Obj. 4: Mathmatical Properties of Fundamental Equations.

1. Euler Equation.
2. Gibbs – Duhem Relation.
3. Structure of thermodynamic Formulism.
4. E.O.S. (and Fundamental Eq.) for common sys.

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1. Euler Equation

Given the 1^{st}-order & homogeneous nature of Fundamental Eqs.

$$\underline{U(\lambda S, \lambda X_1, \lambda X_2 \cdots \lambda X_t)} = \underline{\lambda U(S, X_1, X_2 \cdots X_t)}$$

treat λ as a variable. Diff. w/ respect to λ.

$$\frac{\partial U(\lambda S, \lambda X_1 \cdots \lambda X_t)}{\partial \underbrace{(\lambda S)}_{f = f(\lambda)}} \cdot \underline{\frac{\partial(\lambda S)}{\partial \lambda}} + \cdots \frac{\partial U(\lambda S, \lambda X_1 \cdots \lambda X_t)}{\partial(\lambda X_t)} \cdot \frac{\partial(\lambda X_t)}{\partial \lambda}$$

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product rule: $h = f \cdot g$. $\frac{d}{dx} h = \frac{d}{dx}(f \cdot g)$

$$= \frac{df}{dx} \cdot g + \frac{dg}{dx} \cdot f$$

$$\underbrace{\frac{\partial \lambda}{\partial \lambda} \cdot S}_{= S} + \underbrace{\frac{\partial S}{\partial \lambda}}_{0} \cdot \lambda$$

$$= \underbrace{\frac{\partial \lambda}{\partial \lambda}}_{1} \cdot U(S, X_1, \cdots X_t) + \underbrace{\frac{\partial U(S, X_1, \cdots X_t)}{\partial \lambda}}_{0} \cdot \lambda$$

$$= U(S, X_1, \cdots X_t)$$

This should be true for arbitrary λ. Now let $\lambda = 1$.

$$\Rightarrow \underbrace{\frac{\partial U(S, X_1 \cdots X_t)}{\partial S}}_{T} \cdot S + \sum_{j=1}^{t} \underbrace{\frac{\partial U(S, X_1 \cdots X_t)}{\partial X_j}}_{P_j} \cdot X_j = U(S, X_1, \cdots X_t)$$

(*)

$$\Rightarrow \boxed{U = TS + \sum_{j=1}^{t} P_j \cdot X_j}$$ Euler Equation.

if we have $X_1 = V$, $X_2 \cdots X_t = N_1 \cdots N_r$

$$\rightarrow \boxed{U = TS - PV + \sum_{i=1}^{r} \mu_i N_i}$$

$$\boxed{P_{j=1} = -P}$$

*. Entropic Form

$$S = \sum_{j=0}^{t} F_j X_j \qquad F_{j=0} = \frac{\partial S}{\partial U} = \frac{1}{T}, \quad \overbrace{F_{j=1}}^{-\frac{P_j}{T}} = \frac{\partial S}{\partial V} = -\left(\frac{-P}{T}\right) = \frac{P}{T}$$

$$\rightarrow \boxed{S = \left(\frac{1}{T}\right)U + \left(\frac{P}{T}\right)V - \sum_{k=1}^{r} N_k \left(\frac{\mu_k}{T}\right)}$$

*. U or S is the sum of the product of their intensive parameters and the corresponding extensive parameters.

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2. Gibbs – Duhem relation.

*. There exists a relationship amongst various intensive parameters.

Why?

$$U = U(S, X_1, \cdots X_t)$$

$\rightarrow$ $(t+1)$ EOS.

$$P_k = P_k(S, X_1, \cdots X_t) \qquad k = 1, \cdots (t+1)$$

$$P_k = P_k(\lambda S, \lambda X_1, \cdots \lambda X_t)$$

For arbitrary λ, true

$$\lambda = 1/X_t$$

$$P_k = P_k\Big(\underbrace{\frac{S}{X_t}}_{\gamma_1}, \underbrace{\frac{X_1}{X_t}}_{\gamma_2}, \cdots \underbrace{\frac{X_{t-1}}{X_t}}_{\gamma_t}, 1\Big)$$

$$\left.\begin{aligned} P_1 &= P_1(\gamma_1, \gamma_2 \cdots \gamma_t) \\ &\vdots \\ P_j &= P_j(\gamma_1, \gamma_2 \cdots \gamma_t) \\ &\vdots \\ P_t &= P_t(\gamma_1, \gamma_2 \cdots \gamma_t) \end{aligned}\right\} \leftrightarrow \left\{\begin{aligned} \gamma_1 &= \gamma_1(P_1, P_2 \cdots P_t) \\ &\vdots \\ \gamma_j &= \gamma_j(P_1, P_2 \cdots P_t) \\ &\vdots \\ \gamma_t &= \gamma_t(P_1, P_2 \cdots P_t) \end{aligned}\right.$$

$$\underline{P_{t+1} = P_{t+1}(\gamma_1, \gamma_2 \cdots \gamma_t)}$$

Now replace $\{\gamma_1 \cdots \gamma_t\}$ in $P_{t+1} = P_{t+1}(\gamma_1, \gamma_2 \cdots \gamma_t)$

by $\gamma_j = \gamma_j(P_1, \cdots P_t)$

$$\Rightarrow P_{t+1} = P_{t+1}(\gamma_1(P_1 \cdots P_t), \gamma_2(P_1 \cdots P_t) \cdots \gamma_t(P_1 \cdots P_t))$$

*. consider Euler Equation.

$$U = TS + \sum_{j=1}^{t} P_j X_j$$

$$dU = \underline{TdS} + \underline{S \cdot dT} + \underline{\sum_{j=1}^{t} P_j dX_j} + \underline{\sum_{j=1}^{t} X_j dP_j}$$

1st law

$$dU = đQ + đW = Tds + \sum_{j=1}^{t} P_j dX_j$$

$$\Rightarrow \boxed{0 = S \cdot dT + \sum_{j=1}^{t} X_j dP_j}$$ ⊛ Gibbs-Duhem Relation.

or $$\sum_{j=0}^{t} X_j dP_j = 0$$

For a single component sys.

$\rightarrow \quad SdT - Vdp + Nd\mu = 0$

$\rightarrow \quad d\mu = -\underbrace{\frac{S}{N}}_{s} dT + \underbrace{\frac{V}{N}}_{v} dP = -s\,dT + v\,dP$

*. variation of any intensive parameter (μ, T, P) can be calculated based on the variations of other intensive parameters.

*. Entropy form of Gibbs-Duhem Relation.

$$\sum_{j=0}^{t} X_j \, dF_j = 0 \qquad F_j = -\frac{P_j}{T} \quad (j \geq 1)$$

$$F_{j=0} = \frac{1}{T}$$

$$\rightarrow \quad U \cdot d\left(\frac{1}{T}\right) + V d\left(\frac{P}{T}\right) - \sum_{k=1}^{r} N_k \, d\left(\frac{\mu_k}{T}\right) = 0$$

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3. structure of thermo.

*. Information contained Fundamental Eq. vs. that contained in EOS.

*. $U = U(S, V, N) \rightarrow$ all-inclusive (thermo. info.)

→ EOS
$$\begin{cases} T = \frac{\partial U}{\partial S} = T(S, V, N) \\ P = -\frac{\partial U}{\partial V} = P(S, V, N) \\ \mu = \frac{\partial U}{\partial N} = \mu(S, V, N) \end{cases}$$

if these are known. you could recover Fundamental Eq. because of

$$U = TS + \sum_{j=1}^{t} P_j X_j$$

1> The totality of all EOS is equivalent to the Fundamental Eq. & contains all thermo. info.

2> what if one of EOS is unknown?