

Physics 127a: Class Notes

Lecture 18: Gases with Internal Degrees of Freedom

Partition Functions

Most gases consist of atoms or molecules with internal degrees of freedom. For example atoms may have spin or orbital angular momenta, as well as electronic excitations, and molecules may also have rotation and vibrations of the internuclear coordinates. In principle the procedure to calculate the effect on the thermodynamics is straightforward. The single particle energy levels are now $\varepsilon_p + E_i$ where the E_i are the various excitation energies. (Of course the excitations do not affect the center of mass energy spectrum ε_p .) We have to sum over the internal levels in the partition functions.

The grand canonical potential becomes

$$\Omega = \mp kT \sum_{\mathbf{p}, i} \ln(1 \pm e^{-\beta(\varepsilon_p + E_i - \mu)}) \quad (1)$$

(upper sign for Fermions, lower sign for Bosons). In the degenerate limit, the internal degrees of freedom affect the occupation of the momentum states (e.g. for Fermions, if a second internal level becomes excited as the temperature is raised, each momentum state can contain two particles, not just one), and it is hard to say anything very general about this expression.

In the nondegenerate limit we can use the canonical partition function instead, which separates

$$Q_N = \frac{1}{N!} Q_1^N \quad \text{with} \quad Q_1 = \sum_{\mathbf{p}} e^{-\beta\varepsilon_p} \sum_i e^{-\beta E_i}. \quad (2)$$

It is convenient to define an internal partition function

$$j(T) = \sum_i e^{-\beta E_i}. \quad (3)$$

The internal degrees of freedom give an additive term in the free energy $A_{int}(T, N)$

$$A = A_p(T, V, N) + A_{int}(T, N) \quad (4)$$

which is *independent of the volume*. Explicitly

$$A = NkT [\ln(\rho\lambda^3) - 1] - NkT \ln j(T). \quad (5)$$

From this we can work out other thermodynamic quantities. For example the chemical potential μ is

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{T, V} = kT \ln \left(\frac{\rho\lambda^3}{j(T)} \right). \quad (6)$$

Since $j(T)$ is independent of volume the equation of state $P(N, V, T)$ is not affected by the internal degrees of freedom. Note if there are just a set of g degenerate internal levels (e.g. spin degeneracy $g = 2s + 1$) then $j(T) = g$, and is independent of temperature. In this case the internal energy is also not affected by the internal degrees of freedom, the entropy gains a constant additive piece $Nk \ln g$, and the chemical potential is changed by $-kT \ln g$.

An application where the chemical potential of gaseous molecules is important is to chemical reactions. Before going into the details of how to calculate $j(T)$ I will describe this application.

Chemical Equilibria

In a multicomponent system with N_α particles of species X_α the thermodynamic identity must be generalized to

$$dE = TdS - PdV + \sum_{\alpha} \mu_{\alpha} dN_{\alpha}, \quad (7)$$

with μ_{α} the chemical potential of the α th species. Legendre transformations give potentials for other equilibria, e.g. for equilibria at constant P, T , use $G = E + PV - TS$ giving

$$dG = -SdT + VdP + \sum_{\alpha} \mu_{\alpha} dN_{\alpha}. \quad (8)$$

Consider a chemical reaction written in the form

$$\sum_{\alpha} \nu_{\alpha} X_{\alpha} = 0 \quad (9)$$

with ν_{α} positive for reactants and negative for products (e.g. the reaction $2H_2 + O_2 \rightleftharpoons 2H_2O$ would be written

$$2H_2 + O_2 - 2H_2O = 0 \quad (10)$$

so that $\nu_1 = 2, \nu_2 = 1, \nu_3 = -2$).

For equilibrium under this chemical reaction, minimizing the appropriate thermodynamic potential (A at constant T, V and G at constant T, P , etc.) gives

$$\sum_{\alpha} \mu_{\alpha} \nu_{\alpha} = 0 \quad (11)$$

(for a reaction of dN_r formula units we have $dN_{\alpha} = \nu_{\alpha} dN_r$). This is the general condition for chemical equilibrium.

For an ideal gas we have evaluated the chemical potential

$$\mu = kT \ln \left(\frac{n_{\alpha} \lambda_{\alpha}^3(T)}{j_{\alpha}(T)} \right) \quad (12)$$

with $n_{\alpha} = N_{\alpha}/V$, $\lambda_{\alpha} = \sqrt{h/2\pi m_{\alpha} kT}$, and j_{α} the partition function of the internal degrees of freedom of the α th species. Note that the energies of the different particles must be measured with a consistent zero of energy: this can be done by including binding energies etc. in the internal energy levels and so j_{α} . Substituting in Eq. (11) gives the *law of mass action*

$$\prod_{\alpha} n_{\alpha}^{\nu_{\alpha}} = K(T) \quad (13)$$

with $K(T)$ the equilibrium constant just a function of temperature for a given reaction

$$K(T) = \prod_{\alpha} \left[\frac{j_{\alpha}(T)}{\lambda_{\alpha}^3(T)} \right]^{\nu_{\alpha}}. \quad (14)$$

An example, important in astrophysics, is the ionization of hydrogen



Using $j_e = 2, j_p = 2$ (from the spin degeneracy) and $j_H = 4e^{\beta E_I}$ with E_I the ionization energy (the Rydberg) and the 4 from the degenerate spin states (at temperatures high compared to the hyperfine splitting) you should be able to derive the *Saha equation*

$$\frac{n_e n_p}{n_H} = \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-E_I/kT} \quad (16)$$

(where $m_H \simeq m_p$ has been used to simplify).

In general, to calculate $j(T)$ Eq. (3) we must look up the energy levels E_i in spectroscopy books, and see which ones are comparable to kT for the temperatures of interest, and then perform the sums to calculate the thermodynamic quantities. In some cases simple approximations give a good account of the energy level structure, and we can proceed more analytically. We will consider this for the example of diatomic molecules in the next lecture.