Gases with internal degrees of freedom [tln59]

Assumptions: molecules are noninteracting; translational, rotational, and vibrational degrees of freedom are independent:

$$H = \sum_{i=1}^{N} \left[H_T^{(i)} + H_R^{(i)} + H_V^{(i)} \right] \;\Rightarrow\; Z_N = \frac{1}{N!}\tilde{Z}^N,\; \tilde{Z} = \tilde{Z}_T \tilde{Z}_R \tilde{Z}_V.$$

Translational motion (classical):

$$H_T^{(i)} = \frac{p_i^2}{2m} \;\Rightarrow\; \tilde{Z}_T = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \;\Rightarrow\; C_V^{(T)} = \frac{3}{2}Nk_B \quad \text{[tex76]}.$$

Rotational motion (classical):

(a) NH_3 (multi-atomic molecule):
Euler angles θ, ϕ, ψ; canonical conjugate momenta p_θ, p_ϕ, p_ψ.
Uniaxially symmetric inertia tensor with principal moments $I_1 = I_2, I_3$.

Hamiltonian: $H_R^{(i)} = \dfrac{p_{i\theta}^2}{2I_1} + \dfrac{p_{i\psi}^2}{2I_3} + \dfrac{(p_{i\phi} - p_{i\psi}\cos\theta_i)^2}{2I_1 \sin^2\theta_i}$.

Ranges: $0 \le \theta_i \le \pi,\; 0 \le \phi_i, \psi_i \le 2\pi,\; -\infty < p_{i\theta}, p_{i\phi}, p_{i\psi} < +\infty.$

$$\Rightarrow\; \tilde{Z}_R = \frac{1}{\pi\hbar^3}\sqrt{(2\pi I_1 k_B T)^2 (2\pi I_3 k_B T)} \;\Rightarrow\; C_V^{(R)} = \frac{3}{2}Nk_B \quad \text{[tex87]}.$$

(b) HCl (two-atomic heteronuclear molecule):
The rotation about the molecular axis is suppressed due to quantum effect.

Hamiltonian: $H_R^{(i)} = \dfrac{p_{i\theta}^2}{2I_1} + \dfrac{p_{i\phi}^2}{2I_1\sin^2\theta_i}, \quad 0 \le \theta_i \le \pi,\; 0 \le \phi_i \le 2\pi.$

$$\Rightarrow\; \tilde{Z}_R = \frac{2I_1 k_B T}{\hbar^2} \;\Rightarrow\; C_V^{(R)} = Nk_B \quad \text{[tex88]}.$$

(c) N_2 (two-atomic homonuclear molecule):
Minor modification: range of one variable ($0 \le \phi \le \pi$).
This change does affect the entropy but not the heat capacity ⇒ [tex88].

Rotational motion (quantum):

Consider a two-atomic molecule.

Angular momentum operator: $\mathbf{L}$. Hamiltonian operator: $H_R = \frac{1}{2I}\mathbf{L}^2$.

Energy levels: $E_{lm} = \frac{l(l+1)\hbar^2}{2I}$; $l = 0, 1, 2, \ldots$; $m = -l, -l+1, \ldots, l$.

Degeneracy: $(2l+1)$-fold.

$$\Rightarrow \; \tilde{Z}_R = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} e^{-\beta E_{lm}} = \sum_{l=0}^{\infty} (2l+1) e^{-\beta l(l+1)\hbar^2/2I} \quad \Rightarrow \quad \text{[tsl32]}$$

Characteristic temperature: $k_B \Theta_R = \frac{\hbar^2}{2I}$.

Low-temperature analysis ($T \ll \Theta_R$) $\Rightarrow$ [tex89].

High-temperature analysis ($T \gg \Theta_R$) $\Rightarrow$ [tex90].

Vibrational motion (quantum):

Hamiltonian: $$H_V = \sum_{l=1}^{f} \left(\frac{p_l^2}{2m_l} + \frac{1}{2} m_l \omega_l^2 q_l^2 \right).$$

Here f is the number of vibrational normal modes, each expressed by a pair (q_l, p_l) of canonical normal mode coordinates.

$$\Rightarrow \; \tilde{Z}_V = \prod_{l=1}^{f} \left[\frac{e^{-\beta\hbar\omega_l}}{1 - e^{-\beta\hbar\omega_l}} \right] \;\Rightarrow\; C_V^{(V)} \overset{T \gg \Theta_V}{\longrightarrow} fNk_B \quad \text{[tex82]}.$$

Characteristic temperature: $k_B \Theta_V = \hbar\omega_l$.

Vibrational modes require much higher temperatures to be activated:

$$\Theta_R = \frac{\hbar^2}{2Ik_B} \sim 10\text{K}, \quad \Theta_V = \frac{\hbar\omega_l}{k_B} \sim 1000\text{K} \quad \Rightarrow \text{[tsl32]}.$$

Fine structure:

If the atomic ground state has zero *orbital* angular momentum ($l = 0$) and nonzero *spin* angular momentum ($s \neq 0$), the entropy acquires an additive constant, $\Delta S = Nk_B \ln(2s+1)$. The heat capacity remains unaffected.

In the presence of an external magnetic field, this system is a paramagnetic gas. The thermodynamics of dilute paramagnetic gases are the theme of [tex22] and [tex133].

If the atomic ground state has $l \neq 0$ and $s \neq 0$, then the L-S coupling produces a fine-structure splitting of the ground-state degeneracy:

$$\tilde{Z}_{FS} = \sum_j (2j+1) e^{-\beta\epsilon_j}, \qquad |l-s| \leq j \leq l+s,$$

where j is the quantum number of the total angular momentum. If the lowest level has $j = j_0$, then the entropy of the atomic gas increases by

$$\Delta S = Nk_B \ln \frac{(2s+1)(2l+1)}{(2j_0+1)}$$

over a temperature range $0 < k_BT \lesssim \Delta E_{LS}$, where ΔE_{LS} measures the total L-S level splitting.

The contribution to the heat capacity, $C_V^{(FS)}$, is a function of T that rises from zero exponentially, exhibits a smooth maximum at $k_BT \sim \Delta E_{LS}$, and then dips back down to zero algebraically.[1]

The functional dependence of $C_V^{(FS)}$ on T is very similar to that of the heat capacity of a Langevin paramagnet as analyzed in [tex85] and [tex86].

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[1] In practical reality, atomic gases with $l \neq 0, s \neq 0$ tend to form molecules or condense at temperatures far above $k_BT \sim \Delta E_{LS}$.