

# Real Gas Effect in Reacting Flow

*This code repository is used to evaluate the advantages of the proposed real gas equation of state (EoS)*

## 1. Code Environment

```
# Cantera used in /opt/cantera_libs/cantera, one can modified code in `src` and build & install by
conda activate cantera
python3 /usr/bin/scons build
python3 /usr/bin/scons install

# The code in this repo can be run by
source /usr/local/bin/setup_cantera
python3 src/xxx.py
```

## 2. Basic Theory

### 1.0 Generalized EoS

Helmholtz Free Energy:  $F \equiv U - TS = A(T, v, n)$ , where  $U$  is the internal energy of the system,  $T$  is the absolute temperature,  $S$  is the entropy of the system.

- 1st law of thermodynamics:  $dU = \delta Q + \delta W$
- 2nd law of thermodynamics:  $\delta Q = TdS$
- pressure work:  $\delta W = -pdV$

Thus we have:

- $dU = TdS - pdV$
- $\Rightarrow dU = d(TS) - SdT - pdV$
- $\Rightarrow d(U - TS) = -SdT - pdV$
- $\Rightarrow dF = -SdT - pdV$

Therefore,

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_V \\ p &= -\left(\frac{\partial F}{\partial V}\right)_T \\ U &= F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V \\ H &= U + pV = F - T\left(\frac{\partial F}{\partial T}\right)_V - V\left(\frac{\partial F}{\partial V}\right)_T \\ C_p &= \left(\frac{\partial H}{\partial T}\right)_p = T\left[\left(\frac{\partial^2 F}{\partial V \partial T}\right)_{V,T}^2 / \left(\frac{\partial^2 F}{\partial V^2}\right)_T - \left(\frac{\partial^2 F}{\partial T^2}\right)_V\right] \\ C_V &= \left(\frac{\partial U}{\partial T}\right)_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V \end{aligned}$$

### 1.1 Ideal Gas

$$p = \frac{nRT}{V_m}$$

where  $V_m$  is the molar volume of the gas .

## 1.2 Van der Waals (vdW) real gas equation 1783

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

where  $b$  is the volume that is occupied by one mole of the molecules. vdW is a cubic type EoS.

## 1.4 Redlich-Kwong (RK) real gas equation 1948

$$p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}V_m(V_m + b)}$$

where  $a$  is a constant that corrects for attractive potential of molecules and  $b$  is a constant that corrects for volume. The constants are different depending on which gas is being analyzed and can be calculated from the critical point data of corresponding gas:

$$a = \frac{1}{9(\sqrt[3]{2} - 1)} \frac{R^2 T_c^{2.5}}{P_c}$$
$$b = \frac{\sqrt[3]{2} - 1}{3} \frac{RT_c}{P_c}$$

Where  $T_c$  is the temperature at the critical point and  $P_c$  is the pressure at the critical point. Noted that  $a$  and  $b$  are solved analytically from the thermodynamic criteria for the critical point:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0.$$

For more details, please refer to original paper or wikipedia of Redlich Kwong equation of state.

## 1.5 Soave modified Redlich-Kwong (SRK) real gas equation 1972

In 1966, Barner noted that the acentric factor  $\omega$  can be used to improve RK EoS. SRK is proposed by Soave as:

$$p = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + b)}$$

where

$$\alpha = \left[1 + (0.480 + 1.574\omega - 0.176\omega^2)(1 - \sqrt{T_r})\right]^2$$
$$a = \frac{1}{9(\sqrt[3]{2} - 1)} \frac{R^2 T_c^2}{P_c}$$
$$b = \frac{\sqrt[3]{2} - 1}{3} \frac{RT_c}{P_c}$$

where  $T_r = T/T_c$  is the reduced temperature of the compound. Noted that  $\frac{1}{\sqrt{T}}$  term in RK is vanished and its effect is put into  $a$  in SRK.

## 1.6 Peng-Robinson (PR) real gas equation 1976

The Peng-Robinson EoS further modified the RK EoS by modifying the attractive term, giving

$$p = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + b) + b(V_m - b)}$$

where

$$\alpha = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - \sqrt{T_r})\right]^2$$
$$a = 0.457235 \frac{R^2 T_c^2}{P_c}$$
$$b = 0.077796 \frac{RT_c}{P_c}$$

## 1.7 PR-RK real gas equation 2005

The limited accuracy of the two-parameter cubic EoS is caused by the inconsistency in the density dependence of its equation rather than the empirical nature of model constants  $a$  and  $b$ . Many researchers proposed three parameters EoS. In 2005, Cismonti and Mollerup have proposed a three-parameter cubic EoS (hereafter RK-PR EoS) by introducing an additional parameter,  $\delta_1$ .

$$p = \frac{RT}{V_m - b} - \frac{a\alpha}{(V_m + \delta_1 b)(V_m + \delta_2 b)}$$

where  $\delta_2$  is not independent and  $\delta_2 = (1 - \delta_1)(1 + \delta_1)$ . And it will degenerate to SRK when  $\delta_1 = 1, \delta_2 = 0$ ; and degenerate to PR when  $\delta_1 = 1 + \sqrt{2}, \delta_2 = 1 - \sqrt{2}$ .

### 1.7 Mixture properties

When handling mixture, to obtain the aggregate parameters  $a_m, b_m$  of the cubic EoS, mixing rules from the van der Waals one-fluid theory is applied:

$$a_m = \sum_i^{N_s} \sum_j^{N_s} X_i X_j a_{ij}$$

$$b_m = \sum_i^{N_s} X_i b_i$$

where  $X_i$  is the mole fraction of the  $i^{th}$  components of the mixture,  $X_j$  is the mole fraction of the  $j^{th}$  components of the mixture. Besides,  $a_{ij}$  is the attractive term between a molecule of species  $i$  and species  $j$ , which is usually calculated by  $a_{ij} = (a_i a_j)^{1/2}$  or  $a_{ij} = (a_i a_j)^{1/2} (1 - \delta_{ij})$ .  $\delta_{ij}$  is an empirically determined binary interaction coefficient characterizing the binary formed by component  $i$  and component  $j$ .

The mixture properties  $(a\alpha)_m$  is similarly:

$$(a\alpha)_m = \sum_{i=1}^N \sum_{j=1}^N X_i X_j (a_{ij} \alpha_{ij})$$

$$(a_{ij} \alpha_{ij}) = \sqrt{a_i a_j \alpha_i \alpha_j}$$

## 2. The calibration model of alpha

The  $\alpha$  is previously calculated by Sovae-type functions like

- In SRK:  $\alpha = [1 + (0.480 + 1.574\omega - 0.176\omega^2)(1 - \sqrt{T_r})]^2$
- In PR:  $\alpha = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - \sqrt{T_r})]^2$

But those are empirical approximations and would lead to notable effects in particular thermodynamically sensitive simulations. Here a **Gaussian Process (GP) based semi-parametric method** is used to utilize the information of experimental data as most as possible.

### 2.1 The GP model

Here we're trying to fit a function that can map the inputs including  $T_r$  to the output  $\alpha$ . Using the concept of Gaussian Process (GP) model, given the observations  $(\mathbf{X}, y)$ , when applying GP to predict the target  $y_*$  at new input  $\mathbf{X}_*$ , one have

$$\mu(y_*) = \mathbf{K}_*^T (\mathbf{K} + \sigma_n^2 \mathbf{I})^{-1} y$$

$$\sigma^2(y_*) = \mathbf{K}_{**} - \mathbf{K}_*^T (\mathbf{K} + \sigma_n^2 \mathbf{I})^{-1} \mathbf{K}_*$$

where  $\sigma_n^2$  is the covariance of estimated Gaussian noise from observed data  $(\mathbf{X}, y)$ ,  $\mathbf{K}$  related terms are the covariance matrices as

$$\mathbf{K} = \text{cov}(\mathbf{X}, \mathbf{X})$$

$$\mathbf{K}_* = \text{cov}(\mathbf{X}, \mathbf{X}_*)$$

$$\mathbf{K}_{**} = \text{cov}(\mathbf{X}_*, \mathbf{X}_*)$$

## 2.2 Kernel functions

The covariance are usually obtained via kernel functions, which are very important for GP's data training. The most famous ones are:

- Squared exponential (or say Radial Basis Function, RBF):

$$\text{cov}(x_i, x_j) = \sigma_F^2 \exp \left( -\frac{d(x_i, x_j)^2}{2\gamma^2} \right)$$

where  $d(x_i, x_j)$  is the Euclidean distance of  $x_i$  and  $x_j$ ,  $l$  is the length scale of kernel size.

- Matern:

$$k(x_i, x_j) = \frac{1}{\Gamma(\nu)2^{\nu-1}} \left( \frac{\sqrt{2\nu}}{l} d(x_i, x_j) \right)^\nu K_\nu \left( \frac{\sqrt{2\nu}}{l} d(x_i, x_j) \right),$$

where  $\Gamma$  is the Gamma function,  $K_\nu$  is the modified Bessel function of order  $\nu$ .

## 2.3 Basis functions

The basis function provides an important ability to model the mean of  $y$  to zero.

$$y(\mathbf{x}) = f(\mathbf{x}; \boldsymbol{\theta}) + b_\theta(\mathbf{x}) + \epsilon$$

where  $\epsilon$  is the (Gaussian) stochastic error in the database,  $f(\mathbf{x}; \boldsymbol{\theta})$  is a basis function that can model  $y(\mathbf{x})$  as much as possible, and  $b_\theta(\mathbf{x})$  is the bias term that can compensate the error between  $f(\mathbf{x}; \boldsymbol{\theta})$  and  $y(\mathbf{x})$ .

To solve this optimization problem, let  $f(\mathbf{x}; \boldsymbol{\theta}) = \theta_3 x_2 + \theta_2 x_1 + \theta_1$  as a linear combination of the input variables  $\mathbf{x}$ , where the input variable are  $\mathbf{x} = [x_1, x_2]$ ,  $x_1$  and  $x_2$  are the input from each dimension; and  $\boldsymbol{\theta} = [\theta_1, \theta_2, \theta_3]$  are corresponding parameters in the linear combination function  $f$ .

The corresponding kernel function then be formed as:

$$k(x_i, x_j) = k_0(x_i, x_j) - h_\theta(x_i)^T \mathbf{H}_\theta h_\theta(x_j)$$

where  $h_\theta(x)$  is the 1st order global sensitivity obtained from:

$$h_\theta(x) = \int_{\mathbf{X}} \nabla_\theta f(\xi) k_0(x, \xi) d\xi$$

the 2nd order global sensitivity, i.e., Hessian matrix is

$$\mathbf{H}_\theta = \int_{\mathbf{X}} \int_{\mathbf{X}} (\nabla_\theta f(\xi)) (\nabla_\theta f(\zeta))^T k_0(\xi, \zeta) d\xi d\zeta$$

The parameter gradient of  $f$  shows

$$\nabla_\theta f(\mathbf{x}) = \frac{\partial}{\partial \boldsymbol{\theta}} f(\mathbf{x}; \boldsymbol{\theta}) = \begin{bmatrix} 1 \\ x_1 \\ x_2 \end{bmatrix}$$

The matrix constructed by gradients' outer product of randomly samples  $\xi, \zeta$

$$(\nabla_\theta f(\xi)) (\nabla_\theta f(\zeta))^T = \begin{bmatrix} 1 \\ \xi_1 \\ \xi_2 \end{bmatrix} \begin{bmatrix} 1 & \zeta_1 & \zeta_2 \end{bmatrix} = \begin{bmatrix} 1 & \zeta_1 & \zeta_2 \\ \xi_1 & \xi_1 \zeta_1 & \xi_1 \zeta_2 \\ \xi_2 & \xi_2 \zeta_1 & \xi_2 \zeta_2 \end{bmatrix}$$

The kernel function  $k_0$  is:

$$k_0(\xi, \zeta) = \sigma_F^2 \exp \left( -\sum_i \frac{(\xi_i - \zeta_i)^2}{2\gamma_i^2} \right) = \sigma_F^2 \exp \left( -\frac{(\xi_1 - \zeta_1)^2}{2\gamma_1^2} \right) \exp \left( -\frac{(\xi_2 - \zeta_2)^2}{2\gamma_2^2} \right)$$

where  $\gamma_1, \gamma_2$  are the parameters of kernel function in dimension  $x_1$  and  $x_2$ .

The corresponding distribution of the evaluated output  $y_*$  at new  $x_*$  should be:

$$\begin{aligned}\mu(y_*) &= f(x_*; \theta) + \mathbf{K}_*^T \left( \mathbf{K} + \frac{\sigma_n^2}{\nu} \mathbf{I} \right)^{-1} [y - f(\mathbf{X}; \theta)] \\ \sigma(y_*) &= \nu + \mathbf{K}_{**} - \nu \mathbf{K}_*^T \left( \mathbf{K} + \frac{\sigma_n^2}{\nu} \mathbf{I} \right)^{-1} \mathbf{K}_*\end{aligned}$$

where  $\nu$  is a measurement of possible noises, its maximum likelihood estimation (MLE)  $\hat{\nu}$  is

$$\hat{\nu} = \frac{1}{N} [y - f(\mathbf{X}; \theta)]^T (\mathbf{K} + g\mathbf{I})^{-1} [y - f(\mathbf{X}; \theta)]$$

where  $g$  is the original possible noise level, which still should be estimated by optimization program.

## 2.4 Thermodynamic Properties

By setting at least two thermo states like  $p, T, \rho$ , one can calculate all the related thermodynamic properties of given mixture. Where pressure  $p$  and temperature  $T$  can be obtained explicitly from the equation of state (EoS). Density can be obtained by first getting  $V_m$  via solving the cubic function:

$$p = \frac{RT}{V-b} - \frac{a\alpha}{V^2 + 2Vb - b^2}$$

Other related thermodynamic properties can be calculated via:

$$\begin{aligned}C_v &= \left( \frac{\partial H}{\partial T} \right)_V - V \left( \frac{\partial p}{\partial T} \right) \\ C_p &= C_v - T \left( \frac{\partial p}{\partial T} \right)^2 / \frac{\partial p}{\partial V} \\ s(T, p) &= \\ e(T, p) &= \\ h(T, p) &= \end{aligned}$$

where the corresponding partial derivatives are:

$$\begin{aligned}\left( \frac{\partial H}{\partial T} \right)_V &= C_{p,0} + V \frac{\partial p}{\partial T} - R + \frac{1}{2\sqrt{2}b} \log \left( \frac{V+b}{V-b} \right) T \frac{\partial^2(a\alpha)_m}{\partial T^2} \\ \frac{\partial p}{\partial T} &= \frac{R}{V-b} - \frac{\partial(a\alpha)_m}{\partial T} \frac{1}{V^2 + 2Vb - b^2} \\ \frac{\partial p}{\partial V} &= -\frac{RT}{(V-b)^2} + 2 \frac{(a\alpha)_m(V+b)}{V^2 + 2Vb - b^2}\end{aligned}$$

The alpha related properties are:

$$\begin{aligned}\frac{\partial(a\alpha)_m}{\partial T} &= \sum_{i=1}^N \sum_{j=1}^N X_i X_j \frac{\partial(a_{ij}\alpha_{ij})}{\partial T} \\ \frac{\partial^2(a\alpha)_m}{\partial T^2} &= \sum_{i=1}^N \sum_{j=1}^N X_i X_j \frac{\partial^2(a_{ij}\alpha_{ij})}{\partial T^2}\end{aligned}$$

where the derivatives of  $(a_{ij}\alpha_{ij})$  are:

$$\begin{aligned}\frac{\partial(a_{ij}\alpha_{ij})}{\partial T} &= \sqrt{a_i a_j} \frac{\partial \sqrt{\alpha_i \alpha_j}}{\partial T} = \frac{1}{2} \sqrt{a_i a_j \alpha_i \alpha_j} \left( \frac{1}{\alpha_i} \frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_j} \frac{\partial \alpha_j}{\partial T} \right) \\ \frac{\partial^2(a_{ij}\alpha_{ij})}{\partial T^2} &= \frac{1}{2} \sqrt{a_i a_j \alpha_i \alpha_j} \left[ \frac{1}{\alpha_i} \frac{\partial^2 \alpha_i}{\partial T^2} + \frac{1}{\alpha_j} \frac{\partial^2 \alpha_j}{\partial T^2} + \frac{2}{\alpha_i \alpha_j} \frac{\partial \alpha_i}{\partial T} \frac{\partial \alpha_j}{\partial T} - \frac{1}{2} \left( \frac{1}{\alpha_i} \frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_j} \frac{\partial \alpha_j}{\partial T} \right)^2 \right]\end{aligned}$$

Finally, we only need to get  $\frac{\partial \alpha}{\partial T}$  and  $\frac{\partial^2 \alpha}{\partial T^2}$ .

- For the original Peng-Robinson EoS framework,

$$\alpha = \left[ 1 + \kappa \left( 1 - \sqrt{T/T_c} \right) \right]^2$$

Therefore,

$$\begin{aligned} \frac{\partial \alpha}{\partial T} &= \frac{\kappa^2}{T_c} - (\kappa^2 + \kappa) \frac{1}{\sqrt{T_c}} T^{-1/2} \\ \frac{\partial^2 \alpha}{\partial T^2} &= \frac{1}{2} (\kappa^2 + \kappa) \frac{1}{\sqrt{T_c}} T^{-3/2} \end{aligned}$$

- For the Gaussian Process's framework without basis function, we have:

$$\alpha(x_*) = \mu(\alpha_*) = \mathbf{K}_*^T (\mathbf{K} + \sigma_n^2 \mathbf{I})^{-1} \alpha_{obs}$$

where  $\alpha_{obs}$  is the given observed data of  $\alpha$  from NIST or experimental data at specific temperatures and pressures. The right hand side (RHS) term  $(\mathbf{K} + \sigma_n^2 \mathbf{I})^{-1} \alpha_{obs}$  is known during the prediction of  $\alpha(x_*)$ , hence is denoted as  $\mathbf{m}$  here. For a single new evaluation point  $x_* = (T_{r,*}, P_{r,*})$ , the  $\mathbf{K}_*$  is matrix of dimension  $N \times 1$ , so:

$$\alpha = \sum_{i=1}^N k_{*,i} m_i$$

where

$$k_{*,i} = \sigma_F^2 \exp \left( -\frac{(T_{r,*} - T_{r,i})^2}{2\gamma_T^2} - \frac{(P_{r,*} - P_{r,i})^2}{\gamma_T^2} \right)$$

Thus,

$$\begin{aligned} \frac{\partial \alpha}{\partial T} &= \sum_{i=1}^N m_i \frac{\partial k_{*,i}}{\partial T} = \sum_{i=1}^N m_i \left( -\frac{1}{T_c} \frac{T_{r,*} - T_{r,i}}{\gamma_T^2} \right) k_{*,i} \\ \frac{\partial^2 \alpha}{\partial T^2} &= \sum_{i=1}^N m_i \frac{\partial^2 k_{*,i}}{\partial T^2} = \sum_{i=1}^N m_i \left( \frac{1}{T_c^2} \frac{(T_{r,*} - T_{r,i})^2}{\gamma_T^4} - \frac{1}{T_c^2} \frac{1}{\gamma_T^2} \right) k_{*,i} \end{aligned}$$

- For the Gaussian Process's framework with basis function, we have:

$$\alpha(x_*) = \mu(\alpha_*) = f(x_*; \theta) + \mathbf{K}_*^T \left( \mathbf{K} + \frac{\sigma_n^2}{\nu} \mathbf{I} \right)^{-1} [y - f(\mathbf{X}; \theta)]$$

Similarly, one can define the known RHS terms as  $\mathbf{m} = \left( \mathbf{K} + \frac{\sigma_n^2}{\nu} \mathbf{I} \right)^{-1} [y - f(\mathbf{X}; \theta)]$ , and  $\alpha = f(x_*; \theta) + \sum_{i=1}^N k_{*,i} m_i$ , with

$$k_{*,i} = k_0(x_*, x_i) - h_\theta(x_*)^T \mathbf{H}_\theta h_\theta(x_i)$$

where

$$\begin{aligned} h_\theta(x_*) &= \int_{\mathbf{X}} \nabla_\theta f(\xi) k_0(x_*, \xi) d\xi \\ h_\theta(x_i) &= \int_{\mathbf{X}} \nabla_\theta f(\xi) k_0(x_i, \xi) d\xi \end{aligned}$$

so  $\mathbf{H}_\theta h_\theta(x_i)$  is a known term and is hereby denoted as  $g_\theta(x_i) = [g_{i,1}, g_{i,2}, g_{i,3}]$ . Therefore,

$$\begin{aligned} k_{*,i} &= k_0(x_*, x_i) - h_\theta(x_*)^T g_\theta(x_i) = k_0(x_*, x_i) - g_{i,1} \sum_{j=1}^N k_0(x_*, x_j) - g_{i,2} \sum_{j=1}^N x_{j,1} k_0(x_*, x_j) - g_{i,3} \sum_{j=1}^N x_{j,2} k_0(x_*, x_j) \\ \frac{\partial k_{*,i}}{\partial T} &= \frac{\partial k_0(x_*, x_i)}{\partial T} - g_{i,1} \sum_{j=1}^N \frac{\partial k_0(x_*, x_j)}{\partial T} - g_{i,2} \sum_{j=1}^N \left[ x_{j,1} \frac{\partial k_0(x_*, x_j)}{\partial T} + \frac{\partial x_{j,1}}{\partial T} k_0(x_*, x_j) \right] - g_{i,3} \sum_{j=1}^N x_{j,2} \frac{\partial k_0(x_*, x_j)}{\partial T} \\ \frac{\partial^2 k_{*,i}}{\partial T^2} &= \frac{\partial^2 k_0(x_*, x_i)}{\partial T^2} - g_{i,1} \sum_{j=1}^N \frac{\partial^2 k_0(x_*, x_j)}{\partial T^2} - g_{i,2} \sum_{j=1}^N \left[ x_{j,1} \frac{\partial^2 k_0(x_*, x_j)}{\partial T^2} + 2 \frac{\partial x_{j,1}}{\partial T} \frac{\partial k_0(x_*, x_j)}{\partial T} \right] - g_{i,3} \sum_{j=1}^N x_{j,2} \frac{\partial^2 k_0(x_*, x_j)}{\partial T^2} \end{aligned}$$

And finally:

$$\frac{\partial \alpha}{\partial T} = \frac{\partial f}{\partial T} + \sum_{i=1}^N m_i \frac{\partial k_{*,i}}{\partial T}$$

$$\frac{\partial^2 \alpha}{\partial T^2} = \frac{\partial^2 f}{\partial T^2} + \sum_{i=1}^N m_i \frac{\partial^2 k_{*,i}}{\partial T^2}$$

## 2.5 Implementation

Reading Alpha related files:

```
setSpeciesCoeffs(species, a, b, w)
-> readAlphaPara(filename, BasisTheta, KernelGamma, KernelSigma)
-> readCSV(filename, para, nrow, ncol)
-> readAlphaData(filename, AlphaX, Alphay)
-> readCSV(filename, para, nrow, ncol)
```

The call stack for calculating density

```
ThermoPhase::setState_TP(t, p)
-> PengRobinsonAlphaGP::setTemperature(t)
-> Phase::setTemperature(t)
-> _updateReferenceStateThermo();
-> updateMixingExpressions();
-> mixAlpha()
-> calculateAB(a, b, aAlpha_mix)
-> PengRobinsonAlphaGP::setPressure(p)
-> densityCalc(t, p, FLUID_PHASE, rhoNow)
-> updateAlpha(t, p)
-> setTemperature(t)
-> solveCubic(t, p, a, b, aAlpha_mix, Vroot)
```

## 2.6 Validation

## 3. Appendix

Using the chain rule from Table 5, Page 4 of [Partial derivatives of thermodynamic state properties for dynamic simulation](#),

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial H}{\partial T} \right)_V - \left( \frac{\partial H}{\partial V} \right)_T \left( \frac{\partial p}{\partial T} \right)_V \left( \frac{\partial p}{\partial V} \right)_T^{-1}$$

where

$$\begin{aligned}
\left(\frac{\partial H}{\partial T}\right)_V &= \left(\frac{\partial F}{\partial T}\right)_V - \left(\frac{\partial F}{\partial T}\right)_V - T\left(\frac{\partial^2 F}{\partial T^2}\right)_V - V\left(\frac{\partial^2 F}{\partial V\partial T}\right)_{T,V} \\
&= -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V - V\left(\frac{\partial^2 F}{\partial V\partial T}\right)_{T,V} \\
\left(\frac{\partial H}{\partial V}\right)_T &= \left(\frac{\partial F}{\partial V}\right)_T - T\left(\frac{\partial^2 F}{\partial T\partial V}\right)_{V,T} - \left(\frac{\partial F}{\partial V}\right)_T - V\left(\frac{\partial^2 F}{\partial V^2}\right)_T \\
&= -T\left(\frac{\partial^2 F}{\partial T\partial V}\right)_{V,T} - V\left(\frac{\partial^2 F}{\partial V^2}\right)_T \\
\left(\frac{\partial p}{\partial T}\right)_V &= -\left(\frac{\partial^2 F}{\partial V\partial T}\right)_{T,V} \\
\left(\frac{\partial p}{\partial V}\right)_T &= -\left(\frac{\partial^2 F}{\partial V^2}\right)_T
\end{aligned}$$

therefore,

$$\begin{aligned}
C_p &= \left(\frac{\partial H}{\partial T}\right)_V - \left(\frac{\partial H}{\partial V}\right)_T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial p}{\partial V}\right)_T^{-1} \\
&= -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V - V\left(\frac{\partial^2 F}{\partial V\partial T}\right)_{T,V} + \left[ T\left(\frac{\partial^2 F}{\partial T\partial V}\right)_{V,T} + V\left(\frac{\partial^2 F}{\partial V^2}\right)_T \right] \left(\frac{\partial^2 F}{\partial V\partial T}\right)_{T,V} / \left(\frac{\partial^2 F}{\partial V^2}\right)_T \\
&= -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V + T\left(\frac{\partial^2 F}{\partial T\partial V}\right)_{V,T} \left(\frac{\partial^2 F}{\partial V\partial T}\right)_{T,V} / \left(\frac{\partial^2 F}{\partial V^2}\right)_T \\
&= T \left[ \left(\frac{\partial^2 F}{\partial V\partial T}\right)_{V,T}^2 / \left(\frac{\partial^2 F}{\partial V^2}\right)_T - \left(\frac{\partial^2 F}{\partial T^2}\right)_V \right]
\end{aligned}$$