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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 ($\sim 10^3$ particles, ~ 10 ns)

Exact thermophysical properties for a given molecular model

FLUID MODEL

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

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

number of segments: N

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

LJ-SAFT

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

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

Galliero et al, IECR, 2005,
Galliero and Boned, PRE, 2009, PRE, 2010

Dilute gas Residual/Excess viscosity

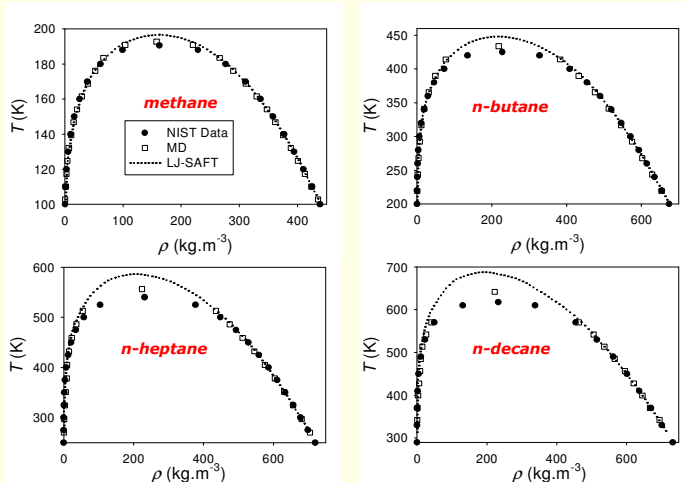
Extended Chapman for η_0 and Rouse approximation for η_{res}

Valid for gas, liquid and supercritical states

RESULTS

VAPOR-LIQUID EQUILIBRIUM

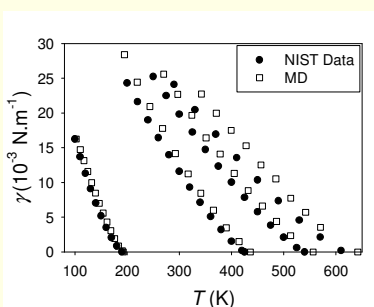
$N=1$ for C1, $N=2$ for C4, $N=3$ for C7 and $N=4$ for C10, σ and ϵ have been adjusted



As well known this fluid model is correct for n-alkanes but $T_c^{SAFT} > T_c^{MD} > T_c$ (\nearrow with N)

Crossover approach is needed to deal with the critical region

SURFACE TENSION



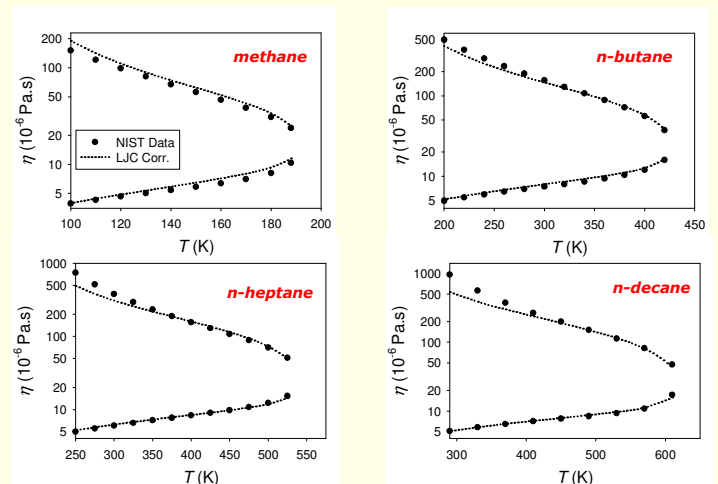
Surface tensions are slightly overestimated

A simple correction of the critical temperature is sufficient

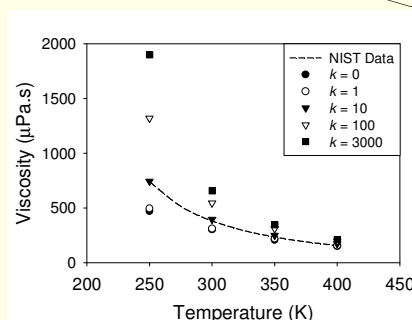
The coupling between DGT/DFT and LJ-SAFT yields good results

Galliero et al., JCP, 2008

SHEAR VISCOSITY



η is well estimated, except at low liquid T when $N \nearrow$
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 $N \nearrow$ (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