

### III.4 Molecular Partition Functions

In the following, the important example of an ideal-gas system is considered again. The system consists of  $N$  *identical but independent, non-interacting particles, each particle has a number of independent degrees of freedom like uncoupled motion along the spatial coordinates  $x$ ,  $y$ , and  $z$ .* In both respects, the microstate energies can be expressed as sum over individual single-particle energies and individual single degrees of freedom. Then, as shown in previous sections, the canonical partition function in *Boltzmann statistics* for the  $N$ -particle system can be written as a *product of partition functions, each for one particle and for one individual degree of freedom.*

One expects that the calculation of the single-particle partition function for translational motion,  $q^{trans}$ , should be the easiest of all. However, this degree of freedom is associated with a *continuous energy spectrum*, which makes the treatment more difficult. Fortunately, one can use a trick: One imagines the particles enclosed in a box with discrete energies given by [Equ.III.55](#). After necessary manipulations have been made in this frame work, and quantities of interest  $X(a)$  have been calculated as functions of the size  $a$  of the box, one performs the transition to an infinitely large box ( $a \rightarrow \infty$ ), where the spectrum becomes indeed continuous. The appropriate quantities for this limit are then

$$X = \lim_{a \rightarrow \infty} X(a) \quad (\text{III.82})$$

For the particles in a finite cubical box of side length  $a$ , the *translational partition function* reads

$$q_a^{trans} = \sum_{n_x, n_y, n_z} e^{-\beta \cdot (\varepsilon_{n_x} + \varepsilon_{n_y} + \varepsilon_{n_z})} = \left( \sum_i e^{-\beta \cdot \varepsilon_i} \right)^3 \quad (\text{III.83})$$

where the particle-in-a-box energy eigen values are given by

$$\varepsilon_i = \frac{h^2}{8ma^2} \cdot n_i^2 \quad (\text{III.84})$$

Performing the transition to the infinite box,  $a \rightarrow \infty$ , the summation over discrete quantum numbers  $n_i$  can be replaced by an integral over continuous quantum numbers  $n$ :

$$q^{trans} = q_{a \rightarrow \infty}^{trans} = \lim_{a \rightarrow \infty} \left[ \int_0^\infty dn e^{-\beta \cdot \frac{h^2}{8ma^2} \cdot n^2} \right]^3 = \left[ \sqrt{\frac{2\pi}{h^2} mkT} \cdot a \right]^3 \quad (\text{III.85})$$

Since the volume is given by  $V = a^3$ , the translational partition function can also be written as

$$q^{trans} = \frac{V}{\lambda_{therm}^3} \propto T^{3/2} \quad (\text{III.86})$$

where the *thermal wave length*  $\lambda_{therm}$  is defined as

$$\lambda_{therm} = \sqrt{\frac{h^2}{2\pi m}} \quad (\text{III.87})$$

This wavelength is similar in magnitude to the *deBroglie wavelength of the gas atom*.

One can now use this single-particle partition function to calculate expectation values for the macro-system, for example the average kinetic energy  $\langle \varepsilon^{trans} \rangle$  per particle. Using the equivalent of [Equ. III.52](#), one obtains

$$\begin{aligned} \langle \varepsilon^{trans} \rangle &= kT^2 \cdot \frac{\partial}{\partial T} \ln q^{trans} = kT^2 \cdot \frac{\partial}{\partial T} \ln T^{3/2} = kT^2 \frac{1}{T^{3/2}} \frac{\partial}{\partial T} T^{3/2} \\ &= kT^2 \frac{\lambda_{therm}^3}{V} \frac{3}{2} V \lambda_{therm}^{-1} \frac{2\pi mk}{h^2} \end{aligned} \quad (III.88)$$

Collecting terms,

$$\langle \varepsilon^{trans} \rangle = \frac{3}{2} kT \quad (III.89)$$

In other words, one regains the **Equipartition Law**, according to which in thermal equilibrium, *every degree of freedom has an energy equal to  $\varepsilon = \frac{1}{2} kT$* . This behavior can be traced back to the *quadratic dependence of the energy on the variable (or quantum number) in the partition integral* (cf. Equ. III.85). Hence, one can say more specifically that, *in thermal equilibrium, any degree of freedom, whose energy (kinetic or potential) depends*

*quadratically on the (momentum or position) variable, has an average thermal energy of  $u = 1/2 kT$ . One also concludes that  $k \equiv k_B$*

□

*At room temperature, this characteristic energy is of the order of*

$$\beta^{-1}(300K) = k \cdot 300K = (1/40)eV = 25meV \quad (\text{III.90})$$

$$q^{\text{electronic}} = \sum_{\varepsilon_i} \Omega_i e^{-\beta\varepsilon_i} = \Omega_0 + \Omega_1 \cdot e^{-\beta\varepsilon_1} + \dots \approx \Omega_0 \quad (\text{III.91})$$

Another term in the partition function of [Equ. III.43](#) is the **electronic partition function**. Expressed in terms of *energy levels and level degeneracies*, this partition function reads

At *normal (room) temperatures, corresponding to energies of the order of  $kT = 25 meV$* , which are smaller than electronic energies ( $\approx 10 eV$ ) by a factor of  $10^3$ , the **electronic partition function represents merely the constant factor  $\Omega_0$** , the degeneracy of the electronic ground state. Typical values for alkali metal atoms are

$$q^{\text{electronic}} = \Omega_0 = 2 \quad (\text{III.92})$$

Similar, even stronger arguments can be made for the nuclear partition function  $q^{\text{nuclear}}$ . Nuclear energy level spacings are of the order of  $(10^5 - 10^6) eV$ . Hence, at room temperatures, the **nuclear partition function can be well approximated by the (spin- $I_{\text{nucl}}$ ) degeneracy of the nuclear ground state:**

$$q^{\text{nuclear}} \sim \Omega_0(I_{\text{nucl}}) = 2 \cdot I_{\text{nucl}} + 1 \quad (\text{III.93})$$

All terms combined give the ***total N-particle partition function of mono-atomic gases in the Boltzmann limit of high temperature***

$$Q(V, T) = \frac{1}{N!} (2I_{\text{nucl}} + 1)^N \cdot (\Omega_0^{\text{electronic}})^N \cdot \left[ \frac{V}{\lambda_{\text{therm}}^3} \right]^N \quad (\text{III.94})$$

Using further ***Stirling's Formula***,  $N! \approx (N/e)^N$ , which is valid for large numbers  $N \gg 1$ , this function simplifies further to

$$Q(V, T) = \left[ (2I_{\text{nucl}} + 1) \cdot (\Omega_0^{\text{electronic}}) \cdot \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \left( \frac{eV}{N} \right) \right]^N \quad (\text{III.94a})$$

*In practice, only the translational part of this partition function is important, because the level degeneracies remain constant in the typical processes considered.*

From this partition function, it is straightforward to regain the *average energy per particle*, essentially in translational motion,

$$\langle \varepsilon^{trans} \rangle = kT^2 \cdot \frac{\partial}{\partial T} \ln T^{\frac{3}{2}} = \frac{3}{2} kT \quad (\text{III.89a})$$

and the contribution of thermal translational motion to the heat capacity per particle,

$$c_V^{trans} = \frac{C_V^{trans}}{N} = \frac{3}{2} k \quad (\text{III.95})$$

Both results are familiar already from the treatment of the kinetic theory of gases.

The *rotation in space* is an important degree of freedom for many complex molecules. The rotational degree of freedom can be excited in collisions between molecules in thermal motion and assumes, therefore, energies typical of the overall temperature of the system. Thus it contributes to the capacity of the system to carry energy, its

*heat capacity has a part dependent on the characteristics of rotational degree of particular molecule of interest.*

The **rotational canonical partition function**  $q^{rot}$  for a single particle can be easily evaluated in the limit of classical **Boltzmann statistics**, valid for relatively high temperatures:

$$q^{rot} = \sum_{j=0}^{\infty} e^{-\beta \varepsilon_j^{rot}} = \sum_{\varepsilon_j^{rot}} \Omega_j(\varepsilon_j^{rot}) e^{-\beta \varepsilon_j^{rot}} \quad (\text{III.96})$$

Here, the rotational partition function has been expressed in both alternatives, as a **sum over single-particle microstates  $j$**  (left) and a **sum over single-particle microstate energy levels  $\varepsilon_j^{rot}$**  (right). It is in fact more practical to use the formulation on the *r.h.s.* of Equ. III.96, because one knows the level degeneracy for rotational levels explicitly. One can choose the index  $j$  to represent the **quantal spin angular momentum**

$$J = \sqrt{j(j+1)} \hbar \quad (\text{III.97})$$

of the molecule. For a generic molecule with no particular symmetry, e.g.,  $CO$ , there are energy levels for every  $j = 0, 1, 2, \dots$

For a molecule of a certain **rotational symmetry** or **symmetry number  $\sigma$** , there are fewer levels. For example, the linear symmetric molecule  $O=C=O$  has  $\sigma = 2$  and a  $180^\circ = 360^\circ/\sigma$  rotational symmetry, rather than the regular  $360^\circ$  symmetry. For reasons explained

by quantum mechanics, this symmetric molecule has only even angular-momentum states, i.e., for  $j = 0, 2, 4, \dots$

$$\Omega_j = 2j + 1 \quad (\text{III.98})$$

*magnetic substates* for the rotational *level* number  $j$ , associated with the magnetic quantum numbers  $-j \leq m \leq +j$ , which all have the *same rotational energy*  $\varepsilon_j^{\text{rot}}$  in the absence of external magnetic fields. This rotational energy of the molecule is related to its *moment of inertia*  $\Theta$  by

$$\varepsilon_j^{\text{rot}} = \frac{j(j+1)\hbar^2}{2\Theta} \quad (\text{III.99})$$

Inserting level degeneracy and energies into Equ. III.85, one obtains for the *single-particle rotational partition function*

$$q^{\text{rot}} = \sum_{j=0}^{\infty} (2j+1) \cdot e^{-\beta \frac{j(j+1)\hbar^2}{2\Theta}} \quad (\text{III.100})$$

Given the moment of inertia  $\Theta$  of the molecule, one can evaluate the rotational partition function. It is convenient to combine the



rotational characteristics of the molecule in one parameter, the "**rotational temperature**"  $T_{rot}$  (or  $\Theta_{rot}$ )

$$T_{rot} = \frac{\hbar^2}{2k\Theta} \quad (\text{III.101})$$

such that the rotational partition function can be expressed as

$$q^{rot} = \sum_{j=0}^{\infty} (2j+1) \cdot e^{-j(j+1)\frac{T_{rot}}{T}} \quad (\text{III.102})$$

One has to realize that the *moment of inertia  $\Theta$  depends on the distribution of the atomic masses of the molecule with respect to the axis of rotation. It is, therefore, in general different for different rotational axes, unless the molecule has certain symmetry.*

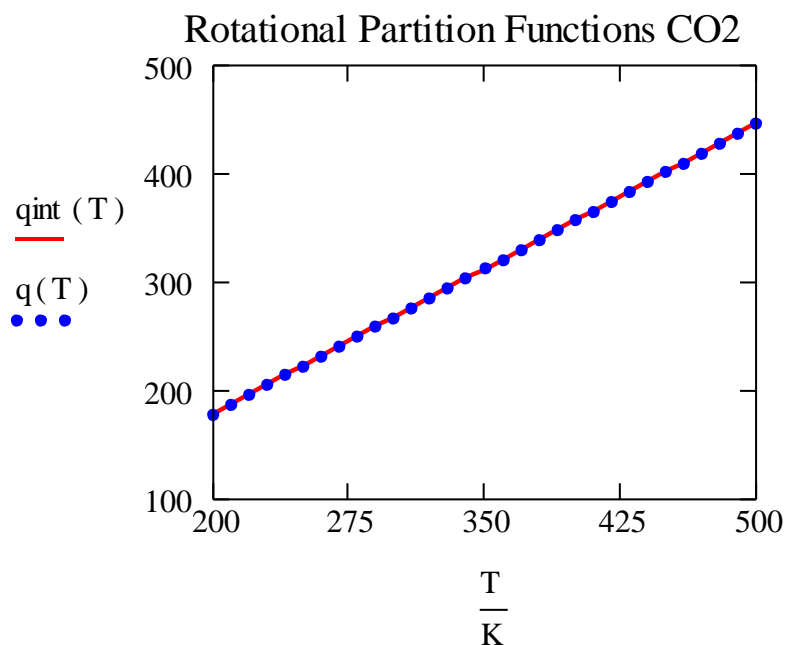
For relatively small molecules such from  $CO_2$  to  $CH_3Cl$ , the magnitude of the rotational temperature is typical from a fraction of one degree to several tens of  $K$ . Hence, at room temperature,  $T_{rot} \ll T$ .

Therefore, the partition sum in Equ. III. 102 is very well approximated by a partition integral

$$q^{rot} \approx \frac{1}{\sigma} \int_0^{\infty} dj(2j+1) \cdot e^{-j(j+1)\frac{T_{rot}}{T}} = \frac{1}{\sigma} \int_0^{\infty} dx e^{-x\frac{T_{rot}}{T}} = \frac{T}{\sigma T_{rot}} \quad (\text{III.103})$$

Making the transition from the exact partition sum to an unrestricted integral over all levels requires a **correction for the double-counting of levels for symmetric molecules**. Therefore, the factor  $1/\sigma$  has been introduced above. In the further evaluation of the integral, the variable transform  $x = j(j+1)$  with  $d\{j(j+1)\}/dx = 2j+1$  has been utilized.

As an example, the figure below shows a comparison of the  $CO_2$



rotational partition sum (points) with the corresponding partition integral (line) [[MATHCAD 252\Rot PF CO2.MCD](#)]. There is obviously very good agreement between the two different

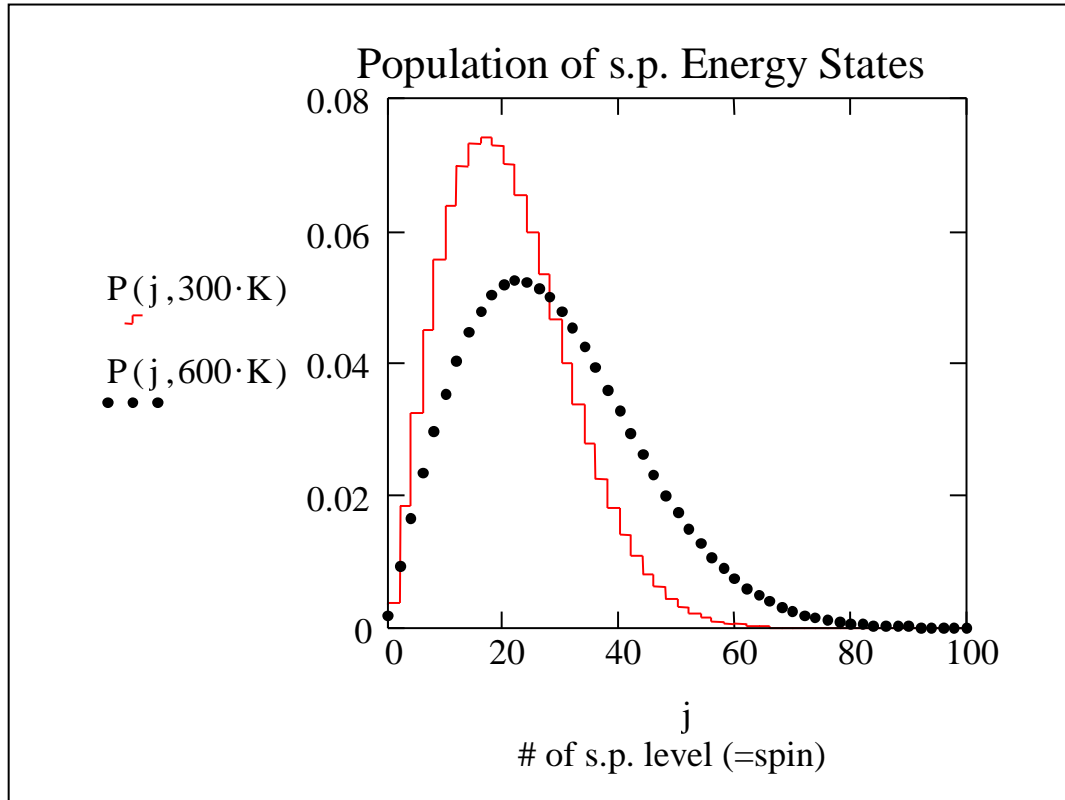
representations already at temperatures somewhat lower than room temperature.

Of practical interest in spectroscopic studies is often the population  $P_j$  of molecular rotational *levels* at the temperature of the sample. These populations are just the terms in the partition sum Equ. III.102, normalized by division by the total sum,

$$P_j = \frac{1}{q^{\text{rot}}} (2j+1) \cdot e^{-j(j+1) \frac{T_{\text{rot}}}{T}} \quad (\text{III.104})$$

Some calculations ([MATHCAD 252\Rot\\_PF\\_CO2.MCD](#)) are shown below for  $\text{CO}_2$  and two different temperatures.

Basically, this function has a triangular shape, folded with a Gaussian. For relatively small angular momenta of the particle, the exponential in Equ. III.104 approaches unity, and the spin



degeneracy determines the population, i.e.,  $P_j \propto (2j+1)$ . For large angular momenta, on the other hand, the Gaussian dominates and the population has approximately the form

$$P_j \propto \exp\left\{-j^2/2\sigma_j^2\right\} \quad (\text{III.105})$$

where  $\sigma_j^2$  is a constant, the so-called *spin cutoff parameter*

$$\sigma_j^2 = \frac{\Theta}{h^2} kT \quad (\text{III.106})$$

With increasing temperature, the peak of the spin distribution, the *most probable spin*, shifts to higher spin values. Simultaneously, the tail of the distribution reaches to higher spins, and the decay becomes more gradual.

The dependence of the populations of energy levels on parameters such as the moment of inertia  $\Theta$  of the molecules presents an interesting spectroscopic tool. It turns out that even fairly small molecules with small  $\Theta$  values, such as *HCl*, are *dominantly in  $j \gg 0$  states already at room temperature*.

Knowing the rotational partition function, for example, in its classical form of Equ. III.103, one can calculate the average energy of rotational motion of a molecule,

$$\langle \varepsilon^{rot} \rangle = kT^2 \frac{\partial}{\partial T} \ln q^{rot} = kT \quad (\text{III.107})$$

The result is quite satisfactory in view of the *Principle of Equipartition of the Energy* mentioned earlier. According to this principle, every degree of freedom in thermal equilibrium carries an

average energy of  $\langle \varepsilon^{\text{TM}} \rangle = (1/2) kT$ . In rotations about a fixed axis, there are two degree of freedom, hence  $\langle \varepsilon^{\text{rotTM}} \rangle = 2 \times (1/2) kT = kT$ . Again, this *result can be traced back to the quadratic dependence of the energy on the associated variable*. Compare Equ. III.102 with Equ. III.85, with the variables  $j$  and  $n$ , respectively.

From the average rotational energy per particle, one can calculate the contribution to the heat capacity per particle due to the rotational degree of freedom. Similar to Equ. III.95, one calculates for the *rotational heat capacity per particle*,

$$c_V^{\text{rot}} = \frac{C_V^{\text{rot}}}{N} = \frac{\partial}{\partial T} \langle \varepsilon^{\text{rot}} \rangle = k \quad (\text{III.108})$$

*In the classical limit of high temperatures or small  $\beta$  values, where the partition sums can be approximated by integrals, the heat capacity per particle and degree of freedom approaches a constant value of  $c_V = (1/2)k$ . This remains true even for molecules that are strictly non-ideal in that they have an internal structure.*

Other degrees of freedom can be treated in much the same manner. Consider, for example, molecules with *vibrational degrees of freedom*, e.g., with oscillation in the direction  $x$ . If the vibration is harmonic, i.e., occurs in a quadratic potential, the quantum-mechanical model of the harmonic oscillator applies. Here, the molecular energy levels can be numbered by the quantum number  $n = 0, 1, \dots$ . The level spacing is equidistant, as determined by the *fundamental (circular) frequency  $\omega$* . This frequency depends on the inertia  $M$  of the oscillator and the linear-force constant defined by Hooke's force law  $F(x) = c(x - x_0)$  as

$$\omega = \sqrt{c / M} \quad (\text{III.109})$$

The single-particle energy levels for such a harmonic oscillator are *sums of kinetic and potential energy*. They can be expressed as

$$E_v = \hbar\omega (v + 1/2) \quad v = 0, 1, 2, \dots \quad (\text{III.110})$$

Here, the ground-state energy  $E_0 = (1/2)\hbar\omega$  is also known as **zero-point fluctuation**.

With this knowledge, one can construct the **vibrational partition function**:

$$q^{\text{vib}} = \sum_{v=0}^{\infty} e^{-\beta\hbar\omega(v+1/2)} \quad (\text{III.111})$$

For the evaluation of this partition function, it is useful to rewrite Equ. III.111 as

$$q^{\text{vib}} = e^{-\frac{1}{2}\beta\hbar\omega} \cdot \sum_{v=0}^{\infty} e^{-\beta\hbar\omega \cdot v} = e^{-\frac{1}{2}\beta\hbar\omega} \cdot \sum_{v=0}^{\infty} (e^{-\beta\hbar\omega})^v = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \quad (\text{III.112})$$

which can also be written as

$$q^{\text{vib}} = \frac{1}{e^{+\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega}} = \frac{1}{2} \sinh^{-1} \left( \frac{\hbar\omega}{2kT} \right) \quad (\text{III.113})$$

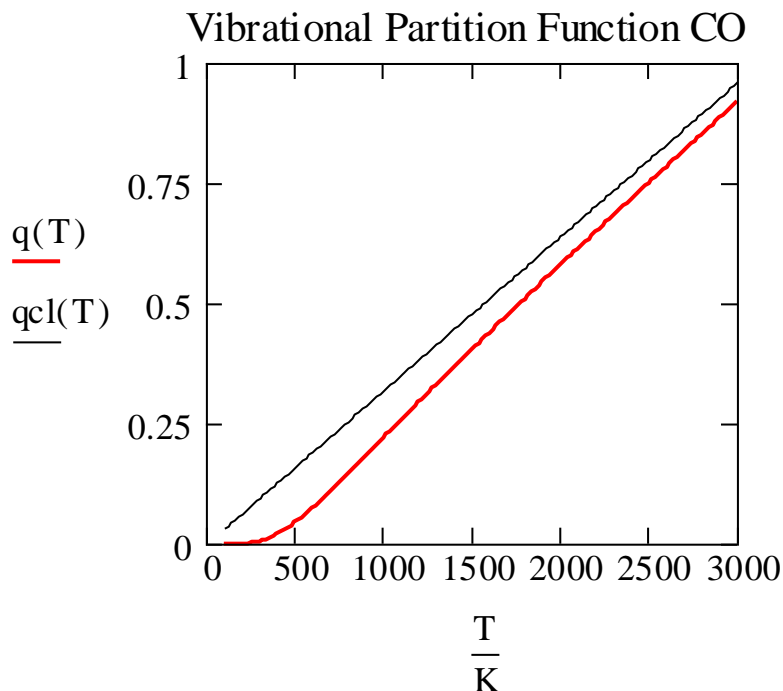
For high temperatures,  $T \gg \hbar\omega$ , the hyperbolic-sine function becomes linear in its argument. Hence,

$$q^{vib} \xrightarrow{T \rightarrow \infty} \frac{kT}{\hbar\omega} = \frac{T}{T_{vib}} \quad (\text{III.114})$$

where  $T_{vib} = \hbar\omega/k$  is the **vibrational temperature**, a quantity characteristic of the molecular oscillator.

For typical diatomic molecules such as  $H_2$  or  $HCl$ , the vibrational temperatures are of the order of several  $10^3 K$ . Hence, the classical limit of very large temperatures  $T \gg T_{vib}$  is difficult to attain for vibrational motion. Essentially, at **temperatures typical for most experiments, vibrational motion has to be described with the quantum-mechanical formalism.**

As an example, the figure compares the quantal vibrational partition function (Equ. III.113) for the diatomic molecule  $CO$  with its classical approximation (Equ. III.114). The vibrational temperature for  $CO$  is  $T_{vib} = 3122 K$  ([MATHCAD 252\Vib PF CO.MCD](#)).



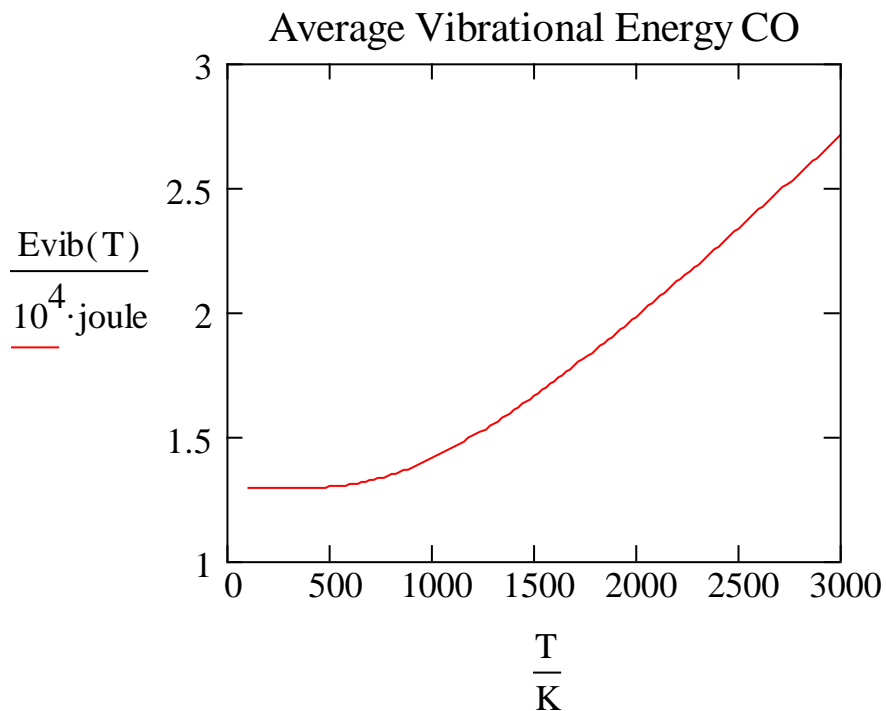
As can be seen from this figure, the absolute values of the vibrational partition function are relatively small, of the order of 1 or less, for the temperature range displayed. At low temperatures, the *quantal partition function is noticeably non-linear*. It is better approached by the classical partition function only at extremely high temperatures, where presumably molecules can no longer exist in stable, bound states.

In spite of these difficulties, it is straightforward to calculate simple quantities like the average vibrational energy and the associated heat capacity:

$$\begin{aligned} \langle \varepsilon^{vib} \rangle &= kT^2 \frac{\partial}{\partial T} \ln q^{vib} = \frac{\partial}{\partial \beta} \ln \left\{ e^{+\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega} \right\} = \\ &= \frac{\frac{\hbar\omega}{2} e^{+\frac{1}{2}\beta\hbar\omega} + \frac{\hbar\omega}{2} e^{-\frac{1}{2}\beta\hbar\omega}}{e^{+\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega}} = \frac{\hbar\omega}{2} \coth\left(\frac{\hbar\omega}{2kT}\right) \end{aligned} \quad (\text{III.115})$$

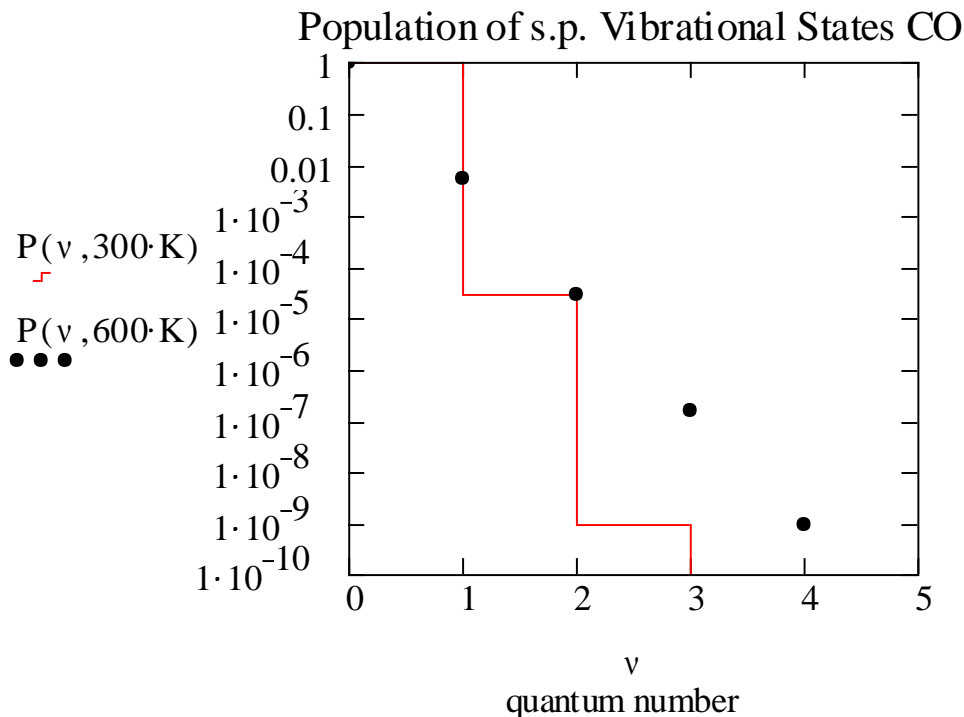


This formula has been evaluated and plotted below for one mole



of  $CO$  { [MATHCAD 252\Vib PF CO.MCD](#) }. One observes that at low temperatures, the average vibrational energy is small and remains constant. This is the region in temperature, where there are only *zero-point vibrations* of the oscillator, and no excited state is populated.

The plot below shows the populations of the first few vibrational

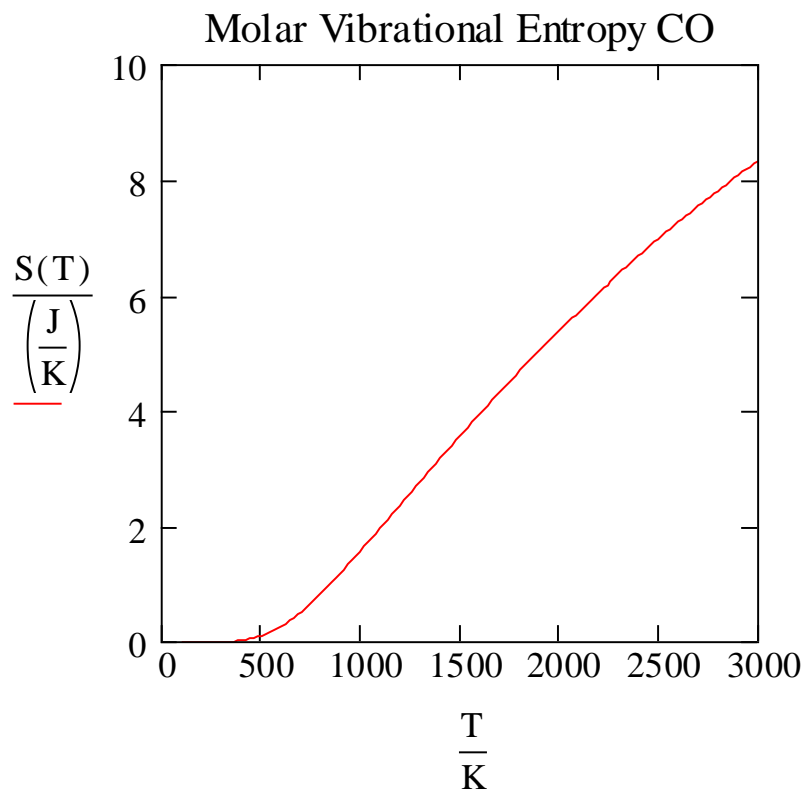


states of  $CO$ , for  $T = 300\text{ K}$  (histogram) and  $T = 600\text{ K}$  (solid dots) {[MATHCAD 252\Vib\\_PF\\_CO.MCD](#)}. It is impressive, how fast the population decreases with increasing principal quantum number. For example,  $P(1)/P(0) \sim 10^{-5}$  for  $T = 300\text{ K}$ . Even for  $T = 600\text{ K}$ , the population of the first excited state ( $\nu = 1$ ) of  $CO$  reaches barely 1% of that of the ground state ( $\nu = 0$ ) of that molecule.

It is also easy to see that in the classical limit of  $T \rightarrow \infty$ , or  $\beta \rightarrow 0$ , the partition function becomes proportional to the temperature:

To appreciate this result in the light of the *Equipartition Principle*, one has to remember that the vibrational energy  $\epsilon^{vib}$  is a sum of kinetic and potential energies. On average, there is an equal amount in kinetic and potential energy for a harmonic oscillator. This explains why the *average vibrational energy is twice the elementary thermal energy  $(1/2)kT$  per degree of freedom*.

However, as shown above, at ordinary temperatures, the thermal energy in vibrational motion is very small, much smaller than the energy in translational or rotational motion. The molecules are typ-



ically not found in a wide range of vibrational states but are mostly gathered in the vibrational ground state. The reason for this is, of course, the *low density of states, or the low entropy associated with*

*vibrational degrees of freedom*. The figure above illustrates the variation of the molar vibrational entropy calculated from [Equ. III.70](#)

$$S(T) = \left[ k \cdot \ln(q^{vib}(T)) + \frac{\langle \epsilon^{vib} \rangle}{T} \right]$$

(III.117)

and the vibrational partition function of Equ. III.113 using again [C:\WINMCAD\Programs\Vib\\_PF\\_CO.MCD](#). One observes from this figure that, even for thousands of degrees of Kelvin, the molar entropy  $S(T)$  is still in the range of only a few  $J/K$ .

This behavior is echoed by the vibrational contribution to the heat capacity. To obtain the heat capacity associated with vibrational motion, one simply differentiates the average energy of Equ. III.103 with respect to  $T$  and obtains

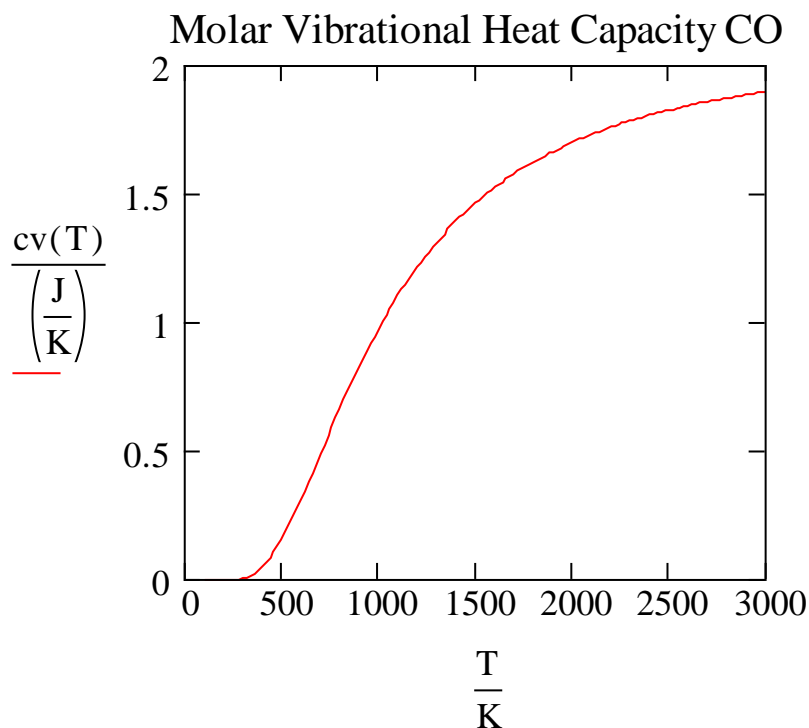
$$c_V^{vib} = \frac{\partial \langle \epsilon^{vib} \rangle}{\partial T} = + \frac{\hbar \omega}{2} \cdot \frac{1}{\sinh^2\left(\frac{\hbar \omega}{2kT}\right)} \cdot \frac{\hbar \omega}{2kT^2} \quad (\text{III.118})$$

and finally

$$c_V^{vib} = k \cdot \left( \frac{\hbar \omega}{2kT} \cdot \sinh^{-1}\left(\frac{\hbar \omega}{2kT}\right) \right)^2 \quad (\text{III.119})$$

Since for small values of the argument,  $\sinh(x) \approx x$ , one obtains immediately,  $c_V^{vib} \approx k$  in the classical limit of large temperatures, as for the other degrees of freedom considered.

The figure below shows the heat capacity calculated for  $CO$ . Its  $T$  dependence illustrates the behavior famous from introductory discussions of quantum mechanics. This is in fact the characteristic  $T$



dependence of the heat capacity for solid materials. Solids form lattices of atoms or molecules that are held in their lattice positions by the interaction forces. These particles have no freedom of translational or rotational motion. Hence, ***vibrational motion is the most important degree of freedom of solids at low to moderately high temperatures.***

The small values of the heat capacity at such temperatures indicate the ***inability of solids to store large amounts of heat energy or entropy.*** What happens, when one forces large amounts of heat into a piece of solid material, e.g., by immersing it into a heat bath of very high temperature or by irradiating it with intense high-energy

radiation, is all too familiar: Like forcing too large an amount of water into a pipe system makes it burst, forcing too large a current of entropy into a solid destroys the lattice structure. The solid *melts*. ***A certain structure (phase) of material can carry entropy only to a maximum amount, after which its structure changes in a 'phase transition'.***

Of course, in the above example, the gas *CO* was considered, which has translational degrees of freedom, in addition to rotational and vibrational ones. The *translational degrees of freedom* have the largest heat capacity. They *dominate the average thermodynamic behavior of gases*. In particular, translational degree of freedom can store the largest amounts of entropy and heat energy.