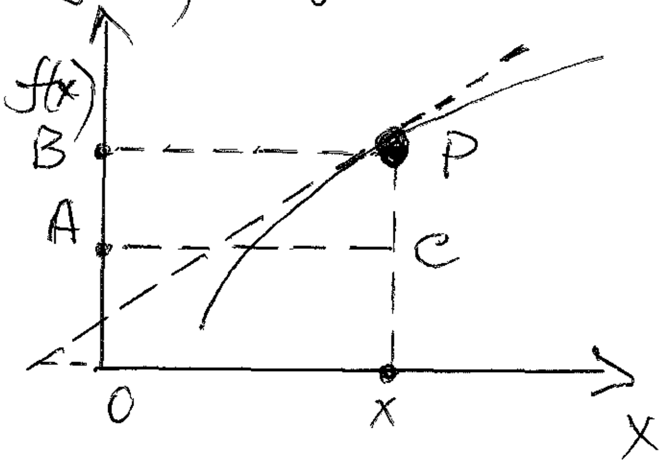
Legendre Transform

Take $A = E - S\left(\frac{\partial E}{\partial S}\right)$ ← Legendre transformation of $E \to A$

Geometrical interpretation of LT

Take $f(x)$ – some function

Suppose, we want to reconstruct $f(x)$ from $f'(x)$.



$f(x) = OB = OA + AB$

$AB = PC = AC\tan\theta$
$= x f'(x)$

$\Rightarrow f(x) = OA + x f'(x)$

$\Rightarrow OA = f(x) - x f'(x)$

Define $y = f'(x)$

$OA \equiv -J(y)$

$J(y) \equiv x y(x) - f(x)$

$$\frac{dJ}{dy} = \frac{dx}{dy}\underbrace{y}_{f'(x)} + x\underbrace{y'_y}_{=1} - \frac{df}{dx}\frac{dx}{dy} = x$$

$\Rightarrow x = \frac{dJ}{dy}$ and $J(y)$ – Legendre transform (LT)

Reconstruction of $f(x)$ from $f'(x)$:

Summary:

1. Define $J(y)$, such that $x = J_y'(y)$
2. Solve for $y(x)$ from this eq.
3. $f(x) = x\,y(x) - J[y(x)]$

For us
$$\left.\begin{array}{l} E \to f(x) \\ x = S \\ J(y) = A \end{array}\right\} \quad y = \frac{\partial E}{\partial S}$$

So $A = J(y) = E - S\dfrac{\partial E}{\partial S}$

The LT of $f(x)$ is defined as

$$\boxed{g(s) = s \cdot x(s) - f[x(s)]}$$

↳ motivation later!

Example 1: non-rel. kinetic energy

$$f(x) = \frac{1}{2}\alpha x^2 \Rightarrow f' = s = \alpha x \Rightarrow x = s/\alpha$$

$$g(s) = s\frac{s}{\alpha} - \frac{1}{2}\alpha\frac{s^2}{\alpha^2} \Rightarrow g(s) = \frac{1}{2\alpha}s^2$$

$\Rightarrow$ The curvatures of $\underset{\alpha}{\underset{\Uparrow}{f}}$ and $\underset{1/\alpha}{\underset{\Downarrow}{g}}$ are

inverses of each other as required.
(higher derivatives relation $\Rightarrow 0=0$)

$\Rightarrow$ This example is the case in classical Mech. of a single non-relativistic particle with mass "m", moving in external potential $V(q)$.

There, $x \to \dot{q}$; $f \to L$; $\alpha \to m$; $s \to P$; $g \to H$;

q is dummy as q is not involved! (q or potential)

Now: $L(\dot{q})$; $P = \frac{\partial L}{\partial \dot{q}}$; $H = \dot{q}\frac{\partial L}{\partial \dot{q}} - L$; $J \to H$

prove this is Hamiltonian!

$$\Rightarrow f + g = s \cdot x \text{ is } L + H = P \cdot \dot{q} \Rightarrow H = P\dot{q} - L = \frac{\partial L}{\partial \dot{q}}\dot{q} - L$$

Example 2:

Microcanonical ensemble $\qquad E(S, V, N)$

$X \to S \qquad f \to E \leftrightarrow sx = f + g$

where $s = f'_x$

$x = \frac{dg}{ds}$

when LT w.r.t. S is

$$\underbrace{\underbrace{S\left(\frac{\partial E}{\partial S}\right)}_{sx}}_{S \to x;\ \frac{\partial E}{\partial S} \to f'_x} - \underbrace{E}_{f} = \underbrace{TS - E}_{g} = -A$$

etc.

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LT motivation

In stat. thermo: the LT appears when different variables are "traded for their LT-conjugates.

Often: one variable is easy to think about, other variable is easy to control.

Example: conjugate to total "E" is the inverse of T (i.e., $\beta = \frac{1}{k_B T}$). But T is used for historical reasons:

$$A = E - TS$$

$\Rightarrow$ obscures the symmetry between β and E, as well as dimensionless nature of the LT.

By contrast, if we define dimensionless quantities $\begin{cases} \mathcal{S} = S/k_B, \\ \mathcal{A} = \beta A \end{cases}$ the duality (symmetry) between them can be expressed as $\mathcal{A}(\beta) + \mathcal{S}(E) = \underbrace{\beta \cdot E}$ (1)

$$\left[\mathcal{S} + \mathcal{A} = \frac{S}{k_B} + \beta(E - TS) = \frac{S}{k_B} + \beta E - \frac{1}{\cancel{\beta} k_B} S \cancel{\beta} = \beta E \right]$$

How does LT enters thermo?

$\Rightarrow$ through the door of Stat. Mech.

($\Rightarrow$ Laplace transform + thermo limit)

67) $\Omega(E) = e^{\mathcal{S}(E)}$; $Z(\beta) = e^{-\mathcal{A}(\beta)}$

$$\frac{d\mathcal{S}}{dE} = \beta; \quad \frac{d\mathcal{A}}{d\beta} = E$$

Why LT?

$\mathcal{S}$ - determines phys. conditions $\mathcal{S}(E)$

E - is not easy to control!

but $\left(\frac{\partial S}{\partial E}\right) \to \beta$ or T is more natural to control!

$\Rightarrow$ We: LT($\mathcal{S}$) - to get the same info coded in Helmholtz free energy $\mathcal{A}$ which is $\mathcal{A}(\beta)$.

$\Rightarrow$ Thermo potentials are LT of thermo functions. $\mathcal{A}$ is LT of E that replaces $S \to T$ as independent variable.

* entalpy is LT of E that replaces $V \to P$ as independent variable

Foundations of Stat. Thermo.

Start: microcanonical ensemble:
equal probability within δE
$\Rightarrow$ closed, isolated system

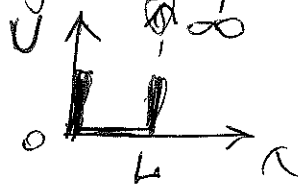
Classical example: gas of N identical particles $\Rightarrow$ free, non-relativ. structureless particles in D-dimensional box of volume $V = L^d$.

$\Rightarrow$ microstate: $2dN$ variables $\to (\vec{x}_i, \vec{p}_i)$
$i = 1 \dots N$

Since $E = \text{const}$:

$$\Rightarrow \underbrace{P(\vec{x}_i, \vec{p}_i)}_{\text{probability}} \propto \delta[E - \underbrace{H(\vec{x}_i, \vec{p}_i)}_{\text{Hamiltonian}}]$$

$$\Rightarrow H = \sum_i h(\vec{x}_i, \vec{p}_i) = \sum_i \left[\frac{p_i^2}{2m} + \underbrace{U(\vec{x}_i)}_{\text{confining pot.}}\right]$$



$\Rightarrow$ Normalization for P:

$$\Omega(E) = \int_{-\infty < x, p < +\infty} \delta(E - H)$$

$\to$ configuration part of $\int \Rightarrow L^{Nd}$ - explicitly
momentum part of $\int \Rightarrow$ surface area of a sphere in Nd

Entropy $S = k_B \ln \Omega \to S \equiv \ln \Omega(E)$

Now proceed (1) math
or (2) physics

Route of Math ($k_B = 1$)

$\Rightarrow$ Solve $\Omega(E) = \int_{x,p} \delta(E-H)$ using Laplace Tr.

$\Rightarrow$ integrand factorizable! (<u>Not easy</u>)

Nd integrations $\rightarrow \underbrace{\int \times \int \times \int \times \ldots \int}_{\text{simple integrals}}$

So, consider Laplace Tr. of $\Omega(E)$:

$$Z(\beta) \equiv \int^{\infty} \Omega(E)\, e^{-\beta E}\, dE$$

Inserting $\Omega^{0}(E) \Rightarrow Z(\beta) = \int_{x,p} e^{-\beta H} \ldots$, and using δ-function

Since $H = \sum$ of individual components:

$$\int_{x,p} e^{-\beta H} = \int_{x,p} \prod_i e^{-\beta h(\vec{x}_i, \vec{p}_i)} = \left[\int_{x,p} d\vec{x}\, d\vec{p}\; e^{-\beta h}\right]^N$$

Remain: use inverse Laplace Tr.:

$$\Omega(E) = \int_C Z(\beta)\, e^{\beta E}\, d\beta$$ where C-contour in the complex β-plane

Defining $\mathcal{A}(\beta) \equiv -\ln Z(\beta) \Rightarrow e^{S(E)} = \int d\beta\, e^{-\mathcal{A}(\beta) + \beta E}$

$\Rightarrow$ integrand: $e^{S(E)} = \int_C e^{-\mathcal{A}(\beta) + \beta E}\, d\beta$

$\mathcal{A}$, E - extensive

Standard method to deal with $\int$ of large exponentials is Saddle Point method

$\Rightarrow$ Saddle point in β defined by setting the <u>first</u> derivative of $\beta E - \mathcal{A}(\beta) \rightarrow 0$:

$$\frac{\partial}{\partial \beta}\left[\beta E - \mathcal{A}(\beta)\right]_{\beta_0} = 0$$

In other words: $\left.\frac{\partial \mathcal{A}}{\partial \beta}\right|_{\beta_0} = E.$ $(*)$

where β_0 should be $\beta_0(E)$!

In this approach, the integrand of

$$Z(\beta) = \int \Omega(E)\, e^{-\beta E}\, dE$$

is well approximated by evaluating the integrand at the Saddle Point, so that,

$$\Omega(E) \simeq e^{\beta_0 E - \mathcal{A}(\beta_0)}$$

Or using $\mathcal{S}(E) = \ln \Omega(E) \Rightarrow \mathcal{S}(E) = \beta_0 E - \mathcal{A}(\beta_0)$

$$\mathcal{S}(E) + \mathcal{A}(\beta_0) = \beta_0 E$$

where β_0 and E related via eq. $(*)$

$\Rightarrow$ this eq. is identical to eq. (1) on p. 66

So, $\boxed{\mathcal{S} \text{ and } \mathcal{A} \text{ are LTs of each other}}$

Hence, for $N \to \infty$, the Laplace Tr. and LT are intimately related!