What is the trace definition in quantum mechanics?

$$\mathrm{Tr}(\hat{A}) = \sum_l \langle l | \hat{A} | l \rangle$$

and orthonormal

where $\{|l\rangle\}$ form a complete set (which one we choose is arbitrary!)

$$= \sum_l \langle \phi_l | \hat{A} | \phi_l \rangle$$

$\{\phi_l\}$ form complete, orthonormal set

(we will use $|l\rangle$, $|\phi_l\rangle$ interchangeably)

With this definition:

$$\mathrm{Tr}\left(e^{-\beta \hat{\mathcal{H}}}\right) = \sum_l \langle \phi_l | e^{-\beta \hat{\mathcal{H}}} | \phi_l \rangle$$

from previous page

$$= \sum_l \langle \phi_l | \left(\sum_m \exp(-\beta E_m) |\psi_m\rangle\langle\psi_m| \right) | \phi_l \rangle$$

$$= \sum_l \sum_m \exp(-\beta E_m) \langle \phi_l | \psi_m \rangle \langle \psi_m | \phi_l \rangle$$

According to the definition of the Tr operation, we can use any complete orthonormal basis to evaluate the trace. Let's use the eigenstates ψ_n of $\hat{\mathcal{H}}$, i.e., $\phi_n \to \psi_n$

$$\Rightarrow \mathrm{Tr}\left(e^{-\beta\hat{\mathcal{H}}}\right) = \sum_{\ell}\sum_{m} \exp(-\beta E_m) \underbrace{\langle\psi_\ell|\psi_m\rangle}_{\delta_{\ell m}} \underbrace{\langle\psi_m|\psi_\ell\rangle}_{\delta_{m\ell}}$$

$$= \sum_m \exp(-\beta E_m)$$

So: $Q_N(V,T) = \sum_m e^{-\beta E_m}$

where E_m are eigenenergies of $\hat{\mathcal{H}}$ (the sum goes over <u>all</u> eigenenergies)

* if we consider the harmonic oscillator, then the entire energy spectrum consists of discrete bound energies.
* if we consider the H-atom, then we have a bound state portion and an unbound scattering portion! The complete set contains b.st. wave fcts. and sc. st. wave fcts.!

$$\hat{\rho}_{can} = \frac{e^{-\beta\hat{\mathcal{H}}}}{\mathrm{Tr}(e^{-\beta\hat{\mathcal{H}}})}$$

$$= \frac{\sum_m e^{-\beta E_m} |\psi_m\rangle\langle\psi_m|}{\sum_{m'} e^{-\beta E_{m'}}}$$

$$= \sum_m \underbrace{\frac{e^{-\beta E_m}}{\sum_{m'} e^{-\beta E_{m'}}}}_{p_m} |\psi_m\rangle\langle\psi_m|$$

$$\left\{ \boxed{\sum_m p_m = 1} \right\}$$

normalization!

So: $\langle \hat{A} \rangle = Tr(\hat{\rho}\,\hat{A})$

$$= Tr\left(\frac{e^{-\beta\hat{\mathcal{H}}}}{Tr(e^{-\beta\hat{\mathcal{H}}})}\,\hat{A} \right)$$

$$= \frac{Tr(e^{-\beta\hat{\mathcal{H}}}\,\hat{A})}{Tr(e^{-\beta\hat{\mathcal{H}}})}$$

$$= \frac{\sum_{\ell} \langle \phi_\ell | e^{-\beta\hat{\mathcal{H}}}\hat{A} | \phi_\ell \rangle}{\sum_m e^{-\beta E_m}}$$

Still need to know what to do with $e^{-\beta\hat{\mathcal{H}}}\hat{A}$...

Insert another complete set:

$$\langle \hat{A} \rangle = \frac{\sum_{\ell} \langle \phi_\ell | e^{-\beta\hat{\mathcal{H}}} \left(\sum_{\ell'} |\phi_{\ell'}\rangle\langle\phi_{\ell'}| \right) \hat{A} | \phi_\ell \rangle}{\sum_m e^{-\beta E_m}}$$

$$= \frac{\sum_{\ell}\sum_{\ell'} \langle \phi_\ell | e^{-\beta\hat{\mathcal{H}}} | \phi_{\ell'} \rangle \langle \phi_{\ell'} | \hat{A} | \phi_\ell \rangle}{\sum_m e^{-\beta E_m}}$$

Now: use the energy eigenstates: $\phi_\ell, \phi_{\ell'} \to \psi_\ell, \psi_{\ell'}$

$$\Rightarrow \langle \hat{A} \rangle = \frac{\sum_{l} e^{-\beta E_l} \langle \psi_l | \hat{A} | \psi_l \rangle}{\sum_{m} e^{-\beta E_m}}$$

$$= \sum_{l} \frac{e^{-\beta E_l}}{\sum_{m} e^{-\beta E_m}} \langle \psi_l | \hat{A} | \psi_l \rangle$$

think of this as a weight factor:

probability to occupy the l'th energy eigenstate

Single-particle example: One-dimensional harmonic oscillator

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m \omega^2 \hat{x}^2$$

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

H_n: Hermite polynomial

eigenstates $\psi_n(x) = \underbrace{\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}}_{\left(\frac{1}{\sqrt{\pi}\, a_{ho}}\right)^{1/2}} \frac{H_n\left(\frac{x}{a_{ho}}\right)}{\left(2^n\, n!\right)^{1/2}} e^{-\frac{1}{2}\left(\frac{x}{a_{ho}}\right)^2}$

where $a_{ho} = \left(\frac{\hbar}{m\omega}\right)^{1/2}$ or HO length characteristic

E_n and $\psi_n(x)$ are being derived in quantum

→ here, we assume them as known / given.

Task 1: Calculate $\hat{\rho}$ in the position representation.

$$\hat{\rho} = \frac{e^{-\beta \hat{\mathcal{H}}}}{Tr(e^{-\beta \hat{\mathcal{H}}})}$$

Start with numerator.

$e^{-\beta \hat{\mathcal{H}}}$ in position representation : $\langle x | e^{-\beta \hat{\mathcal{H}}} | x' \rangle$

We know: $e^{-\beta \hat{\mathcal{H}}} = \sum_m e^{-\beta E_m} |\psi_m\rangle\langle\psi_m|$

$$\Rightarrow \langle x | e^{-\beta \hat{\mathcal{H}}} | x' \rangle = \sum_m e^{-\beta E_m} \psi_m(x)\, \psi_m^*(x')$$

The next step is to plug in the expressions for the eigenstates ⇝ this gives us an infinite sum over Hermite polynomials.

It turns out that the sum reduces to a compact expression.

Without proof:

$$\langle x | e^{-\beta \hat{\mathcal{H}}} | x' \rangle = \frac{1}{(2\pi a_{ho}^2 \sinh(\beta\hbar\omega))^{1/2}} \times$$

$$\exp\left[-\left(\frac{x+x'}{2a_{ho}}\right)^2 \tanh\left(\frac{\beta\hbar\omega}{2}\right) - \left(\frac{x-x'}{2a_{ho}}\right)^2 \coth\left(\frac{\beta\hbar\omega}{2}\right)\right]$$

We can use this result to calculate $\mathrm{Tr}(e^{-\beta \hat{\mathcal{H}}})$:

$$\mathrm{Tr}\left(e^{-\beta\hat{\mathcal{H}}}\right) = \int_{-\infty}^{\infty} \langle x | e^{-\beta \hat{\mathcal{H}}} | x \rangle \, dx$$

see next page

$$= \frac{1}{(2\pi a_{ho}^2 \sinh(\beta\hbar\omega))^{1/2}}$$

$$\times \int_{-\infty}^{\infty} e^{-\tanh\left(\frac{\beta\hbar\omega}{2}\right)\left(\frac{x}{a_{ho}}\right)^2} dx$$

$$= \frac{1}{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)}$$

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

Why is $\mathrm{Tr}\left(e^{-\beta\hat{\mathcal{H}}}\right)$ equal to $\int_{-\infty}^{\infty} \langle x | e^{-\beta\hat{\mathcal{H}}} | x \rangle \, dx$?

A few "bra-ket" rules/reminders:

$$\langle x | y \rangle = \delta(x-y)$$

$$\int |x\rangle\langle x| \, dx = \mathbb{1}$$

$$\Rightarrow |y\rangle = \int |x\rangle \underbrace{\langle x | y \rangle}_{\delta(x-y)} dx = \int |x\rangle \, \delta(x-y) \, dx$$

$$\text{So: } \mathrm{Tr}\left(e^{-\beta\hat{\mathcal{H}}}\right) = \sum_m \langle \psi_m | e^{-\beta\hat{\mathcal{H}}} | \psi_m \rangle$$

inserting two identities $\int |x'\rangle\langle x'| \, dx'$ $\quad$ $\int |x\rangle\langle x| \, dx$

rearranging sums and integrals:
using $\langle x | \psi_m \rangle = \psi_m(x)$
$\langle \psi_m | x' \rangle = \psi_m^*(x')$

$$= \sum_m \iint \psi_m^*(x') \langle x' | e^{-\beta\hat{\mathcal{H}}} | x \rangle \, \psi_m(x) \, dx' dx$$

$$= \iint \underbrace{\sum_m \psi_m^*(x') \psi_m(x)}_{\langle x' | \underbrace{\left(\sum_m |\psi_m\rangle\langle\psi_m|\right)}_{\mathbb{1}} | x \rangle = \delta(x-x')} \langle x' | e^{-\beta\hat{\mathcal{H}}} | x' \rangle \, dx' dx$$

$$= \iint \langle x' | e^{-\beta\hat{\mathcal{H}}} | x \rangle \, \delta(x-x') \, dx' dx$$

$$= \int \langle x | e^{-\beta \hat{H}} | x \rangle \, dx$$

the integration over x' makes the δ-fct. disappear

Alternatively:

$$\mathrm{Tr}\left(e^{-\beta\hat{\mathcal{H}}}\right) = \sum_m e^{-\beta E_m}$$

$$= \sum_m e^{-\beta(m+\frac{1}{2})\hbar\omega}$$

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

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

$$x = e^{-\beta\hbar\omega}$$

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

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

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

in agreement w/ the result on page 164!

So: $\langle x|\hat{\rho}|x'\rangle = \ \ldots$

collect terms from previous pages.

So, we're done with task 1.

Task 2: Look at $\langle x|\hat{\rho}|x\rangle$ in the limits

$\hbar\omega \ll k_B T$ $(\beta\hbar\omega \ll 1) \rightarrow$ classical (high T)

&

$\hbar\omega \gg k_B T$ $(\beta\hbar\omega \gg 1) \rightarrow$ quantum (low T)

$$\langle x|\hat{\rho}|x\rangle = \left(\frac{\tanh(\frac{1}{2}\beta\hbar\omega)}{\pi a_{ho}^2}\right)^{1/2} \exp\left[-\frac{x^2}{a_{ho}^2}\tanh\left(\frac{\beta\hbar\omega}{2}\right)\right]$$

$$\tanh x \overset{\text{small } x}{\approx} x - \frac{1}{3}x^3 + \ldots$$

So: For $\beta\hbar\omega \ll 1$:

$$\langle x|\hat{\rho}|x\rangle \approx \left(\frac{\beta\hbar\omega}{2\pi a_{ho}^2}\right)^{1/2} \exp\left(-\frac{\beta\hbar\omega x^2}{2a_{ho}^2}\right)$$

$$= \left(\frac{m\omega^2}{2\pi kT}\right)^{1/2} \exp\left(-\frac{m\omega^2 x^2}{2kT}\right)$$

For $\beta\hbar\omega \gg 1$:

$$\langle x|\hat{\rho}|x\rangle \approx \frac{1}{(\pi a_{ho}^2)^{1/2}} \exp\left(-\frac{x^2}{a_{ho}^2}\right)$$

purely quantum mechanical density

$\langle x|\hat{\rho}|x\rangle$ gives ~~us~~ the probability density!

Task 3: Calculate $\langle\hat{\mathcal{H}}\rangle$.

$$\langle\hat{\mathcal{H}}\rangle = \mathrm{Tr}(\hat{\rho}\,\hat{\mathcal{H}}) = \mathrm{Tr}\left(\frac{e^{-\beta\hat{\mathcal{H}}}\hat{\mathcal{H}}}{\mathrm{Tr}\,e^{-\beta\hat{\mathcal{H}}}}\right)$$

$\hat{\mathcal{H}}e^{-\beta\hat{\mathcal{H}}} = -\frac{\partial}{\partial\beta}e^{-\beta\hat{\mathcal{H}}}$

$\frac{\frac{\partial}{\partial\beta}f}{f} = \frac{\partial}{\partial\beta}\log f$

$$= -\frac{\partial}{\partial\beta}\log\left(\mathrm{Tr}\left(e^{-\beta\hat{\mathcal{H}}}\right)\right)$$

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

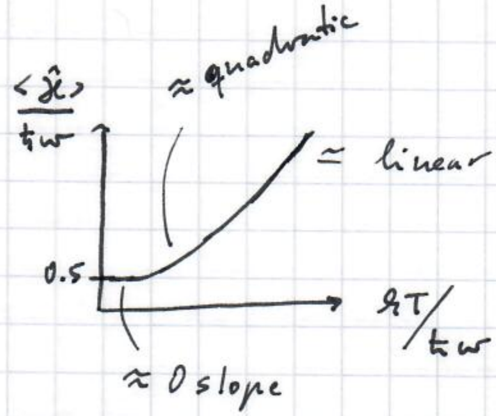
$$= -\frac{\partial}{\partial\beta}\left[-\frac{1}{2}\beta\hbar\omega - \log\left(1-e^{-\beta\hbar\omega}\right)\right]$$

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

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

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

$$\langle \hat{\mathcal{H}} \rangle = \frac{1}{2}\hbar\omega \coth\left(\frac{1}{2}\beta\hbar\omega\right)$$



Alternatively:

$$\langle \hat{\mathcal{H}} \rangle = \sum_{\ell} \overbrace{\frac{e^{-\beta E_\ell}}{\sum_m e^{-\beta E_m}}}^{\text{"weight factor"}} \langle \psi_\ell | \hat{A} | \psi_\ell \rangle$$

$$= \frac{1 - e^{-\beta\hbar\omega}}{e^{-\frac{1}{2}\beta\hbar\omega}} \underbrace{\sum_\ell e^{-\beta E_\ell} \left(\ell + \frac{1}{2}\right)\hbar\omega}_{-\frac{\partial}{\partial\beta}\sum_\ell e^{-\beta E_\ell}}$$

$$\Rightarrow \langle \mathcal{H} \rangle = -\frac{\partial}{\partial\beta} \log \sum_\ell e^{-\beta E_\ell}$$

as before