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
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

- $nC_{10}H_{22}$

Coarse grained models

Low resolution

- Upscaling

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

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))


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

Gives quasi-experimental equilibrium properties
Compatible with developed theories (SAFT, ...)
Less CPU time consumption

BUT

Poor prediction of transport properties

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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

\[
\langle E \rangle = \frac{1}{n} \sum_{i=1}^{n} E_i \quad \langle V \rangle = \frac{1}{n} \sum_{i=1}^{n} V_i
\]

\[
T = \frac{2 \langle K \rangle}{k_B N_f} \quad K = \sum_{i=1}^{n} \frac{m_i v_i^2}{2}
\]

\[
\langle P \rangle = \frac{N k_B T}{V} + \frac{1}{3V} \sum_{i=1}^{n} \overrightarrow{r}_k \overrightarrow{F}_k
\]

\[
C_v = \frac{1}{k_B T^2} (\langle E^2 \rangle - \langle E \rangle^2)
\]

\[
D = \frac{1}{3N} \sum_{i=1}^{n} \int_{0}^{\infty} \langle v_i(t) v_i(0) \rangle
\]

\[
\eta = \frac{1}{6V k_B T} \sum_{\alpha \neq \beta} \int_{0}^{\infty} \langle f^p_{\alpha \beta}(t) f^p_{\alpha \beta}(0) \rangle \, dt
\]
Methodology
Methodology

Choice of the model: Semi-rigid LJC coarse grained

Technique to use: Molecular simulation

Properties assessed?

- Saturated liquid viscosity through Molecular dynamics
- Equilibrium properties (\(w, T_c, LVE\)) through monte carlo simulations

Correlation \(\mu_{\text{liqSat}_T\text{r}07}\)

Correlations \(\rho_{\text{liqSat}_T\text{r}07} W & T_c\)

Optimization: \(m, \sigma, \varepsilon + K_\theta\)

Molecular simulations for prediction of ALL fluid properties
Parametrization
**Parametrization**

**Approaches**

- **Experimental**
- **CoarseGrained**
- **UnitedAtom**
- **AllAtom**
- **Ab initio**

**A Top-down approach based on extended Corresponding States Scheme**

<table>
<thead>
<tr>
<th></th>
<th>Microscopic</th>
<th>Macroscopic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy scale</td>
<td>$\varepsilon$</td>
<td>$T_c$</td>
</tr>
<tr>
<td>Length scale</td>
<td>$\sigma$</td>
<td>$\rho_{\text{liq,}Tr=0.7}$</td>
</tr>
<tr>
<td>Asphericity</td>
<td>$m, \lambda, K$</td>
<td>$\omega$</td>
</tr>
<tr>
<td>Viscosity</td>
<td>$m, \lambda, K$</td>
<td>$\mu_{\text{liq,}Tr=0.7}$</td>
</tr>
</tbody>
</table>

\[
\min F(m, K_\theta) = \left| W_{CG}^{\text{Tr}_{0.7}} - W_{Exp}^{\text{Tr}_{0.7}} \right| + \left| \mu_{\text{Liq Sat,} Tr_{0.7}}^{CG} - \mu_{\text{Exp}}^{\text{Liq Sat,} Tr_{0.7}} \right|
\]

\[
\varepsilon = \frac{k_B T_c}{T_{CG}^{\text{Tr}_{0.7}}} \\
\sigma = \sqrt[3]{\frac{M_\rho_{CG,\text{sat,Liq,}Tr_{0.7}}^{\text{Exp}}}{\rho_{\text{sat,Liq,}Tr_{0.7}}^{\text{Exp}}}}
\]

**Bottom Up:** Iterative Boltzmann Inversion method, Force matching, ...
Reith et al. 2003, Moore et al. 2014...

**Top Down:** Saturation curve fit ($P_{\text{Sat}}^{\text{Liq}}, \rho_{\text{Sat,Liq}}$, $C_p^{\text{Liq}}, H_{\text{Vap}}$ ...), Corresponding states
Lafitte et al. 2006, Mejia et al. 2014, Hoang et al. 2017...

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,...
Our model performs very well for properties not included in the optimization: very good « Representability »
Our Coarse Grained model can do better than most fine models!
CPU time?
CPUtime: AA vs UA vs CG

$\text{tSIM} = 9\text{nS}$  
$T = 500\text{K}$  
$\text{Rho}=800\text{kg/m}^3$

**nC10H22**

- **tCPU vs N**
  - Nbr of molecules

- **tCPU vs Nc**
  - Carbon number

- **tCPU vs rc**
  - $rc\ [\text{A}^*]$  

**nC16H34**

- **tCPU vs N**
  - Nbr of molecules

- **tCPU vs rc**
  - $rc\ [\text{A}^*]$
CPU time, can we do more? A SAFT type model
SAFT theory...

The Model: SemiRigid LJ chains

Molecular simulation (exact properties) → Validation


Real fluids (Exact experimental properties)

+ rigidity

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

\[
\frac{A_{\text{res}}}{N_c kT} = \frac{A_{\text{Mono}}}{N_m kT} + \frac{A_{\text{Chain}}}{N_c kT} + \frac{A_{\text{Assoc}}}{N_c kT} + \frac{A_{\text{Rigidity}}}{N_c kT} + \cdots
\]

Most famous models: PC-SAFT, SAFT-\(\Upsilon\)-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