Nonsmooth Modeling and Optimization of LNG Processes

Paul I. Barton

Process Systems Engineering Laboratory
MIT

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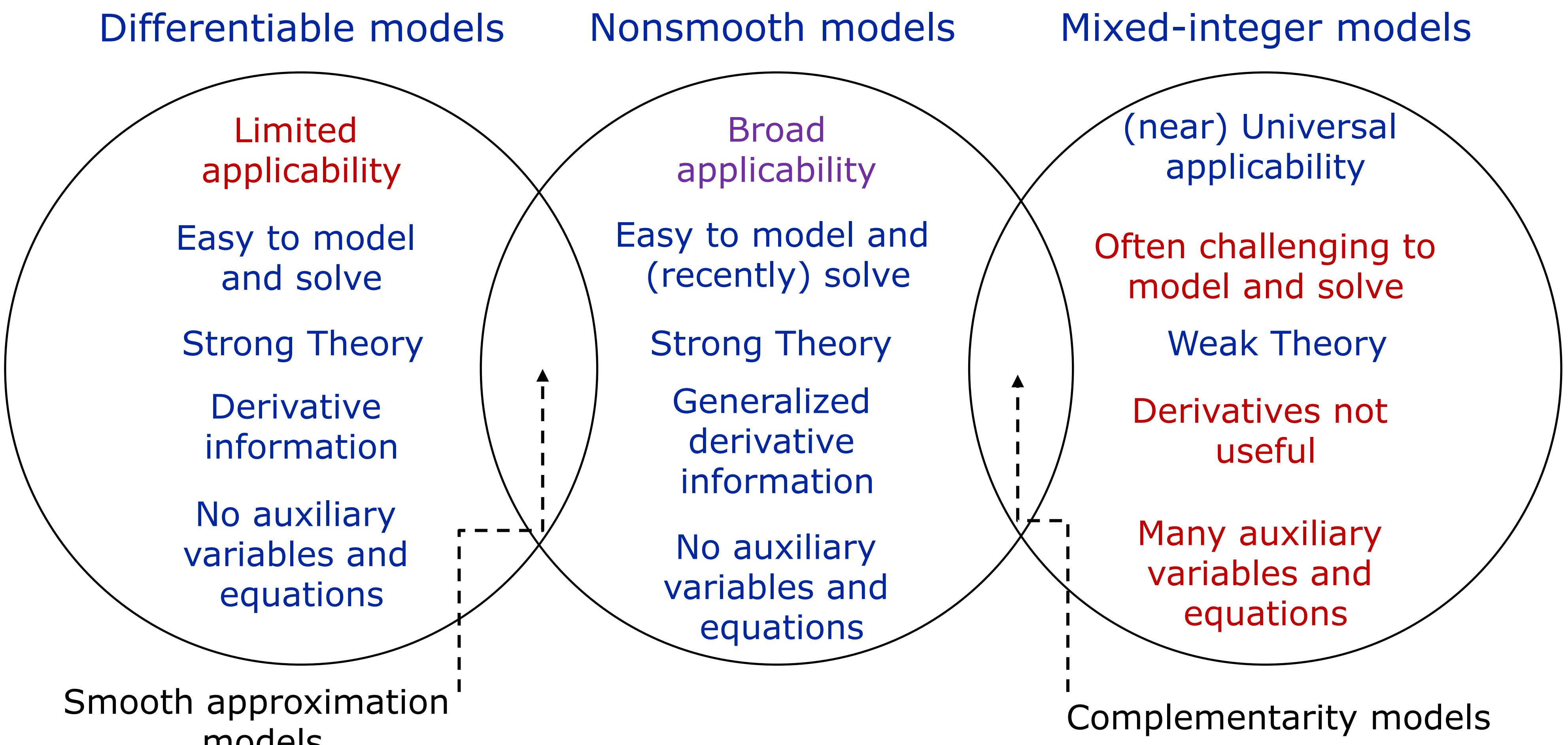
Modeling in Process Systems Engineering

- Trade-off: applicability vs. ease of modeling & solving



Modeling Approaches in PSE

- Nonsmooth equations are a compact and natural modeling framework for many applications that cannot be fully-described by differentiable models
  - No nonphysical variables
  - No nonphysical constraints

Check Valve Flow

$$F = \max\{0, f(\Delta P)\}$$

$$F = f(\Delta P) + s_B$$
$$f(\Delta P) = s_A - s_B$$
$$0 \le s_A \perp s_B \ge 0$$

$$f^L \le f(\Delta P) \le f^U$$
$$F \ge 0,\ F \ge f(\Delta P)$$
$$F \le f^U(1-y_1),\ F \le f(\Delta P) + (f^U - f^L)(1-y_2)$$
$$y_1 + y_2 = 1,\ \mathbf{y} \in \{0,1\}^2$$

Equilibrium Calculations

$$\operatorname{mid}\left\{\frac{V}{F},\ \sum_{i=1}^{n_c} x_i - \sum_{i=1}^{n_c} y_i,\ \frac{V}{F} - 1\right\} = 0$$

$$y_i = \beta k_i x_i,\ \forall i$$
$$\beta - 1 = s_V - s_L$$
$$0 \le L \perp s_L \ge 0$$
$$0 \le V \perp s_V \ge 0$$

$$\begin{bmatrix} V = 0 \\ L > 0 \\ \sum_{i=1}^{n_c} x_i \ge \sum_{i=1}^{n_c} y_i \end{bmatrix} \veebar \begin{bmatrix} V > 0 \\ L > 0 \\ \sum_{i=1}^{n_c} x_i = \sum_{i=1}^{n_c} y_i \end{bmatrix} \veebar \begin{bmatrix} V > 0 \\ L = 0 \\ \sum_{i=1}^{n_c} x_i \le \sum_{i=1}^{n_c} y_i \end{bmatrix}$$

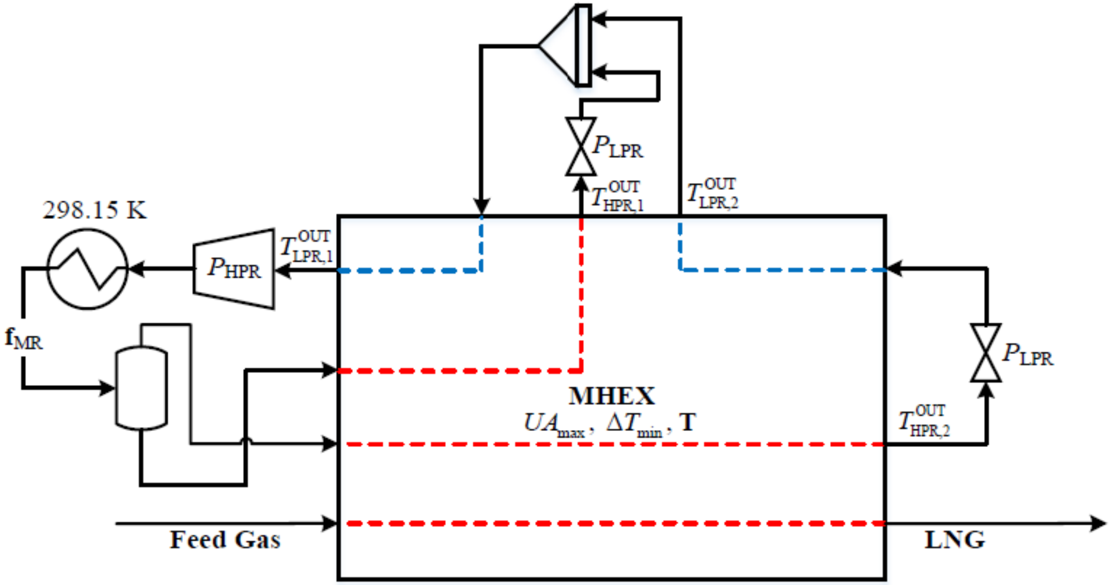
Heat Transfer Feasibility

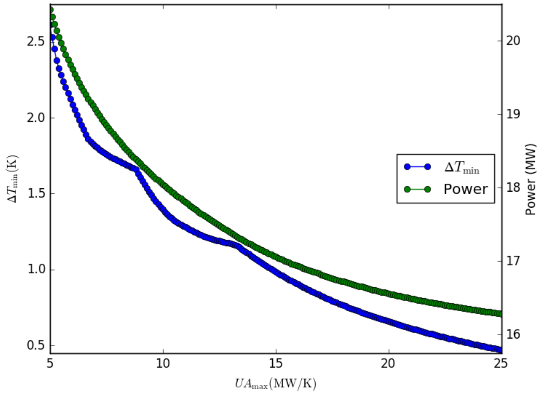
$$\max\{0, T_i^{\text{in}} - T^p\} - \max\{0, T_i^{\text{out}} - T^p\}$$

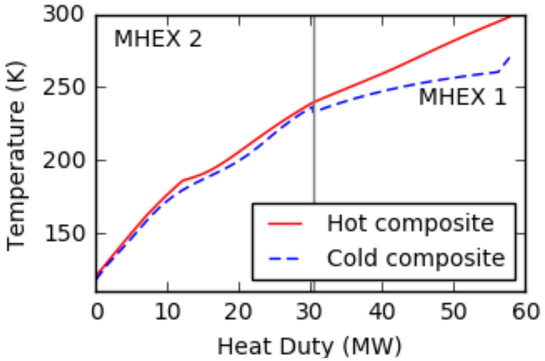
$$\frac{\sqrt{\left(T_i^{\text{in}} - T^p\right)^2 + \beta^2} + T_i^{\text{in}} - T^p}{2} - \frac{\sqrt{\left(T_i^{\text{out}} - T^p\right)^2 + \beta^2} + T_i^{\text{out}} - T^p}{2}$$

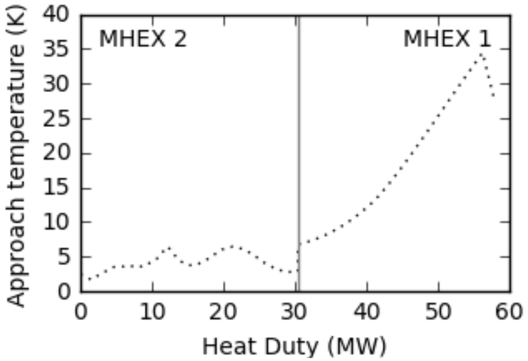
$$T_i^{\text{in}} \ge T_k^{\text{in}} - M(1 - w_{k,i}^1),$$
$$T_i^{\text{out}} \ge T_k^{\text{in}} - M(1 - w_{k,i}^1),$$
$$w_{k,i}^1 \in \{0,1\},$$
$$\vdots$$

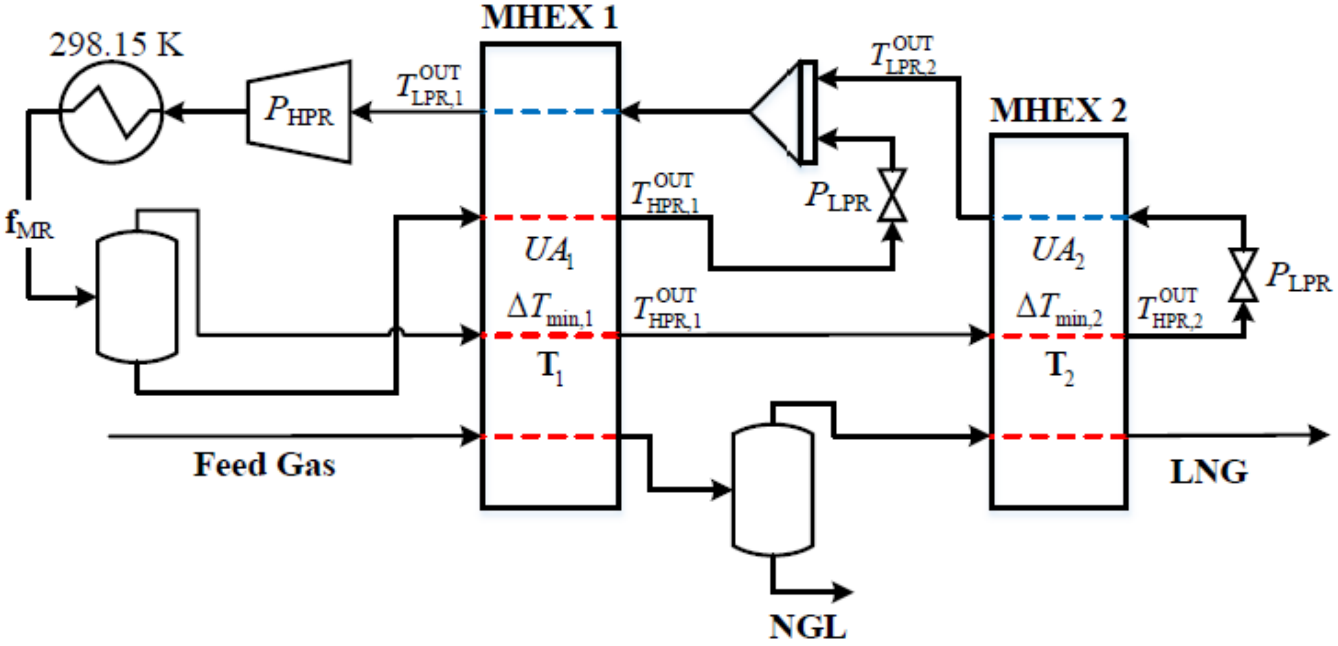
LNG Process Simulation & Optimization





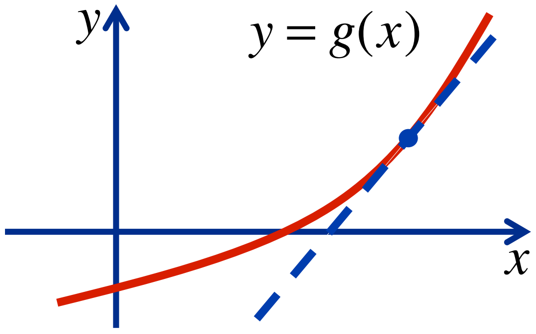


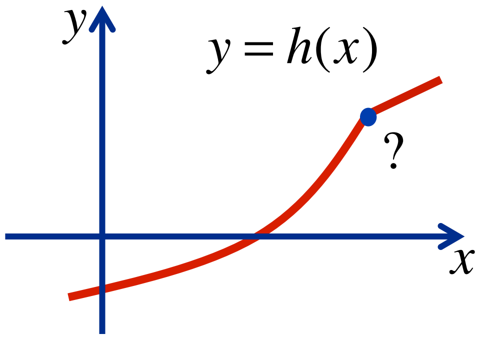




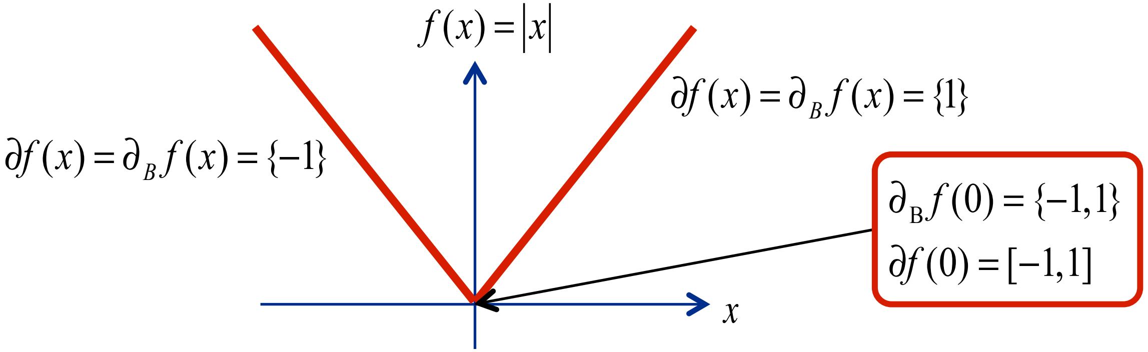
Working with Nonsmooth Functions

- Methods for smooth equation solving and optimization often make use of derivative information
  - e.g. Newton's method:





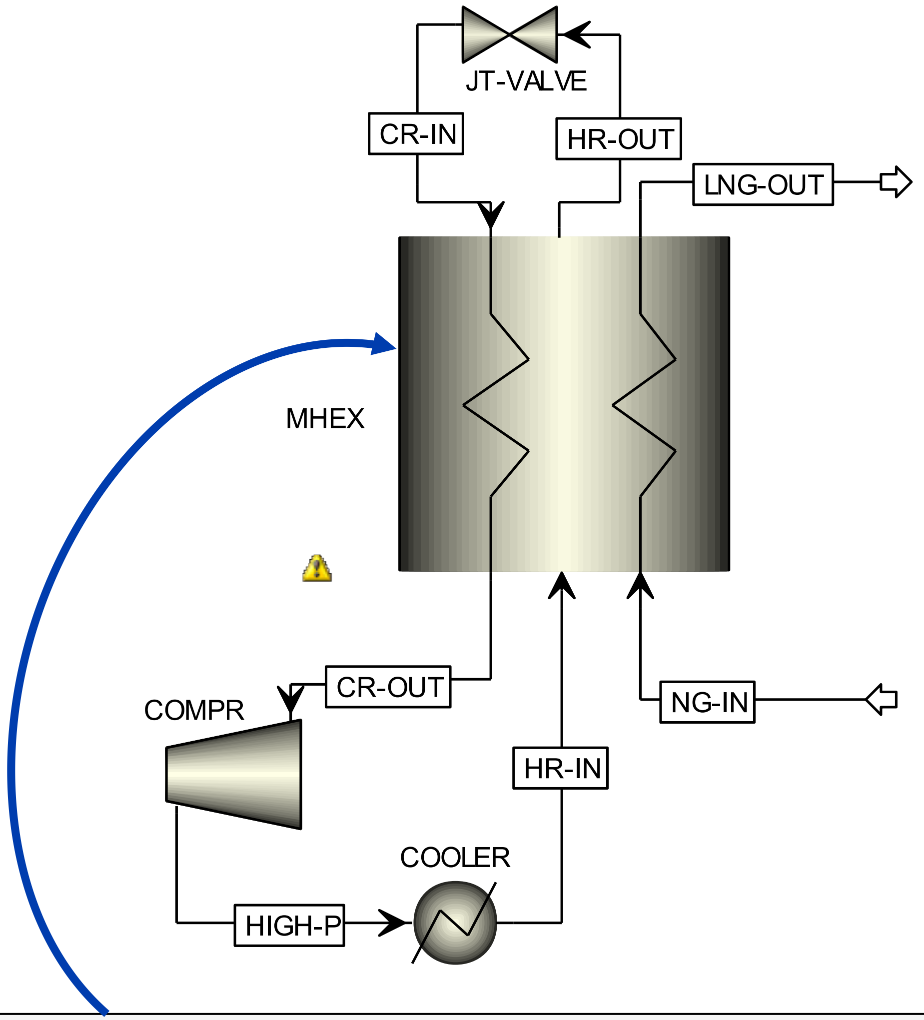
- Analogous methods for nonsmooth systems need generalized derivatives instead

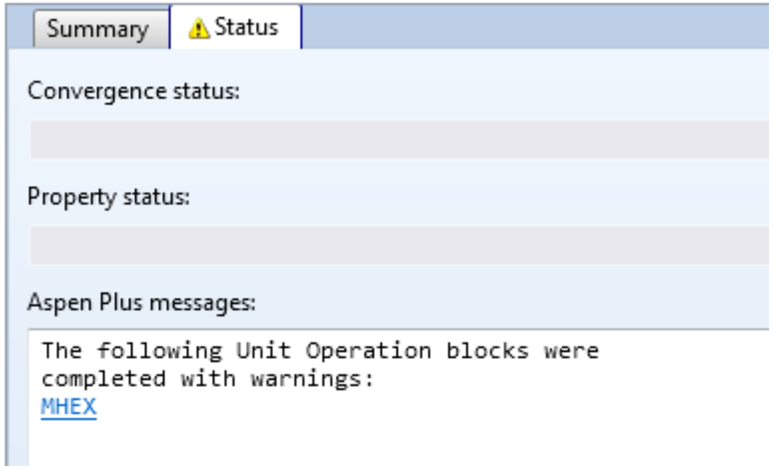


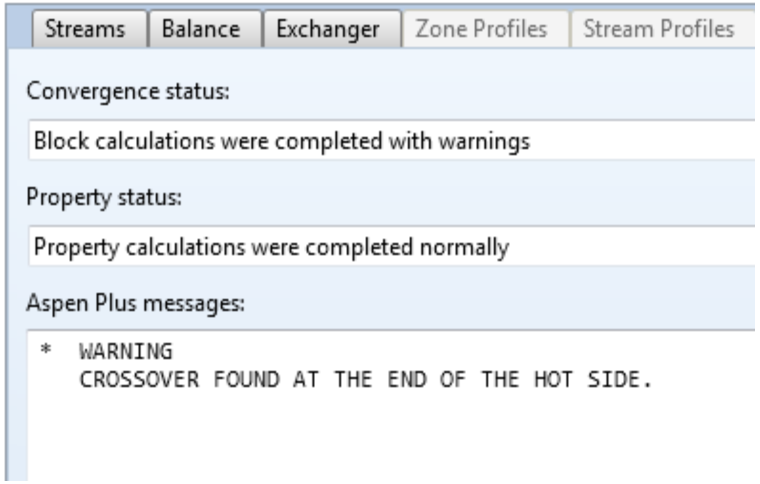
- For most nonsmooth functions, elements of these objects can be calculated using a new variant of automatic differentiation (AD)

K. A. Khan, and P. I. Barton, 2015. A vector forward mode of automatic differentiation for generalized derivative evaluation. Optimization Methods and Software. 30(6):1185-1212.

Limitations of Commercial Software







Input: Pressures, compositions, and all-but-one of the temperatures around the MHEX
Output: The single unknown outlet temperature

Heat Exchanger Modeling

$$F_{C_p}\left(T^{\text{in}} - T^{\text{out}}\right) = f_{C_p}\left(t^{\text{out}} - t^{\text{in}}\right)$$

$$\Delta T_{\min} = \min\left\{T^{\text{in}} - t^{\text{out}}, T^{\text{out}} - t^{\text{in}}\right\}$$

$$Q = UA\Delta T_{LM}$$

- Minimum temperature difference ($\Delta T_{\min}$)
- Total heat transferred (Q)
- Heat transfer coefficient (U)
- Heat transfer area (A)
- Log-mean temperature difference (ΔT_{LM})

Multistream Heat Exchanger Modeling

First Law feasibility:

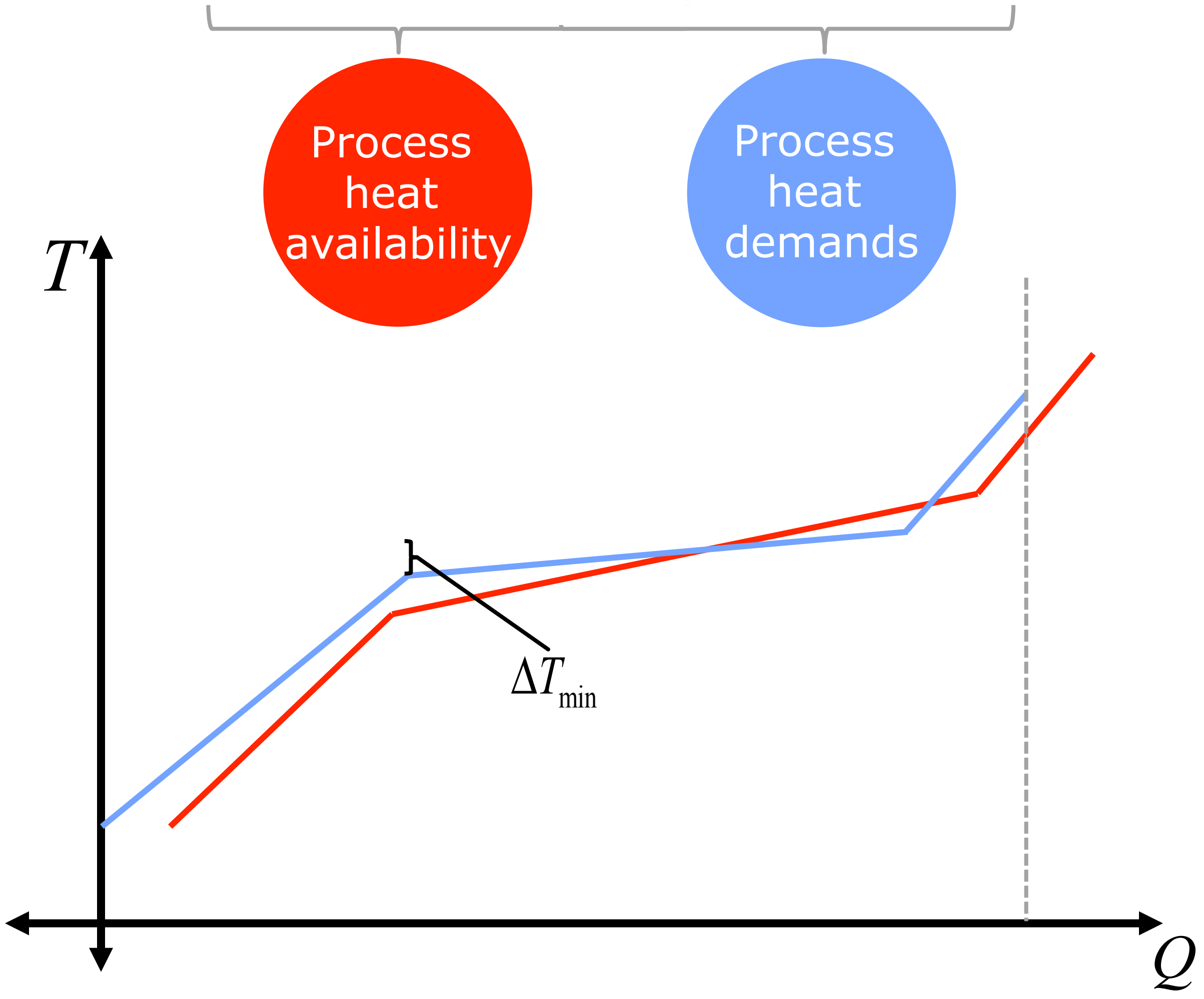
$$\sum_{i \in H} F_{C_p,i}\left(T_i^{\text{in}} - T_i^{\text{out}}\right) = \sum_{j \in C} f_{C_p,j}\left(t_j^{\text{out}} - t_j^{\text{in}}\right)$$

How is Second Law feasibility enforced?

How is the physical area linked with the heat transferred?

Pinch Analysis Approach to MHEX Modeling

- MHEX = (heat integration problem) – (external utilities)



First Law of Thermodynamics

Second Law of Thermodynamics

Enforce feasibility by solving a nonsmooth equation defined by a (modified) pinch location algorithm

$$\min_{p \in P}\left(EBP_C^p - EBP_H^p\right) = 0$$

R. S. Kamath, L. T. Biegler, I. E. Grossmann, 2012. Modeling multistream heat exchangers with and without phase changes for simultaneous optimization and heat integration. AIChE Journal 58 (1), 190–204.

Models for Pinch Location

MINLP Formulation

$$Q_{\mathrm{H}} + \sum_{i\in H} Q_{\mathrm{HOT}_i} = Q_C + \sum_{j\in C} Q_{\mathrm{COLD}_j},$$
$$Q_{\mathrm{H}} \geq \sum_{j\in C} q_{kj}^{hp} - \sum_{i\in H} q_{ki}^{hp}, \quad \forall k\in H,$$
$$Q_{\mathrm{H}} \geq \sum_{j\in C} q_{lj}^{cp} - \sum_{i\in H} q_{li}^{cp}, \quad \forall l\in C,$$
$$Q_{\mathrm{HOT}_i} = F_i c_{\mathrm{p},i}(T_{i,\mathrm{in}} - T_{i,\mathrm{out}}), \quad \forall i\in H,$$
$$Q_{\mathrm{COLD}_j} = F_j c_{\mathrm{p},j}(T_{j,\mathrm{out}} - T_{j,\mathrm{in}}), \quad \forall j\in C,$$
$$q_{ki}^{hp} - Q_{\mathrm{HOT}_i} \leq U(1-w_{ki}^1), \quad \forall(i,k)\in H\times H,$$
$$T_{i,\mathrm{in}} \geq T_{k,\mathrm{in}} - M(1-w_{ki}^1), \quad \forall(i,k)\in H\times H,$$
$$T_{i,\mathrm{out}} \geq T_{k,\mathrm{in}} - M(1-w_{ki}^1), \quad \forall(i,k)\in H\times H,$$
$$q_{ki}^{hp} - F_i c_{\mathrm{p},i}(T_{i,\mathrm{in}} - T_{k,\mathrm{in}}) \leq U(1-w_{ki}^2), \quad \forall(i,k)\in H\times H,$$
$$T_{i,\mathrm{in}} \geq T_{k,\mathrm{in}} - M(1-w_{ki}^2), \quad \forall(i,k)\in H\times H,$$
$$T_{i,\mathrm{out}} \leq T_{k,\mathrm{in}} - \varepsilon + M(1-w_{ki}^2), \quad \forall(i,k)\in H\times H,$$
$$q_{ki}^{hp} \leq U(1-w_{ki}^3), \quad \forall(i,k)\in H\times H,$$
$$T_{i,\mathrm{in}} \leq T_{k,\mathrm{in}} - \varepsilon + M(1-w_{ki}^3), \quad \forall(i,k)\in H\times H,$$
$$T_{i,\mathrm{out}} \leq T_{k,\mathrm{in}} - \varepsilon + M(1-w_{ki}^3), \quad \forall(i,k)\in H\times H,$$
$$w_{ki}^1 + w_{ki}^2 + w_{ki}^3 = 1, \quad \forall(i,k)\in H\times H,$$
$$q_{kj}^{hp} - Q_{\mathrm{COLD}_j} \geq -U(1-z_{kj}^1), \quad \forall(j,k)\in C\times H,$$
$$T_{j,\mathrm{in}} \geq T_{k,\mathrm{in}} - \Delta T_{\min} - M(1-z_{kj}^1), \quad \forall(j,k)\in C\times H,$$
$$T_{j,\mathrm{out}} \geq T_{k,\mathrm{in}} - \Delta T_{\min} - M(1-z_{kj}^1), \quad \forall(j,k)\in C\times H,$$
$$q_{kj}^{hp} - F_j c_{\mathrm{p},j}(T_{j,\mathrm{out}} - (T_{k,\mathrm{in}} - \Delta T_{\min})) \geq -U(1-z_{kj}^2), \quad \forall(j,k)\in C\times H,$$
$$T_{j,\mathrm{in}} \leq T_{k,\mathrm{in}} - \Delta T_{\min} + M(1-z_{kj}^2), \quad \forall(j,k)\in C\times H,$$
$$T_{j,\mathrm{out}} \geq T_{k,\mathrm{in}} - \Delta T_{\min} - \varepsilon - M(1-z_{kj}^2), \quad \forall(j,k)\in C\times H,$$
$$q_{kj}^{hp} \leq U(1-z_{kj}^3), \quad \forall(j,k)\in C\times H,$$
$$T_{j,\mathrm{in}} \leq T_{k,\mathrm{in}} - \Delta T_{\min} - \varepsilon + M(1-z_{kj}^3), \quad \forall(j,k)\in C\times H,$$
$$T_{j,\mathrm{out}} \leq T_{k,\mathrm{in}} - \Delta T_{\min} - \varepsilon + M(1-z_{kj}^3), \quad \forall(j,k)\in C\times H,$$
$$z_{kj}^1 + z_{kj}^2 + z_{kj}^3 = 1, \quad \forall(j,k)\in C\times H,$$
$$q_{li}^{cp} - Q_{\mathrm{HOT}_i} \leq U(1-u_{li}^1), \quad \forall(i,l)\in H\times C,$$
$$T_{i,\mathrm{in}} \geq T_{l,\mathrm{in}} + \Delta T_{\min} - M(1-u_{li}^1), \quad \forall(i,l)\in H\times C,$$
$$T_{i,\mathrm{out}} \geq T_{l,\mathrm{in}} + \Delta T_{\min} - M(1-u_{li}^1), \quad \forall(i,l)\in H\times C,$$
$$q_{li}^{cp} - F_i c_{\mathrm{p},i}(T_{i,\mathrm{in}} - (T_{l,\mathrm{in}} + \Delta T_{\min})) \leq U(1-u_{li}^2), \quad \forall(i,l)\in H\times C,$$
$$T_{i,\mathrm{in}} \geq T_{l,\mathrm{in}} + \Delta T_{\min} - M(1-u_{li}^2), \quad \forall(i,l)\in H\times C,$$
$$T_{i,\mathrm{out}} \leq T_{l,\mathrm{in}} + \Delta T_{\min} - \varepsilon + M(1-u_{li}^2), \quad \forall(i,l)\in H\times C,$$
$$q_{li}^{cp} \leq U(1-u_{li}^3), \quad \forall(i,l)\in H\times C,$$
$$T_{i,\mathrm{in}} \leq T_{l,\mathrm{in}} + \Delta T_{\min} - \varepsilon + M(1-u_{li}^3), \quad \forall(i,l)\in H\times C,$$
$$T_{i,\mathrm{out}} \leq T_{l,\mathrm{in}} + \Delta T_{\min} - \varepsilon + M(1-u_{li}^3), \quad \forall(i,l)\in H\times C,$$
$$u_{li}^1 + u_{li}^2 + u_{li}^3 = 1, \quad \forall(i,l)\in H\times C,$$
$$q_{lj}^{cp} - Q_{\mathrm{COLD}_j} \geq -U(1-v_{lj}^1), \quad \forall(j,l)\in C\times C,$$
$$T_{j,\mathrm{in}} \geq T_{l,\mathrm{in}} - M(1-v_{lj}^1), \quad \forall(j,l)\in C\times C,$$
$$T_{j,\mathrm{out}} \geq T_{l,\mathrm{in}} - M(1-v_{lj}^1), \quad \forall(j,l)\in C\times C,$$
$$q_{lj}^{cp} - F_j c_{\mathrm{p},j}(T_{j,\mathrm{out}} - T_{l,\mathrm{in}}) \geq -U(1-v_{lj}^2), \quad \forall(j,l)\in C\times C,$$
$$T_{j,\mathrm{in}} \leq T_{l,\mathrm{in}} + M(1-v_{lj}^2), \quad \forall(j,l)\in C\times C,$$
$$T_{j,\mathrm{out}} \geq T_{l,\mathrm{in}} - \varepsilon - M(1-v_{lj}^2), \quad \forall(j,l)\in C\times C,$$
$$q_{lj}^{cp} \leq U(1-v_{lj}^3), \quad \forall(j,l)\in C\times C,$$
$$T_{j,\mathrm{in}} \leq T_{l,\mathrm{in}} - \varepsilon + M(1-v_{lj}^3), \quad \forall(j,l)\in C\times C,$$
$$T_{j,\mathrm{out}} \leq T_{l,\mathrm{in}} - \varepsilon + M(1-v_{lj}^3), \quad \forall(j,l)\in C\times C,$$
$$v_{lj}^1 + v_{lj}^2 + v_{lj}^3 = 1, \quad \forall(j,l)\in C\times C.$$

140 equality constraints, 1100 inequality constraints, slightly approximate solution

Smoothed NLP Formulation

$$Q_H + \sum_{i\in H} F_{C_p,i}\left(T_i^{\text{in}} - T_i^{\text{out}}\right) = Q_C + \sum_{j\in C} f_{C_p,j}\left(t_i^{\text{out}} - t_i^{\text{in}}\right),$$
$$AP_C^p - AP_H^p \leq Q_H + \varepsilon, \forall p\in P = H\cup C,$$
$$AP_H^p \equiv \sum_{i\in H} F_i\left(\max\{0, T_i^{\text{in}} - T^p\} - \max\{0, T_i^{\text{out}} - T^p\}\right), \forall p\in P = H\cup C,$$
$$AP_C^p \equiv \sum_{j\in C} f_j\left(\max\{0, t_j^{\text{out}} - (T^p - \Delta T_{\min})\} - \max\{0, t_j^{\text{in}} - (T^p - \Delta T_{\min})\}\right),$$
$$\forall p\in P = H\cup C,$$
$$Q_H \geq 0, \quad Q_C \geq 0, \quad \max\{0, f(x)\} \approx \tfrac{1}{2}\left[\sqrt{f(x)^2 + \beta^2} + f(x)\right].$$

1 equality constraint, 13 inequality constraints, approximate solution

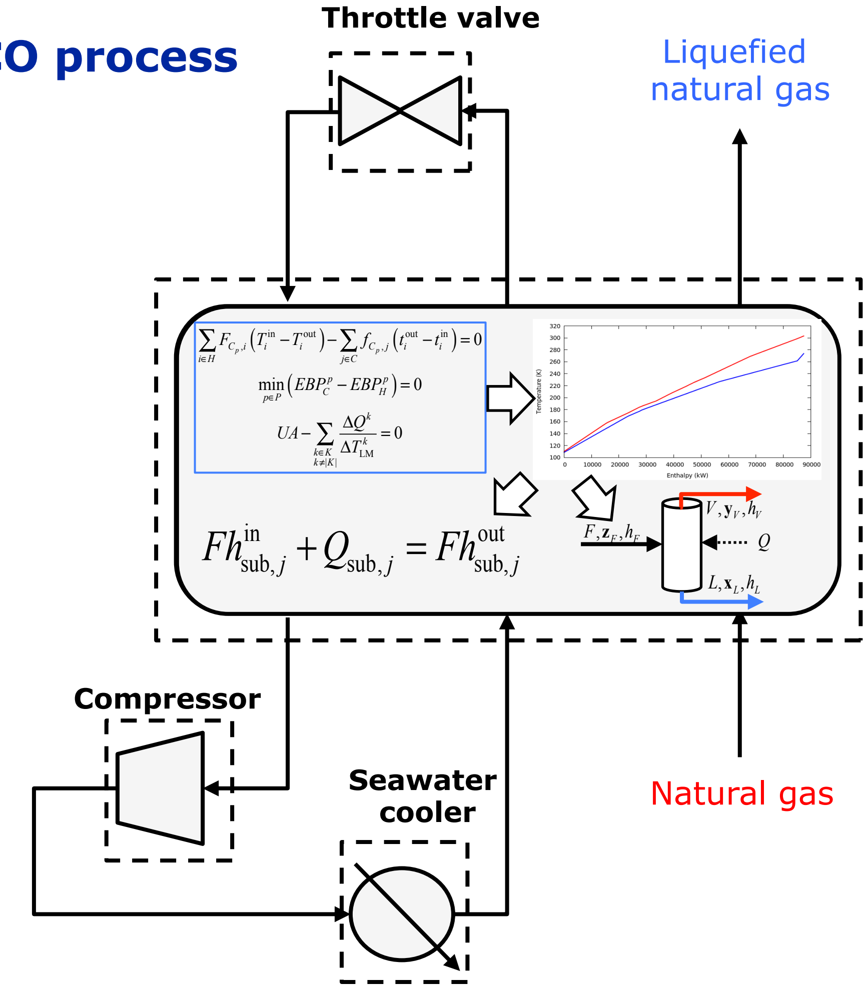
Nonsmooth NLP Formulation

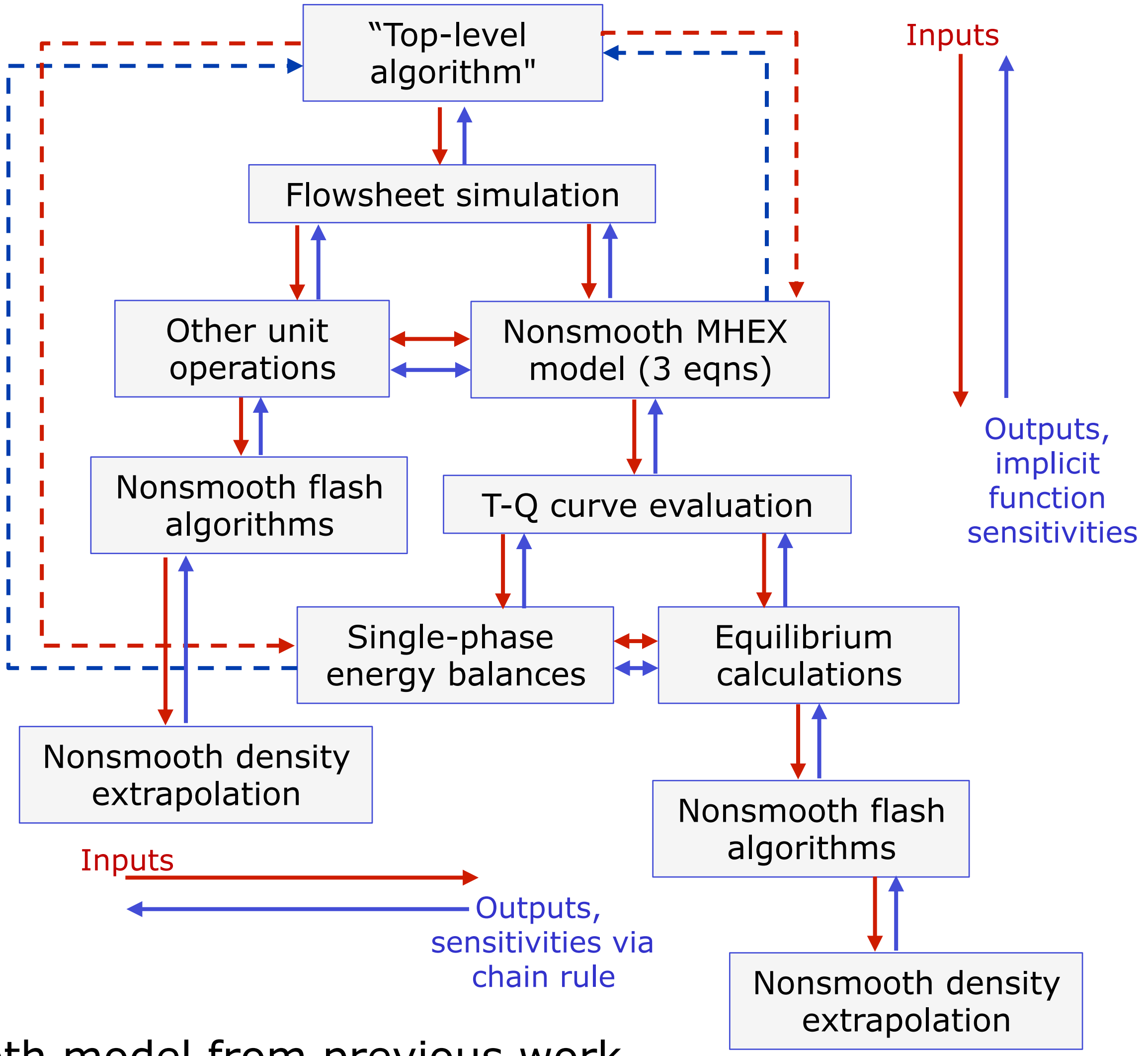
$$Q_H + \sum_{i\in H} F_{C_p,i}\left(T_i^{\text{in}} - T_i^{\text{out}}\right) = Q_C + \sum_{j\in C} f_{C_p,j}\left(t_i^{\text{out}} - t_i^{\text{in}}\right),$$
$$\min_{p\in P}\left(EBP_C^p - EBP_H^p\right) = -Q_C,$$
$$EBP_H^p \equiv \sum_{i\in H} F_i\left(\max\{0, T^p - T_i^{\text{out}}\} - \max\{0, T^p - T_i^{\text{in}}\}\right.$$
$$\left. - \max\{0, T^{\min} - T^p\} + \max\{0, T^p - T^{\max}\}\right), \forall p\in P = H\cup C,$$
$$EBP_C^p \equiv \sum_{j\in C} f_j\left(\max\{0, (T^p - \Delta T_{\min}) - t_j^{\text{in}}\} - \max\{0, (T^p - \Delta T_{\min}) - t_j^{\text{out}}\}\right.$$
$$\left. + \max\{0, (T^p - \Delta T_{\min}) - t^{\max}\} - \max\{0, t^{\min} - (T^p - \Delta T_{\min})\}\right),$$
$$\forall p\in P = H\cup C,$$
$$Q_H \geq 0, \quad Q_C \geq 0$$

2 equality constraints, 2 inequality constraints, exact solution

Nonsmooth Process Modeling for Natural Gas Liquefaction Processes

PRICO process





- Multiphase multistream heat exchanger uses nonsmooth model from previous work
- All flash calculations (PQ,PT,PV,PS) solved with inside-out algorithms

PRICO Process Optimization Formulation

- Process optimization formulation

$$\min_{\mathbf{x}} \ \dot{W}_{\text{comp}}(\mathbf{x})$$

$$\text{s.t.} \quad \mathbf{h}(\mathbf{x}) = \mathbf{0},$$

MHEX overall energy balance
MHEX pinch location function
Substream energy balances

Compressor feed must be superheated

$$\Delta T_{\text{sup}}(\mathbf{x}) \geq \Delta T_{\text{sup,min}},$$

Constraining UA instead of $\Delta T_{\min}$ leads to optimal utilization of MHEX area

$$UA(\mathbf{x}) \leq UA_{\max},$$

$$\mathbf{x}^{\text{LB}} \leq \mathbf{x} \leq \mathbf{x}^{\text{UB}}.$$

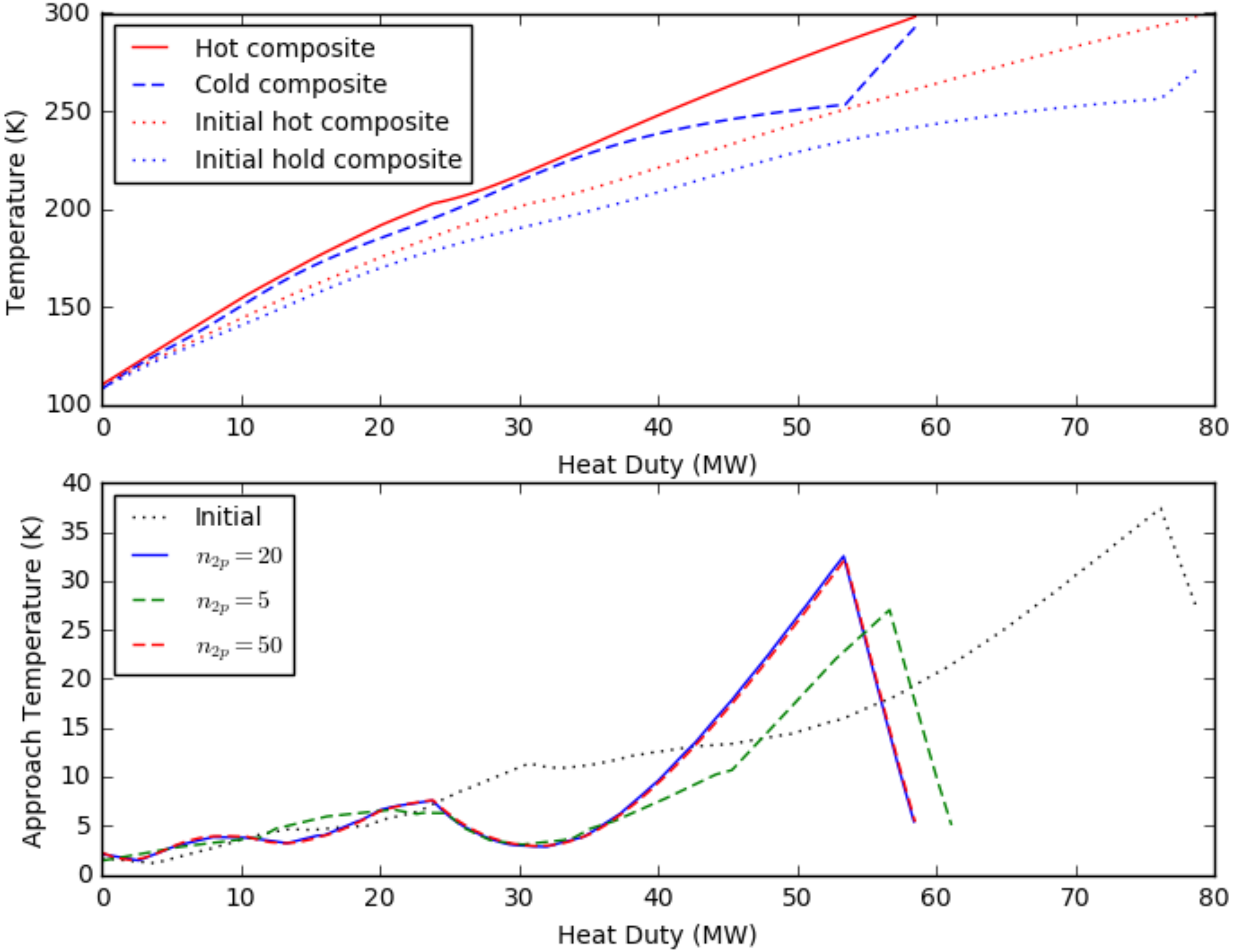
$$\mathbf{x} \equiv (P_{\text{LPR}}, P_{\text{HPR}}, \mathbf{f}_{\text{MR}}, \Delta T_{\min}, T_{\text{LPR}}^{\text{OUT}}, \mathbf{T})$$

Superheated/subcooled substream temperatures

Austbø and Gundersen, 2016. Impact of problem formulation on LNG process optimization. *AIChE J. 62(10):3598-3610*

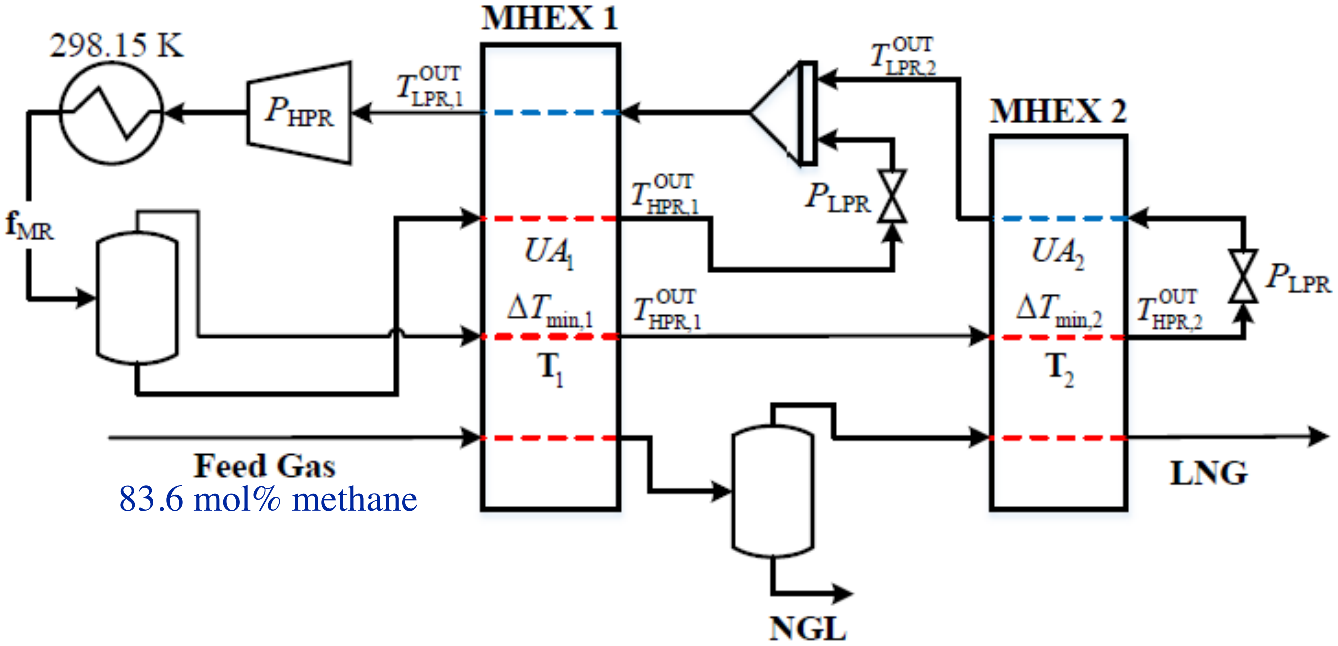
PRICO Process Optimization Studies

- Optimization results with UA_{max} = 12.0 MW/K
  - Feasible initial guess: simulation result
- Compressor power requirement reduced 17.5% for the same MHEX size
- Coarser discretization of the composite curves leads to different solutions
  - Infeasible in higher accuracy models

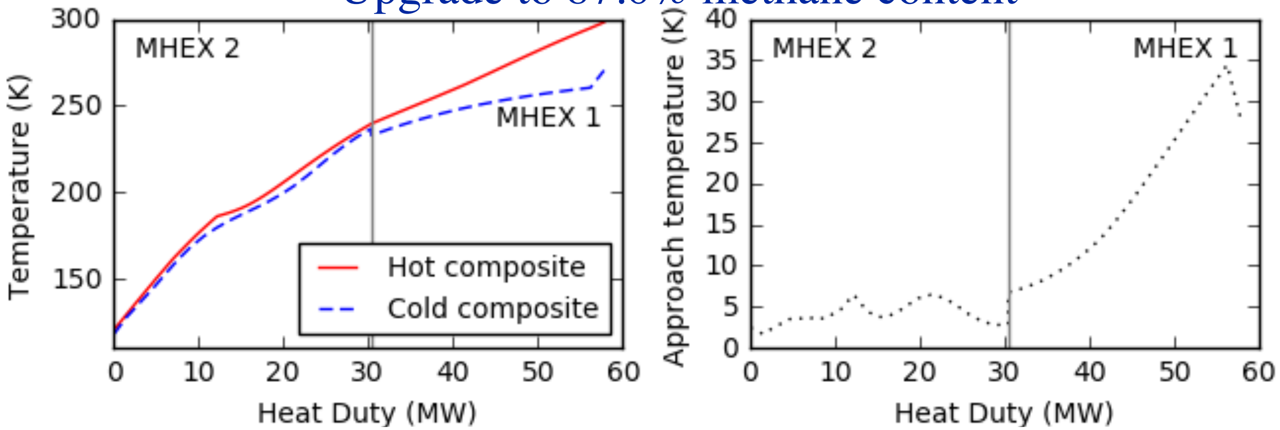


Natural Gas Liquids Extraction

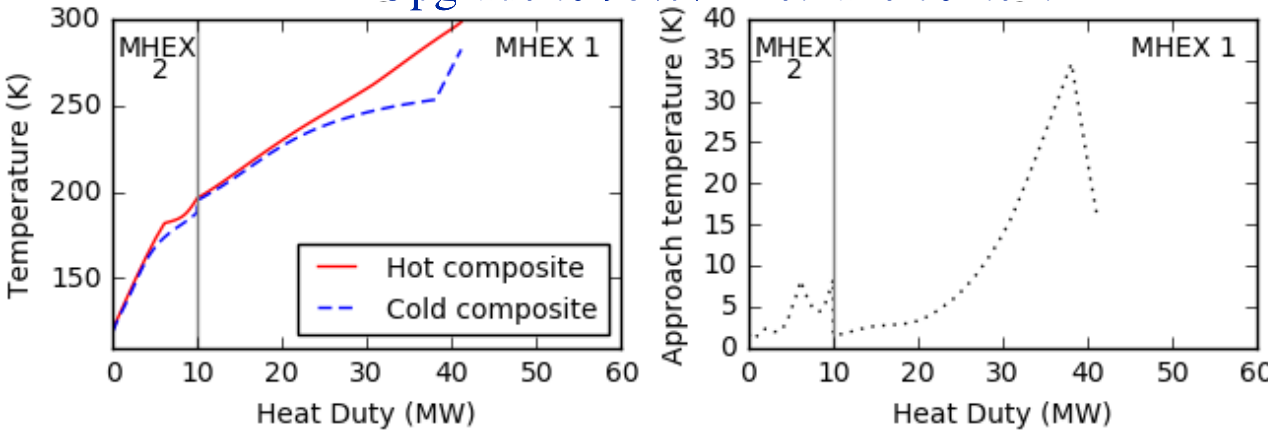
- Problem: very rich feed gas must be upgraded to produce high heating value product
  - Extracted natural gas liquids (NGLs) can be sold as additional product
- Given an overall UA_{max}, optimizer decides on the distribution between the two MHEXs



Upgrade to 87.6% methane content



Upgrade to 95.6% methane content



Dynamic Modeling Frameworks in PSE

- Trade-off: applicability vs. ease of modeling & solving

Smooth DAEs

Limited applicability

Easy to model and solve

Derivative information

Strong existence & uniqueness theory

Nonsmooth DAEs

Broad applicability

Easy to model and solve

Generalized derivative information

(recently) Strong existence & uniqueness theory

Hybrid (Discrete/Continuous) Models

(near) Universal applicability

Often challenging to model and solve

Limited derivative information

Pathological behaviors (hard to exclude a priori)

Smooth approximation models

Complementarity systems

Summary & Conclusions

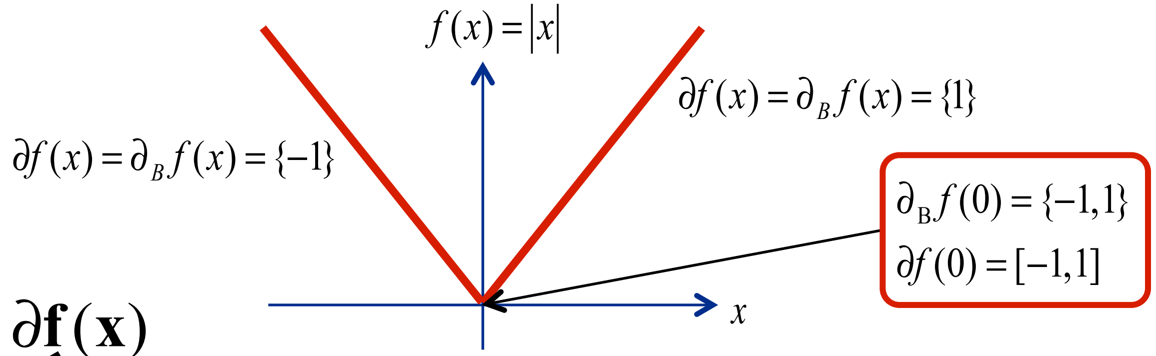
- LD-derivatives enable exact and automatable sensitivity analysis for nondifferentiable process models
- Nonsmooth models represent broad range of conditions, are highly compact & have favorable scaling with regards to high accuracy simulation/optimization
  - Accordingly very robust, even for challenging optimization problems
- Even more complex processes are currently being modeled and studied within this framework
  - e.g. Dual mixed-refrigerant liquefaction processes, processes with distillation, etc.

Acknowledgements

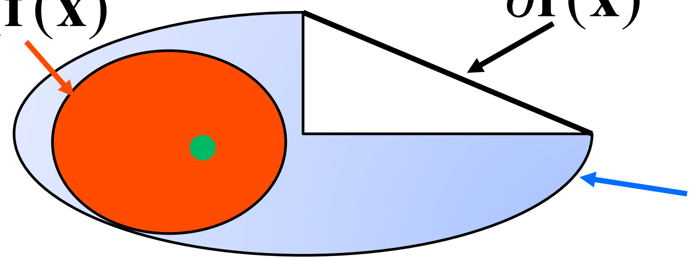
- PSEL labmates
  - Prof. Kamil Khan
  - Dr. Harry Watson
- NTNU collaborators
  - Prof. Truls Gundersen
  - Matias Vikse

Notions of the Generalized Derivative

- There are many generalizations of the derivative:
  - B-subdifferential: $\partial_{\mathrm{B}}\mathbf{f}(\mathbf{x})$
  - Clarke Jacobian: $\partial\mathbf{f}(\mathbf{x})$



- Given $\mathbf{f}:\mathbf{R}^n\rightarrow\mathbf{R}^m$
  - If **f** is *PC*[1]: $\partial_{\mathrm{L}}\mathbf{f}(\mathbf{x})$



  - If **f** is *C*[1]: ● ⟵ $\partial_{\mathrm{L}}\mathbf{f}(\mathbf{x})=\partial_{\mathrm{B}}\mathbf{f}(\mathbf{x})=\partial\mathbf{f}(\mathbf{x})=\{\mathbf{Jf}(\mathbf{x})\}$
- New AD methods calculate generalized derivative elements corresponding to the green dots using "LD-derivatives": $\mathbf{f}'(\mathbf{x};\mathbf{M})$
  - Have programmable rules for LD-derivatives of abs, min, max, mid, etc.
  - Obey a sharp chain rule

K. A. Khan, and P. I. Barton, 2015. A vector forward mode of automatic differentiation for generalized derivative evaluation. Optimization Methods and Software. 30(6):1185-1212.

Solving Nonsmooth Equation Systems

- Semismooth Newton method: calculates next iterate $\mathbf{x}$ by solving linear system:

$$\underbrace{\mathbf{G}(\mathbf{x}^k)}(\mathbf{x}-\mathbf{x}^k) = -\mathbf{f}(\mathbf{x}^k)$$

Element of generalized derivative

- Linear programming (LP) Newton method: calculates next iterate $\mathbf{x}$ by solving LP:

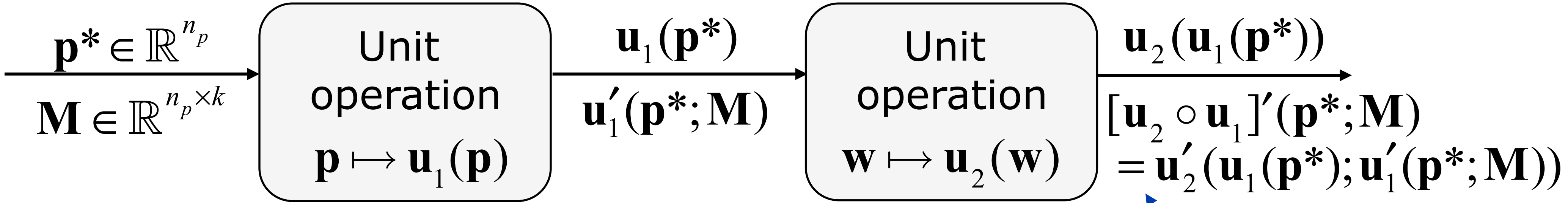
$$\begin{aligned} \min_{\gamma,\mathbf{x}} \quad & \gamma \\ \text{s.t.} \quad & \left\| \mathbf{f}(\mathbf{x}^k) + \mathbf{G}(\mathbf{x}^k)(\mathbf{x}-\mathbf{x}^k) \right\|_\infty \le \gamma \min\left(\left\| \mathbf{f}(\mathbf{x}^k) \right\|_\infty, \left\| \mathbf{f}(\mathbf{x}^k) \right\|_\infty^2 \right) \\ & \left\| (\mathbf{x}-\mathbf{x}^k) \right\|_\infty \le \gamma \left\| \mathbf{f}(\mathbf{x}^k) \right\|_\infty \\ & \mathbf{x} \in X \end{aligned}$$

  - Can be globalized with Armijo-rule linesearch
- Local Q-quadratic convergence rate if $\mathbf{G}(\mathbf{x}^k) = \mathbf{f}'(\mathbf{x};\mathbf{I}_{n\times n}) \in \partial_B \mathbf{f}(\mathbf{x}^k)$

Qi, L., & Sun, J. (1993). A nonsmooth version of Newton's method. Mathematical Programming, 58(1–3), 353–367.
F. Facchinei, A. Fischer, and M Herrich, 2014. An LP-Newton method: nonsmooth equations, KKT systems, and nonisolated solutions. *Mathematical Programming*.

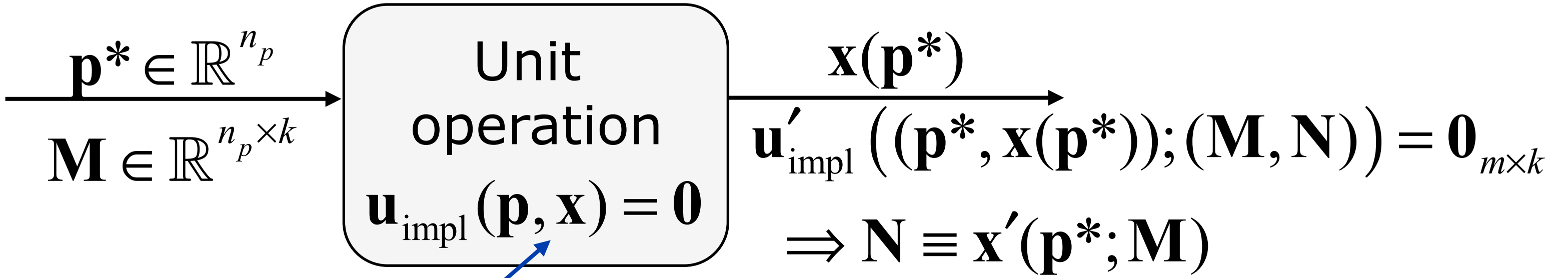
A Nonsmooth Flowsheeting Paradigm

- Explicit unit modules and the chain rule:



By the sharp chain rule

- Implicit unit modules:

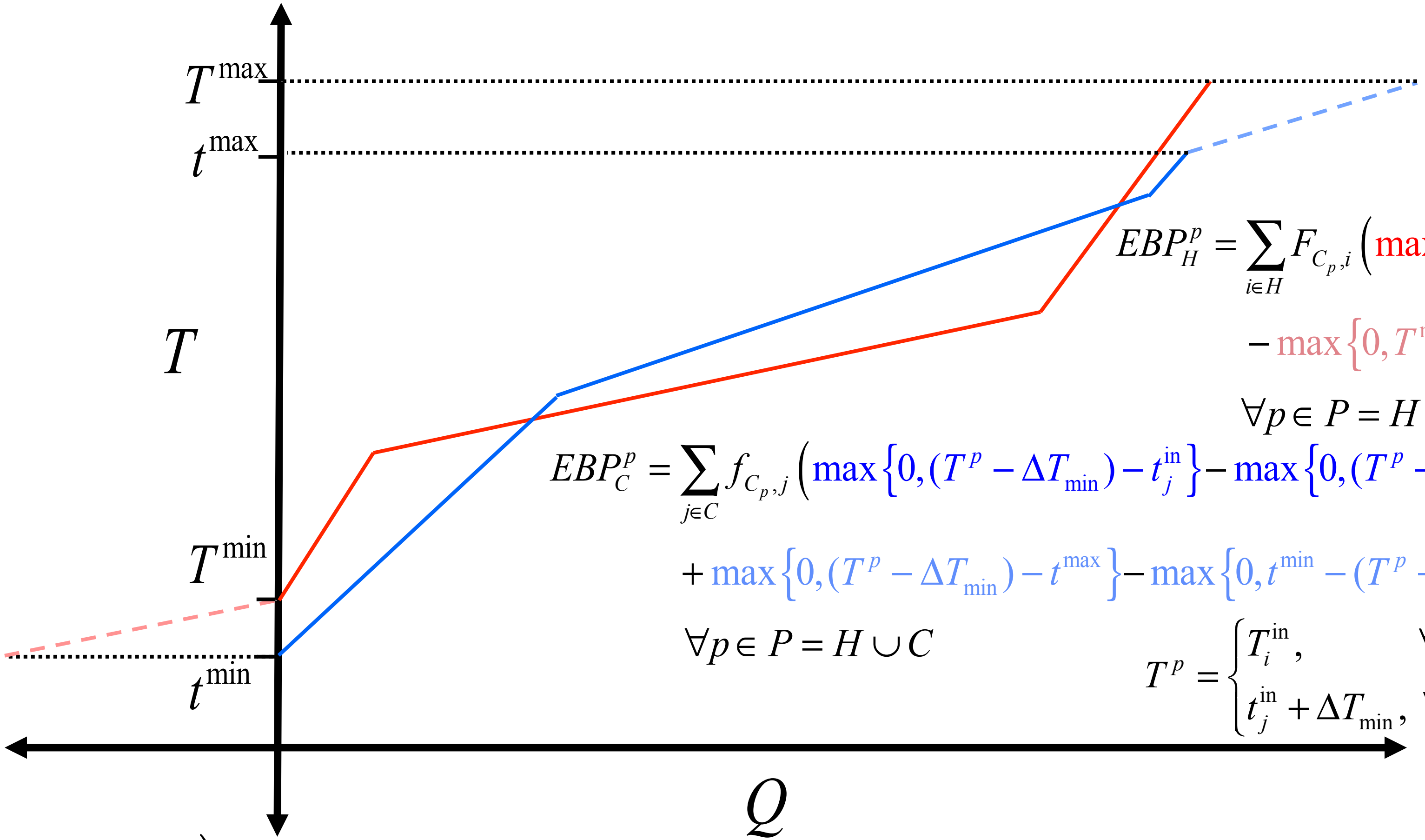


Can use an external algorithm for this subproblem

Can evaluate these sensitivities algorithmically

H. A. J. Watson, M. Vikse, T. Gundersen, P. I. Barton (2017). Reliable Flash Calculations: Part 2. Process flowsheeting with nonsmooth models and generalized derivatives. Ind. & Eng. Chem. Res

MHEX Second Law feasibility constraint



$$EBP_H^p = \sum_{i \in H} F_{C_p,i}\Big(\max\{0, T^p - T_i^{\text{out}}\} - \max\{0, T^p - T_i^{\text{in}}\} - \max\{0, T^{\min} - T^p\} + \max\{0, T^p - T^{\max}\}\Big),$$
$$\forall p \in P = H \cup C$$

$$EBP_C^p = \sum_{j \in C} f_{C_p,j}\Big(\max\{0, (T^p - \Delta T_{\min}) - t_j^{\text{in}}\} - \max\{0, (T^p - \Delta T_{\min}) - t_j^{\text{out}}\} + \max\{0, (T^p - \Delta T_{\min}) - t^{\max}\} - \max\{0, t^{\min} - (T^p - \Delta T_{\min})\}\Big),$$
$$\forall p \in P = H \cup C$$

$$T^p = \begin{cases} T_i^{\text{in}}, & \forall p = i \in H \\ t_j^{\text{in}} + \Delta T_{\min}, & \forall p = j \in C \end{cases}$$

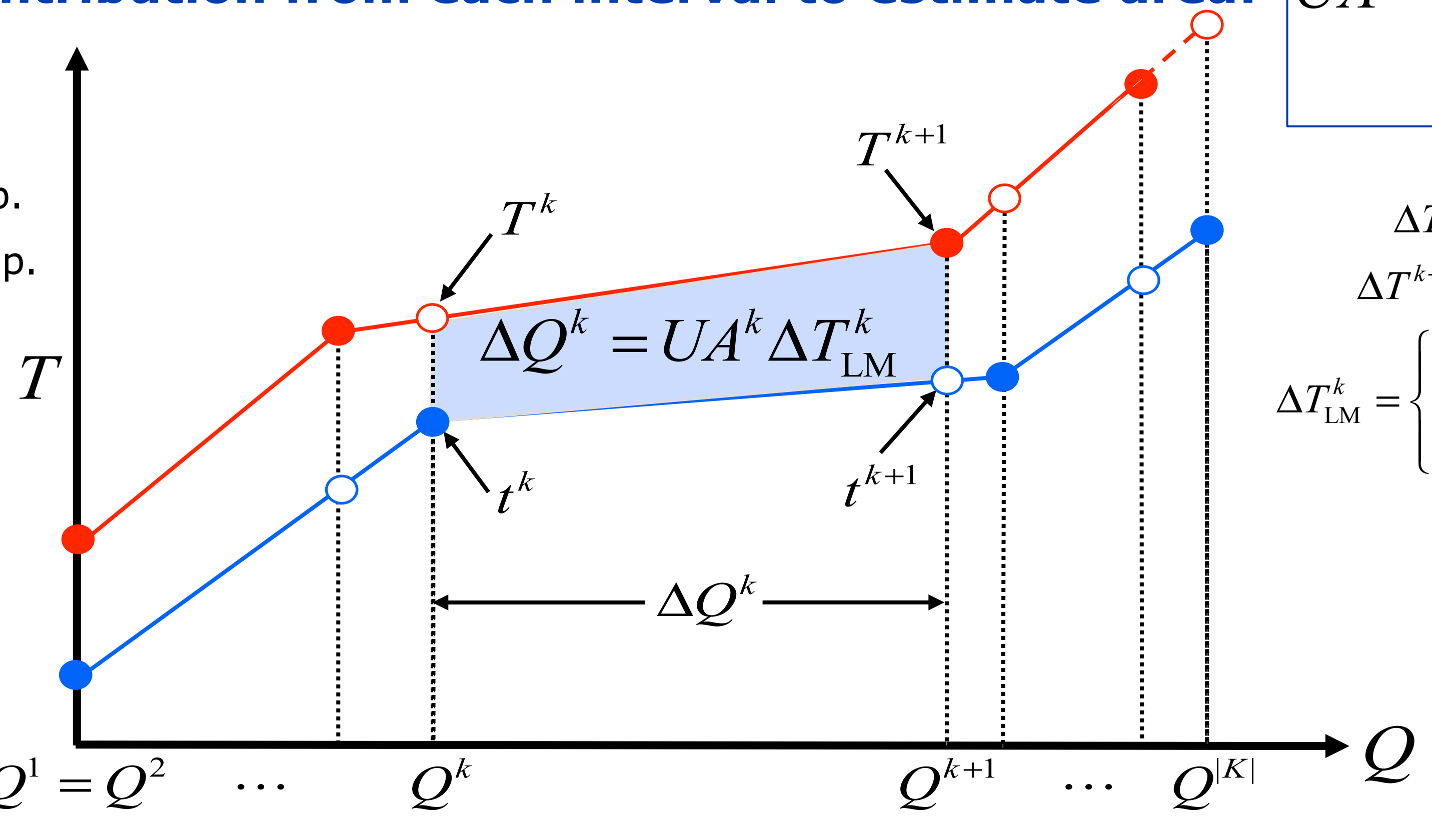
- $\min_{p \in P}\left(EBP_C^p - EBP_H^p\right)$ models the separation between the (extended) composite curves across possible pinch points
  - Equal to zero only when distance between the curves is exactly $\Delta T_{\min}$

MHEX physical area constraint algorithm

- Intervals between non-differentiable points are equivalent to two-stream heat exchangers
  - **4. Sum contribution from each interval to estimate area:**

$$UA = \sum_{\substack{k \in K \\ k \neq |K|}} \frac{\Delta Q^k}{\Delta T^k_{\text{LM}}}$$

- Known hot stream temp.
- Known cold stream temp.
- Unknown hot stream temp.
- Unknown cold stream temp.



1. Sort intervals

```
for i ← 1 to n do
    for j ← 1 to n − 1 do
        a ← min(A[j], A[j+1])
        b ← max(A[j], A[j+1])
        A[j] ← a
        A[j+1] ← b
return A
```

2. Find values/sensitivities of implicitly defined temperatures

$$Q^k - \sum_{i \in H} F_i \left(\max\{0, \boxed{T^k} - T_i^{\text{out}}\} - \max\{0, \boxed{T^k} - T_i^{\text{in}}\} \right) = 0$$

$$\Delta T^k = \max\{\Delta T_{\min}, T^k - t^k\}$$

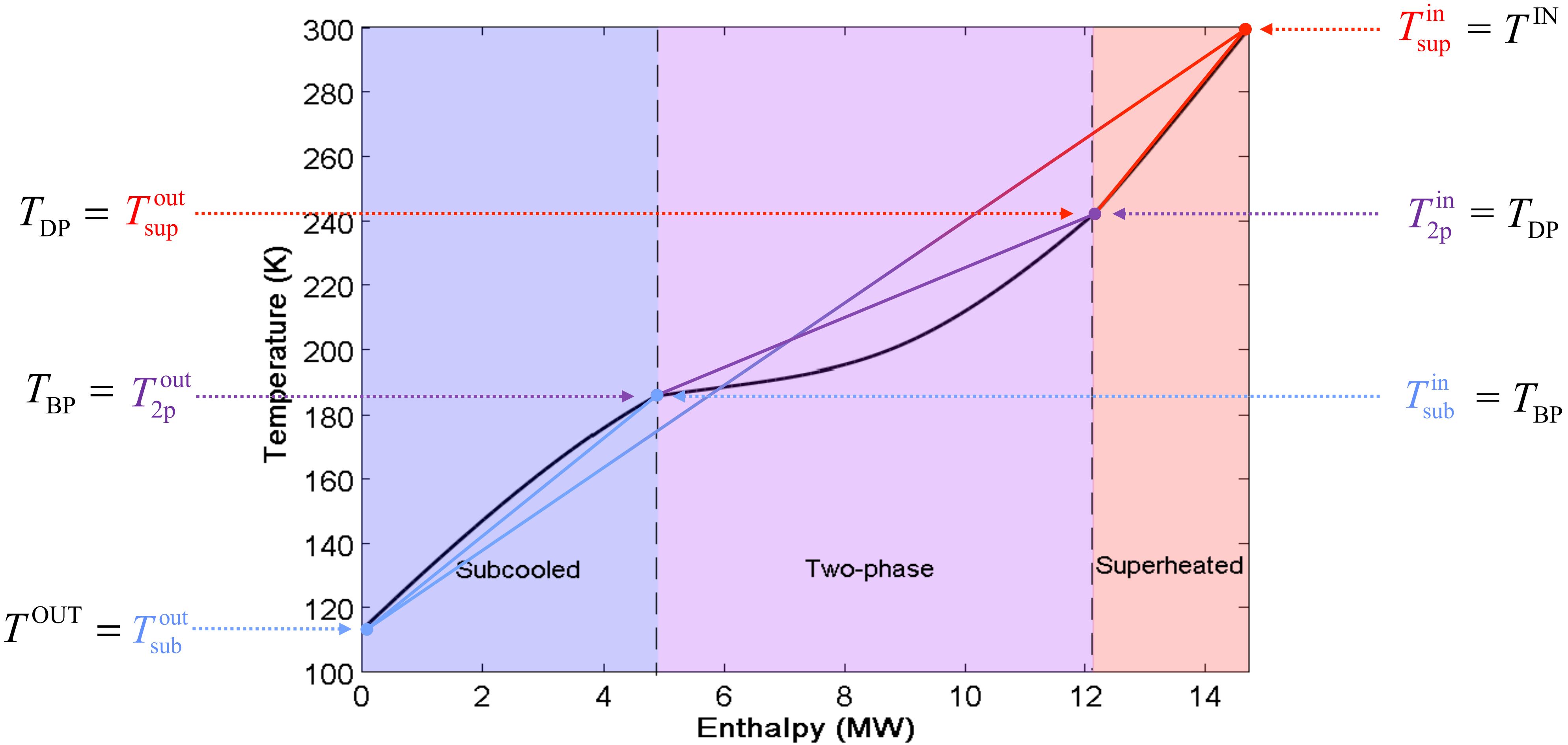
$$\Delta T^{k+1} = \max\{\Delta T_{\min}, T^{k+1} - t^{k+1}\}$$

$$\Delta T^k_{\text{LM}} = \begin{cases} \frac{1}{2}\left(\Delta T^k + \Delta T^{k+1}\right) & \text{if } \Delta T^k = \Delta T^{k+1} \\ \frac{\Delta T^{k+1} - \Delta T^k}{\ln(\Delta T^{k+1}) - \ln(\Delta T^k)} & \text{otherwise} \end{cases}$$

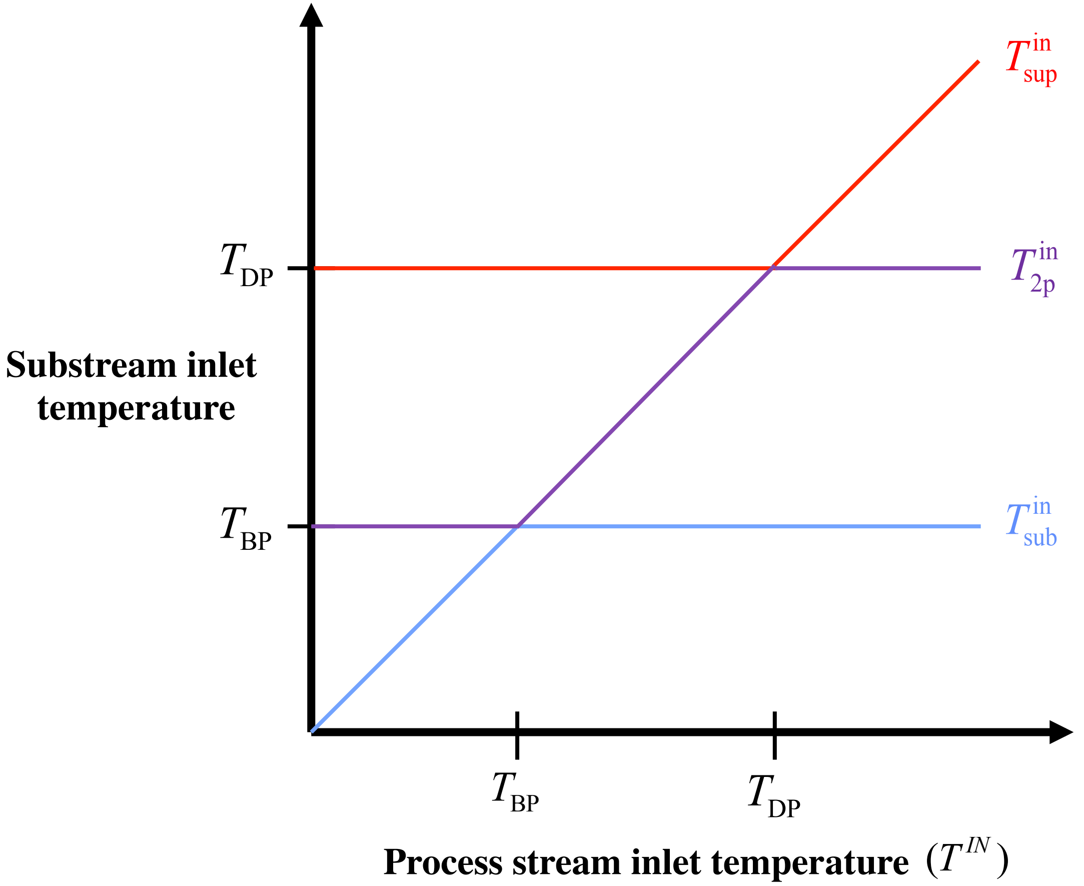
3. Calculate safe log-mean temperature differences

Simulating LNG Processes Realistically

- Need to automatically detect and handle phase changes
  - Calculate correct physical properties, find pinch points, etc.



Detecting and Handling Phase Change Automatically



$$T_{sup}^{in} = \max\{T_{DP}, T^{IN}\}$$

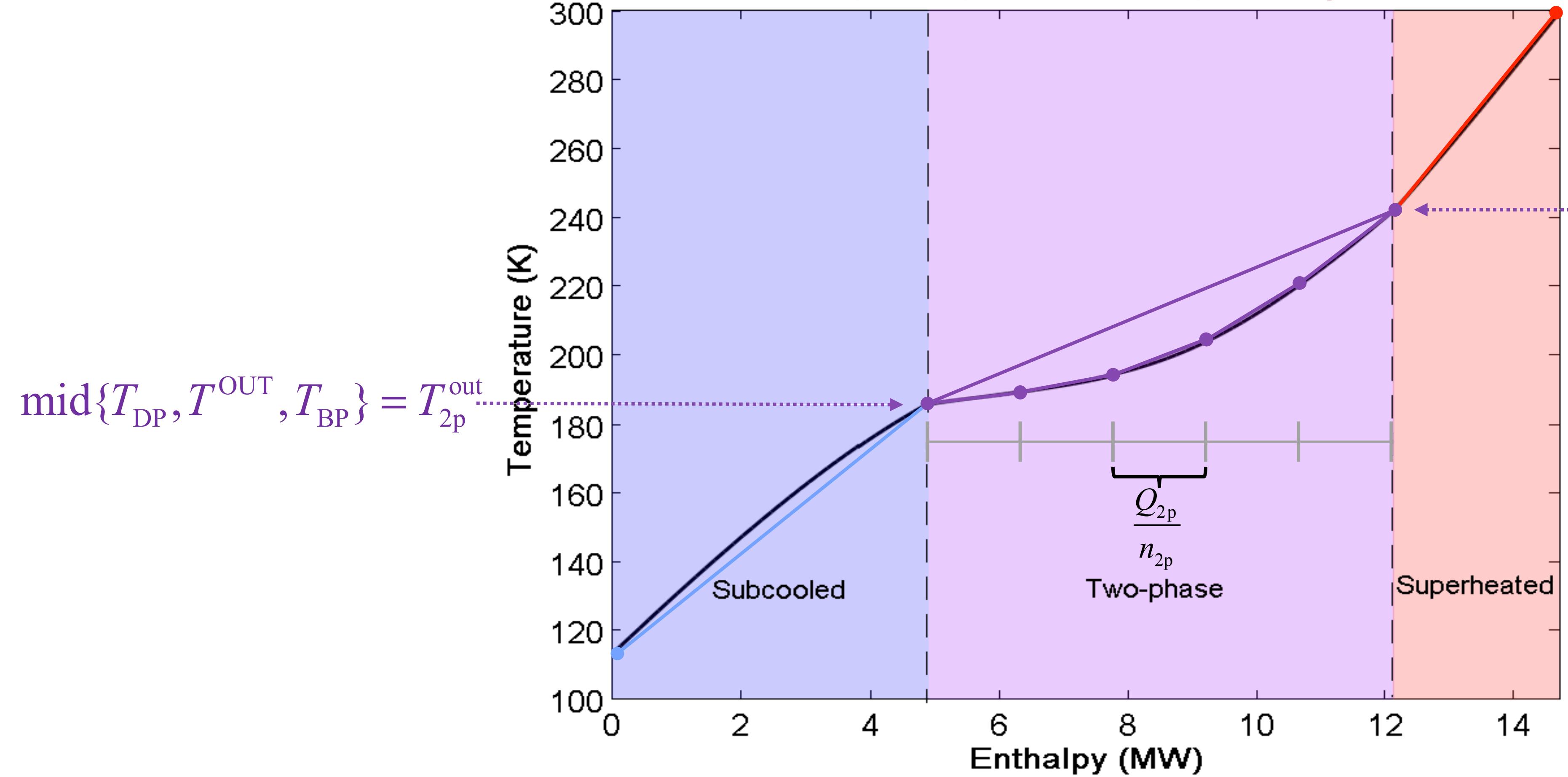
$$T_{2p}^{in} = \mathrm{mid}\{T_{DP}, T^{IN}, T_{BP}\}$$

$$T_{sub}^{in} = \min\{T^{IN}, T_{BP}\}$$

- Temperatures of phase substreams are *PC*[1] functions of the inlet, dew point, and bubble point temperatures

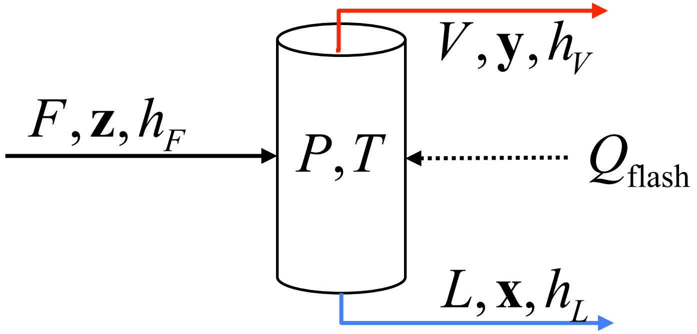
Improving the Piecewise Approximation

- Each substream is further subdivided into piecewise affine segments of equal heat load
  - Inlet/outlet temperatures *implicitly* defined by energy balances and flash calculations



$$F_{C_p,2p}^{i} = \frac{FQ_{2p}}{n_{2p}\left(T_{2p}^{in,i} - T_{2p}^{out,i}\right)}$$

Classical formulation for PQ-flash



- Both outlet streams exist:

$$F = V + L$$

$$Fz_i = Lx_i + Vy_i, \quad i = 1, \ldots, n_c$$

$$y_i = k_i x_i, \quad i = 1, \ldots, n_c$$

$$\sum_{i=1}^{n_c} y_i - \sum_{i=1}^{n_c} x_i = 0$$

$$Vh_V + Lh_L - Fh_F = Q_{\text{flash}}$$

⇒

Rachford-Rice equation

$$\sum_{i=1}^{n_c} \frac{z_i(k_i - 1)}{1 + \frac{V}{F}(k_i - 1)} = 0$$

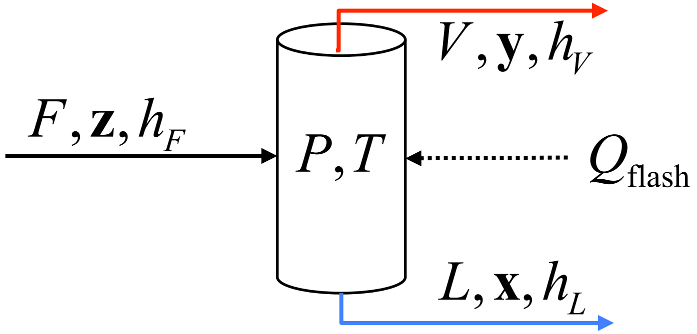
$$Vh_V + Lh_L - Fh_F = Q_{\text{flash}}$$

$$F = V + L$$

$$x_i = \frac{z_i}{1 + \frac{V}{F}(k_i - 1)}, \quad i = 1, \ldots, n_c$$

$$y_i = \frac{k_i z_i}{1 + \frac{V}{F}(k_i - 1)}, \quad i = 1, \ldots, n_c$$

Traversing Phase Regimes in Flash Calculations

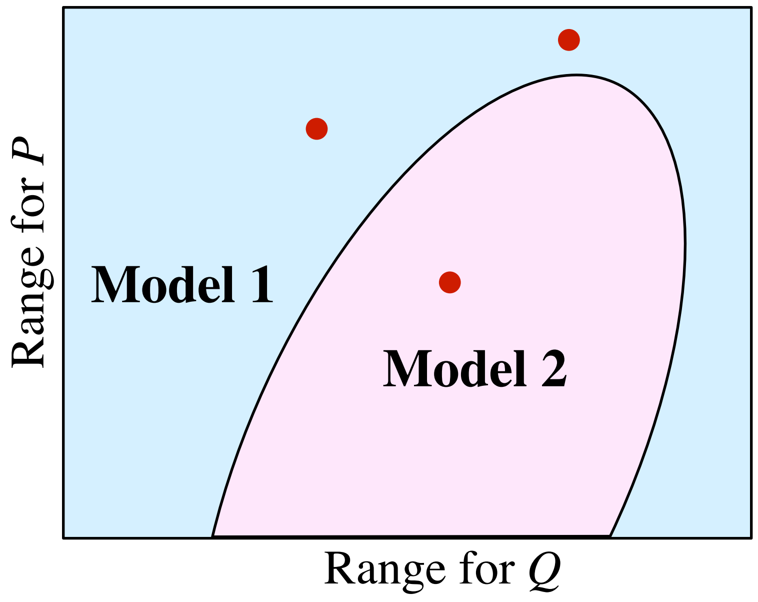


- Consider simulation/optimization in which the flash parameters vary:

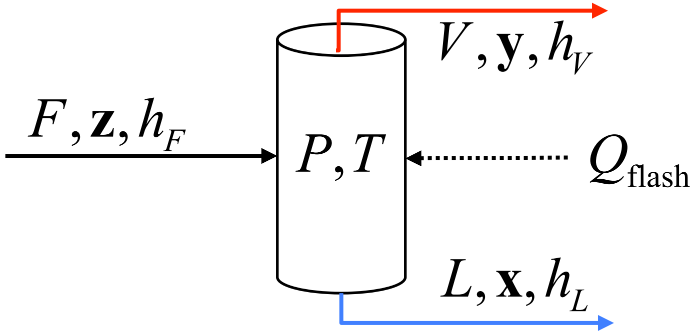
- Need to calculate the outlet state(s):
  - … know that only single-phase points will be chosen
    → satisfy only material and energy balances

  - … know that only two-phase points will be chosen
    → need to include equilibrium constraints

- What if the chosen parameter combinations imply a change of regime between iterations?



Nonsmooth Flash Formulation



- Developed a nonsmooth function which captures all phase conditions:

Liquid only

$$\frac{V}{F} = 0$$

Vapor-liquid equilibrium

$$\sum_{i=1}^{n_c} \frac{z_i(k_i - 1)}{1 + \frac{V}{F}(k_i - 1)} = 0$$

Vapor only

$$\frac{V}{F} = 1$$

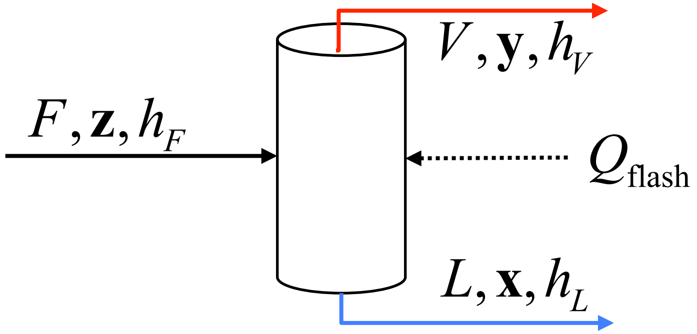
$$\text{mid}\left\{\frac{V}{F},\ -\sum_{i=1}^{n_c} \frac{z_i(k_i - 1)}{1 + \frac{V}{F}(k_i - 1)},\ \frac{V}{F} - 1\right\} = 0$$

- Analogous formulation works for dynamic simulation of evaporators and columns
  - Also proved this formulation follows from Gibbs free energy minimization for a mixture

H. A. J. Watson and P. I. Barton, 2017. Modeling phase changes in multistream heat exchangers. International Journal of Heat and Mass Transfer. 105:207-219.

A. M. Sahlodin, H. A. J. Watson, P. I. Barton, 2016. Nonsmooth Model for Dynamic Simulation of Phase Changes. AICHE Journal, 62(9):3334-3351.

Nonsmooth Flash Formulation



$$\mathbf{z} = (0.2, 0.2, 0.2, 0.2, 0.2)$$

$$\mathbf{k} = (10.0, 3.0, 1.0, 0.3, 0.1)$$

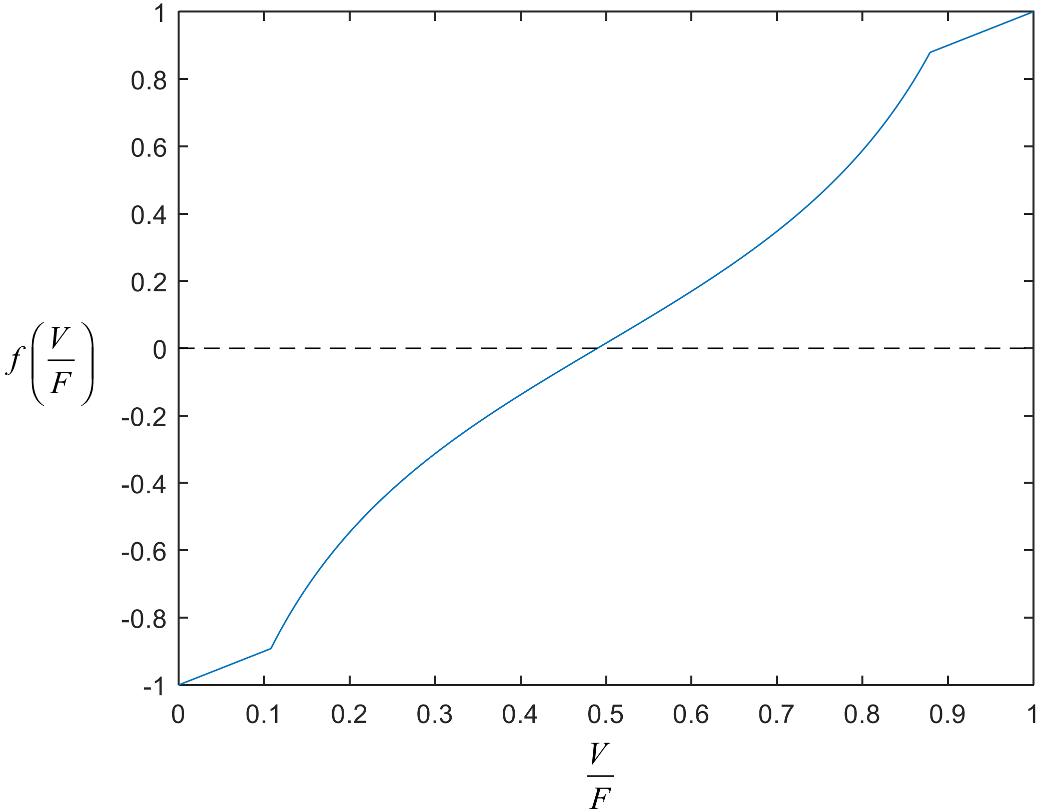
$$\text{mid}\left\{\frac{V}{F},\ -\sum_{i=1}^{n_c}\frac{z_i(k_i-1)}{1+\frac{V}{F}(k_i-1)},\ \frac{V}{F}-1\right\}=0$$

$$Vh_V + Lh_L - Fh_F = Q_{\text{flash}}$$

$$F = V + L$$

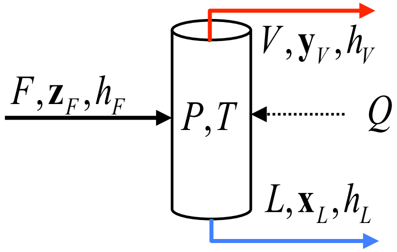
$$x_i = \frac{z_i}{1+\frac{V}{F}(k_i-1)}, \quad i = 1,\ldots,n_c$$

$$y_i = \frac{k_i z_i}{1+\frac{V}{F}(k_i-1)}, \quad i = 1,\ldots,n_c$$



Nonsmooth Inside-Out Algorithm (PQ-flash)

Initialization



Generate surrogate model parameters ($\mathbf{u}$, $A - F$)

Guess R and k_b, calculate physical variables ($\mathbf{x}_L$, $\mathbf{y}_V$, T, V, L)

Inner loop

Converge nonsmooth flash equations in transformed variable space

$$\frac{L}{F}(\Delta h_V - \Delta h_L) - h_F^{\text{id}} - \Delta h_V + h_F + \frac{Q_{\text{flash}}}{F} = 0$$

$$\text{mid}\left(R, \sum_{i=1}^{n_c} p_i - k_b \sum_{i=1}^{n_c} e^{u_i} p_i, R - 1 \right) = 0$$

Evaluate rigorous thermophysical properties ($\mathbf{k}$, Δh_V, Δh_L)

Outer loop

Surrogate models

$$u_i = \ln(k_i / k_b), \ i = 1, \ldots, n_c$$

$$\ln k_b = A + B\left(\tfrac{1}{T} - \tfrac{1}{T_{\text{ref}}}\right)$$

$$\Delta h_V = C + D(T - T_{\text{ref}})$$

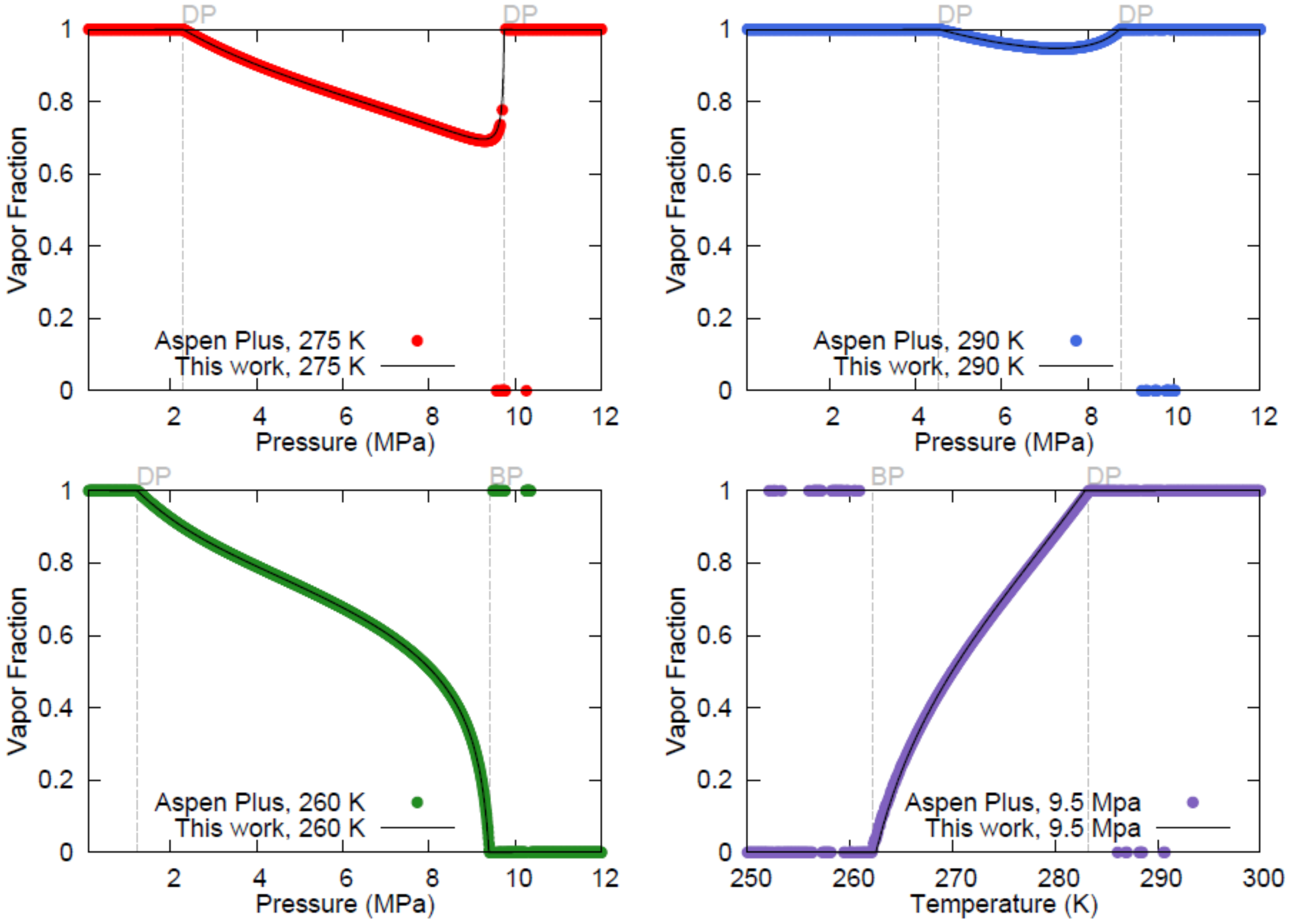
$$\Delta h_L = E + F(T - T_{\text{ref}})$$

End when surrogate model parameters stabilize

J. Boston, H. Britt, 1978. Comput. Chem. Eng., 2(1), 109–122.
H. A. J. Watson, M. Vikse, T. Gundersen, P. I. Barton, 2017. Ind. & Eng. Chem. Res., 56(4): 960-973.

Example – Retrograde Condensation

- PT-flashes on a 5-component hydrocarbon mixture
  - Peng-Robinson cubic equation of state used for both phases
- Top row simulations show retrograde condensation
  - Liquid appears as pressure decreases at const. temperature
- Bottom row simulations are at near-retrograde conditions
- Aspen Plus struggles to correctly determine the high-P phase regime



Pressure-density Behavior of Mixtures

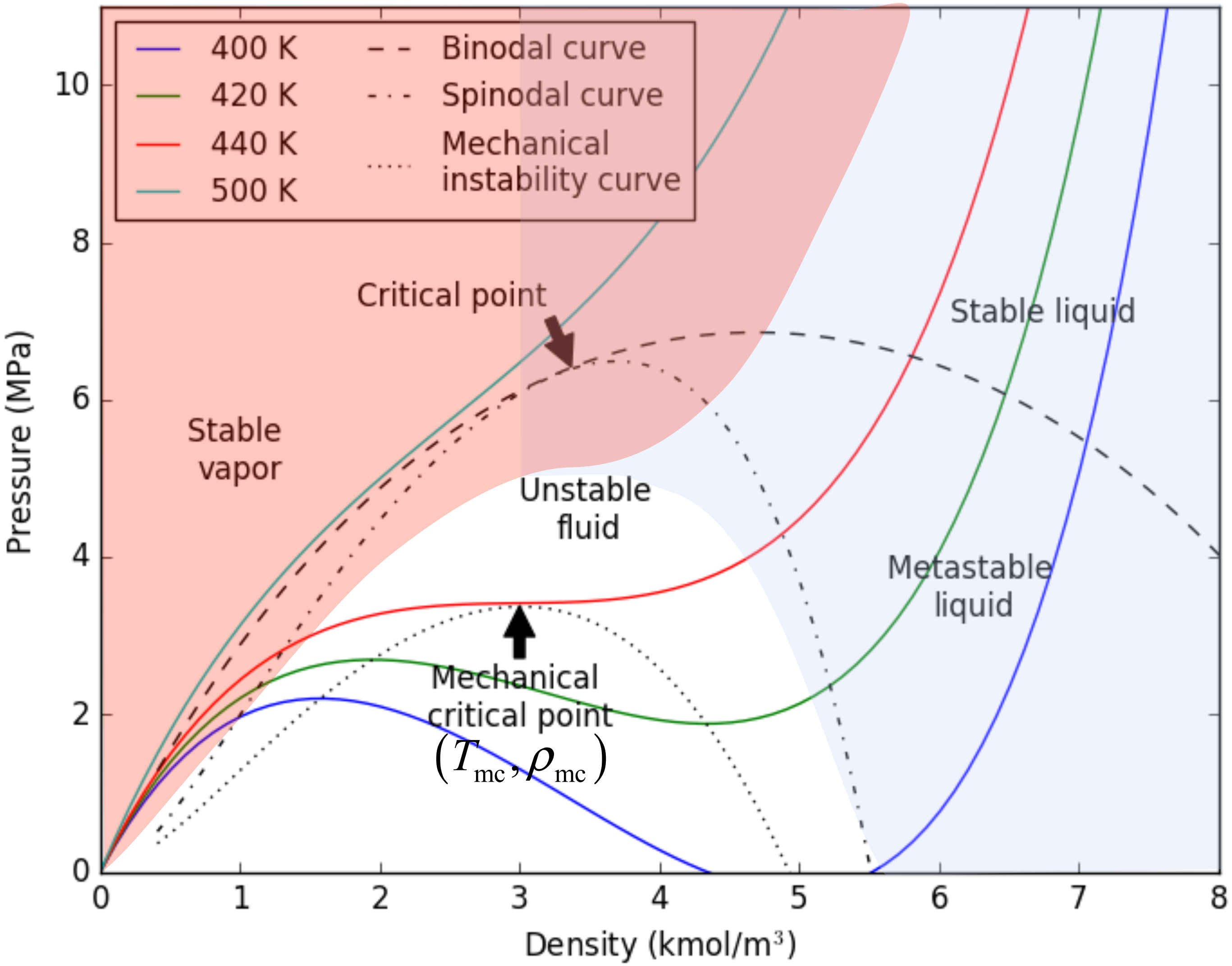
- P-ϱ isotherms for equimolar mixture of ethane and n-heptane
  - Peng-Robinson EOS:

$$P = \frac{\rho RT}{1-b\rho} - \frac{a\rho^2}{1+2b\rho-b^2\rho^2}$$

- Stable liquid and vapor states only truly exist in certain regions
  - … that are expensive to ascertain
  - Can lead to divergence or trivial solution convergence in flash calculations
- Only accept the EOS density for a given phase when:

$$P_\rho \equiv \left(\frac{\partial P}{\partial \rho}\right)_{T,\mathbf{z}} > 0.1RT \quad \text{(liquid and vapor)}$$

$$\rho > \rho_{mc} \quad \text{(liquid)}$$



Mathias, P. M., Boston, J. F., & Watanasiri, S., 1984. Effective utilization of equations of state for thermodynamic properties in process simulation. AIChE Journal, 30(2), 182–186.

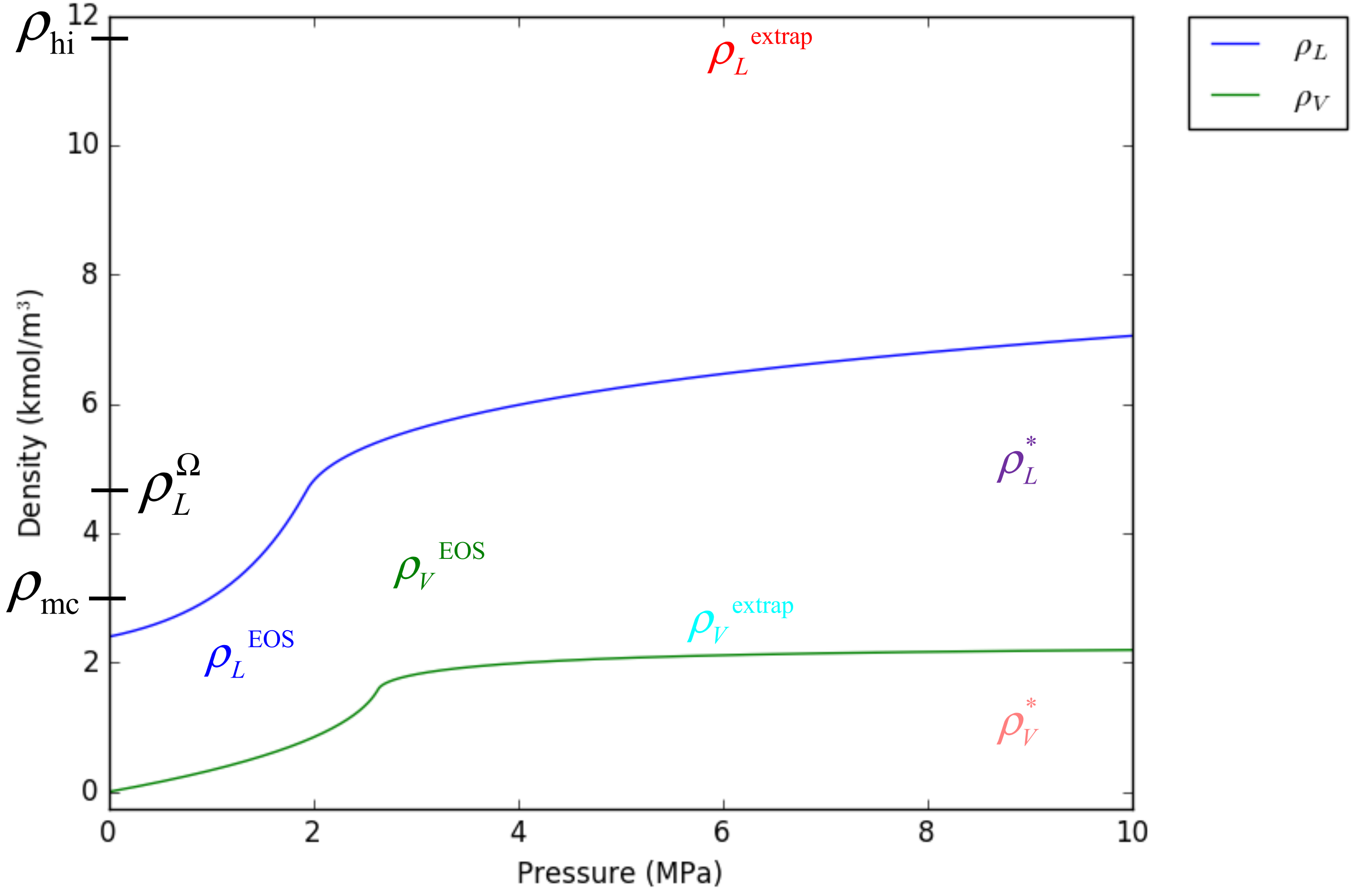
Nonsmooth Extrapolation Algorithm

Algorithm 1 Evaluate liquid density and scaling pressure.

1: **procedure** LIQUID DENSITY EVALUATION

2: Solve the EOS model for ρ_L^{EOS}.

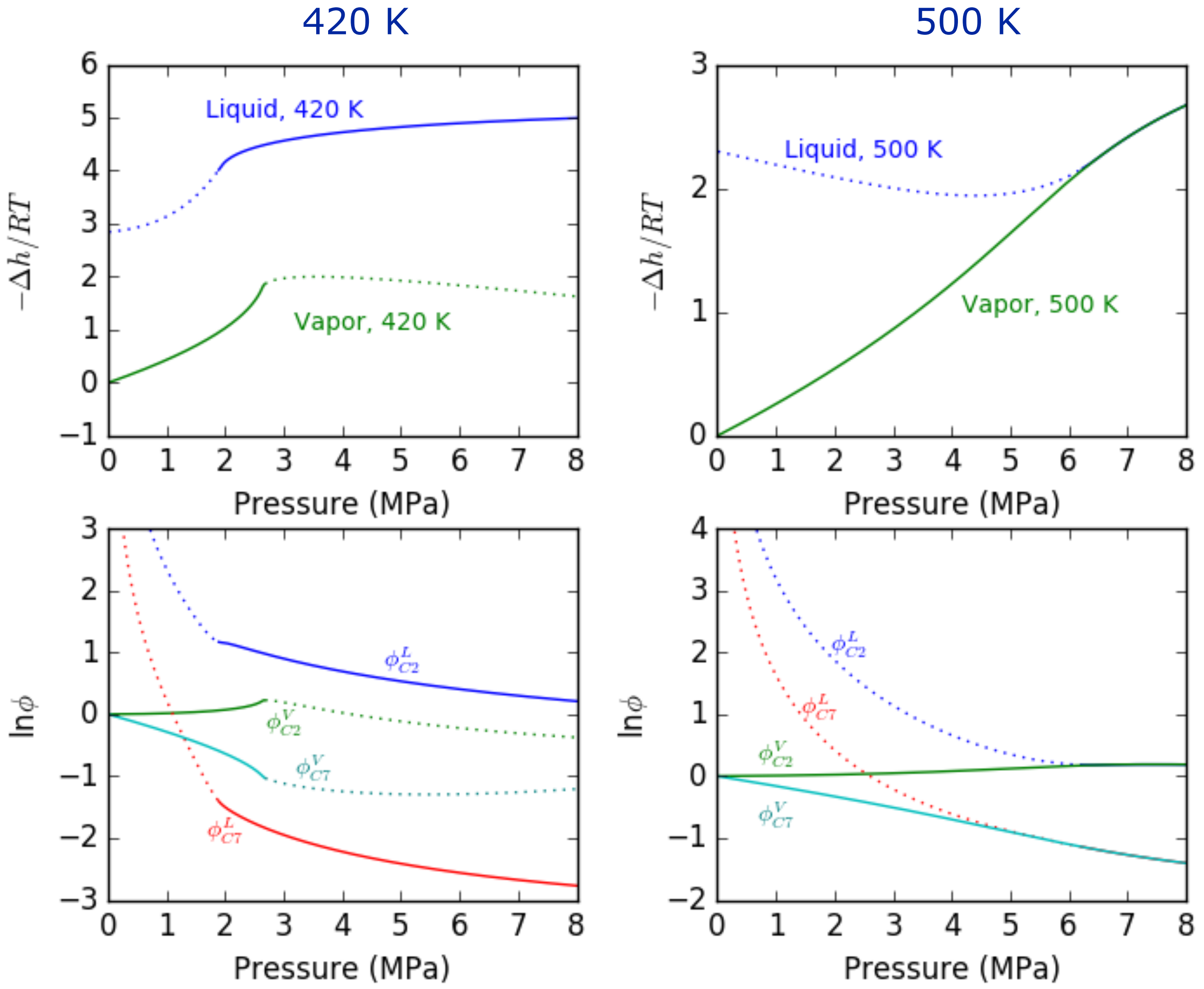
$$P_\rho(\rho, T, \mathbf{x}) = 0.1RT$$

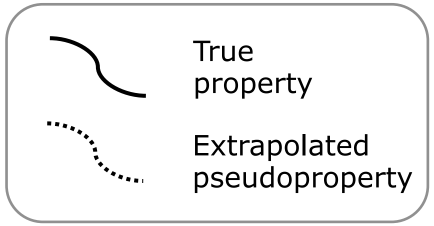


Pseudoproperty Evaluation

Enthalpy departure

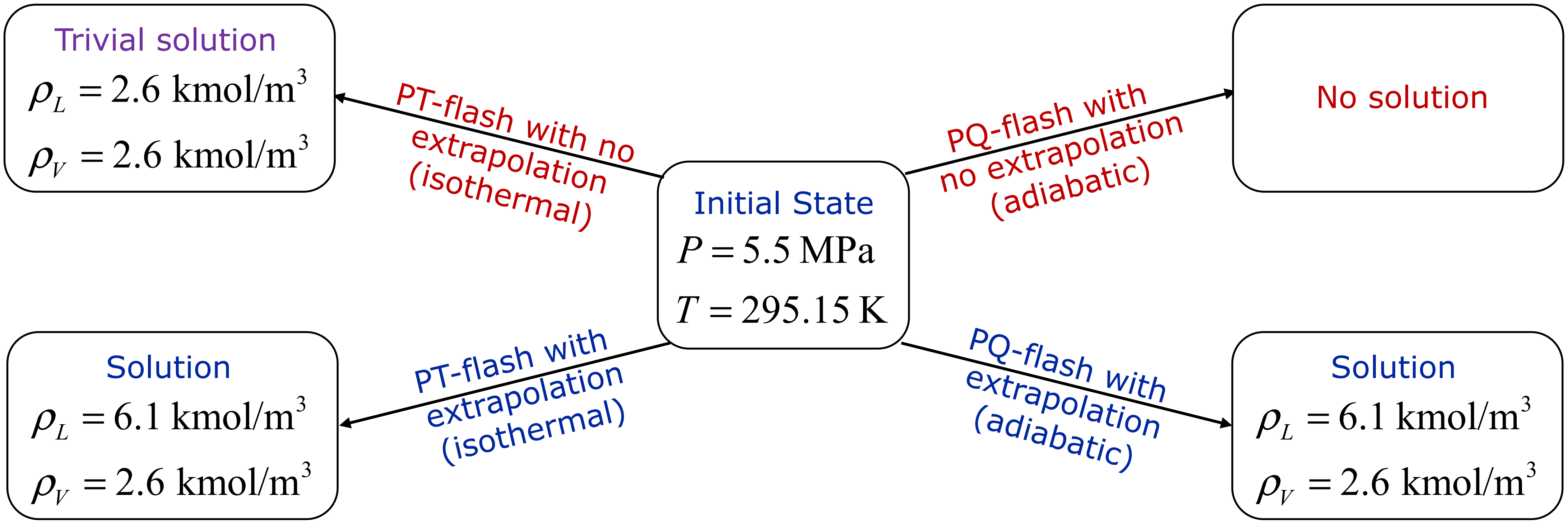
Fugacity coefficients





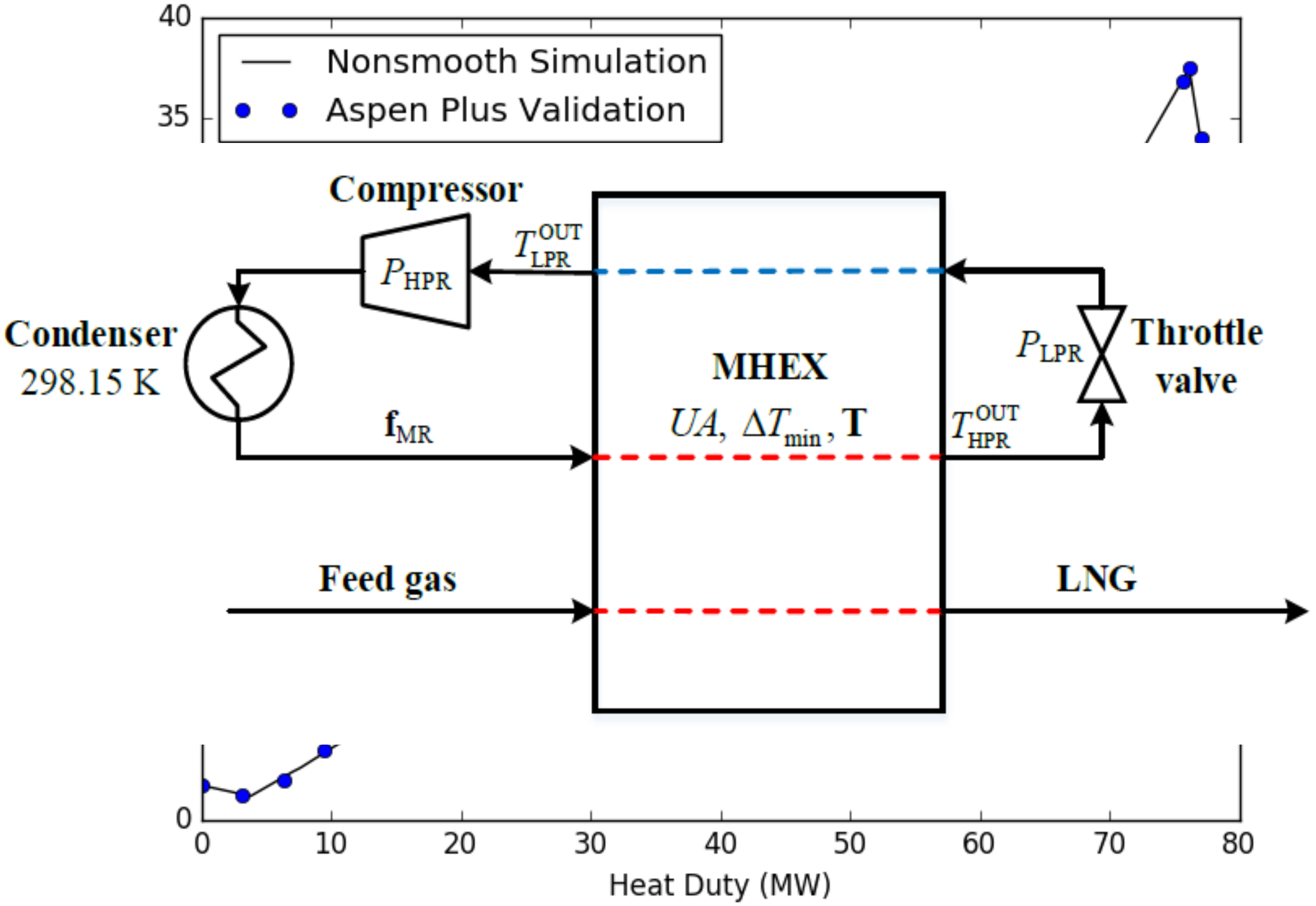
Enabling Impact on Flash Calculations

- Example: natural gas stream in liquefaction process
  - 91.6% C1, 4.93% C2, 1.71% C3, 0.35% n-C4, 0.40% i-C4, 0.01% i-C5, 1.00% N2



PRICO Process Simulation with a Cubic EOS (Peng-Robinson)

- Ex. Simulate liquefying a natural gas mixture using a MHEX with UA = 12.0 MW/K, calculating:
  - Low pressure level (P_{LPR}),
  - Cold temperature outlet ($T_{\mathrm{LPR}}^{\mathrm{OUT}}$),
  - Minimum approach temperature ($\Delta T_{\min}$)
- Nonsmooth model: 27 equations and variables after discretizing cooling curve of *each* stream into:
  - Five affine segments for superheated regime
  - Five affine segments for subcooled regime
  - Twenty affine segments for two-phase regime
    - Denote this as $n_{2\mathrm{p}} = 20$
- Equation-solving problem
  - Simple, automatic initialization procedure
- Isentropic compression power: 18.02 MW
- Profiles:



H. A. J. Watson, M. Vikse, T. Gundersen, P. I. Barton. Submitted. Reliable Flash Calculations: Part 2. Process flowsheeting with nonsmooth models and generalized derivatives.

Robustness and Convergence rate

- How important is exact sensitivity analysis?

- Approximations of LD-derivatives:
  - Concatenated directional derivatives:

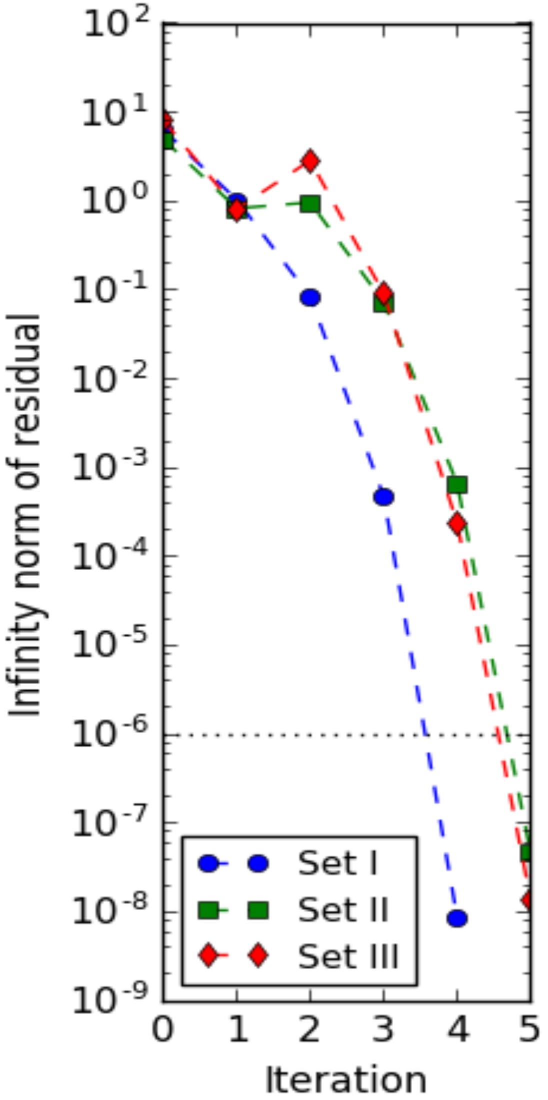
$$\mathbf{f}'(\mathbf{x};\mathbf{I}_{n\times n}) \neq \left[\mathbf{f}'(\mathbf{x};\mathbf{e}_{(1)}) \ \dots \ \mathbf{f}'(\mathbf{x};\mathbf{e}_{(n)})\right]$$

  - Finite differences:

$$\mathbf{f}'(\mathbf{x};\mathbf{e}_{(j)}) \approx \frac{\mathbf{f}(\mathbf{x}+\delta\mathbf{e}_{(j)})-\mathbf{f}(\mathbf{x})}{\delta}$$

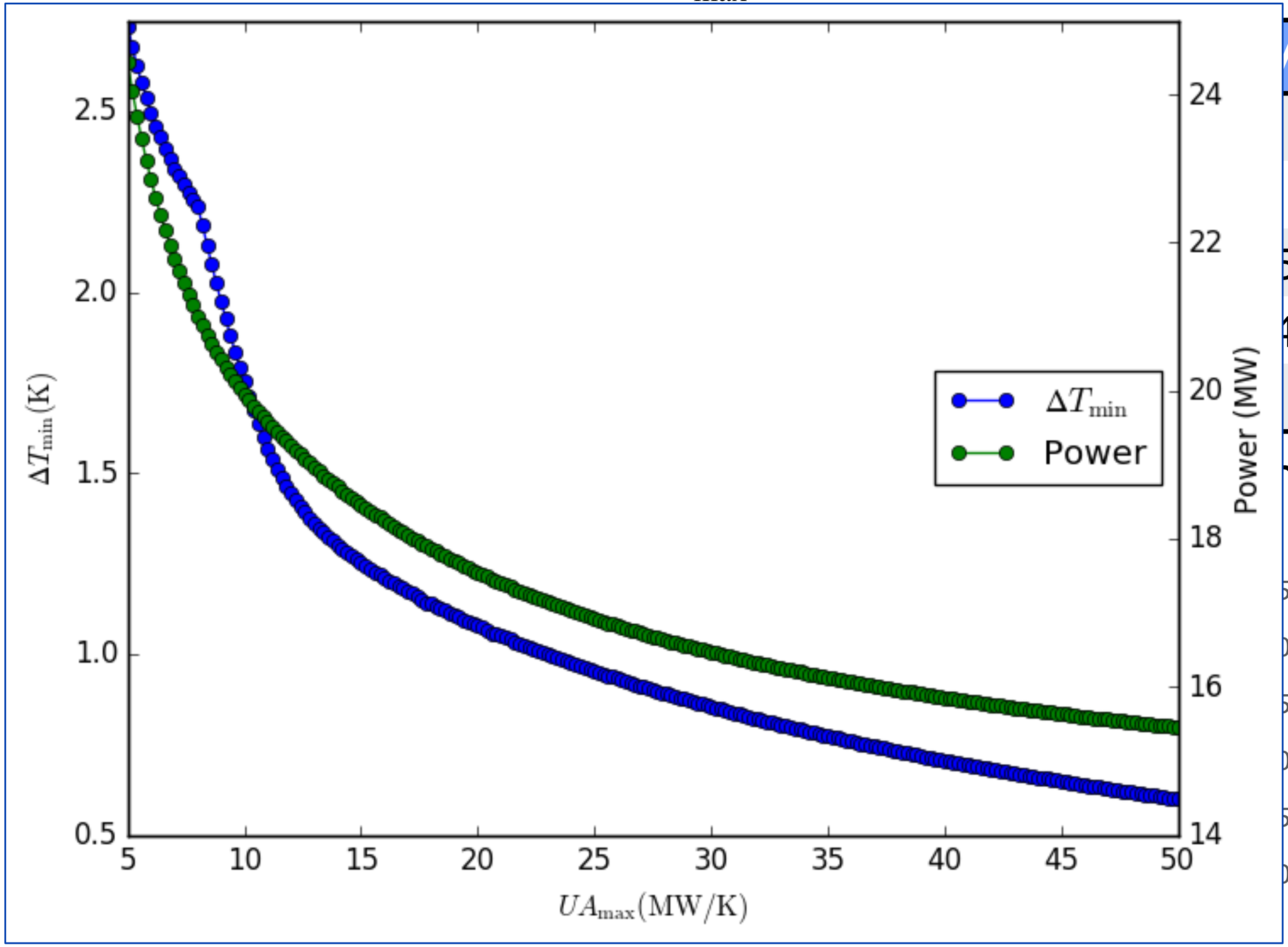
- Variable sets:
  - Set I: $P_{\mathrm{LPR}}, T_{\mathrm{LPR}}^{\mathrm{OUT}}, \Delta T_{\min}$
  - Set II: $f_{\mathrm{MR,C4}}, T_{\mathrm{LPR}}^{\mathrm{OUT}}, \Delta T_{\min}$
  - Set III: $P_{\mathrm{LPR}}, P_{\mathrm{HPR}}, \Delta T_{\min}$

LD derivatives | Directional derivatives | Finite differences



PRICO Process Optimization Studies

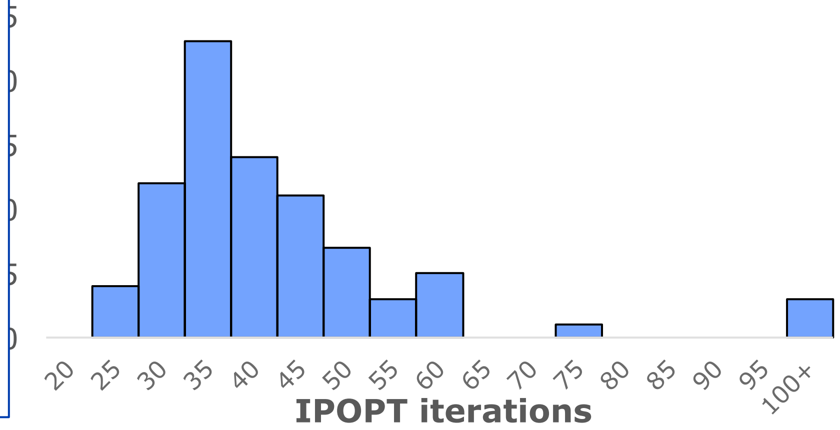
- Varying the value of UA_{max} shows the expected trends (n_{2p} = 20)



/K	20 MW/K	25 MW/K
	32	44
	125	171
5	17.55	16.93
4	7.87	6.47
	2.55	2.75

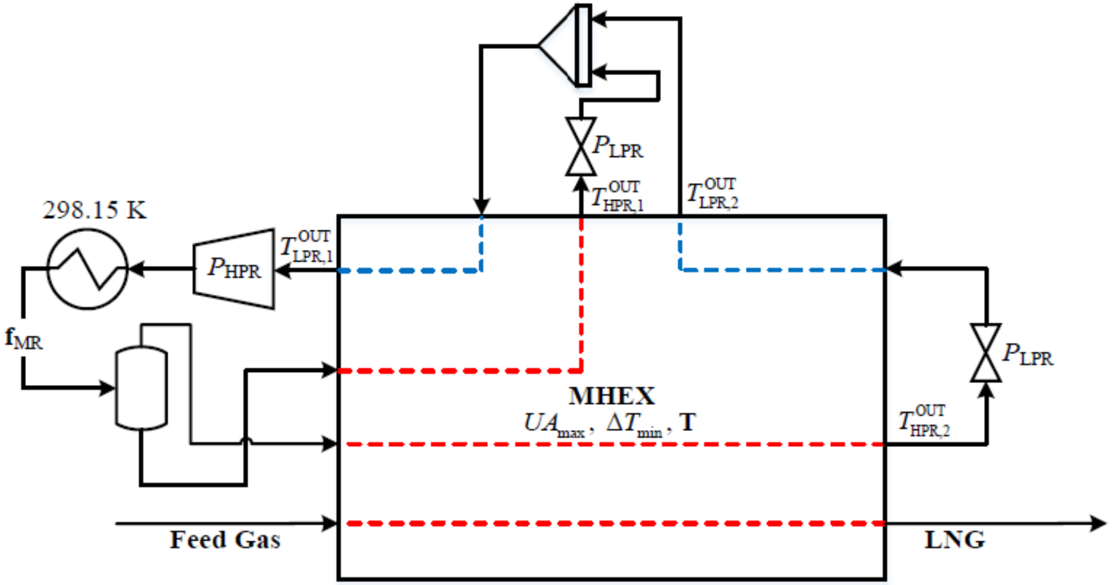
his optimization formulation

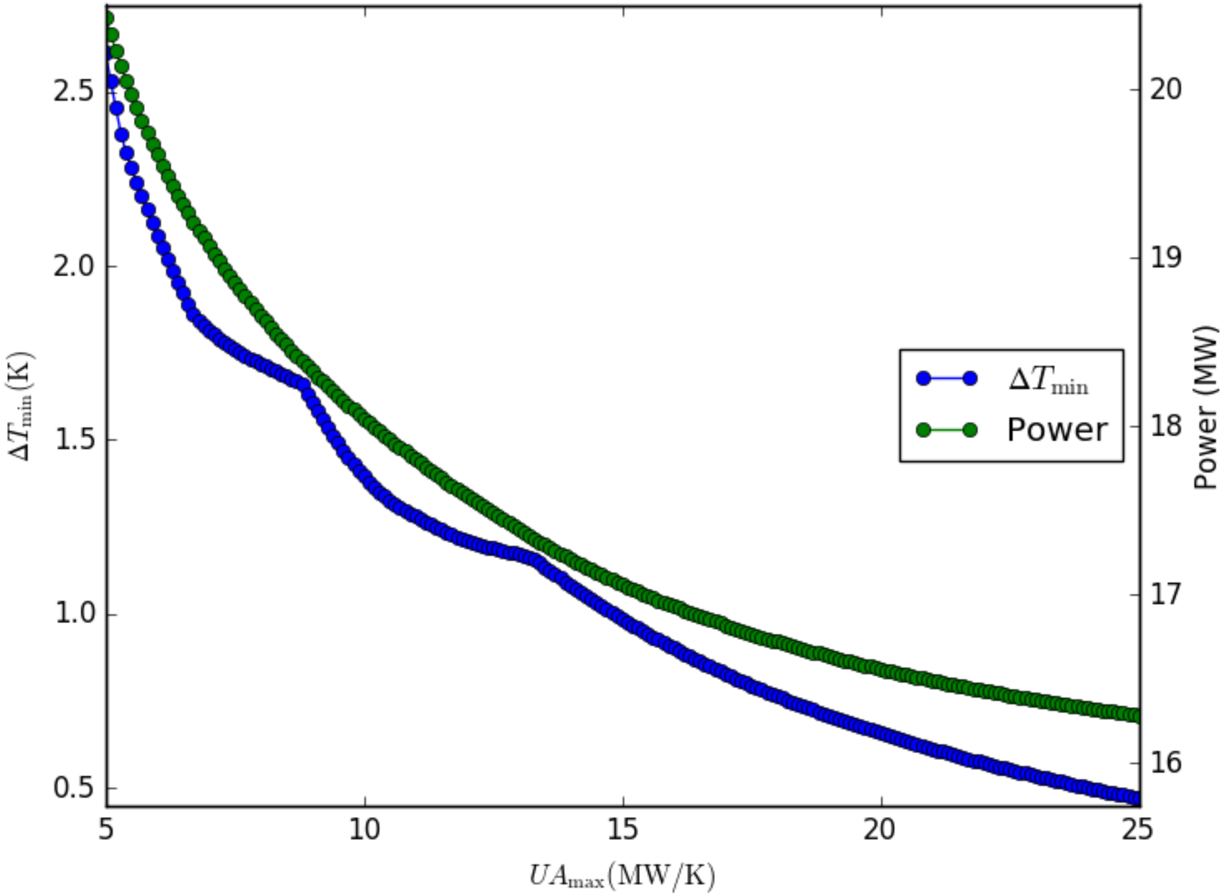
points



PRICO Process with Phase Separation

- This optimization strategy can also handle more complex liquefaction processes reliably





- Phase separation allows for more compact processes with reasonable power consumption

UA_{max} (MW/K)	6.0	8.0	10.0	12.0
IPOPT iterations	41	46	54	41
Power, 80% eff. (MW)	19.61	18.66	18.05	17.59