Composition “Recipes” for Asphalt Simulation

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UNIVERSITY OF
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ARC Product Showcase
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What makes a good pavement?

- Smooth – stays flat over time
- Durable – resists cracking - fatigue, cold
- Easy to repair, Inexpensive, …

What do these mean in terms of
microstructure? nanostructure?

How are they influenced by asphalt chemistry?

How can chemistry hypotheses be tested by simulations and models on the nanoscale?

HYPOTHESIS:
Accurate asphalt chemistry representation on a molecular scale can demonstrate mechanisms consistent with real asphalts

Motivating Questions: why care about this ?

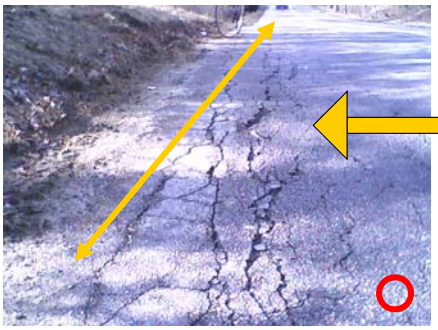
- Why do asphalts with similar G^* but from different crude oil sources behave differently in pavements?
- How do specific molecule types influence G^*, η, J_{nr} ?
- How do additives affect nanometer scales & mechanisms?

Chemo-mechanics chemistry $\Rightarrow$ mechanics

Products: Univ of Rhode Island, Report S

- Asphalt composition "recipes"
  - Compositions of asphalts proposed for use in molecular simulations
- Simulations of Asphalt mechanics & dynamics
  - Display trends consistent with experimental results for real asphalts
  - CAM model, rotation times, zero shear viscosity
- Equation of state approach to estimate free energy in phase models on intermediate scales

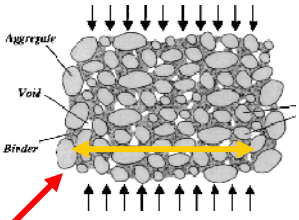
Asphalt over many length scales



10 m of road

zoom in …

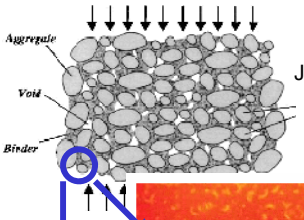
Asphalt over many length scales



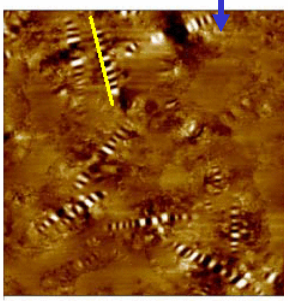
cm of rocks
and asphalt

Calculations by Martin Sadd, Qingli Dai, …
J Mater Civil Eng, 2004

Asphalt over many length scales



Sadd, Dai, …
J Mater Civil Eng



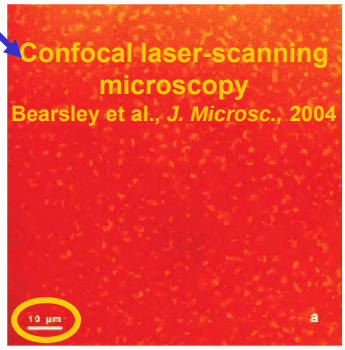
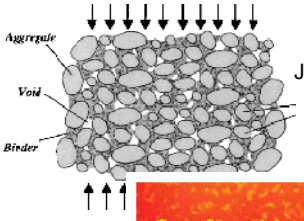


Fig. 1. CLSM image of Safaniya (a) 180/200 and (b) 80/100 bitumen darker maltene matrix. The asphaltene aggregates are typically 2–7 µm

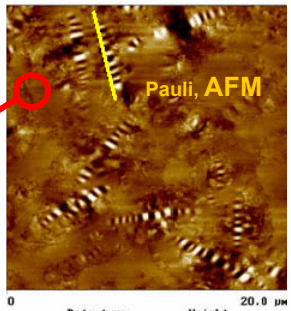
Atomic Force Microscopy,
A. Troy Pauli,
Western Research Institute

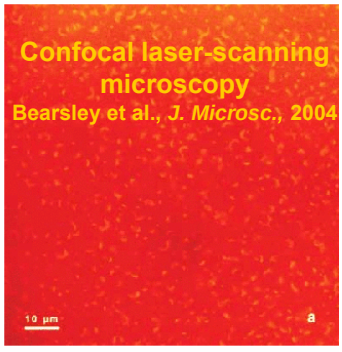
micron scales of textures and phases within asphalt

Asphalt over many length scales



Sadd, Dai, …
J Mater Civil Eng





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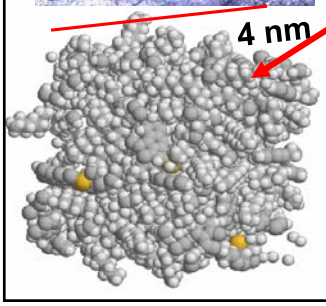
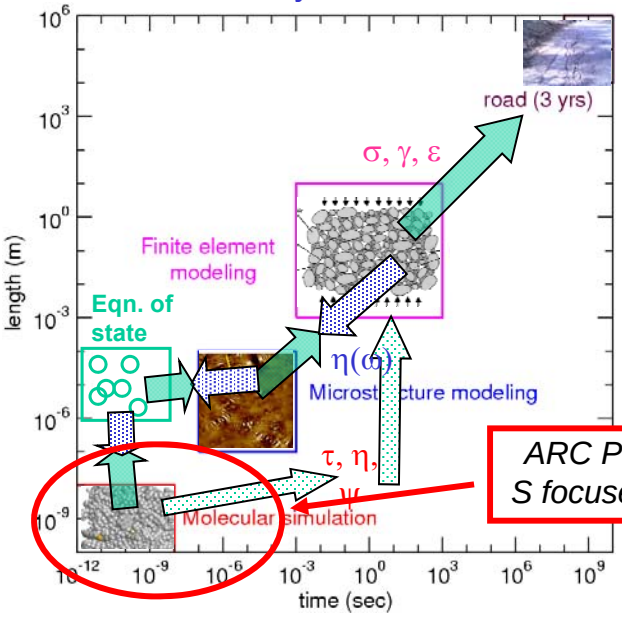


Heterogeneities on ever-smaller scales

ChemoMechanics by Models across Length, Time scales



"pull" from larger scales

"push" from smaller scales

ARC Product S focuses here

MD outputs ⇒ energies ⇒ guide to Microstructure parameters

Benefits of Simulating Asphalt on a Molecular Level

- Analyze how specific molecules contribute to asphalt properties including and beyond rheology
  - Mechanical contributions
  - Oxidation effects
- Differentiate how chemistry implies asphalts from different crude oils differ in properties
- Decipher strategies to modify asphalt mechanical properties and behavior

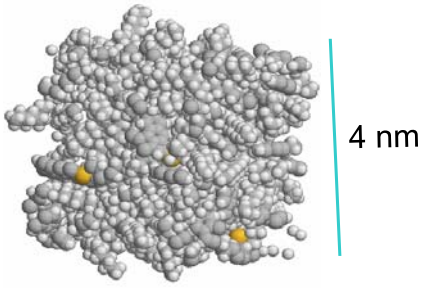
Molecular Dynamics Simulation of Asphalt

f = forces from energy *V*

f = *m* ***a***

x ← ***v***

$$-\frac{\partial V}{\partial \mathbf{x}_i} = m\frac{\partial^2 \mathbf{x}_i}{\partial t^2}$$



time step δt ~ 10^{-15} s = 1 fs
Repeat δt to reach ns+
length scale *L* ~ 1-10 nm
N ~ 10^3 – 10^5 atoms

Multiple computers
Weeks to months

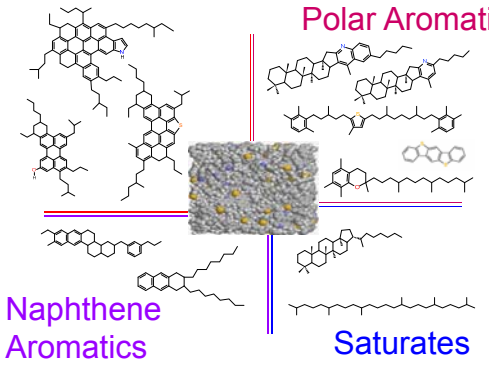
Outputs:

Forces and stresses

Molecule positions
" motions
" rotations

vs. time

Product: Composition "Recipe"



Range of polarities

Structures compatible with geochemistry literature data

Sizes commensurate with SEC data (WRI)

Many classes in bitumen
Many compounds in each

Li and MLG, *Fuel* **115**:347 (2014)

5572 atoms in $(3.8\ nm)^3$ box

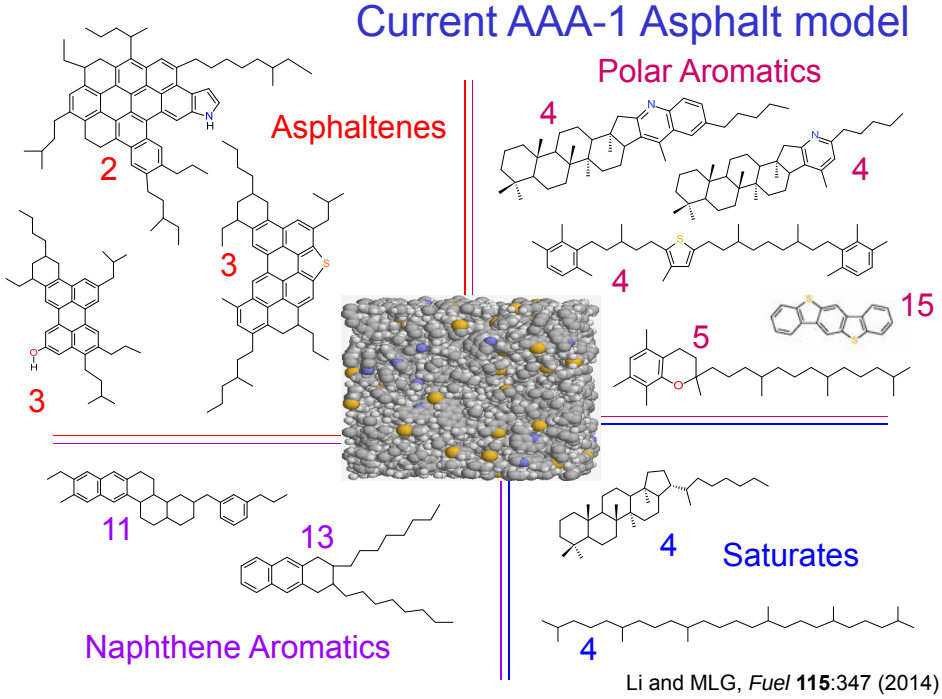
Simulation details
OPLS-aa ff
2 ns NPT for ρ
10+ ns NVT for relaxations
MD (LAMMPS)
MC (Towhee)

Model Asphalt Recipes from the ARC

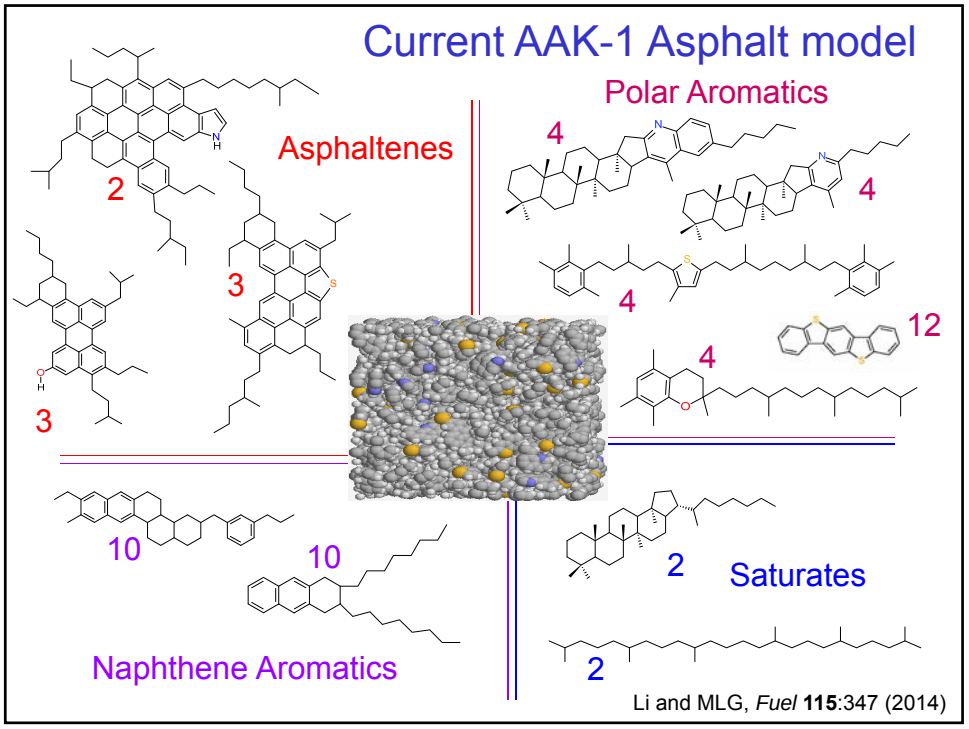
	Compound	AAA	AAK	AAM
S	squalane	4	2	1
	hopane	4	2	1
A	PHPN	11	10	20
	DOCHN	13	10	21
R	quinolinohopane	4	4	10
	thioisorenieratane	4	4	10
	trimethylbenzeneoxane	5	4	10
	pyridinohopane	4	4	10
	benzobisbenzothiophene	15	12	4
A	asphaltene-phenol	3	3	1
	asphaltene-pyrrole	2	2	1
	asphaltene-thiophene	3	3	1

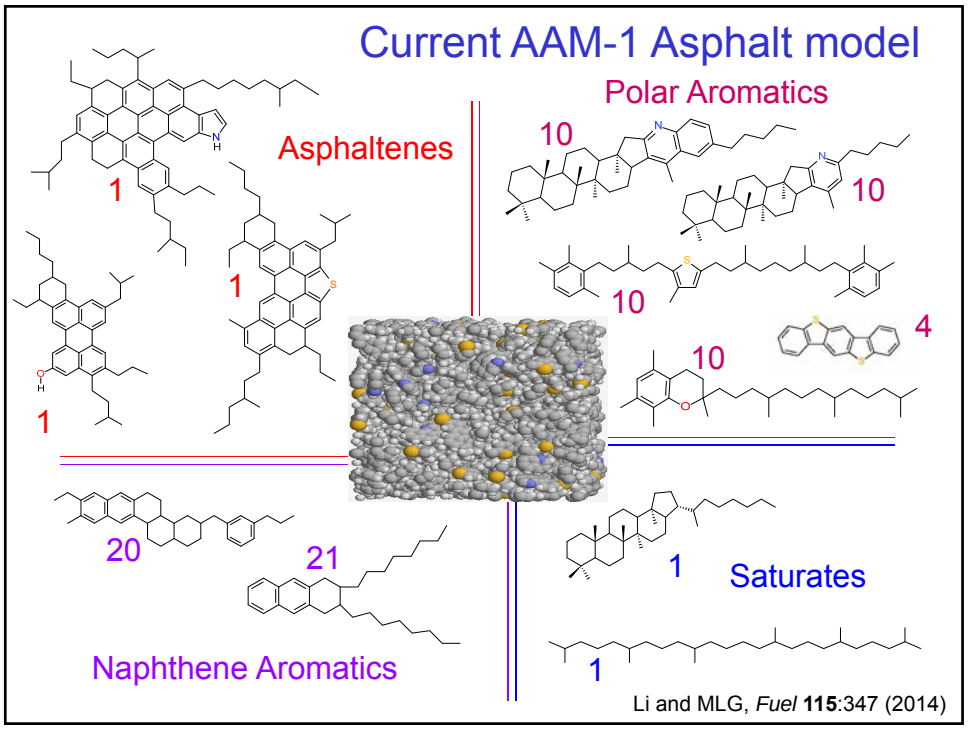
Li and MLG, *Fuel* **115**:347 (2014)

Current AAA-1 Asphalt model

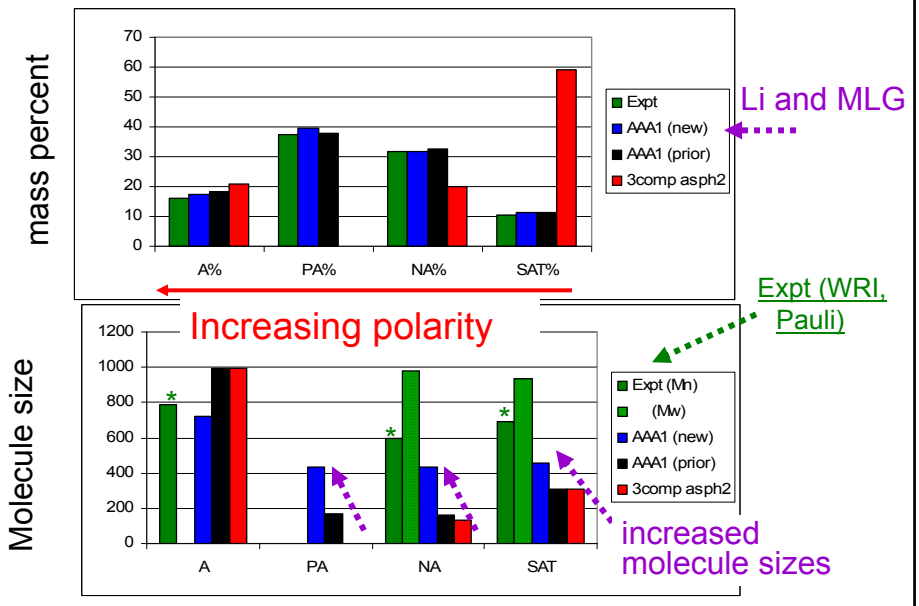


Li and MLG, *Fuel* **115**:347 (2014)


Current AAK-1 Asphalt model
Polar Aromatics
Asphaltenes
4
4
2
3
4
3
12
4
10
10
2
Saturates
2
Naphthene Aromatics
Li and MLG, Fuel 115:347 (2014)


Current AAM-1 Asphalt model
Polar Aromatics
Asphaltenes
10
10
1
1
10
1
10
4
10
20
21
1
Saturates
Naphthene Aromatics
1
Li and MLG, Fuel 115:347 (2014)

Larger molecules prior vs. current AAA-1 models



Current models are closer to *experimental data*

What does it mean to use this product ???

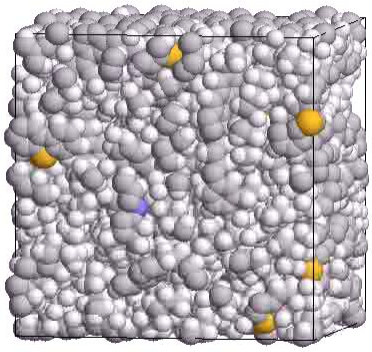
1) Pick a property of interest
   - e.g. mechanical relaxation
2) Find a procedure in literature to simulate this
   - See reports for properties/procedures we use
3) Set up molecules in a simulation box
4) Equilibrate system
   - Loses correlation with initial guess
   - Confirm simulation is making sense
5) Run simulation for awhile (days to weeks)
6) Interpret results
   - Confirm simulation is making sense

Movie of model asphalt, ~nanosecond times

Simulation movies: 12 types of molecules, 72 molecules total

- 77 F, 25 C, 298 K, full simulation box

Slight oscillations, few changes with time

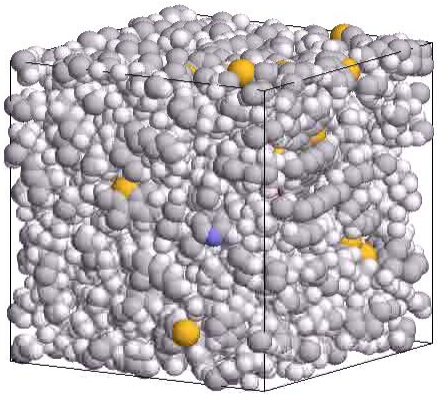


Movie of model asphalt, ~nanosecond times

Simulation movies:

- 140 F, 60 C, 333 K, full simulation box

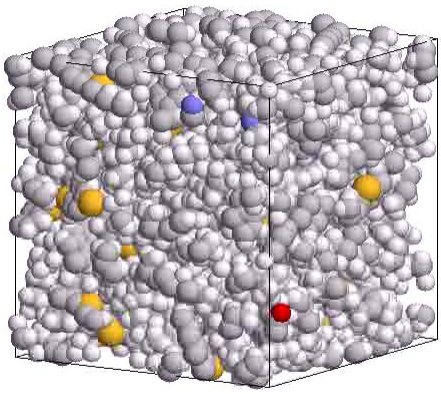
More oscillations, not many changes with time



Movie of model asphalt, ~nanosecond times

Simulation movies:

- 260 F, 127 C, 400 K, full simulation box

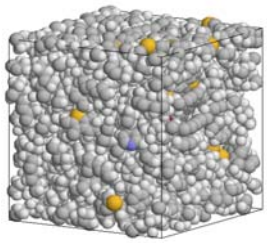


Larger oscillations, more changes with time

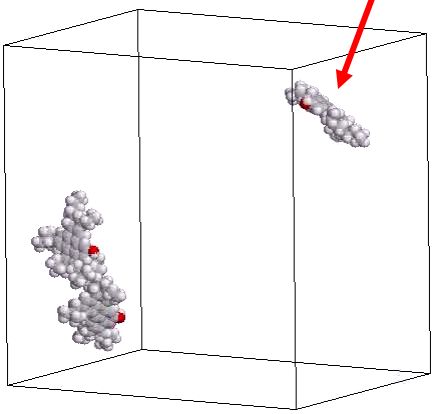
Watch **sulfur**, **nitrogen**, **oxygen** atoms

What do individual molecules do within this bulk model asphalt ?

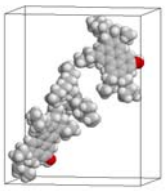
full simulation box →



View only one kind of asphaltene, higher temperature

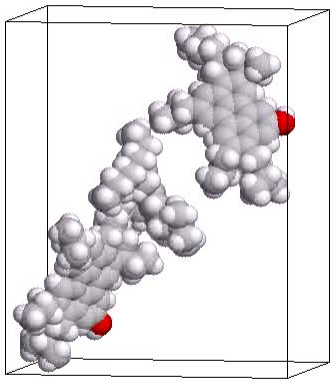


View one asphaltene, room temperature



Asphaltene within bulk model asphalts

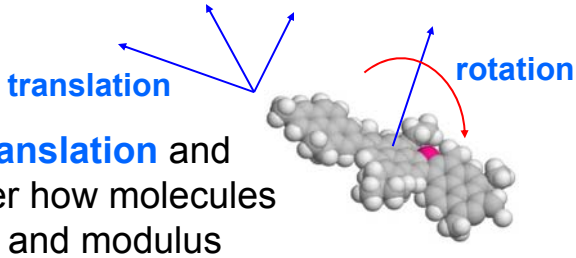
Simulation movie: 77 F, 25 C, 298 K
asphaltene phenol only



Slow rocking motions

Why follow individual molecules ?

- Molecule motions indicate *local environment*
  local surroundings
- **Analogies**:
  - Jog on a sidewalk
  - Jog in a swimming pool
  - Forward roll on grass
  - Forward roll in pool

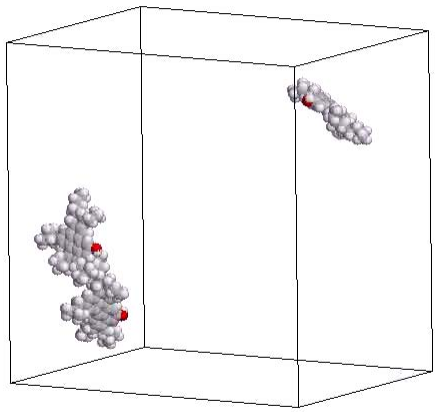


- Use rates of **translation** and **rotation** to infer how molecules affect viscosity and modulus

(‡) following Mondello and Grest, *J. Chem. Phys.* (1997)

Asphaltene within bulk model asphalts

Simulation movie: 320 F, 160 C, 433 K
asphaltene phenol only

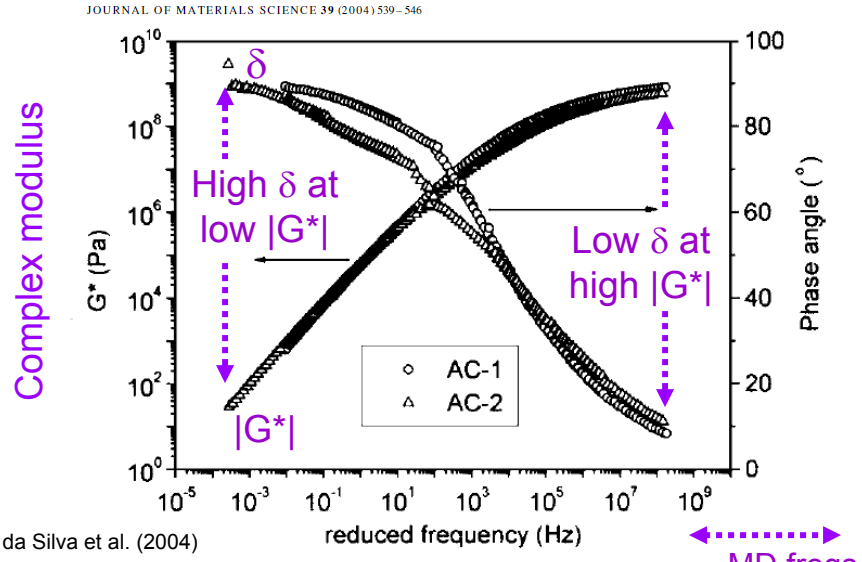


Translate from place to place,

Faster rotations

Side chain motions

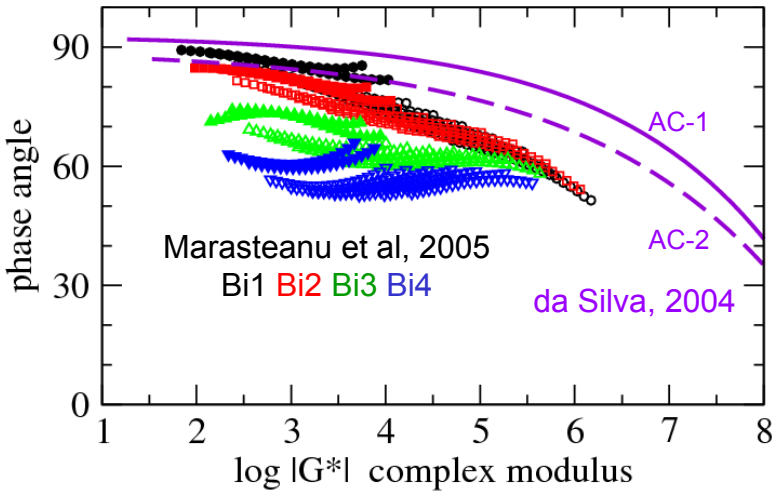
Asphalt Mechanics – |G*|, δ by CAM model



da Silva et al. (2004)

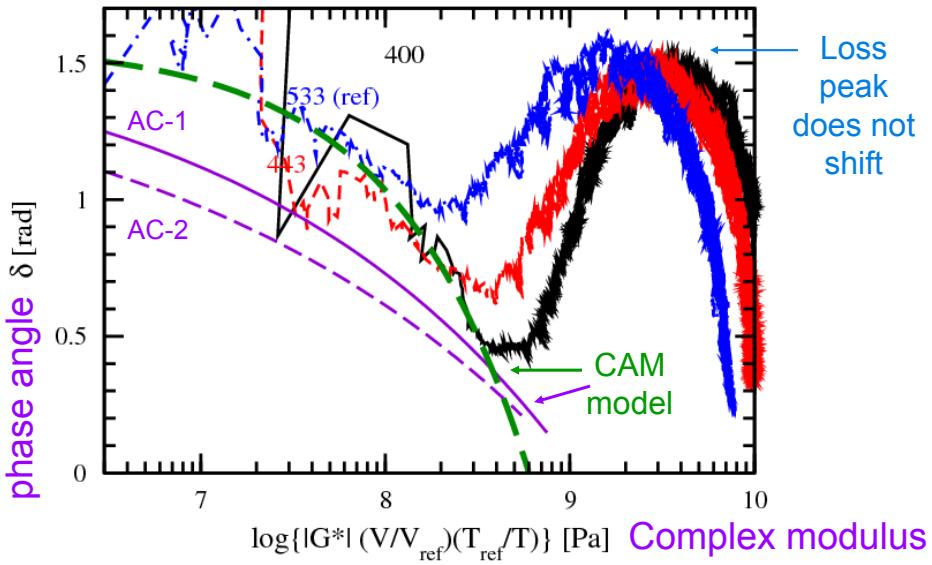
Plot |G*| vs δ for all frequencies …

Asphalt Mechanics: multiple asphalt sources



Asphalts each show different rheology

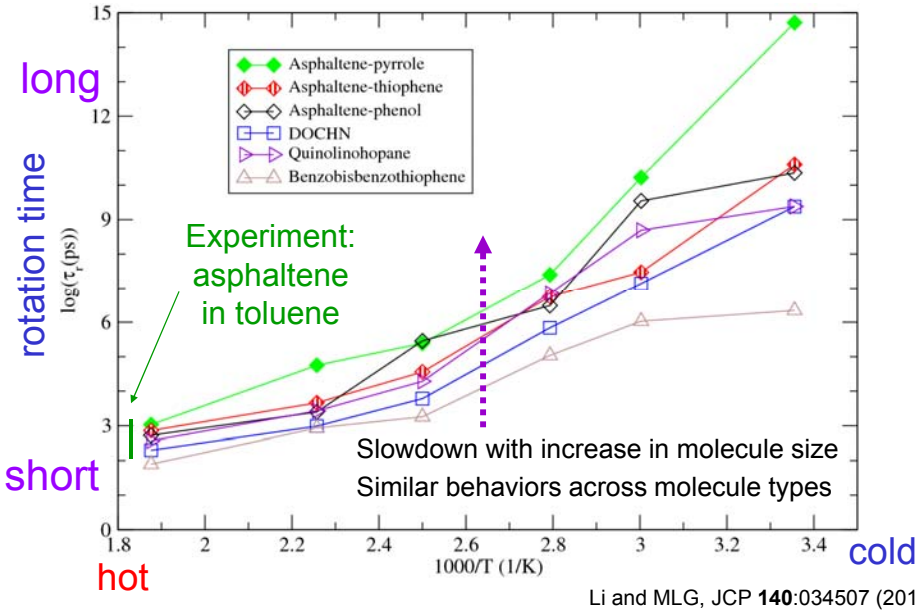
Product: Simulation of Asphalt Mechanics



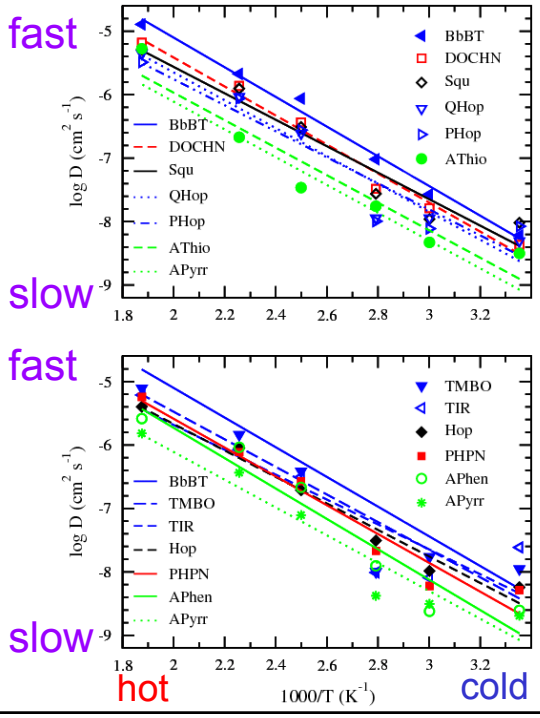
CAM model: equation to relate |G*|, δ, frequency

Masoori and MLG, *J. Chem. Phys.* **141**:124504 (2014)

Rotation Rate in model AAA-1 asphalt



Li and MLG, JCP **140**:034507 (2013)



Translation rate

Diffusion in model asphalts

Similar activation energy

Saturate

Aromatic

Resin

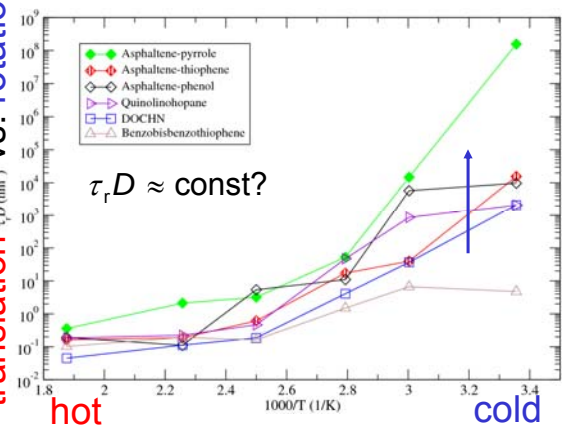
Asphaltene

Prefactor depends on molecule size

Li and MLG, JCP **140**:034507 (2013)

Importance of molecule size: rotation vs. translation

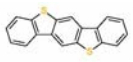
translation vs. rotation



hot cold

Similar rises in resins and asphaltenes

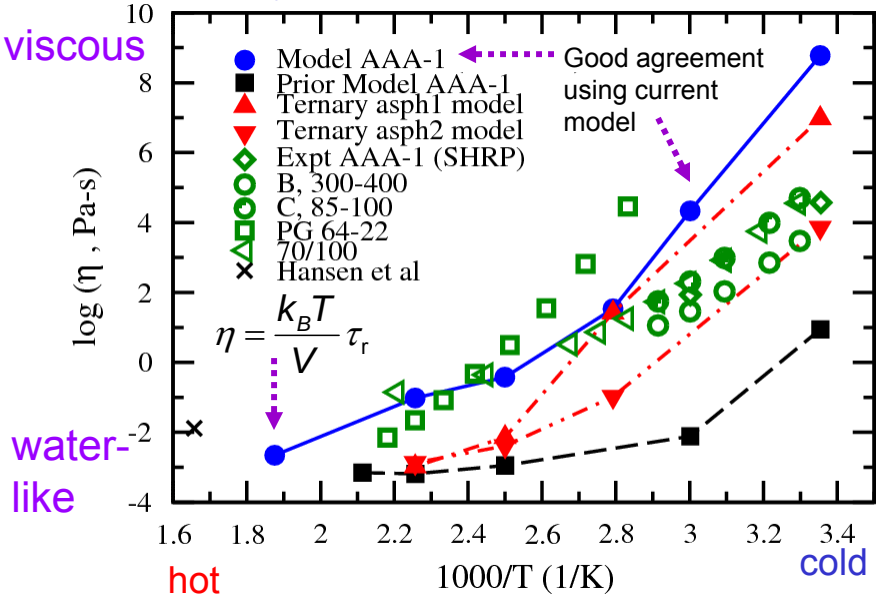
slight rise 5-ring resin



- Most molecules large, rotation slow relative to diffusion
- Smallest molecule, more coupled diffusion and rotation

Larger molecules control mechanical behavior in similar ways

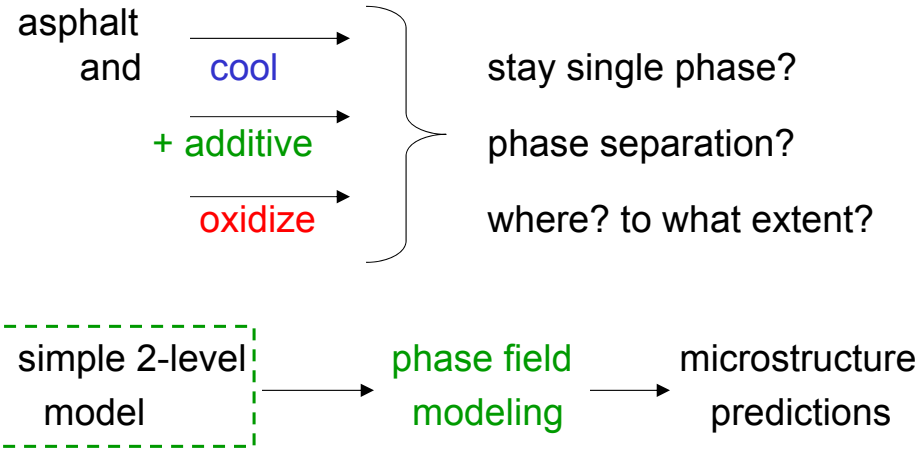
Viscosity Predictions in model asphalts



Li and MLG, JCP **140**:034507 (2013)

PRODUCT: Equation of State for Free Energy

Goal: Free energy vs. (T,P,composition)



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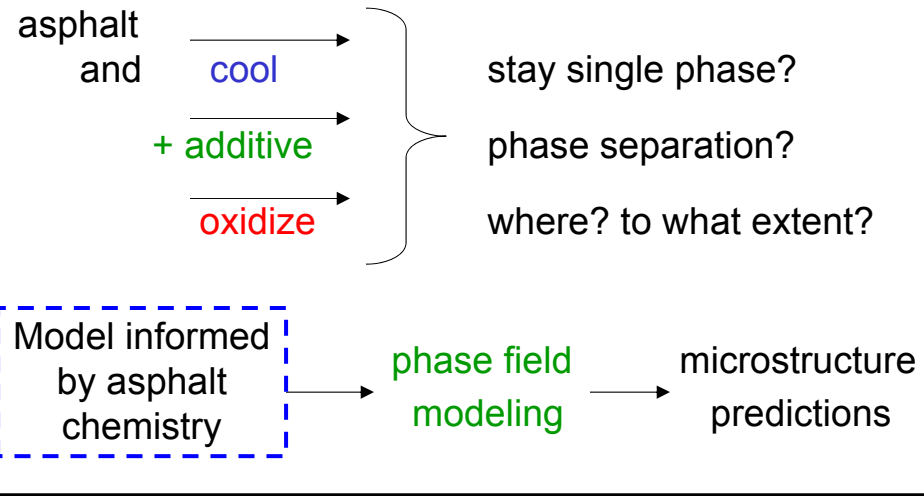
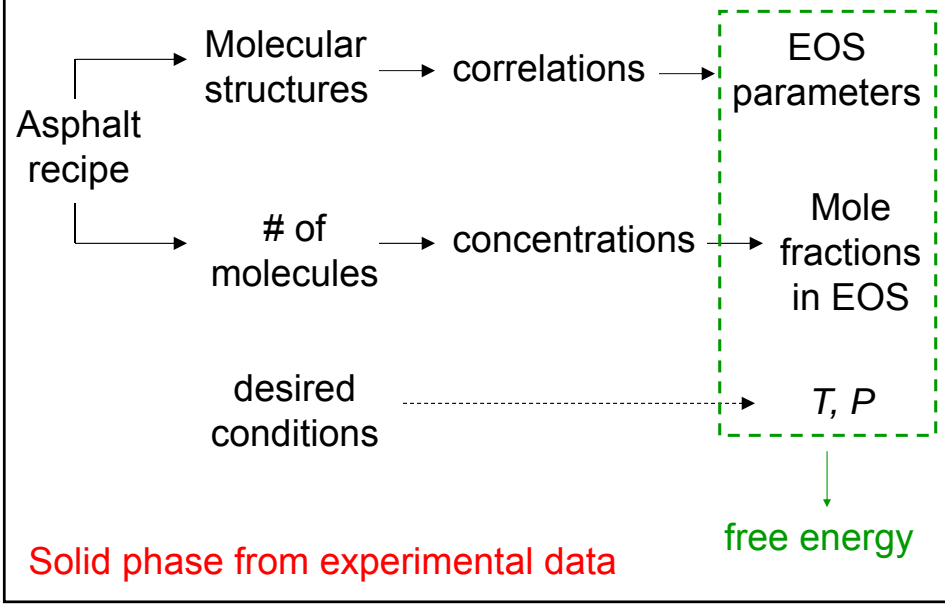
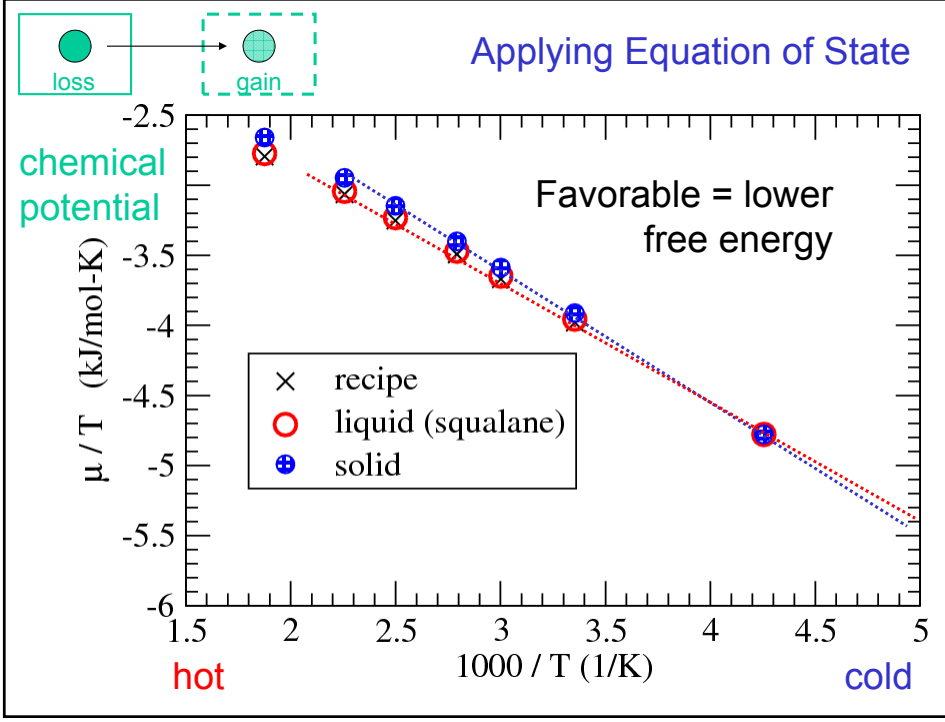


Applying Equation of State

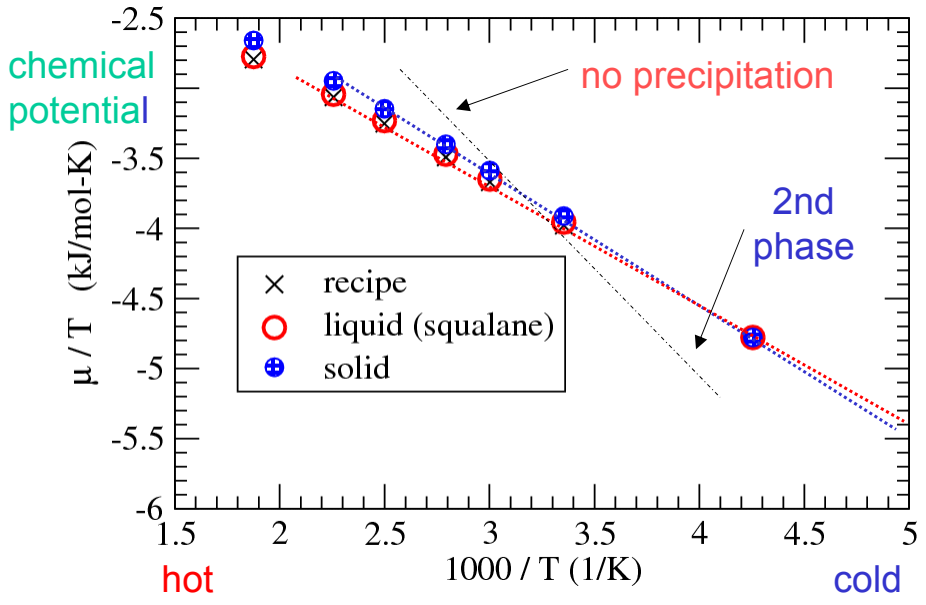


Solid phase from experimental data

Applying Equation of State



Qualitative use - precipitation by lower free energy



Challenges with Next Gen Model Asphalts

	Compound	wt% S	wt% $C_{aromatic}$
S	squalane	0	0
	hopane	0	0
A	PHPN	0	41.3
	DOCHN	0	29.5
R	quinolinohopane	0	19.5
	thioisorenieratane	5.6	33.5
	trimethylbenzeneoxane	0	17.4
	pyridinohopane	0	11.9
	Benzobisbenzothio.	22.1	74.4
A	asphaltene-phenol	0	41.8
	asphaltene-pyrrole	0	40.6
	asphaltene-thiophene	4.5	40.8

wt%	S	C_{arom}
AAA	5.5	28.1
	3.6	39.5
AAK	6.4	31.9
	3.6	40.9
AAM	1.2	24.7
	1.4	33.7

SHRP reports 335, 645

Next Gen models

Need compounds with fewer aromatic C.

Need compounds with more S or many compounds with sulfur.

Polar hopane compounds = promising direction.

sulfides, biological sources of S

Li and MLG, *Fuel* **115**:347 (2014)

Product Summary: Asphalt Simulation Recipes

- *New compositions* that reflect molecules in asphalts (polarity, size) with even more accuracy
- Demonstrations of *asphalt mechanics, rheology, dynamics* using *molecule simulations*
- Equation of state approach for *free energy* (T,P,x_i)
  - Can provide guidance for phase field models

Tools to simulate changes in *composition and environment,* and to infer effects on properties in simulated asphalts

Acknowledgements

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Liqun Zhang, Abiodun Olawepo, Derek Li, Mohammad Masoori – graduate students

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Funding

FHWA / Asphalt Research Consortium ARC (subcontract from Western Research Institute)

Funding on related projects

Rhode Island DOT (Research/Technology - C Franco)

Univ. of Rhode Island Transportation Center (funded by DOT UTC)

Molecular simulation software

Marcus Martin (Towhee - MC), Steve Plimpton (Lammps - MD)