

Legendre transform

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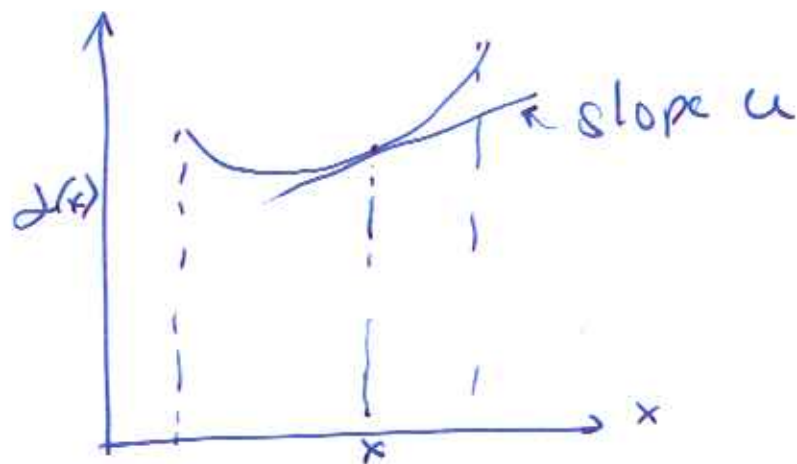
One variable

consider a function $f(x)$ s.t.

$$f''(x) \geq 0$$

(convex function) on some interval

of x



in this case the equation $f'(x) = u$
for any x has only one solution

Define: $F(x, u) = ux - f(x)$

Legendre transform:

$$g(u) = \max_x F(x, u) = \max_x ux - f(x)$$

the maximum x is going to be a

function of u

$$g(u) = ux(u) - f(x(u))$$

$g(u)$ is also a convex function

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Proof: $g'(u) = u x'(u) + x(u) - \frac{\partial \mathcal{L}}{\partial x} \frac{\partial x}{\partial u}$

since $\frac{u}{x(u)} - \frac{\partial \mathcal{L}}{\partial x} = 0$

$$g'(u) = x(u)$$

$$g''(u) = x'(u) = \frac{dx}{du} = \frac{1}{f''(x(u))} \geq 0$$

Remark: this is the form of the Legendre transform used in mechanics

- in thermodynamics usually one uses

$$g(u) = \max_x F(x, u)$$

where $F(x, u) = f(x) - xu$

- in this case $g(u)$ is concave

Many variables

we can also generalize the above to many variables

$f(x_1, \dots, x_n)$ is a function for which

$$C_{ij} = \frac{\partial^2 f}{\partial x_i \partial x_j} \text{ is well-defined}$$

$$\text{let } u_i = \frac{\partial f}{\partial x_i}$$

in this case the Legendre transform

$$\text{looks like: } g(u_1, \dots, u_n) = \sum_i x_i u_i - f(x_1, \dots, x_n)$$

in this case: $\frac{\partial g}{\partial u_i} = x_i + \sum_j x_j \frac{\partial u_j}{\partial x_i}$ (5)

$$- \sum_j \frac{\partial x_j}{\partial x_i} \frac{\partial x_j}{\partial u_i}$$

$$= x_i \quad \left(\text{since } u_i = \frac{\partial x}{\partial x_i} \right)$$

convexity can be shown by considering

$$\frac{\partial^2 g}{\partial u_i \partial u_j} = D_{ij} = \frac{\partial^2 g}{\partial x_i \partial x_j}$$

it is easy to show that

$$\sum_j C_{ij} D_{jk} = \delta_{ik}$$

C_{ij} and D_{ij} are inverses of each other

\Rightarrow both C_{ij} and D_{ij} are positive definite

Massieu functions

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- when we studied free energies (enthalpy, Helmholtz, Gibbs, ...) we arrived at a particular free energy by way of Legendre transform of the internal energy

example: $A = E - TS$

(Helmholtz free energy)

- the Legendre transform changes the independent variables ($E(S, V, N) \rightarrow A(T, V, N)$)
- one can also start with the entropies

$$S(E, V, N)$$

and perform a Legendre transform to switch independent variables

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\Phi = S - \left(\frac{1}{T}\right) E$$

$$d\Phi = dS - d\left(\frac{1}{T}\right) E - \frac{1}{T} dE$$

$$d\Phi = -E d\left(\frac{1}{T}\right) + \frac{P}{T} dV - \frac{\mu}{T} dN$$

Φ is an example of a Massieu function

$$\Phi = \Phi\left(\frac{1}{T}, V, N\right) \quad \text{independent variables } \frac{1}{T}, V, N$$

- the use of the Maxwell functions is more apparent after introduction of partition functions, which are sums ~~over~~ over the available microstates of a given system (5)

- for example: $S = k_B \ln \Omega(E)$

where $\Omega(E)$ is the number of microstates with a given energy E (microcanonical ensemble) \rightarrow partition function

- example: Helmholtz free energy

$$A = -k_B T \ln Q$$

Q - partition function

for constant, T, V, N

- usually the free energy is not ~~is~~ proportional to the logarithm of the partition function

- for the Maxwell functions this always holds

Specific heats / Response functions

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- if we add heat to a system \Rightarrow its temperature will rise.
- under well-controlled circumstances (quasi-static) one expects that the ratio of the heat added to the change in temperature is a material dependent quantity, well-defined

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i.e. $C = \frac{\Delta Q}{\Delta T} \Big|_{\text{constraints}}$

$$dE = Tds - PdV + \mu dN \Rightarrow (dE)_{\substack{V \\ N}} = (Tds)_{\substack{V \\ N}}$$

at constant volume

$$C_V = \frac{dQ}{dT} \Big|_V = \frac{Tds}{dT} \Big|_V = \frac{\partial E}{\partial T} \Big|_V$$

at constant pressure

$$C_P = \frac{dQ}{dT} \Big|_P = \frac{Tds}{dT} \Big|_P = \frac{\partial H}{\partial T} \Big|_P$$

$$\text{since } H = E + PV \Rightarrow dH = Tds + VdP + \mu dN$$

$$(dH)_{\substack{P, N}} = (Tds)_{\substack{P, N}}$$

other response functions of interest

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

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

adiabatic compressibility: $\chi_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S$

we can derive a useful relation between response functions

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1st: consider a function $Z(x, y)$

if exact differential:

$$dZ = \left. \frac{\partial Z}{\partial x} \right|_y dx + \left. \frac{\partial Z}{\partial y} \right|_x dy$$

for the case of $Z(x, y) = A$ (constant)

$$dZ = 0$$

$$\Rightarrow \left. \frac{\partial Z}{\partial x} \right|_y \left. \frac{\partial Z}{\partial y} \right|_x + \left. \frac{\partial Z}{\partial y} \right|_x \left. \frac{\partial Z}{\partial x} \right|_y = 0 \quad \begin{array}{l} \text{(identity)} \\ \text{(useful)} \end{array}$$

$$\text{or} \quad \left. \frac{\partial Z}{\partial x} \right|_y \left. \frac{\partial Z}{\partial x} \right|_y + \left. \frac{\partial Z}{\partial y} \right|_x \left. \frac{\partial Z}{\partial y} \right|_x = -1$$

now, derive relation

$$TdS = T \left. \frac{\partial S}{\partial T} \right|_V dT + T \left. \frac{\partial S}{\partial V} \right|_T dV$$

$$= C_V dT + T \left. \frac{\partial S}{\partial V} \right|_T dV$$

$$T \left. \frac{\partial S}{\partial V} \right|_P = C_V + T \left. \frac{\partial S}{\partial V} \right|_T \left. \frac{\partial V}{\partial T} \right|_P$$

$$C_P = C_V + T \left. \frac{\partial S}{\partial V} \right|_T V \alpha$$

using

$$dF = -SdT - PdV$$

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V$$

~~$$\left. \frac{\partial S}{\partial V} \right|_T \left. \frac{\partial V}{\partial T} \right|_P$$~~

$$C_P = C_V + T \left. \frac{\partial P}{\partial T} \right|_V V \alpha$$

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1 \quad (\text{identity}) \quad (8)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = - \frac{1}{\left(\frac{\partial V}{\partial T}\right)_P} = \frac{\alpha}{\kappa_T}$$

$$C_p = C_v + \frac{TV\alpha^2}{\kappa_T}$$

can also show that $\frac{C_p}{C_v} = \frac{\kappa_T}{\kappa_S}$

Stability Conditions

concavity of entropy \leftrightarrow convexity of energy

- generalize concavity argument to many variables

for example E, V

~~$S(E, V)$~~ one system: $E + \Delta E, V + \Delta V$
other system: $E - \Delta E, V - \Delta V$

$$S(E + \Delta E, V + \Delta V) + S(E - \Delta E, V - \Delta V) \leq S(2E, 2V) = 2S(E, V)$$

results from the properties of the entropy

~~E~~ ~~barrier~~

removal of a barrier \rightarrow has to increase entropy

expansion

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$$S(E + \Delta E, V + \Delta V) + S(E - \Delta E, V - \Delta V) =$$

$$S(E, V) + \frac{\partial S(E, V)}{\partial E} \Delta E + \frac{\partial S(E, V)}{\partial V} \Delta V$$

$$+ \frac{1}{2} \frac{\partial^2 S(E, V)}{\partial E^2} \Delta E^2 + 2 \frac{\partial^2 S(E, V)}{\partial E \partial V} \Delta E \Delta V + \frac{1}{2} \frac{\partial^2 S(E, V)}{\partial V^2} \Delta V^2$$

$$+ S(E, V) - \frac{\partial S(E, V)}{\partial E} \Delta E - \frac{\partial S(E, V)}{\partial V} \Delta V$$

$$+ \frac{1}{2} \frac{\partial^2 S(E, V)}{\partial E^2} \Delta E^2 + 2 \frac{\partial^2 S(E, V)}{\partial E \partial V} \Delta E \Delta V + \frac{1}{2} \frac{\partial^2 S(E, V)}{\partial V^2} \Delta V^2$$

$$\Rightarrow \left[\frac{\partial^2 S(E, V)}{\partial E^2} \Delta E^2 + 2 \frac{\partial^2 S(E, V)}{\partial E \partial V} \Delta E \Delta V + \frac{\partial^2 S(E, V)}{\partial V^2} \Delta V^2 \leq 0 \right]$$

many-variable generalization of concavity

→ now, we consider the same for energies

$$\text{two systems: } E = E_1 + E_2$$

$$V = V_1 + V_2$$

$$S(E_1, V_1) + S(E_2, V_2) \leq S(E, V)$$

→ since $S(E, V)$ is a ~~function of~~ ~~E~~ monotonically increasing function of E , it

follows that there exists a \tilde{E} , such that

$$\tilde{E} \leq E, \quad S(E_1, V_1) + S(E_2, V_2) = S(\tilde{E}, V)$$

- equation: $S(E_1, V_1) + S(E_2, V_2) = S(\bar{E}, V)$

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* entropy is the same on both sides, energy is smaller on the right side

* left-side represents system divided into two subsystems, right-side represents system without barrier

⇒ conclude: for a system divided by a barrier, if the entropy is held fixed, the energy decreases as the system tends towards equilibrium ⇒ equilibrium state is a minimum energy state

$$\Delta E(S, V) \leq 0 \quad (\Delta E)_{S, V} \leq 0$$

- this also implies that the energy (internal) is a convex function of S and V

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stability condition in this case:

$$\boxed{(\Delta S)^2 \frac{\partial^2 E}{\partial S^2} + 2 \Delta S \Delta V \frac{\partial^2 E}{\partial S \partial V} + \frac{\partial^2 E}{\partial V^2} \Delta V^2 \geq 0}$$

- this condition (convexity) can be expressed in terms of a 2×2 matrix

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$$(\Delta S \ \Delta V) \begin{pmatrix} \frac{\partial^2 E}{\partial S^2} & \frac{\partial^2 E}{\partial S \partial V} \\ \frac{\partial^2 E}{\partial S \partial V} & \frac{\partial^2 E}{\partial V^2} \end{pmatrix} \begin{pmatrix} \Delta S \\ \Delta V \end{pmatrix} \geq 0$$

- in general a matrix which satisfies

$$\vec{x}^T (\bar{A}) \vec{x} \geq 0 \quad \text{for any } \vec{x} \text{ is a positive-definite matrix}$$

- diagonalize:

$$\vec{x}^T \bar{A} \vec{x} = \vec{y}^T \bar{\Lambda} \vec{y} \quad \text{where } \bar{\Lambda} = \begin{pmatrix} \lambda_1 & & 0 \\ & \ddots & \\ 0 & & \lambda_n \end{pmatrix}$$

$$\bar{A} = \bar{U}^T \bar{\Lambda} \bar{U} \quad \vec{y} = \bar{U} \vec{x}$$

$$\vec{x}^T \bar{A} \vec{x} = \sum_i \lambda_i y_i^2$$

for positive definite matrix $\sum_i \lambda_i y_i^2 \geq 0$

as a result $\lambda_i \geq 0$ for any i

- for 2×2 matrix

$$\begin{pmatrix} a & b \\ b & c \end{pmatrix} \quad \lambda_1 \geq 0 \quad \lambda_2 \geq 0 \quad \text{is}$$

guaranteed if $a+c \geq 0 \quad ac - b^2 \geq 0$

which means that $a \geq 0 \quad c \geq 0$

let's show this!

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$$\begin{vmatrix} a-\lambda & b \\ b & c-\lambda \end{vmatrix} = 0 \quad (a-\lambda)(c-\lambda) - b^2 = 0$$
$$ac - b^2 - \lambda(a+c) + \lambda^2 = 0$$

$$\lambda = \frac{a+c \pm \sqrt{(a+c)^2 - 4(ac-b^2)}}{2}$$

$$\lambda = \frac{a+c \pm \sqrt{(a-c)^2 + 4b^2}}{2}$$

↓

$$(a+c)^2 \geq (a-c)^2 + 4b^2$$

↓

$$ac - b^2 \geq 0$$

$$a+c \geq 0$$

$$a, c \geq 0$$

- now, we can derive conditions on the response functions based on stability

- consider $G(P, T) \rightarrow$ Gibbs free energy is a concave function of P, T

which means that $-G(P, T)$ is a ~~function~~ convex function of P, T

$$-\left(\frac{\partial^2 G}{\partial T^2}\right)_P \geq 0$$

$$dG = -SdT + VdP$$

$$S = -\frac{\partial G}{\partial T}$$

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$$\left(\frac{\partial S}{\partial T}\right)_P \geq 0$$

$$\frac{C_p}{T} \geq 0 \Rightarrow C_p \geq 0$$

for a system to be stable the constant pressure specific heat must be positive

$$-\left(\frac{\partial^2 G}{\partial P^2}\right)_T \geq 0$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T$$

$$\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial^2 G}{\partial P^2}\right)_T$$

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

$$-\frac{V}{V} \left(\frac{\partial V}{\partial P}\right)_T = +V\kappa_T \geq 0$$

for a system to be stable the constant temperature compressibility must be positive

$$\frac{\partial^2 G}{\partial P \partial T} \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \alpha V$$

$$\Rightarrow \frac{C_p}{T} V \kappa_T - \alpha^2 V^2 \geq 0$$

$$\Rightarrow \boxed{C_p - \frac{\alpha^2 V T}{\kappa_T} \geq 0}$$

recall!

$$C_v = C_p - \frac{\alpha^2 V T}{\kappa_T} \geq 0$$

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for a system to be stable the constant volume specific heat has to be positive

3rd law of thermodynamics

- this law is based on quantum mechanics
- on an operational level it needs to be mentioned that there are techniques which allow ~~approach~~ approaching absolute zero temperature ($T=0K$)
- approaching in this case means to go down to a level where quantum fluctuations dominate over thermal fluctuations (the latter being negligible)
- for example: Bose-Einstein condensates of atomic gases enable going down to the nanokelvin (nK) range

⇒ 3rd law of thermodynamics:

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$$\lim_{T \rightarrow 0} \lim_{V \rightarrow \infty} \frac{1}{V} S(V) = 0$$

$V \rightarrow \infty$ thermodynamic limit \rightarrow means extensive variables are taken to infinity, intensive variables are held constant

- there are systems in which there is something called residual entropy

in this case

$$\lim_{T \rightarrow 0} \lim_{V \rightarrow \infty} \frac{S(V)}{V} = S_0$$

but the key point is that S_0 is independent of thermodynamic variables (pressure, etc.) or the particular phase in which the system finds itself at $T=0K$

- examples of systems with residual entropy

* ice near zero temperature

(Pauling ice rules)

* antiferromagnetic Ising model on a triangular lattice

Metastable states

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- provide a possibility to experimentally verify the 3rd law

- consider a system in which two stable states exist on each side of a 1st order phase transition (phase a, phase b)

$$\frac{L}{T_c} = S^{(a)}(T_c) - S^{(b)}(T_c)$$

one phase being stable / metastable

L - latent heat T_c - phase transition temperature

$$S^{(a)}(T_c) = \int_0^{T_c} \frac{C^{(a)}(T)}{T} dT + S_0$$

(under \int) expressions

$$S^{(b)}(T_c) = \int_0^{T_c} \frac{C^{(b)}(T)}{T} dT + S_0$$

(under \int) = entropies of two phases

S_0 - independent of which phase !!!

L, T_c - available from experiment

$C^{(a)}(T), C^{(b)}(T)$ - available from experiment

\Rightarrow 3rd law can be experimentally verified

\Rightarrow and, of course it has been !!!

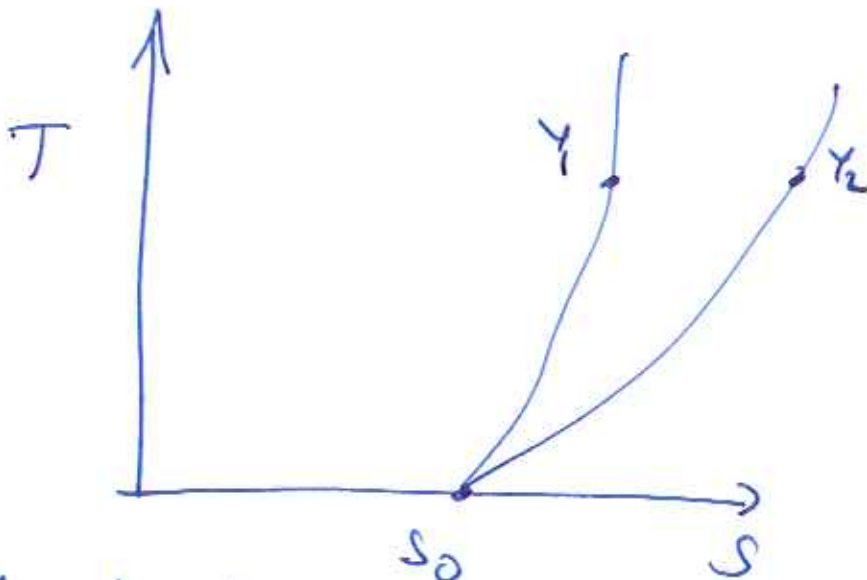
- 3rd law also is a statement about derivatives near $T=0$

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$$S(T; P, V) - S_0 = \int_0^T dT' \frac{C_{P,V}(T')}{T'}$$

as $T \rightarrow 0$ $C_{P,V}(T) \rightarrow 0$ otherwise integral on right hand side diverges

- also:



let Y_1, Y_2 be two different values of some thermodynamic variable Y

~~obviously as $T \rightarrow 0$~~

obviously as $T \rightarrow 0$ $\frac{\Delta S}{Y_1 - Y_2} \rightarrow 0$

$$\Rightarrow \left. \frac{\partial S}{\partial Y} \right|_{\dots} = 0$$

- using Maxwell relations one can show

$$\alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P \rightarrow 0 \quad \text{or} \quad \left. \frac{\partial P}{\partial T} \right|_V \rightarrow 0$$