

Problem 5

Find the probability distribution for the angular velocities of rotation of molecules.

The rotational energy is $\epsilon = \frac{1}{2} (I_1 \Omega_1^2 + I_2 \Omega_2^2 + I_3 \Omega_3^2)$

The classical Gibbs distribution gives the probability density in phase space as $\rho(p, q) = A e^{-E(p, q)/T}$. The probability of finding the system in a region of phase space is

$$dW = \rho(p, q) dp dq = A e^{-\epsilon/T} dp_1 dp_2 dp_3 dq_1 dq_2 dq_3.$$

Since ϵ does not depend on q_i and $p_i = I_i \Omega_i$ we get

$$dW_n = A(I_1 I_2 I_3) \exp\left[-\frac{1}{2T} (I_1 \Omega_1^2 + I_2 \Omega_2^2 + I_3 \Omega_3^2)\right] d\Omega_1 d\Omega_2 d\Omega_3.$$

We require $\int dW_n = 1$ and using $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\pi/a}$ with $a_i = I_i/2T$ we get that

provided A contains I_i and the constant of integration from dq_i :

$$A \cdot \sqrt{\frac{2\pi T}{I_1}} \cdot \sqrt{\frac{2\pi T}{I_2}} \cdot \sqrt{\frac{2\pi T}{I_3}} = 1 \Rightarrow A = (2\pi T)^{-3/2} (I_1 I_2 I_3)^{-1/2}$$

giving us:

$$dW_n = (2\pi T)^{-3/2} (I_1 I_2 I_3)^{-1/2} \exp\left[-\frac{1}{2T} (I_1 \Omega_1^2 + I_2 \Omega_2^2 + I_3 \Omega_3^2)\right] d\Omega_1 d\Omega_2 d\Omega_3$$