Density matrix

$$\boxed{\hat{\rho} = \sum_\alpha p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha|}$$

1

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}] \Rightarrow \text{steady state } [\hat{H}, \hat{\rho}] = 0$$

$\Rightarrow$ advocates for $\hat{\rho} = f(\hat{H})$

Canonical

$$p_n = \frac{1}{Z} e^{-\beta E_n} \iff \hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}}$$

$$\mathrm{Tr}(\hat{\rho}) = 1 \Rightarrow Z = \mathrm{Tr}(e^{-\beta\hat{H}}) = \sum_n e^{-\beta E_n}$$ $\Rightarrow$ validates the approach of chapter 5!

Grand canonical

$$\hat{\rho} = \frac{1}{Q} e^{-\beta\hat{H} + \beta\mu\hat{N}} ; Q(\beta,\mu) = \mathrm{Tr}(e^{-\beta\hat{H} + \beta\mu\hat{N}});$$ [Requires $[\hat{H}, \hat{N}] = 0$ or $\mu = 0$]

Thermodynamic properties:

$$\langle\hat{H}\rangle = \mathrm{Tr}(\hat{\rho}\hat{H}) = \mathrm{Tr}\left(\frac{e^{-\beta\hat{H}}}{Z}\hat{H}\right) = -\frac{1}{Z}\partial_\beta \mathrm{Tr}(e^{-\beta\hat{H}}) = -\frac{1}{Z}\partial_\beta Z$$

$$\langle\hat{H}\rangle = -\partial_\beta \ln Z$$ as in classical stat mech!

Maximum entropy & quantum ensemble

Also works to build quantum ensemble with using the generalization of Gibbs entropy:

$$S = -k_B \mathrm{Tr}(\hat{\rho}\ln\hat{\rho})$$ [Jaynes, Phys Rev 108, 171, (1957)]

Coherence

* In a given basis $|n\rangle$, the diagonal elements of $\hat{\rho}$ give the proba that the system is measured in $|n\rangle$:

$$\langle n|\hat{\rho}|n\rangle = \sum_\alpha p_\alpha \underbrace{\langle n|\psi_\alpha\rangle\langle\psi_\alpha|n\rangle}_{P(E_n | \text{system } \psi_\alpha)} = p(E_n)$$

* If all $|\psi_\alpha\rangle \in \{|n\rangle\}$; then $\langle n|\hat{\rho}|k\neq n\rangle = 0$, none of the states ②
are quantum superpositions between $|n\rangle$ & $|k\rangle$ in the ensemble described by $\hat{\rho}$.
$\Rightarrow$ the system is a statistical mixture of $\{|n\rangle\}$

* Conversely, if $\langle n|\hat{\rho}|k\rangle \neq 0 \Rightarrow$ some states in $\{|\psi_\alpha\rangle\}$ are quantum superposition of $|n\rangle$ & $|k\rangle$.

Ex: $|\psi_+\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\rangle + |\downarrow\rangle\right)$; $|\psi_-\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\rangle - |\downarrow\rangle\right)$; $p_+ = \frac{1}{4}$, $p_- = \frac{3}{4}$

$$\rho = \frac{1}{4}|\psi^+\rangle\langle\psi^+| + \frac{3}{4}|\psi^-\rangle\langle\psi^-| = \frac{1}{8}\left(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow| + |\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\uparrow|\right)$$
$$+\frac{3}{8}\left(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow| - |\uparrow\rangle\langle\downarrow| - |\downarrow\rangle\langle\uparrow|\right)$$

In the basis $|\uparrow\rangle, |\downarrow\rangle$, $\rho = \begin{pmatrix} 1/2 & -1/4 \\ -1/4 & 1/2 \end{pmatrix}$

If $|\psi_+\rangle = |\uparrow\rangle$ & $|\psi_-\rangle = |\downarrow\rangle$; $\rho = \begin{pmatrix} 1/4 & 0 \\ 0 & 3/4 \end{pmatrix}$

A particle in a Box:

$\hat{H} = \frac{\hat{p}^2}{2m}$; $\langle x|\hat{p}|\psi\rangle = -i\hbar\nabla\langle x|\psi\rangle$

$\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$; $\hat{H}|k\rangle = \varepsilon(k)|k\rangle \Rightarrow \langle x|k\rangle = \frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{x}}$; $\varepsilon(\vec{k}) = \frac{\hbar^2k^2}{2m}$

Partition function

$$Z = \mathrm{Tr}\left(e^{-\beta\hat{H}}\right) = \sum_{\vec{k}} e^{-\beta\frac{\hbar^2k^2}{2m}} \simeq \frac{V}{(2\pi)^3}\int d^3\vec{k}\, e^{-\beta\frac{\hbar^2k^2}{2m}} = \frac{V}{(2\pi)^3}\sqrt{\frac{2\pi m k_BT}{\hbar^2}}^{\,3}$$
$$= V\sqrt{\frac{2\pi m k_BT}{h^2}}^{\,3} = \frac{V}{\Lambda^3} \Rightarrow \text{as in classical statistical mechanics.}$$

Density matrix

$$* \; \langle x|\hat{\rho}_c|x'\rangle = \sum_k \frac{e^{-\beta\varepsilon(k)}}{Z}\langle x'|k\rangle\langle k|x\rangle \simeq \frac{\Lambda^3}{V}\frac{1}{(2\pi)^3}\int d^3\vec{k}\, e^{-\frac{\beta\hbar^2k^2}{2m} - i\vec{k}\cdot(\vec{x}-\vec{x}')}$$

$$= \frac{1}{V} \exp\left[-\frac{\pi(\vec{x}-\vec{x}')^2}{2\Lambda^2}\right] \quad \text{since } \frac{2\hbar^2}{mkT} = \frac{1}{\pi}\frac{h^2}{2\pi mkT}$$

* $\langle x|\rho_0|x\rangle = \frac{1}{V}$ as expected
* The statistical mixtures described by the canonical $\hat{\rho}$ comprise states that are quantum superposition of the states $\{|x\rangle\}$. At temperature T, the particle is a wave paquet spread over a scale given by de Broglie thermal wave length.
* Take an observable $\hat{f}$ that is not diagonal in $\{|x\rangle\}$, $\hat{f}|x\rangle = \int d\vec{x}''\, f(x-x'')|x''\rangle$ $\delta(x$

then $\langle\hat{f}\rangle_{stat} = \mathrm{Tr}(\hat{\rho}\hat{f}) = \int d^3\vec{x}\, d^3\vec{x}' \langle x|\hat{\rho}|x'\rangle\langle x'|f|x\rangle$

$$= \frac{1}{V}\int d^3\vec{x}\, d^3\vec{x}'\, e^{-\frac{\pi(\vec{x}-\vec{x}')^2}{2\Lambda^2}} f(\vec{x}-\vec{x}') = \int d^3\vec{u}\, f(\vec{u})\, e^{-\frac{\pi\vec{u}^2}{2\Lambda^2}}$$

If instead we consider the $\hat{\rho}$ that describes a statistical mixture of $|x\rangle$ with weight $1/V$, so that $\langle x|\hat{\rho}|x'\neq x\rangle = 0$, then $\langle\hat{f}\rangle_{\hat{\rho}} = f(0)$.

For instance, consider the translation operator $T_{\vec{a}}|x\rangle = |x+a\rangle$, with $\vec{a}\neq 0$, such that $f(\vec{u}) = \delta(\vec{u}+\vec{a})$,

then $\langle T_{\vec{a}}\rangle = \exp\left[-\frac{\pi\vec{a}^2}{2\Lambda^2}\right]$ in the canonical ensemble. Without the off diagonal element, $\langle T_{\vec{a}}\rangle = 0$ since $\langle x|x+a\rangle = 0$ for $a\neq 0$.

6.2) Quantum gases

To characterize the statistical properties of a system, we thus need to build $\hat{\rho}$.

Canonical ensemble $\hat{\rho} = \frac{1}{Z}\sum_n e^{-\beta E_n}|n\rangle\langle n|$

$\Rightarrow$ construct $|n\rangle$ for a gas of non-interacting particles.

Symmetry properties

If particles are undistinguishable $P(x_1, x_2, \ldots, x_N) = P(x_2, x_1, \ldots, x_N)$

$\Leftrightarrow |\Psi(x_1,x_2,\dots,x_N)|^2 = |\Psi(x_2,x_1,\dots,x_N)|^2 \Rightarrow \Psi(x_2,x_1,\dots,x_N) = e^{i\theta}\Psi(x_1,x_2,\dots,x_N)$

Since swapping x_1 & x_2 twice leads back to $x_1, x_2, \dots, x_N \Rightarrow e^{2i\theta} = 1$

$\Rightarrow \theta = 0$ or π.

Spin statistics theorem: Particles with intrinsic spin s are such that

s integer $\Leftrightarrow$ bosons & $\theta = 0 \Rightarrow \Psi$ fully symmetric

s half integer $\Leftrightarrow$ fermions & $\theta = \pi \Rightarrow \Psi$ fully antisymmetric

Proof: Pauli, 1940, [Phys. Rev. 58, 716, (1940)]

Eigenstates: let us denote by $|k\rangle$ the eigenstates of a single particle.

$|k_1 \dots k_N\rangle = |k_1\rangle \otimes |k_2\rangle \otimes \dots \otimes |k_N\rangle$ is a basis of the full Hilbert space.

that has no particular symmetry properties.

* let us introduce $\eta = 1$ (or "+") for bosons & $\eta = -1$ (or "−") for fermion. We can build the corresponding eigenstate for an N-particle system

$$\boxed{|\Psi\rangle_\eta = \frac{1}{\sqrt{N_\eta}} \sum_{\sigma \in \sigma(N)} (\eta)^{p(\sigma)} |k_{\sigma(1)} \dots k_{\sigma(N)}\rangle}$$ (*), where

- $\sigma(N)$ is the group of permutations of $\{1, \dots, N\}$
- $p(\sigma)$ is the parity of the permutation, i.e. the number of pairwise swaps to go from $1, \dots, N$ to $\sigma(1), \dots, \sigma(N)$
- N_η is a normalization factor such that ${}_\eta\langle\Psi|\Psi\rangle_\eta = 1$

Normalization:

$$ {}_{\eta}\langle\Psi|\Psi\rangle_{\eta} = \frac{1}{N_\eta} \sum_{\sigma_1,\sigma_2} \eta^{P(\sigma_1)+P(\sigma_2)} \langle k_{\sigma_1(1)} - k_{\sigma_1(N)} | k_{\sigma_2(1)} - k_{\sigma_2(N)} \rangle $$

Bosons

$$ {}_{+}\langle\Psi|\Psi\rangle_{+} = \frac{N!}{N_+} \sum_{\sigma} \underbrace{\langle k_1 - k_N | k_{\sigma(1)} - k_{\sigma(N)}\rangle}_{\langle k_1|k_{\sigma(1)}\rangle \cdots\cdots \langle k_N|k_{\sigma(N)}\rangle} $$

Non zero only if $k_i = k_{\sigma(i)}$

number of permutations such that $k_i = k_{\sigma(i)}$

$\Rightarrow \prod_k (n_k)! \Rightarrow N_+ = N! \prod_k n_k!$

Fermions: If two particles are in the same state, $k_i = k_j$, then permuting i & j leaves $|k_{\sigma(1)} - k_{\sigma(N)}\rangle$ unchanged. Introducing $\tilde\sigma = \sigma \circ (i \leftrightarrow j)$, we write

$$ |\Psi\rangle_- = \frac{1}{2\sqrt{N_-}} \left(\sum_{\sigma \in S(N)} (-1)^{P(\sigma)} |k_{\sigma(1)} - k_{\sigma(N)}\rangle + (-1)^{P(\sigma)} |k_{\tilde\sigma(1)} - k_{\tilde\sigma(N)}\rangle \right) $$

$$ = \frac{1}{2\sqrt{N_-}} \left[\left(\sum_{\sigma} (-1)^{P(\sigma)} |k_{\sigma(1)} - k_{\sigma(N)}\rangle \right) - \left(\underbrace{\sum_{\sigma}}_{=\sum_{\tilde\sigma}} (-1)^{P(\tilde\sigma)} |k_{\tilde\sigma(1)} - k_{\tilde\sigma(N)}\rangle \right) \right] = 0 $$

$\Rightarrow$ we cannot have two particles in the same state & the only acceptable σ is $\sigma = \mathrm{Id}$. $\Rightarrow N^- = N!$ Since $n_k = 0, 1$, this is also $N^- = N! \prod_k n_k!$

All in all $$ |\Psi\rangle_\eta = \frac{1}{\sqrt{N! \prod_k n_k!}} \sum_{\sigma \in S(N)} \eta^{P(\sigma)} |k_{\sigma(1)} - k_{\sigma(N)}\rangle $$

While this looks complicated, this will make our life <u>simpler</u> than in classical stat mech.

* Classical SM: state characterized by variables $\sigma_1, -, \sigma_N$
  $\Rightarrow$ define $P(\sigma_1, -, \sigma_N)$ & correct for overcounting $\Rightarrow$ tough

* quantum sn: the state itself is symmetrized correctly. there is only ONE state with n_k particles in state $|k\rangle$

$$\Rightarrow \mathrm{Tr}\left(e^{-\beta\hat{H}}\right) = \sum_{\{\sum_k n_k = N\}} e^{-\beta \sum_k n_k \varepsilon_k} \quad ; \ \varepsilon_k \text{ the energy of state } |k\rangle$$

$\Rightarrow$ No need to correct for overcounting afterwards, the trace includes what is needed.

* Still $\sum_k n_k = N$ leads to a somewhat painful constrained sum

$\Rightarrow$ grand canonical ensemble

Grand canonical partition function

$$Q = \mathrm{Tr}\left(e^{-\beta\hat{H} + \beta\mu\hat{N}}\right) = \sum_{\{n_k\}} e^{\beta\mu \sum_k n_k - \beta \sum_k n_k \varepsilon_k} = \prod_k \sum_{n_k} \left[e^{\beta(\mu - \varepsilon_k)}\right]^{n_k}$$

Fermions: $n_k = 0, 1$ $\qquad Q_- = \prod_k \left(1 + e^{\beta(\mu - \varepsilon_k)}\right)$

Bosons: $n_k \in \mathbb{Z}^+$ $\qquad Q_+ = \prod_k \dfrac{1}{1 - e^{\beta(\mu - \varepsilon_k)}}$

$$\left.\right\} \quad Q_\eta = \prod_k \left[1 - \eta e^{\beta(\mu - \varepsilon_k)}\right]^{-\eta}$$

Comment: Bosons require $\mu < \min_k \varepsilon_k$ for convergence of Q_+.

Then $$P_\eta(\{n_k\}) = \frac{1}{Q_\eta} \prod_k \exp\left[\beta(\mu - \varepsilon_k) n_k\right]$$

occupation statistics:

$$\langle n_k \rangle = -\frac{\partial}{\partial(\beta\varepsilon_k)} \ln Q_\eta = \eta \frac{\partial}{\partial \beta\varepsilon_k} \ln\left(1 - \eta e^{\beta(\mu - \varepsilon_k)}\right) = \eta \frac{\eta e^{\beta(\mu - \varepsilon_k)}}{1 - \eta e^{\beta(\mu - \varepsilon_k)}}$$

$$\boxed{\langle n_k \rangle_\eta = \frac{1}{e^{\beta(\mu - \varepsilon_k)} - \eta}}$$