Auxiliary Functions
Legendre Transforms

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Auxiliary Function

- **The term "auxiliary function" usually refers to the functions created during the course of a proof in order to prove the result.**
- **In thermodynamics, quantities with dimensions of energy were introduced that have useful physical interpretations and simplify calculations in situations where controlled set of variables were used.**

Work

- **In general, work can be divided into two parts:**
  - **work of expansion and contraction, and**
  - **work of the sum of all other forms**
- **Therefore in the reversible case,**

$$\underline{f} \cdot d\underline{X} = -pdV + \sum_i \mu_i dn_i$$

where μ_i will be defined as the chemical potential of species *i*, but not yet at this moment.

Euler's theorem

- **Euler's homogeneous function theorem**

  States that: Suppose that the function *f* is continuously differentiable, then *f* is positive homogeneous of degree n if and only if

$$f(\lambda \underline{x}) = \lambda^n f(\underline{x})$$

- **n= 1, *f* is a first-order homogeneous function**

Euler's theorem

- **Let $f(x_1,\ldots, x_n)$ be a first-order homogeneous function of $x_1,\ldots, x_n$.**
- **Let $u_i = \lambda x_i$**
- **Then $f(u_1,\ldots,u_n) = \lambda f(x_1,\ldots,x_n)$**
- **Differentiate with respect to λ;**

$$\left(\frac{\partial f\left(u_1,\ldots,u_n\right)}{\partial \lambda}\right)_{x_i} = f\left(x_1,\ldots,x_n\right) \qquad (1)$$

Euler's theorem

- **From calculus,**

$$df(u_1,\ldots,u_n) = \sum_{i=1}^{n} (\partial f / \partial u_i)_{u_j} du_i \qquad (2)$$

- **and,**

$$(\partial f / \partial \lambda)_{x_i} = \sum_{i=1}^{n} (\partial f / \partial u_i)_{u_j} (\partial u_i / \partial \lambda)_{x_i}$$

$$= \sum_{i=1}^{n} (\partial f / \partial u_i)_{u_j} x_i \qquad (3)$$

Euler's theorem

- **Substitute back to eq. (1),**

$$f(x_1,\ldots,x_n) = \sum_{i=1}^{n} \left(\partial f / \partial u_i\right)_{u_j} x_i \qquad (4)$$

- **and take $\lambda = 1$,**

$$f(x_1,\ldots,x_n) = \sum_{i=1}^{n} \left(\partial f / \partial x_i\right)_{x_j} x_i \qquad (5)$$

- **This is Euler's theorem for first-order homogeneous functions**

Legendre Transform

- **Recall the 2nd law of thermodynamics,**

$$dS = (1/T)dE - \left(\boldsymbol{f}/T\right) \bullet d\boldsymbol{X}$$

$$dE = TdS + \boldsymbol{f} \bullet d\boldsymbol{X}$$

- **and**

$$\underline{f} \cdot d\underline{X} = -pdV + \sum_i \mu_i dn_i$$

- **we arrive at,**

$$dE = TdS - pdV + \sum_i \mu_i dn_i$$

- **Thus, *$E=E(S,V,n_1,n_2,\ldots n_r)$*, is a natural function of *S*, *V*, and the *n_i's*.**

- **However, experimentally, *T* is much more convenient than *S*.**
- **Assume $f = f(x_1,\ldots,x_n)$ is a natural function of $x_1,\ldots,x_n$.**
- **Then,**

Euler's theorem for first-order homogeneous functions

$$f(x_1,\ldots,x_n) = \sum_{i=1}^{n} \left(\partial f / \partial x_i\right)_{x_j} x_i$$

$$df = \sum_{i=1}^{n} u_i dx_i \quad u_i = \left(\partial f / \partial x_i\right)_{x_j}$$

- **Let**

$$g = f - \sum_{i=r+1}^{n} u_i dx_i$$

- **Then,**

$$dg = df - \sum_{i=r+1}^{n} \left(u_i dx_i + x_i du_i \right)$$

$$= \sum_{i=1}^{r} u_i dx_i + \sum_{i=r+1}^{n} \left(-x_i \right) du_i$$

- **Thus, $g = g(x_1,\ldots,x_r, u_{r+1},\ldots,u_n)$ is a natural function of $x_1,\ldots,x_r$ and the conjugate variables to $x_{r+1},\ldots,x_n$, namely $u_{r+1},\ldots,u_n$.**
- **The function *g* is called a Legendre transform of *f*.**

- **It transform away the dependence upon $x_{r+1},\ldots,x_n$ to a dependence upon $u_{r+1},\ldots,u_n$.**
- **Newton** $\vec{F} = m\vec{a}$
- **Leibniz** $\vec{F} = m\dfrac{d^2 x}{dt^2}$
- **Euler-Lagrange** $\dfrac{d}{dt}\dfrac{\partial L}{\partial \dot{q}_i} - \dfrac{\partial L}{\partial q_i} = 0, \quad L = K - V, \text{'action'}$
- **Hamilton** $\dfrac{\partial H}{\partial q_i} = -\dot{p}_i$

$$\frac{\partial H}{\partial p_i} = \dot{q}_i, \quad H = K + V, \text{'Hamitonian'}$$

See my PPT at https://mestudio.tongji.edu → Teaching → Grad → StatisticalThermo for details

- **It is apparent that this type of transformation allows one to introduce a natural function of *T*, *V*, and *n*, since *T* is simply the conjugate variable to *S*; so as to *p* to *V*.**
- **From the first and second law, we have**

$$E = E(S, V, n)$$

- **We construct a natural function of *T*, *V* and *n*, by subtract from the *E*(*S*, *V*, *n*) the quantity**

$$S \times (\text{variable conjugate to } S) = ST.$$

- **Let** $A(T, V, n) = E - TS$ **called the Helmholtz free energy**
- **Therefore,**

$$dA = -SdT - pdV + \sum_{i=1}^{r} \mu_i dn_i$$

Legendre Transform

- Let $G(T, p, n)$ be the **Gibbs free energy**

  $G = E - TS - (-pV)$
- And $H(S, p, n)$ be **the Enthalpy**

  $H = E - (-pV) = E + pV$
- Therefore,

$$dG = -SdT + Vdp + \sum_{i=1}^{r} \mu_i dn_i$$

$$dH = TdS + Vdp + \sum_{i=1}^{r} \mu_i dn_i$$

Think also about,
volume to U
pressure to H,
natural variables

Maxwell Relations

- Armed with the auxiliary, many types of different measurements can be interrelated.
- Consider,

$$\left(\partial S / \partial V\right)_{T,n}$$

- implies we are viewing *S* as function of the natural function of *T*, *V* and *n*.

Maxwell Relations

- **If** $df = adx + bdy$, **from calculus,**

$$\left(\partial a / \partial y\right)_x = \left(\partial b / \partial x\right)_y$$

- **Recall** $dA = -SdT - pdV + \mu dn$
- **Then we have**

$$\left(\partial S / \partial V\right)_{T,n} = \left(\partial p / \partial T\right)_{V,n}$$

- **and**

$$dG = -SdT - Vdp + \mu dn$$

$$\left(\partial S / \partial p\right)_{T,n} = -\left(\partial V / \partial T\right)_{p,n}$$

Example I

- **Let** $C_v = T(\partial S / \partial T)_{V,n}$

$$dE = TdS - pdV + \sum_i \mu_i dn_i$$

- **then** $\left(\frac{\partial C_v}{\partial V}\right)_{T,n} = T\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_{V,n}\right)_{T,n}$

$$= T\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_{T,n}\right)_{V,n}$$

$$= T\left(\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial T}\right)_{V,n}\right)_{V,n}$$

$$= T\left(\frac{\partial^2 p}{\partial T^2}\right)_{V,n}$$

Quiz X

- **Derive an analogous form for (10 Mins)**

$$\left(\frac{\partial C_p}{\partial p}\right)_{T,n}$$

- Show that for a one component p-V-n system **(10 Mins)**

$$\left(\frac{\partial \mu}{\partial v}\right)_T = v\left(\frac{\partial p}{\partial v}\right)_T$$

- where *v* is the volume per mole. [Hint: show that , where *s* is the entropy per mole.

$$d\mu = -s dT + v dp$$

Example II

- **Let** $$C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,n}$$
- **Viewing *S* as a function of *T*, *V* and *n***
- **We have**

$$(dS)_n = \left(\frac{\partial S}{\partial T}\right)_{V,n}(dT)_n + \left(\frac{\partial S}{\partial V}\right)_{T,n}(dV)_n$$

$$\left(\frac{\partial S}{\partial T}\right)_{p,n} = \left(\frac{\partial S}{\partial T}\right)_{V,n} + \left(\frac{\partial S}{\partial V}\right)_{T,n}\left(\frac{dV}{\partial T}\right)_{n,p}$$

Maxwell Relations

- **Hence** $$\frac{1}{T}C_p = \frac{1}{T}C_v + \left(\frac{\partial p}{\partial T}\right)_{V,n}\left(\frac{\partial V}{\partial T}\right)_{n,p}$$
- **Note that** $$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x$$ Euler's chain rule
- **So** $$\left(\partial p / \partial T\right)_{V,n} = -\left(\partial p / \partial V\right)_{T,n}\left(\partial V / \partial T\right)_{p,n}$$
- **Therefore** $$C_p - C_v = -T\left(\partial p / \partial V\right)_{T,n}\left[\left(\partial V / \partial T\right)_{p,n}\right]^2$$

Euler's theorem

- **From the 2nd law of thermodynamics,**

$$E = E(S, \underline{X})$$

- **the internal energy *E* is extensive, it depends upon *S* and *X*, which are also extensive.**

$$E(\lambda \underline{X}) = \lambda E(S, \underline{X})$$

- **Thus, *E*(*S*,*X*) is a first order homogeneous function of *S* and *X*.**

Euler's theorem

- **Therefore, from Euler's theorem, Eq.5,**

$$E = \left(\partial E / \partial S\right)_{\underline{X}} S + \left(\partial E / \partial \underline{X}\right)_s \underline{X}$$

$$= TS + \underline{f} \cdot \underline{X}$$

where $\underline{X}$ is a vector means system volume

- **And work is,**

$$\underline{f} \cdot d\underline{X} = -pdV + \sum_i \mu_i dn_i$$

Extensive Function

- **This flow naturally as we gave earlier,**

$$dE = TdS - pdV + \sum_{i=1}^{r} \mu_i dn_i$$

- **That is, $\boldsymbol{E = E(S,V, n_1,\ldots,n_r)}$**

- **and Euler's theorem yields,**

$$E = TS - pV + \sum_{i=1}^{r} \mu_i n_i$$

Extensive Function

- **Its total differential is**

$$dE = TdS + SdT - pdV - Vdp + \sum_{i=1}^{r} \left(\mu_i dn_i + n_i d\mu_i \right)$$

- **Therefore,**

$$0 = SdT - Vdp + \sum_{i=1}^{r} \left(n_i d\mu_i \right)$$

This is the Gibbs-Duhem Equation

Extensive Function

- **Recall the definition of Gibbs free energy**
  $\boldsymbol{G = E - TS - (-pV)}$
- **Apply Euler's theorem gives,**

$$dG = \left(TS - pV + \sum_{i=1}^{r} \mu_i dn_i \right) - TS - pV$$

$$= \sum_{i=1}^{r} \mu_i dn_i$$

- **For one component system μ = *G*/*n*, Gibbs free energy per mole**

Quiz (exercise 1.14)

- Show that for a one component p-V-n system

$$\left(\frac{\partial \mu}{\partial v}\right)_T = v\left(\frac{\partial p}{\partial v}\right)_T$$

- where *v* is the volume per mole. [Hint: show that $d\mu = -s dT + v dp$, where *s* is the entropy per mole.