Thermodynamics

Thermodynamic quantities describe macroscopic properties of a system.

(1) Small fluctuations are disconsidered,

e.g., energy of a subsystem $E := \overline{H}$ (mean value of the Hamiltonian)

(2) system is assumed to be in thermodynamic (statistical) equilibrium, or can be divided into smaller subsystems, which are in local equilibrium.

(3) system/subsystem state is fully determined by

- size, number of particles N
- volume, V
- energy, E.

(model: system in a box)

<u>Entropy</u> : $S = S(E, V, N)$

It is usually increasing function of E

(larger energy $\rightarrow$ larger phase-space volume)

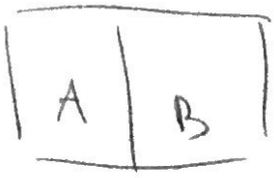
$\Rightarrow$ we can express:

$$\boxed{E = U(S, V, N)}$$

called <u>internal energy</u>

Obs! do **Not** confuse with interaction potential in the Lagrangian.

Consider subsystems A and B in thermod. equilibrium



$$S = S_A + S_B \,, \quad E = E_A + E_B$$

Assume a small energy transfer δE from B to A, keeping volumes and particle numbers fixed:

$$E_A \to E_A + \delta E \,, \qquad \delta E = \left(\frac{\partial U_A}{\partial S_A}\right)\delta S_A$$

$$E_B \to E_B - \delta E \,, \qquad -\delta E = \left(\frac{\partial U_B}{\partial S_B}\right)\delta S_B$$

In therm. equilibrium $S \to \max \Rightarrow \delta S = \delta S_A + \delta S_B = 0$ for small δE.

Hence, $\dfrac{\partial U_A}{\partial S_A} = \dfrac{\partial U_B}{\partial S_B}$ – the equilibrium condition

<u>Temperature</u>: $$\boxed{T = \left(\frac{\partial U}{\partial S}\right)_{\underbrace{V,N}_{\text{at fixed volume and particles number}}}}$$

<u>Obs</u> Temperatures of two bodies in therm. equilibrium are equal $\Rightarrow$ it is easy to measure.

Thermometer

<u>Obs</u>: T [Kelvin, K], U [Joule, J], $S \sim k_B$ [J/K]

The Boltzmann Constant k_B expresses energy in units of Kelvin [K].

<u>Heat</u>: transfer of internal energy other than:

- <u>macroscopic</u> work (geometry and volumes are fixed)
- transfer of mass (number of particles fixed).

This is a <u>microscopic</u> mechanism of energy transfer through interaction of particles near the boundary.

Heat transfered: $\delta Q = \delta U = \frac{\partial U}{\partial S}\delta S = \underline{\underline{T\,\delta S}}$

If heat is transfered between subsystems: $B \to A$

$$\delta S = \delta S_A + \delta S_B = \frac{\delta Q}{T_A} - \frac{\delta Q}{T_B} = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\delta Q.$$

By the second law of thermodynamics:

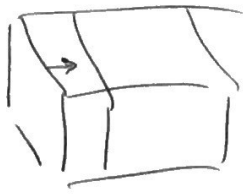
$\delta S \geq 0$ (non-zero is systems are not in equilibrium)

Hence, $T_A < T_B$ for $\delta Q > 0$, i.e., heat (internal energy) is always transfered from a hotter to a colder body.

Adiabatic process:

- external conditions change slowly in time

  Hamiltonian $H = H(p, q, \lambda)$ with $\lambda = \lambda(\varepsilon t)$ and small ε. For example, λ describes a change of a box.



- System is (thermally) isolated.

Obs In practice, adiabatic process (can also model macroscopically) fast changes, such that heat transfer is negligible.

Change of a parameter $\lambda(\varepsilon t)$ leads in general to irreversible processes: $\frac{dS}{dt} \geq 0$. (equality for reversible processes)

$\frac{dS}{dt}$ is a function of $\frac{d\lambda}{dt} = \varepsilon \lambda'$ such that

$$\frac{dS}{dt} = A_0 + A_1\left(\frac{d\lambda}{dt}\right) + A_2\left(\frac{d\lambda}{dt}\right)^2 + \dots \qquad \text{(Taylor)}$$

Equilibrium condition: $\frac{d\lambda}{dt} = 0 \Rightarrow \frac{dS}{dt} = 0 \Rightarrow A_0 = 0$

2nd law of thermodynamics: $\frac{d\lambda}{dt} \geq 0 \Rightarrow A_1 = 0$

Hence, in the leading order

$$\frac{dS}{dt} \sim \left(\frac{d\lambda}{dt}\right)^2 \sim \varepsilon^2$$

When $\varepsilon \to 0$, we have $\dfrac{dS}{d\lambda} = \dfrac{dS/dt}{d\lambda/dt} \sim \dfrac{\varepsilon^2}{\varepsilon} = \varepsilon \to 0$.

Therefore, $S \approx$ const in the <u>adiabatic process</u>.

<u>Adiabatic process is reversible!</u>

In the adiabatic process, we can relate variations of thermodynamic quantities to the Hamiltonian function $H = H(p, q, \lambda)$.

$$\frac{dH(p,q,t)}{dt} = \underbrace{\frac{\partial H}{\partial p}\dot{p} + \frac{\partial H}{\partial q}\dot{q}}_{=0 \text{ because of Ham.'s eqs.}} + \frac{\partial H}{\partial \lambda}\dot{\lambda} = \frac{\partial H}{\partial \lambda}\frac{d\lambda}{dt}$$

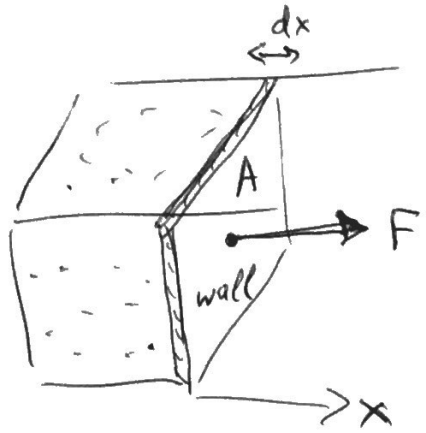
Since the internal energy $\mathcal{U} = \overline{H(p, q, \lambda)}$ (mean) and $S =$ const, we have

$$\left(\frac{\partial \mathcal{U}}{\partial \lambda}\right)_S = \overline{dH/dt} \Big/ d\lambda/dt = \overline{\frac{\partial H(p,q,\lambda)}{\partial \lambda}}$$

(at fixed entropy)

(mean value of the Hamiltonian derivative.)

Pressure



Consider a system in the box.

Let F be the macroscopic force (mean force) acting on the wall from the particles.

If we move the wall slowly (adiabatically) by distance dx, the system will make work $dW = F dx$, which corresponds to the decrease of the internal energy (Hamiltonian) $-\overline{dH(p,q,x)}$

This defines the force as

$$F = -\overline{\frac{\partial H}{\partial x}} \underset{\substack{\uparrow \\ \text{adiabatic}}}{=} -\left(\frac{\partial U}{\partial x}\right)_S$$

Pressure is defined as $P = \frac{F}{A} = \frac{\text{force}}{\text{area of the surface}}$

Since $A dx = dV$ - change of volume, we obtain

$$\boxed{P = -\left(\frac{\partial U}{\partial V}\right)_S}$$

derivative w.r.t. volume at fixed entropy.

Combining with Def. of temperature:

$$\boxed{dU = T dS - P dV}$$

for a system with fixed number of particles N.

Obs Pressures $P_A = P_B$ between two bodies,

from the 3d Newton's law.

Change of ~~energy~~ internal energy is the sum

$$\delta U = \delta Q + \delta R$$

of heat transfered to the system $\delta Q = T\delta S$

and macroscopic (mechanical) work done on the system $\delta R = -PdV$.

Obs: Separation on δQ and δR depends on the process, e.g., it is different for reversible and irreversible proc.

Thermodynamic potentials

Thermod. potential is a function, whose derivative yield thermod. properties:

$$U(S,V) \longrightarrow T = \frac{\partial U}{\partial S}, \quad P = -\frac{\partial U}{\partial V}.$$

To define ~~other~~ new potentials, we use the Legendre transformation:

Consider a function $f(x)$ with $f''(x) > 0$

Define a new variable $y = f'(x) \Rightarrow x = f'^{-1}(y)$.

Define a new function $F(y) = \left(xf' - f\right)_{x = f'^{-1}(y)}$

$$x,\ f(x),\ \underbrace{y = \frac{df}{dx}}_{\text{used as new variable}} \xleftrightarrow{\text{Legendre}} y,\ F(y),\ x = \frac{dF}{dy}$$

<u>Example</u> Hamiltonian vs. Lagrangian with p vs. $\dot{q}$

$$H(q,p) = \dot{q}\frac{\partial L}{\partial \dot{q}} - L = \dot{q}p - L(q,\dot{q})$$

$$p = \frac{\partial L}{\partial \dot{q}} \text{ - momentum} \longleftrightarrow \dot{q} = \frac{\partial H}{\partial p} \text{ speed}$$

For the internal energy $U(S,V)$ we can apply the Legendre transform (with "−" sign) for

$$S \longleftrightarrow T = \frac{\partial U}{\partial S} \quad \text{and} \quad V \longleftrightarrow P = -\frac{\partial U}{\partial V}.$$

Obs: for now, we assume ~~mass to be con~~ $N = \text{const}$ (no mass transfer)

<u>Enthalpy (heat function)</u>: $V \to P$

$$\boxed{H(S,P) = U + PV}$$

with $V = V(S,P)$ expressed from relation $P = -\partial U/\partial V$.

Obs: do NOT confuse with the Hamiltonian! same letter!

$$dH = TdS + VdP \quad \text{or} \quad T = \left(\frac{\partial H}{\partial S}\right)_P,\ V = \left(\frac{\partial H}{\partial P}\right)_S$$

variables fixed

Interpretation: H = internal energy U + work PV to create a space for the system.

Usage: when $P = \text{const} \Rightarrow dH = TdS = dQ$ heat transfered at pressure kept constant.

Free energy (Helmholtz free energy) : $S \to T$

$$\boxed{F(T,V) = \mathcal{U} - TS}$$ with $S(T,V)$ expressed from $T = \left(\frac{\partial \mathcal{U}}{\partial S}\right)_V$

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

At constant temperature $T = \text{const}$,

$$dF = -P\,dV = dR$$ mechanical work done on the body.

Useful for macroscopic equations of motion.

Gibbs free energy : $S \to T$ and $V \to P$

$$\boxed{G(T,P) = \mathcal{U} - TS + PV}$$

$$dG = -S\,dT + V\,dP$$

Potential	Variables	Relations	derivatives
$\mathcal{U}$ internal energy	S, V		$d\mathcal{U} = T\,dS - P\,dV$
H enthalpy	S, P	$\mathcal{U} + PV$	$dH = T\,dS + V\,dP$
F free energy	T, V	$\mathcal{U} - TS$	$dF = -S\,dT - P\,dV$
G Gibbs energy	T, P	$\mathcal{U} - TS + PV$	$dG = -S\,dT + V\,dP$

Heat capacity: $C = \frac{\delta Q}{\delta T} \frac{\text{(heat transfered)}}{\text{(increase of temp.)}} = \frac{T\delta S}{\delta T}$

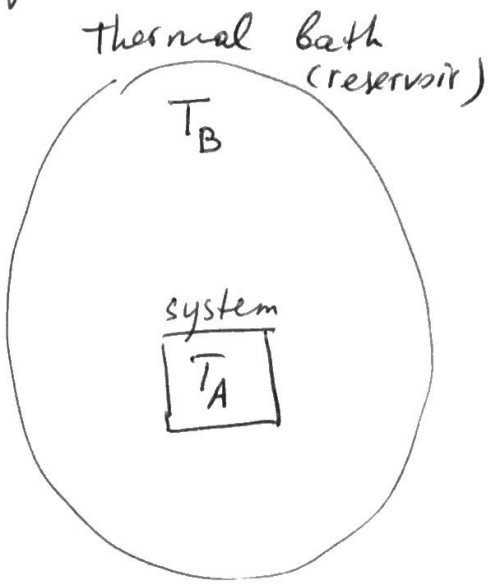
(a) heat transfer, keeping volume constant:

$$C_V = \frac{\delta Q}{\delta T} = \frac{\delta U}{\delta T}$$

(b) heat transfer keeping pressure constant

$$C_P = \frac{\delta Q}{\delta T} = \frac{\delta H}{\delta T}.$$

Thermal potentials in irreversible process.



A: system with non-equilibrium process e.g. chemical reaction.

B: thermal reservoir (bath) - very large system in equilibrium that keeps constant T_B in any interaction with system A.

2^d law of thermod.: $\delta S_A + \delta S_B \geq 0$

Energy conservation: $\delta U_A + \delta U_B = 0$.

System B is in equilibrium $\Rightarrow \delta U_B = T_B \delta S_B - P_B \delta V_B$

where $\delta V_A + \delta V_B = 0$.

Case 1: process at constant temperature $T_A = T_B = T$ and constant pressure $P_A = P_B = P$.

(Volumes will change!)

$$\delta U_A = -\delta U_B = -T\delta S_B + P\delta V_B = -T\delta S_B - P\delta V_B \leq$$

$$\underset{(2^d \text{ law.})}{\leq} T\delta S_A - P\delta V_B \underset{(T,P=\text{const})}{=} \delta(TS_A - PV_B).$$

Hence, $\delta G_A = \delta(U_A - TS_A + PV_A) \leq 0$

<u>Gibbs energy</u> decreases in non-equilibrium process at constant temperature and pressure, and attains min in the equilibrium.

<u>Case 2</u> process at constant temperature $T_A = T_B = T$ and constant volume, $\delta V_A = 0$, $\delta V_B = 0$.

$$\delta U_A = -\delta U_B = -T\delta S_B \leq T\delta S_B = \delta(TS_B).$$

Hence, $\delta F_A = \delta(U_A - TS_A) \leq 0$

<u>Free energy</u>, in non-equilibrium process at fixed temperatures and volumes, decreases and attains min in the equilibrium.

Dependence on the particle number N

$$\mathcal{U} = \mathcal{U}(S, V, N) \Rightarrow d\mathcal{U} = TdS - PdV + \mu dN$$

where $\mu = \left(\frac{\partial \mathcal{U}}{\partial N}\right)_{S,V}$ is called <u>chemical potential</u>

quantities fixed in differentiation.

(energy needed to add a particle)

For other potentials,
$$dH = TdS + VdP + \mu dN$$
$$dF = -SdT - PdV + \mu dN$$
$$dG = -SdT + VdP + \mu dN$$

or
$$\mu = \left(\frac{\partial \mathcal{U}}{\partial N}\right)_{S,V} = \left(\frac{\partial H}{\partial N}\right)_{S,P} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{T,P}.$$

All <u>potentials are additive functions</u> by construction,

e.g., $F_{A+B} = \mathcal{U}_{A+B} - TS_{A+B} = \mathcal{U}_A - TS_A + \mathcal{U}_B - TS_B = F_A + F_B$

because $T_A = T_B = T$ in the therm. equilibrium.

Hence, potentials and also entropy and volume are proportional to N: $\boxed{1 \mid 2 \mid 3 \mid 4 \mid 5}$ ...

Then, potentials depend on N as

$$\mathcal{U}(S,V,N) = N f_{\mathcal{U}}(S/N, V/N)$$
$$H(S,P,N) = N f_H(S/N, P)$$
$$F(T,V,N) = N f_F(T, V/N)$$
$$G(T,P,N) = N f_G(T,P)$$

Obs:

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = f_G(T,P)$$

Hence,

$$G = N\mu(T,P).$$