

# Computer Simulations of Asphalts

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# Models = Simulation or Theory or Correlation

## *Simulation*

- **Choose** actors (here = molecules) + behavior rules + updates  
$$\mathbf{F} = m\mathbf{a}, \quad \mathbf{F} = -\nabla V(\mathbf{x}), \quad \delta t = 10^{-15}\text{s} = 1 \text{ fs}$$
- **Calculate** and **analyze** to see what emerges

## *Theory*

- **Identify** physical processes of importance
- **Derive** and **simplify** equations governing the processes
- **Graph** final results, sometimes analytical solution

## *Correlation*

- **Conduct** experiments on many systems, compare results
- **Develop** / “fit” equations that interrelate exptl results
- **Apply** equations to other systems

	simulation	theory	correlation
underlying physics and chemistry	very detailed	simplified to detailed	sometimes simplified; sometimes unrelated
computational requirements	high to very high	medium to low	very low
extrapolation	additional simulations likely required	excellent if physics is unchanged	risky if not based on underlying physics

# What can molecular simulations say about asphalt?

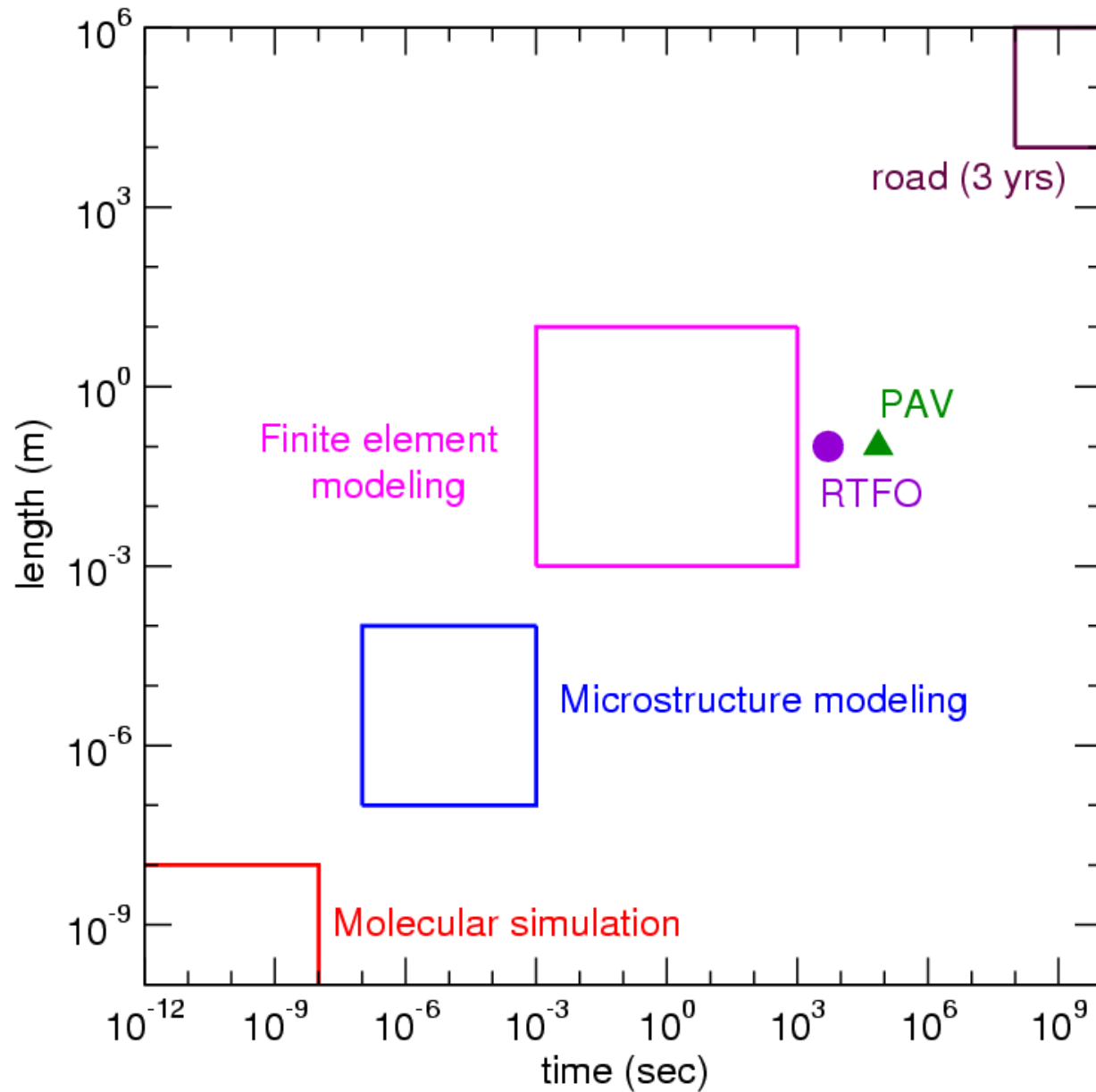
## *“How do I” questions:*

- What are the limits of asphalt simulations?
- What properties/characteristics emerge directly?
- What needs to be known in advance /  
What does simulating molecules mean?

## *“What if” questions:*

- What simple mixtures express physical properties similar to asphalts?
- How do molecules arrange within asphalts?
- What changes do asphalt modifications lead to on the molecular level?
- How do molecules impact high temperature rheology?  
Low temperature shear modulus?

# Molecular simulation length and time scales



# Molecular simulation length scales

Surface Morphology of SHRP Asphalts by AFM  
Troy Pauli and W. Grimes, *ACS Petrol Div Preprint*, spring 2003

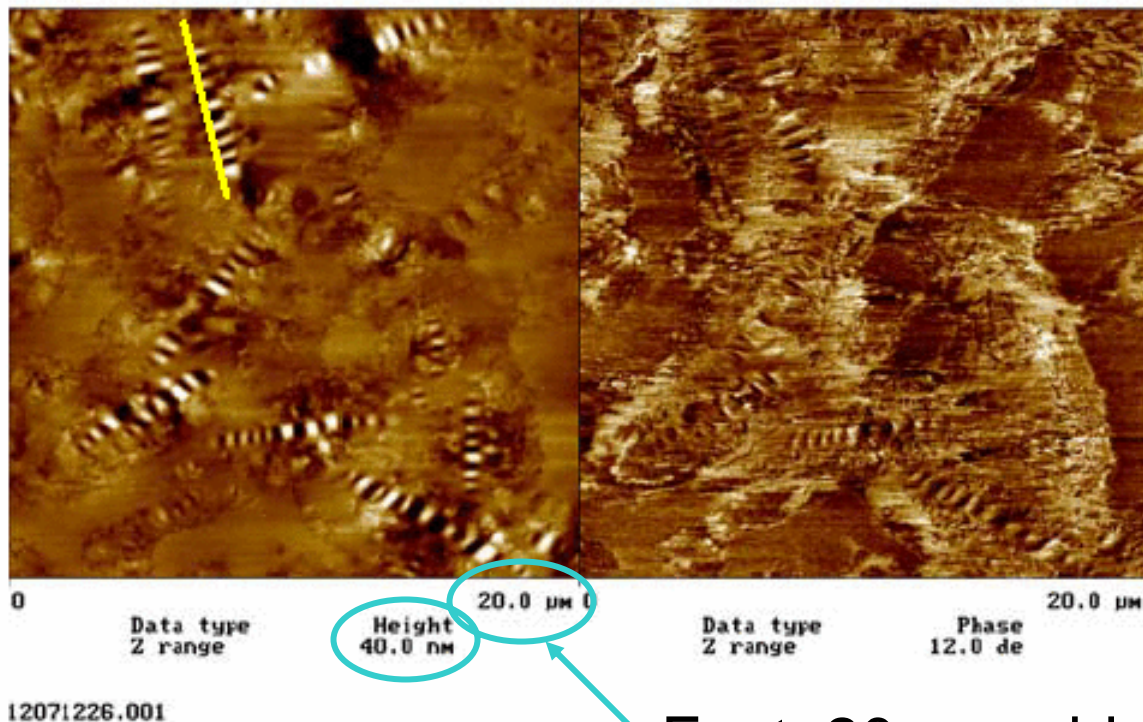
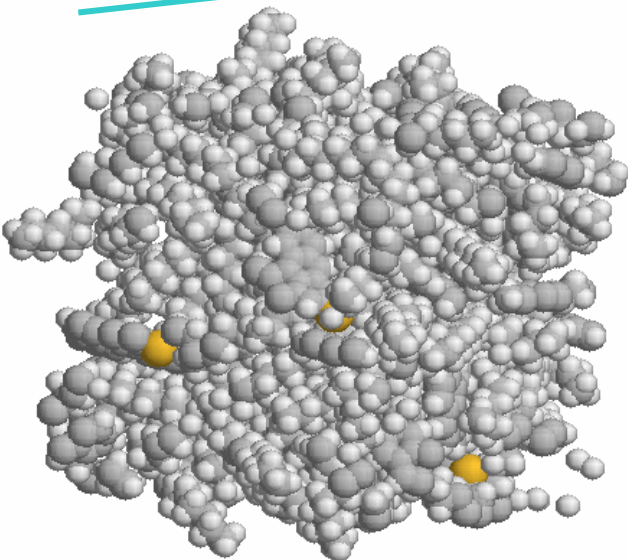
Simulation:

5-10 nm

= 1% of 1  $\mu\text{m}$

=  $\text{--}$  x .01

4 nm




Expt: 20  $\mu\text{m}$  wide

**Figure 3.** Height and phase image of a solvent cast "10  $\mu\text{m}$  thick-film" sample of SHRP core asphalt AAK-1; 20  $\mu\text{m}$  scan area, z-range of 40 nm and phase angle of 12 $^\circ$ .

# Molecular simulation length scales

Confocal laser-scanning microscopy of bitumens with asphaltene aggregates

Bearsley, Forbes, Haverkamp, *J. Microscopy*, **215** pt 2: 149-155 (2004)

**Simulation:** 5-10 nm = 0.1% of 10  $\mu\text{m}$  =  x .001

Expt:  
10  $\mu\text{m}$

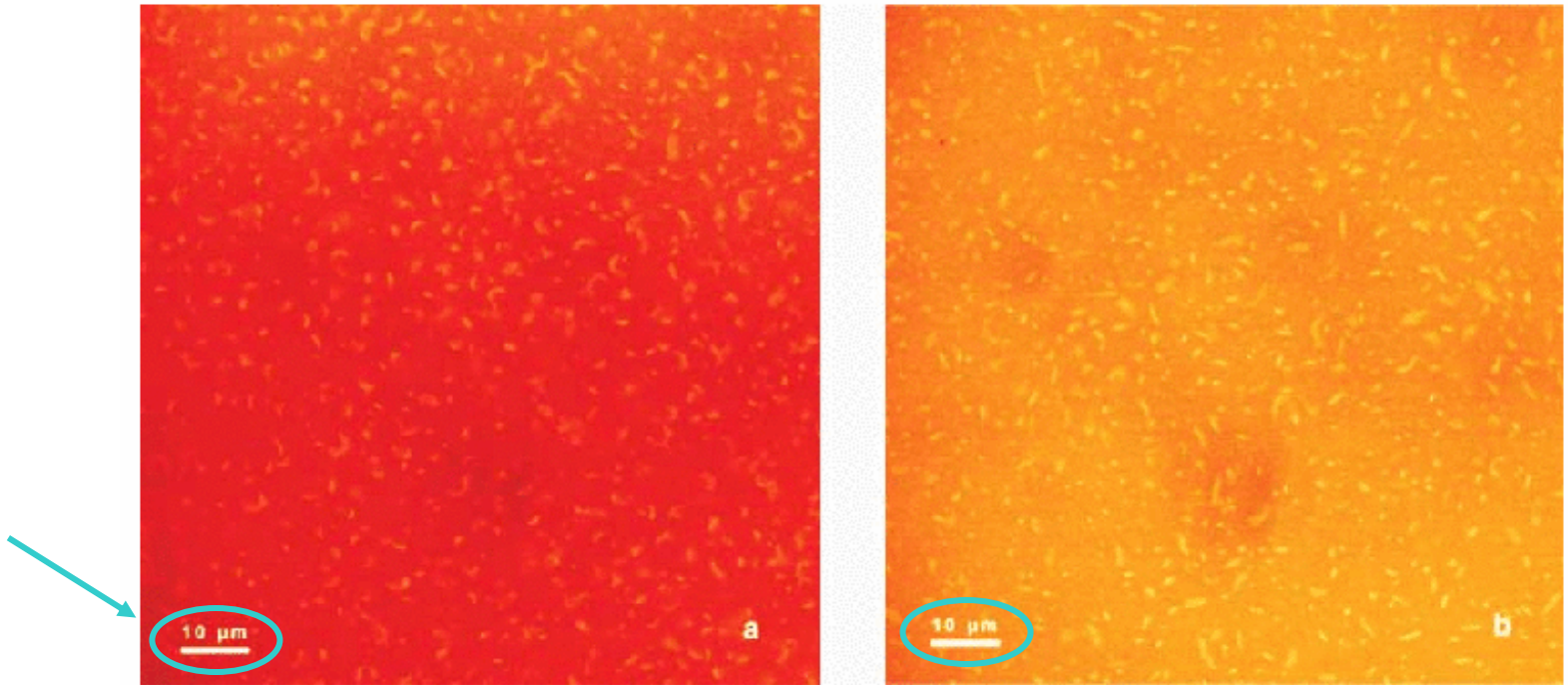


Fig. 1. CLSM image of Safaniya (a) 180/200 and (b) 80/100 bitumen. The light coloured flecks are thought to be asphaltene aggregates dispersed in a darker maltene matrix. The asphaltene aggregates are typically 2–7  $\mu\text{m}$  in size.

# Physical Properties from simulation

- thermodynamic properties
  - equilibrium avgs and fluctuations*
  - density
  - heat capacity
  - expansion coefficient
  - isothermal compressibility
- molecular properties
  - single molecule configurations
  - correlations and orientations between molecules
- transport properties
  - time correlation functions*
  - diffusion coefficient
  - stress relaxation modulus
  - viscosity
  - (frequency-dependent modulus)
  - mean-squared displacement
  - stress fluctuations

total time limited to 10 to 100 ns

average correlation times < total

# Components of Asphalt

Characterization: solvent precipitation, chromatography

**resins, oils** (polar aromatics, naphthene aromatics, ...)

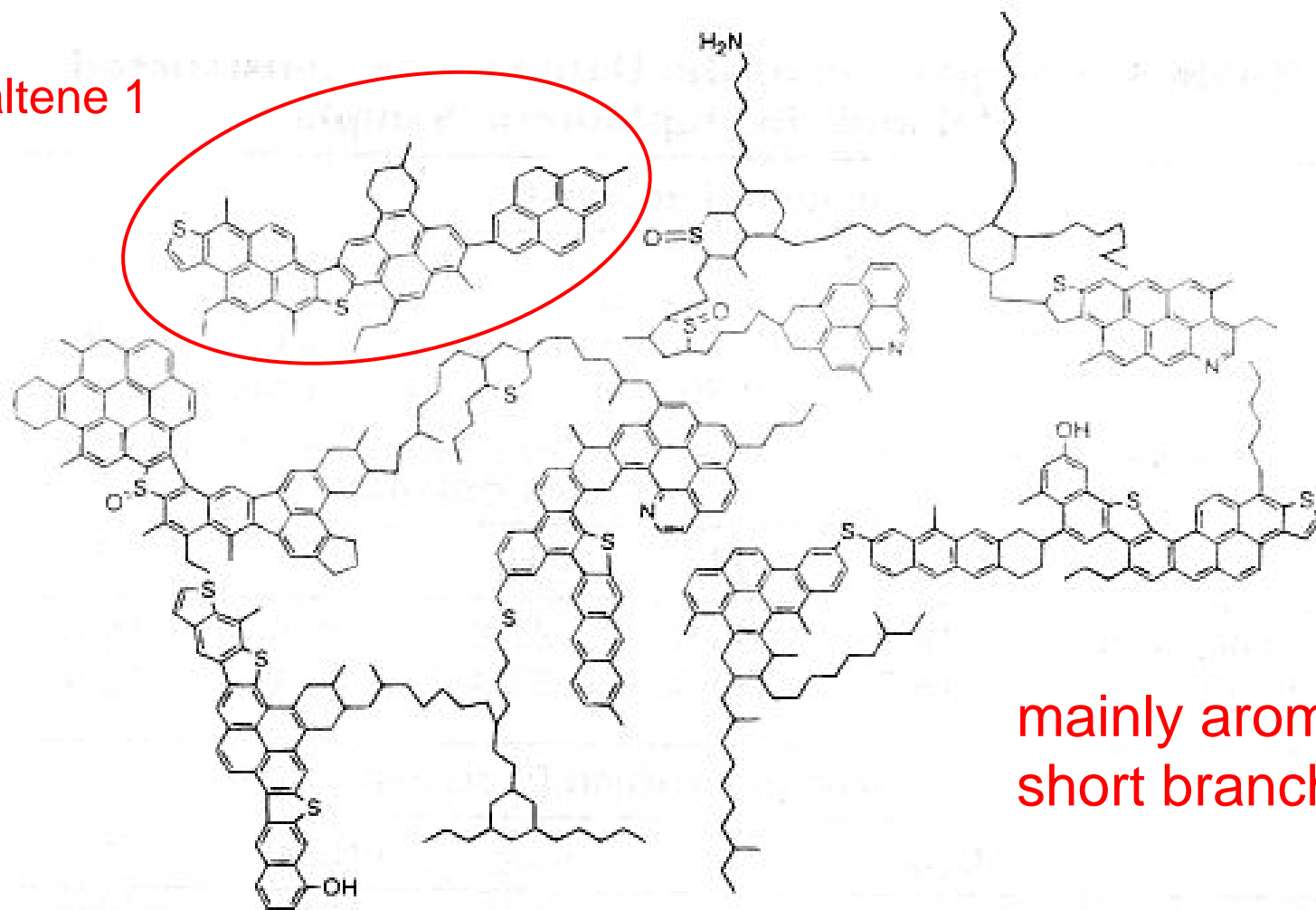
- less viscous than crude oil
- mainly small to moderate size molecules
- polar (resins) or nonpolar (oils) 1,7-dimethylnaphthalene  
n-C<sub>22</sub>  
(straight chain alkane)

**asphaltene**

- heaviest and most aromatic component
- insoluble in n-heptane, soluble in toluene
- Use representative asphaltene molecules

# Some proposed asphaltene molecular structures

asphaltene 1

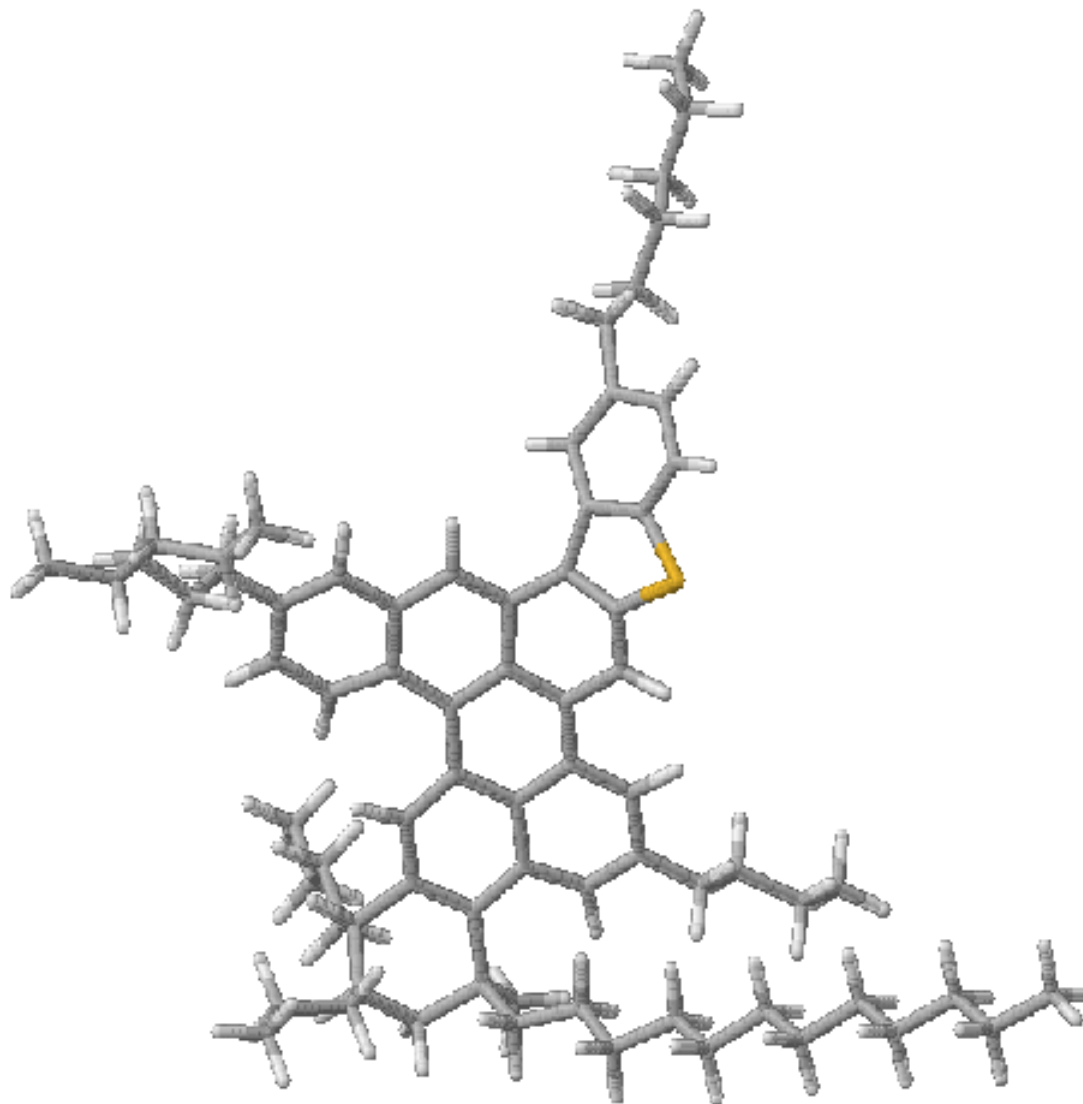


mainly aromatic,  
short branches

**Figure 8.** Chemical structural model for the asphaltene.

asphaltene 2

Groenzin and Mullins; *Energy & Fuels* 14: 677-684 (2000)



anes from  
:ore

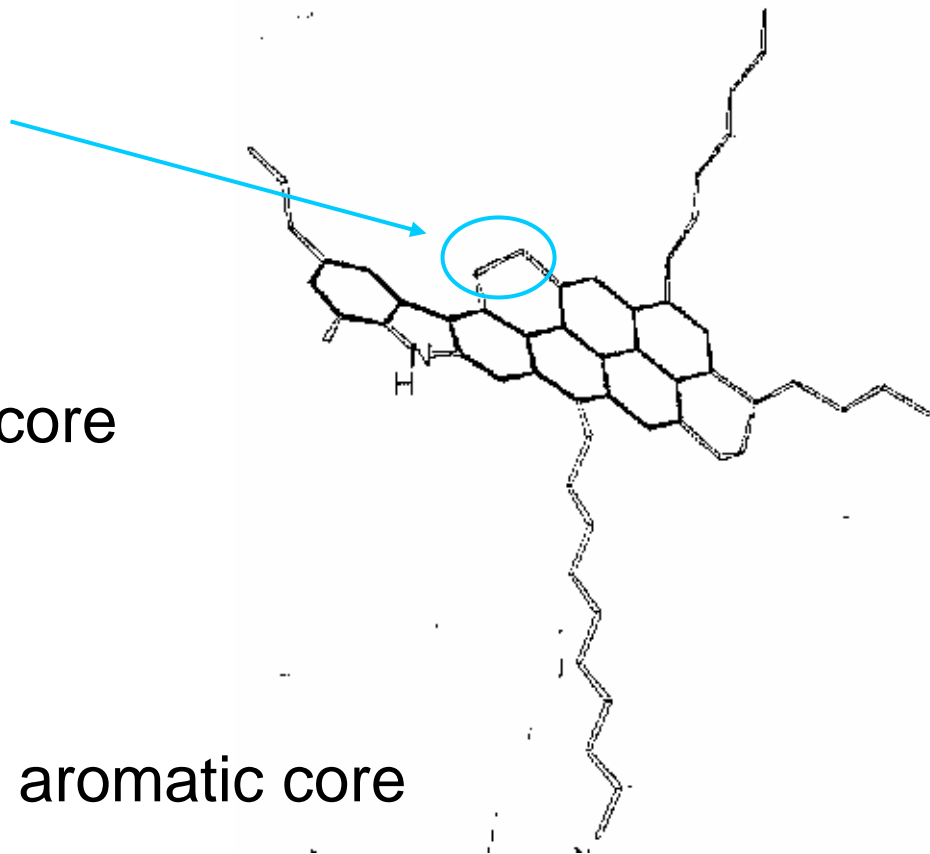
**asphaltene 3** Groenzin and Mullins; *Energy & Fuels* **14**: 677-684 (2000)

Unrealistic chemistry for  
2 alkane carbons in a ring

- bond lengths and angles lead to high ring strain and buckling of aromatic core

Nitrogen functionality

Long branches from single aromatic core



# Initial Model Asphalts

- asphaltene 1 / 1,7-dimethylnaphthalene / n-C<sub>22</sub>
  - asphaltene 2 / 1,7-dimethylnaphthalene / n-C<sub>22</sub>
- 21 wt%
20 wt %
59 wt %
- ↑
↑
↑
- no resin!

too much!

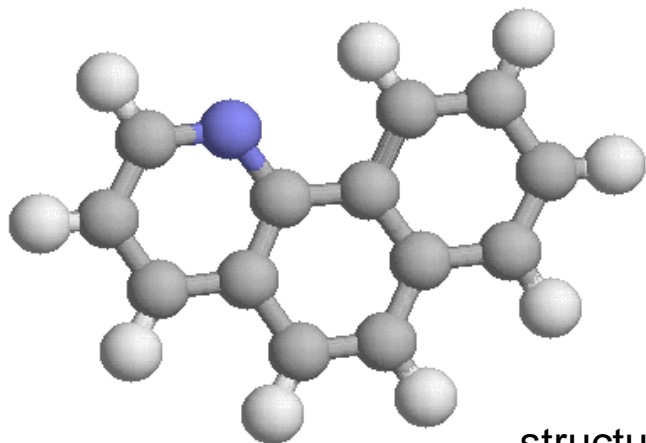
mole percents of aromatic vs alkane C, H in oil, resins, asphaltene are somewhat consistent with literature  
 e.g. Storm, Edwards, DeCanio, Sheu; *Energy & Fuels* **8**: 561-566 (1994)

Expt:      **Ratawi**                      **Alaska North Slope**

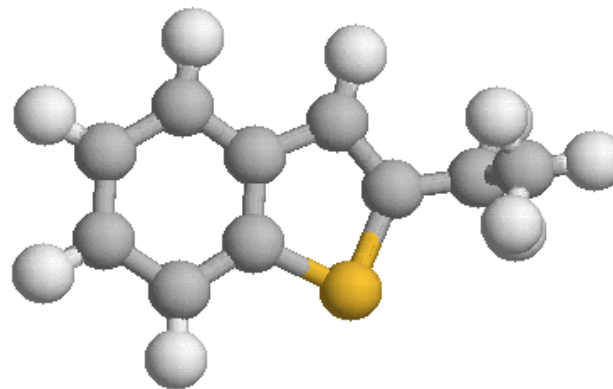
	oil	resins	asphaltenes		oil	resins	asphaltenes
H/C	1.6	1.53	1.22		1.6	1.4	1.4
C(AR)	27.8	41.3	58.1		27.9	42.7	42.7
C(AL)	72.2	58.7	41.9		72.1	57.3	57.3
H(AR)	7.3	10.6	13.7		6.6	10.8	10.8

# Resin-like Molecules

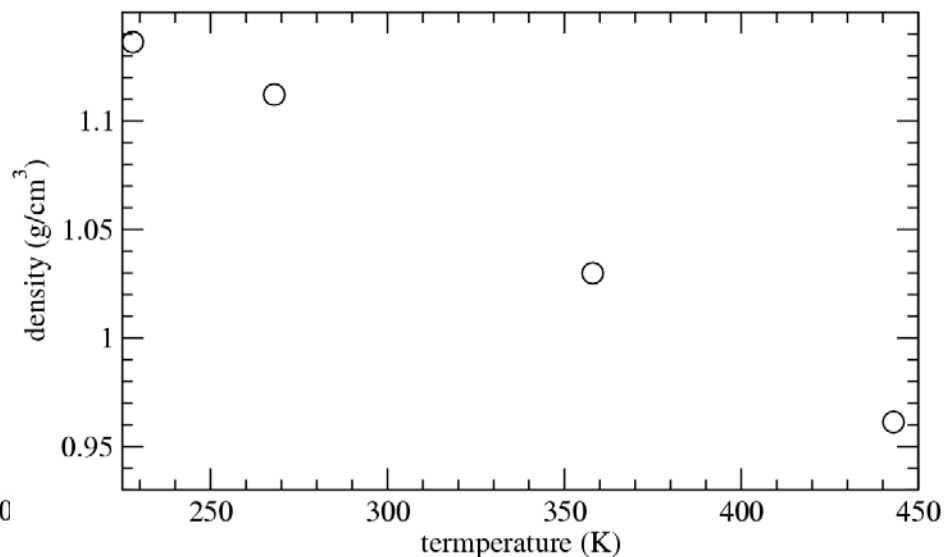
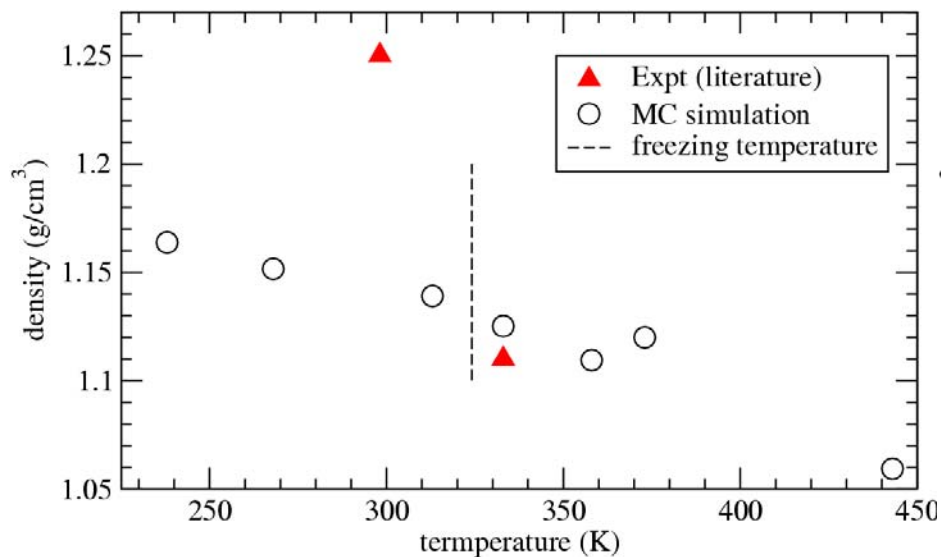
## 7,8-benzoquinoline



## ethylbenzothiophene



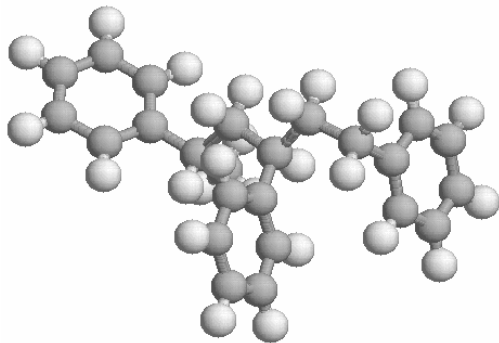
structures from J.-F. Masson and M. A. Lacasse,  
RILEM, 259-274 (2000)



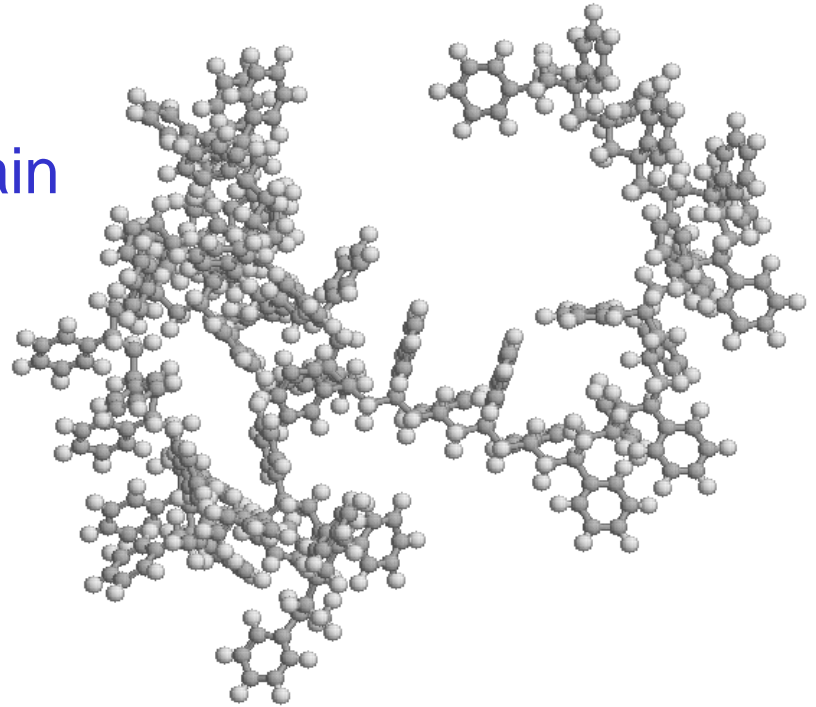
# Polymer Modification

- Real modifier = SBS (linear, branched, ...)
- Simulation: add 1 polystyrene chain
  - 50 repeat units, 805 atoms, **M=5200 g/mol**
  - 5 asphaltene 2, 30 1,7-dimethylnaphthalene, 45 n-C<sub>22</sub>
  - mass fraction PS = 18%

trimer



50-mer chain



molecules present  
in system

Prediction of  
macroscopic  
properties

MD:  $F = ma$ ,  $\delta t = 10^{-15}$  s

**Molecular  
Simulation**  
 $t \sim \text{ns} - \mu\text{s}$   
 $L \sim \text{nm}$

*post-  
process*

packing among chains  
local order / disorder  
local correlations  
occupied vs unoccupied  
("free") volume

MC: prob'ty  $\sim \exp(-\mathcal{H}/k_B T)$

*QM +  
force  
fields*

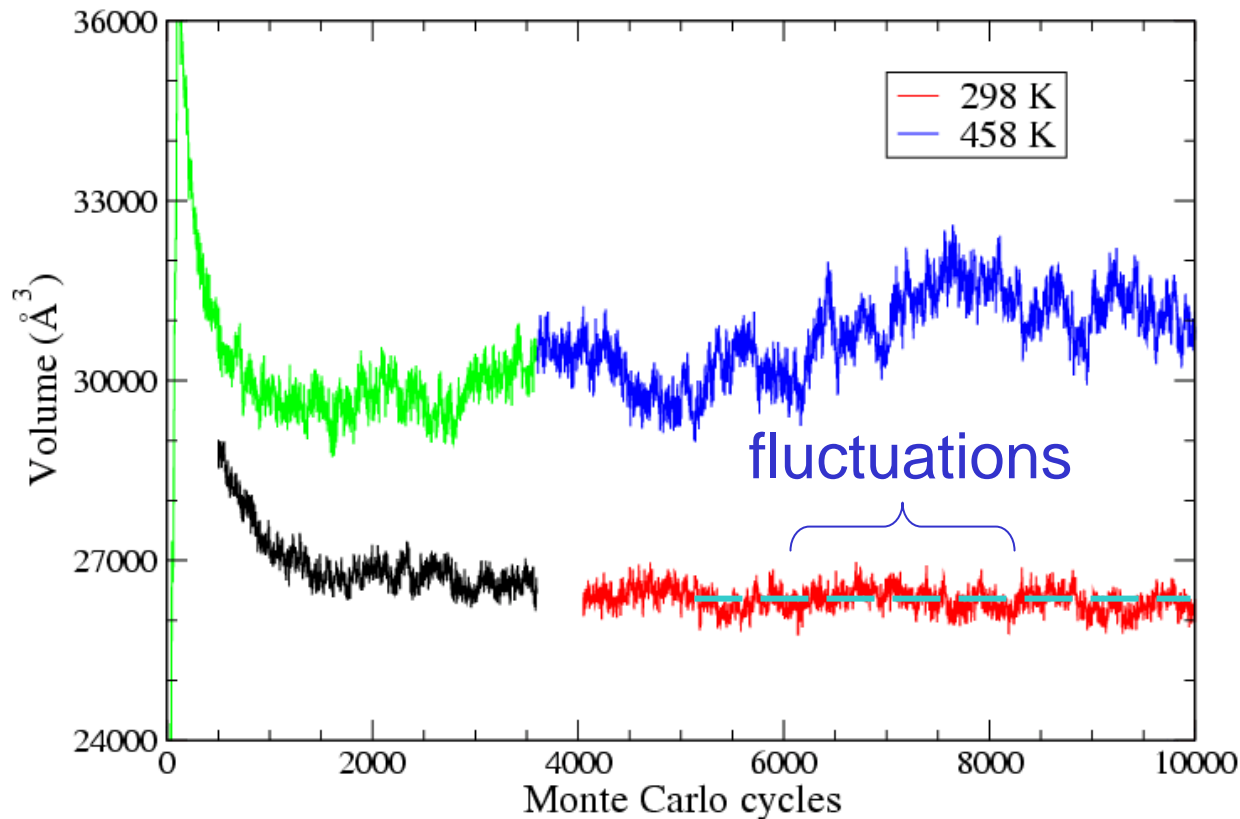
**Classical** forces  
between molecules

Interpretation of  
experiments

# How does molecular simulation provide results?

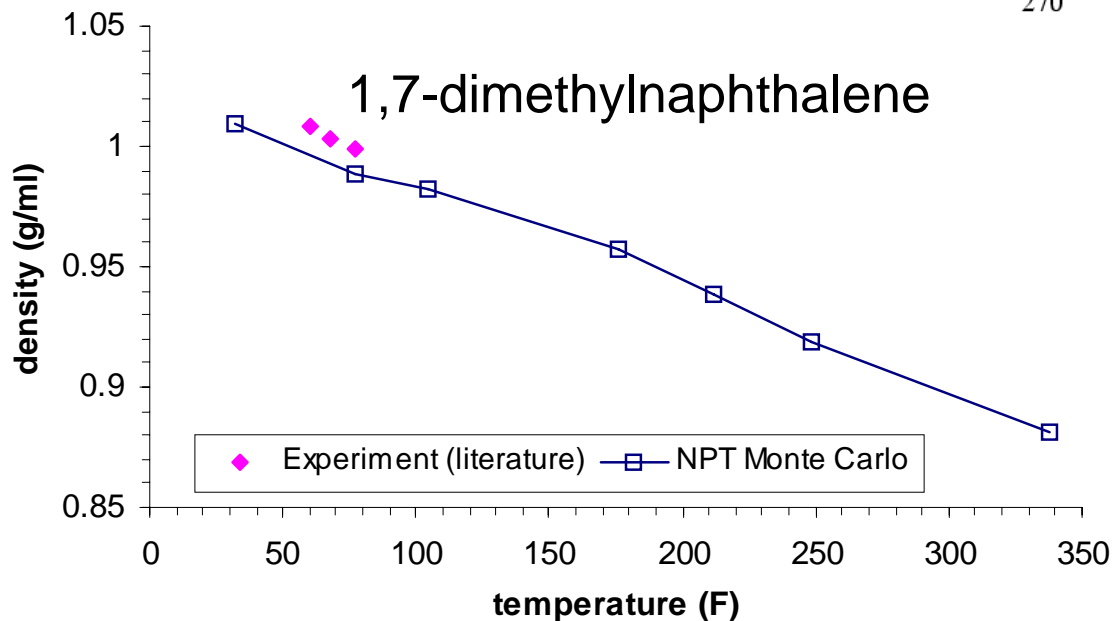
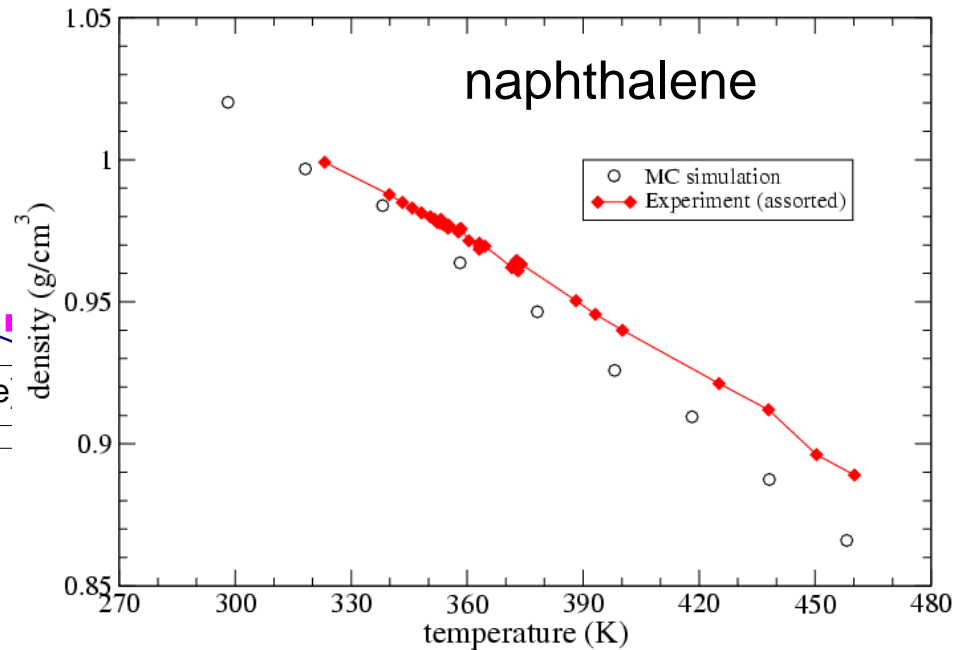
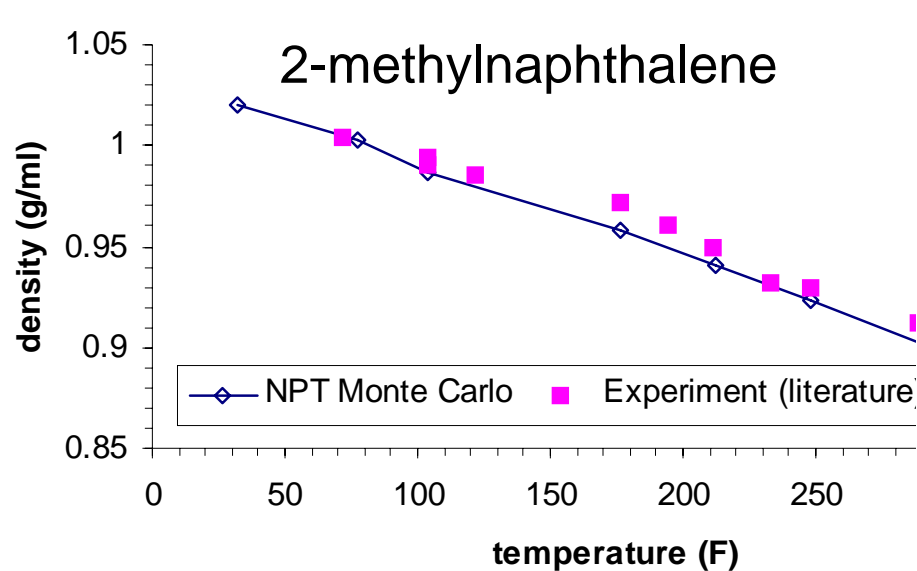
$$\langle \text{physical property} \rangle = \frac{\int X \exp(-\mathcal{H} / k_B T) d\mathbf{x} d\mathbf{p}}{\int \exp(-\mathcal{H} / k_B T) d\mathbf{x} d\mathbf{p}}$$

**ratio** = probability of one state = fraction of time



Example:  
naphthalene  
(as liquid)

# OPLS-aa force field: good results for small molecules



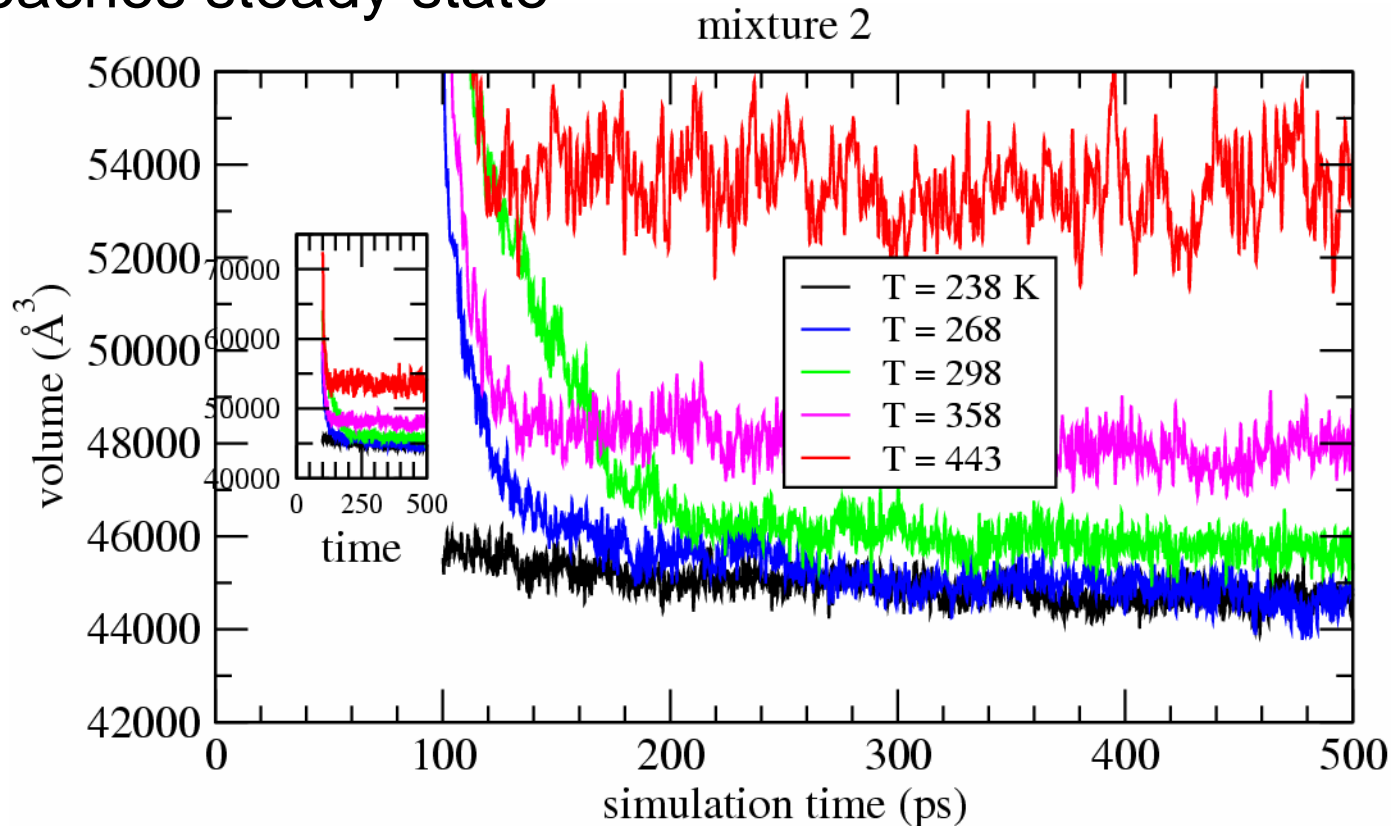
# Simulation evolution

Monte Carlo:

unsuccessful volume equilibration

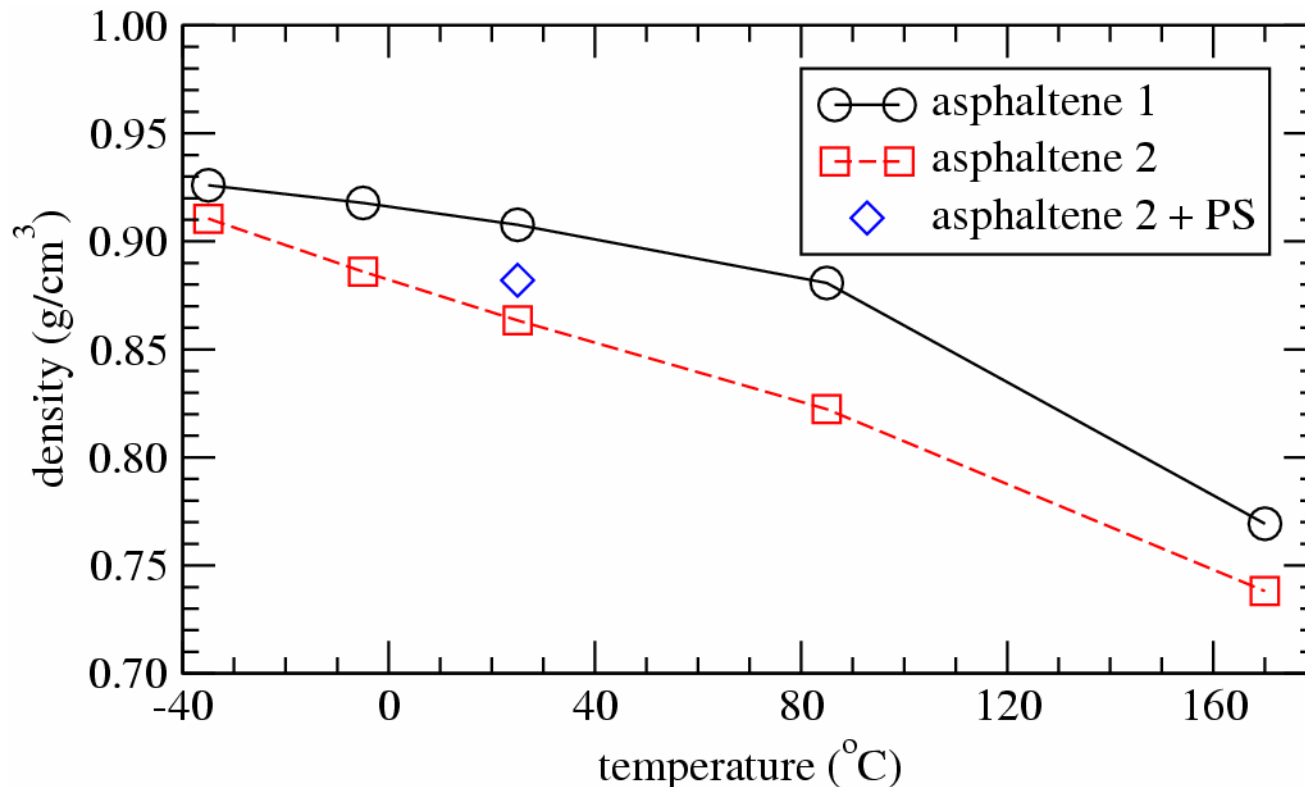
Molecular dynamics:

reaches steady state



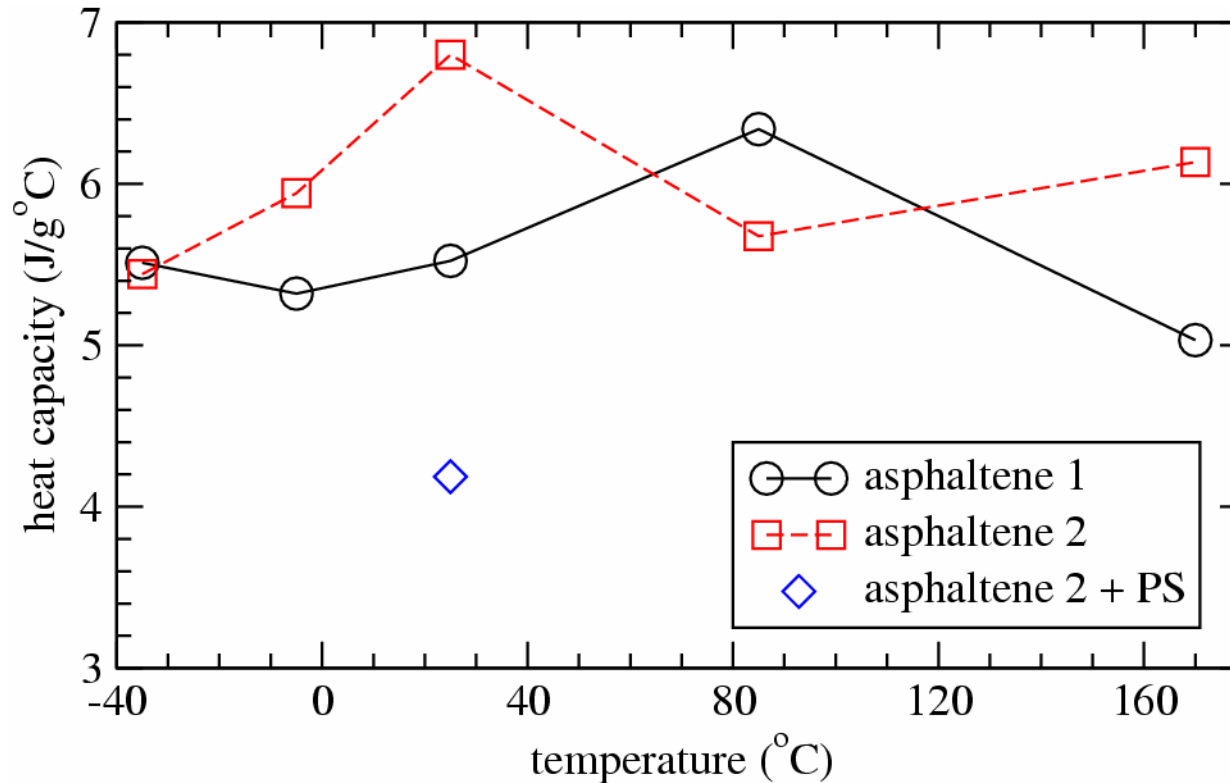
# Mixture density results

- density somewhat below 1 g/cm<sup>3</sup>
  - too much saturate, not enough aromatic
- break in slope (glass transition) at higher temperatures than expected



# mixture heat capacity

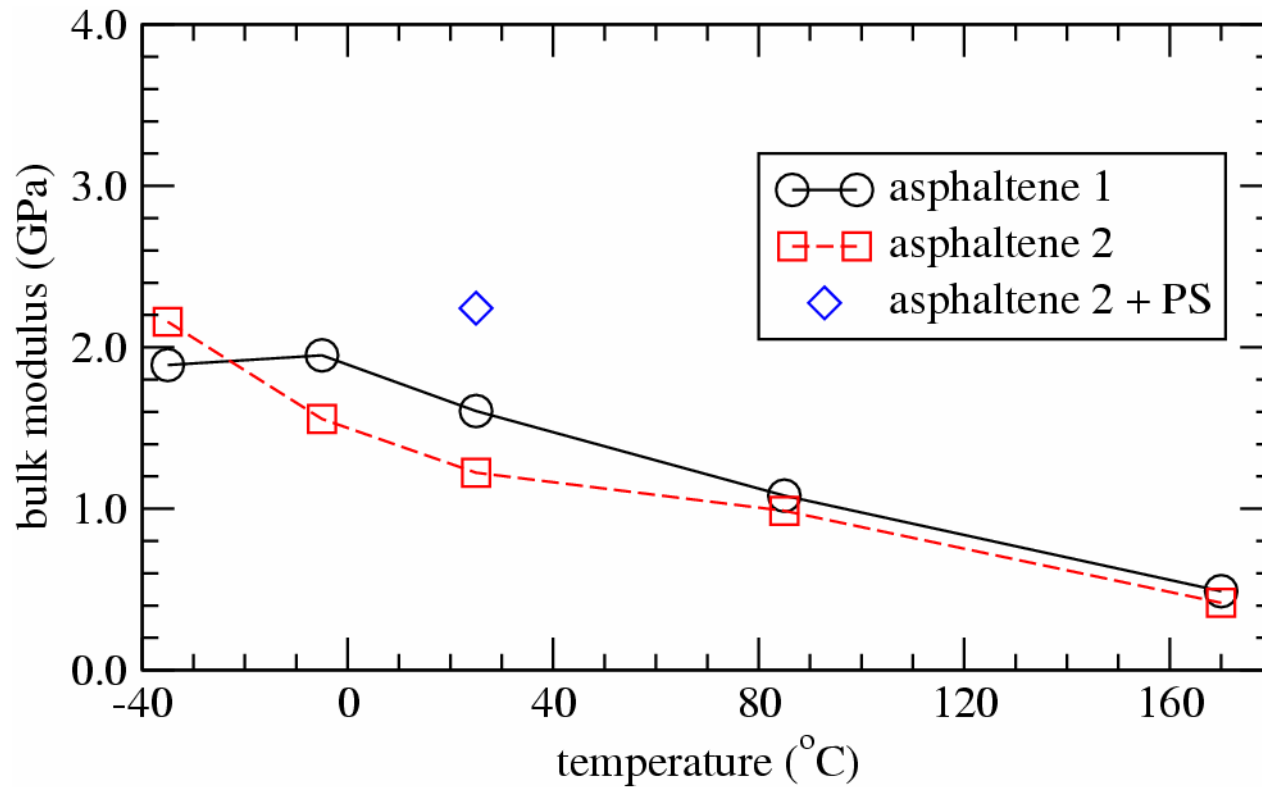
- additional averaging required
- difficult to distinguish step change (glass transition) from scatter



# bulk modulus

$$B = 1/\beta = 1/V (dV/dP)_T$$

Expect step change at glass transition

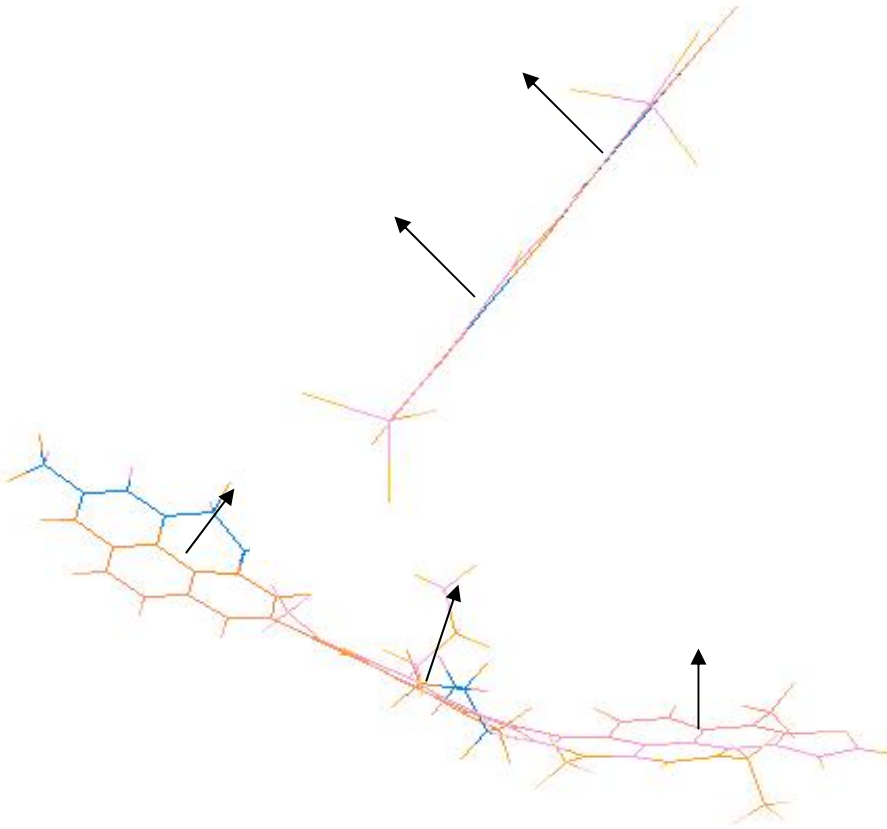


# Orientations of Molecules in Asphalt

- How are asphalt molecules packed together?

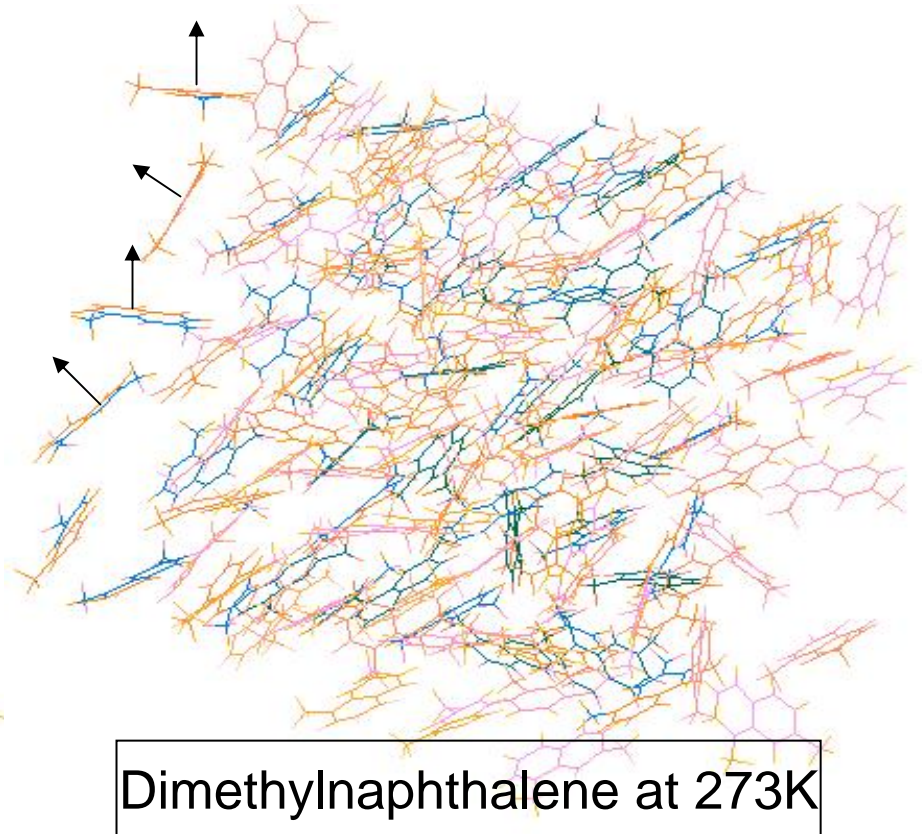
*Intra-molecular* orientation

- angle between two rings

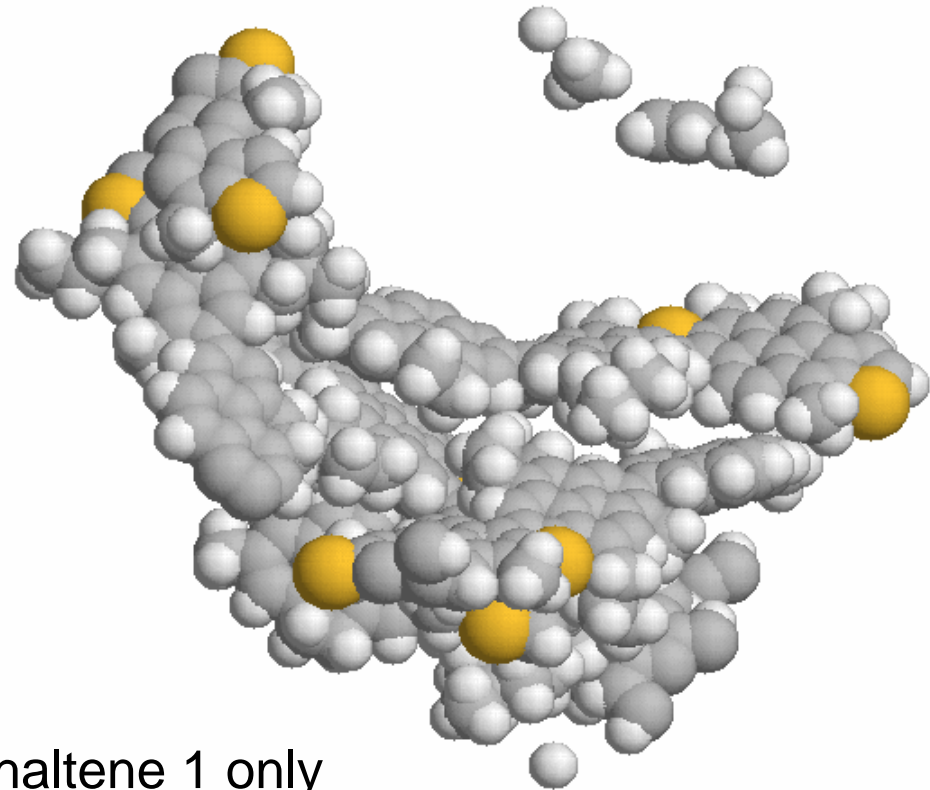
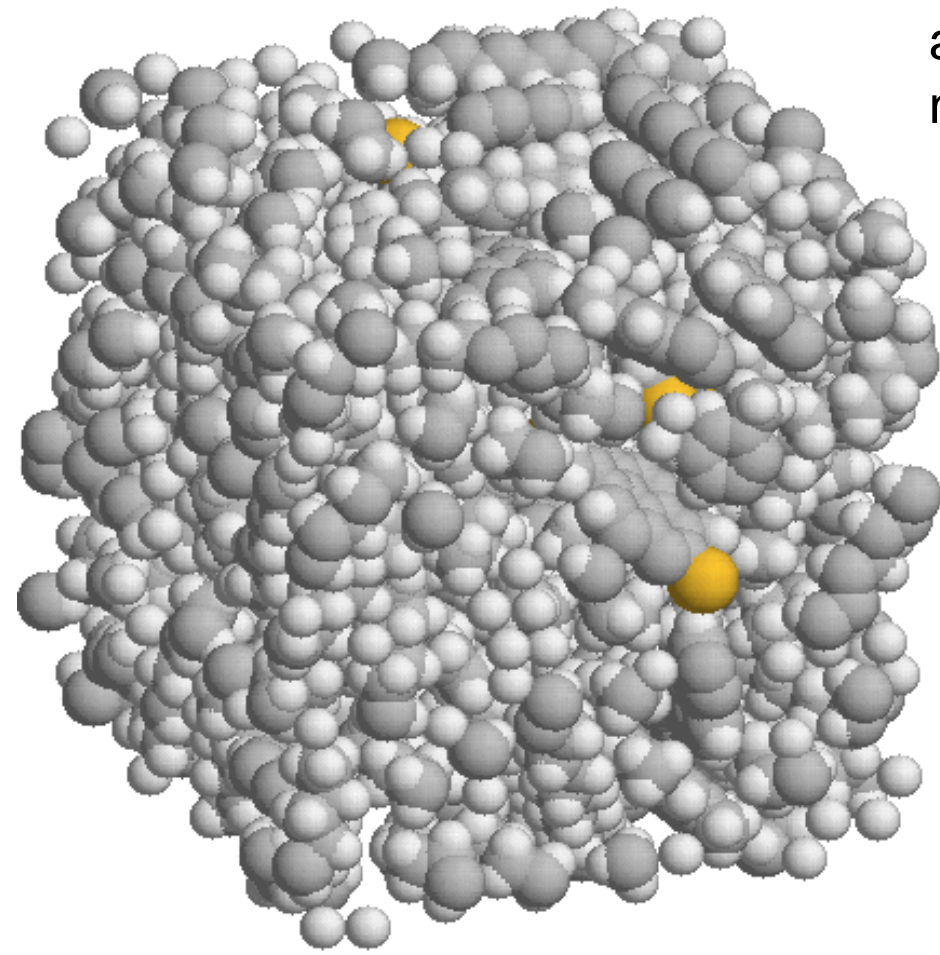


*Inter-molecular* orientation

- angle between planes in two separate molecules

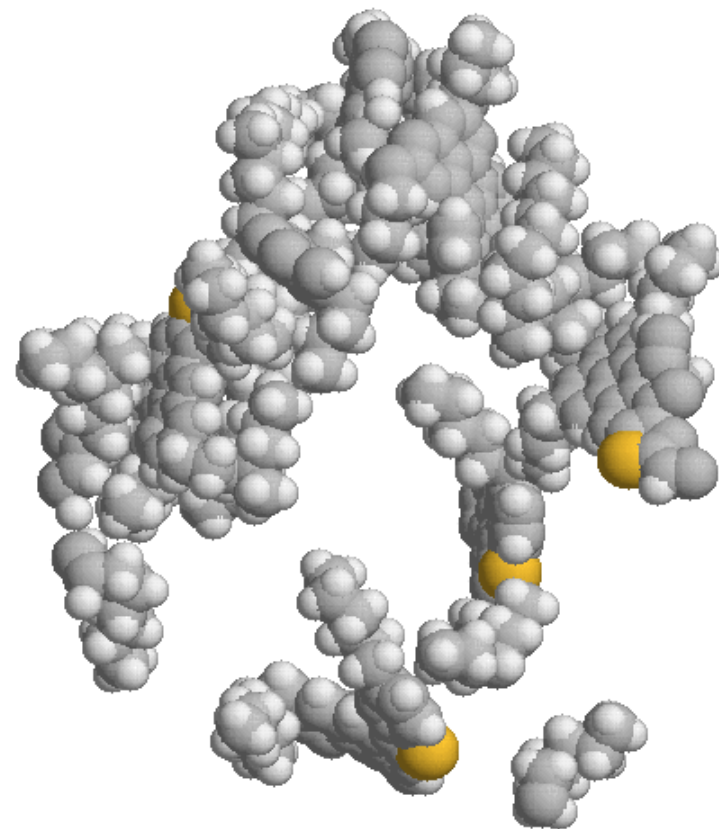
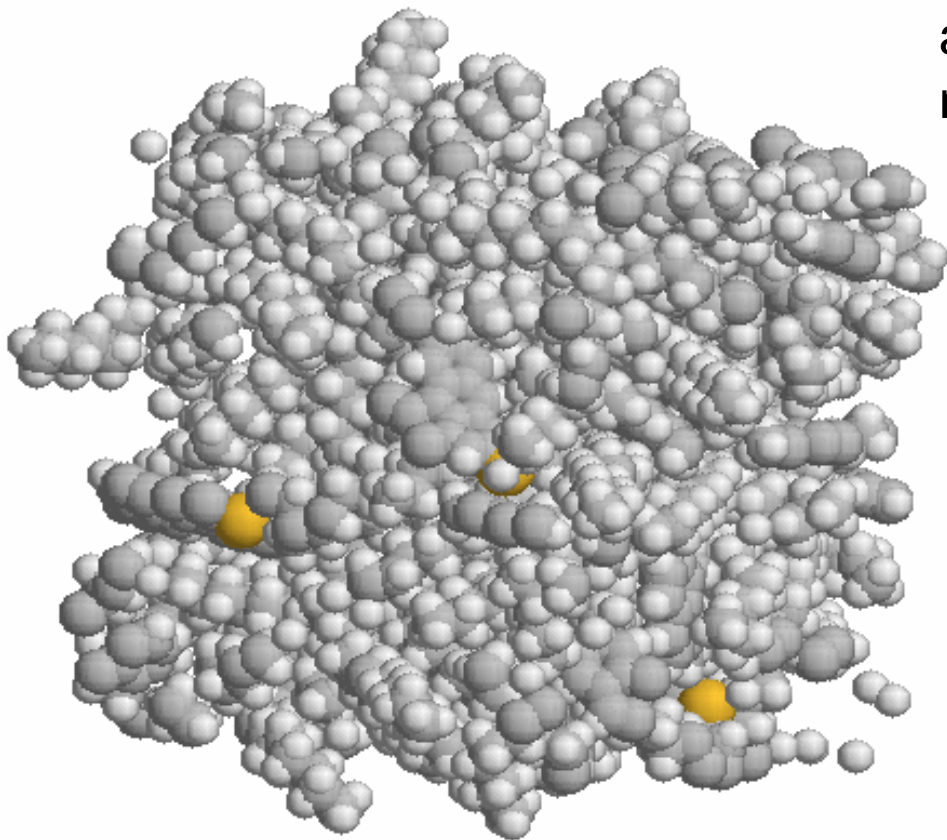


asphaltene 1 / dimethylnaphthalene /  
n-C<sub>22</sub> alkane mixture, -5 °C



viewing asphaltene 1 only

asphaltene 2 / dimethylnaphthalene /  
n-C<sub>22</sub> alkane mixture, 25 °C



viewing asphaltene 2 only

# Stress and Stress Relaxation Modulus

Modulus and compliance relate stress and strain

$$\sigma = G^* \gamma \qquad \gamma = J^* \sigma$$

$$G'' = G^* \sin \delta \qquad 1/J'' = G^* / \sin \delta$$

$$\sigma_{uv} = \text{instantaneous stress} = (\text{KE} + F \cdot r) / V = \langle \sigma \rangle + \delta \sigma(t)$$

stress relaxation modulus from symmetric traceless stress

$$G(t) = \frac{V}{10k_B T} \sum_{u,v} \left\langle \sigma_{uv}^{\text{st}}(0) \sigma_{uv}^{\text{st}}(t) \right\rangle$$

$$\sigma_{xx}^{\text{st}} + \sigma_{yy}^{\text{st}} + \sigma_{zz}^{\text{st}} = 0$$

$$\sigma_{xy}^{\text{st}} = \sigma_{yx}^{\text{st}}$$

# Stress and Zero-frequency Viscosity

stress relaxation modulus

$$G(t) = \frac{V}{10k_B T} \sum_{u,v} \langle \sigma_{uv}^{\text{st}}(0) \sigma_{uv}^{\text{st}}(t) \rangle$$

Complex modulus

$$G^*(\omega) = i\omega \int_0^{\infty} e^{-i\omega t} G(t) dt$$

Zero-frequency viscosity

$$\eta = \int_0^{\infty} G(t) dt = \lim_{\omega \rightarrow 0} G^*(\omega) / \omega$$

Steps:

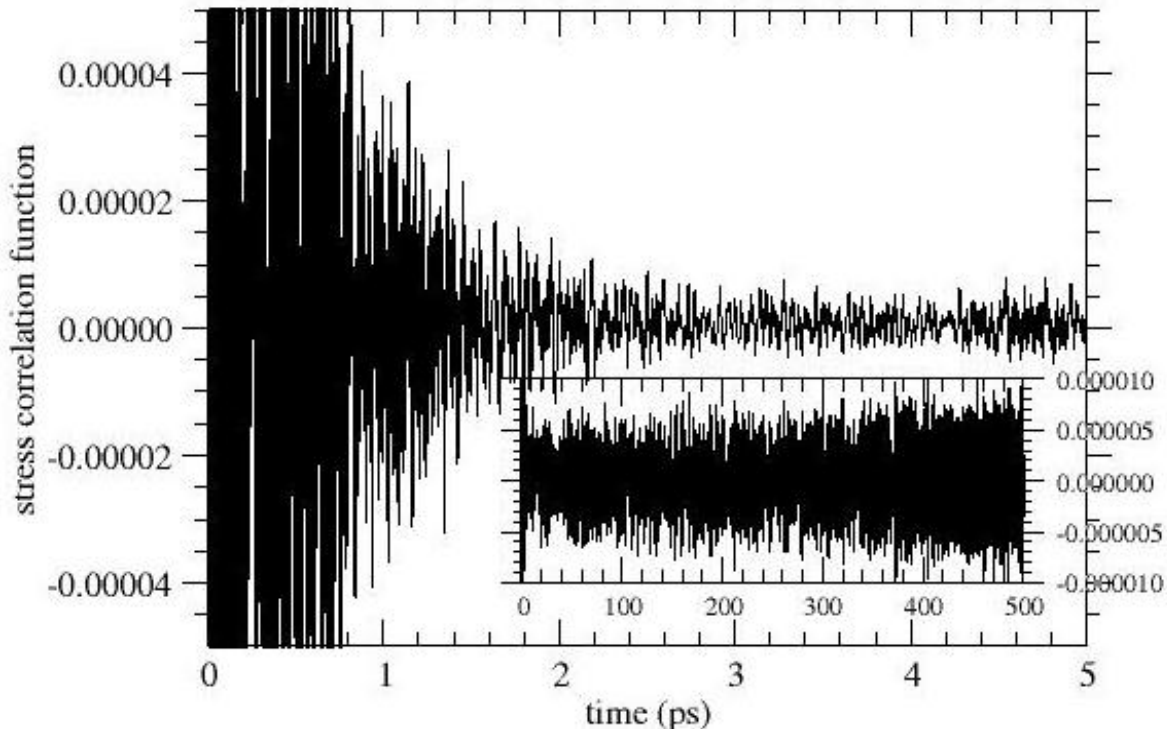
1. Simulate,  $\delta\sigma(t)$
2. Calc.  $G(t)$
3. Integrate to find  $\eta$
4. Fourier transform to find  $G^*(\omega)$

# Stress Relaxation Modulus

$\sigma$  from forces on atoms

$$G(t) = \frac{V}{10k_B T} \sum_{u,v} \langle \sigma_{uv}(0) \sigma_{uv}(t) \rangle$$

asphaltene 2 mixture, T = 443 K



Fast oscillations  
are a converged  
result

Too much detail !

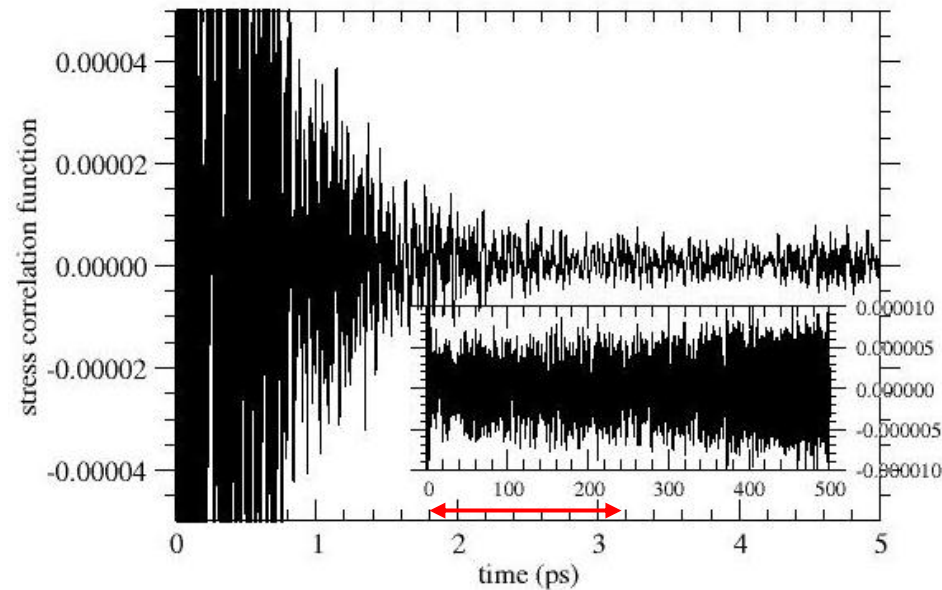
- *fluctuations in correlations* at frequencies of atoms
- $G(t)$  decreases, then noise dominates

# Viscosity estimate

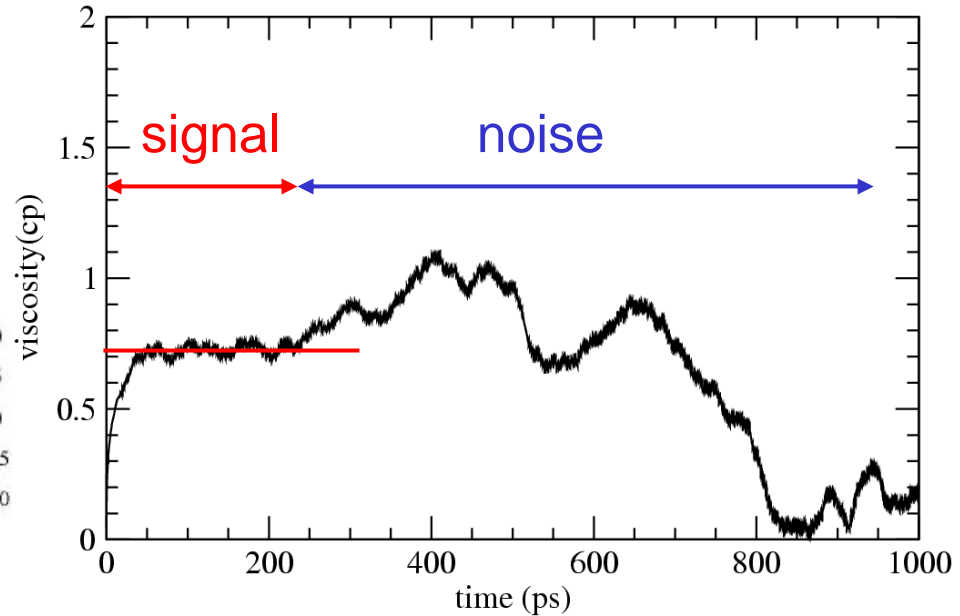
$\sigma$  from forces on atoms

$$\eta = \frac{V}{10k_B T} \int_0^{\infty} \sum_{u,v} \langle \sigma_{uv}(0) \sigma_{uv}(t) \rangle dt$$

asphaltene 2 mixture, T = 443 K



asphaltene 2 mixture, 443 K

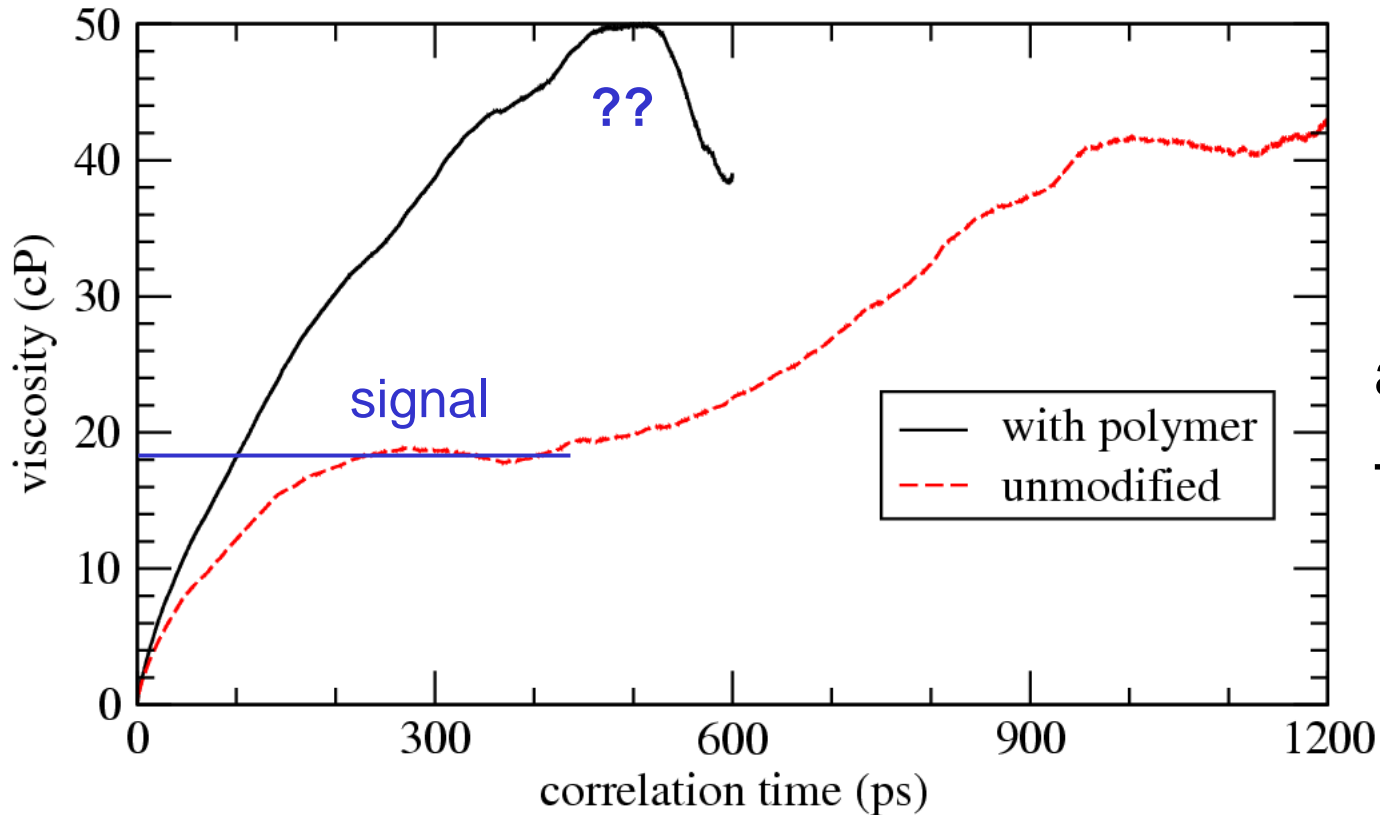


Simulation of time  $10\tau$  averages correlations over  $\tau$

# Unmodified vs Modified Model Asphalt

$\sigma$  from forces on atoms

$$\eta = \frac{V}{10k_B T} \int_0^{\infty} \sum_{u,v} \langle \sigma_{uv}(0) \sigma_{uv}(t) \rangle dt$$



asph 2 mixture

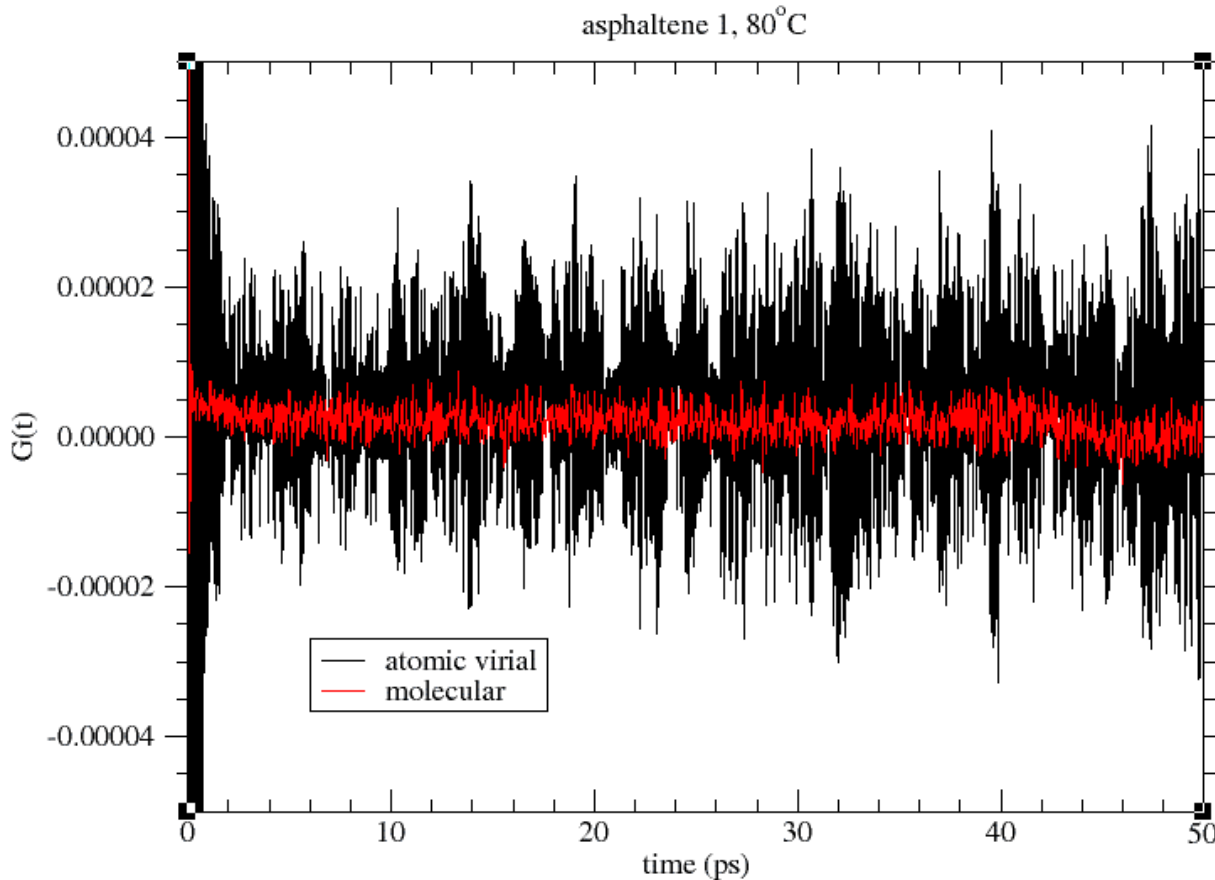
T = 25°C

Polymer: unclear if average converges before noise dominates

# Molecular vs Atomic Stress

Use forces on molecules to calculate  $\sigma$ .

Preliminary results:



Slower oscillations

Easier to converge

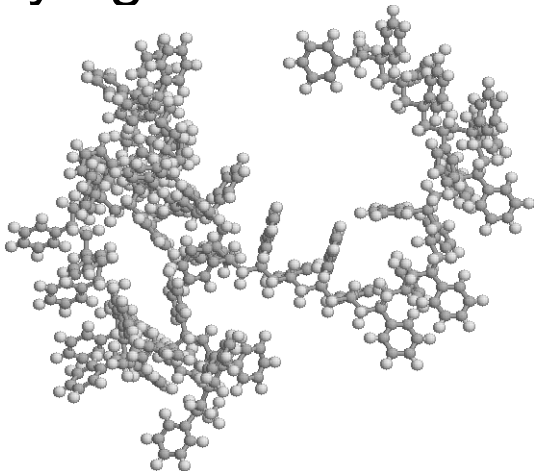
Faster calculation

# Summary of Initial Asphalt Results

- Confirmed density predictions for naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, dimethylnaphthalene, phenanthrene, ternary mixture of small molecules, ...  
(check of method)
- *Bulk modulus* vs.  $T$  provides some evidence of a sub-0 °C glass transition in the model asphalts.
- *Intra- and Inter-molecular orientation* indicate potential for significant packing differences among molecules, depending on the asphaltene.
- *Zero shear viscosity* prediction is consistent for unmodified and modified model asphalt.

# Ongoing work

- Simulations of additional asphaltene / resin / oil mixtures with improved speciation:
  - clarify effect on  $T_g$ 's of model asphalts
  - improved polarity balance for increased density
- Estimates of shear modulus, viscosity;  $t$ - $T$  superposition
- Refine search for  $T_g$  signatures in  $C_p$  and  $V(T)$ .
- Continue to incorporate polymers as asphalt modifiers, studying molecular-level effects.



*Additive:* styrene / butadiene /  
styrene (SBS) copolymer

*shown:* polystyrene

# Modeling uses for Model Asphalts

- Utility of model asphalts:

Create modeling environment to try out new asphalt additives and additive strategies.

- How do molecules impact high temperature rheology? Low temperature shear modulus?
- Requirements:
  - Reasonable length scales
  - Correct balances of aromatic/aliphatic/naphthenic, polar/non-polar, ...
  - Connection to larger scales
  - Creative ideas about what to try

e.g. Sadd et al., *J. Mater. Civ. E.* **16**:107 (2004)

# Advantages of Molecular Simulations

- All properties emerge from same underlying model (i.e. force field for potential energy among atoms)
- Detailed molecular information can be obtained
- Exact chemistry can be studied
- Assist with interpreting experiments that depend on molecular hypotheses

# Limitations of Molecular Simulations

- $N \approx 10^3$  (small) to  $10^5$  or  $10^6$  (large) atoms
- $L < 10$  nm or so
- $t < 10$  ns
  - require time-temperature superposition to access longer times
- Reaching equilibrium can be challenging, especially for complicated molecules
- output = local properties

simulation box  $\approx$  single grain in microstructure

# Correlation - Hansen solubility parameter

- What are the Hansen solubility parameters for each component in a model asphalt?
- Divide each molecule into groups  $i$
- Estimate HSP using

$$\delta_d = \frac{1}{V} \sum_i F_{d,i} \quad \delta_h = \frac{1}{V} \sum_i U_{h,i} \quad \delta_p^2 = \frac{1}{V^2} \sum_i F_{p,i}^2$$

asphaltene 1:       $\delta_d=23.6$        $\delta_p=0.6$        $\delta_h=4.5 \text{ (J/cm}^3\text{)}^{1/2}$

asphaltene 2:       $\delta_d=17.8$        $\delta_p=0.2$        $\delta_h=2.4 \text{ (J/cm}^3\text{)}^{1/2}$

benzoquinoline:       $\delta_d=19.5$        $\delta_p=3.7$        $\delta_h=5.7 \text{ (J/cm}^3\text{)}^{1/2}$

C<sub>2</sub>benzothiophene       $\delta_d=21.1$        $\delta_p=1.6$        $\delta_h=6.0 \text{ (J/cm}^3\text{)}^{1/2}$

# Acknowledgements



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Steve Plimpton (Lammps - MD)

