DE LA RECHERCHE À L'INDUSTRIE

Large cryogenic process cycle modeling

Helmholtz-energy-explicit models for fluid mixtures

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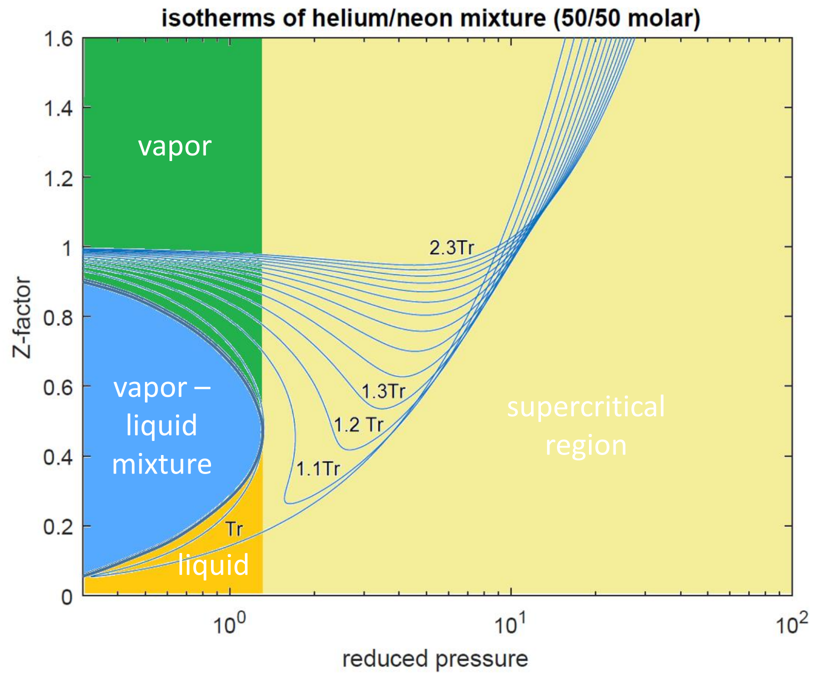
Objectives

- Model the thermal properties of mixtures
  - helium-neon
  - neon-argon
  - helium-argon
- Validate the mixture model with existing Brayton / J-T cycle
- Study the process cycles with large cryogenic installations

Evolution of EoS

- Van der Waals: $$p = \frac{RT}{(v-b)} - \frac{a}{v^2}$$
- Virial expansion: $$\frac{pv}{RT} = Z = 1 + B(T)\rho + C(T)\rho^2 + D(T)\rho^3 + \cdots$$
- Peng-Robinson: $$p = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2}$$
- Helmholtz energy: $$\alpha(\delta,\tau,\bar{x}) = \alpha^0(\rho,T,\bar{x}) + \alpha^r(\delta,\tau,\bar{x})$$ $$\rho_N k_B T\alpha = U - TS$$

Potential that measures the useful work obtainable from a closed thermodynamic cycle



Advantages

- Continuous over liquid/vapor boundary
- It is a function of measurable properties
- Purely analytical derivatives

Helmholtz energy formulation

$$\delta = \frac{\rho}{\rho_r},\ \tau = \frac{T_r}{T}$$

$$\frac{a(\rho,T)}{RT} = \alpha(\delta,\tau) = \alpha^o(\delta,\tau) + \alpha^r(\delta,\tau)$$

Ideal Helmholtz free energy

$$\alpha^o(\delta,\tau) = \frac{h^o_o\tau}{RT_r} - \frac{s^o_o}{R} - 1 + \ln\frac{\delta\tau_o}{\delta_o\tau} + \frac{\tau}{R}c^o_p\left(\frac{1}{\tau} - \frac{1}{\tau_o}\right) + \frac{c^o_p}{R}ln\frac{\tau}{\tau_o}$$

Residual Helmholtz free energy

$$\alpha^r(\delta,\tau) = \sum_{k=1}^{I_{pol}} N_k\delta^{d_k}\tau^{t_k} + \sum_{k=I_{pol}+1}^{I_{pol}+I_{exp}} N_k\delta^{d_k}\tau^{t_k}\exp\Big(-\delta^{l_k}\Big) + \sum_{k=I_{pol}+I_{exp}+1}^{I_{pol}+I_{exp}+I_{crit}} N_k\delta^{d_k}\tau^{t_k}\exp\Big(-\eta_k(\delta-\eta)^2 - \beta_k(\tau-\gamma_k)^2\Big)$$

pure fluid

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mixtures

Ideal Helmholtz free energy

$$\alpha^o(\rho,T,\bar{x}) = \sum_{i=1}^{N} x_i\Big[\alpha^o_{oi}(\rho,T) + \ln x_i\Big]$$

Residual Helmholtz free energy

$$\alpha^r(\delta,\tau,\bar{x}) = \sum_{i=1}^{N} x_i\alpha^r_{oi}(\delta,\tau) + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_ix_jF_{ij}\alpha^r_{ij}(\delta,\tau)$$

Reducing variables

$$\frac{1}{\rho_r(x)} = \sum_{i=1}^{N}\frac{x_i^2}{\rho_{c,i}} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} 2x_ix_j\beta_{v,ij}\gamma_{v,ij}\frac{x_i+x_j}{\beta^2_{v,ij}x_i + x_j}\frac{1}{8}\left(\frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}}\right)^3$$

$$T_r(x) = \sum_{i=1}^{N} x_i^2T_{c,i} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} 2x_ix_j\beta_{T,ij}\gamma_{T,ij}\frac{x_i+x_j}{\beta^2_{T,ij}x_i + x_j}\left(T_{c,i}\cdot T_{c,j}\right)^{0.5}$$

Departure function represents Helmholtz energy from mixing

$$\Delta\alpha^r(\delta,\tau,\bar{x}) = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_ix_jF_{ij}\alpha^r_{ij}(\delta,\tau)$$

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pure fluid

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mixtures

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5+30 variables describing mixture properties
vs
130-150 variables describing pure fluid properties with HEoS

Relation of thermodynamic properties to Helmholtz energy

Property	Relation to Helmholtz free energy
Pressure	$\frac{p(\delta,\tau,\bar{x})}{\rho RT} = 1 + \delta\alpha^r_\delta$
Compression factor	$Z(\delta,\tau,\bar{x}) = 1 + \delta\alpha^r_\delta$
Entropy	$\frac{s(\delta,\tau,\bar{x})}{R} = \tau\left(\alpha^o_\tau + \alpha^r_\tau\right) - \alpha^o - \alpha^r$
Internal energy	$\frac{u(\delta,\tau,\bar{x})}{RT} = \tau\left(\alpha^o_\tau + \alpha^r_\tau\right)$
Enthalpy	$\frac{h(\delta,\tau,\bar{x})}{RT} = 1 + \tau\left(\alpha^o_\tau + \alpha^r_\tau\right) + \delta\alpha^r_\delta$
Isochoric heat capacity	$\frac{c_v(\delta,\tau,\bar{x})}{R} = -\tau^2\left(\alpha^o_{\tau\tau} + \alpha^r_{\tau\tau}\right)$
Isobaric heat capacity	$\frac{c_p(\delta,\tau,\bar{x})}{R} = -\tau^2\left(\alpha^o_{\tau\tau} + \alpha^r_{\tau\tau}\right) + \frac{(1+\delta\alpha^r_\delta-\delta\tau\alpha^r_{\delta\tau})^2}{1+2\delta\alpha^r_\delta+\delta^2\alpha^r_{\delta\tau}}$
Gibbs free energy	$\frac{g(\delta,\tau,\bar{x})}{RT} = 1 + \alpha^o + \alpha^r + \delta\alpha^r_\delta$
Speed of sound	$\frac{w^2(\delta,\tau,\bar{x})M}{RT} = 1 + 2\delta\alpha^r_\delta + \delta^2\alpha^r_{\delta\delta} - \frac{(1+\delta\alpha^r_\delta-\delta\tau\alpha^r_{\delta\tau})^2}{\tau^2(\alpha^o_{\tau\tau}+\alpha^r_{\tau\tau})}$
J - T coefficient	$\mu_{JT}R\rho = \frac{-(\delta\alpha^r_\delta+\delta^2\alpha^r_{\delta\delta}+\delta\tau\alpha_{\delta\tau})}{(1+\delta\alpha^r_\delta-\delta\tau\alpha^r_{\delta\tau})^2-\tau^2(\alpha^o_{\tau\tau}+\alpha^r_{\tau\tau})(1+2\delta\alpha^r_\delta+\delta^2\alpha^r_{\delta\delta})}$

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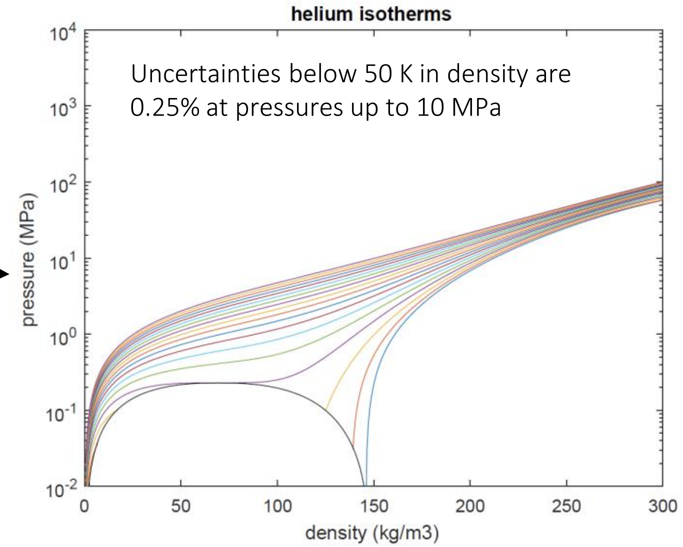

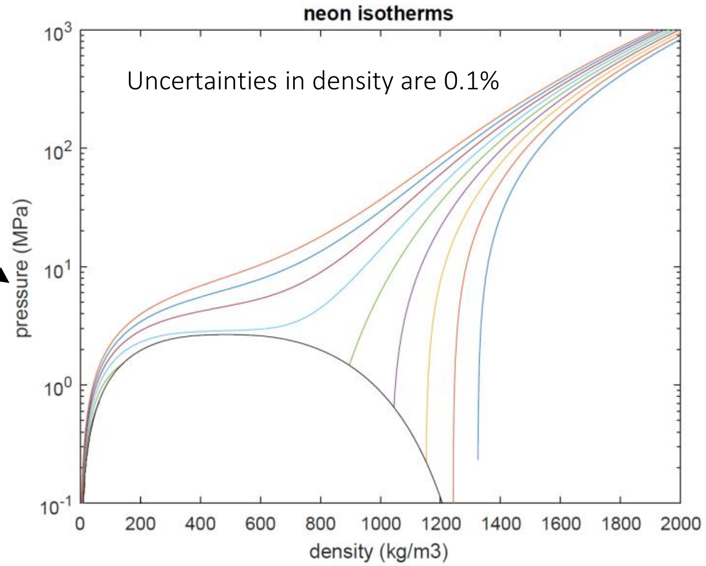

Algorithms

Algorithms employed so far:

- Sum of squares: $SSQ = \sum_{i=0}^{n} c(w_i X_i - \bar{X})^p$ with constrains and points weights
- Complex marching algorithm – no success so far

- The first algorithm is more successful (so far)

Institutes and universities developing the EoS:

- NIST Boulder, U.S.
- Ruhr-Universitat Bochum, Germany
- Kyushu Sangy University, Japan
- Others? NTNU, KIT, …?

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On the way to the HEoS mixture model

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(My) methodology

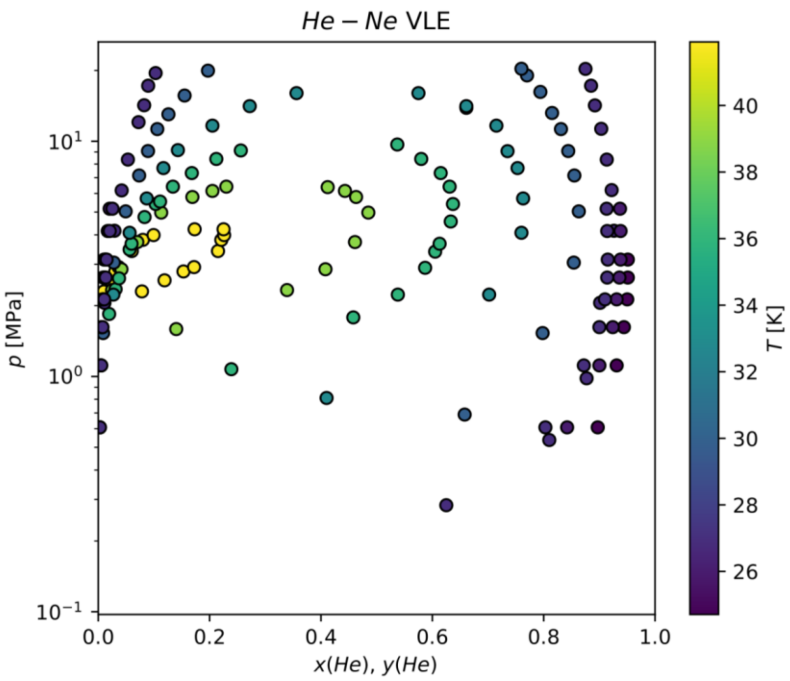
- *Obtain good VLE model*
  - Assess the credibility of all datasets / each diverging experimental point
  - Fit the reducing parameters and the excess function

$$\alpha^{\mathrm{r}}(\delta,\tau,\bar{x}) = \sum_{i=1}^{N} x_i\,\alpha_{\mathrm{o}i}^{\mathrm{r}}(\delta,\tau) + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j F_{ij}\,\alpha_{ij}^{\mathrm{r}}(\delta,\tau)$$

$$\alpha_{ij}^{\mathrm{r}}(\delta,\tau) = \sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}} + \sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}}\,e^{-\eta_{ij,k}(\delta-\varepsilon_{ij,k})^2-\beta_{ij,k}(\delta-\gamma_{ij,k})}$$

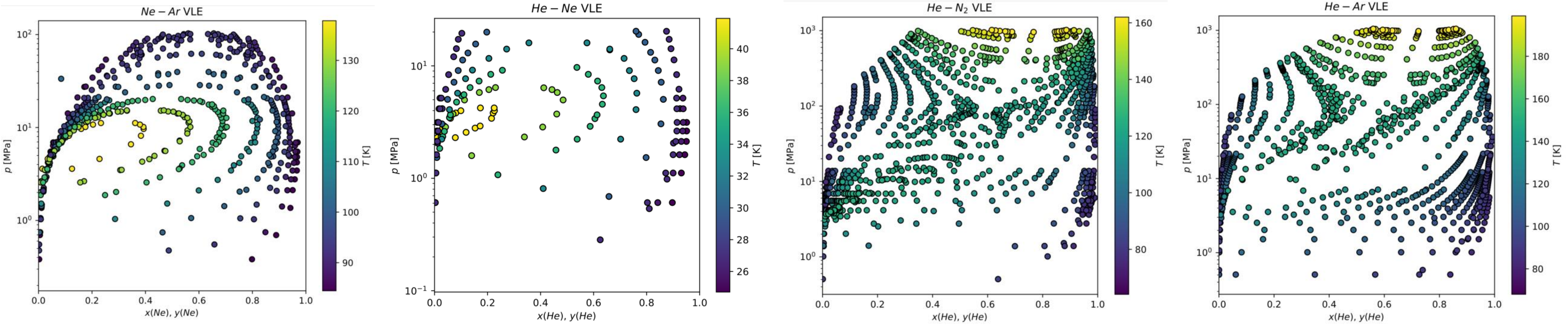
  - Constrain the fugacity coefficients at the phase envelope

- Fit the densities
- Fit the speed of sound (if available)
- Constrain the derivatives

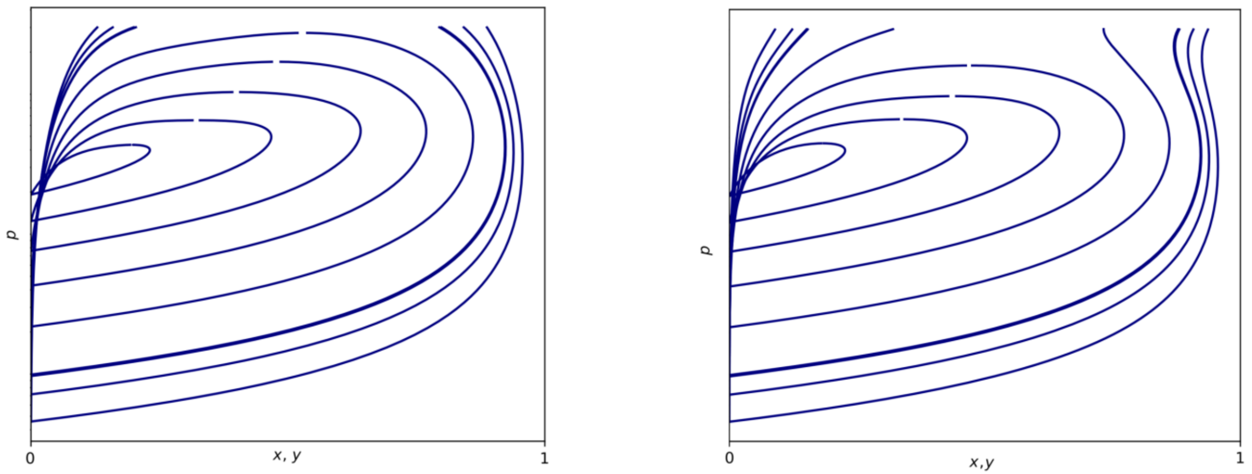


Phase envelope

T_{c1}/T_{c2}	3.4	8.5	24.3	29.0



Closed or open - is there a LLE or just the VLE?



Statistical Associating Fluid Theory (SAFT)

Hard sphere diameter of a segment: $d_{ii} = \int_0^{\sigma_{ii}} \left(1 - exp\left(-\beta u_{ii}^{Mie}(r)\right)\right) dr$

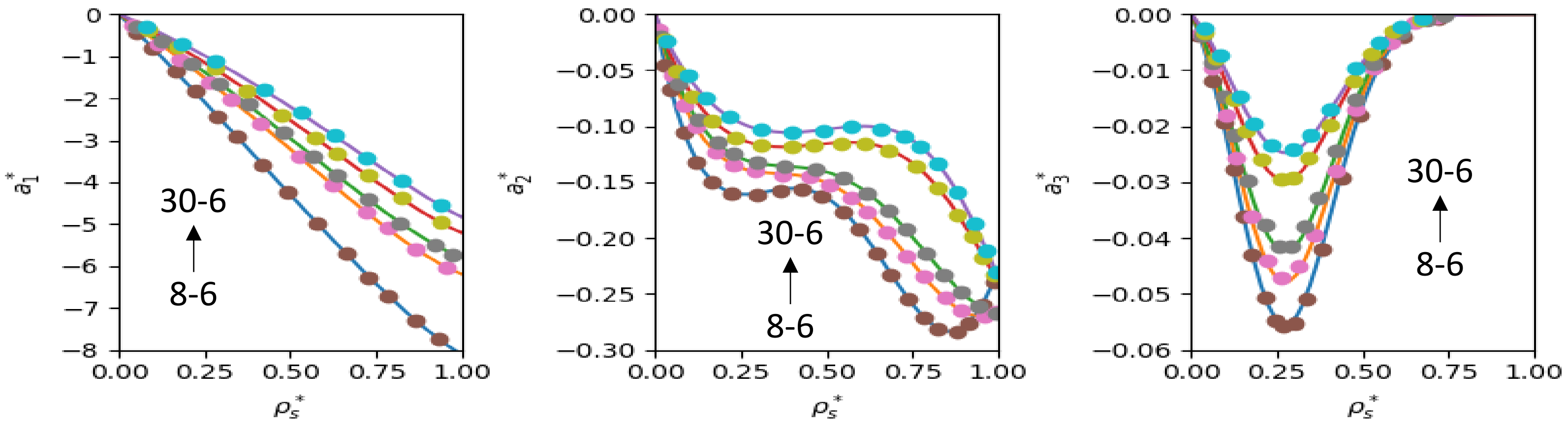
Interaction potential between two species: $u_{ij}^{Mie} = C_{ij}\epsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{\lambda_{r,ij}} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{\lambda_{a,ij}}\right)$

potential depth

distance between
the spherical segments

segment
diameter

1st, 2nd and 3rd order perturbation terms



Quantum effects

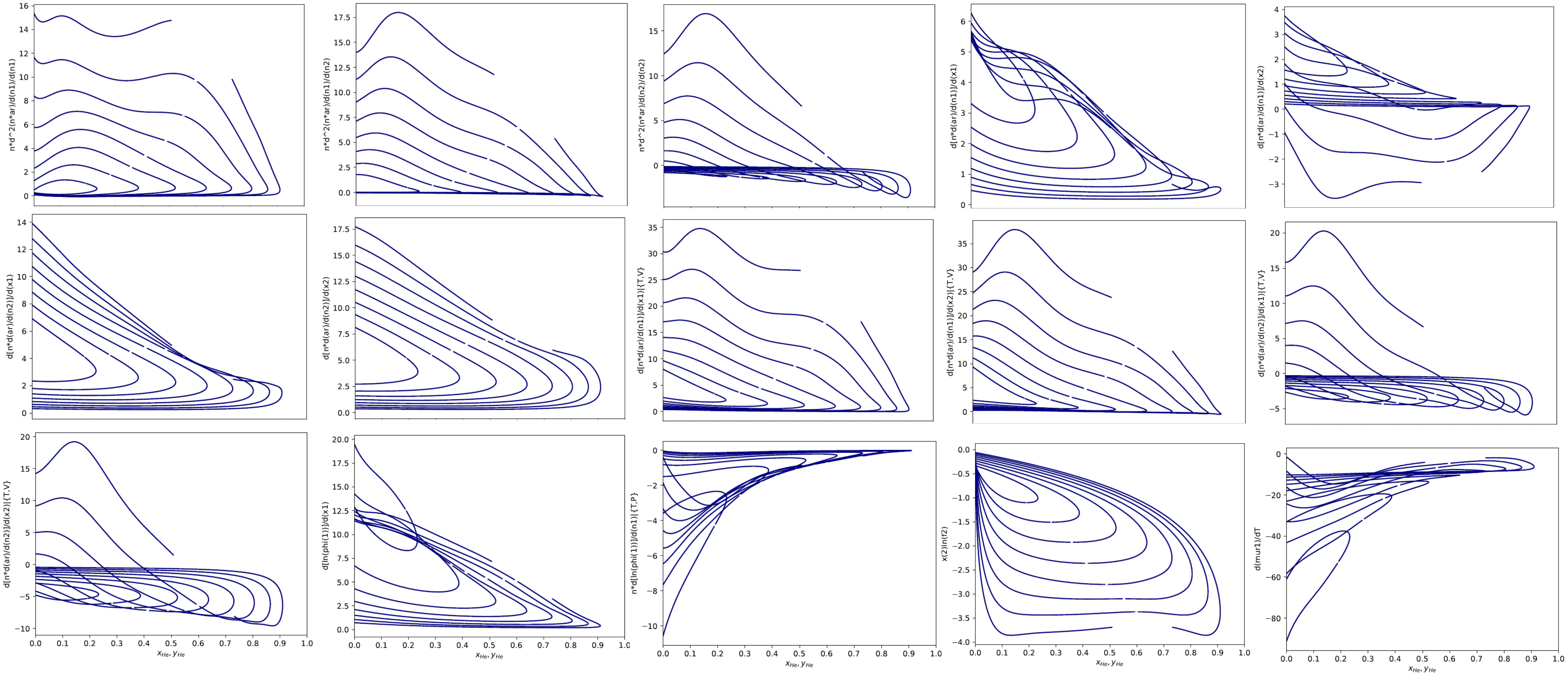
Thermal de Broglie wavelength: $\lambda_{th} = \sqrt{\frac{h^2}{2\pi m k_B T}}$

$d_{eff} \gg \lambda_{th} \Rightarrow$ Maxwell-Boltzmann statistics

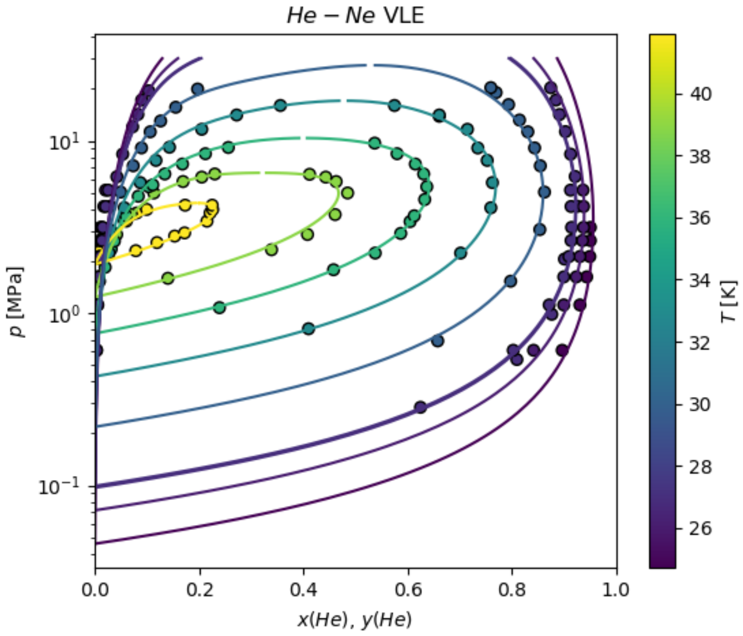
$d_{eff} \sim \lambda_{th} \Rightarrow$ quantum gas (Bose-Einstein, Fermi-Dirac statistics)

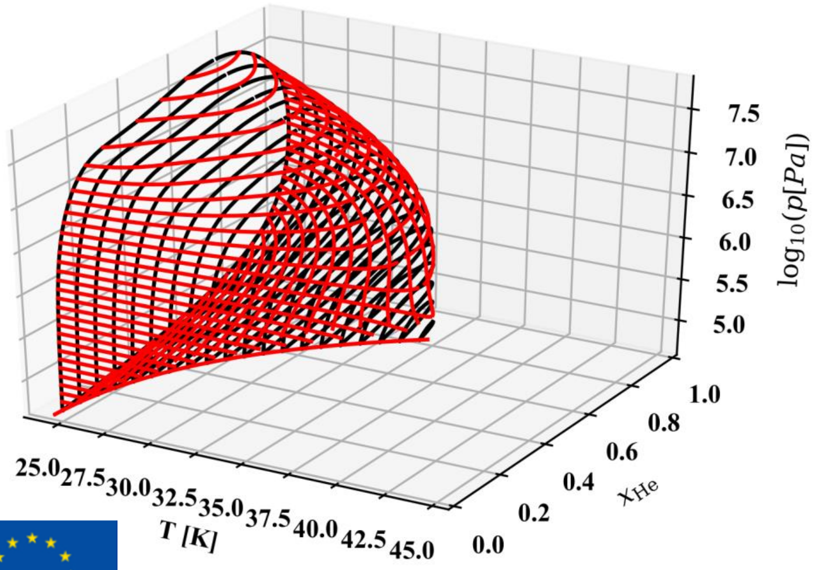
	Tc [K]	m [u]	T [K]	$\lambda_{th}[A]$	$d_{eff}[A]$
He	5.2	4.002	5	3.90	0.31
H2	33.1	2.016	22	2.62	…
Ne	44.4	20.180	30	0.71	0.38
N2	126.2	28.013	80	0.37	…
Ar	150.7	39.948	90	0.29	0.71

Derivatives

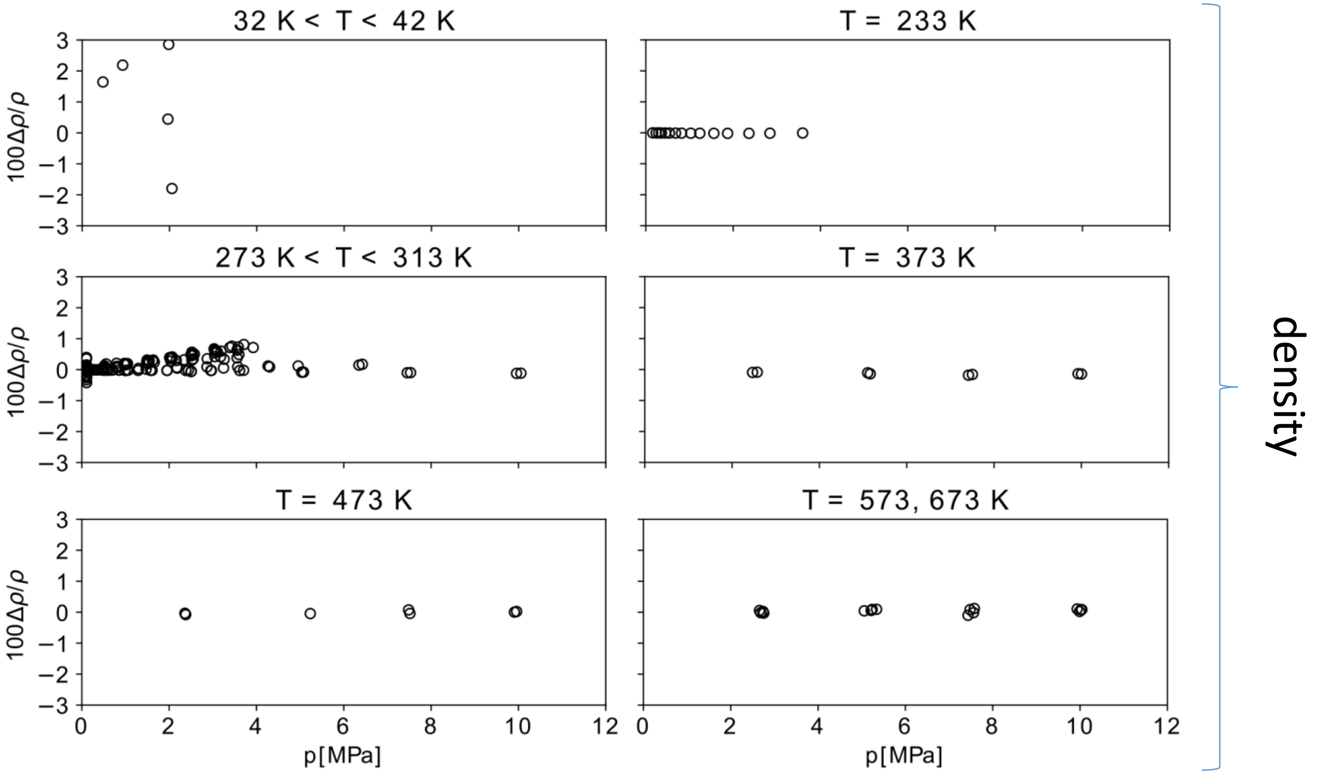


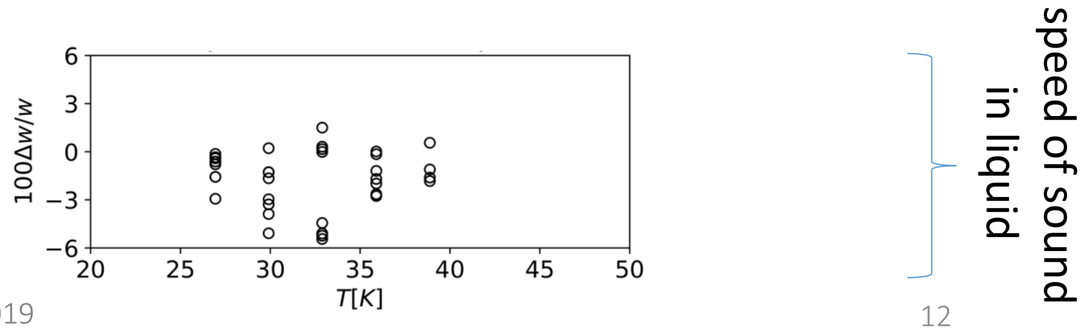
Empirical fit results





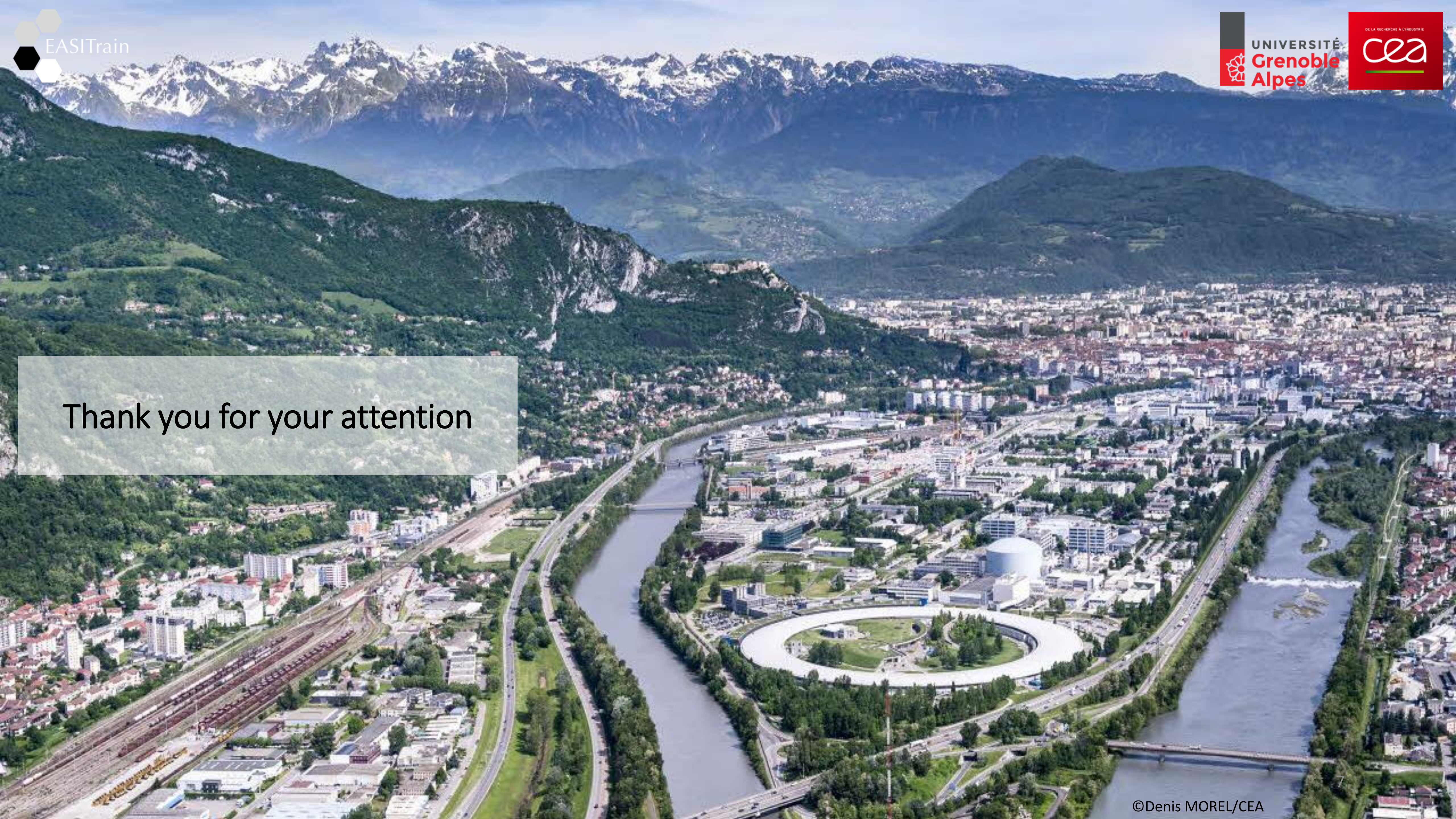
Uncertainty





Next steps

- Finalize the empirical fit for three mixtures (He-Ne, He-Ar, Ne-Ar) and publish the models
- Finalize the general SAFT model for mixtures and release a python library
- Confirm the obtained results / extend the experimental data set



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Thank you for your attention