Density Operator in Statistical Mechanics
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It may be useful to rewrite ensemble theory (micro canonical, canonical, and grand canonical ensemble) in a language that is more natural to a quantum-mechanical treatment, namely the language of the operators and the wavefunctions. As far as the statistics are concerned, this rewriting of the theory may not seem to introduce any new physical ideas as such; nonetheless, it provides us with a tool that is highly suited for studying typical quantum systems. And once we set out to study these systems in detail, we encounter a stream of new, and altogether different, physical concepts

1. Fundamental

We introduce the density operator $\hat{\rho}$. In thermal equilibrium, the expectation value of a macroscopic observable $\hat{B}$,

$$\langle B \rangle = Tr[\hat{\rho}(t)\hat{B}],$$

has to be time independent. This is only possible if $\hat{\rho}(t)$ is time independent:

$$i\hbar \frac{\partial}{\partial t}\hat{\rho} = [\hat{H}, \hat{\rho}], \qquad \text{(Liouville theorem)}$$

This equation is similar to the Heisenberg's equation of motion for the Hermitian operator, except for the sign. Since $\frac{\partial}{\partial t}\hat{\rho} = 0$ (in thermal equilibrium), $[\hat{H}, \hat{\rho}] = 0$. This equation implies that $\hat{\rho}$ is a conserved quantity and is a function of the Hamiltonian $\hat{H}$.

$$\hat{\rho} = \hat{\rho}(\hat{H}).$$

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2. Density operator for the canonical ensemble

The density operator for the canonical ensemble is given by

$$\hat{\rho}_C = \frac{1}{Z_C(\beta)}\exp(-\beta\hat{H}) = \frac{\exp(-\beta\hat{H})}{Tr[\exp(-\beta\hat{H})]},$$

where $\beta = \dfrac{1}{k_B T}$. $\hat{H}$ is the Hamiltonian of the system. $Z_C(\beta)$ is the partition function and is defined by

$$Z_C(\beta) = Tr[\exp(-\beta\hat{H})]$$

We use the basis of energy eigenstate $\left|\phi_n\right\rangle$, where

$$\hat{H}\left|\phi_n\right\rangle = E_n\left|\phi_n\right\rangle$$

Then we get

$$\begin{aligned}\exp(-\beta\hat{H}) &= \sum_n e^{-\beta\hat{H}}\left|\phi_n\right\rangle\left\langle\phi_n\right| \\ &= \sum_n e^{-\beta E_n}\left|\phi_n\right\rangle\left\langle\phi_n\right|\end{aligned}$$

where we use the closure relation. Then the density operator is

$$\hat{\rho}_C = \frac{1}{Z_C(\beta)}\sum_n e^{-\beta E_n}\left|\phi_n\right\rangle\left\langle\phi_n\right| = \sum_n P_n\left|\phi_n\right\rangle\left\langle\phi_n\right|$$

where P_n is a probability and is given by

$$P_n = \frac{1}{Z_C(\beta)}e^{-\beta E_n}$$

The partition function is

$$\begin{aligned}Z_C(\beta) &= Tr[e^{-\beta\hat{H}}] \\ &= \sum_n \left\langle\phi_n\right|e^{-\beta\hat{H}}\left|\phi_n\right\rangle \\ &= \sum_n e^{-\beta E_n}\end{aligned}$$

The average value of operator $\hat{B}$

$$\langle B\rangle_C = Tr(\hat{B}\hat{\rho}_C) = \frac{1}{Tr(e^{-\beta\hat{H}})}Tr(\hat{B}e^{-\beta\hat{H}})$$

The average energy is

$$\langle E\rangle_C = Tr(\hat{H}\hat{\rho}_C) = -\frac{\partial}{\partial\beta}\ln Z_C(\beta)$$

which can be rewritten as

$$\langle E\rangle_C = \frac{1}{Z_C(\beta)}\sum_n \langle\phi_n|\hat{H}e^{-\beta\hat{H}}|\phi_n\rangle = \frac{1}{Z_C(\beta)}\sum_n E_n e^{-\beta E_n} .$$

The energy fluctuation:

$$\begin{aligned}(\Delta E)^2 &= \langle E^2\rangle - \langle E\rangle^2 \\ &= Tr[\hat{H}^2\hat{\rho}] - \left(Tr[\hat{H}\hat{\rho}]\right)^2\end{aligned}$$

Representation of the density operator under the basis of $|\boldsymbol{r}\rangle$

$$\begin{aligned}\langle\boldsymbol{r}|\hat{\rho}|\boldsymbol{r}'\rangle &= \frac{1}{Z_C(\beta)}\int d\boldsymbol{p}\int d\boldsymbol{p}'\langle\boldsymbol{r}|\boldsymbol{p}\rangle\langle\boldsymbol{p}|\exp[-\beta H|\boldsymbol{p}'\rangle\langle\boldsymbol{p}'|\boldsymbol{r}'\rangle \\ &= \frac{1}{Z_C(\beta)}\frac{1}{(2\pi\hbar)^3}\int d\boldsymbol{p}\int d\boldsymbol{p}'\exp(\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r})\langle\boldsymbol{p}|\exp[-\beta H|\boldsymbol{p}'\rangle\langle\boldsymbol{p}'|\boldsymbol{r}'\rangle \\ &= \frac{1}{Z_C(\beta)}\frac{1}{(2\pi\hbar)^3}\int d\boldsymbol{p}\int d\boldsymbol{p}'\exp(\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r})\exp(-\frac{\beta\,\boldsymbol{p}^2}{2m})\langle\boldsymbol{p}|\boldsymbol{p}'\rangle\exp(-\frac{i}{\hbar}\boldsymbol{p}'\cdot\boldsymbol{r}') \\ &= \frac{1}{Z_C(\beta)}\frac{1}{(2\pi\hbar)^3}\int d\boldsymbol{p}\int d\boldsymbol{p}'\exp(\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r})\exp(-\frac{i}{\hbar}\boldsymbol{p}'\cdot\boldsymbol{r}')\exp(-\frac{\beta\,\boldsymbol{p}^2}{2m})\delta(\boldsymbol{p}-\boldsymbol{p}') \\ &= \frac{1}{Z_C(\beta)}\frac{1}{(2\pi\hbar)^3}\int d\boldsymbol{p}\exp[\frac{i}{\hbar}\boldsymbol{p}\cdot(\boldsymbol{r}-\boldsymbol{r}') - \frac{\beta\,\boldsymbol{p}^2}{2m}]\end{aligned}$$

where we use the transformation function

$$\langle\boldsymbol{r}|\boldsymbol{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}}\exp(\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r})$$

$$\langle \boldsymbol{r}|\boldsymbol{p}\rangle^* = \frac{1}{(2\pi\hbar)^{3/2}}\exp(-\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}) = \langle \boldsymbol{p}|\boldsymbol{r}\rangle$$

$$\hat{H} = \frac{1}{2m}\hat{\boldsymbol{p}}^2 \qquad \text{(Hamiltonian for the free particle).}$$

$$\langle \boldsymbol{p}|\boldsymbol{p}'\rangle = \delta(\boldsymbol{p}-\boldsymbol{p}')$$

Here we use the spherical co-ordinate (***p*** co-ordinate) for the integral

$$\begin{aligned}
I &= \int d\boldsymbol{p}\exp[\frac{i}{\hbar}\boldsymbol{p}\cdot(\boldsymbol{r}-\boldsymbol{r}') - \frac{\beta\,\boldsymbol{p}^2}{2m}] \\
&= 2\pi\int_0^\infty p^2\exp(-\frac{\beta\,p^2}{2m})dp\int_0^\pi \exp[\frac{i}{\hbar}p(|\boldsymbol{r}-\boldsymbol{r}'|)\cos\theta] \\
&= \frac{4\pi\hbar}{|\boldsymbol{r}-\boldsymbol{r}'|}\int_0^\infty dp\; p\exp(-\frac{\beta\,p^2}{2m})\sin(\frac{|\boldsymbol{r}-\boldsymbol{r}'|}{\hbar}p) \\
&= \left(\frac{2\pi m}{\beta}\right)^{3/2}\exp[-\frac{m|\boldsymbol{r}-\boldsymbol{r}'|}{2\beta\hbar^2}]
\end{aligned}$$

or

$$\begin{aligned}
\langle \boldsymbol{r}|\hat{\rho}|\boldsymbol{r}'\rangle &= \frac{1}{Z(\beta)}\frac{1}{(2\pi\hbar)^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\exp[-\frac{m|\boldsymbol{r}-\boldsymbol{r}'|}{2\beta\hbar^2}] \\
&= \frac{1}{Z(\beta)}\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}\exp[-\frac{m|\boldsymbol{r}-\boldsymbol{r}'|}{2\beta\hbar^2}]
\end{aligned}$$

Note that

$$
\begin{aligned}
Z(\beta) &= Tr[\exp(-\beta H)] \\
&= \sum_{\boldsymbol{p}} \exp(-\frac{\beta \boldsymbol{p}^2}{2m}) \\
&= \frac{V}{(2\pi\hbar)^3} \int d\boldsymbol{p} \exp[-\frac{\beta \boldsymbol{p}^2}{2m}] \\
&= \frac{V}{(2\pi\hbar)^3} \int_0^\infty 4\pi p^2 dp \exp[-\frac{\beta p^2}{2m}] \\
&= \frac{V}{(2\pi\hbar)^3} \left(\frac{2\pi m}{\beta}\right)^{3/2} \\
&= \frac{V}{\lambda_T{}^3}
\end{aligned}
$$

where λ_T is the thermal length,

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2\beta}{m}}$$

Then we have

$$\langle \boldsymbol{r}|\hat{\rho}|\boldsymbol{r}'\rangle = \frac{1}{V}\exp[-\frac{m|\boldsymbol{r}-\boldsymbol{r}'|}{2\beta\hbar^2}]$$

The diagonal element:

$$\langle \boldsymbol{r}|\hat{\rho}|\boldsymbol{r}\rangle = \frac{1}{V}$$

are just the probabilities for finding a particle at $\boldsymbol{r}$. The iff-diagonal elements have no vlassical analogy.

3. Density operator for the Grand canonical ensemble

The density operator for the grand canonical ensemble is given by

$$\hat{\rho}_G = \frac{1}{Z_G(\beta,\mu)} e^{-\beta(\hat{H}-\mu\hat{N})}$$

where the partition function is given by

$$Z_G(\beta,\mu) = Tr[e^{-\beta(\hat{H}-\mu\hat{N})}]$$

Here, we use the energy-particle representation. Since $[\hat{H},\hat{N}] = 0$, we have simultaneous eigenkets such that

$$\hat{H}\left|E_i(N)\right\rangle = E_i(N)\left|E_i(N)\right\rangle,$$

$$\hat{N}\left|E_i(N)\right\rangle = N\left|E_i(N)\right\rangle$$

Then we get the partition function as

$$\begin{aligned}
Z_G(\beta,\mu) &= Tr[e^{-\beta(\hat{H}-\mu\hat{N})}] \\
&= \sum_{N=0}^{\infty}\sum_{i[N]}\left\langle E_i(N)\right|e^{-\beta(\hat{H}-\mu\hat{N})}\left|E_i(N)\right\rangle \\
&= \sum_{N=0}^{\infty}\sum_{i[N]} e^{-\beta(E_i(N)-\mu N)} \\
&= \sum_{N=0}^{\infty} e^{\beta\mu N}\sum_{i[N]} e^{-\beta E_i(N)} \\
&= \sum_{N=0}^{\infty} \lambda^{\mathrm{N}}\sum_{i[N]} e^{-\beta E_i(N)} \\
&= \sum_{N=0}^{\infty} \lambda^{\mathrm{N}} Z_{CN}
\end{aligned}$$

or

$$Z_G(\beta,\mu) = \sum_{N=0}^{\infty}\lambda^N Z_{CN}(\beta)$$

with

$$\lambda = e^{\beta\mu}$$

The average value of operator $\hat{B}$

$$\langle B\rangle_G = Tr(\hat{B}\hat{\rho}_G) = \frac{1}{Z_G(\beta,\mu)} Tr[\hat{B}e^{-\beta(\hat{H}-\mu\hat{N})}]$$

In the energy-particle representation, we get

$$\begin{aligned}
\langle B\rangle_G &= \frac{1}{Z_G(\beta,\mu)} \sum_{N=0}^{\infty} \sum_{i[N]} \langle E_i(N)|\hat{B}e^{-\beta(\hat{H}-\mu\hat{N})}|E_i(N)\rangle \\
&= \frac{1}{Z_G(\beta,\mu)} \sum_{N=0}^{\infty} \sum_{i[N],j[N]} \langle E_i(N)|\hat{B}|E_j(N)\rangle\langle E_j(N)|e^{-\beta(\hat{H}-\mu\hat{N})}|E_i(N)\rangle \\
&= \frac{1}{Z_G(\beta,\mu)} \sum_{N=0}^{\infty} \lambda^{\mathrm{N}} \sum_{i[N],j[N]} \langle E_i(N)|\hat{B}|E_j(N)\rangle e^{-\beta E_i(N)}\delta_{i,j} \\
&= \frac{1}{Z_G(\beta,\mu)} \sum_{N=0}^{\infty} \lambda^{\mathrm{N}} \sum_{i[N]} \langle E_i(N)|\hat{B}|E_i(N)\rangle e^{-\beta E_i(N)}
\end{aligned}$$

If $\langle B\rangle_{CN}$ is the average value of $\hat{B}$ in the canonical ensemble,

$$\sum_{i[N]} \langle E_i(N)|\hat{B}|E_i(N)\rangle e^{-\beta E_i(N)} = Z_{CN}\langle B\rangle_{CN}.$$

then we have

$$\langle B\rangle_G = \frac{1}{Z_G(\beta,\mu)} \sum_{N=0}^{\infty} \lambda^{\mathrm{N}} Z_{NC}(\beta)\langle B\rangle_{CN}$$

The average number:

$$\frac{\partial}{\partial\mu} Z_G(\beta,\mu) = Tr[\beta\hat{N}e^{-\beta(\hat{H}-\mu\hat{N})}] = \beta Tr[\hat{N}e^{-\beta(\hat{H}-\mu\hat{N})}] = \beta Z_G(\beta,\mu)\langle N\rangle_G$$

or

$$\langle N\rangle_G = k_B T \frac{\partial}{\partial\mu}\ln Z_G(\beta,\mu) = -\frac{\partial}{\partial\mu}\Phi_G$$

where Φ_G is the grand potential and is defined by

$$\Phi_G = -k_B T \ln Z_G(\beta,\mu)$$

The number fluctuation is evaluated as follows.

$$\frac{\partial^2}{\partial\mu^2} Z_G(\beta,\mu) = Tr[\beta^2 \hat{N}^2 e^{-\beta(\hat{H}-\mu\hat{N})}] = \beta^2 Tr[\hat{N}^2 e^{-\beta(\hat{H}-\mu\hat{N})}] = \beta^2 Z_G(\beta,\mu)\left\langle \hat{N}^2 \right\rangle_G$$

leading to

$$\left\langle \hat{N}^2 \right\rangle_G = (k_B T)^2 \frac{1}{Z_G(\beta,\mu)} \frac{\partial^2}{\partial\mu^2} Z_G(\beta,\mu)$$

The number fluctuation:

$$\begin{aligned}
(\Delta N)_G{}^2 &= \left\langle \hat{N}^2 \right\rangle_G - \left\langle \hat{N} \right\rangle_G \\
&= (k_B T)^2 \{ \frac{1}{Z_G(\beta,\mu)} \frac{\partial^2 Z_G(\beta,\mu)}{\partial\mu^2} - \frac{1}{[Z_G(\beta,\mu)]^2} [\frac{\partial Z_G(\beta,\mu)}{\partial\mu}]^2 \} \\
&= (k_B T)^2 \{ \frac{Z_G(\beta,\mu)\frac{\partial^2 Z_G(\beta,\mu)}{\partial\mu^2} - [\frac{\partial Z_G(\beta,\mu)}{\partial\mu}]^2}{[Z_G(\beta,\mu)]^2} \} \\
&= (k_B T)^2 \frac{\partial}{\partial\mu}\frac{\partial}{\partial\mu} \ln Z_G(\beta,\mu) \\
&= k_B T \frac{\partial}{\partial\mu} \left\langle N \right\rangle_G
\end{aligned}$$

or

$$(\Delta N)_G{}^2 = k_B T \frac{\partial}{\partial\mu} \left\langle N \right\rangle_G$$

4. Entropy and density operator for the canonical ensemble

We show that the entropy in the canonical ensemble, is expressed in terms of the density operator $\hat{\rho}_C$ as

$$S = -k_B Tr[\hat{\rho}_C \ln \hat{\rho}_C].$$

((**Proof**))

We note that

$$Z_C(\beta) = Tr[e^{-\beta\hat{H}}] = e^{-\beta F}$$

where F is the Helmholtz free energy and is given by

$$F = -k_B T \ln Z_C(\beta) = -\frac{1}{\beta}\ln Z_C(\beta)$$

Thus we can write the density operator as

$$\hat{\rho}_C = e^{\beta F} e^{-\beta\hat{H}}$$

Then we have

$$\ln\hat{\rho}_C = \beta(F - \hat{H})$$

$$-k_B\langle\ln\hat{\rho}_C\rangle = -k_B\beta(F - \langle H\rangle) = -\frac{1}{T}(F - E) = -\frac{1}{T}(-ST) = S$$

or

$$S = -k_B\langle\ln\hat{\rho}_C\rangle = -k_B Tr[\hat{\rho}_C \ln\hat{\rho}_C]$$

5. Entropy and density operator for the canonical ensemble

We show that the entropy in the grand canonical ensemble, is expressed in terms of the density operator $\hat{\rho}_G$ as

$$S = -k_B Tr[\hat{\rho}_G \ln\hat{\rho}_G]$$

((**Proof**))

We note that

$$Z_G(\beta) = Tr[e^{-\beta(\hat{H}-\mu\hat{N})}] = e^{-\beta J}$$

where Φ_G is the grand potential and is given by

$$\Phi_G = -k_B T \ln Z_G(\beta) = -\frac{1}{\beta} \ln Z_G(\beta)$$

Thus we can write the density operator as

$$\hat{\rho}_G = e^{\beta \Phi_G} e^{-\beta(\hat{H} - \mu \hat{N})}$$

Then we have

$$\ln \hat{\rho}_G = \beta(\Phi_G - \hat{H} + \mu \hat{N})$$

$$\begin{aligned} -k_B \langle \ln \hat{\rho}_G \rangle &= -k_B \beta < \Phi_G - \hat{H} + \mu \hat{N} > \\ &= -\frac{1}{T}(\Phi_G - \langle H \rangle + \mu \langle N \rangle) \\ &= \frac{1}{T}(F - \langle H \rangle) \\ &= -\frac{1}{T}(-ST) = S \end{aligned}$$

or

$$S = -k_B \langle \ln \hat{\rho}_G \rangle = -k_B Tr[\hat{\rho}_G \ln \hat{\rho}_G]$$

So the entropy is independent of the representation of $\hat{\rho}$. The entropy is a genuine mathematical invariant of a quantum system.

In the actual evaluation of thermodynamic average, the similarity of

$$\hat{\rho}_C = \frac{1}{Z_C} \exp(-\beta \hat{H}),$$

to the expression for the time evolution operator

$$\hat{T} = \exp(-\frac{i}{\hbar} \hat{H} t).$$

has often been used. Thus, by putting

$$\beta = \frac{it}{\hbar}.$$

One can treat the inverse temperature as an imaginary time variable.

6. Density operator for the microcanonical ensemble

Since the density operator for the microcanonical ensemble is characterized by a stationary distribution, we have

$$[\hat{\rho}_{MC}, \hat{H}] = 0$$

leading to the simultaneous eigenkets of $\hat{H}$ and $\hat{\rho}_{MC}$. Here we use the energy eigenstates to get the expression of $\hat{\rho}_{MC}$.

$$\hat{H}|E_n\rangle = E_n|E_n\rangle$$

with

$$\langle E_n | E_m\rangle = \delta_{n,m}$$

For an isolated system, the principle of a priori probability states that all possible states of the system have the same probability. Therefore we can write

$$\hat{\rho}_{MC} = \sum_m P_m |E_m\rangle\langle E_m|$$

with

$$P_m = \frac{1}{\Gamma(E)}\begin{cases} 1 & \text{for } E < E_m < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

where the constant P_m can be obtained from the normalization condition

$$Tr[\hat{\rho}_{MC}] = 1$$

We define

$$\begin{aligned}\Gamma(E) &= \Omega(E,N,V)\delta E \\ &= W(E,N,V,\delta E) \\ &= Tr[\sum_{m}^{E<E_m<E+\delta E} |E_m\rangle\langle E_m|] = \sum_{m}^{E<E_m<E+\delta E} 1\end{aligned}$$

$$Tr[\hat{\rho}_{MC}] = \frac{1}{\Gamma(E)} Tr[\sum_{m}^{E<E_m<E+\delta E} |E_m\rangle\langle E_m|] = 1$$

Then we have

$$\hat{\rho}_{MC} = \frac{1}{\Gamma(E)} \sum_{m}^{E<E_m<E+\delta E} |E_m\rangle\langle E_m|$$

The expectation value of the operator $\hat{B}$ in the microcanonical ensemble is

$$\langle B\rangle = \frac{1}{\Gamma(E)} Tr[\sum_{m}^{E<E_m<E+\delta E} \hat{B}|E_m\rangle\langle E_m|]$$

The average energy:

$$\begin{aligned}\langle E\rangle &= \frac{1}{\Gamma(E)} Tr[\sum_{m}^{E<E_m<E+\delta E} \hat{H}|E_m\rangle\langle E_m|] \\ &= \frac{1}{\Gamma(E)} \sum_{m}^{E<E_m<E+\delta E} E_m \\ &\approx E\end{aligned}$$

The entropy S is given by

$$S = k_B \ln \Gamma(E)$$

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7. Probability distribution function for the Microcanonical ensemble (classical mechanics

We define the State density function in the phase space as

$$f({}^N\Gamma) = f(q,p) = f(q_1, q_2, ..., q_{3N}, p_1, p_2, ..., p_{3N})$$

$$f({}^N\Gamma) = \begin{cases} 1 & \text{for } E \text{ to } E+\delta E \\ 0 & \text{otherwise} \end{cases}$$

Using the property of the Dirac delta function, $f({}^N\Gamma)$ can be rewritten as

$$f({}^N\Gamma) = \delta(E - H_N(q,p))\delta E$$

where $H_N(q,p)$ is the N-particle Hamiltonian. The total number of states for E to $E+\delta E$

$$\Gamma(E) = W(N,E,V,\delta E) = \Omega(N,E,V)\delta E = \int d^N\Gamma f({}^N\Gamma)$$

$\Omega(N,E,V)$ is the density of states (units of erg^{-1}). We define the probability distribution function

$$\rho_{MC}({}^N\Gamma) = \frac{f({}^N\Gamma)}{W(N,E,V,\delta E)} = \frac{\delta(E - H_N(q,p))\delta E}{\Omega(N,E,V)\delta E} =$$

where

$$\int d^N\Gamma \rho({}^N\Gamma) = 1$$

The average value of the physical quantity

$$\langle B \rangle_{MC} = \int d^N\Gamma B({}^N\Gamma)\rho_{MC}({}^N\Gamma)$$

The average energy:

$$\langle E \rangle_{MC} = \int d^N\Gamma H_N(q,p)\rho_{MC}({}^N\Gamma) = E$$

$$\langle N \rangle_{MC} = \int d^N\Gamma N\rho_{MC}({}^N\Gamma) = N$$

The entropy $S(N,E,V)$ is defined by

$$S(N,E,V) = k_B \ln W(N,E,V,\delta E)$$

8. Exmaple-1

R. Kubo, Statistical Mechanics: An Advanced Course with Problems and Solutions (North-Holland, 1965).
Chapter 2, Problem 2-29 (p.138)

The Hamiltonian of an electron in magnetic field $\boldsymbol{B}$ is given by

$$H = -\mu_B \hat{\boldsymbol{\sigma}} \cdot \boldsymbol{B}$$

where $\hat{\boldsymbol{\sigma}}$ is the Pauli's spin operator and μ_B stands for the Bohr magneton. Evaluate (i) the density matrix in the diagonalized representation of $\hat{\sigma}_z$, (ii) the density matrix in the diagonalized representation of $\hat{\sigma}_x$ and (iii) the averages of $\hat{\sigma}_z$ in these representations, the z-axis being taken along the field direction.

((**Solution**))
The magnetic moment of spin 1/2 is given by

$$\hat{\boldsymbol{\mu}} = -\left(\frac{2\hat{\boldsymbol{S}}}{\hbar}\right)\mu_B = -\mu_B \hat{\boldsymbol{\sigma}} .$$

The Zeeman energy:

$$\hat{H} = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{B} = \mu_B \hat{\sigma}_Z B$$

The density operator is given by

$$\hat{\rho}_C = \frac{1}{Z_C(\beta)} \exp(-\beta \hat{H}) = \frac{1}{Z_C(\beta)} \exp(-\beta \mu_B B \hat{\sigma}_Z)$$

$\hat{U}$ is the unitary operator

$$\left|+x\right\rangle = \hat{U}\left|+z\right\rangle, \qquad \left|-x\right\rangle = \hat{U}\left|-z\right\rangle$$

where

$$\hat{U} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}, \qquad \hat{U}^{+} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}.$$

The partition function $Z_C(\beta)$ is

$$Z_C(\beta) = Tr[\exp(-\beta\mu_B B\hat{\sigma}_Z)] = \exp(-\beta\mu_B B) + \exp(\beta\mu_B B) = 2\cosh(\beta\mu_B B)$$

(a) The density matrix under the basis of $\{|+z\rangle, |\text{-z}\rangle\}$.

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

(b) The density matrix under the basis of $\{|+x\rangle, |\text{-x}\rangle\}$.

$$\begin{aligned}
\hat{\rho}_x &= \hat{U}^{+}\hat{\rho}_z\hat{U} \\
&= \frac{1}{2\cosh(\beta\mu_B B)}\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1\end{pmatrix}\begin{pmatrix} e^{-\beta\mu_B B} & 0 \\ 0 & e^{\beta\mu_B B}\end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1\end{pmatrix} \\
&= \frac{1}{4\cosh(\beta\mu_B B)}\begin{pmatrix} 2\cosh(\beta\mu_B B) & -2\sinh(\beta\mu_B B) \\ -2\sinh(\beta\mu_B B) & 2\cosh(\beta\mu_B B)\end{pmatrix} \\
&= \frac{1}{2}\begin{pmatrix} 1 & -\tanh(\beta\mu_B B) \\ -\tanh(\beta\mu_B B) & 1\end{pmatrix}
\end{aligned}$$

(c)

The average of $\hat{\sigma}_z$ under the basis of $\{|+z\rangle, |\text{-z}\rangle\}$

$$\langle\sigma_z\rangle = Tr[\rho_z\sigma_z] = -\tanh(\beta\mu_B B)$$

since

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

(c)

The average of $\hat{\sigma}_z$ under the basis of $\{|+x\rangle, |\text{-x}\rangle\}$.

$$\begin{aligned}\langle\sigma_z\rangle &= Tr[\hat{\rho}_z\hat{\sigma}_z] \\ &= Tr[\hat{U}^+\hat{\rho}_z\hat{U}\hat{U}^+\hat{\sigma}_z\hat{U}] \\ &= -\tanh(\beta\mu_B B)\end{aligned}$$

Note that

$$\begin{aligned}\hat{U}^+\hat{\rho}_z\hat{U}\hat{U}^+\hat{\sigma}_z\hat{U} &= \frac{1}{2}\begin{pmatrix} 1 & -\tanh(\beta\mu_B B) \\ -\tanh(\beta\mu_B B) & 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ &= \frac{1}{2}\begin{pmatrix} -\tanh(\beta\mu_B B) & 1 \\ 1 & -\tanh(\beta\mu_B B) \end{pmatrix}\end{aligned}$$

and

$$\begin{aligned}\hat{U}^+\hat{\sigma}_z\hat{U} &= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \\ &= \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \\ &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\end{aligned}$$

9. Example-1

The entropy is given by

$$S = -k_B Tr[\hat{\rho}_C \ln\hat{\rho}_C]$$

In the above example, the density operator is given by

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

Using the Mathematica the entropy is obtained as

$$\begin{aligned}S &= -\frac{1}{1+e^{2\beta\mu_B B}}\ln\left(\frac{1}{1+e^{2\beta\mu_B B}}\right) - \frac{e^{2\beta\mu_B B}}{1+e^{2\beta\mu_B B}}\ln\left[\frac{1+\tanh(\beta\mu_B B)}{2}\right] \\ &= \ln[2\cosh(\beta\mu_B B)] - \beta\mu_B B\tanh(\beta\mu_B B)\end{aligned}$$

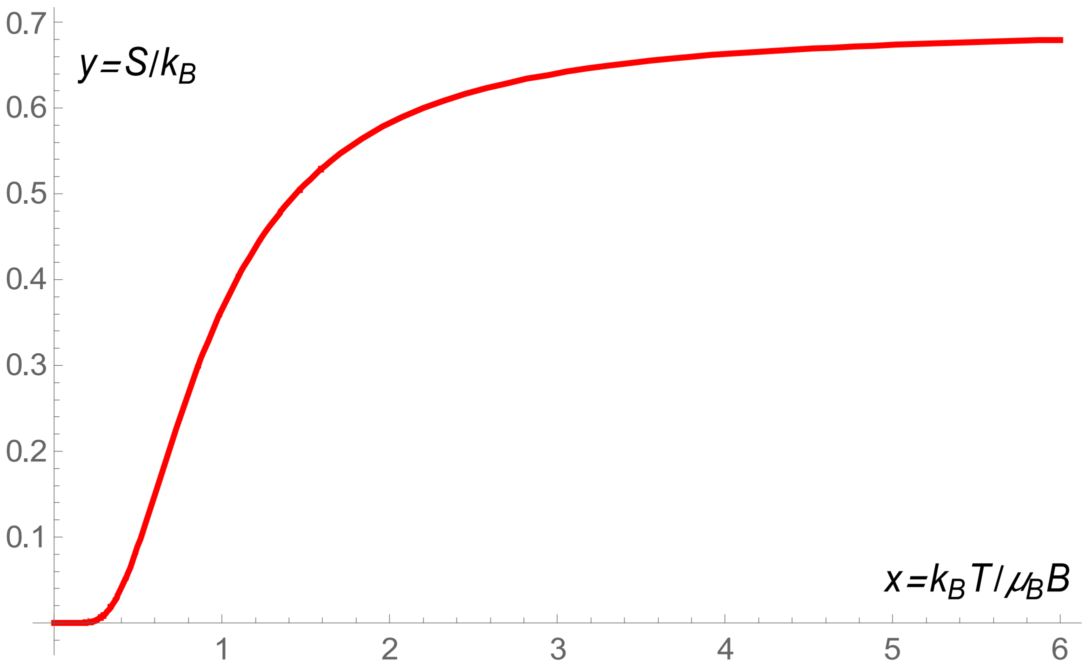
((Mathematica))

```
Clear["Global`*"];
ρ1 = 1/(2 Cosh[α]) ( Exp[-α]    0
                       0      Exp[α] );
M1 = -Tr[ρ1 . MatrixLog[ρ1]] // FullSimplify
```

$$-\frac{\text{Log}\left[\frac{1}{1+e^{2\alpha}}\right]+e^{2\alpha}\,\text{Log}\left[\frac{1}{2}\,(1+\text{Tanh}[\alpha])\right]}{1+e^{2\alpha}}$$

```
M2 = Log[2 Cosh[α]] - α Tanh[α];

h1 = Plot[M1 /. α → 1 / x, {x, 0, 6},
   PlotStyle → {{Red, Thick}}];
h2 = Plot[M2 /. α → 1 / x, {x, 0, 6},
   PlotStyle → {{Blue, Thick}}];
h3 =
  Graphics[
   {Text[Style["y=S/k_B", Black, Italic, 12],
     {0.5, 0.65}],
    Text[Style["x=k_BT/μ_BB", Black, Italic, 12],
     {5.5, 0.05}] }];
Show[h1, h3]
```



Show[h2, h3]

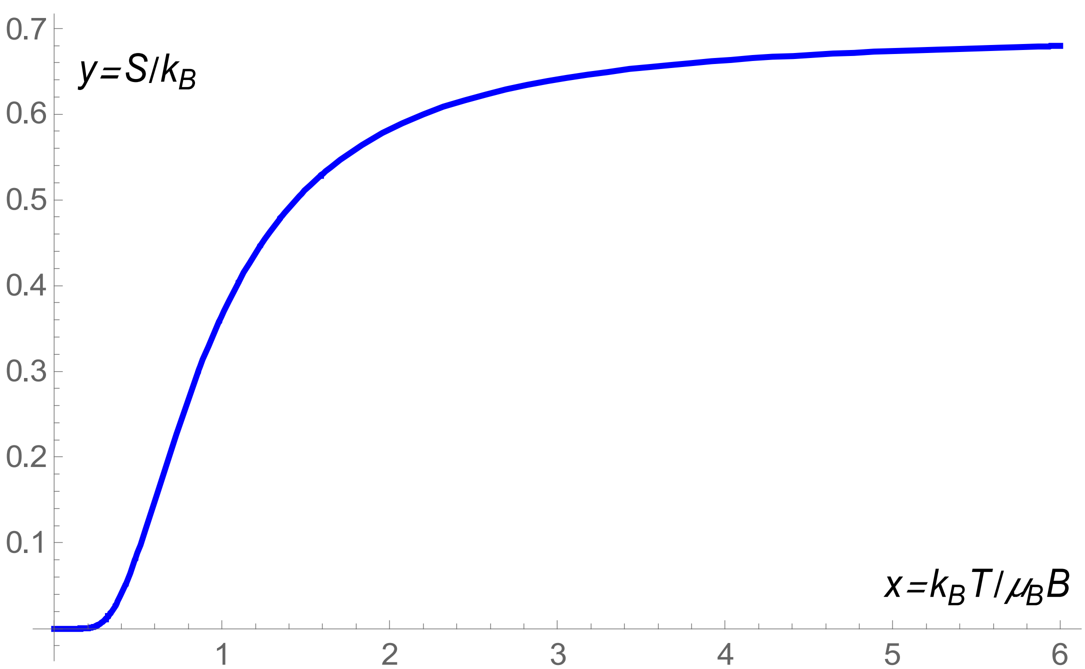
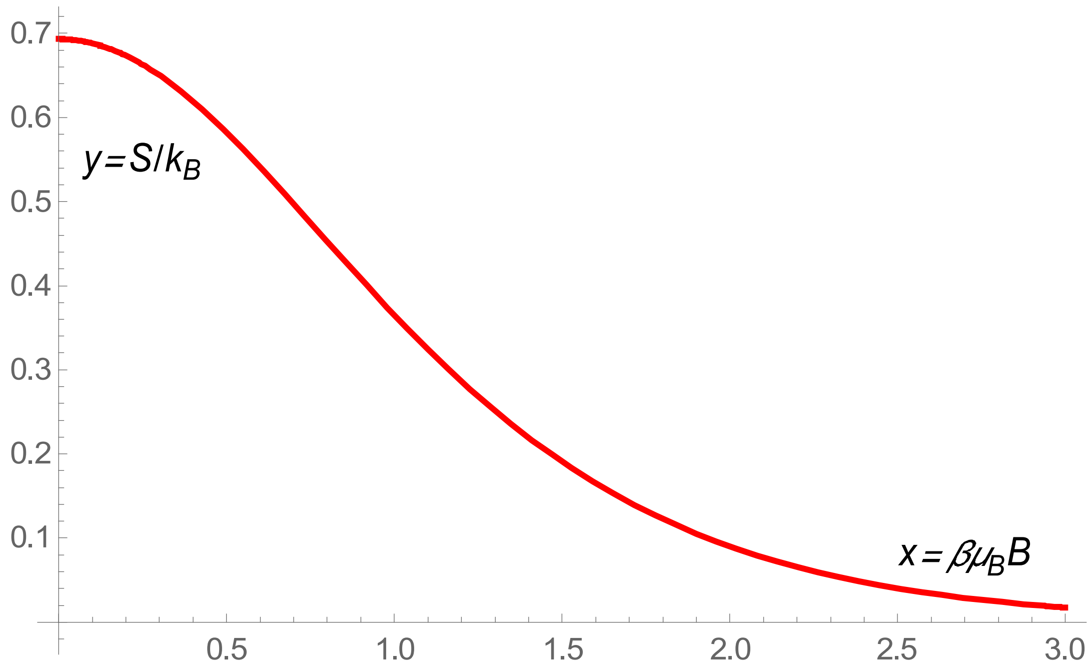
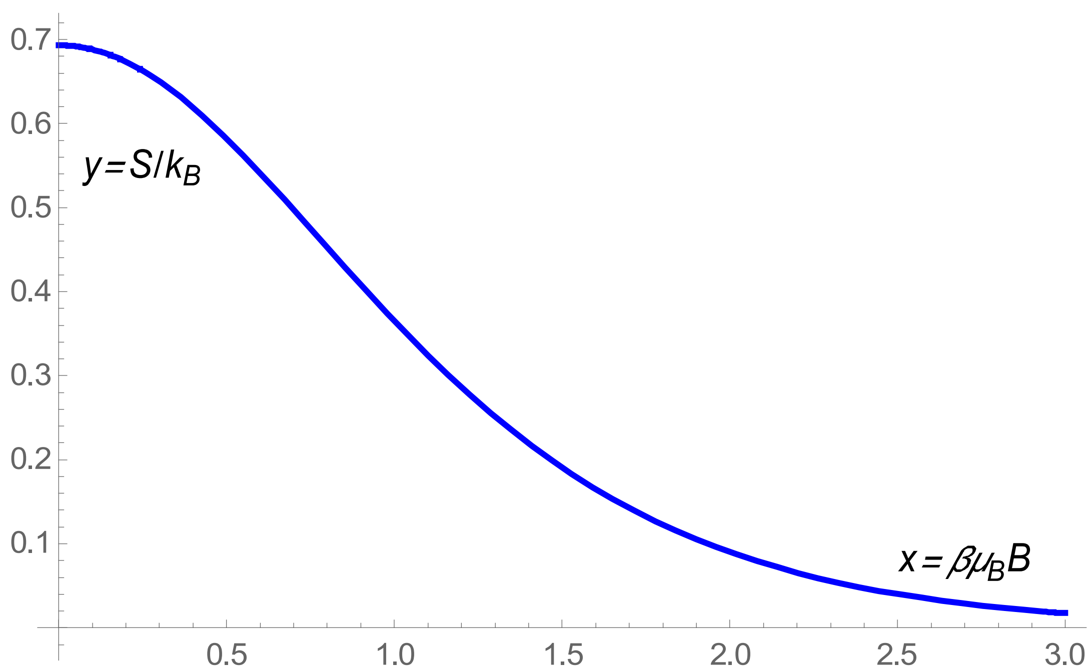


Fig. Entropy vs temperature at the fixed B.




```
Show[h2, h3]
```



10. Example-2

R. Kubo, Statistical Mechanics: An Advanced Course with Problems and Solutions (North-Holland, 1965).

Chapter 2, Problem 2-30 (p.138)
Evaluate the matrix elements of the density matrix

$$\hat{\rho} = \frac{1}{Tr[e^{-\beta\hat{H}}]} e^{-\beta\hat{H}}$$

where

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega^2\hat{q}^2$$

of a one-dimensional harmonic oscillator in the $|q\rangle$ representation. Discuss, in particular, the limiting case of

$$\frac{\hbar\omega}{k_B T} = \beta\hbar\omega << 1$$

Hint: The eigenfunction $\psi_n(q)$ for the eigenvalue

$$E_n = (n + \frac{1}{2})\hbar\omega$$

is given by

$$\psi_n(q) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{H_n(\xi)}{\sqrt{2^n n!}} e^{-\xi^2/2} \qquad \text{with } \xi = \sqrt{\frac{m\omega}{\hbar}} q$$

The Hermite polynomials $H_n(\xi)$ are defined by

$$H_n(\xi) = (-1)^n e^{\xi^2} \left(\frac{d}{d\xi}\right)^n e^{-\xi^2} = \frac{e^{\xi^2}}{\sqrt{\pi}} \int_{-\infty}^{\infty} du(-2iu)e^{-u^2+2i\xi u}$$

Use the last expression in the integral form.

((**Solution**))

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega^2\hat{q}^2 \qquad \text{(one-dimensional simple harmonics)}$$

$$\hat{H}\left|n\right\rangle = \hbar\omega(n+\frac{1}{2})\left|n\right\rangle$$

The density matrix in the basis of $\left|q\right\rangle$

$$\begin{aligned}\left\langle x\right|\exp(-\beta\hat{H})\left|y\right\rangle &= \sum_{n,n'}\left\langle x|n\right\rangle\left\langle n\right|\exp(-\beta\hat{H})\left|n'\right\rangle\left\langle n'|y\right\rangle \\ &= \sum_{n,n'}\exp[-\beta(n+\frac{1}{2})\hbar\omega]\delta_{n,n'}\left\langle n|n'\right\rangle\left\langle x|n\right\rangle\left\langle n'|y\right\rangle \\ &= \sum_{n}\exp[-\beta(n+\frac{1}{2})\hbar\omega]\left\langle x|n\right\rangle\left\langle n|y\right\rangle\end{aligned}$$

The wave function is given by

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

with

$$H_n(x) = \frac{\exp(x^2)}{\sqrt{\pi}}\int_{-\infty}^{\infty}du(-2iu)^n\exp[-u^2+2ixu]$$

Then we get

$$\begin{aligned}\left\langle x\right|\exp(-\beta\hat{H})\left|y\right\rangle &= \sum_{n}\exp[-\beta(n+\frac{1}{2})\hbar\omega]\left\langle x|n\right\rangle\left\langle n|y\right\rangle \\ &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/2}\exp[-\frac{m\omega(x^2+y^2)}{2\hbar}] \\ &\times\sum_{n}\frac{1}{2^n n!}\exp[-\beta(n+\frac{1}{2})\hbar\omega]H_n(\sqrt{\frac{m\omega}{\hbar}}x)H_n(\sqrt{\frac{m\omega}{\hbar}}y)\end{aligned}$$

where

$$\begin{aligned}H_n(\sqrt{\frac{m\omega}{\hbar}}x)H_n(\sqrt{\frac{m\omega}{\hbar}}y) &= \frac{1}{\pi}\exp[\frac{m\omega(x^2+y^2)}{\hbar}] \\ &\times\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}dv(-2iu)^n(-2iv)^n\exp[-u^2-v^2+2i\sqrt{\frac{m\omega}{\hbar}}(xu+yv)\end{aligned}$$

Thus we have

$$\langle x|\exp(-\beta\hat{H})|y\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2}\frac{1}{\pi}\exp[\frac{m\omega(x^2+y^2)}{2\hbar}-\beta\frac{\hbar\omega}{2})]$$
$$\times\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}dv\exp[-u^2-v^2+2i\sqrt{\frac{m\omega}{\hbar}}(xu+yv)]\sum_n\frac{1}{n!}(-2uv)^n e^{-n\beta\hbar\omega}$$
$$=\left(\frac{m\omega}{\pi\hbar}\right)^{1/2}\frac{1}{\pi}\exp[\frac{m\omega(x^2+y^2)}{2\hbar}-\beta\frac{\hbar\omega}{2})]$$
$$\times\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}dv\exp[-u^2-v^2+2i\sqrt{\frac{m\omega}{\hbar}}(xu+yv)-2uve^{-\beta\hbar\omega}]$$

where

$$\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}dv\exp[-u^2-v^2+2i\sqrt{\frac{m\omega}{\hbar}}(xu+yv)-2uve^{-\beta\hbar\omega}] = \pi(1-e^{-2\beta\hbar\omega})^{-1/2}$$
$$\times\exp[-\frac{m\omega e^{\beta\hbar\omega}(-2xy+e^{\beta\hbar\omega}(x^2+y^2))}{\hbar(e^{2\beta\hbar\omega}-1)}]$$

((**Mathematica**)) Proof of the above integral using the Mathematica

```
Clear["Global`*"];

f1 = Exp[-u^2 - v^2 + 2 ⅈ Sqrt[m ω/ℏ] (x u + y v) -
    2 u v Exp[-β ℏ ω]];

Integrate[Integrate[f1, {v, -∞, ∞}], {u, -∞, ∞}] //
  Simplify[#, {β > 0, ω > 0, ℏ > 0, m > 0}] &
```

$$\frac{e^{-\frac{e^{\beta\omega\hbar}m\left(-2xy+e^{\beta\omega\hbar}\left(x^2+y^2\right)\right)\omega}{\left(-1+e^{2\beta\omega\hbar}\right)\hbar}}\pi}{\sqrt{1-e^{-2\beta\omega\hbar}}}$$

Then we have

$$\langle x|\exp(-\beta\hat{H})|y\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \frac{e^{-\frac{\beta\hbar\omega}{2}}}{\sqrt{1-e^{-2\beta\hbar\omega}}}$$

$$\times\exp[\frac{m\omega(x^2+y^2)}{2\hbar} - \frac{m\omega e^{\beta\hbar\omega}(-2xy+e^{\beta\hbar\omega}(x^2+y^2))}{\hbar(e^{2\beta\hbar\omega}-1)}]$$

$$= \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \frac{e^{-\frac{\beta\hbar\omega}{2}}}{\sqrt{1-e^{-2\beta\hbar\omega}}}$$

$$\times\exp[\frac{m\omega(x^2+y^2)}{2\hbar} - \frac{m\omega(x^2-2e^{-\beta\hbar\omega}xy+y^2)}{\hbar(1-e^{-2\beta\hbar\omega})}]$$

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

$$\times\exp[\frac{m\omega}{2\hbar}\{-(x^2+y^2)\coth(\beta\hbar\omega) + \frac{2xy}{\sinh(\beta\hbar\omega)}\}]$$

Note that

$$-(x^2+y^2)\coth(\beta\hbar\omega) + \frac{2xy}{\sinh(\beta\hbar\omega)} = -\frac{1}{2}\{(x+y)^2\tanh(\frac{\beta\hbar\omega}{2}) + (x-y)^2\coth(\frac{\beta\hbar\omega}{2})\}\ \{$$

Thus we have

$$\langle x|\exp(-\beta\hat{H})|y\rangle = \left(\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right)^{1/2}$$

$$\times\exp[-\frac{m\omega}{4\hbar}\{(x+y)^2\tanh(\frac{\beta\hbar\omega}{2}) + (x-y)^2\coth(\frac{\beta\hbar\omega}{2})\}]$$

When $\beta\hbar\omega \ll 1$,

$$\sinh(\beta\hbar\omega) \approx \beta\hbar\omega, \qquad \tanh(\frac{\beta\hbar\omega}{2}) \approx \frac{\beta\hbar\omega}{2}, \qquad \coth(\frac{\beta\hbar\omega}{2}) \approx \frac{2}{\beta\hbar\omega}.$$

So we get the approximate form as

$$\langle x|\exp(-\beta\hat{H})|y\rangle = \left(\frac{m}{2\pi\hbar^2\beta\hbar}\right)^{1/2}$$

$$\times\exp[-\frac{m\omega^2\beta}{8}(x+y)^2 - \frac{m}{2\hbar^2\beta}(x-y)^2]$$

$$= \exp(-\frac{m\omega^2\beta}{2}x^2)\,\delta(x-y)$$

Here we use the definition of the Dirac delta function

$$\lim_{\varepsilon\to 0}\sqrt{\frac{\varepsilon}{2\pi}}\exp[-\frac{1}{2}\varepsilon(x-y)^2] = \delta(x-y)\,.$$

---

11. Example-3

R. Kubo, Statistical Mechanics: An Advanced Course with Problems and Solutions (North-Holland, 1965).
Chapter 2, Problem 2-31 (p.139)

Evaluate $\langle\hat{q}^2\rangle$ and $\langle\hat{p}^2\rangle$ from the density matrix in the $|q\rangle$ representation obtained in the Example-2 for a one-dimensional harmonic oscillator.

((**Solution**))

$$\langle x^2\rangle = \frac{1}{Z(\beta)}Tr[\hat{x}^2\exp(-\beta\hat{H})]\,,\qquad \langle p^2\rangle = \frac{1}{Z(\beta)}Tr[\hat{p}^2\exp(-\beta\hat{H})]$$

$$Tr[\hat{x}^2\exp(-\beta\hat{H})] = \int dx\langle x|\hat{x}^2\exp(-\beta\hat{H})|x\rangle$$

$$= \int x^2 dx\langle x|\exp(-\beta\hat{H})|x\rangle$$

$$= \left(\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right)^{1/2}\int_{-\infty}^{\infty}x^2\exp[-\frac{m\omega}{\hbar}x^2\tanh(\frac{\beta\hbar\omega}{2})]dx$$

$$= \left(\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right)^{1/2}\frac{\sqrt{\pi}}{2}[\left(\frac{m\omega}{\hbar}\right)\tanh\left(\frac{\beta\hbar\omega}{2}\right)]^{-3/2}$$

where

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

The partition function:

$$\begin{aligned}
Z(\beta) &= Tr[\exp(-\beta\hat{H})] = \int dx\langle x|\exp(-\beta\hat{H})|x\rangle \\
&= \int dx\langle x|\exp(-\beta\hat{H})|x\rangle \\
&= \left(\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right)^{1/2}\int_{-\infty}^{\infty}\exp[-\frac{m\omega}{\hbar}x^2\tanh(\frac{\beta\hbar\omega}{2})]dx \\
&= \left(\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right)^{1/2}\left(\frac{\pi}{\frac{m\omega}{\hbar}\tanh(\frac{\beta\hbar\omega}{2})}\right)^{1/2}
\end{aligned}$$

Then we have

$$\begin{aligned}
\langle x^2\rangle &= \frac{1}{Z(\beta)}Tr[\hat{x}^2\exp(-\beta\hat{H})] \\
&= \left(\frac{\frac{m\omega}{\hbar}\tanh(\frac{\beta\hbar\omega}{2})}{\pi}\right)^{1/2}\frac{\sqrt{\pi}}{2}[\left(\frac{m\omega}{\hbar}\right)\tanh\left(\frac{\beta\hbar\omega}{2}\right)]^{-3/2} \\
&= \frac{\hbar}{2m\omega}\coth(\frac{\hbar\omega\beta}{2})
\end{aligned}$$

$$\ln Z = \frac{1}{2}\ln\left(\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right) + \frac{1}{2}\ln\left(\frac{\pi}{\frac{m\omega}{\hbar}\tanh(\frac{\beta\hbar\omega}{2})}\right)$$

$$\langle\varepsilon\rangle = -\frac{\partial}{\partial\beta}\ln Z = \frac{\hbar\omega}{2}\coth(\frac{\hbar\omega\beta}{2})$$

Since

$$\langle\varepsilon\rangle = \frac{1}{2m}\langle p^2\rangle + \frac{1}{2}m\omega^2\langle x^2\rangle$$

$$\langle p^2\rangle = m^2\omega^2\langle x^2\rangle = m^2\omega^2\frac{\hbar}{2m\omega}\coth(\frac{\hbar\omega\beta}{2}) = \frac{m\hbar\omega}{2}\coth(\frac{\hbar\omega\beta}{2})$$

((Note))

$$\begin{aligned}
Tr[\hat{p}^2\exp(-\beta\hat{H})] &= \int dx\langle x|\hat{p}^2\exp(-\beta\hat{H})|x\rangle \\
&= \int dx\int dx''\langle x|\hat{p}^2|x''\rangle\langle x''|\exp(-\beta\hat{H})|x\rangle \\
&= \int dx\int dx''\langle x|x''\rangle\left(\frac{\hbar}{i}\frac{\partial}{\partial x''}\right)^2\langle x''|\exp(-\beta\hat{H})|x\rangle \\
&= \int dx\int dx''\delta(x-x'')\left(\frac{\hbar}{i}\frac{\partial}{\partial x''}\right)^2\langle x''|\exp(-\beta\hat{H})|x\rangle
\end{aligned}$$

where

$$\begin{aligned}
\langle x''|\exp(-\beta\hat{H})|x\rangle &= \left(\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right)^{1/2} \\
&\times\exp[-\frac{m\omega}{4\hbar}\{(x''+x)^2\tanh(\frac{\beta\hbar\omega}{2})+(x''-x)^2\coth(\frac{\beta\hbar\omega}{2})\}]
\end{aligned}$$

Using the Mathematica we get

$$\langle p^2\rangle = \frac{1}{Z(\beta)}Tr[\hat{p}^2\exp(-\beta\hat{H})] = \frac{m\hbar\omega}{2}\coth(\frac{\hbar\omega\beta}{2})$$

((**Mathematica**))

```
Clear["Global`*"];
```

$$g1 = \sqrt{\frac{m\,\omega}{2\,\pi\,\hbar\,\mathrm{Sinh}[\beta\,\hbar\,\omega]}}\;\mathrm{Exp}\left[\frac{-m\,\omega}{4\,\hbar}\,(x2+x)^2\,\mathrm{Tanh}\left[\frac{\beta\,\hbar\,\omega}{2}\right]-\frac{m\,\omega}{4\,\hbar}\,(x2-x)^2\,\mathrm{Coth}\left[\frac{\beta\,\hbar\,\omega}{2}\right]\right];$$

$$g2 = -\hbar^2\,D[g1,\{x2,2\}]\;//\;\mathrm{FullSimplify};$$

$$g3 = g2\;/.\;x2\to x\;//\;\mathrm{FullSimplify}$$

$$\frac{1}{2\sqrt{2\,\pi}}\,e^{-\frac{m\,x^2\,\omega\,\mathrm{Tanh}\left[\frac{\beta\,\omega\,\hbar}{2}\right]}{\hbar}}\,\hbar\,\mathrm{Csch}[\beta\,\omega\,\hbar]\left(\frac{m\,\omega\,\mathrm{Csch}[\beta\,\omega\,\hbar]}{\hbar}\right)^{3/2}\left(-8\,m\,x^2\,\omega\,\mathrm{Sinh}\left[\frac{\beta\,\omega\,\hbar}{2}\right]^4+\hbar\,\mathrm{Sinh}[2\,\beta\,\omega\,\hbar]\right)$$

$$g4 = \mathrm{Integrate}[g3,\{x,-\infty,\infty\}]\;//\;\mathrm{FullSimplify}[\#,\{m>0,\hbar>0,\beta>0,\omega>0\}]\;\&$$

$$\frac{1}{8}\,m\,\omega\,\hbar\,\mathrm{Csch}\left[\frac{\beta\,\omega\,\hbar}{2}\right]^3\,\mathrm{Sinh}[\beta\,\omega\,\hbar]$$

$$Z1 = \sqrt{\frac{m\,\omega}{2\,\pi\,\hbar\,\mathrm{Sinh}[\beta\,\hbar\,\omega]}}\;\sqrt{\frac{\pi}{\frac{m\,\omega}{\hbar}\,\mathrm{Tanh}\left[\frac{\beta\,\hbar\,\omega}{2}\right]}};$$

$$\frac{g4}{Z1}\;//\;\mathrm{FullSimplify}[\#,\{m>0,\hbar>0,\beta>0,\omega>0\}]\;\&$$

$$\frac{1}{2}\,m\,\omega\,\hbar\,\mathrm{Coth}\left[\frac{\beta\,\omega\,\hbar}{2}\right]$$