Thermodynamical Engineering

Christian JALLUT

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01 Introduction
What do we face with for physico-chemical processes modelling?

Properties of matter:
• phases: solid (crystals), liquid, vapour, amorphous domains, coexisting phases;
• mixtures of many components: 14 million of molecules could be synthesized in 2005*;
• multiple scales of analysis (18 g of water: $6.02 \times 10^{23}$ molecules).

*Charpentier JC (2009), Perspective on multiscale methodology for product design and engineering, Comp. and Chem. Eng., 33, 936-946
Macroscopic Thermodynamics for process modelling and control

Combination of

- First principles: extensive variables balance equations;
- Constitutive equations: thermodynamic properties of phases or Thermodynamic model.
Balance equations for extensive variables in one phase systems

Distributed parameters phases

\[ \frac{d}{dt} \iiint_{V} \rho q \, dV = - \iint_{A} \varphi_{q} n \, dA + \iiint_{V} \sigma_{q} \, dV \]

\[ \frac{\partial \rho q}{\partial t} + \text{div} \varphi_{q} = \sigma_{q} \]

Lumped parameters phases

\[ \frac{d}{dt} (\rho V q) = \Sigma_{q} + \sum_{k} F_{q}^{k} \]

\( \sigma_{q} \) : extensive variable source term density
\( \rho \) : mass density
\( q \) : extensive variable per unit of mass
\( \varphi_{q} \) : extensive variable flux
\( F_{q} \) : flow of extensive variable
\( \Sigma_{q} \) : extensive variable source term
\( V \) : fixed volume of boundary \( A \)

Bird et al. (2007), Transport Phenomena, Wiley and Sons
Maxwell equations: magnetic and electric flows 
balance equations

\[
\begin{align*}
\int_\Gamma E \cdot dl &= -\frac{d}{dt} \int_A B \cdot n \, dA \\
\int_\Gamma H \cdot dl &= \frac{d}{dt} \int_A D \cdot n \, dA + \int_A i \cdot n \, dA
\end{align*}
\]

\(E\): electric field intensity (V.m\(^{-1}\))

\(H\): magnetic field intensity (A.m\(^{-1}\))

\(B\): magnetic flux (Wb.m\(^{-2}\))

\(D\): electric flux (C.m\(^{-2}\))

\(i\): charge flux or current surface density (A.m\(^{-2}\))

\(A\): surface with boundary \(\Gamma\)

First law: the total energy of a material system is neither destroyed nor created

The stored energy is the sum of different forms of energy ("domains" in the Bond Graph vocabulary):

- Energy stored in matter considered as a whole:
  - Kinetic energy;
  - Potential energy.

- Energy stored in elementary particles population (atoms, molecules):
  - Electric and magnetic energies;
  - Internal energy of a phase;
  - Internal energy of an interface separating two phases.
A fundamental constitutive equation for the internal energy of a phase
Energy conjugated variables pairs

Mechanical energy stored per unit of mass:
- kinetic energy variation: \( de_k = w \cdot dp \) (velocity, momentum);
- gravitational potential energy variation: \( de_p = gdz \) (weight, altitude).

Electromagnetic energy variation (given per unit of volume from Maxwell equations):
\[
d\left( \rho e_{em} \right) = H \cdot dB + E \cdot dD.
\]

\( p, z, B, D \) are involved in extensive variables balances.

What about the internal energy variation of a phase?
How can we vary the internal energy of a phase?

- by changing its volume (deformation energy, mechanical as well as spatial domains);

- by changing its content of matter (material domain);

- by providing or removing heat: a form of energy that is exchanged when spatial temperature gradients exist (thermal domain).
A constitutive equation for the internal energy $U$

An open uniform phase is considered (for solids, isotropic compression).

Internal energy and mass balance equations:

$$\frac{dU}{dt} = P_{ext} \frac{dV_{ext}}{dt} + \Phi + \sum_{i=1}^{C} F_i \left( u_i^* + P_i v_i^* \right) = P_{ext} \frac{dV_{ext}}{dt} + \Phi + \sum_{i=1}^{C} F_i h_i^*$$

heat flux

enthalpy

per mass unit

$$\frac{dM_i}{dt} = F_i \text{ (mass basis)}$$

* pure constituent

$C$ is the number of constituents
Second law: a pair of conjugated variables \((T,S)\) is assumed to be associated to the thermal domain. Entropy can be created

Entropy balance equation with a source term

\[
\frac{dS}{dt} = \frac{\Phi}{T_{\text{ext}}} + \sum_{i=1}^{C} F_i \cdot s_i^* + \sum_{s} s_{i}^* \geq 0
\]

per mass unit
From the balance equations of a real process to a constitutive equation for $U$

By eliminating $\Phi$ between the two balance equations, one find:

$$\frac{dU}{dt} = -P_{\text{ext}} \frac{dV}{dt} + T_{\text{ext}} \frac{dS}{dt} + \sum_{i=1}^{C} F_i \left(h_i^* - T_{\text{ext}} s_i^*\right) - T_{\text{ext}} \Sigma_s$$

Gibbs equation

Reversible version:

$$\begin{aligned}
P_{\text{ext}} &= P : \text{mechanical equilibrium} \\
T_{\text{ext}} &= T : \text{thermal equilibrium} \\
h_i^* - T_{\text{ext}} s_i^* &= h_i - T s_i = \mu_i : \text{material equilibrium} \\
\Sigma_s &= 0
\end{aligned}$$

$$\frac{dU}{dt} = -P \frac{dV}{dt} + T \frac{dS}{dt} + \sum_{i=1}^{C} F_i \mu_i$$
Domains coupling for $U$

**Gibbs equation: Thermodynamical domain**

$$dU = T(S,V,M_1,\ldots,M_C) dS - P(S,V,M_1,\ldots,M_C) dV + \sum_{i=1}^{C} u_i(S,V,M_1,\ldots,M_C) dM_i \text{ (mass basis)}$$

or for the unit of mass

$$du = T(s,v,\omega_1,\ldots,\omega_{C-1}) ds - P(s,v,\omega_1,\ldots,\omega_{C-1}) dv + \sum_{i=1}^{C} u_i(s,v,\omega_1,\ldots,\omega_{C-1}) d\omega_i \quad \omega_i: \text{i component mass fraction}$$

**Mechanical domain:**

$$de_m = w(p) \cdot dp + gdz$$

**Electromagnetical domain:**

$$d(\rho e_{em}) = H(B) \cdot dB + E(D) \cdot dD$$

Astarita G (1990), Thermodynamics. An advanced textbook for chemical engineers, Plenum
Entropy production derivation

Gibbs equation is assumed to be valid locally

Lumped parameter phases

\[
\frac{dU}{dt} = T \frac{dS}{dt} - P \frac{dV}{dt} + \sum_{i=1}^{C} \mu_i \frac{dM_i}{dt} \quad \text{(mass basis)}
\]

Distributed parameters phases

\[
\frac{Du}{Dt} = T \frac{Ds}{Dt} - P \frac{Dv}{Dt} + \sum_{i=1}^{C} \mu_i \frac{D\omega_i}{Dt}
\]

De Groot and Mazur (1984), Non-equilibrium thermodynamics, Dover
Example: entropy production within a CSTR (Continuous Stirred Tank Reactor)

By combining the balance equations and the Gibbs equation one finds:

\[
\Sigma S = \sum_{i=1}^{C} F_i^{in} \cdot \left( (h_i^{in} - TS_i^{in}) - \mu_i \right) + (P - P_{ext}) f_v + \Phi \left( 1 - \frac{T}{T_{ext}} \right) + \left( -\sum_{i=1}^{C} v_i \mu_i \right) r_V
\]

Couenne et al. (2006), Bond graph modelling for chemical reactors, *MCMDS*, 12(2-3), 159-174

Entropic production within a CSTR (Continuous Stirred Tank Reactor)

Remark on the mixing term with respect to Prigogine and coll. work

\[
\sum_{i=1}^{C} F_{i}^{in} \cdot \left( (h_{i}^{in} - T_{s_i}^{in}) - \mu_{i} \right)
\]

\( (h_{i}^{in} - T_{s_i}^{in}) - \mu_{i} \) is not a driving force for \( F_{i}^{in} \)
that is a purely convected flow.

Favache et al. (2009), Thermodynamics and chemical systems stability: The CSTR case study revisited, *J. of Process Control*, 19, 371-379

Thermodynamic model
What is a Thermodynamic model?

A set of algebraic equations to calculate *Thermodynamic properties of a phase (liquid, solid, vapour)* like volume, internal energy...as functions of measurable state variables like temperature, composition, pressure,.....

Constraints for a Thermodynamic model:

- thermodynamic properties are assumed to be state functions leading to exact differential forms:

\[
f(x_1, x_2, ...) \\
df = \sum_i \frac{\partial f}{\partial x_i} \, dx_i \\
\frac{\partial^2 f}{\partial x_i \partial x_j} = \frac{\partial^2 f}{\partial x_j \partial x_i}
\]

- Gibbs equation has to be satisfied;

- phase stability constraints have to be satisfied.
Example: one phase made of a pure component (molar or mass basis), \( u \) as a function of \( T \) and \( v \)

A change of state variable is needed since the temperature is measured

\[
\begin{align*}
    u(s,v), \quad d\omega_i &= 0 \\
    du &= Tds - Pdv
\end{align*}
\]

By defining \( \left( \frac{\partial u}{\partial T} \right)_v = c_v(T,v) \), the following constitutive relations can be derived from the Gibbs equation. It can be easily checked that \( du = Tds - Pdv \).

\[
\begin{align*}
    du &= c_v(T,v) dT + \left( T \left( \frac{\partial P}{\partial T} \right)_v - P \right) dv \\
    ds &= \frac{c_v(T,v)}{T} dT + \left( \frac{\partial P}{\partial T} \right)_v dv
\end{align*}
\]
A Thermodynamic model for one phase of a pure component

In order to integrate $du = c_v(T,v)\,dT + T\left(\frac{\partial P}{\partial T}\right)_v - P\right)\,dv$ from an arbitrary reference state, the needed Thermodynamic model is:

- the heat capacity $c_v(T,v)$;

- an equation of state (EOS). Example: Peng-Robinson, 1976 (Van der Waals family for fluids)………..

$$\left(P + \frac{a_{PR}(T)}{v(v+b_{PR})+b_{PR}(v-b_{PR})}\right)(v-b_{PR}) = RT$$
Example: heat transfer within an electrical solid conductor and rigid body. A partial energy balance is written with a source term coming from electromagnetic domain.

Internal energy balance equation:

\[ \frac{\partial \rho u}{\partial t} + \text{div}\varphi = \rho \frac{\partial u}{\partial t} + \text{div}\varphi = E \cdot i \]

Constitutive equations:
- Fourier model for heat conduction: \( \varphi = -\lambda \text{grad}T \);
- for a rigid solid, \( du = c_v(T) dT \).

\[ \rho c_v(T) \frac{\partial T}{\partial t} + \text{div}(-\lambda \text{grad}T) = E \cdot i \]
One phase made of \( C \) components, principle of representation: example of \( U \) (on a molar basis)

The internal energy of a uniform phase as a function of \( P \) and \( T \) has to be a first order homogeneous function with respect to the quantities of matter \( N_i's \):

\[
U(P, T, \lambda N_1, ..., \lambda N_C) = \lambda U(P, T, N_1, ..., N_C)
\]

then (Euler theorem):

\[
U(P, T, N_1, ..., N_C) = \sum_{i=1}^{C} N_i \frac{\partial U(P, T, N_i)}{\partial N_i} = \sum_{i=1}^{C} N_i u_i(P, T, z_1, ..., z_{C-1})
\]

\( u_i(P, T, z_1, ..., z_{C-1}) \) is the partial molar internal energy and \( z_i \) is the \( i^{th} \) component molar fraction. \( u_i \) is a zero order homogeneous function with respect to \( N_i's \).

For one mole of mixture, in order to deal with distributed parameters phases:

\[
u(P, T, z_1, ..., z_{C-1}) = \sum_{i=1}^{C} z_i u_i(P, T, z_1, ..., z_{C-1})
\]
Variables classification

**Extensive variables** $U(P,T,N_1,\ldots,N_C), V(P,T,N_1,\ldots,N_C) \ldots \text{: first order homogeneous functions with respect to } N_i's$.

**Intensive variables**: zero order homogeneous function with respect to $N_i's$:

\[ u(P,T,z_1,\ldots,z_{C-1}), v(P,T,z_1,\ldots,z_{C-1}) \ldots \text{ quantities per unit of mole (or mass)} \]

\[ T(P,T,z_1,\ldots,z_{C-1}), P(v,T,z_1,\ldots,z_{C-1}), \mu_i(P,T,z_1,\ldots,z_{C-1}) \text{ effort variables, driving forces} \]
Highly specialized literature

Models are available for mixtures as well as for pure components, particularly for fluid phases:

- equations of state: calculation of a correction to the ideal gas model;
- excess or activity coefficients models for condensed phases: calculation of a correction to ideal solution model.


Sandler SI (1999), Chemical and Engineering Thermodynamics, third edition, Wiley and Sons

Vidal J (2003), Thermodynamics. Application in chemical engineering and the petroleum industry, Technip

Phase stability
A stable phase

The phase under consideration is stable if it remains in the same state after some perturbations:

- a liquid remains a liquid;
- a solid remains a solid;
- a vapour remains a vapour.
A condition that a Thermodynamic model of a stable phase should satisfy

Let us consider an isolated lumped parameter phase that is split into two sub-systems. The trajectory back to equilibrium is such that:

\[ \frac{dS}{dt} = \Sigma \geq 0 \]

\[ S(Z_k) \geq \frac{S(Z_k - \Delta Z_k) + S(Z_k + \Delta Z_k)}{2} \]

\( Z_k \): extensive variables \((U, V, N_1, ..., N_C)\)

The entropy, as a property of a stable phase, should be a concave function with respect to extensive variables.

Callen HB (1985), Thermodynamics and an introduction to thermostatics, 2nd edition, Wiley and Sons.
Local phase stability (metastability): example of a pure component (the unit of mass or one mole are considered)

Local phase stability around \((u_0, v_0)\): tangent plane criterion applied locally

\[
s(u, v) \approx s(u_0, v_0) + \left( \frac{\partial s}{\partial u} \right)_0 du + \left( \frac{\partial s}{\partial v} \right)_0 dv + \frac{1}{2} \left[ \begin{array}{cc} du & dv \\ \frac{\partial^2 s}{\partial u^2} & \frac{\partial^2 s}{\partial u \partial v} \\ \frac{\partial^2 s}{\partial v \partial u} & \frac{\partial^2 s}{\partial v^2} \end{array} \right]_0 \left[ \begin{array}{c} du \\ dv \end{array} \right]
\]

Tangent plane equation

Negative definite matrix

It can be deduced that

\[
c_v > 0 \quad \left( \frac{\partial P}{\partial v} \right)_T < 0
\]

Sandler SI (1999), Chemical and Engineering Thermodynamics, third edition, Wiley and Sons
Phase stability with respect to composition at given $P$ and $T$: the Gibbs free energy convexity

The tangent plane to the Gibbs free energy surface of a stable phase must lie everywhere under the Gibbs free energy surface.

The tangent plane criterion is used in process modelling and simulation.

Baker et al. (1982), Gibbs energy analysis of phase equilibria, *SPE Journal*, October, 731-742

Phase instability: apparition of at least two phases

Figure taken from Callen (1985): $S$ as function of extensive variables

Phase instability between B and F: $S$ is not as high as possible. The unstable curve is replaced by a straight line. H is made of B and F phases at equilibrium.

$$S_H = \lambda S_B + (1 - \lambda) S_F$$

$$0 \leq \lambda \leq 1$$

Necessary equilibrium conditions between B and F from common tangent conditions:

- $T_B = T_F$: thermal;
- $P_B = P_F$: mechanical;
- $\mu^B_i = \mu^F_i$: material.

Callen HB (1985), Thermodynamics and an introduction to thermostatics, 2nd edition, Wiley and Sons
From Thermodynamic models of existing phases, one can calculate equilibrium conditions.

Mainly for fluid phases, some models can represent two phases:

- Van der Waals family EOS: liquid, vapour and supercritical domain;
- some activity coefficient or excess models: two liquid phases.
Van der Waals EOS family: example of a pure component

Isothermal curve: surface of I = surface of II (Maxwell rule)

Figure taken from Callen (1985). Necessary equilibrium conditions:
• the unstable part is replaced by a straight line such that:
  - $\mu_O = \mu_D$ : material;
  - $T_O = T_D$ : thermal;
  - $P_O = P_D$ : mechanical;
  - $v = \lambda v_O + (1-\lambda)v_D$

Example: global $P$, $v$, $T$ behaviour of O$_2$ fluid phases.

Peng-Robinson EOS.
Figure taken from Sandler (1999).

Callen HB (1985), Thermodynamics and an introduction to thermostatistics, 2nd edition, Wiley and Sons

Sandler SI (1999), Chemical and Engineering Thermodynamics, third edition, Wiley and Sons
Necessary and sufficient conditions of equilibrium

Isothermal and isobaric curves of molar Gibbs free energy as a function of the composition of a binary mixture

2 is the true equilibrium point:
- common tangent condition: \( \mu^L_B = \mu^V_B \);
- the tangent line is everywhere under the \( g \) function (\( g \) is as low as possible).

Figure taken from Baker et al. (1996)

Baker et al. (1982), Gibbs energy analysis of phase equilibria, *SPE Journal*, October, 731-742
Excess model: example of the NRTL model

Isothermal and isobaric curves of molar Gibbs free energy as a function of the composition of a binary mixture.

Figure taken from Wasylkiewicz et al. (1996)

Two liquid phases $L_1$ and $L_2$ at equilibrium: the unstable part is removed by a straight line.

Common tangent condition: $\mu_1^{L_1} = \mu_1^{L_2}$.

Dynamic stability

Use of availability as Lyapunov function for a one phase system

\[ A: \text{distance between the tangent plane and the entropy function} \]

Linear case: \[ A = -\delta^2 S \]


At least one constraint on an extensive variable has to be taken in order \( S \) to be strictly concave


Hoang et al. (2013), Thermodynamics based stability analysis and its use for nonlinear stabilization of the CSTR, *Computers and Chemical Engineering*, 58, 156-177
5

Process modelling: some examples
General considerations

From the Gibbs equation

Energetic representation: entropy, volume and material balances

\[ dU = Ts - PdV + \sum_{i=1}^{C} \mu_i dN_i \] (molar basis)

Leads to Irreversible Port Hamiltonian approach where \( U \) is the Hamiltonian


General considerations

Entropic representation: internal energy, volume and material balances (the classical Chemical Engineering approach).

\[ dS = \frac{dU}{T} + \frac{P}{T} dV - \sum_{i=1}^{C} \frac{u_i}{T} dN_i \] (molar basis)

This approach leads to generalized Port Hamiltonian representation with \( S \) or \(-S\) as Hamiltonian functions

Garcia-Sandoval et al. (2017), Generalized Hamiltonian representation of thermo-mechanical systems based on an entropic formulation, *J. of Process Control*, 51, 18 – 26

Hoang et al. (2011), The port Hamiltonian approach to modeling and control of Continuous Stirred Tank Reactors, *J. of Process Control*, 21, 1449 – 1458
Example of one stable phase system
Gas phase isochoric jacketed CSTR

Fundamental modelling assumptions:

- *the content of the reactor remains at the gaseous state*;
- the content of the reactor is perfectly mixed so that the state variables are *spatially uniform* (lumped parameter system);
- the outlet flows state is the same as the one inside the reactor.
Gas phase isochoric jacketed CSTR

Inputs: jacket fluid temperature $T_j$ (control variable), inlet total molar flow rate $F_{in}$, inlet composition $y_{k\,in}$ or $c_{k\,in}$, inlet temperature and pressure $T_{in}, P_{in}$

Outputs: temperature $T=T_{out}$, pressure $P=P_{out}$, composition ($y_{k} = y_{k\,out}$ or $c_{k} = c_{k\,out}$), outlet total molar flow rate $F_{out}$
Gas phase isochoric jacketed CSTR

Material balance of component $k = 1..C$ (molar basis)

$$\frac{dN_k}{dt} = \frac{dVc_k}{dt} = V \frac{dc_k}{dt} = F_{\text{in}}^k y_{k,\text{in}} - F_{\text{out}}^k y_{k,\text{out}} + r_k V$$

Internal energy balance

$$\frac{dU}{dt} = \frac{d(H - PV)}{dt} = \frac{dH}{dt} - \frac{d(PV)}{dt} = \frac{dH}{dt} - V \frac{dP}{dt} = F_{\text{in}}^h h_{\text{in}} - F_{\text{out}}^h h_{\text{out}} + \Phi$$

Volume balance

$$\frac{dV}{dt} = 0$$

Gas phase isochoric jacketed CSTR

Constitutive equations

Chemical reactions rates

\[ r_k = \sum_{j=1}^{N_r} v^j_k r_j(T, c_1, \ldots, c_C) \]

Heat transfer model: heat flux exchanged with a fluid flowing through the jacket

\[ \Phi = K(T_j - T) \]

A Thermodynamic model
Gas phase isochoric jacketed CSTR

Since the reactor content is assumed to remain in the gaseous phase state, its entropy is a concave function of extensive variables $N_i$ and $U$.

In the case of an isolated reactor, the entropy production can be used as a Lyapunov function candidate.

In the case of an open reactor, it can be used as a storage function for passivity properties studies.

Application in the case of an ideal gas.

Garcia-Sandoval et al. (2015), Stability analysis and passivity properties for a class of chemical reactors: internal entropy production approach, *Comp. and Chem. Eng.*, 75, 184-195

Examples of two phases systems: two phases are assumed to exist and be stable
Finite dimension continuous distillation columns modelling

The column is represented by a network of plates/stages where liquid and vapour phases are brought into contact.

Two models for stages:
- equilibrium model: liquid and vapour phases are assumed to be at equilibrium;
- rate model: non equilibrium model.


Taylor R, Krishna R (1993), Multicomponent mass transfer, Wiley and Sons
Equilibrium model: the stage is considered as a whole

Balance equations

\[ \frac{dN_i^k}{dt} = L_i^{k-1} + V_i^{k+1} - L_i^k - V_i^k \]

Energy

\[ \frac{dU_i^k}{dt} = L_i^{k-1}h_i^{k-1} + V_i^{k+1}h_i^{k+1} - L_i^kh_i^k - V_i^kh_i^k \]

Equilibrium constraints

\[
\begin{align*}
\mu_{vi}^k(P_i^k,T_i^k,y_i^k,...,y_{C-1}^k) &= \mu_{il}^k(P_i^k,T_i^k,x_{C-1}^k,....,x_{C-1}^k) \\
T_v^k &= T_{l_i}^k = T^k \\
P_v^k &= P_{l_i}^k = P^k
\end{align*}
\]

Rouchon P. (1990), Dynamic simulation and non linear control of distillation columns, PhD thesis (in French), ENS Mines de Paris

Rate model: each phase in the stage is considered

Each phase is assumed to be perfectly mixed

Balance equations

\[ \frac{dN_{ij}^k}{dt} = V_{ij}^{k+1} - V_{ij}^k + F_{ij}^k \]

\[ \frac{dN_{ij}^k}{dt} = L_{ij}^{k-1} - L_{ij}^k - F_{ij}^k \]

Energy

\[ \frac{dU_{ij}^k}{dt} = V_{ij}^{k+1}h_{ij}^{k+1} - V_{ij}^k h_{ij}^k + \Phi_k \]

\[ \frac{dU_{ij}^k}{dt} = L_{ij}^{k-1}h_{ij}^{k-1} - L_{ij}^k h_{ij}^k - \Phi_k \]

An hydrodynamic model is needed

A Thermodynamic model is needed


Rate model: each phase in the stage is considered

\[ V_i^k, y_i^k, h_v^k \]

\[ L_i^{k-1}, x_i^{k-1}, h_l^{k-1} \]

**Stage k**

Vap  | Liq

Equilibrium constraints are assumed at the interface for temperature and chemical potential

\[ \mu_{vl}(P^k, T^k, y_1^k, ..., y_{C-1}^k) = \mu_{li}(P^k, T^k, x_1^k, ..., x_{C-1}^k) \]

\[ T_v^{k,l} = T_l^{k,l} = T^k \]

\[ P_v^k = P_l^k = P^k \]

Double-film model: lumped flux expressions according to global driving forces.

Figure taken from Krishnamurthy and Taylor (1985), *AIChE J.*, 31(3), 449 – 456
Phases formation or disappearance
Use of the tangent plane criterion for process simulations: example of the equilibrium flash system

During the simulation course, discrete events: phase apparition or disappearance. Two methods:
• necessary equilibrium conditions for trial sets of phases combinations;
• tangent plane stability test with respect to phases compositions.

Hybrid system

Liquid(s)-phase equilibrium flash

Flash: equilibrium stage

or

Flash: equilibrium stage

Liquid(LL)

Liquid-Liquid (LL)

Figure taken from Müller and Marquardt (1997).
NRTL excess model.

Apparition of solid phase particles in a fluid phase (crystallisation/solidification/precipitation processes…)

Blandin et al. (2001), Kinetics identification of salicylic acid precipitation through experiments in a batch stirred vessel and a T-mixer, *Chem. Eng. J.*, 81, 91-100

Wu et al. (2015), Population balance modelling for the charging process of a PCM cold energy storage tank, *Int. J. Heat and Mass Transf.*, 85, 647-655

Principle of modelling: if the system is assumed to be perfectly mixed, the model is based on Population Balance Equations only.

For one category of particles characterized by one size $L$, a number size distribution of $L$ per unit of volume is defined:

$$f(L, t)$$
Population balance equation in a perfectly mixed batch system

\[ \frac{\partial f}{\partial t} + \text{div}_L w_L f = \frac{\partial f}{\partial t} + \frac{\partial f w_L}{\partial L} = \sigma_f \]

\( f w_L \): the flux in the size space where the velocity \( w_L \) gives the way the size \( L \) changes with time;

\( \sigma_f \): the source term includes death, birth terms as well as agglomeration and breaking terms.


Example of source term: primary homogeneous nucleation in crystallisation processes

Definition of the mechanical energy of an interface between two phases $a$ and $b$: stored energy change due to a change of the surface (Gibbs sharp interface model)

\[ \gamma_{ab} dA_{ab} \]

When the interface surface increases, more matter is present in the vicinity of the interface. To bring matter from the volume to the interface, one has to exert a force.

Adamson AW and Gast AP (1997), Physical chemistry of surfaces, Wiley and Sons

Hunter RJ (1987), Foundations of colloïd science, Oxford University Press
Primary homogeneous nucleation source term: example of spherical particles

Apparition of the solid phase of a pure component from a liquid phase containing this component.

This solid phase birth term is calculated for a given size $R_c$: one does not really gives a model of the phase apparition that is supposed to exist at size $R_c$.

Only $R_c$ and the corresponding source term are calculated.

\[
G_{in} = N \mu_l
\]

\[
G_{fin} = N \mu_s + \gamma_{sl} A_{sl}
\]

Adamson AW and Gast AP (1997), Physical chemistry of surfaces, Wiley and Sons
Primary homogeneous nucleation source term

\[ \Delta G = -\rho_s \frac{4}{3} \pi R^3 (\mu_l - \mu_s) + \gamma_{sl} 4\pi R^2 \]

\[ \frac{\partial \Delta G}{\partial R} = 0 \]

\[ R_c = \frac{2\gamma_{sl}}{\rho_s (\mu_l - \mu_s)} \]

\[ \Delta G_{\text{max}} = \frac{16\pi (\gamma_{sl})^3}{3 (\rho_s (\mu_l - \mu_s))^2} \]

Constitutive equations or data are needed for \( \gamma_{sl}, \rho_s, (\mu_l - \mu_s) \)

Adamson AW and Gast AP (1997), Physical chemistry of surfaces, Wiley and Sons
Phase separation kinetics modelling

Example of experimental results

Water/citric acid crystallisation process according to citric acid initial concentration in the liquid phase (from LAGEPP)

Chatre C, Emmelin C, Cogné C (2018), Influence of Arizona Test Dust (ATD) on the freezing process of high altitude clouds, 6th Sino-French Joint Workshop on Atmospheric Environment, Orléans, 10-12 september 2018
Two ways

Cahn-Hillard approach: the state variables are composition variables. The driving force for diffusion includes surface energy.

Allen-Cahn approach, “Phase field”: the state variables are order parameters.


Example: solidification process phase field modelling

Order parameter:
- $\phi = 0$: liquid phase
- $\phi = 1$: solid phase

Gradient model with respect to the potential $E$

$$\tau \frac{\partial \phi}{\partial t} = -\frac{\delta E}{\delta \phi}$$

One energy balance applied to the two phases

$$\frac{\partial T}{\partial t} = \Delta T + K(\phi) \frac{\partial \phi}{\partial t}$$

solidification energy source term


Example: solidification process

Potential $E$

$$E = \iiint_V \left( \frac{\varepsilon^2}{2} |\text{grad} \phi|^2 + f(\phi, T) \right) dV$$

Volume contribution

(a) $\Delta f < 0$

(b) $\Delta f = 0$

(c) $\Delta f > 0$

FIGURE 3. Graphs of $f(\phi)$. If $\phi = 0$ and $\phi = 1$ correspond the liquid phase and the solid phase respectively, the relation between the temperature $T$ and the equilibrium temperature $T_r$ are (a) $T < T_r$, (b) $T = T_r$, (c) $T > T_r$.

Figure taken from Kobayashi, 2010


Example: solidification process

Pure water

Initial conditions:
liquid phase at \( T < 0^\circ C \)
Solid germs at some points

Boundary conditions:
\( T < 0^\circ C \)

Morphogenesis of the crystal

Ahoure C (2019), Master of Chemical Engineering thesis (under progress) at LAGEPP

Ahoure C et al. (2019), abstract submitted to SFGP 2019 (French Congress of Chemical Engineering), Nantes, october 15 – 17, 2019
Conclusion
Thermodynamical Engineering

Balance equations

Thermodynamic model(s) for phases under consideration: the main problem

Number phases, possibly unknown
Number of components, possibly polar or ions (Coulombic forces)

Modelling

First principles
Constitutive equations