

## Thermodynamics is a funny subject. . .

*The first time you go through it, you don't understand it at all.*

*The second time you go through it, you think you understand it, except for one or two small points.*

*The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you any more.*

Arnold Sommerfeld

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# Some notes on thermodynamics

## Construction of (in-)coherent thermodynamic laws

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# Generality of Thermodynamics

Thermodynamics describes **average** properties of **macroscopic** matter in **equilibrium**.

**Macroscopic matter:** large objects that consist of many atoms and molecules.

**Average properties:** properties (such as volume, pressure, temperature etc.) that do not depend on the detailed positions and velocities of atoms and molecules of macroscopic matter. Such quantities are called thermodynamic coordinates, variables or parameters.

**Equilibrium:** state of a macroscopic system in which all average properties do not change with time.

- Thermodynamics predicts that these properties of a system in equilibrium **are not independent from each other**. Therefore, if we measure a subset of these properties, we can calculate the rest of them using thermodynamic relations.
- Thermodynamics also provides an approximate description of relatively **slow processes**. During such slow processes, system is in quasi-equilibrium because in the process **the system goes through a sequence of nearly equilibrium states**.

## Motivation

For the purpose of CFD calculations, thermodynamic properties must be calculated

- over a wide range of states
- starting from different couples of input variables
- a check must be made whether the calculated thermodynamic point is located in a pure region or in the VLE region (Vapor-Liquid Equilibrium)

### Difficulties on the construction of coherent thermodynamic laws

- 1 How to obtain an *accurate* (and useful in CFD) description of a pure region?
- 2 How to obtain the *same values* for all thermodynamic variables by performing calculations with different couples of input variables, but corresponding to the same thermodynamic state?
- 3 How to obtain an *accurate* description of the transition from a pure region to the VLE region?
- 4 CFD requires extremely fast algorithms for thermodynamic properties of working fluids because they are frequently used in the inner iteration cycles of the process calculations. How to balance accuracy and reasonable computing times?

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1. EoS for pure phases: one component with one-phase (liquid or vapour)
2. EoS with liquid-vapour phase transition
3. Some analytical EoS
4. Working with real values and VLE region
5. What I haven't told you

## Notations I

- EoS Equation of state

In this talk, all variables are *intensive*

- $\tau > 0$  specific volume (and  $\varrho = 1/\tau$  specific density)
- $\varepsilon$  specific internal energy
- $s$  specific (physical) entropy
- $T$  temperature
- $P$  pressure
- $\mu$  Gibbs potential or free enthalpy or chemical potential (synonyms for a one-component system)
- $h$  enthalpy
- $f$  free energy (or Helmholtz potential)
- $c$  speed of sound
- $c_P$  specific heat at constant pressure (isobar heat capacity)
- $c_V$  specific heat at constant volume (isochoric heat capacity)

## Notations II

### A physicists' convention:

to avoid confusion when we compute partial derivative performing changes of thermodynamic variables, we shall specify outside a vertical bar the list of the independent variables maintained constant.

For instance if we think of  $P$  as being a function of  $T$  and  $\tau$ , we write

$$\left. \frac{\partial P}{\partial \tau} \right|_T$$

to denote partial derivative of  $P$  in  $\tau$  with  $T$  held constant.

If we write

$$\left. \frac{\partial P}{\partial \tau} \right|_s$$

we think of  $P$  as being another function which variables are  $\tau$  and  $s$ .

## 1. EoS for pure phases: one component with one-phase (liquid or vapour)

- 1.1 A complete EoS
- 1.2 Legendre's transform
- 1.3 Thermodynamic potentials and state function
- 1.4 Entropy as a complete EoS

# A complete EoS – I

## Complete equation of state (= Fundamental equation)

Specific **internal energy**  $\varepsilon$  is everywhere uniquely (and smoothly) determined by its **specific volume**  $\tau$  and its **specific entropy**  $s$ :

$$\begin{aligned}\varepsilon: \mathbb{R}^+ \times \mathbb{R} &\rightarrow \mathbb{R}^+ \\ (\tau, s) &\mapsto \varepsilon(\tau, s)\end{aligned}$$

The fundamental thermodynamics relation is

$$d\varepsilon = -P d\tau + T ds$$

where  $P$  is the pressure and  $T$  the temperature so that

$$(\tau, s) \mapsto P \stackrel{\text{def}}{=} - \left. \frac{\partial \varepsilon}{\partial \tau} \right|_s \qquad (\tau, s) \mapsto T \stackrel{\text{def}}{=} \left. \frac{\partial \varepsilon}{\partial s} \right|_\tau$$

$(\tau, s) \mapsto P$  and  $(\tau, s) \mapsto T$  are called **incomplete EoS**.

## A complete EoS – II

Standard thermodynamics requires that

- $T \stackrel{\text{def}}{=} \left. \frac{\partial \varepsilon}{\partial s} \right|_{\tau} > 0$
- Hessian matrix is positive definite, *i.e.*

$$\det(H_{\varepsilon}) = \left. \frac{\partial^2 \varepsilon}{\partial \tau^2} \right|_s \left. \frac{\partial^2 \varepsilon}{\partial s^2} \right|_{\tau} - \left( \left. \frac{\partial^2 \varepsilon}{\partial \tau^2} \right|_s \right)^2 > 0,$$

$$\left. \frac{\partial^2 \varepsilon}{\partial \tau^2} \right|_s > 0$$

$$\left. \frac{\partial^2 \varepsilon}{\partial s^2} \right|_{\tau} > 0$$

Let us note that this implies that  $\varepsilon$  is strictly convex but the converse is wrong.

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If  $\varepsilon$  is not strictly convex (for example when the graph of  $\varepsilon$  contains a line or a plane), the geometry has the physical interpretation of phase transition.

# Legendre's transform – I

- $\tau$  and  $s$  are independent variables while  $P$  and  $T$  are derivatives
- It is often more convenient to have  $P$  and  $T$  as independent variables because they are simpler to measure or control in experiments
- Our goal is to derive functions of variables  $P$  and/or  $T$  that **contain all information** about the system of interest as the complete EoS  $(\tau, s) \mapsto \varepsilon$ .
- These functions (thermodynamic potentials) can be obtained by a mathematical trick called the **Legendre transform**.

## Legendre's transform – II

Let  $H$  a convex l.s.c. and proper function:

$$H: \mathbb{R}^n \rightarrow (-\infty, +\infty]$$

$$\mathbf{p} \mapsto H(\mathbf{p})$$

- $H^*$  is likewise convex, l.s.c. and proper and  $(H^*)^* = H$
- If  $H$  is  $\mathcal{C}^2$  and strictly convex then

$$H^*: \mathbb{R}^n \rightarrow (-\infty, +\infty]$$

$$\mathbf{q} \mapsto H^*(\mathbf{q}) \stackrel{\text{def}}{=} \mathbf{p}(\mathbf{q}) \cdot \mathbf{q} - H(\mathbf{p}(\mathbf{q})) \quad \text{with } \mathbf{p} = \mathbf{p}(\mathbf{q}) \text{ solving } \mathbf{q} = \nabla H(\mathbf{p}).$$

The Legendre transform  $H^*$  of  $H$  is

$$H^*: \mathbb{R}^n \rightarrow (-\infty, +\infty]$$

$$\mathbf{q} \mapsto H^*(\mathbf{q}) \stackrel{\text{def}}{=} \sup_{\mathbf{p} \in \mathbb{R}^n} (\mathbf{p} \cdot \mathbf{q} - H(\mathbf{p}))$$

There are 3 possible Legendre transforms of  $(s, \tau) \mapsto \varepsilon$ , according as to whether we transform

- in the variable  $s$  only,
- in  $\tau$  only,
- or in  $(s, \tau)$  together.



## Legendre's transform – III

It is customary in thermodynamics to take the negative of the mathematical Legendre transform:

$$-\sup \{ \dots \} = \inf \{ - \dots \}$$

- The Helmholtz free energy  $f$  (sometimes noted  $a$ ) is

$$f(T, \tau) = \inf_s (\varepsilon(s, \tau) - Ts) \stackrel{*}{=} \varepsilon(s, \tau) - Ts \quad \text{where } s = s(T, \tau) \text{ solves } T = \left. \frac{\partial \varepsilon}{\partial s} \right|_{\tau}$$

- The enthalpy  $h$  is

$$h(s, P) = \inf_{\tau} (\varepsilon(s, \tau) + P\tau) \stackrel{*}{=} \varepsilon(s, \tau) + P\tau \quad \text{where } \tau = \tau(s, P) \text{ solves } -P = \left. \frac{\partial \varepsilon}{\partial \tau} \right|_s$$

- The Gibbs potential (= chemical potential = free enthalpy)  $\mu$  is

$$\mu(T, P) = \inf_{(s, \tau)} (\varepsilon(s, \tau) + P\tau - Ts)$$

$$\stackrel{*}{=} \varepsilon(s, \tau) + P\tau - Ts \quad \text{where } s = s(T, P) \text{ and } \tau = \tau(T, P) \text{ solve } \begin{cases} T = \left. \frac{\partial \varepsilon}{\partial s} \right|_{\tau} \\ -P = \left. \frac{\partial \varepsilon}{\partial \tau} \right|_s \end{cases}$$

★ because  $\varepsilon$  is  $\mathcal{C}^2$  strictly convex.

## Thermodynamic potentials and state function

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Potential	Natural variables	Conjugate variables	Differential	Maxwell relations
$\varepsilon$	$(s, \tau)$	$T = \left. \frac{\partial \varepsilon}{\partial s} \right _{\tau}$ $P = - \left. \frac{\partial \varepsilon}{\partial \tau} \right _s$	$d\varepsilon = Tds - Pd\tau$	$\left. \frac{\partial T}{\partial \tau} \right _s = - \left. \frac{\partial P}{\partial s} \right _{\tau}$
$h = \varepsilon + P\tau$	$(s, P)$	$T = \left. \frac{\partial h}{\partial s} \right _P$ $\tau = \left. \frac{\partial h}{\partial P} \right _s$	$dh = Tds + \tau dP$	$\left. \frac{\partial T}{\partial P} \right _s = \left. \frac{\partial \tau}{\partial s} \right _P$
$f = \varepsilon - Ts$	$(T, \tau)$	$s = - \left. \frac{\partial f}{\partial T} \right _{\tau}$ $P = - \left. \frac{\partial f}{\partial \tau} \right _T$	$df = -sdT - Pd\tau$	$\left. \frac{\partial s}{\partial \tau} \right _T = \left. \frac{\partial P}{\partial T} \right _{\tau}$
$\mu = \varepsilon - Ts + P\tau$	$(T, P)$	$s = - \left. \frac{\partial \mu}{\partial T} \right _P$ $\tau = \left. \frac{\partial \mu}{\partial P} \right _T$	$d\mu = -sdT + \tau dP$	$\left. \frac{\partial s}{\partial P} \right _T = - \left. \frac{\partial \tau}{\partial T} \right _P$

By exploiting the  
exactness of differentials

- The internal energy  $\varepsilon$  is strictly convex in  $(s, \tau)$
- The enthalpy  $h$  is strictly concave in  $P$ , strictly convex in  $s$
- The Helmholtz free energy  $f$  is strictly concave in  $T$ , strictly convex in  $\tau$
- The Gibbs free energy  $\mu$  is strictly concave in  $(T, P)$

# Entropy as a complete EoS – I

Owing  $T > 0$ , the relation  $(\tau, s) \mapsto (\tau, \varepsilon)$  is a local diffeomorphism so we can define a **complete equation of state** as

$$\begin{aligned}s: \mathbb{R}^+ \times \mathbb{R}^+ &\rightarrow \mathbb{R} \\ (\tau, \varepsilon) &\mapsto s(\tau, \varepsilon)\end{aligned}$$

The **fundamental thermodynamics relation**  $Tds = d\varepsilon + Pd\tau$  implies that

$$\left. \frac{\partial s}{\partial \varepsilon} \right|_{\tau} = \frac{1}{T} > 0, \qquad \left. \frac{\partial s}{\partial \tau} \right|_{\varepsilon} = \frac{P}{T},$$

The entropy has a **definite negative Hessian matrix**, thus  $s$  is strictly concave.

## Entropy as a complete EoS – II

Remark:

- we can compute other 3 potentials (and 4 Maxwell's relations) using Legendre's transform of  $(\tau, \varepsilon) \mapsto s$ :

- the ??? function

$$r\left(\frac{P}{T}, \varepsilon\right) = \inf_{\tau} \left( s(\tau, \varepsilon) - \frac{P}{T} \tau \right) \stackrel{*}{=} s(\tau, \varepsilon) - \frac{P}{T} \tau \quad \text{where } \tau = \tau\left(\frac{P}{T}, \varepsilon\right) \text{ solves } \frac{P}{T} = \left. \frac{\partial s}{\partial \tau} \right|_{\varepsilon}$$

- the Massieu function

$$j\left(\tau, \frac{1}{T}\right) = \inf_{\varepsilon} \left( s(\tau, \varepsilon) - \frac{\varepsilon}{T} \right) \stackrel{*}{=} s(\tau, \varepsilon) - \frac{\varepsilon}{T} \quad \text{where } \varepsilon = \varepsilon\left(\tau, \frac{1}{T}\right) \text{ solves } \frac{1}{T} = \left. \frac{\partial s}{\partial \varepsilon} \right|_{\tau}$$

- the Planck function

$$r\left(\frac{P}{T}, \frac{1}{T}\right) = \inf_{(\tau, \varepsilon)} \left( s(\tau, \varepsilon) - \frac{P}{T} \tau - \frac{\varepsilon}{T} \right) \stackrel{*}{=} s(\tau, \varepsilon) - \frac{P}{T} \tau - \frac{\varepsilon}{T}$$

where  $\tau = \tau\left(\frac{P}{T}, \varepsilon\right)$  and  $\varepsilon = \varepsilon\left(\frac{P}{T}, \frac{1}{T}\right)$  solve  $\begin{cases} \frac{P}{T} = \left. \frac{\partial s}{\partial \tau} \right|_{\varepsilon} \\ \frac{1}{T} = \left. \frac{\partial s}{\partial \varepsilon} \right|_{\tau} \end{cases}$

- if  $P > 0$  then  $(\tau, s) \mapsto (\varepsilon, s)$  is also a local diffeomorphism and we can compute other 3 potentials (and 4 Maxwell's relations) using Legendre's transform of  $(\varepsilon, s) \mapsto \tau$

## 2. EoS with liquid-vapour phase transition

- 2.1 Principal facts and ideas
- 2.2 Maxwell construction with cubic law
- 2.3 What about the speed of sound in the VLE region?

# First Order Phase Transitions: Phase Equilibrium

- A **phases** is a part of a system, **uniform** in chemical composition and physical properties.
- A **phase transition** is **an abrupt** or a **qualitative change** of some macroscopic property of a **thermodynamic system** as a function of a thermodynamic coordinate.

For example, in a liquid-vapor phase transition, density of the material undergoes an abrupt change.

- When two phases are at equilibrium they have **the same  $T$  and  $P$ , and the  $\mu$**  of any substance must have the same value in all phases in which that substance appears

$$(P, T) \mapsto \mu_k$$

The surfaces intersect along the coexistence curve.

The transparent yellow extensions of the surface represent metastable states.

The slope of the (white) isotherms in the pressure direction is the volume.

Source <http://www.public.iastate.edu/~jolls/>

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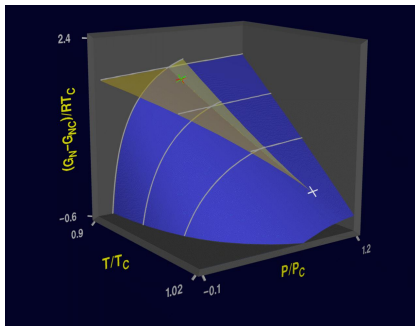
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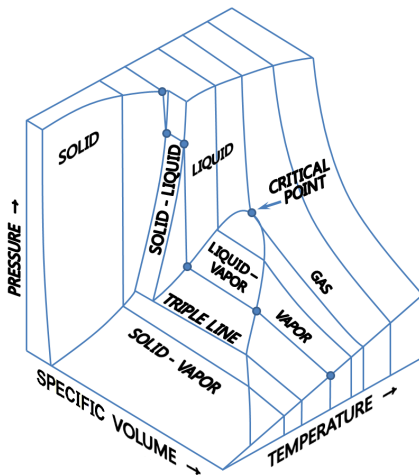
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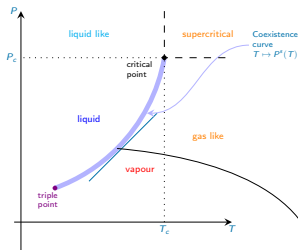
Source <http://www.public.iastate.edu/~jolls/>



# The $(\tau, T) \mapsto P$ surface



# Projections of the $(\tau, T) \mapsto P$ surface



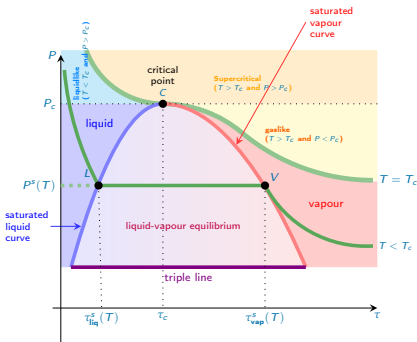
## Clausius-Clapeyron

$$\begin{aligned} \frac{dP^s}{dT}(T) &= \frac{s_{\text{vap}}^s(T) - s_{\text{liq}}^s(T)}{\tau_{\text{vap}}^s(T) - \tau_{\text{liq}}^s(T)} \\ &= \frac{1}{T} \frac{h_{\text{vap}}^s(T) - h_{\text{liq}}^s(T)}{\tau_{\text{vap}}^s(T) - \tau_{\text{liq}}^s(T)} \end{aligned}$$

$$\mu_{\text{liq}}(P, T) = \mu_{\text{vap}}(P, T) \implies T \mapsto P^s(T)$$

$$\left. \frac{\partial \mu_{\text{liq}}}{\partial T} \right|_P \neq \left. \frac{\partial \mu_{\text{vap}}}{\partial T} \right|_P \implies s_{\text{liq}}^s(T) \neq s_{\text{vap}}^s(T)$$

$$\left. \frac{\partial \mu_{\text{liq}}}{\partial P} \right|_T \neq \left. \frac{\partial \mu_{\text{vap}}}{\partial P} \right|_T \implies \tau_{\text{liq}}^s(T) \neq \tau_{\text{vap}}^s(T)$$

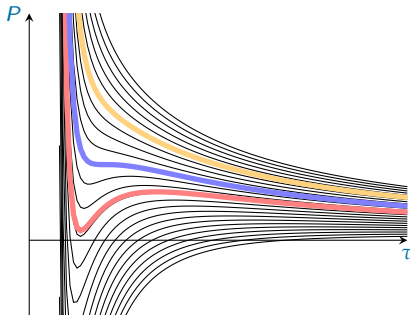


## Maxwell construction with cubic law

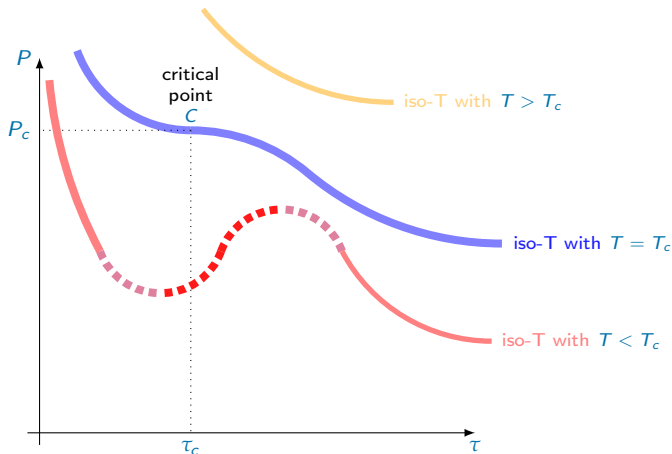
"Cubic EoS" is an incomplete EoS  $(\tau, T) \mapsto P$  that can be written as a polynomial of degree 3 in  $\tau$  (e.g. Van der Waals, Peng Robinson, Soave Redlich Kwong...)

E.g. reduced Van der Waals law

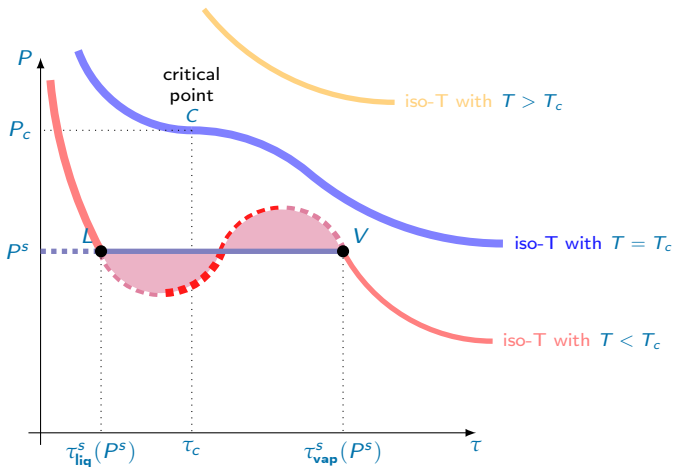
$$(\tau, T) \mapsto P \stackrel{\text{def}}{=} \frac{8T}{3\tau - 1} - \frac{3}{\tau^2}$$



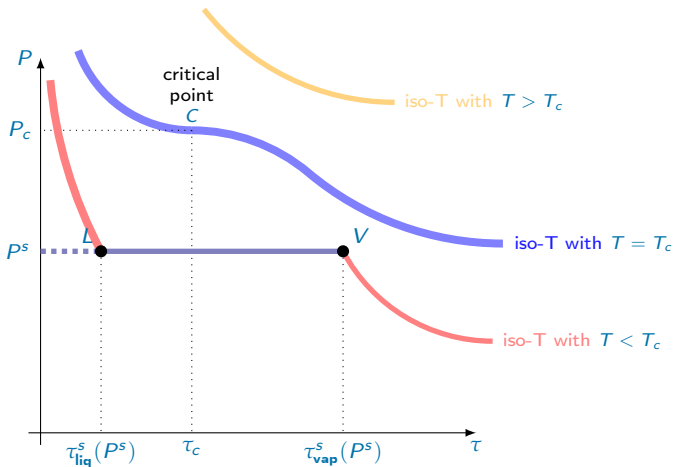
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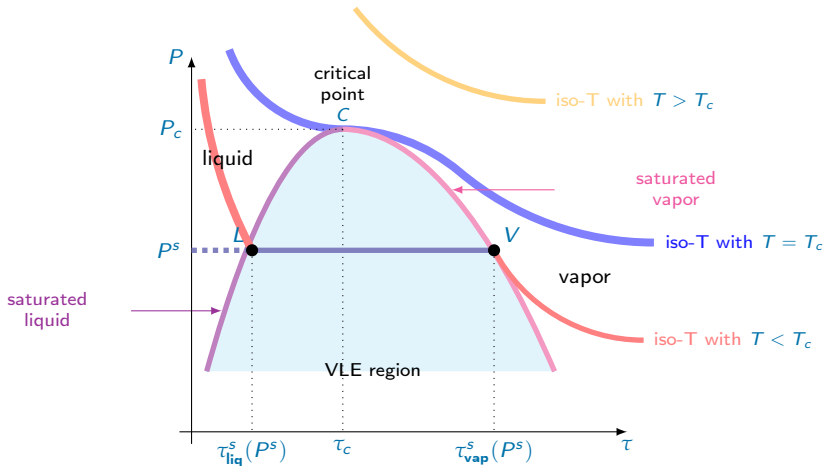
# Maxwell construction with cubic law



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## What about a complete EoS with phase transition?

- In an ideally isolated system, all internal processes lead to an **increase in the total entropy of the system**. When the entropy reaches its maximum value, the system is at equilibrium.
- In a system with liquid and vapor with no chemical reactions, the equilibrium condition is that the temperature, pressure, and Gibbs free energy must be equal in both phases in VLE region. This condition is equivalent to compute the **concave hull of an entropy**:

① If we have one EoS  $(T, P) \rightarrow s$  describing both phases (e.g. Van der Waals), then  $s$  is not concave and we define

$$(T, P) \mapsto s^{CH}(T, P) = co\{s(T, P)\}$$

(cf. Ph. Hillig, H. Martin)

② If we have two EoS  $(T, P) \rightarrow s_i$  (e.g. NAG), one for each pure phase, then

$$(T, P) \mapsto s^{CH}(T, P) = co\left\{\max_{i=1,2} \{s_{i,CH}(T, P), s_{i,eq}(T, P)\}\right\}$$

(cf. Ph. Barboux, Ph. Hillig, H. Martin, R. Sanyal, ...)

where  $co$  is the concave envelope (i.e. the smallest concave function greater than or equal to  $s$  in some region)



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[cf. Ph. Helluy, H. Mathis]

- If we have two EoS  $(\tau, \varepsilon) \mapsto s_x$  (e.g. NASG), one for each pure phase, then

$$(\tau, \varepsilon) \mapsto s^{\text{eq}}(\tau, \varepsilon) = \text{co} \left\{ \max_{(\tau, \varepsilon)} \left\{ s_{\text{liq}}(\tau, \varepsilon), s_{\text{vap}}(\tau, \varepsilon) \right\} \right\}$$

[cf. Th. Barberon, Ph. Helluy, H. Mathis, N. Seguin ...]

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- In a system with liquid and vapor with no chemical reactions, **the equilibrium condition is that the temperature, pressure, and Gibbs free energy must be equal in both phases in VLE region**. This condition is equivalent to compute the **concave hull of an entropy**:

- If we have one EoS  $(\tau, \varepsilon) \mapsto s$  describing both phases (e.g. Van der Waals), then  $s$  is not concave and we define

$$(\tau, \varepsilon) \mapsto s^{\text{eq}}(\tau, \varepsilon) = \text{co} \left\{ s(\tau, \varepsilon) \right\}$$

[cf. Ph. Helluy, H. Mathis]

- If we have two EoS  $(\tau, \varepsilon) \rightarrow s_\kappa$  (e.g. NASG), one for each pure phase, then

$$(\tau, \varepsilon) \mapsto s^{\text{eq}}(\tau, \varepsilon) = \text{co} \left\{ \max_{(\tau, \varepsilon)} \{ s_{\text{liq}}(\tau, \varepsilon), s_{\text{vap}}(\tau, \varepsilon) \} \right\}$$

[cf. Th. Barberon, Ph. Helluy, H. Mathis, N. Seguin ...]

where **co** is the concave envelope (*i.e.* the smallest concave function greater than or equal to  $s$  in some region)

Pure region

oooooooo

Maxwell construction with cubic law

VLE region

oooo●o

Analytical

oooo

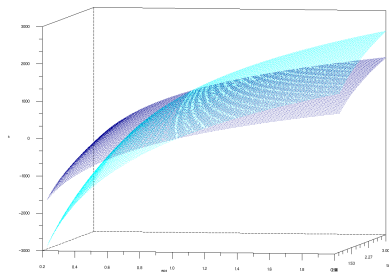
Real life

oooooooooooo

What I haven't told you

# Concave envelope

$$(\tau, \varepsilon) \mapsto s_{\text{liq}}(\tau, \varepsilon), s_{\text{vap}}(\tau, \varepsilon)$$



Pure region

oooooooo

Maxwell construction with cubic law

VLE region

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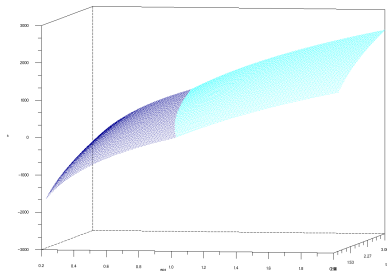
Real life

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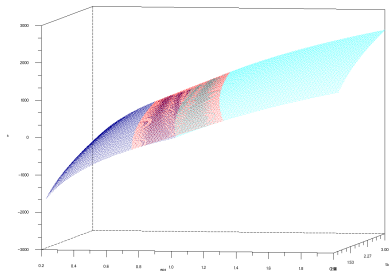
Real life

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Pure region

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Maxwell construction with cubic law

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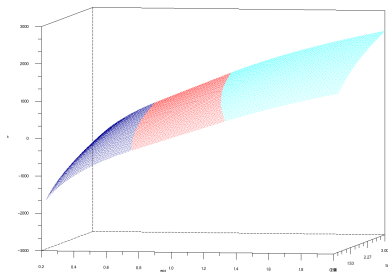
Real life

oooooooooooo

What I haven't told you

# Concave envelope

$$(\tau, \varepsilon) \mapsto \text{co} \left\{ \max_{(\tau, \varepsilon)} \{ s_{\text{liq}}(\tau, \varepsilon), s_{\text{vap}}(\tau, \varepsilon) \} \right\}$$



What about the speed of sound in the VLE region?

## What about the speed of sound in the VLE region?

Let  $\mathbf{w} \stackrel{\text{def}}{=} (\tau, \varepsilon)$ .

$$c^2(\mathbf{w}) = \tau^2 \left( P^{\text{eq}}(\mathbf{w}) \frac{\partial P^{\text{eq}}}{\partial \varepsilon} \Big|_{\tau} - \frac{\partial P^{\text{eq}}}{\partial \tau} \Big|_{\varepsilon} \right) = \overset{0}{-\tau^2 T^{\text{eq}}(\mathbf{w})} \quad [P^{\text{eq}}(\mathbf{w}), -1] H_{S^{\text{eq}}}(\mathbf{w}) \begin{bmatrix} P^{\text{eq}}(\mathbf{w}) \\ -1 \end{bmatrix} \overset{\leq 0}{\leq 0}$$

### Hessian matrix of $\mathbf{w} \mapsto S^{\text{eq}}$

- for all  $\mathbf{w}$  in pure phase region

$$\mathbf{v}^T H_{S^{\text{eq}}}(\mathbf{w}) \mathbf{v} < 0 \quad \forall \mathbf{v} \neq \mathbf{0},$$

- for all  $\mathbf{w}$  in VLE region

$$\exists! \mathbf{v}(\mathbf{w}) \neq \mathbf{0} \text{ s.t. } (\mathbf{v}(\mathbf{w}))^T H_{S^{\text{eq}}}(\mathbf{w}) \mathbf{v}(\mathbf{w}) = 0.$$

Theorem (G.F., S. Kokh, G. Allaire – M2AN 2012)

$\forall \mathbf{w}$  in VLE region,  $\mathbf{v}(\mathbf{w}) \not\perp [P^{\text{eq}}(\mathbf{w}), -1]$



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### 3. Some analytical EoS

- 3.1 How to define a complete EoS
- 3.2 From an incomplete  $(\tau, T) \mapsto P$  EoS to a complete  $(\tau, \varepsilon) \mapsto s$  EoS
- 3.3 Some examples

## How to define a complete EoS

- It is very common in practice to specify the EoS of a material via a specification of the function  $(\tau, T) \mapsto P$ . Such a formulation is just an incomplete EoS.
- In the compressible Euler equations it is necessary to specify the incomplete EoS  $(\varepsilon, \tau) \mapsto P$ .

In these cases, the difficulty is to obtain an accurate function for pure phases also coherent with saturation.

### Idea

Derive a complete EoS that is compatible with a given incomplete EoS, by finding a temperature and specific entropy that satisfies the first law of thermodynamics.

From an incomplete  $(\tau, T) \mapsto P$  EoS to a complete  $(\tau, \varepsilon) \mapsto s$  EoS

## From an incomplete $(\tau, T) \mapsto P$ EoS to a complete $(\tau, \varepsilon) \mapsto s$ EoS I

### Goal

Find the internal entropy  $s = s(\tau, \varepsilon)$  for a particular material for which the incomplete equation of state can be written as

$$P(\tau, T) = \frac{rT}{\tau - b} - v(\tau)$$

where  $r > 0$  is the universal gas constant,  $b \geq 0$  is material-specific constant and  $v$  is a function of  $\tau$  (e.g. for Van der Waals  $v(\tau) = \frac{a}{\tau^2}$ ).

- The complete equation of state can be obtained by integration of

$$\begin{aligned} ds &= \frac{P}{T} d\tau + \frac{1}{T} d\varepsilon \\ &= \left( \frac{r}{\tau - b} - \frac{1}{T} v(\tau) \right) d\tau + \frac{1}{T} d\varepsilon \end{aligned}$$

From an incomplete  $(\tau, T) \mapsto P$  EoS to a complete  $(\tau, \varepsilon) \mapsto s$  EoS

## From an incomplete $(\tau, T) \mapsto P$ EoS to a complete $(\tau, \varepsilon) \mapsto s$ EoS II

- The entropy  $s$  is an exact differential form, so that

$$\left. \frac{\partial \left( \frac{1}{T} \right)}{\partial \tau} \right|_{\varepsilon} = \left. \frac{\partial \left( \frac{P}{T} \right)}{\partial \varepsilon} \right|_{\tau} = -v(\tau) \left. \frac{\partial \left( \frac{1}{T} \right)}{\partial \varepsilon} \right|_{\tau} \quad \text{i.e.} \quad \underbrace{\left. \frac{\partial \left( \frac{1}{T} \right)}{\partial \tau} \right|_{\varepsilon} \left. \frac{\partial \varepsilon}{\partial \left( \frac{1}{T} \right)} \right|_{\tau}}_{\left. \frac{\partial \varepsilon}{\partial \tau} \right|_{\frac{1}{T}}} = -v(\tau).$$

thus we can define  $\frac{1}{T}$  as any function of  $\varepsilon - \int v(\tau) d\tau$ .

- Finally we compute the complete EoS by integration of

$$ds = \frac{P}{T} d\tau + \frac{1}{T} d\varepsilon.$$

We note that, given  $\tau \mapsto v(\tau)$ ,

- there is no uniqueness on the choice of  $T$  (and then on  $s$ )!
- if  $(\tau, \varepsilon) \mapsto s$  is not concave everywhere, we replace  $s$  by its concave envelope.

**Van der Waals:**  $P(\tau, T) = \frac{rT}{\tau-b} - v(\tau)$  and  $v(\tau) = \frac{a}{\tau^2}$

$\frac{1}{T}$  must be a function  $\varepsilon + \int v(\tau) d\tau = \varepsilon + \frac{a}{\tau}$ , e.g.

$$\frac{1}{T} = \frac{c_v}{\frac{a}{\tau} + \varepsilon}$$

and the complete EoS can be obtained by integration of

$$ds = \frac{P}{T} d\tau + \frac{1}{T} d\varepsilon = \left( \frac{r}{\tau-b} - \frac{a}{\tau^2} \frac{c_v}{\frac{a}{\tau} + \varepsilon} \right) d\tau + \left( \frac{c_v}{\frac{a}{\tau} + \varepsilon} \right) d\varepsilon.$$

We start by integrating in  $\varepsilon$ :

$$s(\tau, \varepsilon) = \int \frac{1}{T} d\varepsilon + \omega(\tau) = \int \frac{c_v}{\frac{a}{\tau} + \varepsilon} d\varepsilon + \omega(\tau) = c_v \ln \left( \frac{a}{\tau} + \varepsilon \right) + \omega(\tau)$$

and then

$$\left. \frac{\partial s}{\partial \tau} \right|_{\varepsilon} = -\frac{a}{\tau^2} \frac{c_v}{\frac{a}{\tau} + \varepsilon} + \omega'(\tau).$$

Since  $\left. \frac{\partial s}{\partial \tau} \right|_{\varepsilon} = \frac{P}{T} = \frac{r}{\tau-b} - \frac{c_v}{\tau} \frac{a}{\frac{a}{\tau} + \varepsilon}$  then  $\omega'(\tau) = \frac{r}{\tau-b}$  and finally

$$s(\tau, \varepsilon) = c_v \ln \left( \frac{a}{\tau} + \varepsilon \right) + r \ln(\tau - b) + s_0.$$



## Some examples

## Some examples

EoS	$v(\tau)$	$\varepsilon - \int v(\tau) d\tau$	$\frac{1}{\tau}$
Noble-Abel Stiffened Gas	$a$	$\varepsilon - a\tau$	$\frac{c_v}{\varepsilon - a\tau + ab - q}$
Van der Waals	$\frac{a}{\tau^2}$	$\varepsilon + \frac{a}{\tau}$	$\frac{c_v}{\varepsilon + \frac{a}{\tau}}$
Soave Redlich Kwong	$\frac{a}{\tau(\tau+b)}$	$\varepsilon + \frac{a}{b} \ln\left(\frac{\tau+b}{\tau}\right)$	$\frac{c_v}{\varepsilon + \frac{a}{b} \ln\left(\frac{\tau+b}{\tau}\right)}$
Peng Robinson	$\frac{a}{\tau^2 + 2b\tau - b^2}$	$\varepsilon + \frac{a}{2\sqrt{2}b} \ln\left(\frac{\tau+(1+\sqrt{2})b}{\tau+(1-\sqrt{2})b}\right)$	$\frac{c_v}{\varepsilon + \frac{a}{2\sqrt{2}b} \ln\left(\frac{\tau+(1+\sqrt{2})b}{\tau+(1-\sqrt{2})b}\right)}$
Martin Hu	$\frac{a_1}{(\tau-b)(\tau-b_1)} - \frac{a_2}{(\tau-b)^2(\tau-b_1)}$	...	...
No name 1	$\frac{a}{\tau(\tau-b)}$	$\varepsilon + \frac{a}{b} \ln\left(\frac{\tau}{\tau-b}\right)$	$\frac{c_v}{\varepsilon + \frac{a}{b} \ln\left(\frac{\tau}{\tau-b}\right)}$
No name 2	$\frac{a}{(\tau-b)^2}$	$\varepsilon + \frac{a}{\tau-b}$	$\frac{c_v}{\varepsilon + \frac{a}{\tau-b}}$

## 4. Working with real values and VLE region

- 4.1 A cubic EoS (e.g. Van der Waals)
- 4.2 A complete EoS for pure phases (e.g. Stiffened Gas)
- 4.3 An incomplete EoS

## A cubic EoS (e.g. Van der Waals)

In general, we work with a reduced version of the EoS by defining the following dimensionless quantity

$$P_R \stackrel{\text{def}}{=} \frac{P}{P_c}, \quad T_R \stackrel{\text{def}}{=} \frac{T}{T_c}, \quad \tau_R \stackrel{\text{def}}{=} \frac{\tau}{\tau_c}$$

where  $(\tau_c, P_c, T_c)$  is the critical point. We obtain the reduced EoS (which is the same for all fluids).

### Van der Waals

$$(\tau, T) \mapsto P \stackrel{\text{def}}{=} \frac{rT}{\tau - b} - \frac{a}{\tau^2}, \quad \tau > b.$$

The critical point  $(\tau_c, P_c, T_c)$  is defined as the only point such that  $\left. \frac{\partial P}{\partial \tau} \right|_T = 0$  and  $\left. \frac{\partial^2 P}{\partial \tau^2} \right|_T = 0$ .

We have  $T_c = \frac{8a}{27br}$ ,  $\tau_c = 3b$  and  $P_c = \frac{a}{27b^2}$  so that

$$(\tau_R, T_R) \mapsto P_R \stackrel{\text{def}}{=} \frac{8T_R}{3\tau_R - 1} - \frac{3}{\tau_R^2}, \quad \frac{1}{3} < \tau_R < +\infty.$$

A complete EoS for pure phases (e.g. Stiffened Gas)

## A complete EoS for pure phases (e.g. Stiffened Gas) I

Having chosen the expression of entropy, how to determine the parameters describing each pure phase to best fit with saturated curves?

$$s = c_v \ln(\varepsilon - q - \pi\tau) + c_v(\gamma - 1) \ln(\tau) + s_0$$

Each phase is described by its own SG EoS, so that we have to compute five constants for each phase:

- specific heat at constant volume  $c_{v_K}$
- adiabatic coefficient  $\gamma_K$
- reference pressure  $\pi_K$
- binding energy  $q_K$
- reference entropy  $(s_0)_K$

A complete EoS for pure phases (e.g. Stiffened Gas)

## A complete EoS for pure phases (e.g. Stiffened Gas) II

Method from [O. Le Metayer, R. Saurel]

For a given temperature  $\bar{T}$ , the experimental data needed for the computation are the pressure at saturation  $P_{\text{exp}}^s(\bar{T})$ , the enthalpies at saturation  $h_{\kappa,\text{exp}}^s(\bar{T})$  and the volumes at saturation  $\tau_{\kappa,\text{exp}}^s(\bar{T})$ .

- Step I: computation of  $c_{p\kappa}$  and  $q_\kappa$ .

Analytical expression of the SG enthalpy:  $h_\kappa(T, P) = q_\kappa + c_{p\kappa} T$  (independent of  $P$ ). We performs a linear approximation of the experimental enthalpies between two reference states  $T_0$  and  $T_1$  (or by least-square approximation):

$$c_{p\kappa} = \frac{h_{\kappa,\text{exp}}^s(T_1) - h_{\kappa,\text{exp}}^s(T_0)}{T_1 - T_0}, \quad q_\kappa = h_{\kappa,\text{exp}}^s(T_0) - c_{p\kappa} T_0$$

A complete EoS for pure phases (e.g. Stiffened Gas)

## A complete EoS for pure phases (e.g. Stiffened Gas) III

- Step II: computation of  $\pi_\kappa$ .

At saturation, there is an algebraic relation between the temperature and the pressure, e.g. we can write  $P = P^s(T)$ . Thus for the specific volumes at saturation we have

$$\tau_\kappa^s(T) = \tau_\kappa(T, P^s(T)) = \frac{(c_{p_\kappa} - c_{v_\kappa})T}{P^s(T) + \pi_\kappa}, \quad \Rightarrow \quad \frac{\tau_\kappa^s(T_1)}{\tau_\kappa^s(T_0)} = \frac{(P^s(T_0) + \pi_\kappa) T_1}{(P^s(T_1) + \pi_\kappa) T_0},$$

so that we can determine an averaged value of the coefficient  $\pi_\kappa$  using experimental values of the volume and the pressure at saturation

$$\pi_\kappa = \frac{T_0 \tau_{\kappa,\text{exp}}^s(T_1) P_{\text{exp}}^s(T_1) - T_1 \tau_{\kappa,\text{exp}}^s(T_0) P_{\text{exp}}^s(T_0)}{T_1 \tau_{\kappa,\text{exp}}^s(T_0) - T_0 \tau_{\kappa,\text{exp}}^s(T_1)}.$$

- Step III: computation of  $c_{v_\kappa}$  and  $\gamma_\kappa$ .

$$c_{v_\kappa} = c_{p_\kappa} - \frac{P_{\text{exp}}^s(T_0) + \pi_\kappa}{T_0} \tau_{\kappa,\text{exp}}^s(T_0) \quad \Rightarrow \quad \gamma_\kappa = \frac{c_{p_\kappa}}{c_{v_\kappa}}$$

A complete EoS for pure phases (e.g. Stiffened Gas)

## A complete EoS for pure phases (e.g. Stiffened Gas) IV

- Step V: computation of  $q'_k$ .

At thermodynamic equilibrium, the two Gibbs potentials are equal:

$$A \ln(P^s(T) + \pi_g) - B \ln(P^s(T) + \pi_\ell) - C(\ln T - 1) + \frac{D}{T} + q'_\ell - q'_g = 0$$

with

$$A \stackrel{\text{def}}{=} c_{p_g} - c_{v_g}, \quad B \stackrel{\text{def}}{=} c_{p_\ell} - c_{v_\ell}, \quad C \stackrel{\text{def}}{=} c_{p_g} - c_{p_\ell}, \quad D \stackrel{\text{def}}{=} q_g - q_\ell.$$

By convention, we take  $q'_\ell = 0 \text{ J} \cdot \text{K}^{-1}$  and determine the coefficient  $q'_g$  using experimental values of the pressure at saturation

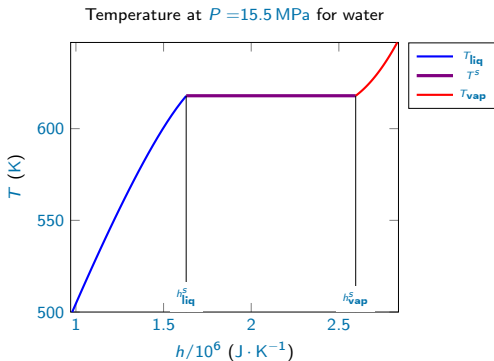
$$q'_g = A \ln(P_{\text{exp}}^s(T_0) + \pi_g) - B \ln(P_{\text{exp}}^s(T_0) + \pi_\ell) - C(\ln T_0 - 1) + \frac{D}{T_0}$$

and finally

$$(s_0)_k = q'_k - c_{v_k} \gamma_k \ln(c_{v_k}) - c_{v_k}(\gamma_k - 1) \ln(\gamma_k - 1).$$

A complete EoS for pure phases (e.g. Stiffened Gas)

## What about SG EoS for liq-vap phase transition at high pressure?



- SG EoS:  $T_K(h, P) = \frac{h - q_K}{c_{p,K}}$
- NASG EoS:  $T_K(h, P) = \frac{h - q_K - b_K P}{c_{p,K}}$

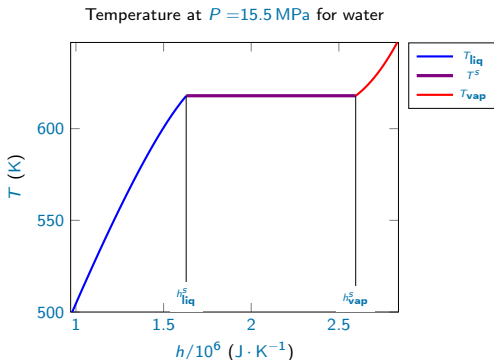
IAPWS

cf. talk O. Hurisse



A complete EoS for pure phases (e.g. Stiffened Gas)

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- NASG EoS:  $T_{\kappa}(h, P) = \frac{h - q_{\kappa} - b_{\kappa} P}{c_{p, \kappa}}$

IAPWS

cf. talk O. Hurisse

## An incomplete EoS

## An incomplete EoS – I

Tabulated laws at  $p = p_0$ 

Do you really want a complete EoS?

Or do you want just an incomplete EoS respecting some conditions (e.g. positivity, monotonicity, saturation etc.)?

For instance: how to define the incomplete EoS  $(h, p = p_0) \mapsto T$  accurate with table values?

Pure region  
○○○○○○○○

An incomplete EoS

# An incomplete EoS – II

Tabulated laws at  $p = p_0$

VLE region  
○○○○○○○

Analytical  
○○○○○

Real life  
○○○○○○●●○○○

What I haven't told you

Source: <http://webbook.nist.gov/chemistry/fluid/>

Isobaric Data for P = 15.500 MPa

Temperature (K)	Pressure (MPa)	Density (kg/m <sup>3</sup> )	Volume (m <sup>3</sup> /kg)	Internal Energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (J/g·K)	Cv (J/g·K)	Cp (J/g·K)	Sound Spd. (m/s)	Joule-Thomson (K/MPa)	Viscosity (Pa·s)	Therm. Cond. (W/m·K)	Phase
500.00	15.500	842.78	0.0011865	960.31	978.70	2.5569	3.2180	4.5615	1293.7	-0.063913	0.00012092	0.65713	liquid
510.00	15.500	829.75	0.0012052	1006.0	1024.6	2.6478	3.1869	4.6282	1257.5	-0.046444	0.00011562	0.64849	liquid
520.00	15.500	816.02	0.0012255	1052.3	1071.3	2.7384	3.1575	4.7054	1219.1	-0.026471	0.00011071	0.63869	liquid
530.00	15.500	801.52	0.0012476	1099.5	1118.8	2.8289	3.1299	4.7956	1178.5	-0.0034116	0.00010612	0.62763	liquid
540.00	15.500	786.13	0.0012721	1147.6	1167.3	2.9195	3.1043	4.9023	1135.3	0.023516	0.00010179	0.61518	liquid
550.00	15.500	769.71	0.0012992	1196.8	1216.9	3.0106	3.0809	5.0303	1089.4	0.055400	9.7660e-05	0.60122	liquid
560.00	15.500	752.06	0.0013297	1247.4	1268.0	3.1026	3.0600	5.1871	1040.3	0.093800	9.3664e-05	0.58562	liquid
570.00	15.500	732.91	0.0013644	1299.6	1320.8	3.1961	3.0425	5.3845	987.40	0.14106	8.9743e-05	0.56829	liquid
580.00	15.500	711.87	0.0014048	1354.1	1375.9	3.2918	3.0292	5.6422	929.85	0.20089	8.5823e-05	0.54917	liquid
590.00	15.500	688.30	0.0014529	1411.4	1433.9	3.3911	3.0222	5.9968	866.29	0.27962	8.1811e-05	0.52826	liquid
600.00	15.500	661.14	0.0015125	1472.9	1496.4	3.4960	3.0252	6.5254	794.32	0.38929	7.7568e-05	0.50554	liquid
610.00	15.500	628.22	0.0015918	1541.0	1565.7	3.6106	3.0478	7.4353	708.82	0.55766	7.2839e-05	0.48067	liquid
617.94	15.500	594.38	0.0016824	1603.8	1629.9	3.7151	3.1010	8.9500	621.43	0.78902	6.8327e-05	0.45847	liquid
617.94	15.500	101.93	0.0098106	2444.1	2596.1	5.2788	3.6331	14.001	433.40	7.3328	2.3108e-05	0.12136	vapor
620.00	15.500	98.412	0.010161	2465.4	2622.9	5.3220	3.4715	12.096	442.47	7.3549	2.3106e-05	0.11519	vapor
630.00	15.500	87.170	0.011472	2541.7	2719.5	5.4767	3.0236	8.0341	473.67	7.3025	2.3305e-05	0.099545	vapor
640.00	15.500	80.172	0.012473	2597.5	2790.8	5.5891	2.7765	6.4068	495.54	7.1500	2.3642e-05	0.092124	vapor
650.00	15.500	75.074	0.013320	2643.5	2849.9	5.6807	2.6053	5.4819	513.12	6.9630	2.4030e-05	0.087694	vapor
660.00	15.500	71.073	0.014070	2683.4	2901.5	5.7595	2.4762	4.8741	528.11	6.7611	2.4442e-05	0.084820	vapor
670.00	15.500	67.786	0.014752	2719.3	2948.0	5.8294	2.3748	4.4414	541.30	6.5526	2.4866e-05	0.082897	vapor
680.00	15.500	65.004	0.015384	2752.3	2990.7	5.8927	2.2933	4.1171	553.17	6.3425	2.5298e-05	0.081615	vapor
690.00	15.500	62.595	0.015976	2782.9	3030.6	5.9509	2.2266	3.8653	564.01	6.1338	2.5733e-05	0.080792	vapor
700.00	15.500	60.473	0.016536	2811.9	3068.2	6.0050	2.1715	3.6648	574.02	5.9283	2.6169e-05	0.080316	vapor

## An incomplete EoS – III

Tabulated laws at  $p = p_0$

- In tables we can find  $\{h_i, (c_p)_i\}_{i \in \mathcal{I}_k}$  for a given pressure  $p = p_0$
- Since  $Tds = dh - \tau dP$  then

$$\frac{1}{c_p} = \left. \frac{\partial T}{\partial h} \right|_P$$

- Approximation of  $(h, p = p_0) \mapsto \frac{1}{(c_p)_k}$  by least squares on the set  $\{h_i, (c_p)_i\}_{i \in \mathcal{I}_k}$  and

$$T_k(h, p = p_0) \stackrel{\text{def}}{=} T^s(p_0) + \int_{h_k^s(p_0)}^h \frac{1}{(c_p)_k} dh$$

(e.g. if  $1/c_p$  is approximated by a polynomial of degree 1,  $T$  is a polynomial of degree 2)

### Properties

$(h, p = p_0) \mapsto T_k(h, p = p_0)$  is

- continuous
- positive
- strictly increasing
- saturation exactly holds

# An Asymptotic Simplified Low Mach Model for the core of a PWR

$$\rho(t, \mathbf{x}) = \rho_0 + \bar{\rho}(t, \mathbf{x}) \text{ with } \frac{\bar{\rho}(t, \mathbf{x})}{\rho(t, \mathbf{x})} = \mathcal{O}(M^2)$$

$$\begin{cases} \operatorname{div} \mathbf{u} = \frac{\beta(h, p_0)}{p_0} \Phi \\ \partial_t h + \mathbf{u} \cdot \nabla h = \tau(h, p_0) \Phi \\ \partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u} + \tau(h, p_0) \nabla \bar{p} = \tau(h, p_0) \operatorname{div}(\sigma(\mathbf{u})) + \mathbf{g} \end{cases}$$

- Unknowns
- Given quantities
- Boundary conditions
- EoS
- How to compute EoS with real values

An incomplete EoS

# An Asymptotic Simplified Low Mach Model for the core of a PWR

$$p(t, \mathbf{x}) = p_0 + \bar{p}(t, \mathbf{x}) \text{ with } \frac{\bar{p}(t, \mathbf{x})}{p(t, \mathbf{x})} = \mathcal{O}(M^2)$$

$$\begin{cases} \operatorname{div} \mathbf{u} = \frac{\beta(h, p_0)}{p_0} \Phi \\ \partial_t h + \mathbf{u} \cdot \nabla h = \tau(h, p_0) \Phi \\ \partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u} + \tau(h, p_0) \nabla \bar{p} = \tau(h, p_0) \operatorname{div}(\sigma(\mathbf{u})) + \mathbf{g} \end{cases}$$

- Unknowns

- $(t, \mathbf{x}) \mapsto \mathbf{u}$  velocity
- $(t, \mathbf{x}) \mapsto h$  enthalpy
- $(t, \mathbf{x}) \mapsto \bar{p}$  dynamic pressure

- Given quantities

- Boundary conditions

- EoS

- How to compute EoS with real values

# An Asymptotic Simplified Low Mach Model for the core of a PWR

$$\rho(t, \mathbf{x}) = \rho_0 + \bar{\rho}(t, \mathbf{x}) \text{ with } \frac{\bar{\rho}(t, \mathbf{x})}{\rho(t, \mathbf{x})} = \mathcal{O}(M^2)$$

$$\begin{cases} \operatorname{div} \mathbf{u} = \frac{\beta(h, \rho_0)}{\rho_0} \Phi \\ \partial_t h + \mathbf{u} \cdot \nabla h = \tau(h, \rho_0) \Phi \\ \partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u} + \tau(h, \rho_0) \nabla \bar{p} = \tau(h, \rho_0) \operatorname{div}(\sigma(\mathbf{u})) + \mathbf{g} \end{cases}$$

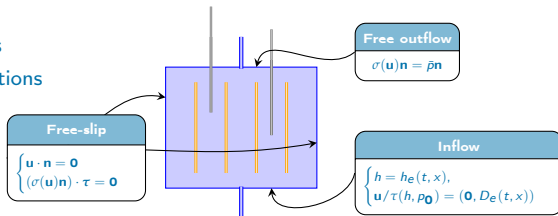
- Unknowns
- Given quantities
  - $(t, \mathbf{x}) \mapsto \Phi \geq 0$  power density
  - $\mathbf{g}$  gravity
  - $\rho_0$  thermodynamic pressure (constant)
- Boundary conditions
- EoS
- How to compute EoS with real values

# An Asymptotic Simplified Low Mach Model for the core of a PWR

$$\rho(t, \mathbf{x}) = \rho_0 + \bar{\rho}(t, \mathbf{x}) \text{ with } \frac{\bar{\rho}(t, \mathbf{x})}{\rho(t, \mathbf{x})} = \mathcal{O}(M^2)$$

$$\begin{cases} \operatorname{div} \mathbf{u} = \frac{\beta(h, p_0)}{p_0} \Phi \\ \partial_t h + \mathbf{u} \cdot \nabla h = \tau(h, p_0) \Phi \\ \partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u} + \tau(h, p_0) \nabla \bar{p} = \tau(h, p_0) \operatorname{div}(\sigma(\mathbf{u})) + \mathbf{g} \end{cases}$$

- Unknowns
- Given quantities
- Boundary conditions



- EoS
- How to compute EoS with real values



# An Asymptotic Simplified Low Mach Model for the core of a PWR

$$p(t, \mathbf{x}) = p_0 + \bar{p}(t, \mathbf{x}) \text{ with } \frac{\bar{p}(t, \mathbf{x})}{p(t, \mathbf{x})} = \mathcal{O}(M^2)$$

$$\begin{cases} \operatorname{div} \mathbf{u} = \frac{\beta(h, p_0)}{p_0} \Phi \\ \partial_t h + \mathbf{u} \cdot \nabla h = \tau(h, p_0) \Phi \\ \partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u} + \tau(h, p_0) \nabla \bar{p} = \tau(h, p_0) \operatorname{div}(\sigma(\mathbf{u})) + \mathbf{g} \end{cases}$$

- Unknowns
- Given quantities
- Boundary conditions
- EoS  $(h, p_0) \mapsto \tau \implies (h, p_0) \mapsto \beta \stackrel{\text{def}}{=} p_0 \left. \frac{\partial \tau(h, p_0)}{\partial h} \right|_{p_0}$  dilatibility coefficient
  - Liquid and vapour are characterized by their thermodynamic properties:  $(h, p_0) \mapsto \tau_\kappa$
  - In the mixture, full equilibrium between liquid and vapour phases:  $T = T^s(p_0)$  and we define values at saturation:  $h_\kappa^s(p_0) \stackrel{\text{def}}{=} h_\kappa(p_0, T^s(p_0))$  and  $\tau_\kappa^s(p_0) \stackrel{\text{def}}{=} \tau_\kappa(h_\kappa^s, p_0)$

$$\tau(h, p_0) = \begin{cases} \tau_\ell(h, p_0), & \text{if } h \leq h_\ell^s(p_0), \\ \tau_m(h, p_0) & \text{if } h_\ell^s(p_0) < h < h_g^s(p_0), \\ \tau_g(h, p_0), & \text{if } h \geq h_g^s(p_0), \end{cases}$$

- How to compute EoS with real values

## An incomplete EoS

## An Asymptotic Simplified Low Mach Model for the core of a PWR

$$p(t, \mathbf{x}) = p_0 + \bar{p}(t, \mathbf{x}) \text{ with } \frac{\bar{p}(t, \mathbf{x})}{p(t, \mathbf{x})} = \mathcal{O}(M^2)$$

$$\begin{cases} \operatorname{div} \mathbf{u} = \frac{\beta(h, p_0)}{p_0} \Phi \\ \partial_t h + \mathbf{u} \cdot \nabla h = \tau(h, p_0) \Phi \\ \partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u} + \tau(h, p_0) \nabla \bar{p} = \tau(h, p_0) \operatorname{div}(\sigma(\mathbf{u})) + \mathbf{g} \end{cases}$$

- Unknowns
- Given quantities
- Boundary conditions
- EoS
- How to compute EoS with real values
  - Construction of the tabulated values  $\beta_i$  using relation  $\beta = \frac{p}{c\sqrt{T}} \sqrt{\frac{1}{c_v} - \frac{1}{c_p}}$
  - Approximation of  $h \mapsto \beta_\kappa(h)$  by least squares on  $\{h_i, \beta_i\}_{i \in \mathcal{I}_\kappa}$
  - Deduction of  $\tau_\kappa(h, p) = \tau_\kappa^s(p) + \int_{h_\kappa^s(p)}^h \frac{\beta_\kappa(h)}{p} dh$

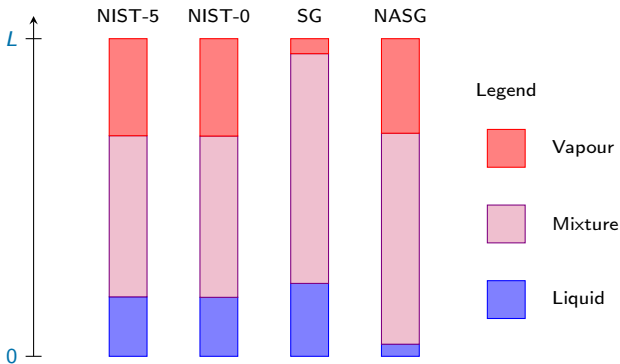
$$h \mapsto \beta_\kappa(h) = p_0 \left. \frac{\partial \tau(h, p_0)}{\partial h} \right|_{p_0} \text{ exactly holds}$$

$h \mapsto \tau_\kappa(h)$  is continuous, positive, strictly increasing and saturation exactly holds

An incomplete EoS

## Influence of EoS: asymptotic 1d solution

Schematic comparison of the phases repartition in the core for different EoS  
(exact steady state solution)



Pure region  
○○○○○○○○

VLE region  
○○○○○○○

Analytical  
○○○○○

Real life  
○○○○○○○○○○○○

What I haven't told you

## 5. What I haven't told you

# What I haven't told you – I

## Model

- Extensive vs intensive parameters
- An arbitrary system with  $r > 1$  components and/or  $M$  phases [cf. talks of O. Hurisse, R. Privat, H. Mathis, S. Müller, F. Smai]
- Miscible mixture [cf. talk of H. Mathis]
- Metastability [cf. talk of F. James]
- Second order phase transition, supercritical etc.
- Partial equilibrium/disequilibrium [cf. talks of O. Hurisse, T. Flåtten]

## EoS

- Other analytical (incomplete) EoS, like SAFT [cf. R. Privat]
- Library (especially written in Python) for water, in general based on IAPWS [cf. O. Hurisse or M. DiLorenzo, Ph. Lafont ...]

# What I haven't told you – II

## Computation

- How to compute the equilibrium entropy for using in CFD [cf. talk of O. Hurisse]
  - Concave hull used to define the entropy at equilibrium can be computed by an inf-convolution and FLT [cf. H. Mathis and Ph. Helluy]
  - The entropy at equilibrium can be interpreted as a solution of a maximisation problem w.r.t. mass/volume/energy fractions  
To compute the solution of this problem we have to solve a system of algebraic equations. [cf. Th. Barberon, Ph. Helluy, N. Seguin]  
A trick to simplify this system to obtain only one equation can be to use an approximation of saturated curves  $\tau_K^S$  and  $\varepsilon_K^S$  parametrized by  $P$  or  $T$ . [cf. G. Allaire, G.F., O. Hurisse, S. Kokh, ...]
- the problem to find tabulated values for other species than water (e.g. sodium)

A cartoon illustration of Homer Simpson sitting up in bed. He has a grumpy expression, with heavy-lidded eyes and a frown. He is wearing a light blue long-sleeved shirt and a purple blanket is pulled up to his chest. His right arm is raised, with his index finger pointing upwards. The background is a pink wall with two framed pictures: one of a yellow dog and another of a cartoon character. To the left of the bed is a red alarm clock on a nightstand. The overall scene is dimly lit, suggesting it might be early morning or late evening.

Thank you for your attention

and

sorry for my broken English

IN THIS HOUSE, WE OBEY  
THE LAWS OF  
THERMODYNAMICS!

# Transformation rules I

Considering a general implicit function  $f$  linking three variables  $x$ ,  $y$  and  $z$ :  $f(x, y, z) = 0$ . If the function can be inverted, it will be possible to write the explicit forms  $x = x(y, z)$ ,  $y = y(x, z)$  and  $z = z(x, y)$ . Some rules for transforming partial derivatives (valid for  $C^1$  functions) are used in thermodynamics:

$$\left. \frac{\partial x}{\partial y} \right|_z = \frac{1}{\left. \frac{\partial y}{\partial x} \right|_z} \quad \text{[reciprocity relation]}$$

$$\left. \frac{\partial x}{\partial y} \right|_z \left. \frac{\partial y}{\partial z} \right|_x \left. \frac{\partial z}{\partial x} \right|_y = -1 \quad \text{[cyclic relation]}$$

Composite derivative rule:

let  $F(x, y) = G(a(x, y), b(x, y))$  then

$$\left. \frac{\partial F}{\partial x} \right|_y = \left. \frac{\partial G}{\partial a} \right|_b \left. \frac{\partial a}{\partial x} \right|_y + \left. \frac{\partial G}{\partial b} \right|_a \left. \frac{\partial b}{\partial x} \right|_y$$

$$\left. \frac{\partial F}{\partial y} \right|_x = \left. \frac{\partial G}{\partial a} \right|_b \left. \frac{\partial a}{\partial y} \right|_x + \left. \frac{\partial G}{\partial b} \right|_a \left. \frac{\partial b}{\partial y} \right|_x$$

if  $a(x, y) = x$  then

$$\left. \frac{\partial F}{\partial x} \right|_y = \left. \frac{\partial G}{\partial x} \right|_b + \left. \frac{\partial G}{\partial b} \right|_x \left. \frac{\partial b}{\partial x} \right|_y$$

$$\left. \frac{\partial F}{\partial y} \right|_x = \left. \frac{\partial G}{\partial b} \right|_x \left. \frac{\partial b}{\partial y} \right|_x$$