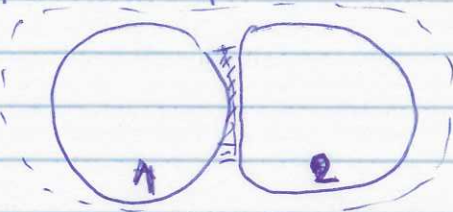


Thermodynamic stability and convexity

$$S(U, N, V)$$

Take 2 copies and put in thermal contact



isolated;

total system has
 $2U, 2N, 2V$

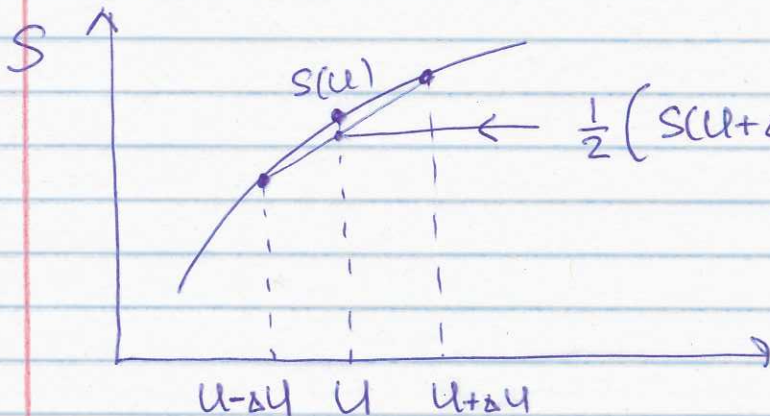
The system must be stable against macroscopic fluctuation of energy

$$E_1 \rightarrow E + \Delta E$$

$$E_2 \rightarrow E - \Delta E$$

$$S(U + \Delta U, N, V) + S(U - \Delta U, N, V) \leq 2S(U, V, N)$$

For any ΔU . (If this were " $>$ ", then ^{U, V, N} cannot be equilibrium since ~~then could~~ increase the entropy by partitioning).



Geometrically, any cord joining two points on the $S(U)$ curve must lie below the curve.

$\Rightarrow S(U)$ must be concave

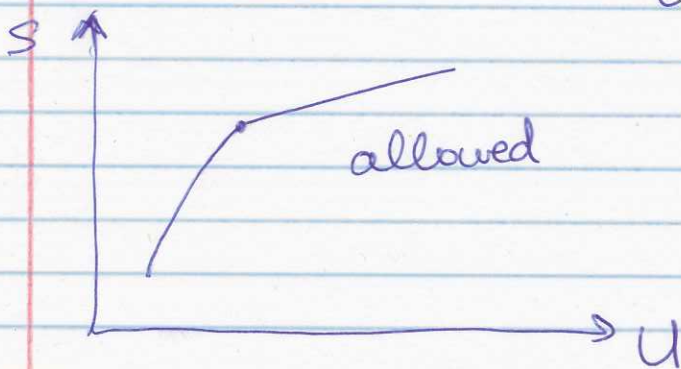
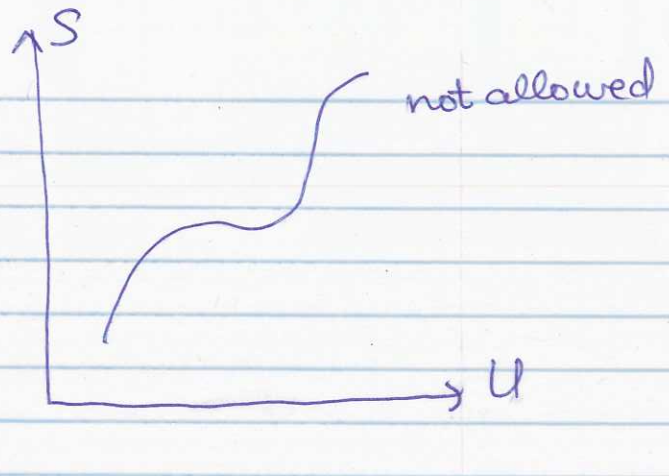
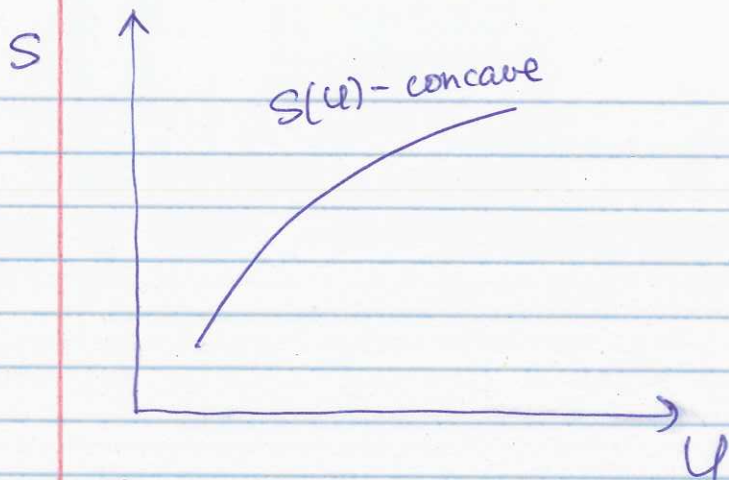
$$\left(\frac{\partial^2 S}{\partial U^2} \right)_{N, V} \leq 0$$

- differential condition;

the cord condition is stricter

- does not require differentiability

example
of stability
conditions



$$\frac{\partial^2 U}{\partial S^2} \geq 0$$

Interchanging axes, \$U(S)\$ is a ~~convex~~ convex function.

Immediate corollary

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V = \frac{T}{\left(\frac{\partial T}{\partial S} \right)_V} = \frac{T}{\left(\frac{\partial^2 U}{\partial S^2} \right)_V} > 0$$

$T = \left(\frac{\partial U}{\partial S} \right)_V$

Similarly ~~convex~~ \$S\$ must be ~~convex~~ concave function of \$V, N\$

$$\left(\frac{\partial^2 S}{\partial V^2} \right)_{U, N} \leq 0 \quad , \quad \left(\frac{\partial^2 S}{\partial N^2} \right)_{U, V} \leq 0$$

Legendre transformations and thermodynamic potentials

$$dU = TdS - PdV \quad \left. \vphantom{dU} \right\} \text{ suggests that } U(S, V) \text{ is particularly natural}$$

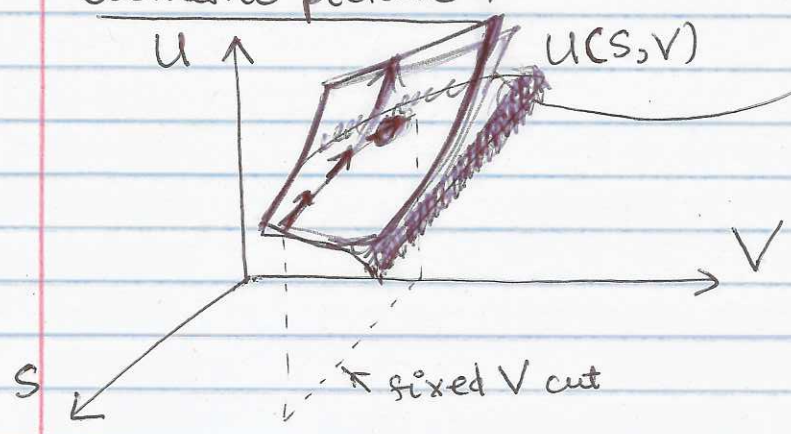
- compare with

$$dU = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{T\left(\frac{\partial P}{\partial T}\right)_V - P} dV$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V$$

On the other hand, S is not easily controllable. Thus mathematical problem: given $U(S, V)$, find function $F = F\left(\left(\frac{\partial U}{\partial S}\right)_V, V\right)$ equivalent to $U(S, V)$, where derivative $\left(\frac{\partial U}{\partial S}\right)_V$ is new variable - namely, T .

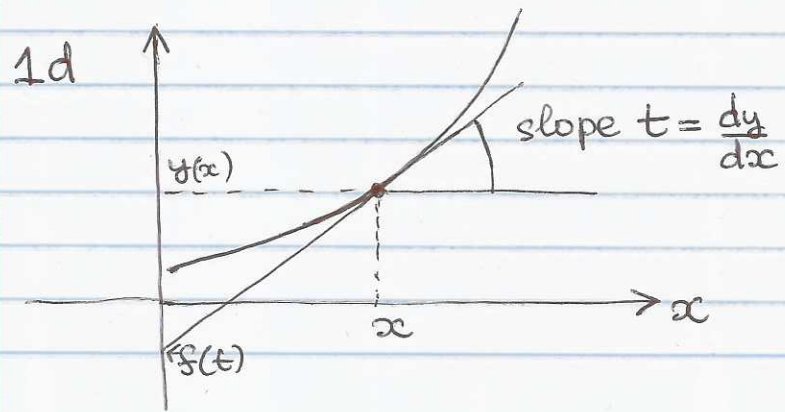
Geometric picture:



Surface is represented in terms of points S, V . Goal: represent the surface in terms of tangent coordinate

$$T = \left(\frac{\partial U}{\partial S}\right)_V$$

and point coordinate V



Specification of tangent line requires slope $t = \frac{dy}{dx}$ and

intercept $f(t) = y(x) - tx$

Old representation:
Surface (here, curve) is
specified by $(x, y(x))$

New representation:
Surface specified by
 $(t, S(t))$

Legendre transformation

More precisely:

$t = \frac{dy}{dx}(x) \rightarrow$ solve for $x = x(t)$;
define $S(t) = y(x(t)) - tx(t)$

assumes
 $\frac{dy}{dx}(x)$ is a
monotonic
fnctn of x
 $\Rightarrow y'' > 0$ everywhere
(or $y'' < 0$
everywhere)

$$t = \frac{dy}{dx}$$

$$S(t) = y(x) - tx$$

enveloping curve
of these lines;
here this is true
by construction

lines specified by slope t
and intercept $S(t)$

Inverse Legendre transformation is given by

$$x = -\frac{dS}{dt}(t)$$

$$y(x) = S(t) + xt$$

Proof:

Indeed, solve $t = \frac{dy}{dx}(x)$ for $x = x(t)$

$$\Rightarrow S(t) = y(x(t)) - tx(t)$$

$$\Rightarrow \frac{dS}{dt} = \underbrace{\frac{dy}{dx}(x(t))}_{"t"} \frac{dx}{dt} - x(t) - t \frac{dx}{dt} = -x(t)$$

In differential form: $dy = \frac{dy}{dx} dx = t dx$
 $dS = dy - t dx - dt \cdot x = -x dt$

Remarks on Legendre transformation

* Sufficient and necessary condition for Legendre transform to be well defined:

$$t = \frac{dy}{dx}(x) = y'(x) \text{ must be solvable for } x = x(t)$$

$\Leftrightarrow y'(x)$ is strictly monotonic \Leftrightarrow

$y''(x) > 0$ everywhere, i.e. $y(x)$ convex

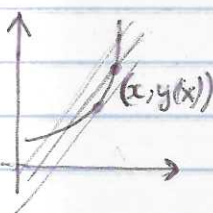
or $y''(x) < 0$ everywhere, i.e. $y(x)$ concave

In thermodynamics, $U(S)$ ~~must~~ must be convex,

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V > 0.$$

* Alternative expression for Legendre transform.:

Assuming $y(x)$ is differentiable and convex; then



$$S(t) = \min_x \{ y(x) - tx \}; \quad \text{— indeed, minimize wrt } x:$$

$$\frac{dy}{dx}(x) = t; \quad \text{second deriv} = \frac{d^2 y}{dx^2} > 0 \rightarrow \text{minimum}$$

$$y(x) = \max_t \{ S(t) + xt \}. \quad \text{— indeed,}$$

$$\frac{d^2 S}{dt^2} = -\frac{dx}{dt} = -\frac{1}{\frac{dt}{dx}} = -\frac{1}{y''} < 0$$

Maximization $\Rightarrow \frac{dS}{dt}(t) + x = 0$

\uparrow S is concave

* Legendre transform. for several variables.

$$dy = \sum_i t_i dx_i$$

$$dS = -\sum_i x_i dt_i$$

$$y = y(x_1, x_2, \dots, x_n);$$

$$t_i = \frac{\partial y}{\partial x_i}(x_1, x_2, \dots) \Rightarrow \text{solve for } \vec{x} = \vec{x}(\vec{t})$$

$$S(t_1, t_2, \dots) = y(\vec{x}(\vec{t})) - t_1 x_1(\vec{t}) - t_2 x_2(\vec{t}) - \dots$$

Application of Legendre transforms to thermodynamics:
Thermodynamic potentials

① Take $u = u(S, V)$. Choose $\left(\underbrace{\left(\frac{\partial u}{\partial S} \right)_V}_T, V \right)$ as indep. variables
 $du = Tds - pdv$

$$F(T, V) = u - TS \quad \text{--- Helmholtz free energy}$$

Inverse : $S = - \left(\frac{\partial F}{\partial T} \right)_V$

Since V is a "spectator" indep. variable

$$\left(\frac{\partial F}{\partial V} \right)_T = \left(\frac{\partial u}{\partial V} \right)_S \quad \text{--- general property of Legendre transformation.}$$

(Explicitly, $F(T, V) = u(S(T, V), V) - TS(T, V)$)

$$\left(\frac{\partial F}{\partial V} \right)_T = \left(\frac{\partial u}{\partial S} \right)_V \cdot \left(\frac{\partial S}{\partial V} \right)_T + \left(\frac{\partial u}{\partial V} \right)_S - T \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial u}{\partial V} \right)_S$$

$$\left(\frac{\partial F}{\partial V} \right)_T = \left(\frac{\partial u}{\partial V} \right)_S = -p$$

Directly in differential form:

$$dF = du - Tds - SdT = -SdT - pdv$$

② Take $u = u(S, V)$; choose $\left(S, \left(\frac{\partial u}{\partial V} \right)_S \right)$ as new indep. variables.

$$-p = \left(\frac{\partial u}{\partial V} \right)_S$$

$$H(S, p) = u - \left(\frac{\partial u}{\partial V} \right)_S V = u + pV \quad \text{--- enthalpy}$$

$$dH = du + dp \cdot V + pdv = Tds + Vdp$$

③ Take $U = U(S, V)$; choose $\left(\frac{\partial U}{\partial S}\right)_V, \left(\frac{\partial U}{\partial V}\right)_S$ as new indep. variables:

$$T = \left(\frac{\partial U}{\partial S}\right)_V$$

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

$$G(T, p) = U - \left(\frac{\partial U}{\partial S}\right)_V S - \left(\frac{\partial U}{\partial V}\right)_S V = U - TS + pV$$

- Gibbs free energy (Gibbs potential)

$$dG = dU - dT \cdot S - SdT + pdV + dpV = -SdT + Vdp$$

Generalization to case with generalized coords X_i and generalized forces J_i :

$$dU = Tds + \sum_i J_i dX_i$$

Helmholtz free energy:

$$F = U - TS$$

$$dF = -SdT + \sum_i J_i dX_i$$

Gibbs free energy:

$$G = U - TS - \sum_i J_i X_i$$

$$dG = -SdT - \sum_i X_i dJ_i$$

Traditionally, particle number N_j is treated ~~separately~~ separately from other coordinates.

$$\delta W = \sum_j \mu_j dN_j \text{ - "chemical work"}$$

$$dU = Tds + \vec{J} \cdot d\vec{X} + \vec{\mu} \cdot d\vec{N}$$

$$\Omega = U - TS - \vec{\mu} \cdot \vec{N} \text{ - "grand potential"}$$

$$d\Omega = -SdT + \vec{J} \cdot d\vec{X} - \vec{N} \cdot d\vec{\mu}$$

(approach to equilibrium of a thermally isolated system)
 Significance of entropy; adiabatic process; work in an adiabatic process

Significance of thermodynamic potentials

Entropy

Recall discussion of 2nd law and corollaries:

* For any process $A \rightarrow B$

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

"=" if $A \rightarrow B$ is reversible

Here δQ is heat received by the system;

$\frac{\delta Q}{T}$ can be viewed as entropy supplied to the system by reservoir; and the above inequality can be viewed as: entropy increase in the system \geq entropy supplied by reservoir.

* For an adiabatic process,

$$0 \leq S(B) - S(A)$$

Meaning: for thermally isolated system, entropy can only increase. Equilibrium state is state of maximum entropy consistent with external conditions.

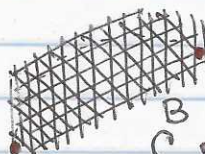
Remark: Note that in the above we did not assume any mechanical isolation - the system can be performing some mechanical work during the process

* Work done by an adiabatic process

$$-W_{ad, A \rightarrow B} = U(B) - U(A), \quad W_{ad, A \rightarrow B} = U(A) - U(B);$$

$S(B) \geq S(A)$

Consider an arbitrary reversible process $A \rightarrow B$



$$Tds = du + \delta w$$

$$\int_{A, \text{rev.}}^B Tds = U(B) - U(A) + W_{A \rightarrow B, \text{rev}}$$

$$W_{A \rightarrow B, \text{rev.}} \geq W_{A \rightarrow B, \text{adiabatic}}$$

← HW problem

Significance of thermodynamic potentials:

$F(T, V)$
Helmholtz free energy: isothermal processes

* For any isothermal process $A \rightarrow B$

work done by the system: $W_{A \rightarrow B} = \Delta Q - \Delta U \leq T(S(B) - S(A)) - (U(B) - U(A))$

$$\Delta Q = \int_A^B \delta Q = T \int_A^B \frac{\delta Q}{T} \leq T(S(B) - S(A))$$

↑
since $T = \text{const}$

$$W_{A \rightarrow B} \leq -\left(F(B) - F(A)\right); \quad \text{"=" if reversible}$$
$$\Delta F \leq -\Delta W$$

* For any process at constant T and V
(more generally, with ~~constant~~ ^{constant} mechanical coordinates so that no mechanical work is performed)

$$\Delta F \leq -\Delta W = 0, \quad \Delta F \leq 0$$

⇒ Equilibrium state of a mechanically isolated system
(constant V ; more generally, constant X_i & not doing any work)

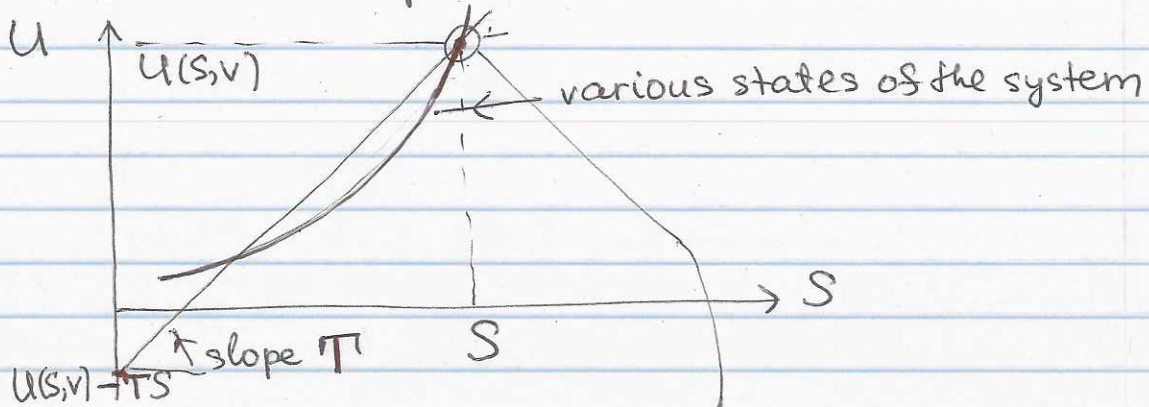
maintained at constant temperature is state minimizing the free energy consistent with given T, V

Recall discussion of Legendre transform:

$$F(T, V) = \min_S \left\{ \underbrace{U(S, V) - TS}_{\text{Legendre transform}} \right\}$$

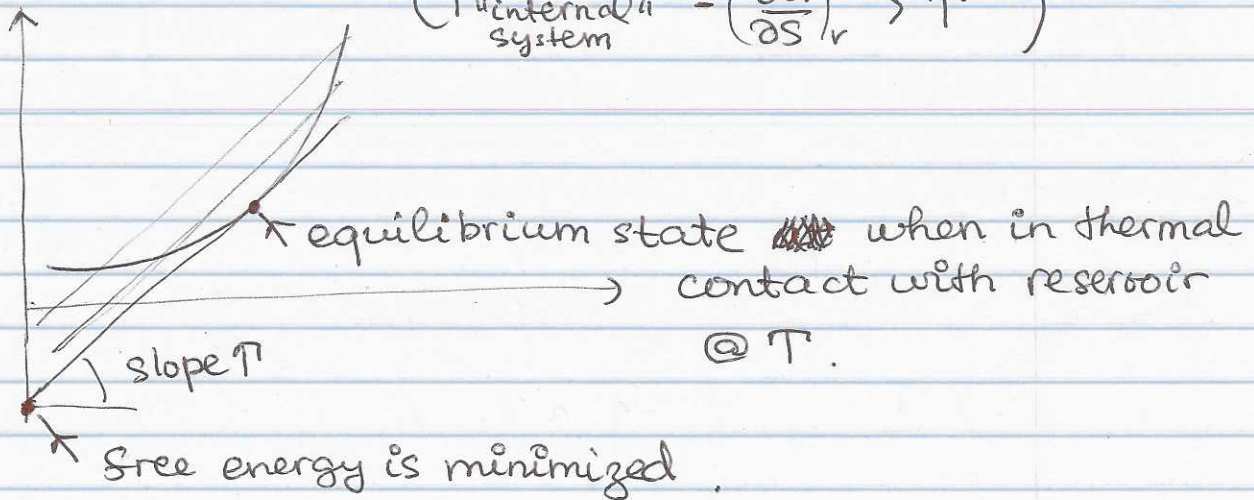
can be viewed as free energy at given T, V
in a non-equilibrium state
parametrized by S

Geometric interpretation



this would be non-equilibrium state if the system is brought in thermal contact with reservoir T

$$\left(T_{\text{internal system}} = \left(\frac{\partial U}{\partial S} \right)_V > T \right)$$



Significance of thermodynamic potentials

Gibbs free energy $G(T, p)$: isobaric processes

* For any process at constant T and p
(more generally, with constant generalized forces)

$$\boxed{\Delta G = \Delta U - T\Delta S + p\Delta V \leq 0}$$

$$\left(\Delta S \geq \int \frac{\delta Q}{T} = \frac{1}{T} \int \delta Q = \frac{1}{T} (\Delta U + p\Delta V) \right)$$

\uparrow const T \uparrow const p

\Rightarrow Equilibrium state of a system at $T, p = \text{const}$ is minimum of Gibbs free energy.

$$G_{\text{eq}}(T, p) = \min_{\text{all states with given } T, p} G$$

cf. Legendre transform

$$G(T, p) = \min_{S, V} \{ U(S, V) - TS + pV \}$$

Enthalpy $H(S, p)$

* For a thermally isolated process at constant p

$$\Delta H = \Delta U + p\Delta V = 0 \text{ if there is no friction}$$
$$\Delta Q = \Delta U + p\Delta V = 0$$

In general, $0 = \Delta Q = \Delta U + p\Delta V + \underbrace{\text{work expended against friction}}_{\neq 0}$

$$\Rightarrow \Delta U + p\Delta V \leq 0$$

$$\boxed{\Delta H \leq 0}$$

$$H(S, p) = \min_V \{ U(S, V) + pV \}$$