



ESDU-SPD-M14-1

Sept.10: Thermodynamic modelling of asphaltene-oil systems using SAFT

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Sub-Project D: Thermodynamics and
molecular modelling

**Thermodynamic modelling
of asphaltene-oil systems
using SAFT**

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Outline

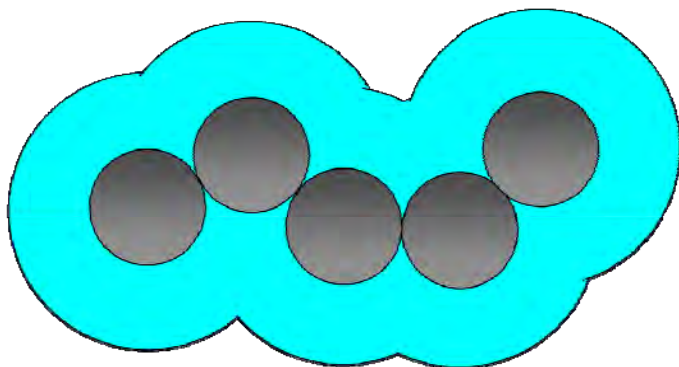
- SAFT-VR: brief reminder of relevant details
- Review of modelling within CROF project
 - relation of *asphaltene + oil* to *polymer + solvent* systems
 - PAM
- Relating asphaltene precipitation to familiar oil phase diagrams (bubble and dew curves)
 - new multicomponent-multiphase-flash algorithm
 - reinforces interpretation of precipitation as a liquid-liquid instability
- Progress in molecular simulation of asphaltenic systems

SAFT-VR equation of state

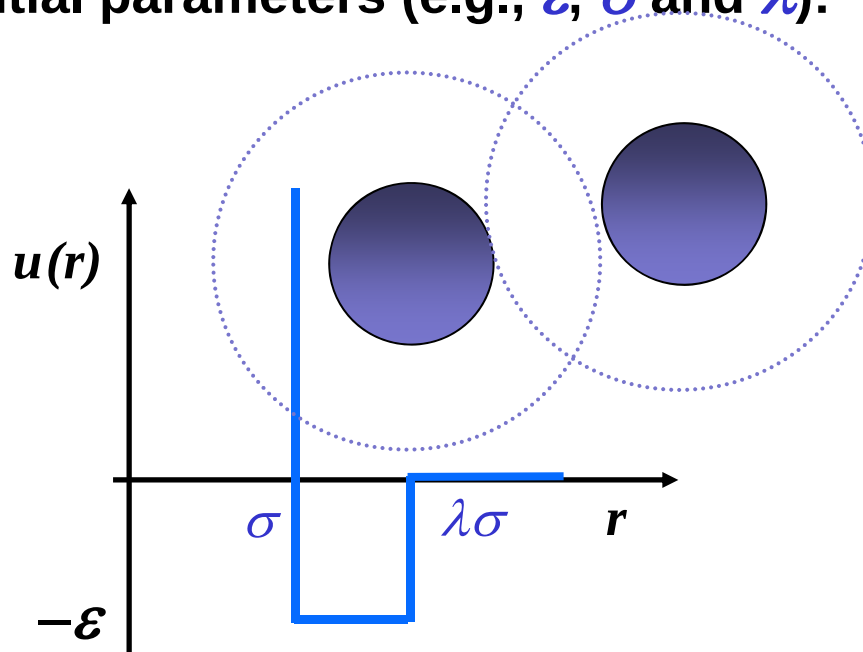
- Free-energy Equation of State

- from statistical thermodynamics $\Rightarrow$ *molecular based*
- free energy A is a function of m (#(chain segments)) and the intermolecular-potential parameters (e.g., ϵ , σ and λ):

“MW”



$m = 5$ (e.g., $C_{13}H_{28}$)

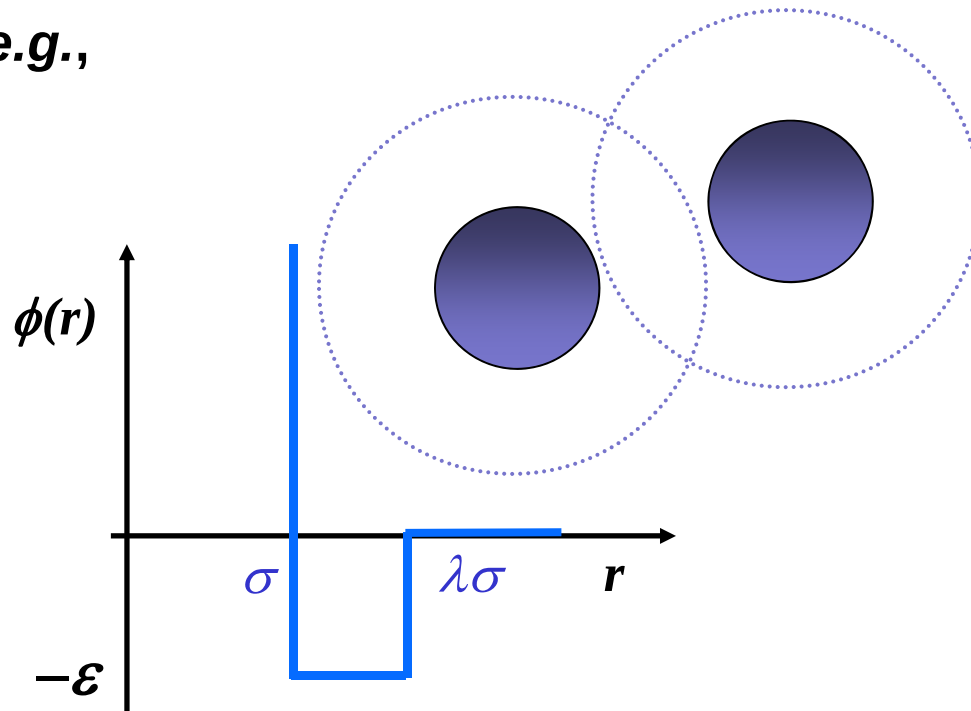


- e.g., $p = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$

Gil-Villegas *et al.*, *J. Chem. Phys.*, **106**, 4168 (1997).

Modelling real fluids

- Choose an intermolecular potential (the model):
e.g.,



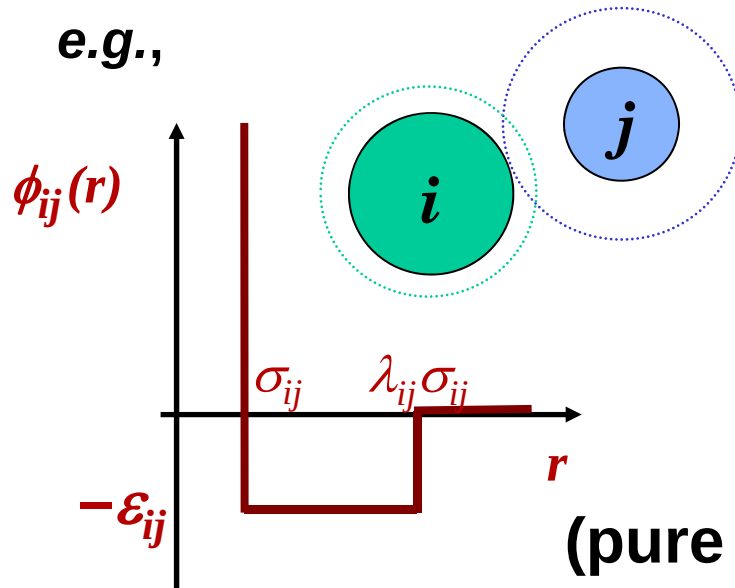
Potential parameters then define the fluid:

$$\epsilon; \lambda; \sigma; (m)$$

Modelling real fluids: mixtures

- Pure-component model predetermined
- Choose an intermolecular potential (the model):
 - almost invariably of same form as pure-component potential

e.g.,



Potential parameters
(pure and **mixture**) then define the fluid:

$$\sigma_i; \varepsilon_i; \lambda_i; (m_i); \sigma_j; \varepsilon_j; \lambda_j; (m_j); \sigma_{ij}; \varepsilon_{ij}; \lambda_{ij}$$

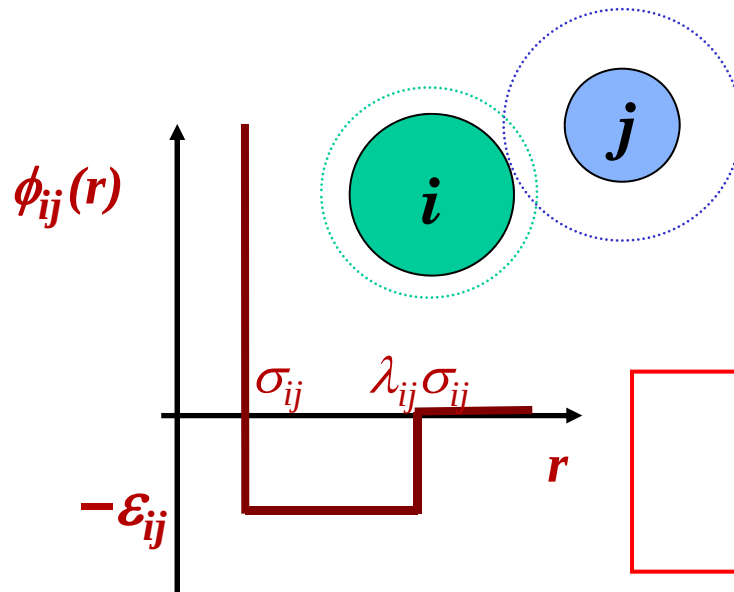
Modelling real fluids: mixtures

- Assume Lorentz rule for σ_{ij} :
$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$$

- Obtain ε_{ij} ; λ_{ij}
 - Expressed as k_{ij} and l_{ij} , where:

$$\varepsilon_{ij} = (1 - k_{ij}) \sqrt{\varepsilon_i \varepsilon_j}$$

$$\lambda_{ij} = (1 - l_{ij}) \frac{(\lambda_i \sigma_i + \lambda_j \sigma_j)}{(\sigma_i + \sigma_j)}$$



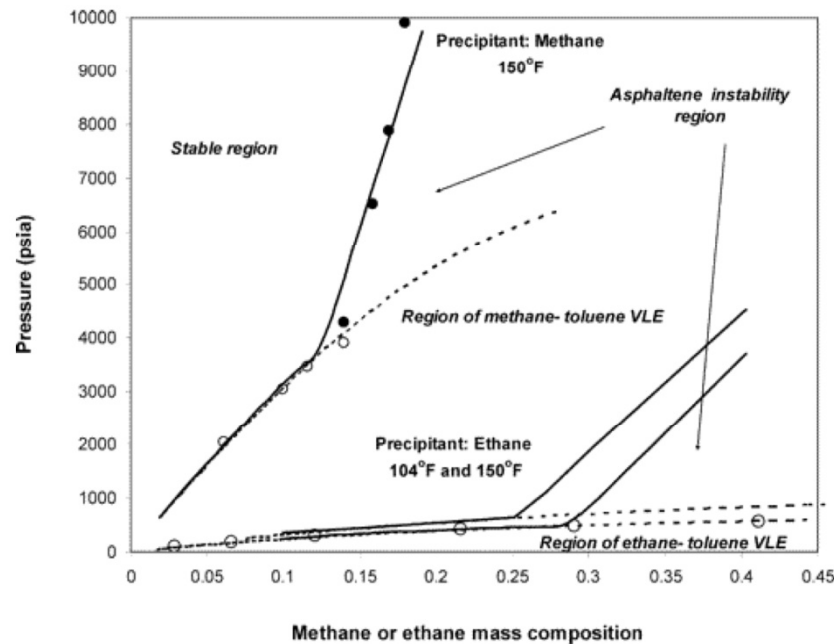
k_{ij} from theoretically derived combining rules

Thrust of our modelling

- **Analogy between phase equilibria of solvent / gas + polymer and heavy-crude-oil phase behaviour**
 - instability on raising or lowering temperature
 - instability on addition of light component (e.g., low alkane or CO₂)
- **Phase diagrams of the same form ...**

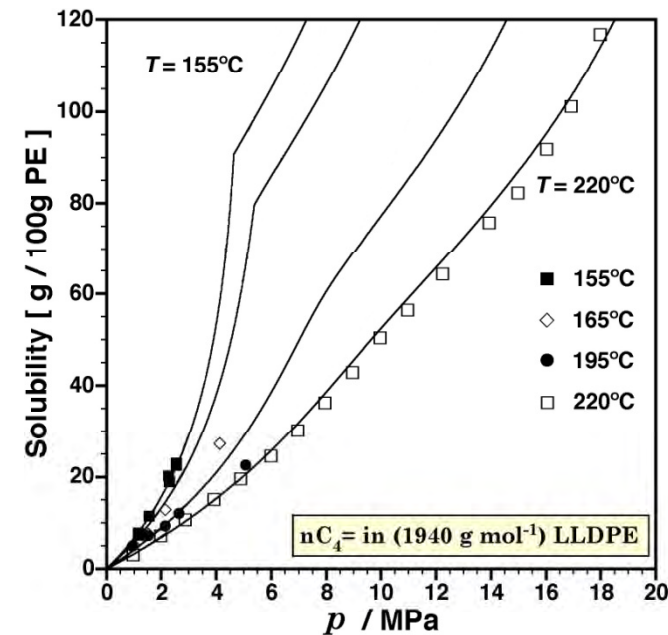
Asphaltene + oil (“alkane”) cf Polymer + solvent

Precipitation of asphaltene by methane or ethane



Ting, Chapman *et al.*

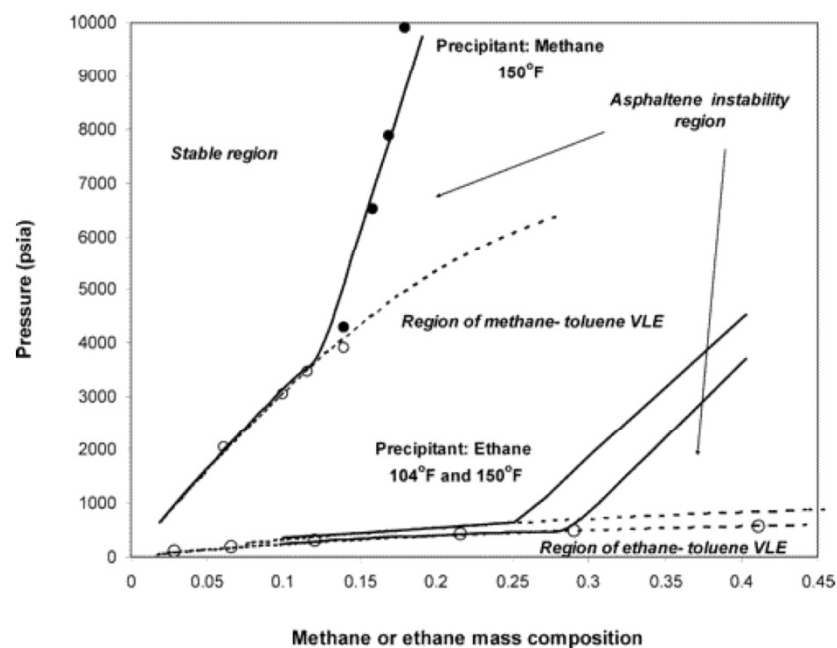
Solubility of butene in polyethylene



Butene + polyethylene,
 Haslam *et al.* (2006)

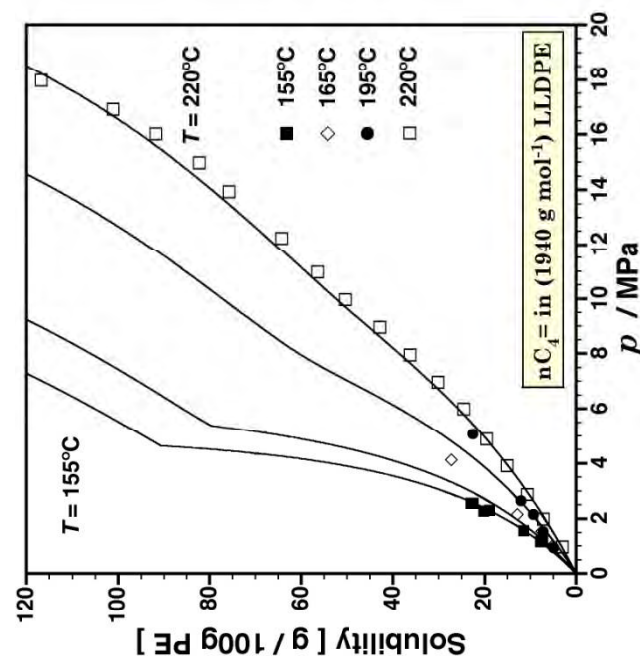
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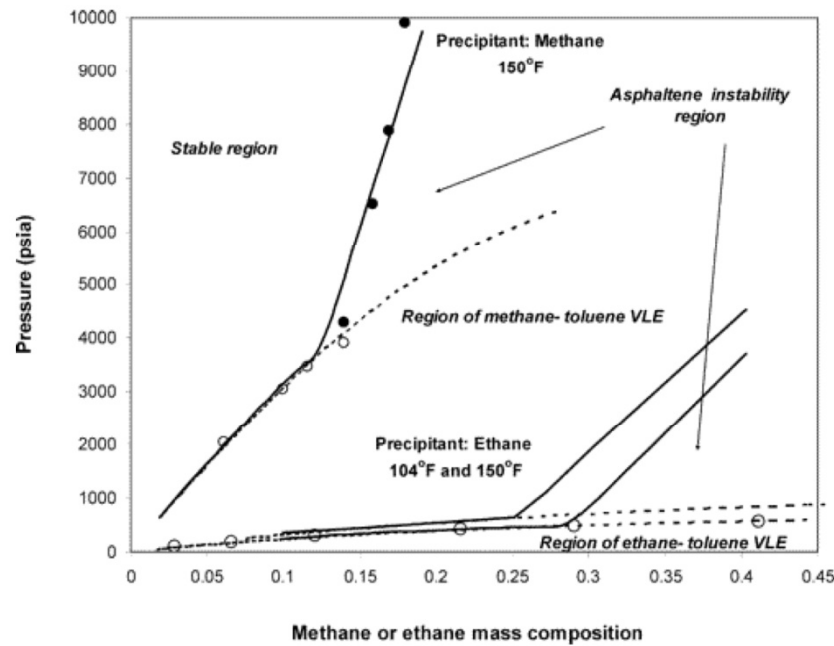
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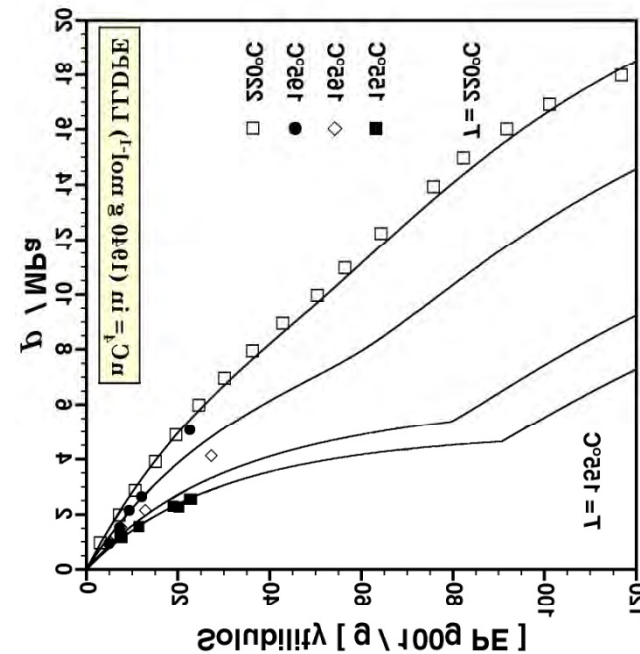
Asphaltene + oil cf Polymer + solvent

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Ting, Chapman *et al.*

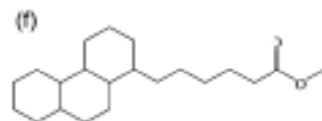
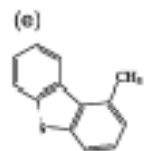
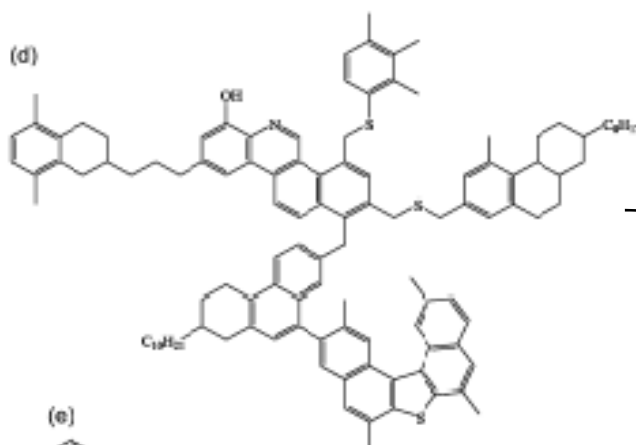
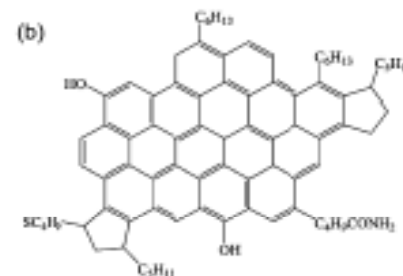
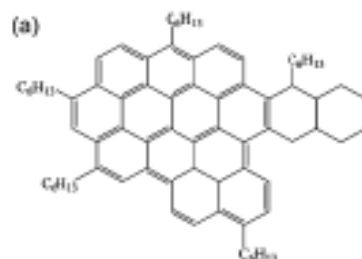
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Fundamentally a “small molecule” + polymer phase equilibrium

- **Models of asphaltene fluids**



***cf* polystyrene:**

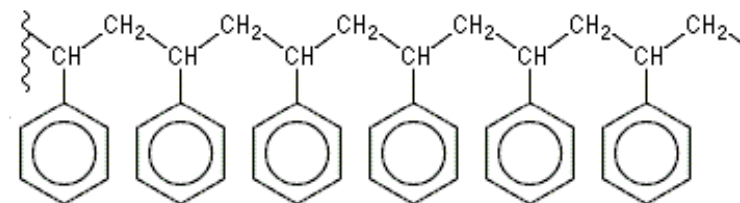
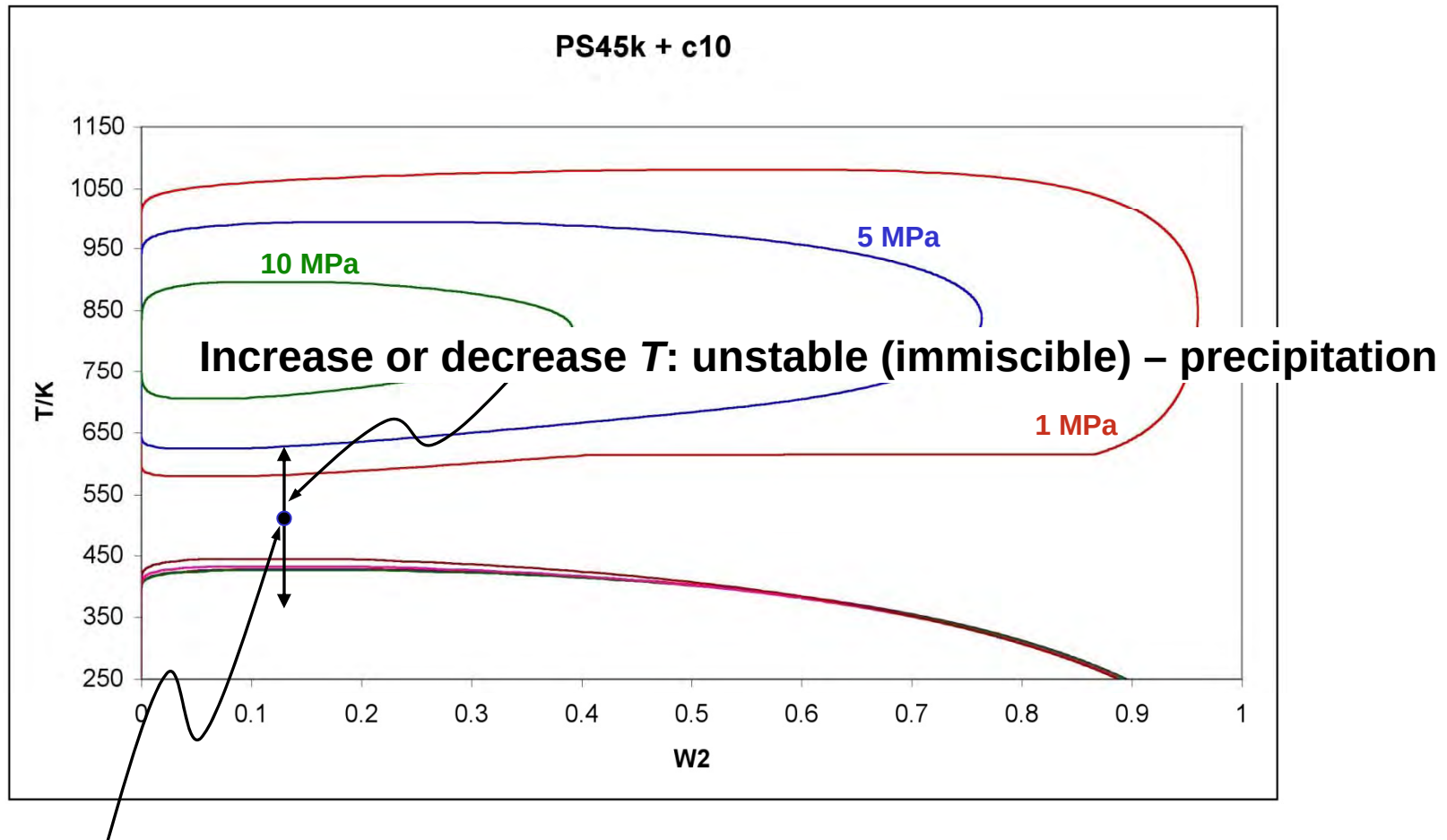


Figure 1. Planar (2D) structures of model asphalters and resins. (a) Model BC5,² stable continental asphaltene from a Venezuelan crude oil. MW: 1003, formula: $C_{50}H_{16}$. (b) Model CO2,²¹ unstable continental asphaltene from a Venezuelan crude oil. MW 1208, formula: $C_{50}H_{12}NO_{1.5}$. (c) Model asphaltene from a Mayan crude oil.²² MW: 794, formula: $C_{37}H_{10}NS$. (d) Model archipelago asphaltene.²³ MW 1653, formula: $C_{118}H_{31}NOS_2$. (e) Model resin from an Athabasca sand oil.¹⁹ MW 194, formula: $C_{17}H_{14}S$. (f) Model resin from an Athabasca sand oil.¹⁹ MW 320, formula: $C_{15}H_{14}O$.

PAM

- **Model asphaltenes as polystyrene**
 - model $(\varepsilon, \lambda, \sigma, m)$ a simple function of molecular weight
 - understand how to model PS + alkane (oil)
 - successful description of PS + alkane phase equilibria
 - Kao *et al* (2009)
- **Polystyrene-Asphaltene Mapping**
 - polystyrene “equivalent” to a given asphaltene

Polystyrene + decane



Stable (miscible) region – no precipitation