Thermodynamics of materials

08. Equilibrium and Stability II

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Thermodynamic Stability Criteria

- Thermodynamic equilibrium states can be stable, metastable, or unstable.
- Unstable equilibrium system: Thermodynamic condition will spontaneously evolve with small perturbations.
- Stable equilibrium system: With any perturbations, a thermodynamic conditions will spontaneously fall back to the equilibrium state.
- Several approaches that we can employ to derive the same set of stability criteria.

Thermodynamic Stability Criteria

- Entropic representation: Entropy is maximized for and isolated system maintaining the same total internal energy, volume and amount of substance.
- Energy representation: Internal energy at constant entropy, pressure, number of moles will be minimized at the equilibrium.
- Entropy production: An equilibrium state is subjected to a perturbation, the entropy produced arising from perturbing a stable equilibrium state is negative.

Thermodynamic Stability Criteria

- For example, small perturbation of the system can be related to the amount of amount produced dS^{ir}

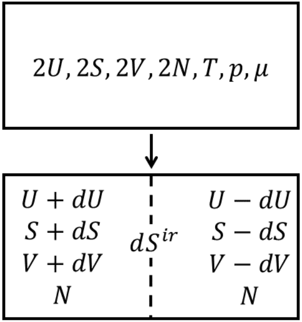
$$dS^{\text{ir}} = \frac{Dd\xi}{T}$$

- When $dN = 0$,

$$\begin{aligned} dS^{\text{ir}} &= \frac{Dd\xi}{T} \\ &= dS \text{ when } dU = dV = 0 \\ &= \frac{-dU}{T} \text{ when } dS = dV = 0 \\ &= \frac{-dH}{T} \text{ when } dS = dp = 0 \\ &= \frac{-dF}{T} \text{ when } dT = dV = 0 \end{aligned}$$

Thermodynamic Stability Criteria

- Let's consider a simple stable equilibrium system with total value of $2U$, $2S$, $2V$ and $2N$ moles hypothetically separated into two identical systems with small perturbations $\pm dU$, $\pm dS$ and $\pm dV$.



Thermodynamic Stability Criteria

- Following Kopndepudi and Prigogin, the entropy produced ΔS^{ir} from small perturbation dS, dT, dV and dp to a stable equilibrium state can be obtained by

$$\Delta S^{\text{ir}} = \delta^2 S = -\frac{1}{T}(dSdT - dVdp) < 0$$

- When the original state is an equilibrium state, all the thermodynamic variables are uniform, and

$$\delta S = 0$$

- The increase in the internal energy due to the perturbations in entropy dS and volume dV in the initially equilibrium state with energy U, and volume V while maintaining constant overall S and V.

$$\Delta U = -T\Delta S^{\text{ir}} = dSdT - dVdp > 0$$

Thermodynamic Stability Criteria

- The perturbations in temperature and pressure can be represented in terms of perturbations in entropy and volume

$$dT = \left(\frac{\partial T}{\partial S}\right)_V dS + \left(\frac{\partial T}{\partial V}\right)_S dV$$

$$dp = \left(\frac{\partial p}{\partial S}\right)_V dS + \left(\frac{\partial p}{\partial V}\right)_S dV$$

- Then we have

$$\begin{aligned}\Delta U = dS &\left[\left(\frac{\partial T}{\partial S}\right)_V dS + \left(\frac{\partial T}{\partial V}\right)_S dV\right] \\ - dV &\left[\left(\frac{\partial p}{\partial S}\right)_V dS + \left(\frac{\partial p}{\partial V}\right)_S dV\right] > 0\end{aligned}$$

Thermodynamic Stability Criteria

- Proceed to

$$\Delta U = \left(\frac{\partial T}{\partial S}\right)_V (dS)^2 + \left(\frac{\partial T}{\partial V}\right)_S dS dV - \left(\frac{\partial p}{\partial S}\right)_V dV dS + \left(\frac{\partial p}{\partial V}\right)_S (dV)^2 > 0$$

- When $dV = 0$,

$$\Delta U = \left(\frac{\partial T}{\partial S}\right)_V (dS)^2 = \left(\frac{\partial^2 U}{\partial S^2}\right)_V (dS)^2 > 0$$

Since $(dS)^2 > 0$,

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V > 0$$

is the condition for stability.

Thermodynamic Stability Criteria

- When $dS = 0$,

$$\Delta U = \left(\frac{\partial p}{\partial V}\right)_S (dV)^2 = \left(\frac{\partial^2 U}{\partial V^2}\right)_S (dV)^2 > 0$$

Since $(dV)^2 > 0$,

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_S > 0$$

is the condition for stability.

Thermodynamic Stability Criteria

- From $dU = TdS - pdV$, we have

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \qquad -p = \left(\frac{\partial U}{\partial V}\right)_S$$

we have

$$\Delta U = \left(\frac{\partial^2 U}{\partial S^2}\right)_V (dS)^2 + 2\left(\frac{\partial^2 U}{\partial S \partial V}\right) dSdV + \left(\frac{\partial^2 U}{\partial V^2}\right)_S (dV)^2 > 0$$

can be rearranged to

$$\Delta U = \left(\frac{\partial^2 U}{\partial S^2}\right)_V \left[dS + \frac{\frac{\partial^2 U}{\partial S \partial V}}{\left(\frac{\partial^2 U}{\partial S^2}\right)_V} dV \right]^2 + \left[\left(\frac{\partial^2 U}{\partial V^2}\right)_S - \frac{\left(\frac{\partial^2 U}{\partial S \partial V}\right)^2}{\left(\frac{\partial^2 U}{\partial S^2}\right)_V} \right] (dV)^2 > 0$$

Thermodynamic Stability Criteria

- Since

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V > 0$$

for a stable equilibrium state,

$$\left[\left(\frac{\partial^2 U}{\partial V^2}\right)_S - \frac{\left(\frac{\partial^2 U}{\partial S \partial V}\right)^2}{\left(\frac{\partial^2 U}{\partial S^2}\right)_V}\right] = \left[\frac{\left(\frac{\partial^2 U}{\partial S^2}\right)_V \left(\frac{\partial^2 U}{\partial V^2}\right)_S - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2}{\left(\frac{\partial^2 U}{\partial S^2}\right)_V}\right] > 0$$

therefore,

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V \left(\frac{\partial^2 U}{\partial V^2}\right)_S - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2 > 0$$

is the condition for a stable equilibrium.

Thermodynamic Stability Criteria

- The first criterion is

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_{V,N} = \frac{T}{C_V} > 0 \rightarrow C_V > 0$$

- The second criterion is

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_S = -\left(\frac{\partial p}{\partial V}\right)_S = \frac{1}{V\beta_S} > 0 \rightarrow \beta_S > 0$$

- The third criterion is

$$\left[\left(\frac{\partial^2 U}{\partial V^2}\right)_S - \frac{\left(\frac{\partial^2 U}{\partial S \partial V}\right)^2}{\left(\frac{\partial^2 U}{\partial S^2}\right)_V}\right] = \left(\frac{\partial^2 F}{\partial V^2}\right)_T > 0$$

Thermodynamic Stability Criteria

- Similarly, under constant overall T and p, for small perturbations,

$$\Delta G = -T\Delta S^{\text{ir}} = dSdT - dV\,dp > 0$$

- We express the perturbations in entropy and volume in terms of perturbations in temperature and pressure,

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$$

proceed to

$$\Delta G = \left(\frac{\partial S}{\partial T}\right)_p (dT)^2 + \left(\frac{\partial S}{\partial p}\right)_T dTdp - \left(\frac{\partial V}{\partial T}\right)_p dTdp - \left(\frac{\partial V}{\partial p}\right)_T (dp)^2 > 0$$

Thermodynamic Stability Criteria

- In other words,

$$\Delta G = -\left(\frac{\partial^2 G}{\partial T^2}\right)_p (dT)^2 - \frac{\partial^2 G}{\partial p \partial T} dT dp - \frac{\partial^2 G}{\partial p \partial T} dT dp - \left(\frac{\partial^2 G}{\partial p^2}\right)_T (dp)^2 > 0$$

- For a thermodynamic stable state,

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_p < 0 \qquad \left(\frac{\partial^2 G}{\partial p^2}\right)_T < 0$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_p \left(\frac{\partial^2 G}{\partial p^2}\right)_T - \left(\frac{\partial^2 G}{\partial T \partial p}\right)^2 > 0$$

- It implies that

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_p = -\frac{C_p}{T} < 0 \to C_p > 0$$

$$\left(\frac{\partial^2 G}{\partial p^2}\right)_T = -V\beta_T < 0 \to \beta_T > 0$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_p \left(\frac{\partial^2 G}{\partial p^2}\right)_T - \left(\frac{\partial^2 G}{\partial T \partial p}\right)^2$$
$$= \frac{C_p V \beta_T}{T} - V^2\alpha^2 = \frac{V C_p \beta_S}{T} = \frac{V C_V \beta_T}{T} > 0$$

Thermodynamic Stability Criteria

- We can conclude that for a system at stable(metastable) equilibrium, the thermodynamic energy functions are convex functions of their extensive variables and concave functions of their intensive variables,

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V > 0 \qquad \left(\frac{\partial^2 U}{\partial V^2}\right)_S > 0$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_p < 0 \qquad \left(\frac{\partial^2 G}{\partial p^2}\right)_T < 0$$