



ESDU SPD-M4-2

Advances in characterising asphaltenes combining macro- and micro-ATR-FTIR imaging

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Unamended
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Sub-Project D: Thermodynamics and molecular modelling

Modelling Asphaltenes using SAFT or related approaches

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and Stephen Richardson**

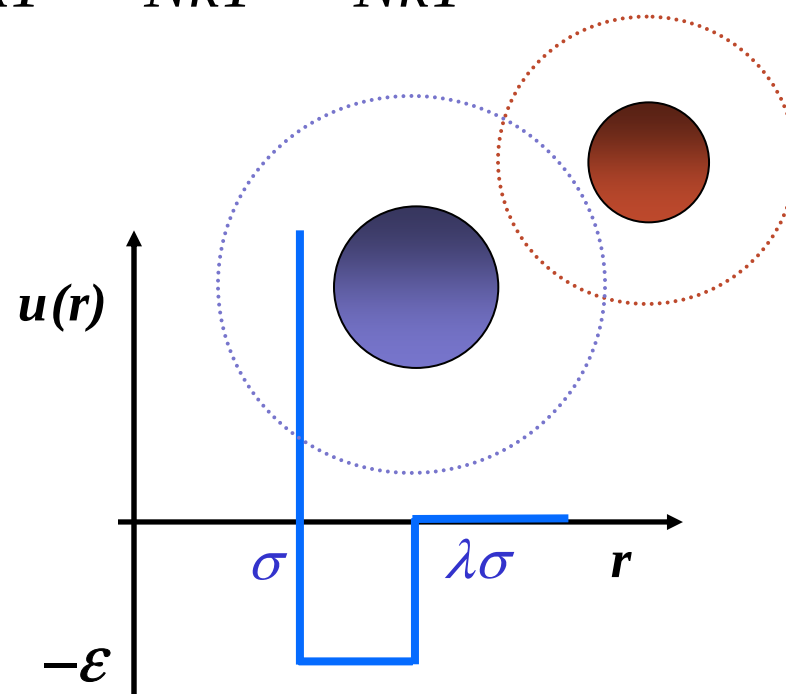
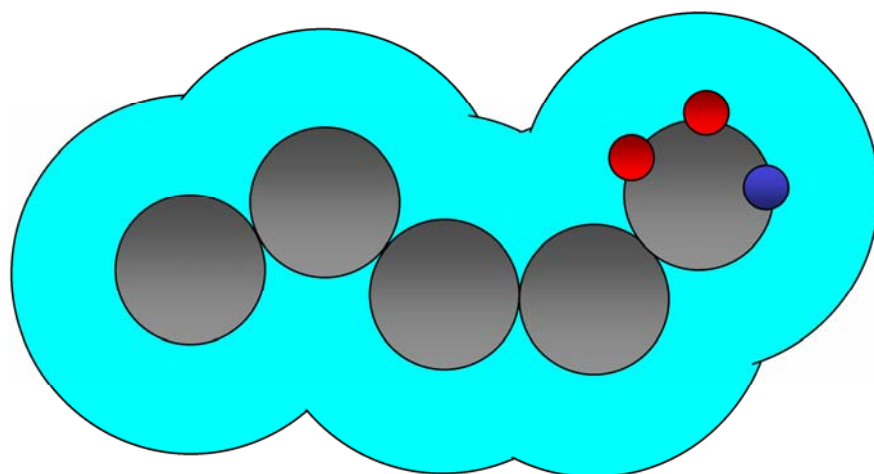
Outline

- **Reminder**
 - **Statistical Associating Fluid Theory (SAFT)**
 - Free-energy equation of state
 - SAFT-VR
- **Previous successful applications of SAFT to asphaltene systems**
- **Polystyrene as a “prototype” asphaltene**

SAFT-VR equation of state

- Free-energy Equation of State

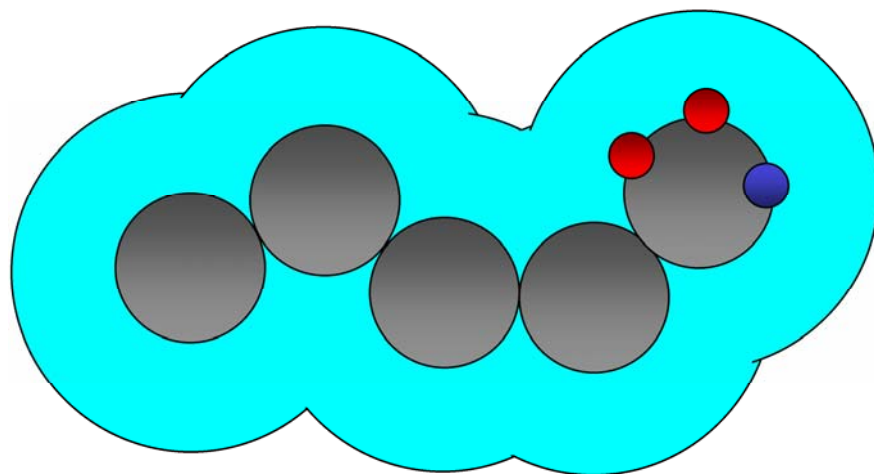
$$\frac{A(m, \sigma, \lambda, \varepsilon, u^{\text{assoc.}})}{NkT} = \frac{A^{\text{ideal}}}{NkT} + \frac{A^{\text{mono.}}}{NkT} + \frac{A^{\text{chain}}}{NkT} + \frac{A^{\text{assoc.}}}{NkT}$$



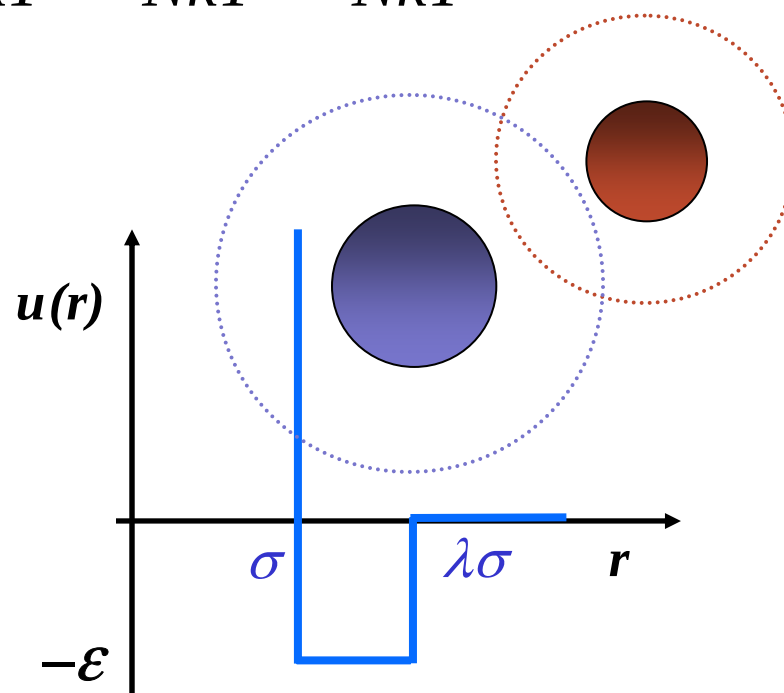
SAFT-VR equation of state

- Free-energy Equation of State

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chain of m square-well spheres;
 $m = 1$ for, e.g., water, methane



Gil-Villegas, Galindo, Whitehead, Mills, Jackson, Burgess, *J. Chem. Phys.*, **106**, 4168 (1997)

Recent examples of modelling complex fluids

- **Complex phase equilibria of:**
 - **Alkanes**
 - **Aromatics**
 - **Polymers**
 - polythene
 - polystyrene
 - **Electrolytes**
 - **...**
 - **Asphaltenes**

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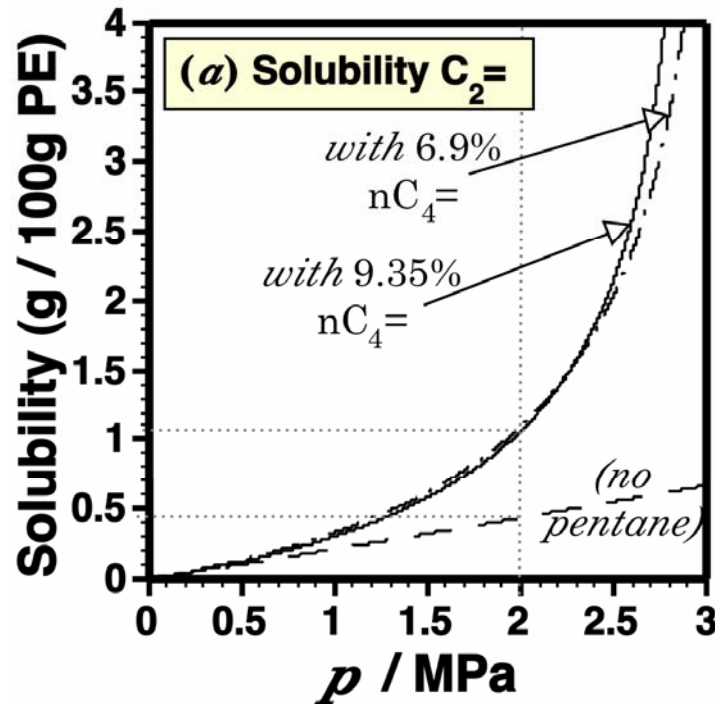
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Recent examples of modelling complex fluids

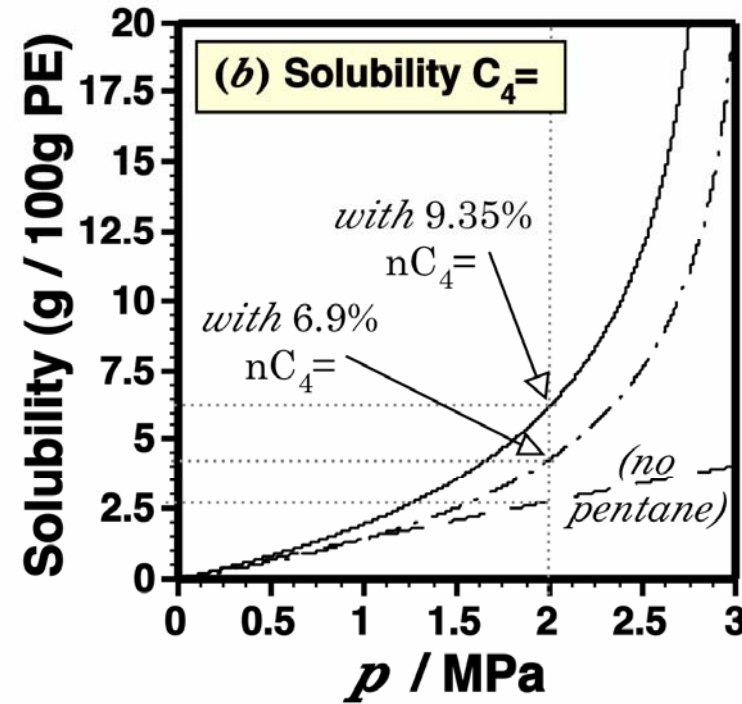
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Co-absorption of gases in PE during manufacture by GPR

PE, $nC_2=$, $nC_4=$ + N_2



PE, $nC_2=$, $nC_4=$ + (N_2 + nC_5)



Using SAFT-VR

predict enhanced solubility of $C_2=$ and $C_4=$ by replacing N_2 with C_5

Co-absorption of gases in PE during manufacture by GPR

Experiment	Activity [gPE gCAT ⁻¹ hr ⁻¹]	MW [g mol ⁻¹]	Percentage change
2 litre reactor but-1-ene co-monomer <i>Inert</i> : 13.4 bar Nitrogen	1908	12000	Reference
5.3 litre reactor but-1-ene co-monomer <i>Inert</i> : 13.4 bar Nitrogen	1929	10000	Reference
5.3 litre reactor but-1-ene co-monomer <i>Inert</i> : 3 bar Pentane, 10.4 bar Nitrogen	2547	11000	32 % increase

Successful **prediction** of solubility (“absorption”) in a macromolecular system **based on thermodynamic phase equilibrium**.

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Asphaltene models

- Models of asphaltene fluids

Asphaltene and Resin Molecules in Crude Oils

Energy & Fuels, Vol. 20, No. 1, 2006 329

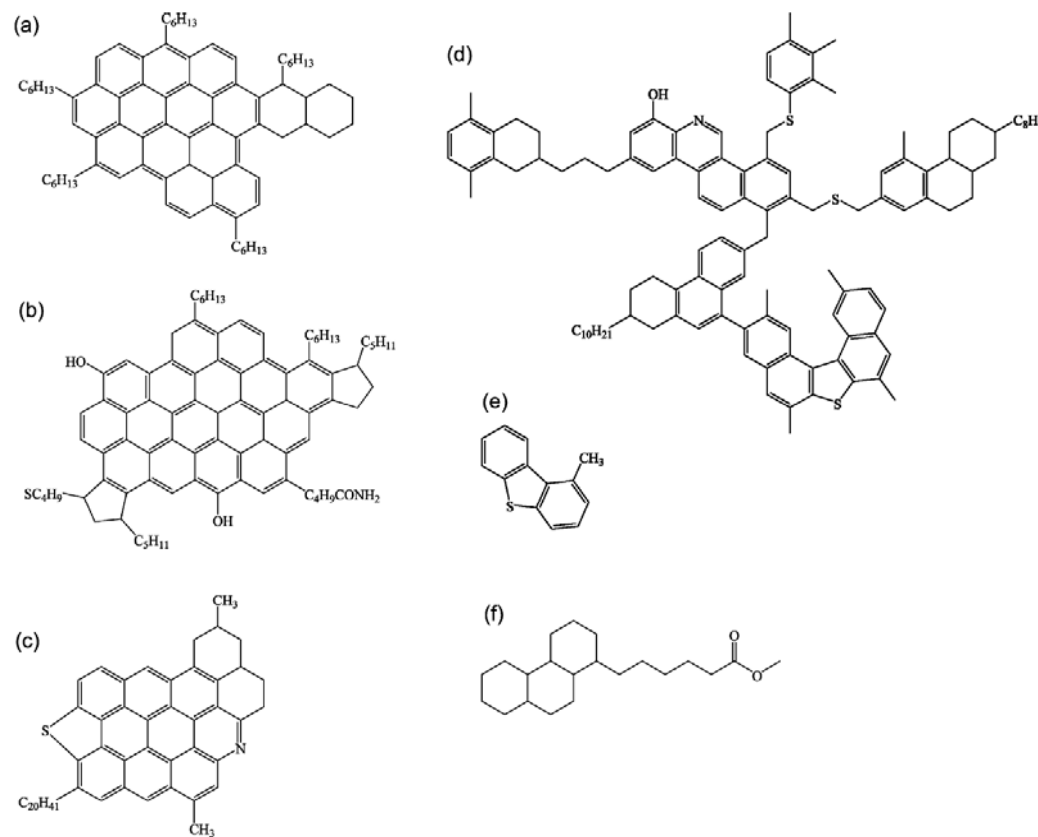


Figure 1. Planar (2D) structures of model asphaltenes and resins. (a) Model BC5,²¹ stable continental asphaltene from a Venezuelan crude oil. MW: 1003, formula: $C_{76}H_{60}$. (b) Model CO2,²¹ unstable continental asphaltene from a Venezuelan crude oil. MW 1208, formula: $C_{83}H_{62}NO_3S$. (c) Model asphaltene from a Mayan crude oil.³² MW: 794, formula: $C_{57}H_{43}NS$. (d) Model archipelago asphaltene.³³ MW 1653, formula: $C_{116}H_{133}NOS_3$. (e) Model resin from an Athabasca sand oil.¹⁸ MW 198, formula: $C_{13}H_{10}S$. (f) Model resin from an Athabasca sand oil.¹⁸ MW 320, formula: $C_{21}H_{36}O_2$.

Ashpaltenic systems with SAFT: pseudocomponents

- **Wu, Prausnitz and Firoozabadi (1998, 2000)**
 - Light gases treated as a medium through Hamaker constant
 - Asphaltenes modelled as spheres with association sites
 - System: asphaltene + resin in a medium

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- Beunrostro-Gonzalez *et al.* (2004)
 - Light gases treated as a medium through Hamaker constant
 - Asphaltenes modelled as chains with association sites
 - System: asphaltene + resin in a medium