

Statistical Mechanics: Introduction

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January 20, 2017

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Classical physics

Classical mechanics in the microscopic world, deals with a large number of particles that are the constituent of matter. It is assumed that the laws of classical physics can be applied at the molecular level:

$$F_i = F_i(r_1, \dots, r_n, \dot{r}_i) \quad (1)$$

F_i depends on the positions of the rest of the particles plus a friction term. Now if the force only depends on the individual terms we say that is pairwise additive:

$$F_i(r_1, \dots, r_n, \dot{r}_i) = \sum_{j \neq i} F_{i,j}(r_i - r_j) + F^{\text{ext}}(r_i, \dot{r}_i) \quad (2)$$

Newton's second law:

$$m_i \ddot{r}_i = F_i(r_1, \dots, r_n, \dot{r}_i) \quad (3)$$

Thermodynamics

- Phenomenological theory of macroscopic matter.
- Provides general relations between macroscopic properties
- Based on experimental observations

Problems

Classical mechanics

- Newton's laws predict the future and past (trajectories) if we know positions and velocities
- Newton's laws are reversible in time. Time reversal symmetry.
- Small number of degrees of freedom
- Interparticle forces are highly non-linear
- Enormous dynamical complexity $N \sim 10^{23}$
- No analytical solution

But...

Thermodynamics

- Self-consistent framework with no reference to the microscopic world
- 2nd and 3rd laws prescribes and arrow of time

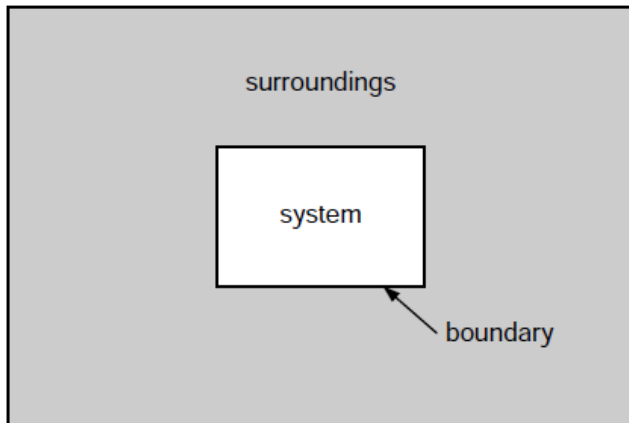
Statistical Mechanics

Reconciliation of macroscopic thermodynamics with the microscopic laws of motion, required the development of a new field, statistical mechanics.

Main innovative ideas:

- Macroscopic observables do not strongly depend on the detailed dynamical motion of every particle, but rather on gross averages.
- Apply microscopic mechanical laws in a statistical fashion *i.e* probabilities, becoming a link between macroscopic thermodynamics and microscopic classical mechanics.
- Concept of an ensemble: Collection of systems that share common macroscopic properties.

Basic Concepts: 1. A thermodynamic system



Basic Concepts: 1. A thermodynamic system

- A macroscopic system
- Universe divided into system and its surroundings
- Isolated system: No exchange of material or energy via heating
- Surroundings produce change in the system

Basic Concepts: 2. Equilibrium

Thermodynamic state does not change with time, except for very small fluctuations.

- Time independence
- History independence. No memory.
- Relative simplicity

Operationally, a system is in equilibrium if its properties can be consistently described by the laws of thermodynamics

Basic Concepts: 3. Fundamental Thermodynamic Parameters

- Pressure (P)
- Volume (V)
- Temperature (T)
- Number of Moles (n)
- ...

A thermodynamic state is specified by providing all values of P,V,T,n. These are measurable quantities that can be obtained experimentally.

Basic Concepts: 4. Equation of state

Relationship among the thermodynamic parameters prescribing how these parameters vary from one equilibrium state to another

$$g(n, P, V, T) = 0 \quad (4)$$

Example:

$$PV - nRT = 0 \quad (5)$$

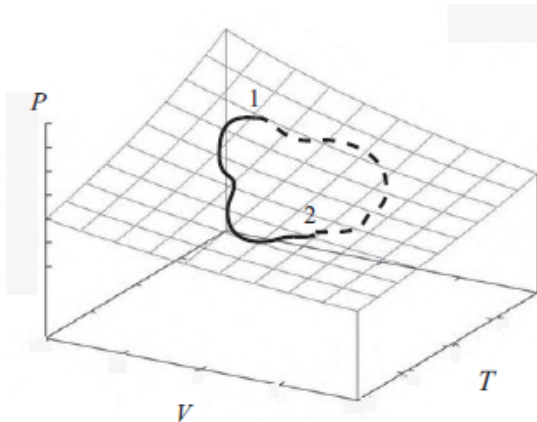
Basic Concepts: 5. Thermodynamic transformation

A change in the thermodynamic state of the system.

- Reversibly: Change is carried out slowly enough, so the system can adjust to each new external condition. It can retrace its history along the same path between the end points.
- Irreversibly: The opposite

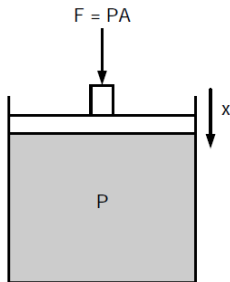
Basic Concepts: 6. State function

$f(n, P, V, T)$, any function that only depends on the initial and final states. It is not path dependent.



Basic Concepts: 7. Thermodynamic Work

In order to change the volume of a system, a mechanical compression or expansion (work) must be performed on it.



$$dW_{rev} = -PdV \quad (6)$$

Basic Concepts: 8. Heating

In order to change the temperature of a system, "heating" or "cooling" must be performed.

$$dQ_{rev} = CdT \quad (7)$$

C = Specific Heat Capacity. Heating needed to change the temperature of 1 mole by 1 degree.

The First Law : Definition

$$\Delta E = \Delta Q_{rev} + \Delta W_{rev} = \Delta Q_{irrev} + \Delta W_{irrev} \quad (8)$$

- Conservation of energy statement.
- Work is defined with respect to the system, *i.e.* compression is positive.
- ΔE is an state function, ΔQ and ΔW are not.

Reversible vs Irreversible work

$$\Delta W_{irrev} = -P_{ext}\Delta V \quad (9)$$

$$\Delta W_{rev} = -\int_{V_1}^{V_2} PdV \quad (10)$$

$$P_{ext} < P_{int}$$

$$\Delta W_{rev} < \Delta W_{irrev} \quad (11)$$

An due to the first law:

$$\Delta Q_{rev} > \Delta Q_{irrev} \quad (12)$$

Entropy Definition

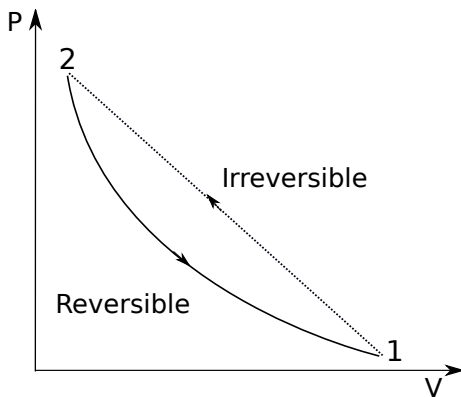
- By fact we know that real systems are not reversible.
- We know that Temperature equalize upon thermal contact
- So lets define a function that is related to T

$$S \equiv \frac{Q_{rev}}{T} \quad (13)$$

$$\Delta S \equiv \int_1^2 \frac{dQ_{rev}}{T} \quad (14)$$

$$dS \equiv \frac{dQ_{rev}}{T} \quad (15)$$

The second law



What about the entropy of the full cycle ?

$$dQ_{rev} > dQ_{irrev}$$

$$\oint \frac{dQ}{dT} = \int_1^2 \frac{dQ_{irrev}}{dT} + \int_2^1 \frac{dQ_{rev}}{dT} > 0 \quad (16)$$

$$\int_2^1 \frac{dQ_{rev}}{dT} > \int_1^2 \frac{dQ_{irrev}}{dT} \quad (17)$$

$$\Delta S_{2 \rightarrow 1} > \int_1^2 \frac{dQ_{irrev}}{dT} \quad (18)$$

The second law

$$\frac{dQ}{T} \leq dS \quad (19)$$

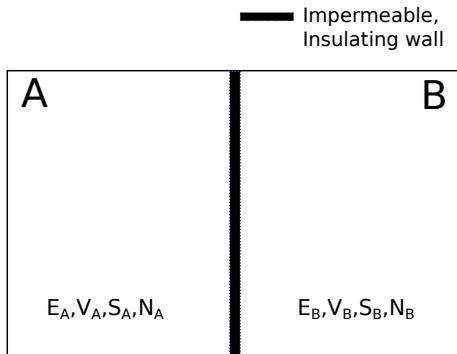
and for an isolated system

$$0 \leq dS \quad (20)$$

in other words, irreversibility.

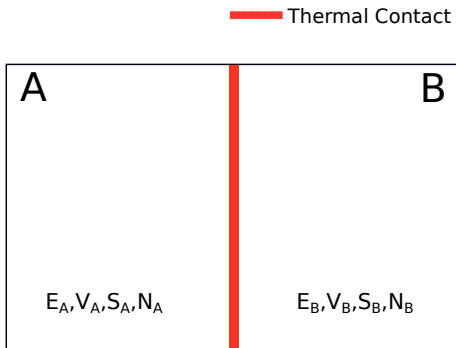
The thermodynamic temperature

Composite system partitioned into A and B



- Total Energy, $E_A + E_B$
- Total Volume, $V_A + V_B$
- Total N, $N_A + N_B$
- $S_T(E_A, V_A, N_A, E_B, V_B, N_B) = S_A(E_A, V_A, N_A) + S_B(E_B, V_B, N_B)$

The Partition is replaced by a conducting impermeable wall, and we let the system evolved towards equilibrium.



- $\Delta S_T \geq 0$
- at equilibrium: $\Delta S_T = 0$

$$dS_T = \left(\frac{\partial S_A}{\partial E_A} \right)_{V_A, N_A} dE_A + \left(\frac{\partial S_B}{\partial E_B} \right)_{V_B, N_B} dE_B \quad (21)$$

Due to energy conservation $dE_A = -dE_B$

$$dS_T = \left[\left(\frac{\partial S_A}{\partial E_A} \right)_{V_A, N_A} - \left(\frac{\partial S_B}{\partial E_B} \right)_{V_B, N_B} \right] dE_A \quad (22)$$

$dS = 0$ at equilibrium.

$$\left(\frac{\partial S_A}{\partial E_A} \right)_{V_A, N_A} = \left(\frac{\partial S_B}{\partial E_B} \right)_{V_B, N_B} \quad (23)$$

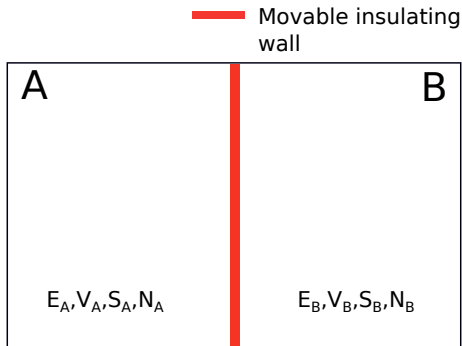
Empirically, it is known that temperatures equate upon thermal contact, thus the entropy must be related to temperature.

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial E} \right)_{V,N} \quad (24)$$

Thus, at thermal equilibrium: $\frac{1}{T_A} = \frac{1}{T_B}$ or $T_A = T_B$

The thermodynamic pressure I

The Partition is replaced by a movable insulating impermeable wall, and we let the system evolved towards equilibrium.



- $\Delta S_T \geq 0$
- at equilibrium: $\Delta S_T = 0$

$$dS_T = \left(\frac{\partial S_A}{\partial V_A} \right)_{E_A, N_A} dV_A + \left(\frac{\partial S_B}{\partial V_B} \right)_{E_B, N_B} dV_B \quad (25)$$

Due to Volume conservation $dV_A = -dV_B$

$$dS_T = \left[\left(\frac{\partial S_A}{\partial V_A} \right)_{E_A, N_A} - \left(\frac{\partial S_B}{\partial V_B} \right)_{E_B, N_B} \right] dV_A \quad (26)$$

$dS = 0$ at equilibrium.

$$\left(\frac{\partial S_A}{\partial V_A} \right)_{E_A, N_A} = \left(\frac{\partial S_B}{\partial V_B} \right)_{E_B, N_B} \quad (27)$$

Empirically, it is known that pressures equate upon movable contact, thus the entropy must be related to pressure.

$$\frac{P}{T} \equiv \left(\frac{\partial S}{\partial V} \right)_{E,N} \quad (28)$$

Thus, at pressure equilibrium: $\frac{P_A}{T} = \frac{P_B}{T}$ or $P_A = P_B$

The third law

Definition of the absolute value of entropy

$$\lim_{T \rightarrow 0} S = 0 \quad (29)$$

Which implies that all heat capacities go to zero at low T

$$S(T_2, V) - S(T_1, V) = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT \quad (30)$$

$$T_1 \rightarrow 0, C_V \rightarrow 0$$

The fundamental thermodynamic relation

$$\Delta E = \Delta Q + \Delta W \text{ (any process)}$$

$$dW = -pdV + \mu dN + \dots \text{ (reversible process)}$$

$$dQ = TdS \text{ (reversible process)}$$

Thermodynamic Potential

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN + \dots \quad (31)$$

The total variation of S is:

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN \quad (32)$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}, \quad -\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V}$$

The fundamental thermodynamic relation

$$dE = TdS - PdV + \mu dN + \dots \quad (33)$$

The total variation of E is:

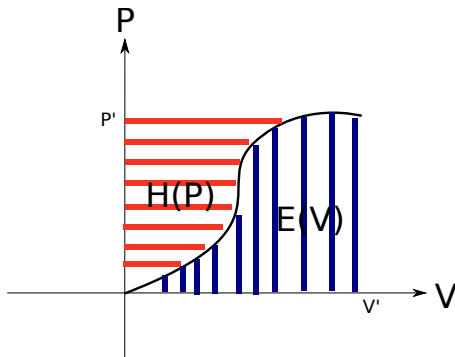
$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV + \left(\frac{\partial E}{\partial N}\right)_{S,V} dN \quad (34)$$

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N}, \quad P = -\left(\frac{\partial E}{\partial V}\right)_{S,N}, \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

The Legendre transform

Consider a function $E(V)$ of one variable. The Legendre transform allows to replace the independent variable V by the derivative $\frac{\partial E}{\partial V}$, which is convenient in thermodynamics given that state variables are usually defined as derivatives.

- $\frac{\partial E(V)}{\partial V} = P(V)$
- $\frac{\partial H(P)}{\partial P} = V(P)$
- $E(V) = \int_0^{V'} P(V) dV$
- $H(P) = \int_0^{P'} V(P) dP$
- $H(P) + E(V) = P'V'$



The Legendre transform II

We define the Legendre transform of the function $E(V)$ as

$$H(P) = PV - E(V) \quad (35)$$

Thus for any function $f(x(y))$ the Legendre transform $f^*(y(x))$ is defined as:

The Legendre Transform

$$f^*(y(x)) = \frac{\partial f(x(y))}{\partial x} x(y) - f(x(y)) \quad (36)$$

or

$$-f^*(y(x)) = f(x(y)) - \frac{\partial f(x(y))}{\partial x} x(y) \quad (37)$$

The Enthalpy: H

The Enthalpy, H , is the negative Legendre transform of the energy, switching from volume to pressure.

$$H(P, S, N) \equiv E(V, S, N) - \frac{\partial E}{\partial V} V(p) \quad (38)$$

Enthalpy

$$H(P, S, N) = E + PV \quad (39)$$

$$dH = TdS + VdP + \mu dN + \dots \quad (40)$$

*Even though not explicitly stated, all other control variables are kept fixed.

The Enthalpy: H II

The total variation of H is:

$$dH = \left(\frac{\partial H}{\partial S} \right)_{P,N} dS + \left(\frac{\partial H}{\partial P} \right)_{S,N} dP + \left(\frac{\partial H}{\partial N} \right)_{S,P} dN \quad (41)$$

$$T = \left(\frac{\partial H}{\partial S} \right)_{P,N}, \quad V = \left(\frac{\partial H}{\partial P} \right)_{S,N}, \quad \mu = \left(\frac{\partial H}{\partial N} \right)_{S,P}$$

The Helmholtz free energy : A

The Helmholtz free energy, A , is the negative Legendre transform of the energy, switching from entropy to temperature.

$$A(V, T, N) \equiv E(V, S, N) - \frac{\partial E}{\partial S} S(T)^* \quad (42)$$

Helmholtz free energy

$$A(V, T, N) = E - TS \quad (43)$$

$$dA = -SdT - PdV + \mu dN + \dots \quad (44)$$

*Even though not explicitly stated, all other control variables are kept fixed.

Helmholtz free energy: A II

The total variation of A is:

$$dA = \left(\frac{\partial A}{\partial T} \right)_{V,N} dT + \left(\frac{\partial A}{\partial V} \right)_{T,N} dV + \left(\frac{\partial A}{\partial N} \right)_{V,T} dN \quad (45)$$

$$S = - \left(\frac{\partial A}{\partial T} \right)_{V,N}, \quad V = - \left(\frac{\partial A}{\partial V} \right)_{T,N}, \quad \mu = \left(\frac{\partial A}{\partial N} \right)_{T,V}$$

The Gibbs free energy : G

The Gibbs free energy, G, is the negative Legendre transform of the enthalpy, switching from entropy to temperature.

$$G(P, T, N) \equiv H(P, S, N) - \frac{\partial H}{\partial S} S(T)^* \quad (46)$$

Gibbs free energy

$$G(P, T, N) = H - TS \quad (47)$$

$$dG = -SdT + VdP + \mu dN + \dots \quad (48)$$

*Even though not explicitly stated, all other control variables are kept fixed.

Gibbs free energy: A II

The total variation of G is:

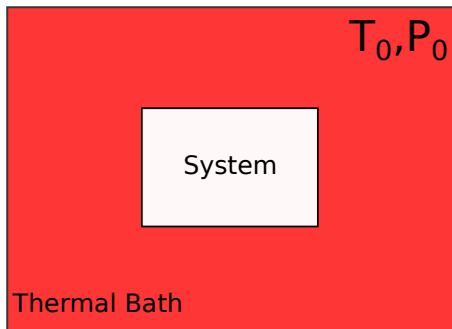
$$dG = \left(\frac{\partial G}{\partial T} \right)_{P,N} dT + \left(\frac{\partial G}{\partial P} \right)_{T,N} dP + \left(\frac{\partial G}{\partial N} \right)_{P,T} dN \quad (49)$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P,N}, \quad V = \left(\frac{\partial G}{\partial P} \right)_{T,N}, \quad \mu = \left(\frac{\partial G}{\partial N} \right)_{T,P}$$

Spontaneous Changes

For the free energies, what spontaneous changes will occur?

- Typical experimental setup
- Total entropy of combined system:
- Spontaneous change, ΔQ_{rev} absorbed by the system
- Volume change ΔV



Spontaneous Changes II

1st Law: $dQ = dE + P_0 dV - \mu dN$

The total change in Entropy has two parts:

- dS for the system.
- $-\frac{Q_{rev}}{T_0}$ for the thermal bath.

$$dS_{Tot} = dS - \frac{dQ_{rev}}{T_0} = \frac{T_0 dS - dE - P_0 dV + \mu dN}{T_0} \geq 0 \quad (50)$$

or

$$dE - T_0 dS + P_0 dV - \mu dN \leq 0 \quad (51)$$

$$d[E - T_0 S + P_0 V - \mu N] \leq 0 \quad (52)$$

The therm within brackets is known as the "availability"

Spontaneous Changes III

- N,V,E constant $dA = -T_0S$
- N,V,T constant $dA = d[E - T_0S]$
- N,P,T constant $dA = d[E + P_0V - T_0S]$ or $d[H - TS]$

Spontaneous Changes

- NVE constant, $\Delta S \geq 0$
- NVT constant, $\Delta A \leq 0$
- NPT constant, $\Delta G \leq 0$

Summary

- The first Law : $\Delta E = \Delta Q + \Delta W$
- Entropy from Carnot Cycle: $\Delta S \equiv \int_1^2 \frac{dQ_{rev}}{T}$
- Second Law: $0 \leq TdS$, for an isolated system.
- Fundamental thermodynamic relation : $dE = TdS - PdV + \mu dN + \dots$
- Free energies from Legendre transforms:
 - ▶ $A(V, T, N) = E - TS, dA = -SdT - PdV + \mu dN + \dots$
 - ▶ $G(P, T, N) = H - TS, dG = -SdT + VdP + \mu dN + \dots$

Spontaneous Changes

- ▶ NVE constant, $\Delta S \geq 0$
- ▶ NVT constant, $\Delta A \leq 0$
- ▶ NPT constant, $\Delta G \leq 0$

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