The Free Quantum Molecular Gas

General Considerations

• *Idea:* We want to calculate the contribution to the heat capacity of a molecular gas arising from the fact that energy can be stored in the internal degrees of freedom of each molecule. The dynamics of the centers of mass of the N molecules will be treated classically, but, as we will see, we would not get results consistent with observations unless we treat the internal degrees of freedom quantum mechanically.

• *Molecular Hamiltonian:* If the n atoms in each molecule are identical (the treatment can be generalized to the case of different atoms), and T is low enough that the atoms are only slightly displaced from their equilibrium positions $\vec{q}_i = \vec{q}_i^*$ ($i = 1, ..., n$) and the probability of electron transitions to higher energy states can be neglected, we can use $H = \sum_{I=1}^{N} H_1(q_{(I)}, p_{(I)})$, with single-molecule Hamiltonian

$$H_1(q,p) = \sum_{i=1}^{n} \frac{\vec{p}_i^2}{2m} + V(\vec{q}_1, ..., \vec{q}_n) \ ,$$

$$V(\vec{q}_1, ..., \vec{q}_n) = V^* + \tfrac{1}{2} \sum_{i,\,j=1}^{n} \sum_{\alpha,\,\beta=1}^{3} \left. \frac{\partial^2 V}{\partial q_{i,\alpha} \partial q_{j,\beta}} \right|_{q=q*} u_{i,\alpha}\, u_{j,\beta} + \mathcal{O}(u^3) \ ,$$

where V^* is the equilibrium value of the molecular potential energy, and the $u_{i,\alpha} := q_{i,\alpha} - q_{i,\alpha}^*$ are the deviations of the configuration variables from their equilibrium values. If we now identify the $3n$ normal modes for the system by diagonalizing the matrix $\partial^2 V/\partial q_{i,\alpha} \partial q_{j,\beta}$, then in adapted coordinates $\tilde{u}_s$ and $\tilde{p}_s$,

$$H_1 = V^* + \sum_{s=1}^{3n} \left[\frac{1}{2m} \tilde{p}_s^2 + \frac{K_s}{2} \tilde{u}_s^2 \right] \ .$$

• *Heat capacity:* This single-molecule Hamiltonian H_1 is a sum of terms depending separately on center-of-mass, molecular orientation and deformation variables, meaning that the translational, rotational and vibrational degrees of freedom of each molecule are uncoupled. Then, general results imply that the heat capacity will be, both classically and quantum mechanically, a sum of three corresponding terms,

$$C_{\mathrm{mol}} = C_{\mathrm{t}} + C_{\mathrm{r}} + C_{\mathrm{v}} \ .$$

Furthermore, the small-perturbation Hamiltonian is a sum of quadratic terms, so classically, based on the equipartition theorem, we would expect the contribution from each molecule to the heat capacity to be $C_1 = \tfrac{1}{2}(6n - 3 - r) k_{\mathrm{B}}$, where we have subtracted from the $6n$ terms in H_1 the ones for which $K_s = 0$, i.e., the 3 overall translations and the r effective rotations. This would imply that the systems does not satisfy the third law, and it is not what is actually measured experimentally.

Diatomic molecule: Vibrational degree of freedom

• *Diatomic molecule in general:* In this case, $n = 2$ and $r = 2$ (the third rotation, around the axis, corresponds to no change in the molecule), so the number of terms that contributes to H_1 is $6n - 3 - r = 7$ (3 overall translation momenta, 2 from the vibrational p and u, and 2 from rotational angles) and classically we expect to find a molecular contribution to the mean energy of $\bar{\epsilon} = (\tfrac{3}{2} + \tfrac{2}{2} + \tfrac{2}{2}) k_{\mathrm{B}} T = \tfrac{7}{2} k_{\mathrm{B}} T$.

• *Classically:* For small-amplitude oscillations, the vibrational degree of freedom behaves like a simple harmonic oscillator. If ω is its angular frequency, the vibrational part of the 1-molecule partition function is

$$Z_{1,\mathrm{v}}^{(\mathrm{cm})} = \int \frac{\mathrm{d}q\,\mathrm{d}p}{h}\, \mathrm{e}^{-\beta(p^2/2\mu + \mu\omega^2 q^2/2)} = \frac{k_{\mathrm{B}}T}{\hbar\omega}$$

(μ is the reduced mass), consistently with the principle of equipartition, and therefore, for N molecules,

$$C_{\mathrm{v}}^{(\mathrm{cm})} = N k_{\mathrm{B}} \ .$$

• *Quantum mechanically:* The states of the simple harmonic oscillator are quantized. If we use n to label the states, the corresponding energy eigenvalues for a single oscillator are $\epsilon_n = (n + \frac{1}{2})\hbar\omega$ and

$$Z_{1,\mathrm{v}}^{(\mathrm{qm})} = \sum_n \mathrm{e}^{-\beta\epsilon_n} = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta\,(n+1/2)\,\hbar\omega} = \frac{\mathrm{e}^{-\beta\hbar\omega/2}}{1 - \mathrm{e}^{-\beta\hbar\omega}} \ ,$$

which goes like $k_{\mathrm{B}}T/\hbar\omega$ as $T \to \infty$. Therefore we get

$$\bar{\epsilon}_{\mathrm{v}}^{(\mathrm{qm})} = -\frac{\partial}{\partial\beta}\ln Z_{1,\mathrm{v}}^{(\mathrm{qm})} = \tfrac{1}{2}\,\hbar\omega + \hbar\omega\,\frac{\mathrm{e}^{-\beta\hbar\omega}}{1 - \mathrm{e}^{-\beta\hbar\omega}}$$

(the terms correspond to zero-point energy and thermal fluctuations, respectively) and, for N oscillators,

$$C_{\mathrm{v}}^{(\mathrm{qm})} = N\,\frac{\partial\,\bar{\epsilon}_{\mathrm{v}}^{(\mathrm{qm})}}{\partial T} = Nk_{\mathrm{B}}\left(\frac{\hbar\omega}{k_{\mathrm{B}}T}\right)^2 \frac{\mathrm{e}^{-\beta\hbar\omega}}{(1 - \mathrm{e}^{-\beta\hbar\omega})^2} \ ,$$

which vanishes as $T \to 0$, consistently with the third law, and approaches Nk_{B} [expand the exponentials] for $T \gg \theta_{\mathrm{v}} = \hbar\omega/k_{\mathrm{B}}$, a temperature usually in the thousands of degrees (810 K for Cl_2 ... 6140 K for H_2).

Diatomic molecule: Rotational degrees of freedom

• *Classically:* The rotational part of the Hamiltonian only has a kinetic energy term,

$$H_{1,\mathrm{rot}} = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) = \frac{L^2}{2I} \ ,$$

so, by a calculation of the same type as the previous ones,

$$Z_{1,\mathrm{rot}}^{(\mathrm{cm})} = \frac{2I\,k_{\mathrm{B}}T}{\hbar^2} \qquad \text{and} \qquad C_{\mathrm{r}}^{(\mathrm{cm})} = Nk_{\mathrm{B}} \ .$$

consistently with the principle of equipartition but not with the third law.

• *Quantum mechanically:* The rotational states can be labelled by a non-negative integer l and an integer $m = -l, ..., l$, such that the square of the angular momentum vector is $l\,(l+1)\,\hbar^2$. Therefore,

$$Z_{1,\mathrm{rot}}^{(\mathrm{qm})} = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} \mathrm{e}^{-\beta\hbar^2 l(l+1)/2I} = \sum_{l=0}^{\infty}(2l+1)\,\mathrm{e}^{-l(l+1)\,\theta_{\mathrm{r}}/T} \ ,$$

where $\theta_{\mathrm{r}} := \hbar^2/2Ik_{\mathrm{B}}$. We can find good approximations for this sum in two limiting cases. For high values of T, the argument of the sum varies slowly with l, so we can replace l by a continuous variable x and the sum by an integral (in which we then introduce $x \mapsto y := x(x+1)$),

$$T \gg \theta_{\mathrm{r}}: \quad Z_{1,\mathrm{rot}}^{(\mathrm{qm})} \approx \int_0^{\infty}\mathrm{d}x\,(2x+1)\,\mathrm{e}^{-\theta_{\mathrm{r}}x(x+1)/T} = \int_0^{\infty}\mathrm{d}y\,\mathrm{e}^{-\theta_{\mathrm{r}}y/T} = \frac{T}{\theta_{\mathrm{r}}} = Z_{1,\mathrm{rot}}^{(\mathrm{cm})} \ ,$$

and we see that $C_{\mathrm{r}}^{(\mathrm{qm})} \approx Nk_{\mathrm{B}}$, as expected. For low values of T, the terms in the sum decrease very rapidly as l increases. If we consider only the first two terms,

$$T \ll \theta_{\mathrm{r}}: \quad Z_{1,\mathrm{rot}}^{(\mathrm{qm})} = 1 + 3\,\mathrm{e}^{-2\theta_{\mathrm{r}}/T} + \mathcal{O}(\mathrm{e}^{-6\theta_{\mathrm{r}}/T}) \qquad \text{and} \qquad C_{\mathrm{r}}^{(\mathrm{qm})} \approx 6\,Nk_{\mathrm{B}}\,\theta_{\mathrm{r}}\,\mathrm{e}^{-2\theta_{\mathrm{r}}/T} \to 0 \ .$$

The rotational temperature θ_{r} is usually in the range 1–100 K (0.36 K for Cl_2 ... 85.4 K for H_2), so the rotational degrees of freedom of a gas are excited at much lower temperatures than the vibrational ones.

Reading

• *Course textbook:* Kennett, §§4.4 and 4.5.
• *Other texts:* Chandler, §4.9; Halley, Part of Ch 5; Kardar, §6.1; Pathria & Beale, §6.5; Schwabl, §5.1.