Fluid properties modeling

Jakub Tkaczuk [1,*], Eric Lemmon [2], Ian Bell [2], Francois Millet [1], Nicolas Luchier [1]

[1] Université Grenoble Alpes, CEA IRIG-dSBT, F-38000 Grenoble, France
[2] National Institute of Standards and Technology, Boulder, Colorado 80305, United States
* jakub.tkaczuk@cea.fr

Abstract

Based upon the conceptual design reports for the FCC cryogenic system, the need for more accurate thermodynamic property models of mixtures was identified. Both academic institutes and world-wide industries have identified the lack of reliable equation of state for mixtures used at very low temperatures. Detailed cryogenic architecture modeling and design cannot be assessed without valid fluid properties. Therefore, the latter is the focus of this work. Initially driven by the FCC study, the modeling was extended to other fluids beneficial for scientific and industrial application beyond the FCC needs. The properties are modeled for the mixtures of some noble gases with the use of multi-fluid Helmholtz-energy-explicit models: helium-neon, neon-argon, and helium-argon. The on-going studies are performed at CEA-Grenoble, France and at the National Institute of Standards and Technology, U.S.

Helmholtz energy equation of state

The Helmholtz free energy $\alpha(\delta,\tau)$ is a thermodynamic potential, which measures useful work obtainable from a closed system. Defining the equation of state (EoS) as a Helmholtz energy-explicit function can be particularly advantageous.

- it is continuous over the phase boundary;
- it is a function of measurable properties;
- it has purely analytical derivatives.

EoS is formulated as a sum of the ideal Helmholtz energy α^o and the residual Helmholtz energy α^r, being a function of the reduced density and reduced temperature

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

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

Thanks to the Helmholtz energy definition, the properties themselves can be easily calculated, for example

$$Z(\delta,\tau,\bar{x}) = 1 + \delta \frac{\partial \alpha^r}{\partial \delta}\bigg|_{\tau}.$$

Fitting process

The equation is being fitted to data with a simple but very successful algorithm, constantly developed and improved at NIST.
Multiple weighted data points are used to model the behavior of the thermodynamic properties and minimize the sum of squares. The model accuracy depends on the availability and the quality of data.

For the considered mixtures of noble gases the available data is usually limited. For helium and neon, data is limited both in pressure and temperature. However, more data is available for some other cryogenic mixtures of noble gasses.

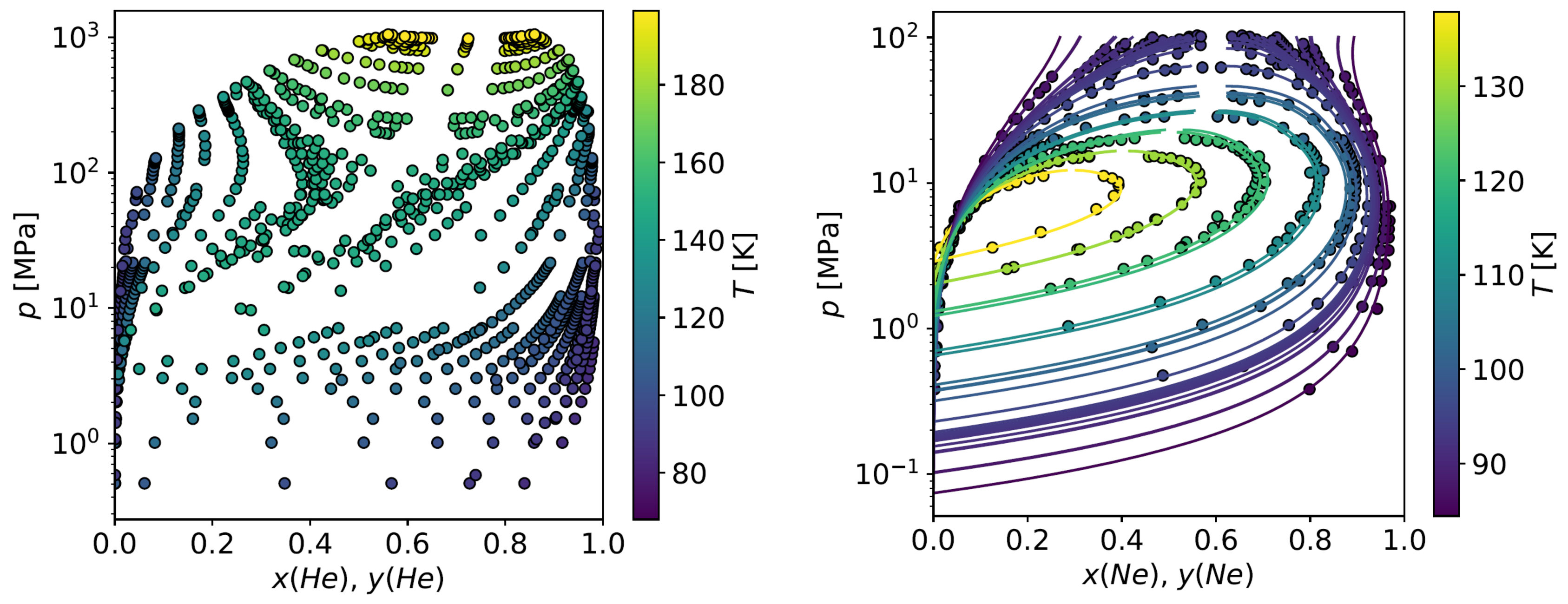

Fig. 1. Available data for helium-argon (left) and neon-argon (right) with developed VLE isotherms for neon-argon only

EASITrain – European Advanced Superconductivity Innovation and Training. This Marie Skłodowska-Curie Action (MSCA) Innovative Training Networks (ITN) has received funding from the European Union's H2020 Framework Program under Grant Agreement no. 764879

Phase envelope

With the available data points, a shape of the vapor-liquid equilibrium and the occurrence of liquid-liquid equilibrium can be defined (most probably no LLE for helium-neon).

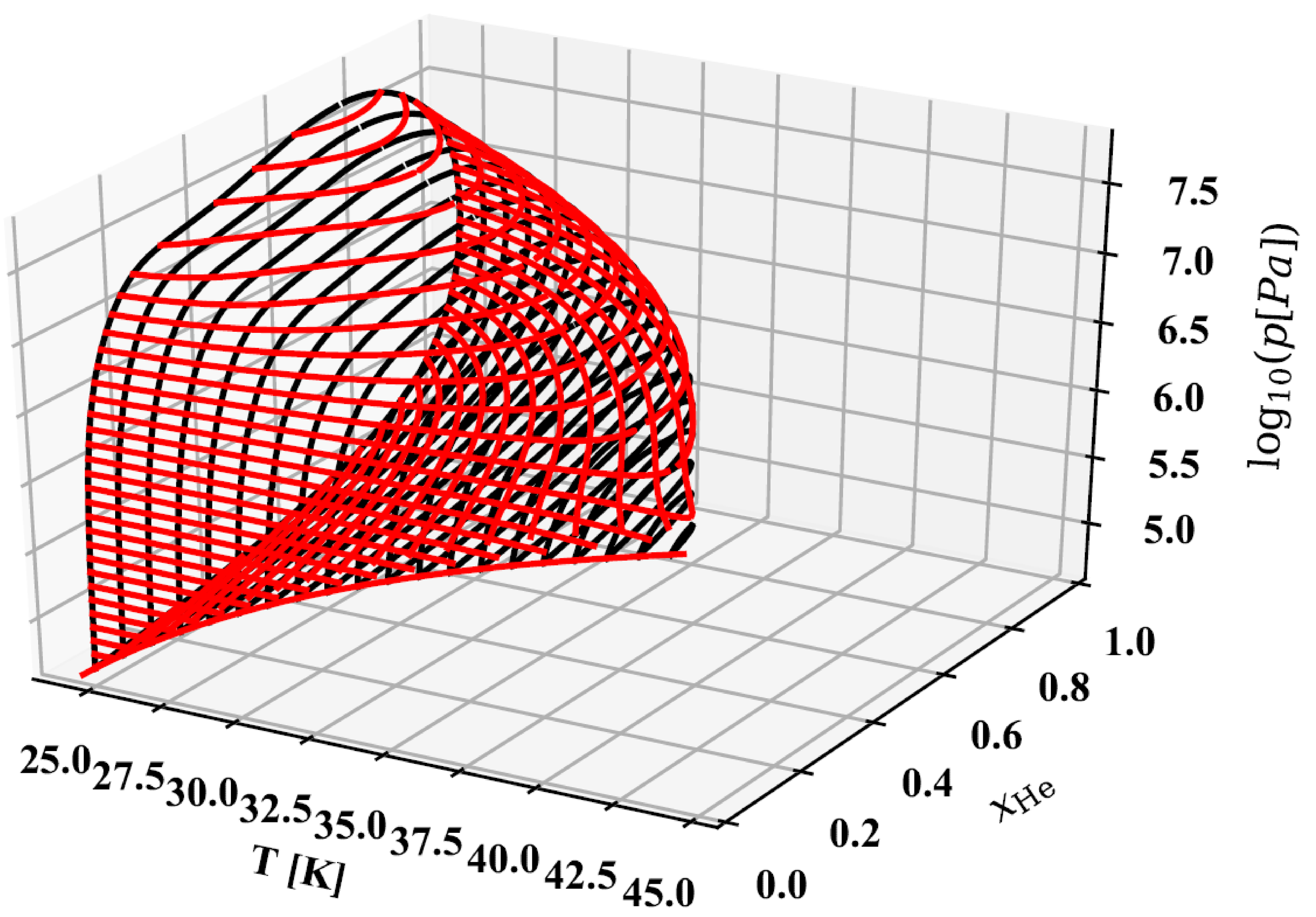

Fig. 2. Helium-neon phase envelope (red lines – isobars, black lines – isotherms)

Uncertainty

Model accuracy can be evaluated with respect to the experimental data. It is important to notice that there is no vapor density above 42 K and below 230 K for helium-neon mixture, additionally low temperature measurements are characterized by high uncertainty, therefore were not fitted with high weights.

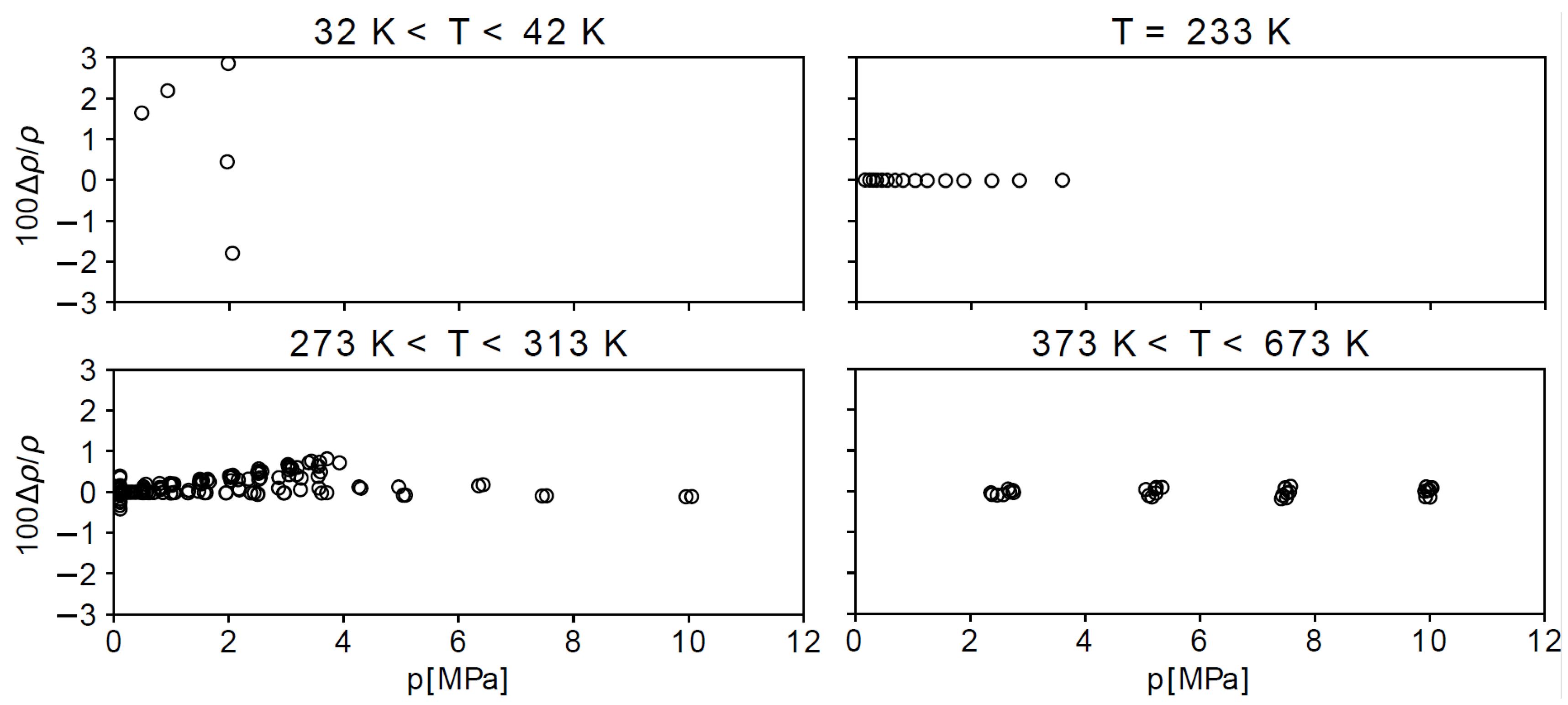

Fig. 3. Error in density for developed helium-neon model

Second property, used for this model development is speed of sound in liquid. Here the error is slightly higher than for density.

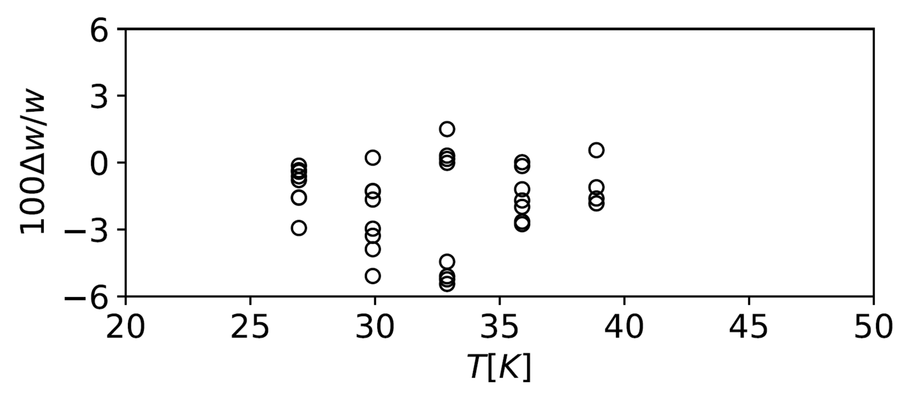

Fig. 4. Error of speed of sound in liquid fitting

Conclusions

The helium-neon model is successfully developed with a reasonable uncertainty (accordingly to the available data). The possibility of performing additional measurements is investigated. Together with this mixture, Helmholtz EoS are developed for another cryogenic mixtures.

References

References listed for helium-neon mixture only.

[1] J. Brewer and G. W. Vaughn, *Measurement and correlation of some interaction second virial coefficients from -125º to 50ºC. I,* J. Chem. Phys. **50**, 2960-2968 (1969)
[2] C. K. Heck and P. L. Barrick, *Liquid-vapor equilibria of the neon-helium system*, Adv. Cryo. Eng. **12**, 714-718 (1967)
[3] L. Holborn and J. Otto, *Uber die Isothermen einiger Gase bis 400º und ihre Bedeutung fur das Gasthermometer, Zeit. fur Physik* **23**, 77-94 (1924)
[4] J. Kestin et al., *Density dependence and composition dependence of the viscosity of neon-helium and neon-argon mixtures*, Physica A **106**, 415-442 (1981)
[5] C. M. Knobler, J. J. M. Beenakker and H. F. P. Knaap, *The second virial coefficient of gaseous mixtures at 90ºK*, Physica **25**, 909-916 (1959)
[6] M. Knorn, *Vapour-liquid equilibria of the neon-helium system,* Cryogenics, **7**, 177 (1967)
[7] V. V. Paskov, E. V. Konovodchenko and O. V. Evdokumova, *Speed of sound in the solution of helium with cryogenic liquids*, J. Eng. Phys. **4**, 603-608 (1985)
[8] E. Thornton, *Viscosity and thermal conductivity of binary gas mixtures: xenon-krypton, xenon-argon, xenon-neon and xenon-helium*, Proc. Phys. Soc. **76**, 104-112 (1960)
[9] W. F. Vogl and K. R. Hall, Compressibility data and virial coefficients for helium, neon and one mixture, Physica **3**, 529-535 (1972)