Physics 112: Lecture 15

Notes for the Fall 2017 Physics 112 Course taught by Professor Holzapfel
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October 12, 2017

1   Gibbs Factor - Average Energy

Recall that from last time, we found the Gibbs factor. To simplify our expressions a bit, we might introduce a factor Λ, defined by:

$$\Lambda = e^{M/\tau}$$

for an ideal gas, we know that $M = \tau \ln(n/n_Q)$, so we have for an ideal gas that $\Lambda = (n/n_Q)$ simply. Substituting this into our Gibb's 'grand sum', we find that:

$$\zeta = \sum \Lambda^N e^{-\epsilon_s/\tau}$$

Once again, we can see that there are two ways to change the entropy of the universe: the right hand component is given by energy exchange with a reservoir, and the left hand side is given by particle energy with a reservoir. Now, recalling the equation we had for the average number of particles from last lecture, we find that:

$$\langle N \rangle = \Lambda \frac{d}{d\Lambda} \ln \zeta$$

Now, we can find the average energy of the system if we want:

$$U = \langle \epsilon_s \rangle = \frac{\sum \epsilon_s e^{\beta(NM - \epsilon_s)}}{\zeta}$$

where $\beta = 1/\tau$. Notice now that:

$$\langle NM - \epsilon \rangle = \langle N \rangle M - U = \frac{1}{\zeta} \frac{\partial \zeta}{\partial \beta} = \frac{\partial}{\partial \beta} \ln \zeta$$

Now, rearranging and solving for the energy, we find that:

$$U = \langle N \rangle M - \langle NM - \epsilon \rangle = \left(\frac{M}{\beta} \frac{\partial}{\partial M} - \frac{\partial}{\partial \beta} \right) \ln \zeta$$

Just as a sanity check, we can recall from the partition function (when we weren't considering the exchange of particles), we had that:

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau} = -\frac{\partial}{\partial \beta} Z$$

which is just like the temperature term we had in our derivation of the energy in terms of the Gibbs sum.

2 Gas molecules binding to a bigger structure

Now, changing tack a little bit, consider the case where we have a molecule, and gas molecules binding onto our parent molecule. Now, as each of the gas molecules come in to bind; they lower the energy of the system, since it takes energy for them to pop off and escape since they are bound. Now, we might say that if one gas molecule is bound, we have a system energy of $-I$. Then, as the second gas molecule comes in, the system energy only drops by $I/2$, so the energy is $-3I/2$. For this simple case (where we can't have more than two gas molecules bound), we have:

$$\zeta = 1 + e^{(M+I)/\tau} + e^{(2M+3I/2)/\tau}$$

Now, we can find the average number $\langle N \rangle$ of particles bound either by definition (summing $NP(N)$), or by using our formulas derived earlier, $\langle N \rangle = \tau(\partial \ln \zeta / \partial M)$, and we get the same answer, regardless of whether we use the simple method or the complex method[1]. The result is:

$$\langle N \rangle = \frac{e^{(M+I)/\tau} + 2e^{(2M+3I/2)/\tau}}{\zeta}$$

Now, for the case where the gas molecules are an ideal cas, we know that $n/n_Q = e^{M/\tau}$, so substituting in we find that:

$$\langle N \rangle = \frac{(n/n_Q)e^{I/\tau} + 2(n/n_Q)^2 e^{3I/2\tau}}{\zeta}$$

We can also use our formula for the average energy for this system, by taking some derivatives.

3 Gibbs Free Energy

Recall that for the case when our system is in equilibrium with only a thermal reservoir, we defined the Helmholtz Free Energy, which is minimized in this case. In our new system, which is allowed to exchange particles with the reservoir, we will define the Gibbs Free Energy, the quantity we minimise when our system is in equilibrium with a reservoir of particles and energy.

$$G = U - \tau\sigma + pV$$

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[1] I won't claim which is which

The idea being that when we add particles to the system, it doesn't get more and more dense; it simply expands in size so the density stays constant, the chemical potential stays constant.

$$dG = dU - \tau d\sigma - \sigma d\tau + pdV + Vdp = 0$$

in equilibrium. If, say, we had a system in contant with a thermal reservoir and a pressure reservoir, we have that:

$$dG_s = dU_s - \tau d\sigma_s + pdV_s$$

Which, as commented on, looks like the thermodynamic identity! Substituting in the real thermodynamic identity:

$$\tau d\sigma_s = dU_s - MdN_s + pdV_s$$

we finally find that:

$$dG_s = MdN_s$$

so we have related the Gibbs free energy to the exchange of particles (IN THE CASE WHERE THE SYSTEM IS IN CONTACT WITH BOTH A THERMAL RESERVOIR AND A PRESSURE RESERVOIR). Notice that we can sum our thermodynamc identity into our total differential for the Gibbs free energy:

$$dG = MdN - \sigma d\tau + Vdp = \left(\frac{\partial G}{\partial N}\right)_{\tau p} dN + \left(\frac{\partial G}{\partial \tau}\right)_{N,p} d\tau + \left(\frac{\partial G}{\partial p}\right)_{N,\tau} dp$$

giving us the three relations:

$$\left(\frac{\partial G}{\partial N}\right)_{\tau,p} = M; \qquad \left(\frac{\partial G}{\partial \tau}\right)_{N,p} = -\sigma; \qquad \left(\frac{\partial G}{\partial p}\right)_{N,\tau} = V$$