Lecture 22 – Thermodynamics of phase equilibrium

A. The Fundamental Equation

In the last lecture, we learned that there are two important state functions – energy and entropy – that describe a system. There was a law for each.

1st law: $dU = \delta Q + \delta W$

2nd law: $dS = \delta Q_{rev}/T$, $\oint dS \geq 0$

We can combine what we know about both entropy and energy from these two laws into a single equation.

$$dU = \delta Q + \delta W$$

$$dU = \delta Q_{rev} + \delta W_{rev}$$ the first law also holds for reversible processes

$$\delta Q_{rev} = TdS$$ Definition of entropy

$$dW_{rev} = \sum_j F_j\, dX_j$$ Work for a reversible path

$$= -PdV + \sum_{i=1}^{N} \mu_i\, dn_i$$ For an isotropic fluid with N components

$$\boxed{dU = TdS - PdV + \sum_{i=1}^{N} \mu_i\, dn_i}$$ FE – Energy Representation

This expression is called the Fundamental Equation of Thermodynamics. It represents the combined 1st and 2nd laws. A simple rearrangement gives us the entropy representation of the Fundamental Equation.

$$\boxed{dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{1}{T} \sum_{i=1}^{N} \mu_i\, dn_i}$$ FE – Entropy Representation

If we roll back our assumption of an isotropic fluid, we get the more general expression

$$dU = TdS + \sum_j F_j\, dX_j$$

Note the sign convention is opposite from mechanics, except for $-PdV$

$F_j = \left(\frac{\partial U}{\partial X_j}\right)_{S, X_i}$: generalized forces X_j: generalized displacements

Integrating one of these expressions tells us

$S(U, V, n_1, n_2, \ldots, n_N)$ or $S(U, \underline{X})$ Entropy representation

$U(S, V, n_1, n_2, \ldots, n_N)$ or $U(S, \underline{X})$ Energy representation

This is our equilibrium manifold. It tells us the complete thermodynamic information about our system! If we know this function, we know how all of the pieces relate, we can calculate any reversible process, we can find phase behavior, we can compute P, T, μ, ρ, etc. If it is an equilibrium property, we can get it.

Ex: Entropy of a monoatomic ideal gas

$$S = S_0 + nR \ln\left[\left(\frac{U}{U_0}\right)^{\frac{3}{2}}\left(\frac{V}{V_0}\right)\right] \qquad S = S(U, V, n)$$

Equivalent to Sackur-Tetrode when

$V_0 = N\lambda_0^3 \quad \lambda_0 = h/(2\pi m k_B T_0)^{1/2}$

$U_0 = \frac{3}{2} N k_B T_0 \quad S_0 = \frac{5}{2} N k_B$

"Quantum crossover" reference state at T_0 with density of 1 atom per thermal cell volume ($\rho_0 = \frac{N}{V_0} = \frac{1}{\lambda_0^3}$)

$$\frac{S}{Nk_B} = \ln\left(\frac{V}{N\lambda^3}\right) + \frac{5}{2}$$

$$= \ln\left(\frac{\lambda_0^3}{\lambda^3}\frac{V}{N\lambda_0^3}\right) + \frac{5}{2} = \ln\left[\left(\frac{T}{T_0}\right)^{\frac{3}{2}}\frac{V}{V_0}\right] + \frac{5}{2} = \ln\left[\left(\frac{U}{U_0}\right)^{\frac{3}{2}}\frac{V}{V_0}\right] + \frac{5}{2}$$

$$\frac{S}{nR} = \frac{S_0}{nR} + \ln\left[\left(\frac{U}{U_0}\right)^{\frac{3}{2}}\frac{V}{V_0}\right]$$

$n = N/N_A$, $R = k_B N_A \Rightarrow nR = Nk_B$

Solve for $U(S, V, n)$

$$\frac{S - S_0}{nR} = \ln\left[\left(\frac{U}{U_0}\right)^{\frac{3}{2}}\frac{V}{V_0}\right] \Rightarrow \left(\frac{U}{U_0}\right)^{\frac{3}{2}}\frac{V}{V_0} = \exp\left(\frac{\Delta S}{nR}\right)$$

$$\frac{U}{U_0} = \left(\frac{V_0}{V}\right)^{2/3}\exp\left(\frac{\Delta S}{nR}\right)^{2/3} \Rightarrow \boxed{U = U_0\left(\frac{V}{V_0}\right)^{-2/3}\exp\left(\frac{2}{3}\frac{\Delta S}{nR}\right)}$$

B. Equations of State

For simplicity, I am going to do the following for an isotropic, pure component fluid. I will note more general expressions as needed. The fundamental equations $S(U,V,n)$ and $U(S,V,n)$ can be written as total differentials

$$dS = \left(\frac{\partial S}{\partial U}\right)_{n,V} dU + \left(\frac{\partial S}{\partial V}\right)_{n,U} dV + \left(\frac{\partial S}{\partial n}\right)_{U,V} dn \qquad \text{total derivative}$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dn \qquad \text{fundamental equation}$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{n,V} dS + \left(\frac{\partial U}{\partial V}\right)_{n,S} dV + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn \qquad \text{total derivative}$$

$$dU = TdS - PdV + \mu dn \qquad \text{fundamental equation}$$

Focusing on the energy representation (again for brevity and simplicity), by comparing the total differential and fundamental equation, we see that

$$T = \left(\frac{\partial U}{\partial S}\right)_{n,V} \qquad P = -\left(\frac{\partial U}{\partial V}\right)_{n,V} \qquad \mu = \left(\frac{\partial U}{\partial n}\right)_{S,V}$$

Comments: ($F_i - X_i - T$ relations)

- Each of these expressions are equations of state.

  $P = P(n,V,T)$ — P-V-T EoS (no heat capacity info)

  $T = T(U,n,V)$ — U-V-T EoS (no PVT data)

  $\mu = \mu(n,V,T)$ — μ-V-T EoS (redundant for pure component)

- Only 2 of the 3 are independent. This is a consequence of the fact that $U(S,V,n)$ is extensive. When the system size doubles, the energy doubles. In the language of mathematics U is a homogeneous function of degree 1: $U(\lambda S, \lambda V, \lambda n) = \lambda U(S,V,n)$. This leads to the Gibbs-Duhem equation that constrains the EoS. (no time to go deeper)
- If we know the equations of state, then we can reconstruct the entire fundamental equation. "full information" = PVT + $\tilde{C}_V$

- Classical thermodynamics tells us this structure, but we don't know the equations of state. We can get those empirically or by statistical thermodynamics. Each material (and mixture) has its own fundamental equation. Classical thermo just tells us there is one.
- These are the "property relationships" from the box in our last lecture.

Example: Equations of state for monoatomic ideal gas

$$U = U_0 \left(\frac{V}{V_0}\right)^{-2/3} \exp\left(\frac{2}{3}\frac{\Delta S}{nR}\right) \qquad \Delta S = S - S_0$$

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

$$T = \frac{\partial}{\partial S}\left[U_0 \left(\frac{V}{V_0}\right)^{-2/3} \exp\left(\frac{2}{3}\Delta S/nR\right)\right] = U_0 \left(\frac{V}{V_0}\right)^{-2/3} \frac{2}{3}\frac{1}{nR} \exp\left(\frac{2}{3}\Delta S/nR\right)$$

$$\frac{U}{U_0}\left(\frac{V}{V_0}\right)^{2/3}$$

$$T = \frac{2}{3}\frac{U}{nR} \quad \Rightarrow \quad \boxed{U = \frac{3}{2}nRT}$$

U(T) does not have the same amount of information as U(S,V,n)

2) $P = -\left(\frac{\partial U}{\partial V}\right)_{n,V}$

$$P = -\frac{\partial}{\partial V}\left[U_0 \left(\frac{V}{V_0}\right)^{-2/3} \exp\left(\frac{2}{3}\Delta S/nR\right)\right] = +U_0 \exp\left(\frac{2}{3}\Delta S/nR\right)\left(+\frac{2}{3}\right)\left(\frac{V}{V_0}\right)^{-5/3}\frac{1}{V_0}$$

$$U/U_0 \left(V/V_0\right)^{2/3}$$

$$P = \frac{2}{3}U\frac{V_0}{V}\frac{1}{V_0}$$

$$P = \frac{2U}{3V} \quad \Rightarrow \quad P = \frac{2}{3}\frac{1}{V}\frac{3}{2}nRT \quad \Rightarrow \quad \boxed{P = nRT/V}$$

3) $\mu = \left(\frac{\partial U}{\partial n}\right)_{S,V}$ (careful: U_0 and V_0 are functions of n)

$$\mu = \frac{\partial}{\partial n}\left[U_0 \left(\frac{V}{V_0}\right)^{-2/3} \exp\left(\frac{2}{3}\Delta S/nR\right)\right] \qquad \text{let } U_0 = \tilde{U}_0 n,\ V_0 = \tilde{V}_0 n$$

$$= \frac{\partial}{\partial n}\left[n\tilde{U}_0 \left(\frac{V}{n\tilde{V}_0}\right)^{-2/3} \exp\left(\frac{2}{3}\frac{\Delta S}{nR}\right)\right] \qquad \text{use chain rule}$$

$$\mu = \tilde{u}_0\left(\frac{V}{n\tilde{v}_0}\right)^{-2/3}\exp\left(\frac{2}{3}\frac{\Delta S}{nR}\right) + \left(\frac{2}{3}\right)n^{-1/3}\, n\tilde{u}_0\left(\frac{V}{\tilde{V}_0}\right)^{-2/3}\exp\left(\frac{2}{3}\frac{\Delta S}{nR}\right)$$

($n^{2/3}$; common factor)

$$+ n\tilde{u}_0\left(\frac{V}{n\tilde{v}_0}\right)^{-2/3}\frac{2\Delta S}{3R}\exp\left(\frac{2\Delta S}{3nR}\right)\cdot\frac{-1}{n^2}$$

$$\mu = \tilde{u}_0\left(\frac{V}{n\tilde{v}_0}\right)^{-2/3}\exp\left(\frac{2}{3}\frac{\Delta S}{nR}\right)\left[1 + \frac{2}{3} - \frac{2}{3}\frac{\Delta S}{nR}\right]$$

($\frac{U}{n\tilde{u}_0}\left(\frac{V}{n\tilde{v}_0}\right)^{2/3}$)

$$\mu = \frac{U}{n}\left(\frac{5}{3} - \frac{2}{3}\frac{\Delta S}{nR}\right) \qquad U = \frac{3}{2}nRT \qquad \frac{\Delta S}{nR} = \ln\left[\left(\frac{U}{U_0}\right)^{3/2}\frac{V}{V_0}\right]$$

($U/U_0 = T/T_0$)

$$\mu = \frac{3}{2}RT\left[\frac{5}{3} - \frac{2}{3}\ln\left(T/T_0\right)^{3/2} - \frac{2}{3}\ln\left(V/V_0\right)\right]$$

$$\frac{\mu}{RT} = \frac{5}{2} - \ln\left[\left(\frac{T}{T_0}\right)^{3/2}\frac{V}{V_0}\right]$$

μ_0 at $V = V_0$, $T = T_0 \Rightarrow \mu_0 = \frac{5}{2}RT$

$\Delta\mu = \mu - \mu_0$

$$\boxed{\frac{\Delta\mu}{RT} = \ln\left[\left(\frac{T}{T_0}\right)^{3/2}\frac{V}{V_0}\right]}$$

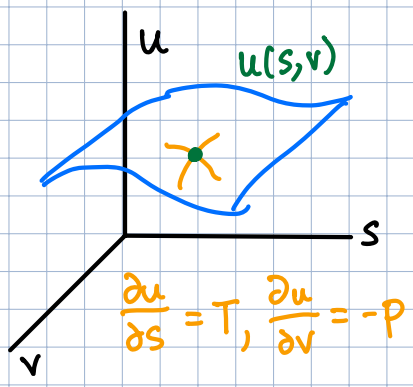
← can make a function of PV, TV, or PV using PVT EoS

C. Thermodynamic Potentials

Everything seems great! We have this state function U or S that gives us the equilibrium state of the system. We can construct it from empirical equations of state that we measure (PVT behavior and heat capacity), or we can use statistical thermo to get those.

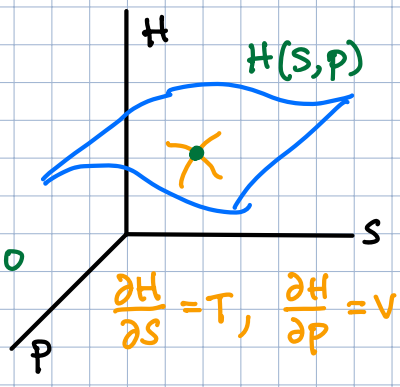
However, $U(S,V,n)$ and $S(U,V,n)$ are annoying. They are in terms of variables we don't have an easy way to measure. There are no "internal energy/entropy meters." But, if we solve for $U(T)$, we lose information. Are there other state functions with all the same information as U and S but depend on variables we can more easily measure? Yes! How do I find them? By a Legendre transform.

A Legendre transform is a change of variables for a surface that replaces an original coordinate with the corresponding derivative (slope of the surface). It gives us different coordinates but with the same amount of information.



$$H = U - V\frac{\partial u}{\partial V}$$

height where the tangent line crosses the intercept at V = 0



Define: Enthalpy $H = U + pV$ $\quad U = U(S,V,n)$

$dU = TdS - pdV + \mu dn$ $\quad$ Swap conjugate variables V & p

$dH = dU + pdV + Vdp$

$\boxed{dH = TdS + Vdp + \mu dn}$ $\quad H = H(S,P,n)$

Define: Helmholtz Free Energy $A = U - TS$ $\quad U = U(S,V,n)$

$dU = TdS - pdV + \mu dn$ $\quad$ Swap conjugate variables S & T

$dA = dU - TdS - SdT$

$\boxed{dA = -SdT - pdV + \mu dn}$ $\quad A = A(T,V,n)$

Define: Gibbs Free Energy $G = H - TS$ $\quad H = H(S,P,n)$

$dH = TdS + Vdp + \mu dn$ $\quad$ Swap conjugate variables S & T

$dG = dH - TdS + SdT$

$\boxed{dG = SdT + Vdp + \mu dn}$ $\quad G = G(T,P,n)$

The most useful are A and G. The Helmholtz free energy is a function of temperature and (specific) volume. The Gibbs free energy is a function of pressure and temperature.

Comments:

- With these thermodynamic potentials, we can now do useful things like compute phase equilibria or evaluate thermodynamic cycles.
- Just like with S & U, the partial derivatives of H, A, and G are given by equations of state.
- There is a whole "calculus of thermodynamics" that helps us relate all of these quantities together. This includes things like Maxwell Relations and it yields useful formulas like $H = H(P,T)$ or using compressibilities (instead of PVT behavior) to construct thermodynamic potentials. This formalism is very useful.
- What do H, A, and G mean physically?

H: Internal energy corrected for the PV work in a flowing system. For a constant pressure system, enthalpy is equal to heat input. $dH = \delta Q$ (const p only)

A: Negative weighted count of the microstates ($A = -k_B T \ln Q$, $Q = \sum_i e^{-\beta E_i}$). Like a "negative entropy" in a const nVT system. Remember that S is constant nVU ($S = k_B \ln \Omega$). Practically, the amount of work one can extract (not locked up as heat) at constant T, V ("thermodynamic potential").

G: Negative weighted count of the microstates ("negative entropy") in a constant nPT system ($G = -k_B T \ln \Xi$, $\Xi = \sum_i e^{-\beta(E+PV)}$). Weighted by the enthalpy. Amount of extractable work ("thermodynamic potential") at constant P, T.

- Thermodynamic square: A mnemonic for remembering the thermodynamic potentials. "Good physicists have studied under very ambitious teachers"

$-S$	U	V
H		A
$-P$	G	T

- Adjacent corners are differentials
- opposite corners are coefficients w/ sign
- opposite corners are conjugate variables

$U = U(S,V)$ $\quad dU = -pdV + TdS$

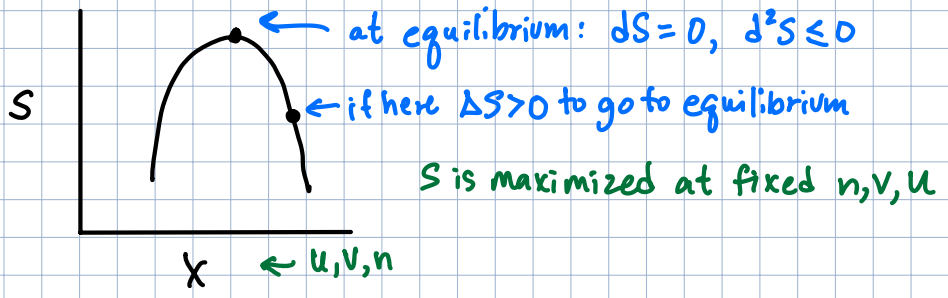
$H = H(S,p)$ $\quad dH = Vdp + TdS$

$A = A(V,T)$ $\quad dA = -pdV - SdT$

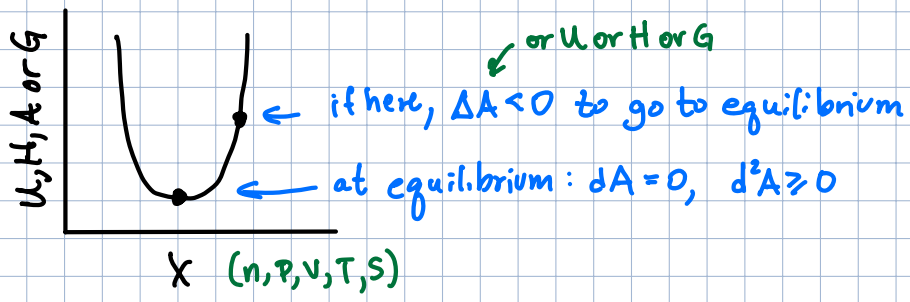
$G = G(p,T)$ $\quad dG = -SdT + Vdp$

D. Extrema Principles beyond Entropy

We learned previously that a system at equilibrium corresponds to an entropy maximum.



What about our potentials: U, H, A & G? Equilibrium corresponds to an energy minimum. This is also an extremum, but the concavity is flipped.



A is minimized at const n,V,T U is minimized at const n,V,S

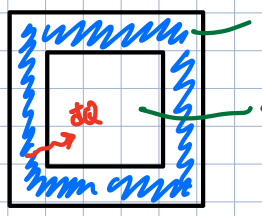
G is minimized at const n,p,T H is minimized at const n,P,S

(Don't usually minimize U or H.)

"Variational principle" of thermodynamics: the system seeks to maximize entropy (at constant n,V,U). Equivalently, the system seeks to minimize the free energy (usually A or G).

(Not to be confused with variational calculus.)

Proof for Helmholtz energy



system at fixed n, V, T

$dS_{univ} = dS_{sys} + dS_{bath} \geq 0$

$dS_{bath} = -\frac{đQ}{T}$

$dU_{sys} = đQ + \cancel{đW}$ (V fixed)

$dS_{bath} = -\frac{1}{T} dU_{sys}$

$A = U - TS$

$dA = dU - TdS - SdT$

$dA = dU - TdS$ const T

$-\frac{dA}{T} = -\frac{dU}{T} + dS$

$dS_{univ} = dS_{sys} - \frac{1}{T} dU_{sys} \geq 0$

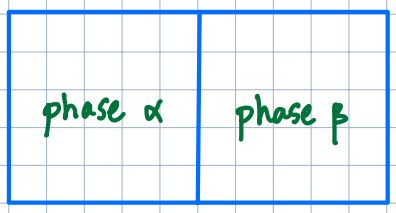
$= -\frac{dA_{sys}}{T} \geq 0$

$\boxed{dA_{sys} \leq 0}$

Analogous results hold for G. We need bath and piston (G is at const T & P).

D. Phase Equilibrium

we are prepared to analyze unary (pure material) phase behavior. Materials that are phase separated have an interface between two different macroscale regions separated in space.



α - β equilibrium

vapor-liquid, solid-liquid,

solid-solid, solid-vapor

What are the equilibrium criteria for the two phases?

$$dU_{tot} = dU_\alpha + dU_\beta \qquad dU = T\,dS - p\,dV + \mu\,dn$$

$$= T_\alpha dS_\alpha + T_\alpha dS_\beta - p_\alpha dV_\alpha - p_\beta dV_\beta + \mu_\alpha dn_\alpha + \mu_\beta dn_\beta$$

The system is isolated at at equilibrium, so

$$dU_{tot} = 0$$

$$dS_\alpha = -dS_\beta \,, \quad dV_\alpha = -dV_\beta \,, \quad dn_\alpha = -dn_\beta$$

Updating our above expression gives

$$0 = (T_\alpha - T_\beta)\,dS_\alpha - (p_\alpha - p_\beta)\,dV_\alpha + (\mu_\alpha - \mu_\beta)\,dn_\alpha$$

The only way this is zero for arbitrary dS, dV, and dn is for

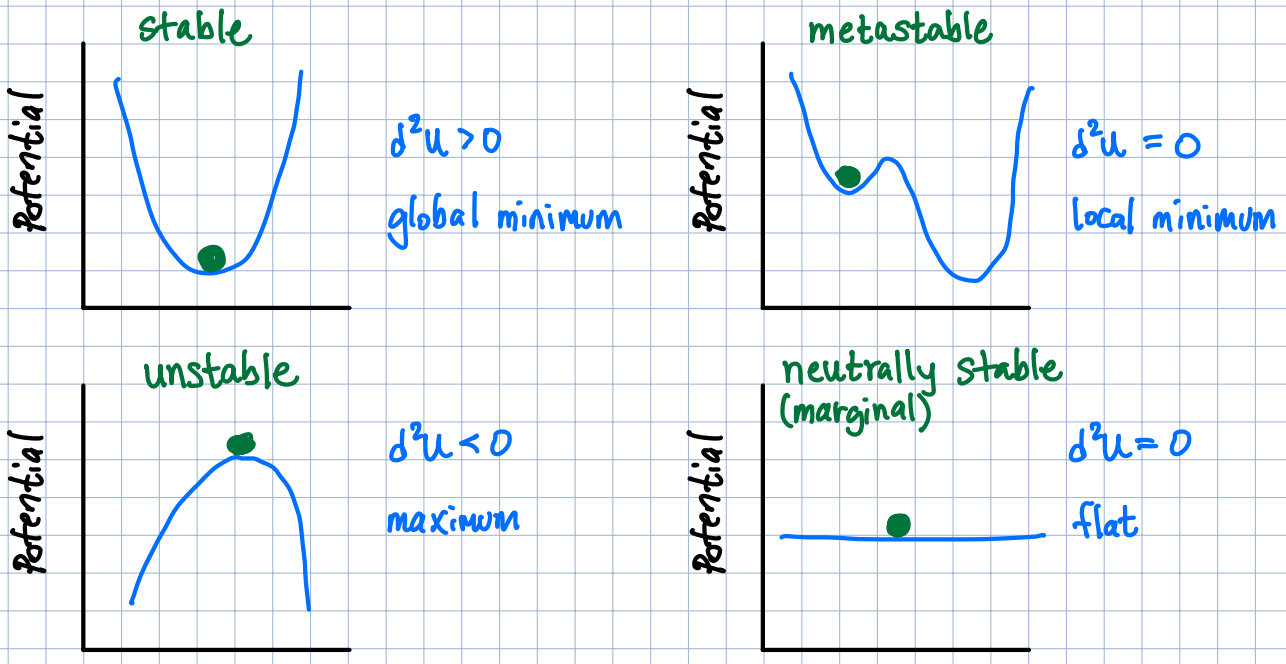
$$\boxed{T_\alpha = T_\beta \qquad p_\alpha = p_\beta \qquad \mu_\alpha = \mu_\beta}$$

Comments:

- Only 2 of 3 are needed because of Gibbs-Duhem
- For mixtures, we need a chemical potential for each component: $\mu_i^\alpha = \mu_i^\beta$
- This is all of the foundation we need for phase equilibrium calculations. The rest is details. They can be very useful, but in stat thermo, we usually have direct access to free energies (e.g., A), so we don't need them.

E. Thermodynamic Stability

We know that entropy is maximized at equilibrium and that free energy is minimized. But what happens if we are purturbed slightly? Do we return to equilibrium or do we "run away"? In other words, are we in a stable state?



How do we mathematically assess thermodynamic stability? Lets look at the Taylor Series for a small perturbation from equilibrium for U.

$$U(S,V,n) = U(z_i)$$

$$U - U^{eq} = \delta U + \frac{1}{2!}\delta^2 U + \frac{1}{3!}\delta^3 U + \dots$$

$$\delta U = \sum_i \frac{\partial U}{\partial z_i}(z_i - z_i^{eq})$$

$$\delta^2 U = \sum_i \sum_j \frac{\partial^2 U}{\partial z_i \partial z_j}(z_i - z_i^{eq})(z_j - z_j^{eq})$$

matrix notation:

$\delta U = \underline{J} \cdot \delta \underline{z}$ (Jacobian)

$\delta^2 U = \delta \underline{z} \cdot \underline{\underline{H}} \cdot \delta \underline{z}$ (Hessian)

$\underline{\underline{H}}$ ↖ symmetric

$$\Delta U = \underline{J} \cdot \delta \underline{z} + \frac{1}{2}\delta \underline{z} \cdot \underline{\underline{H}} \cdot \delta \underline{z} + \dots$$

In order to be at a minimum at U^{eq}, we need

$\delta U = 0$ equilibrium condition

$\delta^2 U \geq 0$ Stability condition

The stability condition is equivalent to the statement that $\underline{\underline{H}}$ must be positive semidefinite. This means all eigenvalues are real and ≥ 0. Another test is if all of the leading principal minors of $\underline{\underline{H}}$ are ≥ 0 (Sylvester's criterion).

For strict stability (not marginal) the Hessian matrix must be positive definite (>0) and not equal to zero.

Example: $u(s,v)$

$$\underline{\underline{H}} = \begin{bmatrix} \frac{\partial^2 u}{\partial s^2} & \frac{\partial^2 u}{\partial s \partial v} \\ \frac{\partial^2 u}{\partial s \partial v} & \frac{\partial^2 u}{\partial v^2} \end{bmatrix} = \begin{bmatrix} u_{ss} & u_{sv} \\ u_{sv} & u_{vv} \end{bmatrix}$$

Stability criteria:

$|u_{ss}| \geq 0$

$u_{ss} u_{vv} - u_{sv}^2 \geq 0$

F. Appendix: Matrix minors

A minor is the determinant of any square submatrix obtained by deleting rows and columns.

Example: 3x3 symmetric matrix

$$\underline{\underline{H}} = \begin{bmatrix} a & b & c \\ b & d & e \\ c & e & f \end{bmatrix}$$

order 1 minors: $|a|, |b|, \ldots$

order 2 minors: $\begin{vmatrix} a & b \\ b & d \end{vmatrix}, \begin{vmatrix} b & c \\ d & e \end{vmatrix}, \ldots$

order 3 minors: $\det(H)$

A principal minor is the determinant of a submatrix obtained by deleting the same rows and columns.

Example: 3x3 symmetric matrix

$$H = \begin{bmatrix} a & b & c \\ b & d & e \\ c & e & f \end{bmatrix}$$

order 1 principal minors: $|a|, |d|, |f|$

order 2 " " : $\begin{vmatrix} a & b \\ b & d \end{vmatrix}, \begin{vmatrix} a & c \\ c & f \end{vmatrix}, \begin{vmatrix} d & e \\ e & f \end{vmatrix}$

order 3 " minor: $\det(H)$

A leading principal minor is only the upper-left principal minors of each order.

Example: 3x3 symmetric matrix

$$H = \begin{bmatrix} a & b & c \\ b & d & e \\ c & e & f \end{bmatrix}$$

order 1 LPM: $|a|$

order 2 LPM: $\begin{vmatrix} a & b \\ b & d \end{vmatrix}$

order 3 LPM: $\det(H)$