Internal energy. Pressure. First law of thermodynamics.

$$\delta Q = \delta W + \delta E$$

- <u>the first law of thermodynamics</u> =

= energy conservation law

$\delta W = -\delta W_{ext}$ — work done by the system = minus work done <u>on</u> the system

E is a function of the state of the system, when the system returns to its initial state,

$$\oint dE = 0$$

$$E = \frac{\sum_i \varepsilon_i e^{-\frac{\varepsilon_i}{T}}}{\sum_i e^{-\frac{\varepsilon_i}{T}}} = \frac{\partial Z}{\partial(-\frac{1}{T})} \cdot \frac{1}{Z} = T^2 \frac{\partial \ln Z}{\partial T}$$

Thus, knowing the partition function allows one to obtain the internal energy immediately

Energy is an <u>extensive</u> property: the total energy of a system is a sum of internal energies of constituent parts

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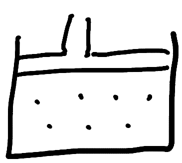
The state of the system depends also on external fields (they modify effectively the parameters of the Hamiltonian) = External forces. For instance,



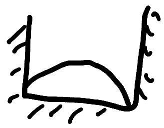
Gas under a piston

Or external field

Consider again a quantum system with energy

Consider again a quantum system with energy levels $\varepsilon_i = \varepsilon_i(\lambda)$, λ - external parameter.

Examples: particle in a box



$$\varepsilon_i = \frac{\pi^2 \hbar^2 i^2}{2mL^2} \quad \text{(similarly in 3D)}$$

$+ \, \vec{p} \, -$ - a rigid dipole $\quad -\vec{p}\vec{E}$

Harmonic oscillator: $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2 x^2}{2}$

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

Consider a very small change of the external parameter λ

$$\delta\varepsilon_i = \underbrace{\left(\frac{\partial \varepsilon_i}{\partial \lambda}\right)_{w_i}}_{\text{a generalised force } -f_i} \delta\lambda$$

$$\delta\varepsilon_i = -f_i \, \delta\lambda$$

The change of the average energy in the process we consider

$$\delta E = \sum_i \delta\varepsilon_i w_i = -\sum_i f_i w_i \, \delta\lambda = -\Lambda \, \delta\lambda$$

Λ - average force; $\Lambda = -\left(\sum f_i w_i\right)_{w_i}$

Quite often we will be talking about pressure

$$(\delta E)_{w_i} = -P\,\delta V$$

(... $P = \left(\frac{\partial E}{\ldots}\right)$)

$(\delta E)_{w_i} =$

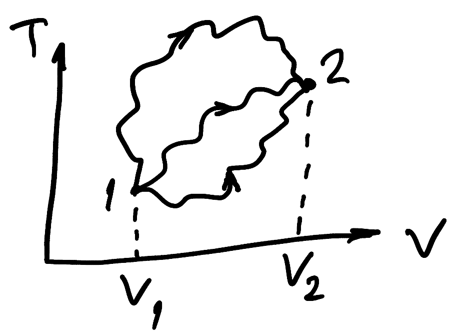
(Landau Lifshitz : $P = -\left(\frac{\partial E}{\partial V}\right)_S$)

Note that the generalised force is a function of temperature : $\Lambda = \Lambda(T, \lambda)$

Work done on the system when its volume changes from V_1 to V_2 :

$$W_{ext} = -\int_{V_1}^{V_2} P(V, T)\, \delta V$$

- depends on the path which the system follows



A generic slow process

Let's consider now a more generic process, in which there is heat exchange between the system and the environment. The temperature of the system may change.

$$\delta E = \delta\left(\sum_i \varepsilon_i w_i\right) = \underbrace{\left(\sum_i w_i \delta\varepsilon_i\right)_{w_i}}_{\delta W_{ext}\text{, work}} + \underbrace{\left(\sum_i \varepsilon_i \delta w_i\right)_{\lambda}}_{\text{change of the energy of the}}$$

δW_{ext}, work done on the system

Change of the energy of the system unrelated to the change of field, $= \delta Q$

$$\delta E = \delta W_{ext} + \delta Q$$

$$\delta Q = \delta E + \delta W$$

Let's investigate the microscopic meaning of the amount of heat δQ

$$\delta Q = \Big(\sum_i \varepsilon_i \delta w_i\Big)_\lambda = \delta E - \sum_i w_i \delta\varepsilon_i = \delta E - \frac{\sum_i e^{-\frac{\varepsilon_i}{T}}\delta\varepsilon_i}{Z}$$

$$\delta\Big(\sum_i e^{-\frac{\varepsilon_i}{T}}\Big) = -\frac{1}{T}\sum_i e^{-\frac{\varepsilon_i}{T}}\delta\varepsilon_i + \sum_i \varepsilon_i e^{-\frac{\varepsilon_i}{T}}\frac{\delta T}{T^2}$$

$$\rightarrow \sum_i e^{-\frac{\varepsilon_i}{T}}\delta\varepsilon_i = -T\delta\Big(\sum_i e^{-\frac{\varepsilon_i}{T}}\Big) + \frac{\delta T}{T}\sum_i \varepsilon_i e^{-\frac{\varepsilon_i}{T}}$$

$$\rightarrow \frac{\sum_i e^{-\frac{\varepsilon_i}{T}}\delta\varepsilon_i}{Z} = \underbrace{-\frac{T\delta Z}{Z}}_{-T\delta\ln Z} + \underbrace{\frac{\delta T}{T}\frac{\sum_i e^{-\frac{\varepsilon_i}{T}}\varepsilon_i}{Z}}_{\frac{\delta T}{T}E}$$

Summing up all the terms,

$$\delta Q = \delta E + T\delta\ln Z - E\frac{\delta T}{T} = \delta E + T\delta\Big(\frac{E}{T} + \ln Z\Big)$$

Thus, if the system undergoes some process during which it remains in equilibrium with the environment, then

$$\delta E = -P\,dV + T\delta\Big(\frac{E}{T} + \ln Z\Big)$$