

Worksheet 10 - Solutions

1) Thermal de Broglie wavelength.

We have that

$$\lambda_{Th} = \sqrt{\frac{2\pi \hbar^2}{m k_B T}}$$

and we have that the average interparticle distance goes as

$$\left(\frac{V}{N}\right)^{1/3} = \left(\frac{1}{\rho}\right)^{1/3} = \rho^{-1/3}$$

or, we can also use

$$\frac{1}{\rho \lambda_{Th}^3} \gg 1 \Rightarrow \text{Classical gas.}$$

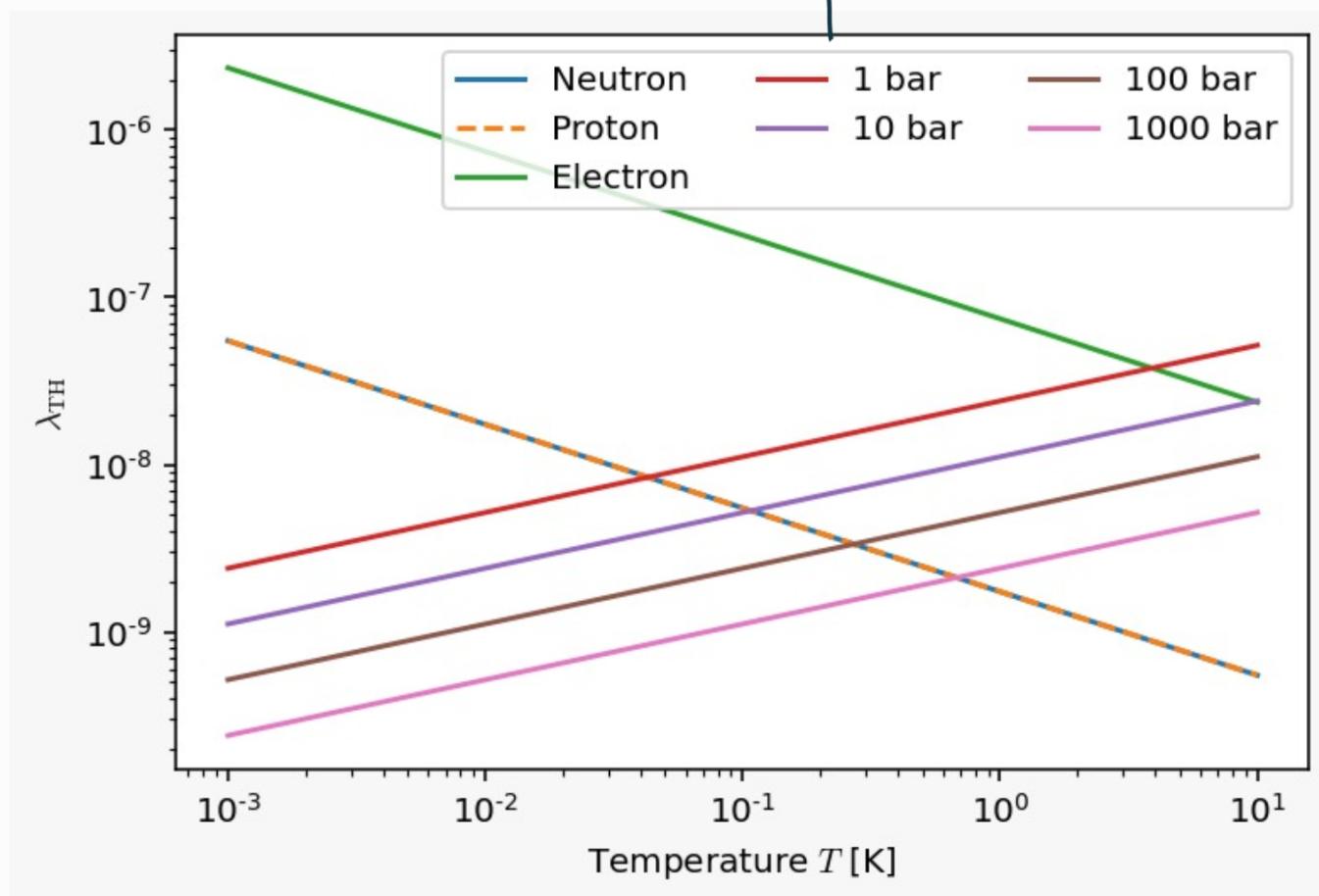
We may compare with an ideal gas (Boltzmann Gas)

$$PV = N k_B T$$

$$\frac{V}{N} = \frac{k_B T}{P}$$

$$\left(\frac{V}{N}\right)^{1/3} = \left(\frac{k_B T}{P}\right)^{1/3}$$

So, if we take several pressures for the ideal gas comparison.



D look that the differences on the three cases is of orders of magnitude, this makes possible to use classical mechanics for nuclei and quantum treatment in some theories

Massless particle
 in this case, what it means to be classical
 or quantum, is the fact that the spectrum
 of, for instance, black bodies, follows the
 classical Rayleigh-Jeans law

$$B_1(T) = \frac{2c k_B T}{\lambda^4}$$

but in the quantum domain, the Planck's law
 is needed

$$B_2(v, T) = \frac{2hv^3}{c^2} \frac{1}{e^{hv/k_B T} - 1}$$

2 Does entropy increase in quantum system

1) let us start with the Schrödinger Equation

$$\partial_t |\Psi(t)\rangle = (i\hbar)^{-1} \hat{H} |\Psi(t)\rangle.$$

$\hookrightarrow |\Psi(t)\rangle = e^{-i\hat{H}\frac{t}{\hbar}} |\Psi(0)\rangle$

and the definition of the density matrix

$$\rho = \sum_n |\Psi_n\rangle \langle \Psi_n|.$$

the time evolution of ρ goes as

$$\begin{aligned}\rho(t) &= \sum_n |\psi_n(t)\rangle\langle\psi_n(t)| \\ &= \sum_n e^{-\frac{i\hat{H}t}{\hbar}} |\psi_n(0)\rangle\langle\psi_n(0)| e^{\frac{i\hat{H}t}{\hbar}} \\ &= e^{-\frac{i\hat{H}t}{\hbar}} \underbrace{\left[\sum_n |\psi_n(0)\rangle\langle\psi_n(0)| \right]}_{\rho(0)} e^{\frac{i\hat{H}t}{\hbar}} \\ &= U(t) \rho(0) U^\dagger(t) \quad \text{with } U(t) = e^{-\frac{i\hat{H}t}{\hbar}}\end{aligned}$$

the time evolution operator.

consider a basis ψ so that ρ is diagonal.

$\{\psi_i\}$ so that

$$i\hbar t/\hbar$$

$$\psi_i(t) = \psi_i(0) e^{i\hbar t/\hbar}$$

$$\psi_j(t) = \psi_j(0) e^{i\hbar t/\hbar}$$

$$\begin{aligned}\langle\psi_j(t)|\psi_i(t)\rangle &= \int dq \psi_i(t) \psi_j^*(t) = \int dq \psi_i(0) \psi_j(0) \\ &\quad \times e^{\frac{i\hbar t}{\hbar}} e^{-\frac{i\hbar t}{\hbar}}\end{aligned}$$

$$= \int d\mathbf{q} \psi_i(0) \psi_j(0) = \langle \psi_j(0) | \psi_i(0) \rangle$$

or for the case of the density matrix

the solution of $\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar} [H, \rho]$

can be written with the time evolution operator

$$\rho(t) = U(t) \rho(0) U^\dagger(t)$$

$$= e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar}$$

So, let us compute the entropy

$$S = \text{Tr} \left[\rho \ln(\rho) \right] = \text{Tr} \left[e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar} \times \ln \left(e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar} \right) \right]$$

and using that for unitary operators

$$f(U^\dagger U) = U f(U) U^\dagger$$

$$S = \text{Tr} \left[e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar} e^{-iHt/\hbar} \ln(\rho(0)) e^{iHt/\hbar} \right]$$

and as the trace is cyclic.

$$S = \text{Tr} \left[e^{\frac{i\hbar t}{\hbar}} e^{-\frac{i\hbar t}{\hbar}} \rho^{(0)} \ln(\rho^{(0)}) \right]$$

$$= \text{Tr} [\rho^{(0)} \ln(\rho^{(0)})] \xrightarrow{\text{---}} S \text{ is time independent.}$$

3 Density matrix of Polarized light.

$$\hat{\rho} = f |\hat{z} \times \hat{z}| + (1-f) |\text{opposite} \times \text{opposite}|$$



Diagonal.

4. Electron Spin.

By definition, we have;

$$\rho = \frac{\exp(-\beta \mathcal{H})}{\text{Tr} [\exp(-\beta \mathcal{H})]}$$

and as $\sigma_i^2 = 1$ for all i ,

$$\exp(a \sigma_i) = \left(1 + \frac{a^2}{2!} + \frac{a^4}{4!} + \dots \right) \mathbb{1} + \left(a + \frac{a^3}{3!} + \frac{a^5}{5!} + \dots \right) \sigma_i$$

$$= \cosh(a \mathbb{1}) + \sinh(a \sigma_i)$$

$$\text{so, } \text{Tr} [\exp(a \sigma_i)] = \text{Tr} [\cosh(a \mathbb{1}) + \sinh(a \sigma_i)] = 2 \cosh(a)$$

$\hookrightarrow \sigma_i$ are traceless

In the case of $\vec{B} = B\hat{z}$

$$\rho = \frac{\exp(\beta \mu_B \sigma_z B)}{2 \cosh(\beta \mu_B B)} = \frac{1}{2 \cosh(\beta \mu_B B)} \begin{pmatrix} e^{\beta \mu_B B} & 0 \\ 0 & e^{-\beta \mu_B B} \end{pmatrix}$$

2) for B_z

$$\rho = \frac{\exp(\beta \mu_B \sigma_z B)}{2 \cosh(\beta \mu_B B)} = \frac{1}{2 \cosh(\beta \mu_B B)} \begin{pmatrix} \cosh(\beta \mu_B B) & \sinh(\beta \mu_B B) \\ \sinh(\beta \mu_B B) & \cosh(\beta \mu_B B) \end{pmatrix}$$

$$\begin{pmatrix} 1/2 & \tanh(\beta \mu_B B)/2 \\ \tanh(\beta \mu_B B)/2 & 1/2 \end{pmatrix}$$

3) The energy for both cases

Note that

$$\text{tr}[\sigma_i \exp(a \sigma_i)] = \text{tr}[\cosh(a \sigma_i) + \sinh(a \mathbb{1})]$$

$$= 2 \sinh(a)$$

so, using $\mathcal{H} = -\mu_B B \sigma_i$,

$$\frac{\text{Tr}[\mathcal{H} \rho]}{\text{Tr}[\rho]} = \frac{\text{Tr}[-\mu_B B \sigma_i \exp(\rho \mu_B \sigma_i B)]}{\text{Tr}[\exp(\rho \mu_B \sigma_i B)]}$$

$$\frac{-2\mu_B B \sinh(\beta \mu_B B)}{2 \cosh(\beta \mu_B B)} = -\mu_B \tanh(\beta \mu_B B)$$

for all directions.

5 Quantum Harmonic Oscillator.

we have that

$$Z = \sum_n \exp(-\beta \hbar \omega (n + 1/2)) = e^{-\beta \hbar \omega / 2} + e^{-3\beta \hbar \omega / 2} + \dots$$

$$= \frac{1}{e^{\beta \hbar \omega / 2} - e^{-\beta \hbar \omega / 2}} = \frac{1}{2 \sinh(\beta \hbar \omega / 2)}$$

so, the average energy

$$\langle E \rangle = -\frac{\partial \ln(Z)}{\partial \beta} = \frac{\hbar \omega}{2} \frac{1}{\tanh(\beta \hbar \omega / 2)}$$

2) we can write \hat{P} as;

$$P = 2 \sinh\left(\frac{\beta \hbar \omega}{2}\right) \left\{ \sum_n |n\rangle \exp(-\beta \hbar \omega (n + 1/2)) \langle n| \right\}$$

and, like in coordinate representation;

$$\langle n | q \rangle = \left(\frac{m \omega}{\pi \hbar}\right)^{1/4} \frac{H_n(\xi)}{\sqrt{2^n n!}} \exp\left(-\frac{\xi^2}{2}\right)$$

where

$$\xi = \sqrt{\frac{m \omega}{\hbar}} q$$

and H_n are the Hermite Polynomials.

$$\langle q | P | q \rangle = 2 \sinh\left(\frac{\beta \hbar \omega}{2}\right) \sum_n \exp(-\beta \hbar \omega (n + 1/2)) \langle q | n \rangle \langle n | q \rangle$$

3) we have that

$$e^A = \sum_{n=0}^{\infty} \frac{1}{n!} A^n$$

and the derivatives

$$\frac{\partial e^A}{\partial x} = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\partial A^n}{\partial x}$$

and as A is an operator

$$\frac{\partial}{\partial x} (A \cdot A \cdots A) = \frac{\partial A}{\partial x} A \cdots A + A \cdot \frac{\partial A}{\partial x} \cdot A \cdots A + \cdots + A \cdot A \cdots \frac{\partial A}{\partial x}$$

we can exchange $\frac{\partial A}{\partial x}$ and A if $[A, \frac{\partial A}{\partial x}] = 0$
suppose that is the case

$$\frac{\partial A}{\partial x} = n \frac{\partial A}{\partial x} A^{n-1}$$

and

$$\frac{\partial e^A}{\partial x} = \frac{\partial A}{\partial x} e^A$$

lastly as trace is cyclic, we can always exchange
orders

$$\text{tr} \left(A \cdots A \cdots \frac{\partial A}{\partial x} \cdots A \right) = \text{tr} \left(\frac{\partial A}{\partial x} \cdot A^{n-1} \right)$$

so

$$\frac{\partial}{\partial x} \text{tr}(e^A) = \text{tr} \left(\frac{\partial A}{\partial x} e^A \right) \quad \text{with no constrain.}$$

4) using that

$$\langle A \rangle = \text{Tr} (A \rho)$$

and as $\partial_m z = 0$

$$\begin{aligned}\frac{\partial}{\partial m} z &= \frac{\partial}{\partial m} \text{Tr} (e^{-\beta \mathcal{H}}) = \text{Tr} \left[\frac{\partial}{\partial m} (-\beta \mathcal{H}) e^{-\beta \mathcal{H}} \right] = 0 \\ &= \text{Tr} \left[\cancel{\frac{p^2}{2m^2}} e^{-\beta \mathcal{H}} \right] + \text{Tr} \left[-\beta \cancel{\frac{m\omega^2 q^2}{2}} e^{-\beta \mathcal{H}} \right] = 0\end{aligned}$$

so

$$\text{Tr} \left[\frac{p^2}{2m} e^{-\beta \mathcal{H}} \right] = \text{Tr} \left[\frac{m\omega^2 q^2}{2} e^{-\beta \mathcal{H}} \right]$$

$$\left\langle \frac{p^2}{2m} \right\rangle = \left\langle \frac{m\omega^2 q^2}{2} \right\rangle$$

5) Using the Hint, for high temp

$$\exp \left(-\beta \frac{p^2}{2m} - \beta \frac{m\omega^2 q^2}{2} \right) \approx e^{-\beta \frac{p^2}{2m}} \cdot e^{-\beta \frac{m\omega^2 q^2}{2}}$$

↓
Ideal gas term.

The matrix element

$$\langle q' | p | q \rangle = \langle q' | e^{-\beta \frac{p^2}{2m}} \cdot e^{-\beta \frac{m\omega^2 q^2}{2}} | q \rangle$$

↓

$$\int d\mathbf{p}' |p' \times p'| = 1$$

$$= \int d\mathbf{p}' \langle q' | e^{-\beta \frac{p^2}{2m}} |p' \times p'| e^{-\beta \frac{m\omega^2 q^2}{2}} |q\rangle$$

$$= \int dp' e^{-\beta \frac{p'^2}{2m}} e^{-\beta \frac{m\omega^2 q^2}{2}} \langle q' | p' X p' | q \rangle$$

$$\downarrow$$

$$\langle q' | p' \rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{-iq \cdot p'/\hbar}$$

$$= \frac{1}{2\pi\hbar} \int dp' \exp\left(i p' (q - q')/\hbar\right) \exp\left(-\beta p'^2/2m\right) \exp\left(-\beta \frac{q^2 m \omega^2}{2}\right)$$

One can complete the square making it a Gaussian integral

$$\langle q' | p' | q \rangle = \frac{1}{2\pi\hbar} e^{\beta q^2 m \omega^2 / 2} \sqrt{2\pi m k_B T} \exp\left(-\frac{m k_B T}{2\hbar^2} (q - q')^2\right)$$

and the normalization

$$Z = \sum_n \exp\left[-\beta \hbar \omega \left(n + \frac{1}{2}\right)\right]$$

$$= e^{-\beta \hbar \omega / 2} + e^{-3\beta \hbar \omega / 2} + \dots$$

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

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

at $T \gg 1$, $\beta \approx 0$, then

$$\lim_{\beta \rightarrow 0} Z = \frac{1 - \beta \hbar \omega / 2 + O(\beta^2)}{1 - (1 - \beta \hbar \omega + O(\beta^2))}$$

$$\approx \frac{1 - \beta \hbar \omega / 2}{1 - 1 + \beta \hbar \omega}$$

$$= \frac{1 - \beta \hbar \omega / 2}{\beta \hbar \omega} = \frac{1}{\beta \hbar \omega} - \frac{1}{2}$$

$$= \frac{k_B T}{\hbar \omega} - \frac{1}{2} \approx \frac{k_B T}{\hbar \omega} \quad \text{as } T \gg 1$$

so

$$\langle q' | \rho | q \rangle = \lim_{T \rightarrow \infty} \sqrt{\frac{m \omega^2}{2 k_B T}} \exp\left(-\frac{m \omega^2}{2 k_B T} q^2\right) \exp\left(-\frac{m k_B T}{2 \hbar^2} (q - q')^2\right)$$

at low temperatures, we keep only the first terms.

$$\begin{aligned} \langle q' | \rho | q \rangle &= \sum_{n, n'} \langle q' | n' X_{n'} | \rho | n X_n | q \rangle \\ &= \frac{\sum_n \exp(-\beta \hbar \omega (n + 1/2)) \cdot \langle q' | n X_n | q \rangle}{\sum_n \exp(-\beta \hbar \omega (n + 1/2))} \end{aligned}$$

we keep only the ground state |0>|0| and for the normalization

$$\langle q' | \rho | q \rangle = \frac{\exp(-\beta \hbar \omega / \kappa)}{e^{\beta \hbar \omega / \kappa} - e^{-\beta \hbar \omega / \kappa}} \langle q' | 0 \rangle \langle 0 | q \rangle$$

so from the part ②

$$\langle q' | \rho | q \rangle_{T=0} \approx \sqrt{\frac{m\omega}{\pi\hbar}} \exp\left[-\frac{m\omega}{2\hbar} (q'^2 + q'^2)\right] (1 - e^{-\beta \hbar \omega})$$

b) calculate $\langle q' | \rho | q \rangle$

we have that

$$\langle q' | \rho | q \rangle = \rho(q', q) = \frac{\langle q' | \exp(-\beta \hat{H}) | q \rangle}{Z}$$

$$= Z \sinh\left(\frac{\beta \hbar \omega}{2}\right) \sum_{n=0}^{\infty} \exp(-\beta \hbar \omega(n+1/2)) \langle q' | n \rangle \langle n | q \rangle$$

with

$$\langle n | q \rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{\text{H}_n(\xi)}{\sqrt{2^n n!}} \exp\left(-\frac{\xi^2}{2}\right)$$

$$\text{where } \xi = \sqrt{\frac{m\omega}{\hbar}}$$

so,

$$\langle q' | \rho | q \rangle = \frac{1}{Z} \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \exp\left(-\frac{1}{2} (\xi^2 + \xi'^2)\right)$$

$$\times \sum_{n=0}^{\infty} \frac{1}{2^n n!} e^{-\beta \hbar \omega (n + \frac{1}{2})} H_n(\xi) H_n(\xi')$$

using the Hermite polynomials integral representation.

$$= \frac{1}{z\pi} \left(\frac{m\omega}{\pi\hbar} \right)^{1/2} \exp \left(\frac{1}{2} (\xi^2 + \xi'^2) \right)$$

$$= \int_{-\infty}^{\infty} du \int_{-\infty}^{+\infty} dv \sum_{n=0}^{\infty} \frac{(-2uv)^n}{n!} e^{-\beta\hbar\omega(n+\frac{1}{2})} e^{-u^2+2i\omega u} e^{-v^2+2i\omega' v}$$

Let us consider the sum first

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

$$= \exp \left(-\frac{1}{2} \beta\hbar\omega \right) \sum_{n=0}^{\infty} \frac{1}{n!} (-2uv \exp(-\beta\hbar\omega))^n$$

$$= \exp \left(-\frac{1}{2} \beta\hbar\omega \right) \times \exp \left(-2uv e^{-\beta\hbar\omega} \right)$$

Hence, the integral becomes

$$\langle q| \hat{p}|q\rangle = \frac{1}{z\pi} \left(\frac{m\omega}{\pi\hbar} \right)^{1/2} \exp \left(\frac{1}{2} (\xi^2 + \xi'^2 - \beta\hbar\omega) \right)$$

$$\times \int_0^{\infty} du \int_0^{\infty} dv \exp \left(-u^2 + 2i\omega u - v^2 + 2i\omega' v - 2i\omega u - 2uv e^{-\beta\hbar\omega} \right)$$

This is a 2D gaussian on the complex plane.

then, we can rewrite the exponent as

$$-\omega^2 + 2i\omega u - \omega^2 + 2is'v - 2i\omega u - 2\omega u e^{-\beta\hbar\omega} = -\frac{1}{2} \overline{w}^T \cdot A \cdot \overline{w} + \frac{i}{2} \overline{b} \cdot \overline{w}$$

square term
imaginary

$$A = 2 \begin{pmatrix} 1 & e^{-\beta\hbar\omega} \\ e^{-\beta\hbar\omega} & 1 \end{pmatrix} \quad \overline{b} = 2 \begin{pmatrix} s \\ s' \end{pmatrix} \quad \overline{w} = \begin{pmatrix} u \\ v \end{pmatrix}$$

So in this way, the integral becomes

$$\int d^n \overline{w} \exp \left(-\frac{1}{2} \overline{w}^T \cdot A \cdot \overline{w} + \frac{i}{2} \overline{b} \cdot \overline{w} \right)$$

$$= \frac{(2\pi)^{n/2}}{[\det(A)]^{1/2}} \exp \left(-\frac{1}{2} \overline{b}^T \cdot A^{-1} \cdot \overline{b} \right)$$

so,

$$\langle a | \hat{\rho} | a \rangle = \frac{1}{Z} \left(\frac{m\omega}{\pi\hbar} \right)^{n/2} \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{(1 - e^{-2\beta\hbar\omega})^{n/2}}$$

$$\times \exp \left\{ \frac{1}{2} (s^2 + s'^2) - \left[(1 - e^{-2\beta\hbar\omega})^{-1} \times (s^2 + s'^2 - 2ss' e^{-\beta\hbar\omega}) \right] \right\}$$

$$= \frac{1}{Z} \left[\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)} \right]^{n/2} \exp \left(-\frac{1}{2} (s^2 + s'^2) \coth(\beta\hbar\omega) + \frac{ss'}{\sinh(\beta\hbar\omega)} \right)$$

and using

$$\tanh(\beta\hbar\omega/2) = \frac{\cosh(\beta\hbar\omega) - 1}{\sin(\beta\hbar\omega)} = \frac{\sinh(\beta\hbar\omega)}{1 + \cosh(\beta\hbar\omega)}$$

we finally get;

$$\langle q' | \hat{P} | q \rangle = \frac{1}{2} \left[\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)} \right]^{1/2}$$

$$\times \exp \left\{ -\frac{m\omega}{4\hbar} \left[(q+q')^2 \tanh\left(\frac{1}{2}\beta\hbar\omega\right) + (q-q')^2 \coth\left(\frac{1}{2}\beta\hbar\omega\right) \right] \right\}$$

6. Quantum Rotor

The Schrödinger eq.

$$-\frac{\hbar^2}{2I} \frac{d^2}{d\theta^2} \psi(\theta) = E \psi(\theta)$$

we get

$$\psi(\theta) = \frac{1}{\sqrt{2\pi}} \exp\left(\pm i \sqrt{\frac{2I}{\hbar^2} E} \theta\right)$$

As it has to be cyclic we get

$$\psi_n(\theta) = \frac{1}{\sqrt{2\pi}} \exp(i n \theta) \quad \text{with } E_n = \frac{\hbar^2 n^2}{2I}$$

and n an integer

2. The Density Matrix

$$\rho = \frac{1}{Z} \sum_n |n\rangle e^{-\beta \hbar^2 n^2 / 2I} \langle n|$$

so

$$\langle \theta' | \rho | \theta \rangle = \frac{1}{Z} \frac{\sum_n e^{in(\theta-\theta')} e^{-\beta \hbar^2 n^2 / 2I}}{\sum_n e^{-\beta \hbar^2 n^2 / 2I}}$$

in the low temperature limit ($\frac{\hbar^2 \beta}{2I} \gg 1$) the ground state dominates

$$\begin{aligned} \langle \theta' | \rho | \theta \rangle &= \frac{1}{Z} \frac{\left[1 + 2e^{-2\beta \hbar^2 / 2I} \cos(\theta - \theta') + \dots \right]}{\left[1 + 2e^{-2\beta \hbar^2 / 2I} + \dots \right]} \\ &= \frac{1}{Z} \left(1 + 2e^{-2\beta \hbar^2 / 2I} \cos(\theta - \theta') \right) \end{aligned}$$

$$\text{as } \sin^2 x = \frac{1 - \cos(2x)}{2} \approx \frac{1}{2} \left(1 + 4e^{-\beta \hbar^2 / 2I} \times \sin^2 \left(\frac{\theta - \theta'}{2} \right) \right)$$

in the high temperature limit, using

$$x \rightarrow n \sqrt{\frac{\hbar^2 \beta}{2I}}$$

$$\sum_n e^{-\beta \hbar^2 n^2 / 2I} \rightarrow \sqrt{\frac{2I}{\hbar^2 \beta}} \int dx e^{-x^2}$$

$$\text{and} \quad \sum_n e^{in(\theta-\theta')} e^{-\beta \hbar^2 n^2 / 2I} \rightarrow \sqrt{\frac{2I}{\hbar^2 \beta}} \int dx e^{-x^2} e^{i\sqrt{\frac{2I}{\hbar^2 \beta}} (\theta - \theta') x}$$

$$= \sqrt{\frac{2I}{\pi^2 p}} e^{-I(\theta-\theta')^2/2p\pi^2} \int dx e^{-x^2}$$

$$\langle \theta' | \rho | \theta \rangle = \frac{1}{2\pi} e^{-\frac{I(\theta-\theta')^2}{2p\pi^2}}$$