FUNDAMENTAL EQUATION

From Postulate I, we know that we can write

$\underline{u} = \underline{u}(\underline{S}, \underline{V}, N_1, \dots N_n)$ Energy Equation

or $\underline{S} = \underline{S}(\underline{u}, \underline{V}, N_1, \dots N_n)$ Entropy Equation

Why? $\underline{V}$ and $\underline{S}$ can always be varied independently

Both equations deserve to be called "Fundamental" -

- They relate quantities appearing in 1st and 2d Law
- Involve only extensive properties (first order in mass) } no external constr. (T, P) on systems

Differential form of Fundam. Equation (F.E) in energy representation } $\boxed{d\underline{u} = Td\underline{S} - Pd\underline{V} + \sum_i \mu_i dN_i}$

Derivatives of F.E

$$\left(\frac{\partial \underline{u}}{\partial \underline{S}}\right)_{\underline{V}, N_1, \dots N_n} = T$$

$$\left(\frac{\partial \underline{u}}{\partial \underline{S}}\right)_{\underline{S}, N_1, \dots N_n} = -P$$

$$\left(\frac{\partial \underline{u}}{\partial N_j}\right)_{\underline{S}, \underline{V}, \underbrace{N_{i[j]}}} = \mu_j$$

} Intensive variables (0th order in mass)

this means all i except j

Euler's theorem (App. C in T+M) states that:

If $f(a, b, kx, ky) = k^n f(a, b, x, y) \Rightarrow$

$$\Rightarrow h f(a,b,x,y) = x\left(\frac{\partial f(a,b,x,y)}{\partial x}\right)_{a,b,y} + y\left(\frac{\partial f(a,b,x,y)}{\partial y}\right)_{a,b,x}$$

Applying Euler's theorem, for $h=1$ (extensive variables)

Integrated form of F.E. $\}$ $\boxed{\underline{U} = T\underline{S} - P\underline{V} + \sum_i \mu_i N_i}$

$\underline{U}$ is still a function of $\underline{S}, \underline{V}, N_1, \dots N_n$ and

$T = T(\underline{S}, \underline{V}, N_1, \dots N_n)$

$P = P(\underline{S}, \underline{V}, N_1, \dots N_n)$

$\mu_i = \mu_i(\underline{S}, \underline{V}, N_1, \dots N_n)$

<u>Digression</u>: Intensive properties are only functions of $n+1$ independently variable <u>intensive</u> props:

$$\underset{\substack{\uparrow \\ \text{an int.} \\ \text{var.}}}{b} = f(\underbrace{c_1, c_2, \dots c_{n+1}}_{\substack{n+1 \text{ indep.} \\ \text{intensive variables}}}, \underset{\substack{\downarrow \\ \text{extent of system}}}{N})$$ according to Postulate I

Euler- Integrates using $h=\phi$

$$\phi = \left(\frac{\partial b}{\partial N}\right)_{c_1, c_2 \dots c_{n+1}} \cdot N \Rightarrow \left(\frac{\partial b}{\partial N}\right)_{c_1, c_2, \dots c_{n+1}} = \phi$$

for example, $\mu = \mu(T,P)$ for a pure component

$\underline{U}$: extensive $\qquad U$: intensive

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

$$\left(\frac{\partial U}{\partial N}\right)_{\underline{S},\underline{V}} \overset{?}{=} \phi \qquad \left(\frac{\partial \underline{U}}{\partial N}\right)_{\underline{S},\underline{V}} = \underbrace{\left(\frac{\partial (NU)}{\partial N}\right)_{\underline{S},\underline{V}}}_{= \mu \text{ from F.E.}} = U + N\left(\frac{\partial U}{\partial N}\right)_{\underline{S},\underline{V}}$$

Since $U \neq \mu$, $\left(\frac{\partial U}{\partial N}\right)_{\underline{S},\underline{V}} \neq \phi$

Now, reconsider the expressions

$\underline{u} = \underline{u}(\underline{S}, \underline{V}, N_1, \dots N_n)$ [1]

$T = T(\underline{S}, \underline{V}, N_1, \dots N_n)$ [2] $P = P(\underline{S}, \underline{V}, N_1, \dots N_n)$ [3]

Often, we would like to work with variables other than $\underline{S}, \underline{V}, \dots N_n$. Why don't we just eliminate $\underline{S}$ by solving [2] and substituting in [1] to get $\underline{u} = \underline{u}(T, \underline{V}, N_1, \dots N_n)$ [4]? What would be "wrong" with this?

$\rightarrow$ When going from $\underline{u}(\underline{S}, \underline{V}, N_1, \dots N_n)$ to $\underline{u}(T, \underline{V}, N_1, \dots N_n)$

we lose information!

Explanation

(A)
$$\left\{ \begin{array}{l} y(x) = x^2 + 5 \\ \dfrac{dy}{dx} = \xi = 2x \Rightarrow x = \dfrac{\xi}{2} \end{array} \right\} y(\xi) = \frac{\xi^2}{4} + 5$$

(B)
$$\left| \begin{array}{l} y(x) = (x+3)^2 + 5 \\ \dfrac{dy}{dx} = \xi = 2(x+3) \end{array} \right\} \Rightarrow y(\xi) = \frac{\xi^2}{4} + 5$$

(A) and (B) are not equivalent for $y(x)$, even though $y(\xi)$ is the same in both cases!

To go from [1] $\underline{u} = \underline{u}(\underline{S}, \underline{V}, N_1, \dots N_n)$ to [4] $\underline{u} = \underline{u}(T, \underline{V}, N_1, \dots N_n)$

we need $T = \left(\dfrac{\partial \underline{u}}{\partial \underline{S}}\right)_{\underline{V}, N_1, \dots N_n} = f(\underline{S}, \underline{V}, N_1, \dots N_n) \Rightarrow$

$$\underline{S} = f^{-1}(T, \underline{V}, N_1, \dots N_n)$$

but to go back from [4] to [1] we need to integrate a Partial Differential Equation, which introduces arbitrary const.

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

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

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

↑
derivative
w.r.t. 1st variable

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

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

Or, in a neat table:

$y^{(0)}$ var.	$y^{(0)}$ der.	$y^{(1)}$ var.	$y^{(1)}$ der.
x_1	ξ_1	ξ_1	$-x_1$
x_2	ξ_2	x_2	ξ_2
$\vdots$	$\vdots$	$\vdots$	$\vdots$
x_n	ξ_n	x_n	ξ_n

Reverse Transform:

$$y^{(0)} = y^{(1)} + \xi_1 x_1$$

Example - 1 D (0 component system - impossible!)

$$y^{(0)}(x) = x^2 + 5$$
$$\frac{dy^{(0)}}{\partial x} = \xi = 2x$$

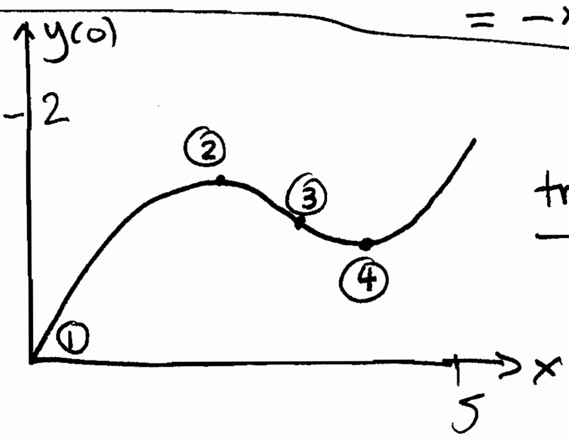
$$\Rightarrow \quad y^{(1)}(\xi) = \frac{\xi^2}{4} + 5 - \frac{\xi^2}{2} = -\frac{\xi^2}{4} + 5$$

reverse transform

$$\frac{dy^{(1)}(\xi)}{d\xi} = -x = -\frac{\xi}{2} \Rightarrow y^{(0)}(x) = y^{(1)}(\xi) + x\xi = -x^2 + 5 + 2x^2 = \underline{\underline{x^2 + 5}} \checkmark$$

$y^{(0)} = \sin(x) + x^2/9$

$\frac{dy^{(0)}}{dx} = \xi = \cos(x) + \frac{2x}{9}$



$\xrightarrow{\text{transform}}$ no analytical solution possible, invert numerically

$y^{(0)} = \sin(x) + x^2/9$