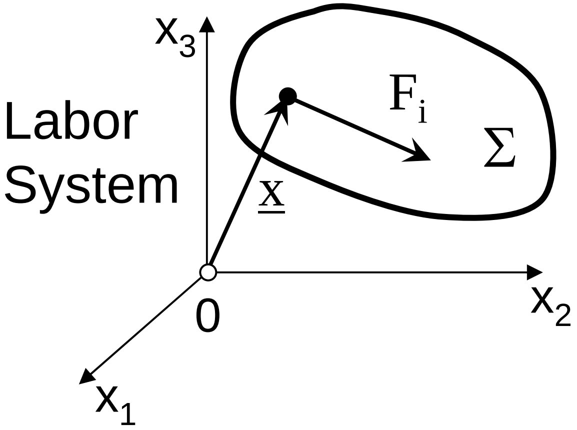
Classical Theory (3): Thermostatics of Continuous Systems with External Forces



Σ: Equilibrium State?

Isolation, Inhomogeneity

External Forces $F_{i\alpha} = -\partial_\alpha \varphi_i(\underline{x})$

Components: $i = 1 \ldots N$

$$S = \int_V S_V(\underline{x})\, dV \to \text{Max.}$$

$$U + W_p = \int_V \left[U_V(\underline{x}) + \sum_{i=1}^{N} \rho_i(\underline{x})\, \varphi_i(\underline{x}) \right] dV = \text{const}$$

$$m_i = \int_V \rho_i(\underline{x})\, dV = \text{const}_i \;,\; i = 1 \ldots N$$

Equilibrium Conditions:

$$T(\underline{x}) = \text{const}$$

$$\partial_\alpha p(\underline{x}) = \sum_i^N \rho_i(\underline{x})\, F_{i\alpha}$$

$$\mu_i(\underline{x}) + \varphi_i(\underline{x}) = \text{const}_i \;,\; i = 1 \ldots N$$

Boundary Conditions

Generalizations: E-M-Fields
Chem. Reactions

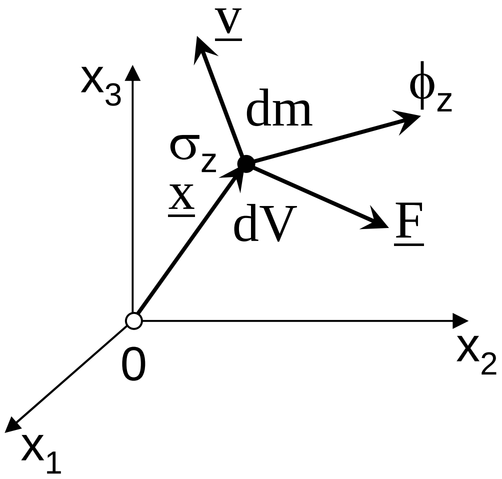
Ref.: J.U. Keller, TIP, Part 1
Thermostatics, W. de Gruyter,
Berlin - New York, 1977.

Thermodynamics of Processes (2)

Continuous System

Fluid, $N \geq 1$ Components

External Forces



Extensive Quantity (Z)

$$Z(t) = \int_V z_V(\underline{x},t)\,dV(\underline{x})$$

$$= \int_m z_m(\underline{x},t)\,dm(\underline{x})$$

$$z_m(\underline{x},t) = \rho(\underline{x},t)\,z_V(\underline{x},t)$$

Balance Equation

$$\dot{Z} = \Phi + P$$

Local Formulation (Lab)

$$\underline{\partial_t z_V + \partial_\alpha \phi_{z\alpha} = \sigma_z}$$

Material Formulation

$$\underline{\rho\, d_t z_m + \partial_\alpha\left(\phi_{z\alpha} - \rho\, v_\alpha z_m\right) = \sigma_z}$$

$$d_t \equiv \frac{d}{dt} = \partial_t + v_\alpha \partial_\alpha \ , \quad \partial_t = \frac{\partial}{\partial t} \ , \quad \partial_\alpha = \frac{\partial}{\partial x_\alpha}$$

Balance Equations of Mass Densities

$\rho_i(\underline{x},t),\ i=1...N$	Partial density of component (i)
$\rho(\underline{x},t)=\sum\limits_i^N \rho_i(\underline{x},t)$	Total mass density
$w_i \quad = \rho_i/\rho$	Mass concentration (i)
$v_i(\underline{x},t)$	Partial velocity
$v \quad = \sum\limits_i w_i v_i$	Velocity of mass element $\Delta m(\underline{x},t)$
$\Gamma_i\ ,\ i\ =1...N$	Chemical production rate (i)
$\sum\limits_i^N \Gamma_i \ =0$	Mass conservation
$J_{i\alpha} \quad = \rho_i(v_{i\alpha}-v_\alpha)$	Diffusion flow (i)

$$Z:\quad z_V=\rho_i\quad ,\ z_m=w_i$$

$$\phi_z=\rho_i v_i\ ,\ \sigma_z=\Gamma_i$$

Local balance

$$\underline{\partial_t\rho_i+\partial_\alpha(\rho_i v_{i\alpha})=\Gamma_i}$$

Material balance

$$\underline{\rho\frac{d}{dt}w_i+\partial_\alpha J_{i\alpha}=\Gamma_i}$$

Balance Equation of Linear Momentum

$P_{\alpha\beta}\left(\underline{x},t\right)$ Stress Tensor
β-component of stress
at α-surface element

$F_i\left(\underline{x},t\right)$ External force acting on component (i)

$$Z: \; z_V = \rho v_\alpha \, , \; z_m = v_\alpha$$

Newton's equation of motion of mass (m)

$$\frac{d}{dt}\int_{V(t)} \rho v_\alpha dV = -\oint_{O(t)} P_{\alpha\beta} dO_\beta + \int_{V(t)} \sum_i^N \rho_i F_{i\alpha} dV$$

Material balance

$$\rho \frac{d}{dt} v_\alpha + \partial_\beta P_{\alpha\beta} = \sum_i^N \rho_i F_{i\alpha}$$

$$\alpha = 1,2,3$$

Local balance

$$\partial_t\left(\rho v_\alpha\right) + \partial_\beta\left(P_{\alpha\beta} + \rho v_\alpha v_\beta\right) = \sum_i^N \rho_i F_{i\alpha}$$

$$\alpha = 1,2,3$$

Internal stress

Convective flow of momentum

Balance Equation of Angular Momentum (AM)

$z_m = \varepsilon_{\alpha\beta\gamma} x_\beta v_\gamma + \sigma_\alpha$ $\alpha = 1,2,3$	Specific angular momentum (α) at $(\underline{x}, t)$
$\varepsilon_{\alpha\beta\gamma} = (1,-1,0)$	Antisymmetric unit-tensor
σ_α	Internal angular momentum (IAM) (Spin of atoms, molecules etc.)
$\Sigma_{\alpha\beta}$	Tensor of IAM-flux
Γ_α	Production density of IAM due to external forces

Momentum balance $(\alpha \to \gamma) / \varepsilon_{\alpha\beta\gamma} x_\beta$, IAM

$$\rho \frac{d}{dt}\left(\varepsilon_{\alpha\beta\gamma} x_\beta v_\gamma + \sigma_\alpha\right) + \partial_\delta \left(\varepsilon_{\alpha\beta\gamma} x_\beta P_{\gamma\delta} + \Sigma_{\alpha\delta}\right) =$$

$$= \varepsilon_{\alpha\beta\gamma} x_\beta \sum_i^N \rho_i F_{i\gamma} + \Gamma_\alpha \left(F_i\right) + \frac{1}{2} \varepsilon_{\alpha\beta\gamma} \left(P_{\beta\gamma} - P_{\gamma\beta}\right) \; (*)$$

Balance for IAM

$$(*) : \underline{x} \to \underline{x} + \underline{a} \;,\; \underline{a} = 0$$

$$\rho \frac{d}{dt} \sigma_\alpha + \partial_\delta \Sigma_{\alpha\delta} =$$

$$= \Gamma_\alpha \left(F_i\right) + \frac{1}{2} \varepsilon_{\alpha\beta\gamma} \left(P_{\beta\gamma} - P_{\gamma\beta}\right)$$

$$\underline{\sigma} = \text{const} : \quad P_{\beta\gamma} = P_{\gamma\beta}$$

Balance for external AM:

$$\rho \frac{d}{dt} \varepsilon_{\alpha\beta\gamma} x_\beta v_\gamma + \partial_\delta \varepsilon_{\alpha\beta\gamma} x_\beta P_{\gamma\delta} =$$

$$= \varepsilon_{\alpha\beta\gamma} x_\beta \sum_i^N \rho_i F_{i\gamma}$$

Balance Equation of Energy

$e = \frac{1}{2} v^2 + u$	Total energy per unit of mass
u	Internal energy per unit of mass
$\phi_{e\alpha} = e \rho v_\alpha + P_{\alpha\beta} v_\beta + J_{u\alpha}$	Energy Flux
$J_{u\alpha}$	Heat flux
$\sigma_e = \sum_i^N \rho_i F_{i\alpha} v_{i\alpha}$	Energy supply by mechanical work of external forces

Material balance(s)

$$\rho \frac{d}{dt} e + \partial_\alpha \left(P_{\alpha\beta} v_\beta + J_{u\alpha} \right) = \sum_i^N \rho_i v_{i\alpha} F_{i\alpha}$$

$$\rho \frac{d}{dt} u + \partial_\beta J_{u\alpha} + P_{\alpha\beta} \partial_\beta v_\alpha = \sum_i^N \rho_i v_{i\alpha} F_{i\alpha}$$

Local balance(s)

$$\partial_t e + \partial_\alpha \left(P_{\alpha\beta} v_\beta + J_{u\alpha} + e \rho v_\alpha \right) =$$

$$= \sum_i^N \rho_i F_{i\alpha} v_\alpha + \sum_i^N F_{i\alpha} J_{i\alpha}$$

$$\partial_t \left(\rho u \right) + \partial_\alpha \left(J_{u\alpha} + \rho u v_\alpha \right) + P_{\alpha\beta} \partial_\beta v_\alpha =$$

$$= \sum_i^N F_{i\alpha} J_{i\alpha}$$

Entropy Balance

Δm: Simple thermodynamic system

Exchange of mass, work, heat

Principle of local equilibrium

Gibbs Fundamental Equation

$$ds = \frac{1}{T} du + \frac{p}{T} d\left(\frac{1}{\rho}\right) - \sum_{i}^{N} \frac{\mu_i}{T} dw_i$$

$$+ \frac{1}{\rho T}\left(E_\alpha d \cancel{D}_\alpha + H_\alpha d \cancel{B}_\alpha\right)$$

$$w_i = \rho_i / \rho \,, \quad i = 1 \ldots N$$

$$du = \ldots \,, \quad d\left(\frac{1}{\rho}\right) = \ldots \,, \quad dw_i = \ldots$$

Material balance

$$\rho \frac{d}{dt} s + \partial_\alpha \left(\phi_s - \rho s v_\alpha\right) = \sigma_s$$

Entropy flow:

$$\phi_{s\alpha} = \frac{1}{T}\left(J_{u\alpha} - \sum_{i}^{N} \mu_i J_{i\alpha}\right) + \rho s v_\alpha$$

Entropy production:

$$\sigma_s = J_{u\alpha} \partial_\alpha \left(\frac{1}{T}\right) + \frac{1}{T}\left(p\delta_{\alpha\beta} - P_{\alpha\beta}\right)\partial_\beta v_\alpha +$$

$$+ \sum_{i}^{N} J_{i\alpha}\left[\frac{F_{i\alpha}}{T} - \partial_\alpha\left(\frac{\mu_i}{T}\right)\right] +$$

$$+ \sum_{i}^{N} \Gamma_i \left(-\frac{\mu_i}{T}\right) \geq 0$$

Process Equations (Flux-Force-Relations)

(Eckart-Onsager-Meixner-Prigogine)

Entropy Production $(*)$

$$\sigma = \sum_i X_i Y_i \geq 0$$

$TX_i = X_i$ ... Forces

$TY_i = -Y_i$ ... Fluxes

$$\underline{Y_i = \sum_k L_{ik} X_k}$$

$$L_{ik} = L_{ki}$$

Onsager (Casimier)-Symmetry

$\left\| L_{ik} \right\| \geq 0$ ... 2nd Law

Linear Independency of Fluxes $\left(Y_i \right)$:

$$\sigma = J_{u\alpha} \partial_\alpha \frac{1}{T} \quad + \quad \frac{1}{T} \left(\rho \delta_{\alpha\beta} - P_{\alpha\beta} \right) \partial_\beta v_\alpha +$$

Heat Transfer   Internal Friction

$$+ \sum_i^{N-1} J_{i\alpha} \left[\frac{1}{T} \left(F_{i\alpha} - F_{N\alpha} \right) - \partial_\alpha \frac{\mu_i - \mu_N}{T} \right]$$

Diffusion

$$+ \sum_{k=1}^{r} \Gamma_k \left(-\frac{A_k}{T} \right) , \qquad A_k = \sum_l^N \gamma_{kl} \mu_l$$

Chemical Reactions

Example: Diffusion and Heat Transfer in 2 Component Fluid System (No internal friction or chemical reactions)

Thermostatic EOS

$$T = T(u, \rho_1, \rho_2)$$

$$p = p(u, \rho_1, \rho_2)$$

$$\mu_i = \mu_i(u, \rho_1, \rho_2), \; i = 1,2$$

Balance Equations

$$\frac{d\rho}{dt} + \rho \partial_\alpha v_\alpha = 0$$

$$\rho \frac{dw_i}{dt} + \partial_\alpha J_{i\alpha} = 0, \; i = 1,2$$

$$\rho \frac{du}{dt} + \partial_\alpha P = \sum_i^2 \rho_i F_{i\alpha}$$

Process Equations

$$J_{i\alpha} = \sum_{k=1}^{2} L_{ik} \left(\frac{F_{k\alpha}}{T} - \partial_\alpha \frac{\mu_k}{T} \right) + L_{iu} \partial_\alpha \frac{1}{T}$$

$$i = 1,2$$

$$J_{u\alpha} = \sum_{k=1}^{2} L_{uk} \left(\frac{F_{k\alpha}}{T} - \partial_\alpha \frac{\mu_k}{T} \right) + L_u \partial_\alpha \frac{1}{T}$$

UQ: $u, \rho_1, \rho_2, \rho, v_\alpha, J_{i\alpha}, J_{u\alpha}$

T, μ_1, μ_2, p

Boundary- and Intial-Conditions.