III, 4. Entropy in an isolated system

To show: The entropy of an isolated system is maximal in equilibrium

(note: We have used this statement several times, but have not justified it so far!)

consider two statistical operators $\hat{\rho}$ and $\hat{\rho}'$ where

$\hat{\rho}$: statistical operator in equilibrium

$\hat{\rho}'$: " " in some non-equilibrium state

assumptions: $\underset{\text{Trace}}{\mathrm{Sp}}\,\hat{\rho} = \mathrm{Sp}\,\hat{\rho}' = 1$

, $\hat{\rho}|n\rangle = p_n |n\rangle$; $\hat{\rho}'|n'\rangle = p_{n'}|n'\rangle$

$\hat{\rho} = \sum_n p_n |n\rangle\langle n|$, $\hat{\rho}' = \sum_n p_n' |n'\rangle\langle n'|$

and $\rho, \hat{\rho}$ hermite operators

define the function

$$\mathcal{H} = \mathrm{Sp}\left(\hat{\rho}' \ln \hat{\rho} - \hat{\rho}' \ln \rho'\right)$$

goal: Estimate an upper limit for $\mathcal{H}$!

$\Rightarrow$

$$\mathcal{H} = Sp\, \hat\rho' \ln\hat\rho - Sp\,\hat\rho' \ln\hat\rho'$$

$$= \sum_n \left(\langle n'|\hat\rho' \ln\hat\rho|n'\rangle - \langle n'|\hat\rho' \ln\hat\rho'|n'\rangle \right)$$

$$= \sum_n p_{n'} \langle n'|\ln\hat\rho|n'\rangle - p_{n'} \ln p_{n'} \langle n'|n'\rangle$$

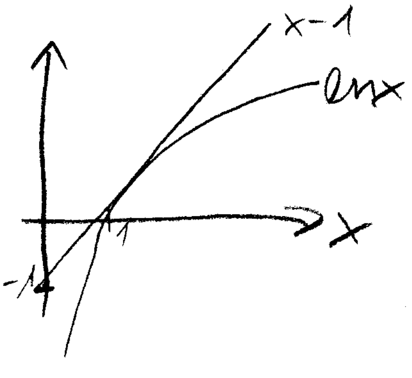
$$= \sum_{n,m} p_{n'} \left(\langle n'|\ln\hat\rho|m\rangle\langle m|n'\rangle - \ln p_{n'} \langle n'|m\rangle\langle m|n'\rangle \right)$$

$$= \sum_{n,m} p_{n'} \left(\ln p_m \, |\langle n'|m\rangle|^2 - \ln p_{n'} \, |\langle n'|m\rangle|^2 \right)$$

$$= \sum_{n,m} p_{n'} \ln \frac{p_m}{p_{n'}} \, |\langle n'|m\rangle|^2$$

one has:

$$\ln x \leq x - 1 \quad \text{for } x > 0$$



application:

$$\underbrace{\frac{p_m}{p_{n'}}}_{\text{ratio of probabilities}} > 0 \quad \Rightarrow \quad \ln \frac{p_m}{p_{n'}} \leq \frac{p_m}{p_{n'}} - 1$$

$$\Rightarrow \mathcal{H} \leq \sum_{n,m} p_{n'} \left(\frac{p_m}{p_{n'}} - 1 \right) |\langle n'|m\rangle|^2$$

$$= \sum_{n,m} p_m \left(\langle n'|m\rangle\langle m|n'\rangle - p_{n'} \langle n'|m\rangle\langle m|n'\rangle \right)$$

$$\mathcal{H} \leq \sum_n \langle n' | \overbrace{\sum_m p_m |m\rangle\langle m|}^{\hat{\rho}} n' \rangle$$

$$- \sum_m \langle m | \underbrace{\sum_n p_n' |n'\rangle\langle n'|}_{\hat{\rho}} m \rangle$$

$$= Sp\,\hat{\rho} - Sp\,\hat{\rho} = 1 - 1$$

note: Trace is independent of the basis!

$$= 0$$

This holds for arbitrary non-equilibrium states characterized by an operator $\hat{\rho}'$!

now apply this to the entropy:

$$S = -k_B\, Sp\,\hat{\rho} \ln \hat{\rho}$$

$$S' = -k_B\, Sp\,\hat{\rho}' \ln \rho'$$

entropy of a non-equilibrium state

$$\Rightarrow \mathcal{H} = Sp(\hat{\rho}' \ln \hat{\rho}) - Sp(\hat{\rho}' \ln \hat{\rho}')$$

$$= Sp(\hat{\rho}' \ln \hat{\rho}) + k_B^{-1} S' \qquad (*)$$

$\rightarrow$

note:

$$Sp(\hat{\rho}' \ln \hat{\rho}) = \sum_n \langle n | \hat{\rho}' \ln \hat{\rho} | n \rangle$$

$$= \sum_n \ln p_n \langle n | \hat{\rho}' | n \rangle$$

probabilities in the <u>equilibrium</u> distribution!

now consider the microcanonical ensemble (isolated system)

$$p_n = \begin{cases} \frac{1}{\Omega(E,N)}, & \text{within the energy shell} \\ 0 & \text{else} \end{cases}$$

$$\Rightarrow Sp(\hat{\rho}' \ln \hat{\rho}_{MK}) = \ln \frac{1}{\Omega} \sum_n \langle n | \hat{\rho}' | n \rangle$$

$$= \ln \frac{1}{\Omega} \underbrace{Sp\, \hat{\rho}'}_{1} = \ln \frac{1}{\Omega} = -\ln \Omega$$

$$= -k_B^{-1} S$$

equilibrium entropy in the microcanonical ensemble

insert in (*)

$$\Rightarrow k_B \mathcal{H} = S' - S$$

now use the inequality of $\mathcal{H}$.

$$\mathcal{H} \leq 0 \quad \Rightarrow S' - S \leq 0$$

$$\Leftrightarrow S' \leq S$$

for any non-equilibrium state!

$\Rightarrow$ all processes in an isolated system, which transform a non-equilibrium state into an equilibrium state behave such the entropy increases!

$\Rightarrow$ 2nd law of thermodynamics:

$$dS \geq 0 \quad \text{in an isolated system}$$

note:

The inequality for $\mathcal{H}$ can also be applied to a canonical system, where $\hat{\rho} = \hat{\rho}_K = \frac{1}{Z_K} \sum_n e^{-\beta E_n} |n\rangle\langle n|$

$$\Rightarrow Sp(\hat{\rho}' \ln \hat{\rho}) = \sum_n \langle n|\hat{\rho}' \ln \hat{\rho}|n\rangle = \sum_n \ln p_n \langle n|\hat{\rho}'|n\rangle$$

$$= \sum_n (-\ln Z_K - \beta E_n) \langle n|\hat{\rho}'|n\rangle$$

$\longrightarrow$

$$\Rightarrow Sp(\hat{\rho}' \ln \hat{\rho})$$

$$= -\ln Z_K \underbrace{Sp\hat{\rho}'}_{1} - \beta \sum_n E_n \langle n|\hat{\rho}'|n\rangle$$

$$= -\ln Z_K - \beta \sum_n \langle n|\hat{\rho}'\hat{H}|n\rangle$$

$$= -\ln Z_K - \beta \underbrace{Sp\,\hat{\rho}'\hat{H}} = -\ln Z_K - \beta U'$$

Average Energy in the non-equilibrium state!

$$= +(k_B T)^{-1} F - \beta U'$$

Free energy in equilibrium

insert in (*)

$$\Rightarrow k_B \mathcal{H} = \frac{1}{T}(F - U') + S' \leq 0$$

$$\Leftrightarrow F \leq U' - TS' = F'$$

Free energy in non-equilibrium

$$\Leftrightarrow \boxed{dF \leq 0}$$

Free energy is <u>minimal</u> in equilibrium!

Similarly one can show:

$dJ \leq 0$ system at fixed T, V, μ

grandcanonical free energy

III.5 Statistical interpretation of heat and work

motivation: In III.4. we have found arguments for the second law ($dS \geq 0$) in an isolated system

What about the first law?

Consider the average energy in a system characterized by a statistical operator $\hat{\rho}$

$$\Rightarrow \quad \bar{E} = \langle H \rangle = \mathrm{Sp}\, \hat{\rho} \hat{H} \qquad \text{with } \mathrm{Sp}\, \hat{\rho} = 1$$

Consider the variation of $\bar{E}$ (at fixed N)

$$d\bar{E} = \mathrm{Sp}\big(\underbrace{d\hat{\rho}}_{\text{change of } \hat{\rho}} \hat{H} + \hat{\rho} \underbrace{d\hat{H}}_{\text{change of } \hat{H}} \big) \qquad (*)$$

On the other hand, one has

$$S = -k_B\, \mathrm{Sp}\, \hat{\rho} \ln \hat{\rho}$$

$$\Rightarrow dS = -k_B\, \mathrm{Sp}\, (d\hat{\rho} \ln \hat{\rho} + 1 \cdot d\hat{\rho})$$

$$= -k_B\, \mathrm{Sp}\, (d\hat{\rho} \ln \hat{\rho}) - k_B\, \mathrm{Sp}(d\hat{\rho})$$

density operator after the change

assume that $\mathrm{Sp}(\hat{\rho} + d\hat{\rho}) = \mathrm{Sp}(\hat{\rho}) = 1$

$\Leftrightarrow \mathrm{Sp}(d\hat{\rho}) = 0\,!$

$$\Rightarrow dS = -k_B\, \mathrm{Sp}(d\hat{\rho} \ln \hat{\rho})$$

Folgerungen:

es gilt: $T dS \geq dE + p dV - \mu dN$ (+)

$$\Rightarrow dF = d(E-TS) = dE - TdS - SdT$$

$$\leq dE - dE - pdV + \mu dN - SdT$$

also: $dF \leq -pdV + \mu dN - SdT$

falls speziell $\underbrace{T, V, N}_{\text{natürliche Variablen von } F\,!}$ konstant: $\boxed{dF \leq 0}$

Veranschaulichung

Betrachte System, das außer von T, V, N noch von weiteren Parametern abhängt (x)

↓

z.B. Magnetisierung
Konzentration einer Komponente
Teilchenzahl eines Subsystems

Folgerung aus $dF \leq 0$:
Im Gleichgewicht stellt sich x (bei festgehaltenen T, V, N) so ein, daß F minimal wird!

z.B. Ferromagnet:

$$H = -J \sum_{i,j} s_i s_j \quad , \quad s_i = \pm 1$$

positive, homogene Kopplung

$\Rightarrow$ F kann geschrieben werden als $\tilde{F}(T, N, m)$
(z.B. Landau-Theorie)
Weiss'sche Theorie

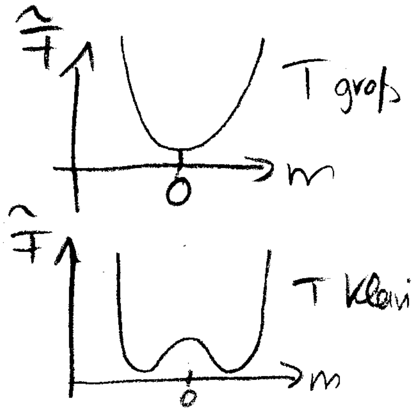
mit $m = \frac{1}{N} \sum_{i=1}^{N} \langle s_i \rangle$
Magnetisierung pro Teilchen

$\Rightarrow$ Gleichgewichts-Wert für m folgt aus der Bedingung:

$$\frac{\partial \hat{F}}{\partial m} = 0 \qquad \frac{\partial^2 \hat{F}}{\partial m^2} > 0$$

qualitatives Verhalten:

- hohe Temperatur: $m = 0$
- tiefe Temperatur: $m \neq 0$



— konsistent mit der Tatsache, daß $F = E - TS$!

denn: hohe T: Entropieterm dominiert $\rightarrow$ Unordnung
tiefe T: Energieterm " $\rightarrow$ Ordnung entsprechend des vorgegebenen Hamiltonian!

analog zur Freien Energie kann man zeigen:

- $dJ \leq -SdT - pdV - Nd\mu \qquad (J = F - \mu N)$

$\Leftrightarrow dJ \leq 0$ für $T, V, \mu = \text{const}$

$\Rightarrow$ Großkanonische Potential ist minimal im Gleichgewicht!

- $dG \leq -SdT + VdP + \mu dN \qquad (G = F + pV)$

$\Rightarrow$ auch G ist minimal im Gleichgewicht