## Quantum statistics

### (1) Density matrix

- pure states - single QM state $|\psi\rangle$ average $\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle$

- mixed states - several/many possible states $|\psi_i\rangle$ occuring with probabilities $p_i$

average $\langle A\rangle = \sum_i p_i \langle\psi_i|\hat{A}|\psi_i\rangle$ requirement $\sum_i p_i = 1$

idea: single system replaced by statistical ensemble of many systems in various pure states, on average the same results

- density matrix $\hat{\rho} = \sum_i p_i |\psi_i\rangle\langle\psi_i|$

$$\langle A\rangle = \sum_i p_i \langle\psi_i|\hat{A}|\psi_i\rangle = \sum_i p_i \langle\psi_i|\left(\sum_n |n\rangle\langle n|\right)\hat{A}\left(\sum_m |m\rangle\langle m|\right)|\psi_i\rangle$$

$$= \sum_{nm}\sum_i \langle m|\psi_i\rangle p_i \langle\psi_i|n\rangle\langle n|\hat{A}|m\rangle = \mathrm{Tr}(\hat{\rho}\hat{A}) \qquad \mathrm{Tr}\,\hat{O} = \sum_m \langle m|\hat{O}|m\rangle$$

- properties of a trace:

cyclic property $\mathrm{Tr}\,\hat{A}\hat{B}\hat{C} = \mathrm{Tr}\,\hat{B}\hat{C}\hat{A}$ $\quad \sum_{n_1 n_2 n_3} \langle n_1|\hat{A}|n_2\rangle\langle n_2|\hat{B}|n_3\rangle\langle n_3|\hat{C}|n_1\rangle$

basis independence $\mathrm{Tr}\, M\sigma M^{-1} = \mathrm{Tr}\,\sigma M^{-1}M = \mathrm{Tr}\,\sigma$

- properties of the density matrix $\hat{\rho} = \sum_i |\psi_i\rangle p_i \langle\psi_i|$

hermitian $\hat{\rho}^{+} = \hat{\rho}$

trace $\mathrm{Tr}\,\hat{\rho} = \sum_n \sum_i \langle n|\psi_i\rangle p_i \langle\psi_i|n\rangle = \sum_i p_i \overbrace{\sum_n |\langle n|\psi_i\rangle|^2}^{1} = 1$

idempotent for pure states $\hat{\rho} = |\psi\rangle\langle\psi| \rightarrow \hat{\rho}^2 = |\psi\rangle\langle\psi|\psi\rangle\langle\psi| = |\psi\rangle\langle\psi| = \hat{\rho}$

- von Neumann equation - reversible dynamics stemming from $i\hbar \frac{d|\psi_i\rangle}{dt} = \hat{H}|\psi_i\rangle$

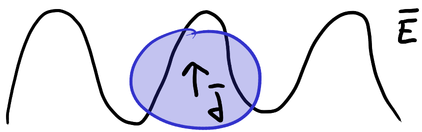
$$\frac{d\hat{\rho}}{dt} = \sum_i p_i \left(\frac{d|\psi_i\rangle}{dt}\langle\psi_i| + |\psi_i\rangle\frac{d\langle\psi_i|}{dt}\right) = \sum_i p_i \frac{1}{i\hbar}\left(\hat{H}|\psi_i\rangle\langle\psi_i| - |\psi_i\rangle\langle\psi_i|\hat{H}\right) = \frac{1}{i\hbar}[\hat{H},\hat{\rho}]$$

## ② Towards equilibrium

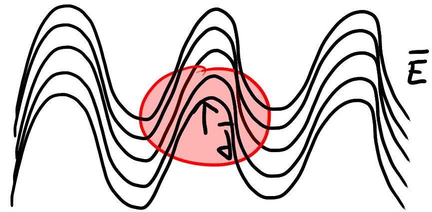
irreversible dynamics – thermalization, evolution towards equilibrium, entropy production

– $p_i$ in the density matrix altered

Ex




no heating, QM evolution driven by $\hat{H}$




heating, $p_i$ of high-energy states grow

- principle of maximal ignorance

  - irreversible processes – system forgets information about initial conditions

  - equilibrium reached at maximal missing information (ignorance)

  - equilibrium state determined solely by equilibrium conditions ($T$, ...)

- Shannon entropy – measure of ignorance

entropy ~ amount of disorder ~ information to reconstruct the state ~

~ how many binary questions needed to identify an element from a random set

illustrative example:

N states $i = 1 \dots N$ occuring

with $P_i = \frac{1}{2^{\ell_i}}$ $\ell_i = 0, 1, 2, \dots$

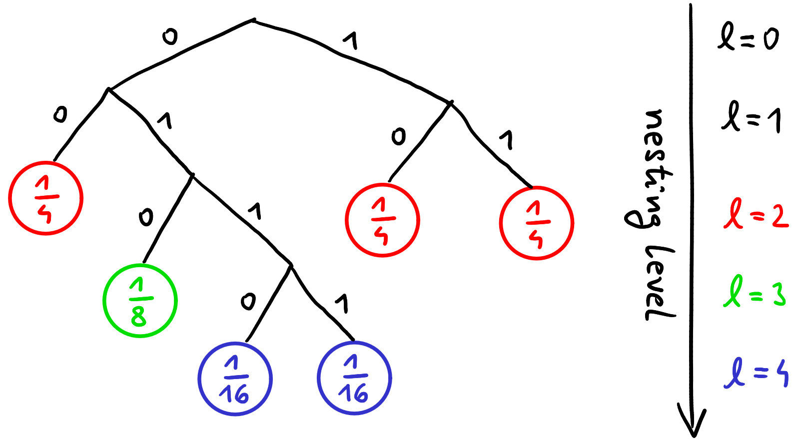
identification via binary questions

→ binary search tree

optimal tree

– yes/no answers come with $P = \frac{1}{2}$

$N = 6 \qquad \{P_i\} = \{\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{8}, \frac{1}{16}, \frac{1}{16}\}$




state $i$ with $P_i = 2^{-\ell_i}$ identified by $\ell_i = -\log_2 P_i$ questions

average number of questions needed : $-\sum_i P_i \log_2 P_i$ ~ entropy

- thermodynamic entropy (von Neumann)

$$S = -k_B \sum_i p_i \ln p_i = -k_B \,\mathrm{Tr}\,\hat{\rho} \ln \hat{\rho} = -k_B \langle \ln \hat{\rho} \rangle$$

entropy limits: pure state – single $p_i = 1 \rightarrow S = 0$

maximally mixed state – all $p_i = \dfrac{1}{\dim \mathcal{H}} \rightarrow S = k_B \ln(\dim \mathcal{H})$

Ex entropy limits of a system containing $N$ spin-$\frac{1}{2}$ moments

- towards equlibrium in thermodynamics

1st law $dU = \delta Q + \delta W$  2nd law $\dfrac{\delta Q}{T} \leq dS$ ($<$ sign for irreversible processes)

$$\left.\begin{array}{l} \text{combination for } \delta W = 0 \text{ (no work done) gives } dU \leq T dS \\ \text{Helmholtz free energy } F = U - TS \rightarrow dF = dU - TdS - SdT \end{array}\right\} dF \leq -S dT$$

at constant $T$ irreversible processes reduce $F$ until equilibrium is reached

$\rightarrow$ $F$ is minimized at const. $T$

## ③ Equilibrium density matrices

- canonical ensemble – constant $T$ and fixed number of particles

→ minimization of $F = U - TS$

in eigenbasis of $\hat{H}$

$$\left.\begin{aligned} U &= \langle \hat{H} \rangle = \sum_i p_i E_i \\ S &= -k_B \langle \ln \hat{\rho} \rangle = -k_B \sum_i p_i \ln p_i \end{aligned}\right\} \quad F = U - TS = \sum_i p_i (E_i + k_B T \ln p_i)$$

minimization of $F$ with respect to $p_i$ under the constraint $\sum_i p_i = 1$

$$\frac{\partial}{\partial p_i}\left[F - \lambda\left(\sum_i p_i - 1\right)\right] = 0 \quad \rightarrow \quad E_i + k_B T \ln p_i + p_i k_B T \frac{1}{p_i} - \lambda = 0$$

implies $p_i = \frac{1}{Z} e^{-\frac{E_i}{k_B T}}$ with the normalization constant $Z = \sum_i e^{-\frac{E_i}{k_B T}}$

converted to operator form $\hat{\rho} = \frac{1}{Z} \sum_i |\psi_i\rangle e^{-\frac{E_i}{k_B T}} \langle \psi_i| = \frac{1}{Z} e^{-\frac{\hat{H}}{k_B T}}$ $\quad Z = \mathrm{Tr}\, e^{-\frac{\hat{H}}{k_B T}}$

- grandcanonical ensemble
  - system coupled to both thermal bath and a reservoir of particles

    constant $T$ and chemical potential $\mu$ → minimization of Gibbs free energy

$$G = U - TS - \mu N = \langle \hat{H} \rangle - k_B T \langle \ln \hat{\rho} \rangle - \mu \langle \hat{N} \rangle = \sum_i p_i \left( E_i + k_B T \ln p_i - \mu N_i \right)$$

minimization of $G$ w.r.t. $p_i$ under the constraint $\sum_i p_i = 1$ gives

grandcanonical density matrix $\hat{\rho} = \frac{1}{Z} e^{-\frac{\hat{H} - \mu \hat{N}}{k_B T}}$ $\quad Z = \mathrm{Tr}\, e^{-\beta(\hat{H} - \mu \hat{N})}$ $\quad \beta = \frac{1}{k_B T}$

## 4 Independent particles: Fermi-Dirac & Bose-Einstein statistics

$\hat{H} = \sum_k \varepsilon_k \hat{n}_k$ occupations $n_k = 0, 1$ fermions

$n_k = 0, 1, 2, \ldots \infty$ bosons

eigenstates given by occupations $E_i = \varepsilon_1 n_1 + \varepsilon_2 n_2 + \varepsilon_3 n_3 + \ldots$

$N_i = n_1 + n_2 + n_3 + \ldots$

grandcanonical partition sum

$$Z_k = \sum_{n_k} e^{-\beta(\varepsilon_k-\mu)n_k}$$

$$Z = \sum_{n_1}\sum_{n_2}\sum_{n_3}\cdots e^{-\beta[(\varepsilon_1-\mu)n_1+(\varepsilon_2-\mu)n_2+(\varepsilon_3-\mu)n_3+\dots]} = \prod_k Z_k$$

occupation average

$$\langle n_k\rangle = \sum_{n_1}\sum_{n_2}\sum_{n_3}\cdots n_k \underbrace{\frac{1}{Z} e^{-\beta[(\varepsilon_1-\mu)n_1+(\varepsilon_2-\mu)n_2+(\varepsilon_3-\mu)n_3+\dots]}}_{p_i}$$

$$= \sum_{n_1}\sum_{n_2}\sum_{n_3}\cdots \frac{1}{Z}\left\{-\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_k} e^{-\beta[(\varepsilon_1-\mu)n_1+(\varepsilon_2-\mu)n_2+(\varepsilon_3-\mu)n_3+\dots]}\right\}$$

$$= \frac{1}{Z}\left(-\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_k}Z\right) = -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_k}\ln Z = -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_k}(\ln Z_1+\ln Z_2+\dots) = -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_k}\ln Z_k$$

fermions $\quad Z_k = 1+e^{-\beta(\varepsilon_k-\mu)} \rightarrow \langle n_k\rangle = n_{FD}(\varepsilon_k) = \dfrac{1}{e^{\beta(\varepsilon_k-\mu)}+1}$

bosons $\quad Z_k = \displaystyle\sum_{n=0}^{\infty} e^{-\beta(\varepsilon_k-\mu)n} = \frac{1}{1-e^{-\beta(\varepsilon_k-\mu)}} \rightarrow \langle n_k\rangle = N_{BE}(\varepsilon_k) = \frac{1}{e^{\beta(\varepsilon_k-\mu)}-1}$