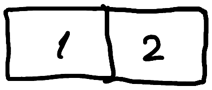
Reminder: thermodynamic function

Entropy

The most generic defintion $\boxed{S = -\mathrm{Tr}\left(\hat{\rho}\ln\hat{\rho}\right)}$



Two subsystems of a bigger system

$$\rho_{12} = \rho_1\rho_2 \longrightarrow \ln\rho_{12} = \ln\rho_1 + \ln\rho_2$$

$\ln\rho$ is an additive function

For a quasi-closed subsystem (= big), it should be a combination of additive of motion: $E, \vec{P}, \vec{L}$

$$\ln\rho = \alpha + \beta E + \cancelto{0}{\vec{\gamma}\vec{P} + \vec{\delta}\vec{L}}$$

in an isotropic system

For a system with discrete levels

$$\ln w_n = \alpha + \beta E_n \quad \text{(in equilibrium)}$$

We may write the average

$$\langle \ln w_n \rangle = \alpha + \beta \bar{E}$$

An additive function

$$S = -\langle \ln w_n \rangle \equiv -\sum_n w_n \ln w_n$$

Generaliseable to the case when the system is not in equilibrium, but consists of several parts which are in local equilibrium

This leads to the above formula

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In a quasistationary process $\boxed{dS = \frac{\delta Q}{T}}$

In an arbitrary process $dS \geq \frac{\delta Q}{T}$

Generic method of solving lots of thermodynamic problems

Ham-n $\hat{H} \longrightarrow$ Eigenenergies E_n

$$\rightarrow Z = \sum_n e^{-\frac{E_n}{T}} \quad \left(= \operatorname{Tr} e^{-\frac{\hat{H}}{T}}\right)$$

$\rightarrow$ Free energy $F = -T \ln Z$

$$\rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad P = -\left(\frac{\partial F}{\partial V}\right)_T$$

That follows from the relation
energy $F = E - TS$ (you can verify it directly)

$$dF = dE - TdS - SdT = -PdV - SdT$$

what if the number of particles is variable?

Consider the grand-canonical partition function

$$\tilde{Z} = \operatorname{Tr}\left(e^{\frac{\mu \hat{N} - \hat{H}}{T}}\right)$$

and use the grand-canonical potential

$$\Omega = -T \ln \tilde{Z}$$

and use the grand ...

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Then use it instead of F

<u>Other important thermodynamic functions</u>

$$F = E - TS$$

$$\varphi = E - TS + PV$$

$$H = E + PV$$

Each of them is a function of 2 variables

$$dF = -S\,dT - P\,dV + \mu\,dN$$

$$d\varphi = -S\,dT + V\,dP + \mu\,dN$$

$$dH = T\,dS + V\,dP + \mu\,dN$$

By differentiating twice, you can obtain Maxwell's relations

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$