

# 10.40 Lectures 23 and 24

## Computation of the properties of ideal gases

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(In preparation for Lectures 23 and 24, also read T&M, 10.1.5-10.1.7).

### Outline

- Degrees of freedom
- Computation of the thermodynamic properties of a monatomic ideal gas
- Computation of the thermodynamic properties of polyatomic ideal gases, including diatomic ideal gases
- Summary of thermodynamic functions

### 23.1 Degrees of freedom

We have discussed *translational*, *electronic*, and *nuclear* degrees of freedom. Diatomic and polyatomic molecules have two additional internal degrees of freedom, *vibrational* and *rotational* degrees of freedom.

Excluding electronic and nuclear degrees of freedom, atoms and molecules have a total of  $3N_{\text{atoms}}$  degrees of freedom, where  $N_{\text{atoms}}$  is the number of atoms in a molecule (or atom). Linear molecules have 2 rotational degrees of freedom and non-linear molecules have 3 rotational degrees of freedom. The rest of the degrees of freedom,  $3N_{\text{atoms}}-5$  for linear molecules and  $3N_{\text{atoms}}-6$  for non-linear molecules are considered to be vibrational degrees of freedom. From now on, we approximate these vibrational degrees of freedom as normal modes, i.e. modes of simple harmonic oscillators. We will also ignore nuclear degrees of freedom from now on.

### 23.2 Computation of the thermodynamic properties of a monatomic ideal gas

We have  $N$  *independent* and *indistinguishable* particles. Let's label these particles,  $a, b, \dots$ . Particle  $a$  can take on energy levels  $\varepsilon_{aj}$ , where as before,  $j$  is just an index refering each of the possible states. Particle  $b$  can take on energy levels  $\varepsilon_{bj}$ , etc. Designate the partition function of each particle with the symbol  $q$ . Thus,

$$q_a = \sum_j e^{-\beta\varepsilon_{aj}},$$
$$q_b = \sum_j e^{-\beta\varepsilon_{bj}},$$

etc.

Then, the energy for the entire system, will be

$$E_{i,j,\dots} = \varepsilon_{ai} + \varepsilon_{bj} + \dots \quad (1)$$

Thus,  $Q$  should be of the form

$$\sum_{i,j,\dots} e^{-\beta E_{i,j,\dots}} = q^N,$$

where  $q$  is the partition function for an individual particle.

However, since each particle is indistinguishable, the  $\varepsilon$ 's in equation 1 can be permuted in  $N!$  ways. Thus, in order to avoid overweighting each quantum state, we must divide  $q^N$  by  $\frac{1}{N!}$ . This leads to

$$Q = \frac{1}{N!} q^N.$$

Now, we need to compute  $q$  for a single atom. We know that from quantum mechanics, the energy levels of a particle due to their *translational degrees of freedom* are

$$\varepsilon_j = \varepsilon_{l_x l_y l_z} = \frac{h^2(l_x^2 + l_y^2 + l_z^2)}{8mV^{2/3}},$$

where  $h$  is Planck's constant, equal to  $6.626 \times 10^{-34}$  J s;  $l_x, l_y, l_z = 1, 2, 3, \dots$ ;  $m$  is the mass of the particle; and  $V$  is the volume occupied by the particle. The numbers  $l_x, l_y, l_z$  are the quantum numbers designating the translational quantum level. Let  $R^2 = l_x^2 + l_y^2 + l_z^2 = \frac{8mV^{2/3}\varepsilon}{h^2}$ . Then, the number of states with energy  $< \varepsilon$  is

$$\Phi(\varepsilon) = \frac{\pi R^3}{6} = \frac{\pi}{6} \left( \frac{8m\varepsilon}{h^2} \right)^{3/2} V.$$

This result can be visualized by thinking of the quantum energy levels as points on a 3D Cartesian grid in an octet of a sphere.

Let us remind ourselves of the difference between the designation of *states* and *energy levels*, as shown in Figure 1. Thus,

$$q = \sum_{\text{states } j} e^{-\beta \varepsilon_j} = \sum_{\text{levels } i} \omega_i e^{-\beta \varepsilon_i},$$

where  $\omega_i$  is the *degeneracy* of level  $i$ . (The degeneracy is the number of states with energy  $\varepsilon_i$ .)

Write

$$q = \sum_{l_x}^{\infty} \sum_{l_y}^{\infty} \sum_{l_z}^{\infty} e^{-\beta \varepsilon_{l_x l_y l_z}}.$$

For states with energies that are very close together, we can replace  $\sum$ 's with  $\int$ 's. How close do they need to be? How close are they? Thus,

$$q = \int_0^{\infty} \omega(\varepsilon) e^{-\beta \varepsilon} d\varepsilon,$$

where the number of states between  $\varepsilon$  and  $\varepsilon + d\varepsilon$  are

$$\begin{aligned} \omega(\varepsilon) d\varepsilon &= \frac{d\Phi}{d\varepsilon} d\varepsilon \\ &= \frac{\pi}{4} \left( \frac{8m}{h^2} \right)^{3/2} V \varepsilon^{1/2} d\varepsilon. \end{aligned}$$

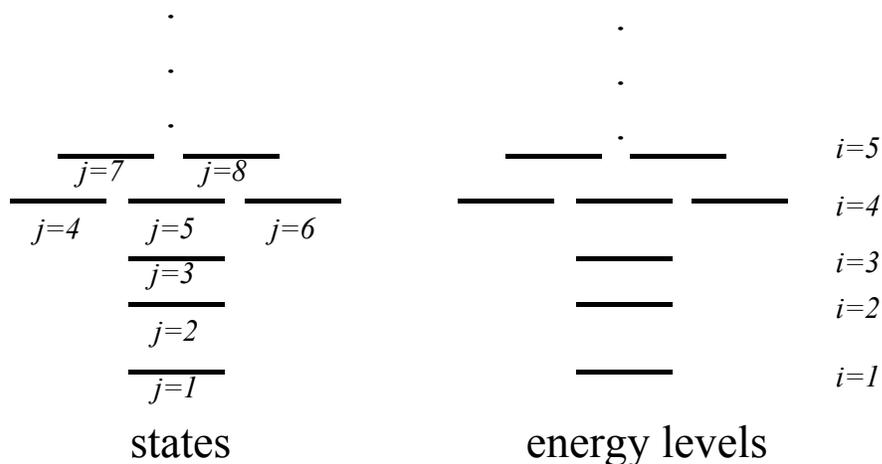


Figure 1: Difference between states and energy levels.

Plugging this into the integral yields

$$\begin{aligned}
 q &= \frac{\pi}{4} \left( \frac{8m}{h^2} \right)^{3/2} \underline{V} \int_0^\infty \varepsilon^{1/2} e^{-\beta\varepsilon} d\varepsilon \\
 &= \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \underline{V}.
 \end{aligned}$$

Thus,

$$q = \frac{V}{\Lambda^3},$$

where  $\Lambda \equiv \left( \frac{h^2}{2\pi mkT} \right)^{1/2}$  and is called the thermal deBroglie wavelength. It gives the characteristic wavelength of a gas. Note that this  $q$  will be designated as  $q_t$  below for "translational" (see below).

From all of this, we can determine the partition function of the system,

$$Q = \frac{1}{N!} q^N = \frac{1}{N!} \left( \frac{V}{\Lambda^3} \right)^N.$$

Now, recalling the formulas for the thermodynamic quantities in terms of  $Q$  yields

$$\begin{aligned}
 \underline{A} &= -kT \ln Q \\
 &= -kT(-N \ln N + N + N \ln q) \\
 &= -NkT \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} e \right]
 \end{aligned}$$

or in intensive form,

$$A = -kT \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V e \right],$$

and

$$\begin{aligned} P &= kT \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N} \\ &= NkT \left( \frac{\partial \ln q}{\partial V} \right)_{T,N} \\ &= \frac{NkT}{V}, \end{aligned}$$

and

$$\begin{aligned} \underline{U} &= kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N} \\ &= NkT^2 \frac{d \ln T^{3/2}}{dT} \\ &= \frac{3}{2} NkT, \end{aligned}$$

and,

$$\begin{aligned} \underline{C}_v &= \left( \frac{\partial \underline{U}}{\partial T} \right)_{V,N} \\ &= \frac{3}{2} Nk. \end{aligned}$$

Recalling an expression for  $\underline{S}$ ,

$$\begin{aligned} \underline{S} &= \frac{\underline{U} - \underline{A}}{T} \\ &= Nk \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} e^{5/2} \right]. \end{aligned}$$

Also,  $\underline{H} = \underline{U} + P\underline{V} = \underline{U} + NkT$  and  $\underline{G} = \underline{A} + P\underline{V} = \underline{A} + NkT$ .

Next, we may need to consider internal degrees of freedom of the atom, such as *electronic* and *nuclear degrees of freedom*. Thus, we can write the partition function as

$$Q = \frac{1}{N!} (q_t q_e q_n)^N,$$

where  $q_t$  is the translational partition function,  $q_e$  is the electronic partition function, and  $q_n$  is the nuclear partition function. For most systems, the first excited electronic state and nuclear state are at  $\approx 20 \text{ kcal mol}^{-1}$  and  $20,000 \text{ kcal mol}^{-1}$  respectively. Thus, they do not play a significant role at temperatures of interest. *Note that there are important exceptions to this rule of thumb, such as with the alkali metal atoms and halogens, but we will not concern ourselves with these in this course.*

We often need to take into account degenerate electronic states of atoms that are a result of their spins. For example, H has a net spin of  $\frac{1}{2}$ , meaning that it has two spin degrees of freedom at the ground state energy level,  $\omega_e = 2$  and  $q_e = 2$ . Thus an additional factor of  $Nk \ln \omega_e$  must be added to the formula for the entropy given above, and an additional factor of  $NkT \ln \omega_e$  must be added to the formula for the Helmholtz free energy given above.

### 23.3 Computation of the thermodynamic properties of polyatomic ideal gases, including diatomic ideal gases

Recall that

$$Q = \frac{1}{N!} q^N.$$

First, we assume that all of the degrees of freedom are separable. Thus,

$$q(\underline{V}, T) = q_t(\underline{V}, T) q_r(T) q_v(T) q_e(T).$$

where  $q_t$  is the translational partition function,  $q_r$  is the rotational partition function,  $q_v$  is the vibrational partition function, and  $q_e$  is the electronic partition function. We discussed  $q_t$  and  $q_e$  last time. We note here that if we choose the electronic energy of separated atoms as the electronic reference state, then we can define  $D_e$  as the dissociation energy, the energy needed to atomize the molecule.

Now, we need to compute  $q_r$  and  $q_v$ .

#### 23.3.1 Vibrational degrees of freedom

From quantum mechanics, the energy levels of a harmonic oscillator are:

$$\begin{aligned} \varepsilon_n &= \left(n + \frac{1}{2}\right) h\nu, \\ n &= 0, 1, 2, \dots, \end{aligned} \tag{2}$$

where  $h$  is Planck's constant and  $\nu$  is the frequency. The vibrational partition function is then

$$q_v = \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}},$$

where  $\Theta_v = h\nu/k$ . (You can verify this yourself.)

Then,

$$\begin{aligned} \underline{A}_v &= -NkT \ln q_v \\ &= NkT \left[ \frac{\Theta_v}{2T} + \ln \left( 1 - e^{-\Theta_v/T} \right) \right], \end{aligned}$$

$$\begin{aligned} \underline{U}_v &= NkT^2 \left( \frac{\partial \ln q_v}{\partial T} \right) \\ &= Nk \left( \frac{\Theta_v}{2} + \frac{\Theta_v}{e^{\Theta_v/T} - 1} \right), \end{aligned}$$

$$\begin{aligned} \underline{C}_{Vv} &= \left( \frac{\partial \underline{U}}{\partial T} \right)_{V,N} \\ &= Nk \left( \frac{\Theta_v}{T} \right)^2 \frac{e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2}, \end{aligned}$$

and,

$$\begin{aligned} \underline{S}_v &= \frac{\underline{U}_v - \underline{A}_v}{T} \\ &= Nk/T \left( \frac{\Theta_v}{e^{\Theta_v/T} - 1} \right) - Nk \ln \left( 1 - e^{-\Theta_v/T} \right). \end{aligned}$$

We also emphasize that the terms  $\frac{\Theta_v}{2}$  in the expressions for  $\underline{U}_v$  and  $\underline{A}_v$  above are a result of the fact that the ground state of the harmonic oscillator has a finite energy level as seen in equation 2. The term  $\frac{1}{2}h\nu = (\frac{k\Theta_v}{2})$  is called the *zero point energy* of the vibration.

We note that for a diatomic molecule, for example, the measured bond dissociation energy,  $D_0$ , is not the energy of atomization described at the beginning of the lecture. This is because the zero point energy adds a destabilizing contribution. Thus,

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

This can be easily generalized for polyatomic molecules.

### 23.4 Rotational degrees of freedom

From quantum mechanics, the energy levels of a rigid, linear rotator are

$$\begin{aligned}\varepsilon_j &= \frac{j(j+1)h^2}{8\pi^2 I}, \\ j &= 0, 1, 2, \dots,\end{aligned}$$

where  $I$  is the moment of inertia. Note that for a diatomic molecule consisting of atoms 1 and 2,  $I = \mu d^2$ , where  $\mu$  is the reduced mass ( $\mu = \frac{m_1 m_2}{m_1 + m_2}$ ) and  $d$  is the bond length. This can be generalized for polyatomic molecules. (See books on classical mechanics.)

For diatomic and non-linear polyatomic molecules, the rotational partition function is then

$$\begin{aligned}q_r &= \sum_{j=0}^{\infty} \omega_j e^{-\beta\varepsilon_j} \\ &= \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\Theta_r/T},\end{aligned}$$

where

$$\Theta_r = \frac{h^2}{8\pi^2 I k}$$

At high  $T$ ,

$$\begin{aligned}q_r &\rightarrow \int_0^{\infty} (2j+1) e^{-j(j+1)\Theta_r/T} dj \\ &= \frac{T}{\Theta_r} = \frac{8\pi^2 I k T}{h^2}.\end{aligned}$$

Note that in order to eliminate double counting, symmetry must be taken into account. The symmetry number is symbolized as  $\sigma$ , and for a diatomic molecule,  $\sigma = 1$  if the molecule is unsymmetrical and  $\sigma = 2$  if the molecule is symmetrical.

A non-linear polyatomic molecule will have 3 rotational degrees of freedom, and obviously the 3 different moments of inertia will almost always be different. For these species,

$$q_r = \frac{\pi^{1/2}}{\sigma} \left( \frac{8\pi^2 I_A k T}{h^2} \right)^{1/2} \left( \frac{8\pi^2 I_B k T}{h^2} \right)^{1/2} \left( \frac{8\pi^2 I_C k T}{h^2} \right)^{1/2},$$

where  $\sigma$  is again the symmetry factor, which can take on many values, up to 12, and  $I_A, I_B, I_C$  are the three principle moments of inertia. (We ignore the derivation here, because it is somewhat complicated. It can be found in a book on classical mechanics.)

This equation can be written more compactly as

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

From this equation, we can derive the thermodynamic functions:

$$\begin{aligned} \underline{A}_r &= -NkT \ln \left[ \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \right], \\ \underline{E}_r &= \frac{3}{2} NkT, \\ \underline{C}_{Vr} &= \frac{3}{2} Nk, \\ \underline{S}_r &= Nk \ln \left[ \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3 e^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \right]. \end{aligned}$$

### 23.5 Summary of thermodynamic functions

Below is a summary of the thermodynamic functions, excluding nuclear and excited electronic degrees of freedom.

#### 23.5.1 Monatomic ideal gas

$$\begin{aligned} \underline{A} &= -NkT \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} e \right]; \\ \underline{U} &= \frac{3}{2} NkT; \\ \underline{C}_V &= \frac{3}{2} Nk; \\ \underline{S} &= Nk \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} e^{5/2} \right]. \end{aligned}$$

Also,  $\underline{H} = \underline{U} + P\underline{V} = \underline{U} + NkT$  and  $\underline{G} = \underline{A} + P\underline{V} = \underline{A} + NkT$ .

#### 23.5.2 Diatomic and linear polyatomic ideal gas

$$\begin{aligned} -\frac{\underline{A}}{kT} &= \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} e \right] + \ln \left[ \frac{8\pi^2 IkT}{\sigma h^2} \right] - \sum_{i=1}^{3N_{\text{atoms}}-5} \left[ \frac{\Theta_{i,v}}{2T} + \ln \left( 1 - e^{-\Theta_{i,v}/T} \right) \right] + \frac{D_e}{kT} + \ln \omega_e; \\ \frac{\underline{U}}{kT} &= \frac{3}{2} + \frac{2}{2} + \sum_{i=1}^{3N_{\text{atoms}}-5} \left[ \frac{\Theta_{i,v}}{2T} + \frac{\Theta_{i,v}/T}{e^{\Theta_{i,v}/T} - 1} \right] - \frac{D_e}{kT}; \\ \frac{\underline{C}_V}{k} &= \frac{3}{2} + \frac{2}{2} + \sum_{i=1}^{3N_{\text{atoms}}-5} \left[ \left( \frac{\Theta_{i,v}}{T} \right)^2 \frac{e^{\Theta_{i,v}/T}}{(e^{\Theta_{i,v}/T} - 1)^2} \right]; \end{aligned}$$

$$\frac{S}{k} = \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} e^{5/2} \right] + \ln \left[ \frac{8\pi^2 I k T e}{\sigma h^2} \right] + \sum_{i=1}^{3N_{\text{atoms}}-5} \left[ \frac{\Theta_{i,v}/T}{e^{\Theta_{i,v}/T} - 1} - \ln \left( 1 - e^{-\Theta_{i,v}/T} \right) \right] + \ln \omega_e.$$

Note that  $m$  is the mass of the molecule. Also,  $H = U + PV = U + kT$  and  $G = A + PV = A + NkT$ .

### 23.5.3 Non-linear polyatomic ideal gas

$$-\frac{A}{kT} = \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} e \right] + \ln \left[ \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \right] - \sum_{i=1}^{3N_{\text{atoms}}-6} \left[ \frac{\Theta_{i,v}}{2T} + \ln \left( 1 - e^{-\Theta_{i,v}/T} \right) \right] + \frac{D_e}{kT} + \ln \omega_e;$$

$$\frac{U}{kT} = \frac{3}{2} + \frac{3}{2} + \sum_{i=1}^{3N_{\text{atoms}}-6} \left[ \frac{\Theta_{i,v}}{2T} + \frac{\Theta_{i,v}/T}{e^{\Theta_{i,v}/T} - 1} \right] - \frac{D_e}{kT};$$

$$\frac{C_V}{k} = \frac{3}{2} + \frac{3}{2} + \sum_{i=1}^{3N_{\text{atoms}}-6} \left[ \left( \frac{\Theta_{i,v}}{T} \right)^2 \frac{e^{\Theta_{i,v}/T}}{(e^{\Theta_{i,v}/T} - 1)^2} \right];$$

$$\frac{S}{k} = \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} e^{5/2} \right] + \ln \left[ \frac{\pi^{1/2} e^{3/2}}{\sigma} \left( \frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \right] + \sum_{i=1}^{3N_{\text{atoms}}-6} \left[ \frac{\Theta_{i,v}/T}{e^{\Theta_{i,v}/T} - 1} - \ln \left( 1 - e^{-\Theta_{i,v}/T} \right) \right] + \ln \omega_e.$$

Note that  $m$  is the mass of the molecule. Also,  $H = U + PV = U + kT$  and  $G = A + PV = A + NkT$ .