Thermodynamic Information

$E(S,V,N)$ } Fundamental equations, contain
$S(E,V,N)$ } complete thermodynamic description

Since $T = \left.\frac{\partial E}{\partial S}\right)_{V,N} = T(S,V,N)$ we could (in principle) solve this for $S = S(T,V,N)$ and substitute in the energy F.E. to obtain $E(T,V,N)$

The reverse process involves integration and thus introduces constants → we have lost information!

Example $f(x) = x^2 + 1$ (1)

derivative $\xi = \frac{df}{dx} = 2x \Rightarrow x = \frac{\xi}{2} \overset{(1)}{\Rightarrow} f(\xi) = \frac{\xi^2}{4} + 1$

but - given $f(\xi)$, we cannot recover (1)!

[e.g. $g(x) = (x+1)^2 + 1 \quad \xi = \frac{dg}{dx} = 2(x+1) \Rightarrow g(\xi) = \frac{\xi^2}{4} + 1$]

Solution: $\boxed{\text{Legendre Transforms}}$

Basis function $y^{(0)}(x_1, x_2, \ldots x_n)$ ← this means "basis"

$$dy^{(0)} = \underbrace{\xi_1 dx_1 + \xi_2 dx_2 + \cdots \xi_n dx_n}_{\text{derivatives}}$$

First Transform : $y^{(1)}(\xi_1, x_2, \cdots x_n) = y^{(0)} - \xi_1 x_1$

$$dy^{(1)} = -x_1 d\xi_1 + \xi_2 dx_2 + \cdots \xi_n dx_n$$

note that 1st derivative of $y^{(1)}$ is $-x_1$; both $y^{(1)}$ and x_1 are now considered functions of $\xi_1, x_2, \ldots x_n$

Example 7.2 – 1D (1 component system – unphysical)

$y^{(0)}(x) = e^x \qquad \xi = \frac{dy^{(0)}}{dx} = e^x \Rightarrow x = \ln \xi$

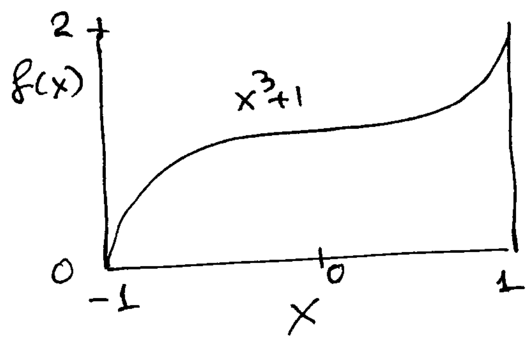
$y^{(1)}(\xi) = y^{(0)} - \xi x = e^{(\ln \xi)} - \xi \ln \xi = \xi - \xi \ln \xi$

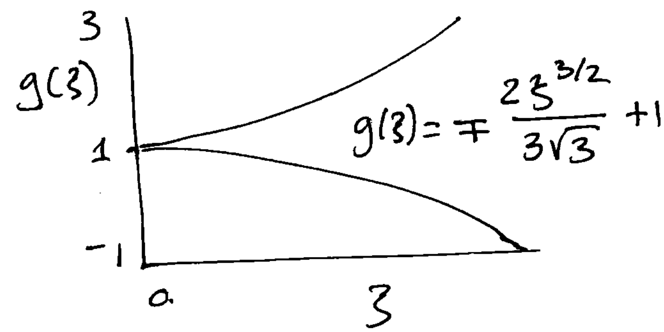
$(y^{(1)})^{(1)} = ? \qquad \frac{\partial y^{(1)}}{d\xi} = \cancel{1} - \ln \xi - \cancel{1} = p \Rightarrow \xi = e^{-p}$

$y^{(1)} - (e^{-p}) \cdot p = e^{-p} - \cancel{e^{-p}}(-p) - \cancel{e^{-p} \cdot p} = e^{-p}$

set $x = -p$ ⤳ recover original function

Example (Notes 4.4) $f(x) = x^3 + 1$ $\qquad \xi = 3x^2 \Rightarrow x = \pm\sqrt{\frac{\xi}{3}}$





Functions become multivalued – (physically represents multiple phases)

Multiple Transforms

$y^{(j)}(\xi_1, \xi_2, \dots \xi_j, x_{j+1} \dots x_n) = y^{(1)} - \sum_{i=1}^{j} \xi_i x_i$

$dy^{(j)} = -x_1 d\xi_1 - x_2 d\xi_2 - \dots - x_j d\xi_j + \xi_{j+1} dx_{j+1} + \dots + \xi_n dx_n$

All of these transforms preserve the information content of the original equation, $y^{(0)}$, which can be obtained from differentiations.

Applications to Thermodynamics

$E = y^{(0)}$ | $y^{(1)} = E - TS \equiv A$ | $y^{(2)} = E - TS + PV \equiv G$

var.	deriv.	var.	deriv.	var.	deriv.
S	T	T	$-S$	T	$-S$
V	$-P$	V	$-P$	$-P$	$-V$
N_1	μ_1	N_1	μ_1	N_1	μ_1
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
N_n	μ_n	N_n	μ_n	N_n	μ_n

Different ordering

$E = y^{(0)} = E(V, S, \{N_i\}) \Rightarrow y^{(1)} = E + PV \equiv H$

Different basis

$G = y^{(0)} = G(T, P, \{N_i\}) \Rightarrow y^{(1)} = G + TS$ ($= H$ again)

The total Legendre transform of $y^{(0)} = E(S, V, \{N_i\})$ corresponds to the Gibbs-Duhem relationship

$$E - TS + PV - \sum_i \mu_i N_i = 0 \quad \text{(from Euler's Theorem)}$$

How about $y^{(0)} = S$ $\qquad dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$ $\quad (C=1)$

var.	deriv.
E	$1/T$
V	P/T
N	$-\mu/T$

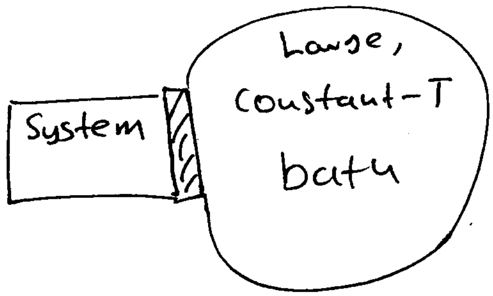
$$y^{(1)} = S - \frac{E}{T} \quad \left(= -\frac{A}{T}\right) \rightarrow$$

var.	deriv.
$1/T$	$-E$
V	P/T
N	$-\mu/T$

So that, $\quad -E = \dfrac{\partial}{\partial(1/T)}\left(-A/T\right)$ $\quad$ (non-obvious)

All of these functions are called "thermodynamic potentials"

Coupling to external Bath



$S_{world} = S + S_{bath}$ is maximum at equilibrium

$E_{world} = E + E_{bath}$ is constant

$$S_{bath} = \frac{E_{bath}}{T} + \underbrace{\frac{P_{bath} V_{bath}}{T} - \frac{\mu_{bath} N_{bath}}{T}}_{\text{constants at const-}T}$$

integrated f.E. for bath

$$\Rightarrow S_{bath} = \frac{E_{world} - E}{T} + (\text{constants}) = -\frac{E}{T} + (\text{constants})$$

$$S_{world} = S - \frac{E}{T} + (\text{constants}) \quad \text{is } \underline{\text{max}} \text{ at equil.}$$

$$\Rightarrow S - \frac{E}{T} = -\frac{A}{T} \quad \text{is } \underline{\text{max}} \text{ at equil. @ const } T, V, N$$

$-\frac{A}{T}$ is the Legendre Transform of $S(E,V,N)$

<u>In general</u>: The thermodynamic potential function being minimized/maximized at equilibrium is the Legendre Transform with the proper variables (corresponding to equilibrium constraints)

E.g. @ const $T, V, N \longrightarrow A$ is min

[Legendre Transform of $E(S,V,N)$]

Const. $T, P, N \rightarrow G$ is min
Const. $S, V, N \rightarrow H$ is min } etc

Example 7.3

The heat capacity of a substance is $c_v(T,v) = \alpha T^2 v^2$
$S = \epsilon = 0$ @ $T=0$ for all v. Compute $e(s,v)$, $h(s,P)$, $a(T,v)$ and $g(T,P)$ [intensive, per particle]

$$C_v = \left(\frac{\partial e}{\partial T}\right)_v \quad (1) \qquad de = Tds - Pdv \quad \text{(intensive } c=1\text{)}$$

$$\Rightarrow C_v = T \left.\frac{\partial s}{\partial T}\right)_v \quad (2)$$

$$(1) \Rightarrow e = \int C_v dT = \frac{\alpha}{3} T^3 v^2 + \cancel{\text{const}(v)} \quad (3)$$

$$(2) \Rightarrow s = \int \frac{C_v}{T} dT = \frac{\alpha}{2} T^2 v^2 + \cancel{\text{const.}(v)} \quad (4)$$

Since $S = e = 0$ @ $T=0$ both const. are 0

$e(s,v) = ?$ solve (4) for T, subst. in (3)

$$T = \left(\frac{2s}{\alpha v^2}\right)^{1/2} \qquad e = \frac{\alpha}{3}\left(\frac{2s}{\alpha v^2}\right)^{3/2} v^2 \Rightarrow e(s,v) = \left(\frac{8}{9\alpha}\right)^{1/2} s^{3/2} v^{-1} \quad (5)$$

For $a(T,v) = e - Ts \overset{(3)}{=} \frac{\alpha}{3} T^3 v^2 - \frac{\alpha}{2} T^3 v^2 = -\frac{\alpha}{6} T^3 v^2$

For $h(s,P)$ we need the pressure P

$$P = -\left.\frac{\partial e}{\partial v}\right)_s \overset{(5)}{=} \left(\frac{8}{9\alpha}\right)^{1/2} s^{3/2} v^{-2} \Rightarrow v = \left(\frac{8}{9\alpha}\right)^{1/4} P^{-1/2} s^{3/4}$$

$$h = e + Pv = \left(\frac{8}{9\alpha}\right)^{1/2} s^{3/2} \left[\left(\frac{8}{9\alpha}\right)^{1/4} P^{-1/2} s^{3/4}\right]^{-1} + P\left[\quad\right]$$

$$= \left(\frac{128}{9\alpha}\right)^{1/4} P^{1/2} s^{3/4}$$

$g = a + Pv$ (same way)