**Appendix: Some Things To Know**

**Some Thermodynamics Stuff**

Suppose we have interrelated variables x, y, z, w. Let’s consider the following identities. First



Now consider:



Assuming we know what these partials are, what we’d like to do is find a formula for the derivative of one of the independent variables w/r to another independent variable. For instance, suppose we want to know how y changes with x if we hold w and z constant. Then we have:



So remember the general form:



OK, now let's consider another case where we have two functions u = u(x,y,z) and v = v(x,y,z). Then the total differential of the first is:



But now suppose that we want to consider u as a function of v,y,z instead. What is the total differential now? Well it would be:



But another way to compute the differential is this. Basically what we're doing is switching out the x for the v, and so we need to take v = v(x,y,z), invert it and solve for x to get x = x(v,y,z). And now form the total differential. It would work like this:



Now these two expressions for du in terms of dv, dy, and dz are identical. So we have the equalities...



This isn't really that abstruse. It’s just using the chain rule on the function u(v,y,z) and u(x(v,y,z),y,z). And equating the coefficients of the various respective differentials. The first case just gives us a way to switch out a derivative w/r to x for a derivative w/r to another variable, v (i.e. the chain rule). The second gives us a way to switch out an x constraint for a v constraint. So altogether,



Now to apply this stuff, partial derivatives encountered in thermodynamics frequently must be manipulated into a more manageable form. Our general goal is to reduce all derivatives to T∂S/∂T)V = CV or some variation on derivatives of p by N, V, or T which can be evaluated via the equation of state.

*Derivatives among conjugates (sort of)*

First let’s suppose that we just want to manipulate derivatives amongst p,V,T into a different form. Then we would use the cyclic rule. For instance we could make the manipulation…



*Derivatives of potential w/r to natural variable*

What if we have a derivative of a potential w/r to one of its natural variables, holding the other natural variable constant? Then we just use the Maxwell relation. For instance,



*Derivatives of potential w/r to unnatural variable*

What if the variable we’re differentiating w/r to and holding constant isn’t one of the natural variables? Then I would say write the potential in terms the potential with those natural variables, and then use Maxwell relations as necessary. For instance, consider ∂U/∂V)T. The potential whose natural variables are T and V is F. And so we’d write:



Then we’d use the F potential again, equating its cross partials to get: ∂S/∂V)T = ∂p/∂T)V. So then we have:



And consider another case. Since we’re differentiating w/r to T and holding p constant. This makes G the natural potential. So…



If we want to simplify Cp, we won’t find it from equating cross partials of Gibbs potential in this case. What we would like to do is switch out the p constraint for a V constraint. So that will require using the last complicated differential relation.

*Switching constraints*

We would have:



Then the last S derivative *can* be manipulated using a Maxwell relation from the Gibbs potential. And we have:



So now we have:



Filling this in…



When we talk about heat of reactions, it will be of interest to determine H(T,p). How could this be measured?

**Mathematical Properties/Definitions**

Start with these I guess,











Think of how <x|xʹ> = δ(x-xʹ) and then insert a complete set of states.







you can cyclically permute the matrices appearing in commutator products too.

**Matsubara Sums**

Want to calculate sums of the form



where νn = 2πn/β and ωn = 2πn1/2/β, where n1/2 = ± (1/2), ± (3/2,), etc. We can use a contour integral



where the contour C is basically an infinitely large circle. We need to choose g(z) so that it has a pole of 1/β at iωn, iν­n­. Some possibilities include…



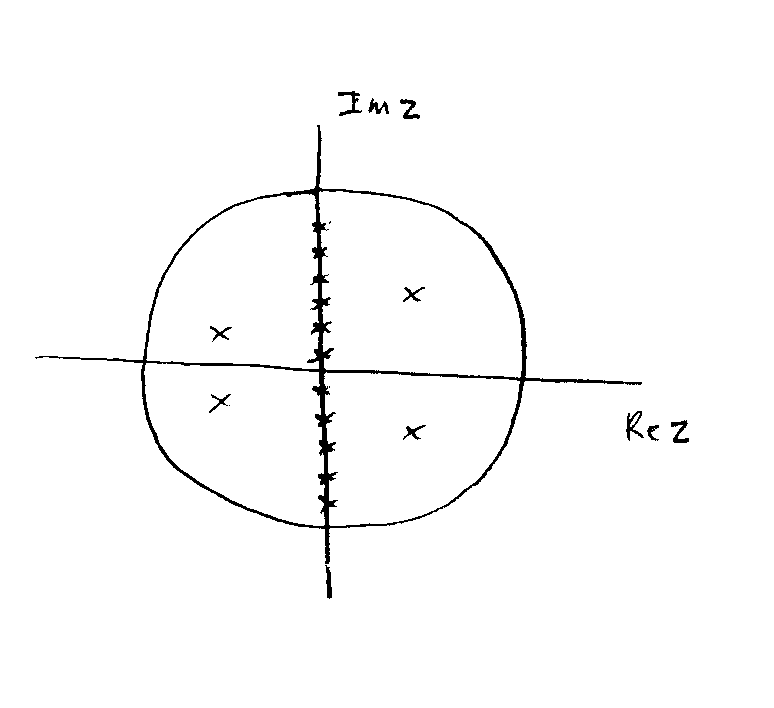
where ε = ± for fermions/bosons. The fermi/bose distribution function does have poles in the right place since,



and since the pole is first order, the residue is:



How we proceed from here depends on the properties of f(z) itself. Suppose that f(z) has no branch cuts, then we can choose a circular contour that will extend out to infinity.



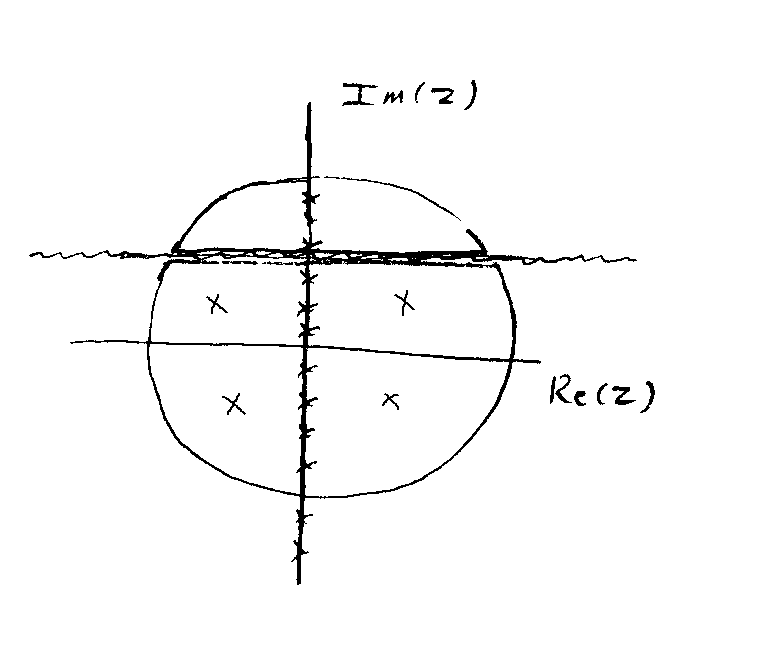
Supposing also that f(z)g(z) goes to 0 faster than 1/|z|, the contour integral will be zero. This implies of course that the sum of the residues is zero, and hence that the sum of the residues of g = - sum of the residues of f. Hopefully f has just a few residues at various points (not equal to iωn, or iν­­n if boson or fermion) in the Argand plane and we can then replace an infinite sum with a small finite sum. So we have:



and more compactly,



If f(z) does have a branch cut, and hoping it doesn’t fall on a Matsubara frequency we can integrate around the cut, and still use Cauchy's theorem.



Then we’ll have:



and so,



So just recall that the integral around both contours (assuming a single branch cut) is equal to 2πi × sum of the residues, and also that the outside part of the contour integral goes to 0 (hopefully), while the inside part (the CW integral over the branch cuts remains finite). But consider a way to avoid branch cuts. Say we wanted to evaluate the following sum:



where



Since the self energies, Σ, and π, have branch-cuts on the real axis in general, it might be complicated to perform the frequency summation because we’d have to integrate around the branch cuts too (it might not be complicated either – who knows). But in order to avoid this, what we do is express the GF’s in their Lehman representation,



which returns us to our original case, but with an integral over the spectral functions left over.

**Some useful equations**

Might note,



and similar things can be shown.