

DATE

# Review of Statistical Mechanics - Phy-

# Thermodynamics

DATE

Macroscopic and microscopic state:

Consider a single particle  $\rightarrow$  State is defined as  $(\vec{r}, \vec{p})$

the initial condition completely specifies the problem.

So that given  $(\vec{r}(0), \vec{p}(0))$ ,  $(\vec{r}(t), \vec{p}(t))$  is uniquely defined. The state of this system is then represented by a point in the phase-space (also called  $\Gamma$  space).

As the system evolves, the time evolution of the system can be ~~represented by the evolution of the~~ represented by a trajectory in the phase space.

Now consider  $N$  such particles. The state ~~then~~ of the system is then represented by the set  $\{\vec{r}_i, \vec{p}_i\}$ .

There are  $6N$  degrees of freedom (no constraints), and hence there are  $6N$  initial conditions. It is evident that these states are microstate of the system. If we consider a chain of non-interacting spins then we have for single spin  $\uparrow$  two states up & down

$\uparrow \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \downarrow$

State. Therefore, the total number of possible states ~~is~~  $2^N$ . Once again, these correspond to microstates of the system.

~~Details~~ There is, however, ~~and~~ some combinations of these microscopic ~~parameters~~ <sup>coordinates</sup> which are ~~not~~ time independent. For example, for the spin system the quantity  $M = \sum_i S_i$ , where  $S_i$  can take value  $\pm 1$

is time independent.  $M$  is the magnetization of the system.

Such quantities are called macroscopic quantities and they describe the macroscopic states of the system. For example, for a hydrostatic system, the three macroscopic or thermodynamic coordinates are  $P$ ,  $V$ ,  $T$ , &  $N$  etc.

Imagine you have a bottle of ~~water~~<sup>fluid</sup>. The first question that comes to mind is what is the fluid? That means we want to chemical composition of the solvent. If it's a mixture of two solvents - say water and glycerol then tell at what proportions they are mixed.

So the number  $N_1, N_2$  of the molecules turn out to be one of the macroscopic quantity. Volume of the fluid is a similar macroscopic coordinate and so are the pressure and temperature. But from an atomistic point of view, we have specified very little. The number of molecules in this solvent is of the order  $10^{23}$  and therefore there is a huge number of microstates. ~~infinitely~~

But only a few of these atomistic coordinates or combinations of them are pertinent macroscopically.

Then the general question that arises at this point is that for any arbitrary system how do we identify our thermodynamic coordinates? This is in turn determined by the type of measurement / experiment, and hence determines the scope and structure of thermodynamics.

However, there two key attributes in choosing macroscopic coordinates - Macroscopic measurements are extremely slow on the ~~atomistic~~ atomic or molecular scale of time as they are extremely coarse on the atomic scale of distance.

\* What is it that you measure in Thermodynamics - the responses from atoms such as heat capacities, force constants, thermal response.

+ phase diagrams of system - example hydro<sup>DATE</sup> systems.

For example, if we ~~not~~ measure the pressure exerted by the solvent on the container walls - then typically such measurements take fractions of a second. On the other hand within this time scale, of few fractions of a second, a large number of atomic reorientations have occurred since a typical atomic time scale  $10^{-15}$  sec.

Thermodynamics is the branch of Physics that deals with such macroscopic coordinates. The scope of thermodynamics does not take into account any microscopic interaction of the system, but rather the macroscopic properties system.

~~temperature~~ ~~is~~ ~~of~~ ~~a~~ ~~system~~ ~~is~~ ~~defined~~ ~~by~~ ~~the~~ ~~zeroth~~ ~~law~~  
~~state~~ ~~variables~~ ~~On~~ ~~the~~ ~~other~~ ~~hand~~, ~~Statistical~~ ~~mechanics~~ provides a more comprehensive picture taking into account the microscopic interactions in the system. As an example, the temperature of a system is defined via the zeroth law of thermodynamics, while statistical mechanical description of temperature relates it to the average kinetic energy of the molecules. ~~Conversely, a microscopic state of a system is defined by the coordinates & momenta of the system while for the thermodynamics~~ \* +

## Review of Thermodynamics

Zneth law - the zeroth law describes the transitive nature of thermal equilibrium.

If two systems A & B are separately in equilibrium with C then they are also in equilibrium with each other.

The theorem might appear to be deceptively simple, but it has a very important conclusion.— the existence of an important state functions: the empirical temperature  $\theta$  such that the systems are in equilibrium at this <sup>same</sup> temperature.

Suppose the equilibrium state of a system A, B, C are described by coordinates  $\{A_1, A_2, \dots\}$ ,  $\{B_1, B_2, \dots\}$  and  $\{C_1, C_2, \dots\}$ . Now the equilibrium between A & B & C means that there is a constraint between the coordinates of A & C such that the change in one of the coordinates must be accompanied by the change in others. Hence

$$f_{AC}(A_1, A_2, \dots, C_1, C_2, \dots) = 0$$

Similarly for equilibrium between B & C we have

$$f_{BC}(B_1, B_2, \dots, C_1, C_2, \dots) = 0$$

From the above relations, we can invert to express one of the coordinates say  $C_1$  in terms of others

$$C_1 = f_{AC}(A_1, A_2, \dots, C_2, C_3, \dots)$$

$$C_1 = f_{BC}(B_1, B_2, \dots, C_2, \dots)$$

$$\Rightarrow f_{AC}(A_1, A_2, \dots, C_2, \dots) = f_{BC}(B_1, B_2, \dots, C_2, \dots) \quad \text{--- (1)}$$

Now, by zeroth law we should have

$$f_{AB}(A_1, A_2, \dots, B_1, B_2, \dots) = 0 \quad \text{--- (2)}$$

I can now choose any set of parameters  $\{A, B\}$  and substitute in ①. The resulting equality must hold for any parameters in C. ~~If we do~~ Further, any variation in these parameters moving along the manifold ~~is~~ defined by ② equation ① will remain ~~variant~~ valid irrespective of the state of C. One can therefore ignore the coordinates C in eq. ①, and the condition for equilibrium between A and B reduces to

$$\theta_A(A_1, A_2, \dots) = \theta_B(B_1, B_2, \dots)$$

The equilibrium is therefore ~~as~~ defined by the function  $\theta$  of the thermodynamic coordinates. This function specifies the equation of state and isotherms of A are defined by the condition  $\theta_A(A_1, A_2, \dots) = \theta$ . We have thus come to the ~~conclu~~ conclusion that there exists a function that constraints the parameters of each system in thermal equilibrium.

### First law

The first ~~law~~ law is a statement of the conservation of energy.

The amount of work required to change the state of an otherwise adiabatically isolated system depends only on the initial and final states and not on the means by which the work is performed ~~or~~ or on the intermediate stages of the process.

~~Since for an adiabatic process, the heat exchange is zero,~~  
The statement is very similar to the conservation of

mechanical energy. In fact we can define an internal energy  $U(x)$  (where  $x$  are the thermodynamic coordinates) such that

$$\cancel{\Delta W} = U(x_f) - U(x_i)$$

If the adiabatic constraints are removed then the work done is no longer equal to the change in the internal energy. ~~For this reason~~ The difference is the heat intake of the system from the surroundings

$$\Delta Q = \Delta U - \Delta W$$

$\Delta Q$  and  $\Delta W$  are no longer state functions.— they will now depend on the ~~other~~ external factors such as the means of doing work etc. For an infinitesimal change we have

$$\cancel{dQ} = dU - \cancel{dW}$$

Not perfect differentials

$$dU = \sum_i \frac{\partial U}{\partial x_i} dx_i \rightarrow \text{perfect differential.}$$

Convention: signs of work and heat indicate energy added to the system.

The above equation is the statement of the 1<sup>st</sup> Law.

Typically, one can divide the thermodynamic coordinates  $\vec{x}$  in two sets — a set of generalized coordinates  $\vec{q}$ , and a set of generalized forces  $\vec{F}$ .

such that for an infinitesimal quasi-static process  
we can define work as

$$dW = \sum_i F_i dx_i$$

↓  
A transformation

Ex:

System	Forces	Disp.
Wire	Tension $F$	$l \times \theta L$
Film	Surface tension $\sigma$	Area $A$
Fluid	Pressure - $P$	Volume $V$
Magnet	Magnetic Field $H$	Magnetization $M$

which is performed sufficiently slowly such that the system is always in equilibrium.

Take, at every stage of the process we can the thermodynamic coordinates are defined.  
 $E_x$  - the chemical work  
pulling a spring  $w = \int F dL$

Chemical Reaction	Chemical Potential $\mu$	Particle number $n$

→ Negative sign since the force exerted by the wall on the system carries a neg. sign.  
The displacements are usually extensive parameters - they depend on the system size. On the other hand, the forces are intensive variables and are independent of size. The generalized forces are also indicators of equilibrium. For example, the pressure, surface tension / film are all uniform in the system in equilibrium.

[Temperature also indicates equilibrium. What is the gen. displacement  $\beta$  corresponding to temp.?]

Response functions - they are usually the quantities that characterize the macroscopic system and are experimentally measured from the thermodynamic coordinates. Heat capacities, force constants and thermal response are some examples of response function.

$$C_V = \left( \frac{\partial Q}{\partial T} \right)_V = \left( \frac{dU - dW}{dT} \right)_V = \left( \frac{dU + PdV}{dT} \right)_V = \left( \frac{dU}{dT} \right)_V$$

$$(C_p = \frac{\partial Q}{\partial T})_P = \frac{dU + PdV}{dT} = \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P$$

Fare constants: isothermal compressibility  $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$

magnetic susceptibility  $\chi_T = \frac{1}{V} \left(\frac{\partial M}{\partial B}\right)_T$

thermal response: expansion coefficient:  $\alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$

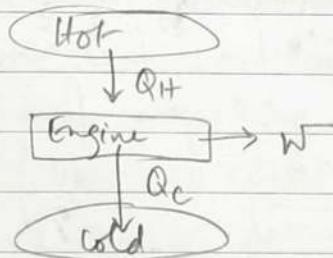
### Second Law

Typically all macroscopic processes are irreversible, particularly those that involve work or exchange of heat. The notion of irreversibility is encoded in the second law.

A thermodynamic system attains its equilibrium state via an irreversible process. The 2nd law provides us with the concept of yet another thermodynamic coordinate entropy  $S$ , which never decreases in any natural process — i.e. a process that takes place in isolation and equilibrium under such conditions is characterized by maximum entropy.

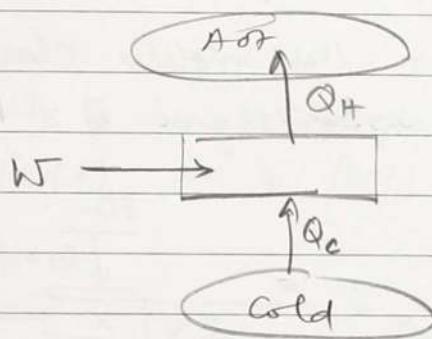
Historically the formulation of 2nd law took place after the advent of heat engines. An idealized heat engine works by taking  $Q_H$  heat from a hot reservoir, ~~and~~ doing some work  $W$  and dumping  $Q_C$  heat to a cold reservoir.

The efficiency is then defined as



$$\eta = 1 - \frac{Q_C}{Q_H}$$

A refrigerator is a heat engine running backward.



The efficiency is now defined as  $\eta_R = \frac{Q_C}{W}$

1<sup>st</sup> law rules out processes that produce work without consuming any energy — perpetual motion of first kind.

2<sup>nd</sup> law rules out processes which do not violate the conservation of energy but are able to do work — for example converting water to ice — perpetual motion of second kind. The observation that heat flows from a hot body to a cold one is the essence of 2<sup>nd</sup> law.

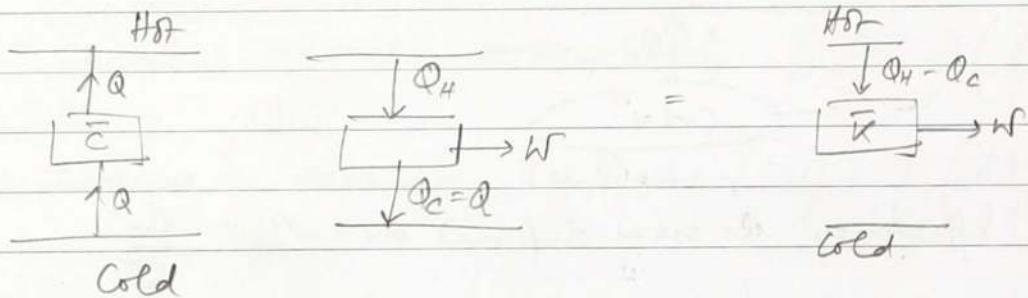
Kelvin's Statement No process is possible whose sole result is the complete conversion of heat into work.

Clausius's Statement No process is possible whose sole result is the transfer of heat from a cold body to a hot body without doing any external work.

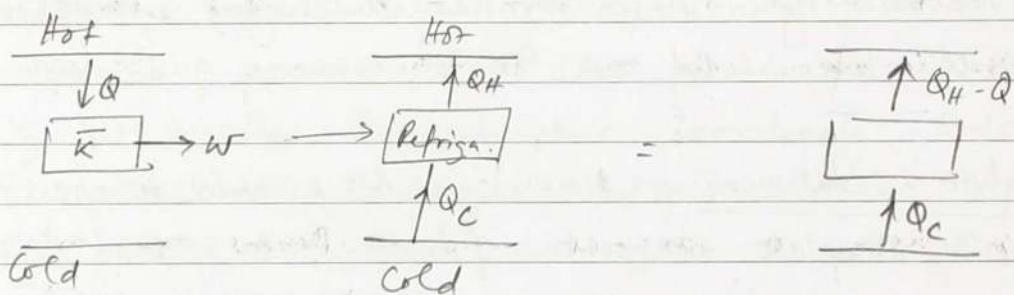
A perfect heat engine is ruled out by the 1<sup>st</sup> statement.  
A perfect refrigerator is ruled out by the 2<sup>nd</sup> statement.

Proof of equivalence:

Suppose we have a machine that violates Clausius's statement by taking heat  $Q$  from a cooler region to a hotter one.



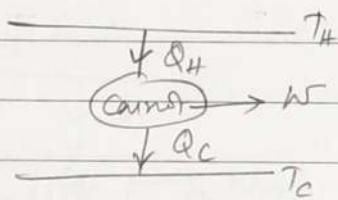
Now we put a heat engine that takes  $Q_h$  from hot-reservoir and dumps  $Q_c$  to cold reservoir and performs work  $W$ . Now the output can be adjusted so that  $Q_c = Q$ . Hence the combined system takes  $Q_h - Q$  heat and does work  $W$  thus violating Kelvin's statement.



Now suppose we violate Kelvin's statement. We extract heat  $Q$  from Hot and completely convert it to work. The work is used to run a refrigerator. The net effect is to transfer heat from cold to a hot body without doing any work and thus violating Clausius's statement.

Carnot Engine

A Carnot engine is a reversible engine that runs in a cycle with all the heat exchanges taking place at constant temperature  $T_C$  (Cold) and  $T_H$  (Hot)



A reversible process is one that can be run backward in time by simply reversing its inputs and outputs. It is the thermodynamic equivalent of frictionless motion in mechanics. Since time reversibility implies equilibrium a reversible process must be a quasistatic process. The converse is not generally true.

Zeroth law allows us to select isotherms at  $T_C$  &  $T_H$ . We need to connect these isotherms by adiabatic processes. Since heat is not a state function ~~is~~ apriori we do not know how to construct such adiabats. Let's take ideal gas as the working substance.

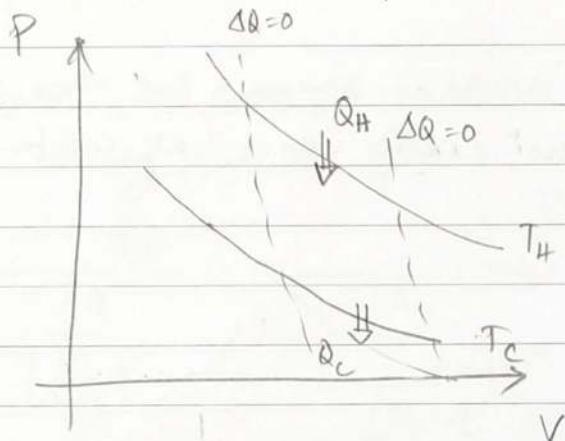
$$\text{Then } U = \frac{3}{2} NKT = \frac{3}{2} PV$$

$$dQ = dU + PdV = \frac{3}{2} d(PV) + PdV = 0$$

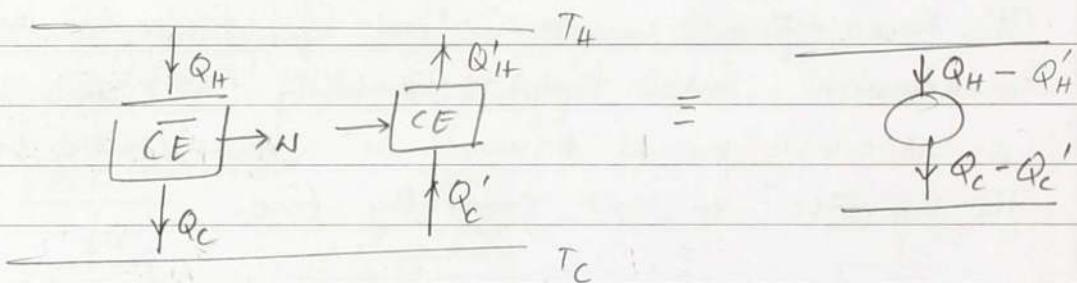
$$\therefore \frac{5}{2} PdV + 3VdP = 0$$

$$PV^{\frac{5}{3}} = \text{const.}$$

For an adiabatic process:  $PV^r = \text{const}$ .



Carnot's theorem  $\rightarrow$  No engine operating between two reservoirs is more efficient than a Carnot engine operating between them.



Take a non Carnot engine (CE) and use it to run a Carnot engine backward as a refrigerator.

The net effect of the combined machine is to transfer an amount of heat  $Q_H - Q'_H = Q_C - Q'_C$ .  
 $\Rightarrow Q_H - Q'_H$  can not be negative, then it violates Clausius' theorem.

$$Q_H \geq Q'_H$$

Since the work done is same we have

$$\frac{W}{Q_H} \leq \frac{W}{Q'_H} \quad \eta_{\text{Carnot}} \geq \eta_{\text{non-Carnot}}$$

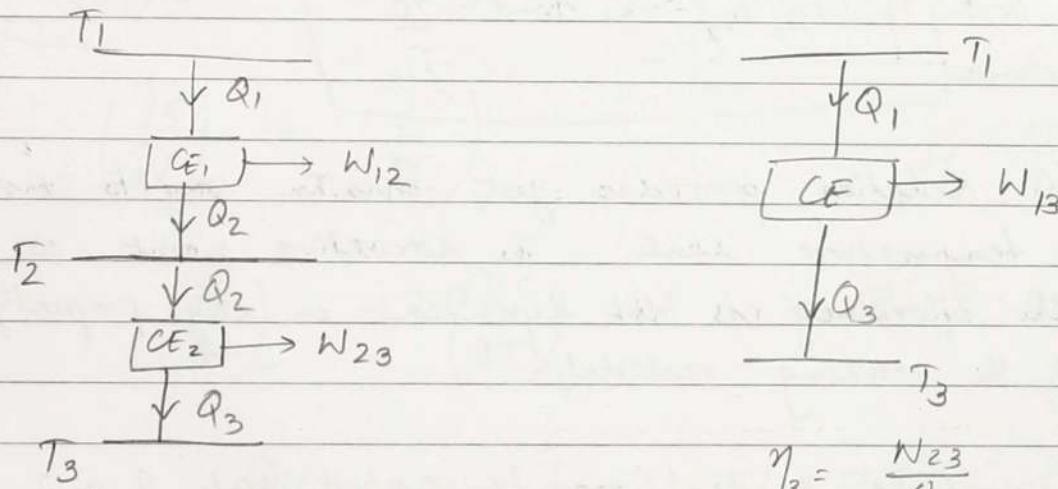
$\Rightarrow$  All Carnot engines have the same universal efficiency

$$\eta(T_c, T_h)$$

↓

Derivation of  $\eta(T_c, T_h)$

Consider 2 Carnot engines



$$\eta_3 = \frac{W_{23}}{Q_2}$$

$$W_{13} = W_{12} + W_{23}$$

$$\eta_1(T_1, T_2) = \frac{W_{12}}{Q_1}$$

$$Q_2 = Q_1 - W_{12} = Q_1 [1 - \eta(T_1, T_2)]$$

$$Q_3 = Q_2 - W_{23} = Q_2 [1 - \eta(T_2, T_3)]$$

$$Q_3 = Q_1 - W_{13} = Q_1 [1 - \eta(T_1, T_3)]$$

$$Q_3 = Q_1 [1 - \eta(T_2, T_3)] [1 - \eta(T_1, T_2)]$$

$$[1 - \eta(T_2, T_3)] [1 - \eta(T_1, T_2)] = [1 - \eta(T_1, T_3)]$$

$$\Rightarrow [1 - \eta(T_1, T_2)] = \frac{f(T_2)}{f(T_1)}$$

which by convention is set as  $\frac{T_2}{T_1}$

→ The temperatures  $T_H$  &  $T_C$  are all positive. If a negative temp existed then a system operating between it and a positive temp would extract heat from both reservoirs and convert them to work, violating Kelvin's statement.

$$\Rightarrow 1 - \eta(T_2, T_1) = \frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

$$\frac{Q_2}{T_2} = \frac{Q_1}{T_1}$$

$$\left( \frac{Q_2}{T_2} - \frac{Q_1}{T_1} \right) = 0$$

ans  $\eta(T_H, T_C) = 1 - \frac{T_C}{T_H}$

This relation provides yet another way to construct a temperature scale. The attractive point is that the efficiency is not dependent on any property of the working material.

Equivalence of ideal gas temperature scale  $\theta$  and thermodynamic temperature  $T$ .

use ideal gas as the working substance for the Carnot cycle.

$$PV = Nk_B\theta \rightarrow \text{ideal gas temperature}$$

$$\frac{T_H}{T_C} = \frac{\theta_H}{\theta_C} \rightarrow \text{thermodynamic temp scale}$$

ideal gas  $U$  is a function of  $\theta$ . To see this we look at the 1<sup>st</sup> law

$$dU = Tds - Pdv$$

$$U = U(T, V) \quad \text{and} \quad S = S(T, V)$$

→  $T=0$  can not be reached. Since for  $T=0$ ,  $\eta=1$  and thus we have extracted heat converted it completely to work violating Kelvin's statement]

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$dU = T \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial S}{\partial V}\right)_T dV - PdV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$PV = Nk_B T$$

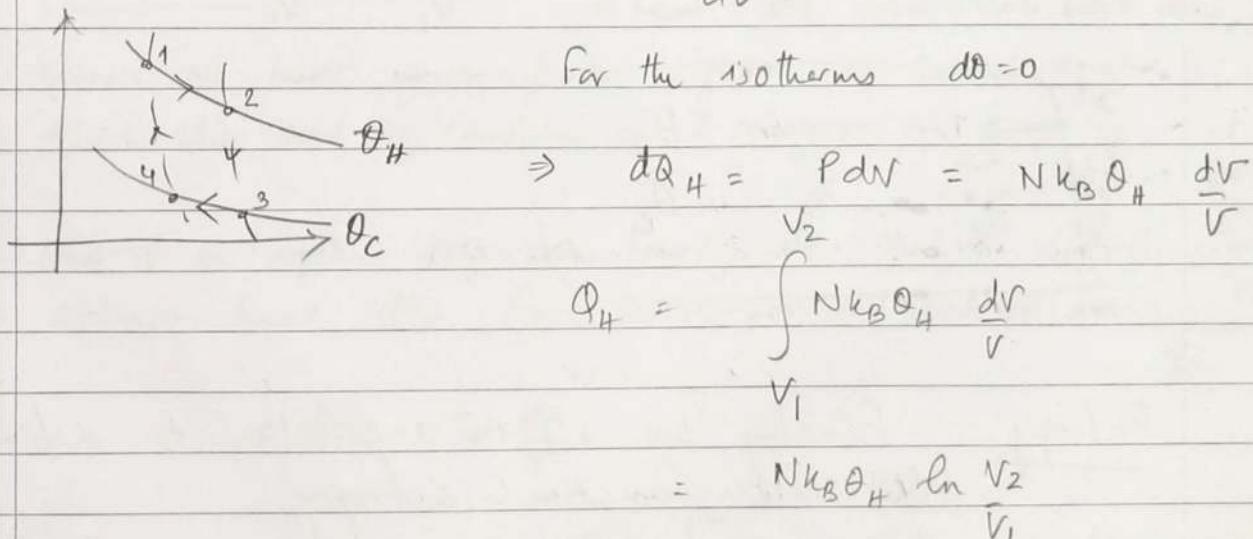
$$\frac{\partial P}{\partial T} = \frac{Nk_B}{V} = \frac{P}{T}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P = P - P = 0.$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \Rightarrow U = U(T)$$

$U$  is only a function  $\theta$ .

$$dQ = du + PdV = \frac{dU}{d\theta} d\theta + PdV$$



Similarly  $Q_C = Nk_B \theta_C \ln \frac{V_3}{V_4}$

$$\Rightarrow \frac{Q_H}{\bar{\varrho}_c} = \frac{\theta_H}{\theta_c} \frac{\ln(v_2/v_1)}{\ln(v_3/v_4)}$$

For the adiabatic processes we have

$$dQ=0 \Rightarrow \frac{du}{d\theta} d\theta + \frac{Nk_B\theta}{v} dw = 0$$

$$\frac{dw}{v} = - \frac{1}{Nk_B\theta} \frac{dE}{d\theta} d\theta$$

$$\ln\left(\frac{v_3}{v_2}\right) = - \frac{1}{Nk_B} \int_{\theta_c}^{\theta_H} \frac{1}{\theta} \frac{dE}{d\theta} d\theta$$

$$\ln\left(\frac{v_4}{v_1}\right) = - \frac{1}{Nk_B} \int_{\theta_c}^{\theta_H} \frac{1}{\theta} \frac{dE}{d\theta} d\theta$$

$$\Rightarrow \frac{v_3}{v_2} = \frac{v_4}{v_1} \Rightarrow \frac{v_2}{v_1} = \frac{v_3}{v_4}$$

$$\boxed{\frac{Q_H}{\bar{\varrho}_c} = \frac{T_H}{T_C} = \frac{\theta_H}{\theta_c}}$$

Entropy Finally we are in a position to define the state function entropy.

Recall that for the Carnot engine we had

$$\frac{\varnothing_2}{T_2} = \frac{\varnothing_1}{T_1} \Rightarrow \left[ \frac{\varnothing_2}{T_2} - \frac{\varnothing_1}{T_1} \right] = 0.$$

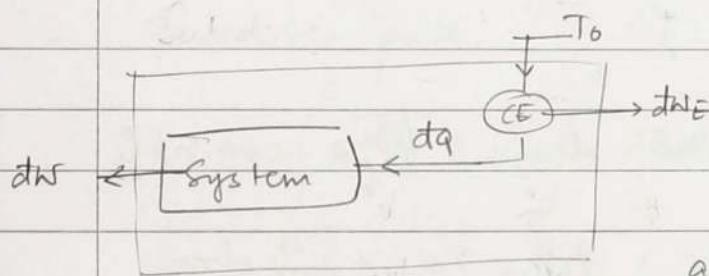
$$\oint \frac{dQ}{T} = 0.$$

$\frac{dQ}{T}$  is then already a state function since it does not depend on the path, just like internal energy.

The more general statement is given by Clausius's theorem.

For any cyclic transformation (reversible or not)

$\oint \frac{dQ}{T} \leq 0$ , where  $dQ$  is the heat increment supplied to the system at temperature  $T$ .



Subdivide the cycle into a series of infinitesimal cycles in which the system receives a heat  $dQ$  and does work  $dW$

Direct all heat given to the system to Carnot engine whose other end is connected to a reservoir at temp  $T_0$ .

Now if the system receives heat  $dQ$  then the Carnot engine extracts heat  $dQ_R$  from the reservoir. And we have

$$dQ_R = T_0 \frac{dQ}{T}$$

At the end of the cycle, the system and the Carnot engine comes back to its initial state.

The net effect is to extract heat  $Q_R = \int dQ_R$  and convert ~~heat~~ it to work  $W = Q_R$  (since  $dU = 0$ ).

The net work  $W$  is a sum total of work done by the Carnot engine and by the system during the cycle.

By Kelvin's statement we have  $Q_R = W \leq 0$

$$\Rightarrow T_0 \int \frac{dQ}{T} \leq 0 \Rightarrow \int \frac{dQ}{T} \leq 0.$$

The equality is valid for a reversible process

$$\int \frac{dQ}{T} = 0 \quad \text{ex} \rightarrow \text{Carnot engine.}$$

We then define <sup>the</sup> state function entropy  $S$

$$S(B) - S(A) = \int_A^B \frac{dQ}{T}$$

The 1<sup>st</sup> law can be written down for a reversible process as

$$dU = Tds + dw = Tds + \sum J_i dx_i$$

Now that we have identified the generalized displacement corresponding to  $T$ , we are in a position to identify the number of independent variables. If there are  $n$  generalized forces then the number of independent variables are  $(n+1)$ . The intensive variables are given by

$$\left( \frac{\partial S}{\partial V} \right)_{x_i} = \frac{1}{T} \quad \text{and} \quad \left( \frac{\partial S}{\partial x_i} \right)_{V, x_j \neq i} = -\frac{J_i}{T}$$

$$dU = Tds - PdV$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \quad \left(\frac{\partial S}{\partial V}\right)_P = +\frac{P}{T}$$

$$dU = Tds + PdV + \mu dN$$

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

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

Consider an irreversible change from A to B. Make a complete cycle by returning from B to A via a reversible path.

$$\int_A^B \frac{dq}{T} + \int_B^A dq_{rev} \leq 0 \quad \text{Clausius's Theorem}$$

$$\int_A^B \frac{dq}{T} \leq S(B) - S(A)$$

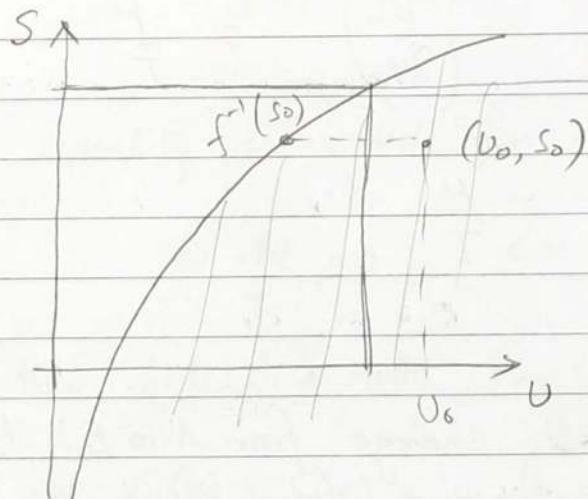
In a differential form this implies that  $-ds \geq \frac{dq}{T}$ .

In particular, consider adiabatically isolating a number of subsystems, each initially in thermal equilibrium. As they come to a joint equilibrium, the net  $\delta q = 0$ . This means  $\delta S \geq 0$ . Thus, an adiabatic system attains a maximum value of entropy in equilibrium, since spontaneous internal changes can only increase S. Thus the

direction of increasing entropy points out the arrow of time and the path to equilibrium.

Consider a thermodynamic system characterized by  $U, S$  and  $\{X\}$ . If the system is left to itself then it will move towards equilibrium. Thus we have

$$\delta S \geq 0$$



The above figure shows the schematic variation of the entropy with  $V$  for fixed values of  $\{X\}$ . The solid line is the equilibrium value of  $S$  and the entire region below the line corresponds to all processes, including non-equilibrium processes. If we look at the entropic formulation of the system, then for states with same value of  $S$  and  $\{X\}$ , the equilibrium state has the minimum energy. Thus, if the system with fixed value of  $S$  and  $\{X\}$  is left to itself then  $\delta U \leq 0$ .

This is the energy minimum principle.

We see that the entropy maximum and energy minimum are equivalent statements.

To make this explicit, consider a state with coordinates  $(U_0, S_0)$ . Also, the equilibrium line is defined by  $S = f(U)$ .

The entropy maximum principle tells us that for the arbitrary state

$$S_0 \leq f(U_0)$$

Now, suppose that  $f$  is a monotonically increasing function.

$$\Rightarrow x < y \quad f(x) < f(y).$$

$$\text{if } f(x) = z \quad x = f^{-1}(z)$$

$$\begin{aligned} x &< y \\ f^{-1}(z) &< y \end{aligned}$$

$$z < f(y)$$

$$\text{we thus have } U_0 \geq f^{-1}(S_0)$$

$f^{-1}(S_0)$  is the ~~value~~ value of energy for an entropy  $S_0$ . Thus, we see that energy is minimum at equilibrium. The whole argument is true only when  $S$  at equilibrium is a monotonically increasing function of  $U$ .

$$\Rightarrow \left( \frac{\partial S}{\partial U} \right)_{ex} \geq 0 \quad \Rightarrow T \geq 0$$

So the equivalence of the two statements is due to positivity of the temp. scale.

Extensivity of the internal Energy  $U(S, V, N)$

$U = U(S, V, N)$  → is a function of  $S, V, N$  alone

The intensive variables are given by

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

Each intensive variable is conjugate to the extensive variables to which it couples in the expression for  $dU$ .

Eqn ① are called equations of state

All thermodynamics is able to tell us is that  $U$  must be a function of the extensive variables. It, however, does not provide us with the exact functional dependence of  $U$  on its variables. Once the later is known, all thermodynamic coordinates can be evaluated explicitly.

One of the scopes of stat mech is precisely that of providing us with an explicit expression for  $U$  on the entropy  $S$ .

There is in principle no reason for all independent-thermodynamic coordinates to be extensive in nature.

Indeed, later on we will see that the thermodynamic potentials will be functions of independent variables that includes one or more intensive variable.

The extensive property of the free energy or alternatively the entropy can be made more precise.

Imagine a system consisting of  $\lambda$  copies of a certain subsystem. For each subsystem the entropy, volume and particle number is given by  $S, V, N$ .

If we consider the whole system then the values are  $\lambda S, \lambda V, \lambda N$ , and the internal energy would be  $U(\lambda S, \lambda V, \lambda N)$ . By the extensivity property

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \quad \forall \lambda > 0$$

Such functions are called homogeneous functions of degree 1.

If a function  $f(x_1, x_2, \dots, x_r)$  obeys the property

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_r) = \lambda^k f(x_1, x_2, \dots, x_r)$$

for arbitrary  $\lambda$ , then the function is a homogeneous function of degree  $k$ .

Take a derivative of both sides w.r.t.  $\lambda$

$$\sum_i \frac{\partial f(\lambda x_i)}{\partial \lambda} x_i = k \lambda^{k-1} f(x_1, x_2, \dots)$$

Putting  $\lambda=1$ , we have

$$\sum_{i=1}^r x_i \frac{\partial f}{\partial x_i} = k f$$

→ Generalized form  
of Euler relation.

In the case of internal Energy  $U$ , we have

$$U = \left(\frac{\partial U}{\partial S}\right) S + \left(\frac{\partial U}{\partial V}\right) V + \left(\frac{\partial U}{\partial N}\right) N$$

$$U = TS - PV + \mu N$$

$$dU = TdS + SdT - PdV + Vdp + \mu dN + Nd\mu$$

$$dU = TdS - PdV + \mu dN + SdT - Vdp + Nd\mu$$

$$\Rightarrow SdT - Vdp + Nd\mu = 0$$

Gibb's - Duhem Relation

Note that the Gibb's Duhem relation is a consequence of the homogeneity property of the internal Energy.

Gibbs Duhem relation in the entropic formulation

$$\text{If I use } S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$$

and the Euler relation then I have

$$S = U\left(\frac{\partial S}{\partial U}\right) + V\left(\frac{\partial S}{\partial V}\right) + N\left(\frac{\partial S}{\partial N}\right)$$

$$S = \frac{U}{T} + \frac{PV}{T} - \frac{\mu N}{T}$$

$$dS = \frac{du}{T} + Vd\left(\frac{1}{T}\right) + Vd\left(\frac{P}{T}\right) + \frac{PdV}{T}$$

$$+ Nd\left(\frac{\mu}{T}\right) - \frac{\mu}{T}dN$$

$$\Rightarrow Vd\left(\frac{1}{T}\right) + Vd\left(\frac{P}{T}\right) - Nd\left(\frac{\mu}{T}\right) = 0$$

Ex Classical ideal gas  $\rightarrow$  See how far thermodynamics can provide information.

$$PV = Nk_B T$$

$$U = \frac{3}{2} N k_B T$$

$$\Rightarrow N d\left(\frac{\mu}{T}\right) = U d\left(\frac{3 N k_B}{2 U}\right) + V d\left(\frac{N k_B}{V}\right)$$

$$N d\left(\frac{\mu}{T}\right) = \frac{3 U k_B}{2 U} dN + \frac{3 N k_B U}{2} \left(-\frac{1}{U^2}\right) dU$$

$$+ \frac{V k_B}{V} dN + V N k_B \left(-\frac{1}{V^2}\right) dV$$

$$N d\left(\frac{\mu}{T}\right) = \frac{5}{2} U_B dN - \frac{3}{2} N k_B \frac{dU}{U} - \frac{dV}{V} N k_B$$

$$d\left(\frac{\mu}{k_B T}\right) = \frac{5}{2} \frac{dN}{N} - \frac{3}{2} \frac{du}{u} - \frac{dv}{v}$$

$$\frac{\mu}{k_B T} = \ln \left[ \frac{N^{5/2}}{k_B U^{3/2} V} \right]$$

$u$  is an arbitrary constant.

$$S = \frac{3}{2} N k_B + N k_B - \frac{\mu N}{T}$$

$$= \frac{5}{2} N k_B + N k_B \ln \left[ \frac{k_B U^{3/2} V}{N^{5/2}} \right]$$

$$= N k_B \left[ \ln \left( \frac{k_B U^{3/2} V}{N^{5/2}} \right) + \frac{5}{2} \right]$$

$K$  is determined by the third equation of state that would give  $\frac{\mu}{T}$  as a function  $g(U, V, N)$ .

Homogeneity of the internal energy and the entropy means that we can define densities for extensive variables. Choose  $\lambda = \frac{1}{N}$ .

$$\text{then we have } U\left(\frac{s}{N}, \frac{v}{N}, 1\right) = \frac{1}{N} U$$

$$s = \frac{S}{N}, \quad v = \frac{V}{N} \quad \text{and we get}$$

$$U = Nu(s, v)$$

$$\text{Similarly, } S\left(\frac{U}{N}, \frac{v}{N}, 1\right) = \frac{1}{N} S$$

$$NS(u, v) = S$$

Note that by definition intensive variables have to be homogeneous functions of degree zero.

$$T(S, V, N) = T\left(\frac{s}{N}, \frac{v}{N}, 1\right)$$

Further, this implies that we can write the intensive variables as

$$T = T(s, v) \quad p = p(s, v) \quad \text{and} \quad \mu = \mu(s, v)$$

Consequently, we can have a relation  $T = T(p, \mu)$  so that not all the intensive variables are independent. This implies that one of the independent thermodynamic coordinate must be an extensive variable.

## Partial Derivatives.

Suppose there exists partial derivatives between coordinates  $x, y, z$

$$f(x, y, z) = 0$$

Then  $x$  can be imagined as a function of  $y, z$ .

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

Similarly

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

So that

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left[ \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \right] + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x dz + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y \right] dz$$

Choosing  $x$  and  $z$  as independent coordinates, the above equation must be true for all variations of  $dx$  and  $dz$ .

Thus, if  $dz = 0$  and  $dx \neq 0$ , then we have

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

Choosing  $dx = 0$ , &  $dt \neq 0$  we get -

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = - \left(\frac{\partial x}{\partial z}\right)_y \Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$$

For a PVT system, the second theorem yields

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = - \left(\frac{\partial P}{\partial T}\right)_V$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \kappa = - \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial P}{\partial T}\right)_V = - \frac{\beta}{\kappa}$$

$$P = P(T, V)$$

$$\begin{aligned} dP &= \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \\ &= \frac{\beta}{\kappa} dT - \frac{1}{\kappa V} dV \end{aligned}$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$\text{Choose } dz = 0 \quad \text{then} \quad \left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_z$$

Exact differential  $f(x, y)$

$$df = \left( \frac{\partial f}{\partial x} \right)_y dx + \left( \frac{\partial f}{\partial y} \right)_x dy \\ = A(x, y) dx + B(x, y) dy.$$

Since the derivatives are equal then we have

$$\boxed{\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x}} \rightarrow \text{Integrability condition}$$

$$\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x} = \frac{\partial f}{\partial xy}$$

$$dG = x'(x, y) dx + y'(x, y) dy$$

$$\frac{\partial x'}{\partial y} \neq \frac{\partial y'}{\partial x} \rightarrow \text{Inexact differential}$$

Consider for a moment  $dG = 0$

$$\Rightarrow \frac{dy}{dx} = -\frac{x'}{y'}$$

Since the RHS is known, the derivative can be computed at each point in the  $(x, y)$  plane. The solution simply consists of drawing a system of curves in  $x-y$  plane such that the tangent at any point is given by the above equation. This therefore defines a family of curves  $\sigma(x, y) = C$

$$\frac{d\sigma}{dx} = \frac{\partial \sigma}{\partial x} + \frac{\partial \sigma}{\partial y} \frac{dy}{dx} = 0$$

$$\frac{\partial \sigma}{\partial x} + \frac{\partial \sigma}{\partial y} \left( -\frac{x'}{y'} \right) = 0$$

$$y' \frac{\partial \sigma}{\partial x} = x' \frac{\partial \sigma}{\partial y} = \frac{xy'}{z}$$

$$\Rightarrow x' = z \frac{\partial \sigma}{\partial x} \quad y' = z \frac{\partial \sigma}{\partial y}$$

$$dG_1 = z \left( \frac{\partial \sigma}{\partial x} dx + \frac{\partial \sigma}{\partial y} dy \right) = z d\sigma$$

$$d\sigma = \frac{dG_1}{z}$$

In two dimension, the pffain  $dG_{20}$  always admits an integrating factor. Thus, for a 2D thermodynamic system, the second law is a theorem.

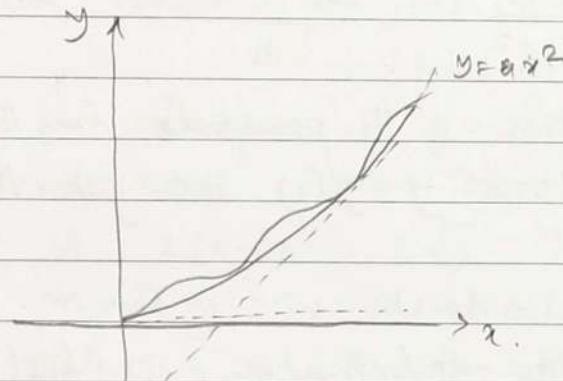
### Legendre Transformation

In the fundamental relations, we have  $U$  or  $S$  as a function of extensive variables. This may not be convenient in some cases and one needs to trade one or several extensive variables for equal number of intensive variables. The way to do this is using Legendre transformation.

The basic idea of Legendre transformation can be explained by using a function of one variable.

We represent it as a curve  $y = f(x)$ .

Take for example  $y = ax^2$



$y = x^2 + (1 - \cos 2\pi x)/\pi$  is second curve and the dashed line are tangents to the curve  $y = ax^2$ .

Suppose we now take the actual curve out of the picture and only look at tangents. This still provides us with an equal insight into the nature of the curve. Of course, if there are fewer tangents, then it is difficult to reconstruct the curve, since a different curve can also have same tangents. But then we can specify tangents at every possible point. How do we do that?

Tangents can be written down as

$$y = mx + c$$

At a point on the parabola,  $\frac{dy}{dx} \Big|_{x_0} = 2ax_0 = m$

The equation of the tangent then takes the form

$$(y - y_0) = m(x - x_0)$$

$$y = mx + (y_0 - mx_0)$$

$$\Rightarrow C = y_0 - mx_0 = ax_0^2 - 2ax_0^2 = -ax_0^2$$

$$\Rightarrow C = -\frac{am^2}{4a^2} = -\frac{m^2}{4a}$$

Which is the equation of the parabola in the Legendre transformation. From  $y = y(x)$  we got the curve  $C = C(m)$

To see that no information is lost, we now discuss how to recover the curve  $y = y(x)$  from Legendre transformed equation  $C = C(m)$ . Now, suppose  $(x, y)$  is a point where we want to reconstruct the curve. The eqn of the tangent at this point is

$$y = mx + C$$

$$C = y - mx$$

$$m = -2ax_0$$

$$dC = dy - m dx - x dm$$

$$m = \frac{dy}{dx} \Rightarrow dy = m dx$$

$$dC = -x dm \quad x = -\frac{dc}{dm} = \frac{m}{2a}$$

$$\Rightarrow y = \frac{m^2}{2a} + C = \frac{m^2}{2a} - \frac{m^2}{4a} = +\frac{m^2}{4a}$$

$$\Rightarrow y = ax^2$$

It is important to realize that we need to know  $c$  as a function of  $m$  in order to retain all the information about  $y = y(x)$ .

Consider for example  $y = x^2$  and  $y = (x-1)^2$ . In the former case  $m = 2x = 2\sqrt{y}$  and in the latter  $m = 2(x-1) = 2\sqrt{y}$ . The two relations between  $m$  and  $y$  are identical. More generally, for any constant value of  $a$ , the function  $y(a-a)$  would have the same relation between  $y$  and  $m$ . So given  $y = g(m)$  we will not be able to distinguish between two curves  $y(x)$ ,  $y(x-a)$ .

Take home message: if we want to change from  $x$  to  $m$ , then we can certainly do it, but we have to define a new function  $c$ . Retaining the old function  $y$  will not help us to reconstruct the curve.

Ex  $L = L(q, \dot{q}, t)$

Suppose I want to eliminate  $\dot{q}$ . Then define the derivative

$$p = \frac{\partial L}{\partial \dot{q}} \quad \text{--- ①}$$

$$C = L - p\dot{q} \quad \text{--- ②}$$

By convention this is defined as  $-H$ , where  $H$  is the Hamiltonian of the system.

$$-H = L - p\dot{q}$$

You can eliminate  $L, \dot{q}$  using ① & ②.

\* Helmholtz free energy is useful for isothermal transformations in the absence of mechanical work  $dH_f = 0$

## Thermodynamic Potentials

We have  $U(S, V, N)$ . Suppose we want to eliminate  $S$ . Then using the Legendre transformation

$$F = U - S \left( \frac{\partial U}{\partial S} \right)_{V, N} = U - TS$$

Now, we know  $U = U(S, V, N)$  and therefore  $T = \left( \frac{\partial U}{\partial S} \right)_{V, N}$  is  $T = T(S, V, N)$ .

The entropy  $S$  can be eliminated and then we have  $F = F(T, V, N)$ . To see this explicitly we look at

$$\begin{aligned} dF &= du - Tds - SdT \\ &= Tds - pdv + \mu dN - Tds - SdT \\ &= -SdT - pdv + \mu dN \end{aligned}$$

Showing that  $F = F(T, V, N)$

\*

We emphasize that during the process of constructing  $F(T, V, N)$ , no information has been lost. Such relations are fundamental relations of type 2.

Note that if we specified  $F = F(S, V, N)$  or  $U = U(T, V, N)$  we would not have known all thermodynamic properties of the system.

We can now write down the various partial derivatives of  $F$ .

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

$$\text{and } \left( \frac{\partial F}{\partial N} \right)_{T, V} = \mu$$

\* Gibbs free energy is useful for isothermal transformations in presence of constant- external force.

DATE

Eliminating  $V$  as an independent coordinate we have

$$H = U - V \left( \frac{\partial U}{\partial V} \right)_{S,N} = U + PV$$

$$\begin{aligned} dH &= dU + PdV + Vdp \\ &= Tds + Vdp + \mu dN \end{aligned}$$

Eliminating  $S, V$  bolt

$$G_1 = U - S \left( \frac{\partial U}{\partial S} \right)_{V,N} - V \left( \frac{\partial U}{\partial V} \right)_{S,N}$$

$$= U - TS + PV$$

$$\begin{aligned} dG_1 &= dU - Tds - SdT + PdV + Vdp \\ &\quad - SdT + Vdp + \mu dN \end{aligned}$$

\*

All thermodynamic potentials are extensive with respect to their extensive parameters only.

$$\Rightarrow F(T, \bar{v}, \bar{N}) = \lambda F(T, v, N)$$

$$H(\bar{s}, P, \bar{N}) = \lambda H(s, P, N)$$

$$G(T, P, \bar{N}) = \lambda G(T, P, N)$$

For Gibbs Potential in particular, this has an interesting consequence. If we construct the Euler relation then we have

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

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

$$\Rightarrow G = \mu N$$

$$g(T, P) = \mu$$

For the other thermodynamic potentials we have

$$F = N f(T, v) \quad H = N h(p, s)$$

Finally we define the grand potential

$$\Omega(T, M, N) = F - \mu N = U - TS - \mu N$$

This is done by eliminating  $(S, N)$ .

Since  $U = TS - PV + \mu N$  we have

$$\Omega = -PV$$

The extensive property of  $\Omega$  translates to

$$\Omega = V \omega(T, \mu) = N \tilde{\omega}(T, \mu)$$

$$\text{where } \tilde{\omega} = g \omega$$

Therefore  $P = -\omega(T, \mu)$ .

Maxwell's relation

$$dU = T ds - pdV + \mu dN$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} ds + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

$$\left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_{V,N}\right)_{S,N} = \left(\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_{S,N}\right)_{V,N}$$

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

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

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

Jacobians

$$\frac{\partial(f,g)}{\partial(x,y)} = \begin{vmatrix} \left(\frac{\partial f}{\partial x}\right)_y & \left(\frac{\partial f}{\partial y}\right)_x \\ \left(\frac{\partial g}{\partial x}\right)_y & \left(\frac{\partial g}{\partial y}\right)_x \end{vmatrix}$$

$$\frac{\partial(g,f)}{\partial(x,y)} = \frac{\partial(f,g)}{\partial(y,x)} = - \frac{\partial(f,g)}{\partial(x,y)}$$

$$\frac{\partial(f,y)}{\partial(x,y)} = \left(\frac{\partial f}{\partial x}\right)_y$$

further,  $\frac{\partial(x,y)}{\partial(f,g)} = \begin{vmatrix} \left(\frac{\partial x}{\partial f}\right)_g & \left(\frac{\partial x}{\partial g}\right)_f \\ \left(\frac{\partial y}{\partial f}\right)_g & \left(\frac{\partial y}{\partial g}\right)_f \end{vmatrix} = - \left[ \frac{\partial(f,g)}{\partial(x,y)} \right]^{-1}$

$$= \left( \frac{\partial x}{\partial f} \right)_g \left( \frac{\partial y}{\partial g} \right)_f - \left( \frac{\partial y}{\partial f} \right)_g \left( \frac{\partial x}{\partial g} \right)_f$$

$$dx = \left( \frac{\partial x}{\partial f} \right)_g df + \left( \frac{\partial x}{\partial g} \right)_f dg \quad df = \left( \frac{\partial f}{\partial x} \right)_y dx + \left( \frac{\partial f}{\partial y} \right)_x dy$$

$$dy = \left( \frac{\partial y}{\partial f} \right)_g df + \left( \frac{\partial y}{\partial g} \right)_f dg \quad dg = \left( \frac{\partial g}{\partial x} \right)_y dx + \left( \frac{\partial g}{\partial y} \right)_x dy$$

$$dx = \left[ \left( \frac{\partial x}{\partial f} \right)_g \left( \frac{\partial f}{\partial x} \right)_y + \left( \frac{\partial x}{\partial g} \right)_f \left( \frac{\partial g}{\partial x} \right)_y \right] dx + \left[ \left( \frac{\partial x}{\partial f} \right)_g \left( \frac{\partial f}{\partial y} \right)_x + \left( \frac{\partial x}{\partial g} \right)_f \left( \frac{\partial g}{\partial y} \right)_x \right] dy$$

$$dx=0, \quad dy \neq 0 \quad \Rightarrow \quad \left( \frac{\partial x}{\partial f} \right)_g \left( \frac{\partial f}{\partial y} \right)_x = - \left( \frac{\partial x}{\partial g} \right)_f \left( \frac{\partial g}{\partial y} \right)_x$$

$$dy = \left[ \left( \frac{\partial y}{\partial f} \right)_g \left( \frac{\partial f}{\partial x} \right)_y + \left( \frac{\partial y}{\partial g} \right)_f \left( \frac{\partial g}{\partial x} \right)_y \right] dx + \left[ \left( \frac{\partial y}{\partial f} \right)_g \left( \frac{\partial f}{\partial y} \right)_x + \left( \frac{\partial y}{\partial g} \right)_f \left( \frac{\partial g}{\partial y} \right)_x \right] dy$$

$$dy=0 \quad dx \neq 0 \quad \left( \frac{\partial y}{\partial f} \right)_g \left( \frac{\partial f}{\partial x} \right)_y = - \left( \frac{\partial y}{\partial g} \right)_f \left( \frac{\partial g}{\partial x} \right)_y$$

$$\left( \frac{\partial x}{\partial f} \right)_g \left( \frac{\partial y}{\partial g} \right)_f \left( \frac{\partial f}{\partial y} \right)_x \left( \frac{\partial g}{\partial x} \right)_y = + \left( \frac{\partial x}{\partial g} \right)_f \left( \frac{\partial y}{\partial g} \right)_g \left( \frac{\partial f}{\partial x} \right)_y \left( \frac{\partial g}{\partial y} \right)_x$$

$$\frac{\left(\frac{\partial x}{\partial g}\right)_f \left(\frac{\partial y}{\partial g}\right)_g}{\left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial g}{\partial x}\right)_y} \left[ \left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial g}{\partial y}\right)_x - \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial g}{\partial x}\right)_y \right]$$

$$\left(\frac{\partial x}{\partial g}\right)_f = \left(\frac{\partial x}{\partial y}\right)$$

$$\frac{\partial(f,g)}{\partial(x,y)} \frac{\partial(x,y)}{\partial(u,v)} = \begin{vmatrix} \left(\frac{\partial f}{\partial x}\right)_y & \left(\frac{\partial f}{\partial y}\right)_x \\ \left(\frac{\partial g}{\partial x}\right)_y & \left(\frac{\partial g}{\partial y}\right)_x \end{vmatrix} \begin{vmatrix} \left(\frac{\partial x}{\partial u}\right)_v & \left(\frac{\partial x}{\partial v}\right)_u \\ \left(\frac{\partial y}{\partial u}\right)_v & \left(\frac{\partial y}{\partial v}\right)_u \end{vmatrix}$$

upper left-corner of the product-matrix is

$$\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial u}\right)_v + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial u}\right)_v.$$

this is simply equal to  $\left(\frac{\partial f}{\partial u}\right)_v$

$$\frac{\partial(f,g)}{\partial(x,y)} \frac{\partial(x,y)}{\partial(u,v)} = \frac{\partial(f,g)}{\partial(u,v)}$$

Now choose  $f = u = f$  and  $v = g$

$$\Rightarrow \frac{\partial(f,g)}{\partial(x,y)} \frac{\partial(x,y)}{\partial(f,g)} = \frac{\partial(f,g)}{\partial(f,g)} = 1$$

$$du = Tds - pdV + \mu dN$$

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

$$= \frac{\partial(M,S,N)}{\partial(N,S,V)}$$

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

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

$$\frac{\partial(T, S, V)}{\partial(N, S, V)} = \frac{\partial(\mu, V, N)}{\partial(S, V, N)} = \frac{\partial(N, \mu V)}{\partial(N, S, V)}$$

$$\frac{\partial(P, S, V)}{\partial(\mu, S, N)} = 1 \quad \frac{\partial(T, S, N)}{\partial(P, V, N)} = 1 \quad \frac{\partial(T, S, V)}{\partial(N, \mu, V)} = 1$$

$$dF = -SdT - pdV + \mu dN$$

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

$$\Rightarrow \frac{\partial(T, S, N)}{\partial(T, V, N)} = \frac{\partial(P, V, N)}{\partial(T, V, N)}$$

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

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

$$\frac{\partial(P, V, T)}{\partial(\mu, N, T)} = 1$$

$$\hookrightarrow \frac{\partial(S, T, V)}{\partial(N, T, V)} = -\frac{\partial(\mu, N, V)}{\partial(T, N, V)}$$

$$\frac{\partial(T, S, V)}{\partial(T, N, V)} = \frac{\partial(\mu, N, V)}{\partial(T, N, V)}$$

$$\frac{\partial(T, S, V)}{\partial(N, \mu, V)} = 1$$

$$dH = TdS + Vdp + \mu dN$$

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

$$\frac{\partial(V, P, N)}{\partial(S, P, N)} = \frac{\partial(T, S, N)}{\partial(P, S, N)}$$

$$\frac{\partial(P, V, N)}{\partial(T, S, N)} = 1$$

$$\frac{\partial(P, V, N)}{\partial(P, S, N)} = \frac{\partial(T, S, N)}{\partial(P, S, N)}$$

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

$$\frac{\partial(V, P, S)}{\partial(N, P, S)} = \frac{\partial(H, N, S)}{\partial(P, N, S)}$$

$$\frac{\partial(P, S, V)}{\partial(P, N, S)} = \frac{\partial(H, N, S)}{\partial(P, N, S)}$$

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

$$\frac{\partial(P, S, V)}{\partial(\mu, N, S)} = 1$$

$$\frac{\partial(T, S, P)}{\partial(N, S, P)} = \frac{\partial(H, N, P)}{\partial(S, N, P)}$$

$$\frac{\partial(S, T, P)}{\partial(S, N, P)} = \frac{\partial(H, N, P)}{\partial(S, N, P)}$$

$$\frac{\partial(S, T, P)}{\partial(\mu, N, P)} = 1$$

$$dG = -SdT + Vdp + \mu dN$$

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

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

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

$$dS = -SdT - pdV - Nd\mu.$$

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

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

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

No new conditions are provided by these two.

The additional relation comes from  $\Omega - \mu N$

$$A = \Omega - \mu N$$

$$\begin{aligned} dA &= du - \mu dN - N d\mu = Tds - pdV + \mu dN - \\ &\quad \mu dN - Nd\mu. \\ &= Tds - pdV - N d\mu. \end{aligned}$$

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

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

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

$$\begin{aligned} \frac{\partial(T,S,\mu)}{\partial(V,S,\mu)} &= -\frac{\partial(P,V,\mu)}{\partial(S,V,\mu)} \\ \frac{\partial(T,S,\mu)}{\partial(P,V,\mu)} &= f \end{aligned}$$

In total there are six independent Maxwell's relation.

Example :

$$\frac{Q}{C_V} = \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial V}\right)_P} = \frac{\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial S}{\partial V}\right)_T}$$

$$= \left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial V}{\partial S}\right)_T$$

$$= \frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial P}\right)_S} = \frac{R_T}{R_S}$$

$$\frac{C_V}{T} = \left(\frac{\partial S}{\partial T}\right)_V = \frac{\underline{\partial(S,V)}}{\underline{\partial(T,V)}} = \frac{\underline{\partial(S,V)}}{\underline{\partial(T,P)}} \frac{\underline{\partial(T,P)}}{\underline{\partial(T,V)}}$$

$$= \begin{vmatrix} \left(\frac{\partial S}{\partial T}\right)_P & \left(\frac{\partial S}{\partial P}\right)_T \\ \left(\frac{\partial V}{\partial T}\right)_P & \left(\frac{\partial V}{\partial P}\right)_T \end{vmatrix} \begin{vmatrix} \left(\frac{\partial T}{\partial T}\right)_V & \left(\frac{\partial T}{\partial V}\right)_T \\ \left(\frac{\partial P}{\partial T}\right)_V & \left(\frac{\partial P}{\partial V}\right)_T \end{vmatrix}$$

$$= \left[ \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T - \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \right] \left(\frac{\partial P}{\partial V}\right)_T$$

$$= \left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$= \frac{Q}{T} - \left(\frac{\partial S}{\partial V}\right)_T \alpha_p V$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = - \frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \frac{\alpha_p}{k_T}$$

$$\frac{G}{T} = \frac{Q}{T} - \frac{\alpha_p^2}{k_T} V$$

$$Q - G = \frac{TV \alpha_p^2}{k_T}$$

Internal Energy of an ideal gas.

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$dU = T dS - P dV = T \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial S}{\partial V}\right)_T dV - P dV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P$$

$$PV = Nk_B T$$

$$= T \left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\frac{\partial P}{\partial T} = \frac{Nk_B}{V} = \frac{P}{T}$$

$$= P - P = 0.$$

## Stability Conditions

Concavity of entropy. — Equilibrium state maximizes the entropy.

Denote all other thermodynamic variables as  $X$ , other than the internal energy  $U$  *including*

Suppose we have two systems with variables  $X_1$  &  $X_2$

Bring them together. Combined system  $(X_1 + X_2)$

$$S(X_1 + X_2) \geq S(X_1) + S(X_2)$$

entropy can not decrease in the equilibration process.

Think about now a single system. Suppose its extensive variables can be partitioned into  $X_1$  and  $X_2$  such that the above inequality is violated. The system as a whole would be unstable and break into smaller systems with extensive variables  $X_1$  and  $X_2$ . The above inequality therefore represents the stability condition for a system.

A function with the above property is called a concave function. The meaning of this property can be understood geometrically if we define a new set of variables

$$X_1 = \lambda Y_1, \quad X_2 = (1 - \lambda) Y_2$$

where  $0 < \lambda < 1$ .

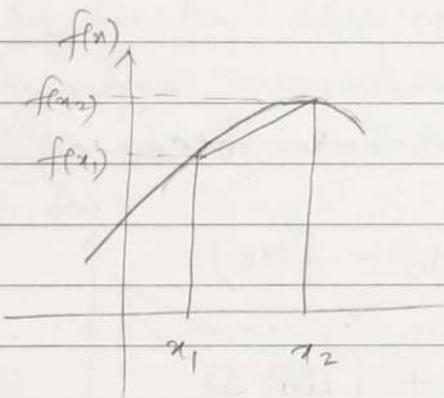
$$\Rightarrow S(\lambda y_1 + (1-\lambda)y_2) \geq S(\lambda y_1) + S((1-\lambda)y_2)$$

Using the homogeneity property of entropy we have

$$S(\lambda y_1 + (1-\lambda)y_2) \geq \lambda S(y_1) + (1-\lambda) S(y_2)$$

To understand the geometrical significance consider only one independent variable which we denote by  $x$ .

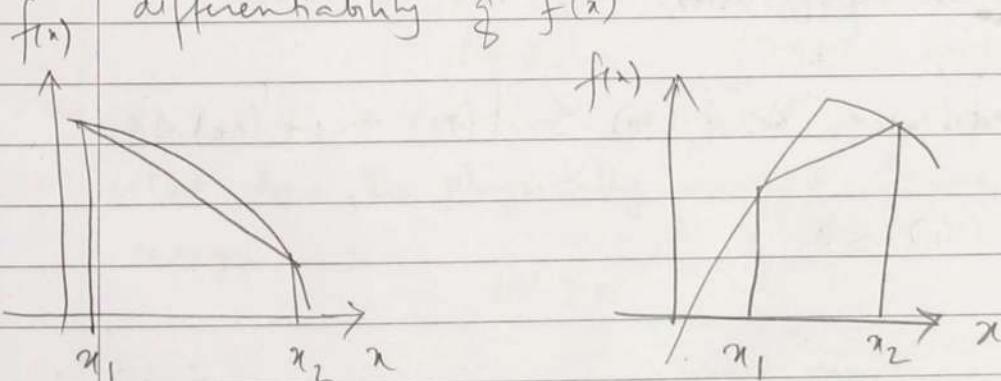
$$f(\lambda x_1 + (1-\lambda)x_2) \geq \lambda f(x_1) + (1-\lambda) f(x_2)$$



Now  $\lambda x_1 + (1-\lambda)x_2$  denotes a point somewhere between  $x_1$  and  $x_2$ . Thus,  $f(\lambda x_1 + (1-\lambda)x_2)$  would denote a value of the function at some intermediate point.

On the other hand the r.h.s denotes a point on the straight line joining  $f(x_1)$  and  $f(x_2)$ . Essentially, this means that the chord between any two points on the curve must be below the curve.

Such a definition does not require the condition of differentiability of  $f(x)$ .



If the derivatives of  $f(x)$  exist, then we can write.  
 $x_1 = x_0$  and  $x_2 = x_0 + \Delta x$ .

$$f(x_0 + (1-\lambda)(x_0 + \Delta x)) \geq \lambda f(x_0) + (1-\lambda) f(x_0 + \Delta x)$$

$$\Rightarrow f(x_0 + (1-\lambda)\Delta x) \geq \lambda f(x_0) + (1-\lambda) f(x_0 + \Delta x)$$

$$f(x_0 + (1-\lambda)\Delta x) - f(x_0) \geq -(1-\lambda) f(x_0) + (1-\lambda) f(x_0 + \Delta x)$$

$$\frac{f(x_0 + (1-\lambda)\Delta x) - f(x_0)}{(1-\lambda)} \geq \frac{f(x_0 + \Delta x) - f(x_0)}{\Delta x}$$

In the limit  $\lambda \rightarrow 1$ , the L.H.S. becomes

$$f'(x_0) \Delta x \geq f(x_0 + \Delta x) - f(x_0)$$

$$\Rightarrow f(x_0 + \Delta x) \leq f(x_0) + f'(x_0) \Delta x$$

The r.h.s. is nothing but the tangent at the point  $x_0$ , so that the inequality means that the tangent lies above the curve.

If the second derivative exists then we expand the L.H.S. as in a Taylor series

$$f(x_0) + \Delta x f'(x_0) + \frac{(\Delta x)^2}{2} f''(x_0) \leq f(x_0) + f'(x_0) \Delta x$$

$$\Rightarrow f''(x_0) \leq 0$$

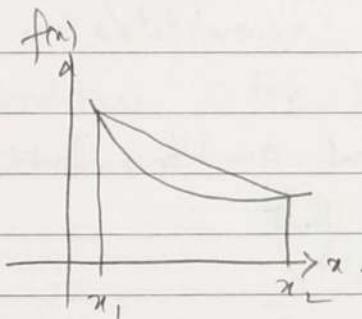
This implies that for the entropy we have the stability condition

$$d^2S \leq 0.$$

We can also work in the energy representation where the internal energy  $U$  is expressed in terms of the extensive variables  $\xi$ . Then the energy minimum principle implies that

$$U(\lambda\xi_1 + (1-\lambda)\xi_2) \leq \lambda U(\xi_1) + (1-\lambda)U(\xi_2).$$

Any function which obeys this is a convex function. The geometrical interpretation is obvious in this case. The chord should lie above the curve.



Further, if the derivatives of  $U(\xi)$  exist, then the condition translates to  $d^2U \geq 0$ .

Similarly, for the other thermodynamic potentials we have

$$dF \leq 0 \quad (T, V, N) \text{ constant}$$

$$dT \geq 0 \quad (S, P, N) \text{ const.}$$

$$dG \geq 0 \quad (T, P, N) \text{ const.}$$

$$d\Omega \geq 0 \quad (T, V, M) \text{ const.}$$

What does this physically imply? Consider the internal energy

$$dU \geq 0.$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

We consider only variations in  $S, V$  and hold  $N$  constant

$$\begin{aligned} d^2U &= d(dU) = \frac{\partial(dU)}{\partial S} dS + \frac{\partial(dU)}{\partial V} dV \\ &= \left(\frac{\partial U}{\partial S}\right)_V (dS)^2 + 2 \frac{\partial^2 U}{\partial S \partial V} dS dV + \left(\frac{\partial^2 U}{\partial V^2}\right)_S (dV)^2 \geq 0 \end{aligned}$$

using the values of the first derivative

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

we have

$$\left(\frac{\partial T}{\partial S}\right)_V (dS)^2 + 2 \left(\frac{\partial T}{\partial V}\right)_S dS dV - \left(\frac{\partial P}{\partial V}\right)_S (dV)^2 \geq 0$$

Now we are faced with the mathematical question that what are the conditions on  $A, B, C$  such that

$$Ax^2 + Bxy + Cy^2 \geq 0$$

for all values of two real parameters  $x, y$ .

Clearly  $A \geq 0$  and  $C \geq 0$  since if we choose

$$x=0, y \neq 0 \quad \text{we have } Cy^2 \geq 0$$

$$\text{and } x \neq 0, y=0 \quad \text{we have } Ax^2 \geq 0$$

These are necessary conditions, but not sufficient.

Suppose we have a relation

$$A_1x_1^2 + A_2x_2^2 \geq 0$$

then the condition of inequality implies that  $A_1 \geq 0$

$$A_2 \geq 0$$

We can recast the earlier inequality in the form

$$A \left( x + \frac{B}{A} y \right)^2 + \left( C - \frac{B^2}{A} \right) y^2 \geq 0$$

$$\Rightarrow C \geq \frac{B^2}{A} \quad \Rightarrow \quad B^2 \leq AC$$

Note that together with the previous constraints, the conditions are superfluous.

Say  $B^2 \leq AC$  and  $A \geq 0$ .

$$\Rightarrow C \geq 0$$

and vice versa. However, we will consider all three conditions. For the condition  $d^2U \geq 0$ , we have therefore

$$\left( \frac{\partial T}{\partial S} \right)_V \geq 0 \quad \Rightarrow T \left( \frac{\partial T}{\partial S} \right)_V \geq 0$$

$\Rightarrow C_V \geq 0$   $\rightarrow$  if temperature is raised, its energy must increase.

The second condition gives  $\left( \frac{\partial P}{\partial V} \right)_S \leq 0$ .

$$\Rightarrow -V \left( \frac{\partial P}{\partial V} \right)_S \geq 0 \quad \Rightarrow K_S \geq 0.$$

If pressure is applied then volume must decrease.

Finally, we have  $\left[ \left( \frac{\partial T}{\partial V} \right)_S \right] \leq - \left( \frac{\partial T}{\partial S} \right)_V \left( \frac{\partial P}{\partial V} \right)_S$

$$\Rightarrow - \left( \frac{\partial T}{\partial V} \right)_S \left( \frac{\partial P}{\partial S} \right)_V + \left( \frac{\partial T}{\partial S} \right)_V \left( \frac{\partial P}{\partial V} \right)_S \leq 0$$

$$\Rightarrow \frac{\partial(T, P)}{\partial(S, V)} \leq 0$$

$$\Rightarrow \frac{\partial(T, P)}{\partial(T, V)} \cdot \frac{\partial(T, V)}{\partial(S, V)} \leq 0$$

$$\Rightarrow \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial T}{\partial S}\right)_V \leq 0$$

Since  $C_V \geq 0$  we have

$$\left(\frac{\partial P}{\partial V}\right)_T \leq 0$$

or the isothermal compressibility  $K_T \geq 0$

$$\text{Further, } C_P - C_V = \frac{T V \alpha_P^2}{K_T}$$

Since  $C_V \geq 0$   $K_T > 0 \Rightarrow C_P \geq 0$

$$\text{Now, } C_V = T \left(\frac{\partial S}{\partial T}\right)_V = -T \left(\frac{\partial F}{\partial T^2}\right)_V$$

$$C_P = -T \left(\frac{\partial S}{\partial T}\right)_P = -T \left(\frac{\partial G}{\partial T^2}\right)_P$$

$$K_T = \left[V \left(\frac{\partial F}{\partial V^2}\right)_T\right]^{-1} = -\frac{1}{V} \left(\frac{\partial G}{\partial P^2}\right)_T$$

$C_P > 0$   $C_V > 0$  and  $K_T > 0$  implies that

$$\left(\frac{\partial F}{\partial T^2}\right)_V < 0 \quad \left(\frac{\partial F}{\partial V^2}\right)_T > 0$$

$$\left(\frac{\partial \tilde{G}}{\partial T^2}\right)_P < 0 \quad \left(\frac{\partial \tilde{G}}{\partial P^2}\right)_V < 0$$

Thus, as a consequence of stability, the Helmholtz free energy is a concave function of  $T$  and a convex function of  $V$ , while the Gibbs free energy  $G$  is a concave function of both  $(T, P)$ .

$$\text{Finally consider } \left(\frac{\partial N}{\partial \mu}\right)_{T,V} = \frac{\partial (N, V, T)}{\partial (\mu, V, T)}$$

$$= \frac{\partial (N, V, T)}{\partial (N, P, T)} \frac{\partial (N, P, T)}{\partial (P, V, T)} \frac{\partial (P, V, T)}{\partial (\mu, V, T)}$$

$$\frac{\partial (P, V, T)}{\partial (\mu, V, T)} = 1 = \frac{\partial (N, V, T)}{\partial (N, P, T)} \frac{\partial (N, P, T)}{\partial (P, V, T)} \frac{\partial (P, V, T)}{\partial (\mu, V, T)}$$

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

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

$$\text{But } \mu = \mu(T, P) \Rightarrow \left(\frac{\partial P}{\partial \mu}\right)_{N,T} = \left(\frac{\partial P}{\partial \mu}\right)_{V,T} = \left(\frac{\partial P}{\partial \mu}\right)_T = \frac{N}{V}$$

$$\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = -\frac{N^2}{V^2} \left(\frac{\partial V}{\partial P}\right)_{N,T} = \frac{N^2}{V} k_T$$

$$\because k_T > 0 \Rightarrow \left(\frac{\partial N}{\partial \mu}\right)_{T,V} > 0$$

Thus, the particle number at fixed value of  $(V, T)$  must be an increasing function of the chemical function  $\mu$ .

$G \geq 0 \quad G_r \geq 0 \rightarrow \text{thermal stability}$

$K_T \geq 0 \quad K_S \geq 0 \rightarrow \text{Mechanical stability}$

$\left(\frac{\partial N_i}{\partial \mu_j}\right)_{T, P, N_{k \neq i}} \geq 0 \rightarrow \text{Chemical stability.}$

Ex. Consider a mixture of particles A, B. The Gibb's free energy is given by

$$G = n_A \mu_A^\circ(P, T) + n_B \mu_B^\circ(P, T) + RT \ln \frac{x_A}{n}$$

$$+ RT \ln \frac{x_B}{n} + \frac{n_A n_B}{n}$$

$$\text{with } x_A = \frac{n_A}{n} \quad \text{and } x_B = \frac{n_B}{n}$$

$$\text{and } n = n_A + n_B$$

Plot region of thermodynamic instability in  $x_A - T$  region.

$$\begin{aligned} \mu_A = \left( \frac{\partial G}{\partial n_A} \right)_{P, T, n_B} &= \mu_A^\circ(P, T) + RT \ln \frac{x_A}{n} + \frac{RT n_A}{x_A} \frac{\partial x_A}{\partial n_A} \\ &\quad + \frac{x_B}{n} - \frac{n_A n_B}{n^2} \frac{\partial n}{\partial n_A} \end{aligned}$$

$$x_A = \frac{n_A}{n_A + n_B}$$

$$n_A + n_B$$

$$\frac{\partial x_A}{\partial n_A} = \frac{1}{n_A + n_B} - \frac{n_A}{(n_A + n_B)^2} = \frac{1}{(n_A + n_B)} \left[ 1 - \frac{n_A}{n_A + n_B} \right] = \frac{n_B}{n^2} = \frac{x_B}{n}$$

$$\mu_A = \mu_A^0(P, T) + RT \ln(x_A) + \frac{RT n_A}{n} \frac{x_B}{n} + \frac{x_B}{n} - \frac{x_A x_B}{n^2}$$

$$\frac{\partial \mu_A}{\partial n_A} = \frac{RT}{x_A} \frac{\partial x_A}{\partial n_A} + RT \frac{\partial}{\partial n_A} \left( \frac{x_B}{n} \right) + \frac{x_B}{n^2} - \frac{x_B}{n^2}$$

$$+ \frac{x_A x_B}{n^3} \frac{\partial n}{\partial n_A}$$

$$= \frac{RT}{x_A} \frac{x_B}{n^2} - \frac{RT x_B}{n^2} - 2 \frac{x_B}{n^2} + 2 \frac{x_A x_B}{n^3}$$

$$x \ln x = (\ln x - 1)$$

$$f(n) \ln f(n) = \ln f(n) - f'(n)$$

$$\frac{RT(1-x_A)}{x_A} - RT(1-x_A) - 2x(1-x_A)$$

$$+ 2x x_A(1-x_A) \geq 0.$$

$$x_A n_A + x_B n_B = n_A.$$

$$RT(1-x_A) - RT x_A(1-x_A) - 2x x_A(1-x_A)$$

$$n_A \frac{\partial x_A}{\partial n_A} + x_A + n_B \frac{\partial x_A}{\partial n_A} = 1$$

$$+ 2x x_A(1-x_A)$$

$$n \frac{\partial x_A}{\partial n_A} = 1 - x_A = x_B$$

$$\frac{RT}{x_A} - \frac{RT}{1-x_A} - 2x + 2x x_A \geq 0$$

$$\frac{\partial x_A}{\partial n_A} = \frac{x_B}{n}$$

$$RT - RT x_A - 2x x_A + 2x x_A \geq 0$$