Thermodynamics of materials
07. Equilibrium and Stability I

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Maximum Entropy Principle

- A stable equilibrium state is at the global minimum in the potential energy function with respect to an extensive thermodynamic variable of a system and is stable against any arbitrary fluctuations.

- We first consider the condition of equilibrium for an isolated system with an initial amount of entropy S and chemical matter N enclosed in a volume V with grid walls that are impermeable to any chemical species and non-conducting to heat or entropy transfer.

$$dS^{\mathsf{e}} = dV^{\mathsf{e}} = dN^{\mathsf{e}} = dU = 0$$

- During the evolution of the isolated system from an initially non-equilibrium state to the equilibrium state,

$$dS = dS^{\mathsf{e}} + dS^{\mathsf{ir}} = dS^{\mathsf{ir}} = \frac{D}{T}d\xi > 0$$

Maximum Entropy Principle

- After the system reaches equilibrium, there is no more entropy creation

$$dS = dS^{\text{ir}} = \frac{D}{T} d\xi = 0$$

i.e., the entropy is maximized after the system reaches equilibrium.

- For an isolated system at thermodynamic equilibrium, its entropy S is maximized at constant energy $dU = 0$ and constant volume $dV = 0$ and substance $dN = 0$.

$$\left(dS\right)_{U,V,N} = 0 \qquad \left(\delta^2 S\right)_{U,V,N} < 0$$

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Minimum Internal Energy Principle

- The above maximum entropy principle formulated based on an isolated system can be employed to derive minimum internal energy principle is; for isolated system;

$$dV = dV^{\mathsf{e}} = 0 \qquad dN = dN^{\mathsf{e}} = 0$$

- According to the first law,

$$dU = TdS^{\mathsf{e}}$$

the sum of entropy is entropy transferred from the surrounding, dS^{e}, and entropy produced amount dS^{ir},

$$dS = dS^{\mathsf{e}} + dS^{\mathsf{ir}}$$

therefore,

$$dU = TdS^{\mathsf{e}} = TdS - TdS^{\mathsf{ir}}$$

Minimum Internal Energy Principle

- Under constant entropy, $dS = 0$,

$$dU = -TdS^{\text{ir}} = -Dd\xi \leq 0$$

- For a system at thermodynamic equilibrium, its entropy S is maximized at constant entropy $dS = 0$ and constant volume $dV = 0$ and substance $dN = 0$.

$$\left(dU\right)_{S,V,N} = 0 \qquad \left(\delta^2 U\right)_{S,V,N} > 0$$

enthalpy must keep decreasing during an irreversible process if the pressure and entropy of the system are kept constant. At equilibrium, the internal energy has the minimum value.

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Minimum Enthalpy Principle

- After the system establishes thermodynamic equilibrium,

$$dU = TdS^{\text{e}} - pdV = TdS - TdS^{\text{ir}} - pdV$$

  proceed to

$$dU + pdV = TdS^{\text{e}} = TdS - TdS^{\text{ir}}$$

- Under constant entropy and pressure,

$$dU + pdV = d(U + pV) = dH = -TdS^{\text{ir}} = -Dd\xi \leq 0$$

- After the system establishes thermodynamic equilibrium, enthalpy H reaches minimum. At equilibrium,

$$\left(dH\right)_{S,p,N} = 0 \qquad \left(\delta^2 H\right)_{S,p,N} > 0$$

- Therefore, at equilibrium, the enthalpy H of a system is minimized at constant entropy S, constant pressure p, and constant amount of substance N, and any perturbation to the equilibrium state while keeping the S, p and N of the system constant will increase the enthalpy H of the system.

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Minimum Helmholtz Free Energy Principle

- The combined first and second law for a closed system at constant volume,

$$dU = TdS^{\mathsf{e}} = T\left(dS - dS^{\mathsf{ir}}\right) = TdS - TdS^{\mathsf{ir}}$$

proceed to

$$dU - TdS = -TdS^{\mathsf{ir}}$$

- If we assume that the temperature of the system is constant, we get

$$dU - TdS = d(U - TS) = dF = -TdS^{\mathsf{ir}} = -Dd\xi \leq 0$$

- The Helmholtz free energy keep decreasing during and irreversible process if the temperature and volume remain constant.

Minimum Helmholtz Free Energy Principle

- After the system establishes thermodynamic equilibrium, the Helmholtz free energy reaches minimum. At equilibrium,

$$\left(dF\right)_{T,V,N} = 0 \qquad \left(\delta^2 F\right)_{T,V,N} > 0$$

- Therefore, at equilibrium, the Helmholtz free energy F of a system is minimized at constant T, V and N.

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Minimum Gibbs Free Energy Principle

- The combined first and second law of thermodynamics for a closed system is

$$dU = T\big(dS - dS^{\text{ir}}\big) - pdV = TdS - TdS^{\text{ir}} - pdV$$

proceed to

$$dU - TdS + pdV = -TdS^{\text{ir}}$$

- Assume that T, p constant,

$$dU - TdS + pdV = d(U - TS - pV) = dG = -TdS^{\text{ir}} = -Dd\xi \leq 0$$

- At equilibrium, the Gibbs free energy reaches minimum.

$$\big(dG\big)_{T,p,N} = 0 \qquad \big(\delta^2 G\big)_{T,p,N} > 0$$

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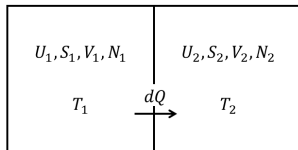
Equilibrium condition for temperature T

- Consider an isolated system containing two hypothetical subsystems separated by a wall which is fixed, allowing entropy or heat transfer.
- Since the energy and entropy is conserved

$$dU_{\text{tot}} = dU_1 + dU_2 = 0$$

$$dS_{\text{tot}} = dS_1 + dS_2 = 0$$

- Since the wall is fixed,

$$dV_1 = dV_2 = 0 \qquad dN_1 = dN_2 = 0$$

- Since we have

$$dU_1 = -dQ \qquad dU_2 = dQ$$

then

$$dS_{\text{tot}} = dS_1 + dS_2 = \frac{dU_1}{T_1} + \frac{dU_2}{T_2} = \left(\frac{1}{T_2} - \frac{1}{T_1} \right) dQ = 0$$

- Since dQ is an arbitrary value, to conserve the entropy,

$$T_1 = T_2$$

i.e., the temperature of an isolated system at thermodynamic equilibrium is uniform throughout the system.
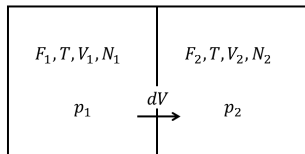
- Consider a composite system at $dT = 0$, $dV = 0$ and $dN = dN_1 = dN_2 = 0$, the differential form for F is

$$dF = -SdT - pdV + \mu dN$$

- The total change of Helmholtz free energy is

$$dF_{\text{tot}} = dF_1 + dF_2 = -p_1 dV_1 - p_2 dV_2$$

- Since

$$dV = dV_1 + dV_2 = 0$$

we have

$$dF_{\text{tot}} = \left(p_2 - p_1\right)dV_1 = 0$$

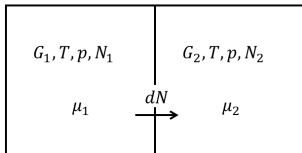- Since the change dV_1 is arbitrary, the pressure has to be uniform at equilibrium,

$$p_1 = p_2$$

- The differential form for the Gibbs free energy is

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

- Consider two subsystems with chemical potentials μ_1 and μ_2 and the same temperature,

$$dG = \mu dN$$

- If the wall separating the two subsystems is allowed mass transfer, then

$$dG_{\text{tot}} = dG_1 + dG_2 = -\mu_1 dN + \mu_2 dN$$

- At equilibrium,

$$dG_{\text{tot}} = 0 = \left(\mu_2 - \mu_1\right)dN \rightarrow \mu_2 = \mu_1 = \mu$$

it requires that the chemical potential be uniform in the system.

General Equilibrium Conditions for Potentials

- When

$$dT = dp = d\mu = 0$$

  we assume that the equilibrium is achieved.

- If any potentials is not uniform, gradient in any of the potentials, the system is not equilibrium.

- A thermal potential or temperature gradient leads to thermal transport or heat transfer or entropy transfer.

- A pressure gradient leads to volume flow.

- Chemical potential gradients of chemical species lead to mass transfer.

- If there are potential gradients, kinetic processes are expected to take place. For example, there can be phase transitions or chemical reactions if they reduce the chemical potential. All reactions produce entropy.

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- A potential is the amount of specific form of energy per unit amount of the corresponding matter, the energy intensity.
- Field: A fiend is defined by the negative gradient of a potential.

$$\vec{E} = -\nabla \phi$$

- Driving force: negative difference between a final state and initial state

$$D = -\Delta\mu = \mu^{\text{initial}} - \mu^{\text{final}}$$