The absolute necessity of getting them* right: I

*Surface tension predictions for high pressure column operations

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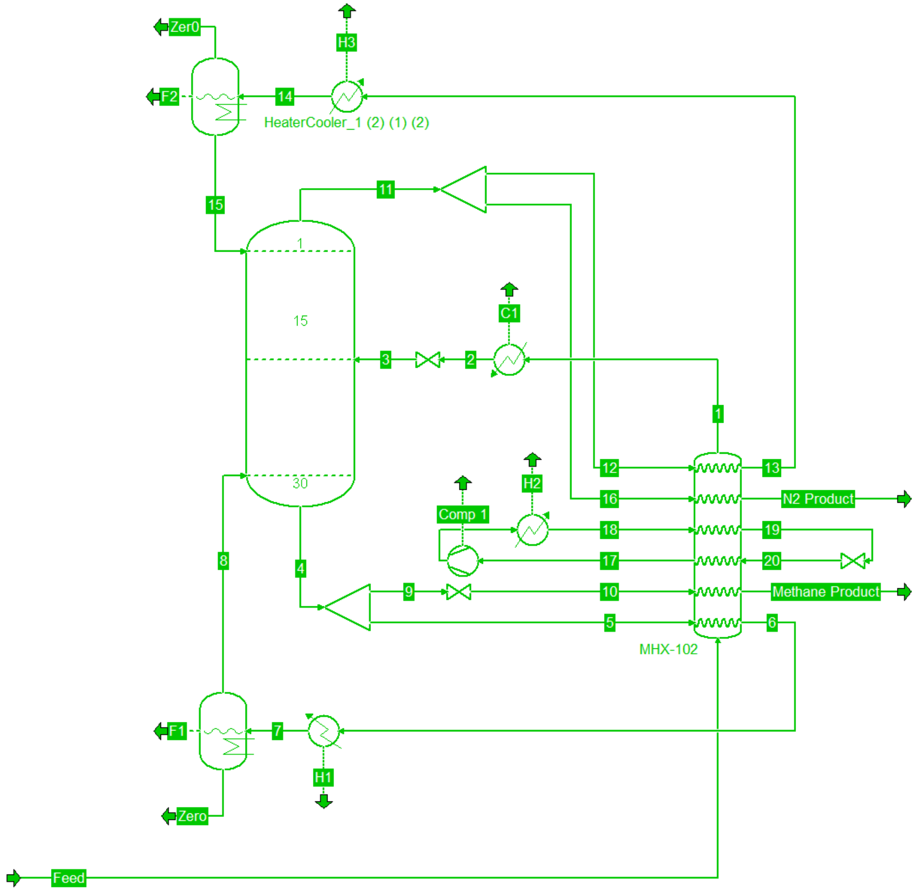
b Consultant



Kister Distillation Symposium 2023: Legacy of Dr. Walter Stupin: Distillation Simulations Are Only Good when the VLE and Physical Properties Predictions Are Good

At this meeting in 2004 Dan Summers showed this plot…

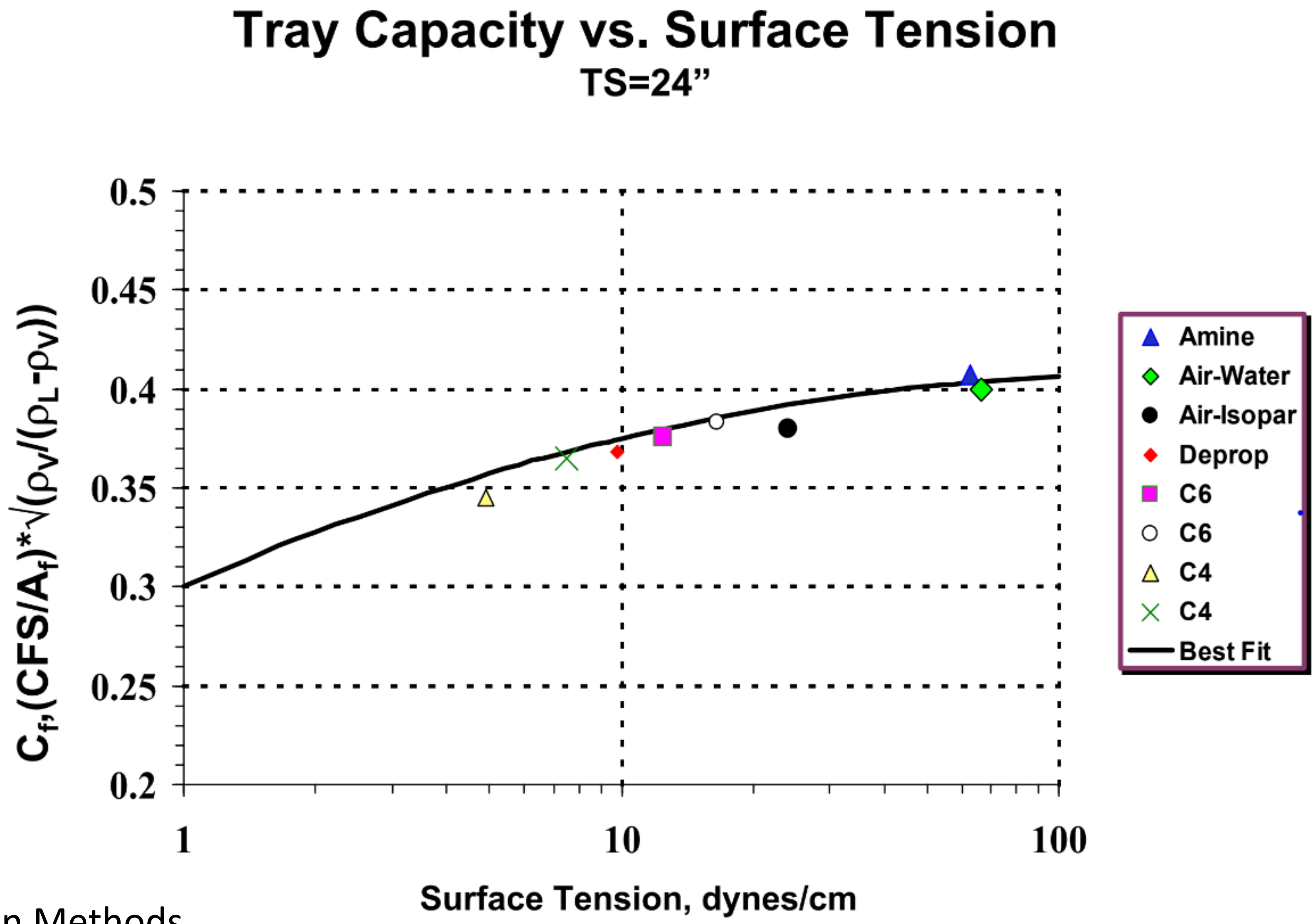
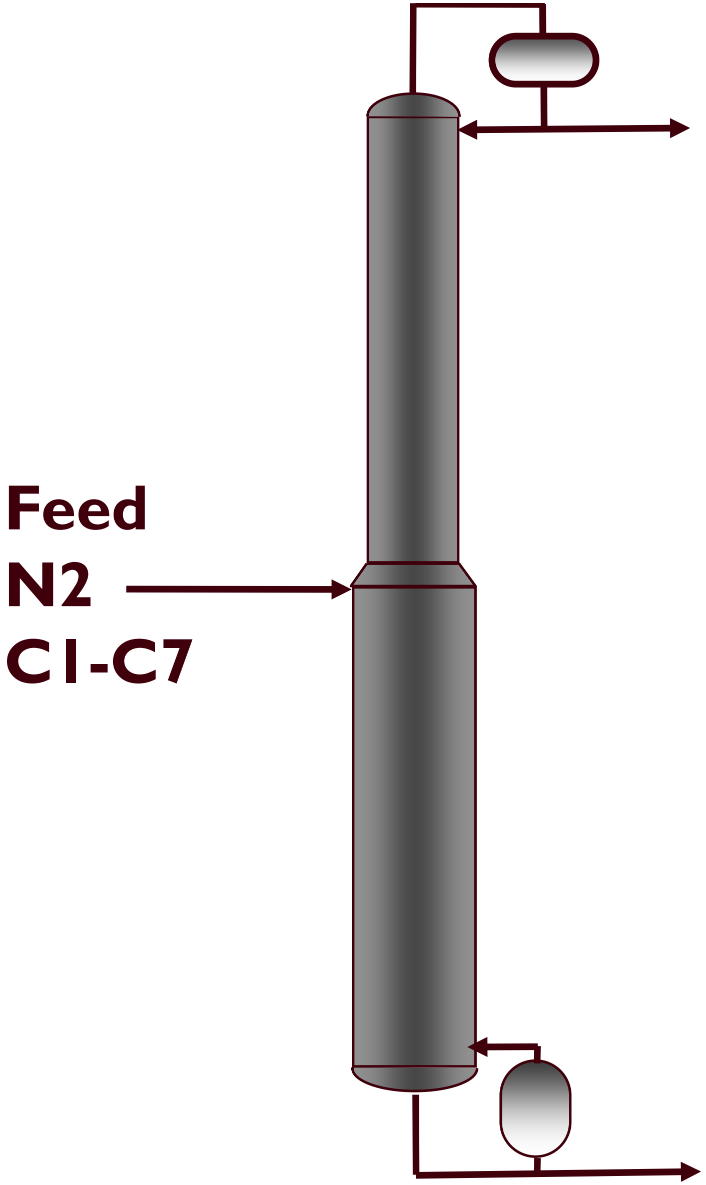


Figure 7

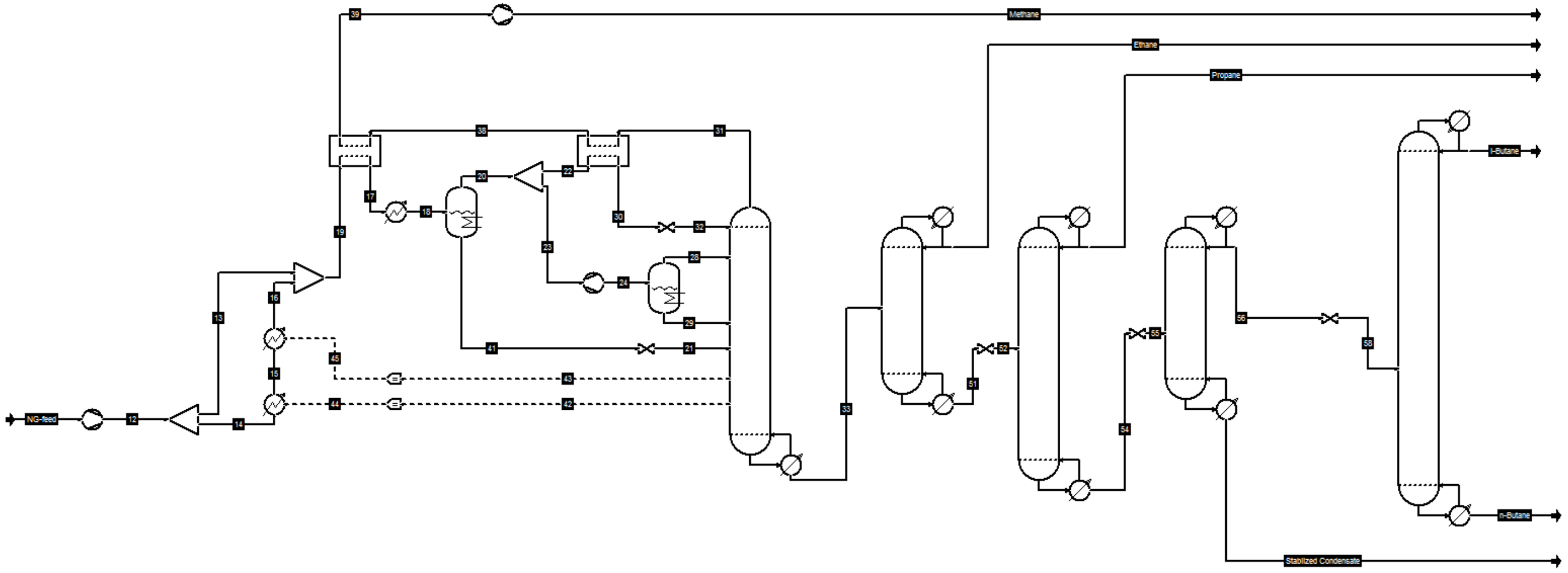
Summers, Daniel R. 2004, Commercial Tray Design Methods and Software: Pencils to Pentiums, Paper 100d presented at the AIChE Spring National Meeting, Distillation Honors Session: Dale Nutter

I get questions…



Does your program have the Weinaug-Katz model for surface tension?

Quiz: What happened next?



This is just a picture of a chemical process. It has no known relationship to this quiz question!

Engineers A, B, and C work for different companies.

Companies A, B, and C use different process simulation programs.

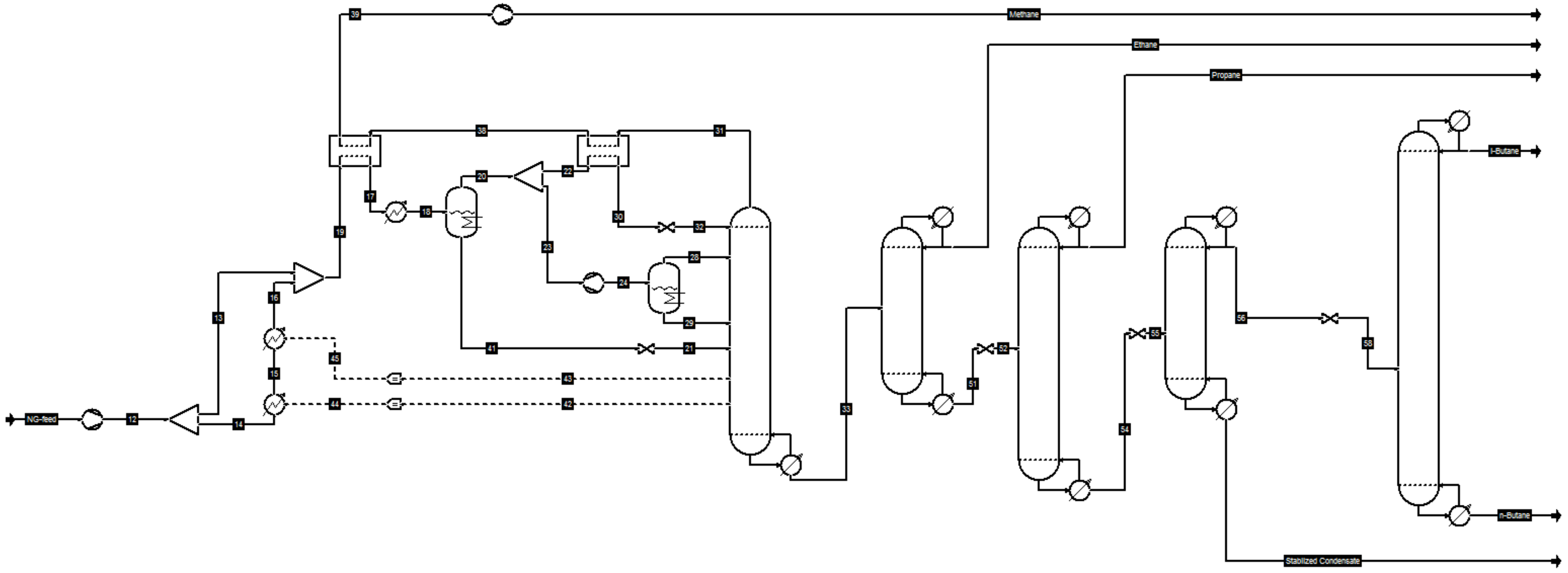
Engineers A, B, and C select the models to use.

Project managers A, B, and C insist that all parties use the same property models.

Simulation systems A, B, and C, don't have the same model for surface tension.

How did Companies A, B, and C resolve this?

Quiz: What happened next?



This is just a picture of a chemical process. It has no known relationship to this quiz question!

Would it matter if Engineers A, B, and C used different models for surface tension?

Why σ is important to chemical engineers

The importance of surface tension in design of separation equipment can only be understated. **Over prediction of surface tension, particularly when significantly below10 dyn/cm, can lead to significant undersizing of vapor−liquid separations equipment.**[169]

Gupta, S., Elliott, J.R., Anderko, A., Crosthwaite, J., Chapman, W.G., Lira, C.T., **2023**.
Current Practices and Continuing Needs in Thermophysical Properties for the Chemical Industry.
Ind. Eng. Chem. Res. 62, 3394–3427. https://doi.org/10.1021/acs.iecr.2c03153

Reference 169

McCarley, K., December 2021. Finding the Capacity of a Distillation Column. CEP 23–28.

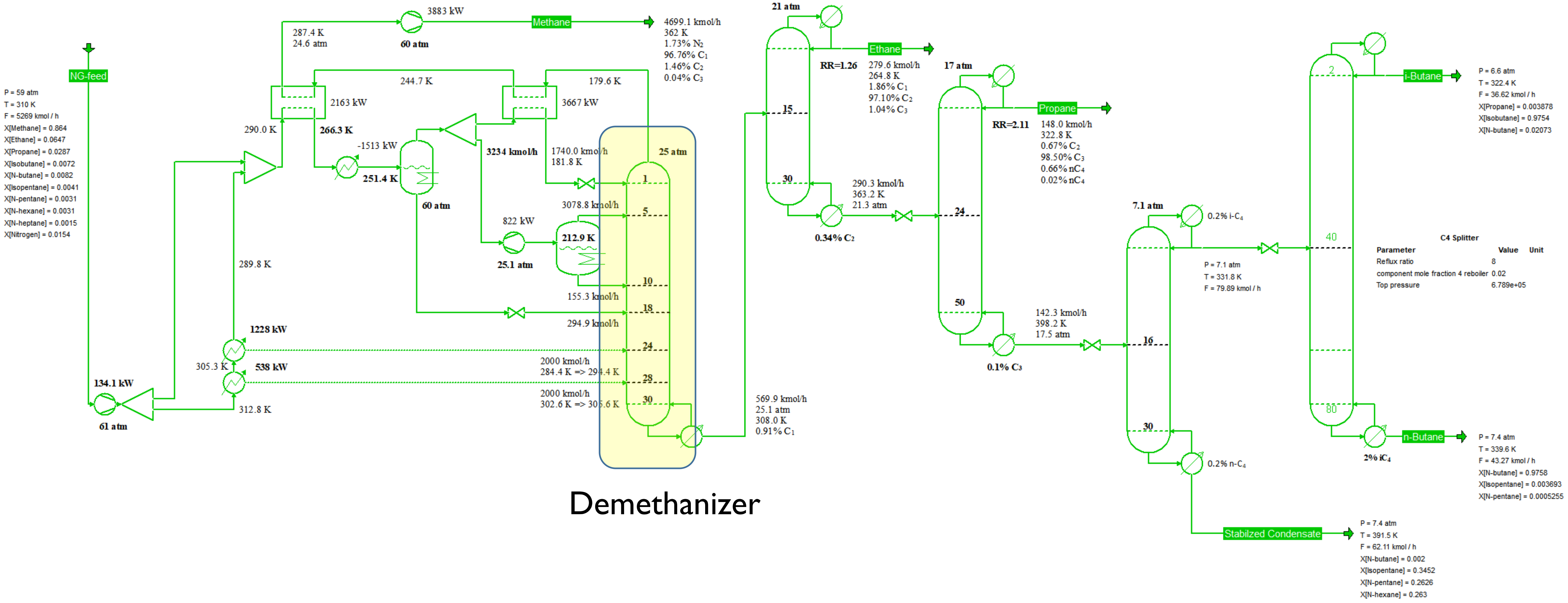
How low can it (σ) go?

Process[+]	**Key components**	**Pressure**	**Surface tension (dyne/cm)**
Demethanizer from natural gas train	$CH_4 – C_2H_6$	25 atm	
CO_2 – Ethane separation	$CO_2 – C_2H_6$	23.7 atm	
Ortloff process	$CH_4 – CO_2$	4.3 MPa	
Nitrogen rejection unit	$N_2 – CH_4$	2650 kPa	
C_4 splitter*	$i\text{-}C_4H_{10} – n\text{-}C_4H_{10}$	658 kPa	

[+] All process simulations are available from http://chemsep.com/downloads/index.html

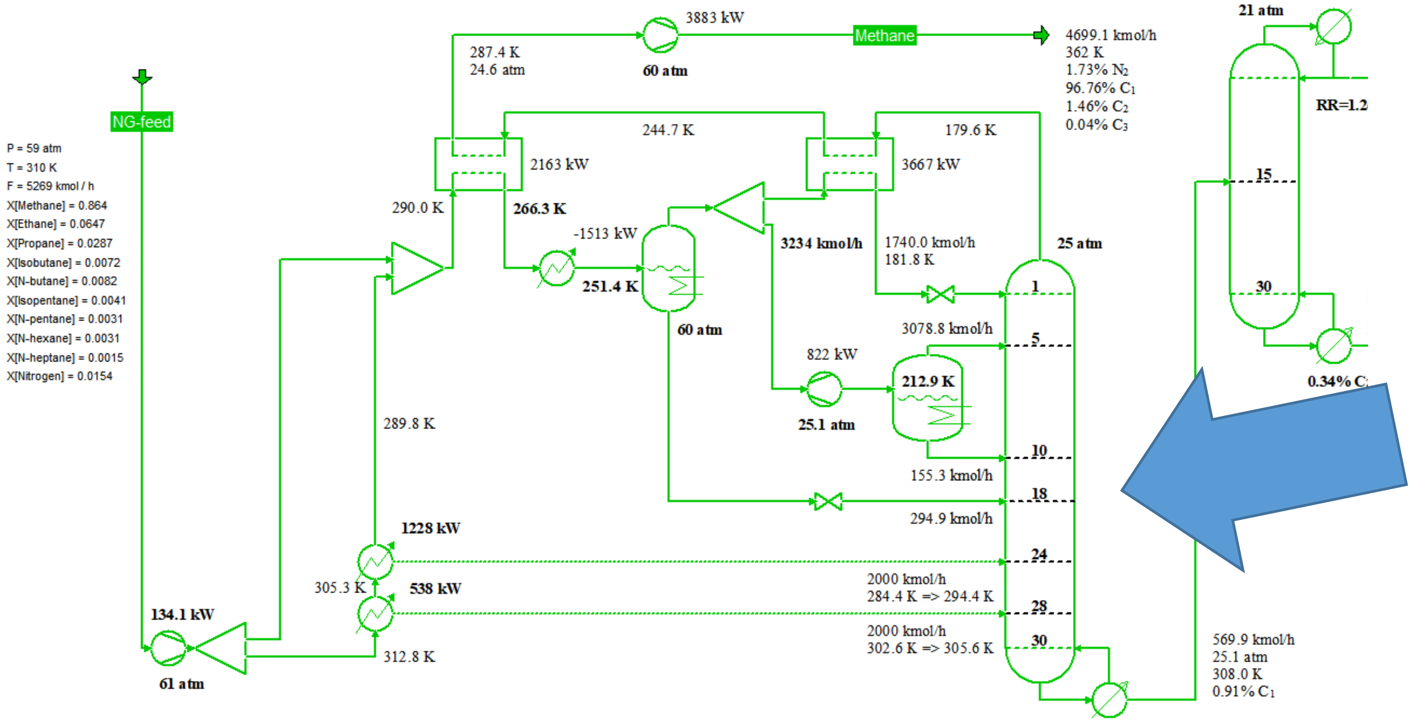
* Not *normally* operated at a pressure high enough for low σ but...

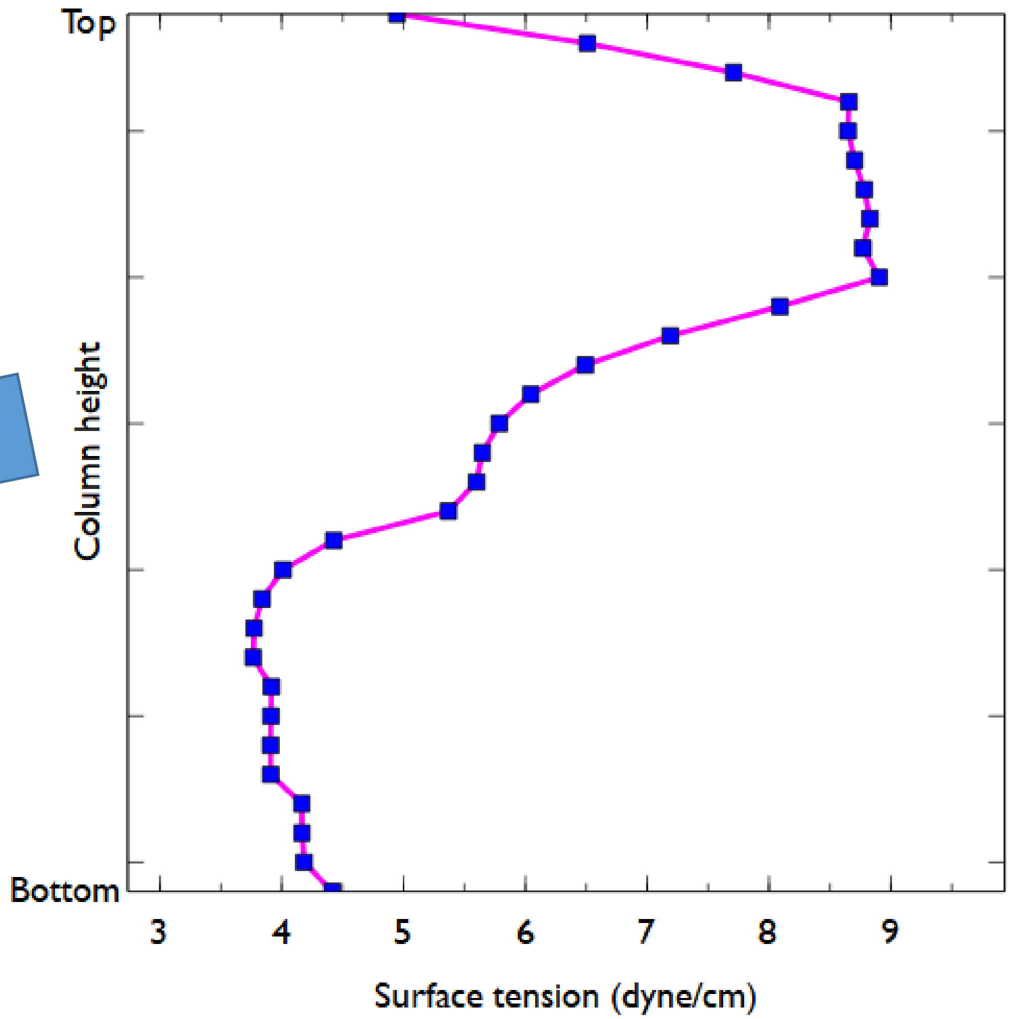
Natural Gas Train – After Luyben (2013)



Luyben, W.L., 2013. Control of a Train of Distillation Columns for the Separation of Natural Gas Liquid. Industrial & Engineering Chemistry Research 52, 10741–10753. https://doi.org/10.1021/ie400869v

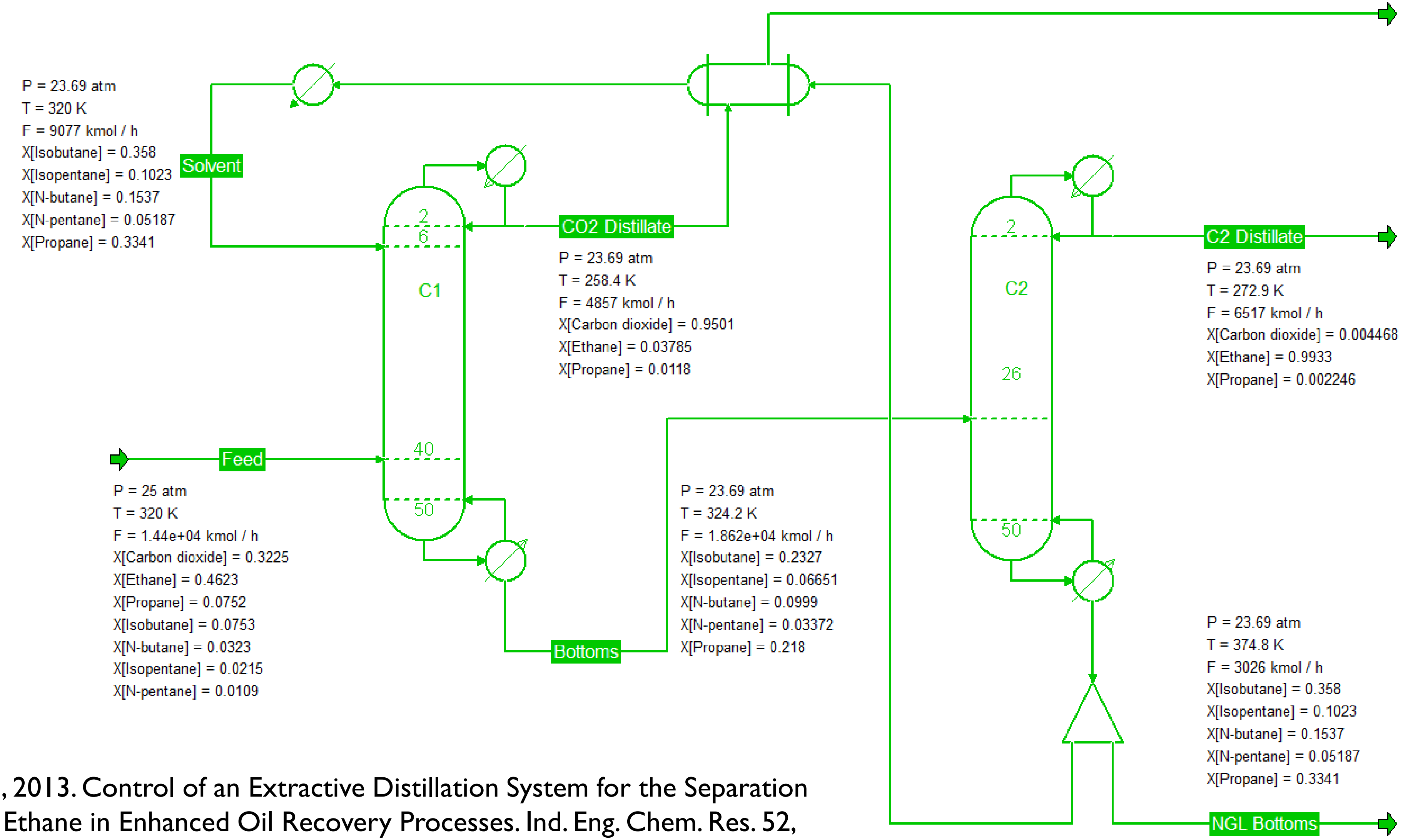
Natural Gas Train – After Luyben (2013)





Surface tension profile for the demethanizer

CO_2 – Ethane Extractive Disillation with LNG – After Luyben (2013)



P = 23.69 atm
T = 320 K
F = 9077 kmol / h
X[Isobutane] = 0.358
X[Isopentane] = 0.1023
X[N-butane] = 0.1537
X[N-pentane] = 0.05187
X[Propane] = 0.3341

P = 23.69 atm
T = 258.4 K
F = 4857 kmol / h
X[Carbon dioxide] = 0.9501
X[Ethane] = 0.03785
X[Propane] = 0.0118

P = 23.69 atm
T = 272.9 K
F = 6517 kmol / h
X[Carbon dioxide] = 0.004468
X[Ethane] = 0.9933
X[Propane] = 0.002246

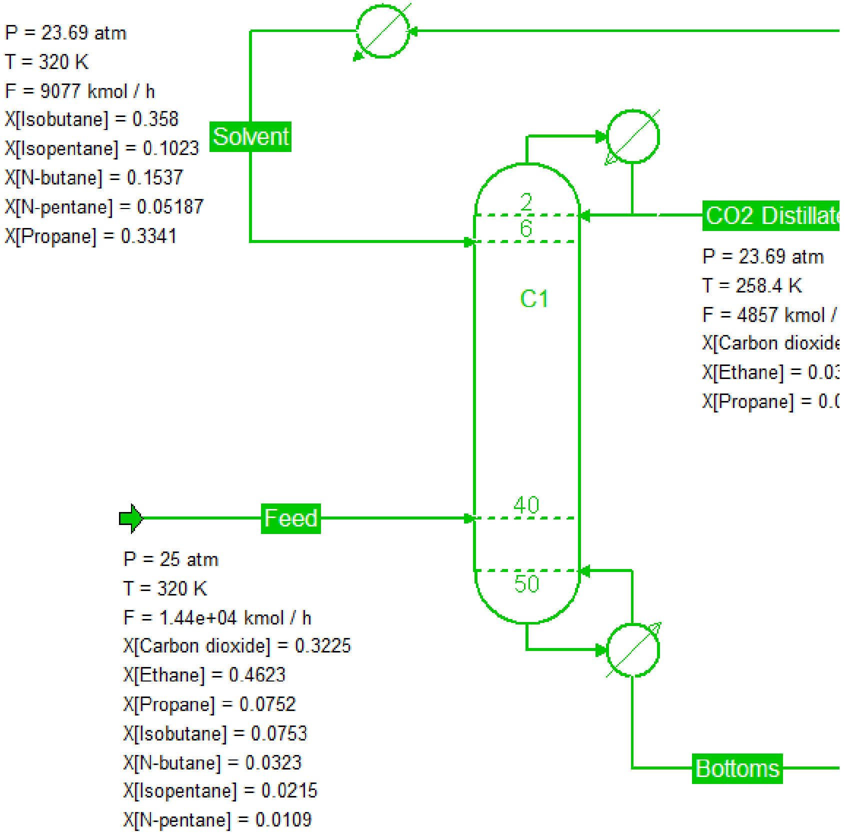
P = 25 atm
T = 320 K
F = 1.44e+04 kmol / h
X[Carbon dioxide] = 0.3225
X[Ethane] = 0.4623
X[Propane] = 0.0752
X[Isobutane] = 0.0753
X[N-butane] = 0.0323
X[Isopentane] = 0.0215
X[N-pentane] = 0.0109

P = 23.69 atm
T = 324.2 K
F = 1.862e+04 kmol / h
X[Isobutane] = 0.2327
X[Isopentane] = 0.06651
X[N-butane] = 0.0999
X[N-pentane] = 0.03372
X[Propane] = 0.218

P = 23.69 atm
T = 374.8 K
F = 3026 kmol / h
X[Isobutane] = 0.358
X[Isopentane] = 0.1023
X[N-butane] = 0.1537
X[N-pentane] = 0.05187
X[Propane] = 0.3341

Luyben, W.L., 2013. Control of an Extractive Distillation System for the Separation of CO2 and Ethane in Enhanced Oil Recovery Processes. Ind. Eng. Chem. Res. 52, 10780–10787. https://doi.org/10.1021/ie401602c

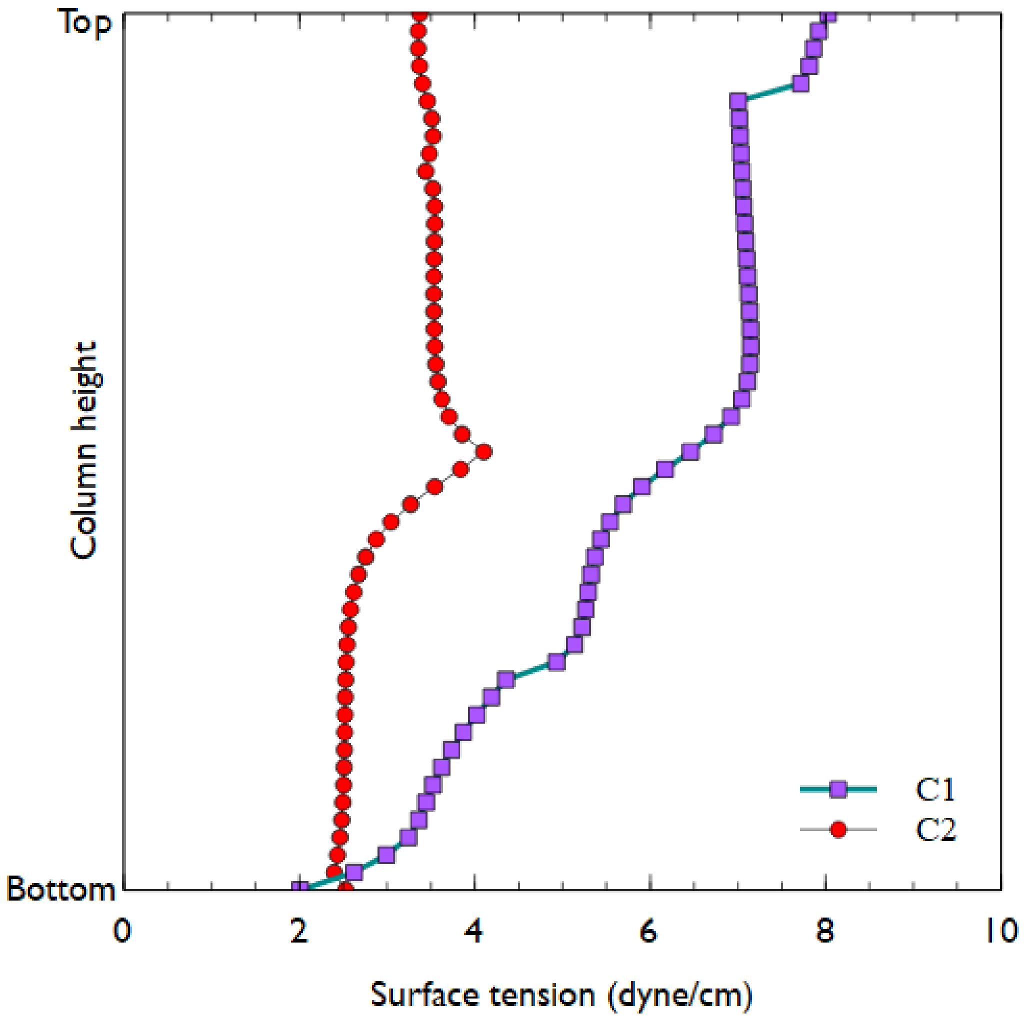
CO_2 – Ethane Extractive Disillation with LNG – After Luyben (2013)



P = 23.69 atm
T = 320 K
F = 9077 kmol / h
X[Isobutane] = 0.358
X[Isopentane] = 0.1023
X[N-butane] = 0.1537
X[N-pentane] = 0.05187
X[Propane] = 0.3341

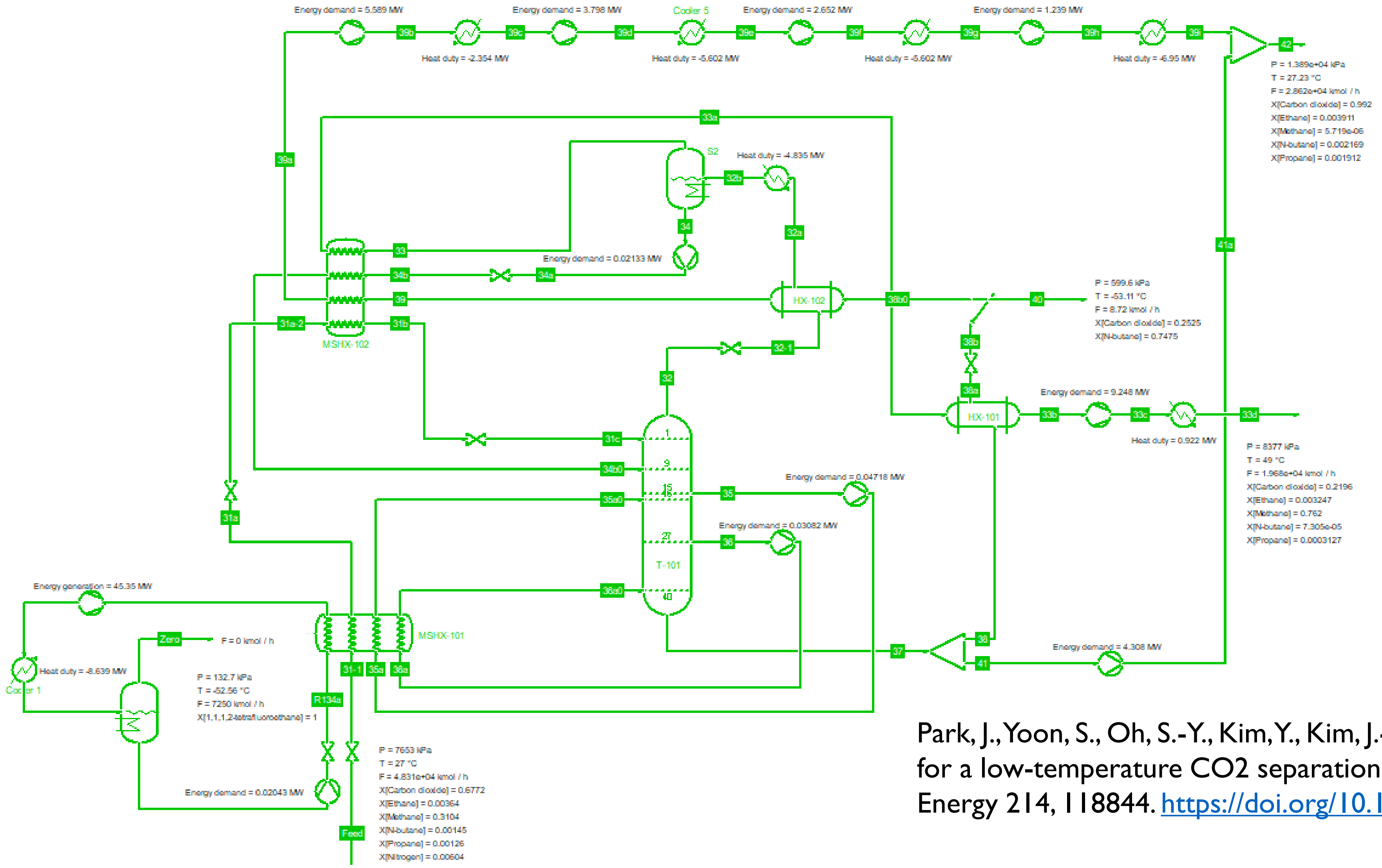
P = 23.69 atm
T = 258.4 K
F = 4857 kmol /
X[Carbon dioxid
X[Ethane] = 0.03
X[Propane] = 0.

P = 25 atm
T = 320 K
F = 1.44e+04 kmol / h
X[Carbon dioxide] = 0.3225
X[Ethane] = 0.4623
X[Propane] = 0.0752
X[Isobutane] = 0.0753
X[N-butane] = 0.0323
X[Isopentane] = 0.0215
X[N-pentane] = 0.0109



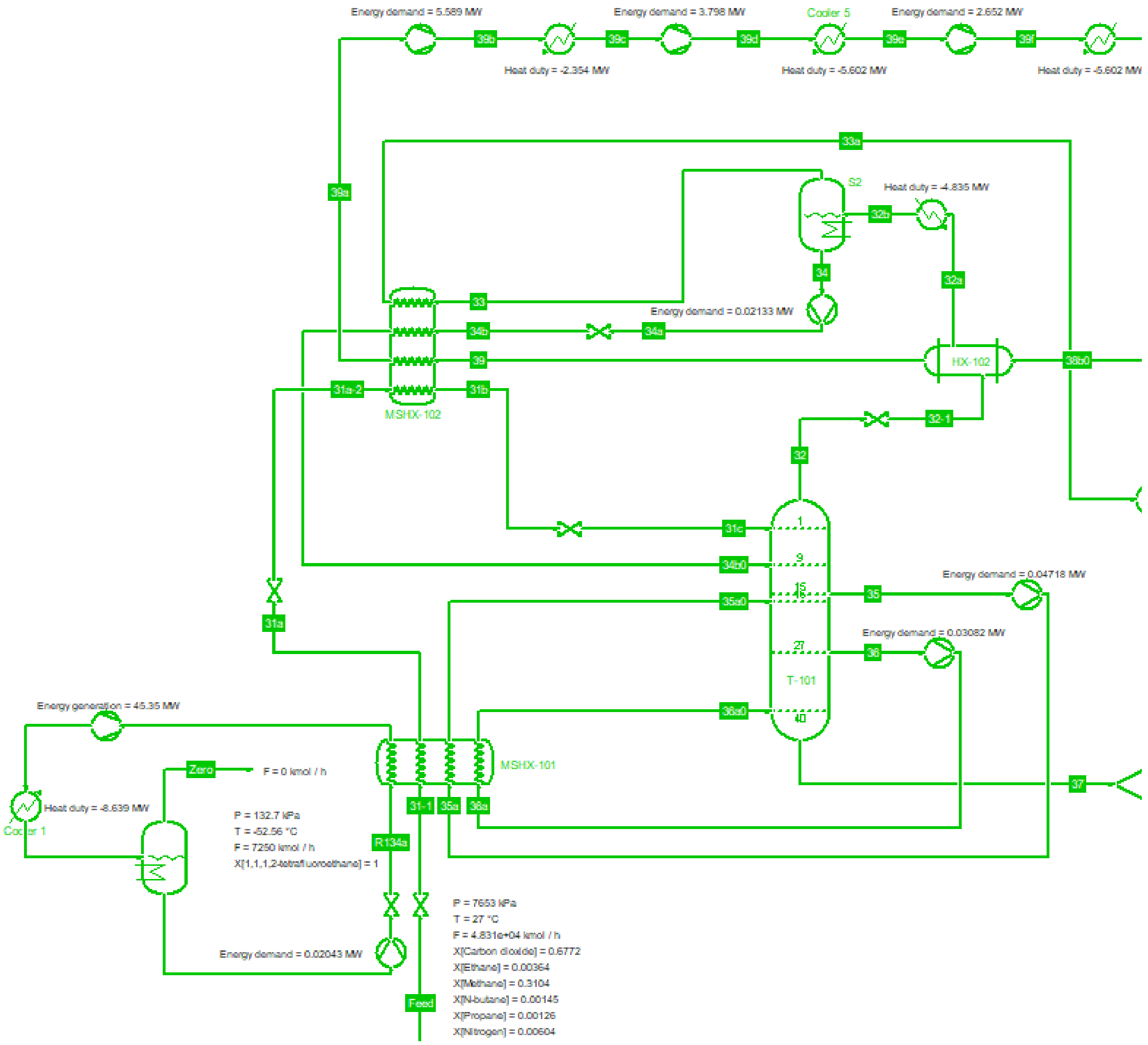
Surface tension profiles in both columns

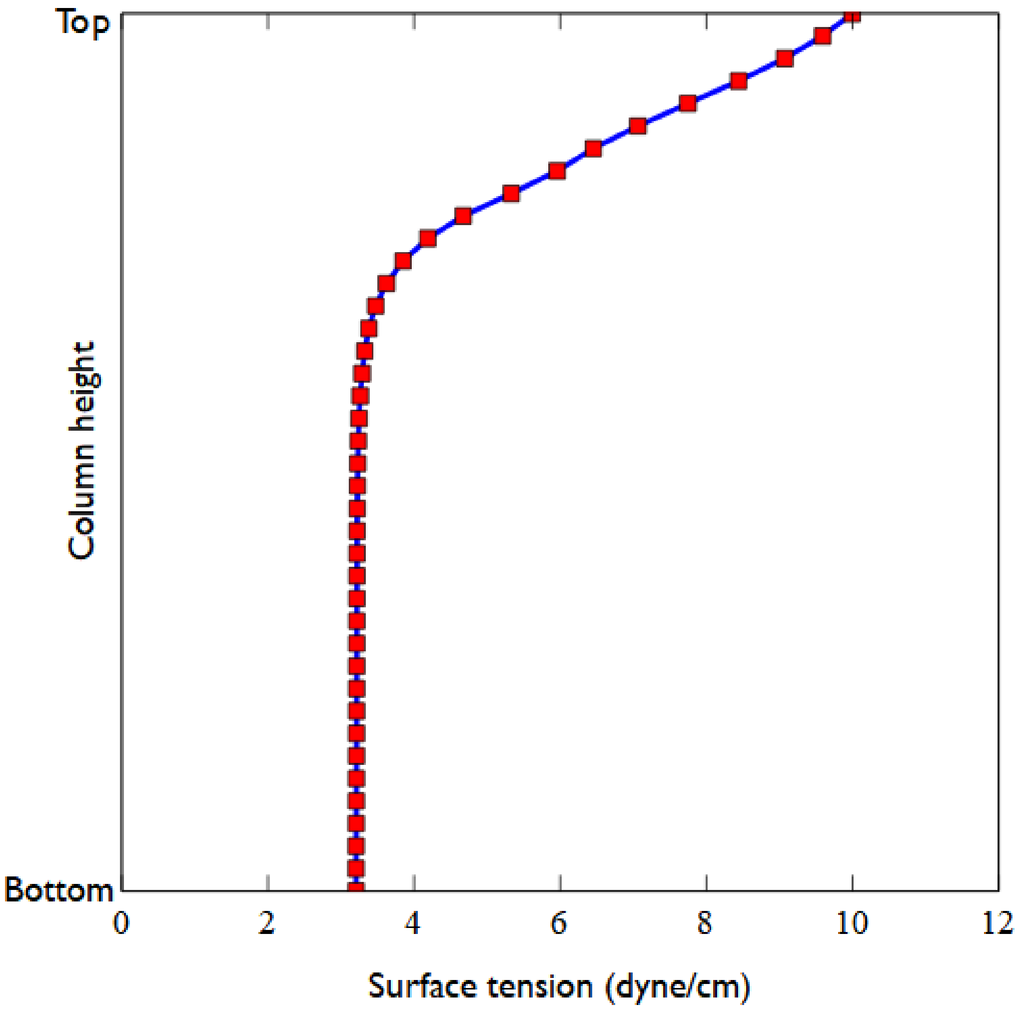
Ortloff Process for CO_2 Separation – After Park et al. (2021)



Park, J., Yoon, S., Oh, S.-Y., Kim, Y., Kim, J.-K., 2021. Improving energy efficiency for a low-temperature CO2 separation process in natural gas processing. Energy 214, 118844. https://doi.org/10.1016/j.energy.2020.118844

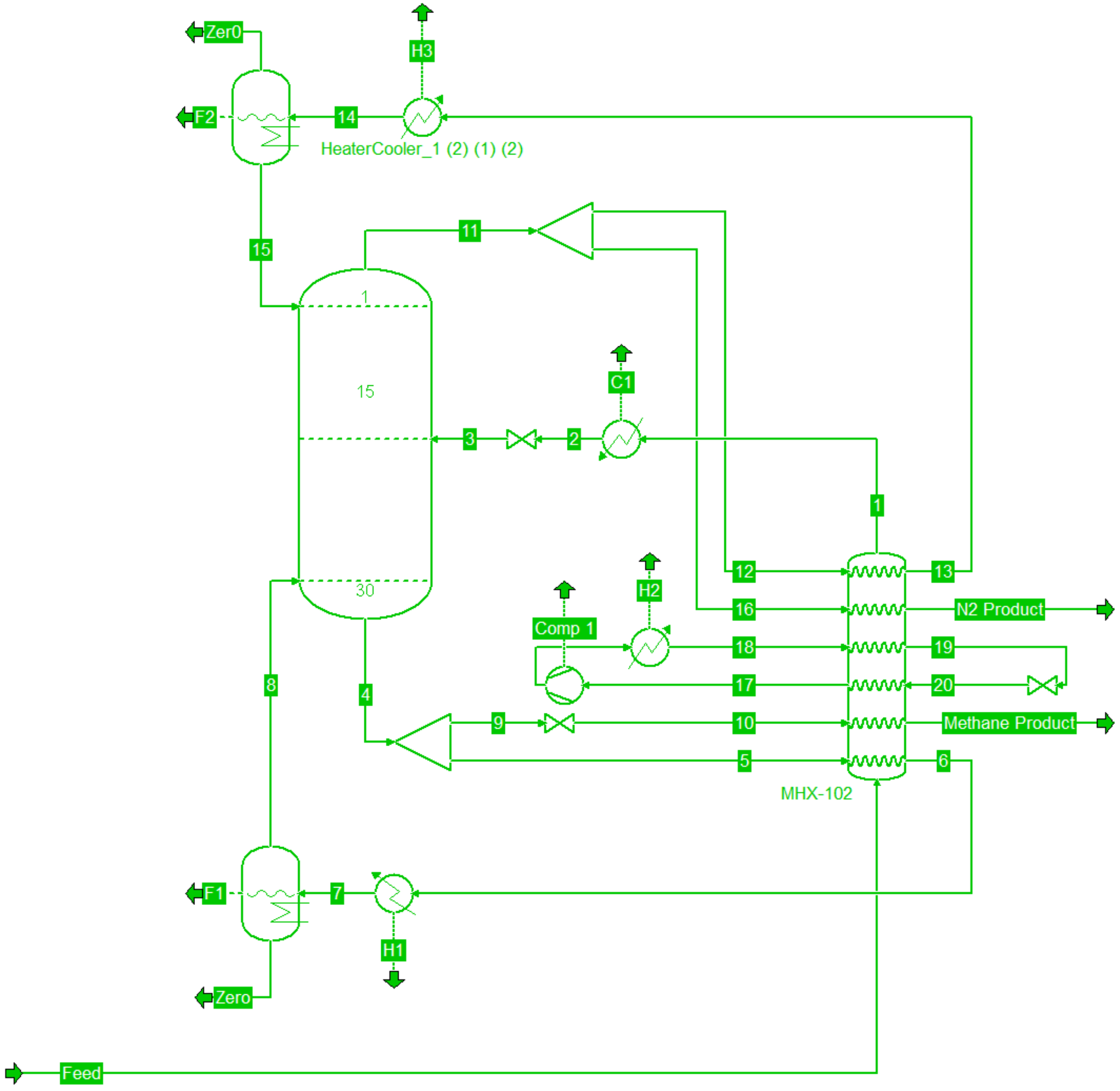
Ortloff Process for CO_2 Separation – After Park et al. (2021)

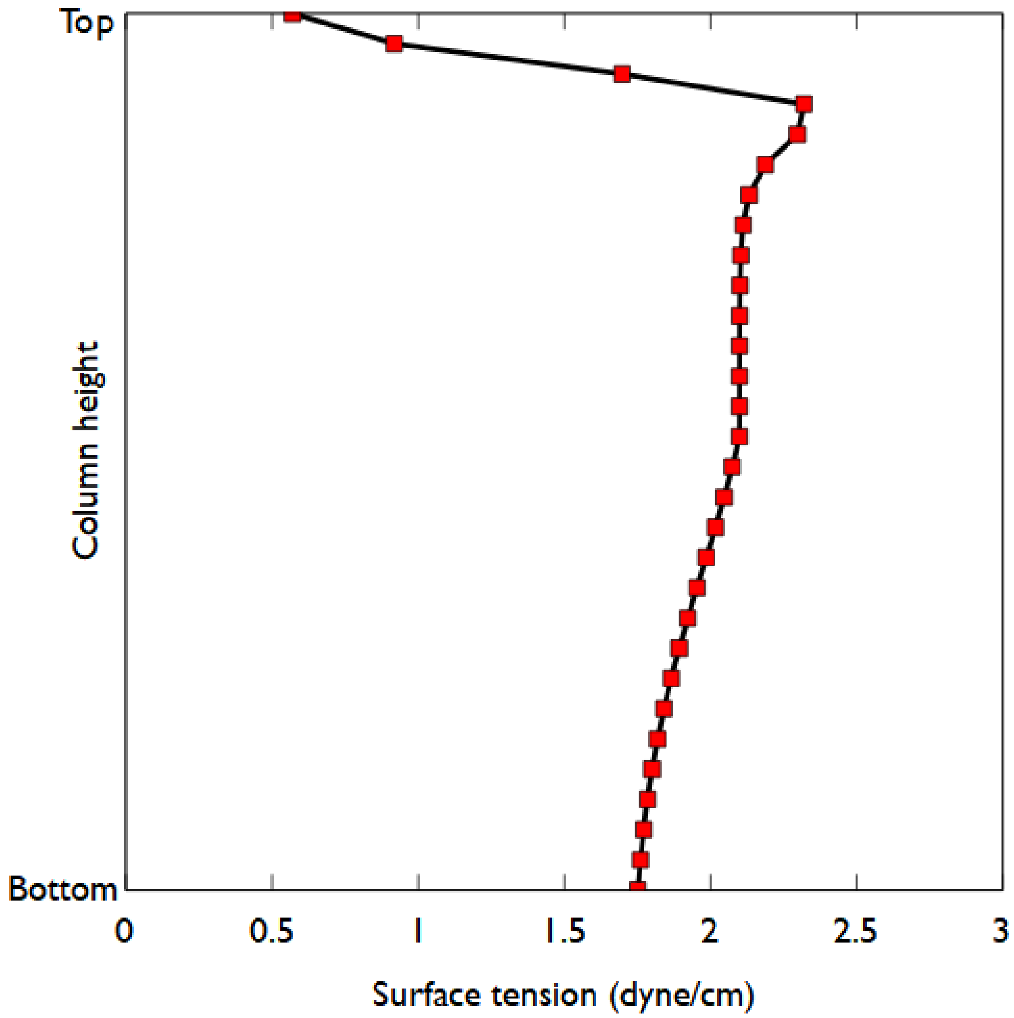




Surface tension profile in column

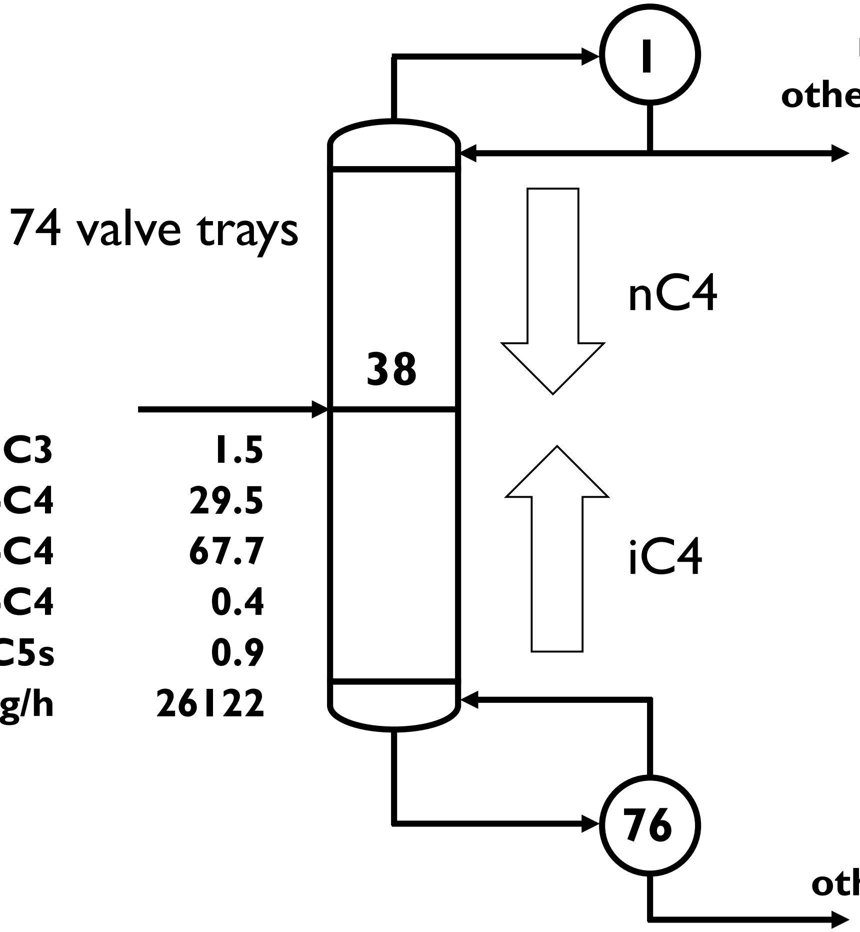
Nitrogen Rejection Unit after Hamedi et al. (2018)





Surface tension profile in column

Industrial C4 Splitter – After Klemola and Ilme (1996)



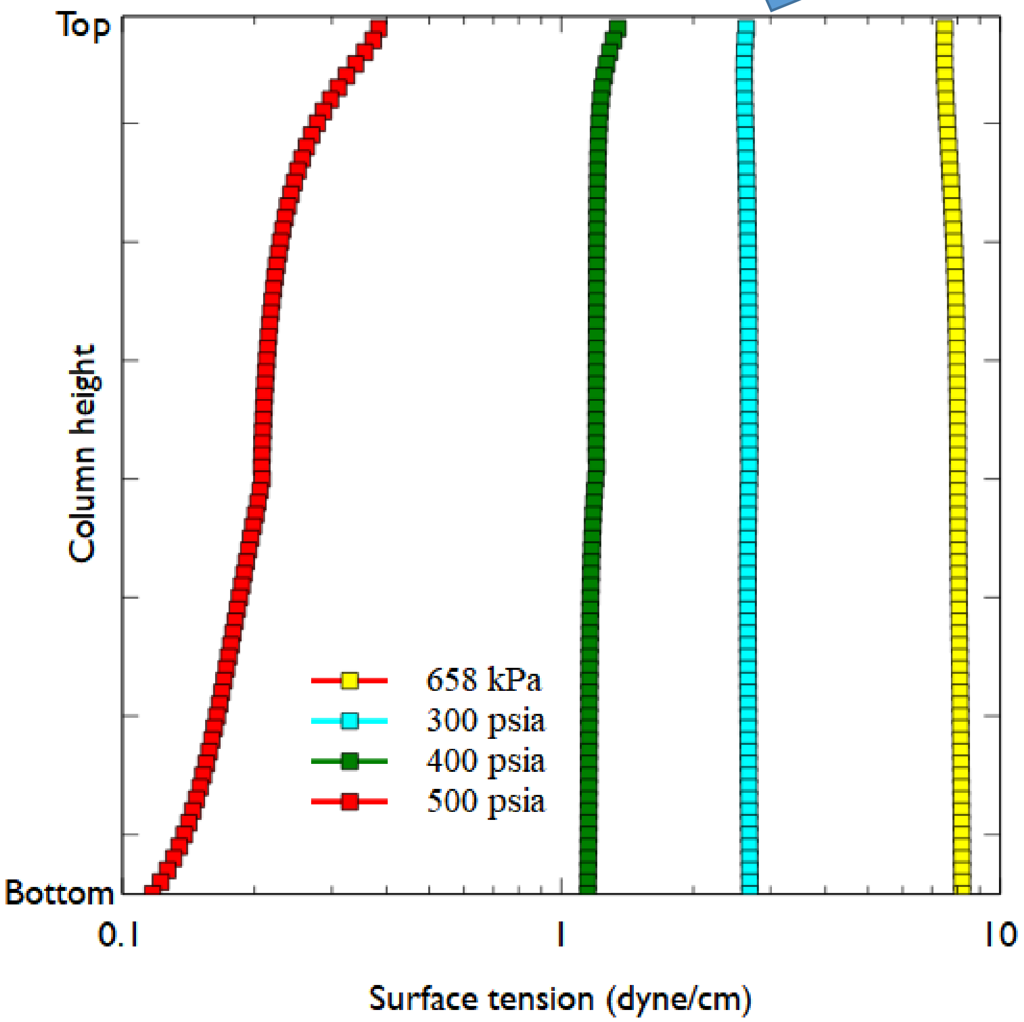
C3	5
i-C4	93.7
n-C4	0.7
other-C4	0
C5s	0
kg/h	8122

C3	1.5
i-C4	29.5
n-C4	67.7
other-C4	0.4
C5s	0.9
kg/h	26122

C3	0
i-C4	0.5
n-C4	97.9
other-C4	0.4
C5s	1.5
kg/h	18000

Klemola, K.T., Ilme, J.K., 1996. Distillation efficiencies of an industrial-scale i-butane/n-butane fractionator. Industrial & engineering chemistry research 35, 4579–4586. https://doi.org/10.1021/ie960390r

Note log scale



Surface tension profiles if operated at the high pressures used in testing

How low can it (σ) go?

Process	**Key components**	**Pressure**	**Surface tension (dyne/cm)**
Demethanizer from natural gas train	$CH_4 - C_2H_6$	25 atm	2 – 9
CO_2 – Ethane separation	$CO_2 - C_2H_6$	23.7 atm	2 – 8 & 2 – 3
Ortloff process	$CH_4 - CO_2$	4.3 MPa	3 – 10
Nitrogen rejection unit	$N_2 - CH_4$	2650 kPa	0.5 – 2
C_4 splitter	$i\text{-}C_4H_{10} - n\text{-}C_4H_{10}$	658 kPa	10
C_4 splitter (test pressure)	$i\text{-}C_4H_{10} - n\text{-}C_4H_{10}$	400 psia	1
C_4 splitter (test pressure)	$i\text{-}C_4H_{10} - n\text{-}C_4H_{10}$	500 psia	0.1 – 0.3

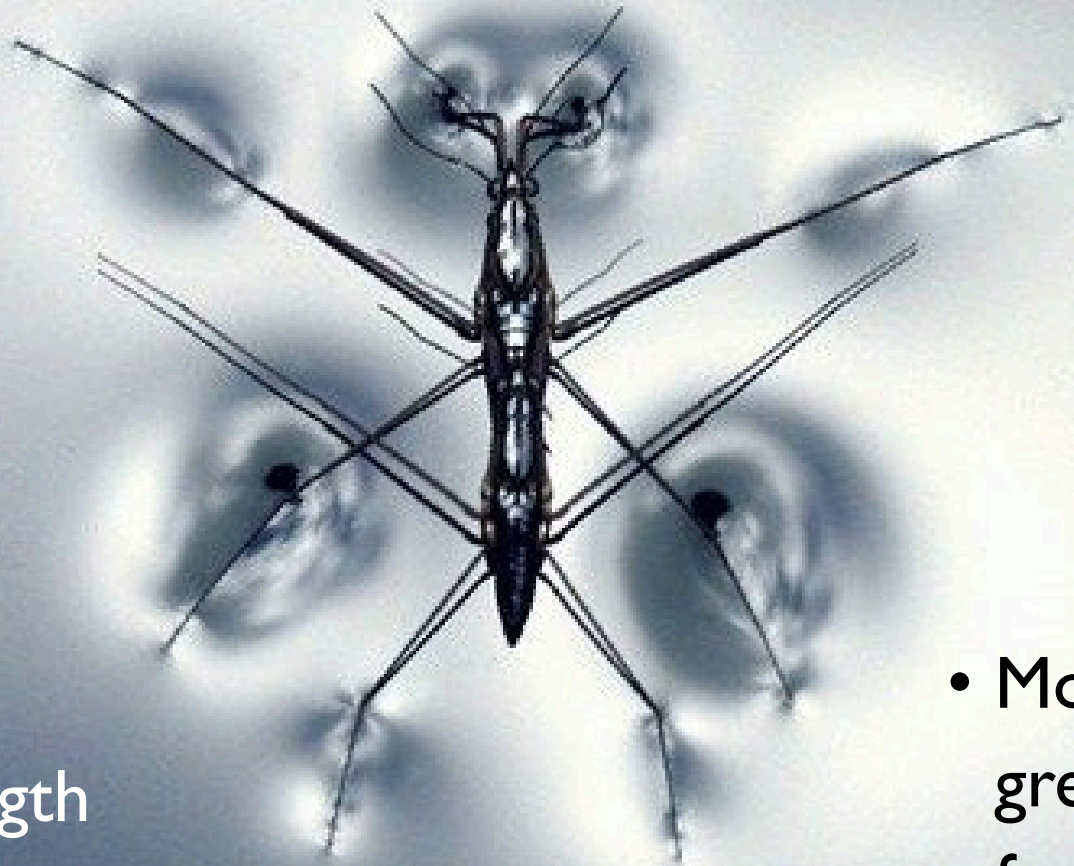
- **I have "seen" column (simulations) where $\sigma < 0.1\ dyne/cm$**

Questions *you* might now be asking...

1. What is surface tension anyway?
2. From where did we get those values for σ?
3. Are they realistic?
4. Where and how does surface tension impact distillation design?
5. What are the consequences of incorrect estimates of σ?

1. What is surface tension?

- Tendency of fluid interface to minimize exposed surface area



- Units of σ: force/length $\left(\frac{\mathrm{mN}}{\mathrm{m}}\right)$ or energy/area $\left(\frac{\mathrm{mJ}}{\mathrm{m}^2}\right)$

- Molecules at interface feel greater attractive forces from liquid than vapor

From internet: Ownership unstated

2. From where did we get those values for σ?

- From a model
  - That was embedded in some process simulation software
- Follow-up question....
  - Which model?

Surface tension of mixtures: Often limited choices

Mixture Surface Tension Model	ChemSep$^+$	Aspen*	ChemCAD*	Symmetry*
Molar average	✓	✓		✓
Power law	✓	✓		✓
Weinaug – Katz	✓	✓	✓	
Lee – Chien	✓			
Winterfeld – Scriven – Davis	✓			
Brock – Bird	✓			
Other general models	✓			✓
Other special models		✓		✓

* As seen in the written documentation we consulted

$^+$ChemSep simulates columns and provides physical properties in CAPE-OPEN compliant systems

4. Where and how does surface tension impact distillation design?

Fair (1982): Tray flooding

$$u_{N,flood} = C_{SB}\left(\frac{\boldsymbol{\sigma}}{20}\right)^{0.2}\left(\frac{\rho_L - \rho_V}{\rho_V}\right)^{1/2}$$

Stupin-Kister (2002): Ultimate capacity

$$C_1 = \left(\frac{1.4}{1 + 1.4\sqrt{\Delta\rho/\rho_V}}\right)\left(\frac{4g}{C_D}\right)^{1/4}\left(\frac{\boldsymbol{\sigma}\Delta\rho}{\rho_V^2}\right)^{1/4} - 1.4L_s$$

$$C_2 = \left(\frac{1.12}{1 + 1.4\sqrt{\Delta\rho/\rho_V}}\right)\left(\frac{4g}{C_D}\right)^{1/4}\left(\frac{\boldsymbol{\sigma}\Delta\rho}{\rho_V^2}\right)^{1/4}$$

$$C_{s,ult} = \min(C_1, C_2)$$

Tyn-Calus (1975): Diffusion coefficients in dilute binary

$$\frac{Đ^{\circ}_{1,2}\mu_2}{T} = 8.93 * 10^{-8}\left(\frac{V_1^{1/6}}{V_2^{1/3}}\right)\left(\frac{\wp_2}{\wp_1}\right)^{0.6}$$

$$\wp = \boldsymbol{\sigma}^{1/4}V$$

Bravo-Fair (1982): Random packing

$$\frac{a_e}{a_p} = 0.498\left(\frac{\boldsymbol{\sigma}^{0.5}}{Z^{0.4}}\right)\left(\frac{\mu_L L}{\rho_L\boldsymbol{\sigma} g_c}\right)^{0.392}\left(\frac{6G}{a_p\mu_G}\right)^{0.392}$$

Billet-Schultes (1993): Structured and random packing

$$\frac{a_e}{a_p} = 1.5(a_p d_h)^{-0.5}\left(\frac{u_L d_h}{\nu_L}\right)^{-0.2}\left(\frac{u_L^2\rho_L d_h}{\boldsymbol{\sigma}}\right)^{0.75}\left(\frac{u_L^2}{g d_h}\right)^{-0.45}$$

- There are *many* more such models…

What properties were used in correlation development?

Property	**Bravo-Fair (1982)**	**Billet-Schultes (1999)**
Gas density (kg/m^3)	0.26 – 28.2	0.07 – 97
Liquid density (kg/m^3)	497 – 833	361 – 1237
Gas viscosity $(10^6 \times m^2/s)$		0.14 – 126
Liquid viscosity $(10^6 \times m^2/s)$		0.14 – 1.66
Surface tension $(dyne/cm)$	**6* & 15 – 27**	**0.7 – 74**

*** Data from Billet (1967) for i-Butane – n-Butane at 165 psia**
Details of source not provided by Bravo (1981)

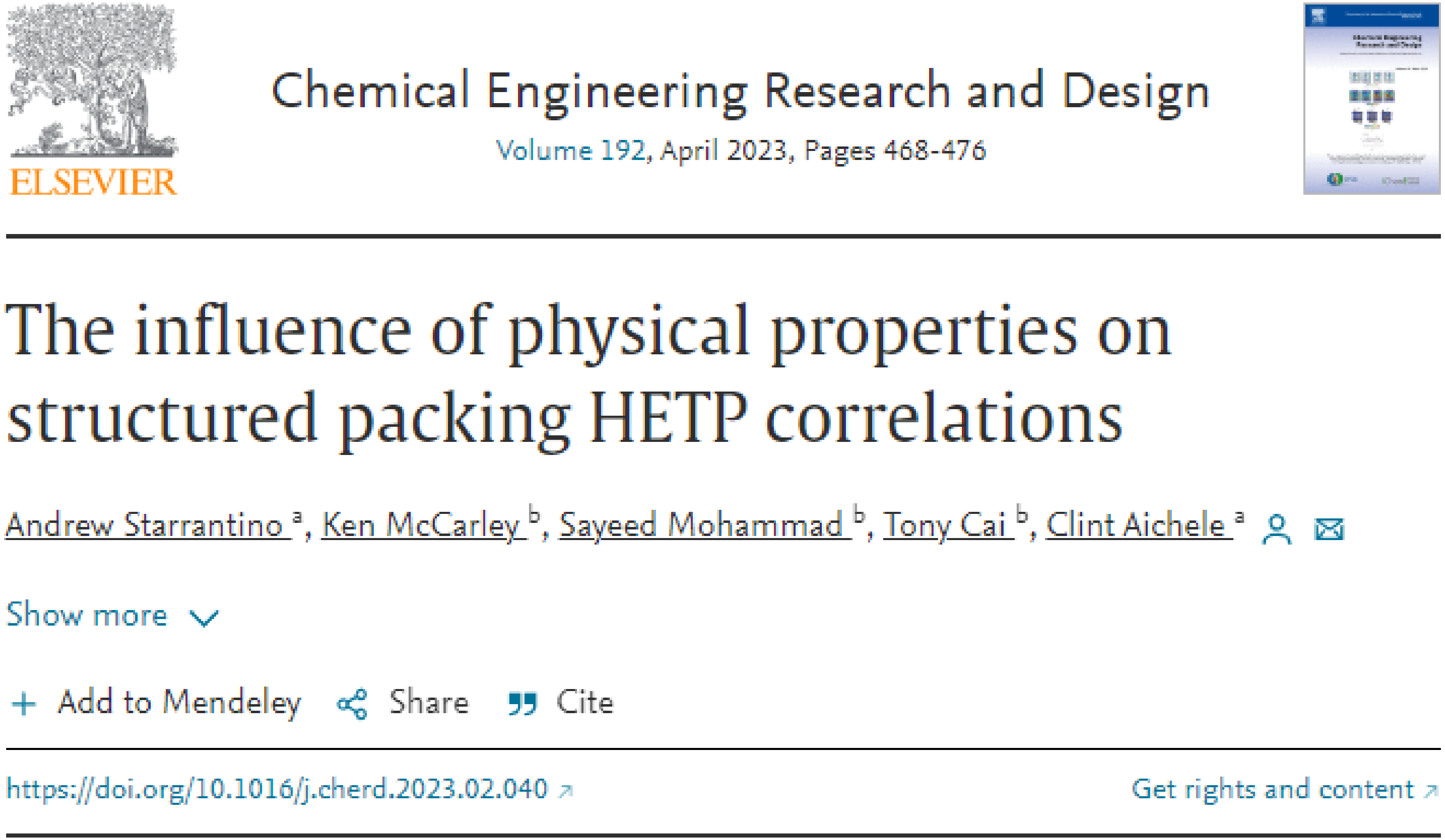
- **Often, we unknowingly use a correlation outside its known range**

Important test systems

Test Mixture	Pressure(s)
Cyclohexane – n-Heptane	5, 24 psia
n-Butane – i-Butane*	**165 psia**
i-Propanol – Water	14.7 psia
Ethylbenzene – Styrene	1, 7 psia
Methanol – Ethanol	14.7 psia
Ethanol – Water	14.7 psia
n-Heptane – Toluene	14.7 psia

- Only standard test system with low surface tension (because tests typically done at "high" pressure)
- Surface tension data for this mixture not available in Dortmund Data Bank or NIST

Recommended Reading



ELSEVIER

Chemical Engineering Research and Design

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The influence of physical properties on structured packing HETP correlations

Andrew Starrantino [a], Ken McCarley [b], Sayeed Mohammad [b], Tony Cai [b], Clint Aichele [a]

https://doi.org/10.1016/j.cherd.2023.02.040

5. What are the consequences of incorrect estimates of σ?

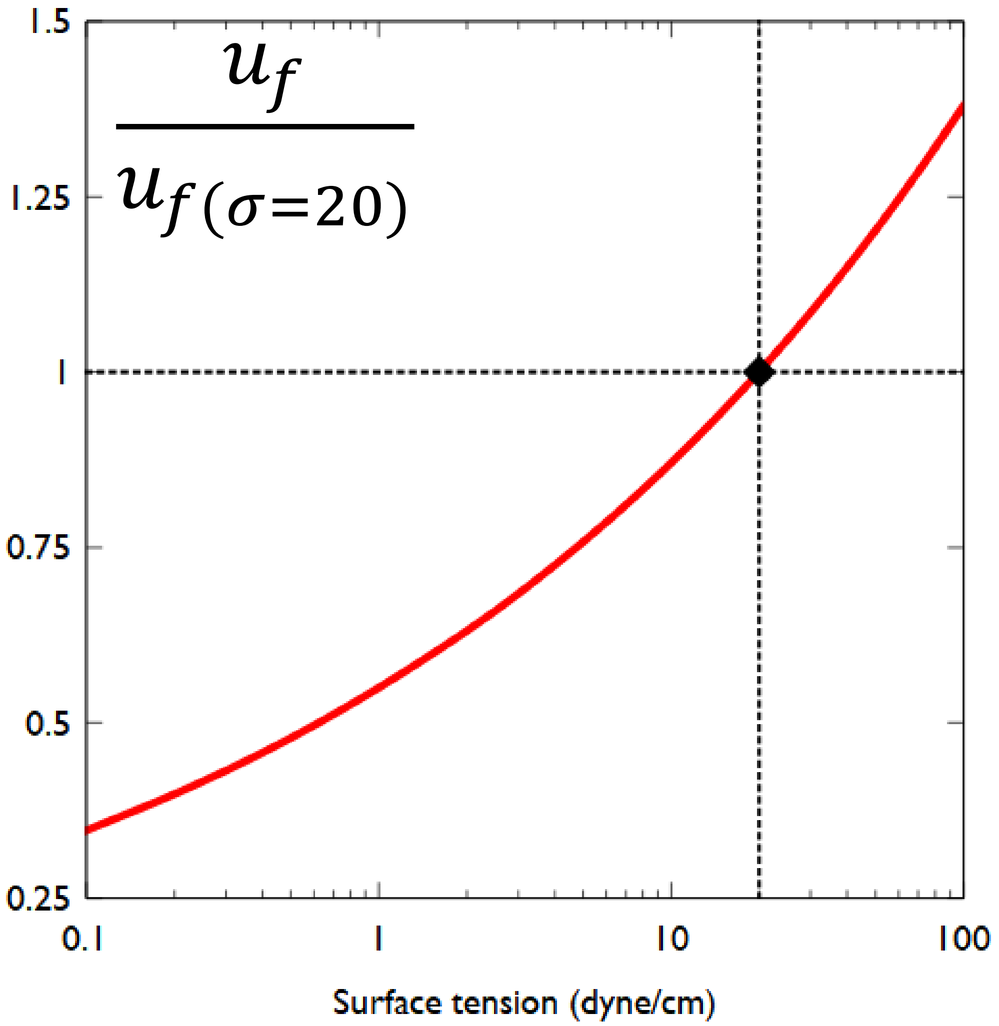
Possible impact of design methodology

- Two different designs for some demethanizer column

Design model	Design I	Design II
Pressure drop and flood	Leva GPDC	Billet and Schultes
Design criterion	75% of flood	75% of flood
Mass transfer coefficient	Bravo – Fair	Billet and Schultes
Diameter	12 ft	16 ft

- Total annualized cost of Design I is much less than that of Design II
- But will either work?
- One of these things does not like the other
  - If I fix the designs and flip the models
    - Design I will not work
    - Design II does work
    - Or so the simulations tell me!
- Surface tension not totally to blame, but it is a part of the story

How σ shows up in distillation design: Trays

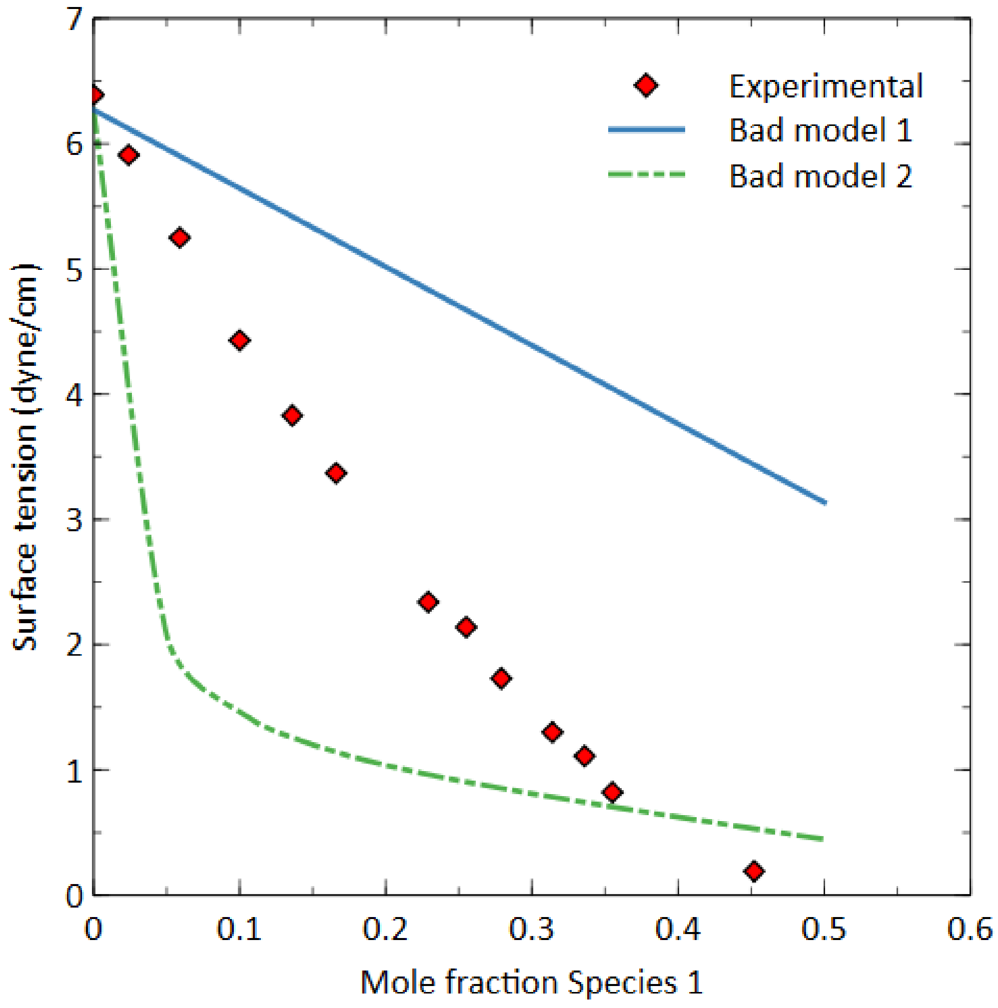


Relative flood velocity from
Fair (1982) flooding correlation

Fair (1982): Tray flooding

$$u_{N,flood} = C_{SB}\left(\frac{\sigma}{20}\right)^{0.2}\left(\frac{\rho_L - \rho_V}{\rho_V}\right)^{1/2}$$

How bad can it be?

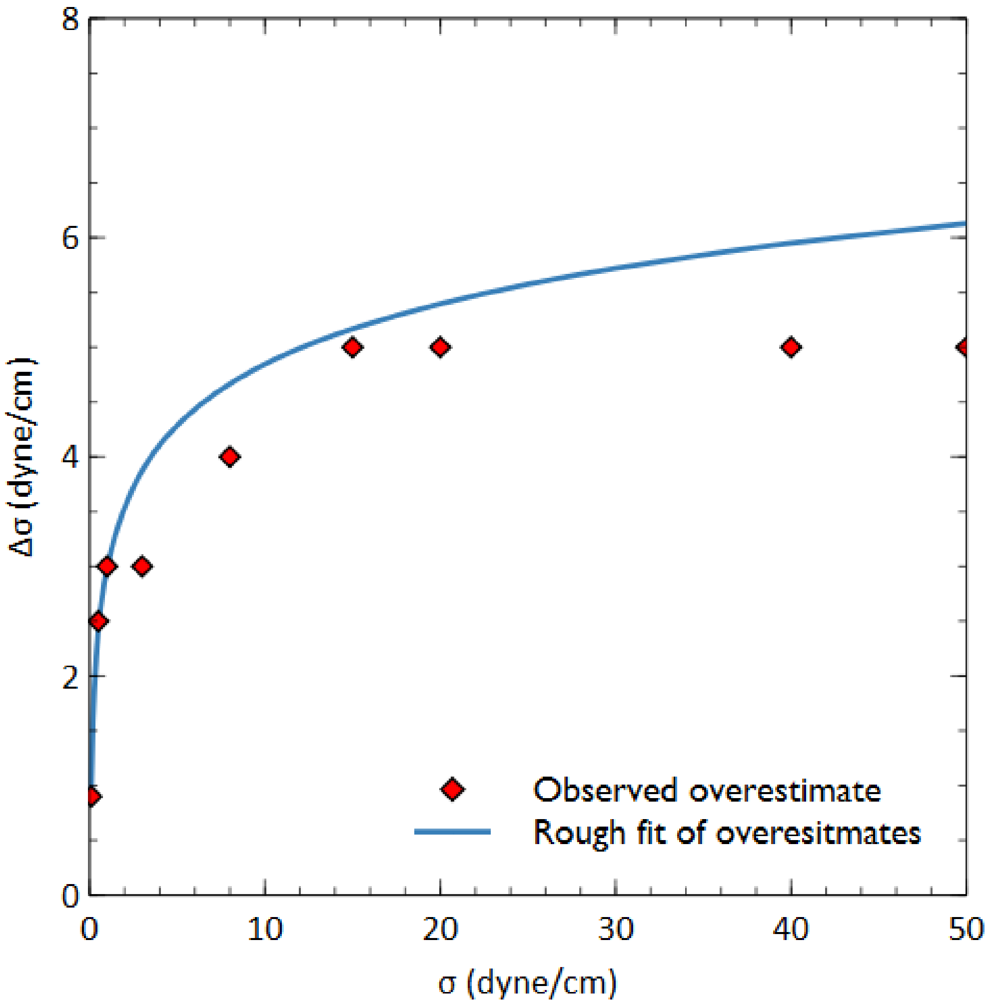


How bad can it be?

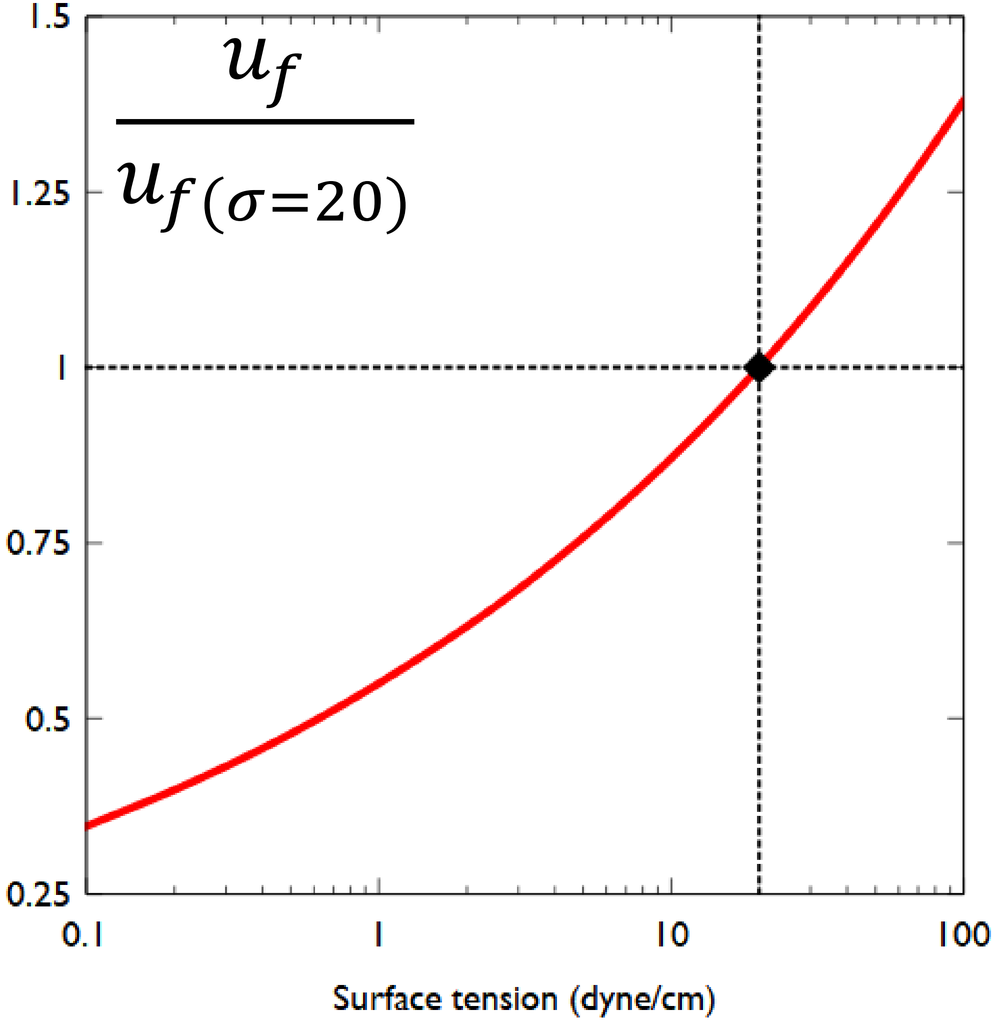
- Very approximate fit to some observed overestimates

$$\Delta\sigma = 3 - \frac{0.02}{\sigma} + 0.8\ln(\sigma)$$

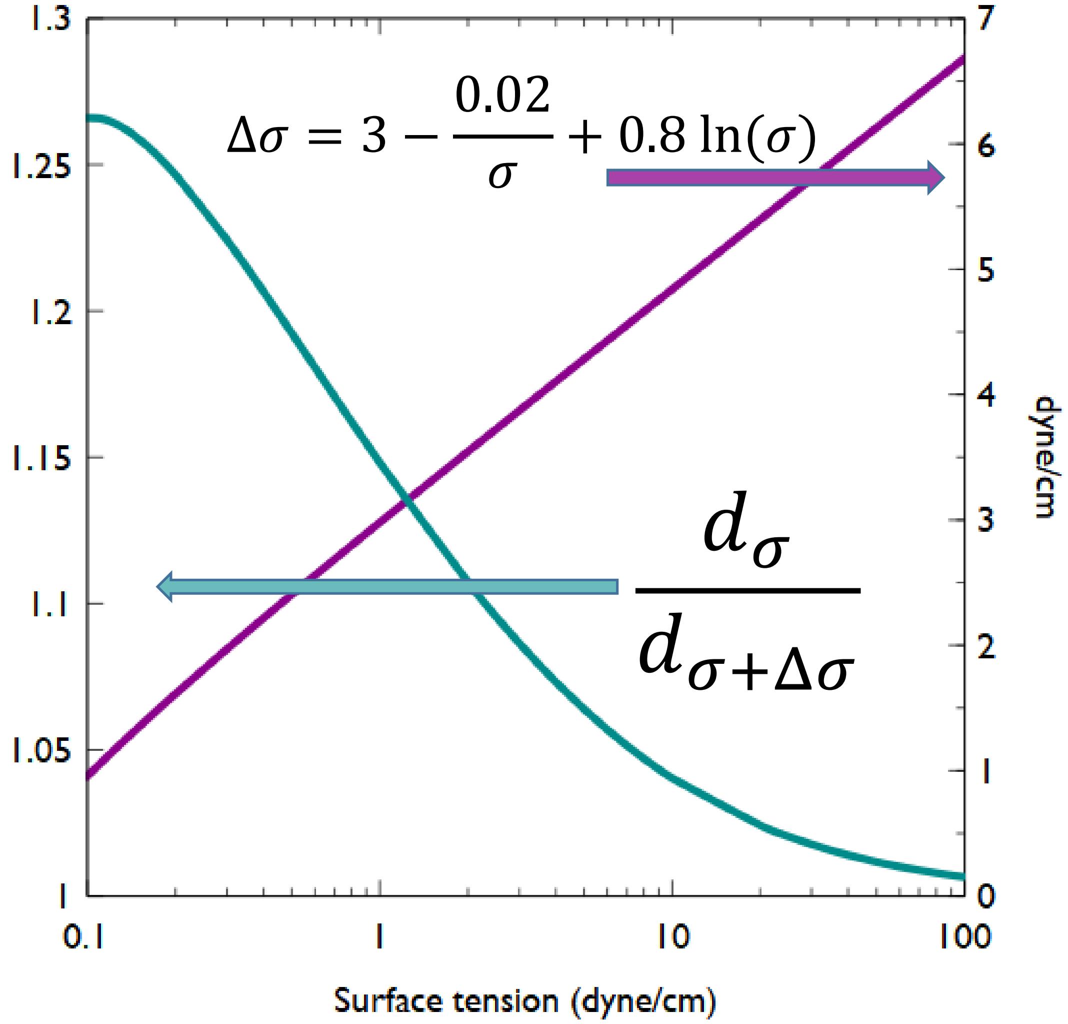
- $\Delta\sigma = \sigma_{estimated} - \sigma_{measured}$



How σ shows up in distillation design: Trays



Relative flood velocity from
Fair (1982) flooding correlation



Relative diameter assuming error
roughly inversely proportional to σ

How σ shows up in distillation design: Stupin–Kister Ultimate Capacity

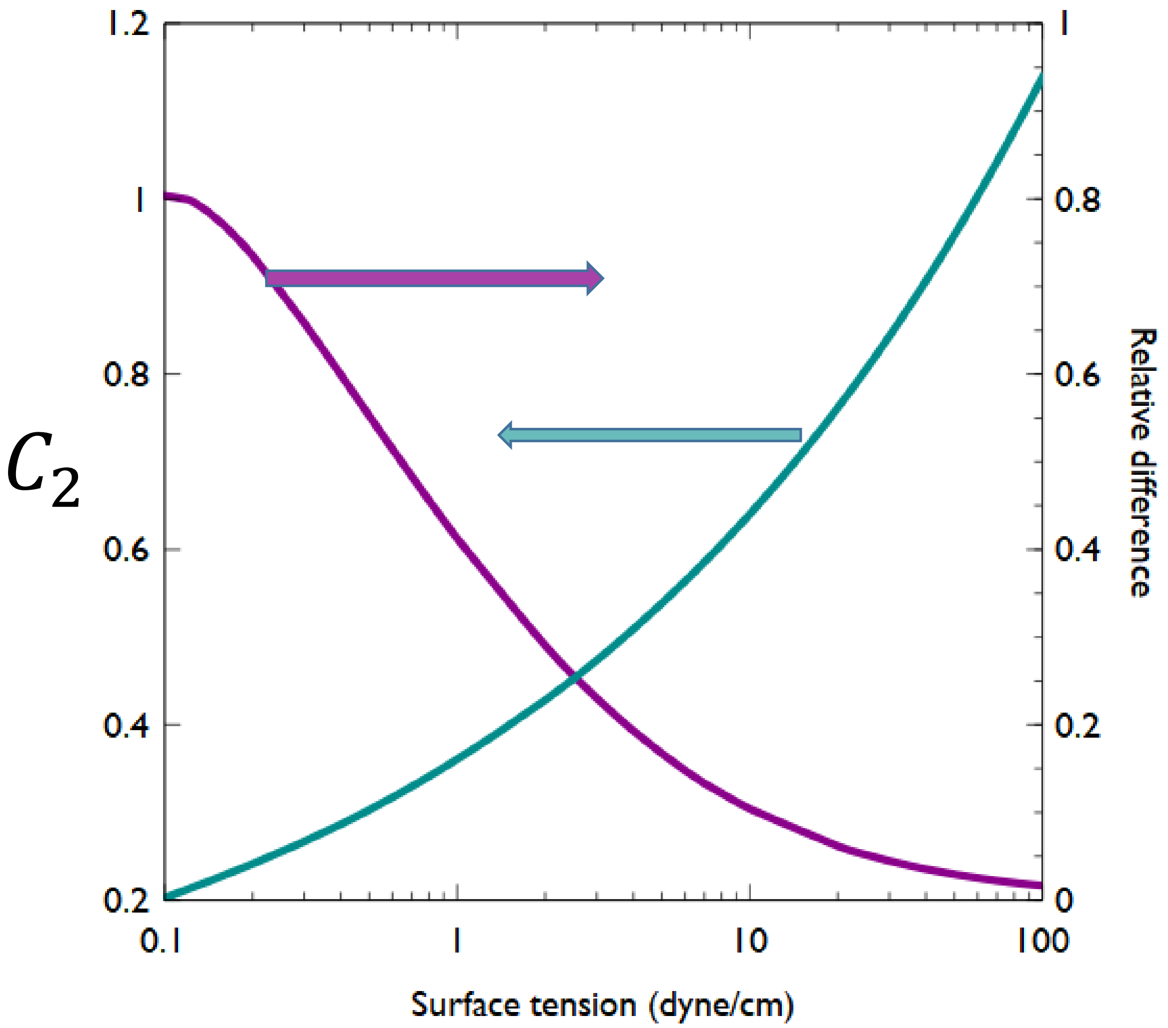
$$C_1 = \left(\frac{1.4}{1 + 1.4\sqrt{\Delta\rho/\rho_V}}\right)\left(\frac{4g}{C_D}\right)^{1/4}\left(\frac{\sigma\Delta\rho}{\rho_V^2}\right)^{1/4} - 1.4L_s$$

$$C_2 = \left(\frac{1.12}{1 + 1.4\sqrt{\Delta\rho/\rho_V}}\right)\left(\frac{4g}{C_D}\right)^{1/4}\left(\frac{\sigma\Delta\rho}{\rho_V^2}\right)^{1/4}$$

$$C_{s,ult} = \min(C_1, C_2)$$

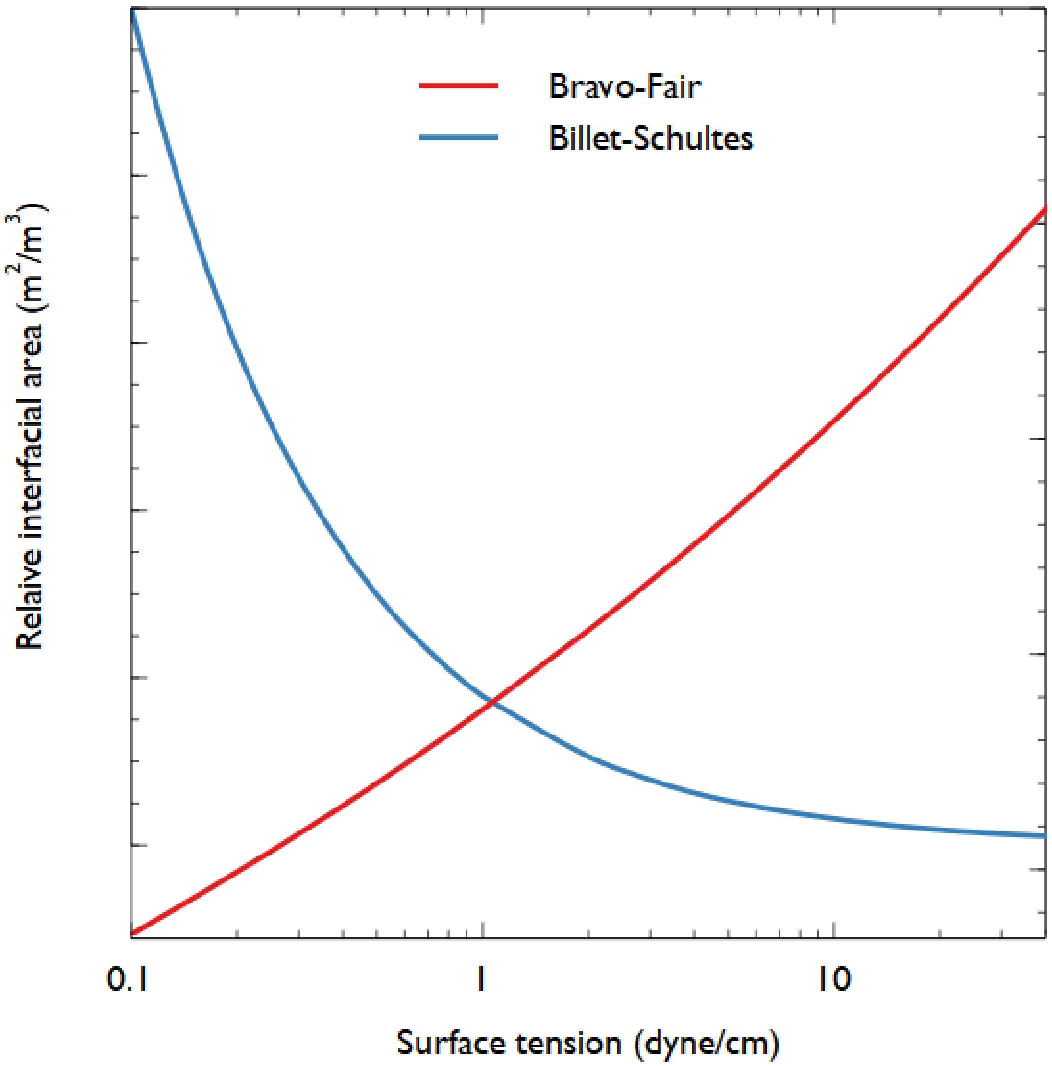
- Lots of assumptions made in these calculations
- Properties for a high pressure demethanizer
- When $\sigma = 1\ dyne/cm$, error in C_2 could be 40%

Stupin, W.J., Kister, H.Z., 2003. System Limit: The Ultimate Capacity of Fractionators. Chemical Engineering Research and Design 81, 136–146. https://doi.org/10.1205/026387603321158294



Stupin – Kister C_2 assuming error roughly inversely proportional to σ

How σ shows up in distillation design: Packing



Surface tension dependency for Bravo-Fair and Billet-Schultes models

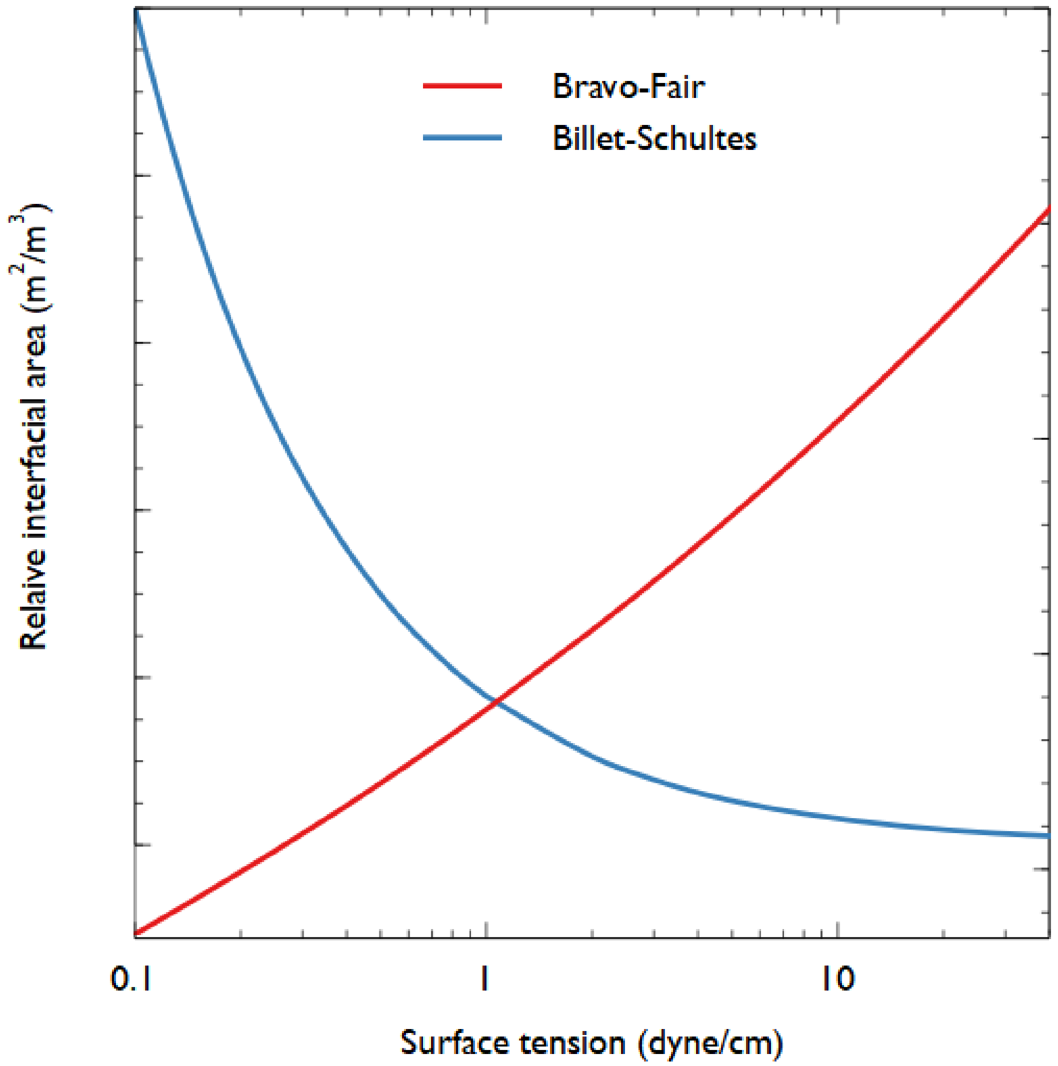
Bravo-Fair (1982): Random packing

$$\frac{a_e}{a_p} = 0.498\left(\frac{\boldsymbol{\sigma}^{0.5}}{Z^{0.4}}\right)\left(\frac{\mu_L L}{\rho_L \boldsymbol{\sigma} g_c}\right)^{0.392}\left(\frac{6G}{a_p \mu_G}\right)^{0.392}$$

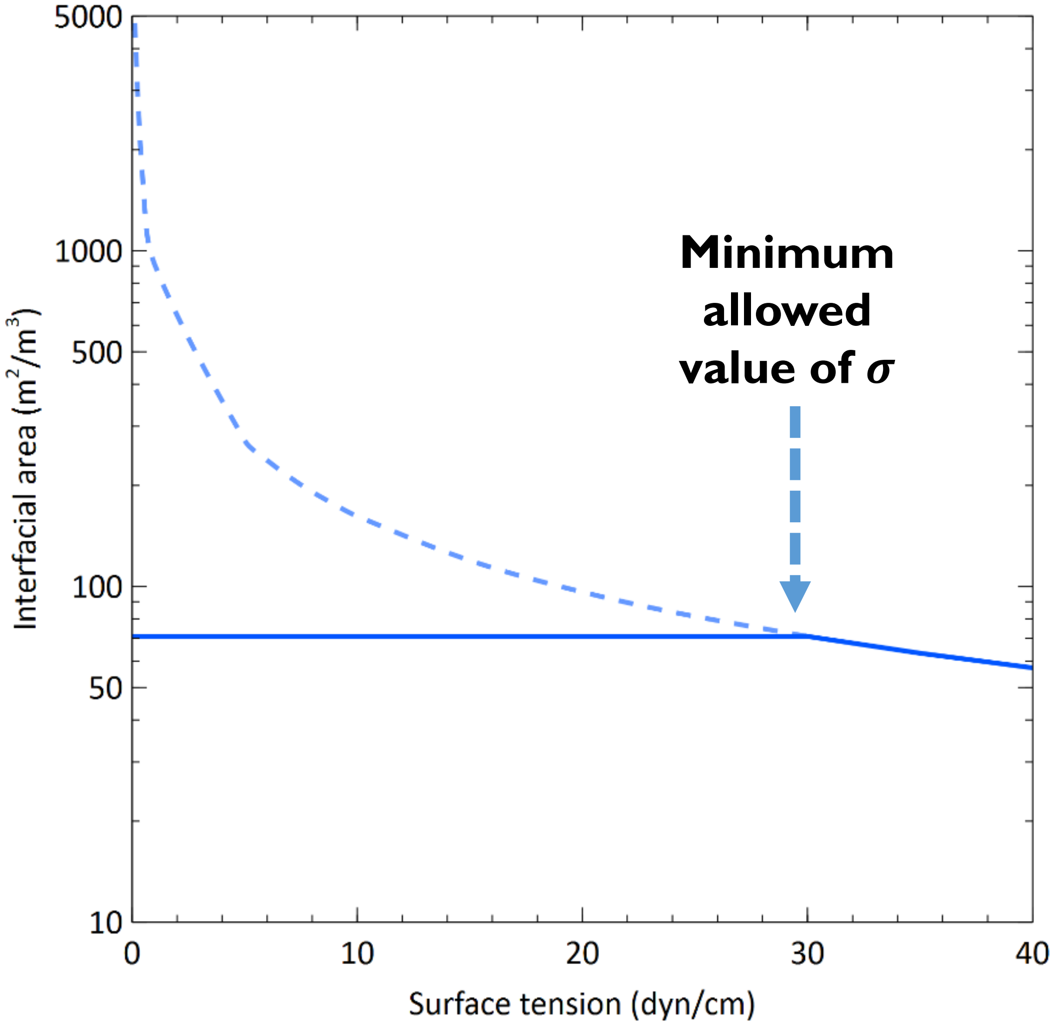
Billet-Schultes (1993): Structured and random packing

$$\frac{a_e}{a_p} = 1.5(a_p d_h)^{-0.5}\left(\frac{u_L d_h}{\nu_L}\right)^{-0.2}\left(\frac{u_L^2 \rho_L d_h}{\boldsymbol{\sigma}}\right)^{0.75}\left(\frac{u_L^2}{g d_h}\right)^{-0.45}$$

How σ shows up in distillation design: Packing

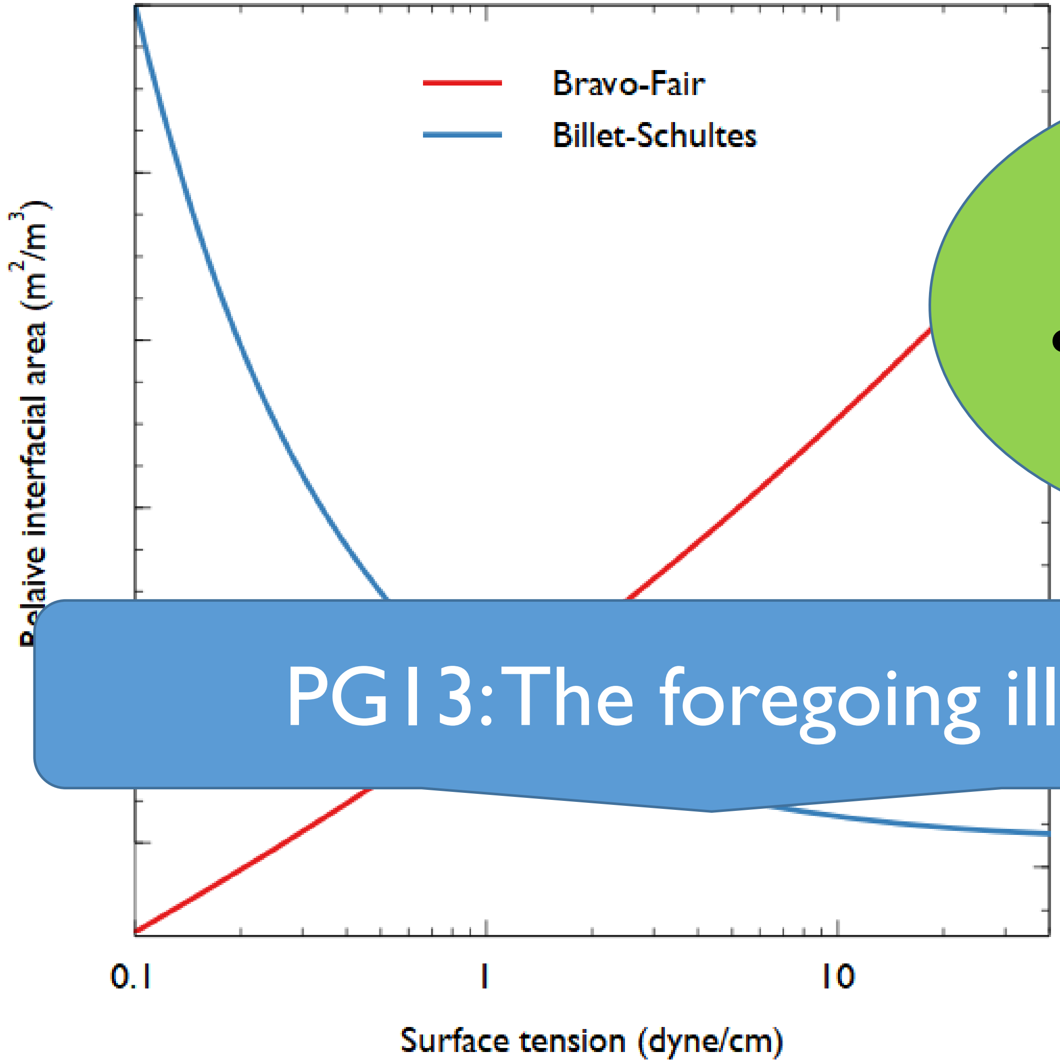


Surface tension dependency for Bravo-Fair and Billet-Schultes models



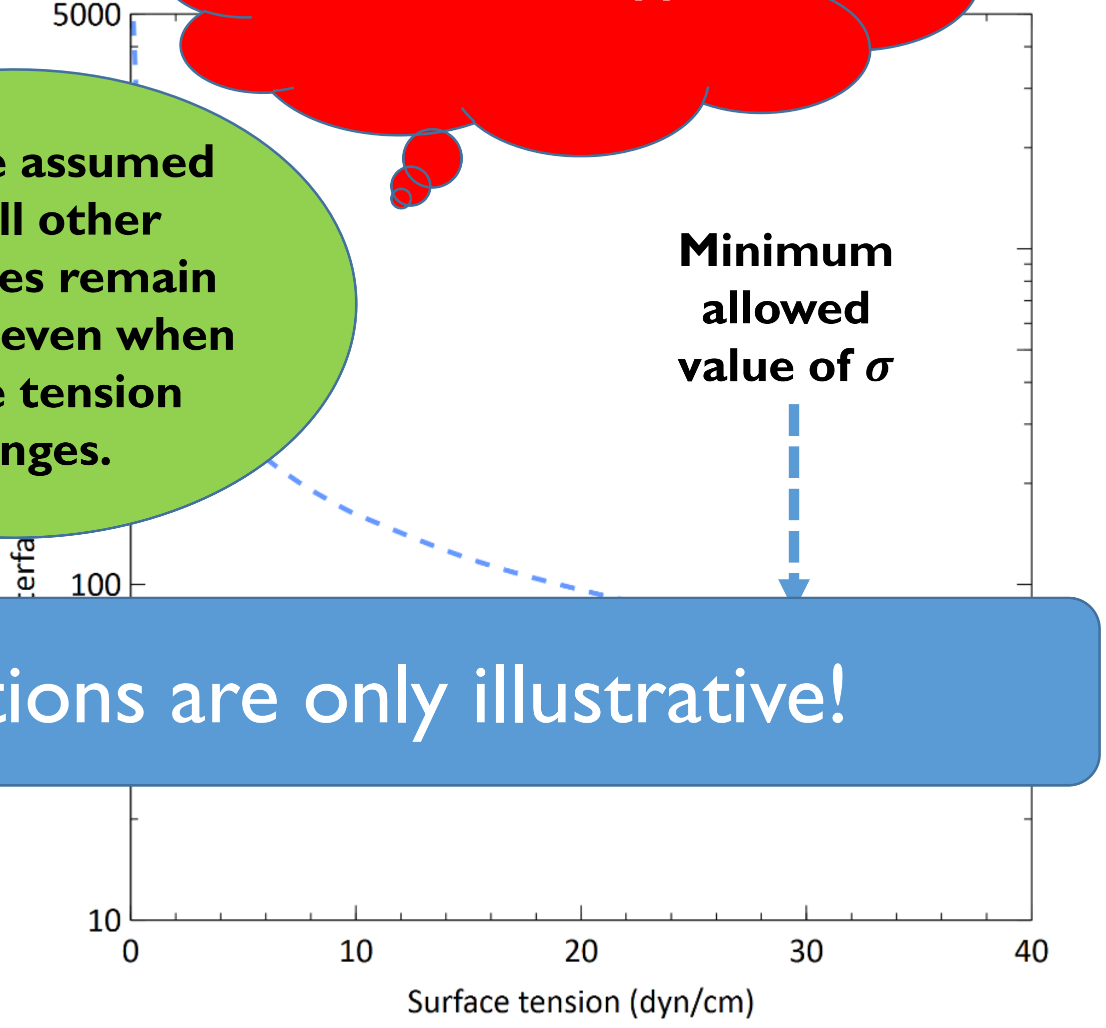
Billet-Schultes (1999) interfacial area for some demethanizer

This is your MPAA warning!



Surface tension dependency for Bravo-Fair and Billet-Schultes models

We have assumed that all other properties remain constant even when surface tension changes.



This cannot happen!!!

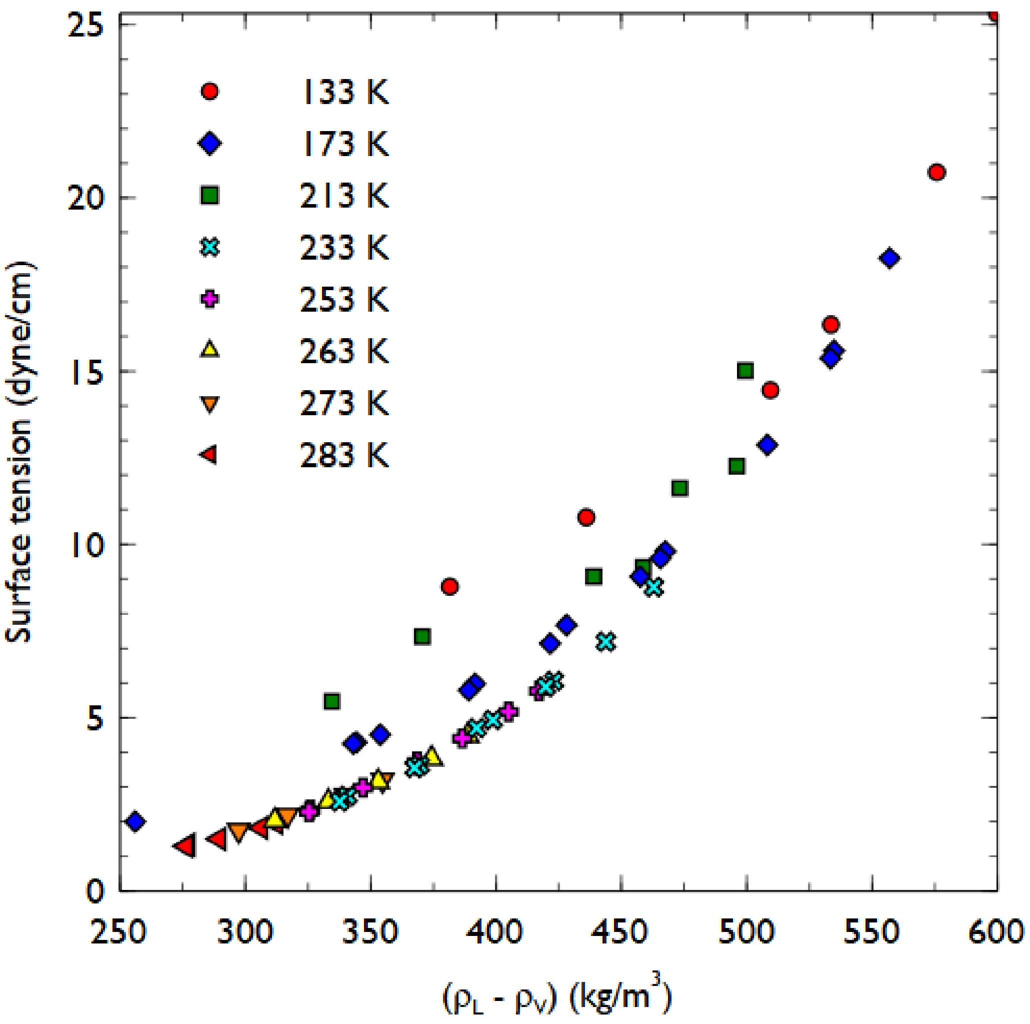
Minimum allowed value of σ

PG13: The foregoing illustrations are only illustrative!

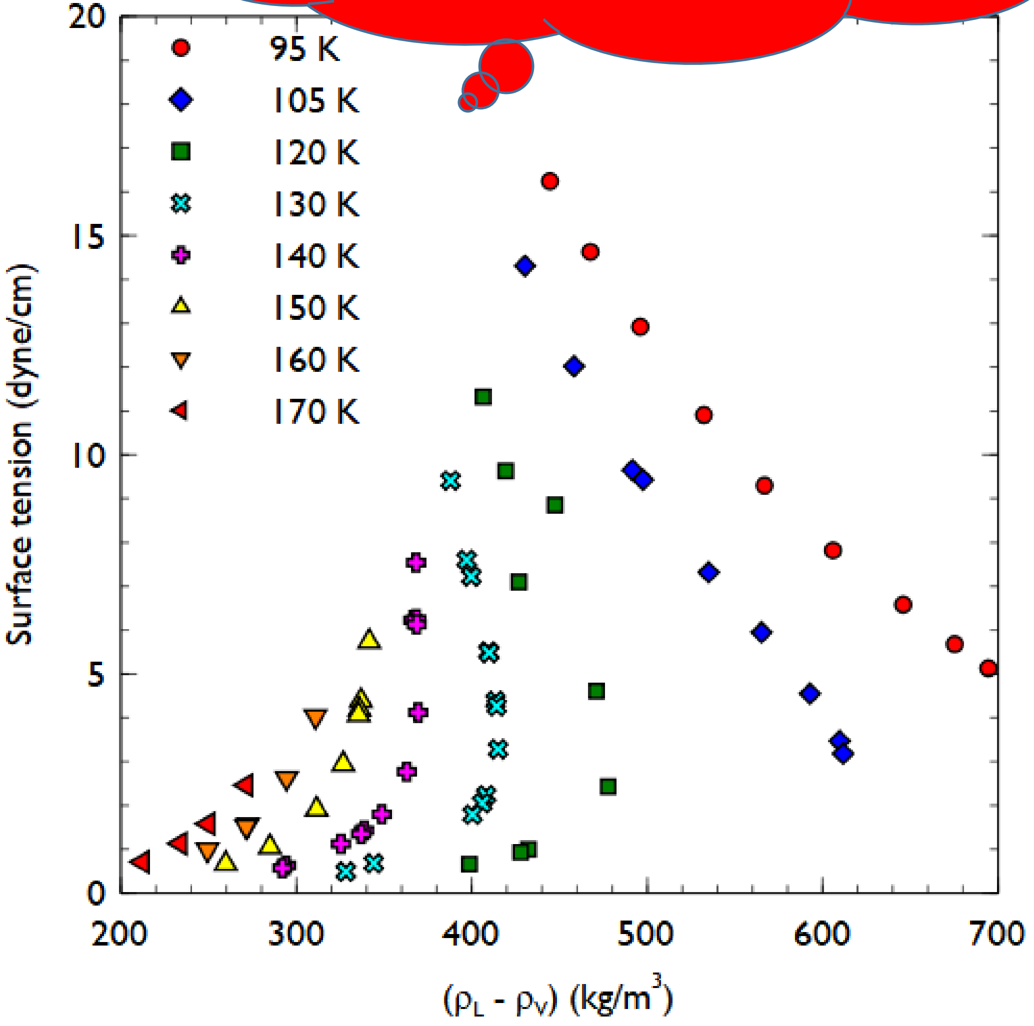
Billet-Schultes (1999) interfacial area for some demethanizer

σ versus $\Delta\rho = (\rho_L - \rho_V)$

Thermodynamics:
It's not just for VLE!

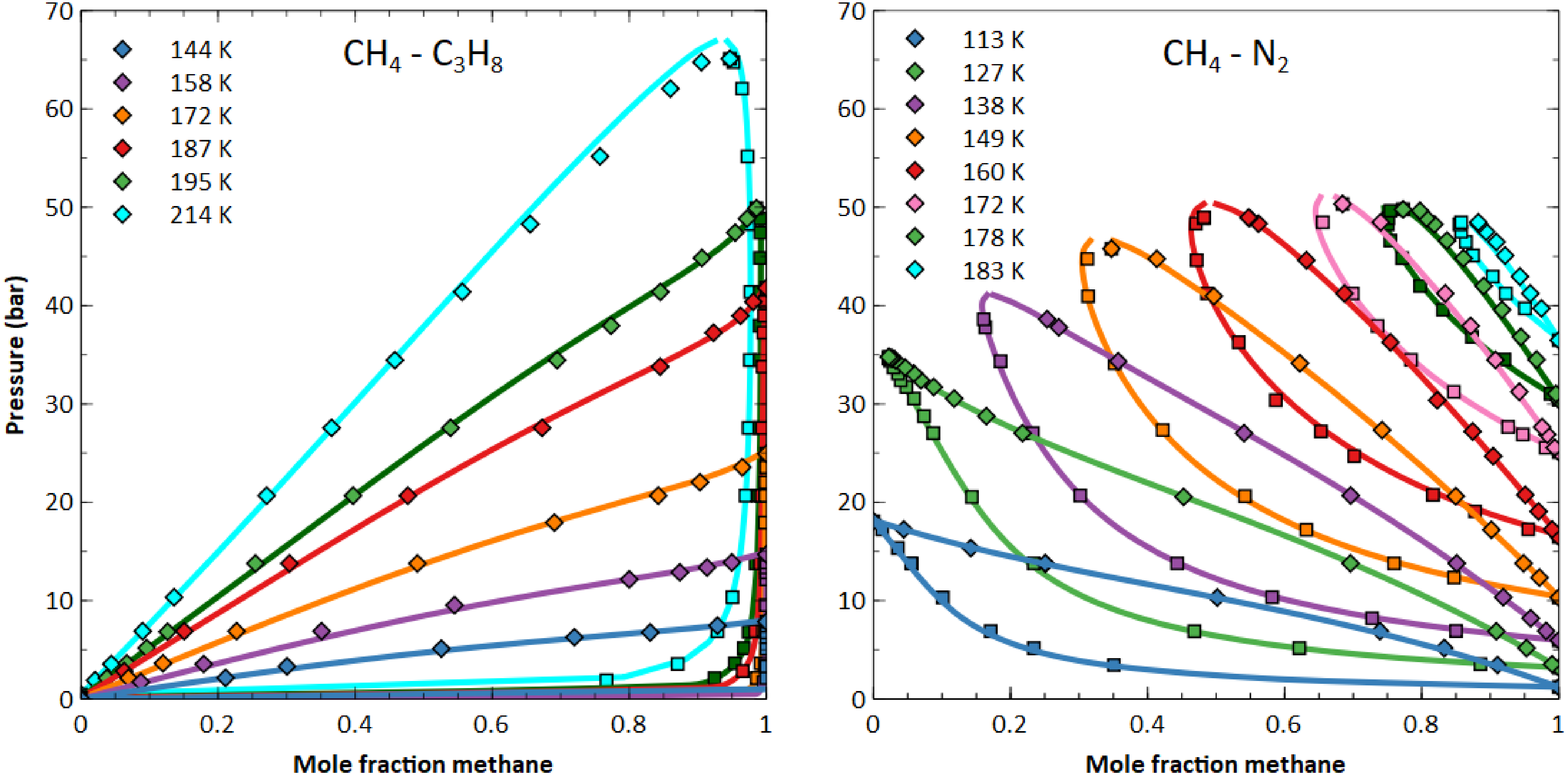


Methane - Ethane



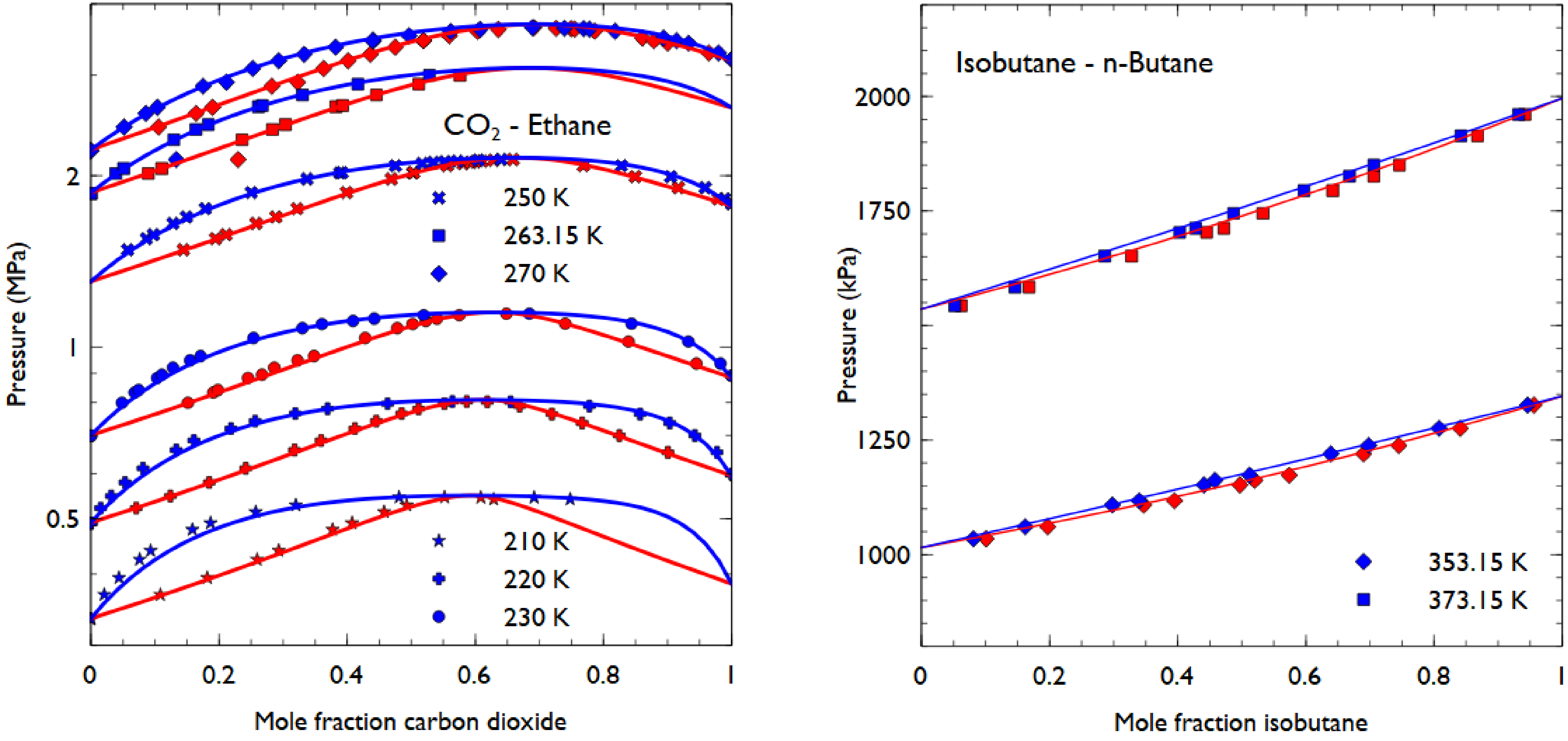
Nitrogen – Methane

Thermodynamics rules, OK!



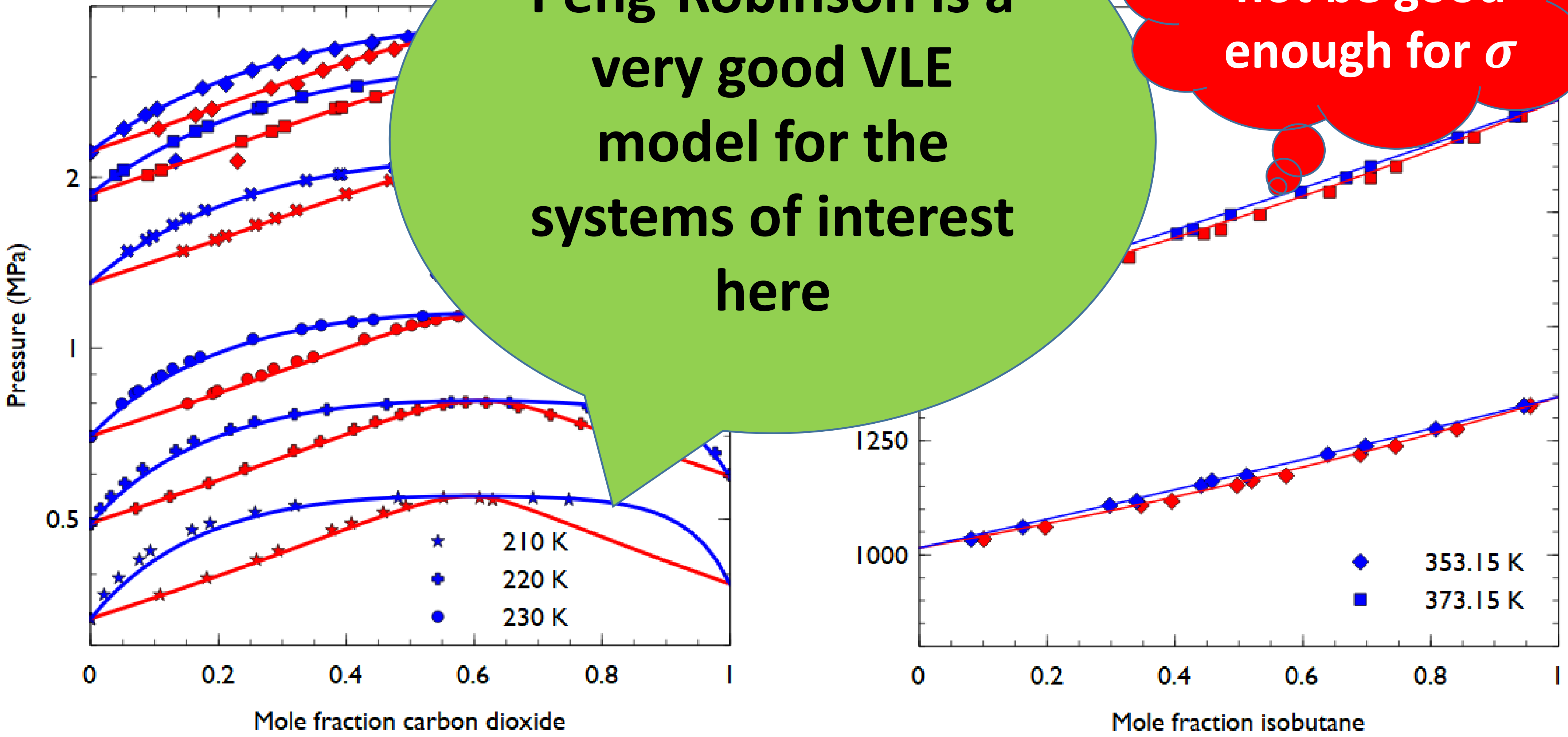
VLE predictions from the Peng-Robinson EOS

Thermodynamics rules, OK!



More VLE predictions from the Peng-Robinson EOS

Thermodynamics rules. P



Peng-Robinson is a very good VLE model for the systems of interest here

But, it may not be good enough for σ

More VLE predictions from the Peng-Robinson EOS

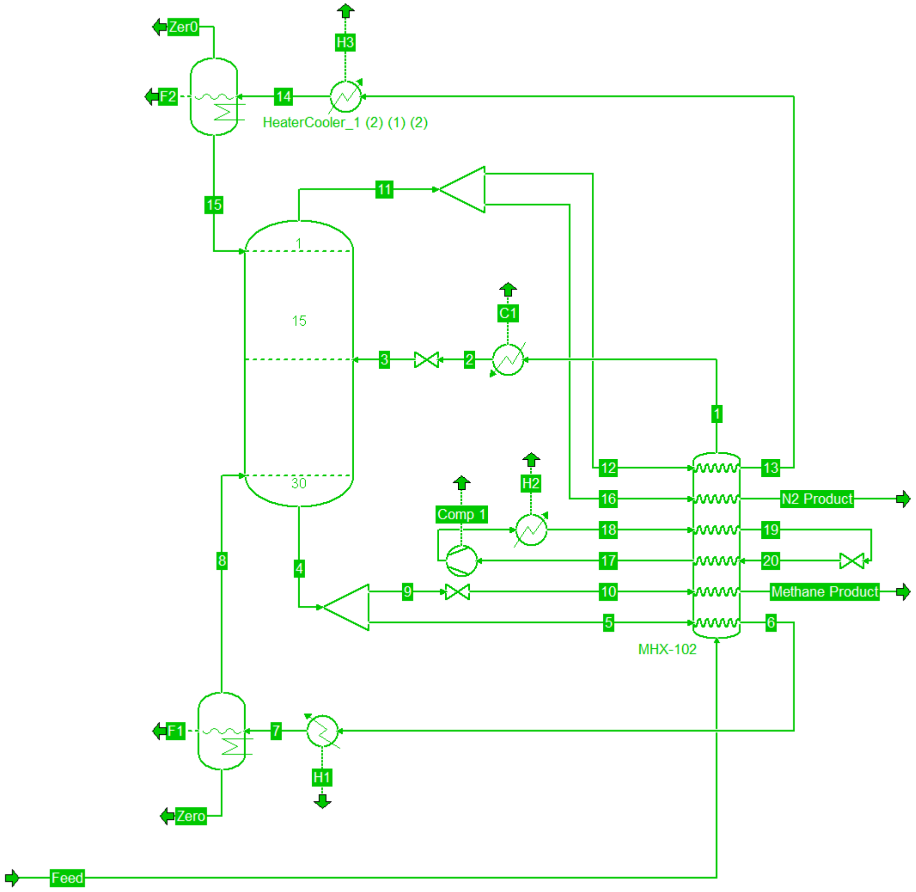
The absolute necessity of getting them* right: II

*Surface tension predictions for high pressure column operations

Ruan de Villiers[a]
Attilio Praderio[b]
Hendrik A. Kooijman[a]
Ross Taylor[a]

a Clarkson University, Potsdam, New York
b Consultant

Kister Distillation Symposium 2023: Legacy of Dr. Walter Stupin: Distillation Simulations Are Only Good when the VLE and Physical Properties Predictions Are Good



In Part I we asked these questions

1. What is surface tension anyway?
2. From where did we get those values for σ?
3. Are they realistic?
4. Where and how does surface tension impact distillation design?
5. What are the consequences of incorrect estimates of σ?

But we did not yet answer question 3.

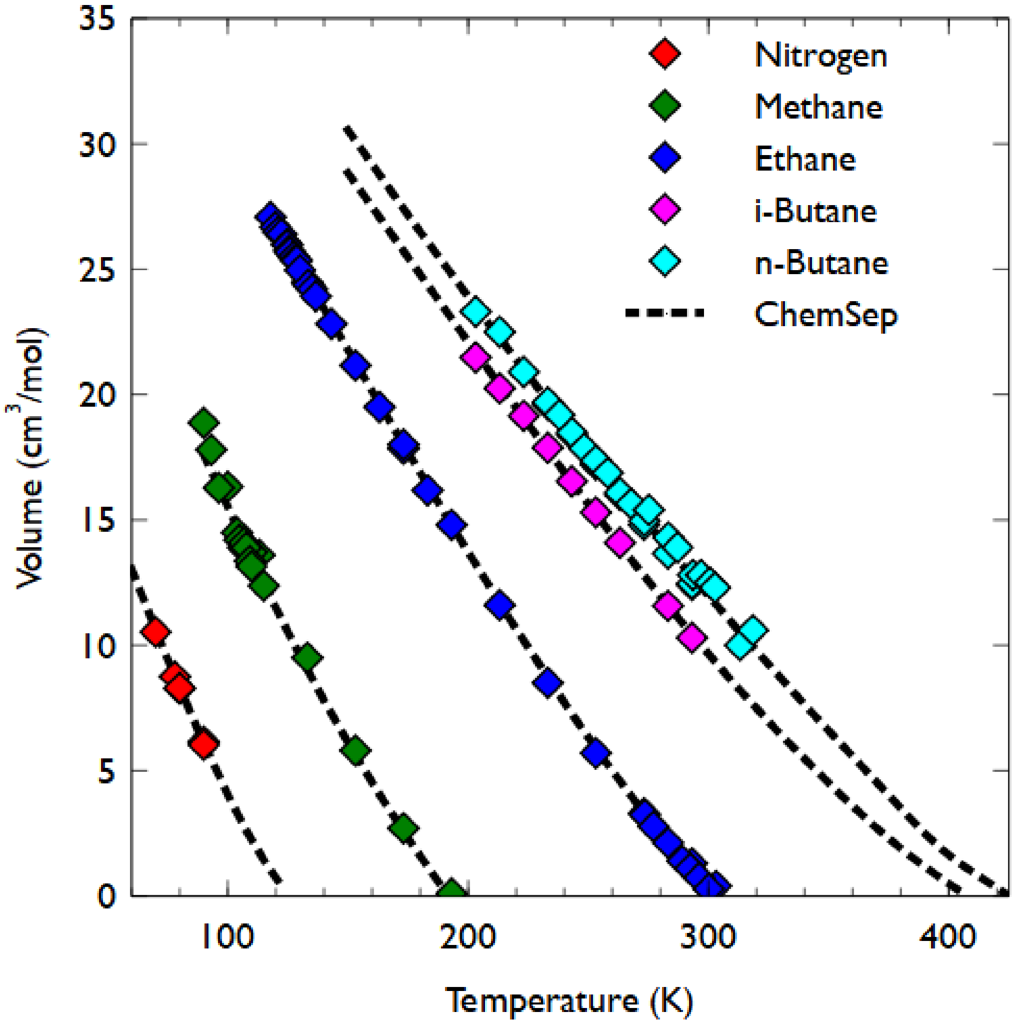
3. Are our estimates of σ realistic?

Pure component surface tension

- Pure component surface tension easy to fit to data

$$\sigma = A + \exp\left(\frac{B}{T} + C + DT + ET^2\right)$$

- (but only if data exists)!
- Correlation parameters often fit to predictions of pure component σ. (e.g. many compounds in DIPPR)
- $\sigma \rightarrow 0$ as $T \rightarrow T_c$



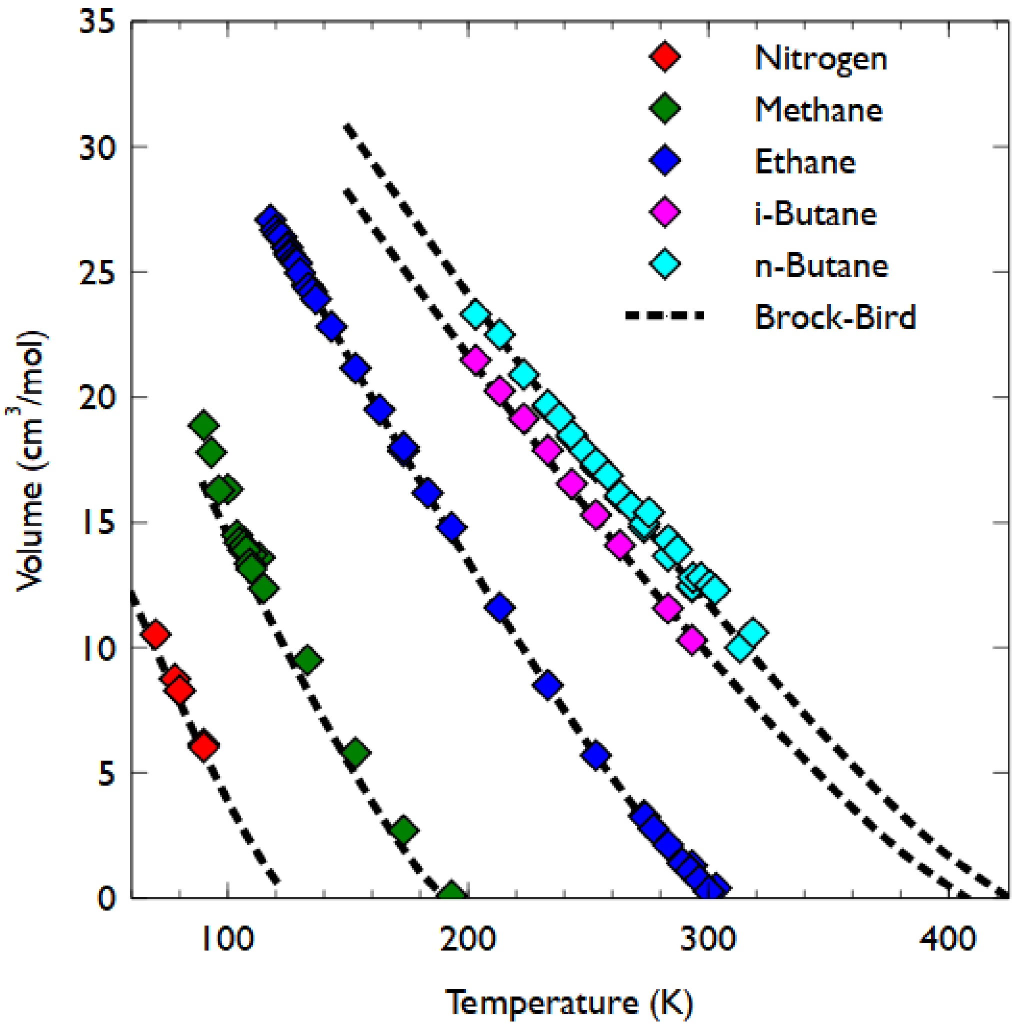
Surface tension of a few pure components
Model is the ChemSep T-correlation

Brock & Bird (1955)

$$\sigma = 4.601 \times 10^{-7} \times (P_c)^{2/3}(T_c)^{1/3}Q(1 - T_r)^{11/9}$$

$$Q = 0.1207\left(1 + \left(\frac{T_{b,r}}{1 - T_{b,r}}\right)\ln\left(\frac{P_c}{101325}\right)\right) - 0.281$$

- Requires only critical properties and boiling point
- Useful predictive model for pure components
- Can be used for mixtures with pseudo-critical properties and molar average boiling point



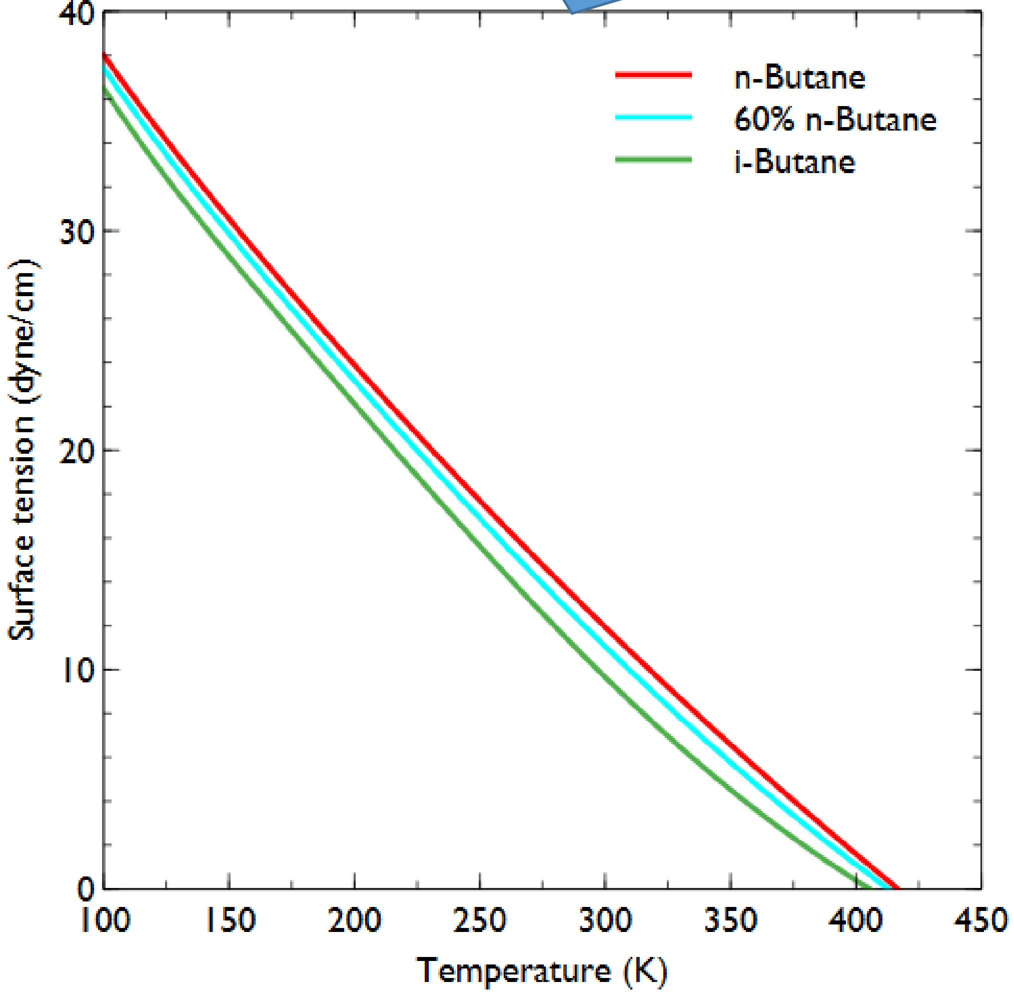
Surface tension of a few pure components
Model is Brock – Bird (1955)

Chemical Engineers like mole fraction averages!

Model is mole fraction weighted average
No data published for this mixture

$$\sigma = \sum_{i=1}^{c} x_i \sigma_i$$

- Simple model that uses only pure component surface tensions (for which we have reliable models)

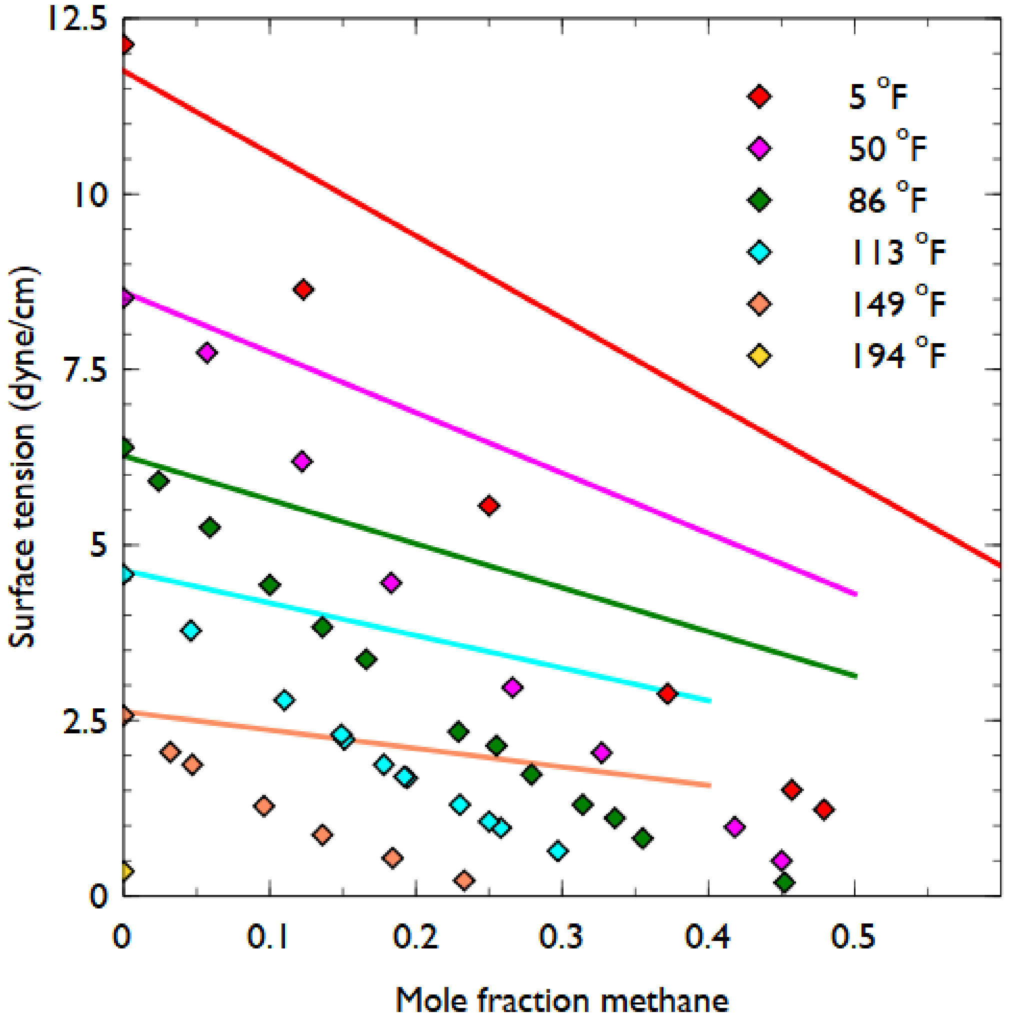


Surface tension of i-butane – n-butane
(a very important test system)

even when they **should NOT!** (like mole fraction averages)

$$\sigma = \sum_{i=1}^{c} x_i \sigma_i$$

- Simple model that uses only pure component surface tensions (for which we have reliable models)
- Highly inaccurate when conditions exceed critical point of one (or more) components
- Sometimes the only available model
- and the worst possible choice!

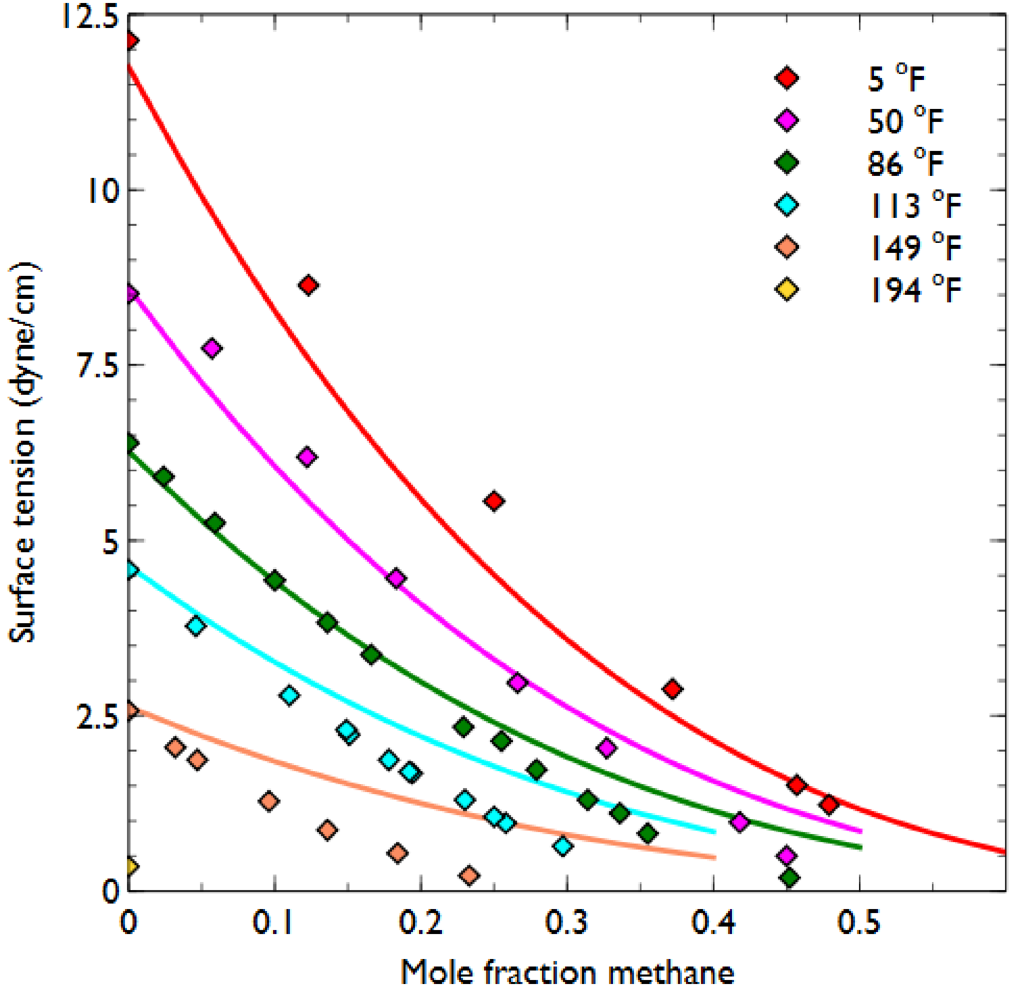


Surface tension of methane – propane
Model is mole fraction weighted average

Mixture surface tension: Power law

$$\sigma^r = \sum_{i=1}^{c} x_i \sigma_i^r$$

- Only requires pure component surface tensions (for which we have reliable models)
- AND the exponent r

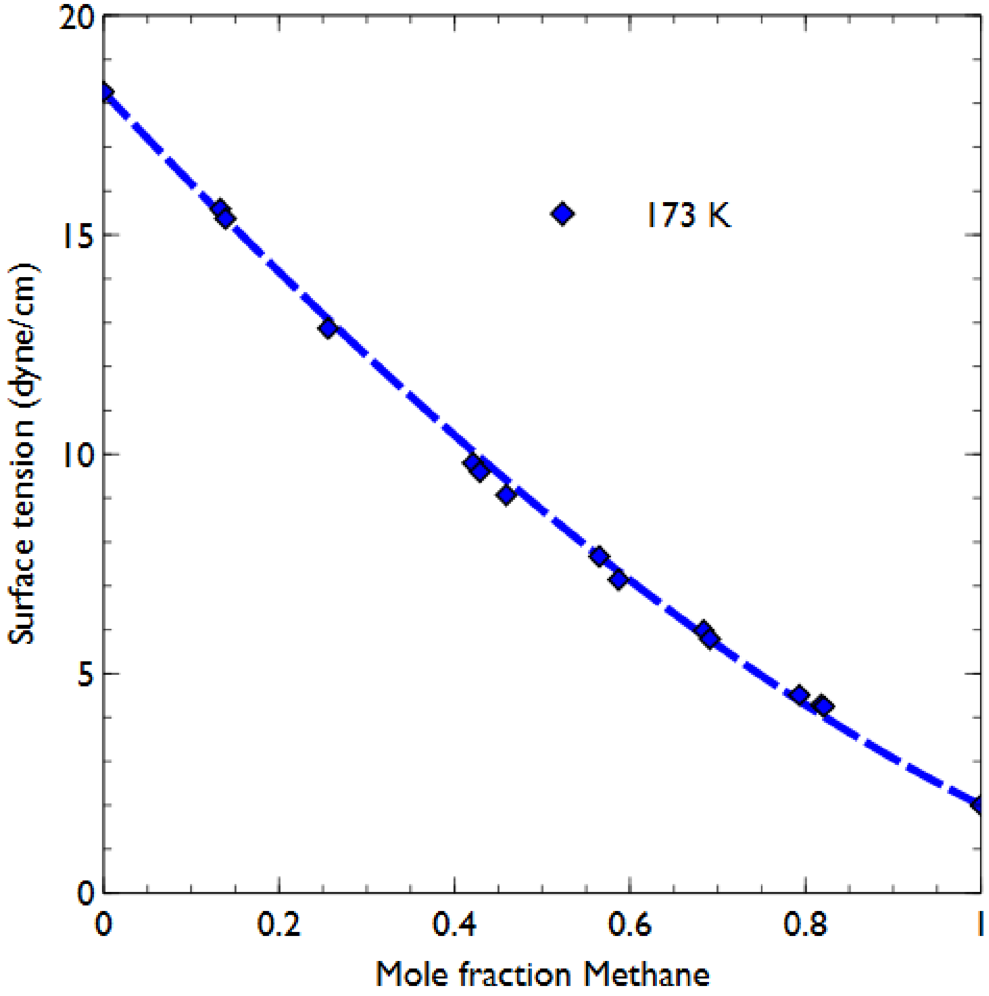


Surface tension of methane – propane
Exponent: $r = 0.3$

Mixture surface tension: Power law

$$\sigma^r = \sum_{i=1}^{c} x_i \sigma_i^r$$

- Only requires pure component surface tensions (for which we have reliable models)
- AND the exponent r
- Plot at right inspired by equivalent shown by Dan Summers two days ago
- BUT…

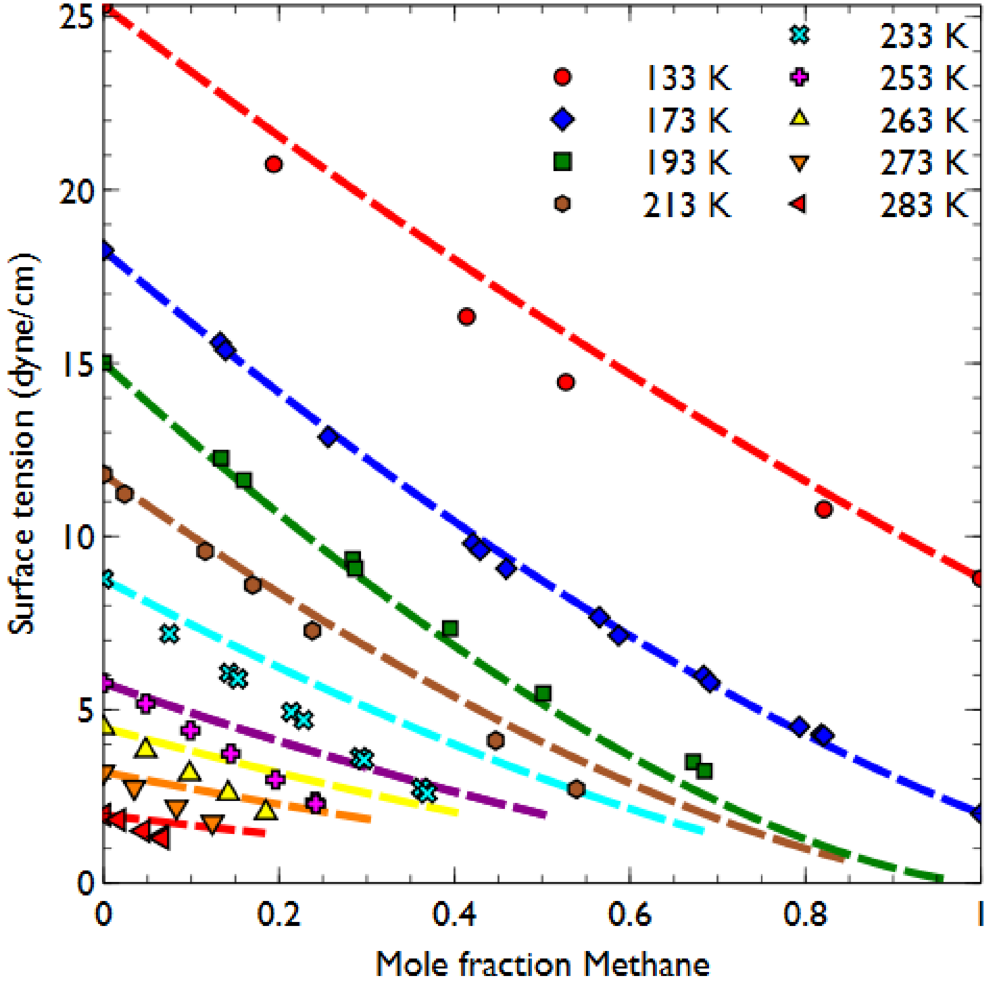


Surface tension of methane – ethane
Exponent: $r = 0.65$

Mixture surface tension: Power law

$$\sigma^r = \sum_{i=1}^{c} x_i \sigma_i^r$$

- Only requires pure component surface tensions (for which we have reliable models)
- AND the exponent r
- Plot at right inspired by equivalent shown by Dan Summers two days ago
- BUT at other temperatures

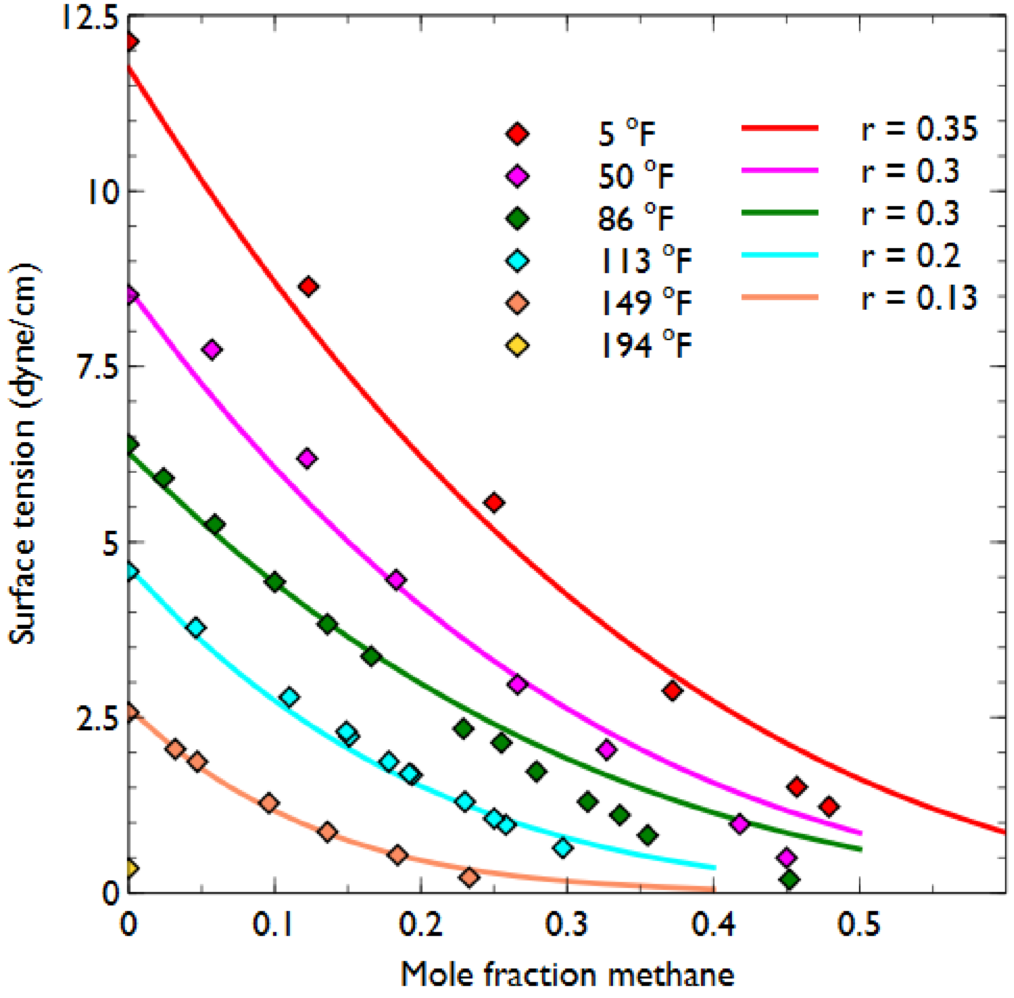


Surface tension of methane – ethane
Exponent: $r = 0.65$

Mixture surface tension: Power law

$$\sigma^r = \sum_{i=1}^{c} x_i \sigma_i^r$$

- Only requires pure component surface tensions (for which we have reliable models)
- AND the exponent r
- Better to make r a function of temperature
- But that function is not knowable
- r can negative (we have seen as low as -11)



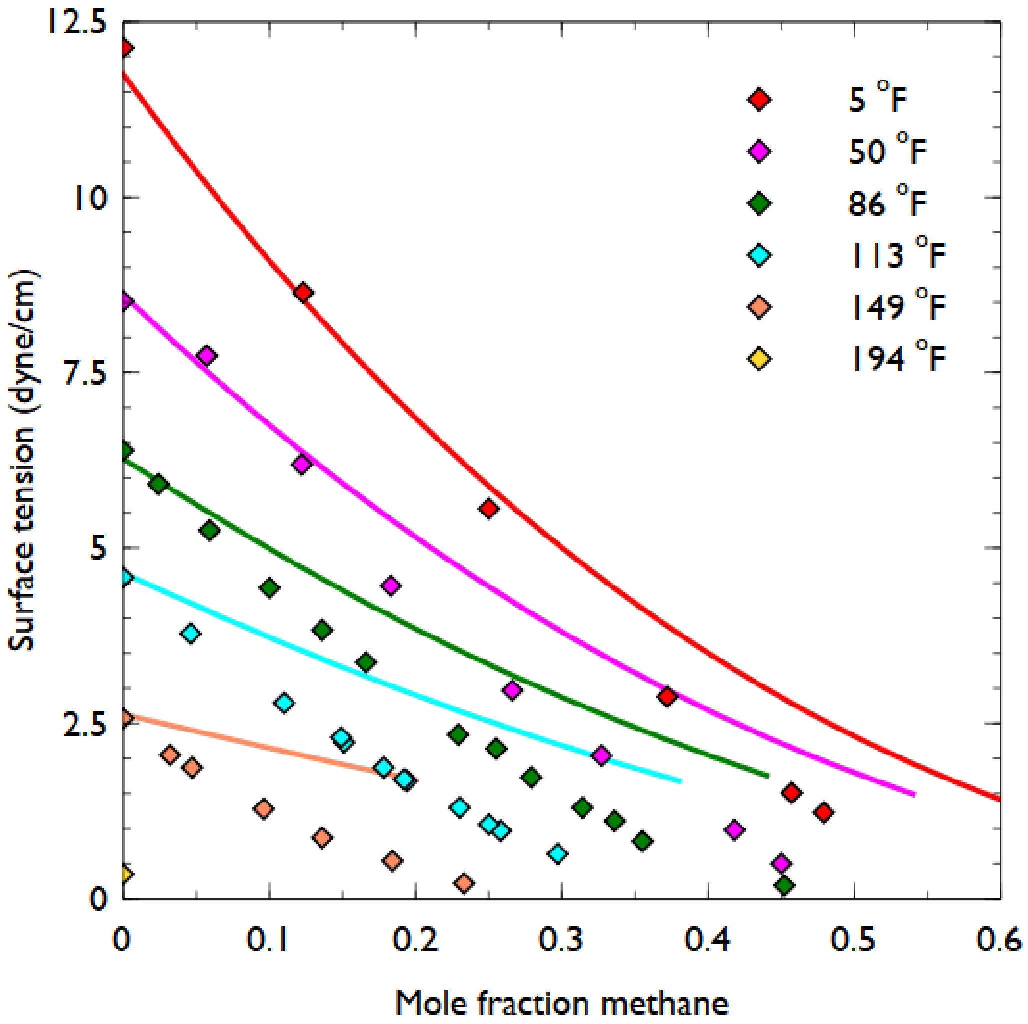
Surface tension of **methane – propane**

Winterfeld – Scriven – Davis Model

$$\sigma = \sum_{i=1}^{c}\sum_{j=1}^{c}(\rho^*)^2 \frac{x_i}{\rho_i^L}\frac{x_j}{\rho_j^L}\sqrt{\sigma_i\sigma_j}$$

$$\frac{1}{\rho^*} = \sum_{i=1}^{c}\frac{x_i}{\rho_i^L}$$

- Simple model that uses pure component densities and σ_i
- Requires accurate pure component liquid densities
- Only useful far from any critical point (mixture or pure component)



Parachor-based methods: Introduction

- (Merriam-Webster) *Parachor:*
  an empirical constant for a liquid that relates the surface tension to the molecular volume

$$\sigma^{1/4} = \wp^L \rho_t^L - \wp^V \rho_t^V$$

- Created by Samuel Sugden in 1924 following rearrangement of an equation proposed by D. B. McLeod (*Trans. Faraday Soc.*, 1923, **19**, 38)

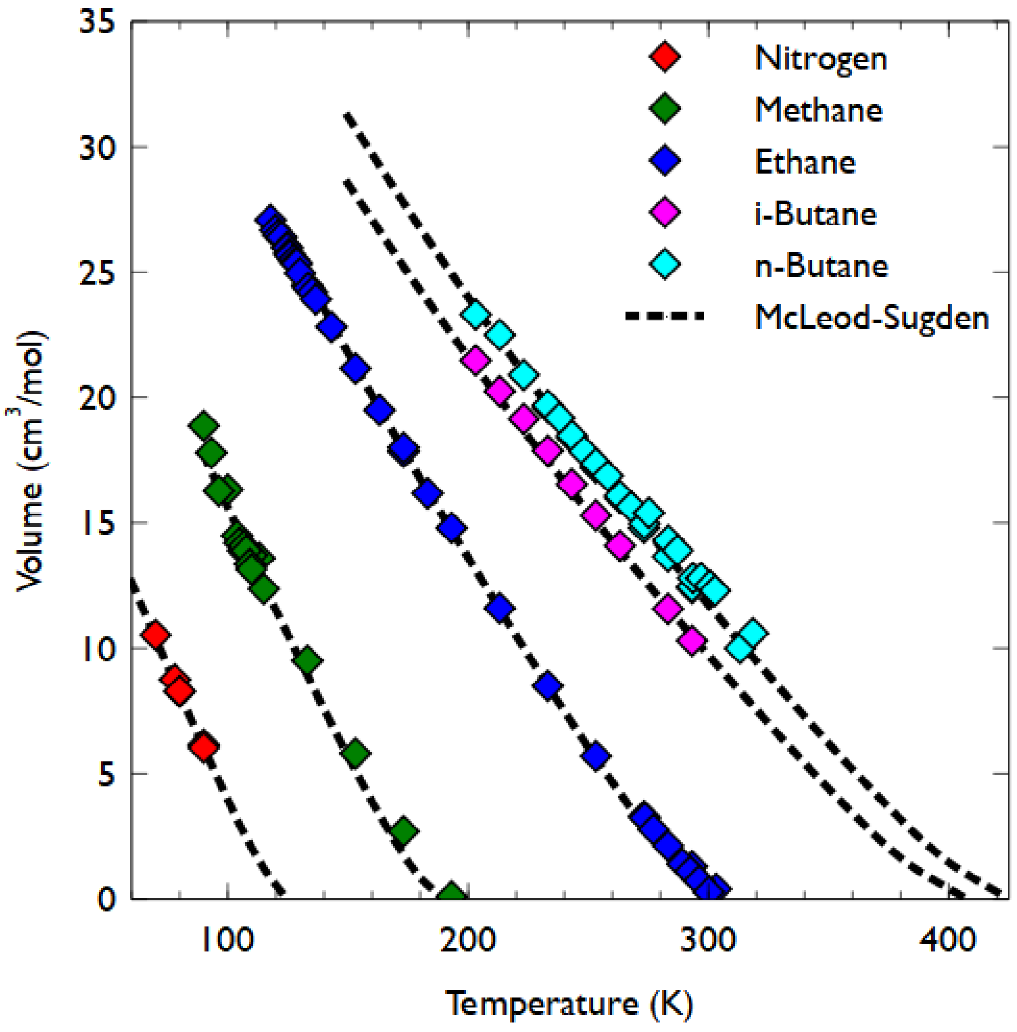
$$\sigma = C(\rho_t^L - \rho_t^V)^4$$

- Evidence suggests that $\wp$ is not a strong function of temperature

- The parachor has some justification from statistical mechanics (Boudh-Hir & Mansoori, *J. Phys. Chem.,* 1990, **94**, 8362-8364)

Parachor-based methods: Pure components

- McLeod-Sugden model quite good for many pure components
- Parachor can be fit to data or predicted from group contributions
- Model has correct behavior when approaching critical point (σ ⟶ 0)
- Model needs accurate liquid density – especially important near critical point



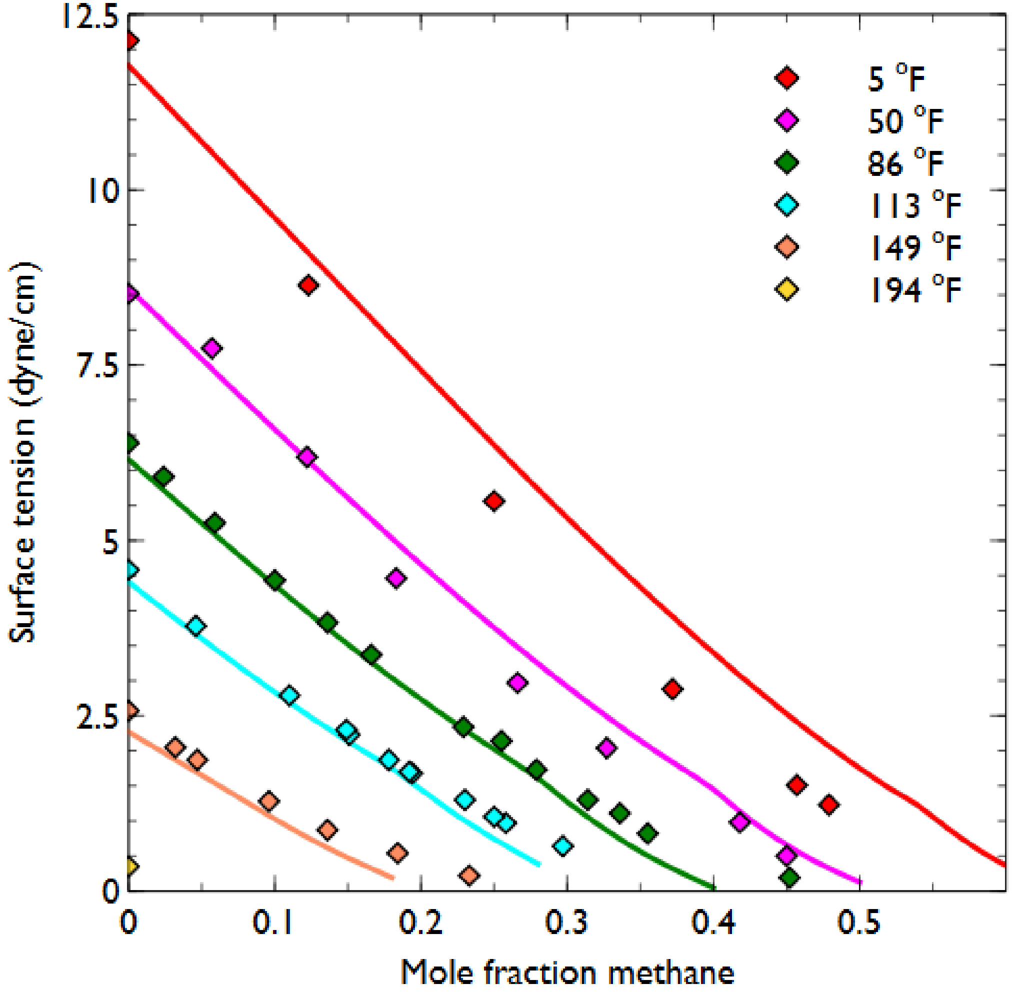
Surface tension of various pure components
Model is McLeod – Sugden

Parachor-based methods: Mixtures – I

- McLeod-Sugden model adapted for mixtures by Weinaug – Katz (1943)

$$\sigma^{1/4} = \wp^L \rho_t^L - \wp^V \rho_t^V$$

$$\wp^L = \sum_{i=1}^{c} \wp_i x_i \quad \wp^V = \sum_{i=1}^{c} \wp_i y_i$$



Surface tension of methane – propane
Model is Weinaug – Katz

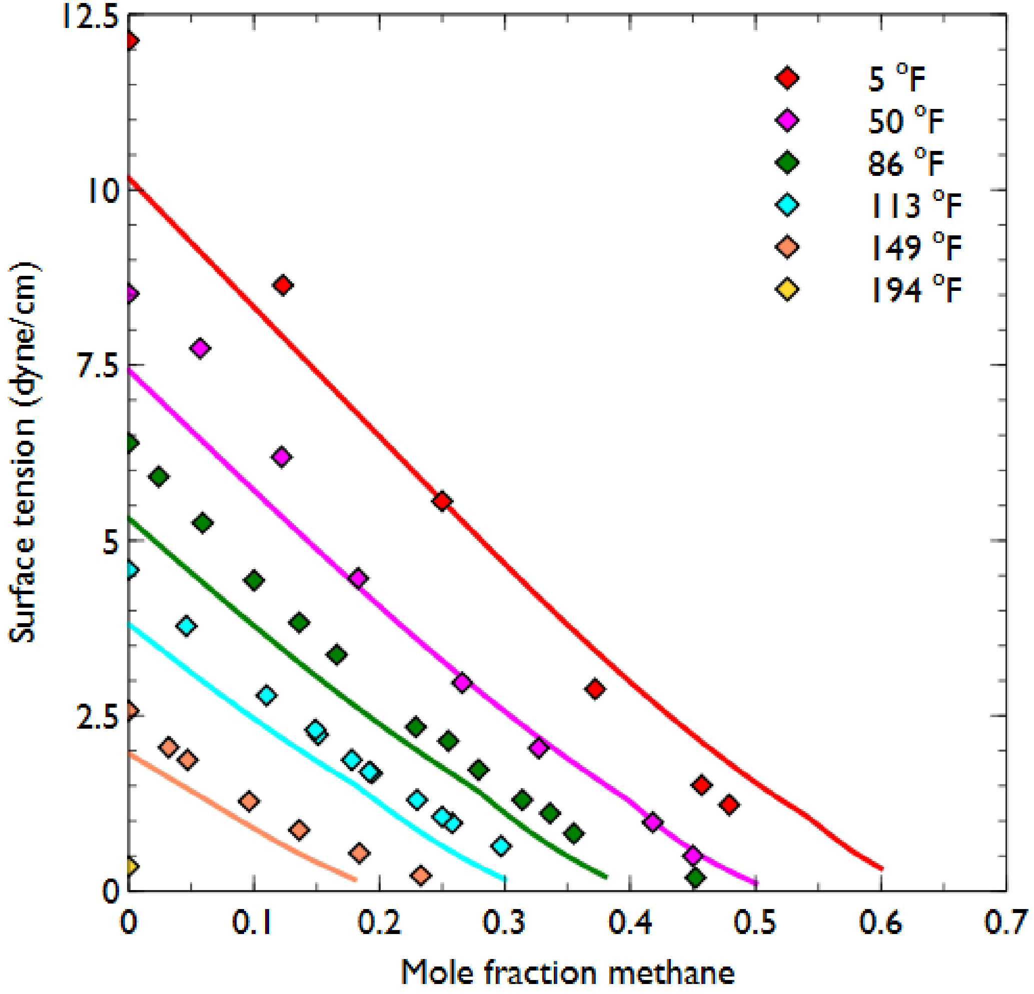
Parachor-based methods: Mixtures – II

- Other parachor-based mixture models are adapted versions of Weinaug – Katz
- Lee – Chien (2007) model uses pseudo-critical parameters that are mole fraction averages of the corresponding pure component properties

$$\wp^* = \frac{(A_c^*)^{1/4} V_c^*}{B^*}$$

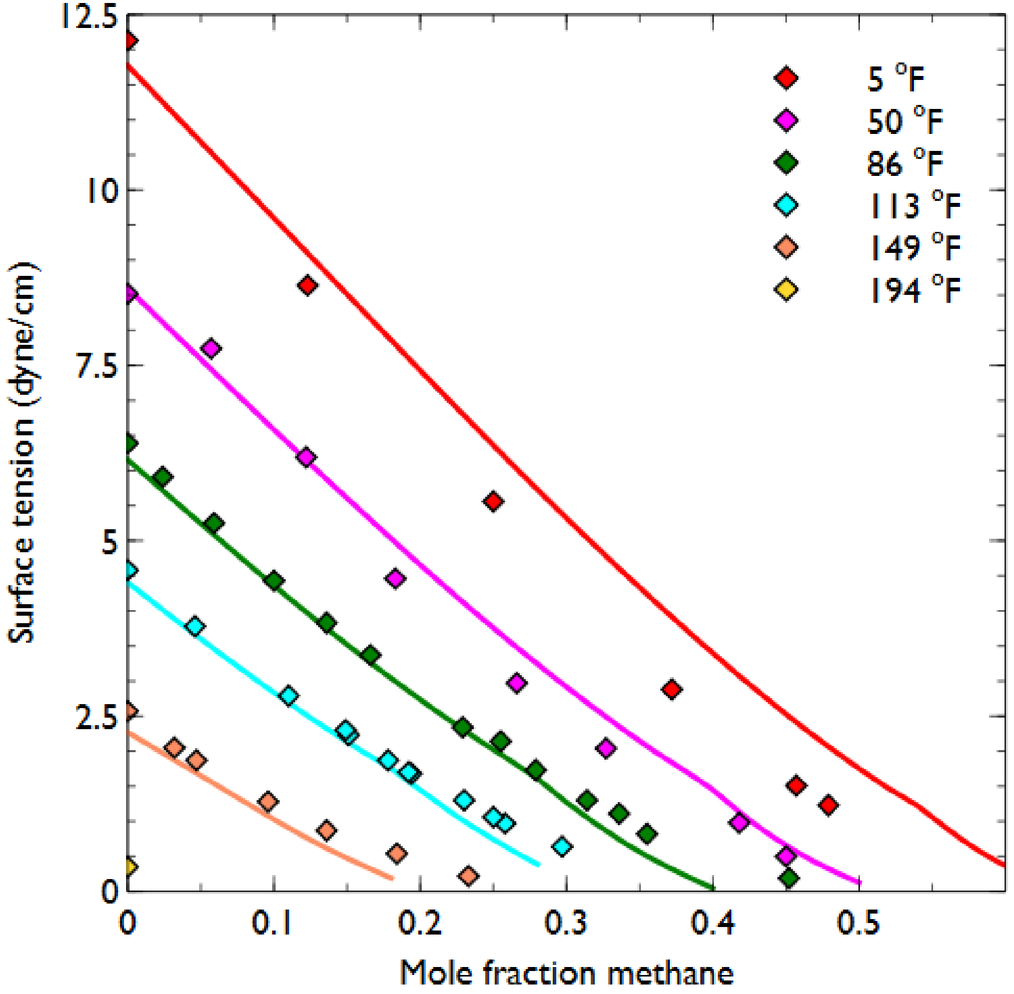
$$A_c^* = 4.601 \times 10^{-7} \times (P_c^*)^{2/3} (T_c^*)^{1/3} \times (0.133\alpha_c^* - 0.281)$$

- B^* is specified for a few important chemicals, otherwise estimated from the critical compressibility

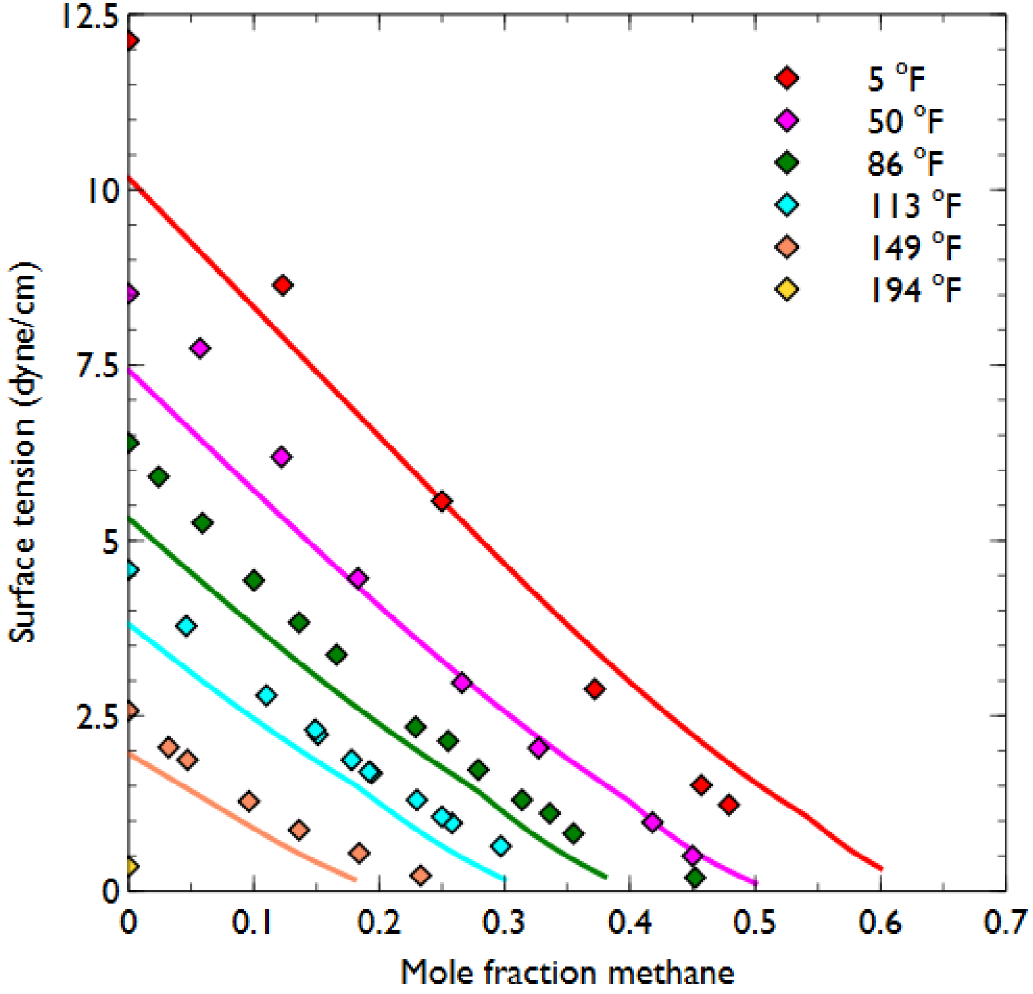


Surface tension of methane – propane
Model is Lee – Chien

Parachor-based methods: Weinaug – Katz vs Lee – Chien



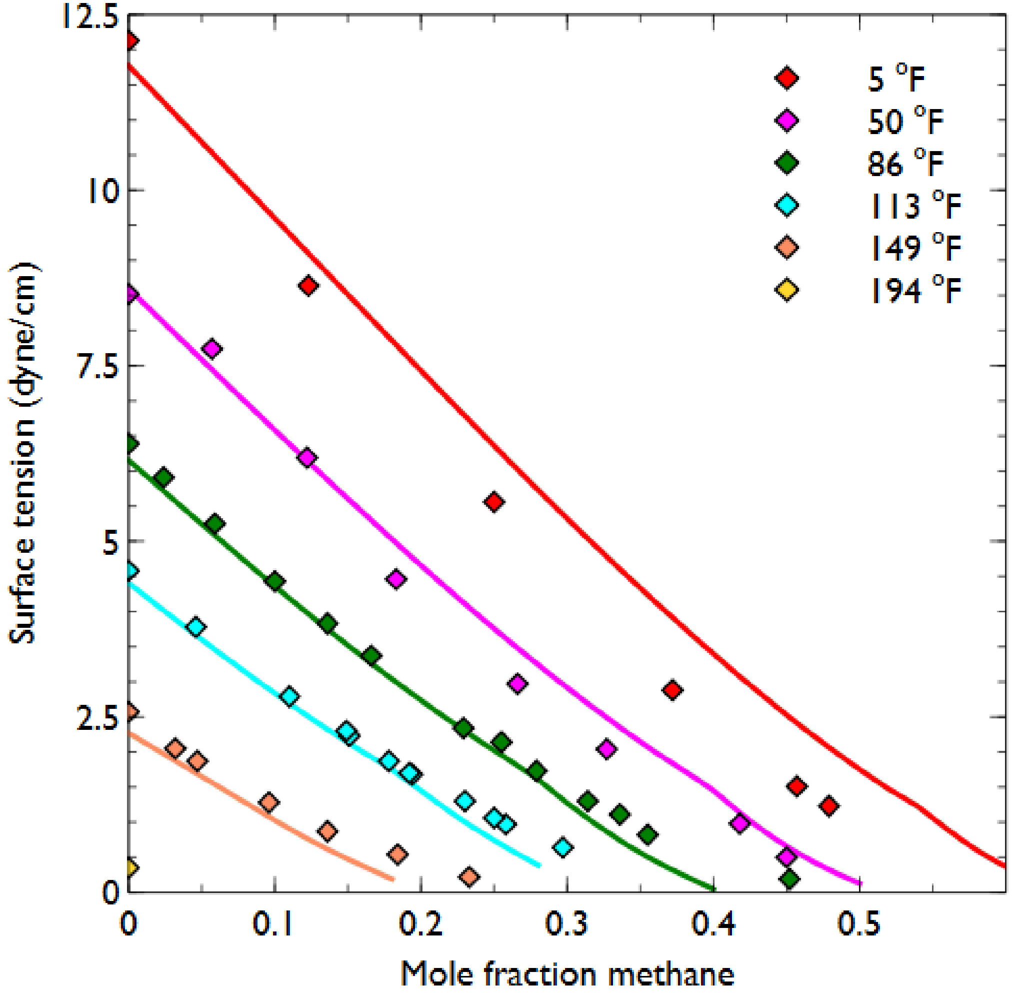
Surface tension of methane – propane
Model is Weinaug - Katz



Surface tension of methane – propane
Model is Lee – Chien

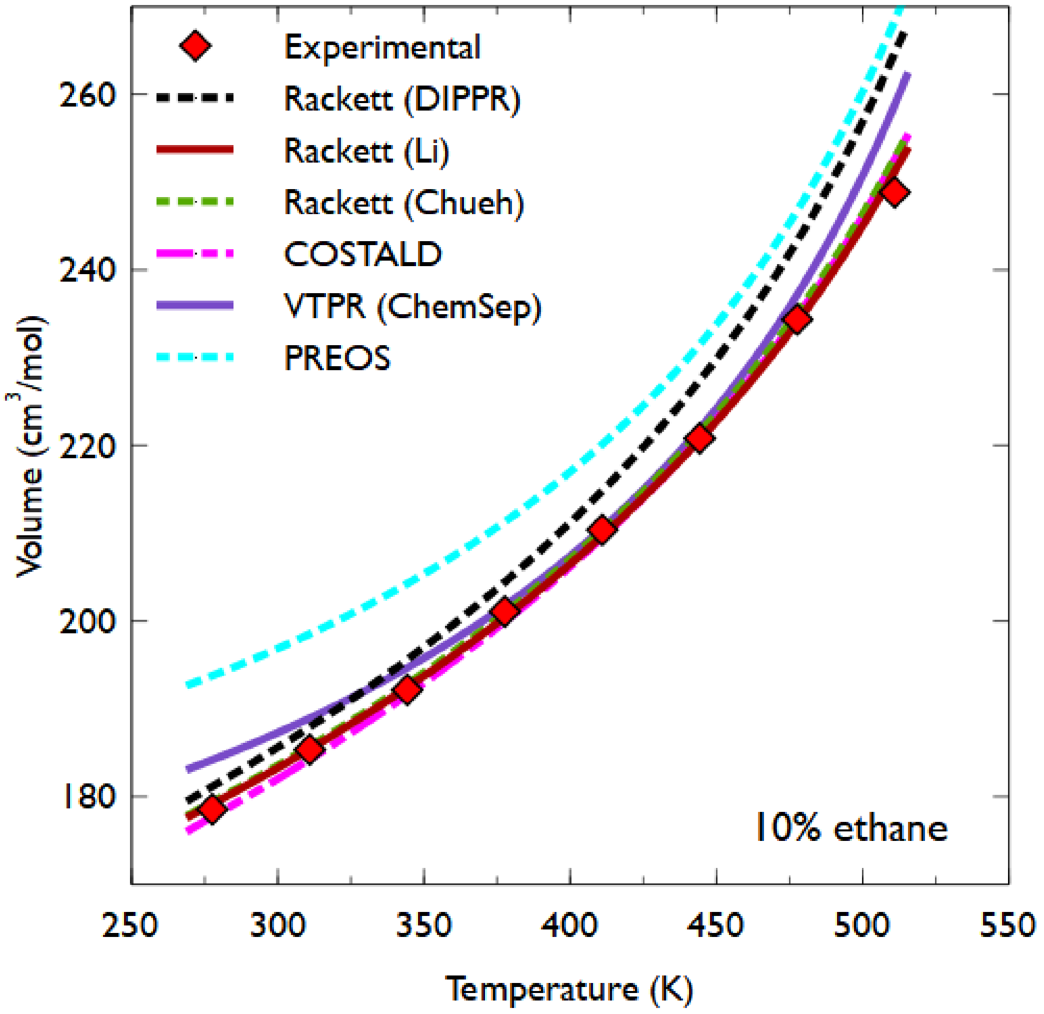
Parachor-based methods: SWOT

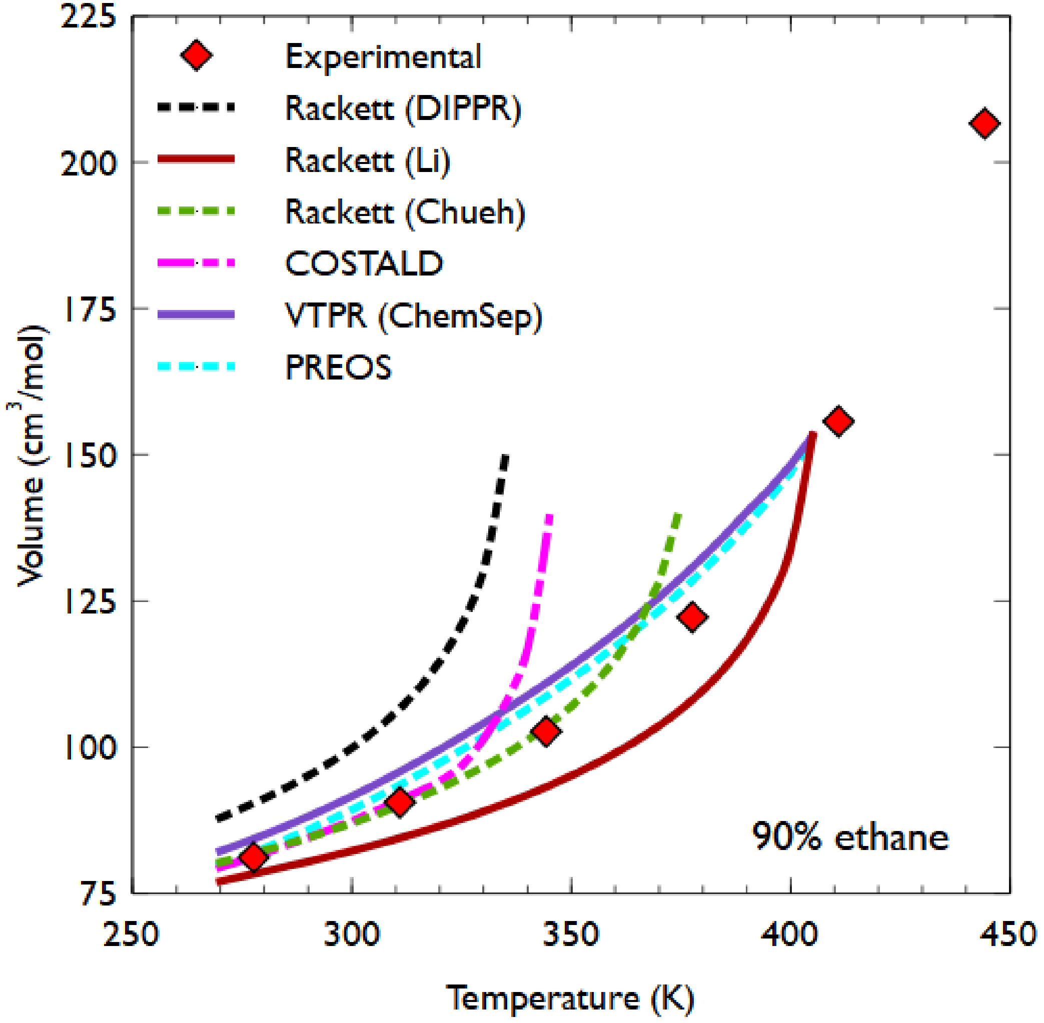
- Does NOT use pure component densities or σ_i (although...)
- Correct behavior when approaching critical point ($\sigma \longrightarrow 0$)
- Can be used when some components are above their own critical points
- Model somewhat sensitive to liquid density estimation method
- Needs accurate liquid density near (pseudo)-critical point



Surface tension of methane – propane
Model is Weinaug – Katz

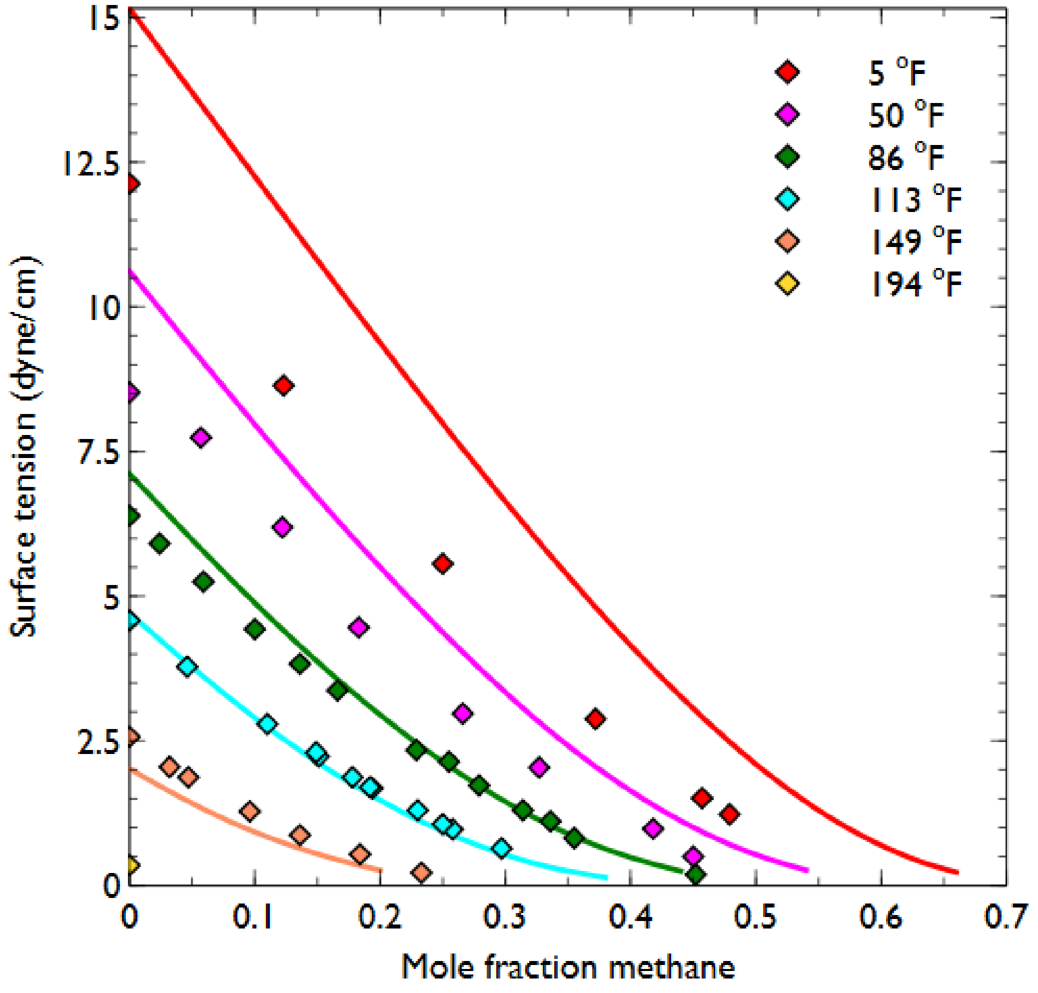
Accurate liquid densities not always possible





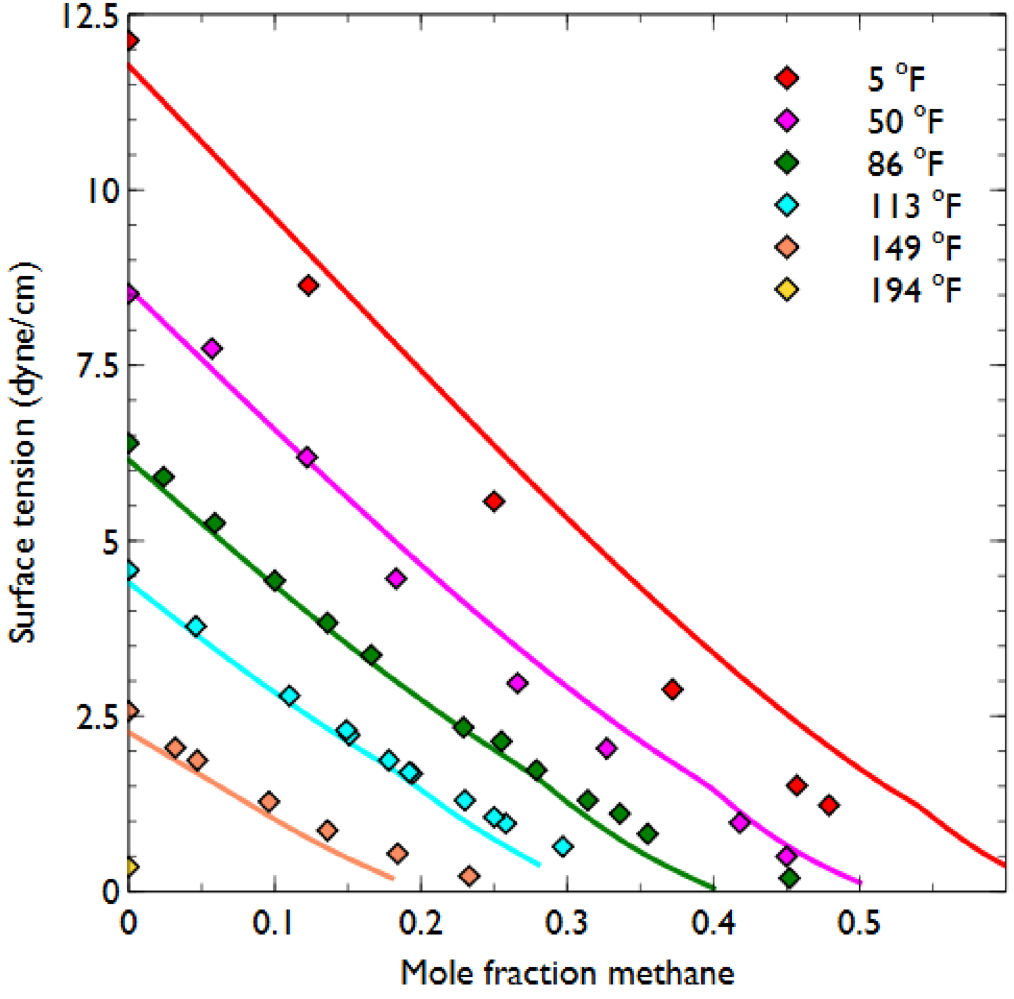
Molar volume ($1/\rho$) for ethane – n-decane mixtures

Parachor-based methods: Know how liquid density is estimated!



Surface tension of methane – propane

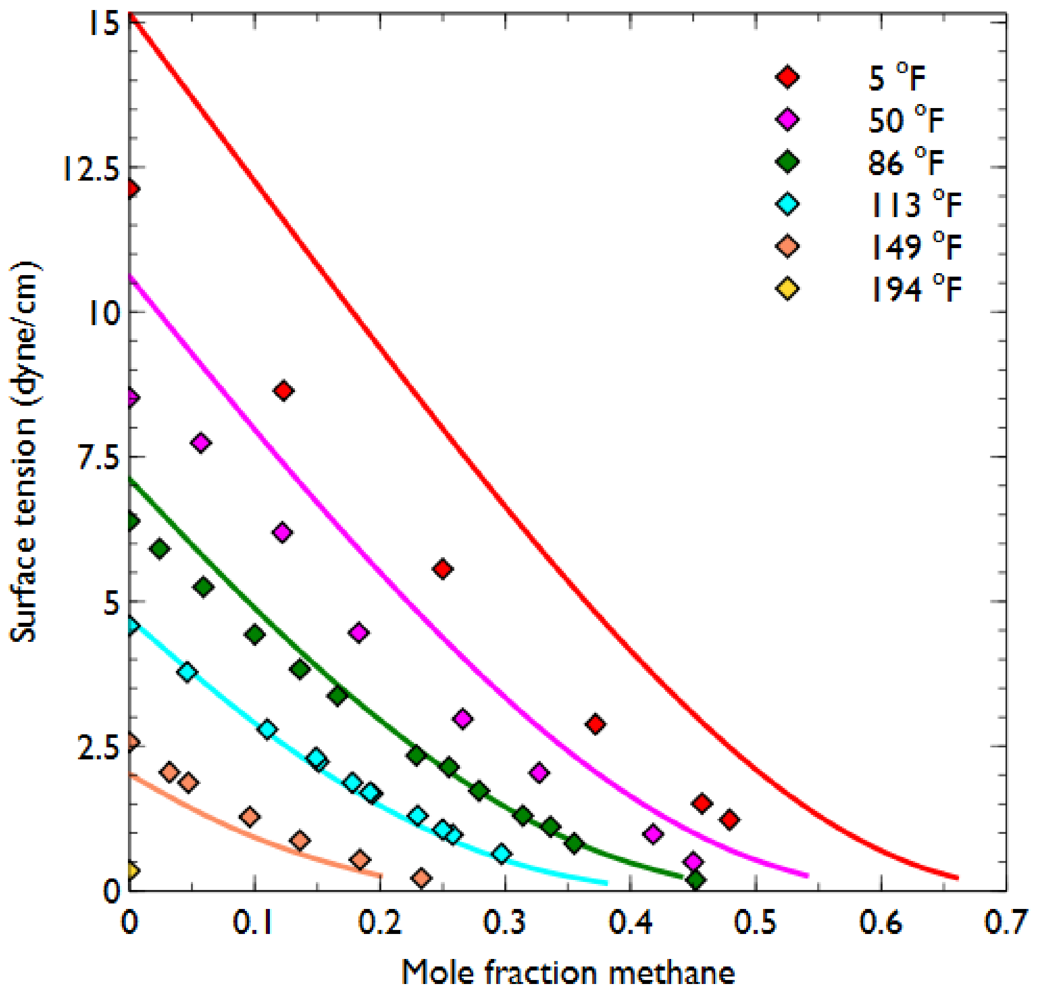
Weinaug – Katz with PR for liquid density



Surface tension of methane – propane

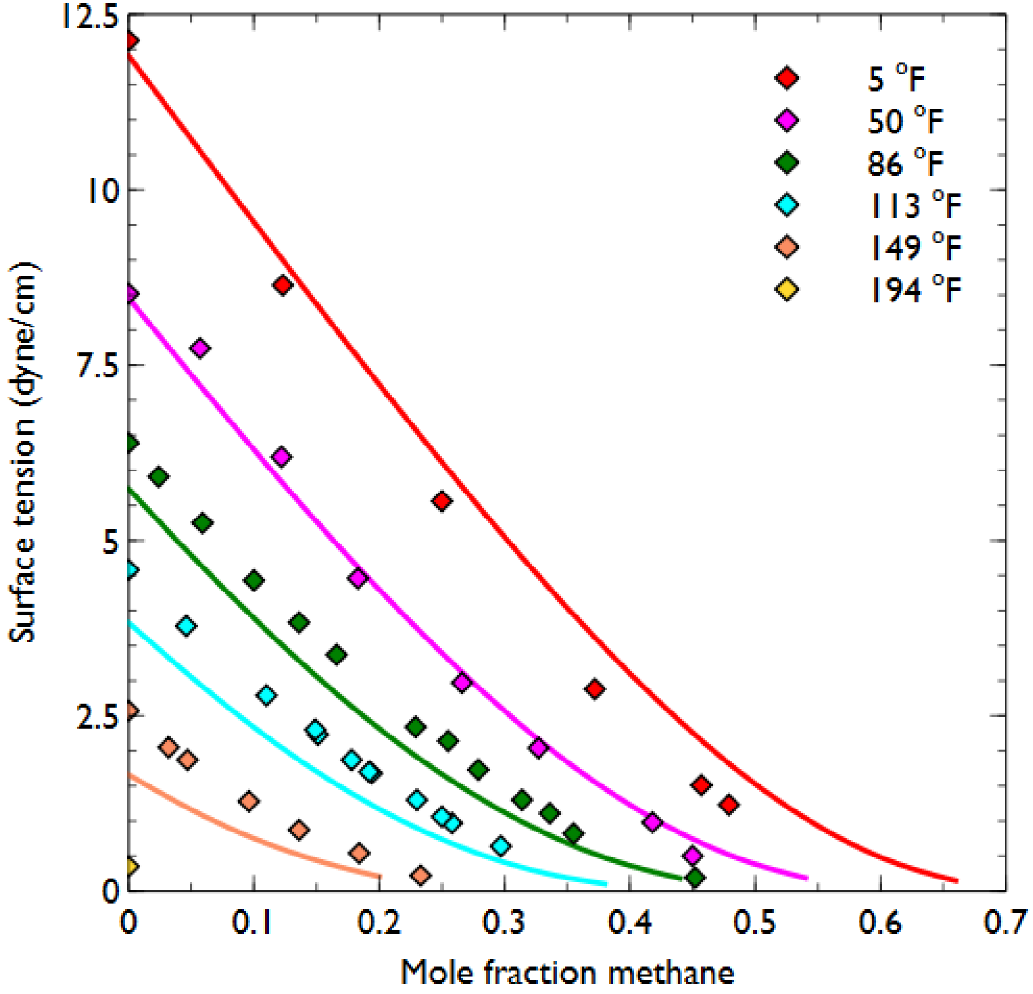
Weinaug – Katz with COSTALD for liquid density

Parachor-based methods: Volume translation helps, sometimes!



Surface tension of methane – propane

Weinaug – Katz with PR for liquid density

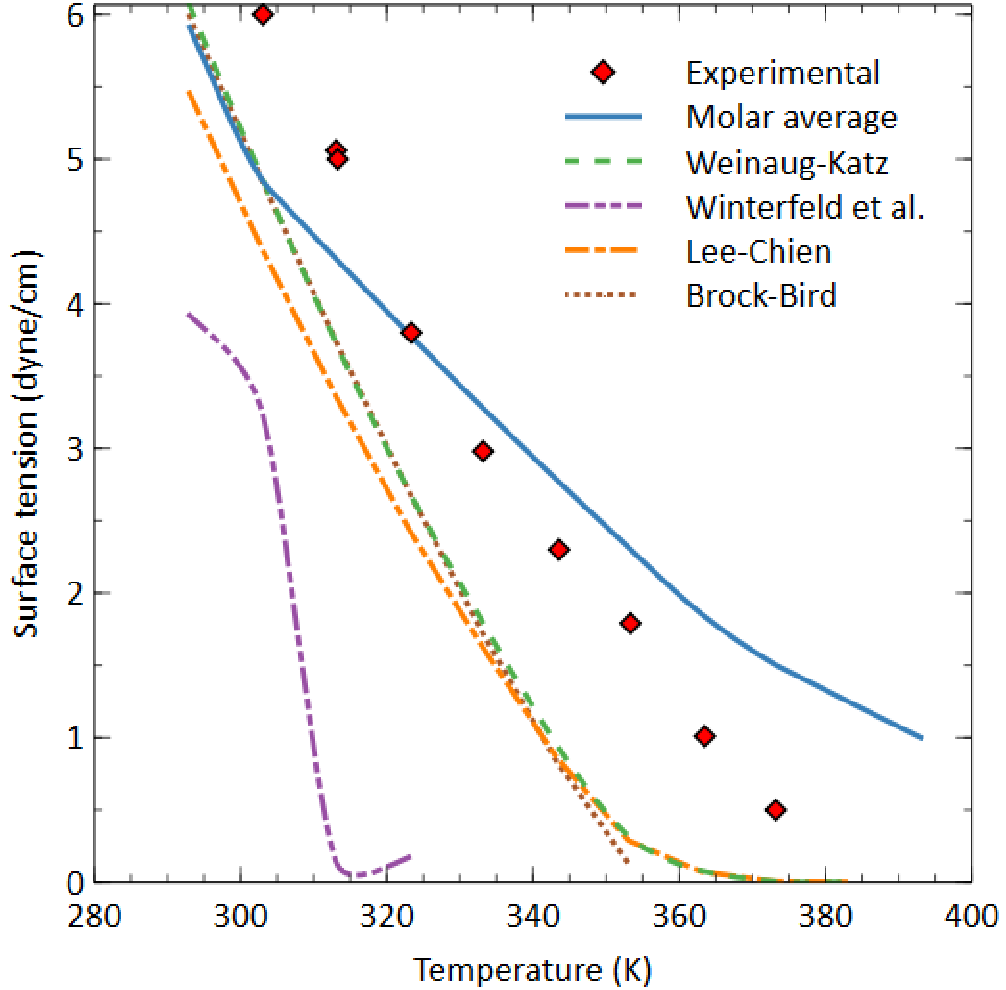


Surface tension of methane – propane

Weinaug – Katz with Volume Translated PR EOS for liquid density

Surface tension of mixtures: Summary to this point

- No model in common use performs well all the time!
- Many models should not be used when the system temperature exceeds the critical temperature of a species in the mixture!
- Many simulators have only a limited choice of models, some of which are not very good much of the time.
- Some simulators do not readily disclose what mixture σ model they use!
  - Or, if they do tell you, it is well hidden
  - Often the default choice is the molar average, often, but not always the worst possible choice



σ For a mixture of C1, C2, C3, C4, C7

A new question *you* should now be asking

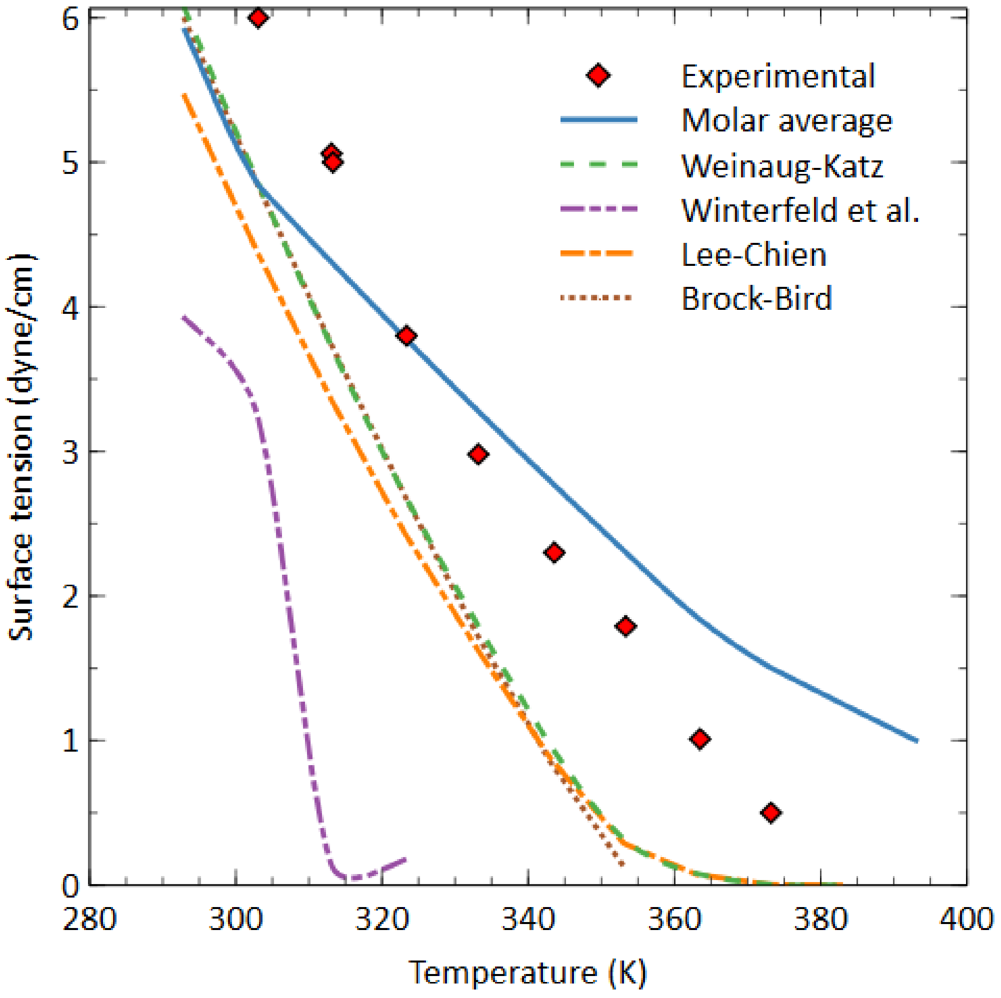
1. Do we have to accept poor estimates of σ?

or, posed another way...

2. Is there anything we can do to improve estimates of σ?

Surface tension of mixtures: What is needed

- Ideally, a model that can be used for all mixtures all of the time
- Failing that, a model that has superior accuracy (compared to most current mixture models) and…
- Can be used when some components are above their own critical points and…
- Is easy to program and rapid in execution (in a computer program)



σ For a mixture of C1, C2, C3, C4, C7

1. Other models for σ

- Density Gradient Theory (DGT)

- *Cubic equation of state (EOS) for σ*

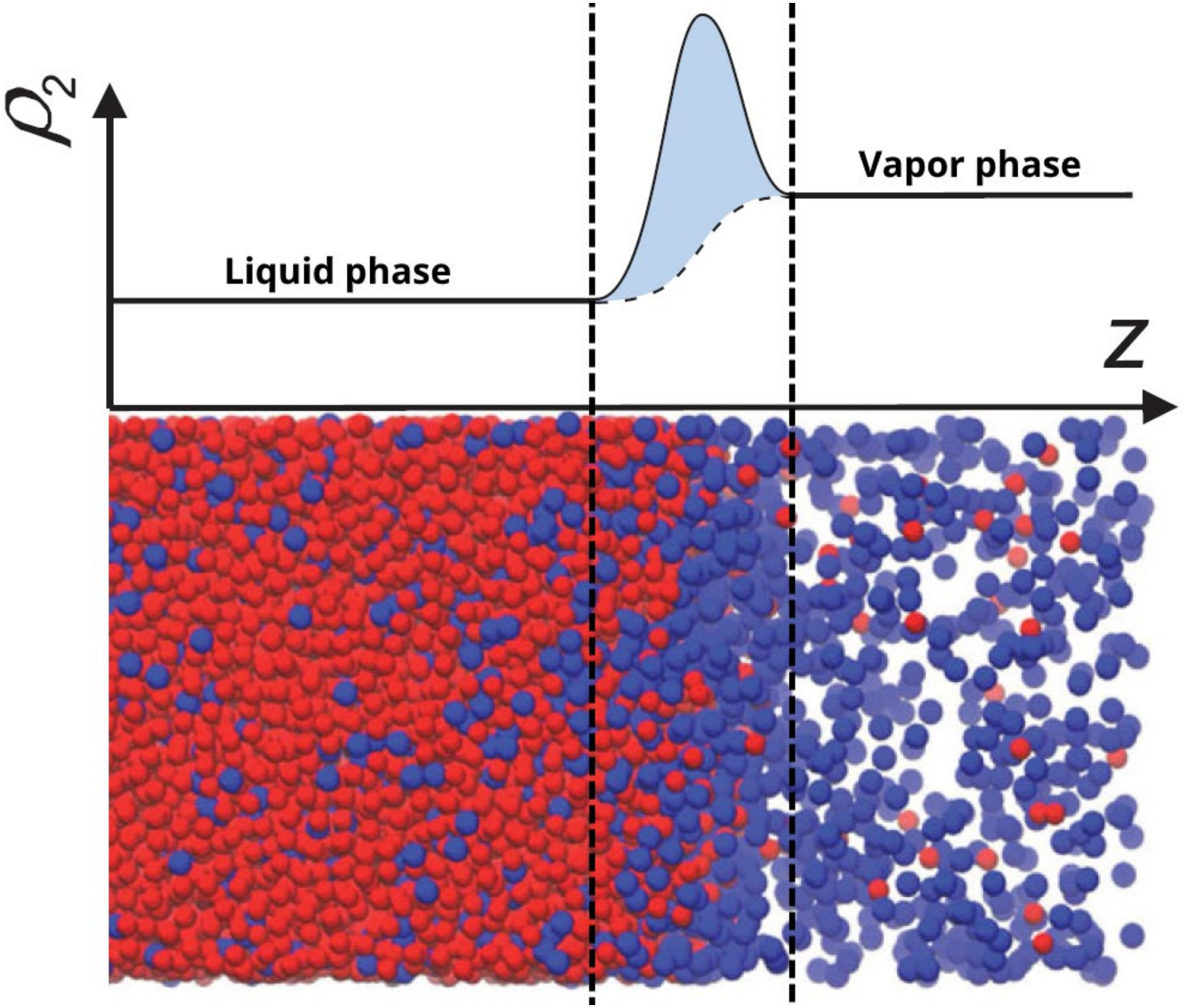
- Shardt-Elliott model

- DGT has been around for some time; the other two are very new

- But are any of them superior to what is now available?

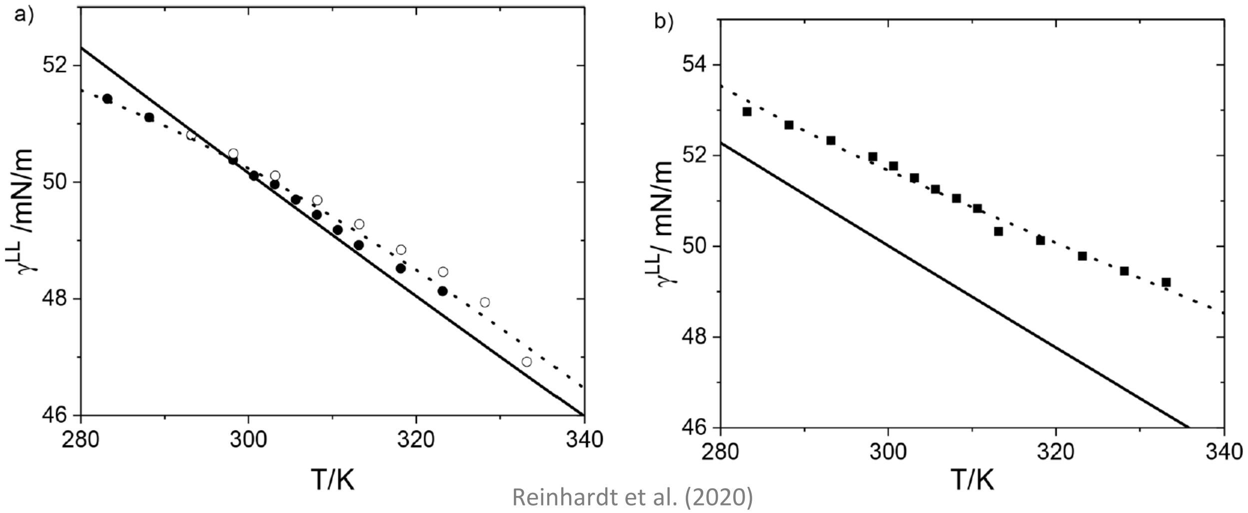
Density Gradient Theory (DGT)

- Interface "phase" between two bulk fluid phases
- Smooth & continuous density profile connecting two bulk values
- Can be used with any conditions/mixture, *including above pure component critical points*!

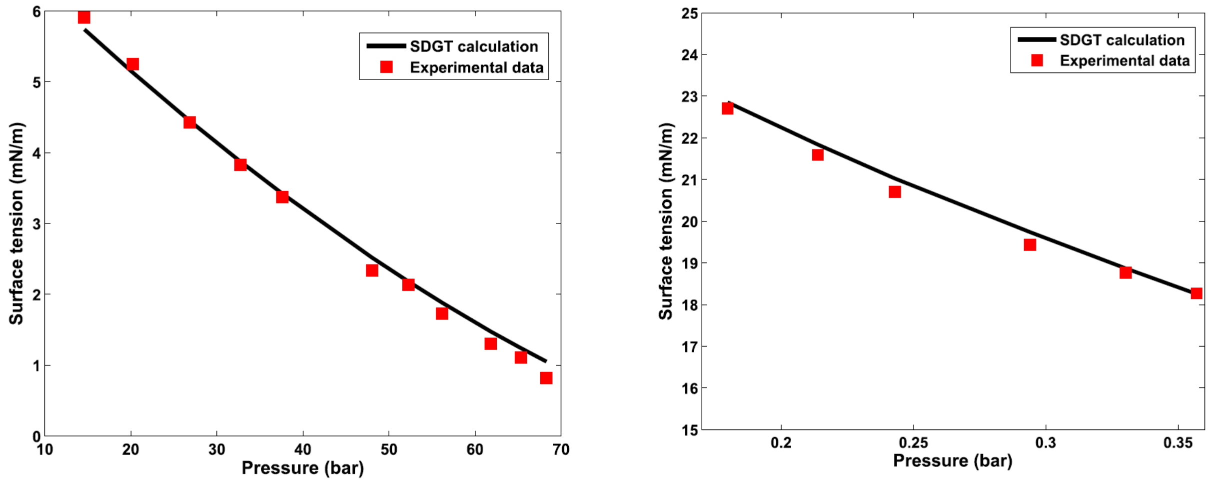


DGT performance: Some Published Results*

*There are many more like these



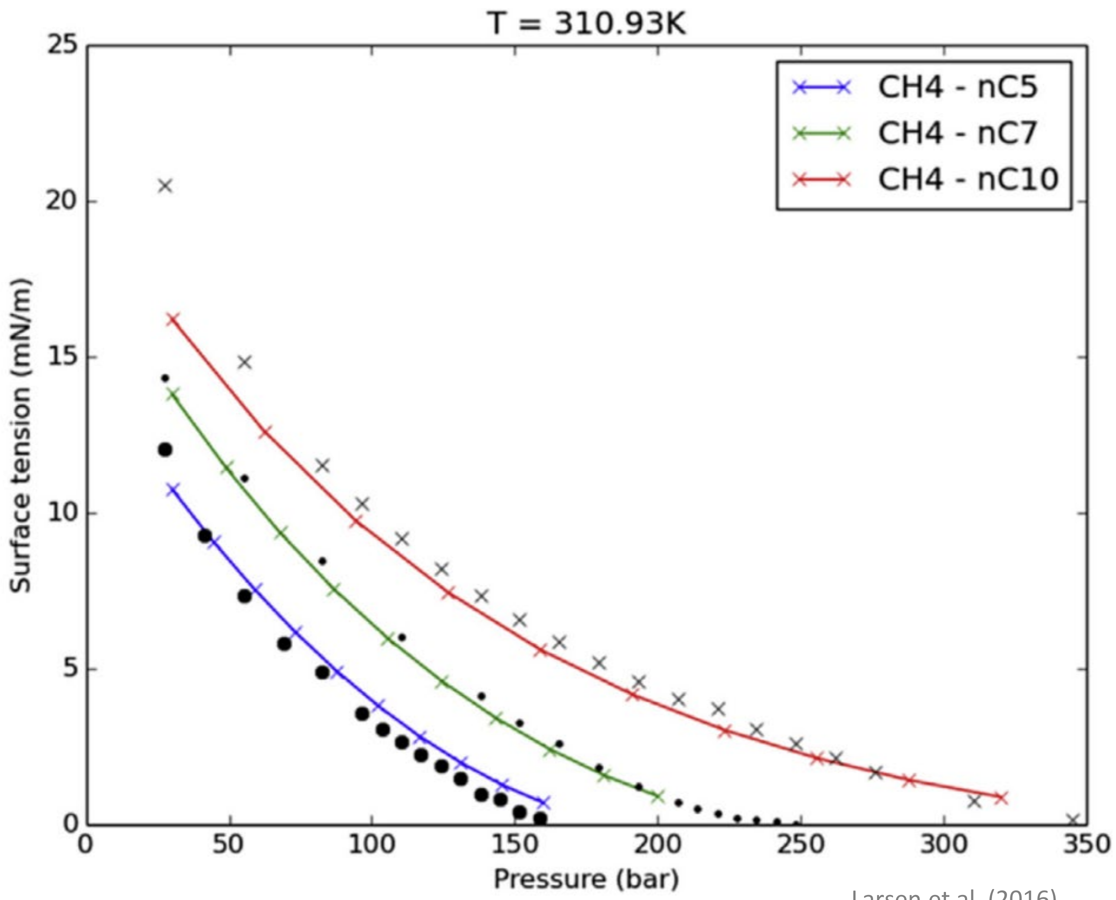
Reinhardt et al. (2020)



(a) Methane–propane, $T = 303.15$ K.

Mu et al. (2017)

(b) Pentane–toluene, $T = 288.15$ K.



Larsen et al. (2016)

DGT – Some math required

- Assumption of NVT (“canonical”) ensemble
- To calculate surface tension, find density (ρ_i) profiles that minimize the Helmholtz energy of the system (equilibrium)

surface tension

position relative to interface

$$\sigma = \int_{-\infty}^{\infty}\left[\left(\frac{1}{2}\sum_i\sum_j c_{ij}\overbrace{\frac{d\rho_i}{dz}\frac{d\rho_j}{dz}}^{\text{density gradients}}\right)+\left(\sum_i \rho_i\overbrace{(\mu_i-\mu_i^*)}^{\text{chemical potentials}}-\underbrace{(P-P^*)}_{\text{pressures}}\right)\right]dz$$

cross-influence parameter

density

Solving DGT

Problem #1

result

$$\sigma = \int_{\underbrace{-\infty}_{\text{replace with finite, quantized interval}}}^{\infty} \left[\left(\frac{1}{2} \sum_i \sum_j c_{ij} \overbrace{\frac{d\rho_i}{dz} \frac{d\rho_j}{dz}} \right) + \left(\sum_i \rho_i \overbrace{(\mu_i - \mu_i^*)}^{\text{from EOS}} - \underbrace{(P - P^*)}_{\text{from EOS}} \right) \right] dz$$

Problem #2

- #1: Need density (and density gradient) profiles across width of the interface
  - Requires one of a variety of solution algorithms

PC influence parameters: Also fit to data (calculable sometimes)

- #2: Need cross-influence parameter

$$c_{ij} = (1 - \beta_{ij})\sqrt{c_i c_j}$$

Binary interaction parameter (BIP): Can be fit to data; often set to zero

Under the influence

- Cross-influence parameters (c_{ij}) need PC influence parameters (c_i)…

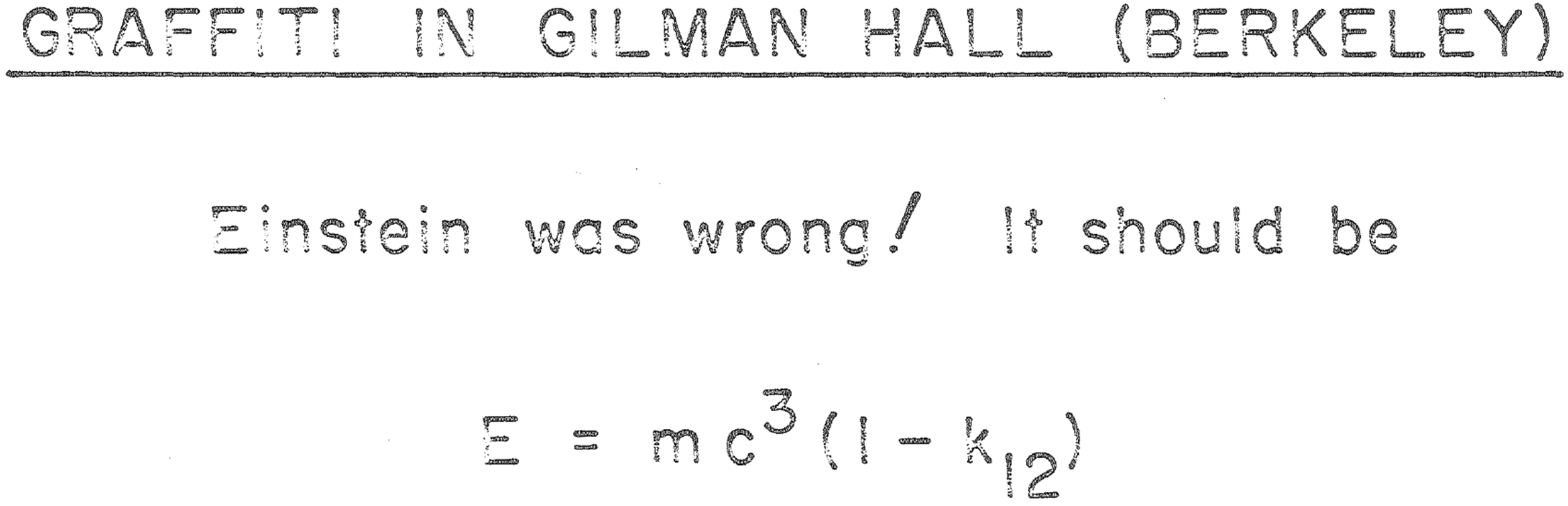
$$c_{ij} = \left(1 - \beta_{ij}\right)\sqrt{c_i c_j}$$

  - Requires a lot of math and various assumptions to obtain workable equations
  - Functions for c_i exist for a couple EOS
    - Even then, only seems to perform well for PC-SAFT EOS
  - Fit to experimental PC σ data in practice
- …and BIPs (β_{ij}) fit to binary σ data

Where there’s a BIP… there’s ignorance

> “The importance of binary parameters is not difficult to understand… Nevertheless, there is always the suspicion that a binary parameter is just a correction factor to hide our ignorance. Just how deep this suspicion is, was revealed to me some years ago in the men's room of Gilman Hall (University of California, Berkeley) where I found the graffiti shown [below].”

– J.M. Prausnitz
State-of-the-Art Review of Phase Equilibria, 1980



GRAFFITI IN GILMAN HALL (BERKELEY)

Einstein was wrong! It should be

$$E = mc^3(1 - k_{12})$$

Prausnitz (1980)

DGT strengths

- Applicable up to true mixture critical point

- Works for any* mixture of chemical species at any conditions

- Permits any EOS/thermodynamic model

- Can be applied to liquid-liquid interfaces as well

DGT weaknesses

- Computationally intensive – hundreds of EOS evaluations per σ calculation
- Requires σ data for all species or accurate c_i model
- Requires binary σ data for cases when $\beta_{ij} = 0$ does not suffice
- Many flavors of DGT algorithms; not all work all of the time
- Requires accurate bulk fluid density estimates
- Nearly always uses a non-cubic equation of state
  - (e.g a version of SAFT, and there are too many versions of SAFT)

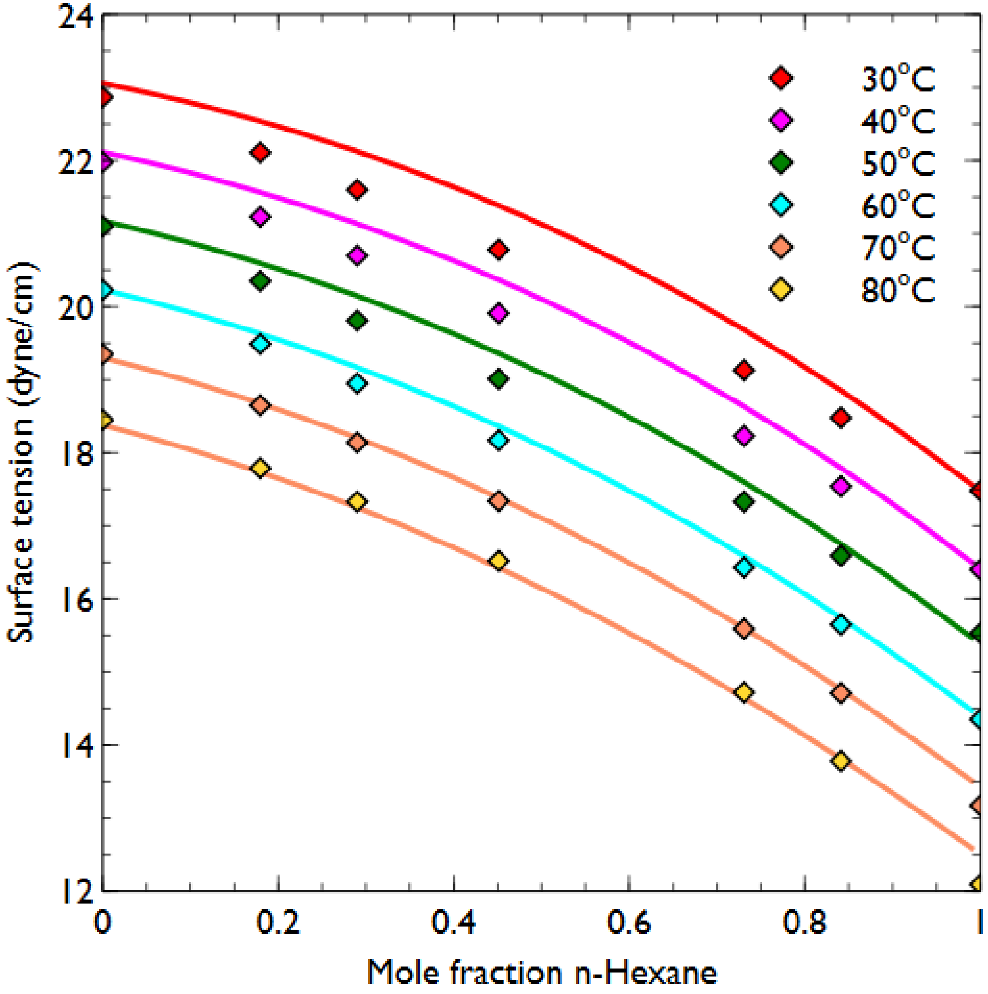
- **Challenging to implement correctly!**

Mulero et al. Cubic σ-EOS

- Cubic EOS for surface tension (Mulero et al., 2022):

$$P_c - P = \frac{R^* T \sigma}{M_m - b_m \sigma} - \frac{a_m \sigma^2}{M_m^2 + M_m \sigma (b_m + c_m) - c_m b_m \sigma^2}$$

- P_c from simple molar average
- Computationally trivial
- So far only developed for alkanes
- Results for low MW alkanes much less satisfactory (so far)
- **(!)** Paper of Mulero et al. incorrectly omits critical pressure from EOS in some places



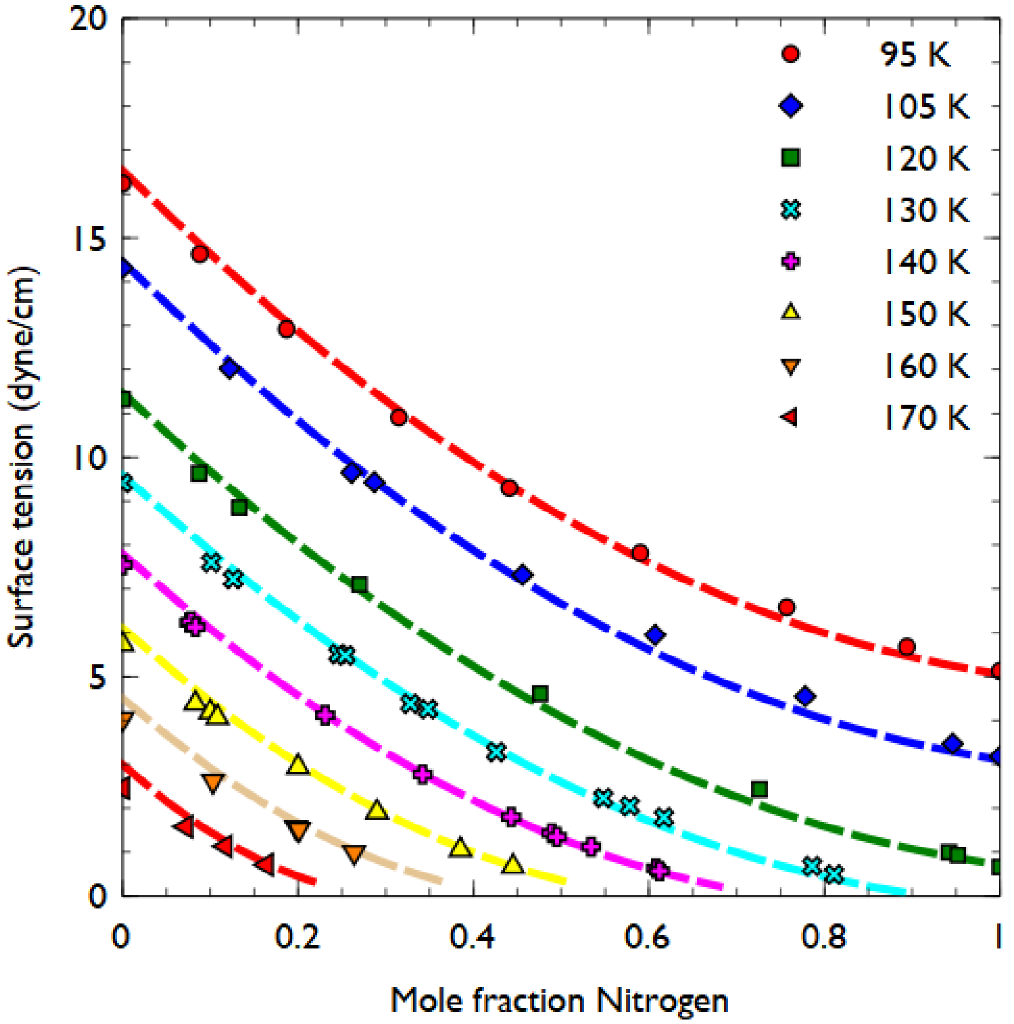
Surface tension for n-Hexane – n-Decane

Shardt – Elliott Model

$$\sigma = \sigma_2 - \left(1 + \frac{b x_2^r}{1 - a x_2^r}\right) x_1^r (\sigma_2 - \sigma_1)$$

$$x_1^r = \frac{x_1}{x_1^c} \qquad x_2^r = 1 - x_1^r$$

- x_1^r reduced (scaled) mole fraction
- x_1^c mole fraction at the critical point
- a and b are adjustable parameters (BIPs)
- In illustration at right (and on the next slide) $a = 0$ and b tuned only to the top line of data points

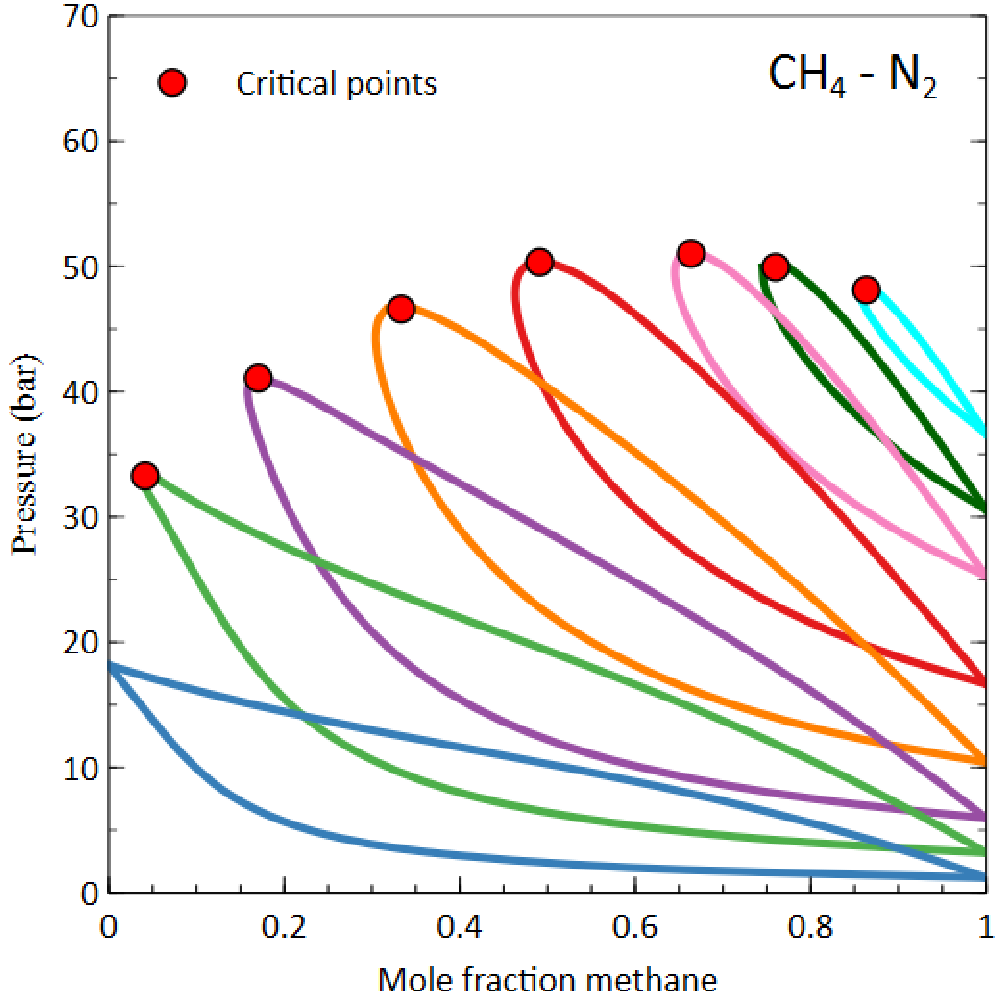


Surface tension for Methane – Nitrogen

How does Shardt – Elliott work?

1. Find critical point of mixture at specified temperature.

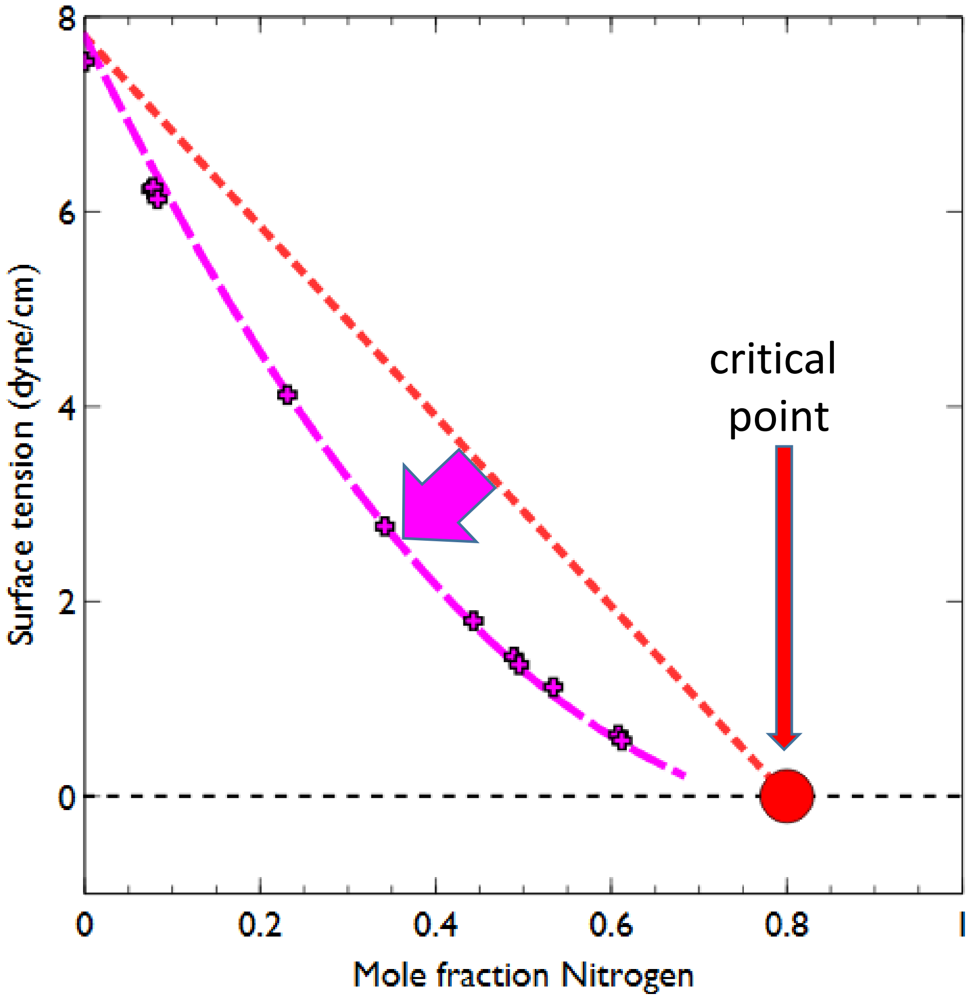
   This is a phase equilibrium calculation.



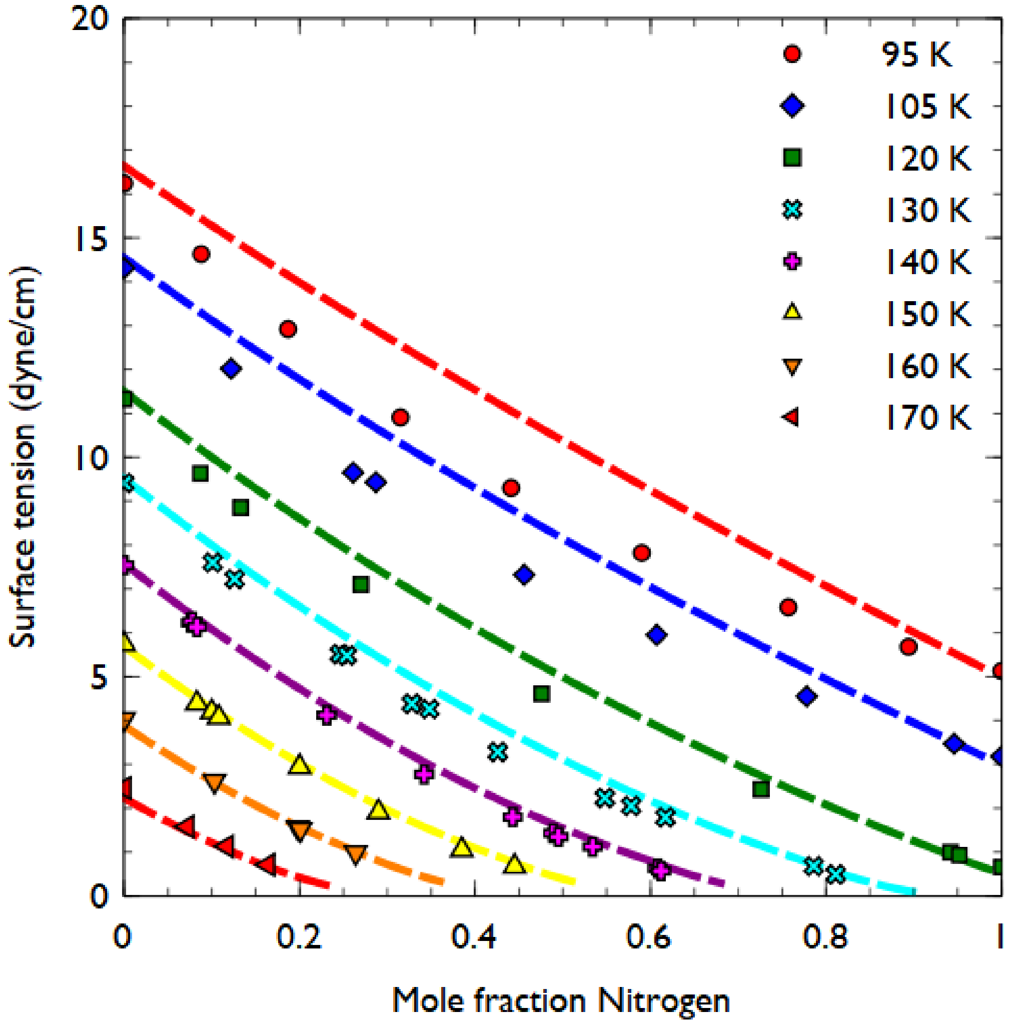
How does Shardt – Elliott work?

1. Find critical point of mixture at specified temperature

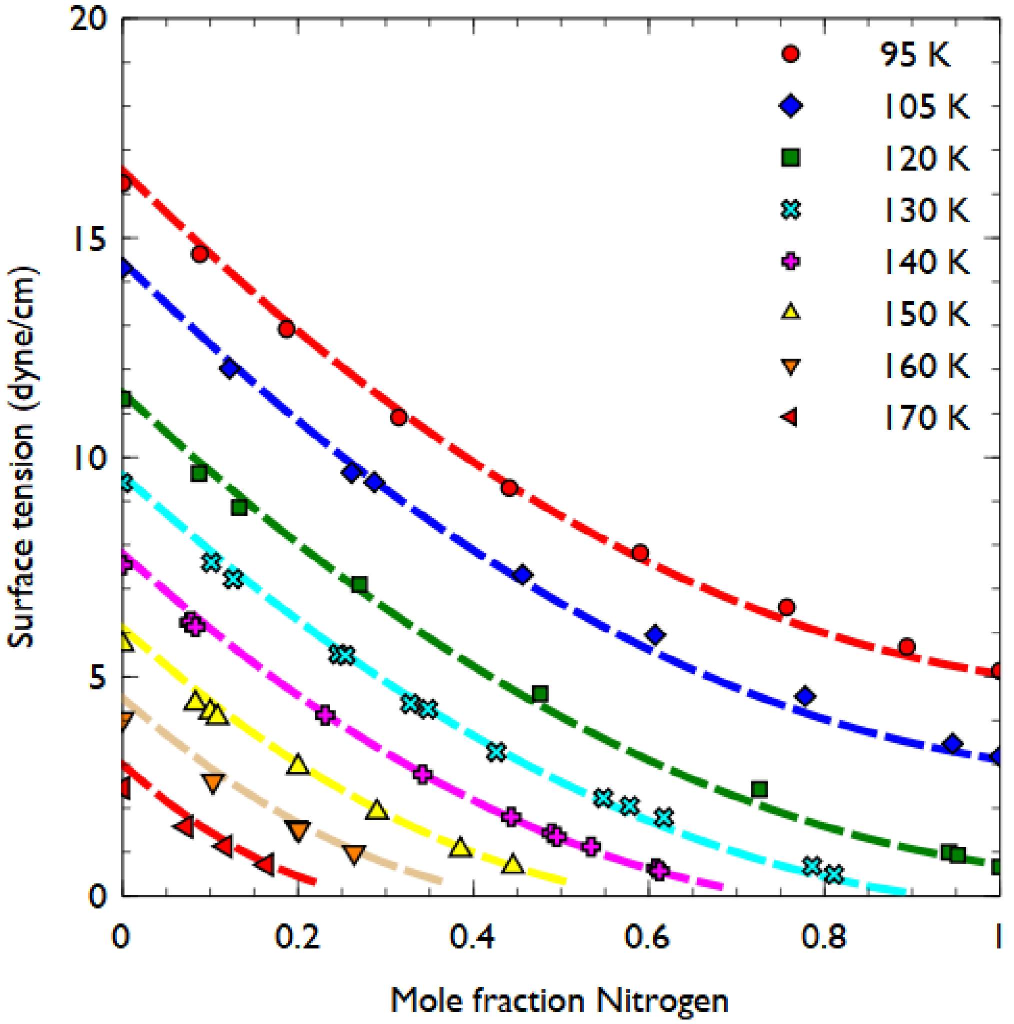
   This is a phase equilibrium calculation.
2. At the critical point $\sigma \to 0$
3. Draw straight line from pure component point on left side axis to critical point.
4. Adjust BIPs to move from straight-line approximation to curve that better represents the data
5. BIPs can be fit to data at a single temperature. In our examples we kept $a = 0$



Weinaug – Katz vs Shardt – Elliott: Methane - Nitrogen

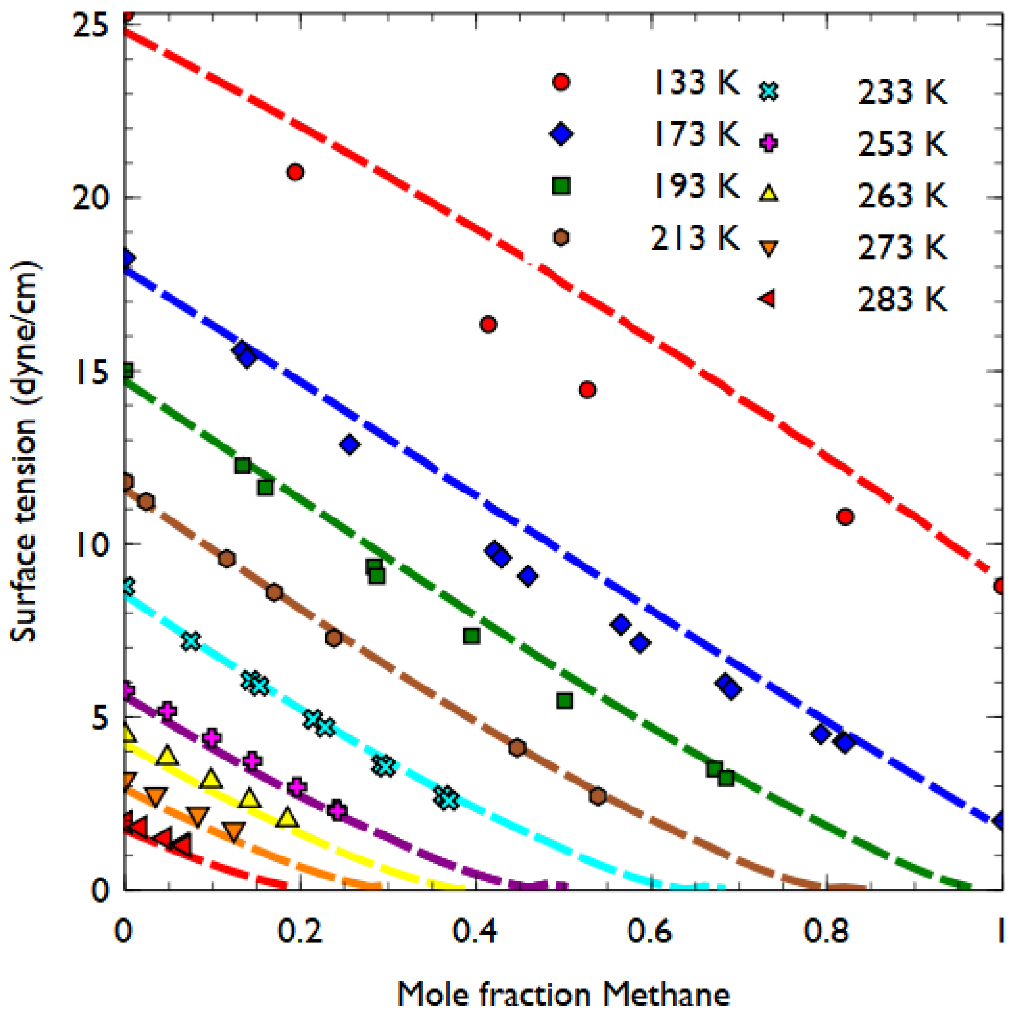


Weinaug – Katz

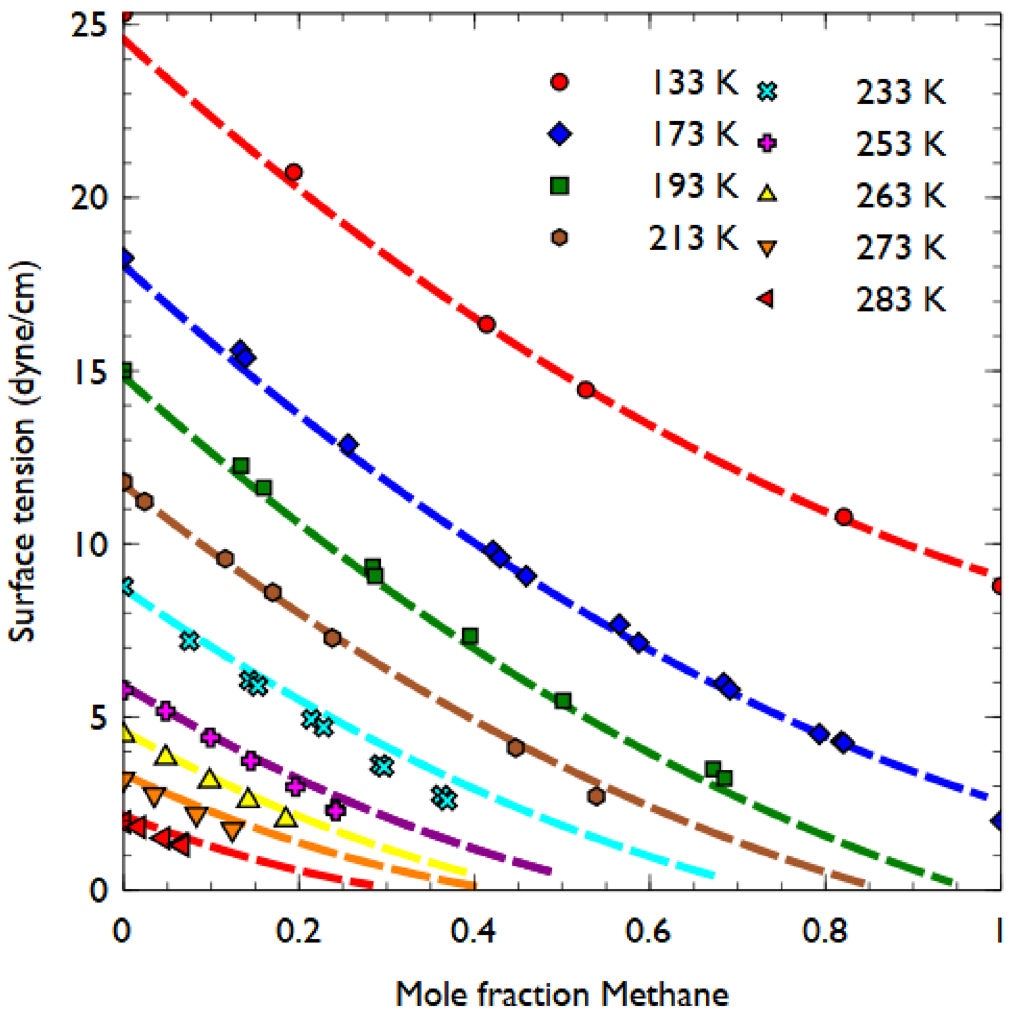


Shardt - Elliott

Weinaug – Katz vs Shardt – Elliott: Methane – Ethane



Weinaug - Katz



Shardt - Elliott

Where do we go from here?

We, the presenters of this paper, think

1. Currently, there is no surface tension model that is always useful and usable
2. Density gradient theory is
   - Likely to prove the best and most versatile approach
   - May be too time consuming or too difficult to use in routine column simulations
3. Shardt – Elliott
   - Appears very promising
   - Is much simpler than DGT
   - Needs BIPs for best results

We, the presenters of this paper, plan to…

1. Release a new version of ChemSep that contains
   - The Shardt – Elliott model for multicomponent systems (binary is there now, available soon)
   - Density gradient theory (Not yet there, quite some work to include this)
   - ChemSep Lite is free so you will be able to experiment with these models
2. Pursue some ideas we have for predicting missing Shardt – Elliott BIPs

Here is the Shardt – Elliott for multicomponent mixtures

$$\sigma\left(x_{i,r},T\right)=\sum_{i=1}^{n}\left[x_{i,r}(T)\sigma_i(T)\right]+\sum_{i=1}^{n}\left\{\left[\frac{x_{i,r}(T)}{\sum_{j=1}^{n}\left(\frac{x_{j,r}(T)}{1-a_{ji}}\right)}\right]\sum_{j=1}^{n}\left[\frac{b_{ji}}{a_{ji}}\left(\frac{1}{1-a_{ji}}\right)x_{j,r}(T)\left(\sigma_i(T)-\sigma_j(T)\right)\right]\right\}$$

- Designed to accommodate components above their critical points
- Broad applicability… but requires mixture critical composition
- Best results obtained with 2 adjustable parameters per binary-pair
- Less computationally-demanding than DGT (but that critical point is not trivial)
- Not yet in ChemSep

Where do you go from here?

You, our audience, should ask some more questions (of yourselves)

1. What is σ in systems of interest to me?
2. From where did I get those estimates? (Bonus points if measured)
3. Should I believe them? (Probably not)
4. What are the consequences *for me* of incorrect estimates of σ?

5. Pressure your experimentalist friends to measure surface tension in
    - iC4 – nC4 mixtures
    - Mixtures of industrial significance
    - Mixtures with more than two components
    - (and to publish the results)
    - So we can develop better models

Surface tension at work