RECAP

- FOR A SYSTEM WITH A FIXED No OF PARTICLES IN CONTACT WITH A HEAT RESERVOIR AT TEMP T, THE CANONICAL PARTITION FUNCTION IS

$$\boxed{Z = \sum_n e^{-E_n/k_B T}}$$

WHERE $n = 1, 2, 3, \ldots$ LABELS THE ENERGY E'STATES.

THE PROBABILITY OF THE SYSTEM OCCUPYING STATE n IS

$$\boxed{\rho_n^{(eq)} = \frac{e^{-E_n/k_B T}}{Z}}$$

- FOR A SYSTEM CONSISTING OF N IDENTICAL BUT DISTINGUISHABLE PARTICLES

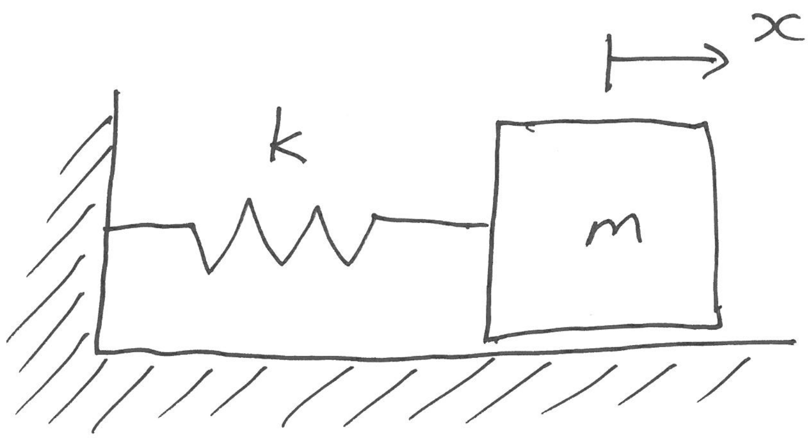
$$\boxed{Z = (Z_1)^N}$$

MAXWELL–BOLTZMANN STATISTICS

WHERE Z_1 IS THE CANONICAL PARTITION FUNCTION FOR JUST 1 OF THE PARTICLES

THE CLASSICAL SIMPLE HARMONIC OSCILLATOR (SHO)

- THE ARCHETYPAL EXAMPLE OF A CLASSIC SHO IS A MASS ON A SPRING



m = mass OF SHO

k = SPRING CONSTANT

x = DISPLACEMENT OF MASS FROM EQUILIBRIUM

- THE <u>RESTORING FORCE</u> ON THE MASS DUE TO THE SPRING IS

$$F = -kx$$

HOOKE'S LAW

AND SO THE EQUATION OF MOTION FOR THE MASS IS

$$m\ddot{x} = -kx$$

$$\Rightarrow \quad \ddot{x} + \frac{k}{m}x = 0$$

$$\Rightarrow \quad \boxed{\ddot{x} + \omega^2 x = 0} \quad (1)$$

$$\omega = \sqrt{\frac{k}{m}}$$

CLASSICAL SOLUTIONS TO (1)

$$\boxed{x(t) = A\cos\omega t + B\sin\omega t}$$

ω – FREQUENCY OF OSCILLATION.

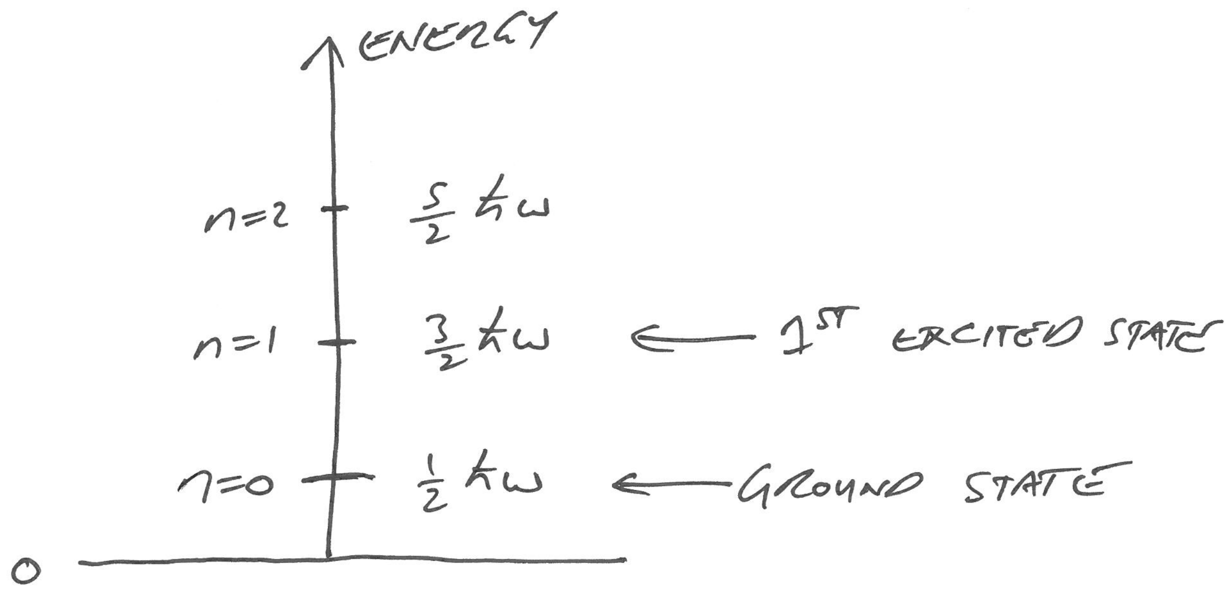
THE QUANTUM SHO:

A SINGLE 1D SHO OF FREQUENCY

$$\omega = \sqrt{\frac{k}{m}}$$

WHEN QUANTISED (i.e. AFTER WE APPLY THE RULES OF QM) HAS ENERGY LEVELS

$$E_n = \left(n + \tfrac{1}{2}\right)\hbar\omega \qquad n = 0, 1, 2, \ldots$$



THE CANONICAL PARTITION FUNCTION FOR A SINGLE SHO IS

$$Z_1 = \sum_{\text{STATES}} e^{-E_{\text{STATE}}/k_B T}$$

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

$$= e^{-\hbar\omega/2k_B T} \boxed{\sum_{n=0}^{\infty} \left(e^{-\hbar\omega/k_B T}\right)^n}$$

SEE ASIDE

$$= e^{-\hbar\omega/2k_B T} \times \boxed{\frac{1}{1 - e^{-\hbar\omega/k_B T}}}$$

<u>ASIDE</u>: LET $S = \sum_{n=0}^{p} x^n \qquad |x|<1$

THEN $S = 1 + x + x^2 + \cdots + x^p$

$$\Rightarrow \quad xS = x + x^2 + x^3 + \cdots + x^{p+1}$$

$$\Rightarrow \quad S - xS = 1 - x^{p+1}$$

$$\Rightarrow \quad S = \frac{1 - x^{p+1}}{1-x}$$

So $$\sum_{n=0}^{\infty} x^n = \lim_{p\to\infty} \sum_{n=0}^{p} x^n = \lim_{p\to\infty}\left(\frac{1-x^{p+1}}{1-x}\right)$$

$$= \frac{1}{1-x} \qquad \text{FOR } |x|<1$$

So

$$P_n^{(eq)} = \frac{e^{-\varepsilon_n/k_BT}}{Z_1}$$

= PROBABILITY TO BE IN THE STATE WITH QUANTUM No° n

• WHAT IS THE AVERAGE ENERGY OF THE SINGLE 1D SHO WHEN IN CONTACT WITH A HEAT BATH?

$$\bar{\varepsilon} = \sum_{n=0}^{\infty} \varepsilon_n P_n^{(eq)}$$

$$= \sum_{n=0}^{\infty} \varepsilon_n \frac{e^{-\varepsilon_n/k_BT}}{Z_1}$$

$$= \frac{1}{Z_1} \sum_{n=0}^{\infty} \varepsilon_n e^{-\varepsilon_n/k_BT}$$

TRICK: NOTICE THAT

$$\frac{\partial}{\partial T}\left(e^{-\varepsilon_n/k_BT}\right) = e^{-\varepsilon_n/k_BT} \times \frac{\varepsilon_n}{k_BT^2}$$

So $$k_BT^2 \frac{\partial}{\partial T}\left(e^{-\varepsilon_n/k_BT}\right) = \varepsilon_n e^{-\varepsilon_n/k_BT}$$

THUS

$$\bar{\varepsilon} = \frac{1}{Z_1} k_BT^2 \frac{\partial}{\partial T}\left(\sum_{n=0}^{\infty} e^{-\varepsilon_n/k_BT}\right)$$

$$= \frac{1}{Z_1} k_BT^2 \frac{\partial Z_1}{\partial T}$$

$$= k_BT^2 \frac{\partial}{\partial T}(\ln Z_1)$$

$$\Longrightarrow \boxed{\bar{\varepsilon} = k_BT^2 \frac{\partial}{\partial T}(\ln Z_1)}$$

So for a SHO

$$\ln Z_1 = \ln\left[\frac{e^{-\hbar\omega/2k_BT}}{1-e^{-\hbar\omega/k_BT}}\right]$$

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

$$\Rightarrow \frac{\partial \ln Z_1}{\partial T} = \frac{\hbar\omega}{2k_BT^2} - \frac{1}{1-e^{-\hbar\omega/k_BT}} \times \left((-1)e^{-\hbar\omega/k_BT}\right) \times \left(\frac{\hbar\omega}{k_BT^2}\right)$$

So $$\bar{E} = k_BT^2 \frac{\partial \ln Z_1}{\partial T}$$

$$= \frac{\hbar\omega}{2} + \frac{\hbar\omega\, e^{-\hbar\omega/k_BT}}{1-e^{-\hbar\omega/k_BT}}$$

$$\Rightarrow \boxed{\bar{\varepsilon} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}} \text{ --- (A)}$$

GROUND STATE ENERGY

CONTRIBUTION TO $\bar{\varepsilon}$ FROM ALL OTHER ENERGY LEVELS

WE CAN ALSO WRITE

$$\bar{\varepsilon} = \sum_{n=0}^{\infty} \varepsilon_n P_n^{(eq)} = \sum_{n=0}^{\infty} \hbar\omega(n+\tfrac{1}{2}) P_n^{(eq)}$$

$$= \hbar\omega\left(\sum_{n=0}^{\infty} n P_n^{(eq)} + \frac{1}{2} \sum_{n=0}^{\infty} P_n^{(eq)} \right)$$

1

$$= \hbar\omega\left(\bar{n} + \frac{1}{2}\right)$$

$$\Rightarrow \boxed{\bar{\varepsilon} = \frac{\hbar\omega}{2} + \hbar\omega\bar{n}} \text{ --- (B)}$$

WHERE $\bar{n} = \sum_{n=0}^{\infty} n P_n^{(eq)}$

IS THE AVERAGE ENERGY LEVEL VALUE.

COMPARING (A) & (B) WE FIND

$$\boxed{\bar{n} = \frac{1}{e^{\hbar\omega/k_B T} - 1}}$$

LIMITS FOR HIGH & LOW TEMP

- HIGH TEMP : $\dfrac{\hbar\omega}{k_B T} \ll 1$ $\quad$ [ie $\hbar\omega \ll k_B T$]

ENERGY LEVEL SPACING

"AVERAGE THERMAL ENERGY"

RECALL THAT

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$

SO FOR $x << 1$

$$e^x \approx 1 + x$$

SO FOR $\frac{\hbar\omega}{k_B T} << 1$ $\quad e^{\hbar\omega/k_B T} \approx 1 + \frac{\hbar\omega}{k_B T}$

SO

$$\bar{\mathcal{E}} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

$$\approx \frac{\hbar\omega}{2} + \frac{\hbar\omega}{1 + \frac{\hbar\omega}{k_B T} - 1} \qquad \left(\frac{\hbar\omega}{k_B T} << 1\right)$$

$$= \frac{\hbar\omega}{2} + k_B T$$

SO FOR HIGH TEMP

$$\bar{E} \approx \frac{\hbar\omega}{2} + k_B T$$

GROUND STATE ENERGY

FROM EQUIPARTITION THEOREM : $\frac{1}{2} k_B T$ PER PARTICLE PER DoF

(HERE 2 DoF - KE + PE)

• FOR LOW TEMP $\frac{\hbar\omega}{k_B T} >> 1$

HERE $e^{\hbar\omega/k_B T} \rightarrow \infty$ AS $T \rightarrow 0$

AND SO

GROUND STATE ENERGY

$$\bar{E} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1} \rightarrow \frac{\hbar\omega}{2} \quad \text{AS } T \rightarrow 0$$

AS $T \rightarrow 0$ THE OSCILLATOR "FREEZES OUT" INTO THE LOWEST ENERGY STATE