Diffusion coefficients in CAPE-OPEN

An open discussion

Current definition in Thermo 1.1

- **Two temperature dependent properties:**
  - **selfDiffusionCoefficientGas**

    "Self-diffusion coefficient in gas phase at 1 atm", m^2/s

  - **selfDiffusionCoefficientLiquid**

    "Self-diffusion coefficient in liquid phase on saturation line", m^2/s

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No real issues here.

Current definition in Thermo 1.1

- **Single phase property ‘diffusionCoefficient’**
  - “Binary diffusion coefficients for all species in mixture relative to all other species”
  - Intensive, rank=2 (matrix), m^2/s, no basis
  - Issues:
    - What kind of diffusion coefficient is meant?
      - Fick, Maxwell-Stefan, Irreversible Thermodynamics?
    - Number-of-compounds x number-of-compounds?
      - Matrix size depends on model used...
    - What velocity reference frame is used?
      - Molar/mass/volume zero average velocity plane?

Possible useful property definitions

- diffusionCoefficientAtInfiniteDilution’
- ‘diffusionCoefficientMaxwellStefan’
- ‘diffusionCoefficientFick’

Possible useful property definitions

- ‘diffusionCoefficientAtInfiniteDilution’
  - Element i,j pertains to diffusion of compound i in pure j
  - Intensive, rank=2 (matrix), m^2/s, no basis
  - Composition independent (T,P-dependent)
  - Molar and mass reference frames are equivalent for binary Fick systems
  - Model choice independent: at infinite dilution Fick and Maxwell-Stefan numerically equal
  - Matrix:
    - Dimension n_{comp} x n_{comp}
    - Asymmetric (however many gas models are composition independent and therefore symmetric)
    - Diagonal: self-diffusion coefficients

Possible useful property definitions

- ‘diffusionCoefficientMaxwellStefan’
  - Element i,j describes inverse drag between compounds i and j:

$$d_i = -\sum_j \frac{x_i x_j \left(u_i - u_j\right)}{Đ_{i,j}} \quad \text{or} \quad d_i = \sum_j \frac{\left(x_i N_j - x_j N_i\right)}{c_t Đ_{i,j}}$$

  - Intensive, rank=2 (matrix), m^2/s, no basis
  - T,P,X-dependent
  - Reference frame independent
  - Matrix:
    - Dimension n_{comp} x n_{comp}
    - Symmetric
    - Diagonal not really useful (packing?)

Possible useful property definitions

- ‘diffusionCoefficientFick’
  - For the binary case: $N = -D\nabla c$ or $N = -c_t D \nabla x$
  - T,P,X-dependent
  - Reference frame dependent
  - Not so well defined for multi-component diffusion, multiple alternatives possible
    - A possible route is via Maxwell-Stefan

Multi component Fick via Maxwell Stefan

- Equal fluxes for Fick and Maxwell-Stefan models leads to

$$D = B^{-1}\Gamma$$

$$B_{i,i} = \frac{x_i}{Đ_{i,n}} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{x_k}{Đ_{i,k}} \quad \text{and} \quad B_{i,j} = -x_i\left(\frac{1}{Đ_{i,j}} - \frac{1}{Đ_{i,n}}\right)$$

- $\Gamma_{i,j} = \delta_{i,j} + x_i \frac{\partial \ln \gamma_i}{\partial x_j}$

- Trying to reconstruct this relation without eliminating a compound leads to singular *B*
- This is under elimination of compound *n* as $\sum N = 0$ and $\sum \nabla x = 0$
- Dimension (n_{comp} - 1) x (n_{comp} - 1)
- Reference frame of molar average zero velocity
- Which compound to eliminate? Who decides?

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Multi component Fick via Maxwell Stefan

- Possible to construct a *D* for which $N = -c_t D \nabla x$ without eliminating a compound
- Multiple alternatives exist
- Useful?

Summary

- ‘diffusionCoefficient’ as it stands
  - poor CAPE-OPEN definition, not useful. Deprecate?
- ‘diffusionCoefficientAtInfiniteDilution’
  - input to other models (not directly applied)
  - CAPE-OPEN definition useful?
- ‘diffusionCoefficientMaxwellStefan’
  - matrix packing is special case
  - CAPE-OPEN definition useful?
- ‘diffusionCoefficientFick’
  - useful to expose: resolves first order derivative issues
  - format, model, shape, attributes? Discussion required.