

Lecture 1

Fundamentals of Thermodynamics

Statistical mechanics is the theory that analyzes meso- or macroscopic systems composed of many particles. Such systems are too big to be analyzed by brute force, by writing down EoMs and conservation laws. These systems are characterized by fluctuations, both in time and space.

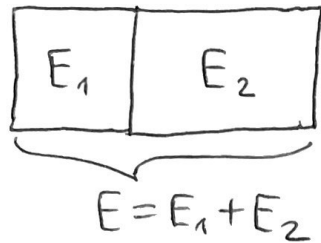
Thermodynamics is the study of systems in "equilibrium" and the corresponding conservation laws (usually, just energy conservation).

First law of thermodynamics

Internal energy \equiv total energy of the system E

E is postulated to have two properties:

(i) E is extensive



(ii) E is conserved

Change in E = energy flow in or out of the system, due to mechanical work or thermal exchange:

$$dE = \underbrace{dQ}_{\substack{\text{diff.} \\ \text{heat} \\ \text{flow}}} + \underbrace{dW}_{\substack{\text{diff.} \\ \text{work done on} \\ \text{the system} \\ \text{(by manipulating} \\ \text{mechanical constraints)}}} \quad \leftarrow \text{First law}$$

In general, $dW = \underbrace{\vec{f}}_{\substack{\text{generalized} \\ \text{force}}} \cdot \underbrace{d\vec{X}}_{\substack{\text{diff. change in} \\ \text{mechanical} \\ \text{extensive} \\ \text{variable}}}$

E.g., $dW = -\underbrace{P_{\text{ext}}}_{\substack{\uparrow \\ \text{external} \\ \text{pressure}}} d\underbrace{V}_{\substack{\uparrow \\ \text{volume of} \\ \text{the system}}}$

Manipulate systems through ^{mechanical} work:
 mechanical constraints (pistons etc)
 —||— —||— through heat
 exchange: adiabatic walls prevent it

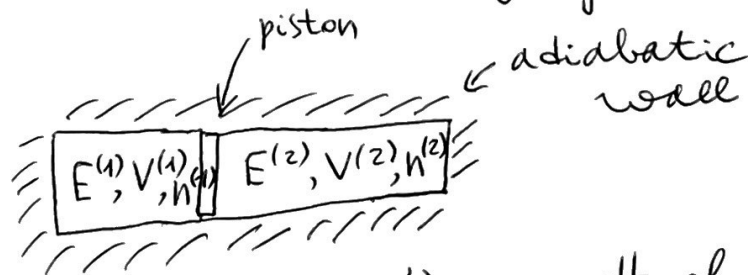
δ \equiv inexact differential

Once, say, δW is transferred through work it is indistinguishable from the same amount of energy transferred through δQ . Thus, there is a state function E , but no W or Q .

Equilibrium states: terminal states described by a small number of variables macroscopically $\Rightarrow E, \vec{X}$.

E, V, n_1, \dots, n_r ^{# species}
 \uparrow volume $n_i = \#$ of particles of species i

Ex.



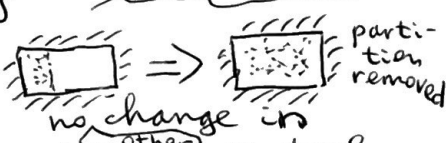

Note that $\dim(\vec{X}) \ll \#$ of microscopic degrees of freedom (DoF)

Experimentally, if the system is indep. of time (t), initial conditions, and there are no flows of energy or matter, it can be assumed to be in equilibrium.

Thermodynamics answers questions like: (a) what happens if the piston moves in the Fig. above?
 (b) what if the piston moves AND the adiabatic wall is removed from the system? etc.

Second law of thermodynamics

There is an extensive function of state $S(E, \bar{X})$ s.t. $S \uparrow$ as $E \uparrow$.

If state B is adiabatically accessible from state A, $S_B \geq S_A$. Ex.:  \Rightarrow  partition removed
no change in other control variables

If, in addition, B is reversibly accessible from A \Rightarrow B \rightarrow A can be done adiabatically too, yielding $S_A \geq S_B$

$$\boxed{S_A = S_B}$$

In other words,

$$\Delta S = S_B - S_A = \begin{cases} \emptyset & \text{reversible adiabatic processes} \\ \neq \emptyset & \text{irreversible -||- -||-} \end{cases}$$

Reversible processes can be retraced by infinitesimal changes in control vars \Rightarrow \Rightarrow goes through a sequence of states within the manifold of equilibrium states. Each intermediate state is at thermal equil. (quasi-static thermodynamic process). Most natural processes are irreversible.

$S(E, \vec{X}) \equiv$ entropy

$$dS = \left(\frac{\partial S}{\partial E} \right)_{\vec{X}} dE + \left(\frac{\partial S}{\partial \vec{X}} \right)_E \cdot d\vec{X}$$

$$= (\delta Q)_{\text{rev}} + \vec{f} \cdot d\vec{X}$$

for a reversible process

Then

$$dS = \left(\frac{\partial S}{\partial E} \right)_{\vec{X}} (\delta Q)_{\text{rev}} + \left[\left(\frac{\partial S}{\partial \vec{X}} \right)_E + \left(\frac{\partial S}{\partial E} \right)_{\vec{X}} \vec{f} \right] \cdot d\vec{X}$$

Note that $(\delta Q)_{\text{rev}} = 0$ for a reversible adiabatic process

Then, since $dS = 0$,

$$\left(\frac{\partial S}{\partial \vec{X}}\right)_E = - \left(\frac{\partial S}{\partial E}\right)_{\vec{X}} \vec{f} \quad (1)$$

Eq'n (1) holds for non-adiabatic reversible processes as well, since all the quantities are functions of state. Thus, we can consider a process where $A \rightarrow B$ reversibly with say $(\delta Q)_{\text{rev}} > 0$, s.t. $\Delta S = S_B - S_A > 0$.

Then we reverse the process:

$$(\delta Q)'_{\text{rev}} = -(\delta Q)_{\text{rev}} \quad \& \quad \Delta S' = -\Delta S.$$

Eq. (1) holds for both A & B states.

By assumption, $S \uparrow$ as $E \uparrow$, s.t.

$$\left(\frac{\partial S}{\partial E}\right)_{\vec{X}} \geq 0 \quad \text{or} \quad \left(\frac{\partial E}{\partial S}\right)_{\vec{X}} \geq 0.$$

We define thermodynamic temperature:

$$T \equiv \left(\frac{\partial E}{\partial S}\right)_{\vec{X}} \geq 0$$

T is intensive (indep. of system size)

Now, Eq. (1) gives:

$$\left(\frac{\partial S}{\partial \vec{X}}\right)_E = -\frac{\vec{f}}{T}, \text{ or}$$

$$dS = \underbrace{\frac{1}{T} dE}_{\left(\frac{\partial S}{\partial E}\right)_{\vec{X}}} - \underbrace{\frac{\vec{f}}{T} \cdot d\vec{X}}_{\left(\frac{\partial S}{\partial \vec{X}}\right)_E}.$$

alternatively,

$$dE = \underbrace{T dS}_{dQ} + \underbrace{\vec{f} \cdot d\vec{X}}_{dW} \Rightarrow E = E(S, \vec{X})$$