Investigation of the thermophysical properties of binary system CO 2 and Hydro-fluoro-olefins

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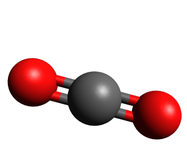
Introduction

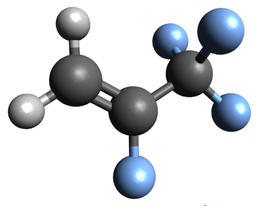
- In the context of reduction of global greenhouse gas emissions, the development and study of refrigerants with low Global Warming Potential (GWP) is crucial. Fluorinated gases are currently considered as promising low-GWP refrigerants. These compounds are used as pure or as components of refrigerant blends. The knowledge of their thermophysical properties is of great importance in the design and optimization process of air-conditioning and refrigeration systems.
- In the following, we illustrate how molecular simulations are used to predict relevant properties for refrigerants fluid mixtures. The studies are applied to the mixture CO_2+CH_2CFCF_3 (R1234yf). Equilibrium properties, including liquid-vapour equilibrium, phase density, enthalpy of vaporization, enthalpy of mixing, specific heat, are obtained using Monte Carlo simulations. Transport properties (viscosity and thermal conductivity) are predicted by means of molecular simulation techniques.

Molecular Simulations

- Systems studied



Carbon dioxide



2,3,3,3 tetrafluoropropene (R1234yf)

- Force fields
  - CO_2: TraPPE model[1]. All atom model, rigid molecule, multipole described with partial charges
  - R1234yf: Raabe model[2]. All atom model, flexible molecule, multipole described with partial charges
- Monte Carlo simulations
  - Gibbs code (CNRS-UPSud/IFPEN)[3;4]
  - ELV: Gibbs ensemble[5] at constant pressure[6]
- Molecular Dynamics simulations
  - Newton code (CNRS-UPSud)[7]
  - Viscosity: equilibrium molecular dynamics and Green-Kubo relationship
  - Thermal conductivity: non equilibrium Heat Exchange Algorithm[8]

Conclusion

- Molecular simulation is able to predict several thermophysical properties for the CO_2-R1234yf mixture
- New *numerical data* have been produced for thermal conductivity. Predicted values show a reasonnable agreement with RefProp data for pur components.
- The full set of data can be used to compute quantities of interest for applications in cooling and heating devices such as the Prandtl number ($C_p\eta/\lambda$)

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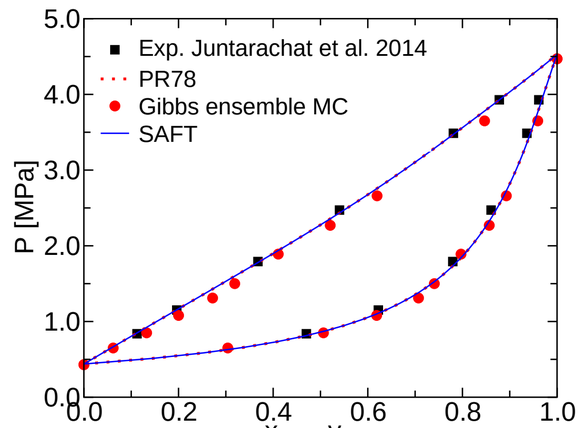
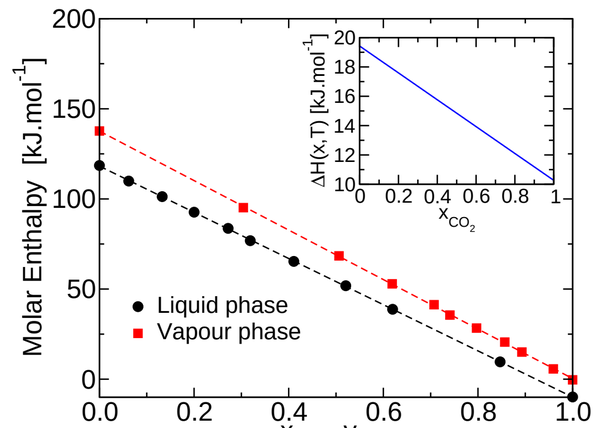
Liquid-vapour equilibrium

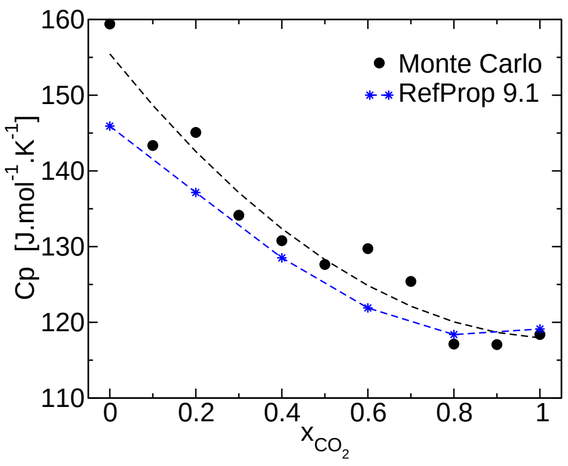




ELV curve (left) at 283 K including experimental data[9], PR78 correlation (with adjustable k_{ij}), Multipolar SAFT-Mie (courtesy P. Paricaud, ENSTA ParisTech, Univ. Paris-Saclay)[10] and GIBBS predictions. Enthalpy of liquid and gas phases along the bubble and dew curves (right). Insert: enthalpy difference versus composition.

Specific Heat

- $T = 283$ K, $P = 6$ MPa



- Specific heat at constant pressure

$$C_p(P,T) = C_p^{id}(T) + C_p^{res}(P,T)$$

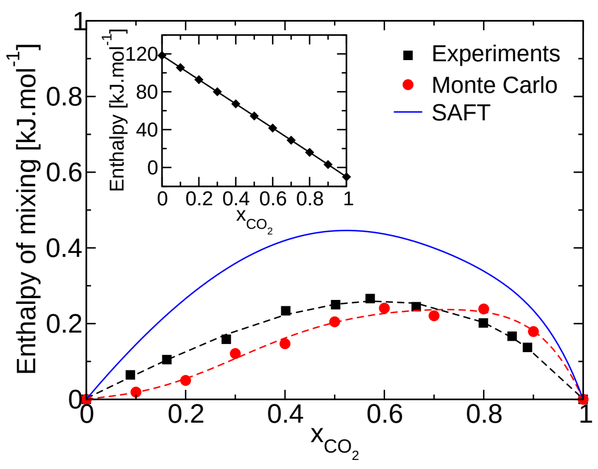
- C_p^{res} from fluctuations in NpT ensemble[11]

$$C_p^{res}(P,T) = \frac{1}{k_B T^2}\left(\langle U_{ex}\hat{H}\rangle - \langle U_{ex}\rangle\langle\hat{H}\rangle\right) + \frac{P}{k_B T^2}\left(\langle V\hat{H}\rangle - \langle V\rangle\langle\hat{H}\rangle\right) - Nk_B$$

- $C_p^{id}(T)$ from NIST (CO_2) and Kato *et al.*[12] (R1234yf) using speed of sound measurements

Mixing enthalpy

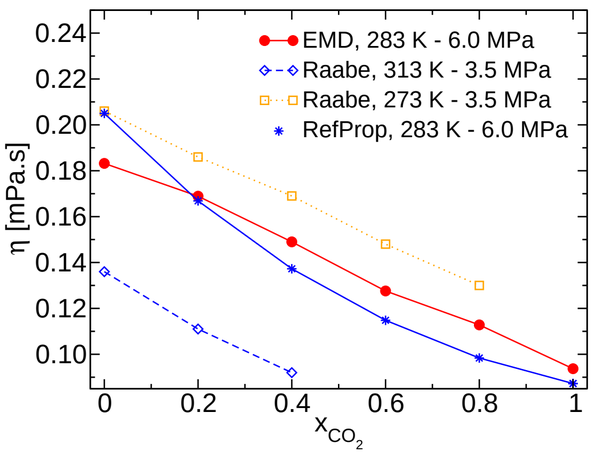
- $T = 283$ K, $P = 6$ MPa



- Experimental data obtained using a customized BT2-15 calorimeter from Setaram, courtesy J.Y. Coxam (Univ. Blaise Pascal, Clermont-Ferrand)[10]
- SAFT model: Multipolar SAFT-Mie model, courtesy P. Paricaud (ENSTA ParisTech, Univ. Paris Saclay)[10]
- Monte Carlo simulations in the NpT ensemble

Transport properties

- $T = 283$ K, $P = 6$ MPa

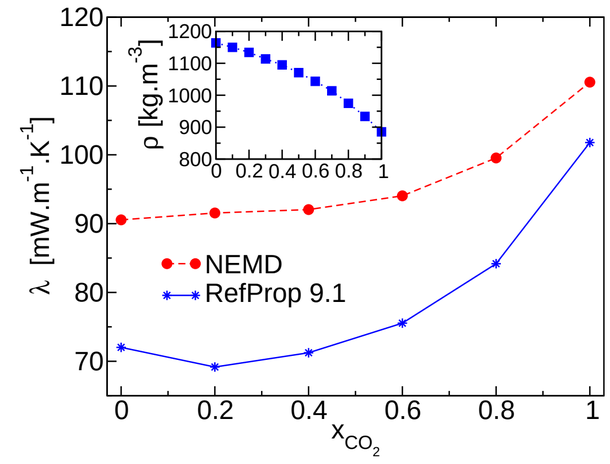


$$\eta = \frac{V}{10k_B T}\int_0^\infty \langle \boldsymbol{\sigma}(t)\cdot\boldsymbol{\sigma}(0)\rangle_{NVT}$$

with[13]

$$\boldsymbol{\sigma} = \left(\sigma_{xx}, \sigma_{yy}, \sigma_{zz}, \sqrt{2}\sigma_{xy}, \sqrt{2}\sigma_{xz}, \sqrt{2}\sigma_{yz}\right)$$

- $T = 283$ K, $P = 6$ MPa



$$\lambda = -\frac{J_{q,z}}{\nabla T} = -\frac{\Delta K}{L_x L_y \delta t}\frac{L_z}{\Delta T}$$

with ΔK the kinetic energy exchanged between hot and cold boundary layers[8]

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