STRUTTURA DELLA MATERIA 1

Problems on molecules – mainly diatomics

Nicola Manini

first delivered: 10, 16, 17 Nov. 2020; last revised Nov. 19, 2024

1 "Megaproblem" on adiabatic molecular mechanics

Let the adiabatic potential energy of the $H^{35}Cl$ molecules be expressed by the relation:

$$V_{\rm ad}(R) = -\frac{a}{R^3} + \frac{b}{R^9}\,,$$

as a function of the interatomic distance R, where a and b are positive constants.

1. Fit a and b on the observed vibrational quantum $\bar{\nu}_0 = 2890$ cm^{-1} and rotational energy spacing $B = \hbar^2/I$ amounting to 21.3 cm^{-1}.
2. Evaluate the molecular bond energy of $H^{35}Cl$, taking also the zero-point motion into account.
3. Estimate, based on the harmonic approximation, the number of bound vibrational states.
4. If the $H^{35}Cl$ bond is stretched by $\delta R = 10$ pm, what is the restoring force? How does this result change in the harmonic approximation?
5. If the $H^{35}Cl$ is pulled by a force $F = 1$ nN, what is the new equilibrium length?
6. What is the most populated rotational level at 300 K and 1103 K?
7. What fraction of molecules is in the $l = 2$ rotational state at 100 K?
8. What fraction of molecules is in any excited vibrational state at 300 K and 1103 K?

1.1 Solution

1. Model side:
   Compute the first derivative of $V_{\rm ad}(R)$:

   $$V'_{\rm ad}(R) = \frac{3a}{R^4} - \frac{9b}{R^{10}}\,,$$

   i.e. − the radial force. Search the equilibrium distance:

   $$V'_{\rm ad}(R) = 0 \qquad \Longrightarrow \qquad a = \frac{3b}{R^6} \qquad \Longrightarrow \qquad R_{\rm M} = \left(\frac{3b}{a}\right)^{1/6}$$

Evaluate the potential-energy curvature:

$$V''_{\rm ad}(R) = \frac{-4\cdot 3a}{R^5} - \frac{-10\cdot 9b}{R^{11}} = -\frac{12a}{R^5} + \frac{90b}{R^{11}}\,.$$

Compute it at the equilibrium distance:

$$V''_{\rm ad}(R_{\rm M}) = -12a\left(\frac{a}{3b}\right)^{5/6} + 90b\left(\frac{a}{3b}\right)^{11/6} = \left(-12\cdot 3^{-5/6} + 90\cdot 3^{-11/6}\right)\frac{a^{11/6}}{b^{5/6}} = 6\times 3^{1/6}\times\frac{a^{11/6}}{b^{5/6}}\,.$$

Experimental side:
Compute the reduced mass

$$\mu = \frac{1\,\text{a.m.u.}\times 35\,\text{a.m.u.}}{1\,\text{a.m.u.} + 35\,\text{a.m.u.}} = 0.972\,\text{a.m.u.}$$

related to the momentum of inertia by $I = \mu R_{\rm M}^2 = \hbar^2/B$. Which allows us to compute the experimental equilibrium interatomic distance

$$R_{\rm M} = \left(\frac{I}{\mu}\right)^{1/2} = \left(\frac{\hbar^2}{B\mu}\right)^{1/2} = \frac{\hbar}{(B\mu)^{1/2}} = 1.276\times 10^{-10}\,\text{m}\,,$$

because $B = hc\times 21.3\ \text{cm}^{-1} = 4.23\times 10^{-22}$ J.

The other experimental quantity, the vibrational frequency, is related to the curvature $K \equiv V''_{\rm ad}(R_{\rm M})$ of the adiabatic potential, because

$$\omega = \sqrt{\frac{K}{\mu}}\,.$$

Therefore the "spring constant"

$$K = \mu\omega^2 = \mu\left(\frac{\hbar\omega}{\hbar}\right)^2 = 478.4\,\text{kg s}^{-2}\,,$$

because $\hbar\omega = hc\times 2890\ \text{cm}^{-1} = 5.741\times 10^{-20}$ J.

By equating model expressions and experimental data

$$\left\{\begin{array}{lcl} K &=& V''_{\rm ad}(R_{\rm M}) = 6\times 3^{1/6}\times\frac{a^{11/6}}{b^{5/6}} \\ R_{\rm M} &=& \left(\frac{3b}{a}\right)^{1/6} \end{array}\right.\,,$$

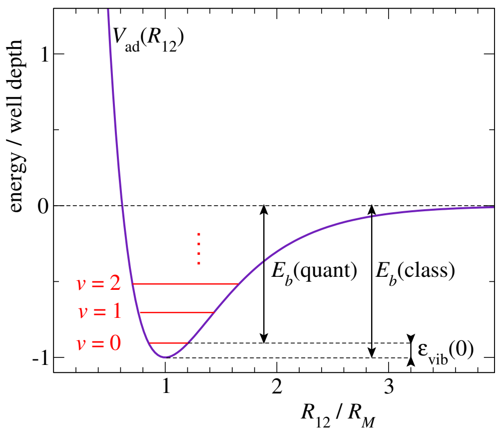
we obtain a system of 2 equations in a and b that we solve. Solutions:

$$a = \frac{1}{18}KR_{\rm M}^5 = 8.990\times 10^{-49}\,\text{kg}\,\text{m}^5\,\text{s}^{-2} = 89.90\,\text{kg}\,\text{Å}^5\,\text{s}^{-2}$$

$$b = \frac{1}{54}KR_{\rm M}^{11} = 1.293\times 10^{-108}\,\text{kg}\,\text{m}^{11}\,\text{s}^{-2} = 129.3\,\text{kg}\,\text{Å}^{11}\,\text{s}^{-2}.$$

2. Depth of the well:

$$-V_{\rm ad}(R_{\rm M}) = -a\left(\frac{a}{3b}\right)^{3/6} + b\left(\frac{a}{3b}\right)^{9/6} = 2\times 3^{-3/2}\times\frac{a^{3/2}}{b^{1/2}} \equiv \frac{1}{27}KR_{\rm M}^2$$
$$= 2.885\times 10^{-19}\ \text{J} = 1.801\ \text{eV}\,.$$



Zero-point energy:

$$\mathcal{E}_{\mathrm{vib}}(0) \simeq \frac{1}{2}\hbar\omega = 2.87 \times 10^{-20}\ \mathrm{J} = 0.179\ \mathrm{eV}\,.$$

Therefore

$$E^{\mathrm{diss}} = -V_{\mathrm{ad}}(R_{\mathrm{M}}) - \mathcal{E}_{\mathrm{vib}}(0) = 2.597 \times 10^{-19}\ \mathrm{J} = 1.621\ \mathrm{eV}\,.$$

3. N bound states ($v = 0, 1 ... N$), can be estimated by equating

$$\hbar\omega \left(N + \frac{1}{2}\right) \simeq -V_{\mathrm{ad}}(R_{\mathrm{M}})\,.$$

Whence

$$N \simeq= -\frac{V_{\mathrm{ad}}(R_{\mathrm{M}})}{\hbar\omega} - \frac{1}{2} = 4.5\,.$$

Which yields a fair first guess $N = 4$ or 5 bound vibrational states.

4. By definition of potential energy, the restoring bond force is

$$F = -V'_{\mathrm{ad}}(R) = -V'_{\mathrm{ad}}(R_{\mathrm{M}} + \delta R) = -\frac{3a}{(R_{\mathrm{M}} + \delta R)^4} + \frac{9b}{(R_{\mathrm{M}} + \delta R)^{10}} = -2.739\ \mathrm{nN}\,.$$

In the harmonic approximation

$$F = -K\,(R - R_{\mathrm{M}}) = -K\,\delta R = -4.784\ \mathrm{nN}\,.$$

Quite different!! A 10 pm distortion is sufficient to violate substantially the harmonic approximation...

5. The equilibrium condition:

$$0 = F - V'_{\mathrm{ad}}(R) = F - \frac{3a}{R^4} + \frac{9b}{R^{10}}$$

provides an equation in the unknown equilibrium distance R. Simplify:

$$F\,R^{10} - 3aR^6 + 9b = 0$$

or, in terms of R_{M}:

$$F\,R^{10} - \frac{K R_{\mathrm{M}}^5}{6} R^6 + \frac{K R_{\mathrm{M}}^{11}}{6} = 0\,.$$

This equation can be solved, e.g. numerically, substituting e.g. $R = R_{\mathrm{M}}$ and $R = R_{\mathrm{M}} + \delta R$ (see previous question), and then bisecting to $R = R_{\mathrm{M}} + \delta R/2$, etc., targeting to make the left hand of the equation as close as possible to 0.

Result: $R_{\mathrm{eq}} = R_{\mathrm{M}} + 2.403\,\mathrm{pm} = 1.300 \times 10^{-10}$ m.

6.

$$\mathcal{E}_{\rm rot}(l) = \frac{\hbar^2 l(l+1)}{2\mu R_{\rm M}^2} = \frac{B}{2} l(l+1)\,.$$

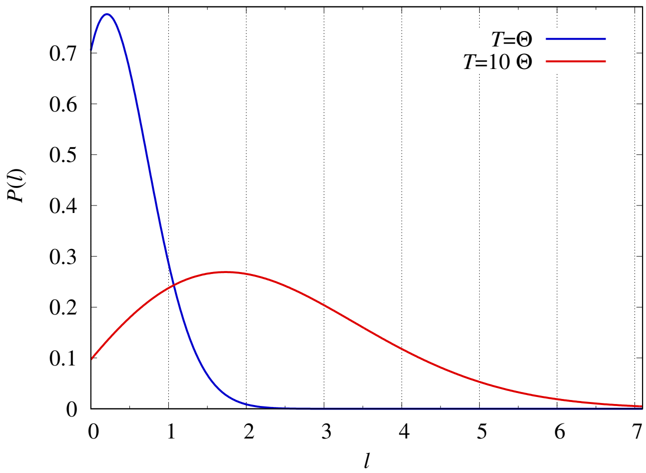
According to Boltzmann statistics for the internal degrees of freedom of molecules

$$P(l) = \frac{(2l+1)e^{-\beta\mathcal{E}_{\rm rot}(l)}}{Z_{1\,\rm rot}}\,.$$

Therefore, on average, the number of molecules in each rotational level is

$$N(l) = N_{\rm tot} \times P(l)\,.$$

The most populated level l is obtained by maximizing $N(l)$ as a function of l. Because $l = 0, 1, 2, 3, ...$ the simplest method for this maximization is a direct substitution of a few successive l's.



Alternatively, one can pretend that l is a continuous variable, take the derivative of $N(l)$ w.r.t. l, and set $N'(l)$ to 0:

$$N'(l) = \frac{N_{\rm tot}}{Z_{1\,\rm rot}}\left[-\beta\frac{B}{2}e^{-\beta Bl(l+1)/2}(2l+1)^2 + e^{-\beta Bl(l+1)/2}\times 2\right] = 0\,.$$

Dropping the irrelevant nonzero factor $N_{\rm tot}e^{-\beta\mathcal{E}_{\rm rot}(l)}/Z_{1\,\rm rot}$, we simplify to

$$\frac{\beta B}{2}(2l+1)^2 = 2\,,$$

$$(2l+1)^2 = \frac{4}{\beta B}\,,$$

$$2l+1 = \frac{2}{(\beta B)^{1/2}}\,.$$

In terms of $\Theta_{\rm rot} \equiv B/(2k_{\rm B}) = 22.81$ K, we can write the most populated l-level as

$$l^{\rm most} = -\frac{1}{2} + \frac{1}{(\beta B)^{1/2}} = -\frac{1}{2} + \left(\frac{T}{2\Theta_{\rm rot}}\right)^{1/2}.$$

For $T = 300$ K, we obtain $l^{\rm most} = 2.63$, indicating that the actual value is either 2 or 3, and one has to substitute these values in the population formula anyway.

We get $N(2) = \frac{N_\text{tot}}{Z_{1\,\text{rot}}} \times 3.68$ and $N(3) = \frac{N_\text{tot}}{Z_{1\,\text{rot}}} \times 3.79$, proving that the most populated level is $l = 3$.

For $T = 1103$ K, we obtain $l^\text{most} = 5.4994$, indicating that the actual value is either 5 or 6. We substitute these values in the population formula: $N(5) = \frac{N_\text{tot}}{Z_{1\,\text{rot}}} \times 7.25105$ and $N(6) = \frac{N_\text{tot}}{Z_{1\,\text{rot}}} \times 7.25362$, proving that the most populated level is $l = 6$.

Note that for this question we neither needed nor computed $Z_{1\,\text{rot}}$!

7.
$$\frac{N(2)}{N_\text{tot}} = P(2) = \frac{(2\times 2+1)e^{-\beta\mathcal{E}_\text{rot}(2)}}{Z_{1\,\text{rot}}},$$

so for this question we do need to evaluate $Z_{1\,\text{rot}}$!

At $T = 100$ K we cannot rely on the high-T approximate expression $Z_{1\,\text{rot}} \simeq T/\Theta_\text{rot} = 2/(\beta B) = 6.526$. To compute it more accurately & reliably, we carry out a truncated summation:

$$Z_{1\,\text{rot}} = \sum_{l=0}^{\infty}(2l+1)e^{-\beta\mathcal{E}_\text{rot}(l)} \simeq \sum_{l=0}^{10}(2l+1)e^{-\frac{\Theta_\text{rot}}{T}l(l+1)} = 6.87021\,.$$

(Note that $Z_{1\,\text{rot}}$ is larger than the approximate expression, and by adding more $l > 10$ terms it would get even larger. The infinitely many $l > 10$ omitted terms contribute less than 10^{-8} anyway.)

We now use the accurate value of $Z_{1\,\text{rot}}$ to compute

$$\frac{N(2)}{N_\text{tot}} = \frac{5e^{-\frac{\Theta_\text{rot}}{T}\times 2\times 3}}{Z_{1\,\text{rot}}} = 0.290\,.$$

8. Also for this question, there is no need to evaluate the relevant partition function, here Z_vib.

Indeed the number of molecules in a generic vibrational state v is:

$$\frac{N(v)}{N_\text{tot}} = P(v) = \frac{e^{-\beta\mathcal{E}_\text{vib}(v)}}{Z_\text{vib}} = \frac{e^{-\beta\hbar\omega(v+\frac{1}{2})}}{Z_\text{vib}}\,.$$

Therefore the fraction of molecules in any excited state (i.e. $v > 0$) is:

$$f_\text{exc} = \frac{\sum_{v=1}^{\infty} N(v)}{\sum_{v'=0}^{\infty} N(v')} = \frac{\sum_{v=1}^{\infty} P(v)}{\sum_{v'=0}^{\infty} P(v')} = \frac{\sum_{v=1}^{\infty} e^{-\beta\hbar\omega(v+\frac{1}{2})}}{\sum_{v'=0}^{\infty} e^{-\beta\hbar\omega(v'+\frac{1}{2})}} = \frac{\sum_{v=1}^{\infty} e^{-\beta\hbar\omega v}}{\sum_{v'=0}^{\infty} e^{-\beta\hbar\omega v'}}\,.$$

Now, we introduce a new summation index $v'' = v - 1$, so that both summations start from 0:

$$f_\text{exc} = \frac{\sum_{v''=0}^{\infty} e^{-\beta\hbar\omega(v''+1)}}{\sum_{v'=0}^{\infty} e^{-\beta\hbar\omega v'}} = e^{-\beta\hbar\omega}\frac{\sum_{v''=0}^{\infty} e^{-\beta\hbar\omega v''}}{\sum_{v'=0}^{\infty} e^{-\beta\hbar\omega v'}} = e^{-\beta\hbar\omega}\,,$$

because the two summations are now obviously identical.

Numerically, we obtain

$$f_\text{exc}(T = 300\text{ K}) = 9.5\times 10^{-7}\,,$$

$$f_\text{exc}(T = 1103\text{ K}) = 0.023\,.$$

2 Written test 18/11/2019, problem 3

Si considerino i livelli elettronici molecolari derivati dagli orbitali atomici 2p della molecola O_2. Tali livelli si classificano in orbitali σ e π a seconda del loro momento angolare $\hbar m$ lungo l'asse della molecola. Si assuma che le energie degli orbitali $\sigma - \sigma^*$ e $\pi - \pi^*$ risultino dalla diagonalizzazione delle seguenti matrici:

$$\begin{pmatrix} E_{2\mathrm{p}} & -\Delta_m \\ -\Delta_m & E_{2\mathrm{p}} \end{pmatrix}$$

con $E_{2\mathrm{p}} = -8$ eV e $\Delta_m = \Delta_m(R) = \epsilon_m \exp(-R/\lambda_m)$, dove $\epsilon_m = (1+|m|)\times 12$ eV e $\lambda_m = (2-|m|)\times 72$ pm. Tenendo conto delle occupazioni di tali livelli molecolari e delle regole di Hund si mostri che alla distanza d'equilibrio $R_M = 121$ pm la molecola è paramagnetica ($S = 1$). Si determini inoltre la distanza interatomica al di sotto della quale le occupazioni di stato fondamentale dei livelli elettronici prevedono uno stato diamagnetico con tutti gli spins appaiati.

2.1 Solution

1. The eigenvalues of a 2×2 matrix with equal diagonal elements are trivially:

$$\mathcal{E}_\pm = E_{2\mathrm{p}} \pm |\Delta_m|.$$

Substituting the expressions for the parameters:

$$\mathcal{E}_\pm(m=0) = -8 \text{ eV} \pm 12 \text{ eV} \times \exp(-R/144 \text{ pm})$$

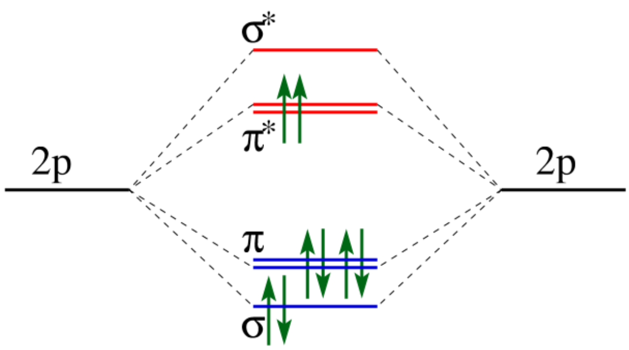
and

$$\mathcal{E}_\pm(m=\pm 1) = -8 \text{ eV} \pm 24 \text{ eV} \times \exp(-R/72 \text{ pm})$$

For $R = R_\mathrm{M} = 121$ pm:

$$\mathcal{E}_\pm(m=0) = \begin{cases} (+) & -2.812 \text{ eV} & \sigma^* \\ (-) & -13.179 \text{ eV} & \sigma \end{cases},$$

$$\mathcal{E}_\pm(m=\pm 1) = \begin{cases} (+) & -3.530 \text{ eV} & \pi^* \\ (-) & -12.471 \text{ eV} & \pi \end{cases},$$



Therefore, the ground state, with 8 electrons occupying the 12 2p-derived levels following the aufbau rule, is $^3\Sigma$.

2. At different R, the level order can change, in particular we are interested to the distance where σ^* crosses down below π^*. To identify this crossing distance, we equate:

$$\mathcal{E}_+(m=0) = \mathcal{E}_+(m=\pm 1),$$

i.e.

$$-8 \text{ eV} + 12 \text{ eV} \times \exp(-R/144 \text{ pm}) = -8 \text{ eV} + 24 \text{ eV} \times \exp(-R/72 \text{ pm}) .$$

Solution:

$$\exp(-R/144 \text{ pm}) = 2 \times \exp(-R/72 \text{ pm}) ,$$
$$\frac{-R}{144 \text{ pm}} = \ln 2 + \frac{-R}{72 \text{ pm}} ,$$
$$-R = 144 \text{ pm} \times \ln 2 - 2R ,$$
$$R = 144 \text{ pm} \times \ln 2 = 99.81 \text{ pm} .$$

For any R smaller than this distance, the $\sigma^* - \pi^*$ order is inverted, and therefore standard aufbau occupancies imply an electronic $^1\Sigma$ ground state.

3 Written test 18/06/2007, problem 3

Nello spettro rotovibrazionale di HCl gassoso si osserva la transizione $(v = 0, l = 2) \to (v = 1, l = 3)$ alla frequenza di 88380 GHz. Si determini la frequenza della linea omologa nello spettro di DCl, sapendo che la distanza d'equilibrio molecolare è di 1.27 Å. Si stimi inoltre la differenza di energia di dissociazione delle due molecole.

3.1 Solution

1. For HCl compute the reduced mass

$$\mu_{\text{HCl}} = \frac{1\,\text{a.m.u.} \times 35\,\text{a.m.u.}}{1\,\text{a.m.u.} + 35\,\text{a.m.u.}} = 0.972\,\text{a.m.u.}$$

and the momentum of inertia

$$I_{\text{HCl}} = \mu_{\text{HCl}} R_{\text{M}}^2 = 2.6039 \times 10^{-47} \text{ kg m}^2.$$

Correspondingly, the characteristic rotational energy

$$\frac{\hbar^2}{2I_{\text{HCl}}} = 2.1355 \times 10^{-22} \text{ J} = 1.3329 \text{ meV} .$$

The rotational contribution to the rotovibrational transition in HCl is therefore:

$$\Delta E^{\text{rot HCl}} = (3 \times 4 - 2 \times 3) \frac{\hbar^2}{2I_{\text{HCl}}} = 1.2813 \times 10^{-21} \text{ J} = 7.997 \text{ meV} .$$

By difference, we obtain the vibrational contribution:

$$\hbar\omega^{\text{vib HCl}} = \hbar\, 2\pi\, \nu^{\text{obs}} - \Delta E^{\text{rot HCl}}$$
$$= \hbar\, 2\pi\, 88380 \text{ GHz} - 1.2813 \times 10^{-21} \text{ J} = 5.728 \times 10^{-20} \text{ J} = 357.5 \text{ meV} .$$

Because $\omega = \sqrt{K/\mu}$ and K is independent of the isotopic mass, the corresponding vibrational quantum of DCl, can be obtained by suitable rescaling by the square root of the reduced mass:

$$\hbar\omega^{\text{vib DCl}} = \hbar\omega^{\text{vib HCl}} \times \sqrt{\frac{\mu_{\text{HCl}}}{\mu_{\text{DCl}}}} = \hbar\omega^{\text{vib HCl}} \times \sqrt{\frac{(35 \times 1)/(35+1)\,\text{a.m.u.}}{(35 \times 2)/(35+2)\,\text{a.m.u.}}}$$
$$= \hbar\omega^{\text{vib HCl}} \times \sqrt{\frac{35/36}{70/37}} = 4.1062 \times 10^{-20} \text{ J} = 256.3 \text{ meV} .$$

Likewise, we obtain the rotational quantum for DCl by suitable rescaling by the reduced mass:

$$\frac{\hbar^2}{2I_{\rm DCl}} = \frac{\hbar^2}{2I_{\rm HCl}} \times \frac{35/36}{70/37} = 1.0974 \times 10^{-22}\ {\rm J} = 0.685\ {\rm meV}\,.$$

We now combine back these two energies to reconstruct the energy of the homologous rovibrational transition:

$$\hbar\, 2\pi\, \nu^{\rm homol\ DCl} = \hbar\omega^{\rm vib\ DCl} + 6\,\frac{\hbar^2}{2I_{\rm DCl}} = 4.1720 \times 10^{-20}\ {\rm J} = 260.4\ {\rm meV}\,.$$

Whence

$$\nu^{\rm homol\ DCl} = 62964\ {\rm GHz}\,.$$

2. As the adiabatic potential is identical, the difference in dissociation energy (alias binding energy) is entirely due to a different zero-point contribution:

$$\begin{aligned}\Delta E_{\rm diss} &= E_{\rm diss\ DCl} - E_{\rm diss\ HCl} = -\mathcal{E}_{\rm vib\ DCl}(0) + \mathcal{E}_{\rm vib\ HCl}(0)\\ &\simeq -\frac{1}{2}\,\hbar\omega^{\rm vib\ DCl} + \frac{1}{2}\,\hbar\omega^{\rm vib\ HCl} = 8.109 \times 10^{-21}\ {\rm J} = 50.61\ {\rm meV}\,.\end{aligned}$$

4 Problem involving Statistics

In countless problem one is required to evaluate thermodynamic quantities such as the molecular or molar heat capacity of molecular gases.
We start with the derivations of the relevant equations.
The relevant degrees of freedom are of two kinds: translational and internal. The standard internal degrees of freedom of molecules are rotations and vibrations, although in special cases other degrees of freedom (e.g. spin) may also play a role.
These are the fundamental relations valid at high temperature:

$$Z \simeq \frac{(Z_1)^N}{N!}\,, \tag{1}$$

and

$$Z_1 = Z_{1\,{\rm tr}}\, Z_{1\,{\rm int}}\,. \tag{2}$$

They connect the statistics of the entire gas to that of a single molecule.

4.1 Translational heat capacity

Evaluate the contribition the translational energy and heat capacity of the molecular centers of mass of a hot gas of molecules or atoms. Evaluate it per molecule, per mole and per unit mass.

4.1.1 Solution

Let a molecule/atom move in a macroscopically large cubic box of volume $V = L\times L\times L$ with periodic boundary conditions. The allowed values of the $u = x, y, z$ wave vector components are

$$k_u = \frac{2\pi}{L}\, n_u\,, \qquad n_u = 0, \pm1, \pm2, \pm3, \ldots \tag{3}$$

Each $\vec{k}$ is associated to a plane-wave eigenfunctions

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{L^{3/2}} \exp(i\,\vec{k}\cdot\vec{r}),$$

with translational kinetic energy

$$\mathcal{E}_{\vec{n}} = \frac{\hbar^2|\vec{k}|^2}{2M} = \frac{(2\pi\hbar)^2}{2ML^2}\,(n_x^2+n_y^2+n_z^2)\,. \tag{4}$$

The translational single-particle partition function $Z_{1\,\mathrm{tr}}$ is the summation of the Boltzmann factors over the quantum numbers n_x, n_y, n_z:

$$Z_{1\,\mathrm{tr}} = \sum_{\vec{n}} \exp(-\beta\mathcal{E}_{\vec{n}}) = \sum_{n_x\,n_y\,n_z} \exp\left(-\beta\frac{[2\pi\hbar]^2}{2ML^2}\,[n_x^2+n_y^2+n_z^2]\right). \tag{5}$$

For large $L \to \infty$, the discrete translational energy levels are practically equivalent to a "continuum", because the ratio $\beta(2\pi\hbar)^2/(2ML^2) \ll 1$, therefore the single-particle contribution to $Z_{1\,\mathrm{tr}}$ changes very little for a unit increment of n_u.
Under this conditions we can approximate the triple n_u sum in Eq. (5) by the triple integral

$$\begin{aligned} Z_{1\,\mathrm{tr}} &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left(-\frac{\beta[2\pi\hbar]^2}{2ML^2}[n_x^2+n_y^2+n_z^2]\right) dn_x\,dn_y\,dn_z \\ &= \int_{-\infty}^{\infty} \exp\left(-\frac{\beta[2\pi\hbar]^2}{2ML^2}n_x^2\right) dn_x \times [\text{ same with } x\to y] \times [\text{ same with } x\to z] \\ &= \left[\int_{-\infty}^{\infty} \exp\left(-\frac{\beta[2\pi\hbar]^2}{2ML^2}n_u^2\right) dn_u\right]^3 . \end{aligned} \tag{6}$$

In the final passages, we show that this expression factorizes into the product of three identical integrals, namely the cube of one of them.
This is a Gaussian-type integral, with general expression:

$$\int_{-\infty}^{\infty} \exp\left(-\frac{x^2}{2a^2}\right) dx = \sqrt{2\pi}\,a\,.$$

We identify the dimensionless constant a^2 with $(ML^2)/[\beta(2\pi\hbar)^2]$, i.e.

$$a = \frac{M^{1/2}L}{\beta^{1/2}2\pi\hbar} = \frac{(Mk_{\mathrm{B}}T)^{1/2}L}{2\pi\hbar}\,.$$

We obtain

$$Z_{1\,\mathrm{tr}} = \left(\sqrt{2\pi}\frac{M^{1/2}L}{\beta^{1/2}\,2\pi\hbar}\right)^3 = \left(\frac{L}{\hbar}\sqrt{\frac{Mk_{\mathrm{B}}T}{2\pi}}\right)^3 = \left(\frac{L}{\Lambda}\right)^3 = \frac{V}{\Lambda^3}\,, \tag{7}$$

where we have introduced the *thermal length*

$$\Lambda = \hbar\sqrt{\frac{2\pi}{Mk_{\mathrm{B}}T}}\,. \tag{8}$$

Substitute the result (7) for the single-particle partition function into the global partition function (1) of the ideal gas

$$Z = \frac{(Z_{1\,\mathrm{tr}})^N}{N!}\,(Z_{1\,\mathrm{int}})^N = \frac{V^N}{N!\,\Lambda^{3N}}\,(Z_{1\,\mathrm{int}})^N\,. \tag{9}$$

From this expression one can obtain the translational contribution to all thermodynamical quantities.

For the present problem, we evaluate the internal energy:

$$\begin{aligned} U_{\rm tr} &= -\frac{\partial}{\partial \beta}\ln Z_{\rm tr} = -\frac{\partial}{\partial \beta}\ln\frac{V^N}{N!\,\Lambda^{3N}} = -\frac{\partial}{\partial \beta}\left[\ln(V^N) - \ln(N!) - \ln(\Lambda^{3N})\right] \\ &= \frac{\partial \ln(\Lambda^{3N})}{\partial \beta} = 3N\frac{\partial \ln \Lambda}{\partial \beta} = 3N\frac{\partial}{\partial \beta}\ln\left(\hbar\sqrt{\frac{2\pi\beta}{M}}\right) \\ &= 3N\frac{\partial}{\partial \beta}\left[\ln\hbar + \ln\left(\frac{2\pi\beta}{M}\right)^{1/2}\right] = 3N\frac{\partial}{\partial \beta}\left[\frac{1}{2}\ln\left(\frac{2\pi\beta}{M}\right)\right] \\ &= \frac{3}{2}N\frac{\partial}{\partial \beta}\left[\ln(2\pi) + \ln(\beta) - \ln(M)\right] = \frac{3}{2}N\frac{\partial \ln(\beta)}{\partial \beta} = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2}Nk_{\rm B}T\,. \end{aligned} \tag{10}$$

Here we have used repeatedly the elementary properties of the logarithm function [$\ln(ab) = \ln(a) + \ln(b)$ and $\ln(a^b) = b\ln(a)$], and the fact that the β derivative is carried out at fixed volume and number of particles. From this formula we immediately obtain the translational heat capacity at fixed volume:

$$C_{V\,\rm tr} = \frac{\partial U_{\rm tr}}{\partial T} = \frac{3}{2}Nk_{\rm B} \tag{11}$$

of a gas of N molecules at high temperature.
The problem requests this contribution "per molecule". It is sufficient to set $N = 1$ in Eq. (11):

$$C_{V\,\rm tr\ 1\ molecule} = \frac{3}{2}\,k_{\rm B}\,.$$

For the heat capacity "per mole", we set instead $N = N_{\rm A}$, the Avogadro constant representing the number of molecules in a mole:

$$C_{V\,\rm tr\ 1\ mole} = \frac{3}{2}N_{\rm A}k_{\rm B}\,.$$

To obtain the heat capacity per unit mass, one proceeds to evaluate the correct value of N to be plugged in Eq. (11), by counting the number of molecules in 1 kg:

$$N_{1\ \rm kg} = \frac{1\ \rm kg}{\text{molecular mass}}\,.$$

For example, the molecular mass of a ^{1}H^{35}Cl molecule is $(35+1)$ a.m.u $= 36$ a.m.u $\simeq 5.98\times 10^{-26}$ kg. As a result, $N_{1\ \rm kg} = 1.673\times 10^{25}$ must be inserted in Eq. (11) to obtain the translational heat capacity per kg of ^{1}H^{35}Cl. For natural isotopic mixtures, one should use the abundance-weighted average atomic masses, as reported in the periodic table of elements. E.g. natural HCl has an average molecular mass $(35.4527+1.0079)$ a.m.u $= 36.4606$ a.m.u $\simeq 6.05\times 10^{-26}$ kg.

4.2 Distribution of the translational degrees of freedom

Evaluate the statistical distribution of the translational energy of the center of mass of a hot gas of molecules or atoms.

4.2.1 Solution

This quantity is the product of 2 ingredients:

1. the energy-density of translational states, i.e. how many translational states are to be found in a given small energy interval

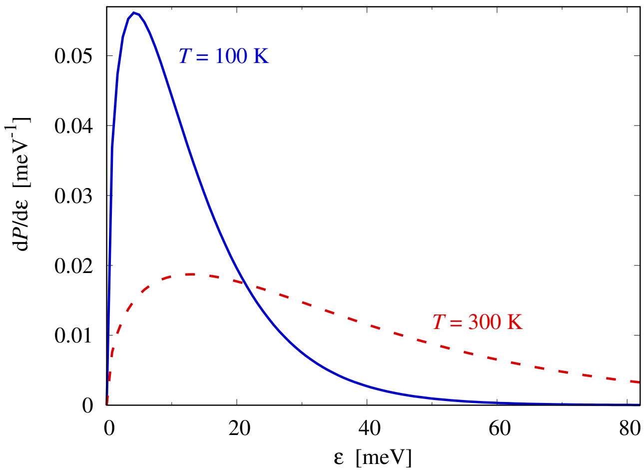
2. the probability to find a particle in one such energy state.

Let us calculated them separately:

1. According to Eq. (4), the kinetic energy is proportional to the squared length of the $\vec{n}$ vector
$$\mathcal{E}_{\vec{n}} = A|\vec{n}|^2 \,,$$
with $A = (2\pi\hbar)^2/(2ML^2)$. The $\vec{n}$ points are evenly distributed with unit density. Therefore the number of states with kinetic energy $\mathcal{E}_{\vec{n}} \leq \mathcal{E}$ (an arbitrarily given energy value) is practically identical to the volume of the sphere with radius $|\vec{n}| = \sqrt{\mathcal{E}/A}$ in the $\vec{n}$-space, namely
$$\#\text{states}(\mathcal{E}_{\vec{n}} \leq \mathcal{E}) = \frac{4\pi}{3}\left(\frac{\mathcal{E}}{A}\right)^{3/2} .$$
The density of states is the derivative of this total number of states taken with respect to the energy:
$$g_{\text{tr}}(\mathcal{E}) = \frac{d\#\text{states}(\mathcal{E}_{\vec{n}} \leq \mathcal{E})}{d\mathcal{E}} = \frac{d}{d\mathcal{E}}\frac{4\pi}{3}\left(\frac{\mathcal{E}}{A}\right)^{3/2} = \frac{4\pi}{3}\frac{1}{A^{3/2}}\frac{d\mathcal{E}^{3/2}}{d\mathcal{E}} = \frac{2\pi}{A^{3/2}}\mathcal{E}^{1/2}. \quad (12)$$
Indeed, due to the fundamental theorem of calculus,
$$\begin{aligned}\#\text{states}(\mathcal{E}_1 \leq \mathcal{E}_{\vec{n}} \leq \mathcal{E}_2) &= \#\text{states}(\mathcal{E}_{\vec{n}} \leq \mathcal{E}_2) - \#\text{states}(\mathcal{E}_{\vec{n}} \leq \mathcal{E}_1)\\ &= \int_{\mathcal{E}_1}^{\mathcal{E}_1}\frac{d\#\text{states}(\mathcal{E}_{\vec{n}} \leq \mathcal{E})}{d\mathcal{E}}\,d\mathcal{E} \equiv \int_{\mathcal{E}_1}^{\mathcal{E}_1} g_{\text{tr}}(\mathcal{E})\,d\mathcal{E} \,.\end{aligned}$$
In expression (12) we substitute the value of A and $V = L^3$, obtaining
$$\begin{aligned}g_{\text{tr}}(\mathcal{E}) &= \frac{2\pi}{\left[\frac{(2\pi\hbar)^2}{2ML^2}\right]^{3/2}}\mathcal{E}^{1/2} = 2\pi\left[\frac{2ML^2}{(2\pi\hbar)^2}\right]^{3/2}\mathcal{E}^{1/2} = 2\pi\frac{(2M)^{3/2}L^3}{(2\pi\hbar)^3}\mathcal{E}^{1/2}\\ &= \frac{(2M)^{3/2}L^3}{(2\pi)^2\hbar^3}\mathcal{E}^{1/2} = \frac{M^{3/2}\,V}{\sqrt{2}\,\pi^2\,\hbar^3}\mathcal{E}^{1/2}. \quad (13)\end{aligned}$$

2. The other factor is simply the Boltzmann probability of having a particle with energy $\mathcal{E}$:
$$\frac{e^{-\beta\mathcal{E}}}{Z_{1\,\text{tr}}} = \frac{e^{-\beta\mathcal{E}}}{V/\Lambda^3} = \frac{\Lambda^3}{V}e^{-\beta\mathcal{E}} = \frac{\hbar^3}{V}\left(\frac{2\pi\beta}{M}\right)^{3/2}e^{-\beta\mathcal{E}}. \quad (14)$$

Then, combining the two terms, the requested single-particle kinetic-energy probability distribution is
$$\begin{aligned}\frac{dP(\mathcal{E})}{d\mathcal{E}} &= g_{\text{tr}}(\mathcal{E})\,\frac{e^{-\beta\mathcal{E}}}{Z_{1\,\text{tr}}} = \frac{M^{3/2}V}{\sqrt{2}\pi^2\hbar^3}\mathcal{E}^{1/2} \times \frac{\Lambda^3}{V}e^{-\beta\mathcal{E}} \quad (15)\\ &= \frac{M^{3/2}V}{\sqrt{2}\pi^2\hbar^3}\mathcal{E}^{1/2} \times \frac{\hbar^3}{V}\left(\frac{2\pi\beta}{M}\right)^{3/2}e^{-\beta\mathcal{E}} = \frac{2}{\sqrt{\pi}}\,\beta^{3/2}\,\mathcal{E}^{1/2}\,e^{-\beta\mathcal{E}}.\end{aligned}$$



4.3 Rotational heat capacity

Evaluate the rotational contribution to the heat capacity of a hot gas of diatomic molecules. Evaluate it per molecule, per mole and per unit mass.

4.3.1 Solution

The rotational levels (rigid-rotor approximation):

$$\mathcal{E}_{\rm rot}(l) = \frac{|\vec{L}|^2}{2\mu R_{\rm M}^2} = \frac{\hbar^2}{2\,I}\, l(l+1)\,. \tag{16}$$

Given the characteristic energy $\hbar^2/(2\,I)$ it is convenient to define the characteristic temperature

$$\Theta_{\rm rot} = \frac{\hbar^2}{2Ik_{\rm B}}.$$

This quantity allows us to write the dimensionless ratio

$$\beta\,\frac{\hbar^2}{2I} = \frac{\Theta_{\rm rot}}{T}$$

more compactly.
In terms of these quantities, the *rotational* partition function

$$Z_{1\,\rm rot} = \sum_{l=0}^{\infty}(2l+1)\,\exp\left(-\beta\frac{\hbar^2}{2I}\,l[l+1]\right) = \sum_{l=0}^{\infty}(2l+1)\,\exp\left(-\frac{\Theta_{\rm rot}}{T}\,l[l+1]\right)\,. \tag{17}$$

Note the $(2l+1)$ degeneracy, due to the projection q.n. values $m_l = -l, -l+1, \ldots l$.
The series in Eq. (17) cannot be evaluated in a closed form. However, the characteristic temperature $\Theta_{\rm rot}$ (e.g. 85 K for H_2, 15 K for HCl, 2.9 K for N_2) is often much smaller than the experimental T.
In the common condition that the dimensionless ratio $\Theta_{\rm rot}/T \ll 1$, i.e. $T \gg \Theta_{\rm rot}$, the exponential in Eq. (17) varies slowly with l and numerous terms contribute to the sum

for $Z_{1\,\mathrm{rot}}$: it is a good approximation to replace the summation with an integration:

$$
\begin{aligned}
Z_{1\,\mathrm{rot}} &\simeq \int_0^\infty (2l+1)\,\exp\left[-\frac{\Theta_{\mathrm{rot}}}{T}\,l(l+1)\right]dl \qquad (18)\\
&\text{substitute } y = l(l+1)\,;\ dy = (2l+1)dl\\
Z_{1\,\mathrm{rot}} &\simeq \int_0^\infty \exp\left(-\frac{\Theta_{\mathrm{rot}}}{T}\,y\right)dy\\
&= \frac{1}{-\frac{\Theta_{\mathrm{rot}}}{T}}\left[\exp\left(-\frac{\Theta_{\mathrm{rot}}}{T}\,y\right)\bigg|_{y=\infty} - \exp\left(-\frac{\Theta_{\mathrm{rot}}}{T}\,y\right)\bigg|_{y=0}\right]\\
&= \frac{T}{\Theta_{\mathrm{rot}}} = \frac{1}{\beta\frac{\hbar^2}{2I}}\,.
\end{aligned}
$$

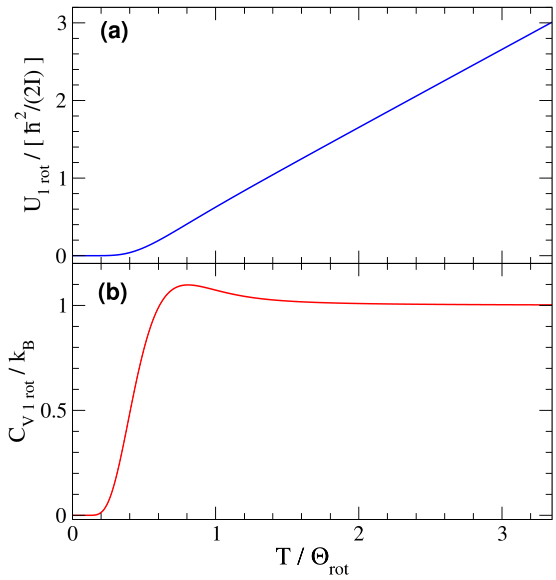
The high-temperature rotational contributions to the thermodynamic functions per molecule are therefore:

$$
\begin{aligned}
F_{1\,\mathrm{rot}} &= \frac{F_{\mathrm{rot}}}{N} \simeq -\beta^{-1}\ln\frac{T}{\Theta_{\mathrm{rot}}} = -k_{\mathrm{B}}T\ln\frac{T}{\Theta_{\mathrm{rot}}} \qquad (19)\\
U_{1\,\mathrm{rot}} &= \frac{U_{\mathrm{rot}}}{N} = -\frac{\partial}{\partial\beta}\ln Z_{1\,\mathrm{rot}} \simeq -\frac{\partial}{\partial\beta}\ln\left(\beta\frac{\hbar^2}{2I}\right)^{-1} = \frac{\partial}{\partial\beta}\ln\left(\beta\frac{\hbar^2}{2I}\right) \qquad (20)\\
&= \frac{\partial}{\partial\beta}\left[\ln(\beta)+\ln\left(\frac{\hbar^2}{2I}\right)\right] = \frac{\partial\ln(\beta)}{\partial\beta} = \frac{1}{\beta} = k_{\mathrm{B}}T\\
C_{V\,1\,\mathrm{rot}} &= \frac{C_{V\,\mathrm{rot}}}{N} = \frac{\partial U_{1\,\mathrm{rot}}}{\partial T} \simeq \frac{\partial k_{\mathrm{B}}T}{\partial T} = k_{\mathrm{B}} \qquad (21)\\
S_{1\,\mathrm{rot}} &= \frac{S_{\mathrm{rot}}}{N} = \frac{U_{1\,\mathrm{rot}}}{T} + k_{\mathrm{B}}\ln Z_{1\,\mathrm{rot}} \simeq k_{\mathrm{B}}\left(1+\ln\frac{T}{\Theta_{\mathrm{rot}}}\right). \qquad (22)
\end{aligned}
$$

These approximate expressions apply only for high temperature $T \gg \Theta_{\mathrm{rot}}$. At lower temperature $T \simeq \Theta_{\mathrm{rot}}$, truncating the series (17) to a finite number of terms $l \leq l_{\mathrm{max}} \simeq 1 + 2\sqrt{T/\Theta_{\mathrm{rot}}}$ approximates $Z_{1\,\mathrm{rot}}$ better. The lowest meaningful truncation, with $l_{\mathrm{max}} = 1$, is

$$
Z_{1\,\mathrm{rot}} = \sum_{l=0}^{l_{\mathrm{max}}}(2l+1)\,\exp\left(-\frac{\Theta_{\mathrm{rot}}}{T}\,l[l+1]\right) \simeq 1 + 3\exp\left(-2\frac{\Theta_{\mathrm{rot}}}{T}\right). \qquad (23)
$$

This expression is accurate when $T \ll \Theta_{\mathrm{rot}}$, which is an experimentally unrealistic condition.
Repeating the calculation with a larger l_{max}, one can extend the validity of the truncated expression to intermediate $T \sim \Theta_{\mathrm{rot}}$. In this way, we obtain the following temperature dependence of the rotational internal energy and heat capacity per molecule:



Note that for $T \gg \Theta_{\text{rot}}$ the curves recover the results of Eqs. (20) and (21). Note also how radically flat these curves become for $T \to 0$.
The analogous specific heat capacities per mole and per kg are obtained by multiplying the per-molecule result by the same factors N discussed above for the translational contribution.

4.4 Vibrational heat capacity

Evaluate the vibrational contribition to the heat capacity of a hot gas of diatomic molecules. Evaluate it per molecule, per mole and per unit mass.

4.4.1 Solution

In the harmonic approximation, the *vibrational* states form an equally-spaced ladder

$$\mathcal{E}_{\text{vib}}(v) = \hbar\omega \left(v + \frac{1}{2} \right) . \tag{24}$$

We can evaluate the series for $Z_{1\,\text{vib}}$. Compared to the rotational case, this series can be evaluated in closed form. This produces an *exact* expression for the vibrational partition function, applicable at any temperature.
For compactness of notation, we define the dimensionless ratio

$$x = \beta\hbar\omega = \frac{\Theta_{\text{vib}}}{T} .$$

Here we have also introduced a characteristic temperature $\Theta_{\text{vib}} = \hbar\omega/k_{\text{B}}$.
Let us calculate the partition function:

$$\begin{aligned} Z_{1\,\text{vib}} &= \sum_{v=0}^{\infty} \exp\left(-\beta\hbar\omega \left[v + \frac{1}{2}\right]\right) = \sum_{v=0}^{\infty} \exp\left(-x \left[v + \frac{1}{2}\right]\right) \\ &= \sum_{v=0}^{\infty} \exp\left(-\frac{x}{2}\right) \exp\left(-xv\right) = \exp\left(-\frac{x}{2}\right) \sum_{v=0}^{\infty} \exp(-v\,x) \\ &= \exp\left(-\frac{x}{2}\right) \sum_{v=0}^{\infty} [\exp(-x)]^v = \exp\left(-\frac{x}{2}\right) \frac{1}{1 - \exp(-x)} \\ &= \frac{1}{\exp\left(x/2\right) - \exp\left(-x/2\right)} = \frac{1}{2\sinh(x/2)} . \end{aligned} \tag{25}$$

In the third line we have used the sum of the geometric series $\sum_{n=0}^{\infty} a^n = 1/(1-a)$, valid for $|a| < 1$.
The main vibrational thermodynamic functions are then:

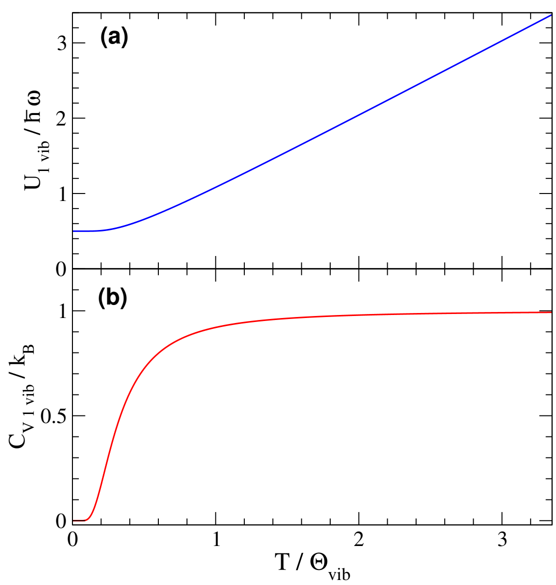
$$
\begin{aligned}
F_{1\,\mathrm{vib}} = \frac{F_{\mathrm{vib}}}{N} &= -\frac{1}{\beta}\ln Z_{1\,\mathrm{vib}} \\
&= -k_{\mathrm{B}}T\ln\left(\exp\left(-\frac{x}{2}\right)\frac{1}{1-\exp(-x)}\right) \\
&= -k_{\mathrm{B}}T\left[\ln\left(e^{-x/2}\right)+\ln\left(\frac{1}{1-e^{-x}}\right)\right] \\
&= k_{\mathrm{B}}T\left[\frac{x}{2}+\ln\left(1-e^{-x}\right)\right] \\
&= \frac{\hbar\omega}{2}+k_{\mathrm{B}}T\ln\left(1-e^{-x}\right) \\
&= k_{\mathrm{B}}T\ln(2\sinh(x/2))
\end{aligned}
\tag{26}
$$

$$
\begin{aligned}
U_{1\,\mathrm{vib}} = \frac{U_{\mathrm{vib}}}{N} &= -\frac{\partial}{\partial\beta}\ln Z_{1\,\mathrm{vib}} \\
&= -\frac{\partial}{\partial\beta}\ln\left(\exp\left(-\frac{x}{2}\right)\frac{1}{1-\exp(-x)}\right) \\
&= -\frac{\partial}{\partial\beta}\left[\ln\left(\exp\left(-\frac{x}{2}\right)\right)+\ln\left(\frac{1}{1-\exp(-x)}\right)\right] \\
&= -\frac{\partial}{\partial\beta}\left[-\frac{x}{2}-\ln\left(1-\exp(-x)\right)\right] = \frac{\partial}{\partial\beta}\left[\frac{x}{2}+\ln\left(1-\exp(-x)\right)\right] \\
&= \frac{\partial}{\partial x}\left[\frac{x}{2}+\ln\left(1-\exp(-x)\right)\right]\times\frac{\partial x}{\partial\beta} \\
&= \left[\frac{1}{2}+\frac{\exp(-x)}{1-\exp(-x)}\right]\times\frac{\partial(\beta\hbar\omega)}{\partial\beta} = \hbar\omega\left[\frac{1}{2}+\frac{e^{-x}\times e^{x}}{(1-e^{-x})\times e^{x}}\right] \\
&= \frac{\hbar\omega}{2}+\frac{\hbar\omega}{e^{x}-1}
\end{aligned}
\tag{27}
$$

$$
\begin{aligned}
C_{V\,1\,\mathrm{vib}} &= \frac{C_{V\mathrm{vib}}}{N} = \frac{\partial}{\partial T} U_{1\,\mathrm{vib}} \\
&= \frac{\partial}{\partial T}\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^x - 1}\right) = \hbar\omega \frac{\partial}{\partial T}\frac{1}{e^x - 1} = \hbar\omega \frac{\partial}{\partial x}\frac{1}{e^x - 1} \times \frac{\partial x}{\partial T} \\
&= \hbar\omega \left[-\frac{e^x}{(e^x - 1)^2}\right] \times \frac{\partial[\hbar\omega/(k_\mathrm{B} T)]}{\partial T} = -\hbar\omega\,\frac{e^x}{(e^x-1)^2}\,\frac{\hbar\omega}{k_\mathrm{B}}\,\frac{(-1)}{T^2} \\
&= \hbar\omega\,\frac{e^x}{(e^x-1)^2}\,\frac{\hbar\omega}{k_\mathrm{B} T^2} = \frac{e^x}{(e^x-1)^2}\,\frac{(\hbar\omega)^2}{k_\mathrm{B}^2 T^2} \times k_\mathrm{B} \\
&= k_\mathrm{B}\,\frac{x^2\,e^x}{(e^x-1)^2} \\
&= k_\mathrm{B}\,\frac{x^2\,e^x}{e^{2x} - 2e^x + 1} = k_\mathrm{B}\,\frac{x^2}{e^x - 2 + e^{-x}} \\
&= k_\mathrm{B}\,\frac{x^2}{2\cosh(x) - 2} \\
&= k_\mathrm{B}\,\frac{x^2}{e^{-x}\,[e^x - 1]^2} = k_\mathrm{B}\,\frac{x^2}{\left[e^{-x/2}(e^x-1)\right]^2} \\
&= k_\mathrm{B}\,\frac{x^2}{\left(e^{x/2} - e^{-x/2}\right)^2} = k_\mathrm{B}\left[\frac{x}{2\sinh(x/2)}\right]^2 \\
&= k_\mathrm{B}\left[\frac{x/2}{\sinh(x/2)}\right]^2
\end{aligned} \tag{28}
$$

$$
\begin{aligned}
S_{1\,\mathrm{vib}} &= \frac{S_\mathrm{vib}}{N} = \frac{U_{1\,\mathrm{vib}}}{T} + k_\mathrm{B}\ln Z_{1\,\mathrm{vib}} \\
&= \frac{1}{T}\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^x - 1}\right) + k_\mathrm{B}\ln\left(\exp\left(-\frac{x}{2}\right)\frac{1}{1 - \exp(-x)}\right) \\
&= \frac{\hbar\omega}{2T} + \frac{\hbar\omega}{T}\,\frac{1}{e^x - 1} + k_\mathrm{B}\left(-\frac{x}{2}\right) - k_\mathrm{B}\ln\left(1 - e^{-x}\right) \\
&= k_\mathrm{B}\frac{x}{e^x - 1} - k_\mathrm{B}\ln\left(1 - e^{-x}\right).
\end{aligned} \tag{29}
$$

We plot the temperature dependence of the vibrational internal energy and heat capacity per molecule:



Note that for $T \gg \Theta_{\rm rot}$ ($x \to 0$) the curves recover the classical equipartition limit $C_{V\,1\,\rm vib} \to k_{\rm B}$. Note also how radically flat these curves become for $T \to 0$ ($x \to \infty$). The analogous specific heat capacities per mole and per kg are obtained by multiplying the per-molecule result by the same factors N discussed above for the translational contribution.

4.5 Total heat capacity

Evaluate the total heat capacity of a hot gas of diatomic molecules. Evaluate it per molecule, per mole and per unit mass.

4.5.1 Solution

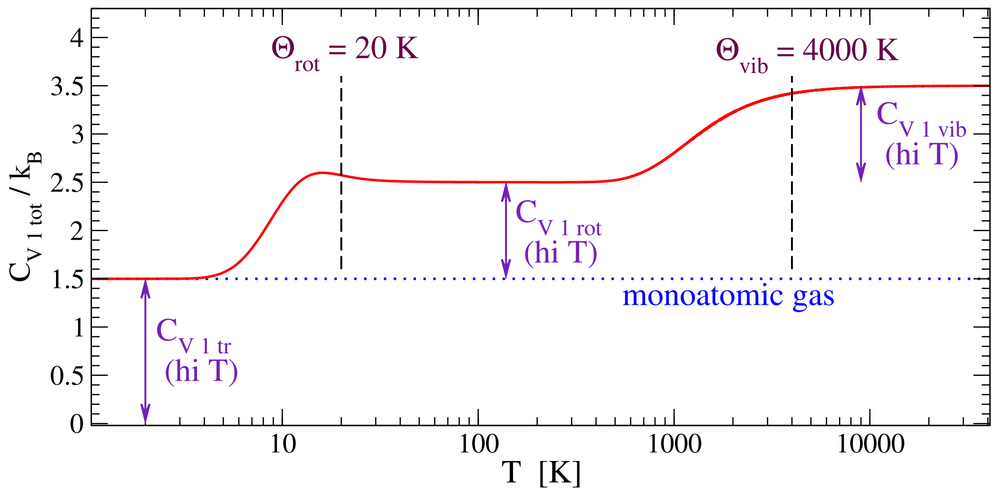
The main issue here is not to forget any of the contributions!
The translational rotational and vibrational contributions to the molecular heat capacity combine additively.
The reason is that the partition function is multiplicative, and

$$Z_1 = Z_{1\,\rm tr}\, Z_{1\,\rm int} = Z_{1\,\rm tr}\, Z_{1\,\rm rot}\, Z_{1\,\rm vib}\,. \tag{30}$$

Then all thermodynamical function, including the heat capacity, are proportional to (derivatives of)

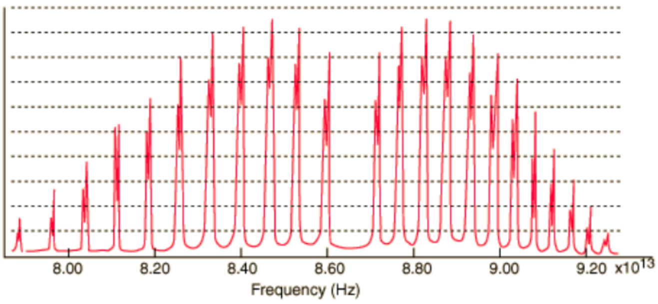
$$\ln Z_1 = \ln Z_{1\,\rm tr} + \ln Z_{1\,\rm rot} + \ln Z_{1\,\rm vib}\,. \tag{31}$$

Given that $\Theta_{\rm rot} \ll \Theta_{\rm vib}$ [e.g. $\Theta_{\rm rot} \simeq 20$ K and $\Theta_{\rm vib} \simeq 4000$ K] the overall heat capacity behaves qualitatively as follows:



Warnings:
In practice, inter-molecular interactions lead to liquid and solid phases for $T \sim T_{\rm boil}$, and usually $\Theta_{\rm rot} \sim T_{\rm boil}$ making it hard to observe the rotational unfreezing.
Even if intermolecular interactions could be neglected, quantum statistical effects would make the low-temperature translational heat capacity deviate from $^3\!/_2 k_{\rm B}$, and the entire separation between internal and translational degrees of freedom invalid.
At high temperature $T \sim 10^4$ K anharmonic and molecular-dissociation effects affect significantly the vibrational and rotational heat-capacity contributions.

5 Written test 09/09/2004, problem 3



La figura a lato rappresenta lo spettro di assorbimento infrarosso di HCl gassoso. Considerando solamente la componente isotopica prevalente $H^{35}Cl$, si determinino a partire dai dati sperimentali:

- la costante elastica del potenziale adiabatico nell'approssimazione armonica;
- la distanza d'equilibrio tra i nuclei di H e di Cl;
- una stima (precisione del 30%) della temperatura del campione.

5.1 Solution

1. In this molecule,

$$\mu = \frac{1\,\text{a.m.u.} \times 35\,\text{a.m.u.}}{1\,\text{a.m.u.} + 35\,\text{a.m.u.}} = 0.972\,\text{a.m.u.}$$

From the experimental spectrum

$$\omega = 2\pi\nu = 2\pi \times 8.64 \times 10^{13}\ \text{Hz} = 5.429 \times 10^{14}\ \frac{\text{rad}}{\text{s}}$$

Recall that the harmonic angular frequency

$$\omega = \sqrt{\frac{K}{\mu}}\,.$$

Therefore the "spring constant"

$$K = \mu\omega^2 = 475.8\,\text{kg s}^{-2}.$$

2. The spacing between successive rotational lines

$$\Delta E^{\text{rot}} = \frac{\hbar^2}{\mu R_{\text{M}}^2}\,.$$

In the exp spectrum the spacing is slightly irregular, therefore it is advisable to average out across e.g. 6 spacings, spanning a frequency interval $\simeq 0.40 \times 10^{13}$ Hz. Accordingly:

$$\Delta E^{\text{rot}} = \hbar \times 2\pi \frac{0.40 \times 10^{13}\ \text{Hz}}{6} = 4.417 \times 10^{-22}\ \text{J}\,.$$

By inverting the relation between ΔE^{rot} and R_{M}, we obtain

$$R_{\text{M}} = \frac{\hbar}{\sqrt{\mu \Delta E^{\text{rot}}}} = 1.249 \times 10^{-10}\ \text{m}.$$

3. In principle one should fit the temperature so that the Boltzmann probability expression

$$P(l) = \frac{(2l+1)\, e^{-\beta \mathcal{E}_{\rm rot}(l)}}{Z_{1\,\rm rot}}\,,$$

best approximates the experimental intensity pattern. This method is far too complicated and unnecessary for the required 30% accuracy.

We just identify the most populated l level, by the most intense rotational line.

In the R branch $l = 2$ and $l = 3$ lines have essentially the same intensity, but in the P branch $l = 3$ is certainly more intense. This value can be put into contact with the equation

$$\frac{\Theta_{\rm rot}}{T}(2l^{\rm most} + 1)^2 = 2\,,$$

obtained by maximizing the numerator in the Boltzmann probability expression.

We extract T

$$T = \frac{\Theta_{\rm rot}}{2}(2l^{\rm most} + 1)^2$$

To evaluate T we need

$$\Theta_{\rm rot} = \frac{\hbar^2}{2Ik_{\rm B}} = 16\ {\rm K}\,.$$

We substitute this value and $l^{\rm most} = 3$ as determined from the experimental intensities:

$$T = \frac{49}{2}\Theta_{\rm rot} = 392\ {\rm K} \simeq 400\ {\rm K}\,.$$

6 Written test 15/02/2021, problem 2 – Ortho- and Para-Hydrogen

L'identità degli atomi componenti la molecola H_2 impone che nel ket globale, il fattore che descrive lo spin nucleare e quello che descrive il moto adiabatico rotovibrazionale abbiano la *stessa* parità per scambio dei due atomi. In concreto, $I_{\rm tot} = 0$ implica L pari (paraidrogeno) e $I_{\rm tot} = 1$ implica L dispari (ortoidrogeno). Data la temperatura rotazionale $\theta_{\rm rot} = 87$ K, si valuti la frazione d'equilibrio di paraidrogeno sul totale a $T = 300$ K e a $T = \theta_{\rm rot}$.

The rotational energy levels are

$$\mathcal{E}_{\rm rot}(l) = \frac{|\vec{L}|^2}{2\mu R_{\rm M}^2} = \frac{\hbar^2}{2\,I}\, l(l+1)\,.$$

These levels are related to the given

$$\theta_{\rm rot} = \frac{\hbar^2}{2Ik_{\rm B}}.$$

Even-l states contribute the partition function the following sum of Boltzmann weights:

$$Z_{1\,\rm even} = \sum_{l\ \rm even} (2l+1)\ \exp\left(-\frac{\theta_{\rm rot}}{T}\, l[l+1]\right)\,.$$

Likewise, odd-l states contribute

$$Z_{1\,\mathrm{odd}} = \sum_{l\ \mathrm{odd}} (2l+1)\ \exp\left(-\frac{\theta_{\mathrm{rot}}}{T}\, l[l+1]\right)\,.$$

The odd-l states are associated to nuclear spin 1, therefore each of them comes with an extra degeneracy 3. Therefore

$$Z_1 = Z_{1\,\mathrm{even}} + 3\,Z_{1\,\mathrm{odd}}\,.$$

Accordingly, the average fraction of parahydrogen equals

$$f_{\mathrm{para}} = \frac{N_{\mathrm{even}}}{N} = \frac{Z_{1\,\mathrm{even}}}{Z_1} = \frac{Z_{1\,\mathrm{even}}}{Z_{1\,\mathrm{even}} + 3\,Z_{1\,\mathrm{odd}}}\,.$$

In the $T \gg \theta_{\mathrm{rot}}$ limit both partition functions approximate 50% of the usual high-temperature limit:

$$Z_{1\,\mathrm{even}},\ Z_{1\,\mathrm{odd}} \to \frac{1}{2}\,\frac{T}{\theta_{\mathrm{rot}}}\,.$$

In this limit, with similar $Z_{1\,\mathrm{even}} \simeq Z_{1\,\mathrm{odd}}$

$$f_{\mathrm{para}} \to \frac{1}{4} = 25\%\,.$$

This high-temperature limit applies approximately to $T = 300$ K.
For $T = \theta_{\mathrm{rot}}$ instead, one must evaluate the partition function with the method of the truncated series, e.g.:

$$Z_{1\,\mathrm{even}} \simeq 1 + 5e^{-6} + 9e^{-20} = 1.012393$$
$$Z_{1\,\mathrm{odd}} \simeq 3e^{-2} + 7e^{-12} = 0.4060$$

(the largest neglected term $\simeq 10^{-12}$). With these data,

$$f_{\mathrm{para}} \simeq 45.4\%\,.$$