

## 7.7: Internal Degrees of Freedom

Many particles, such as atoms, molecules have internal degrees of freedom. This can be due to atomic energy levels, due to vibrational and rotational states for molecules, etc. Very often one has to consider mixtures of particles where they can be in different internal states as well. For example, in a sodium lamp where the atoms are at a high temperature, some of the atoms are in an electronic excited state while some are in the ground state. Of course, the translational degrees of freedom are important as well. In principle, at the classical level, the internal dynamics has its own phase space and by including it in the integration measure for the partition function, we can have a purely classical statistical mechanics of such systems. However, this can be grossly inadequate. Even though in many situations, the translational degrees of freedom can be treated classically, it is necessary to take account of the discreteness of states and energy levels for the internal degrees of freedom. The question is: How do we do this?

The simplest strategy is to consider the particles in different internal states as different species of particles. For example, consider a gas of, say, argon atoms which can be in the ground state (call them A) and in an excited state (call them A\*). The partition function would thus be

$$Z = \sum_{N_A, N_{A^*}} z_A^{N_A} z_{A^*}^{N_{A^*}} Q_{N_A, N_{A^*}} \quad (7.7.1)$$

If we ignore interatomic forces, considering a gas of free particles,  $Q_N = \frac{(Q_1)^N}{N!}$ , so that

$$Z = \exp(Z_A Q_{1_A}) + (Z_{A^*} Q_{1_{A^*}}) \quad (7.7.2)$$

The single particle partition function which we have used so far is of the form

$$Q_1 = \int \frac{d^3x d^3p}{(2\pi\hbar)^3} \exp\left(-\beta \frac{p^2}{2m}\right) \quad (7.7.3)$$

This is no longer good enough since A and A\* have difference in energies for the internal degrees of freedom and this is not reflected in using just  $\frac{p^2}{2m}$ . Because of the equivalence of mass and energy, this means that  $m_A$  and  $m_{A^*}$  are different. From the relativistic formula

$$E_p = \sqrt{m^2 c^4 + c^2 p^2} \approx mc^2 + \frac{p^2}{2m} + \dots \quad (7.7.4)$$

we see that this difference is taken account of if we include the rest energy in  $Q_1$ . (Here  $c$  is the speed of light in vacuum.) Thus we should use the modified formula

$$\begin{aligned} Q_1 &= \int \frac{d^3x d^3p}{(2\pi\hbar)^3} \exp\left(-\beta \left[ mc^2 + \frac{p^2}{2m} \right]\right) \\ &= e^{-\beta mc^2} V \frac{mkT}{2\pi\hbar^2} \end{aligned} \quad (7.7.5)$$

even for nonrelativistic calculations. If there are degenerate internal states, the mass would be the same, so in  $\log Z$  we could get a multiplicity factor. To see how this arises, consider a gas of particles each of which can have  $g$  internal states of the same energy (or mass). Such a situation is realized, for example, by a particle of spin  $s$  with  $g = 2s + 1$ . If we treat each internal state as a separate species of particle, the partition function would be

$$Z = \sum_{\{N_i\}} z_1^{N_1} z_2^{N_2} \dots z_g^{N_g} Q_{N_1, N_2, \dots, N_g} \quad (7.7.6)$$

Each of the  $\mu_i$  will specify the average number in the distribution for each internal state. However, in many cases, we do not specify the numbers for each state, only the total average number is macroscopically fixed for the gas. Thus all  $z_i$  are the same giving a single factor  $z^N$ ,  $N = \sum N_i$ , in Equation 7.7.6. Correspondingly, if we have no interparticle interactions, we get

$$Z = \exp\left(z \sum Q_i\right) = \exp(z g Q_1) \quad (7.7.7)$$

where we used the fact that all masses are the same. We see the degeneracy factor  $g$  explicitly.

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