

Lecture 12  
**Objectives**

1. Be able to write down the semi-classical partition function.
2. Be able to state the assumptions associated with the semi-classical partition function.
3. Be able to change from sum over states to sum over levels.
4. Be able to write expressions for the following molecular partition functions:
  - (a) Nuclear
  - (b) Electronic
  - (c) Vibrational
  - (d) Rotational

## Statistical Mechanics of Ideal Gases

1. Review.

Recall that we wrote down an approximate expression for the partition function as

$$Q = \frac{Z Q_{\text{int}}}{\Lambda^{3N} N!}$$

What is  $Z$ ? What is  $\Lambda$ ? Recall that the configuration integral is

$$Z = \int \cdots \int \exp[-\beta U(\vec{q}^N)] d\vec{q}^N$$

What is  $Z$  for an ideal gas?

Using  $Z = V^N$  we get

$$Q = \frac{V^N}{\Lambda^{3N} N!} Q_{\text{int}} = \frac{V^N}{\Lambda^{3N} N!} (q_n q_e q_v q_r)^N$$

What are the approximations involved in this equation?

- (a) The Hamiltonian is separable into  $H = H_{\text{cm}} + H_{\text{int}}$
- (b)  $Q_{\text{cm}}$  can be treated classically
- (c)  $H_{\text{int}}$  can be separated into contributions due to nuclear, electronic, vibrational and rotational modes, and these are independent. I.e.,

$$\epsilon_{\text{int}} = \sum_i \epsilon_{n,i} + \sum_i \epsilon_{e,i} + \sum_i \epsilon_{v,i} + \sum_i \epsilon_{r,i}$$

This leads to

$$q_{\text{int}} = q_n q_e q_v q_r$$

The next task is to find out how to get the  $\epsilon_{i,j}$  where  $i$  is the mode and  $j$  is the energy level.

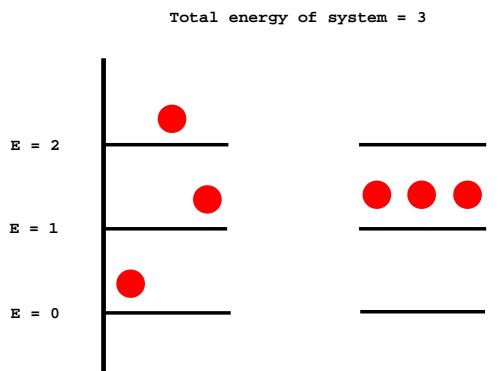


Figure 1: System with possible energy states  $\epsilon_i = 0, 1, 2$ . The degeneracy of the system with  $E = 3$  is 2.

- Sum over states vs. sum over energy levels. We can replace the sum over quantum states with a sum over energy levels by multiplying each energy level by its degeneracy. E.g., consider a system of three balls which can occupy different energy states. If the total energy of the system is 3 (arbitrary units) then how many ways can the balls be arranged to give this energy? Therefore, we change from sum over states to sum over energy levels

$$Q = \sum_{\text{states}} \exp(-\beta E_i) = \sum_{\text{levels}} \omega_i \exp(-\beta E_i)$$

where  $\omega_i$  is the degeneracy of energy level  $i$ .

- Nuclear-spin partition function.  $\Delta\epsilon_n$  is very large. This has two consequences. **What are the two consequences?** (1) Only the ground state level will be occupied. (2) The nuclear-spin partition function must be treated quantumly. Taking the zero to be the ground state energy we write

$$q_n = \omega_0 e^{-\beta\epsilon_0} = \omega_0 e^{-0} = \omega_0$$

Where  $\omega_i$  is the degeneracy of energy level  $i$ . This is included because we have implicitly switched from doing a sum over states to a sum over energy levels. You can look  $\omega_0$  up in tables.

Note that  $q_n$  will only contribute to the entropy and free energies, because all derivatives of  $\ln q$  are zero ( $q$  is a constant) at terrestrial temperatures. See Table 2.1 again.

- Electronic Partition Function.

The electronic and vibrational partition functions are often lumped together when we do calculations. We shall discuss each separately here.

The electronic partition function can be written as a sum over energy levels by including the degeneracy of each energy level

$$q_e = \sum_i \omega_i e^{-\beta\epsilon_{e,i}} = \omega_0 e^{-\beta\epsilon_{e,0}} + \omega_1 e^{-\beta\epsilon_{e,1}} + \omega_2 e^{-\beta\epsilon_{e,2}} + \dots$$

We can choose the zero of energy for the electronic energy levels to be  $\epsilon_0 = 0$  and get

$$q_e = \omega_0 + \omega_1 e^{-\beta\epsilon_{e,1}} + \dots$$

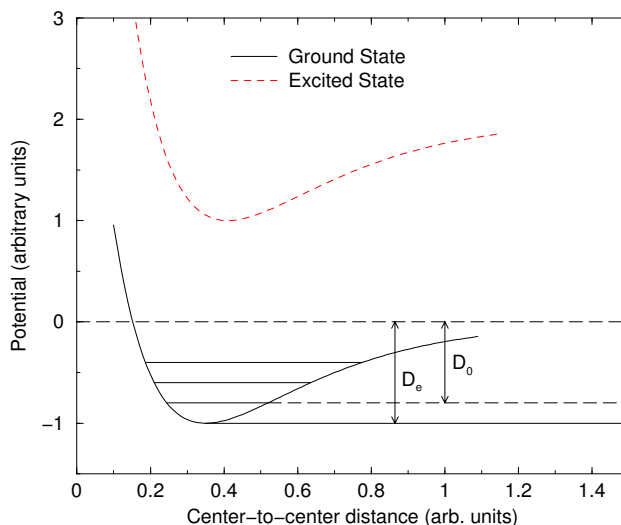


Figure 2: Schematic of the vibrational states in a diatomic potential well. Note the difference between the dissociation energy  $D_0$  and the well depth,  $D_e$ .

where now  $\epsilon_{e,i}$  is actually  $\epsilon_{e,i} - \epsilon_{e,0}$ . Now we employ a common transformation used in statistical mechanics to change energies to frequencies, by dividing the energy by Planck's constant,  $h = 6.6262 \times 10^{-27}$  erg s. Thus,

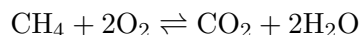
$$\epsilon_i = h\nu_i$$

and

$$q_e = \omega_0 + \omega_1 e^{-\beta h\nu_{e,1}} + \dots$$

The electronic energy level spacings are typically large compared to room temperature, so it is often the case that only the ground states are populated. However, there are some very important exceptions, e.g., atomic oxygen, nitric oxide, etc.

5. Shift of reference. We will often want to change the reference from the zero of energy being the bottom of the energy well to the zero being the separated atoms. This is motivated by doing calculations for chemical reactions and calculating the change of energy on reaction. For example consider the reaction



In order to compute the ideal gas equilibrium constant from classical thermodynamics we must have the heat of formation of each of the molecules *from their elements*. In statistical mechanics this is the same as changing the zero of energy from the *molecules* in their ground state, to the *atoms* in their ground state.

See Fig. 2. This represents the intramolecular potential between atoms of a diatomic molecule. The horizontal lines represent allowed vibrational modes. If the vibrations become too large the molecule will dissociate. The dissociation energy is  $D_0$  and this corresponds to the distance from the lowest vibrational mode to the dissociated atoms, i.e., the energy required

to take a molecule from its ground vibrational state to completely dissociated. But, this is not the bottom of the potential well. We shall shortly see that the lowest vibrational mode is a distance  $(1/2)h\nu$  above the bottom of the electronic well. The zero of electronic energy is taken as the bottom of the well, relative to the separated atoms. The well depth is  $D_e$ , and we subtract this quantity from the electronic eigen energies. This gives

$$q_e = \omega_0 e^{\beta D_e} + \omega_1 e^{-\Theta_{e,1}/T} + \dots$$

where  $\Theta_{e,1} = (\epsilon_1 - D_e)/k$ , is the characteristic temperature for the first excited electronic state.

6. Vibrational partition functions. We have already seen that the vibration and electronic states are related by the depth of the energy well. We will discuss this further.

- (a) Calculating the number of vibrational modes. We first need to find out how many “ways” a molecule can vibrate. These are called the vibrational modes. For a diatomic molecule it is easy to see that there is only one vibrational mode, the stretching of the bond between the two atoms. How about for  $\text{CO}_2$ ? Draw on the board the four modes. (1) In phase stretch, (2) out of phase stretch, (3) scissor, and (4) rotate  $90^\circ$  scissor. How about  $\text{H}_2\text{O}$ , or  $\text{NO}_2$ ? Put up a copy of Example 2.6. How can we tell *a priori* how many modes there will be? In order to specify the state of a molecule you start with  $3m$  degrees of freedom, where  $m$  is the number of atoms, i.e., the three coordinates for each atom. You specify the center of mass, that gets rid of three. If the molecule is nonlinear there will be three rotations, one through each of the three principal axes. If the molecule is linear there are only two rotations, because there are only two principal axes (show this by holding up a pen or pencil; you can rotate about the x and y axes, but the z-axis doesn't give anything.) Therefore, the number of vibrational modes is just the number of degrees of freedom left

$$F_v = 3m - 3 - F_r = 3(m - 1) - F_r$$

where  $F_r = 3$  for nonlinear and  $F_r = 2$  for linear molecules.

- (b) The Quantum harmonic oscillator problem. Now we know how many modes to look for. How do we find the energies of these modes? Recall that we are looking for  $\epsilon_{v,i}$ . The energies are the eigenvalues of the solution to the quantum harmonic oscillator problem. Without proof, we write down the solution

$$\epsilon_{v,i} = \left(i + \frac{1}{2}\right) h\nu$$

for  $i = 0, 1, 2, \dots$ , and  $\nu$  is the characteristic frequency. This is the same  $\nu$  as appears in the electronic problem,

$$D_e - D_0 = \frac{1}{2} h\nu$$

- (c) Finding  $q_v$  from  $\epsilon_{v,i}$ . We recall that

$$q = \sum_i e^{-\beta \epsilon_i}$$

For a diatomic molecule

$$q_v = \sum_i \exp \left[ -\beta \left( i + \frac{1}{2} \right) h\nu \right]$$

$$q_v = e^{-\beta h\nu/2} \sum_{i=0}^{\infty} e^{-i\beta h\nu}$$

We use a math trick to sum this exactly. We note that

$$\sum_{n=0}^{\infty} e^{-nx} = \frac{1}{1 - e^{-x}}$$

then, for a diatomic molecule,

$$q_v = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}$$

For polyatomic molecules there are  $F_v > 1$  modes. You can see that if they are independent that they combine as products in  $q_v$ :

$$q_v = \prod_{j=1}^{F_v} \frac{e^{-\beta h\nu_j/2}}{1 - e^{-\beta h\nu_j}}$$

where  $\nu_j$  is the characteristic frequency of the  $j$ th vibrational mode. In analogy to diatomic molecule, we define  $D_0$  for polyatomic molecules as

$$D_0 = D_e - \sum_{j=1}^{F_v} \frac{h\nu_j}{2}$$

Values of  $D_0$  can be looked up in tables, see for example Tables 3.2, 3.3, and 3.4 of the text. For convenience, people also define characteristic vibration temperatures as

$$\Theta_{v,j} = \frac{h\nu_j}{k}$$

This has units of Kelvin, so it is easy to use in formulae for calculations.

## 7. Rotational partition functions.

- (a) Moments of inertia. Rotation of rigid objects about their centers of mass can be described in terms of the three principal moments of inertia of the rigid body. Nonlinear objects always have three moments of inertia, however linear objects have only two moments of inertia, and both moments are equal. The moments of inertia are labeled  $I_A$ ,  $I_B$ , and  $I_C$ .
- (b) The Three Tops.
  - i. Spherical tops have all three moments of inertia equal, example:  $\text{CCl}_4$ ,  $\text{CH}_4$ , etc.
  - ii. Symmetric tops have two moments of inertia equal, example:  $\text{CH}_3\text{Cl}$ .
  - iii. Asymmetric tops have three distinct moments of inertia, example:  $\text{H}_2\text{O}$ .

One can calculate the moments of inertia from geometric information. Note that this invokes the rigid rotor, harmonic oscillator approximation. Rotational constants can also be measured experimentally from spectroscopy by measuring the characteristic rotational temperature, defined by

$$\Theta_i = \frac{h^2}{8\pi^2 k I_i}$$

The constant  $\Theta$  has units of temperature (K), and this is what we look up in tables (see, e.g., Table 3.4).

## (c) Linear molecules.

The quantum mechanical linear rigid rotor problem can be solved exactly. The energy levels are

$$\epsilon_{r,J} = J(J+1)k\Theta, \quad J = 0, 1, \dots,$$

where  $\Theta$  is defined above. These are the energies levels, not quantum levels, so we must find the degeneracy of each energy level before we find the partition function. The degeneracy is

$$\omega(J) = 2J + 1$$

There is an additional problem for homonuclear molecules due to over counting identical states. This gives rise to something called the symmetry number,  $\sigma$ . For a homonuclear diatomic molecule  $\sigma = 2$ . For heteronuclear molecules  $\sigma = 1$ . For polyatomic molecules  $\sigma$  is the number of distinct rotations that produce indistinguishable configurations. Be careful about determining  $\sigma$ . This is a simple treatment of symmetry numbers, and not the whole story.

With this in mind, we can write

$$q_r = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) \exp(-J(J+1)\Theta_r/T)$$

This expression is exact, but it is not very convenient. When  $\Theta_r \ll T$  we can invoke classical mechanics and turn the sum into an integral. This gives a high temperature approximation,

$$q_r = \frac{T}{\sigma\Theta_r}$$

Use this equation **only** if  $\Theta_r \ll T$ . See the tables, and compare with the temperature of interest.

## (d) Nonlinear molecules.

For nonlinear molecules, there can be three different moments of inertia. The **high temperature** approximation gives

$$q_r = \frac{1}{\sigma} \left( \frac{\pi T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2}$$

If any of the moments of inertia are identical, just repeat the values of  $\Theta$  in the above equation.

8. Summary of molecular partition functions.  
Examine Table 3.5 from the book.
9. Formulae for calculating thermodynamic properties.  
Examine Tables 3.6 and 3.7 from the book.