Kanonische Gesamtheit $\langle E \rangle = U$ (Austausch von Wärme)

$$\rho = \sum_n W_n |\psi_n\rangle\langle\psi_n| \qquad H|\psi_n\rangle = E_n|\psi_n\rangle$$

$$W_n = \text{const} \cdot \exp\left[-\frac{qE_n}{k_B}\right] = \frac{1}{Z} e^{-\beta E_n}$$

$$S = -k_B \sum_n W_n \ln W_n = -k_B \sum \frac{1}{Z} e^{-\beta E_n}(-\ln Z - \beta E_n)$$
$$= k_B \ln Z + k_B \beta \frac{1}{Z} \sum e^{-\beta E_n} \cdot E_n = k_B \ln Z + k_B \beta U$$

$$Z = \sum_n e^{-\beta E_n}$$

$$\frac{\partial}{\partial \beta} Z = -\sum_n E_n e^{-\beta E_n} = -ZU$$

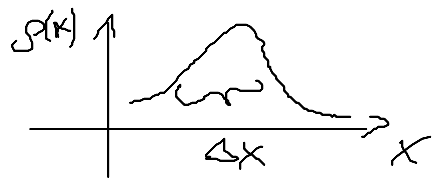
$$\frac{\partial}{\partial \beta} \ln Z = -U \quad \Rightarrow \quad U(\beta),\ \beta(U)$$

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} = k_B \beta + k_B U \frac{\partial \beta}{\partial U} + k_B \frac{\partial \ln Z}{\partial \beta} \frac{\partial \beta}{\partial U} = k_B \beta$$

$$\boxed{\beta = \frac{1}{k_B T}}$$

$$TS = U + k_B T \ln Z \quad \Rightarrow \quad \boxed{F = -k_B T \ln Z} \text{ freie Energie}$$
$$F(T,V,N) = U - TS$$

Fluktuationen (Schwankungen)



Größe X (stochastisch) $\rho(X)$ (Verteilungsfkt)

$$\int dx\, \rho(x) = 1$$

$$\langle x \rangle = \int dx\, \rho(x) \cdot x$$

$$\delta x = x - \langle x \rangle \text{ mit } \langle \delta x \rangle = \langle x \rangle - \langle x \rangle = 0$$

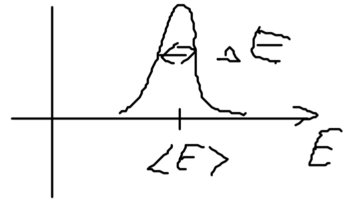
$\langle (\delta x)^2 \rangle$ = Schwankungen, Breite der Verteilungsfkt

$$= \langle (x^2 - 2x\langle x \rangle + \langle x \rangle^2) \rangle$$
$$= \langle x^2 \rangle - (\langle x \rangle)^2$$

kanonisch

$\Delta E^2 \sim N \Rightarrow \Delta E \sim \sqrt{N}$

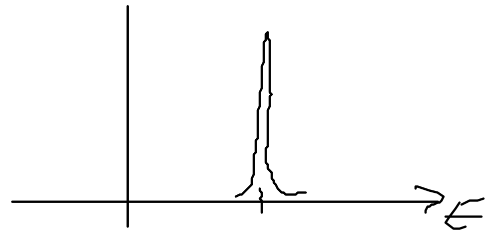
Maß für Stärke der Schwankungen: $\frac{\Delta E}{\langle E \rangle} \sim \frac{1}{\sqrt{N}}$



mikrokanonisch

von beiden Ensemble leicht gleich.

für $N \to \infty$



Großkanonische Gesamtheit

Austausch von Wärme und Teilchen