Spring 2000 # 6

Consider a heteronuclear diatomic molecule with moment inertia I.

a) Using classical statistical mechanics, calculate the specific heat of the system at temperature T.

→ The system has two rotational degrees of freedom. By the equipartition theorem the energy is therefore $E = 2(\frac{1}{2}kT)$. The specific heat is given by $C_v = \left(\frac{\partial E}{\partial T}\right)_v$

$$\boxed{C_v = k}$$

b) In quantum mechanics, the system has energy levels:

$$E_j = \frac{\hbar^2}{2I} j(j+1) \qquad j = 0,1,2 \cdot$$

Where the jth level is $(2j+1)$-fold degenerate. Find the partition function Z and average energy $\langle E \rangle$ as a function of T.

$$Z = \sum e^{-\beta E}$$

$$\boxed{Z = \sum_{j=0}^{\infty} \left[ \underbrace{(2j+1)}_{\text{degeneracy}} \exp\left(\frac{-\hbar^2}{2IkT} j(j+1)\right)\right]}$$

$$\boxed{\langle E \rangle = \frac{\sum_j \frac{\hbar^2}{2I} j(j+1)(2j+1) \exp\left(\frac{-\hbar^2}{2IkT} j(j+1)\right)}{\sum_j (2j+1) \exp\left(\frac{-\hbar^2}{2IkT} j(j+1)\right)}}$$

c) By simplifying result to (b), derive expression for heat capacity valid at very low temperatures.

→ Assume T low enough that only 1st two states are occupied (j:

This gives

$$\langle E \rangle = \frac{3\hbar^2 \exp\left(\frac{-\beta\hbar^2}{I}\right)}{I\left(1 + 3\exp\left(\frac{-\beta\hbar^2}{I}\right)\right)}$$

find $C_v$ using chain rule

$$C_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \langle E \rangle}{\partial \beta} \frac{\partial \beta}{\partial T}$$

$$\frac{\partial}{\partial} = \frac{3\hbar^2}{I}\left[\frac{-\hbar^2}{I}\exp\left(\frac{-\hbar^2\beta}{I}\right)\left(1+3\exp\left(\frac{-\beta\hbar^2}{I}\right)\right)^{-1} - \exp\left(\frac{-\hbar^2\beta}{I}\right)\left(1+3\exp\left(\frac{-\beta\hbar^2}{I}\right)\right)^{-2}\left(\frac{-\hbar^2}{I}\right)\right]$$

$$\beta = \frac{1}{kT} \quad \Rightarrow \quad \frac{d\beta}{dT} = -\frac{1}{kT^2}$$

Simplification leads to: $\boxed{C_v = \frac{3\hbar^4}{IkT^2}\frac{\exp\left(\frac{-\hbar^2}{IkT}\right)}{\left(1+3\exp\left(\frac{-\hbar^2}{IkT}\right)\right)^2}}$

This expression is valid when $\exp\left(\frac{-\hbar^2}{2IkT}\cancel{2}(2+1)\right) \approx 0 \qquad (j=2)$

$$+\frac{3\hbar^2}{IkT} >> 1 \quad \Rightarrow \quad \boxed{T << \frac{3\hbar^2}{Ik}}$$

d) Derive a high temperature expression for specific heat.

→ for high T, levels are closely spaced → replace sum with integr

$$\langle E\rangle = \frac{\int_0^\infty \frac{\hbar^2}{2I} j(j+1)(2j+1)\exp\left(\frac{-\hbar^2}{2kTI}j(j+1)\right)dj}{\int_0^\infty (2j+1)\exp\left(\frac{-\hbar^2}{2kTI}j(j+1)\right)dj}$$

Make substitution $\quad u = j(j+1) \qquad du = (2j+1)dj$

$$\langle E\rangle = \frac{\frac{\hbar^2}{2I}\int_0^\infty u\exp\left(\frac{-\hbar^2}{2kTI}u\right)du}{\int_0^\infty \exp\left(-\frac{\hbar^2}{2kTI}u\right)du}$$

$$\int_0^\infty \exp(-\alpha u)du = \frac{1}{-\alpha}\left[e^{-\alpha u}\right]_0^\infty = -\frac{1}{\alpha}\left[0-1\right] = \frac{1}{\alpha} = \frac{2kTI}{\hbar^2}$$

$$\int_0^\infty u\exp(-\alpha u)du = -\frac{d}{d\alpha}\int_0^\infty \exp(-\alpha u)du = -\frac{d}{d\alpha}\left(\frac{1}{\alpha}\right) = \left(\frac{1}{\alpha}\right)^2 = \left(\frac{2}{\hbar}\right.$$

$$\langle E\rangle = \frac{\hbar^2}{2I}\left(\frac{1}{\alpha}\right)^2\alpha = \frac{\hbar^2}{2I\alpha} = \frac{\cancel{\hbar^2}}{\cancel{2I}}\frac{2kIT}{\cancel{\hbar^2}} = kT$$

$\boxed{C_v = k}$ This solution is valid when $\boxed{T >> \frac{\hbar^2}{2Ik}j(j+1)}$