Phys 112 : Lecture 18

Notes for the Fall 2017 Physics 112 Course taught by Professor Holzapfel prepared by Joshua Lin (email: joshua.z.lin@gmail.com)

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1 Quantities of interest of Ideal Gas

Recall from last lecture we found the free energy of the Ideal Gas:

$$F(N, \tau V) = N\tau \left[\ln \left(\frac{n}{n_Q} \right) - 1 \right]$$

Taking the relevant partial derivative we find:

$$P = -\left(\frac{\partial F}{\partial V} \right)_{\tau, N} = \frac{\tau N}{V}$$

which is a result we know and love. Now, we also have that:

$$U = F + \tau \sigma = F - \tau \left(\frac{\partial F}{\partial \tau} \right)_{V,N} = -\tau^2 \left(\frac{\partial}{\partial \tau} \left(\frac{F}{\tau} \right) \right) = \frac{3}{2} N\tau$$

Now, everything we have been doing so far has just been for a monotomic gas molecule with no extra internal degrees of freedom. If we had a more complex molecule, with extra degrees of freedom, we have to ask the question of whether or not these degrees are 'frozen out' or excited, (depending on whether the ambient thermal energy is comparable to the energy of excitation of the internal degree). For every new quadratic degree of freedom, we get another $N\tau$ in our expression for the energy.

We also have that:

$$\sigma = -\left(\frac{\partial F}{\partial \tau} \right)_{V,N} = N \left[\ln \left(\frac{n_Q}{n} \right) + \frac{5}{2} \right]$$

Which is only valid for monotonic atoms with no additional degrees of freedom. In this case, in the presence of additional degrees of freedom, we would be adding to the $5/2$ term in the entropy.

Finally, we can also find the heat capacity at constant volume:

$$C_V = \tau \left(\frac{\partial \sigma}{\partial \tau} \right)_V = \left(\frac{\partial U}{\partial \tau} \right)_V = \frac{\alpha}{2} N$$

where $\alpha = 3$ for monotomic gas molecule. Now:

$$C_P = \tau \left(\frac{\partial \sigma}{\partial \tau} \right)_P = \left(\frac{\partial U}{\partial \tau} \right)_P + P \left(\frac{\partial V}{\partial \tau} \right)_P = C_V + N$$

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2 Internal Energies

Now, let's specifically treat the case where our molecules have internal structure. We have:

$$\epsilon = \epsilon_n + \epsilon_{\text{int}}$$

In the classical limit, we have $n/n_Q << 1$, (i.e. the occupancy is very low), so that we have gibbs sum (for a particular energy level ϵ_n):

$$\zeta = 1 + \lambda e^{-\epsilon/\tau} = 1 + \lambda \sum_{\text{int}} e^{-(\epsilon_n + \epsilon_{\text{int}})/\tau} = 1 + \lambda e^{-\epsilon_n/\tau} Z_{\text{int}}$$

where

$$Z_{\text{int}} = \sum_{\text{int}} e^{-\epsilon_{textint}/\tau}$$

Now, we can calculate the occupancy of this energy level:

$$f(\epsilon_n) = \frac{\lambda Z_{\text{int}} e^{-\epsilon_n/\tau}}{1 + \lambda Z_{\text{int}} e^{-\epsilon_n/\tau}}$$

In the classical limit, where $f(\epsilon_n) << 1$, we have $f(\epsilon_n) \approx \lambda Z_{\text{int}} e^{-\epsilon_n/\tau}$. Now notice that:

$$N = \sum f(\epsilon_n) = \lambda Z_{\text{int}} \sum e^{-\epsilon_n/\tau} = \lambda Z_{\text{int}} n_Q V$$

So, we can understand this result as for additional internal degrees of freedom, our new *effective* absolute activity λ is given by:

$$\lambda = \frac{n}{Z_{\text{int}} n_Q}$$

i.e. the chemical potential is decreased by the partition function for the internal degrees of freedom. This makes sense, since if we have many internal degrees of freedom, we expect many more energy levels to be filled, so the chemical potential ("cost of filling an energy level") drops. More explicitly:

$$\mu = \tau \left[\ln \left(\frac{n}{n_Q} - \ln Z_{\text{int}} \right) \right]$$

We can also look at the new entropy of the system:

$$\sigma' = -\left(\frac{\partial F'}{\partial \tau} \right)_V = -\left(\frac{\partial F}{\partial \tau} \right)_V - \left(\frac{\partial F_{\text{int}}}{\partial \tau} \right)_V = \sigma + \sigma_{\text{int}}$$

In the simple case where all our internal degrees are energy degenerate (e.g. a big spin particle in the absence of any magnetic field), out partition function just becomes $Z_{\text{int}} = (2I + 1)$ where I is the spin, since this is the number of different degenerate states. In this simple case, we have:

$$F_{\text{int}} = -\tau \ln(2I + 1); \qquad \sigma_{\text{int}} = -\left(\frac{\partial F_{\text{int}}}{\partial \tau} \right)_V = \ln(2I + 1)$$

which makes sense, suppose $I = 1/2$, we would have two states (spin up and spin down), and the entropy would go up by a factor of $\ln 2$, corresponding to the multiplicity going up by a factor of 2. We also have:

$$\mu = \tau \left[\ln \left(\frac{n}{n_Q} - \ln(2I + 1) \right) \right]$$

3 Simple Dynamics

By dynamics, I mean that we are now changing our system with simple changes. For example, lets consider a container of ideal gas, changing the volume from V_1 to V_2 by keeping the temperature τ fixed. We know that throughout this process, $PV = N\tau = \text{constant}$. Note that the entropy σ depends on n_Q which depends on V, extracting this dependance we find that the change in entropy:

$$\Delta\sigma = N\ln(V_2/V_1)$$

Now, we can consider the work done in this process (for there must be work done).

$$W_P = \int_{V_1}^{V_2} F_P \cdot dx = \int_{V_1}^{V_2} pAdx = \int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2} \frac{N\tau}{V} dV = N\tau\ln(V_2/V_1)$$

where this work done on the piston. We can now consider the work done on the gas, which is just the negative:

$$W_g = -N\tau\ln(V_2/V_1)$$

And now, pulling everything together, note that the Helmholtz free energy changes:

$$\Delta F = \Delta(U - \tau\sigma) = -\tau\Delta\sigma = -\tau N\ln(V_2/V_1)$$

The Helmholtz energy has gone down, and the gas has 'used' this energy to do work on the piston! By the same token, this is equal to the amount of heat energy that flows from the heat reservoir into the gas, to keep the internal energy (proportional to τ) of the internal gas to be constant, despite doing work on the piston!

Now, we have a name for these kinds of processes. For a process with no heat flow into the gas, we call it an *adiabatic* process. If instead we have no change in entropy, its *isoentropic*. In this latter case, since

$$\sigma \alpha \ln(V\tau^{3/2})$$

so in an isoentropic process, $V\tau^{3/2}$ is conserved (no particle exchange). This can be extended in the case where we have extra quadratic degrees of freedom,:

$$T_1^{alpha/2}V_1 = T_2^{\alpha/2}V_2; \qquad P_1V_1^{(\alpha+2)/\alpha} = P_2V_2^{(\alpha+2)/\alpha}$$

usually here we define $\gamma = (\alpha + 2)/\alpha$ as the adiabatic constant. (Note that these equations hold in the adiabatic proceses).