A Coarse Grained Force Field To Speed Up Molecular Simulations With Better Predictions Of Thermophysical Properties Of Fluids

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Plan

Global Context

Molecular models

The tool: molecular simulation

Methodology to develop the coarse grained force field

Parametrization of the force field

Results: Equilibrium & transport properties + benchmarking

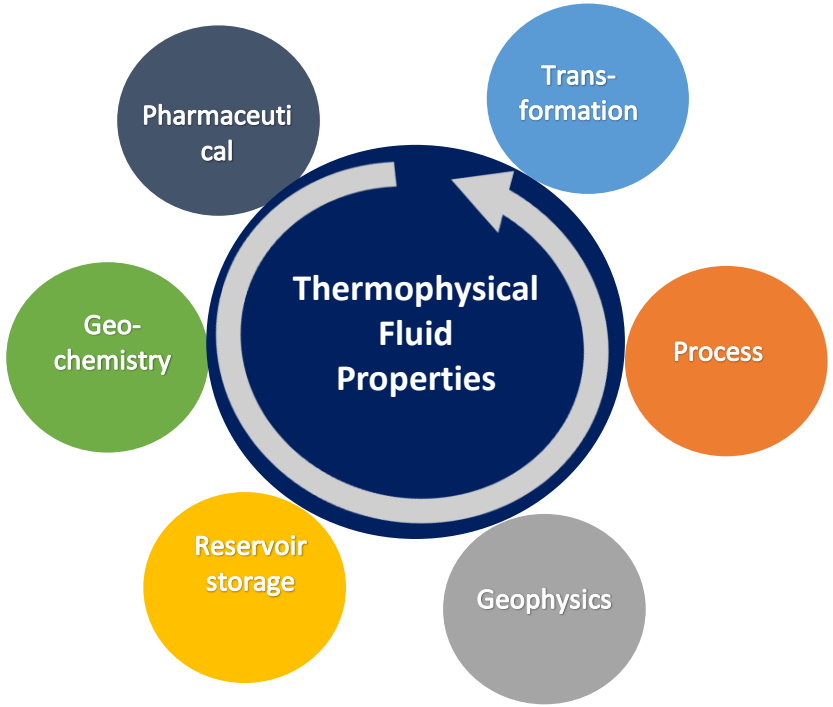
CPU time: fine models vs coarse grained model

A SAFT type EoS model as an alternative to molecular simulation

Context

Global Context

Thermophysical fluid properties (PVT, viscosity …) are crucial for operating/designing many systems



Five main options:

- Experiments *(costs)*
- Machine learning *(black box)*
- Adhoc correlations (*extrapolation*)
- **Theory (*simple model*)**
- **Molecular simulations (*time costs*)**

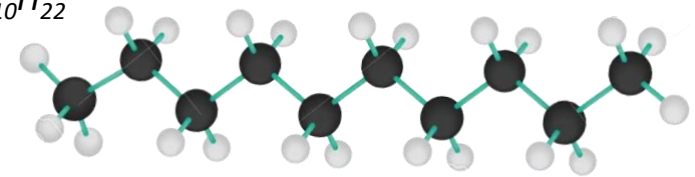
COARSE GRAINED (+ THEORY) FOR AN UNIFIED ALTERNATIVE ?

Molecular models

Molecular Models

All atom models
High resolution

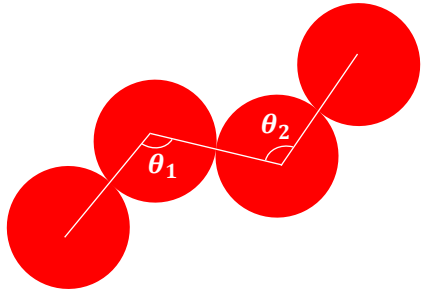
$nC_{10}H_{22}$

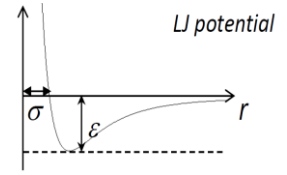


Upsacling

Expected to give quasi-experimental thermophysical data
Applicable to well characterized systems (less cases…)
Dozen of parameters (10 at least!!!)
High CPU time consumption

Coarse grained models
Low resolution





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

Gives quasi-experimental equilibrium properties
Compatible with developed theories (SAFT, …)
Less CPU time consumption
BUT
Poor prediction of transport properties

How to alleviate this weakness on the transport properties prediction?

A use of a Mie potential instead of LJ potential is already explored. Considerable improvements have been shown, but fails for larger molecules at low T.
(Hoang et al.2017 (MieCCG), Rahman et al.2018 (SAFT-Y-Mie))

A molecular rigidity of the bending type? Not fully explored
(Nieto-Draghi et al.2006, Galliéro2014).

Tool: molecular simulation

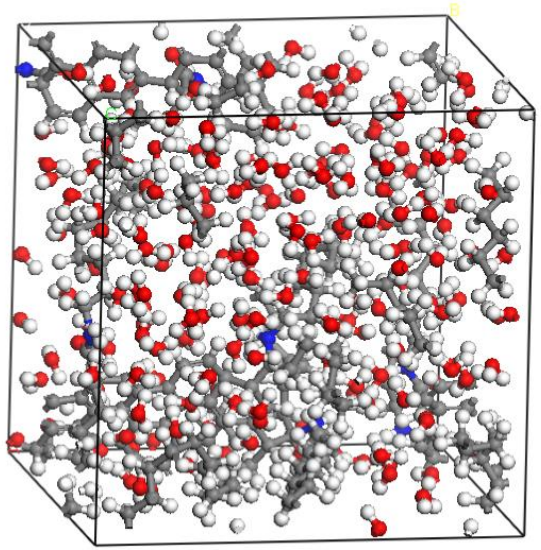
Tool: molecular simulation

Molecular dynamics

Determinist approach

Newton's equation of motions

Verlet velocity integrator



Monte Carlo

Stochastic approach

Boltzmann probability distribution

Metropolis algorithm

Properties assessed through ensemble averages

$$< E >= \frac{1}{n}\sum_{i=1}^{n} E_i \qquad < V >= \frac{1}{n}\sum_{i=1}^{n} V_i \qquad T = \frac{2 < K >}{k_B N_f} \qquad K = \sum_{i=1}^{n} \frac{m_i v_i^2}{2} \qquad < P >= \frac{N k_B T}{V} + \frac{1}{3V}\sum_{i=1}^{n} \overrightarrow{r_k}\overrightarrow{F_k}$$

$$C_v = \frac{1}{k_B T^2}(< E^2 > - < E >^2) \qquad D = \frac{1}{3N}\sum_{i=1}^{n}\int_0^{\infty} < v_i(t) v_i(0) > \qquad \eta = \frac{1}{6V k_B T}\sum_{\alpha \neq \beta}\int_0^{\infty} < J^P_{\alpha\beta}(t) J^P_{\alpha\beta}(0) > dt$$

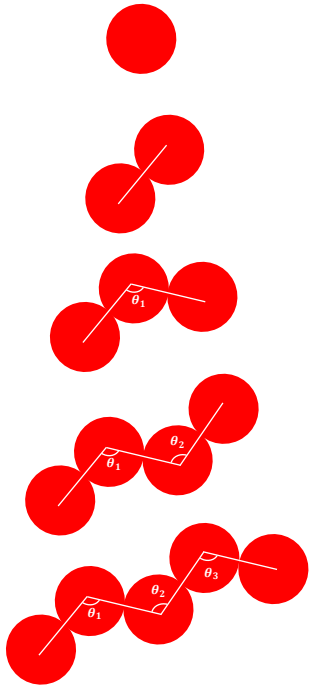
Methodology

Methodology

Choice of the model: → **Semi-rigid LJC coarse grained**

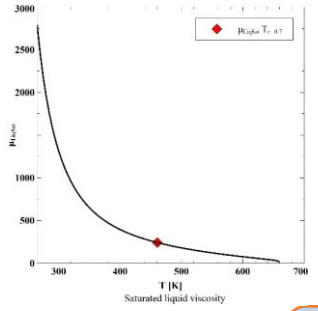
Technique to use: → **Molecular simulation**

Properties assessed? →



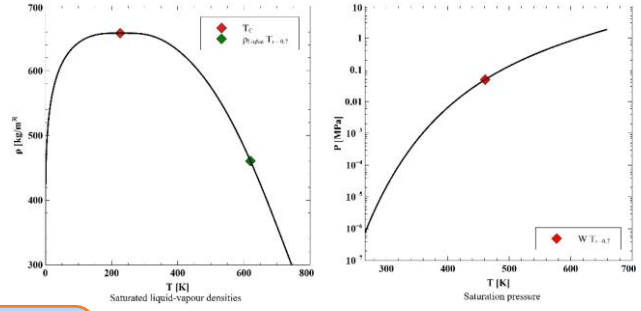
Saturated liquid viscosity through Molecular dynamics

Correlation
μ_{liqSat_Tr07}



Equilibrium properties (w, Tc, LVE) through monte carlo simulations

Correlations
ρ_{liqSat_Tr07} W & Tc



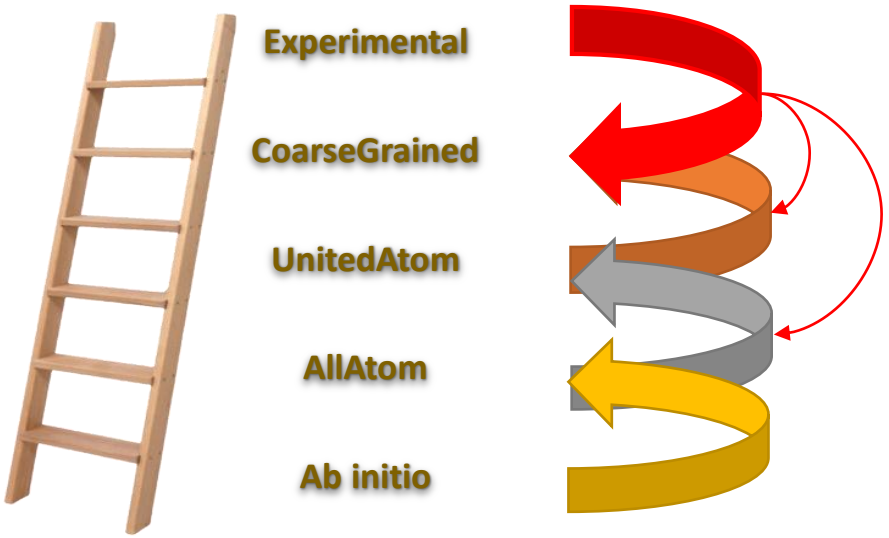
Optimization:
$m, \sigma, \varepsilon + K_\theta$

Molecular simulations for prediction of ALL fluid properties

Parametrization

Parametrization

Approaches



Bottom Up:*Iterative Boltzmann Inversion method, Force matching, …*

Reith et al.2003, Moore et al.2014…

Top Down: Saturation curve fit ($P_{Sat}, \rho_{Sat}^{Liq}, C_p^{Liq}, H_{Vap}$ …), *Corresponding states*

Lafitte et al.2006, Mejía et al.2014, Hoang et al.2017…

A Top-down approach based on extended Corresponding States Scheme

	Microscopic	Macroscopic
Energy scale	ε	T_c
Length scale	σ	$\rho_{liq,Tr=0.7}$
Asphericity	m, λ, K_θ	w
Viscosity	m, λ, K_θ	$\mu_{liq,Tr=0.7}$

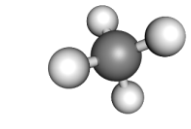
$$minF(m, K_\theta) = \left|W_{Tr0.7}^{CG} - W_{Tr0.7}^{Exp}\right| + \left|\mu_{LiqSat,\,Tr0.7}^{CG} - \mu_{LiqSat,\,Tr0.7}^{Exp}\right|$$

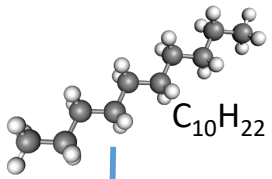
$$\varepsilon = \frac{k_B T_c}{T_c^{CG}} \qquad \sigma = \sqrt[3]{\frac{M\rho_{sat,Liq,Tr0.7}^{CG}}{\rho_{sat,Liq,Tr0.7}^{Exp}}}$$

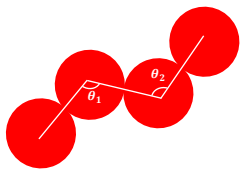
Requires only 4 macroscopic experimental data
Unicity of the solution
Parameters are physically more consistent

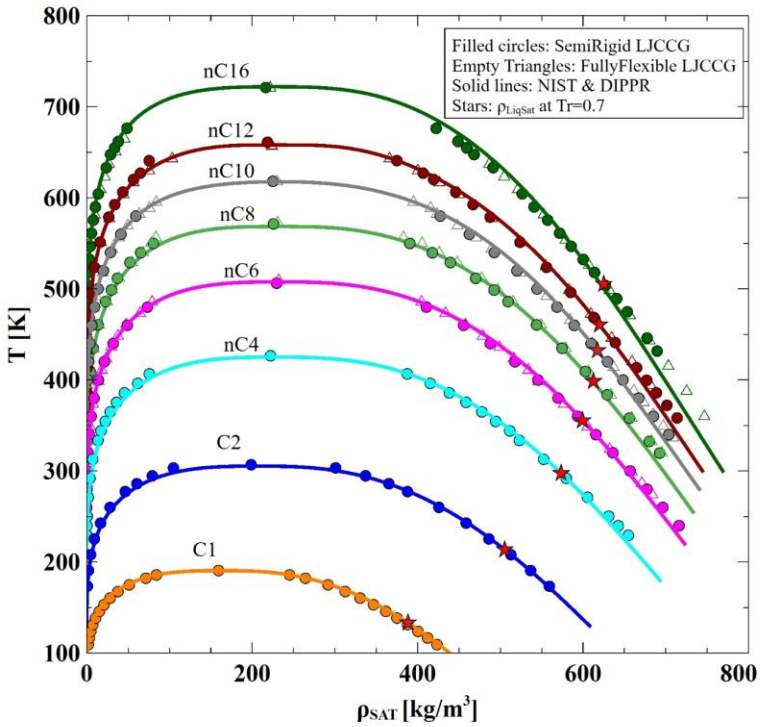
Results

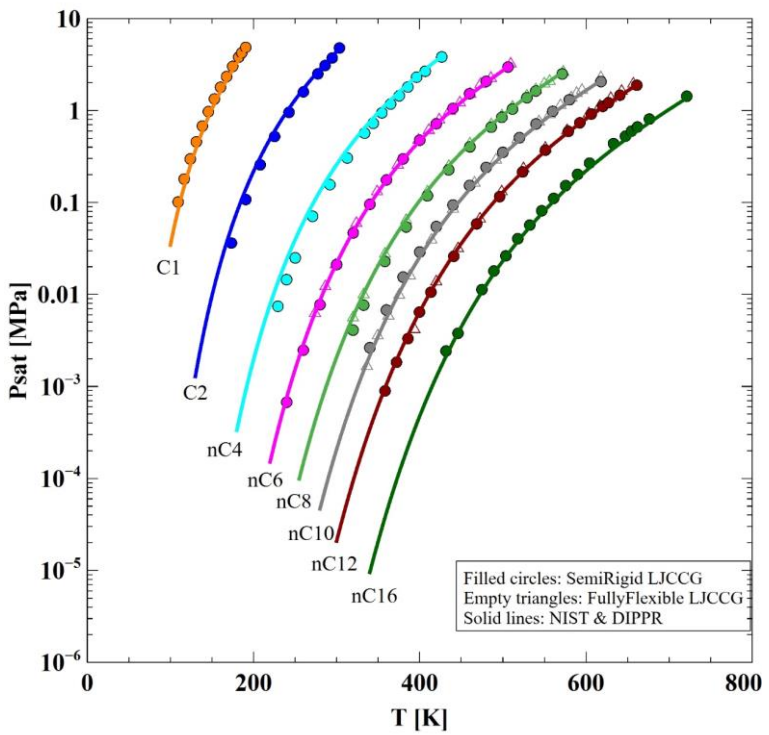
normal alkanes











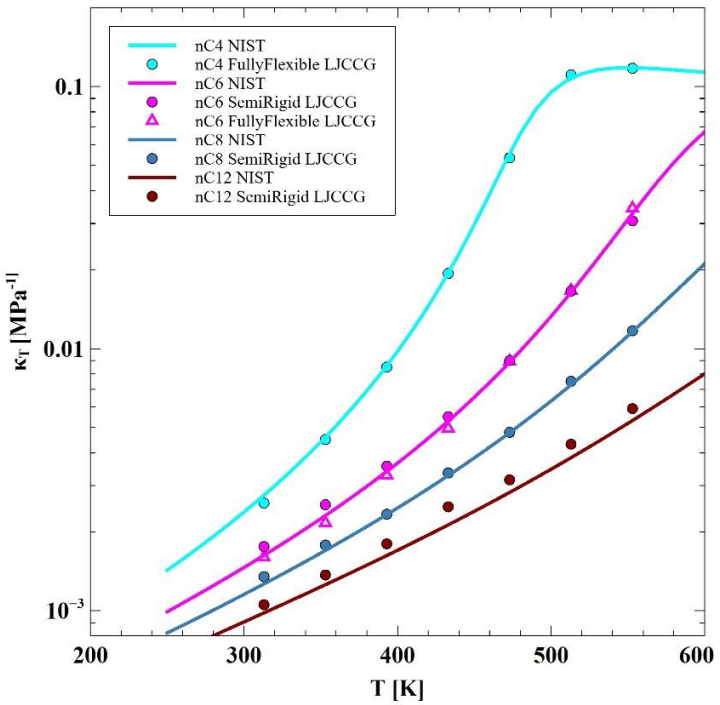
Excellent predictions! → ***« Transferability »***

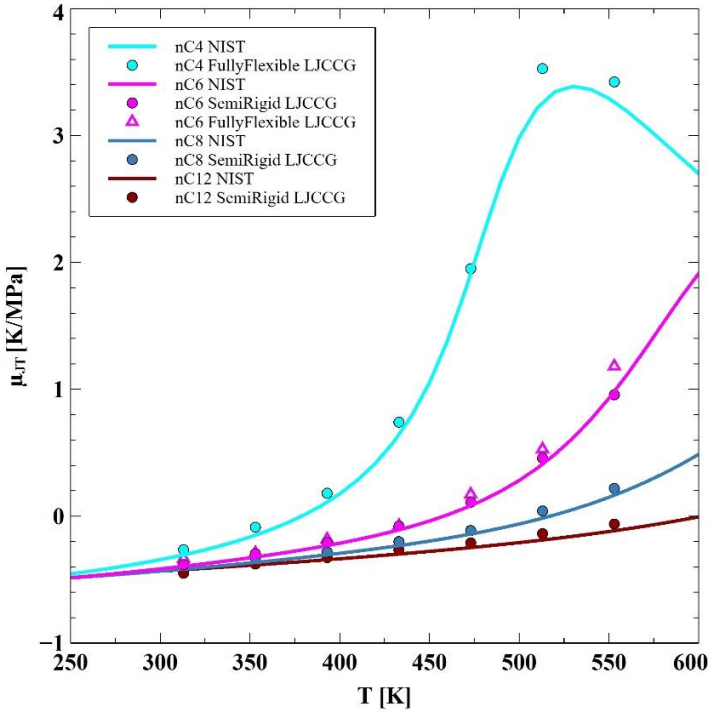
Works very well for iso alkanes, polars,…

Derivative properties

normal alkanes

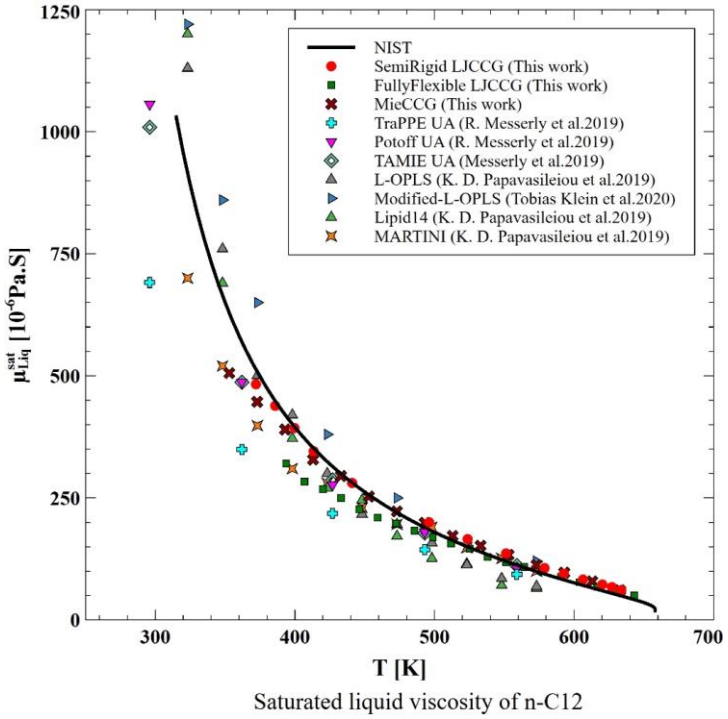
Our model performs very well for properties not included in the optimization: very good
« Representability »



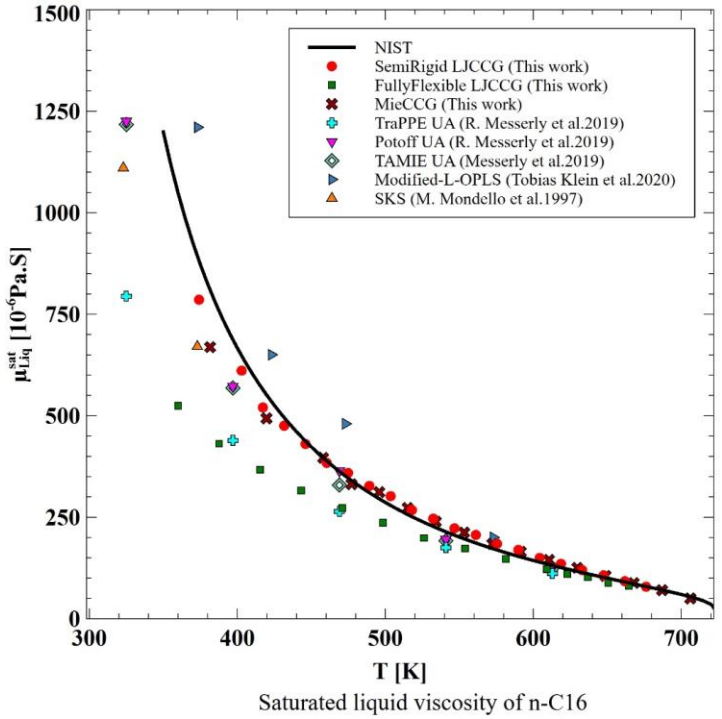


Benchmark

Viscosity



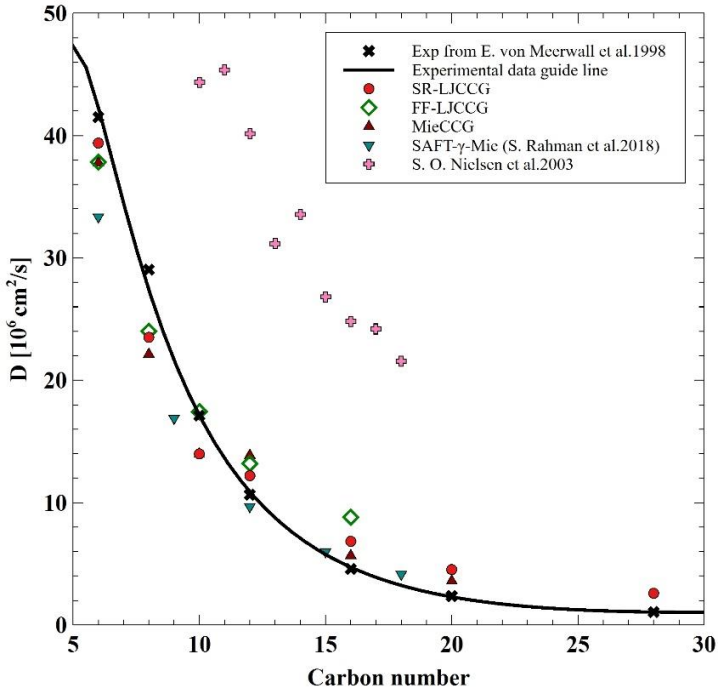
Saturated liquid viscosity of n-C12



Saturated liquid viscosity of n-C16

Diffusivity

T=303K
P=1atm

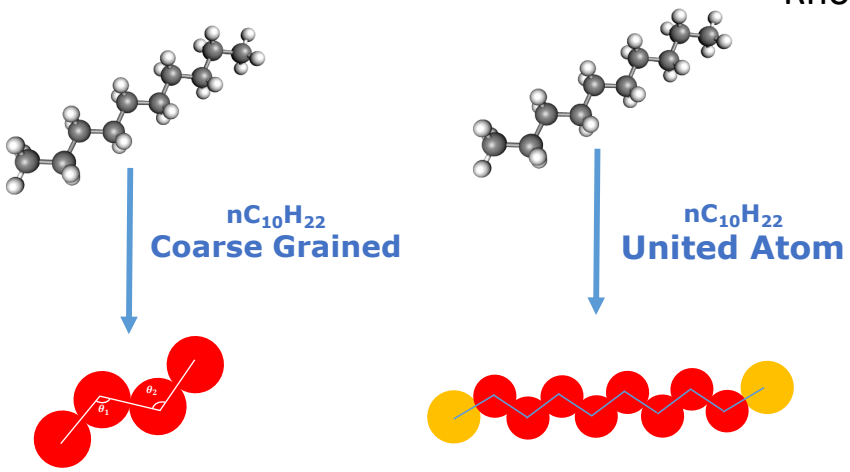


Our Coarse Grained model can do better than most fine models!

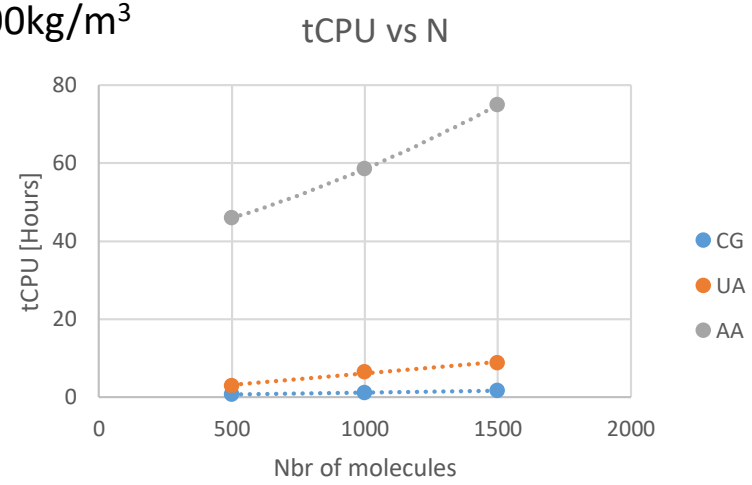
CPU time?

CPUtime: AA vs UA vs CG

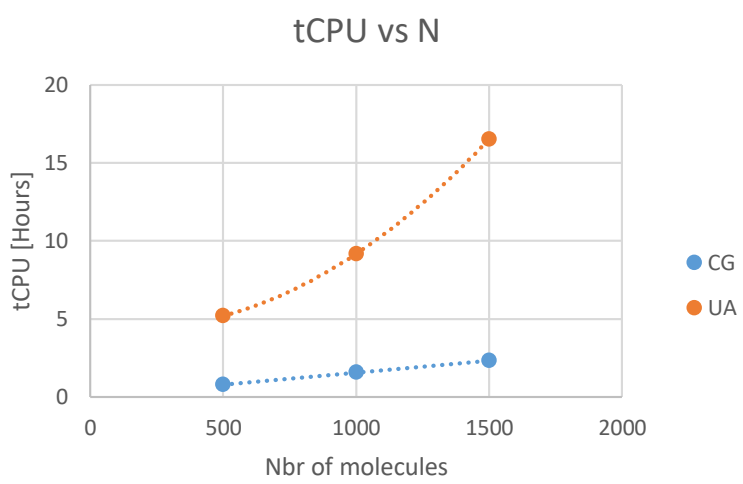
tSIM =9nS
T=500K
Rho=800kg/m^3

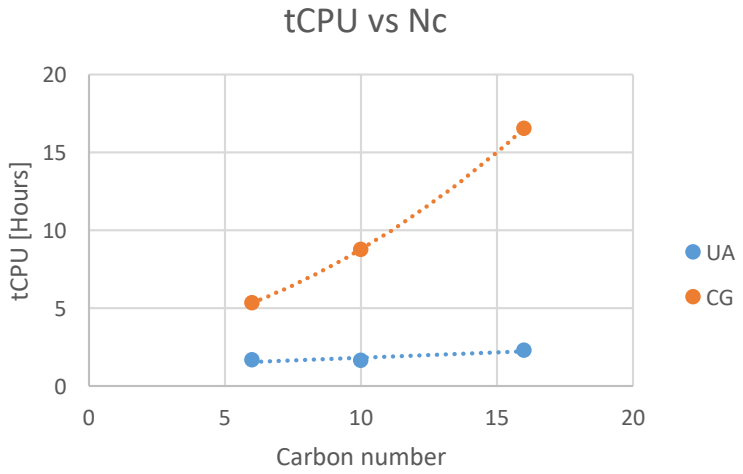


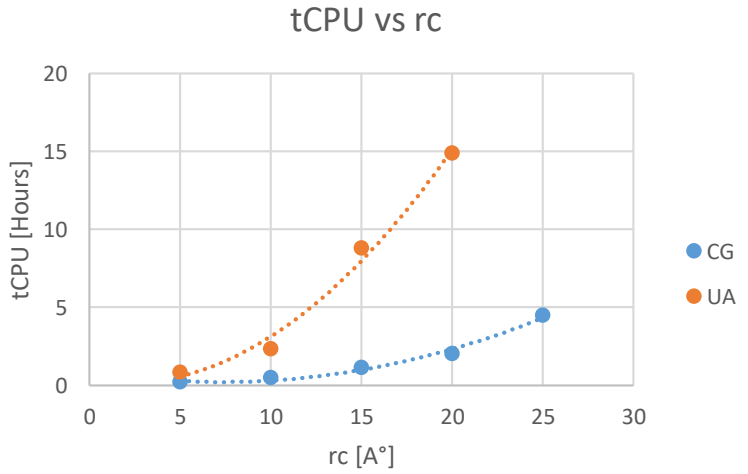
nC10H22

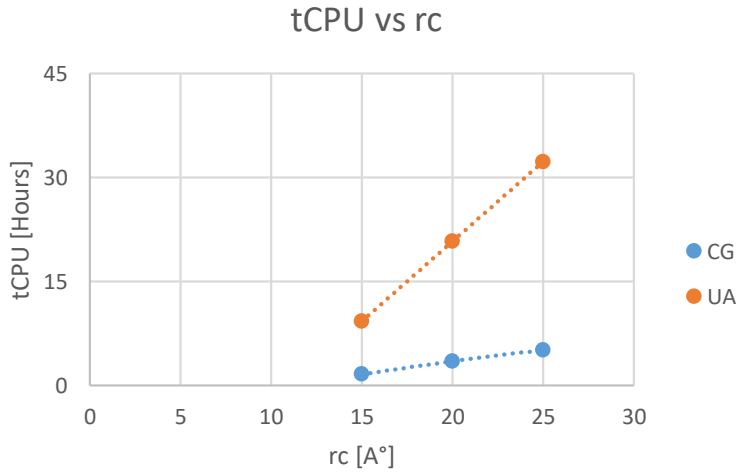


nC16H34





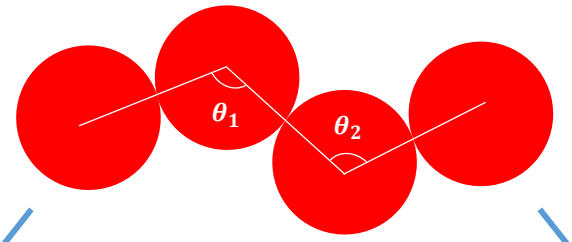




CPU time, can we do more? A SAFT type model

SAFT theory…

The Model:
SemiRigid LJ chains



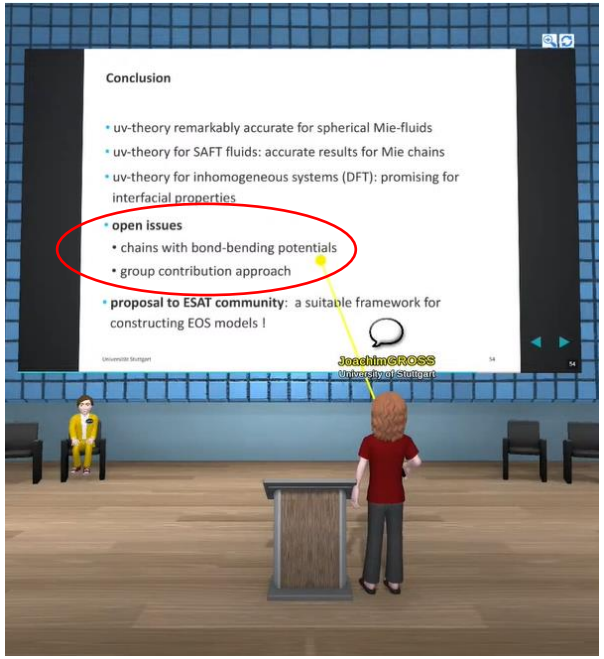
+ rigidity

Molecular simulation
(exact properties)

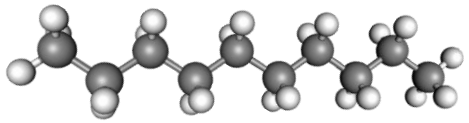
Validation

Thermodynamics Perturbation Theory:
Wertheim1984,1985,1986,1987,1988
(Statistical Association Fluid Theory)

Open issue!!!



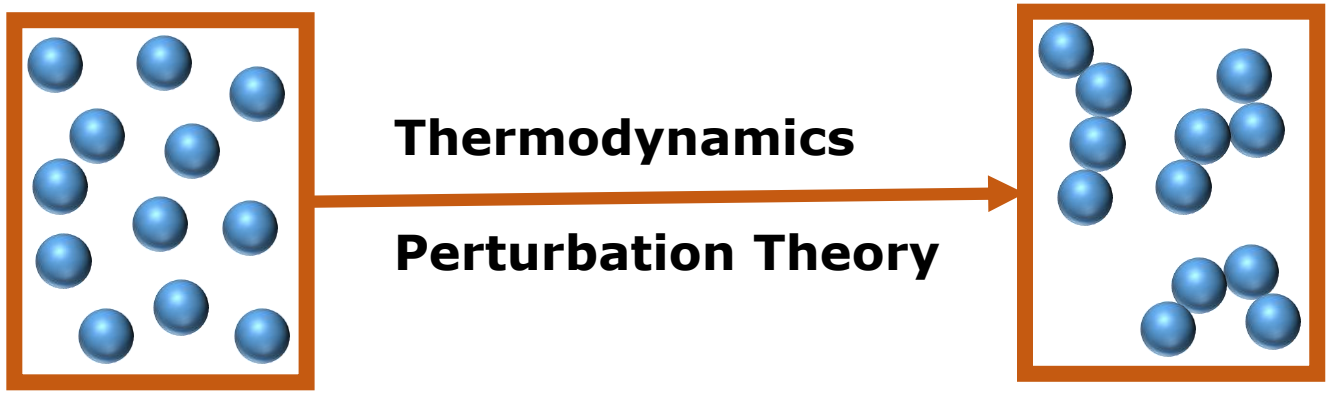
Real fluids
(Exact experimental properties)



SAFT theory…

The SAFT EoS is written in terms of the Helmholtz free energy:

$$\frac{A^{res}}{N_c kT} = \frac{A^{Mono}}{N_m kT} + \frac{A^{Chain}}{N_c kT} + \frac{A^{Assoc}}{N_c kT} + \frac{\boldsymbol{A^{Rigidity}}}{\boldsymbol{N_c kT}} + \cdots$$

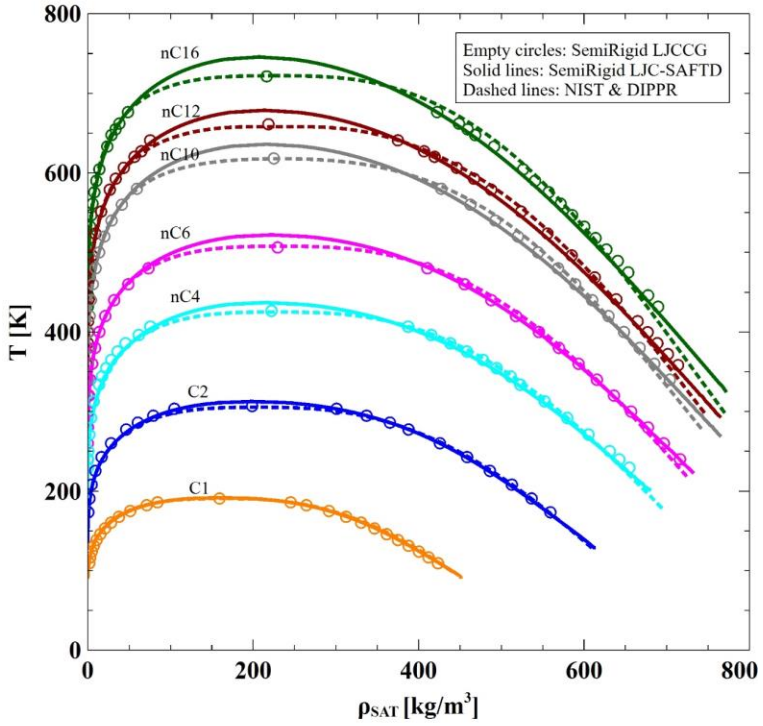


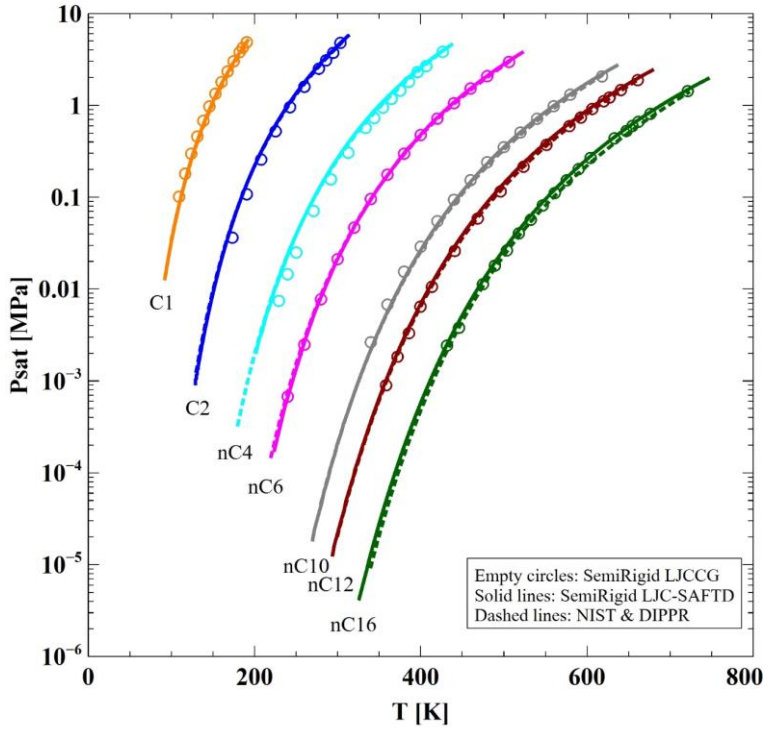
Most famous models: PC-SAFT, SAFT-Y-Mie, Soft-SAFT

SAFT to real Fluids

N-Alkanes

Very accurate predictions





With the SAFT model, results are in seconds!!!

While simulation may take hours, days…

Merci