

Gibbs entropy [tln48]

At thermal equilibrium: $\partial\rho/\partial t = 0$. This condition is satisfied by $\rho = \rho(H)$.

Q: What is the functional dependence of ρ on H ?

A: $\rho(H)$ must maximize the entropy $S(\rho)$ subject to the constraints related to whether the system is isolated, closed, or open.

Q: What is the functional dependence of S on ρ ?

A: The Gibbs entropy can be motivated by Boltzmann's H -function and by Shannon's concept of uncertainty:

- classical system: $S = -k_B \int d^{6N} X \rho(\mathbf{X}) \ln[C_N \rho(\mathbf{X})]$,
- quantum system: $S = -k_B \text{Tr}[\rho \ln \rho]$.

The additive constant C_N in the classical expression allocates a certain phase-space volume element to every microstate:

- distinguishable particles: $C_N = h^{3N}$, $h \simeq 6.62 \times 10^{-34}$ Js,
- indistinguishable particles: $C_N = h^{3N} N!$.

The factor $N!$ is needed to compensate for overcounting indistinguishable permutations of identical particles. No correction is necessary in quantum mechanics, where microstates have definite permutation symmetries.

Q: Why does one microstate require a nonzero phase-space volume element?

A: The Heisenberg uncertainty principle, $\Delta q_i \Delta p_i \geq \frac{1}{2} \hbar$, must be satisfied to accommodate quantum mechanical microstates.

Q: What is the precise size of that volume needed for one microstate?

A: The volume element is h^{3N} for a system with $3N$ degrees of freedom.

Number of microstates in volume element $d^{6N} X$: $\frac{1}{h^{3N}} d^{6N} X = \prod_{i=1}^{3N} \left[\frac{1}{h} dq_i dp_i \right]$.

Illustration: harmonic oscillator (2D phase space).

$$\text{Hamiltonian: } H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 q^2 = \frac{h\omega}{2\pi} \left(n + \frac{1}{2} \right).$$

Classical trajectories are concentric ellipses with axes $2q_{max}, 2p_{max}$.

Energy quantization implies quantized amplitudes:

$$q_{max} = \sqrt{\frac{h}{\pi m \omega} \left(n + \frac{1}{2} \right)}, \quad p_{max} = \sqrt{\frac{h m \omega}{\pi} \left(n + \frac{1}{2} \right)}.$$

Area of ellipse: $A(n) = \pi q_{max} p_{max} = h(n + 1/2) \Rightarrow A(n+1) - A(n) = h$.