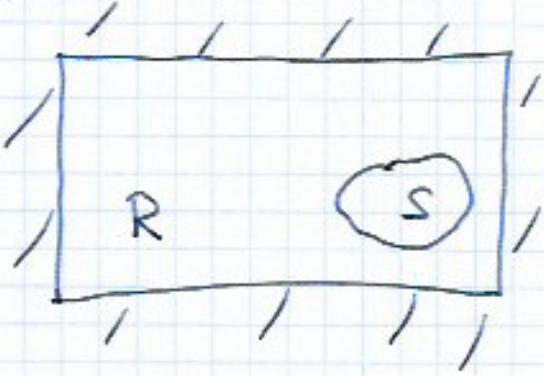
II CANONICAL ENSEMBLE

§1. CANONICAL ENSEMBLE

Isolated system R + S → microcanonical ensemble



S ≪ R

$U = U_R + U_S = \text{const.}$

We investigate a "small" subsystem, which is in thermal equilibrium with a "big" subsystem.

An energy transverse between R and S

thermal interaction

R - reservoir

S - system

Df. A system in a thermal equilibrium with an environment is a canonical ensemble

§2. Boltzmann distribution

A system S has discrete, nondegenerate energy levels ε_s

What is a probability to find a system S in a quantum state ε_s?

$$U = U_R + \varepsilon_S$$

Total number of microstates is

$$\Omega(U_R, U_S) = \Omega(U-\varepsilon_S, \varepsilon_S) = \Omega_R(U-\varepsilon_S)\cdot \overbrace{1}^{\Omega_S(\varepsilon_S)} = \Omega_R(U-\varepsilon_S)$$

From the postulate of equal probability apriori we know that the ratio of probabilities

$\varepsilon_S = \varepsilon_1$ or ε_2

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\Omega_R(U-\varepsilon_1)}{\Omega_R(U-\varepsilon_2)}$$

Using a Boltzmann entropy

$$S = k_B \ln \Omega$$

we get

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{e^{\frac{1}{k_B} S_R(U-\varepsilon_1)}}{e^{\frac{1}{k_B} S_R(U-\varepsilon_2)}} = e^{\frac{1}{k_B}\Delta S_R}$$

$$\Delta S_R = S_R(U-\varepsilon_1) - S_R(U-\varepsilon_2)$$

Since, $R \gg S$ then $\varepsilon_1 \ll U$ and $\varepsilon_2 \ll U$ so we can Taylor expand the entropies

$$S_R(U-\varepsilon_1 {}^{V,N}) \doteq S_R(U,V) - \varepsilon\left(\frac{\partial S_R}{\partial U}\right)_{V,N} + \dots =$$

$$= S_R(U,V,N) - \varepsilon\frac{1}{T} + \dots$$

Therefore

$$\Delta S_R = -\frac{\varepsilon_1 - \varepsilon_2}{T}$$

and

$$\boxed{\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{e^{-\frac{\varepsilon_1}{k_B T}}}{e^{-\frac{\varepsilon_2}{k_B T}}}}$$

up to normalization factor we obtain

$$\boxed{P(\varepsilon) = \frac{1}{Z} e^{-\frac{\varepsilon}{kT}}}$$

- $e^{-\varepsilon/kT}$ - Boltzmann factor
- Z - normalization factor, function of T, V, N
- $P(\varepsilon)$ - probability that the system S, being in the thermal equilibrium with an environment of the temperature T, is in a state ε.

§3. PARTITION FUNCTION

The normalization factor is called a partition function

$$\boxed{Z(T, V, N) = \sum_{s} e^{-\frac{\varepsilon_s}{kT}}}$$

The full thermodynamics can be obtain from the partition function.

Let's compute the <u>internal energy</u>

$$U(T,V,N) = \langle \varepsilon \rangle = \frac{1}{Z}\sum_s \varepsilon_s e^{-\frac{\varepsilon_s}{k_BT}} =$$

$$\boxed{\beta \equiv \frac{1}{k_BT}} \qquad \boxed{\frac{\partial}{\partial\beta} = \frac{\partial (\overset{=\beta^{-1}}{k_BT})}{\partial\beta}\frac{\partial}{\partial k_BT} = -\frac{1}{\beta^2}\frac{\partial}{\partial k_BT} = -k_BT^2\frac{\partial}{\partial T}}$$

$$= -\frac{1}{Z}\frac{\partial}{\partial\beta}\underbrace{\sum_s e^{-\beta\varepsilon_s}}_{Z} = -\frac{\partial}{\partial\beta}\ln Z = (k_BT)^2\frac{\partial \ln Z}{\partial k_BT} =$$

$$= T^2\frac{\partial}{\partial T}k_B\ln Z(T,V,N)$$

$$\boxed{U(T,V,N) = T^2\frac{\partial}{\partial T}k_B\ln Z(T,V,N)}$$

Let's compute

$$\frac{\partial^2\ln Z}{\partial\beta^2} = \frac{\partial^2}{\partial\beta^2}\ln\sum_s e^{-\beta\varepsilon_s} = \frac{\partial}{\partial\beta}\left\{\frac{\sum_s -\varepsilon_s e^{-\beta\varepsilon_s}}{\sum_s e^{-\beta\varepsilon_s}}\right\} =$$

$$= \frac{\sum_s \varepsilon_s^2 e^{-\beta\varepsilon_s}\cdot\sum_s e^{-\beta\varepsilon_s} - \left(\sum_s \varepsilon_s e^{-\beta\varepsilon_s}\right)^2}{\left(\sum_s e^{-\beta\varepsilon_s}\right)^2} =$$

$$= \frac{1}{Z}\sum_s \varepsilon_s^2 e^{-\beta\varepsilon_s} - \left(\frac{1}{Z}\sum_s \varepsilon_s e^{-\beta\varepsilon_s}\right) = \langle\varepsilon^2\rangle - \langle\varepsilon\rangle^2 =$$

$$\equiv \sigma_\varepsilon^2$$

On the other hand $\left(\frac{\partial^2\ln Z}{\partial\beta^2}\right)_{V,N} = -\left(\frac{\partial U}{\partial\beta}\right)_{V,N} = k_BT^2\left(\frac{\partial U}{\partial T}\right)_{V,N}$

Recollect a specific heat

$$C_x = \left(\frac{\delta Q}{\delta T}\right)_x$$

$\uparrow$

at constant x

1st thermodynamic law $dU = \delta Q - pdV$

for isochoric process $dV = 0$

$$\delta Q = \frac{\partial U}{\partial T}dT + \left(\frac{\partial U}{\partial V} + p\right)dV$$

Hence, $\boxed{\sigma_\varepsilon^2 = \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 = k_B T^2 C_V}$

§4. PRESSURE

$\mathcal{E}_s = \mathcal{E}_s(V)$ - energy levels depend on V

e.g. 3d quantum well

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m \underbrace{L^2}_{V^{2/3}}} (n_x^2 + n_y^2 + n_z^2)$$

□

We apply an external force to change a volume by ΔV

If the change is very slow, the system stays in a state $\mathcal{E}_s$, adiabatic (slow) process$^{(*)}$, this gives a reversible thermodynamic process

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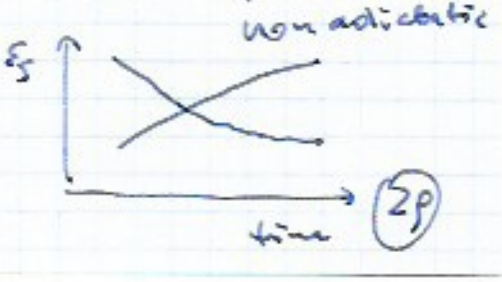
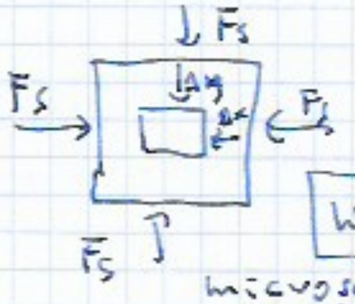
(*) In thermodynamics – adiabatic process $Q = 0$

In (quantum) mechanics – adiabatic process – slow such that the particles are in the same quantum states.



1) A system is in a quantum state with energy $\varepsilon_s(V)$

2) A work performed with volume changes $\Delta V \ll V$ in a reversible process with the constant entropy



$$\Delta V \simeq A(\Delta x + \Delta y + \Delta z)$$

$$\boxed{W_s} = F_s \cdot (\Delta x + \Delta y + \Delta z) = p_s \cdot A(\Delta x + \Delta y + \Delta z)$$

microscopic force

$$= \boxed{p_s \cdot \Delta V}$$

microscopic pressure

3) This work is equal to a change of the system energy

$$\Delta \varepsilon_s = \underbrace{\varepsilon_s(V - \Delta V) - \varepsilon_s(V)}_{\varepsilon_s(V) - \frac{d\varepsilon_s}{dV}\Delta V - \varepsilon_s(V)} = \underset{\substack{\downarrow \\ p_s \Delta V}}{W_s}$$

$$\Rightarrow \quad \boxed{p_s = -\frac{d\varepsilon_s}{dV}}$$

microscopic expression on the pressure of a system in a state with energy ε_s.

4) <u>Macroscopic pressure</u> (just <u>pressure</u>) – we average over all ε_s states

$$p = \langle p_s \rangle = \int d\varepsilon_s\, P(\varepsilon_s) \left(-\frac{d\varepsilon_s}{dV}\right) = -\frac{d}{dV}\langle \varepsilon_s \rangle = -\left(\frac{\partial U}{\partial V}\right)_S$$

$$\Rightarrow \quad \boxed{p = -\left(\frac{\partial U}{\partial V}\right)_\sigma}$$

constant entropy because in reversible processes number of states is conserved.

We have provided, for the first time, a microscopic definition of the pressure!

It is equivalent to the definition from thermodynamics in reversible processes

$$dS(U,V) = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV \overset{!}{=} 0$$

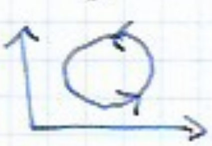
$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_U = - \underset{\frac{1}{T}}{\underset{\shortparallel}{\left(\frac{\partial S}{\partial U}\right)_V}} \underset{-p}{\underset{\shortparallel}{\left(\frac{\partial U}{\partial V}\right)_S}}$$

$$\Rightarrow \boxed{p = T\left(\frac{\partial S}{\partial V}\right)_U}$$ another expression for pressure

§5. HEAT AND 1ST LAW OF THERMODYNAMICS

$\boxed{\text{Thermodynamic reminders}}$

Reversible process – a system and its environment return to the same thermodynamic state in a cycle process



Necessary condition is that the system undergoes through only equilibrium states (not sufficient)

e.g. ·) free motion in vacuum
··) ideal spring oscillations

<u>Ireversible process</u> - such one, which is not reversible

e.g. ·) free motion in the air

··) real spring oscillations

→ There is a heat exchange between the system and the enviorment of different temperatures.

2nd LAW of THERMODYNAMICS

i) Impossibility of a complete change of heat onto a work (no perpetuum mobile of second kind)

ii) A heat flows from a hotter to a colder body in spontaneous process

$$\boxed{T_1} \xrightarrow{Q} \boxed{T_2} \qquad T_1 > T_2$$

⇒ Work and heat are not equivalent ways of transfering the energy

iii) In a cycle (reversible) process

$$\boxed{\oint \left(\frac{\delta Q}{T}\right)_{\text{reversible}} = 0}$$

T - temperature

δQ - elementary heat added (>0) subtracted (<0)

$$\Rightarrow \left(\frac{\delta Q}{T}\right)_{\text{revers}} = dS$$

- ∃ exact form, state function, entropy

iv) Under sponteneous process the entropy change of isolated system never decreases

$$\boxed{\Delta S \geqslant 0}$$

approaching most probable state, as we now know

$\Delta S = 0$ - reversible processes

$\Delta S > 0$ - irreversible processes

1st LAW OF THERMODYNAMICS

In general process $S = S(U, V, N)$

$$dS \neq 0 \Rightarrow dS = \underset{\text{df}\ \shortparallel\ \frac{1}{T}}{\left(\frac{\partial S}{\partial U}\right)_{V,N}} dU + \underset{\text{df.}\ \shortparallel\ \frac{p}{T}}{\left(\frac{\partial S}{\partial V}\right)_{U,N}} dV$$

$\rightarrow \quad T\,dS = dU + p\,dV$

$$\Rightarrow \quad \boxed{dU = T\,dS - p\,dV}$$

1st law of thermodynamics ⇔ conservation of energy

$$[J] = \left[K \cdot \frac{J}{K}\right] - \left[\frac{N}{m^2} \cdot m^3\right] = [J]$$

In general $\boxed{-p\,dV = \delta W}$ a work done on the system

$T\,dS$ − is arbitrary, $T\,dS \geq \delta Q$ (inequality)

In reversible processes $\boxed{T\,dS = \delta Q}$ a heat transfered into the system

NOW $\boxed{dU = \delta Q + \delta W}$ reversible processes

dU ← state function

δQ, δW ← not state function

δQ − heat
δW − work

What is a difference between δQ and δW on a microscopic level?

$$U = \langle \varepsilon \rangle = \sum_s \varepsilon_s \, P(\varepsilon_s)$$

$$dU = \sum_s dP(\varepsilon_s) \cdot \varepsilon_s + \sum_s P(\varepsilon_s) \underbrace{d\varepsilon_s}_{-p_s \, dV} =$$

microscopic pressure

$$= \underbrace{\sum_s \varepsilon_s \, dP(\varepsilon_s)}_{\underline{\delta Q = T\,dS}\ (*)} - \underbrace{\sum_s p_s \, P(\varepsilon_s) \, dV}_{\underline{\delta W = -p\,dV}} =$$

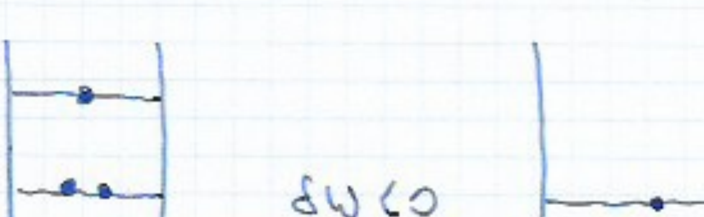
reversible process *

$$dU = \delta Q + \delta W$$

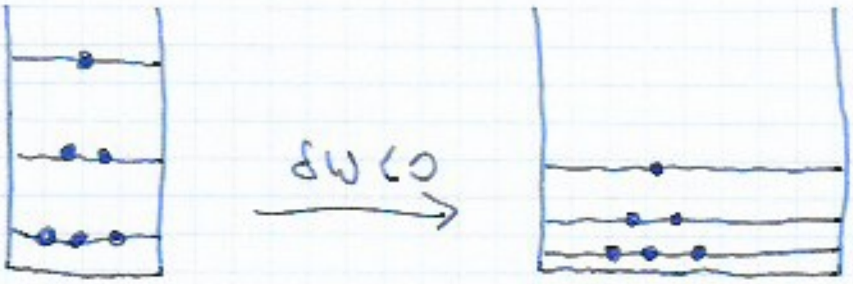
$\boxed{\delta Q = \sum_s \varepsilon_s \, dP(\varepsilon_s)}$ – <u></u>

$\delta Q = \sum_s \varepsilon_s \, dP(\varepsilon_s)$ – heat transfer, unordered way of transfering the energy due to a change in probabilities

$\delta W = -\sum_s p_s \, P(\varepsilon_s) \, dV$ – work, ordered way of transfering the energy due to a change in energy levels



a system gives out a heat, its energy decreases



a system performs a work (expanding), its energy decreases

(*) proof $\delta Q = T\,dS = \sum_s \varepsilon_s \, d\rho(\varepsilon_s)$

$$S = -k_B \sum_s \rho(\varepsilon_s) \ln \rho(\varepsilon_s) \quad , \quad \sum_s \rho(\varepsilon_s) = 1$$

$$\downarrow$$

$$dS = -k_B \sum_s d\rho(\varepsilon_s) \ln \rho(\varepsilon_s) - \qquad \sum_s d\rho(\varepsilon_s) = 0$$

$$- \underbrace{\sum_s \cancel{\rho(\varepsilon_s)} \frac{1}{\cancel{\rho(\varepsilon_s)}} d\rho(\varepsilon_s)}_{=0} =$$

$$= -k_B \sum_s \ln \rho(\varepsilon_s)\, d\rho(\varepsilon_s) = \qquad \rho(\varepsilon_s) = \frac{1}{Z} e^{-\beta \varepsilon_s}$$

$$= -k_B \sum_s \left(-\beta \varepsilon_s - \ln Z \right) d\rho(\varepsilon_s) =$$

$$= \frac{k_B}{k_B T} \sum_s \varepsilon_s \, d\rho(\varepsilon_s) + \ln Z \underbrace{\sum_s d\rho(\varepsilon_s)}_{=0}$$

$$\Rightarrow \quad \boxed{T\,dS = \sum_s \varepsilon_s \, d\rho(\varepsilon_s)}$$

□

Note also:

$$Z = Z(T, V, N)$$

$$S = -k_B \sum_s \frac{e^{-\beta \varepsilon_s}}{Z} \ln\left(\frac{e^{-\beta \varepsilon_s}}{Z} \right) =$$

$$= -k_B \sum_s \frac{e^{-\beta \varepsilon_s}}{Z} (-\beta \varepsilon_s) + k_B \underbrace{\sum_s \underbrace{\frac{e^{-\beta \varepsilon_s}}{Z}}_{\rho(\varepsilon_s)}}_{=1} \ln Z =$$

$$= \frac{1}{T} \sum_s \varepsilon_s \frac{e^{-\beta \varepsilon_s}}{Z} + k_B \ln Z$$

$$\Rightarrow \quad \boxed{S = \frac{U}{T} + k_B \ln Z}$$

$$\Rightarrow \quad \boxed{\left(\frac{\partial S}{\partial U} \right)_{V,N} = \frac{1}{T}}$$

§ 6. FREE ENERGY

Helmholtz free energy

There exists a state function

$$\boxed{F(T, V, N) = U - TS}$$

Legandre's transform

$$\boxed{\text{F - gets minimum (extremum) in equilibrium at constant T (isothermal process)}}$$

$$dF = dU - TdS \qquad (dT = 0)$$

but $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \Rightarrow dU = TdS$

and $\boxed{dF = 0}$ → extremum.

□

Different thermodynamic relations

$$dF = dU - TdS - SdT$$

1st law of thermodynamics $TdS = dU + pdV$ (reversible)

$$\Rightarrow \quad dF = -SdT - pdV$$

$$\Rightarrow \quad \boxed{\begin{aligned} S &= \left(\frac{\partial F}{\partial T}\right)_{V,N} \\ p &= -\left(\frac{\partial F}{\partial V}\right)_{T,N} \end{aligned}}$$

↔ analog of $p = -\frac{\partial U}{\partial V}\Big|_S$

In isothermal processes (T = const) the Helmholtz free energy plays a role of an effective energy in the system.

Note how 1st law of thermodynamics

$$p\,dV = T\,dS - dU$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \underbrace{T\left(\frac{\partial S}{\partial V}\right)_{T,N}}_{\text{entropic pressure}} - \underbrace{\left(\frac{\partial U}{\partial V}\right)_{T,N}}_{\text{energetic pressure}}$$

dominates in gases and elastic polimers (rubber)

dominates in solids

→ The entropic contribution shows that mechanical part $\left(\frac{\partial U}{\partial V}\right)_{T,N}$ does not reflect all possible processes at constant T

e.g. Entropy of a system can be changed with changing its volume even when energy is constant / ideal gas at fixed T, $U = \frac{3}{2} N k_B T$)

system interacts with environment.

→ Free energy - tells us a maximal amount of available work at isothermal processes ($T = \text{cst}$)

$$\Delta F = \underset{\delta Q + \delta W}{\overset{}{\Delta U}} - \underset{\delta Q}{T\Delta S} \quad \text{(revers.)}$$

Only a difference $U - TS$ of total energy is available to be used as a work.

Free energy from partition function

$$F = U - TS \, , \qquad S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$\Rightarrow \quad F = U + T\left(\frac{\partial F}{\partial T}\right)_V$$

$$\Rightarrow \quad U = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)$$

RHS: $-T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)_V = -T^2 \frac{\partial F}{\partial T}\frac{1}{T} - T^2 F\left(-\frac{1}{T^2}\right)_V = F - T\left(\frac{\partial F}{\partial T}\right)_V = \text{LHS}$ $\square$

~~[illegible]~~ This equation is satisfied by

$$\boxed{F = -k_B T \ln Z}$$

proof: We remember $U = k_B T^2 \frac{\partial \ln Z}{\partial T}$

$$\frac{\partial}{\partial T}\left(\frac{F}{T}\right) = -\frac{\partial}{\partial T} k_B \ln Z = -\frac{1}{T^2} U$$

$\square$

The ~~ta~~ Boltzman distribution takes a form

$$\boxed{\begin{aligned} &P(\varepsilon) = \frac{1}{Z} e^{-\beta\varepsilon} = e^{-\beta(\varepsilon - F)} \\ &\text{where} \quad Z = e^{-\beta F} \end{aligned}}$$