

[tex87] Classical rotational free energy of NH₃ gas

Under the assumption that the NH₃ molecule is a rigid body with uniaxially symmetric inertia tensor and principal moments $I_1 = I_2 \neq I_3$, the one-particle Hamiltonian of the free rotational motion reads

$$H_R = \frac{p_\theta^2}{2I_1} + \frac{p_\psi^2}{2I_3} + \frac{(p_\phi - p_\psi \cos \theta)^2}{2I_1 \sin^2 \theta},$$

where $(\theta, p_\theta; \phi, p_\phi; \psi, p_\psi)$ are the Euler angles and their conjugate generalized momenta. The range of these canonical coordinates is $0 \leq \theta \leq \pi$, $0 \leq \phi, \psi \leq 2\pi$, $-\infty < p_\theta, p_\phi, p_\psi < +\infty$.

(a) Show that the canonical partition function for the rotational motion of N molecules is

$$Z_R^N = \pi^{-N} (2\pi k_B T / \hbar^2)^{3N/2} I_1^N I_3^{N/2}.$$

(b) Calculate the rotational Helmholtz free energy $A_R(T, N)$, the rotational entropy $S_R(T, N)$, and the rotational internal energy $U_R(T, N)$.

Solution: