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8.044 Statistical Physics I
Spring 2008

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Polyatomic Gases

Non-interacting, identical $\Rightarrow Z = \frac{1}{N!} Z_1^N$ Find Z_1

Each molecule has $\#$ atoms $\Rightarrow 3\#$ position coordinates

$$3\# = \underbrace{3}_{\text{C.M.}} + \underbrace{n_r}_{\text{rotation}} + \underbrace{(3\# - 3 - n_r)}_{n_v, \text{ vibration}}$$

MONATOMIC
Xe



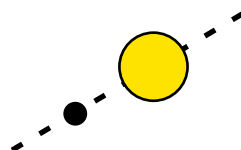
3

0

0

3

DIATOMIC
HS



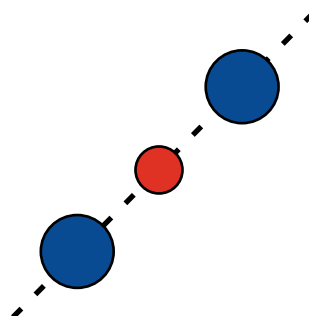
3

2

1

6

LINEAR TRI.
CO₂



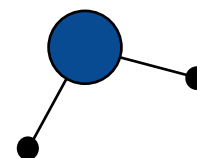
3

2

4

9

NON-LINEAR TRI.
H₂O



3

3

3

9

C.M. Motion:

Particle in a box $\Delta E_s \ll kT \Rightarrow$ classical

Rotation:

(H_2 $\nu_{\text{rot}} = 3.65 \times 10^{12}$ Hz \rightarrow 175 K) \Rightarrow Q.M.

Vibration:

(H_2 $\nu_{\text{vib}} = 1.32 \times 10^{14}$ Hz \rightarrow 6,320 K) \Rightarrow Q.M.

$\mathcal{H} = \mathcal{H}_{\text{CM}} + \mathcal{H}_{\text{vib}} + \mathcal{H}_{\text{rot}} \Rightarrow$ problem separates

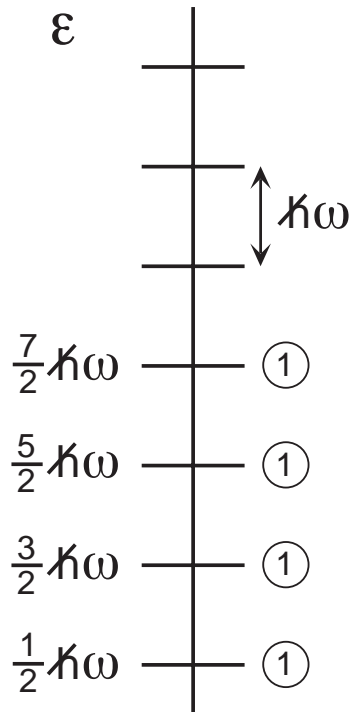
Vibration

$$\mathcal{H}_{\text{vib}} = \sum_{i=1}^{n_v} \left(\frac{1}{2} K_i a_i^2 + \frac{1}{2} \frac{K_i}{\omega_i^2} \dot{a}_i^2 \right)$$

n_v 1 dimensional harmonic oscillators, use Q.M.

$$\hat{\mathcal{H}}\psi_n = \epsilon_n \psi_n \quad \epsilon_n = \left(n + \frac{1}{2} \right) \hbar \omega \quad n = 0, 1, 2, \dots$$

The energy levels are non-degenerate.

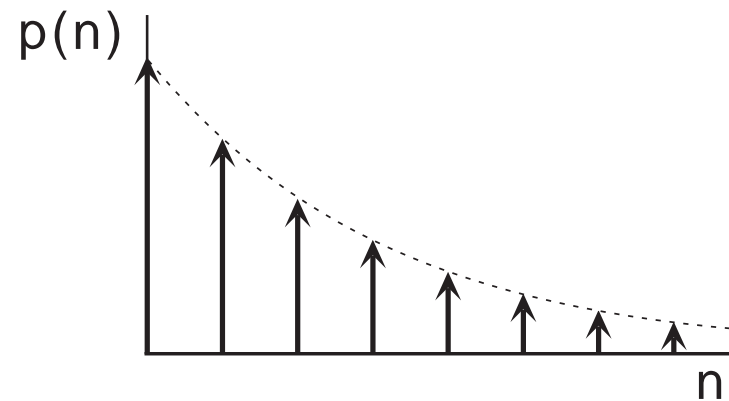


$$p(n) = e^{-(n+\frac{1}{2})\hbar\omega/kT} / \sum_{n=0}^{\infty} e^{-\epsilon_n/kT}$$

$$\begin{aligned} \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\hbar\omega/kT} &= e^{-\frac{1}{2}\hbar\omega/kT} \sum_{n=0}^{\infty} \left(e^{-\hbar\omega/kT}\right)^n \\ &= e^{-\frac{1}{2}\hbar\omega/kT} / \left(1 - e^{-\hbar\omega/kT}\right) \end{aligned}$$

$$p(n) = \left(1 - e^{-\hbar\omega/kT}\right) \left(e^{-\hbar\omega/kT}\right)^n = (1 - b)b^n$$

Geometric or Bose-Einstein



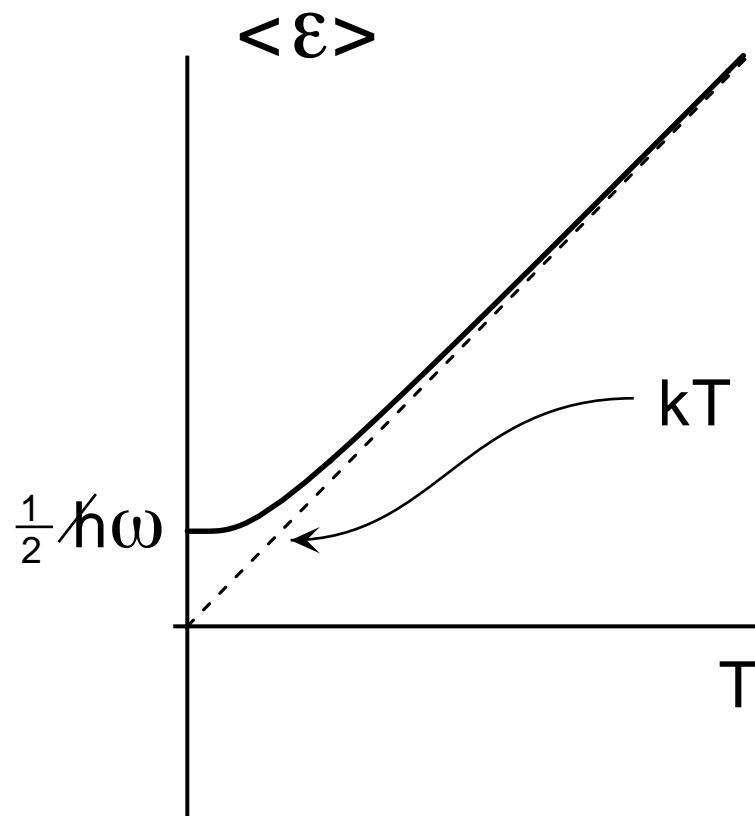
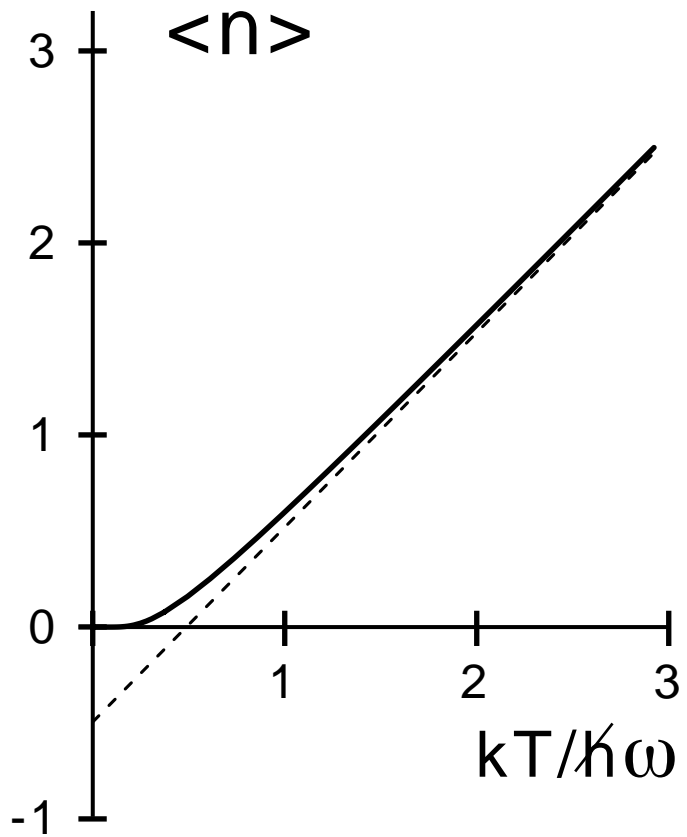
$$\langle n \rangle = \frac{b}{1-b} = \frac{1}{e^{\hbar\omega/kT} - 1}$$

$$\rightarrow e^{-\hbar\omega/kT} \quad \text{when } kT \ll \hbar\omega$$

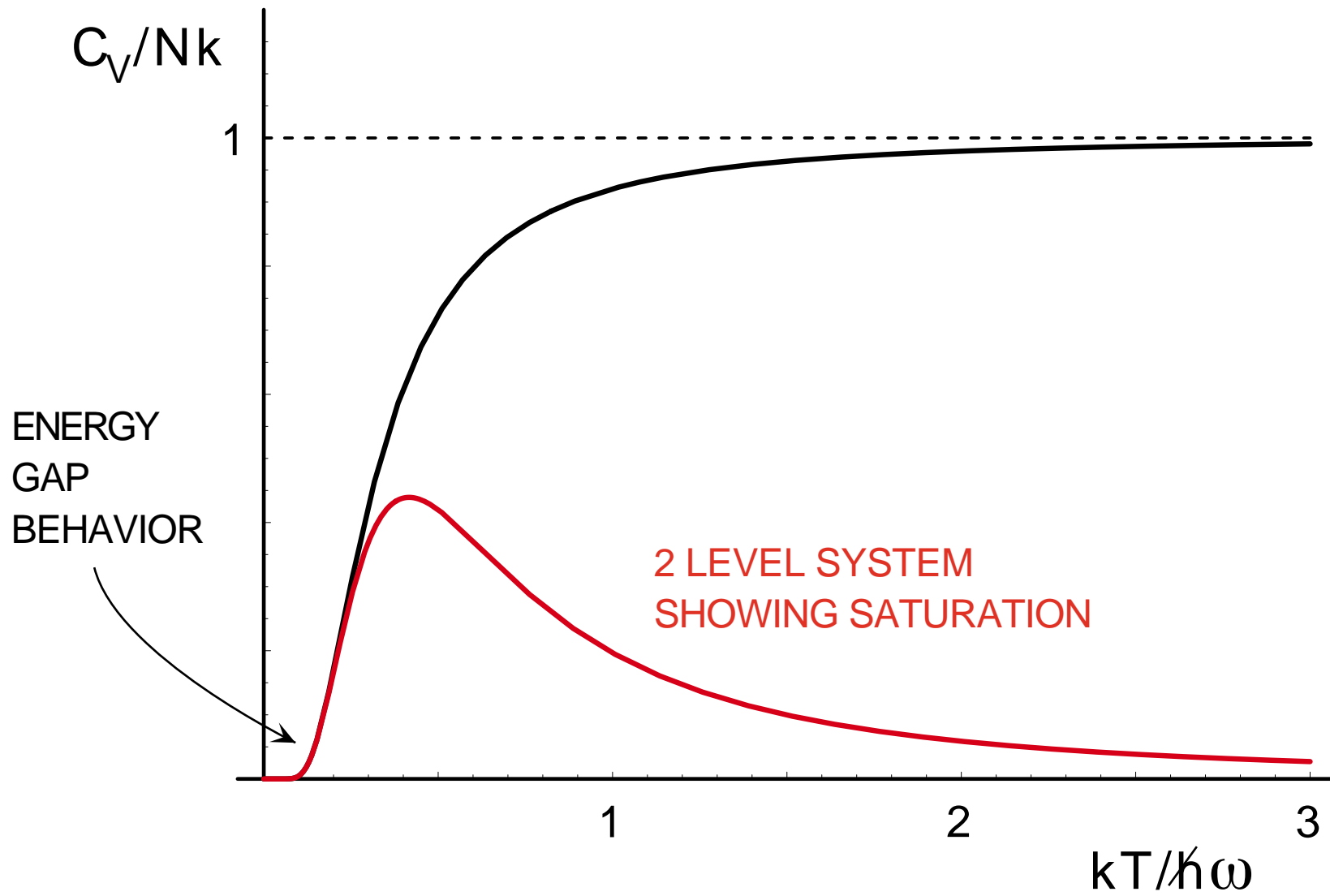
$$\begin{aligned}
\text{For } kT \gg \hbar\omega \quad \langle n \rangle &\rightarrow \frac{1}{1 + \frac{\hbar\omega}{kT} + \frac{1}{2} \left(\frac{\hbar\omega}{kT}\right)^2 \dots - 1} \\
&= \frac{kT}{\hbar\omega} \frac{1}{1 + \frac{1}{2} \left(\frac{\hbar\omega}{kT}\right)} \approx \frac{kT}{\hbar\omega} \left(1 - \frac{1}{2} \left(\frac{\hbar\omega}{kT}\right)\right) \\
&= \frac{kT}{\hbar\omega} - \frac{1}{2}
\end{aligned}$$

$$\langle \epsilon \rangle = \left(\langle n \rangle + \frac{1}{2}\right) \hbar\omega \rightarrow kT \quad kT \gg \hbar\omega \quad (\text{Classical})$$

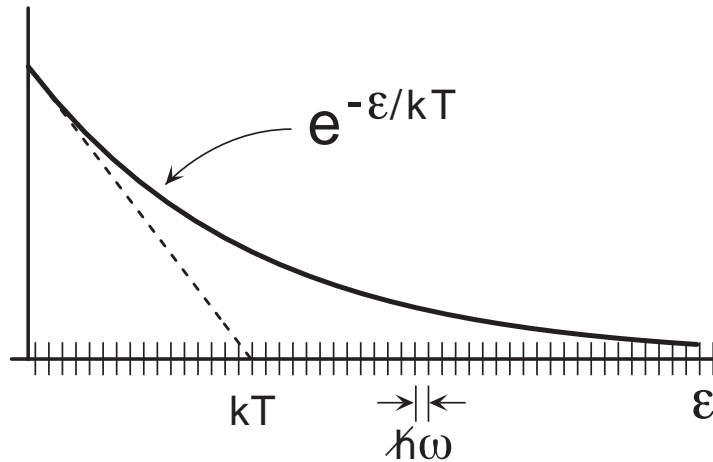
$$\rightarrow \frac{1}{2} \hbar\omega \quad kT \ll \hbar\omega \quad (\text{Ground state})$$



$$\begin{aligned}
C_V &= N \left(\frac{\partial \langle \epsilon \rangle}{\partial T} \right)_V = N \hbar \omega \frac{d \langle n \rangle}{dT} \\
&= Nk \left(\frac{\hbar \omega}{kT} \right)^2 \frac{e^{\hbar \omega / kT}}{(e^{\hbar \omega / kT} - 1)^2} \\
&\rightarrow Nk \left(\frac{\hbar \omega}{kT} \right)^2 e^{-\hbar \omega / kT} \quad kT \ll \hbar \omega \quad (\text{energy gap behavior}) \\
&\rightarrow Nk \quad kT \gg \hbar \omega
\end{aligned}$$



High and low temperature behavior without solving the complete problem Consider first the high T limit.



$\Delta\epsilon$ contains $\frac{\Delta\epsilon}{\hbar\omega}$ states

$$Z_1 = \sum_{n=0}^{\infty} e^{-\epsilon_n/kT}$$

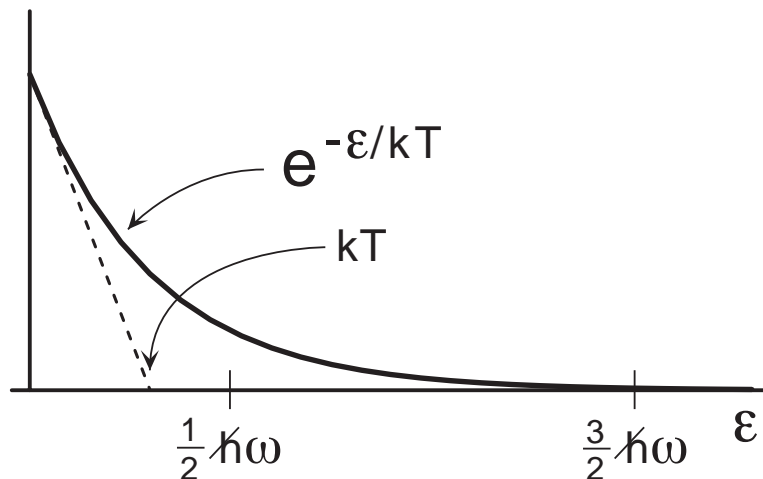
$$\approx \int_0^{\infty} \frac{1}{\hbar\omega} e^{-E/kT} dE = \frac{kT}{\hbar\omega} \int_0^{\infty} e^{-y} dy = \frac{kT}{\hbar\omega} \propto \beta^{-1}$$

$$Z_{\text{vib}} = Z_1^N \propto \beta^{-N}$$

$$U_{\text{vib}} = -\frac{1}{Z} \left(\frac{\partial Z}{\partial \beta} \right)_N = -\beta^N (-N) \beta^{-N-1} = \underline{NkT}$$

$$C_{\text{vib}} = \underline{Nk}$$

Next, consider the low T limit.



⇒ consider only 2 states

$$p(n = 1) \approx \frac{e^{-\frac{3}{2}\hbar\omega/kT}}{e^{-\frac{1}{2}\hbar\omega/kT} + e^{-\frac{3}{2}\hbar\omega/kT}} = \frac{1}{e^{\hbar\omega/kT} + 1} \approx e^{-\hbar\omega/kT}$$

$$p(n = 0) \approx 1 - e^{-\hbar\omega/kT}$$

$$\langle E \rangle = \frac{1}{2}N\hbar\omega \left(1 - e^{-\hbar\omega/kT}\right) + \frac{3}{2}N\hbar\omega e^{-\hbar\omega/kT}$$

$$= \frac{1}{2}N\hbar\omega + N\hbar\omega e^{-\hbar\omega/kT}$$

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = N\hbar\omega \left(\frac{\hbar\omega}{kT^2}\right) e^{-\hbar\omega/kT} = \underline{Nk \left(\frac{\hbar\omega}{kT}\right)^2 e^{-\hbar\omega/kT}}$$