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VI.2 The ensembles

Entropy of a density operator:

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

p_i: eigenvalues

closed system → fixed energy $\langle E \rangle = \mathrm{Tr}\, \hat\rho \hat H$

maximize entropy under constraints $\mathrm{Tr}\,\hat\rho = 1$ and $\mathrm{Tr}\,\hat\rho \hat H = E$

$$0 = \frac{\partial}{\partial \hat\rho} \underbrace{\left[-\mathrm{Tr}\, \hat\rho \ln \hat\rho + \lambda (\mathrm{Tr}\,\hat\rho - 1) + \mu (E - \mathrm{Tr}\,\hat\rho \hat H) \right]}_{q(\hat\rho)}$$

$$q(\hat\rho + \delta\hat\rho) - q(\hat\rho) = -\mathrm{Tr}\left[(\hat\rho + \delta\hat\rho) \ln(\hat\rho + \delta\hat\rho)\right] - \lambda + \lambda \mathrm{Tr}(\hat\rho + \delta\hat\rho)$$
$$+ \mu E - \mu \mathrm{Tr}(\hat\rho + \delta\hat\rho)\hat H + \mathrm{Tr}\,\hat\rho \ln \hat\rho + \lambda - \lambda \mathrm{Tr}\,\hat\rho$$
$$- \mu E + \mu \mathrm{Tr}\,\hat\rho \hat H$$

$$= -\underbrace{\mathrm{Tr}\left[(\hat\rho + \delta\hat\rho) \ln(\hat\rho + \delta\hat\rho)\right]}_{\ast} + \mathrm{Tr}\,\hat\rho \ln \hat\rho + \lambda \mathrm{Tr}\,\delta\hat\rho - \mu \mathrm{Tr}\,\hat H \delta\hat\rho$$

$$\ln(\hat\rho + \delta\hat\rho) = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} (\hat\rho + \delta\hat\rho - \hat I)^n = \underbrace{\sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} (\hat\rho - \hat I)^n}_{\ln \hat\rho} + \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} \sum_{k=0}^{n-1} (\hat\rho - \hat I)^k \delta\hat\rho (\hat\rho - \hat I)^{n-k-1} + O(\delta\hat\rho^2)$$

$$\ast = \mathrm{Tr}(\hat\rho \ln \hat\rho + \delta\hat\rho \ln \hat\rho) + \mathrm{Tr}\left(\hat\rho \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} \sum_{k=0}^{n-1} (\hat\rho - \hat I)^k \delta\hat\rho (\hat\rho - \hat I)^{n-k-1}\right) + O((\delta\hat\rho)^2)$$

$$= -\mathrm{Tr}\, \delta\hat\rho \ln \hat\rho - \mathrm{Tr}\, \hat\rho \hat\rho^{-1} \delta\hat\rho + \lambda \mathrm{Tr}\, \delta\hat\rho - \mu \mathrm{Tr}\, \hat H \delta\hat\rho$$

$$= \mathrm{Tr}\left\{ \delta\hat\rho \left[-\ln \hat\rho - \hat I + \lambda \hat I - \mu \hat H \right] \right\}$$

$$= \sum_{ij} (\delta\hat\rho)_{ij} \left[\ln \hat\rho - \hat I + \lambda \hat I - \mu \hat H \right]_{ji} = 0 \text{ for all } \delta\hat\rho$$

$$\Rightarrow -\ln \hat\rho - \hat I + \lambda \hat I - \mu \hat H = 0 \Rightarrow \hat\rho = e^{\lambda - 1} e^{-\mu \hat H}$$

$\mathrm{Tr}\,\hat{\varrho}=1 \quad \Rightarrow \quad \hat{\varrho} = \frac{e^{-\mu \hat{H}}}{\mathrm{Tr}\, e^{-\mu\hat{H}}}$

comparison with previous derivation of canonical ensemble:

$$\hat{\varrho} = \frac{e^{-\beta\hat{H}}}{\mathrm{Tr}\, e^{-\beta\hat{H}}}$$

partition function $Z = \mathrm{Tr}\, e^{-\beta\hat{H}}$

free energy $\quad F = U - TS = \mathrm{Tr}\,\hat{\varrho}\hat{H} + T k_B\, \mathrm{Tr}\,\hat{\varrho}\ln\hat{\varrho}$

Analogously: $\quad = \mathrm{Tr}\,\hat{\varrho}\hat{H} + T k_B\, \mathrm{Tr}\,\hat{\varrho}\,(-\beta\hat{H} - \ln Z)$

<u>closed and isolated system</u> $\quad \underset{\mathrm{Tr}\hat{\varrho}=1}{=} -k_B T \ln Z$

$$\hat{\varrho} = \frac{\delta(E-\hat{H})}{\mathrm{Tr}\,\delta(E-\hat{H})}$$

<u>open system</u>

$$\hat{\varrho} = \frac{e^{-\beta\hat{H}+\beta\mu'\hat{N}}}{\mathrm{Tr}\, e^{-\beta\hat{H}+\beta\mu'\hat{N}}}$$

grand partition function $\quad Z = \mathrm{Tr}\, e^{-\beta\hat{H}+\beta\mu'\hat{N}}$

grand potential

$$\Omega = U - TS - \mu' N = \mathrm{Tr}\,\hat{\varrho}\hat{H} + T k_B\, \mathrm{Tr}\,\hat{\varrho}\ln\hat{\varrho} - \mu'\,\mathrm{Tr}\,\hat{\varrho}\hat{N}$$

$$= \mathrm{Tr}\,\hat{\varrho}\hat{H} + k_B T\, \mathrm{Tr}\,\hat{\varrho}\,(-\beta\hat{H} + \beta\mu'\hat{N} - \ln Z) - \mu'\,\mathrm{Tr}\,\hat{\varrho}\hat{N}$$

$$\underset{\mathrm{Tr}\hat{\varrho}=1}{=} -k_B T \ln Z$$

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