Microcanonical ensemble [tln49]

Consider an isolated classical system (volume V, N particles, internal energy U). The goal is to determine the thermodynamic potential $U(S,V,N)$ pertaining to that situation, from which all other thermodynamic properties can be derived.

Maximize Gibbs entropy $S = -k_B \displaystyle\int_{U\leq H(\mathbf{X})\leq U+\Delta} d^{6N}X\,\rho(\mathbf{X})\ln[C_N\rho(\mathbf{X})]$

subject to the contraint $\displaystyle\int_{U\leq H(\mathbf{X})\leq U+\Delta} d^{6N}X\,\rho(\mathbf{X}) = 1$ (normalization).

Apply calculus of variation with one Lagrange multiplier:

$$\delta\int d^{6N}X\{-k_B\rho\ln[C_N\rho]+\alpha_0\rho\}=0$$

$$\Rightarrow\quad \int d^{6N}X\,\delta\rho\{-k_B\ln[C_N\rho]-k_B+\alpha_0\}=0.$$

$$\Rightarrow\quad \rho(\mathbf{X})=\frac{1}{C_N}\exp\left(\frac{\alpha_0}{k_B}-1\right)=\text{const}=\begin{cases}\Omega_\Delta^{-1} & U\leq H(\mathbf{X})\leq U+\Delta\\ 0 & \text{otherwise,}\end{cases}$$

where $\Omega_\Delta(U,V,N)=\displaystyle\int_{U\leq H(\mathbf{X})\leq U+\Delta} d^{6N}X$ is the volume of the energy shell.

Thermodyn. potentials: $S(U,V,N)=k_B\ln\left[\dfrac{\Omega_\Delta(U,V,N)}{C_N}\right]\ \Rightarrow\ U(S,V,N)$.

The dependence of S or U on the energy width Δ is undesirable and can, in fact, be avoided. If we replace the shell volume $\Omega_\Delta(U,V,N)$ by the entire volume inside the shell, $\Omega(U,V,N)$, the resulting expression for $S(U,V,N)$ differs only by a term $\propto \ln N$, which is negligible in macroscopic systems.

$$\Rightarrow\quad S(U,V,N)=k_B\ln\left[\frac{\Omega(U,V,N)}{C_N}\right],\ \text{where}\ \Omega(U,V,N)=\int_{H(\mathbf{X})\leq U} d^{6N}X.$$

Consider an isolated quantum system: $H|n\rangle = E_n|n\rangle$.

Maximize $S=-k_B\displaystyle\sum_{E_n<U} p_n\ln p_n$ subject to the constraint $\displaystyle\sum_{E_n<U} p_n = 1$.

$$\Rightarrow\quad p_n=\frac{1}{N_<(U)}\ \text{where}\ N_<(U)=\sum_{E_n<U}.\quad\Rightarrow\quad S=k_B\ln[N_<(U)].$$