

Two lowest energy states:

$$(1) \quad n_x = n_y = n_z = 1, \quad n_x^2 + n_y^2 + n_z^2 = 3,$$

$$(2) \quad 2 \text{ } n\text{'s} = 1 \text{ and } 1 \text{ } n = 2, \quad 1^2 + 1^2 + 2^2 = 6,$$

so

$$\begin{aligned} \varepsilon_1 &= \frac{3h^2}{8mL^2}, & \varepsilon_2 &= \frac{6h^2}{8mL^2}, \\ \frac{h^2}{mL^2} &= \frac{(6.63 \times 10^{-34} \text{ J s})^2}{(1\text{kg})(1 \text{ m})^2} = 4.39 \times 10^{-67} \text{ J}, \\ \varepsilon_1 &= 1.65 \times 10^{-67} \text{ J}, \\ \varepsilon_2 &= 3.30 \times 10^{-67} \text{ J}. \end{aligned}$$

$$\begin{aligned} (b) \quad q_{\text{translation}} &= \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \\ &= \left[\frac{(6.28)(1 \text{ kg})(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}{(6.63 \times 10^{-34} \text{ J s})^2} \right]^{3/2} (1 \text{ m})^3 \\ &= 1.44 \times 10^{70} \frac{\text{accessible states}}{\text{molecule}}. \end{aligned}$$

Quantum effects are clearly not important for objects as large as basketballs.

4. The statistical mechanics of an electron.

Calculate the two lowest energy levels for an electron in a box of volume $V = 1 \text{ \AA}^3$ (This is an approximate model for the hydrogen atom). Calculate the partition function at $T = 300 \text{ K}$. Are quantum effects important?

(a) As above

$$\varepsilon_1 = \frac{3h^2}{8mL^2}, \quad \varepsilon_2 = \frac{3h^2}{4mL^2},$$

where $m = \text{mass of the electron} = 9.11 \times 10^{-31} \text{ kg}$,

$$\frac{h^2}{mL^2} = \frac{(6.63 \times 10^{-34} \text{ J s})^2}{(9.11 \times 10^{-31} \text{ kg})(10^{-10} \text{ m})^2} = 4.82 \times 10^{-17} \text{ J}$$

$$\varepsilon_1 = 1.81 \times 10^{-17} \text{ J},$$

$$\varepsilon_2 = 3.62 \times 10^{-17} \text{ J}.$$

$$(b) \quad q_{\text{translation}} = \left[\frac{(6.28)(9.11 \times 10^{-31} \text{ kg})(4.14 \times 10^{-21} \text{ J})}{(6.63 \times 10^{-34} \text{ J s})^2} \right]^{3/2} (10^{-10} \text{ m})^3$$

$$= 1.25 \times 10^{-5}.$$

The classical approximation is *not* valid (since $q < 10$), and quantum effects are important. Since q cannot be smaller than 1, the value obtained above is an artifact of the assumption that the sum in the partition function can be approximated as an integral for this problem.

5. The translational partition function in two dimensions.

When molecules adsorb on a two-dimensional surface, they have one less degree of freedom than in three dimensions. Write the two-dimensional translational partition function for an otherwise structureless particle.

For each dimension,

$$q_{\text{translation,1D}} = \left(\frac{2\pi mkT}{h^2} \right)^{1/2} L$$

and

$$q_{\text{translation,2D}} = q_{\text{translation,1D}}^2,$$

so if $A = \text{area} = L^2$, then

$$q_{\text{translation,2D}} = \left(\frac{2\pi mkT}{h^2} \right) A.$$

6. The accessibility of rotational degrees of freedom.

Diatomic ideal gases at $T = 300$ K have rotational partition functions of approximately $q = 200$. At what temperature would q become small (say $q < 10$) so that quantum effects become important?

$$q_{\text{rot}} = \frac{8\pi^2 I k T}{\sigma h^2}.$$

If $q_{\text{rot}} = 200$ at $T = 300$ K, then

$$\frac{8\pi^2 I k}{\sigma h^2} = \frac{2}{3}, \quad q_{\text{rot}} = \frac{2}{3} T = 10,$$

and so quantum effects become important when $T = 15$ K.

7. The statistical thermodynamics of harmonic oscillations.

Write the internal energy, entropy, enthalpy, free energy, and pressure for a system of N independent distinguishable harmonic oscillators.

For harmonic oscillators, $q = e^{-h\nu\beta}/(1 - e^{-h\nu\beta})$. For distinguishable particles, $Q = q^N$.

$$(a) \quad \frac{\Delta U}{N} = -\frac{1}{q} \frac{\partial q}{\partial \beta} = \frac{h\nu e^{-h\nu\beta}}{1 - e^{-h\nu\beta}}.$$

$$(b) \quad \frac{S}{kN} = \ln q + \frac{\Delta U}{NkT},$$

$$\frac{S}{kN} = -\ln(1 - e^{-h\nu\beta}) + \left(\frac{h\nu}{kT}\right) \left(\frac{e^{-h\nu\beta}}{1 - e^{-h\nu\beta}}\right).$$

$$(c) \quad F = -kT \ln Q \implies \frac{F}{NkT} = -\ln q = +\ln(1 - e^{-h\nu\beta}).$$

11. Heat capacities of liquids.

- (a) C_V for liquid argon (at $T = 100\text{ K}$) is $18.7\text{ J K}^{-1}\text{ mol}^{-1}$. How much of this heat capacity can you rationalize on the basis of your knowledge of gases?
- (b) C_V for liquid water at $T = 10^\circ\text{C}$ is about $75\text{ J K}^{-1}\text{ mol}^{-1}$. Assuming water has three vibrations, how much of this heat capacity can you rationalize on the basis of gases? What is responsible for the rest?

- (a) Liquid argon is spherical (no rotations and no vibrations), and has only translational freedom, so

$$\begin{aligned}C_V &= \frac{3}{2}nR \\ &= n\left(\frac{3}{2}\right)(8.314\text{ J K}^{-1}\text{ mol}^{-1}) \\ &= 12.47\text{ J K}^{-1}\text{ mol}^{-1}\end{aligned}$$

can be rationalized. The rest must be due to intermolecular interactions.

- (b) $(3/2)nR$ due to translations, plus 0 or $3nR$ for vibrations, depending whether they are strong or weak, plus $(3/2)nR$ for rotations equals $3nR = 24.94\text{ J K}^{-1}\text{ mol}^{-1}$. The rest must be rationalized based on intermolecular interactions and hydrogen bonding.

12. The entropies of CO.

- (a) Calculate the translational entropy for carbon monoxide CO (C has mass $m = 12\text{ amu}$, O has mass $m = 16\text{ amu}$) at $T = 300\text{ K}$, $p = 1\text{ atm}$.
- (b) Calculate the rotational entropy for CO at $T = 300\text{ K}$. The CO bond has length $R = 1.128 \times 10^{-10}\text{ m}$.

Here the gas molecules are indistinguishable. This means that we need to include the correction $1/N!$ in the translation partition function of the N -particle system.

$$\begin{aligned}
\text{(a)} \quad S &= Nk \ln\left(\frac{qe}{N}\right) + \frac{\Delta U}{T} \\
&= nR \left[1 + \ln\left(\frac{q}{N}\right)\right] + \frac{3nR}{2} \\
&= nR \left[\frac{5}{2} + \ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \left(\frac{V}{N}\right)\right],
\end{aligned}$$

$$\frac{S}{n} = R \left[\frac{5}{2} + \ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \left(\frac{kT}{p}\right)\right],$$

$$m = (28)(1.78 \times 10^{-27} \text{ kg}),$$

$$kT = (1.38 \times 10^{23} \text{ J K}^{-1})(300 \text{ K}),$$

$$p = 1.013 \times 10^5 \text{ N m}^{-2},$$

$$h^2 = (6.626 \times 10^{-34} \text{ J s})^2,$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1},$$

$$\Rightarrow \frac{S}{n} = 150.3 \text{ J K}^{-1} \text{ mol}^{-1}.$$

$$\text{(b)} \quad \frac{S}{n} = R(\ln q + 1),$$

$$q = \frac{8\pi^2 \mu R^2 kT}{\sigma h^2},$$

$$\sigma = 1,$$

$$\mu = \frac{(12)(16)}{12 + 16}$$

$$= (6.86) \times (1.67 \times 10^{-27} \text{ kg}),$$

$$\frac{S_{\text{rot}}}{n} = 47.28 \text{ J K}^{-1} \text{ mol}^{-1}.$$