# Cubic Equations of State for Multiphase Flows


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## Framework

The dynamical evolution of a fluid is determined by the principles of conservation of mass, momentum and energy. To obtain a complete description, the conservation laws must be supplemented with constitutive relations to characterize the material properties of the fluid. The thermodynamic properties of a material are given in a relation called *equation of State* (EOS). Thermodynamics imposes mathematical constraints on the EOS.

## 1. Incomplete cubic equation of state

(Four parameters) incomplete cubic EOS:

$$p(\tau,T)=\frac{rT}{\tau-b}-\frac{a\alpha(T)}{\tau(\tau+d)+c(\tau-d)} \tag{1}$$

where

- $\tau$ specific volume
- $T$ temperature
- $p$ pressure
- $a, b, c, d$ parameters
- $r$ related to the universal gas constant
- $\alpha(T)$ satisfies: $\alpha\in\mathcal{C}^2$ and $\alpha(T)\geq 0,\ \alpha(1)=1,\ \alpha'(T)\leq 0,\ \alpha''(T)\geq 0,\ \alpha'''(T)\leq 0.$

Two important classes of cubic EOS, covering significant behaviors of such EOS:

**Van der Waals (VdW)**

$$p(\tau,T)=\frac{rT}{\tau-b}-\frac{a}{\tau^2}$$

**Clausius (Berthelot $\delta=0$)**

$$p(\tau,T)=\frac{rT}{\tau-b}-\frac{a}{T(\tau+\delta)^2}\quad\text{with } \delta\stackrel{\text{def}}{=}\frac{c+d}{2}$$

Other well-known classes of EOS are included in the general form:

- Peng-Robinson class with $c=d=b$
- (Soave-)Redlich-Kwong class with $(\alpha(T)\simeq(C-\sqrt{T})^2)$, $c=0$, $d=b$
- Patel-Teja class with $d=b$

## 2. Construction of a complete cubic EOS using the variables $(\tau,T)$

- We search for the **specific internal energy $e$ as a function of $\tau$ and $T$**
- Denoting $s$ the entropy, we differentiate the Gibbs relation $\mathrm{d}e=T\mathrm{d}s-p\mathrm{d}\tau$ w.r.t. $\tau$ and obtain, using a Maxwell relation

$$\left.\frac{\partial e}{\partial\tau}\right|_T=T\left.\frac{\partial s}{\partial\tau}\right|_T-p=T\left.\frac{\partial p}{\partial T}\right|_\tau-p$$

- Specific heat capacity at constant volume $c_v\stackrel{\text{def}}{=}\left.\frac{\partial e}{\partial T}\right|_\tau$
- $e(\tau,T)$ being an exact differential form, the equality of the mixed partial derivatives leads to a compatibility condition

$$\left.\frac{\partial c_v}{\partial\tau}\right|_T=T\left.\frac{\partial^2 p}{\partial T^2}\right|_\tau \tag{2}$$

- Compute $c_v$ by integration of (2)

$$c_v(\tau,T)=\mathrm{fct}(T)+\int_{\tau_c}^{\tau}T\left.\frac{\partial^2 p(\sigma,T)}{\partial T^2}\right|_\sigma\mathrm{d}\sigma$$

- Incomplete EOS $\implies$ free dependence of the integration "constant" fct w.r.t. $T$

  In this work, independent of $T$: $\mathrm{fct}(T_c)=c_{v,c}$ (simplest choice) for both EOS

$$c_v(\tau,T)=c_{v,c}\qquad\qquad c_v(\tau,T)=c_{v,c}+\frac{2a}{T^2}\left(\frac{1}{\tau+\delta}-\frac{1}{\tau_c+\delta}\right)$$

- $e$ is obtained by integrating the definition of $c_v$ w.r.t. $T$:

$$e(\tau,T)=e_c+(T-T_c)c_{v,c}-a\left(\frac{1}{\tau}-\frac{1}{\tau_c}\right)$$

$$e(\tau,T)=e_c+(T-T_c)c_{v,c}-2a\left(\frac{1}{\tau+\delta}-\frac{1}{\tau_c+\delta}\right)\left(\frac{2}{T}-\frac{1}{T_c}\right)$$

- Possibility to write $e(\tau,T)$ for general cubic EOS (1).

## 3. Use of the complete cubic EOS in CFD

- In compressible flow models, knowledge of the speed of sound is fundamental:

$$c^2(\tau,T)=-\tau^2\left[\left.\frac{\partial p}{\partial\tau}\right|_T-\left(\left.\frac{\partial p}{\partial T}\right|_\tau\right)^2\frac{T}{c_v(\tau,T)}\right]$$

- Changing the thermodynamic variables to $(\tau,p)$:
  - ➥ **Analytic inversion of the temperature** possible for both EOS

$$T(\tau,p)=\frac{(p\tau^2+a)(\tau-b)}{r\tau^2}$$

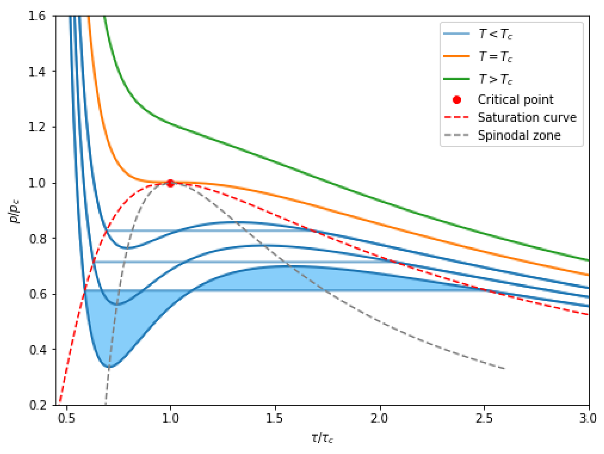
$$T(\tau,p)=\frac{p(\tau-b)}{2r}+\frac{\mathfrak{D}}{2r(\tau+\delta)}\quad\text{where } \mathfrak{D}\stackrel{\text{def}}{=}\sqrt{(\tau-b)\left(p^2(\tau+\delta)^2(\tau-b)+4ar\right)}$$

  Problematic inversion for complicated functions $\alpha(T)$.

  - ➥ It allows to define $\tilde{e}(\tau,p)\stackrel{\text{def}}{=}e(\tau,T(\tau,p))$ $(\star)$
- For asymptotic models dedicated to the low Mach number regime, explicit expression of $h(\tau,p)$ and its derivative $\partial_\tau h(\tau,p)$

## 4. Maxwell construction for determining the saturation values

① For an incomplete cubic EOS $p(\tau,T)$, the isotherm curves are as on the figure below:




- The **critical point** $(\tau_c,T_c,p_c)$ satisfies

$$p_c=p(\tau_c,T_c),\qquad \left.\frac{\partial p}{\partial\tau}\right|_{T_c}(\tau_c,T_c)=\left.\frac{\partial^2 p}{\partial\tau^2}\right|_{T_c}(\tau_c,T_c)=0. \tag{3}$$

- For $T<T_c$, there is a (spinodal) zone where the pressure is increasing: complex valued speed of sound
- **Maxwell equal area construction**: for any fixed $p_*<p_c$, there is a temperature range for which this pressure is associated with three volumes; a gas phase and a liquid phase can coexist.

  For any fixed $p_*$, we compute the **saturation values** $\tau_\ell^s$, $\tau_g^s$, $T^s$ s.th.

$$p(\tau_\ell^s,T^s)=p_*,\qquad p(\tau_g^s,T^s)=p_*,\qquad \int_{\tau_\ell^s}^{\tau_g^s}p(\tau,T^s)-p_*\mathrm{d}\tau=0.$$

- For $\tau\leq\tau_\ell^s$ (resp. $\tau\geq\tau_g^s$): liquid (resp. vapour) pure phase.

② The complete EOS $\tilde{e}(\tau,p)$ is defined piecewise using the saturation values:

$$\tilde{e}(\tau,p)=\begin{cases}(\star) & \text{in pure phases}\\ \varphi(\tau,p)e(\tau_\ell^s(p),T^s(p))+(1-\varphi(\tau,p))e(\tau_g^s(p),T^s(p)) & \text{in the mixture}\end{cases}$$

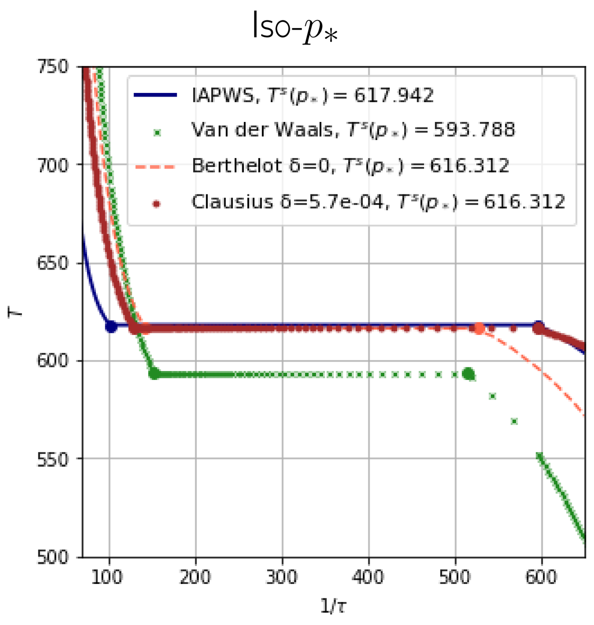
with $\varphi(\tau,p)=\frac{\tau-\tau_g^s(p)}{\tau_\ell^s(p)-\tau_g^s(p)}$. In this case, the speed of sound remains positive.

## 5. Parameter fitting for water at fixed pressure $p_*=155$ bar

Solve the system (3) at the experimental critical values (i.e. $p_c=p_{c,\text{exp}}$, $T_c=T_{c,\text{exp}}$, $\tau_c=\tau_{c,\text{exp}}$)

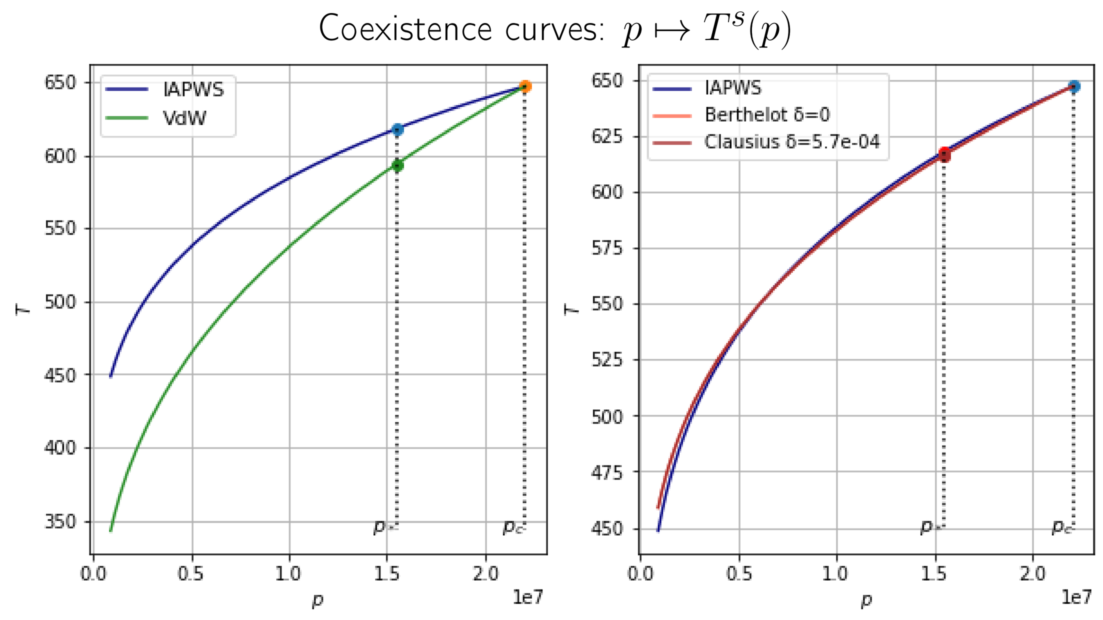
- For the VdW law (and the Berthelot one), the system is overdetermined (only 2 parameters $a$, $b$):
  - ➥ **Relax the value of $r$**: determine $a$, $b$, $r$ instead of satisfying only two critical values
  - ➥ Gives optimal saturation values for any pressure close to $p_c$
- For the Clausius EOS, 3 free parameters ($a$, $b$, $\delta$):
  - ➥ Saturation values are not satisfying for the physical value of $r$
  - ➥ Relaxing $r$ allows to find better saturation values (determining $a$, $b$, $r$ for some adequate $\delta$)
- Comparison of the saturation values for the different EOS with IAPWS data at $p=p_*$

Iso-$p_*$




For these parameters (optimized for $p=p_*$), we obtain the following curves for variable pressures $p\leq p_c$.

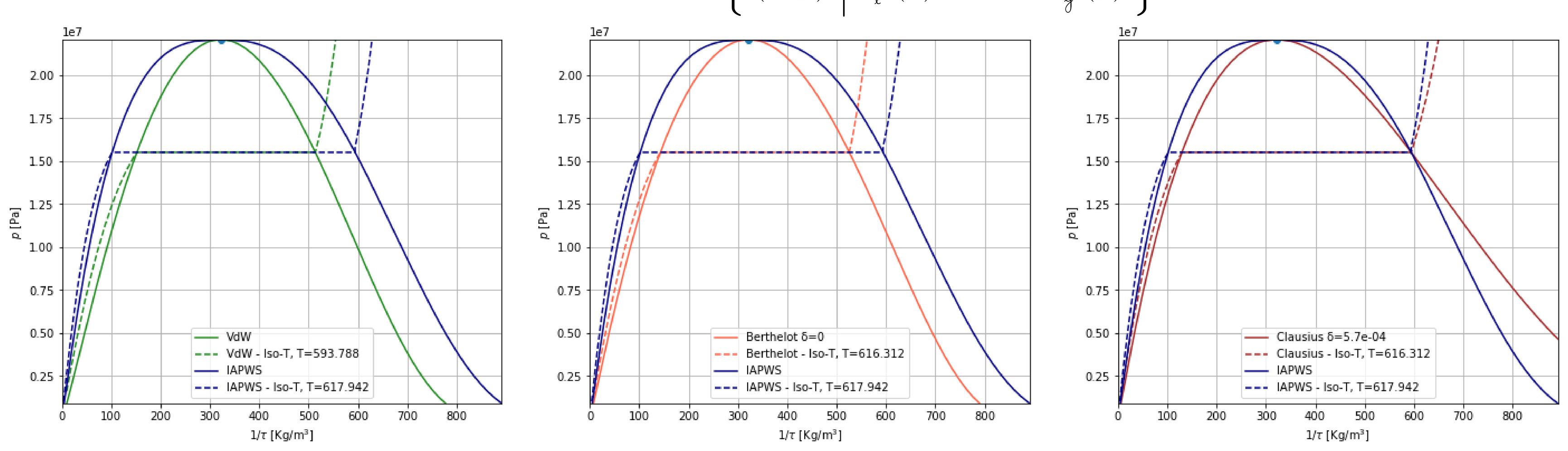
Coexistence curves: $p\mapsto T^s(p)$




- Saturation temperature for different pressures (coexistence curves)
- Discrepancy of the VdW EOS w.r.t. IAPWS for pressures far from $p_c$
- Very good accuracy of the Clausius/Berthelot EOS w.r.t. IAPWS (no visible influence of $\delta$)

Comparison of the phase boundaries $\tau_{\ell/g}^s(p)$ w.r.t. experimental data: better accuracy for Berthelot/Clausius EOS

Mixture at saturation: $\left\{(\tau,p)\ \middle|\ \tau_\ell^s(p)\leq\tau\leq\tau_g^s(p)\right\}$



We also plot the isotherm $\tau\mapsto p(\tau,T^s(p_*))$ for each EOS. Since we fixed $p_*$, the level of the horizontal part of the curve is the same for any EOS. However, the value of $T^s(p_*)$ is different, and thus these isotherm curves do not all correspond to the same temperature.

## References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