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Canonical Formalism:

Examples:

Harmonic Oscillator

Useful for
- Solid state
- Black Body.

Classical case (1 Dim.)

$$H(q_i, p_i) = \frac{1}{2} m \omega^2 q_i^2 + \frac{1}{2m} p_i^2$$

$i = 1, 2, 3, \ldots, N$

N oscillators

for oscillator i

Let's find $Z_1(\beta)$ (single particle partition function because the oscillators are assumed non-interacting)!

$$Z_1(\beta) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta\left(\frac{1}{2}m\omega^2 q^2 + \frac{1}{2m}p^2\right)} \frac{dp\,dq}{h} =$$

$$= \frac{1}{h}\sqrt{\frac{2\pi}{\beta m\omega^2}}\sqrt{\frac{2\pi m}{\beta}} =$$

Using tables for the 2 integrals.

$$= \frac{1}{h}\frac{2\pi}{\beta\omega} = \frac{kT}{\hbar\omega}$$

Then

$$Z_N(\beta) = [Z_1(\beta)]^N = \left(\frac{kT}{\hbar\omega}\right)^N$$

non-interacting.

- Notice that since the oscillators are distinguishable we do not need to divide by $N!$.

$$F = -kT \ln Z_N = NkT \ln\left(\frac{\hbar\omega}{kT}\right)$$

Since $dF = -S\,dT - P\,dV + \mu\,dN$

$$\mu = \frac{\partial F}{\partial N}\Big|_{V,T} = kT \ln\left(\frac{\hbar\omega}{kT}\right)$$

$$P = \frac{\partial F}{\partial V}\Big|_{T,N} = 0$$

$$S = -\frac{\partial F}{\partial T}\Big|_{N,V} = -Nk\ln\frac{\hbar\omega}{kT} + Nk\cancel{T}\,\frac{\cancel{\hbar\omega}/\cancel{kT^2}}{\cancel{\hbar\omega}/\cancel{kT}} =$$

$$= Nk\left[\ln\frac{kT}{\hbar\omega} + 1\right]$$

$$U = -\frac{\partial \ln Z_N}{\partial \beta} = F + TS = NkT\cancel{\ln\left(\frac{\hbar\omega}{kT}\right)} +$$

$$+ NkT\left[\cancel{\ln\frac{kT}{\hbar\omega}} + 1\right] = NkT$$

In agreement with equipartition theorem

$$\bar{\varepsilon} = \frac{kT}{2} f$$

$$f = 2N$$

Also $\quad c_V = \frac{\partial U}{\partial T}\Big|_V = Nk$

We also can find the density of state $g(E)$:

$g(E)$ is the anti-Laplace transform of $Z_N(\beta)$:

$$Z_N(\beta) = \frac{1}{(\hbar\omega\beta)^N} \qquad \frac{1}{\beta^N} \text{ has } \frac{E^{n-1}}{(n-1)!}$$

as $\mathcal{L}^{-1}$

$$g(\varepsilon) = \begin{cases} \dfrac{1}{(\hbar\omega)^N} \dfrac{\varepsilon^{N-1}}{(N-1)!} & \text{for } \varepsilon \geq 0 \\ 0 & \text{for } \varepsilon \leq 0 \end{cases}$$

Quantum mechanical case:

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

$$Z_1(\beta) = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} =$$

geometric series

$$= \frac{1}{e^{\frac{\beta}{2}\hbar\omega} - e^{-\frac{\beta}{2}\hbar\omega}} = \boxed{\frac{1}{2\sinh\frac{\beta\hbar\omega}{2}}}$$

then

$$Z_N(\beta) = [Z_1(\beta)]^N = \left[2 \sinh \frac{\beta \hbar \omega}{2}\right]^{-N}$$

Now

$$U = -\frac{\partial \ln Z_N}{\partial \beta} = N \frac{\frac{\hbar\omega}{2} \cosh \frac{\beta \hbar \omega}{2}}{\sinh \frac{\beta \hbar \omega}{2}} =$$

$$= \frac{N \hbar \omega}{2} \coth \frac{\beta \hbar \omega}{2} =$$

$$= \frac{N \hbar \omega}{2} \frac{\left(e^{\beta \frac{\hbar\omega}{2}} + e^{-\beta \frac{\hbar\omega}{2}}\right)}{\left(e^{\beta \frac{\hbar\omega}{2}} - e^{-\beta \frac{\hbar\omega}{2}}\right)} \Rightarrow$$

$$U = N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right]$$

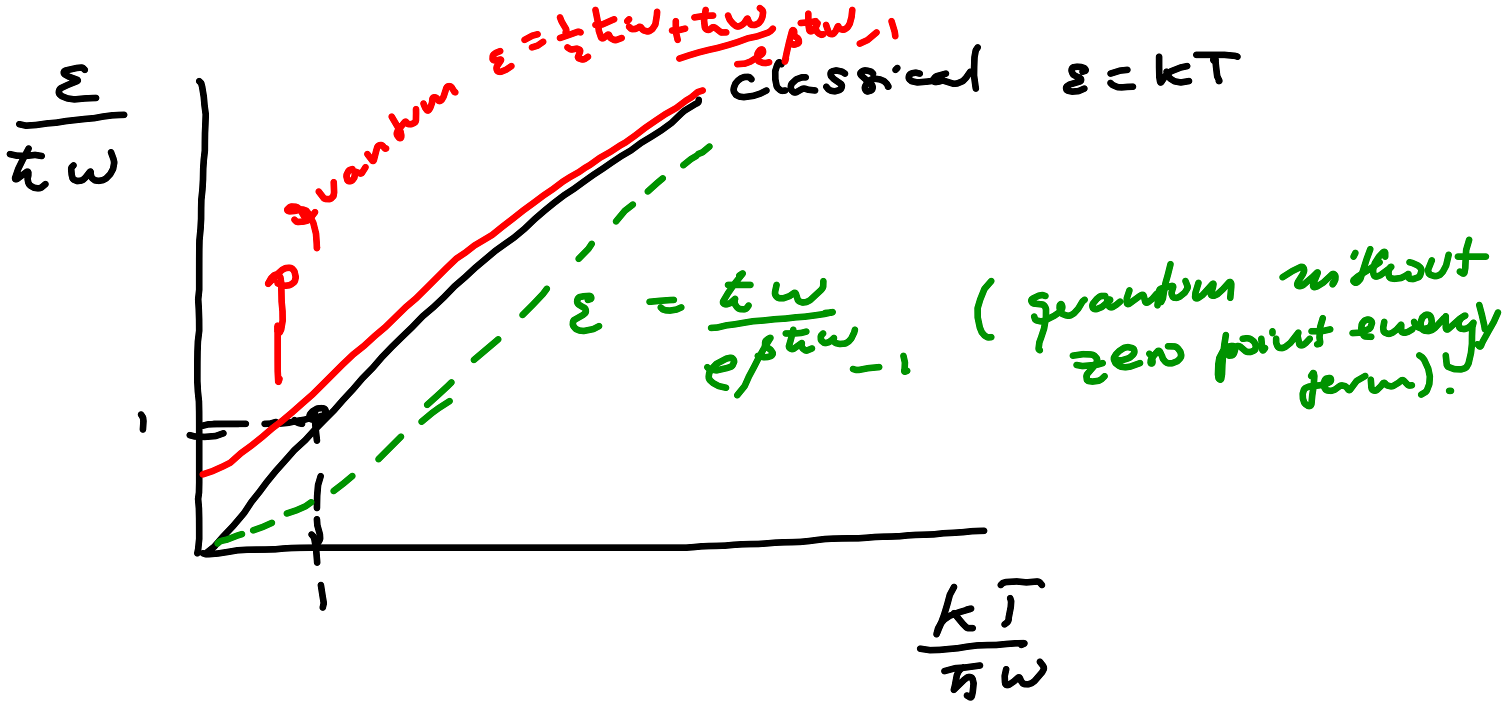
violates equipartition theorem.

However, if $\hbar\omega \ll kT$ (high T when the classical limit is achieved):

$$U \approx N\left[\frac{1}{2}\hbar\omega + \frac{\cancel{\hbar}\omega}{\cancel{1}+\beta\cancel{\hbar}\omega\cancel{-1}}\right] =$$

$$= N\left[\frac{1}{2}\hbar\omega + kT\right] \underset{\hbar\omega \ll kT}{\cong} NkT$$

equipartition fulfilled.



Density of states in quantum case:

$$Z_N(\beta) = e^{-\left(\frac{N}{2}\beta\hbar\omega\right)}\left(1 - e^{-\beta\hbar\omega}\right)^{-N}$$

Now remember that

$$(a+b)^N = \sum_{r=0}^{N} \binom{N}{r} a^r b^{N-r}$$

If N is negative:

$$(a+b)^{-N} = \sum_{r=0}^{\infty} \binom{-N}{r} a^r b^{-N-r} =$$

$$= \sum_{r=0}^{\infty} (-1)^r \binom{N+r-1}{r} a^r b^{-N-r}$$

if $a = 1$ and $b = x$:

$$(1-x)^{-n} = \sum_{r=0}^{\infty} \binom{n+r-1}{r} x^r \quad (1)$$

Using (1) we obtain that

$$Z_N(\beta) = e^{-\frac{N}{2}\beta\hbar\omega} \sum_{r=0}^{\infty} \binom{N+r-1}{r} e^{-\beta r\hbar\omega} =$$

$$= \sum_{r=0}^{\infty} \binom{N+r-1}{r} e^{-\beta\left(\frac{N}{2}\hbar\omega + r\hbar\omega\right)} \quad (2)$$

We know that

$$Z_N(\beta) = \int_0^\infty g(\epsilon)\, e^{-\beta\epsilon}\, d\epsilon \qquad (3)$$

Comparing (2) with (3) we observe that

$$g(\epsilon) = \sum_{r=0}^{\infty} \binom{N+r-1}{r} \delta\left(\epsilon - \left[r + \frac{N}{2}\right]\hbar\omega\right)$$

This tells us that for an oscillator with energy ϵ there are $\binom{N+r-1}{r} = \frac{(N+r-1)!}{r!\,(N-1)!}$

$r = 0, 1, \ldots 2, \ldots$ microstates accessible.

Let's now work in the microcanonical ensemble assuming that we know the energy E of the ensemble of oscillators

Energy $E = N\varepsilon$ is distributed between N identical oscillators each with $\varepsilon_r = (r+\frac{1}{2})\hbar\omega$

$r = 0, 1, 2, \ldots$

Let's $E_R = E - \frac{N}{2}\hbar\omega$

since each oscillator must have at least $\varepsilon \geq \hbar\omega/2$

The number R of energy quanta $\hbar\omega$ left to be distributed among the oscillators is going to be:

$$\underbrace{R}_{\text{integer}} = \frac{E_R}{\hbar\omega} = \frac{E - \frac{N}{2}\hbar\omega}{\hbar\omega} \in \mathbb{Z}$$

$$\therefore \quad E = R\hbar\omega + \frac{N}{2}\hbar\omega$$

To find the number of possible states we need to distribute the R indistinguishable quanta of energy between the N distinguishable oscillators.

This is like the problem of distributing R indistinguishable objects into N distinguishable boxes:

solution:

$$\frac{(R+N-1)!}{R!\,(N-1)!} = \binom{R+N-1}{R} \equiv \binom{R+N-1}{N-1}$$

This is the same number of possible state that we found using the canonical formalism.

Now in microcanonical:

$$S = k \ln \Omega = k \ln \left[\frac{(R+N-1)!}{R!\,(N-1)!} \right] \cong$$

Stirling

$$\cong k \left[\ln (R+N)! - \ln R! - \ln N! \right] \approx$$

$$= k \left[(R+N) \ln (R+N) - R \ln R - N \ln N \right]$$

Since $R = \dfrac{E - \frac{1}{2} N \hbar \omega}{\hbar \omega}$ $\qquad \dfrac{\partial R}{\partial E} = \dfrac{1}{\hbar \omega}$

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_N = \frac{\partial S}{\partial R} \frac{\partial R}{\partial E} = k \left[\ln (R+N) + \overset{1}{\cancel{\frac{(R+N)}{(R+N)}}} - \ln R - 1 \right] \frac{1}{\hbar \omega} \Rightarrow$$

$$\frac{1}{T} = \frac{k}{\hbar\omega} \ln\left(\frac{R+N}{R}\right) = \frac{k}{\hbar\omega} \ln\left[\frac{E + \frac{1}{2}N\hbar\omega}{E - \frac{1}{2}N\hbar\omega}\right]$$

$$\therefore \quad \frac{\hbar\omega}{kT} = \ln\left[\frac{E + \frac{1}{2}N\hbar\omega}{E - \frac{1}{2}N\hbar\omega}\right]$$

$T = T(E)$ in microcanonical

$$e^{\frac{\hbar\omega}{kT}} = \frac{E + \frac{1}{2}N\hbar\omega}{E - \frac{1}{2}N\hbar\omega} \quad (4)$$

Now I will find $E = E(T)$ by reversing the expression

Solving (4) for E we obtain:

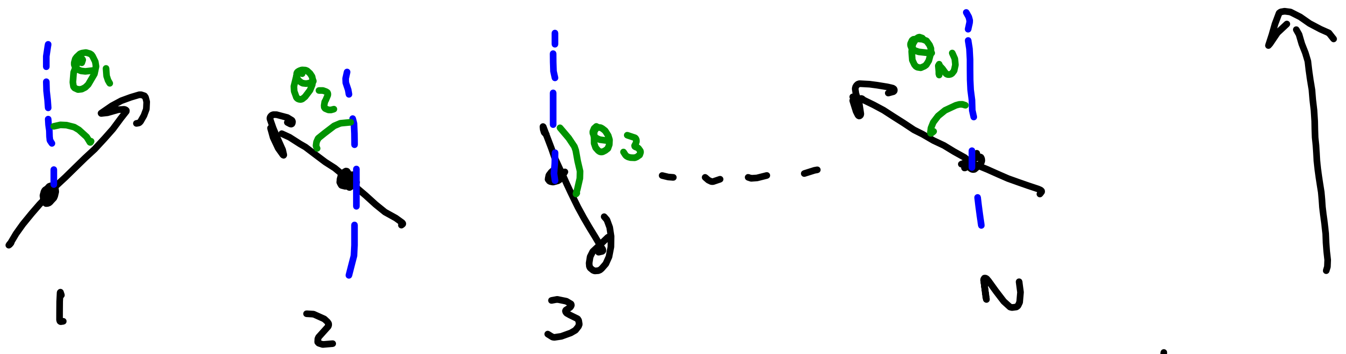
$$\frac{E}{N} = \frac{\hbar\omega}{2} \frac{\left(e^{\frac{\hbar\omega}{kT}} + 1\right)}{e^{\frac{\hbar\omega}{kT}} - 1}$$

Same as in canonical.

Example 2: magnetic dipoles in a magnetic field (model for paramagnetism).

Consider N non-interacting magnetic dipoles with magnetic moment $\bar{\mu}$.

Distinguishable.



$\bar{H} = H\hat{z}$

$-\bar{\mu}\cdot\bar{H}$ (dipole wants to align with H to lower magnetic energy)

at $T \to 0$ $-N\mu_B H$ will be the energy.
All spins ordered.

but kT introduces disorder
as $T \to \infty$ all spins will point randomly.

a) Classical approach:

$$E = \sum_{i=1}^{N} E_i = -\sum_{i=1}^{N} \bar{\mu}_i \cdot \bar{H} =$$

$$= -\mu H \sum_{i=1}^{N} \cos\theta_i \qquad E = E\{\theta_i\}$$

$$Z_N(\beta) = [Z_1(\beta)]^N = \Big[\sum_\theta e^{\beta\mu H\cos\theta}\Big]^N =$$

$$\overset{3D}{=} \left[\int_0^{2\pi}\int_0^{\pi} e^{\beta\mu H\cos\theta} \underbrace{\overbrace{\sin\theta\, d\theta}^{-d(\cos\theta)}\, d\varphi}_{d\Omega}\right]^N =$$

$$= \left[\underbrace{\int_0^{2\pi} d\varphi}_{2\pi} \int_{-1}^{1} e^{\beta\mu H x}\, dx\right]^N = \qquad x = \cos\theta$$

$$= \left[2\pi \left.\frac{e^{\beta\mu H x}}{\beta\mu H}\right|_{-1}^{1}\right]^N = \left[\frac{2\pi}{\beta\mu H}\left(e^{\beta\mu H} - e^{-\beta\mu H}\right)\right]^N$$

Then

$$Z_N(\beta) = \left[\frac{4\pi}{\beta\mu H}\sinh\beta\mu H\right]^N$$

$$\bar{\mu}_z = \frac{M_z}{N} = \langle \mu\cos\theta\rangle = \frac{\sum_\theta \mu\cos\theta\, e^{\beta\mu H\cos\theta}}{\sum_\theta e^{\beta\mu H\cos\theta}} =$$

$$e^{-F/kT} \quad \sum_\theta e^{\beta\mu H\cos\theta}$$

$$= \frac{1}{\beta}\frac{\partial \ln Z_1}{\partial H} = \frac{kT}{N}\frac{\partial \ln Z_N}{\partial H} =$$

$$= -\frac{1}{N}\frac{\partial F}{\partial H}\Big|_T$$