# An Algorithm for Avoiding Trivial Solution Using Inflection Point

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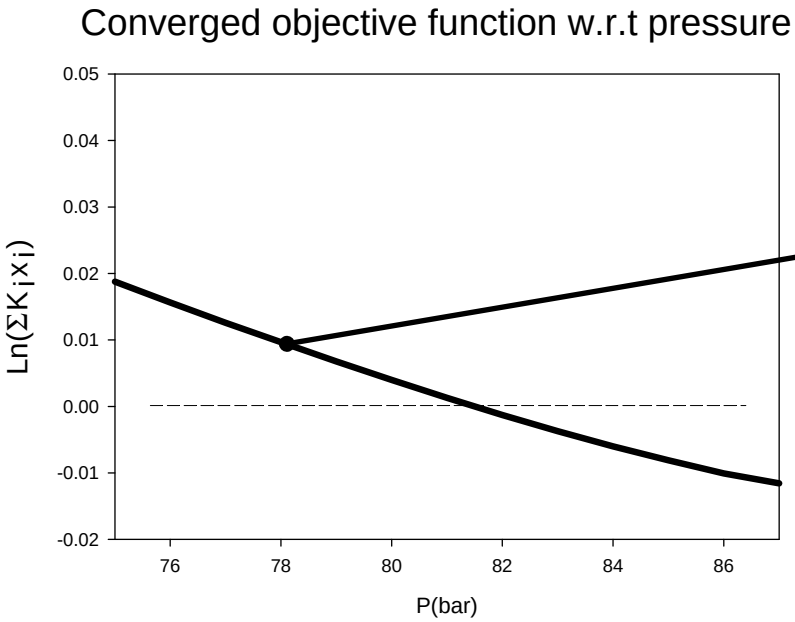
# Trivial Solution in VLE



Outer Loop : Finding equilibrium condition using numerical methods




Inner Loop

Obtaining converged objective function (or composition) for given conditions.

Ex) For Bubble P

$T, P^{guess}, x_i \rightarrow \blacksquare\ y_i^{con}$

But at near critical point, **False solution** occurs (**TS : Trivial solution**)

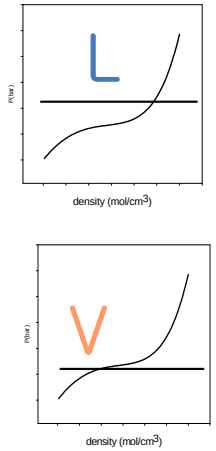
# Trivial Solution in inner Loop

**Given condition**

At $T, P, x_i, y_i^{ini}$

Equation of State

**EOS Solving**




**Thermo Variables**

Possibility owing to initial value

$\Phi_i^L \approx \Phi_i^V$

**Iteration(Inner Loop)**

$y_i^{new}$ for Bubble

$x_i^{new}$ for Dew

$y_i^{new}$ or $x_i^{new}$ Converge?

No

Yes

**False Result**

$y_i = x_i$ after iteration

$\mu_i^L = \mu_i^V$

# TS in subcritical region



If **phase density limit** is not given, TS may occurs at low temperature

Case 1 : For $P_{High}$

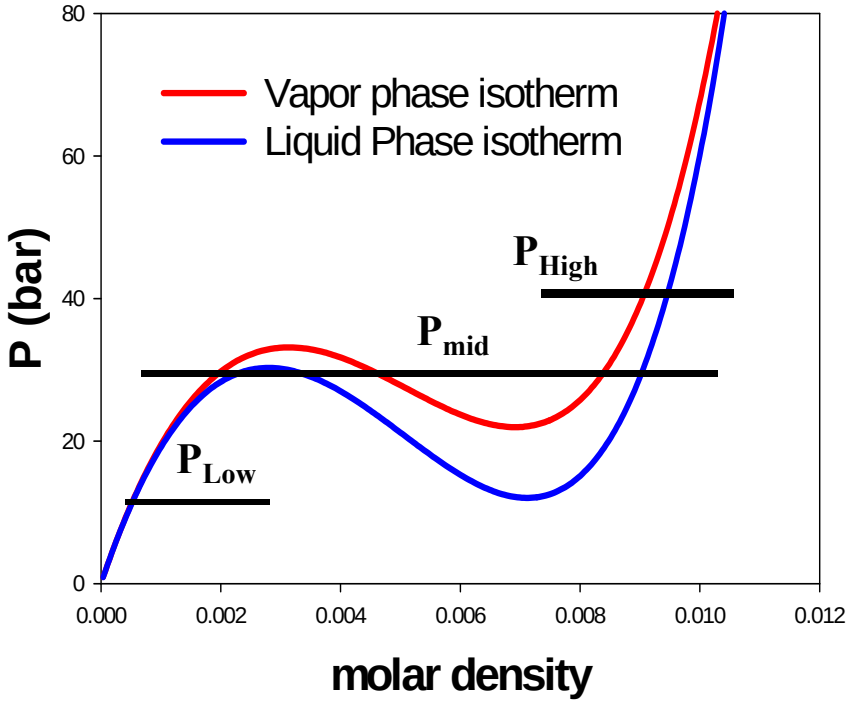
$\rho^V$ ⏲ $\rho^L$ (**liquid like** vapor density)

Case 2 : For $P_{low}$

$\rho^L$ ⏲ $\rho^V$ (**vapor like** liquid density)

Case 3 : For $P_{mid}$

$\rho^L \neq \rho^V$



# Phase limit in subcritical region

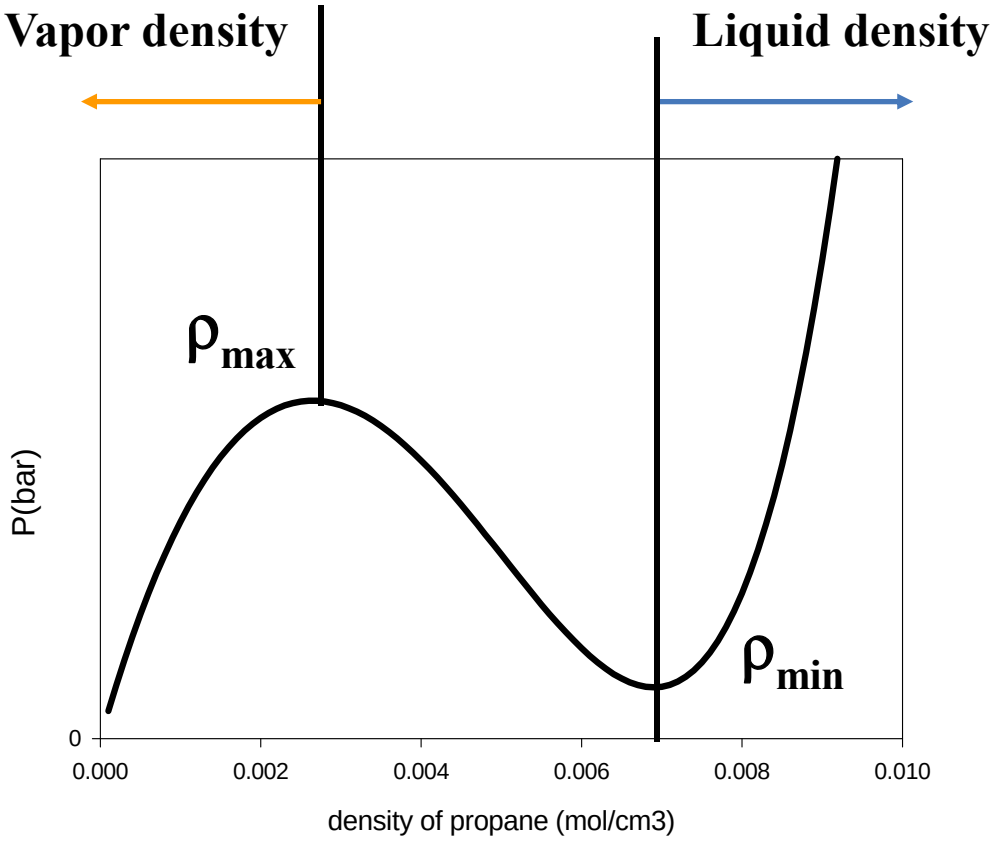
**Limit of phase density**

- **Vapor phase**

  $0 < \rho^{V} < \rho_{max}$

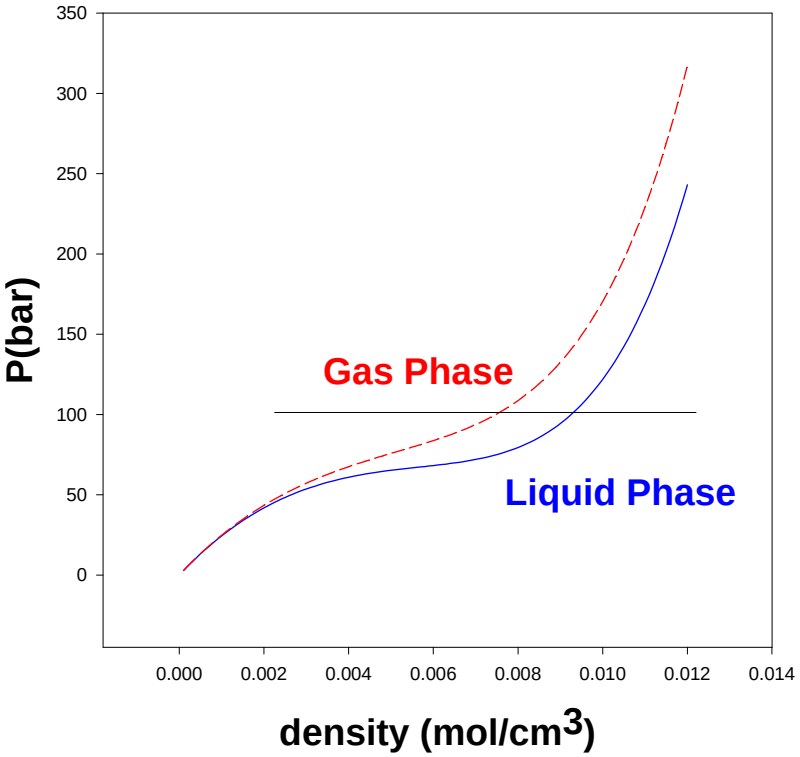
- **Liquid phase**

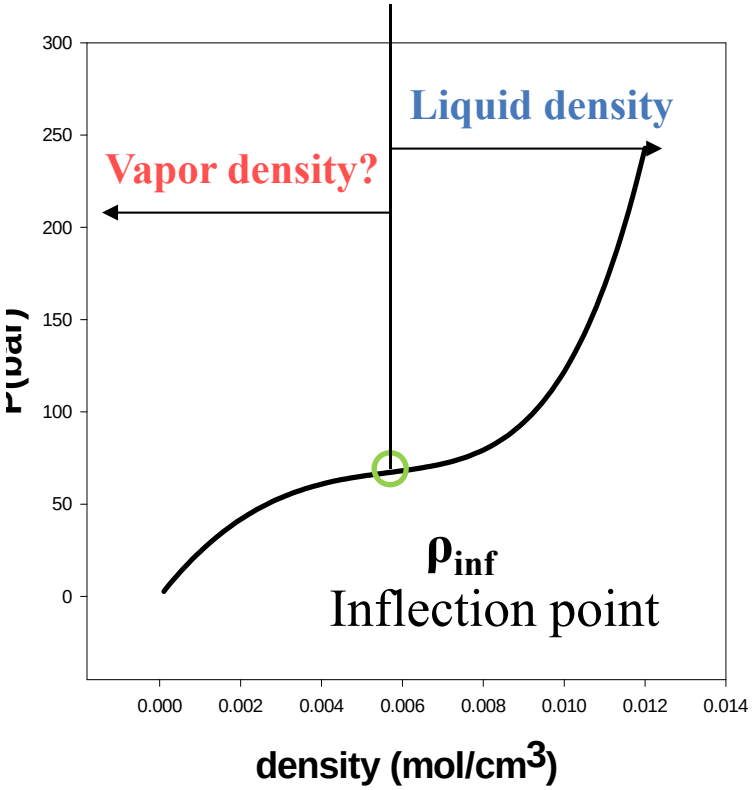
  $\rho^{L} > \rho_{min}$



# Phase limit in supercritical region






## Inflection point

- Vapor phase : $\rho_{inf} < \rho_L$ (almost)
- Liquid Phase : $\rho_{inf} > \rho_V$ (not always)

# TS in inner-loop

- **Aim of Inner-Loop**

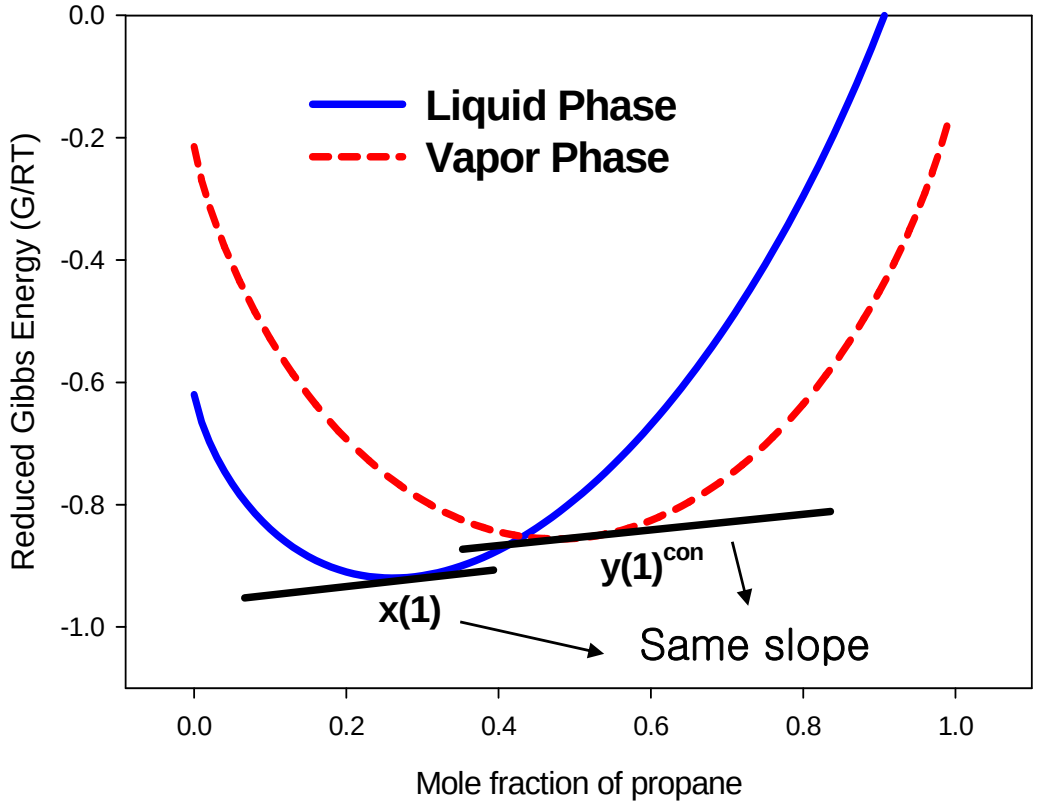
  To find converged composition.

- **Sufficient-Necessary condition of Convergence**

$$\mu_1^L - \mu_2^L = \mu_1^V - \mu_2^V$$

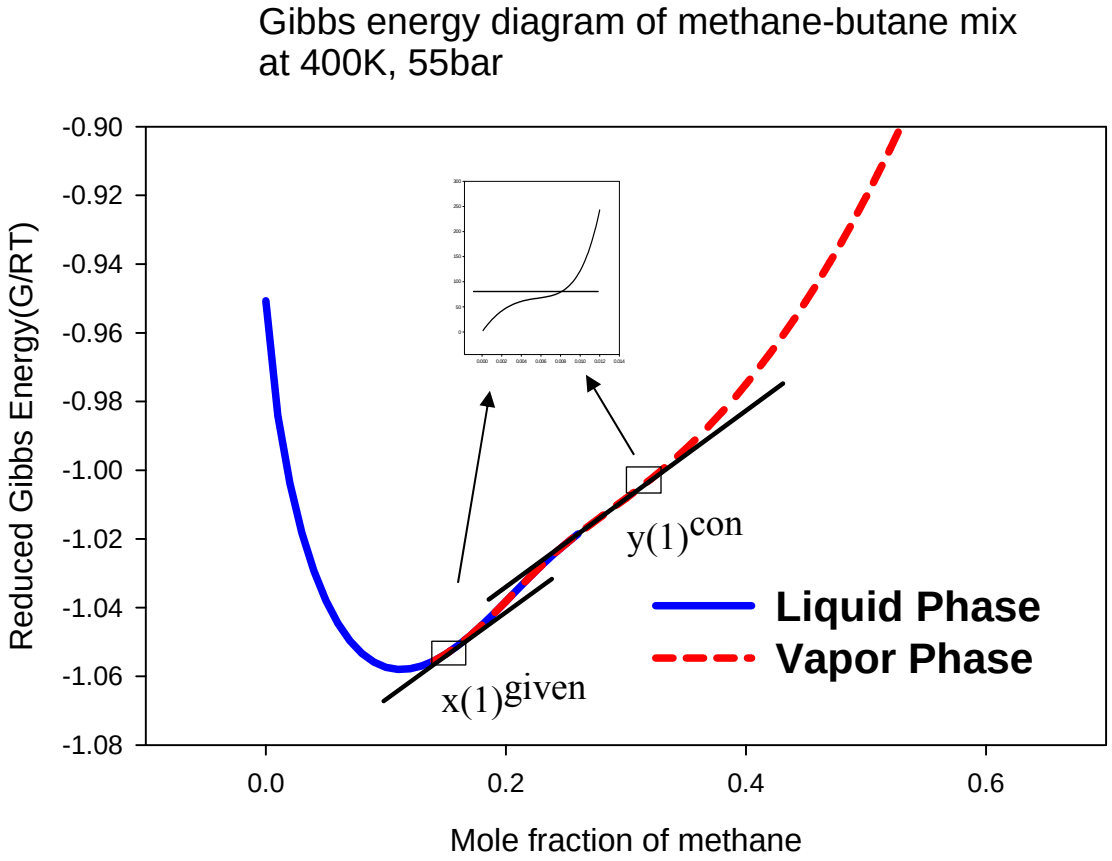
$$dG^L/dx_1 = dG^V/dy_1$$

Interpretation of Inner Loop in Gibbs energy diagram



# TS occurs in inner loop?

❑ Case I : Owing to **bad initial value** (at supercritical T)



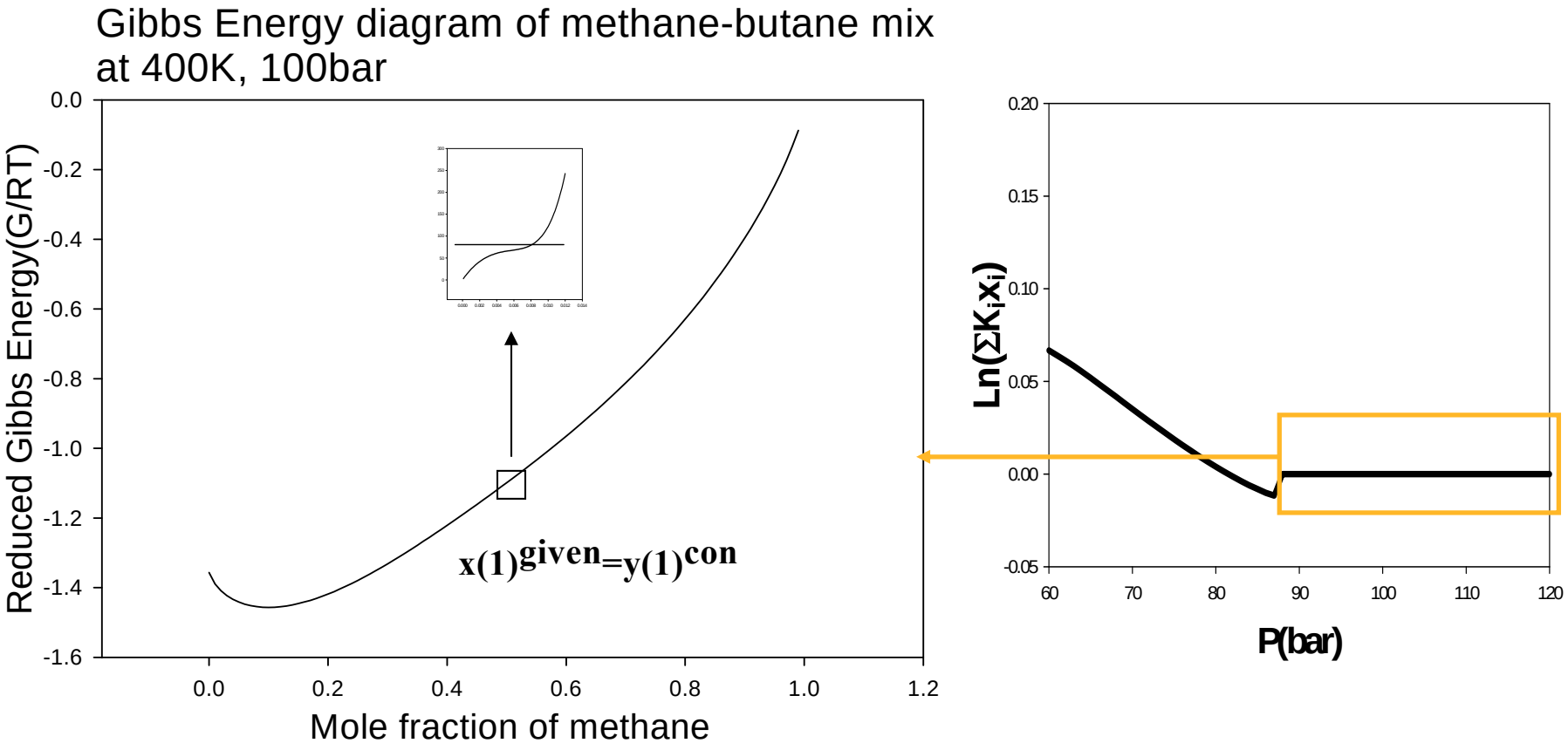

IF $y(1)^{ini}$ is **not far from** $x(1)^{given}$,

$y(1)^{con}$ may **converges** to $x(1)^{given}$ in Inner-Loop

# TS occurs in inner loop?



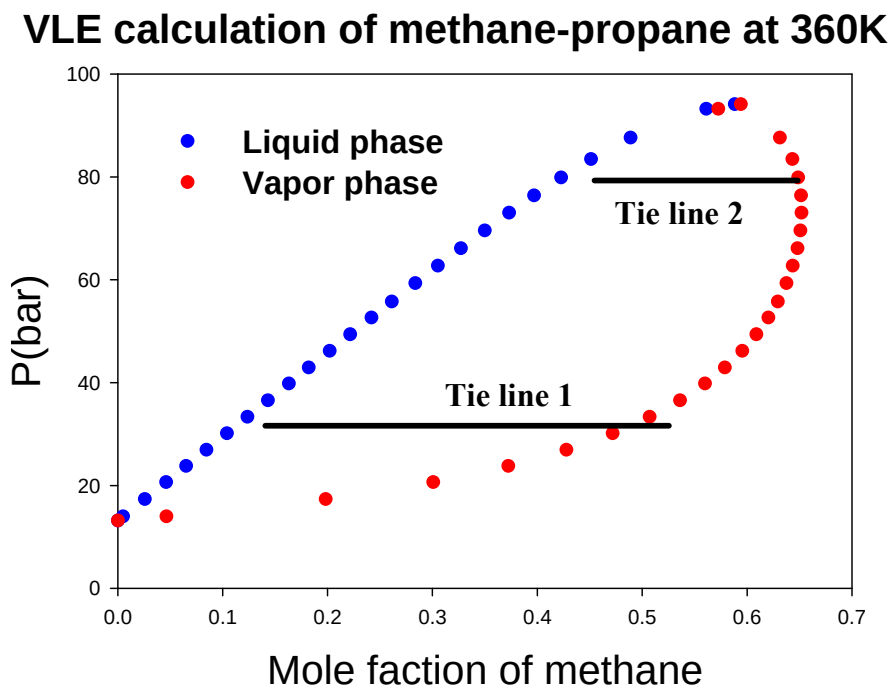
- Case II : **Single Phase** at given condition

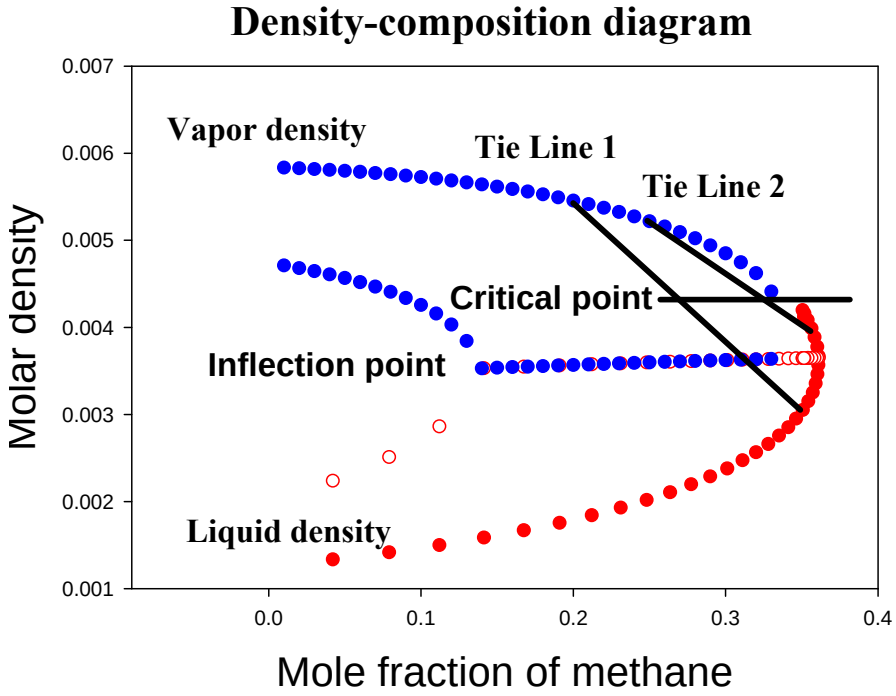


# How to avoid TS ? Inflection point



## ❑ Requirements of Limit of vapor density



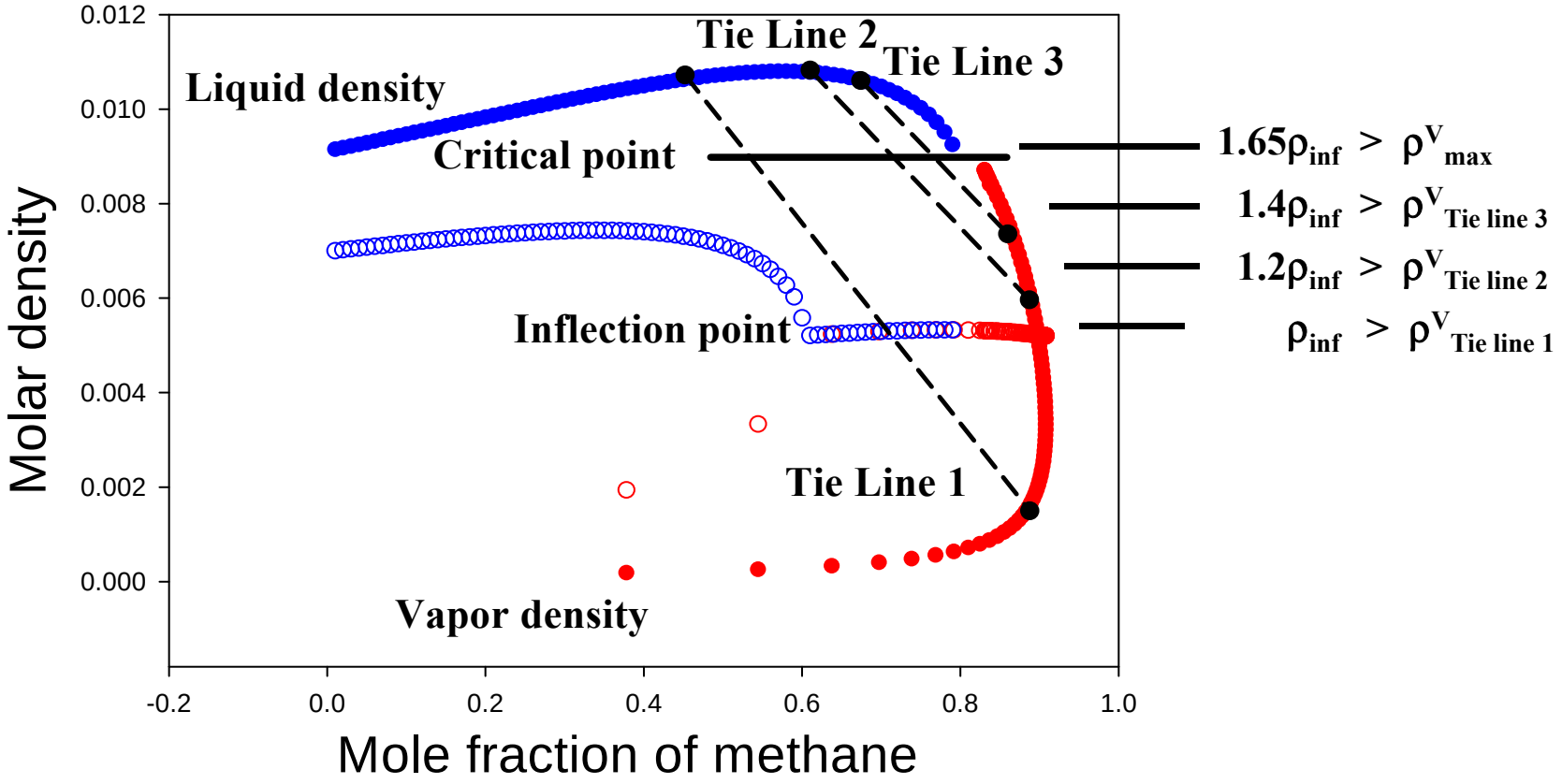

For Tie line 1: **Inflection point** as vapor density limit

Tie line 2: **Increased inflection point** as vapor density limit

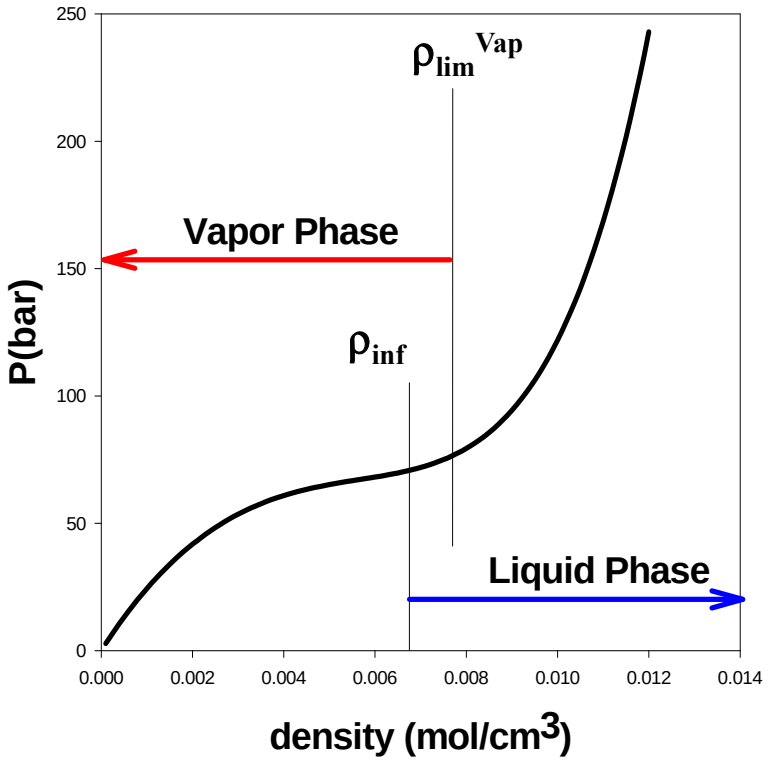
# How to avoid TS ? Inflection point



Density-composition diagram of methane-butane at 300K with SRK EOS



# Pseudo density




- Vapor phase,

  if $P > P_{lim}^{V}$

  $\rho_{pseudo}^{V} = \rho_{lim}^{V}$

  $$\mu_i^V = \mu_i^V(\rho_{\lim}^V) + RT\ln(\frac{P}{P(\rho_{\lim}^V)})$$

- Liquid phase,

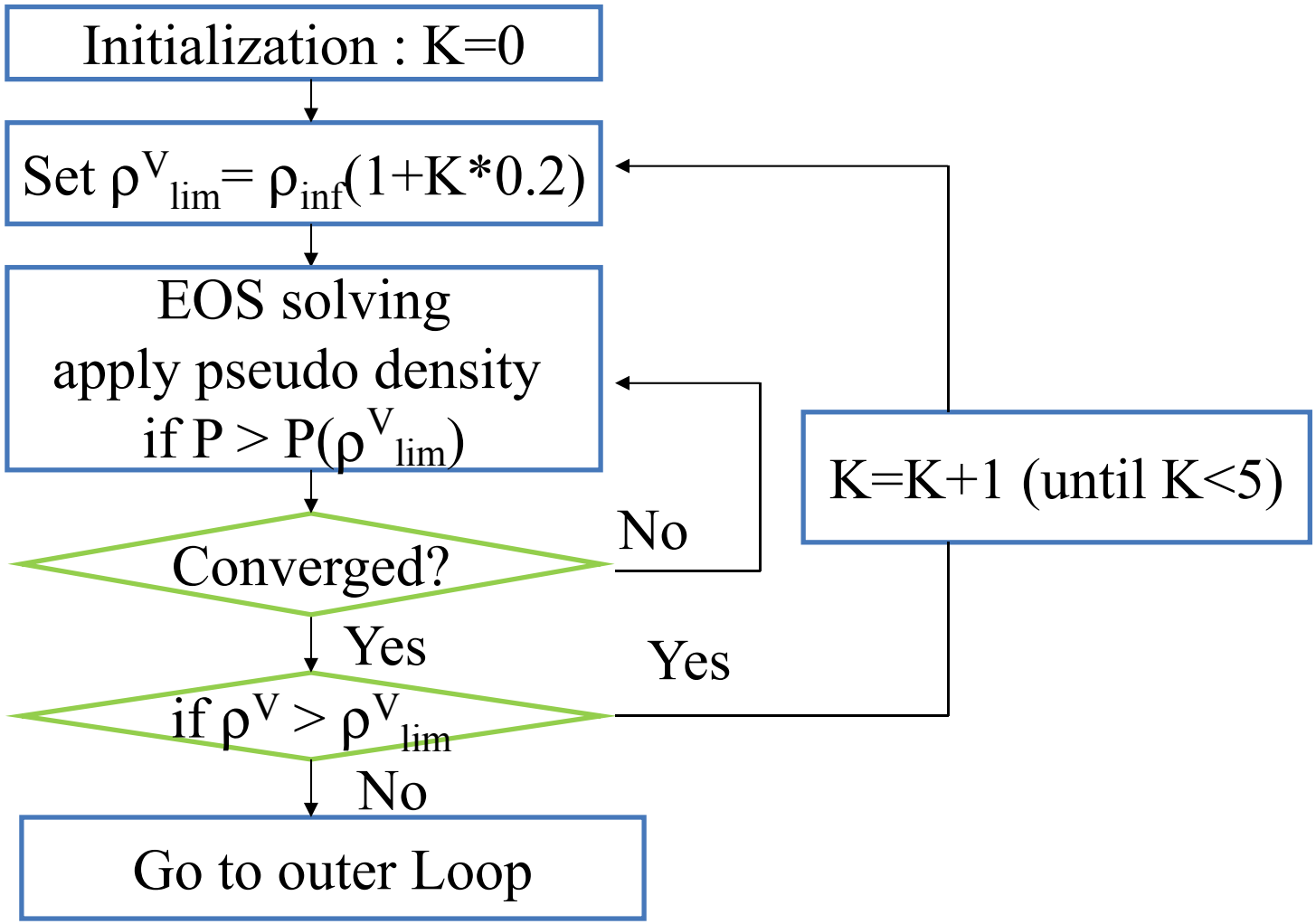
  if $P < P_{inf}$

  $\rho_{pseudo}^{L} = \rho_{inf}$

  $$\mu_i^V = \mu_i^L(\rho_{\inf}^L)$$

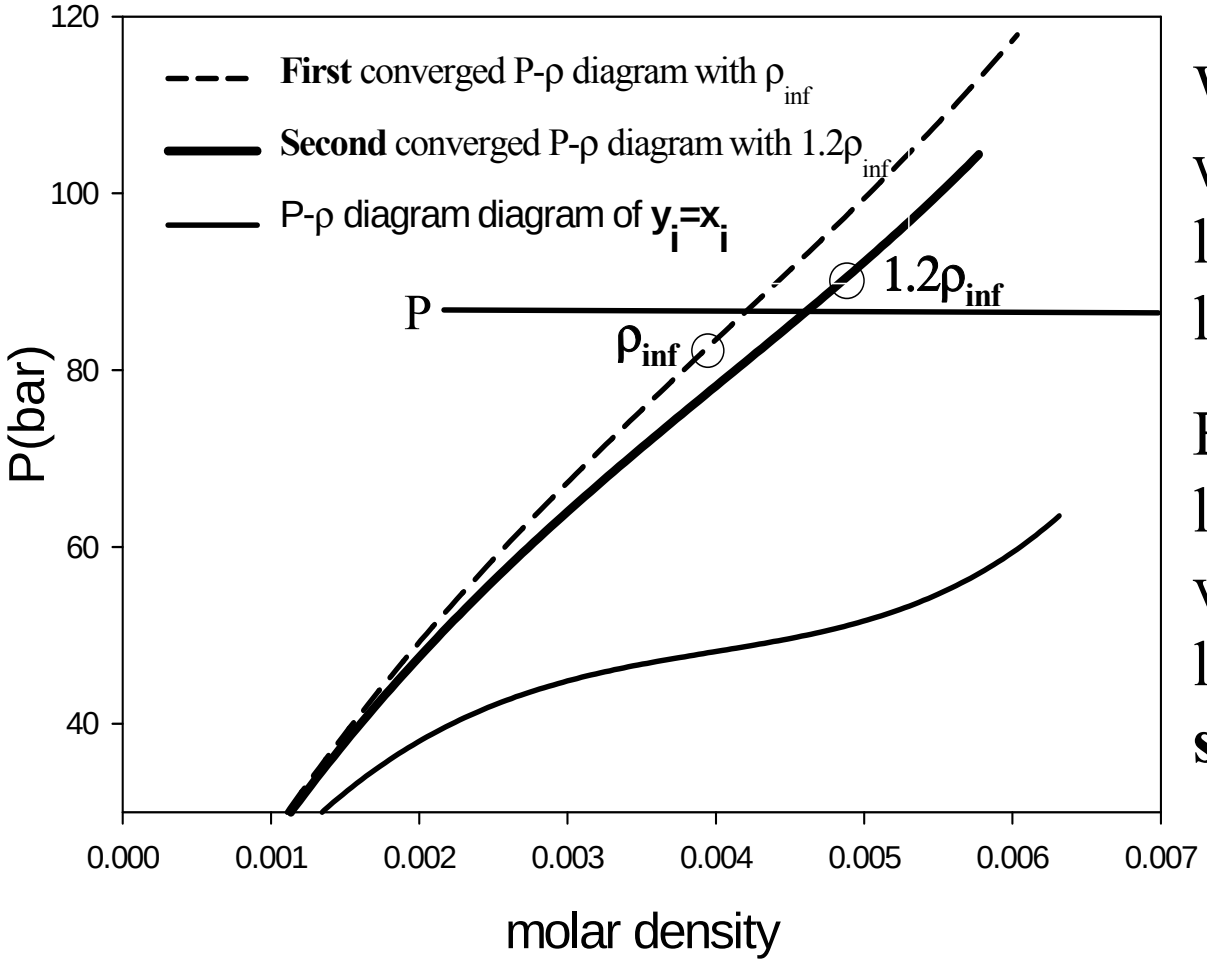
# Step for avoiding TS

- Increases of vapor density limit from inflection point



# Examples :

## Effect of increasement of vapor density limit




When **inflection point** was used as vapor density limit, vapor density is likely to exceed **its limit**.

But when vapor density limit increase by 20%, vapor density is below its limit, **genuine converged status** not **TS**

# Result : Initialization



- Initialization of P and $y_i$ in Bubble P calculations

  - $P^{ini} = \Sigma x_i P_i^s$

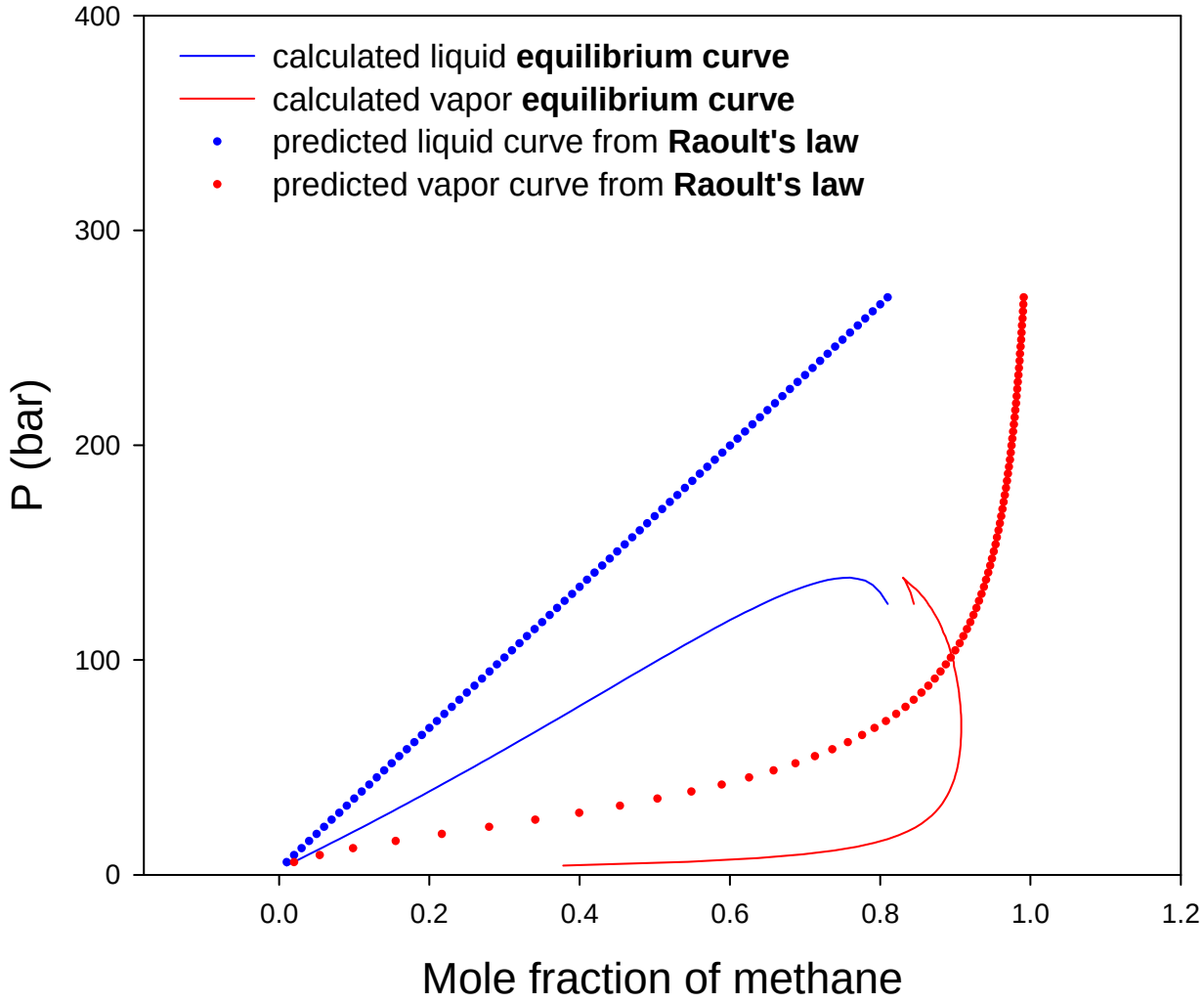
$$\frac{\ln P_i^s - \ln P_{b,i}}{\ln P_{c,i} - \ln P_{b,i}} = \frac{1/T_o - 1/T_{b,i}}{1/T_{c,i} - 1/T_{b,i}}$$

  - $y_i^{ini} = \varphi_i^L / \varphi_i^V$ ($\varphi_i$ : fugacity coefficient of pure components)

# Result : 300K



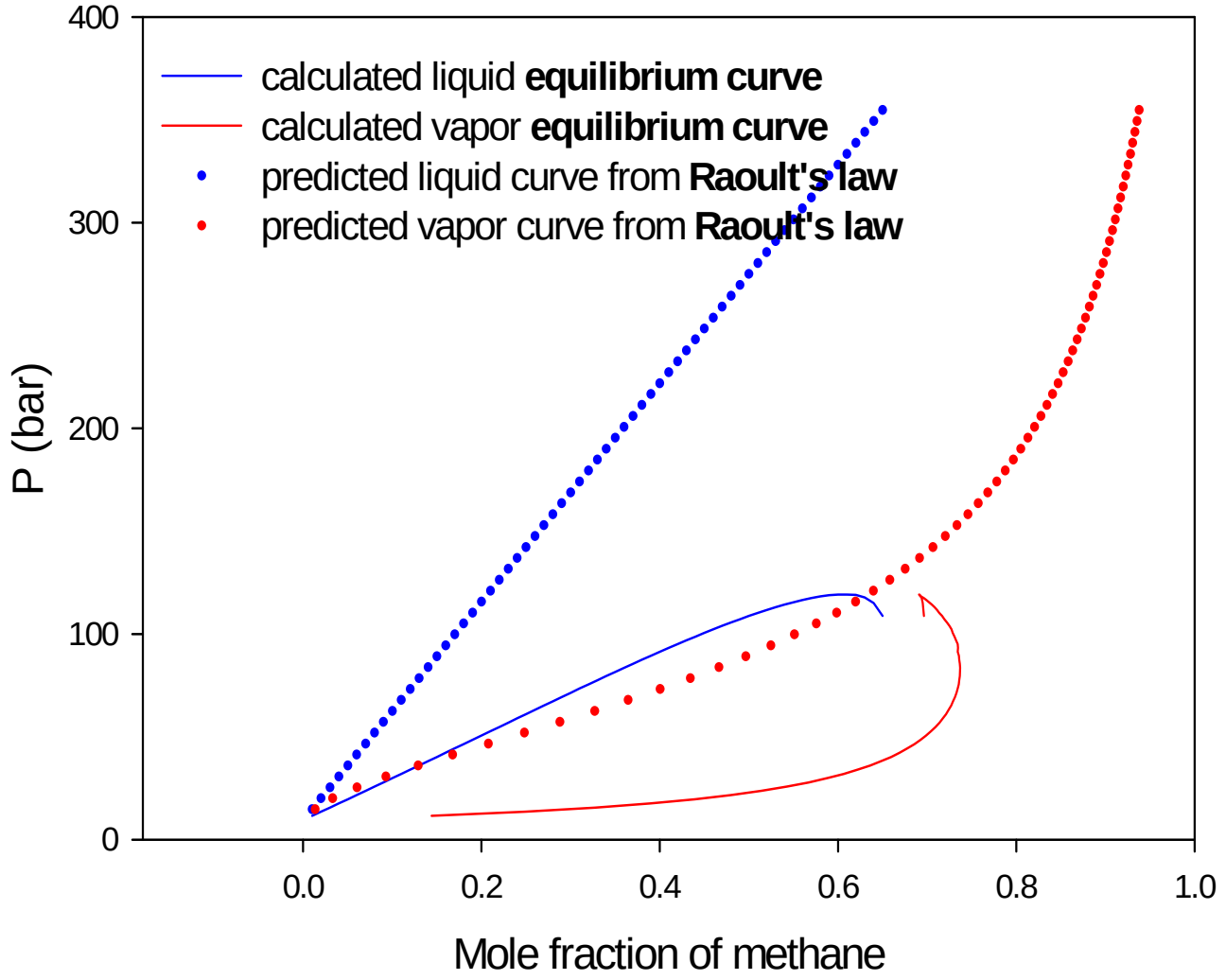
Predicted Equilibrium curve using suggested algorithm



# Result : 350K



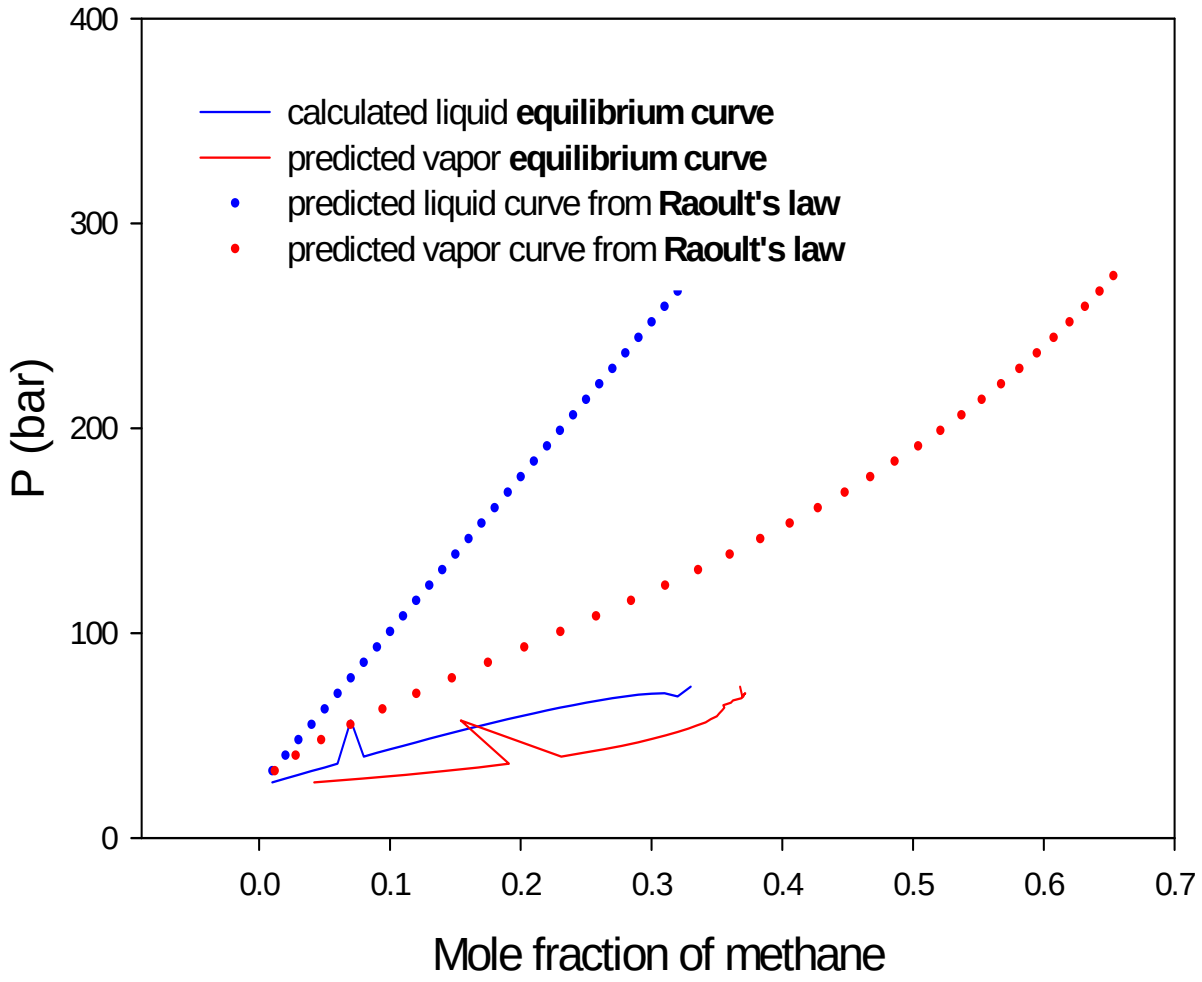
Predicted Equilibrium curve using suggested algorithm



# Result : 400K



Predicted Equilibrium curve using suggested algorithm



# Conclusion



- The reason why TS occurs according to initial variables was shown by Gibbs energy diagram.
- By expanding vapor phase density limit based on inflection point and **pseudo density routine**, genuine converged objective function was obtained regardless of initial value, and this routine works well with calculation for high pressure equilibria