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WEBINAR

Molecular Simulation of Fluids: The SAFT Coarse Graining Technique

Professor Erich Müller
Imperial College London

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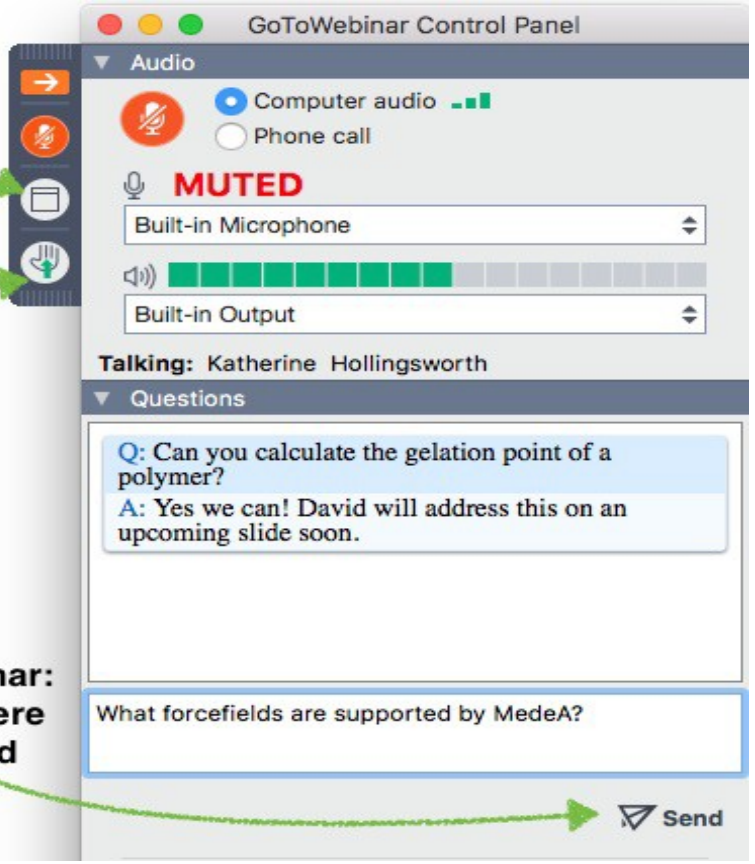

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MOLECULAR SYSTEMS ENGINEERING

Molecular simulation of fluids:

The SAFT coarse graining technique

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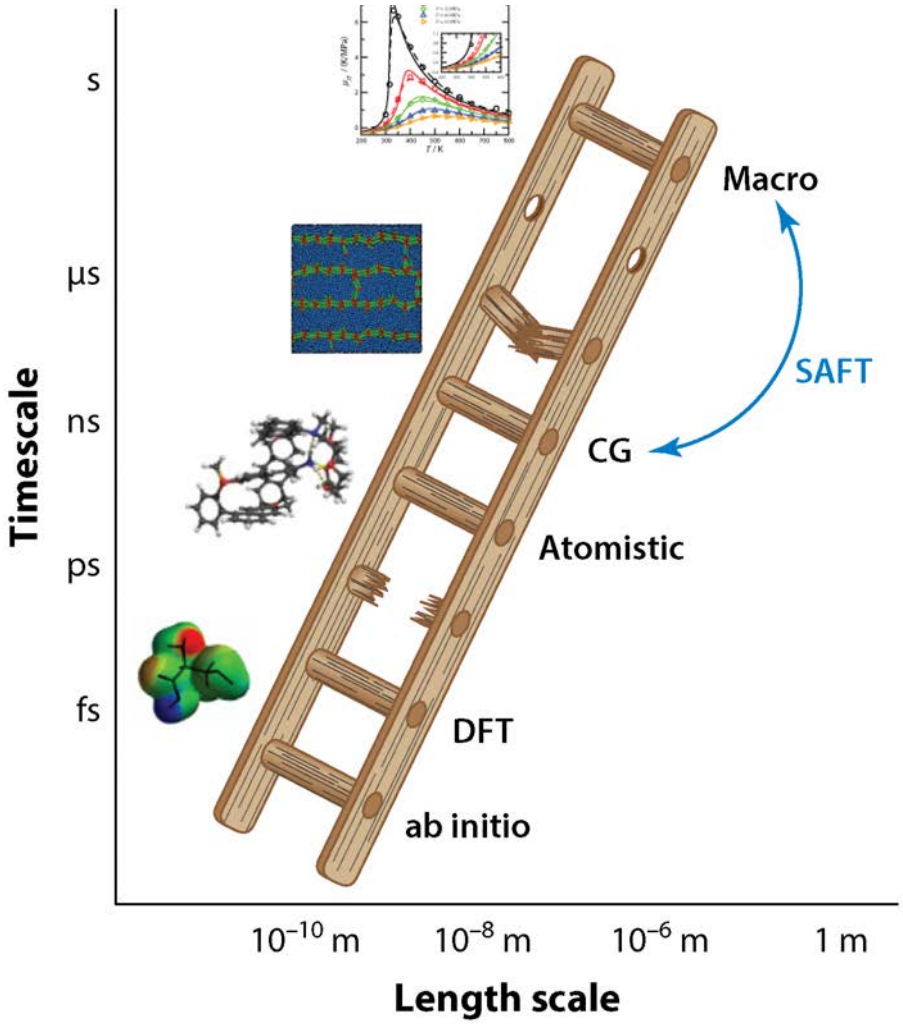
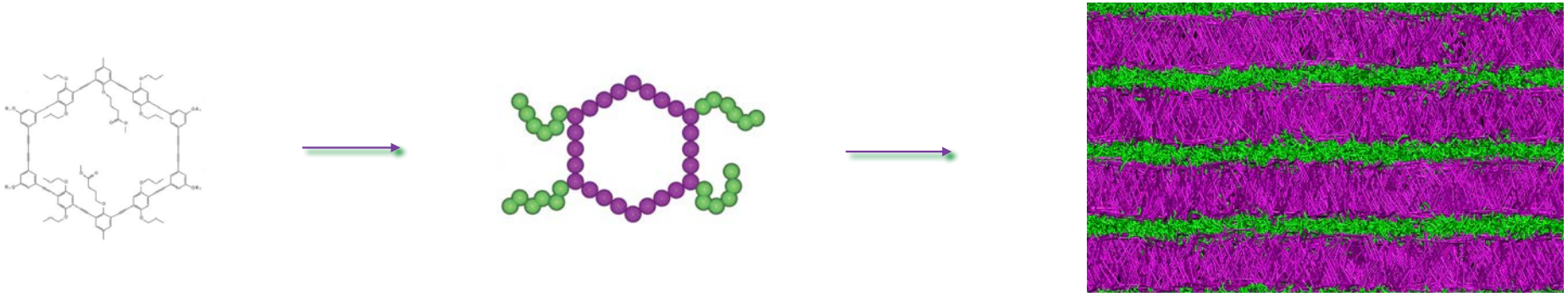


The molecular simulation ladder

Müller, E A, and G Jackson. “Force-Field Parameters From the SAFT-Γ Equation of State for Use in Coarse-Grained Molecular Simulations.” Annu.Rev Chemi Biomol Eng 5, (2014): 405–27.

Coarse Graining

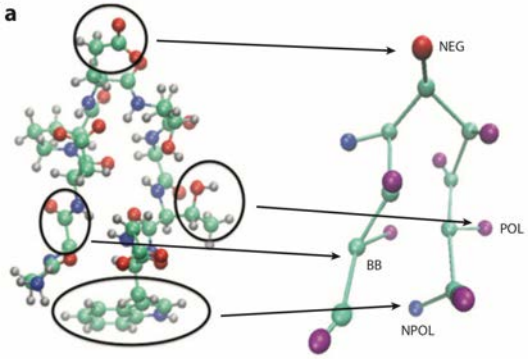
- By removing the detail in the molecular model, significant gains in both the speed of the calculations and the accessible size of the system can be procured.
- Essential if large molecules and/or large time scales are needed e.g. polymer dynamics, multicomponent mixtures, self-assembly of soft matter,
- Risk of GIGO (garbage in, garbage out) as no universally accepted procedure or methodology exists.
- Integrating out degrees of freedom (bottom-up approach) inevitably results in a loss of information with problems of transferability



Avendaño, C, and E A Müller. “Liquid Crystalline Behavior of a Coarse-Grained Model of Shape-Persistent Macrocycles with Flexible Attractive Chains.” Soft Matter 7, (2011): 1694–1701.

Linking scales: Bottom-up approaches

- Iterative-Boltzmann technique: Attempts to match the radial distribution function of an atomistically-detailed model [1]
- Force matching : Attempts to equate the effective intermolecular forces (and angles) between atomistic detailed models and larger force centres. [2]
- Relative Entropy scaling : employs a measure of the entropy to obtain matches between scales [3]
- Machine learning : [4].

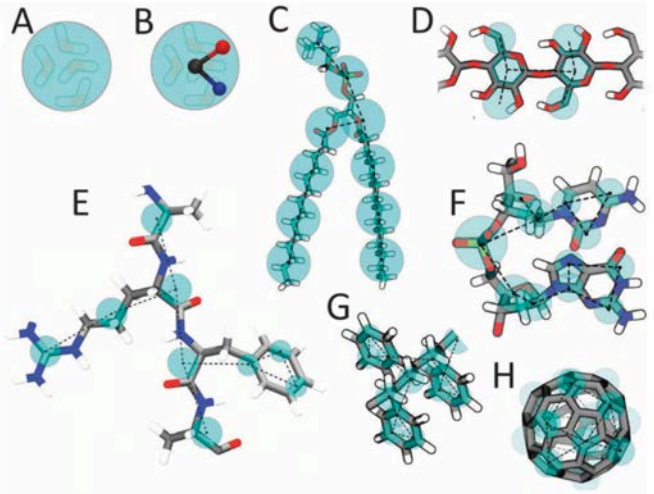


Coarse-grained model of a peptide with at least one CG site per amino acid residue. From {2]

[1] T. C. Moore, C. R. Iacovella, and C. McCabe, “Derivation of coarse-grained potentials via multistate iterative Boltzmann inversion,” J. Chem. Phys. 140, 224104 (2014)
[2] M. G. Saunders and G. A. Voth, “Coarse-graining methods for computational biology.,” Annu. Rev. Biophys., 42, 73–93, (2013).
[3] M. S. Shell, “Coarse-graining with the relative entropy,” in Advances in Chemical Physics (John Wiley & Sons, Inc., 2016), pp. 395–441
[4] P. Gao, X. Yang, and A. M. Tartakovsky, “Learning Coarse-Grained Potentials for Binary Fluids.,” J. Chem. Inf. Model., 60(8), 3731–3745, (2020)

Linking scales: Top-down approaches

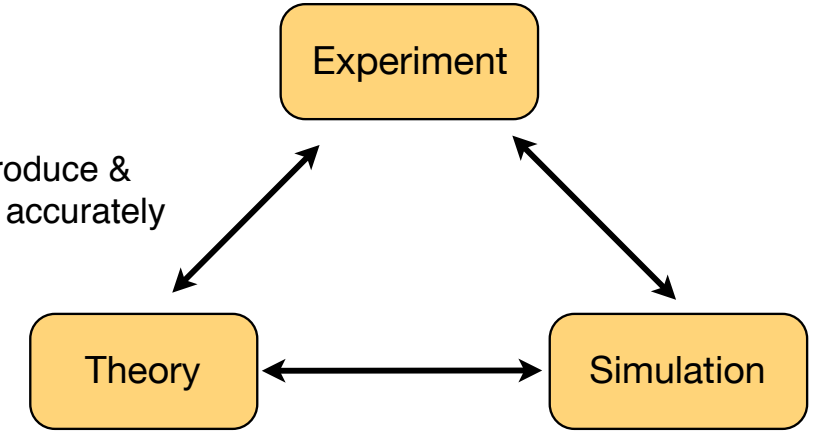
- MARTINI: guides the parameter estimation by matching the experimental water/octanol partition coefficient. Employs a fixed set of equal-sized beads [1]
- SAFT: maps the size, energy and range of the beads to the expected macroscopic volumetric properties of the fluids [2]
- DPD: requires ad-hoc fitting of parameters, e.g. to infinite dilution coefficients [3]



MARTINI mapping of selected molecules. From [1]

[1] S. J. Marrink and D. P. Tieleman, “Perspective on the Martini model,” Chem. Soc. Rev., 42(16) 6801–22, 2013.
[2] E. A. Müller and G. Jackson, “Force-Field Parameters from the SAFT-γ Equation of State for Use in Coarse-Grained Molecular Simulations,” Annu. Rev. Chem. Biomol. Eng., 5, 405–427, 2014.
[3] A. Vishnyakov, M.-T. Lee, and A. V. Neimark, “Prediction of the Critical Micelle Concentration of Nonionic Surfactants by Dissipative Particle Dynamics Simulations,” J. Phys. Chem. Lett., 4(5) 797–802, 2013.

The SAFT approach



SAFT equation of state can reproduce & correlate the experimental results accurately

Simulations based on parameters fit to experimental can be used to explore the molecular level physics

Simulations are used to refine the analytical theory

Transferability

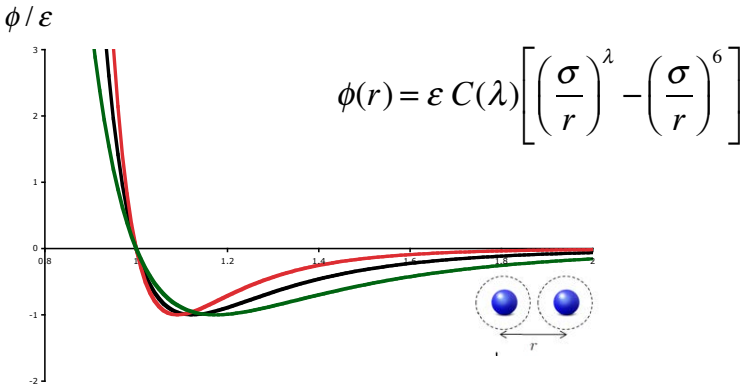
SAFT parameters are transferable to other molecules

Representability

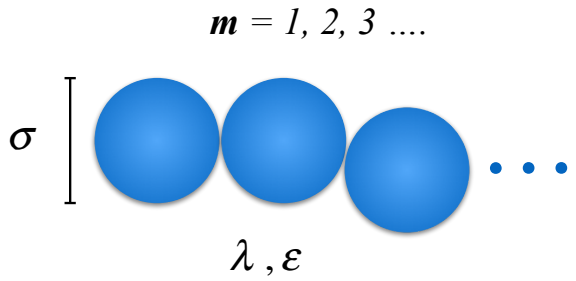
Simulations are used to explore other properties not included in the fit (e.g. interfacial , transport)

SAFT-γ-Mie : Equation of state

- Mie potential



- 4 physical parameters

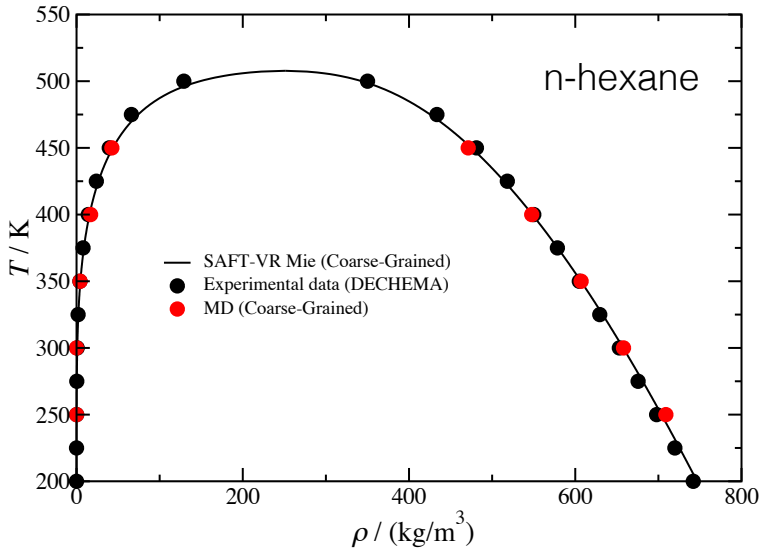


SAFT-γ formulation is unique as it directly relates a macroscopic equation of state with an underlying force field

- third order T expansion

$$a = a^{IDEAL} + a^{MONO} + a^{CHAIN}$$

$$a^{MONO} = m\left[a^{HS} + \beta a_1 + \beta^2 a_2 + \beta^3 a_3\right]$$



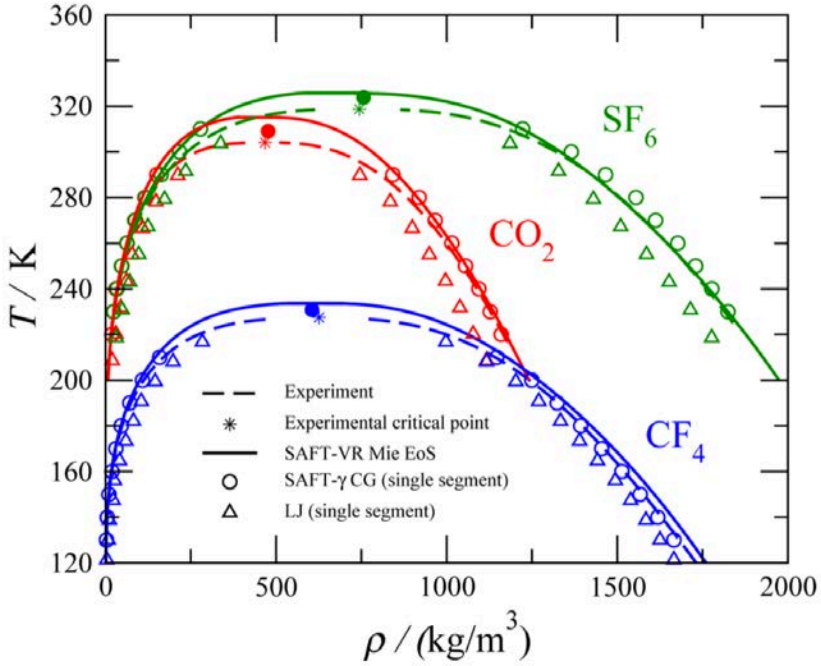
Lafitte, T., et. al (2013).. J. Chem.Phys, 139, 154504. & Papaioannou, V. et al (2014) .J. Chem.Phys, 140, 054107.

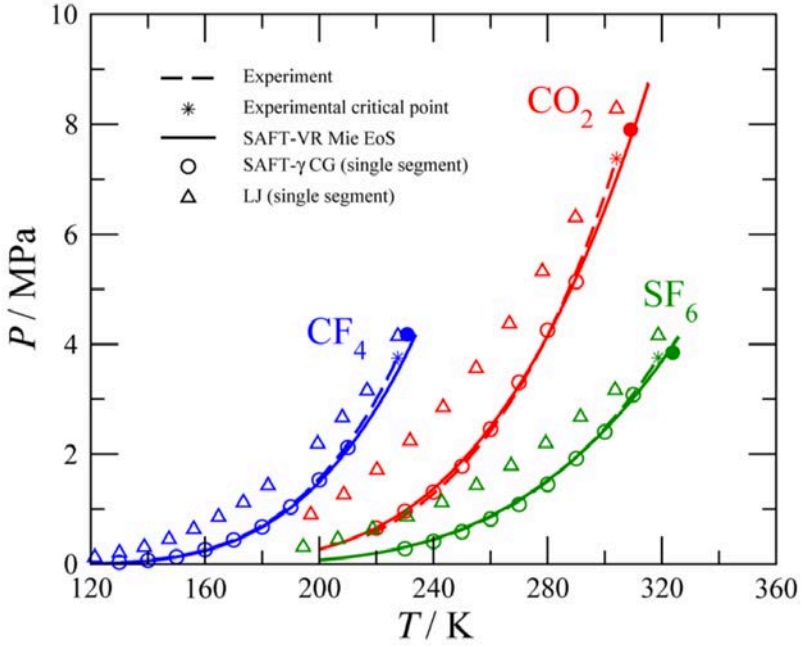
How to obtain the parameters for the EoS / forcefield?

- Fit the EoS to experimental data. Usually information on the vapor-liquid densities and vapour pressures, although we can incorporate other properties (excess volumes, enthalpies, etc.)

- Formulate in terms of corresponding states, hence only need a few pieces of key critical data

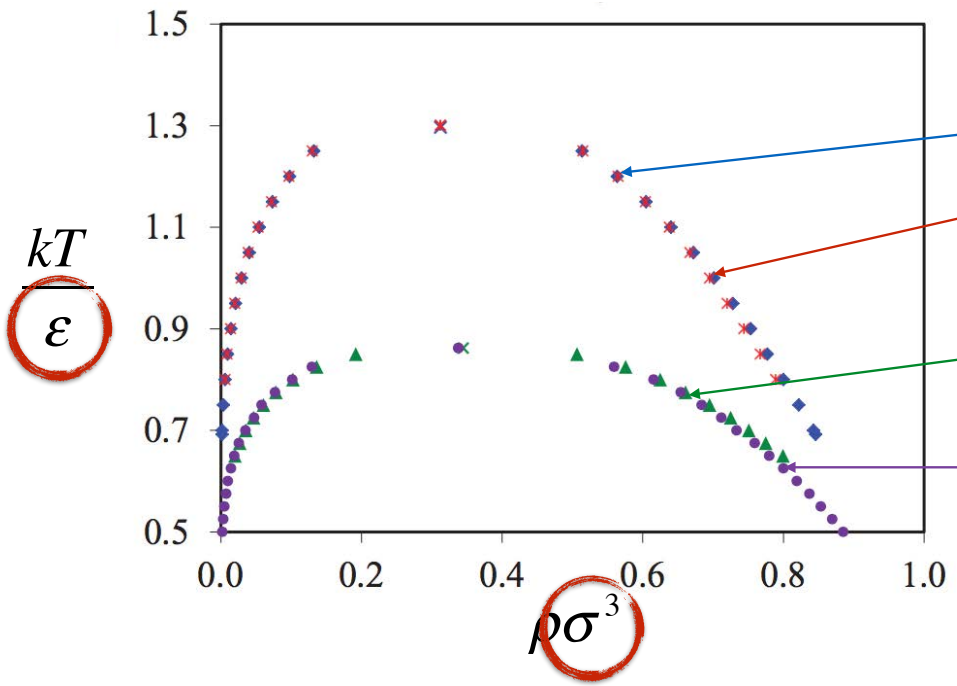
Fitting to experimental VLE data





Conformality of the Mie (m,n) potential

$$u(r) = C\varepsilon\left[\left(\frac{\sigma}{r}\right)^m - \left(\frac{\sigma}{r}\right)^n\right]$$



(12,6)

(9.16,7)

} α = 0.890

(23,6.66)

(14.65,8)

} α = 0.521

scaling parameters

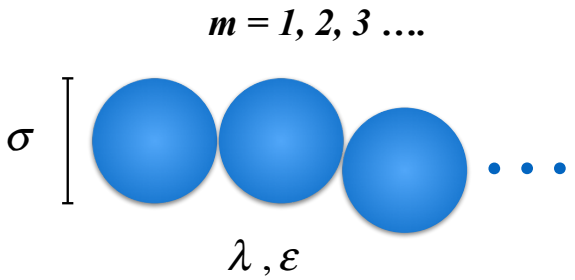
van der Waals parameter

$$\alpha = \frac{1}{\varepsilon\sigma^3}\int_\sigma^\infty u(r)r^2\,dr = \frac{\lambda}{3(\lambda-3)}\left(\frac{\lambda}{6}\right)^{6/\lambda-6}$$

for the (λ,6) potential

Ramrattan, N S, C Avendaño, E A Muller, and A Galindo. “A Corresponding-States Framework for the Description of the Mie Family of Intermolecular Potentials.” Molecular Physics 113, (2015): 932–47.

Three (four) parameter corresponding states



$$m = f(\text{molecular geometry})$$
$$\lambda = f(\alpha) = f(\omega)$$
$$\varepsilon = f(T^*) = f(T_c)$$
$$\sigma^3 = f(\rho^*) = f(\text{density})$$

Since SAFT is an equation of state it can be described in terms of corresponding states, hence **the molecular parameters can be obtained from critical properties**.

Mejía, A., Herdes, C., & Müller, E. A. (2014). Force Fields for Coarse-Grained Molecular Simulations from a Corresponding States Correlation. Ind. Eng. Chem. Res, 53(10), 4131–4141.

bottledsaft.org

SAFT-γ Mie, bottled | Search the bottle | Run your own compound | Build with the blocks | About us

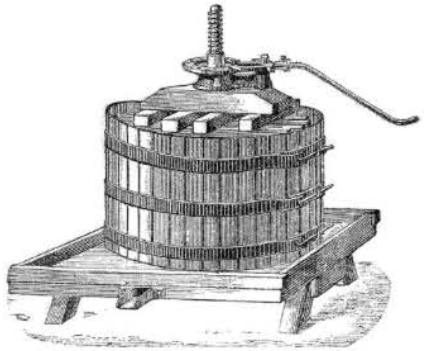
SAFT-γ Mie, bottled

The SAFT-γ Mie force field is a powerful approach to coarse-grained molecular dynamics: the parameters for the model of a substance are computed from its thermophysical properties, removing the need for tuning models to atomistic simulations. The theory also provides a corresponding equation of state. Here we make the power accessible to anyone.

The bottle

"The bottle" is our collection of 6000+ molecules for which we have already computed the force field parameters. You can search by CAS number, name, or chemical formula.

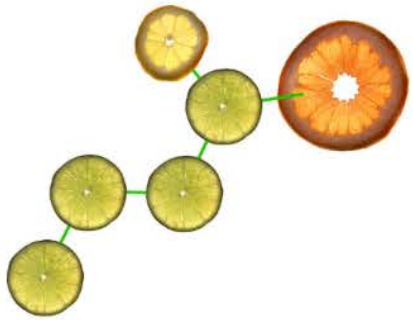
Search the bottle



Press your own

You can create your own model by providing critical properties for the compound you want to study. The M&M correlation instantly gives you the force field parameters.

Run your own compound



Heteronuclear models

We're hoping to extend this such that you can draw the molecule you want. This feature is still work in progress, for now we just have a demo of the interface that gives you back the SMILES.

Build with the blocks

The theory

The SAFT-γ Mie force field forms part of an established top-down coarse graining methodology that enables molecular dynamics simulations of a wide range of components in the vapor and liquid states [1]

References

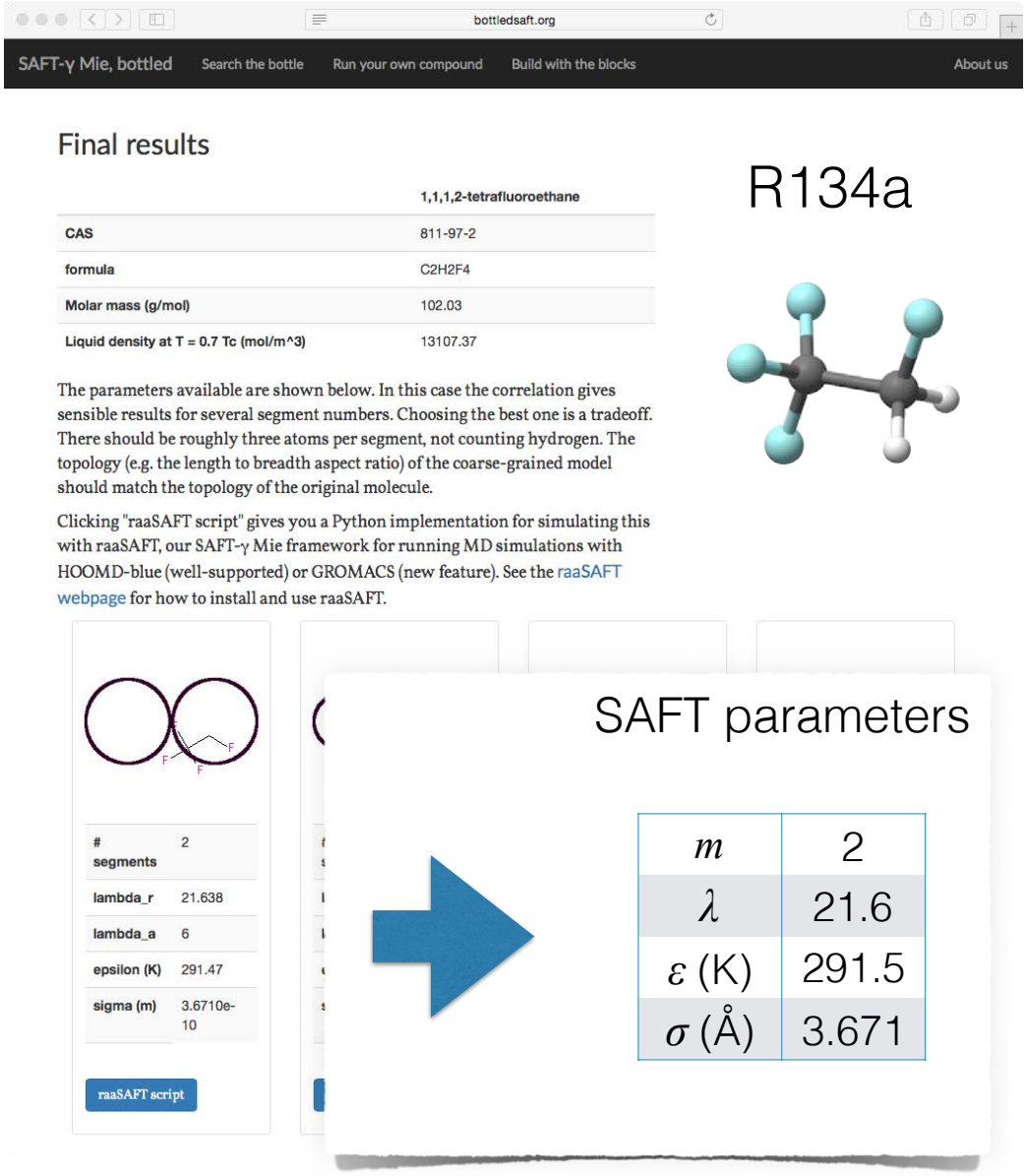
[1] Erich A. Müller and Geo
Chem. Biomol. Eng. **5** (2014):
[2] Andrés Mejía, Carmelo

www.bottledsaft.org

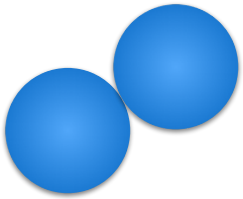
Example

input

T_c	374.1 K
ω	0.3268
$\rho_{0.7}$	13044 mol/m^3



R134a

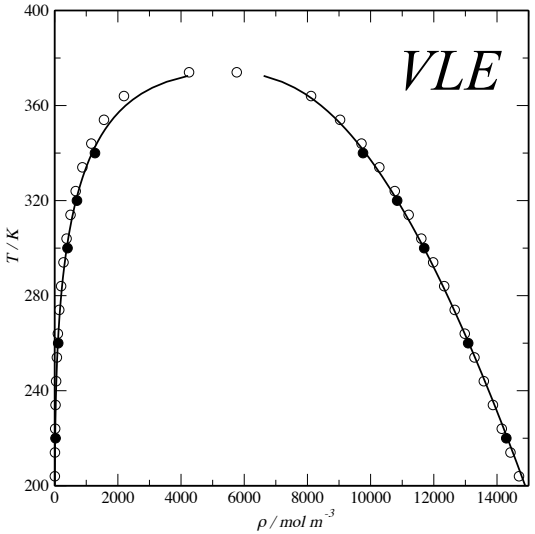


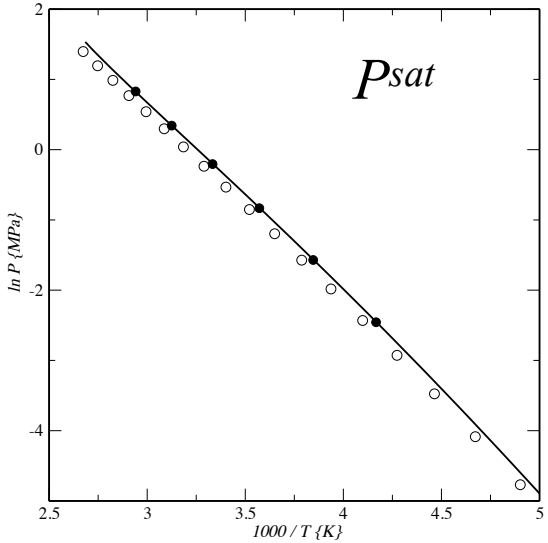
m	2
λ	21.6
ε (K)	291.5
σ (Å)	3.671

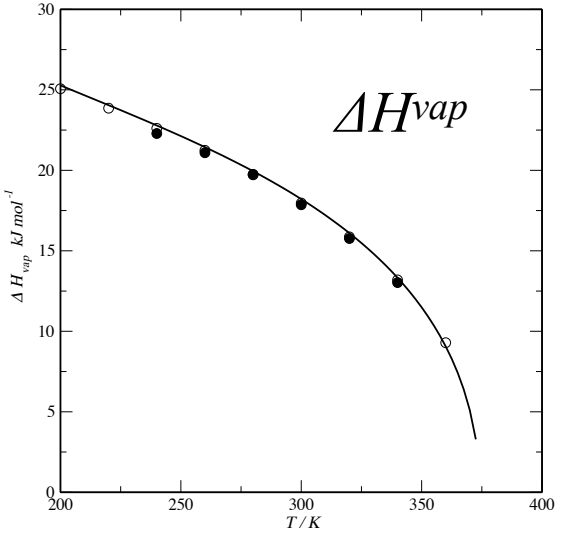
SAFT (EoS)

Experimental data

MD simulations





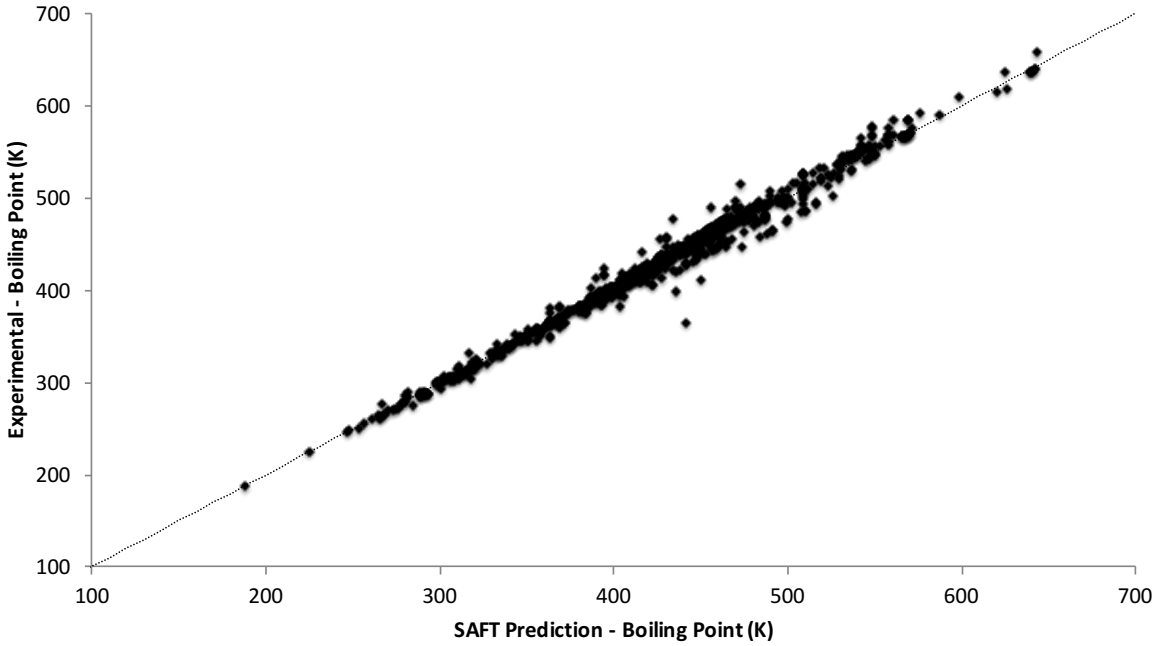


Parameters for 6000+ well-defined chemicals

	m	λ	ε/k_B [K]	σ (nm)
n-alkanes				
methane	1	16.39	170.75	0.3752
ethane	1	27.30	330.25	0.4349
propane	1	34.29	426.08	0.4871
butane	2	13.29	256.36	0.3961
pentane	2	16.06	317.50	0.4248
hexane	2	19.57	376.35	0.4508
heptane	2	23.81	436.13	0.4766
octane	3	16.14	333.70	0.4227
nonane	3	18.31	374.21	0.4406
decane	3	20.92	415.19	0.4584
undecane	4	16.84	348.90	0.4216
dodecane	4	18.41	378.56	0.4351
tetradecane	5	17.66	363.06	0.4183
hexadecane	5	21.20	418.13	0.4432
octadecane	6	19.53	393.74	0.4262
eicosane	6	24.70	453.10	0.4487
aromatics				
benzene	2	14.23	353.93	0.3978
toluene	2	16.95	411.87	0.4266
ethylbenzene	3	12.80	309.69	0.3837
naphthalene	3	12.84	376.50	0.3932
light gases				
nitrogen	1	20.02	122.85	0.3653
carbon dioxide	2	14.65	194.94	0.2848
oxygen	1	17.93	144.02	0.1295
hydrogen sulphide	1	27.38	403.93	0.3801
sulphur dioxide	2	16.06	291.10	0.3091
carbon monoxide	1	21.49	132.83	0.3687
helium	1	14.84	4.44	0.3353
argon	1	14.85	132.04	0.3414
heterocyclics				
pyridine	2	15.52	410.46	0.3899
pyrrolidine	2	19.74	426.12	0.3914
thiolane	2	13.83	391.03	0.4012
thiophene	2	13.58	354.34	0.3832
branched and cyclo-alkanes				
isopentane	2	14.92	298.38	0.4236
isobutane	2	12.94	241.57	0.3974
cyclopentane	2	13.52	312.00	0.3992
cyclohexane	2	14.05	345.94	0.4234
unsaturates				
ethylene	1	25.62	299.49	0.4180
propylene	1	33.65	417.60	0.4721
1-pentene	2	17.50	328.86	0.4183
1-decene	3	18.93	394.49	0.4516
solvents / others				
water	1	8.395	378.87	0.2915
tetrahydrofuran	2	14.85	348.92	0.3840

- Mejía, A., et al. (2014). Force Fields for Coarse-Grained Molecular Simulations from a Corresponding States Correlation. Ind. Eng. Chem. Res, 53(10), 4131–4141.

A quick check



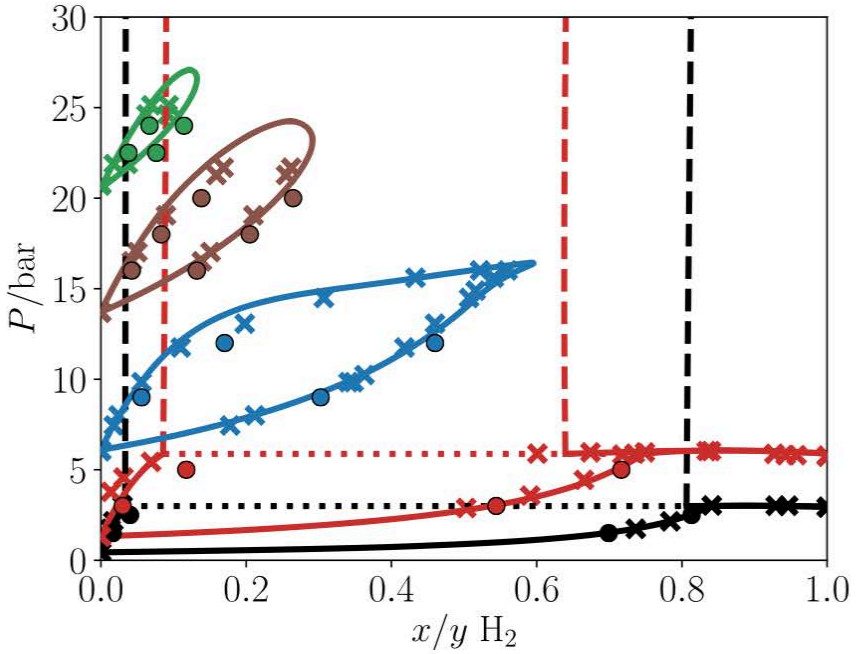
Normal boiling point prediction. AAD 1.15 %

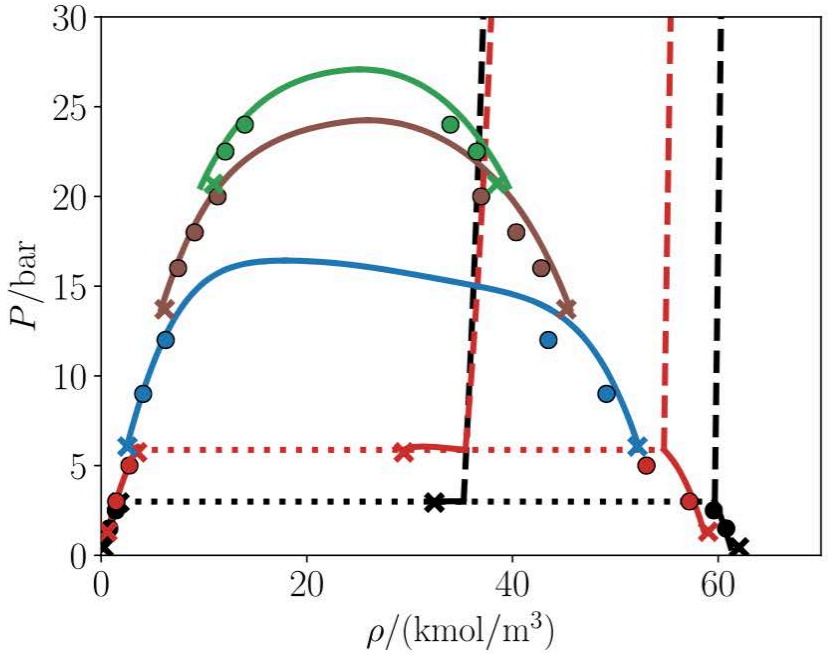
Cryogenic fluids

Adding the Feynman-Hibbs correction

SAFT (EoS)
Experimental data
MD simulations

Hydrogen-Neon mixtures at 25 K, 28 K, 35 K, 40 K and 43 K





A. Aasen, et al. J Chem Phys, 152, 074507 (2020).

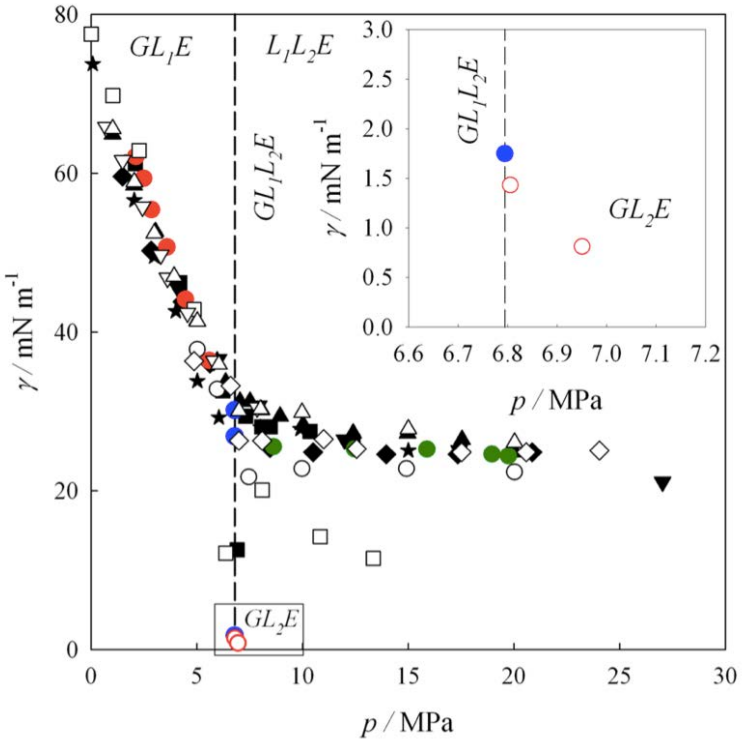
How about transport / interfacial properties?

- Although only volumetric properties are employed for parametrization, the procedure is basically a very broad fit of the effective Helmholtz free energy landscape.

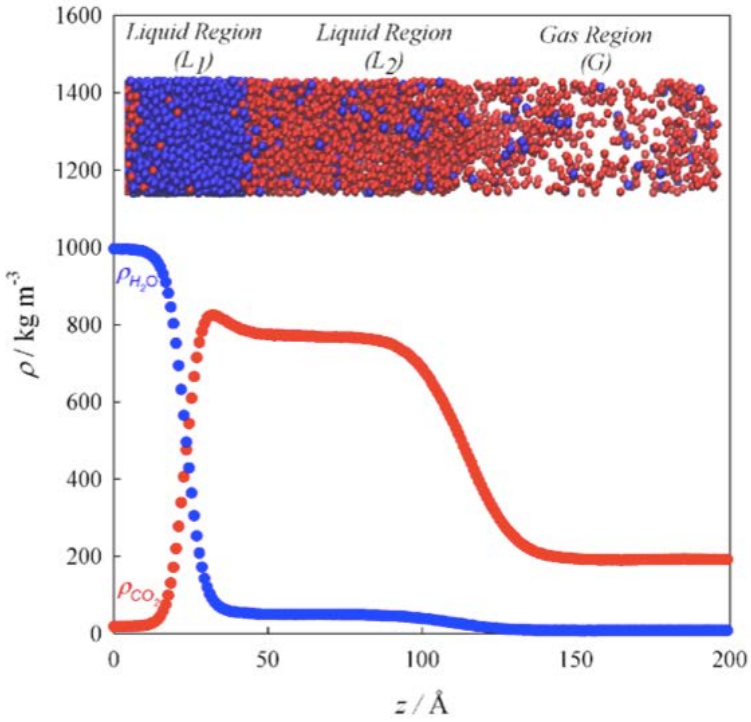
- This seems to be sufficient to produce robust optimised force field parameters which can be employed to explore other properties (e.g. interfacial, transport, etc..)

Resolving discrepancies in experimental data

High pressure CO_2-water interfacial tension



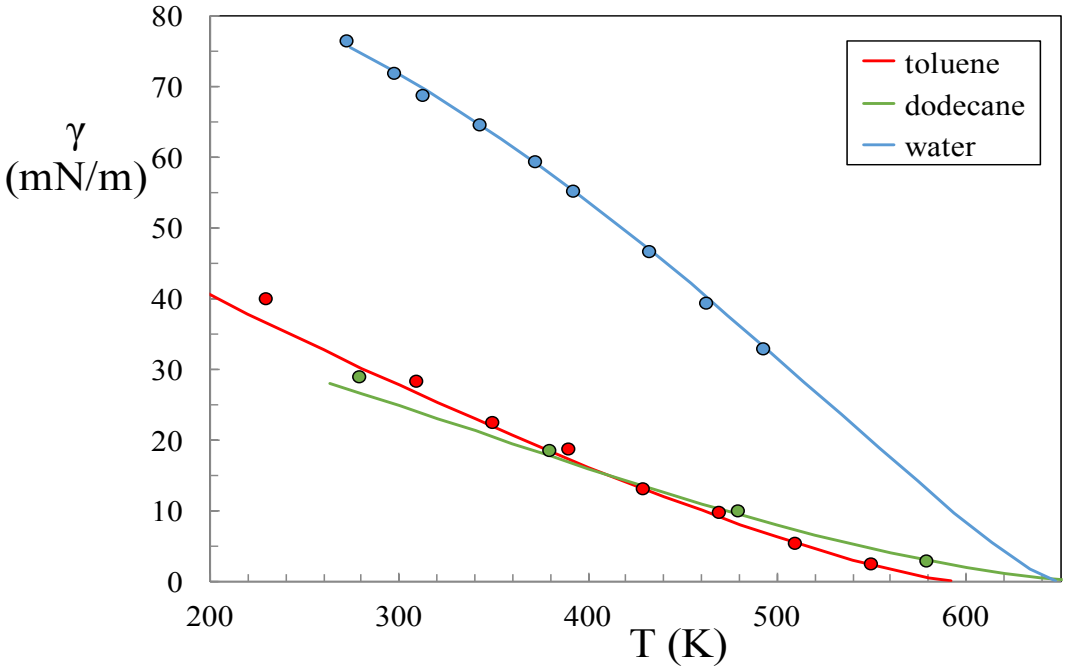
- Experimental data (B&W) show extreme scatter

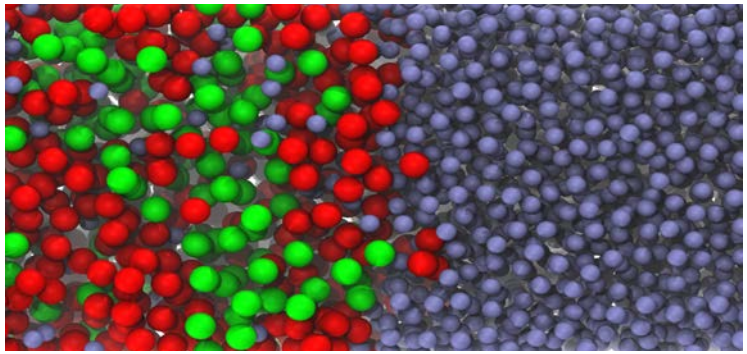


- Large scale CG simulations demonstrate the existence of a liquid-liquid-vapor region (3 phases) which explain the experimental findings

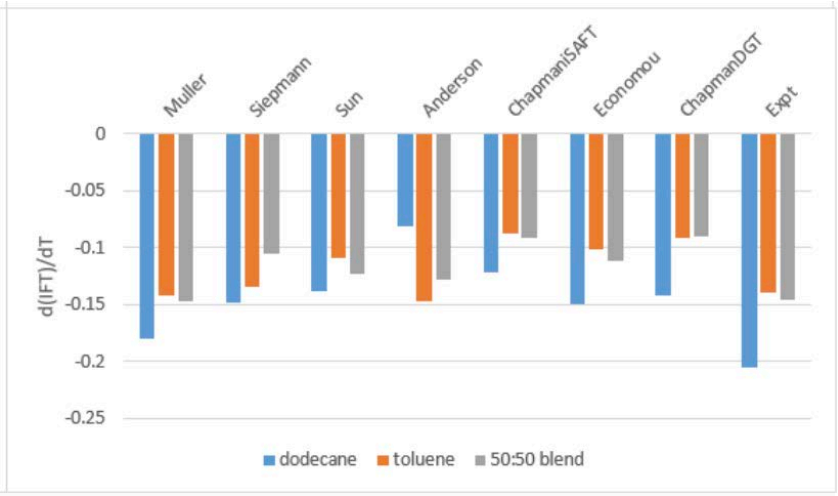
Müller, E. A., & Mejía, A. (2014). J. Phys. Chem. Letters, 5(7), 1267.

Oil/water interfacial tension





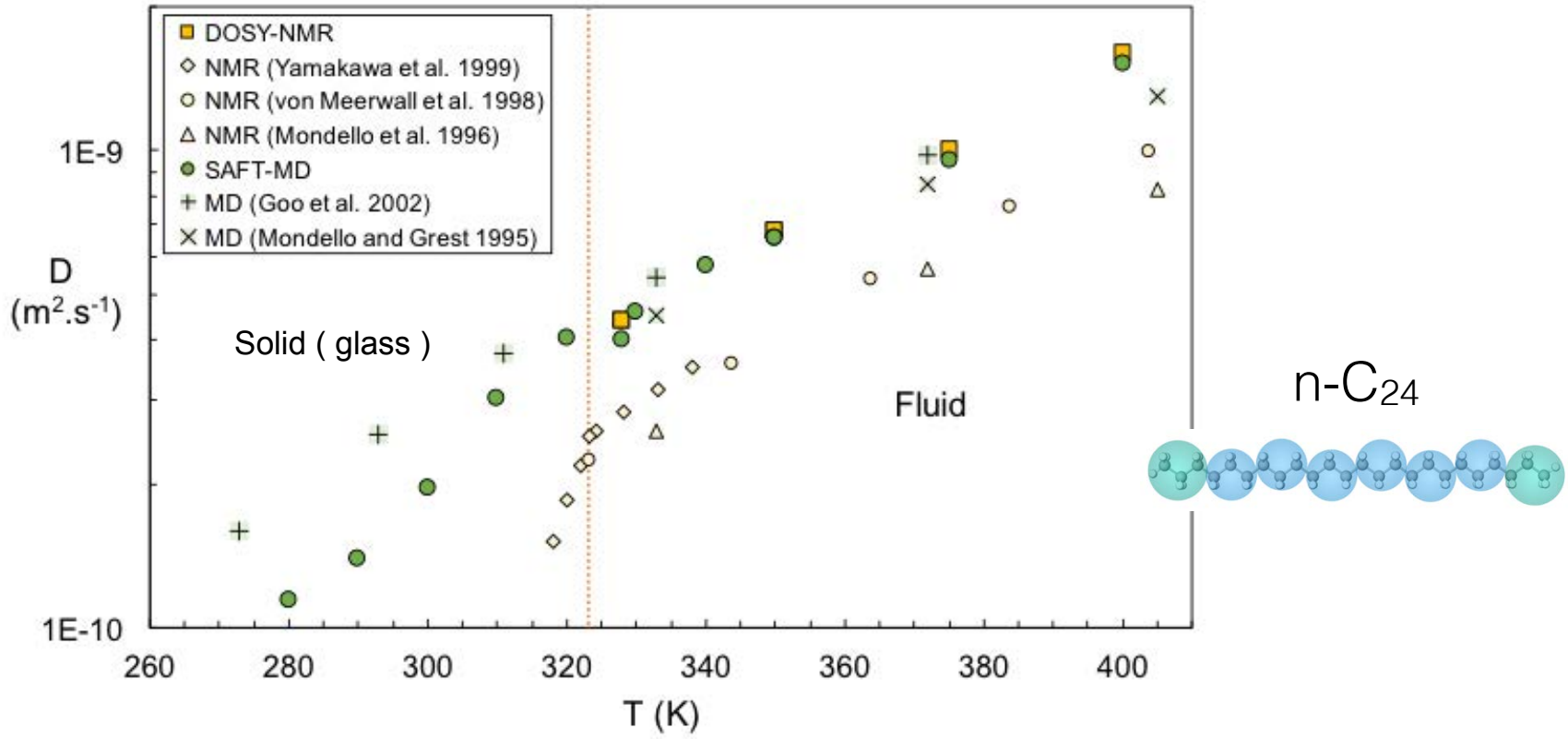
P = 250 psi
T =110-170 C



The MOST ACCURATE modelling technique to determine mixture oil/water IFT at high P and T
AIChE 2016 – Industrial fluid property challenge

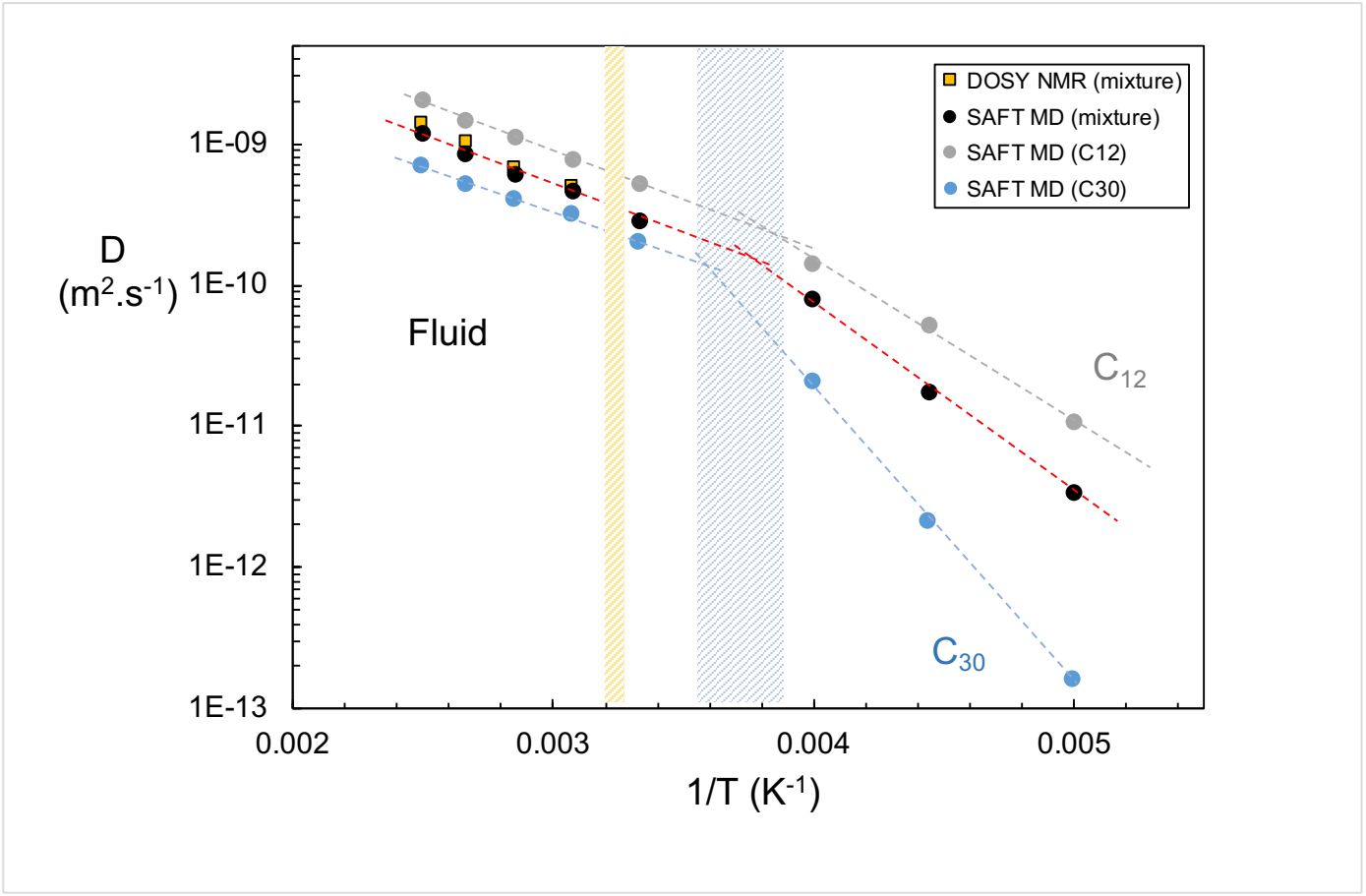
http://fluidproperties.org/results-ninth-challenge

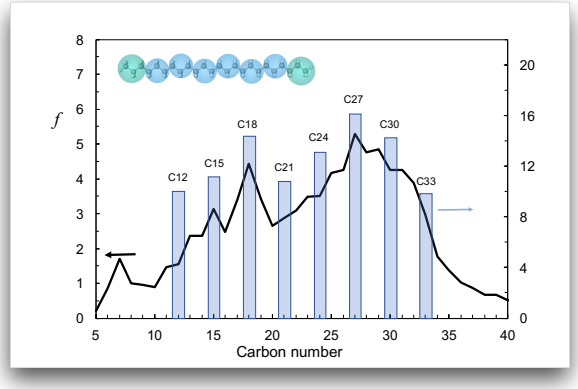
Self-diffusion coefficients



DOSY-NMR : Diffusion ordered spectroscopy nuclear magnetic resonance

Wax appearance temperature





8 component alkane mixture fitted to HPLC data of a real Malaysian crude

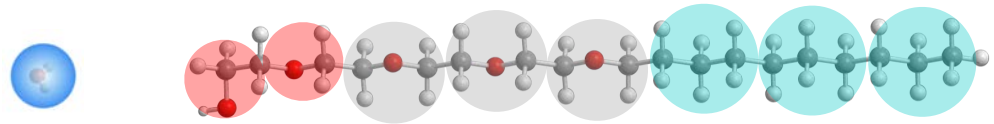
S. Shahruddin, G. Jiménez-Serratos, G. J. P. Britovsek, O. K. Matar, and E. A. Müller, “Fluid-solid phase transition of n-alkane mixtures: Coarse-grained molecular dynamics simulations and diffusion-ordered spectroscopy nuclear magnetic resonance,” Sci Rep, 9, 1002, (2019).

How about complex molecules?

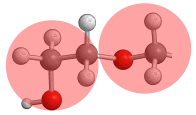
- Fitting parameters are usually done on a per-molecule basis with homogeneous molecules.
- There is no reason why one could could not invoke a **group-contribution** approach.

Ethoxylated Alkyl surfactants

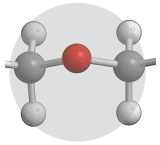
(transferring groups from smaller molecules)



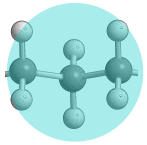
- Break down the molecule into similar moieties
- heteronuclear segment parameters estimated from thermodynamic properties (density, vapour pressure) of simple molecules



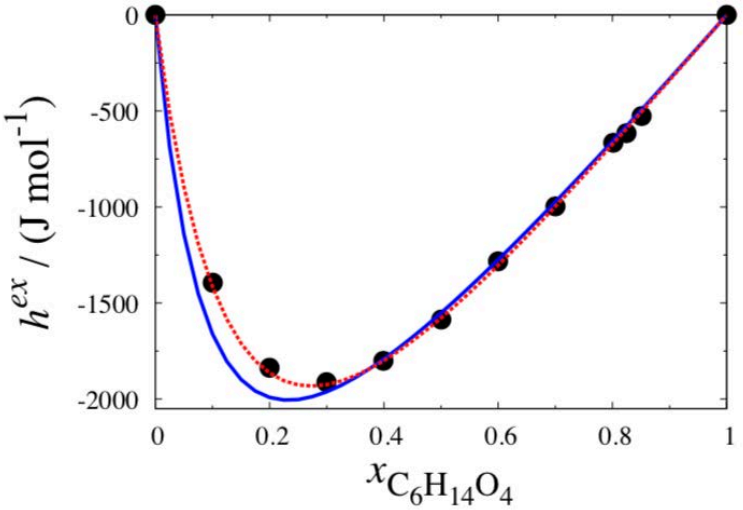
- $OH\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}$
- triethylene glycol



- $\text{-}CH_2\text{-}O\text{-}CH_2\text{-}$
- ethers
- $C_4H_{10}O_2$ to $C_{12}H_{26}O_6$

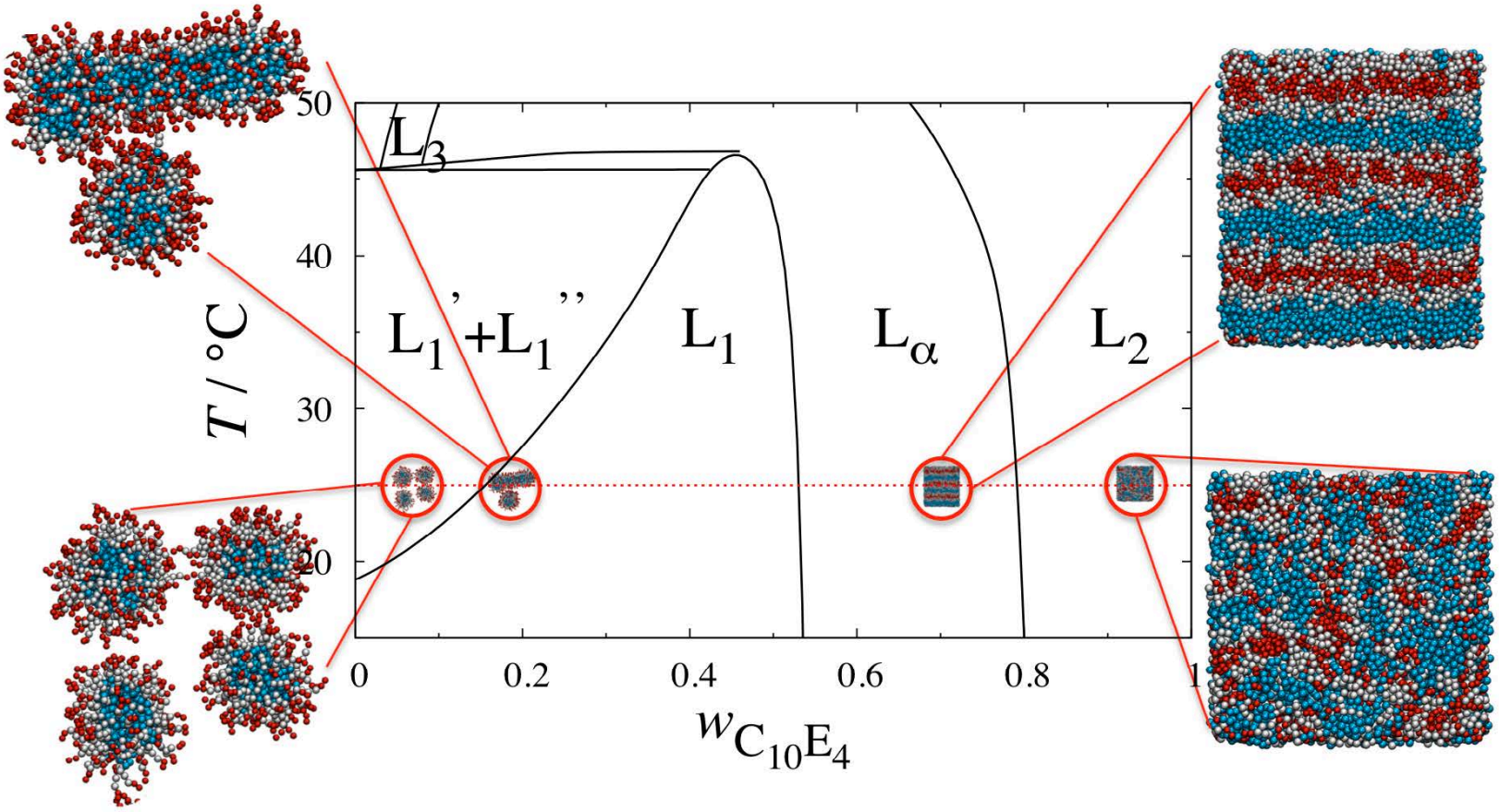


- $\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}$
- alkanes
- C_3H_8 to $C_{24}H_{50}$

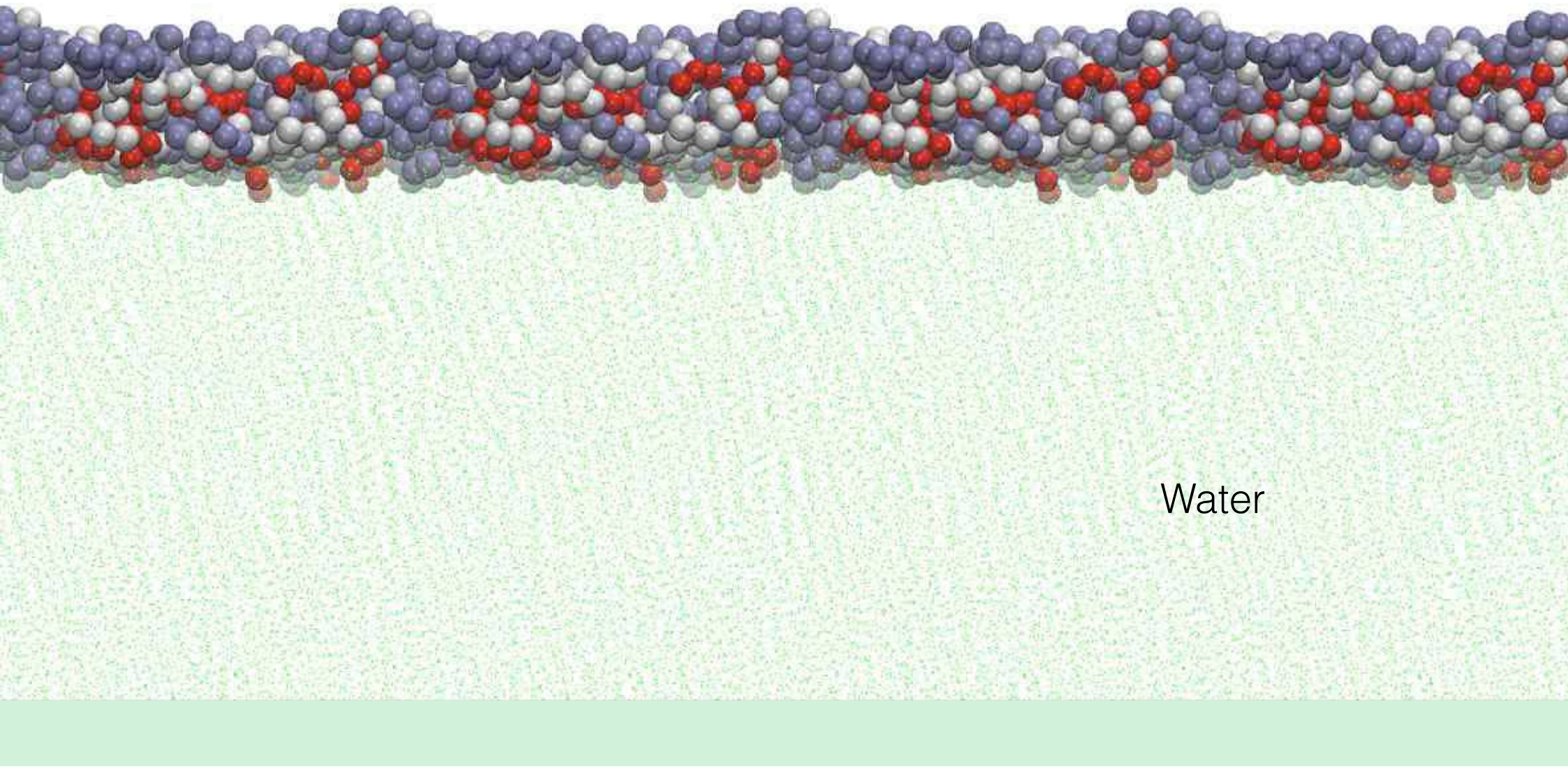


Properties of the mixture (here excess enthalpy of triethylene glycol-water) are used to estimate the unlike interaction between the surfactant and water

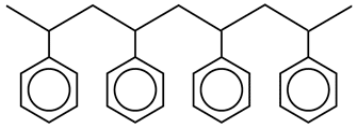
($C_{10}EO_4OH$) in water



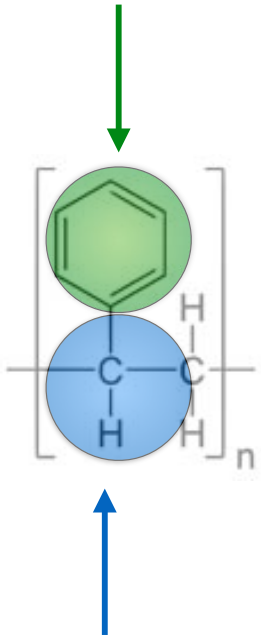
micellar phase L1, lamellar phase Lα, and isotropic phase of inversed micelles L2


Air
Water

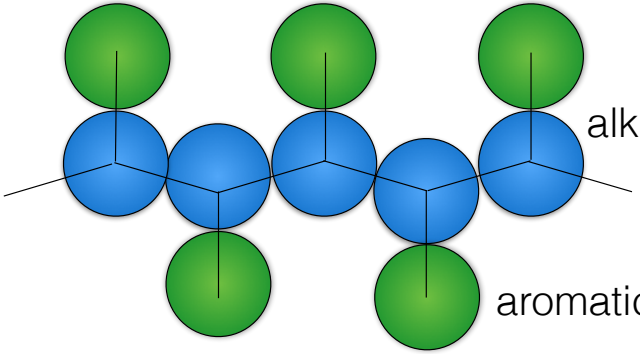
Polystyrene



1/2 toluene molecule

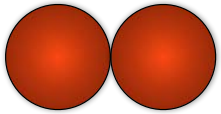


-[CH_2]$_3$- alkane bead



alkane backbone

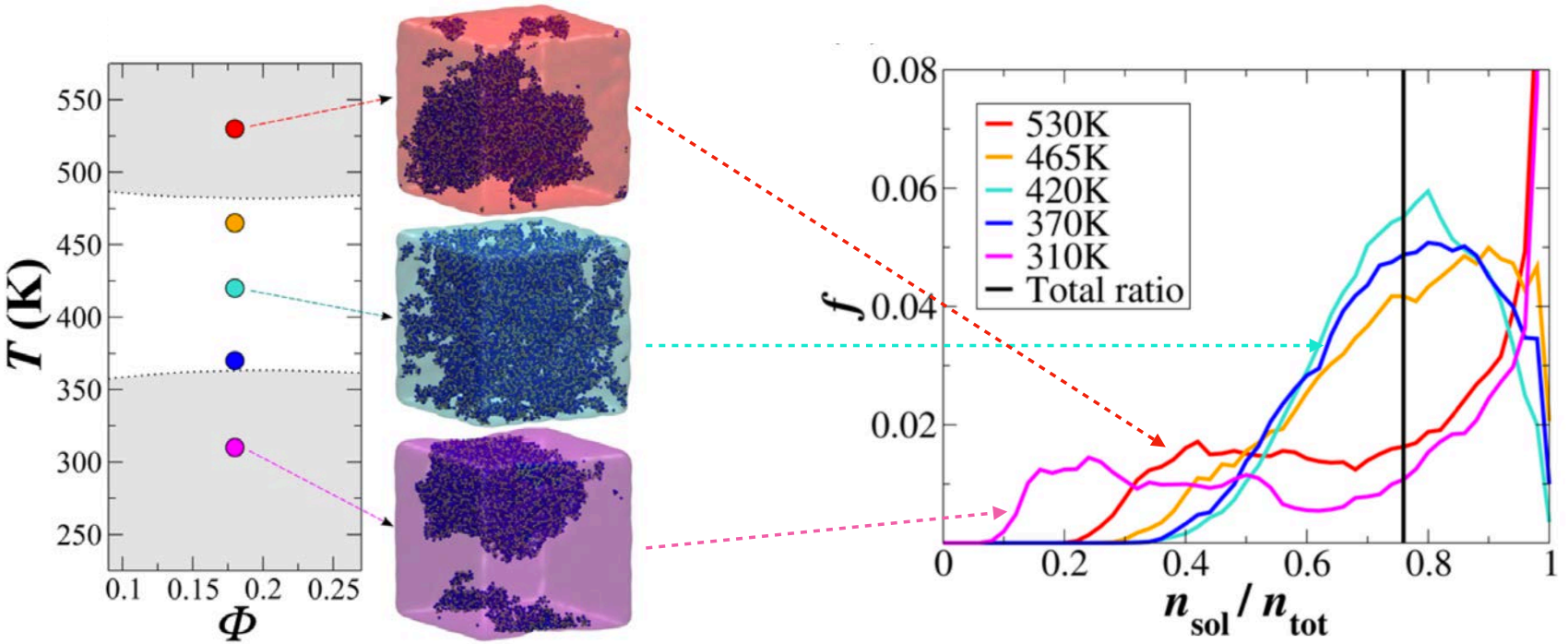
aromatic decorations



hexane (solvent)

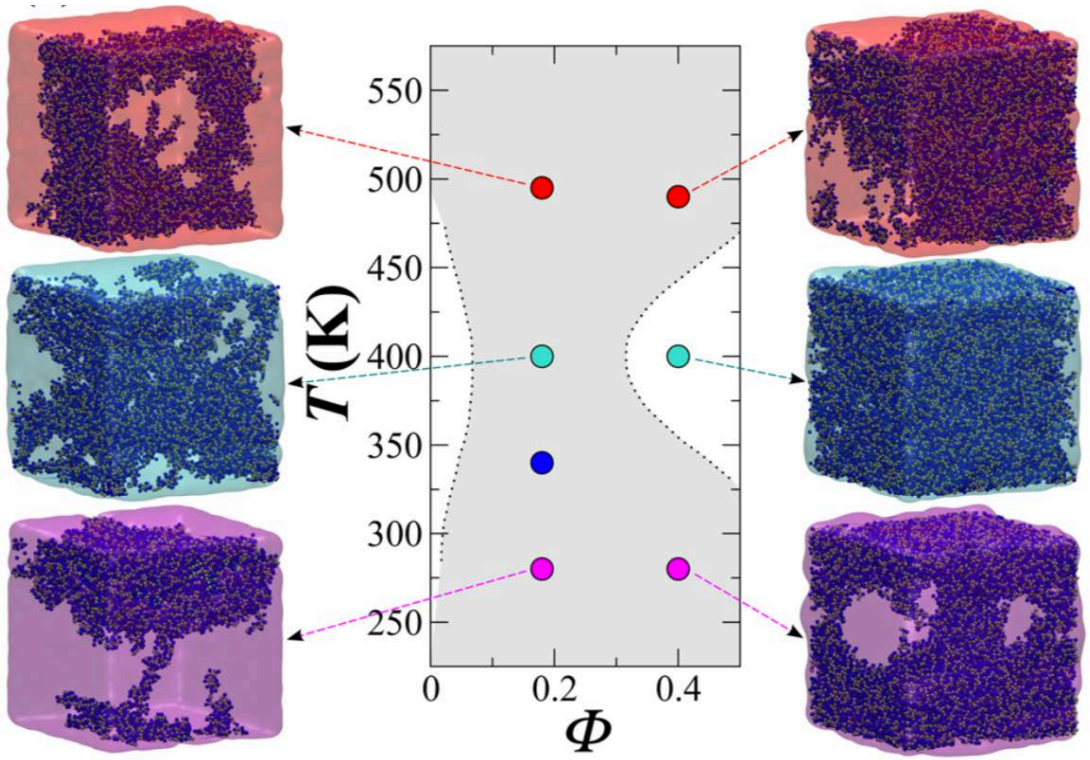
G. Jiménez-Serratos, et al. Macromolecules, 50, 4840–4853 (2017).

PS Mw 4800 g/mol in hexane



local density histograms with $(6)^3$ cells

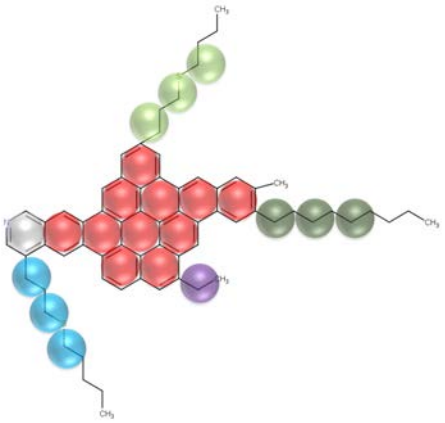
PS Mw 4800 g/mol in heptane



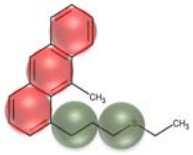
O (10^5 beads)
> 500 ns

“hourglass” phase diagram is accurately predicted with the same model

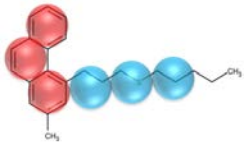
Synthetic live crude simulation (12 components)



Asphaltene A18



Resin A63



Resin A72

Asphaltene A81

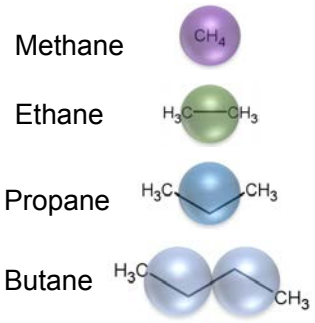
System size: $O(10^4)$ nm3
138000 molecules
2.4M atoms
Temperature: 300K – 800K;
Pressure range: 1 – 500 bar
Time: 0.3 μs
Time step: 0.01 ps
running on 48 cores
Wall time: 1 month (10 ns/day)

Methane

Ethane

Propane

Butane



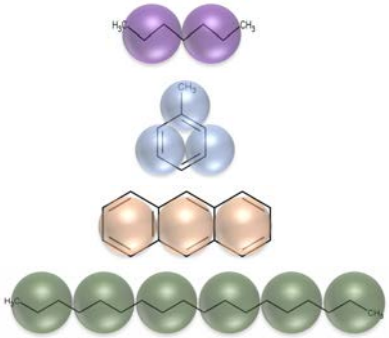
Light ends

Heptane

Toluene

Anthracene

n-C18

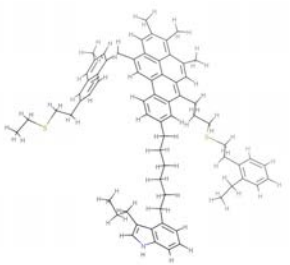


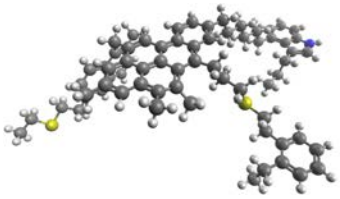
heavy ends

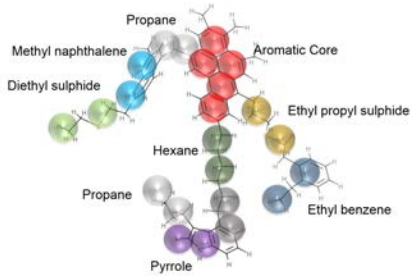
	Wt% in system
Asphaltene 18 (C68H73N1S2)	4.5%
Asphaltene 25 (C70H79N1S2)	1.2%
C1	5.8%
C2	1.9%
C3	2.8%
nC4	5.1%
Saturated n-C7	57.7%
Aromatic Toluene (C7)	3.0%
Aromatic Anthracene (C14)	3.9%
Saturated Wax (n-C18)	9.4%
Resin A (C20H22S1)	2.0%
Resin B (C23H28S1)	2.3%

Twins with different behaviour

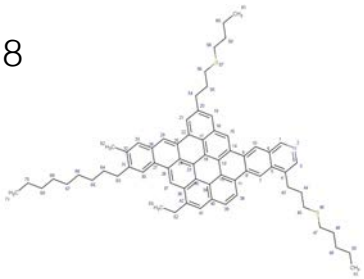
"**good**" archipelago asphaltene A81
10 rings, largest core has 5
DBE 32
MW 984
$C_{69}H_{77}N_1S_2$

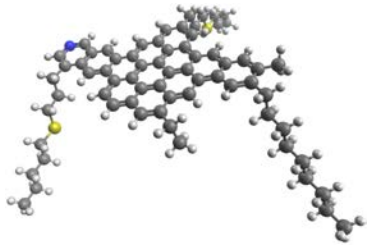


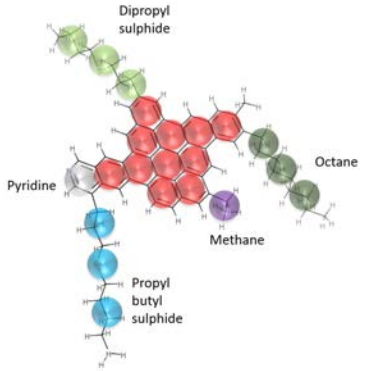




"**bad**" continental asphaltene A18
12 rings, all in one core
DBE 33
MW 968
$C_{68}H_{73}N_1S_2$





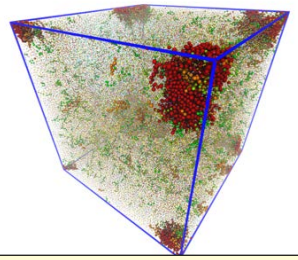


Atomistic Model
(for reference)

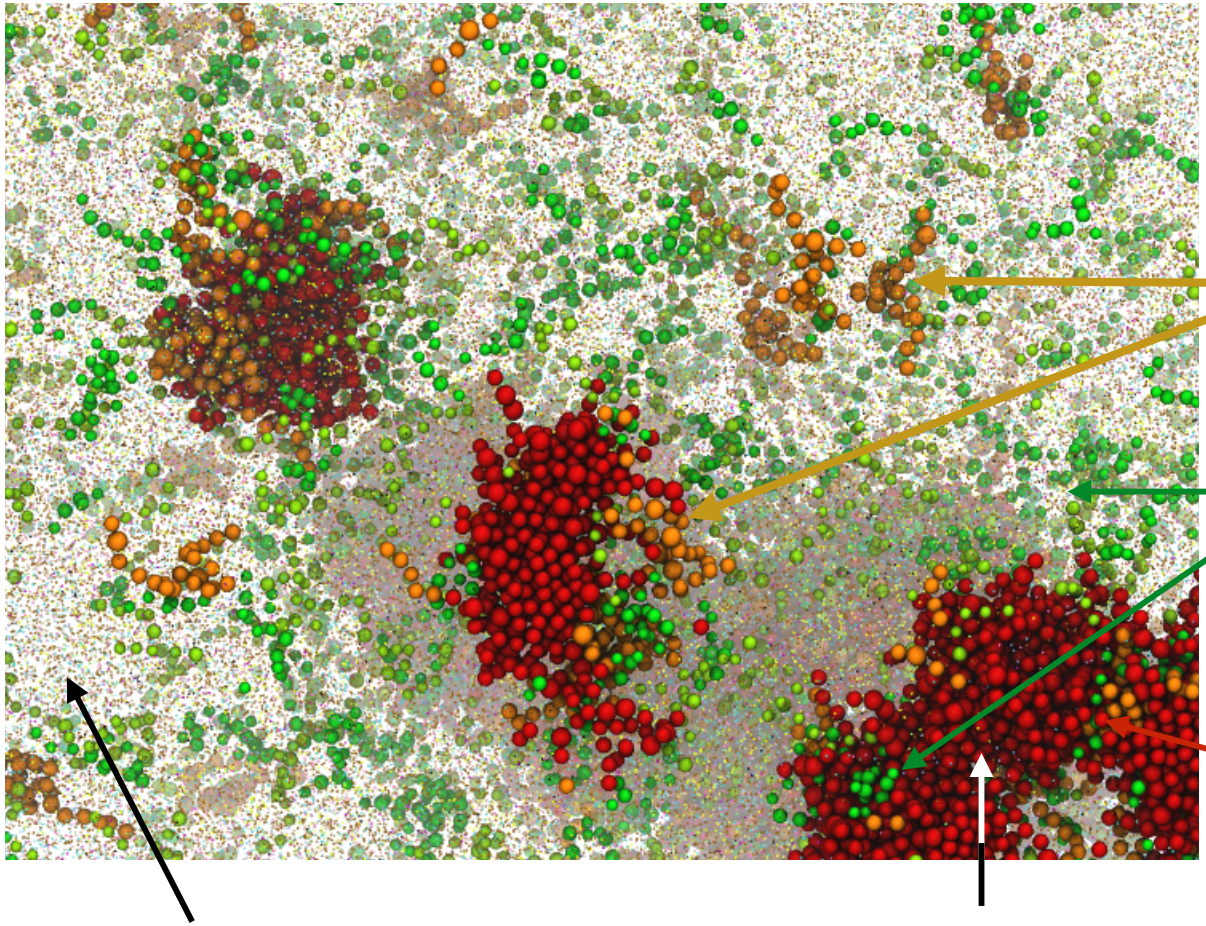
Coarse-grained model

Large scale simulations

410 K , 100 bar
7% w/w asphaltene



An equivalent all-atom simulation would require $O(10^6)$ particles



Archipelago (good) asphaltenes are scattered in the bulk and within the aggregates

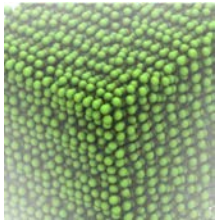
Resins are **not** solvating agents

Continental (bad) asphaltenes form the core of the aggregates

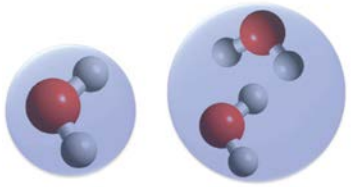
n-alkanes do not form part of the aggregates while **toluene** does (aggregates are loose structures)

Known issues

- Premature solidification - enhanced by the spherical nature of the segments and the propensity of forming an FCC lattice.

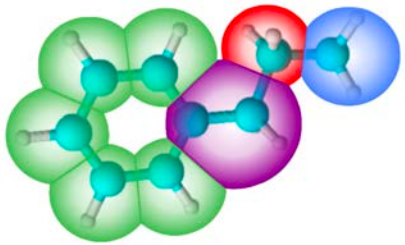


- Charges, electrostatics, etc. - It is challenging to develop the EoS for these systems, hence difficult to parametrize. One can employ “average” potentials which include charges implicitly. e.g. water

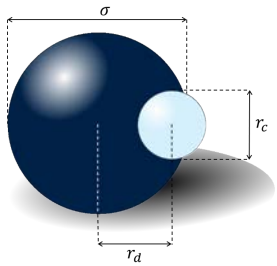


Outlook (the to-do list)

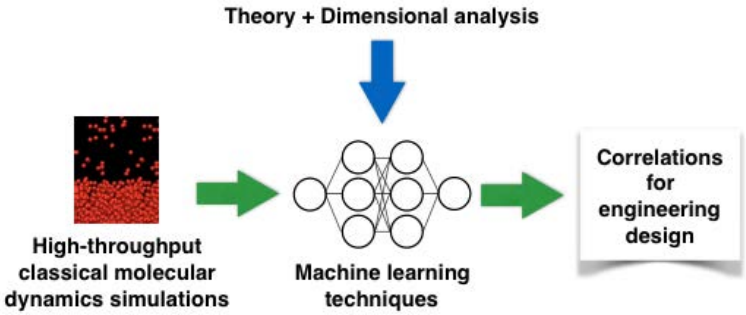
- Fused (or less coarse grained models) informed by the EoS.



- Explicit inclusion of association through molecular models



- Use of machine learning to bypass the EoS



Conclusion

- The use of a top-down approach relieves some of the fundamental issues associated with coarse-graining, in particular the “washing-out” of information when going from a finer to a more coarse scale.

- The SAFT CG approach employs the integrated information contained in the macroscopical thermophysical properties to obtain a surrogate “effective” potential which is transferrable, representative and accurate.

- The use of an analytical equation of state to make the link between the macroscopic properties and the intermolecular potential is the key to the success, but also the limitation in the universal application. Charged systems are particularly challenging.

For a list of current applications of the SAFT CG force field see http://molecularsystemsengineering.org/saft.html

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- Olga Lobanova

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MOLECULAR SYSTEMS ENGINEERING

Question and Answer Session

Professor Erich Müller

Imperial College London

Dr. Marianna Yiannourakou

Materials Design

Questions about Materials Design Webinars

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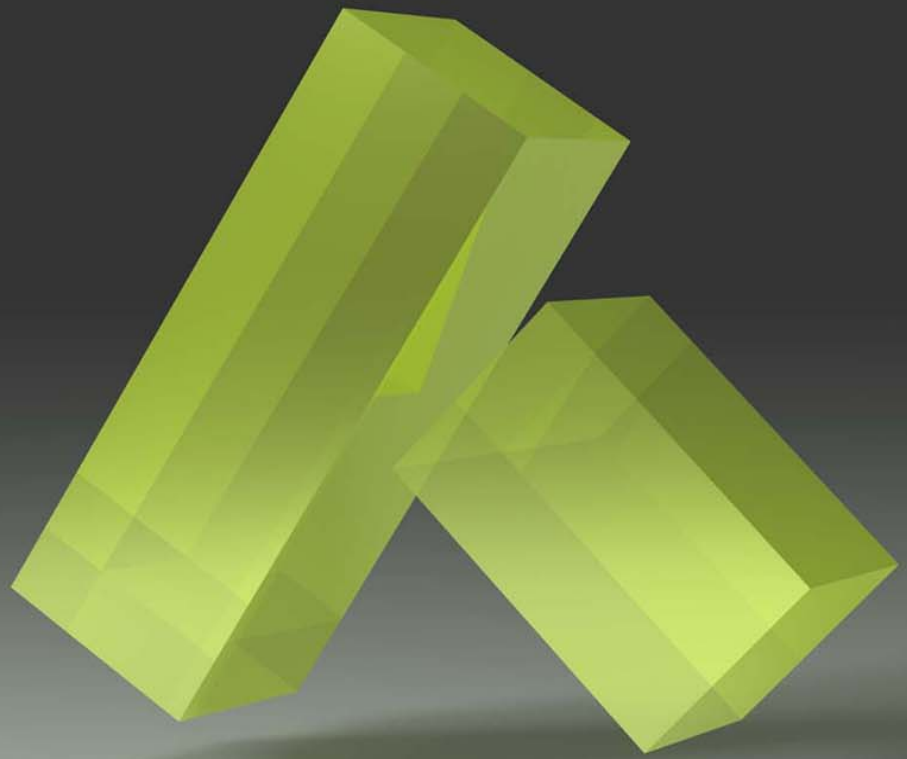

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