
Molecular Modeling and Engineering of Vegetable-Oil Based Lubricants

Mary Jo Biddy*, Mike J. Tupy†, John Curro, and Juan J. de Pablo***

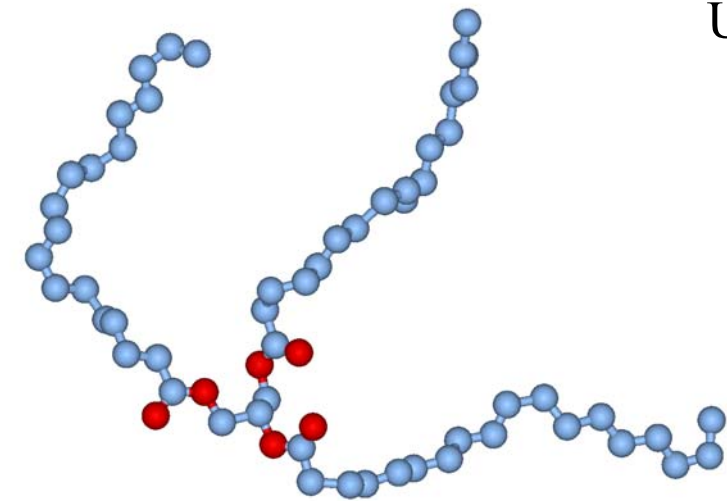
*Department of Chemical and Biological Engineering
University of Wisconsin – Madison

†Cargill Inc.
Wayzata, MN

** Sandia National Laboratories
Albuquerque, NM

Funding Acknowledgements:

- DOE Computational Science Graduate Fellowship
- Cargill Inc.



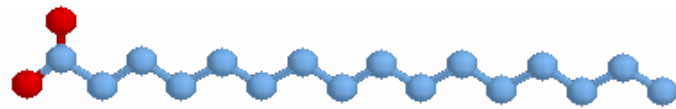
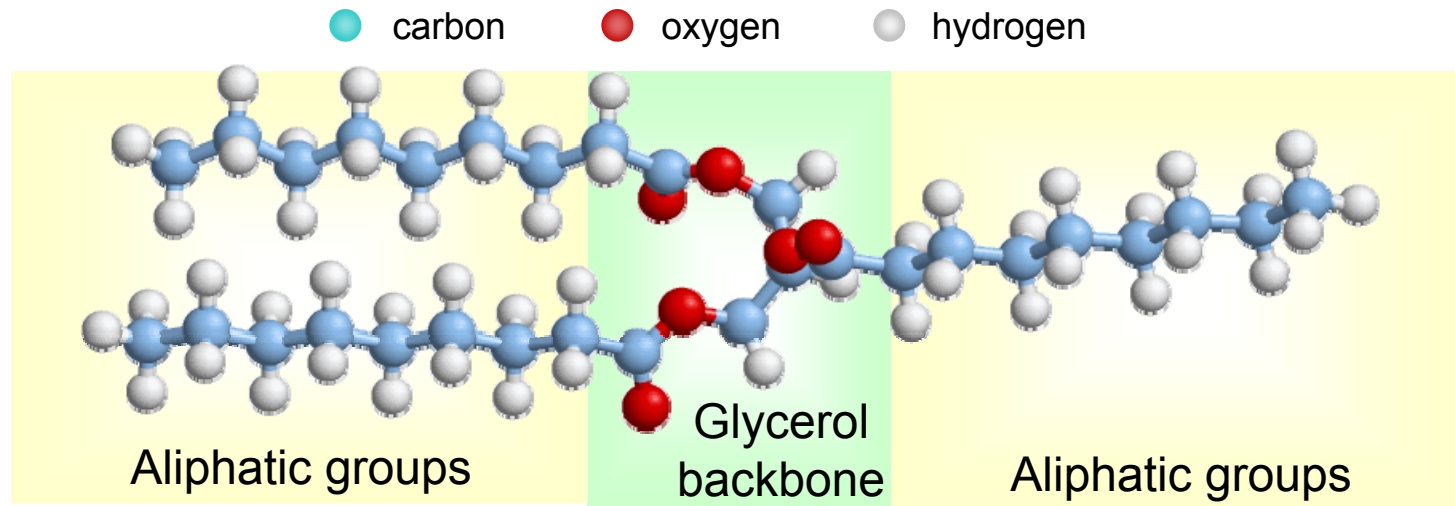
Introduction: Vegetable Oils as Lubricants

- Alternative to petroleum-based products
- Environmentally acceptable lubricants
- Use agricultural feed-stock
 - Biodegradable
 - Minimal health and safety risks
 - Easier disposal
 - Vegetable oils: corn, soybean, canola, cocoa
- Vegetable oil-based lubricants provide improved lubricity compared to petroleum-based products

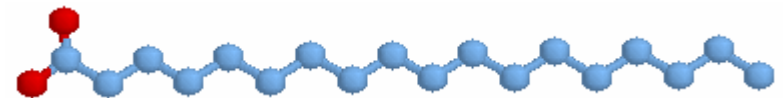
Property	Mineral	Vegetable
Viscosity / Temperature	Fair	Good
Low T properties	Poor	Poor
Oxidation stability	Fair	Poor
Low volatility	Fair	Good
Lubricating properties	Good	Very good
Thermal stability	Fair	Fair



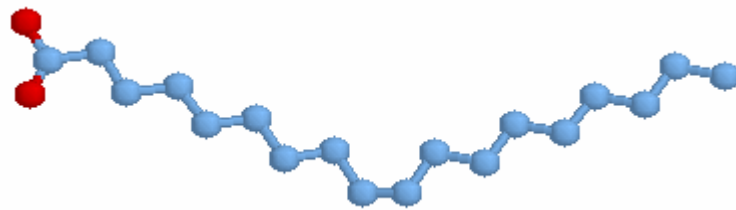
Introduction: Definition of Fatty Acids and Triglycerides



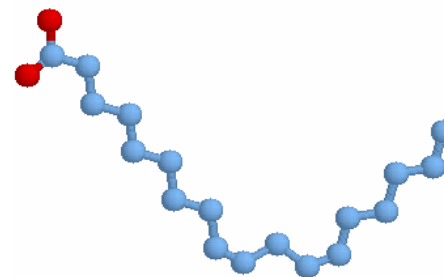
Palmitic acid (P) C16:0



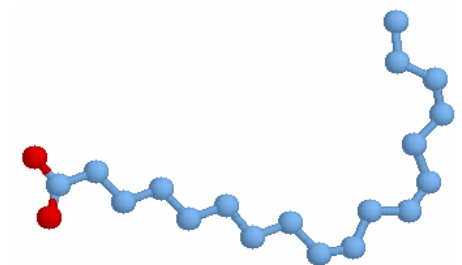
Stearic acid (S) C18:0



Oleic acid (O) C18:1



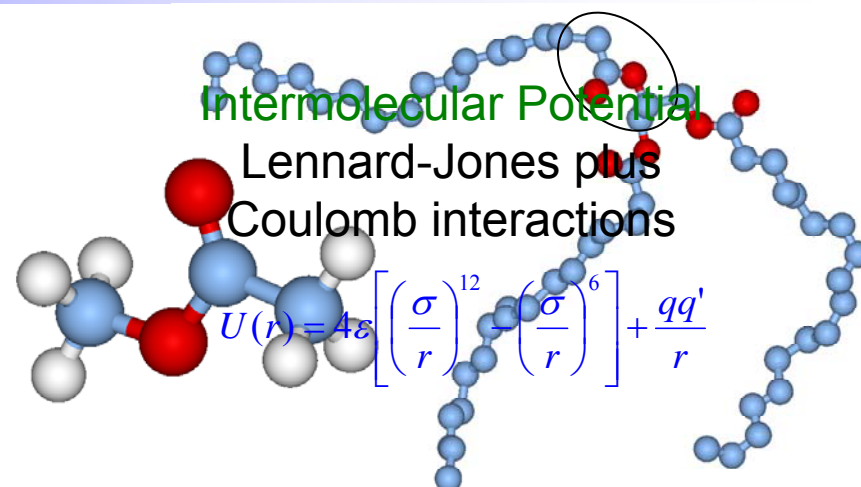
Linoleic acid (Li) C18:2



Linolenic acid (Le) C18:3

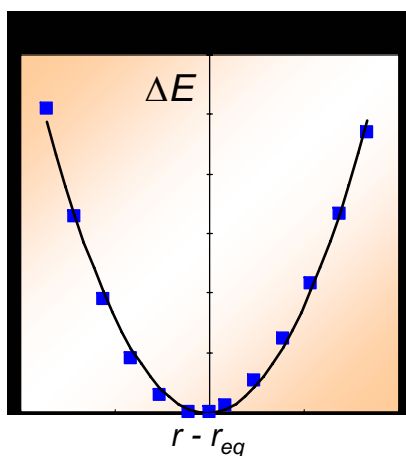
Triglyceride Force Field

- Polar group of TAG: ester linkage
- Model molecule: methyl acetate
- Force field parameters:
→ Quantum Mechanics
(Gaussian MP2/aug-cc-pVDZ)

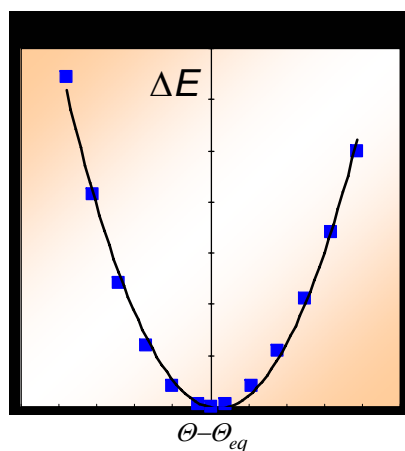


Intramolecular Potentials

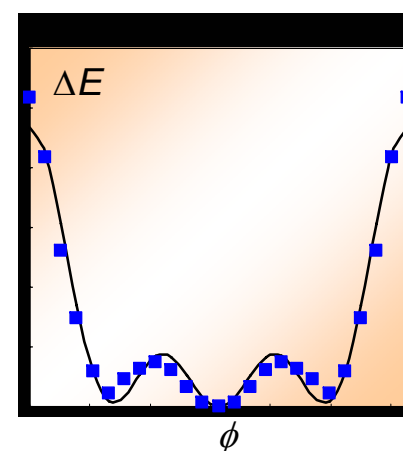
$$U_{bond}(r) = \frac{K_r}{2} (r - r_{eq})^2$$



$$U_{bend}(r) = \frac{K_\theta}{2} (\theta - \theta_{eq})^2$$



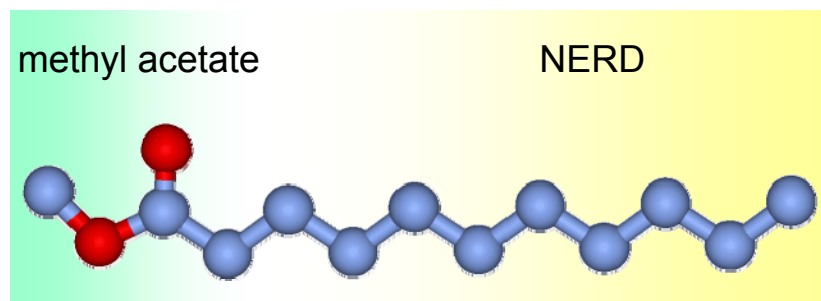
$$U_{torsion}(r) = \sum_{i=0}^3 v_i [1 - \cos(i\phi)]$$



Force Field Testing

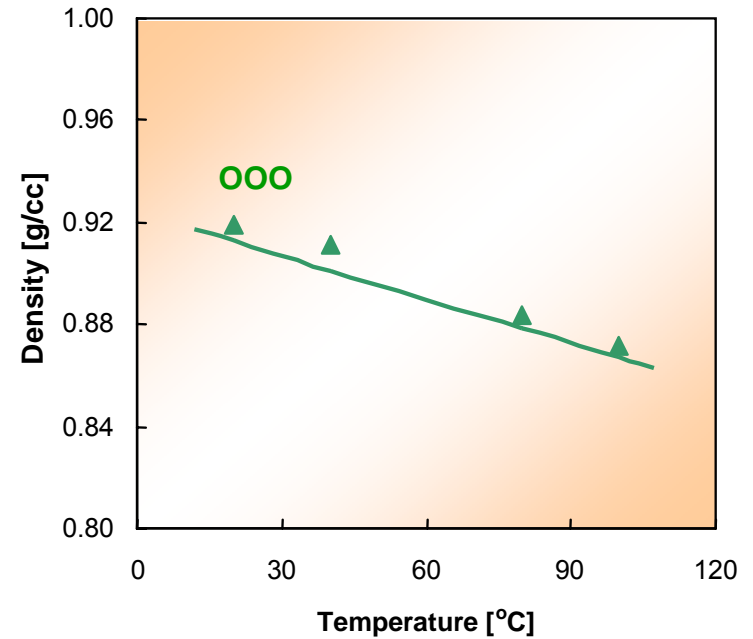
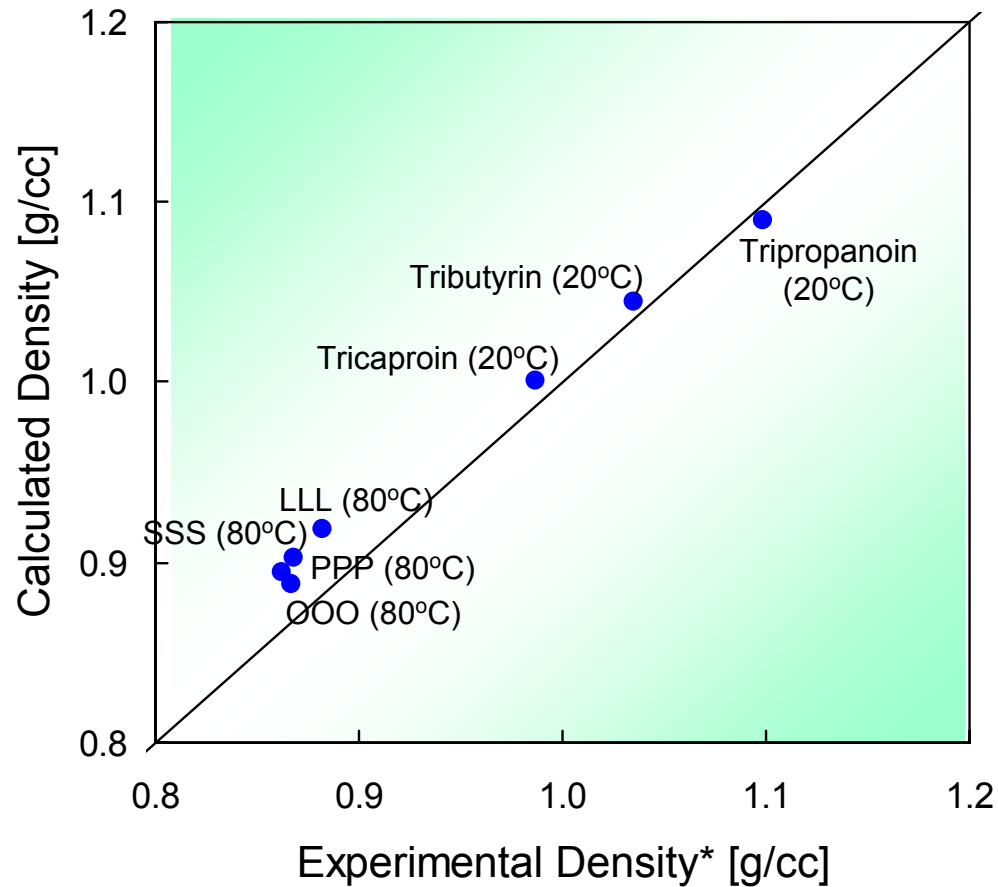
Methyl Acetate

	ρ (g/cm ³)	ΔH (kJ/mol)
This work	0.932	33.5
OPLS	0.897	30.1
Experimental	0.934	32.6



Liquid properties at 25° C		ρ (g/cm ³) calc. / exp.	ΔH (kJ/mol) calc. / exp.
Methyl pentanoate	C ₆ H ₁₂ O ₂	0.886 / 0.895	35.8 / 35.4
Methyl laurate	C ₁₃ H ₂₆ O ₂	0.870 / 0.870	48.6 / —
Methyl palmitate	C ₁₇ H ₃₄ O ₂	0.825 / 0.825	52.2 / —

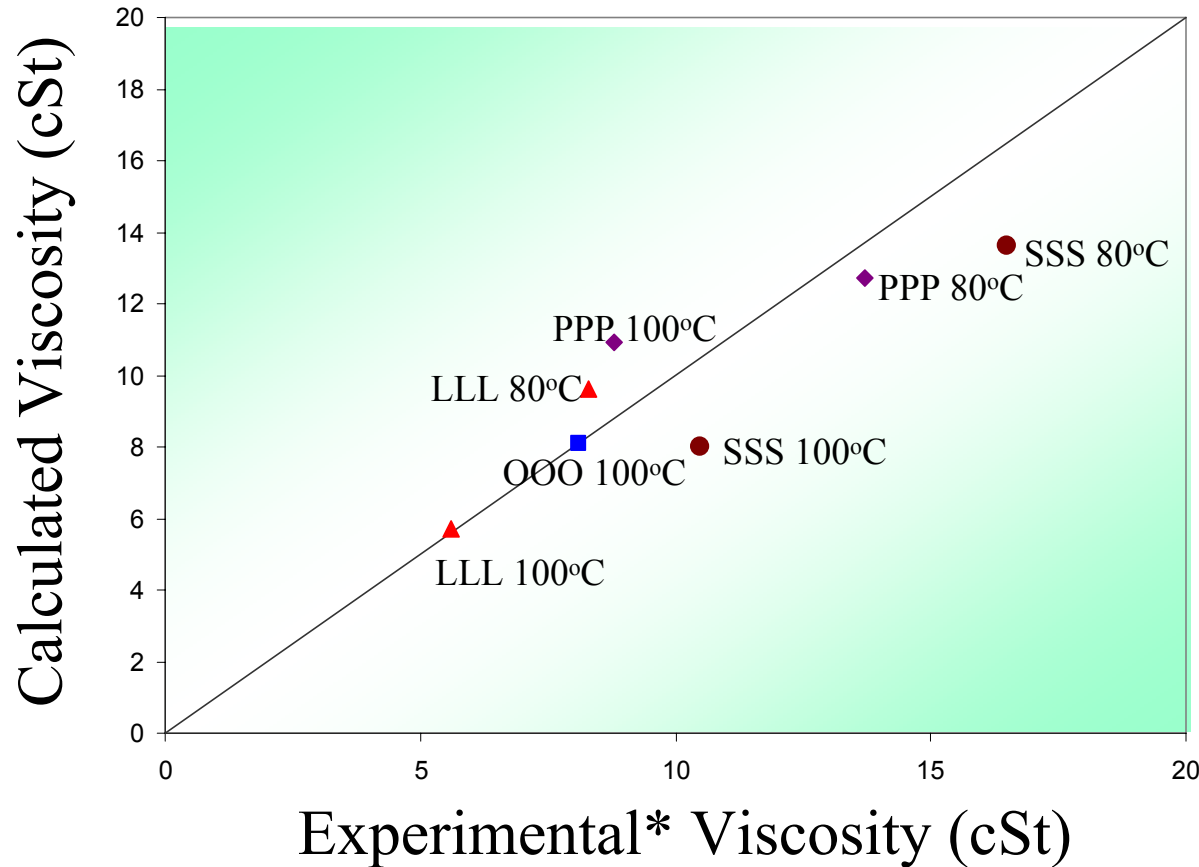
Physical Properties of Triglycerides



	T (°C)	ρ (g/cc)
Trilinolein	80	0.930
Trilinolein	100	0.890
Trilinolenin	80	0.931
Trilinolenin	100	0.902

* Experimental numbers include correlation results

Viscosity Predictions



Green-Kubo Relation

$$\eta = \frac{V}{k_B T \rho} \int_0^\infty \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle dt$$

Simulation Details:

- NVT MD Simulation
- 40 molecules
- Periodic Boundary Conditions
- Reaction Field Correction



* Experimental numbers include correlation results

Vegetable Oil Property Predictions: *Cargill*™ Canola Oils

	Temperature (°C)	Viscosity (cSt)		VI
		Simul.	Exp.	Sim/Exp
Low Oleic	100	9.6 ± 0.9	8.07	
	40	37 ± 4	35.56	248/213
Mid Oleic	100	8.3 ± 0.9	8.423	
	40	40 ± 4	38.95	191/201
High Oleic	100	8.7 ± 0.9	8.59	
	40	36 ± 5	39.93	165/156

These vegetable oils are a combination of the triglycerides OOO, OLiO, OLeO, POO, and SOO

Pour Point

- Accepted industrial standard
- It is the temperature at which an oil no longer flows
- Why is this measurement important?
 - The temperature at which oil can be pumped and adequate oil pressure can be maintained in an engine ranges from 5 to 20°C above the pour point.
 - The lower the pour point temperature the better
- The typical pour point of a commercial petroleum-based oil formulation is around -35 to -40°C.

Experimental Measurement of Pour Point

- A sample of lubricant is chilled in a test jar to a set of defined temperatures.
- At each temperature the test jar is tilted horizontally.
- If the fluid does not flow within 5 seconds, then this is the experimentally determined pour point.
- The recorded pour point is 3°C higher than the experimentally determined point.

Can we use molecular simulations to predict what seems to be a qualitative measurement?

Elastic Constants

- We have investigated pour points using elastic constants to better understand oil gel behavior.
- The expression for the elastic constant is divided into three parts:¹

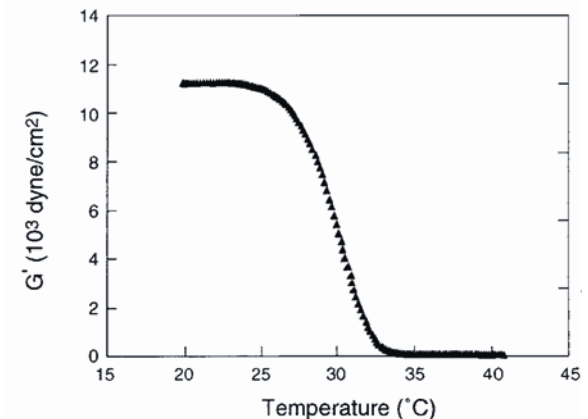
$$C_{ijlm} = C_{ijlm}^{BORN} + C_{ijlm}^{KINETIC} - C_{ijlm}^{STRESS}$$

- Young's Modulus

$$E = \frac{(3\lambda + 2\mu)\mu}{\lambda + \mu}$$

Where $\lambda = C_{xxyy}$ and $\mu = C_{xyxy}$

- A typical Young's Modulus value below T_g :²
 - 3 GPa for PVC with a T_g of 82°C
 - 3.3 GPa for Nylon with a T_g of 50°C
 - 3.3 GPa for PMMA with a T_g of 105°C

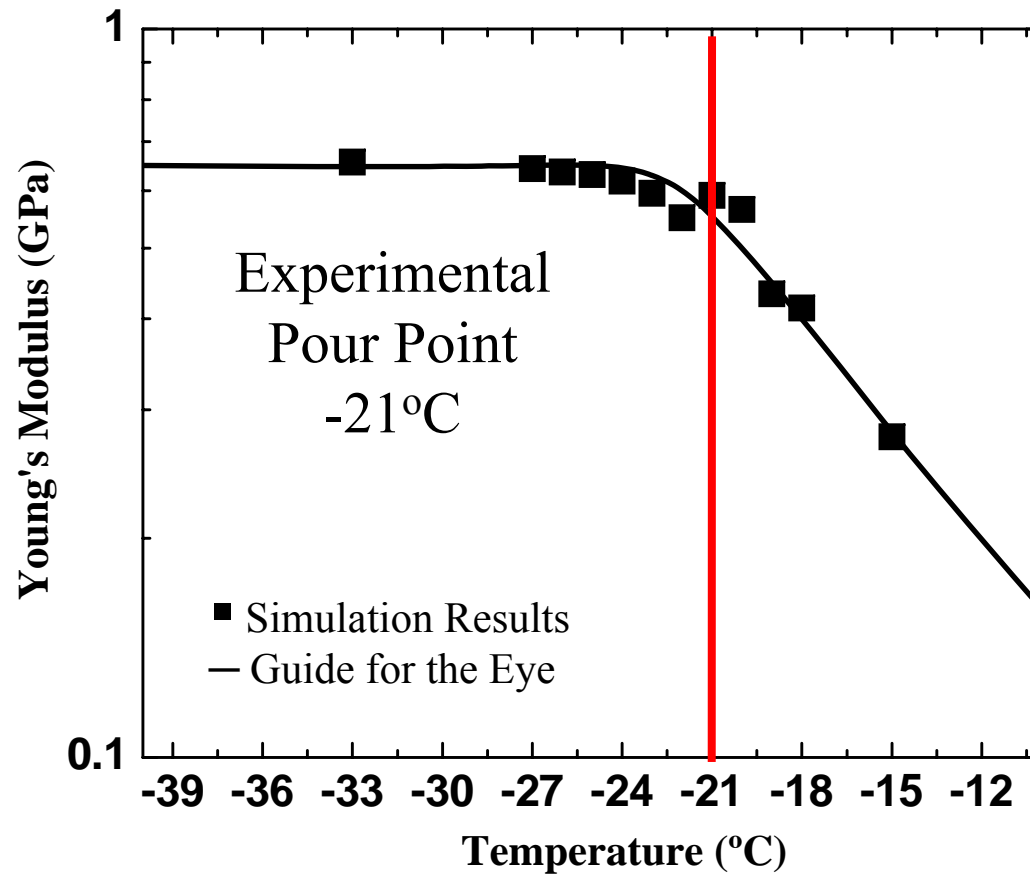


Example of Storage Modulus of Gelatin near gel point³



1. Yoshimoto, K., Papakonstantopolous, G.J., Lutsko, J.F., and de Pablo, J.J., Phys. Rev. B 71(18) 184108, May 2005.
2. Bower, D. An Introduction to Polymer Physics.
3. Gillmore *et. al.*, Journal of Polymer Science Part B, 37(16) 2287, August 1999

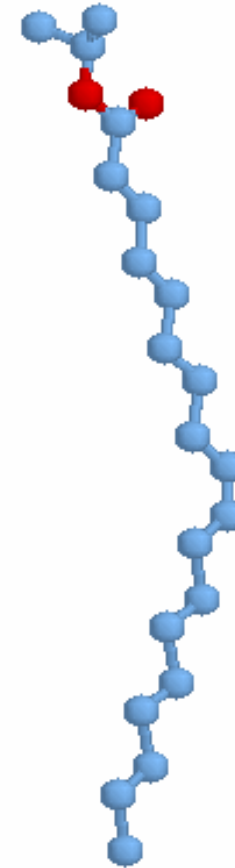
Low Oleic Canola Oil Pour Point



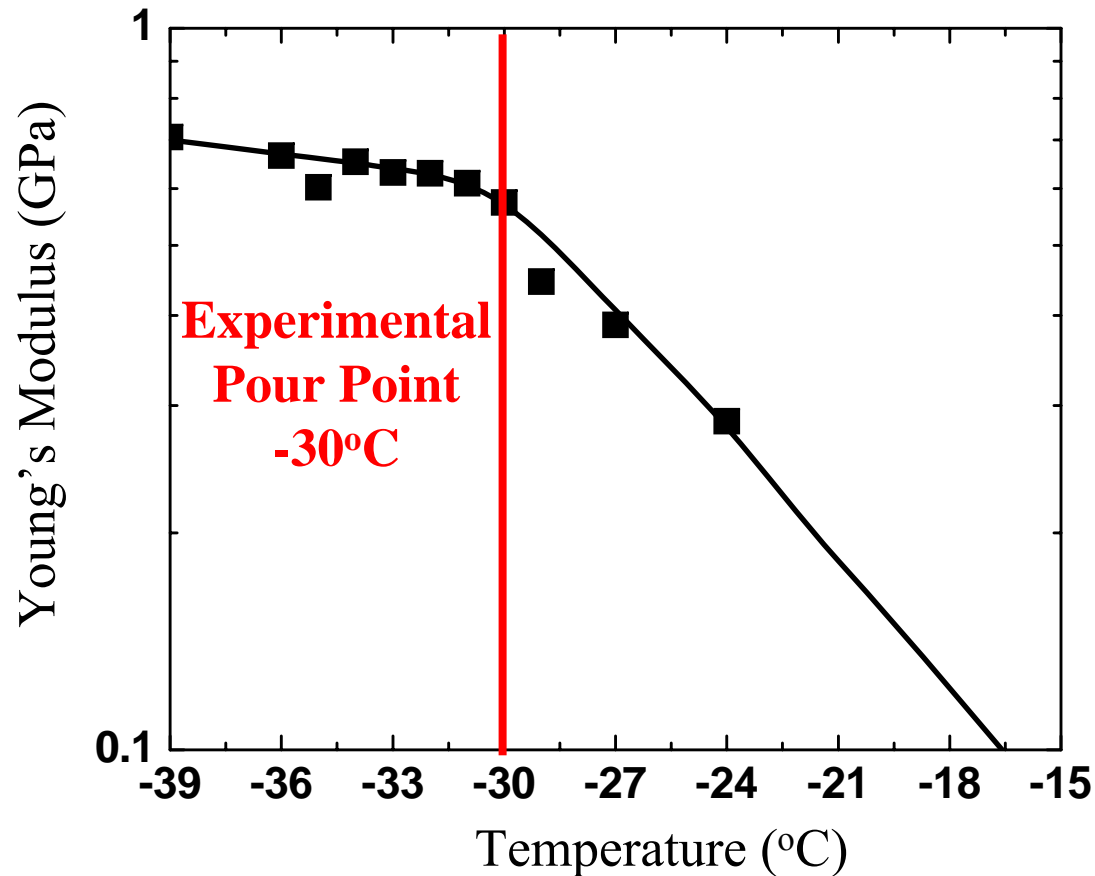
A large increase in the Young's moduli at the pour point temperature is observed for all of the canola oils.

Pour Point Predictions: Pour Point Depression

- Test pour point of low oleic canola oil in the presence of isobutyl oleate
 - Biodegradable pour point depressant
 - Experimental Pour point of -30°C
 - Force field already developed and structure already known
- Two concentrations 20% and 60% (w/w) of isobutyl oleate

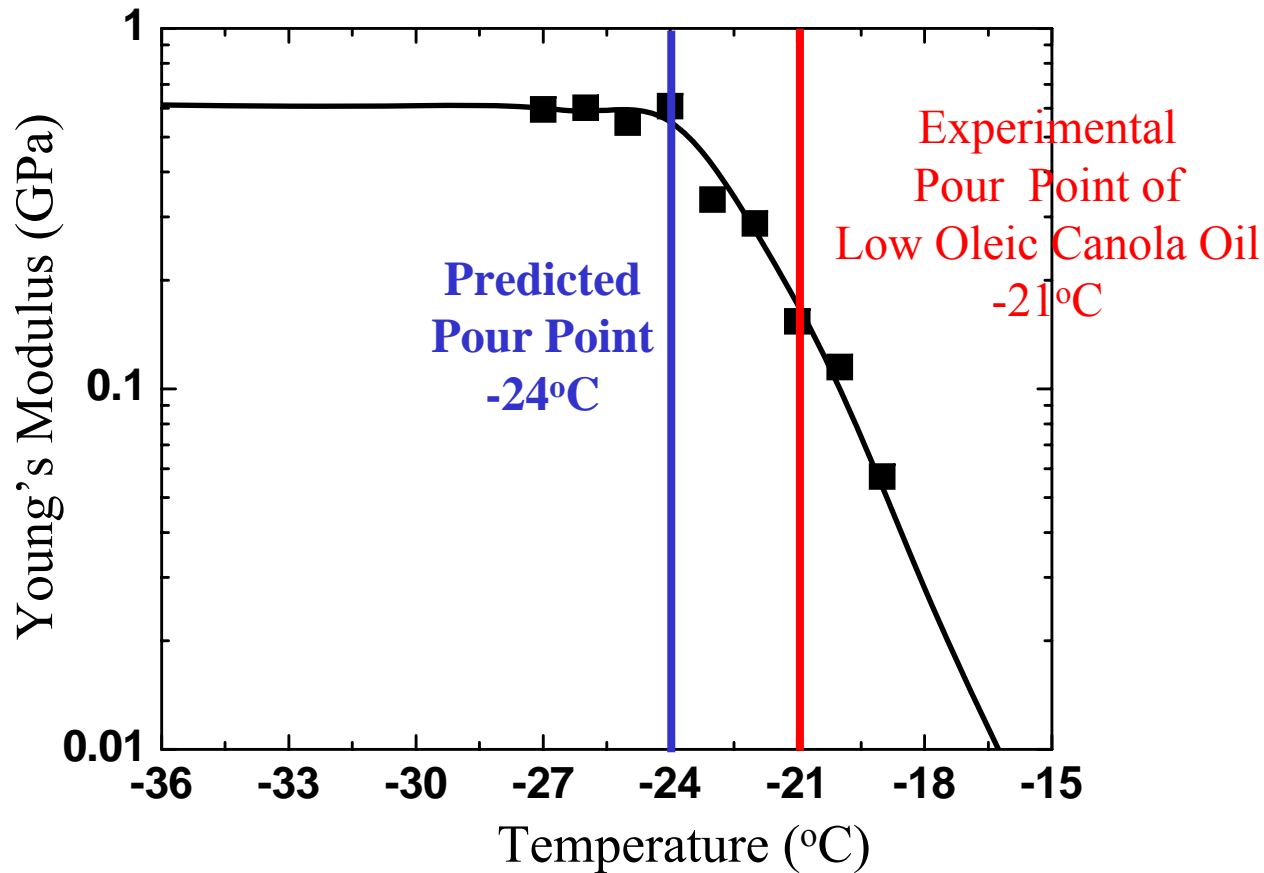


Pour Point Depression Predictions: Pure Depressant



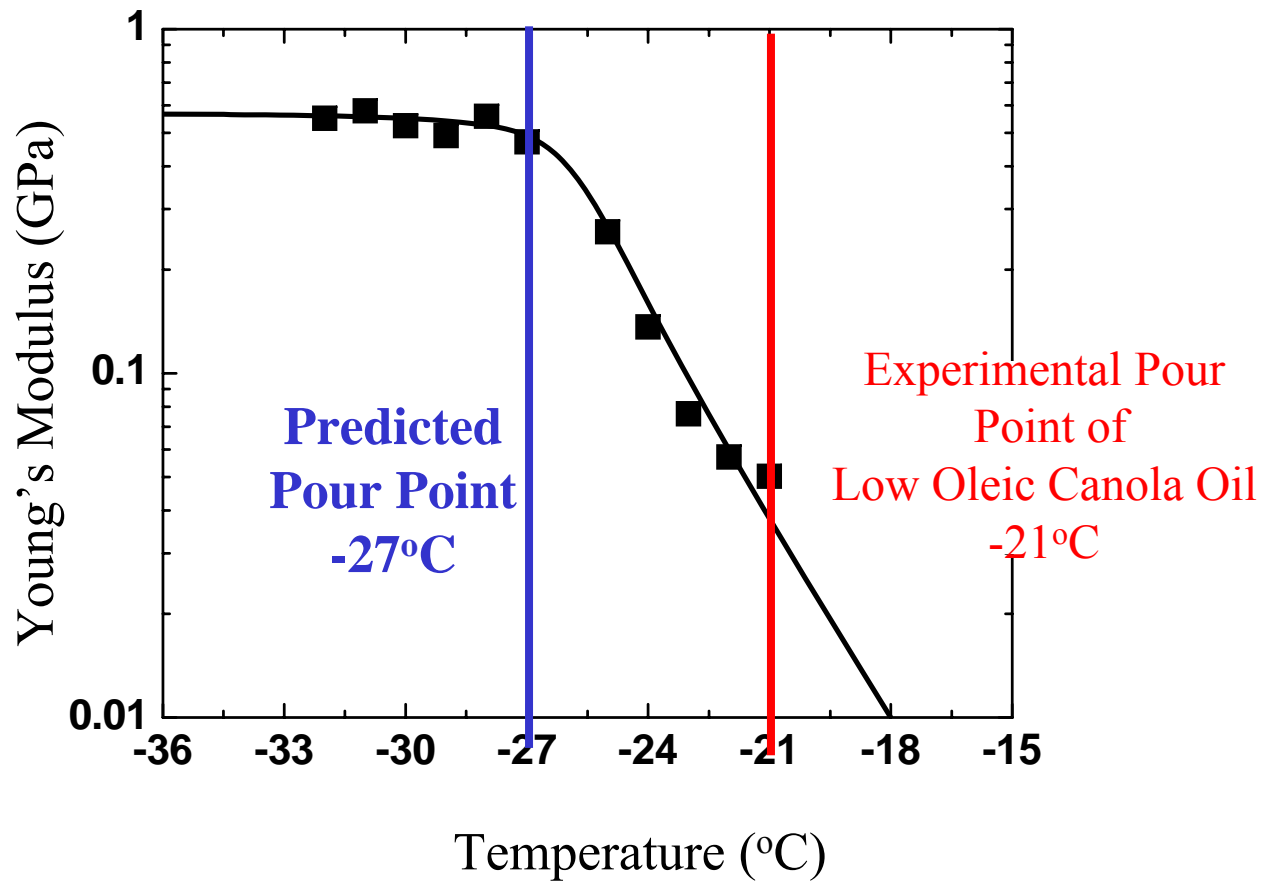
The pour point temperature of the pour point depressant is accurately predicted at -30°C.

Pour Point Depression Predictions: 20% w/w Depressant



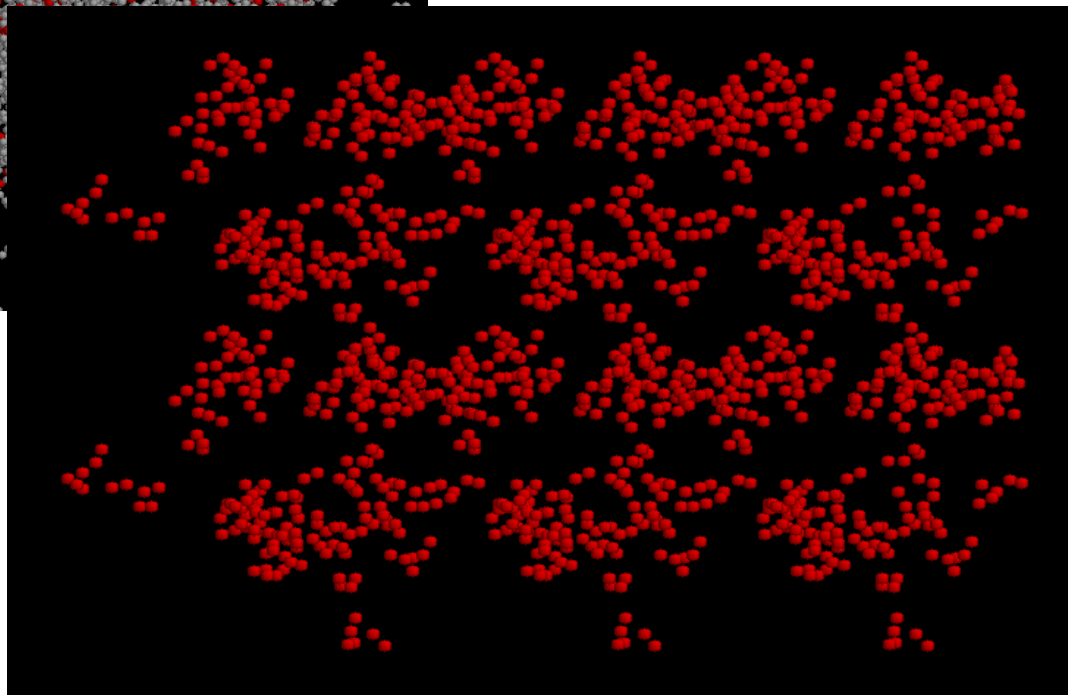
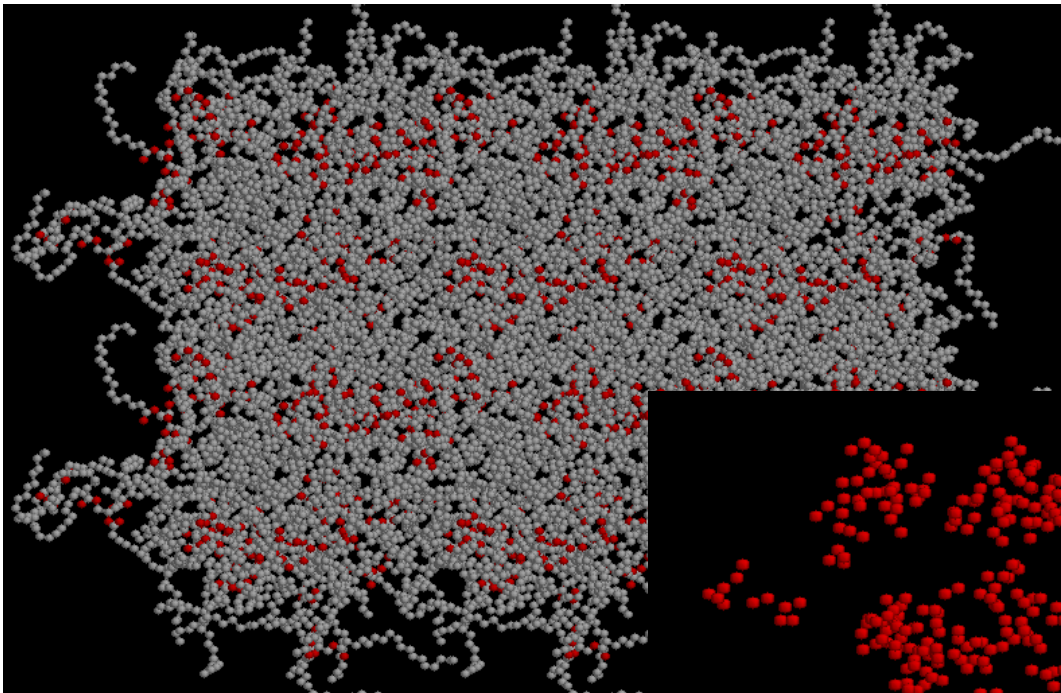
The pour point was lowered by 3°C by adding the pour point depressant.

Pour Point Depression Predictions: 60% w/w Depressant



The pour point temperature is depressed by 6°C by adding a greater amount of depressant.

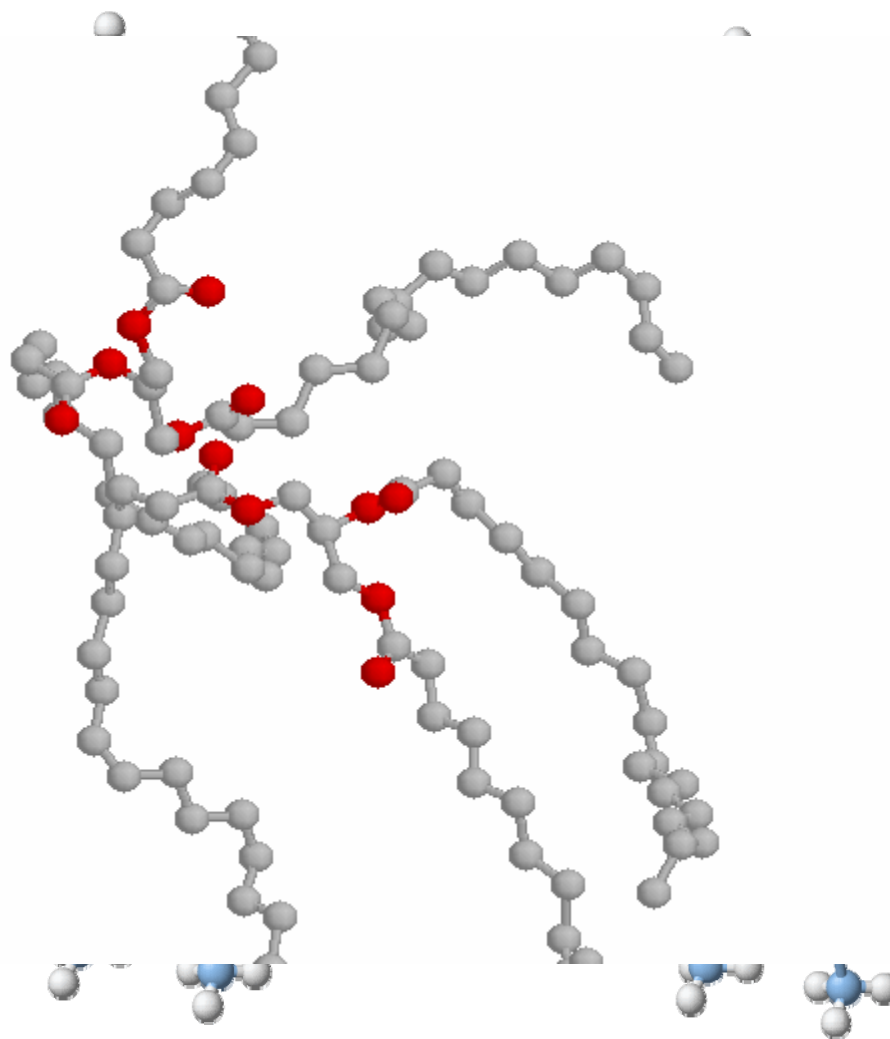
Triglycerides – Self-Assembly?



Ordering of Triglycerides

Molecule
1

Carbonyl Carbon
charge 0.65

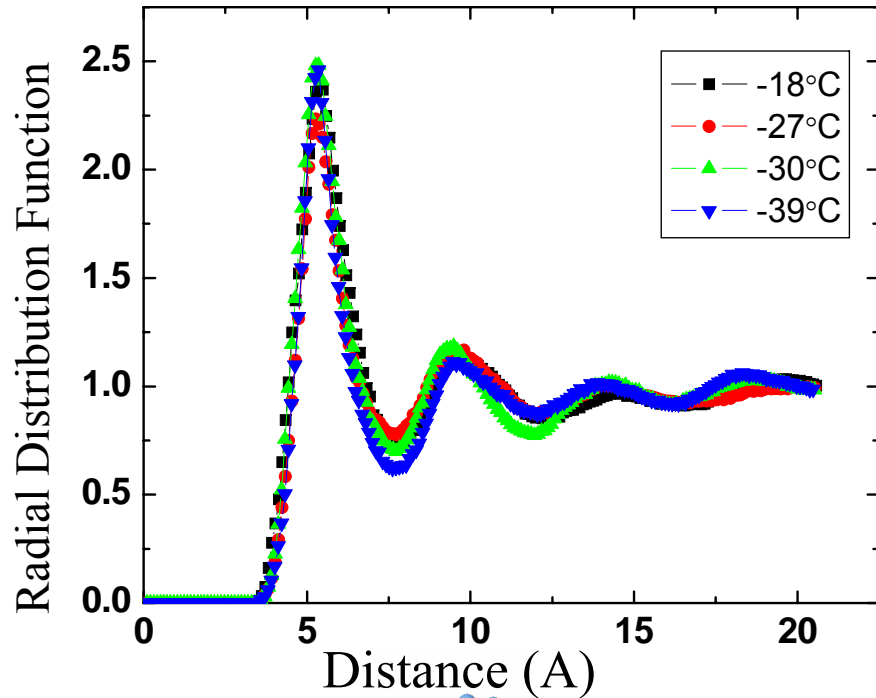


Molecule
2

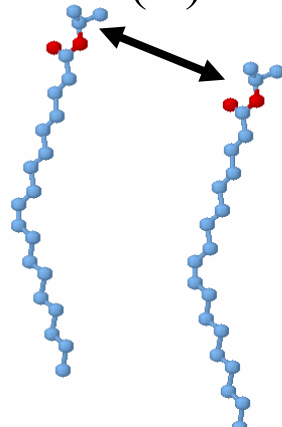
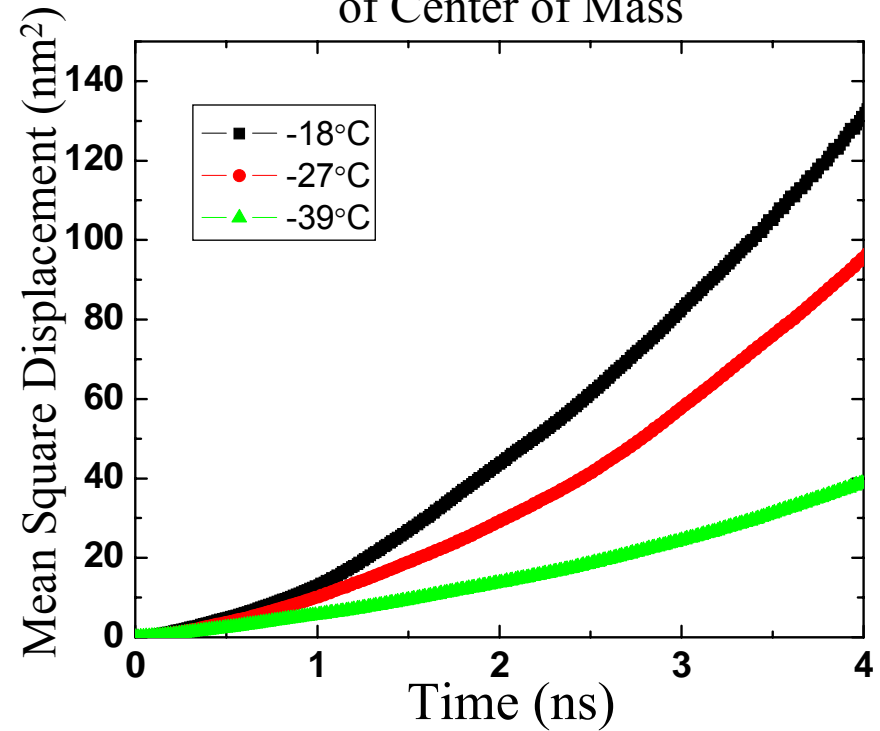
Carbonyl Oxygen
charge -0.5

Pour Point Prediction of Pure Depressant

Radial Distribution Function
between Head Carbons



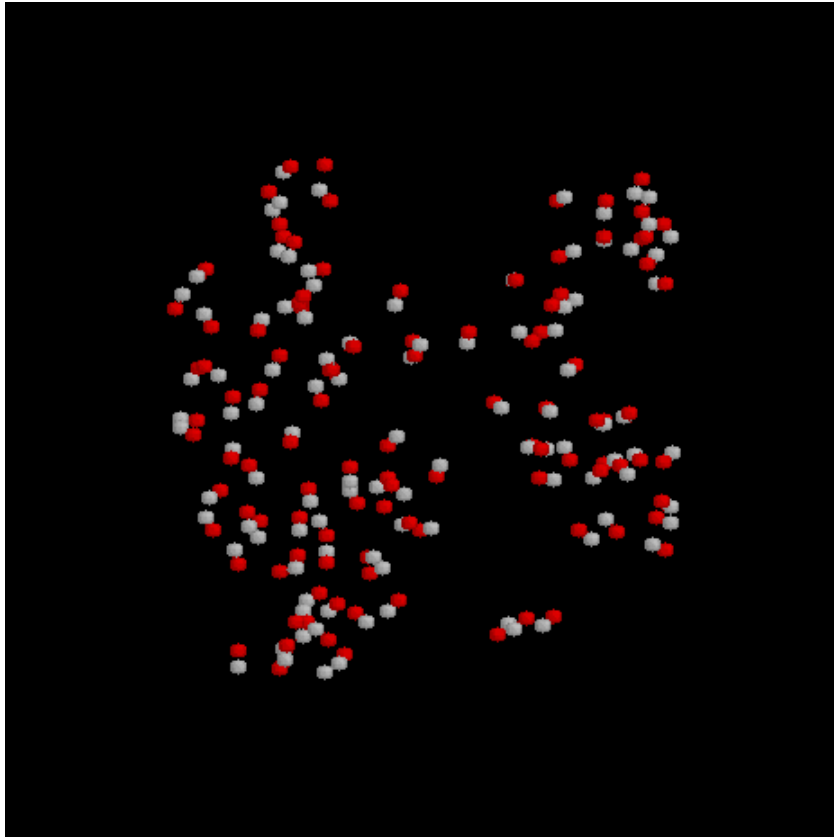
Mean Square Displacement
of Center of Mass



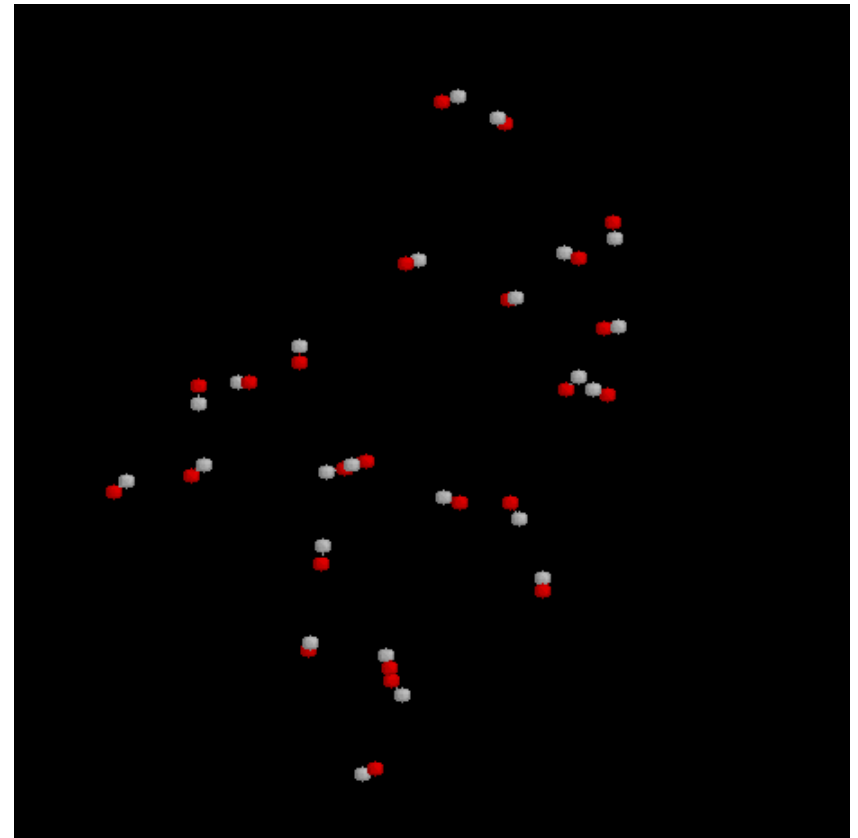
- Experimental pour point of isobutyl oleate is -30°C
- Very little change in structure near this pour point temperature
- A deviation in $\langle r^2 \rangle$ suggests a gel is forming
- High $\langle r^2 \rangle$ values suggest the system is liquid like

Trajectory of Particles for 20% Pour Point Depressant

Trajectory of C=O on glycerol backbone



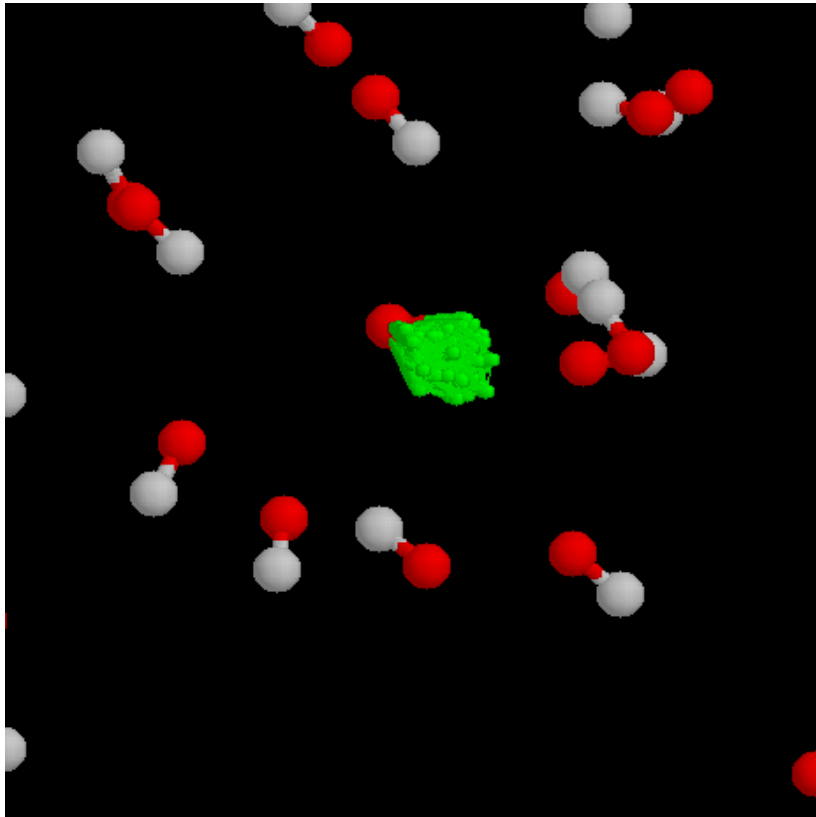
Low Oleic Oil



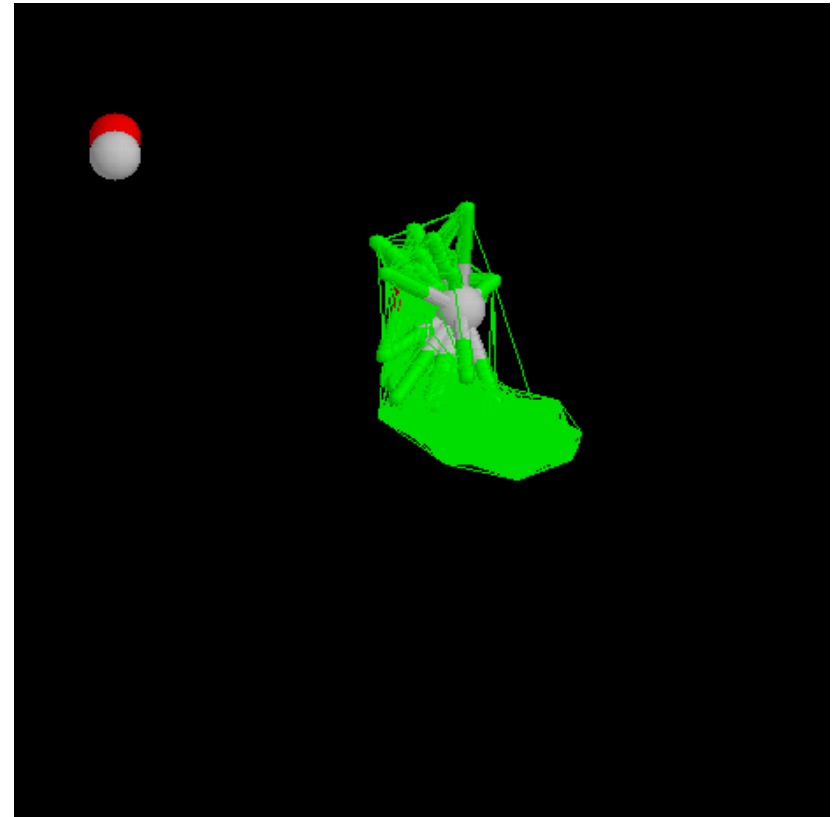
Pour Point Depressants

-27°C

Final Trajectory of Pour Point Depressant



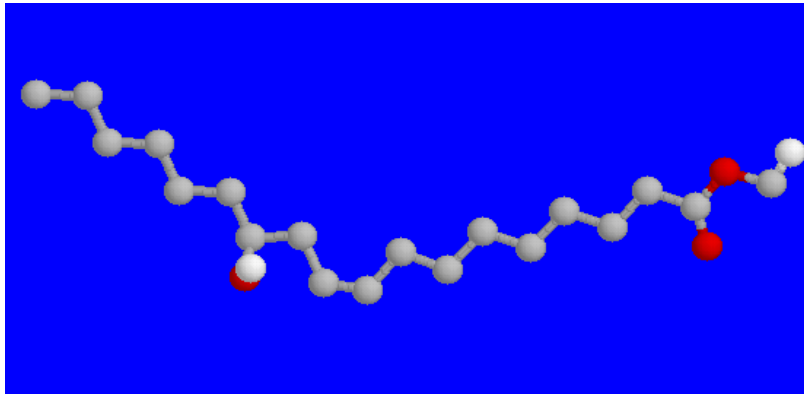
Low Oleic Oil



Pour Point Depressants

Vegetable Oils: Castor Oil

- Has a long history of being recognized as a lubricant
- Is the only vegetable oil with a high content of hydroxyl fatty acids



Ricinoleic fatty acid

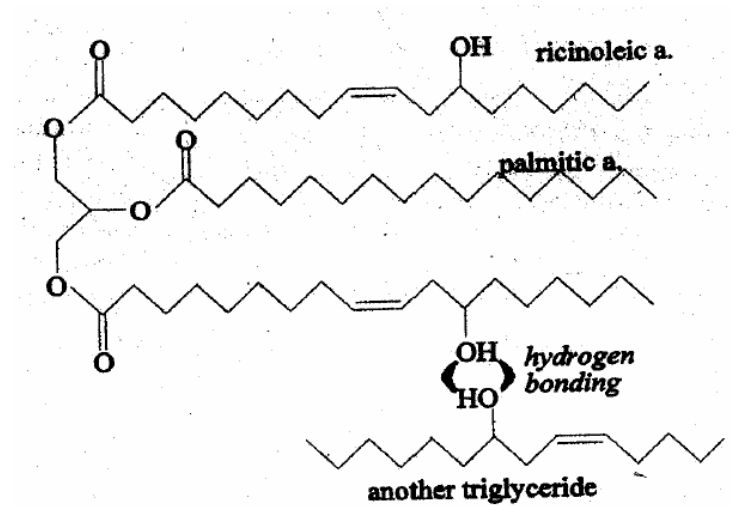
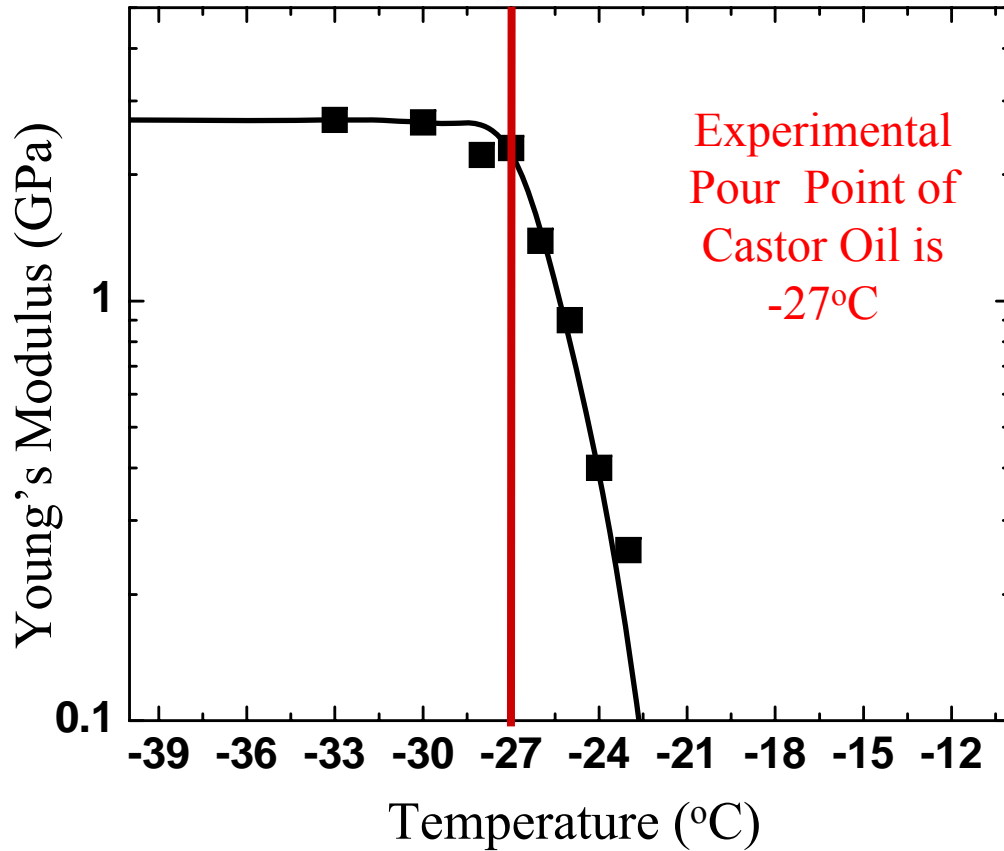
Triglyceride	Percentage
ROO	3
RLiLi	4
RRO	9
RRLi	12
RRR	69

Vegetable Oil Property Predictions: Castor Oil

Temp (°C)	Density (kg/m ³)	Viscosity (cSt)** simul. /exp.	Viscosity Index simul. /exp.
100	924 ± 5	27 ± 2 /19.9	
40	951 ± 4	256 ± 23/252	135/91

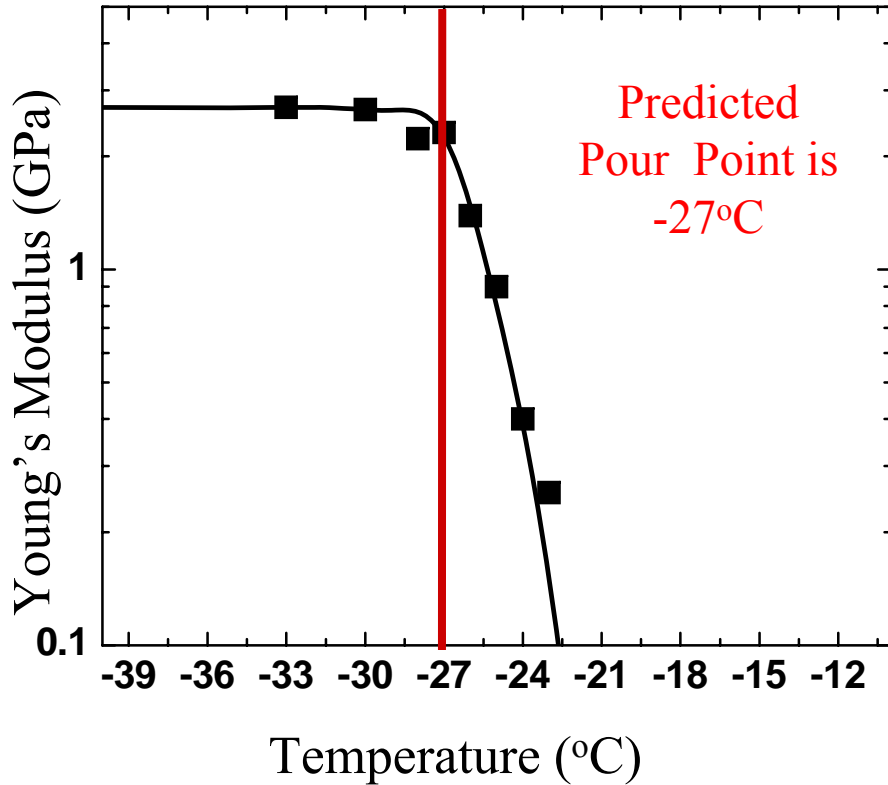
** Triglyceride composition not given for experimental data.

Castor Oil Pour Point

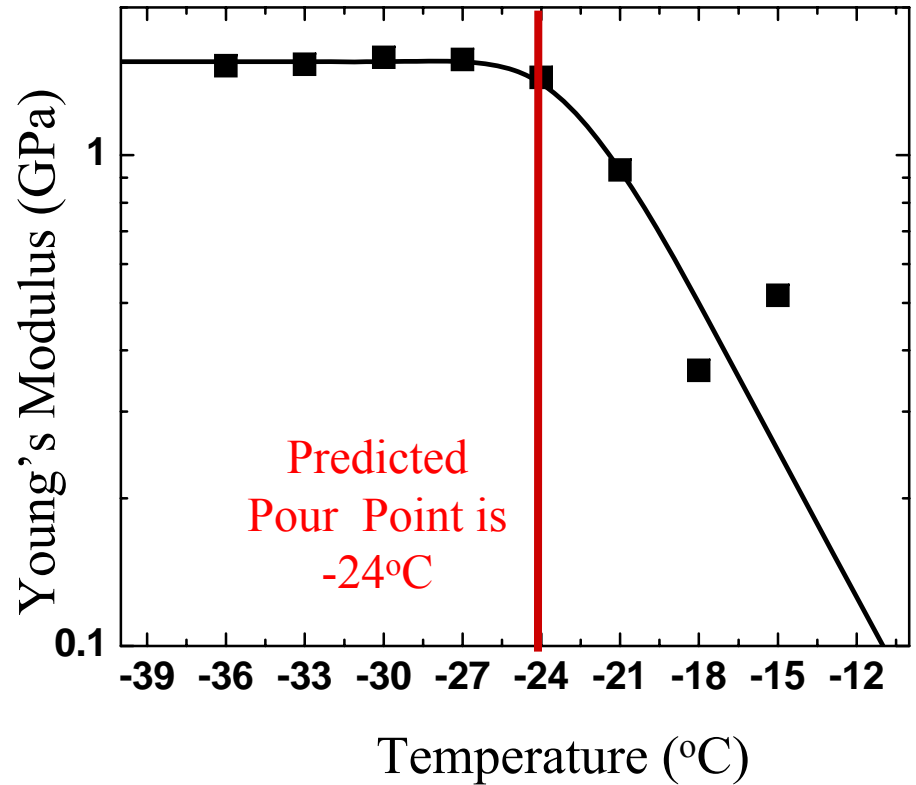


Castor Oil Pour Point – no Double Bond

Pure Castor Oil

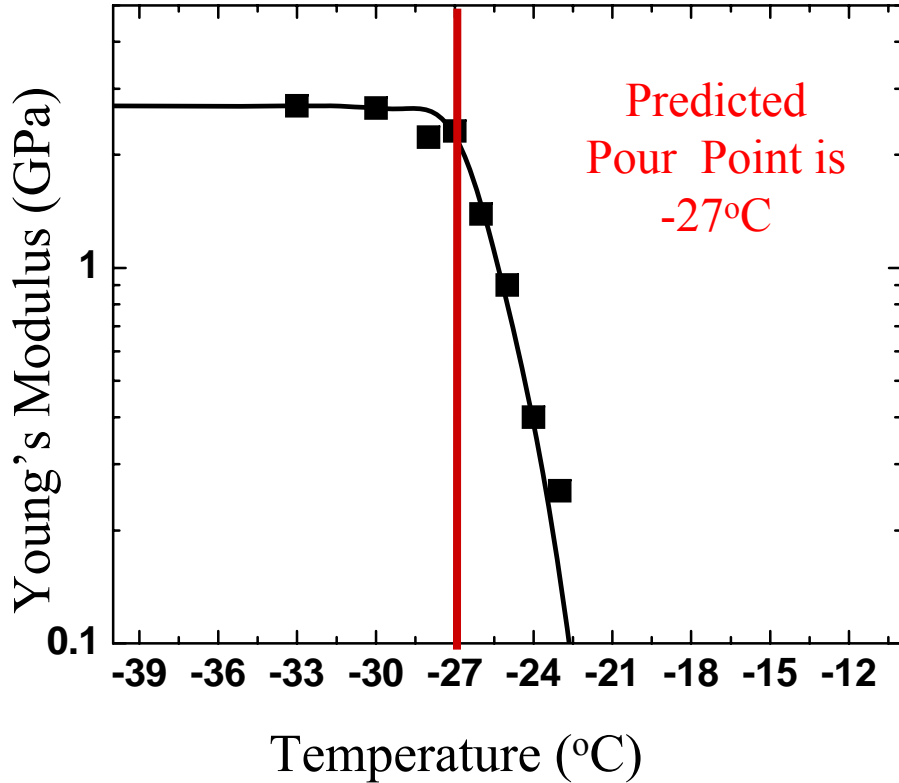


No Double Bond

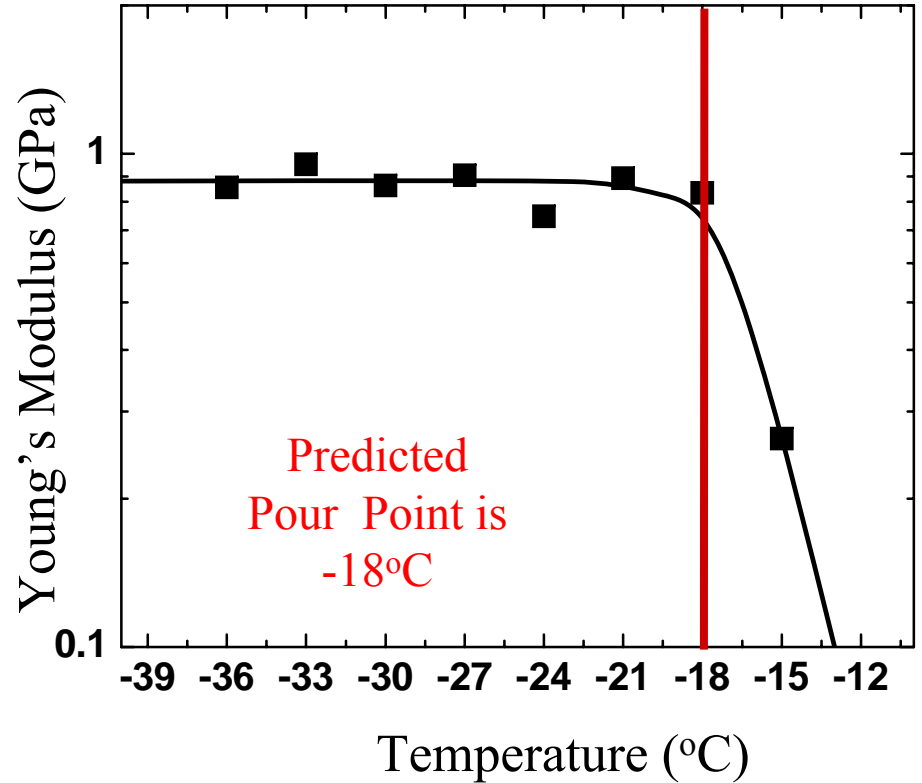


Castor Oil Pour Point – no Hydroxyl Group

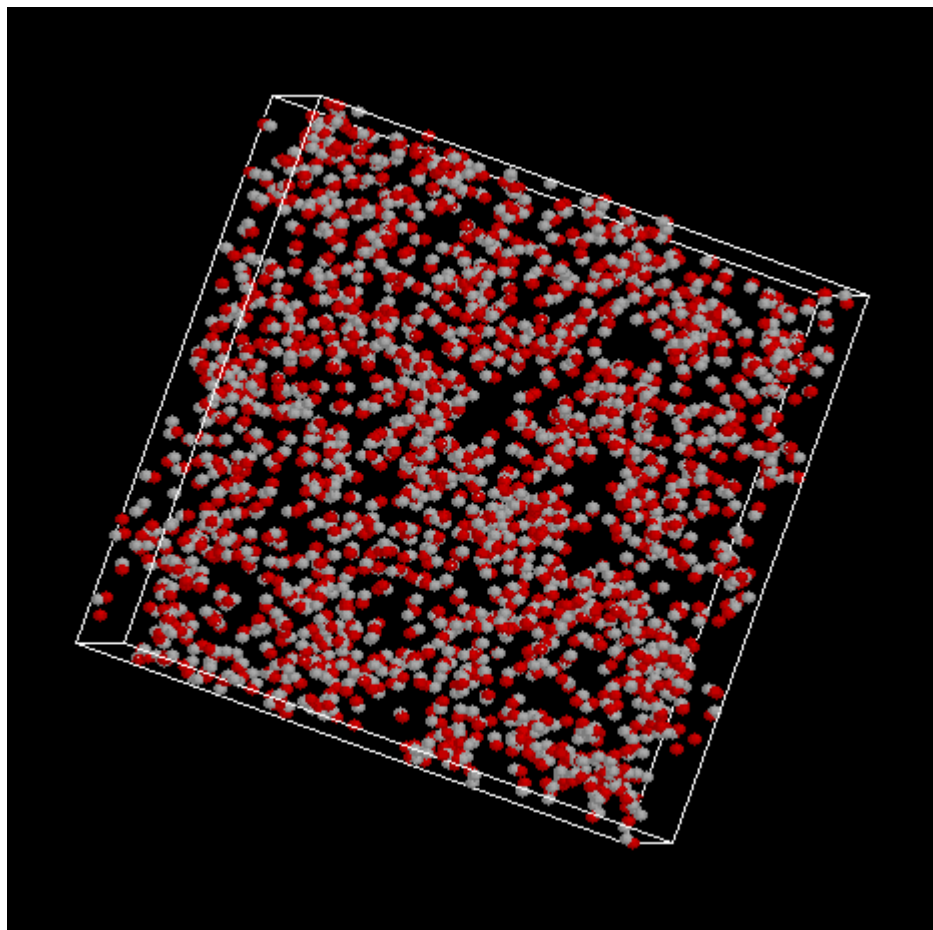
Pure Castor Oil



No Hydroxyl Group

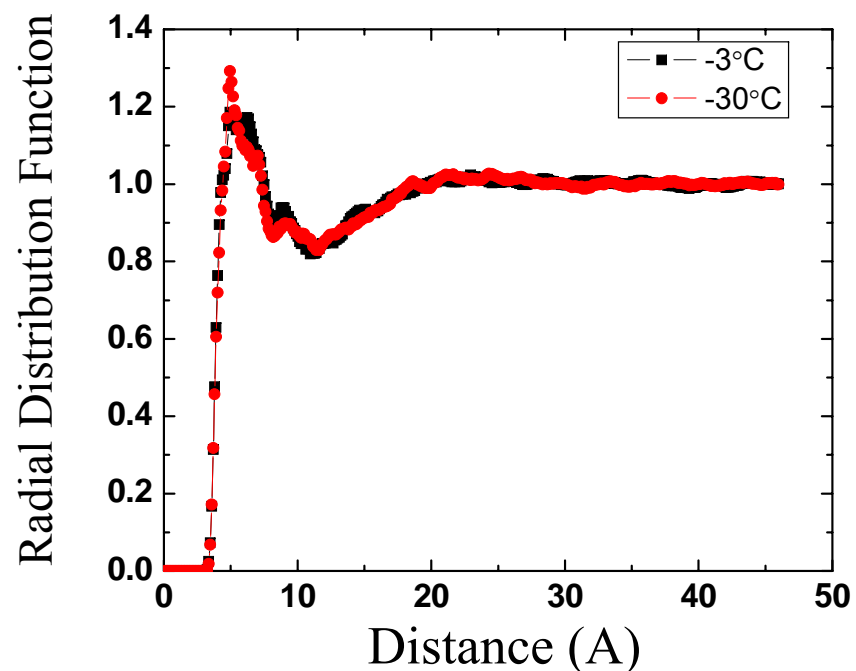


Current Work: Ordering of Triglycerides in Low Oleic Canola Oil



Carbonyl Carbon and Oxygen Atoms
500 molecules
-30°C

Intermolecular Radial Distribution Function between Carbonyl Carbons



Summary

- Successfully developed force-field parameters from *ab initio* calculations
- Accurate force-field for triglycerides and esters
- Good agreement with measured densities and viscosities for both triglycerides and vegetable oils
- Flexible and inexpensive tool for examining different molecular structures
- Accurate modeling method for the prediction of pour points

Acknowledgements

- Professor de Pablo
- Dr. Mike Tupy
- Dr. John Curro
- Dr. Amadeu Sum
- Yioryos Papakonstantopoulos
- Dr. Manolis Doxastakis
- de Pablo Group
- Sandia National Laboratories for supercomputing work
- Funding sources:
DOE CSGF and Cargill

Viscosity Index Definition

$$VI = [(\text{anti log}(N) - 1) / 0.00715] + 100$$

$$N = \frac{(\log H - \log U)}{\log Y}$$

Where:

H is the viscosity of a reference oil with VI of 100 at 40°C whose viscosity matches the oil at 100°C

U is the viscosity of the oil at 40°C

Y is the viscosity of the oil at 100°C

Force Field Development

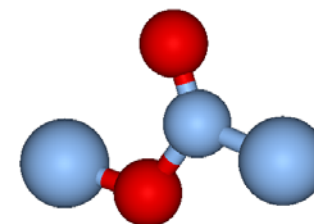
- Calculate physical properties of methyl acetate
- Use MD *NPT* to determine density and heat of vaporization
- Long-range correction for reaction field (continuum dielectric constant ϵ_{RF})

	ϵ (kJ/mol)	σ (Å)	q (a.u.)
CH ₃	0.6347	3.830	0.20
-O-	0.6736	3.472	-0.40
C	0.7185	3.312	0.65
O=	0.7922	2.840	-0.50
CH ₃	0.6253	3.835	0.05

Intermolecular Potential

Lennard-Jones plus
Coulomb interactions

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \frac{qq'}{r}$$



σ, ϵ, q

Elastic Constants

- We have investigated pour points using elastic constants to better understand oil gel behavior.
- The expression for the elastic constant is divided into three parts:

$$C_{ijlm} = \underbrace{-\frac{V_o}{k_b T} \left[\langle \tau_{ij} \tau_{lm} \rangle - \langle \tau_{ij} \rangle \langle \tau_{lm} \rangle \right]}_{\text{Stress Fluctuations}} + \underbrace{2k_b T n (\delta_{im} \delta_{jl} + \delta_{il} \delta_{jm})}_{\text{Kinetic Term}} + \underbrace{\frac{1}{V_o} \left\langle \sum_{\alpha \neq \beta} \chi(q_{\alpha\beta}) q_{\alpha\beta i} q_{\alpha\beta j} q_{\alpha\beta l} q_{\alpha\beta m} g(q_{\alpha}, q_{\beta}; r) \right\rangle}_{\text{Born Term}}$$

where

$$\chi = \left(\frac{\partial^2 V}{\partial r^2} - \frac{1}{r} \frac{\partial V}{\partial r} \right) r^{-2}$$



Yoshimoto, K., Papakonstantopolous, GJ, Lutsko, JF, and de Pablo, JJ, Phys. Rev. B 71(18) 184108, May 2005.