**Specializing to Equilibrium Systems**

Continuing on from previous file,

**Other parameterizations of the entropy**

It is easier to measure S(T,Xj,Nk,ψi) than S(E,Xj,Nk,ψi), since it is easier to measure T, than to measure E. X and N are usually easy enough to determine. So formally, this is how that could proceed. Let’s work out the differential relationship for E(T,Xj,Nk,ψi).



So to get S(T,X,N,ψ) we basically need E(T,X,N,ψ) in addition to the equations of state pj(T,X,N,ψ) and chemical potentials μk(T,X,N,ψ). To get the temperature dependence of E, we can relate it to a heat capacity. The general definition of a heat capacity is this. The heat capacity of a substance, evaluated with parameters α being constant, is:



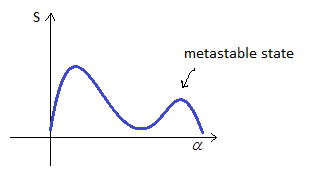
Looking at our dS equation, it is apparent that if α = X,N,ψ, then CX,N,ψ = ∂E/∂T)X,N,ψ. This heat capacity is easy to measure experimentally. Keeping Xj and N­k constant in the energy balance equations, we’d just have: dQ = dE, and so therefore we’d have C = dQ/dT (but be careful to remember that C is defined to be T∂S/∂T and is only equal to dQ/dT incidentally – S can change even if there is no Q, maybe via conversion of mechanical to internal energy). So to measure it we just add heat to the system, measure the increase in temperature, and take the ratio. Now is probably an appropriate time to mention that it turns out that C isn’t always well-defined. Across the phase boundaries it is ∞ as T does not change and yet E (and S) does. So let us introduce another quantity, called the latent heat at constant α.



One can verify again that if α = X,N,ψ then again L = ΔE. And from the energy balance, this would again be L = ΔQ (but this isn’t its primary definition.) For pure substances at least, it seems that L is usually independent of T and X. So this would give us the T dependence – in a manner of speaking – of E. And then we’d need to measure the other derivatives ∂E/∂X)T,N,ψ and ∂E/∂N)T,X,ψ which can be done in a manner similar to discussed above.

**Stability of the Equilibrium State**

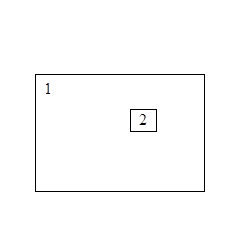
Consider a closed system. Then E, X, N, ψ are fixed, and so is equilibrium S, though perhaps there are fluctuations that will take it away from max S to a lower S. Some of these fluctuations might result in local max S states, and the system might even remain in the local equilibrium state for a while before eventually transitioning to the global max. Such states are called metastable states, illustrated below, where α is an internal parameter that tracks the possible internal states of the system in some sense, perhaps like temperature, pressure, or chemical potential gradients, or net magnetization in the case of spin systems perhaps. But note that such a metastable state would still be characterized overall by the same E, X, N, ψ as the true stable equilibrium state.



Metastable states are ones that are *locally* stable out to some orders in δE, δX, δN, whatever, but not the highest S, etc. in absolute terms – like a local maximum. Super-cooled or super-heated water is an example of a metastable state. And spin systems with a net magnetization in opposite direction of the field is another case. Still, these fluctuations must result in a lower entropy state. This mathematical requirement – that fluctuations indefinitely lower entropy – has physical consequences. Let’s consider them.

**Fluctuations in energy**

Consider a closed system, and let’s isolate a part of it (2). So we have S1(E1,X1,N1,ψ­), and S2(E2,V2,N2,ψ).



Let there be an energy fluctuation in the smaller one, but for now we’ll keep volume and particle number fixed. Then the change in entropy of the system is:



Continuing, we have:



OK. Now T­1 = T2 since we’re looking at fluctuations about equilibrium. And if fluctuations are to reduce the entropy, then we must have:



So thermal stability requires the specific heat capacity be positive.

**Mechanical stability**

Let there be a volume fluctuation in the smaller one. Then the change in entropy of the system is:



He says that we also assume T remains unchanged during this fluctuation. So it’s an isothermal fluctuation? OK. So then we have:



OK. Now T­1 = T2 since we’re looking at fluctuations about equilibrium, and p1 = p2. And if fluctuations are to reduce the entropy, then we must have:



where we’ve made the definition:



If X = V, then κT would be the isothermal compressibility. And since V must be positive, this would require κ be positive as well. What if X = **P**, then **p** = - **v** (due to sign in definition) and it’s a bit ambiguous. But suppose that the X’s are positive. This would require,



is positive as well. Does this mean no negative mass?

**Particle fluctuations**

Now we’ll consider fluctuations in particle number about the equilibrium amount. Such fluctuations can occur via transport or chemical reactions. We have:



and, which is:



As usual the first derivatives are 0. And so we get:



I would expect that these are proportional to N1k, N2k respectively. So I would say, as before



is the condition for stability.