

Application E : The Equipartition Theorem

E. The Equipartition Theorem

- Valid when classical statistical mechanics work [when discreteness can be ignored]

For a system in equilibrium at absolute temperature T , each independent quadratic term of a coordinate or momentum in the Hamiltonian has a mean energy of $\frac{1}{2}kT$.

(E1)

E.g. Classical Ideal Gas (monatomic)

$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} = \sum_{i=1}^N \left(\frac{p_{ix}^2}{2m} + \frac{p_{iy}^2}{2m} + \frac{p_{iz}^2}{2m} \right)$$

$3N$ quadratic in "p" terms

$$\langle E \rangle = 3N \cdot \left(\frac{1}{2}kT \right) = \frac{3}{2} NkT$$

E.g. $3N$ Classical Oscillators

$$H = \sum_{i=1}^{3N} \left[\frac{p_i^2}{2m} + \frac{1}{2} m \omega^2 x_i^2 \right]$$

$3N$ quadratic terms in "p"
 $3N$ quadratic terms in "x"

$$\langle E \rangle = 6N \cdot \frac{1}{2}kT = 3NkT$$

(this gives $C_v^{\text{molar}} = 3R$)

Generally, $H(p_1, p_2, \dots, p_N, x_1, \dots, x_N) = \underbrace{ap_i^2}_{\text{there is a quadratic term}} + \mathcal{E}(p_1, \dots, p_N; x_1, \dots, x_N)$

no "p_i"

$$\begin{aligned}
 \underbrace{\langle ap_i^2 \rangle}_{\substack{\text{contribution to } \langle E \rangle \text{ of} \\ \text{quadratic term}}} &= \frac{\int dp_1 \dots dp_i \dots dp_N dx_1 \dots dx_N (ap_i^2) e^{-\beta H}}{\int dp_1 \dots dp_i \dots dp_N dx_1 \dots dx_N e^{-\beta H}} \\
 &\quad \text{(statistical mechanics average of } (ap_i^2) \text{)} \\
 &= \frac{\int dp_1 \dots dp_i \dots dp_N dx_1 \dots dx_N e^{-\beta \mathcal{E}} e^{-\beta ap_i^2} (ap_i^2)}{\int dp_1 \dots dp_i \dots dp_N dx_1 \dots dx_N e^{-\beta \mathcal{E}} e^{-\beta ap_i^2}} \quad \leftarrow \text{no } p_i \text{ in } \mathcal{E} \\
 &\quad \text{cancelling many (but one) terms} \downarrow \\
 &= \frac{\int_{-\infty}^{\infty} dp_i e^{-\beta ap_i^2} (ap_i^2)}{\int_{-\infty}^{\infty} dp_i e^{-\beta ap_i^2}}
 \end{aligned}$$

$$\langle a p_i^2 \rangle = - \frac{\partial}{\partial \beta} \left(\ln \underbrace{\left[\int_{-\infty}^{\infty} dp_i e^{-\beta a p_i^2} \right]}_{\text{Gaussian integral}} \right) = - \frac{\partial}{\partial \beta} \left(\ln \frac{\sqrt{\pi}}{\sqrt{a\beta}} \right) = \frac{1}{2\beta} = \frac{1}{2} kT \quad (E2)$$

(done)

[same for $b x_i^2$ terms]

Remark: How about $x_i x_j$, $p_i p_j$, $x_i p_j$ terms? Are they quadratic?

$$H = \frac{1}{2} \sum_{i,j}^N \alpha_{ij} y_i y_j \quad \text{can be diagonalized}$$

^ ^ could be coordinates or momenta

Choose a Matrix $\overleftrightarrow{A}$ such that $(\overleftrightarrow{A}^{-1} \overleftrightarrow{\alpha} \overleftrightarrow{A})$ is diagonal $\begin{pmatrix} \lambda_1 & & \\ & \lambda_2 & \\ & & \ddots \\ & & & \lambda_N \end{pmatrix}$

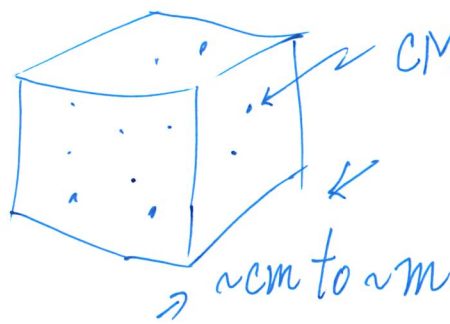
original variables $\rightarrow y_i = \sum_{\ell} A_{i\ell} x_{\ell}$ new variables

then H becomes:
$$H = \frac{1}{2} \sum_{k=1}^N \lambda_k x_k^2$$

thus can apply equipartition theorem

The Heat Capacity of Diatomic Gas as a function of temperature

• Translation



CM (center-of-mass)

"Particle-in-a-big-box problem"

$$E_{n_x, n_y, n_z} = \frac{(n_x^2 + n_y^2 + n_z^2) \pi^2 \hbar^2}{2mL^2}$$

translational states are separated by $\sim 10^{-20}$ eV!
 bigger than electron (not A)
 $L \sim m$

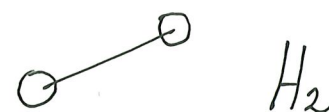
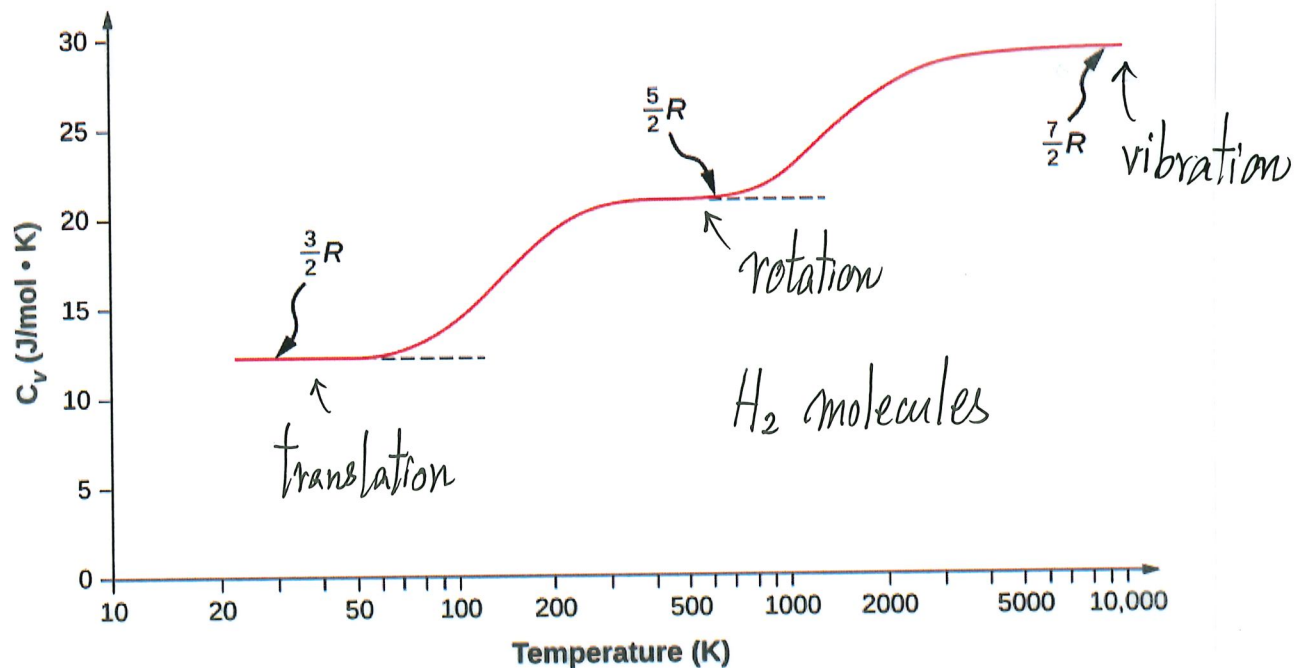
$kT_{\text{room}} \gg \text{spacing}$

$\Rightarrow$ OK to apply Equipartition Theorem to translational Motion

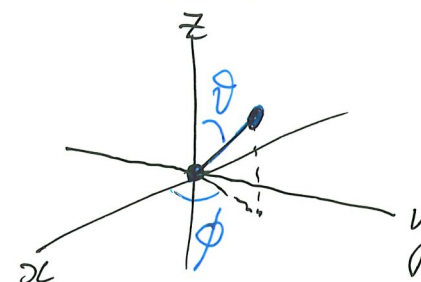
$$\Rightarrow 3N \cdot \frac{1}{2} kT \text{ to } U \Rightarrow \frac{3}{2} Nk \text{ to } C$$

$$\text{OR } \frac{3}{2} R \text{ to } C$$

easily observed at ordinary temperatures



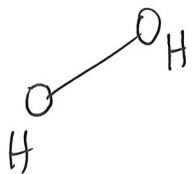
Rotational Motion



Need two angles to specify orientation
(3D rotor QM problem)

when $kT \gg$ rotational energies
 $\Rightarrow 2N \cdot \frac{1}{2} kT$ to energy
 and Nk to C
 or R to C (molar)

rotational levels
(in microwave range)
 $\sim 10^{-3} - 10^{-2} \text{ eV}$



6 variables ($x_1, y_1, z_1, x_2, y_2, z_2$)

CM: (X, Y, Z) "3" translation

Rotation: two angles "2" rotation

Vibration: $\omega = \sqrt{\frac{K}{\mu}}$ (only "one" normal mode)

[in IR or above]
↓

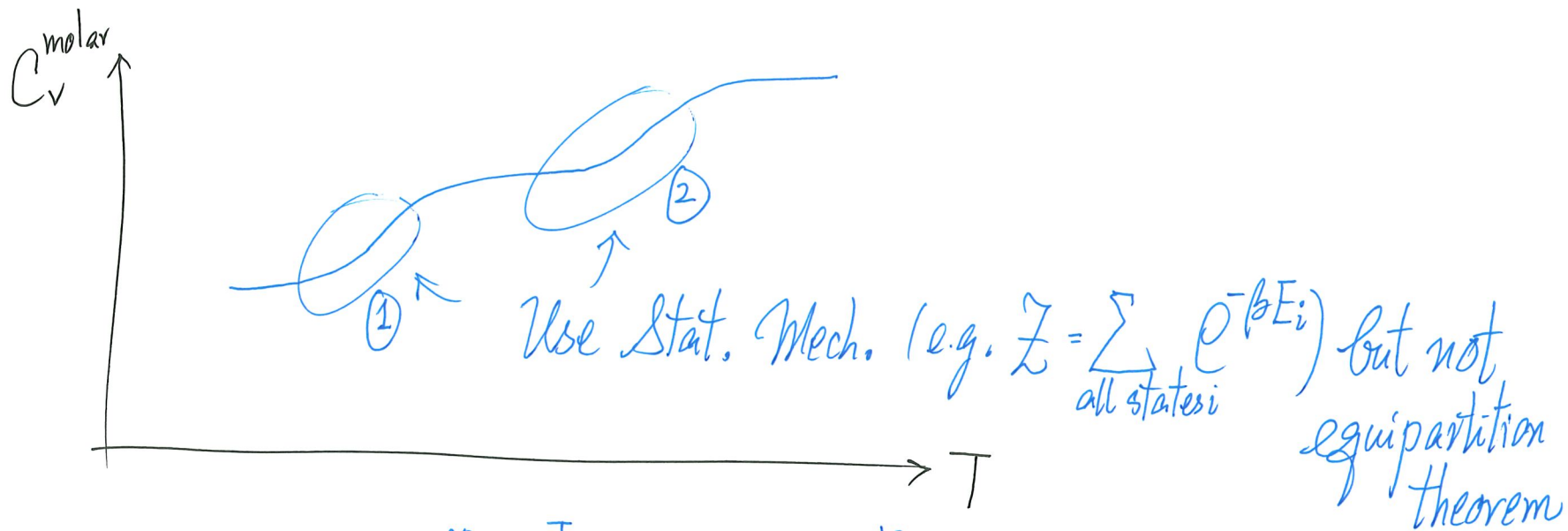
But "1" normal mode means "1" oscillator per molecular
two quadratic terms

contribute $2N \cdot \frac{1}{2} kT$ to energy

Nk to C_v

R to $C_v^{(molar)}$

for sufficiently high temperature



① $Z_{\text{rotation}} = \sum_{J=0}^{\infty} \sum_{m_J=-J}^J e^{-\beta \frac{J(J+1)\hbar^2}{2I}}$ will give the detail

② $Z_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta (n+\frac{1}{2})\hbar\omega}$ will give the detail

$$Z = \frac{1}{N!} Z_{\text{translation}}^N \cdot Z_{\text{rotation}} \cdot Z_{\text{vibration}}$$

$\therefore \mathcal{E}_{\text{each molecule}} = \frac{\vec{p}^2}{2m} + \frac{J(J+1)\hbar^2}{2I} + (n+\frac{1}{2})\hbar\omega$

translation of CM rotational vibrational