Quick Review of Thermodynamics

Plastic Deformation in Crystalline Materials

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Definitions

- **System**: A collection of continuous matter
- **Isolated system**: A system which does not exchange neither energy nor matter with its surrounding

- **Closed system**: A system which does not exchange matter with its surrounding

- **State property**: A property that depends only on the state of the system and not on how it reached that state (e.g.: volume, pressure, temperature, energy, and entropy)

Intensive and Extensive Properties

Intensive properties: properties that do **not** depend on the amount of material in a system
such as temperature, pressure, chemical potential , specific energy, and specific entropy

Extensive properties: properties that depend on the amount of material in a system
such as volume, energy, entropy, and heat capacity

Extensive property	Symbol	SI units	Intensive property**	Symbol	SI units
Volume	V	m^3 or l*	Specific volume***	v	m^3/kg or l*/kg
Internal energy	U	J	Specific internal energy	u	J/kg
Entropy	S	J/K	Specific entropy	s	J/(kg·K)
Enthalpy	H	J	Specific enthalpy	h	J/kg
Gibbs free energy	G	J	Specific Gibbs free energy	g	J/kg
Heat capacity at constant volume	C_V	J/K	Specific heat capacity at constant volume	c_v	J/(kg·K)
Heat capacity at constant pressure	C_P	J/K	Specific heat capacity at constant pressure	c_p	J/(kg·K)

Corresponding extensive and intensive thermodynamic properties

* l = liter, J = joule

Internal Energy *U*

Internal energy arises from total kinetic and potential energies of the atoms within the system.

Kinetic energy can arise from atomic vibration in solids or liquids and from translational and rotational energies of the atoms and molecules within a liquid or gas.

Potential energy arises from the interactions and bonds between atoms within the system.

The First Law of Thermodynamics

Heat is a form of energy

The change in the internal energy ΔU of a system is equal to the heat absorbed by the system ΔQ_{input} and the work done on the system ΔW_{input} by surface traction and body force

$$\Delta U = \Delta Q_{input} + \Delta W_{input}$$

For our purposes, we can treat them as infinitesimally small energy transfers and we can use their specific values (per unit mass):

First Law of Thermodynamics

$$du = \delta q + \delta w$$

- Note that for example $U = \int_V \rho u \, dV$
- δ represents inexact differential; that is there are no functions as $q(P, V)$ and $w(P, V)$ that depend only on the state of the system.

Entropy

- Entropy is understood as a measure of randomness or disorder.

- In statistical mechanics, the Boltzmann principle:

$$\text{entropy of a state} = k_B \ln W$$

  where W is the probability of the state in its mathematical sense; that is, the number of microstates consistent with the given macrostate. k_B is the Boltzmann constant ($k_B = 1.38 \times 10^{-23}$ J/K).

- The units of entropy are [energy]/[temperature].

- Entropy is an extensive property.

- Entropy is usually denoted by S, and its specific by s.

- Entropy of a perfect crystal at 0 K is zero.

Thermal Entropy and Configurational Entropy

■ Thermal (or Vibrational) Entropy S_{th}: associated with atomic vibrations

W = the number of ways in which the thermal energy can be divided among the atoms.

S_{th} increases with T

■ Configuration Entropy S_{config}: In solutions

W = the number of distinguishable ways in which atoms can be arranged.

Entropy in Classical Thermodynamics

In any reversible process, the specific heat input δq and the specific entropy are related by

$$ds = \frac{\delta q_{\text{input}}}{T} \quad (\textit{reversible process})$$

where s is the specific entropy $S = \int_V \rho s dV$

- Although δQ is an imperfect differential, ds is a perfect differential.

- i.e. entropy is a state variable.

Example

- For an ideal gas:

$$Pv = RT$$

  where $v = 1/\rho$ is the specific volume and R the gas constant ($R = k_B N_A$)

- Assume $u = u(T)$

- Note $du = \delta q - Pdv$

- At constant volume process: $dv = 0$, therefire

$$du = \delta q = c_V dT$$

$c_V = (\partial Q/\partial T)_V$ = specific heat capacity.
Because $u = u(T) \Rightarrow c_V = c_V(T)$

$$\delta q = c_V(T)dT + \frac{RT}{v}dv$$

$$\Rightarrow ds = \frac{\delta q}{T} = c_V(T)\frac{dT}{T} + \frac{R}{v}dv$$

$$\Rightarrow s - s_0 = \int_{P_0,v_0}^{P,v} \frac{\delta q}{T} = \int_{T_0}^{T} c_V(T)\frac{dT}{T} + R\ln\frac{v}{v_0}$$

Gibbs Relation

In a reversible relation:

$$\delta q = Tds$$

First thermodynamics law:

$$du = \delta q + \delta w = \delta q - Pdv$$

Therefore:

$$du = Tds - Pdv$$

For a homogeneous system in equilibrium:

$$dU = TdS - PdV$$

Note that:

- S which is an extensive variable is energy conjugate to the intensive variable T
- P is an extensive variable and is energy conjugate to the intensive variable V

Entropy change in an irreversible process:

$$\Delta s \equiv s_f - s_i = \int_i^f \left(\frac{\delta q}{T}\right)_{\text{reversible}}$$

and

$$\oint ds = \oint \left(\frac{\delta q}{T}\right)_{\text{reversible}} = 0$$

The above relations may be be useful for inelastic deformation process.
In an irreversible cyclic process returning to the same state:

$$\oint ds = 0 \text{ but } \oint \left(\frac{\delta q}{T}\right)_{\text{irrevers}} \neq 0$$

In fact:

$$\oint \left(\frac{\delta q}{T}\right)_{\text{irrevers}} < 0$$

■ $\frac{\delta q_{\text{input}}}{T}$ = entropy input from outside carried by the heat

■ In an irreversible cycle the net entropy input is negative ⇒ entropy has been created inside the system by dissipative internal processes

■ Because the internal energy creation is always positive in an irreversible process:

$$\Delta s > \int_i^f \left(\frac{\delta q}{T}\right)_{\text{irrevers}}$$

■ In an isolated system (no heat transfer):

▶ reversible processes: $\Delta s = 0$

▶ irreversible processes: $\Delta s > 0$

■ Real processes are irreversible but energy dissipation might be negligible

Second Law of Thermodynamics

2nd Law of Thermodynamics

It postulates :

❶ existence of entropy as a state function

❷ entropy satisfies

$$\Delta s = s_f - s_i = \int_i^f \left(\frac{\delta q}{T} \right) \quad (\textit{for reversible processes})$$

or

$$\Delta s = s_f - s_i > \int_i^f \left(\frac{\delta q}{T} \right) \quad (\textit{for irreversible processes})$$

Clausius-Duhem Inequality

$$\text{Entropy Input Rate} = \int_V \frac{\rho r}{T} dV + \int_S -\frac{\vec{J}_Q}{T} \cdot \vec{n} dS$$

- r = internal heat supply per unit mass and unit time (possibly from a radiation field)
- $\vec{J}_Q$ = outward heat flux
- If the system is open, we should add:

$$-\int_S \rho s \vec{v} \cdot \vec{n} dS$$

carried by the mass flux

Clausius-Duhem Inequality -II

$$\frac{dS}{dt} = \frac{d}{dt}\int_V s\rho dV \geq \int_V \frac{r}{T}\rho dV - \int_S \frac{\vec{J}_Q}{T}\cdot\vec{n}dS$$

Clausius-Duhem Inequality

$$\frac{ds}{dt} \geq \frac{r}{T} - \frac{1}{\rho}\text{div}\frac{\vec{J}_Q}{T}$$

or

$$\gamma \equiv \frac{ds}{dt} - \frac{r}{T} - \frac{1}{\rho T}\text{div}\vec{J}_Q - \frac{\vec{J}_Q}{\rho T^2}\cdot\nabla T \geq 0$$

γ : internal entropy production rate per unit mass

Equation of State

Difference between 2nd law of thermodynamics and Clausius-Duhem inequality:
2nd law postulates that entropy is a state variable
So we can postulate: $s = s(T, \boldsymbol{\xi})$ where $\boldsymbol{\xi}$ is either all the state variables or limited number of state variables, n.
Similarly:

$$u = u(s, \boldsymbol{\xi}, \boldsymbol{X})$$

where $\boldsymbol{X}$ is the position vector in the reference configuration (usually is dropped)

Thermodynamics temperature T and thermodynamics tensions ψ_i are defined by:

$$T \equiv \left(\frac{\partial u}{\partial s}\right), \quad \psi_i \equiv \left(\frac{\partial u}{\partial \xi_i}\right), \quad i = 1, 2, \cdots, n$$

Therefore we can write:

$$du = Tds + \psi_i d\xi_i, \quad (\text{summation over } i = 1, \cdots, n)$$

Equation of State - II

- For example for a fluid:
  $\xi = v$ and $\psi = -p$
- Note that in this case p is not necessarily equal to the mean pressure $\bar{p} = \sigma_{kk}/3$
- In solids ξ_i = elastic strains. With some caution: ψ_i is stress

Thermodynamics Potentials

Potentials

Helmholtz free energy (denoted also by A or ϕ or ψ):

$$F = U - TS$$

or

$$f = u - Ts$$

Enthalpy:

$$H = U + PV$$

or more generally

$$h = u - \psi_i \xi_i$$

Gibbs free energy:

$$G = H - TS$$

or

$$g = h - sT = u - sT - \psi_i \xi_i$$

Equilibrium

$$F = U - TS \Rightarrow dF = dU - TdS - SdT$$

Let $dU = -PdV + TdS$, thus:

$$dF = -PdV + TdS - TdS - SdT \Rightarrow dF = -PdV - SdT$$

$$H = U + PV \Rightarrow dH = -PdV + TdS + PdV + VdP \Rightarrow dH = TdS + VdP$$

$$G = H - TS \Rightarrow dG = TdS + VdP - TdS - SdT \Rightarrow dG = VdP - SdT$$

Therefore we can say:
For a closed system, the system will be in stable equilibrium if:

- At constant P and T:

$$dG = 0$$

- At constant V and T:

$$dF = 0$$

Chemical Potential

- Up to now, we were considering closed systems with number of particles N = fixed. Now let's consider open systems with variable N

- If we add a small quantity of matter, dN, to a large amount of a phase at constant pressure and temperature, the size of the system will increase by dN and the energy by dG. If dN is small enough, we can write

$$dG = \mu dN$$

  The proportionality constant μ is called *partial molar free energy* or *chemical potential*.

- If there are more than one species of atoms, the chemical potential of the $i-$th component is given by:

$$\mu_i \equiv \left(\frac{\partial G}{\partial N_i} \right)_{P,T,N_{j(j\neq i)}}$$

also $\mu_i = \left(\dfrac{\partial G}{\partial N_i} \right)_{P,T,n_{j(j\neq i)}} = \left(\dfrac{\partial F}{\partial N_i} \right)_{V,T,n_{j(j\neq i)}} = \left(\dfrac{\partial H}{\partial n_i} \right)_{S,P,N_{j(j\neq i)}} = \left(\dfrac{\partial U}{\partial n_i} \right)_{S,V,N_{j(j\neq i)}}$

References and Further Reading:

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