(**r**,t), where **F** is the average force from above, if our volume υ is small enough that a single position is more or less isolated. And then for the last term, the internal torque, I’ll just call it an angular momentum sink, in analogy with what we did for the momentum balance equation.



Again the dependence of the torques on most variables is being suppressed. And so now we have, adding in the chemical reaction term too,



where **L**i(k) is angular momentum imparted to k-species particle from (i) reaction. Looking at the definition of λ, I’m thinking that it’s probably zero, due to the probable fact that ℓi and i are independent variables and the latter averages to zero. Note contraction of ∇·(ℓv) is with v, i.e., ∇jℓivj.

**Energy balance (1st law)**

Now for the really complicated one: the energy balance. Here the particle’s internal parameters will play a non-irrelevant role. So we’ll define the local energy density of species k as:



εs is some term which describes internal degrees of freedom. Here φ is an external potential (which must be time-independent by definition), and Φ is the potential term for the interaction fields, and it’s implicit that i ≠ j. I haven’t explicitly indicated the dependence of the potential on the orientations, θ, and internal variables, s, but this dependence will be accounted for when we take the derivative. Also, Φ(|r-r´|) must implicitly decay fast enough so that energy is an extensive parameter, otherwise we cannot really take a subset of particle within an interacting system, like we’re doing, and declare that the subset’s interaction energy *only* involves the interaction between the particles in the subset. Will also note that borrowing stuff from our momentum analysis we can write, at least for the translational kinetic energy:



The first term could be considered a convective, or bulk, kinetic energy associated with movement of the volume element as a whole. The second term would be fluctuations about that – a sort of internal kinetic energy. And so the total energy can be written as a bulk convective (kinetic) part and an internal part:



where,



u would be the energy of the piece in the ‘entropic’ rest frame of the piece. Anyway, differentiating,



Now the first term can be interpreted as the energy transfer out of the system,



and as per usual, we can write it as a convective and diffusive part:



The convective part tabulates the flux of energy across the system boundary via particle transfer (really just the convective part of particle transfer). The diffussive part can be broken down further into interesting pieces. Consider first the translational kinetic energy part – will assume all particles of same species have same mass:



The first term is zero because of the definition of the average/entropic velocity. The two middle terms in the first line’s product combine to give the second term, which we’ll recognize as the pressure tensor, dotted into the average velocity: **π**·**v**. And the last term we’d recognize as (part of) the heat current, **j**q since it is energy transfer associated with no net velocity. So we can say so far,



where,



**j**extra is close to being the heat current because it is the energy transport in the frame of reference where v = 0 (indeed just go back to **j**ε and set v = 0 and we get jextra). But we need to extract the mechanical rotational work term from **j**extra, right? I want to get from this a term of the form **λ**·**ω**, the rotational analogue of **π**·**v**, but it doesn’t seem to want to come out. Still it must, I think, as we run into entropy balance problems in the NETD formalism if we don’t get it out, and it also doesn’t jive well with our conception of heat as the energy delivered to the object via work which *doesn’t* go into mechanical energy. Hmmmm. So I’m just going to take it out by force. We’ll say,



where,



Pretty sure the φ and Φ terms should decouple from the average, generally speaking, as φ especially, and Φ probably, would just be a constant over the microscopic volume within which we’re averaging. But then we’d be left with the average over , which is zero. So I think we can say something like,



Maybe I’ll change my mind later? A little more explicitly, the angular part of the heat current would be:



Don’t know if that simplifies to anything nice. So the diffusive parts of the energy transfer comprise a translational/angular pressure term and a heat flux term. The pressure term more or less accounts for the energy increase due to a net pressure/torque exerted on the sides of our element. This is basically work. The net pressure would either increase the bulk translational/angular momentum (and thereby energy) via actual net contact force if there is a barrier of some sort between our compartment, or via net particle flux if not, or some combination of the two. The heat term would describe diffusive internal energy flux between either side of our compartment. Notice that it all depends on how the variables , , etc., are correlated with . If they are larger going towards the surface than go away, say, then heat/energy will be transported out through the surface. If larger going back than in, then heat/energy will be transferred inward through the surface. If uncorrelated, i.e., the same either way, then have no heat/energy transfer.

Now let’s look at the second term in the ∂ε/∂t guy. I’m going to define ∂ε/∂s as σ, some sort of generalized force. The σ, **F, τ** and terms will partially cancel, leaving the non-conservative σ, F, τ contributions. For instance, observe for a three particle system:



These non-conservative forces I’ll split into external forces (coming from fields outside the system) and internal forces (coming from particles external to the system but internal to the volume). I’ll call the generic external field terms **σnc**, **Fnc**, **τnc**. Note that strictly speaking, contact forces between particles outside and inside the system average out to no work done, as can explicitly see when we get to Boltzman equation in the stat mech folder. So we can ignore them as in the translational and rotational momentum cases. So then we have:



Now is when I would try to split the external field work terms into bulk ‘work’ and ‘heat’. So we’ll split the σ, F, τ terms, as well as the s and v guys, into their entropic averages and the fluctuations about them. I guess I’ll do this part by part. So first:



where I make the definition <δ> = n, analogous to prior definitions. And we’ll observe the cross-terms go to zero because by their definitions, the fluctuaty terms go to zero when averaged against the density. And apropos the F guys, I’ll split Fnc into the typical two parts: a possible non-conservative field term, Ffield,nc, which I’ll just rename as Fnc, and the internal force from other species Fint. So,



Again, we implicitly observe that the cross-terms go to zero by definition of the fluctuaty part (see definition of entropic velocity and entropic force, above). Despite a superficial resemblance to having split this term into a work + heat contribution, these terms aren’t necessarily either. Take for instance a block sliding on an inclined plane with friction. Friction works by stopping pieces of the bottom layer – and it actually does negligible work. The bottom layer atoms then exert forces on the rest of the block, slowing it down. But we’ll observe the two terms above would both likely be non-zero (but would cancel out) if we extended the control volume to include the entire block. For instance, the first would would have a non-zero average force for sure, and the velocity average is also non-zero, since we’re including in the control volume. So while there is no actual work, our formula would predict there to be. However, if we shrunk the control volume down to include only those constituents that were traveling at substantially the same average velocity, I think we could interpret that term as work, and the other as heat. And then for the last term, I’ll just call it an energy sink, like we’ve done for the analogous momentum and angular momentum term.



We can do similarly for the torque. Then we’ll combine the three fluctuating σnc, Fnc, and τnc terms together and call it an external heat source term: (k). And we’ll put the two force and torque int terms together as one. So then we’ll come to:



All these force and velocity terms are the entropic averages. I guess I’ll throw in a chemical reaction contribution too, and rearrange stuff:



**Entropy balance (2nd law)**

OK so last, let’s consider entropy. Maybe we can define:



where Si is the entropy per particle of that species. We must already be assuming that the particles are in some sort of local equilibrium in order to invoke such an entropy term. This is probably all wrong….but why should that stop us….differentiating we’d get:



The first term is clearly the entropy transfer across the boundary. Let’s split up the velocity into the entropic term and fluctuations about:



The first term would be the reversible convective entropy flux (actually, I don’t think we can reversibly add particles of the same species together, at least within a fixed volume whereby the density may increase and all. So if not then we’ll have to say whatever entropy flux this expression doesn’t capture must get shoveled into the non-equilibrium int term), and the second the diffussive entropy flux. Apropos the first term, we have already defined the entropy per unit volume as Σ<δ(r-r´)Si> = s(**r**,t). Don’t really have a formula for the second term, except that we know this contribution to be from heat flow at least (note for future interest that by integrating this term around the system volume we can see that it is the local temperature at the system boundary which determines what contribution to the entropy is made by the heat flux). So I’ll fill that in. Will also add that there is support for treating this second term as the heat current if look to the Statistical Mechanics folder/Entropy balance file. The term we define as the heat current looks pretty similar to what we have here.



Then the second term in ds/dt has a few contributions, one is from internal heat transfer [say from external field]/internal energy loss terms [say from collisions with other species of particles within the volume], and then the last would be irreversible internal entropy processes. So putting all these together, and customarily combining the two entropy currents together, and also chemical reactions, we’d have:



These identifications are heavily dependent on being able to treat the control volume as in local equilibrium.