

A thermodynamical model for liquid vapor phase change

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1 Introduction

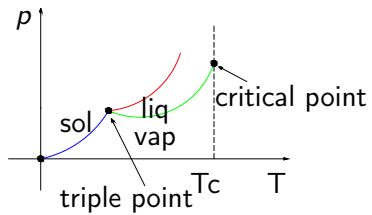
- 1 Introduction
- 2 Thermodynamics and optimization problem
 - Description of a single fluid
 - Description of the phase transition
 - Phase's Rule

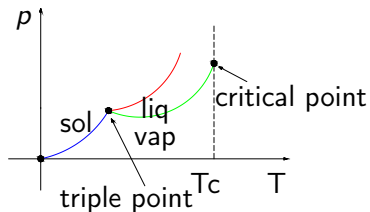
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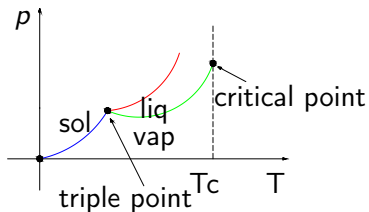


liquid-vapor phase change

↪ Two ways :

↪ Cavitation, Boiling,

↪ Metastable states : Landau Lifshitz : " .. we must distinguish between **metastable** and **stable** equilibrium states. A body in a metastable state **may not return to it** after a sufficient deviation.



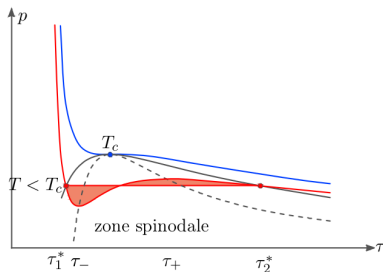
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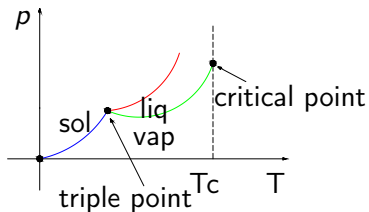
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van der Waals EoS





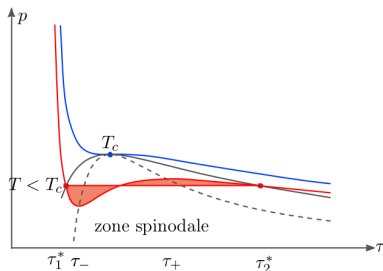
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van der Waals EoS



Experimental observations for metastable states

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Modeling of phase change (fluid's dynamic)

- ① Two fluids model with relaxation terms [Baer Nunziato] :
 - Two Euler-systems, non conservative terms
 - An equation on a rate of presence of one of the two phases.
 - Two Eos
 - Relaxation terms
- ② Model of 1 Eos [Helluy-Seguin, Allaire Faccanoni-Kokh, Helluy Mathis...] :
 - One Euler system mono fluid
 - 1 Eos describing the thermodynamics of the fluid

Goals

- Construct a good thermodynamic model.
- Find the right source terms.
- Construct a relaxation model for non isothermal compressible fluid and allowing the metastable states.

Tools

- Gibb's formalism : construct an optimization problem under constraints of entropy.
- Give the optimal phase rule using concepts of convex analysis.
- Study the optimization problem under constraints to find the set A of equilibria.
- Construct two kinds of dynamical systems :
 - such that the set of equilibria coincides with A
 - Maximize the mixture entropy

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Thermodynamics of a single pure fluid

Consider a fluid of mass $M \geq 0$, covering a volume $V \geq 0$ and characterized by its energy $E \geq 0$.

Gibb's formalism

Using the Gibbs' formalism, the extensive entropy of the fluid S is defined as a function of M , V and E :

$$S : (M, V, E) \mapsto S(M, V, E).$$

S is an extensive quantity i.e. it verifies :

Definition

S is said positively homogeneous of degree 1 (PH1) :

$$\forall \lambda > 0, \quad S(\lambda M, \lambda V, \lambda E) = \lambda S(M, V, E).$$

We assume in the sequel that S is of class C^2 .

Thermodynamical potentials and intensive quantities

- p : fluid's pressure $\frac{p}{T} = \frac{\partial S}{\partial V}(M, V, E)$,
- μ : the chemical potential $\frac{\mu}{T} = -\frac{\partial S}{\partial M}(M, V, E)$,
- T : the temperature $\frac{1}{T} = \frac{\partial S}{\partial E}(M, V, E)$.

p , μ and T are intensive quantities i.e PH0 functions.

We recover the classical thermodynamic extensive Gibbs' relation

$$dS = \frac{-\mu}{T}dM + \frac{p}{T}dV + \frac{1}{T}dE.$$

Using the Euler relation for PH1 function :

$$S(M, V, E) = \frac{-\mu M}{T} + \frac{pV}{T} + \frac{E}{T}.$$

From extensive to intensive form

Define the specific energy $e = \frac{E}{M}$ and the specific volume $\tau = \frac{V}{M}$, then the intensive entropy s for a fixed mass $M > 0$ is defined as

$$s(\tau, e) = S\left(1, \frac{V}{M}, \frac{E}{M}\right) = \frac{1}{M}S(M, V, E).$$

The other potentials T and p are given by

$$\frac{1}{T(\tau, e)} = \frac{\partial s}{\partial e}(\tau, e), \quad \frac{p(\tau, e)}{T(\tau, e)} = \frac{\partial s}{\partial \tau}(\tau, e).$$

Thus we recover the Gibb's relation in intensive form

$$s(\tau, e) = \frac{-\mu(\tau, e)}{T(\tau, e)} + \frac{p(\tau, e)}{T(\tau, e)}\tau + \frac{e}{T(\tau, e)}.$$

In the sequel we assume $\frac{\partial^2 s}{\partial e^2}|_{\tau} < 0$.

van der Waals EoS



van der Waals EoS 1873

$$s(\tau, e) = C_v \ln\left(\frac{a}{\tau} + e\right) + R \ln(\tau - b) + s_0,$$

- R is the universal constant of gas,
- C_v the calorific constant at constant volume,
- s_0 is the entropy of reference,
- a is a measure of the average attraction between particles,
- b is the volume excluded by a mole of particles.

van der Waals EoS

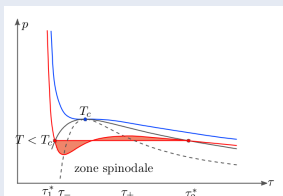
Pressure p and the temperature T of the van der Waals EoS

$$p(\tau, e) = \frac{RC_v}{\tau - b} \left(e + \frac{a}{\tau} \right) - \frac{a}{\tau^2}.$$

$$T(\tau, e) = C_v \left(e + \frac{a}{\tau} \right).$$

van der Waals EoS for isothermal model

$$p(\tau) = \frac{RT}{\tau - b} - \frac{a}{\tau^2}$$



Thermodynamics of phase change

Consider a fluid presented under I subsystems.

Extensive constraints

Energy and mass conservation : $M = \sum_{i=1}^I M_i, \quad E = \sum_{i=1}^I E_i$

Non miscibility of the subsystems : $V = \sum_{i=1}^I V_i,$

where $M_i \geq 0, V_i \geq 0, E_i \geq 0$ are the mass, volume and energy of phase i resp.

Mixture entropy of the system

Out of thermodynamic equilibrium, the entropy Σ of the system is :

$$\Sigma((M_i, V_i, E_i)_i) = \sum_{i=1}^I S(M_i, V_i, E_i).$$

The second law of thermodynamics

For fixed mass M , volume V and energy E , the mixture entropy reaches its maximum at the thermodynamical equilibrium.

Maximization problem

$$S(M, V, E) = \sup_{M_i \geq 0, V_i \geq 0, E_i \geq 0} \left\{ \sum_{i=1}^I S(M_i, V_i, E_i) \right\}$$

under the extensive constraints.

Maximization problem in intensive form

$$s(\tau, e) = \sup_{\tau_i \geq 0, \varphi_i \geq 0, s_i \geq 0} \left\{ \sum_{i=1}^I \varphi_i s(\tau_i, e_i) \right\} \quad (1)$$

The second law of thermodynamics

under the constraints

Intensive constraints

$$\begin{cases} \sum_{i=1}^I \varphi_i = 1, \\ \sum_{i=1}^I \varphi_i \tau_i = \tau, \\ \sum_{i=1}^I \varphi_i e_i = e, \end{cases} \quad (2)$$

where for each phase i

- $\varphi_i = \frac{M_i}{M} \in [0, 1]$ the mass fraction,
- $\tau_i = \frac{V_i}{M_i} \geq 0$ the specific volume,
- $e_i = \frac{E_i}{M_i} \geq 0$ the specific energy.

Gibb's phase rule

Degree of freedom F

Consider a system of

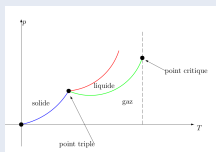
- C components,
- I phases.

Then degree of freedom F is given by :

Gibb's Phase Rule (1875)

$$F = C - I + 2.$$

Interpretation in the phase diagram



Phase's rule for the optimization problem

Let S be a subset in \mathbb{R}^n , we denote by $\text{conv}(S)$ the set of all convex combination of elements of S .

(Theorem of Caratheodory) 1907

Let $S \subset \mathbb{R}^n$ be a set. Then every point $x \in \text{conv}(S)$ can be represented as a convex combination of $(n + 1)$ points of S .

Caratheodory's corollary

Let $f : \mathbb{R}^n \mapsto \mathbb{R} \cup \{+\infty\}$ be an arbitrary function. Then

$$(\text{conv } f)(x) = \inf \left\{ \sum_{i=1}^{n+1} \lambda_i f(x_i) \text{ with } \sum_{i=1}^{n+1} \lambda_i x_i = x \right\},$$

where the inf is taken over all the expressions of x as a convex combination of $(n + 1)$ points.

According to the Caratheodory's theorem $l \leq 3$.

Theorem [H.Ghazi, F.James, H.Mathis,2017]

Consider the maximization problem (4) under the intensive constraints (2), and assume that the entropy function s verifies the inequality

$$\frac{\partial^2 s}{\partial e^2} \Big|_{\tau} < 0.$$

Then

$$l < 3.$$

As $l \leq 2$ we get the following identity

$$e\tau_1 - e\tau_2 + e_2\tau - e_1\tau - e_2\tau_1 + \tau_2e_1 = 0, \quad (3)$$

where τ_i , e_i are the specific volumes, energies of each phase i resp.

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Equilibrium states

Maximization problem under constraints

$$s(\tau, e) = \sup_{\tau_i \geq 0, \varphi_i \geq 0, s_i \geq 0} \left\{ \sum_{i=1}^2 \varphi_i s(\tau_i, e_i) \right\} \quad (4)$$

under the constraints :

$$\begin{cases} \varphi_1 + \varphi_2 = 1, \\ \varphi_1 \tau_1 + \varphi_2 \tau_2 = \tau, \\ \varphi_1 e_1 + \varphi_2 e_2 = e. \end{cases}$$

Characterization of the equilibria

- **Pure liquid or gaseous states** : $\varphi_1 = 0$ (*resp.* $\varphi_2 = 0$), with
 $\tau_2 = \tau, \quad \tau_1 < \tau$ arbitrary and $e_2 = e, \quad e_1 < e$ arbitrary (*resp.*
 $\tau_1 = \tau, \quad \tau_2 > \tau$ arbitrary and $e_1 = e, \quad e_2 > e$ arbitrary).

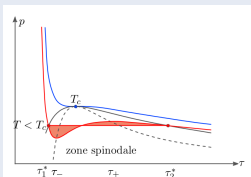
Equilibrium states

Maximization problem under constraints

$$s(\tau, e) = \sup_{\tau_i \geq 0, \varphi_i \geq 0, s_i \geq 0} \left\{ \sum_{i=1}^2 \varphi_i s(\tau_i, e_i) \right\} \quad (4)$$

under the constraints :

$$\begin{cases} \varphi_1 + \varphi_2 = 1, \\ \varphi_1 \tau_1 + \varphi_2 \tau_2 = \tau, \\ \varphi_1 e_1 + \varphi_2 e_2 = e. \end{cases}$$



- **Coexistence states** : $\varphi_1\varphi_2 \neq 0$, then the identity (3) holds with $(\tau_1, \tau_2, e_1, e_2)$ satisfying :

$$\begin{cases} p(\tau_1, e_1) = p(\tau_2, e_2), \\ \mu(\tau_1, e_1) = \mu(\tau_2, e_2), \\ T(\tau_1, e_1) = T(\tau_2, e_2). \end{cases}$$

For a fixed (τ, e) , exist a unique $(\tau_1^*, \tau_2^*, e_1^*, e_2^*)$:

$$s(\tau_2^*, e_2^*) - s(\tau_1^*, e_1^*) = \frac{p^*}{T^*}(\tau_2^* - \tau_1^*) + \frac{1}{T^*}(e_2^* - e_1^*),$$

where $p^* = p(\tau_i^*, e_i^*)$ and $T^* = T(\tau_i^*, e_i^*)$.

At the thermodynamical equilibrium, when the two phases are present, the system is characterized by the equality of pressures, chemical potentials and temperatures.

Dynamical systems

Objective

Construct a dynamical system such that equilibria coincide with the equilibria of the optimisation problem (4).

Possible way

For a fixed (τ, e) , the dynamical system maximizes the entropy defined by :

$$S(\varphi_1, \varphi_2, \tau_1, \tau_2, e_1, e_2) = \varphi_1 s(\tau_1, e_1) + \varphi_2 s(\tau_2, e_2),$$

We obtain two kinds of dynamical system

- Dynamical system with respect to the mass, volume and energy fractions.
- Dynamical system constructed with scale of energy and volume.

First choice of dynamical systems

For a fixed (τ, e) , we consider the following dynamical system :

$$\begin{cases} \dot{\alpha} = \alpha(1 - \alpha) \left(\frac{p_1}{T_1} - \frac{p_2}{T_2} \right), \\ \dot{\varphi} = \varphi(1 - \varphi) \left(\frac{\mu_2}{T_2} - \frac{\mu_1}{T_1} \right), \\ \dot{\xi} = \xi(1 - \xi) \left(\frac{1}{T_1} - \frac{1}{T_2} \right), \end{cases}$$

- $\alpha = \frac{V_1}{V}$: the volume fraction of phase 1.
- $\varphi = \frac{M_1}{M}$: the mass fraction of phase 1.
- $\xi = \frac{E_1}{E}$: the energy fraction of phase 1.
- $\tau_1 = \frac{\alpha\tau}{\varphi}$, $\tau_2 = \frac{(1 - \alpha)\tau}{1 - \varphi}$, $s_1 = \frac{\xi s}{\varphi}$, $s_2 = \frac{(1 - \xi)s}{1 - \varphi}$.

Stability of the dynamical system

Theorem

For a fixed (τ, e) and according to the latter system we get :

- 1 $\dot{S}(t) \geq 0$ where

$$S(\alpha, \varphi, \xi; \tau, e) = \varphi s\left(\frac{\alpha\tau}{\varphi}, \frac{\xi e}{\varphi}\right) + (1 - \varphi) s\left(\frac{(1 - \alpha)\tau}{1 - \varphi}, \frac{(1 - \xi)e}{1 - \varphi}\right).$$

- 2 If $(\alpha(0), \varphi(0), \xi(0)) \in]0, 1[^3$ then $(\alpha(t), \varphi(t), \xi(t)) \in]0, 1[^3$.
- 3 The thermodynamic equilibrium is an equilibrium for the dynamical system.
- 4 If $(\alpha(0), \varphi(0), \xi(0))$ is a mixture state then the unique equilibrium is $(\alpha^*, \varphi^*, \xi^*)$ defined by the unique couples (τ_1^*, e_1^*) and (τ_2^*, e_2^*) .

Disadvantage

Problem in pure phases !!!

Second choice of the dynamical system

For $\Delta\tau = \tau_2 - \tau_1$, $\Delta e = e_2 - e_1$.

$$\begin{cases} \dot{\varphi} = \varphi(1 - \varphi)(s_1 - s_2 + \varphi(\Delta\tau(\frac{p_1}{T_1} - \frac{p_2}{T_2}) + \Delta e(\frac{1}{T_1} - \frac{1}{T_2}))) + \\ \frac{1}{T_2}(\Delta e + \Delta\tau p_2), \\ \dot{\Delta\tau} = \varphi(1 - \varphi)(\Delta\tau)^2(\frac{p_2}{T_2} - \frac{p_1}{T_1}), \\ \dot{\Delta e} = \varphi(1 - \varphi)(\Delta e)^2(\frac{1}{T_2} - \frac{1}{T_1}). \end{cases}$$

Advantages

- ↪ Same properties as the first dynamical system.
- ↪ No problem in pure phases.

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Conclusion

- ↪ Construction of a maximization problem allowing the thermodynamic equilibria.
- ↪ Establish the phase rule.
- ↪ Construction of two dynamical systems which contain the thermodynamic equilibria.

Perspectives

- ↪ Coupling the dynamical systems with PDEs.
- ↪ Establish a good approximation for the source terms.

Thank you for your attention !