Thermodynamic and Transport properties of fluids: towards a single LJ-SAFT like molecular model valid for n-alkanes ?

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THERMODYNAMIC AND TRANSPORT PROPERTIES OF FLUIDS: TOWARDS A LJ-SAFT MOLECULAR MODEL VALID FOR N-ALKANES

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We study the limitations of the Lennard-Jones Chain fluid model (LJ-SAFT) to describe simultaneously all thermophysical properties (equilibrium and transport) of some n-alkanes along the vapor-liquid equilibrium line

MODELS AND THEORY

MOLECULAR DYNAMICS

Molecules movements numerically computed (Newton equations)

Spatial and temporal averages (~10^3 particles, ~10 ns)

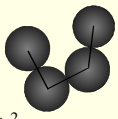
Exact thermophysical properties for a given molecular model

FLUID MODEL

Freely jointed Lennard-Jones spheres (Lennard-Jones Chain)

$$U_{LJ} = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) + \text{internal bonds}$$

number of segments: N



Internal rigidity is included by $U_{flex} = k\varepsilon\left(\theta - \theta_0\right)^2$

LJ-SAFT

No H-bonding, no polar and flexible ⇨ $A^{LJC} = A^{LJ} + A^{chain}$

A^{LJ} using the reference term of Kolafa & Nezbeda, (FPE 1994)
A^{chain} using the chain term of Johnson et al. (JPC 1994)

Accurate apart close to the critical point

VISCOSITY MODEL OF LJC

Based on MD results
Galliero et al, IECR, 2005, Galliero and Boned, PRE, 2009, PRE, 2010

$$\eta(T,\rho) = \eta_0(T) + \eta_{res}(T,\rho)$$

Dilute gas — Residual/Excess viscosity

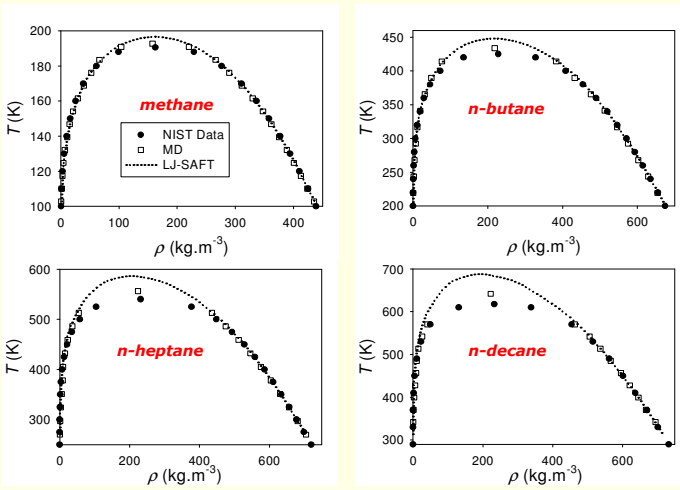
Extended Chapman for η_0 and Rousse approximation for η_{res}

Valid for gas, liquid and supercritical states

RESULTS

VAPOR-LIQUID EQUILIBRIUM

N=1 for C1, N=2 for C4, N=3 for C7 and N=4 for C10, σ and ε have been adjusted

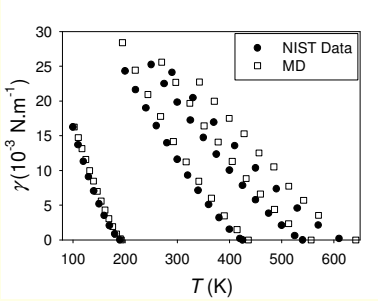


As well known this fluid model is correct for n-alkanes

but $T_c^{SAFT} > T_c^{MD} > T_c$ (↗ with N)

Crossover approach is needed to deal with the critical region

SURFACE TENSION



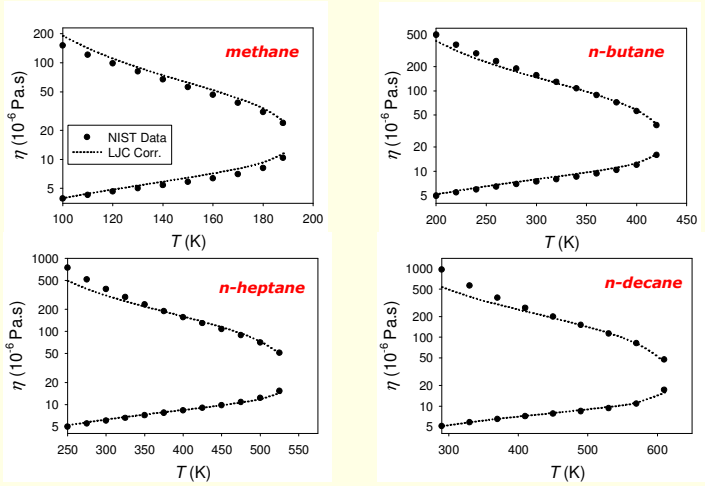
Surface tensions are slightly overestimated

A simple correction of the critical temperature is sufficient

The coupling between DGT/DFT and LJ-SAFT yields good results

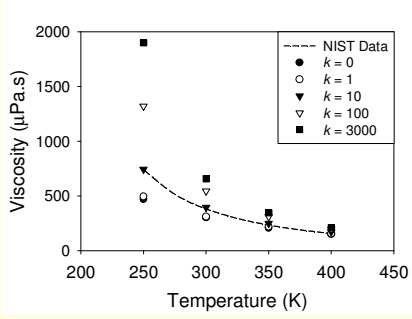
Galliero et al., JCP, 2008

SHEAR VISCOSITY



η is well estimated, except at low liquid *T* when *N*↗

This weakness is related to the flexibility of the chain



η is highly affected by the rigidity while thermodynamic (fluid phase) only weakly

This degree of freedom (rigidity) can be used to improve simply the fluid model

Concerning thermal conductivity, λ_0 is out of range when *N*↗ (internal degrees of freedom) but the λ_{res} of LJC is correct

Internal degrees of freedom (such as rigidity) should be included in a SAFT like approach