Ensemble averages

All thermodynamic quantities of a closed system can be inferred from the canonical partition function $Z_N$ via the associated thermodynamic potential:

$$Z_N = \frac{1}{C_N} \int_{\Gamma} d^6N X \exp (-\beta H(X)), \quad \beta = \frac{1}{k_BT}.$$ 

Further properties of the system can be obtained from the canonical probability density $\rho(X)$ via equilibrium expectation values of arbitrary dynamical variables $f(X)$:

$$\langle f \rangle = \int_{\Gamma} d^6N X \rho(X) f(X), \quad \rho(X) = \frac{1}{Z_N C_N} \exp (-\beta H(X)).$$ 

From such expectation values, we can recover thermodynamic quantities and calculate fluctuations thereof, which are related to response functions, i.e. different thermodynamic quantities. Other expectation values, e.g. correlation functions, cannot be inferred directly from $Z_N$.

- Uncertainty about microstate and entropy:
  $$S = -k_B \int_{\Gamma} d^6N X \rho(X) \ln[C_N \rho(X)].$$

- Average value $H$ and internal energy:
  $$\langle H \rangle = \int_{\Gamma} d^6N X \rho(X) H(X) = \frac{1}{Z_N C_N} \int_{\Gamma} d^6N X H(X) e^{-\beta H(X)}$$
  $$\Rightarrow \langle H \rangle = -\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z_N = \frac{\partial}{\partial \beta} (\beta A)$$

  Use $\frac{\partial}{\partial \beta} = \left( \frac{\partial T}{\partial \beta} \right) \frac{\partial}{\partial T} = -k_B T^2 \frac{\partial}{\partial T}$ \Rightarrow \langle H \rangle = A - T \frac{\partial A}{\partial T} = A + TS = U.$$

- Energy fluctuations and heat capacity:
  $$\langle H^2 \rangle - \langle H \rangle^2 = \frac{1}{Z_N} \frac{\partial^2 Z_N}{\partial \beta^2} - \left[ \frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} \right]^2 = \frac{\partial}{\partial \beta} \left[ \frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} \right]$$
  $$\Rightarrow \langle H^2 \rangle - \langle H \rangle^2 = \frac{\partial^2}{\partial \beta^2} \ln Z_N = -\frac{\partial U}{\partial \beta} = k_B T^2 \frac{\partial U}{\partial T} = k_B T^2 C_V.$$