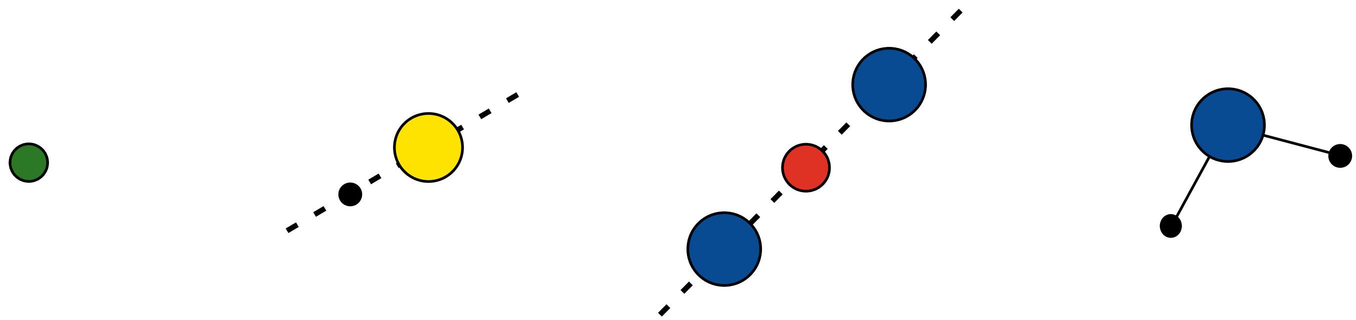
Polyatomic Gases

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	DIATOMIC	LINEAR TRI.	NON-LINEAR TRI.
Xe	HS	CO_2	H_2O



3	3	3	3
0	2	2	3
<u>0</u>	<u>1</u>	<u>4</u>	<u>3</u>
3	6	9	9

C.M. Motion:

Particle in a box ΔEs $\ll kT \Rightarrow$ 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

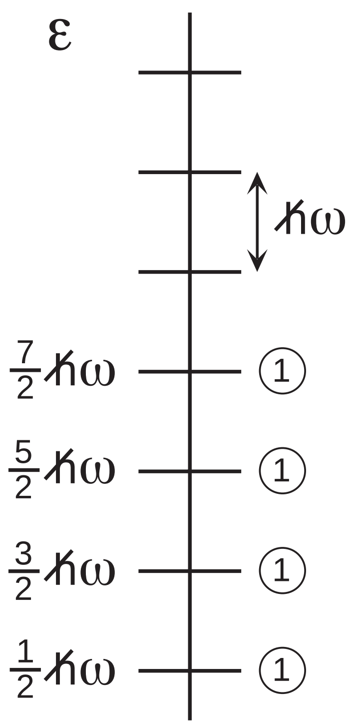
Vibration

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

n_v 1 dimensional harmonic oscillators, use Q.M.

$$\widehat{\mathcal{H}} \psi_n = \epsilon_n \psi_n \qquad \epsilon_n = (n + \tfrac{1}{2}) \hbar\omega \quad n = 0, 1, 2, \cdots$$

The energy levels are non-degenerate.



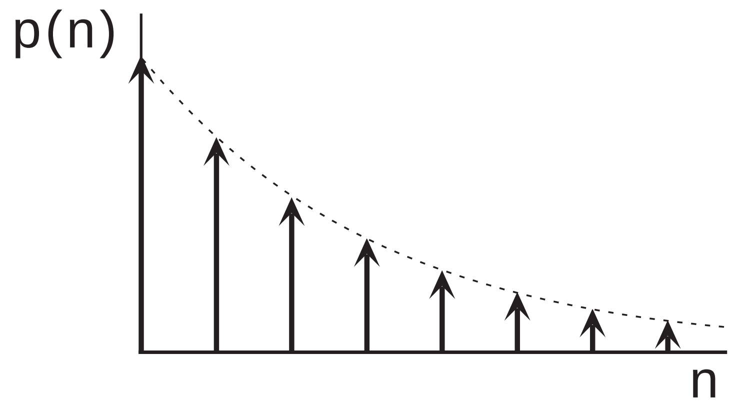
$$p(n) = e^{-(n+\frac{1}{2})\hbar\omega/kT} \Big/ \sum_{n=0}^{\infty} e^{-\epsilon_n/kT}$$

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

$$= e^{-\frac{1}{2}\hbar\omega/kT} \Big/ \left(1 - e^{-\hbar\omega/kT}\right)$$

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

Geometric or Bose-Einstein



$$< n > \; = \; \frac{b}{1-b} = \frac{1}{e^{\hbar\omega/kT} - 1}$$

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

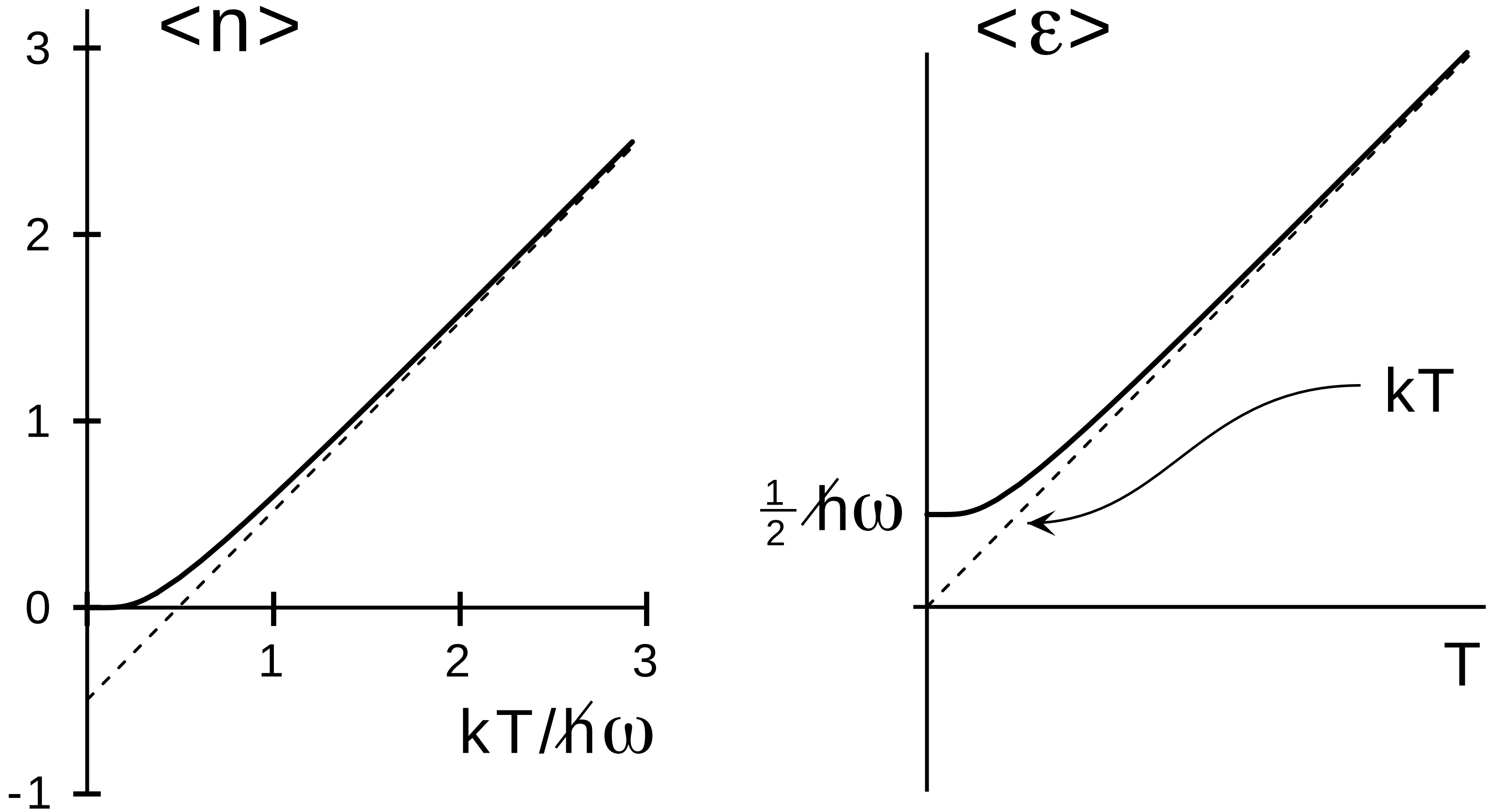
For $kT \gg \hbar\omega \quad < n > \; \rightarrow \; \dfrac{1}{1 + \frac{\hbar\omega}{kT} + \frac{1}{2}\left(\frac{\hbar\omega}{kT}\right)^2 \cdots - 1}$

$$= \frac{kT}{\hbar\omega}\,\frac{1}{1 + \frac{1}{2}\left(\frac{\hbar\omega}{kT}\right)} \approx \frac{kT}{\hbar\omega}\left(1 - \frac{1}{2}\left(\frac{\hbar\omega}{kT}\right)\right)$$

$$= \frac{kT}{\hbar\omega} - \frac{1}{2}$$

$< \epsilon >= (< n > + \frac{1}{2})\hbar\omega \; \rightarrow \; kT \quad kT \gg \hbar\omega$ (Classical)

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



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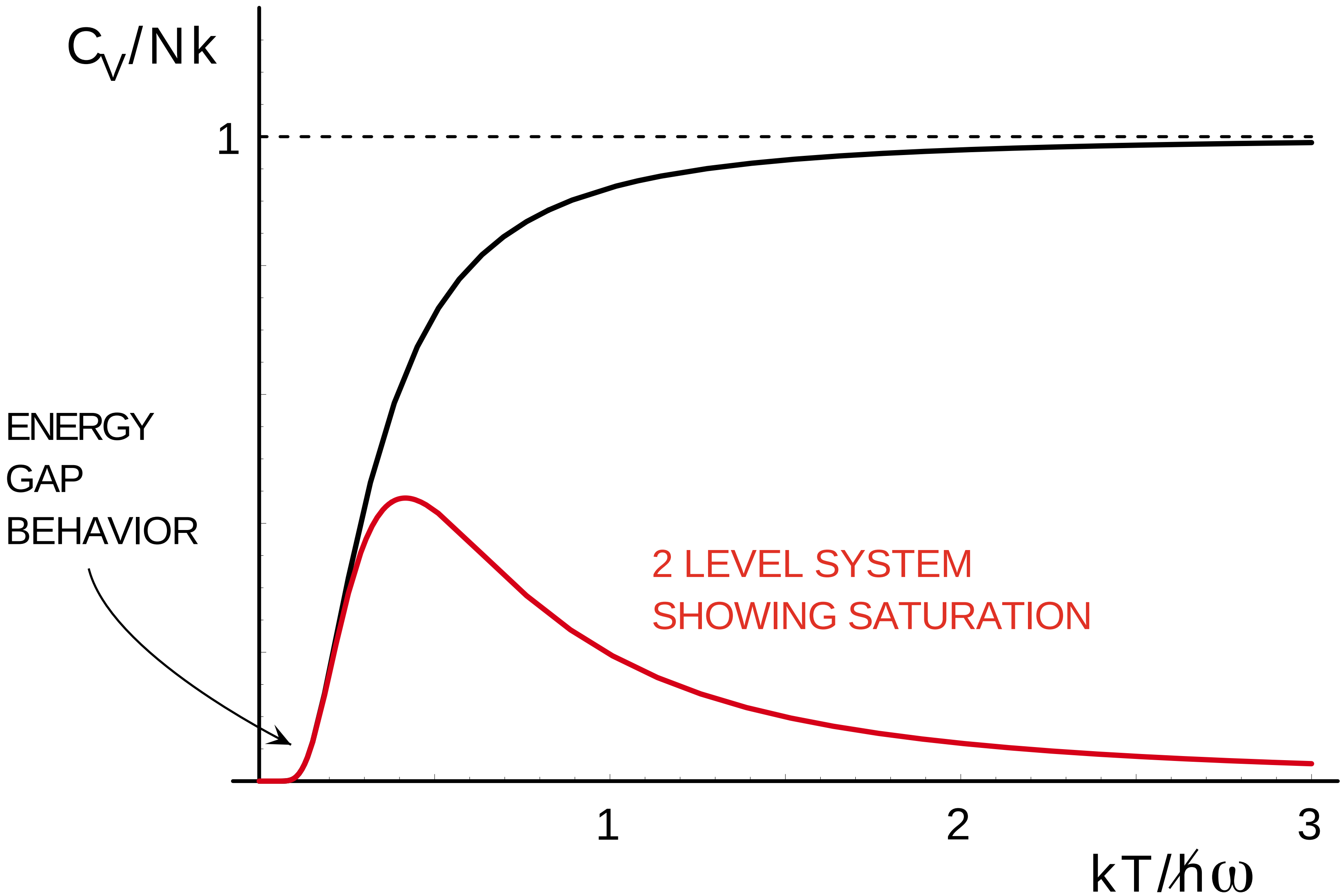
$$
\begin{aligned}
C_V &= N\left(\frac{\partial < \epsilon >}{\partial T}\right)_V = N\hbar\omega\frac{d < n >}{dT} \\
&= Nk\left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT} - 1\right)^2} \\
&\to Nk\left(\frac{\hbar\omega}{kT}\right)^2 e^{-\hbar\omega/kT} \quad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


C_V/Nk
1
ENERGY
GAP
BEHAVIOR
2 LEVEL SYSTEM
SHOWING SATURATION
1
2
3
$kT/\hbar\omega$

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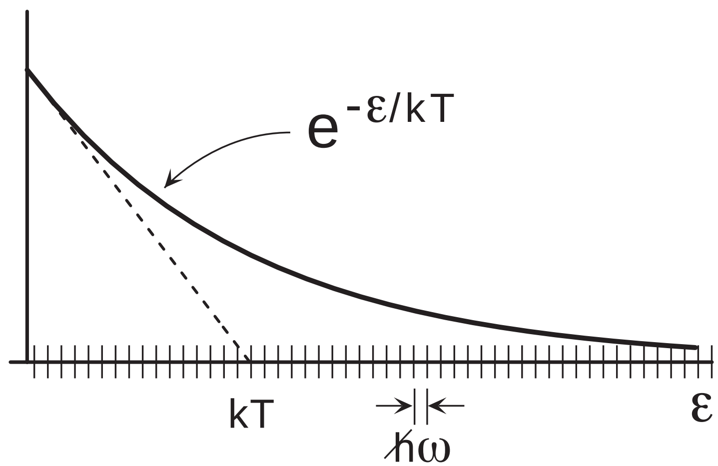
High and low temperature behavior without solving the complete problem Consider first the high T limit.



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

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

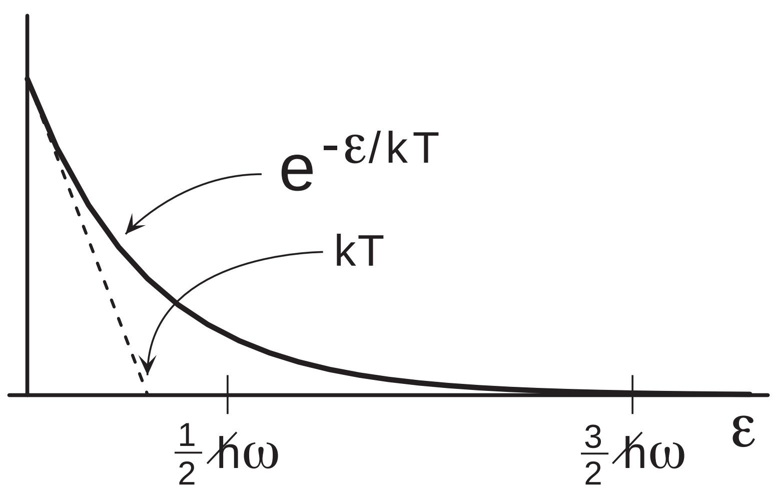
$$\approx \int_0^\infty \frac{1}{\hbar\omega} e^{-E/kT}\, dE = \frac{kT}{\hbar\omega}\int_0^\infty e^{-y}\, dy = \frac{kT}{\hbar\omega} \propto \beta^{-1}$$

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

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

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

Next, consider the low T limit.



$\Rightarrow$ consider only 2 states

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

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

$$< E >= \tfrac{1}{2}N\hbar\omega\left(1 - e^{-\hbar\omega/kT}\right) + \tfrac{3}{2}N\hbar\omega e^{-\hbar\omega/kT}$$

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

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