13. *Statistical Mechanics and Thermodynamics* (Fall 2005)

The hydrogen molecule comes in two forms, in which the spin degrees of freedom of the two protons are in a spin triplet state (the "ortho" case) or in a spin singlet state (the "para" case) respectively. The rotational energies of a hydrogen molecule are given by

$$E(L) = \frac{\hbar^2}{2I} L(L+1)$$

with I the moment of inertia and L the orbital angular momentum quantum number.

(a) In the ortho case, only odd L values are allowed and in the para case only even values. Why?

(b) Assuming that Boltzmann statistics are valid, find an expression for the specific heat of an ideal gas of hydrogen molecules for both the low temperature and the high temperature limits.

(c) Suppose protons were bosons instead of fermions. What would the low-temperature specific heat be then?

(a) protons are spin ½ (Fermions)

- Review QM → Identical particles ⇒ two-particle wave-fcn $\psi(x_1, x_2)$ in 1D (indistinguishable)

Under exchange, you can't tell apart s.t.

$$|\psi(x_1, x_2)|^2 = |\psi(x_2, x_1)|^2$$

Bosons: both symmetrical $\psi(x_1, x_2) = \psi(x_2, x_1)$

Fermions: both antisymmetrical $\psi(x_1, x_2) = -\psi(x_1, x_2)$

⇒ ensures linear superposition obeys above

for a two proton Hydrogen molecule (Fermion), the overall wavefcn must be antisymmetric

⇒ In general, for both in common eigenstate $\vec{S}^2$ and S_z

$$\Psi(x_1, s_1; x_2, s_2) = \psi(x_1, x_2)\,\chi(s_1, s_2)$$

this is helpful b/c we know how spin behaves!

for two spin ½,

Para $S=0$ singlet $|\chi(s=0, s_z=0)\rangle = \frac{1}{\sqrt{2}}(|\uparrow_1\downarrow_2\rangle - |\downarrow_1\uparrow_2\rangle)$ (anti-symmetric)

Ortho $S=1$ Triplet

$$\left.\begin{aligned} &|\chi(s=1, s_z=1)\rangle = |\uparrow_1\uparrow_2\rangle \\ &|\chi(s=1, s_z=0)\rangle = \frac{1}{\sqrt{2}}(|\uparrow_1\downarrow_2\rangle + |\downarrow_1\uparrow_2\rangle) \\ &|\chi(s=1, s_z=-1)\rangle = |\downarrow_1\downarrow_2\rangle \end{aligned}\right\}\ \text{(symmetric)}$$

Finally, we can answer initial question:

By consequence of overall wavefcn antisymmetrization of protons (Fermions)

(1) the ortho case (triplet) must have an antisymmetric spatial wavefcn

⇒ $\psi(x_1, x_2) = -\psi(x_2, x_1)$ ⇒ But parity says $\hat{P}|nLM\rangle = (-1)^L|nLM\rangle$

Thus, $\boxed{\text{L must be odd}}$

(2) the para case (singlet) must have a symmetric spatial wvfcn

$\psi(x_1, x_2) = \psi(x_2, x_1)$ ⇒ By parity $\boxed{\text{L must be even}}$

(b) Using Boltzmann Statistics → find specific heat (high/low limit)

- Ideal Gas of H molecules
- assumption (per Wes Campbell): assume that the ideal gas is composed of para ($g_s=1$) and ortho ($g_s=3$) in equal parts for each spin state and frozen-in

Deriving from scratch: $T_{rot} = \frac{\hbar^2}{2Ik}$

$$Z_1 = \sum_{L=0}^{\infty} g_L e^{-\beta E_L} = g_L \sum_{L=0}^{\infty} (2L+1) e^{-L(L+1) T_{rot}/T}$$

However, we can see from the multiplicity of the spin state + odd/even L states

$$Z_1 = Z_1^{para} + Z_1^{ortho} \quad \text{and} \quad Z = Z_1^N$$

g_s weighting factor for multiplicity (see assumption) for single H molecule

$$Z_1^{para} = (1/4)\sum_{\text{even } L} (2L+1) e^{-L(L+1) T_{rot}/T}$$

$$Z_1^{ortho} = (3/4)\sum_{\text{odd } L} (2L+1) e^{-L(L+1) T_{rot}/T}$$

The heat capacity is given by $C_v = \left(\frac{dU}{dT}\right)_v$

let $x = T_{rot}/T$, $U = \sum_i P_i \varepsilon_i = \sum_i \left(\frac{e^{-\beta\varepsilon_i}}{Z}\right)\varepsilon_i = -\sum_i \frac{1}{Z}\frac{\partial}{\partial\beta} e^{-\beta\varepsilon_i}$

$$= -\frac{1}{Z}\frac{\partial}{\partial\beta}\sum_i e^{-\beta\varepsilon_i} = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{\partial \ln Z}{\partial\beta} = -\frac{\partial \ln Z}{\partial x}\frac{\partial x}{\partial\beta}$$

$$= -k T_{rot} \frac{\partial \ln Z}{\partial x}$$

$$U = -N k T_{rot}\left(\frac{1}{Z_1}\frac{\partial Z_1}{\partial x}\right)$$

$$= -N k T_{rot}\left(\frac{1}{Z_1}\right)\left\{\frac{\partial Z_1^{para}}{\partial x} + \frac{\partial Z_1^{ortho}}{\partial x}\right\}$$

$$C_v^{para/ortho} = \frac{d}{dT}\left(-\frac{N k T_{rot}}{Z_1}\frac{\partial Z_1^{para/ortho}}{\partial x}\right)$$

for $x >> 1$ (as $T \to 0$) $\quad Z_1 \simeq \frac{1}{4}(1)$ (keeping only leading terms) $\quad L=0$

para (singlet): $\quad d_x Z_1^{para} \simeq \left(\frac{1}{4}\right)\left\{\underset{(L=0)}{0} + \underset{(L=2)}{5 \cdot -6e^{-6x}} + \underset{(L>2)}{\mathcal{O}(e^{-L(L+1)x})}\right\}$

$$\simeq -30 e^{-6x}$$

$$\lim_{x>>1} C_v^{para} \simeq \frac{d}{dT}\left(-N k T_{rot}\,(\cancel{4})\cdot\left(\frac{1}{\cancel{4}}\right)(-30 e^{-6x})\right)$$

$x = T_{rot}/T$

$$C_v^{para} \simeq 30 N k T_{rot}(-6e^{-6x})\left(-\frac{T_{rot}}{T^2}\right) \Rightarrow \boxed{\lim_{x>>1} C_v^{para} \simeq 30 N k x^2 e^{-6x}}$$

ortho (triplet): $\quad (L=1)$

$$d_x Z_1^{ortho} \simeq \frac{3}{4}\left\{(3)(-2)e^{-2x}\right\}$$

$$\lim_{x>>1} C_v^{ortho} \simeq \frac{d}{dT}\left(-N k T_{rot}\,(\cancel{4})\cdot\left(\frac{3}{\cancel{4}}\right)\left(-6e^{-2x}\right)\right) = N k T_{rot}(18)(-2)e^{-2x}\left(-\frac{T_{rot}}{T^2}\right)$$

$$\boxed{\lim_{x>>1} C_v^{ortho} \simeq 36 N k x^2 e^{-2x}}$$

Tot heat capacity

$$\boxed{\lim_{T\to 0} C_v \approx N k x^2 \{36 e^{-2x} + 30 e^{-6x}\}}$$

for $x \ll 1$ $(T \to \infty)$: we can see that more state can be occupied at high temps, thus allowing integral approx

$$Z_1 \sim \int_0^\infty dL\,(2L+1)\, e^{-L(L+1)x} = \int_0^\infty dL\, \frac{d}{dL}\left(e^{-L(L+1)x}\right)$$

$$Z_1 \approx -\frac{g_s}{x}\left[e^{-L(L+1)x}\right]_0^\infty = -g_s/x\,(0-1)$$

$$Z_1 \simeq g_s/x \Rightarrow U = -kT_{rot}\frac{N\partial \ln Z}{\partial x}$$

$$\approx -NkT_{rot}\frac{\partial}{\partial x}\left(\ln(g_s) - \ln(x)\right)$$

$$= NkT_{rot}\left(\frac{1}{x}\right) = NkT$$

$$\boxed{\lim_{x \ll 1} C_V \sim Nk}$$

(c) Suppose they were Bosons @ low-temp

- Boltzmann still applies
- Bosons require symmetric overall wavefcn

(1) ortho (triplet) $\rightarrow$ symmetric
spatial $\rightarrow$ symmetric
$\Rightarrow L$ is even

(2) para (singlet) $\rightarrow$ antisymmetric
spatial $\rightarrow$ antisymmetric
$\Rightarrow L$ is odd

We can then say that the Boson gas would have the parity switched in the partition fcn b/t ortho/para.

$$Z_1^{para} = (1/4)\sum_{odd\ L}(2L+1)\, e^{-L(L+1)T_{rot}/T}$$

$$Z_1^{ortho} = (3/4)\sum_{even\ L}(2L+1)\, e^{-L(L+1)T_{rot}/T}$$

$$C_V^{para/ortho} = \frac{d}{dT}\left(-\frac{NkT_{rot}}{Z_1}\frac{\partial Z_1^{para/ortho}}{\partial x}\right)$$

for $x \gg 1$ (as $T \to 0$) $Z_1 \simeq 3/4$ (keeping only leading terms)

para (singlet): $d_x Z_1^{para} \simeq \left(\frac{1}{4}\right)\left\{3 \cdot -2e^{-2x}\right\} \simeq -\frac{3}{2}e^{-2x}$

$$C_V \sim -NkT_{rot}\left(4/\cancel{3}\right)\left(-\cancel{3}/\cancel{2}\right)\left(-\cancel{2}e^{-2x}\right)\left(-\frac{T_{rot}}{T^2}\right)$$

$$\boxed{\lim_{x \gg 1} C_V^{para} \sim 4Nkx^2 e^{-2x}}$$

ortho (triplet): $d_x Z_1^{ortho} \simeq \left(\frac{3}{4}\right)\left\{0 + 5(-6)e^{-6x}\right\}$

$$C_V^{ortho} \sim -NkT_{rot}\left(4/3\right)\left(-30\left(-6e^{-6x}\right)\right) - \frac{T_{rot}}{T^2}$$

$$\boxed{\lim_{x \gg 1} C_V^{orth} \sim 240Nkx^2 e^{-6x}}$$

$$\boxed{\lim_{x \gg 1} C_V \sim Nkx^2\left\{4e^{-2x} + 240e^{-6x}\right\}}$$

total C_V is similar but the heat capacity $C_V^{ortho} \ll C_V^{para}$ (opposite of fermions)