

**Putting Polymer Aggregates to Work:
An Industrial Perspective on the Use of Neutron
Scattering for Probing Polymers in Solution**

H. E. King, Jr.

**ExxonMobil Research and Engineering Co.
Corporate Strategic Research
Annandale, NJ 08801
hubert.e.king@exxonmobil.com**

**American Conference on Neutron Scattering
Knoxville, TN
June, 2002**

Neutron Scattering Influences Technologies for a Wide Range of ExxonMobil Businesses

DOWNSTREAM



Neutron Scattering Research at ExxonMobil

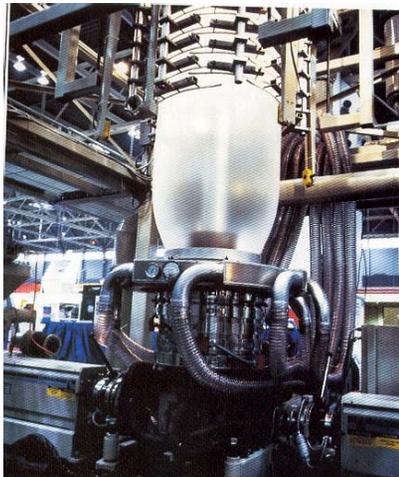
Neutron scattering is unique probe for the structure and dynamics of hydrocarbon-based materials

- Develop new materials and additives
- Improve methods to extract and process petroleum products

UPSTREAM



CHEMICALS



ExxonMobil Programs at the NCNR, NIST

Mechanisms of Dispersion of Organo Clay in Fluids
Dispersion and Suspension of Soot Flocs in Engine Lubricants
Factors Affecting the Flow of Complex Fluids in Porous Media
Determination and Control of Polymer Blend Miscibility
Reducing Crystallization of Hydrates in Crude Oils
Phase Behavior and Compatibility of Mixed Oils
Inhibition of Crystallization of Waxes in Fuels
Structure and Aggregation of Asphaltenes
Imaging Hydrogen Flow in Fuel Cells

ExxonMobil Partnership with NIST

In partnership with NIST since 1985, ExxonMobil has been a member of the participating research team that operates, maintains, and conducts basic research on the 30 meter small-angle neutron scattering (SANS) instrument at NG-7, and the Neutron Spin Echo (NSE) Spectrometer at NG-5.

DiBlock Copolymers as Wax Crystal Modifiers

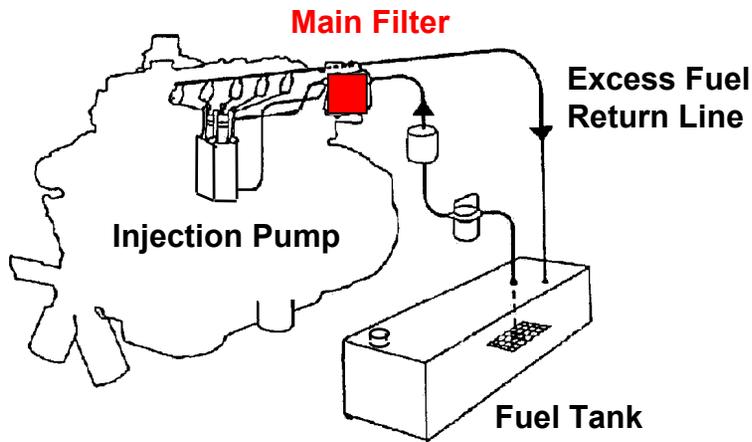
D. Richter
D. Schneiders
M. Monkenbusch
L. Wilner
L. Fetters
J. Huang
M. Lin
K. Mortensen
B. Fargo
W. Leube
D. Adamson
P. Dounis
R. Lovegrove
P. Wright
C. Symon

Facilities

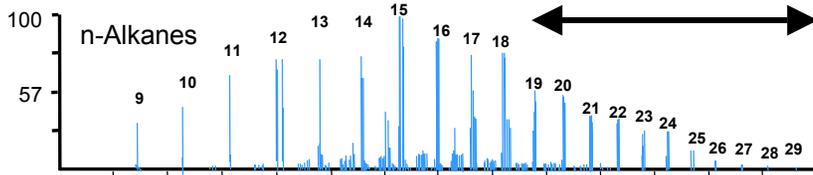
KFA Jülich
LLB Saclay
NIST Gaithersburg
ILL Grenoble

Macromolecules 30, 1053 (1997)
Energy and Fuels 14, 419 (2000)
Macromolecules 35. 861 (2002)

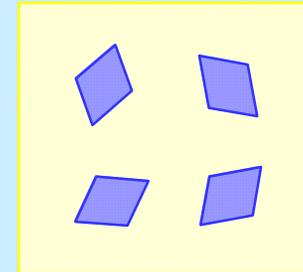
Initial Startup of Diesel Engine in Cold Weather Causes Filter Blockage by Wax Crystals



Wax Crystals are High Carbon Number N-Alkanes

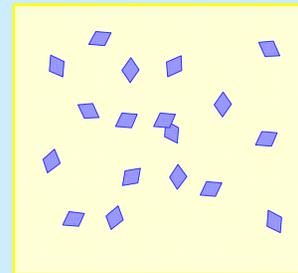


•Unmodified Wax Produces Large, Flat Crystal Plates

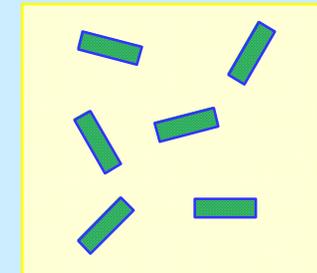


•Modified Wax Produces Smaller, More Compact Crystals

Nucleators

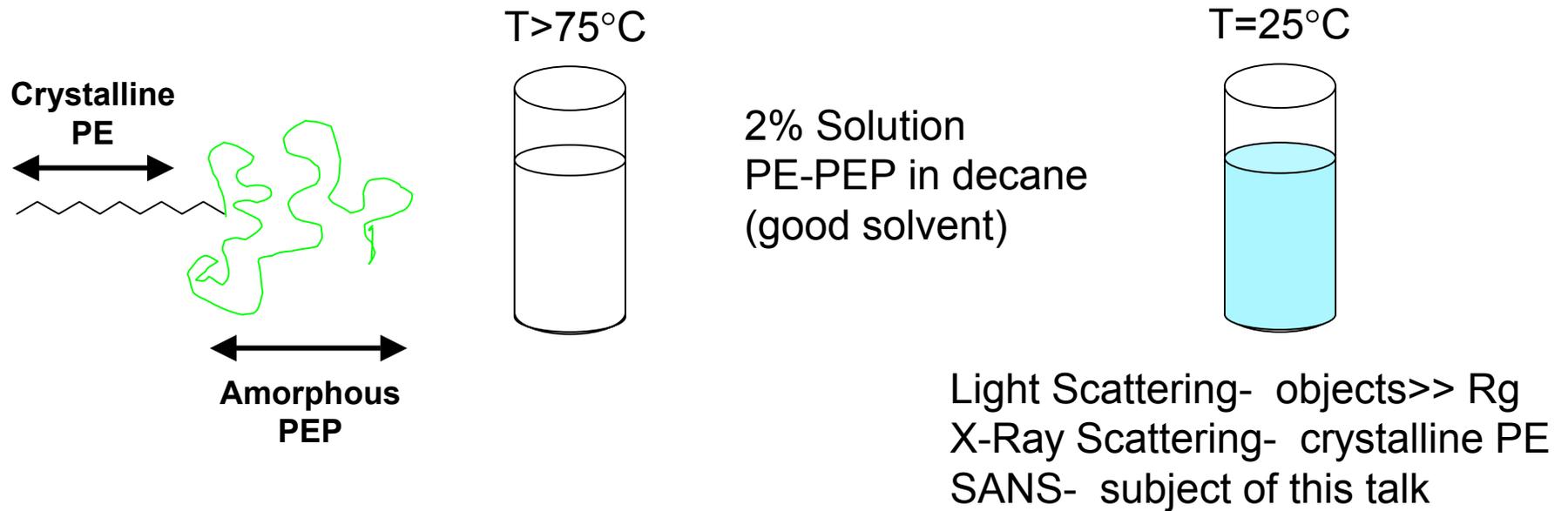


Growth Arrestors



•Polymeric Additives Control Crystallization

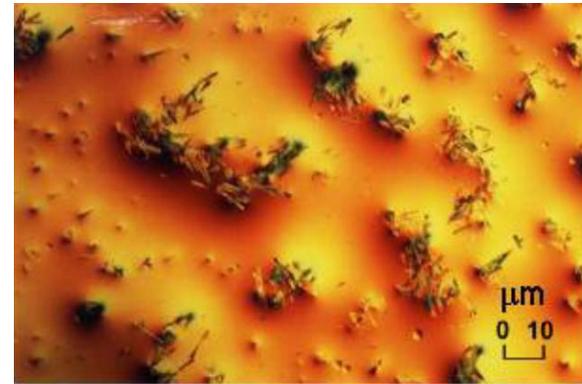
Self-Assembly of PE-PEP Diblock Copolymers Key to Wax Crystal Modification



Effect of PE-PEP Diblock on Wax Crystals in Diesel Fuel



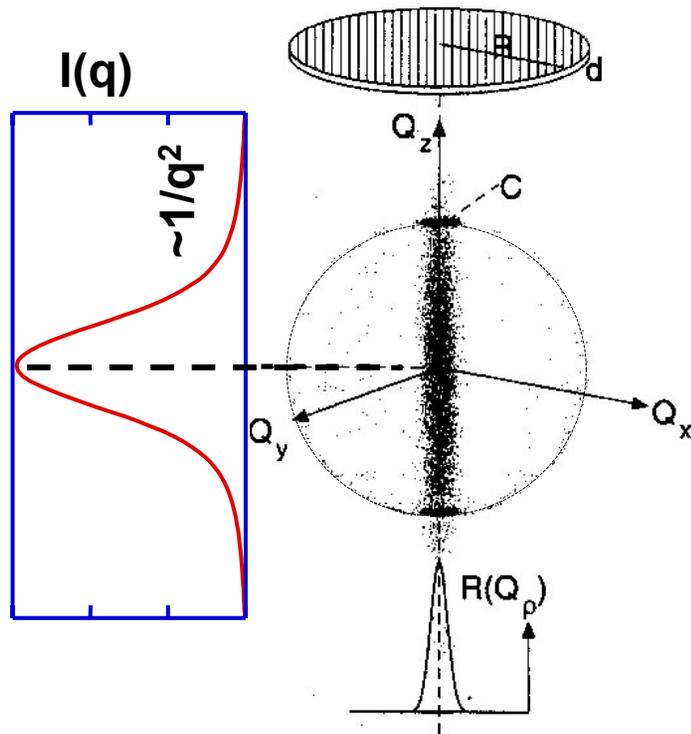
No Modifier



Polymeric Modifier

Structure of PE-PEP "Hairy" Plate

Scattering from Disks



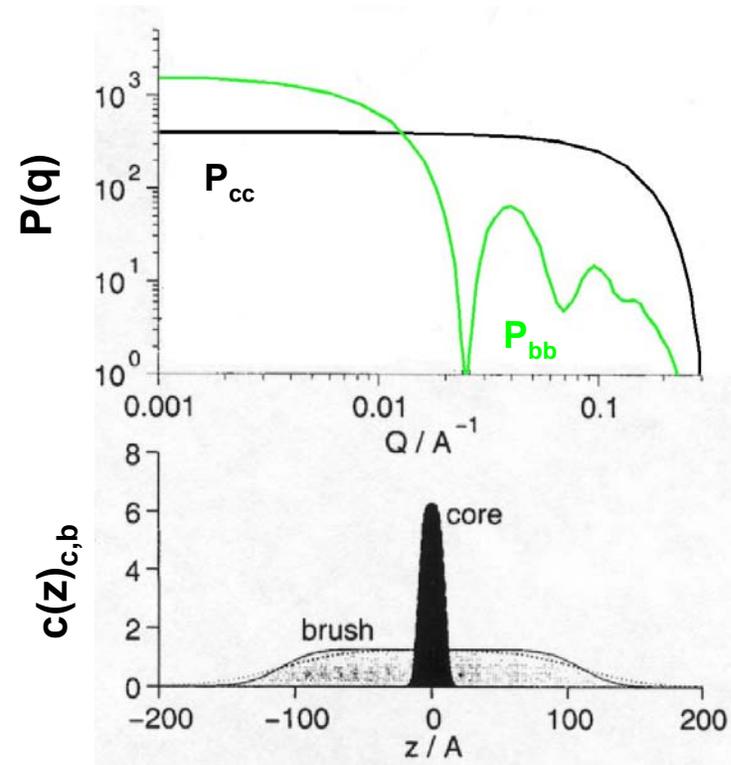
$$\langle I(\mathbf{q}) \rangle_{\theta} = (\pi R^2)^2 \frac{D(qR/2)}{(qR/2)}$$

$$D(u) = \exp(-u^2) \int_0^u \exp(t^2) dt$$

$$u \rightarrow \infty, \quad D(u) \rightarrow 1/u^2$$

Scattering from Core/Brush Structure

$$P(\mathbf{q}) = \Delta\rho_b^2 P_{bb}(\mathbf{q}) + 2\Delta\rho_b\Delta\rho_c P_{bc}(\mathbf{q}) + \Delta\rho_c^2 P_{cc}(\mathbf{q})$$

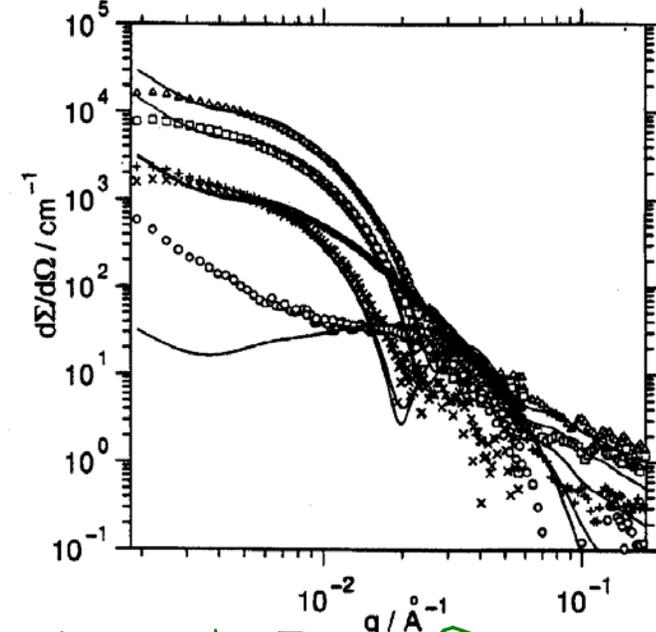


$$\frac{d\Sigma}{d\Omega}(\mathbf{q}) = \phi \frac{\phi_{PE}}{V_{PE}} P(\mathbf{q}) (\pi R^2)^2 \frac{D(qR/2)}{(qR/2)}$$

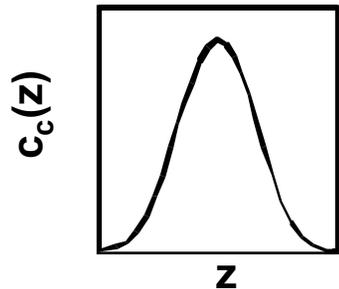
Contrast Variation Allows Full Structure Determination of Hairy Plate

5 scattering length contrasts
1.5k PE - 5k PEP diblock

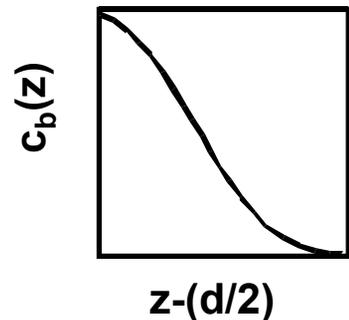
$$\begin{bmatrix} I^{(1)}(q) \\ \vdots \\ I^{(i)}(q) \\ \vdots \\ I^{(N)}(q) \end{bmatrix} = \begin{bmatrix} (\Delta\rho_b^{(1)})^2 & \Delta\rho_b^{(1)}\Delta\rho_c^{(1)} & (\Delta\rho_c^{(1)})^2 \\ \vdots & \vdots & \vdots \\ (\Delta\rho_b^{(i)})^2 & \Delta\rho_b^{(i)}\Delta\rho_c^{(i)} & (\Delta\rho_c^{(i)})^2 \\ \vdots & \vdots & \vdots \\ (\Delta\rho_b^{(N)})^2 & \Delta\rho_b^{(N)}\Delta\rho_c^{(N)} & (\Delta\rho_c^{(N)})^2 \end{bmatrix} \begin{bmatrix} P_{bb}(q) \\ P_{bc}(q) \\ P_{cc}(q) \end{bmatrix}$$



Core model:
Gaussian
smeared step

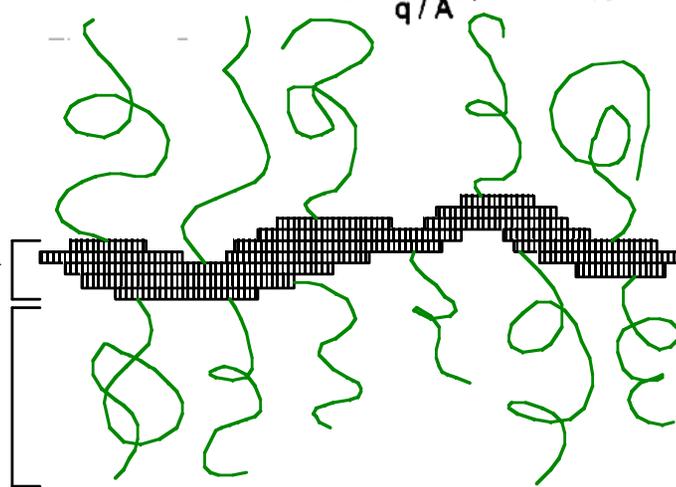


Hair model:
Gaussian
smeared step



$d=18\text{\AA}$

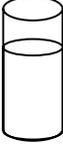
$L_p=120\text{\AA}$



PEP $R_g = 28\text{\AA}$ unperturbed radius of gyration

Crystallization Control from Wax Incorporation In "Hair"

$T > 75^\circ\text{C}$

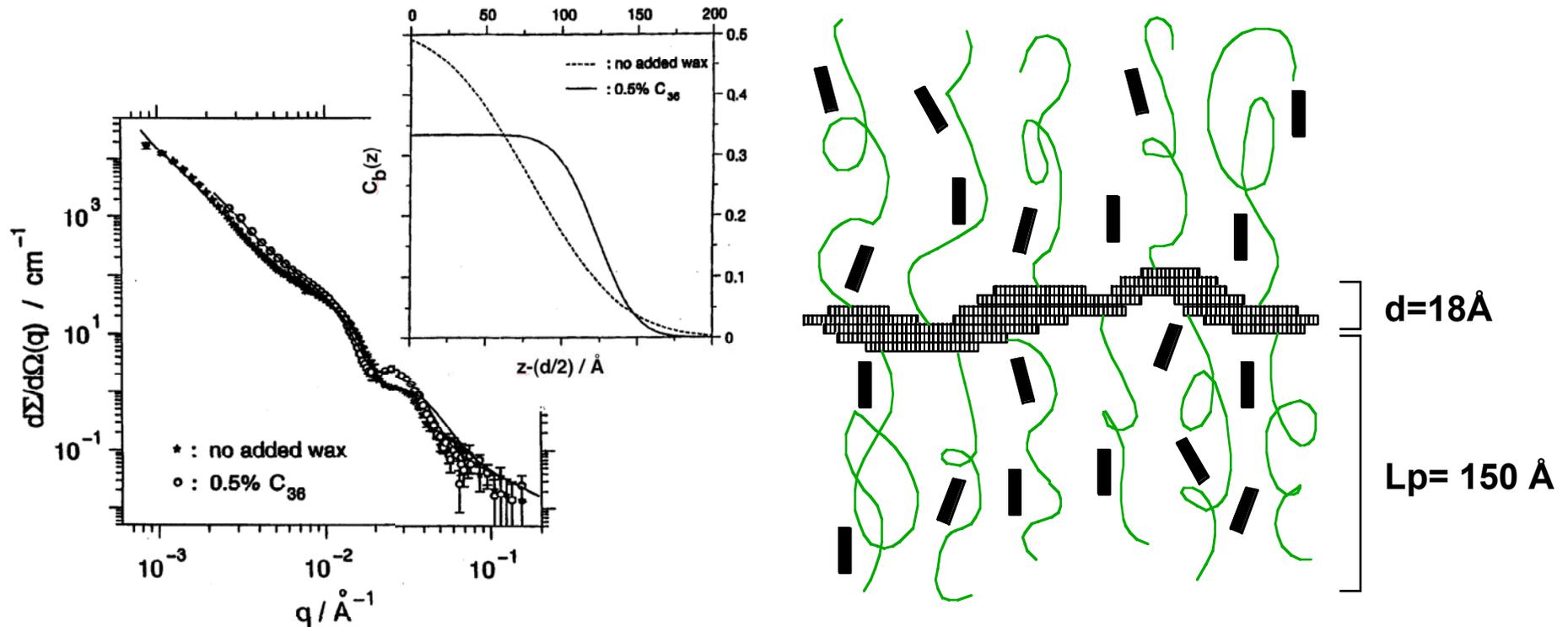


2% Solution PE-PEP
in decane + 0.5% C36-wax



$T = 25^\circ\text{C}$

- **Brush contrast- core and wax contrast matched**
 - Wax Incorporation Stretches "hair"; Molecular Interaction



Shape of hairy plate (d/L_p ratio) is controlled by Mw and branch content. Thermodynamic modeling successful in predicting this relationship. Modeling used to optimize performance.

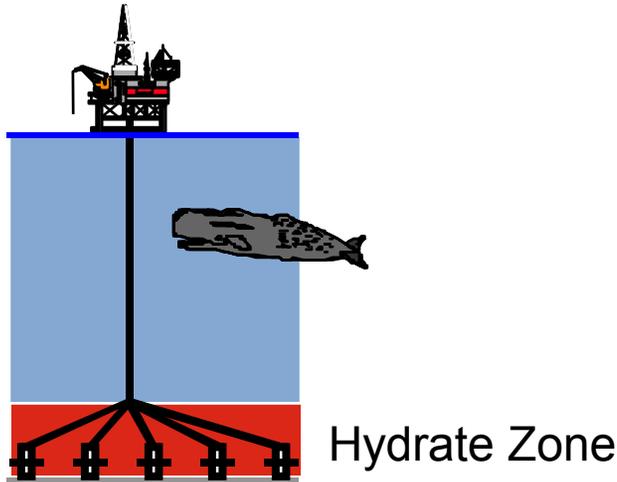
Kinetic Inhibitors for Natural Gas Hydrate Crystallization

T. Sun
E. Smelik
J. Hutter
M. Lin
H. King

Facilities
NIST, Gaithersburg

American Mineralogist 82, 88 (1997)
Macromolecules 29, 3175 (1996)
Macromolecules 33, 2670 (2000)
J. Chemical Physics 112, 2523 (2000)

Hydrates: A Significant Problem for Oil and Gas Production



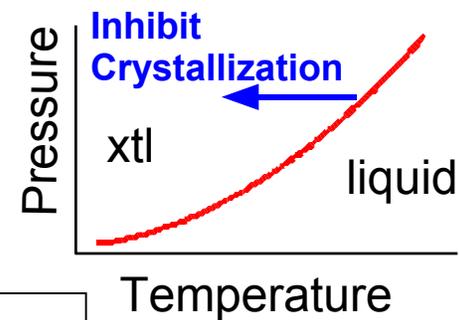
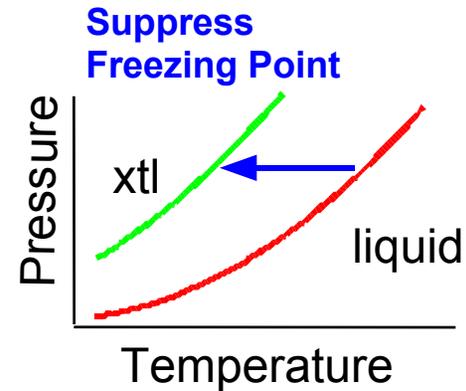
- **Oil and gas pipelines**
 - Hydrates of hydrocarbons and water form at elevated P and low T
 - Block pipelines

Thermodynamic: (current practice)

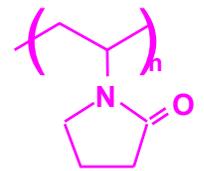
- Insulate the pipeline
- Add an antifreeze (alcohol)
 - Expensive
 - Potential for environmental impact

Kinetic:

- Inhibitors affect crystal formation/morphology
 - Effective at <0.5 wt%
 - slow/inhibit hydrate formation at given ΔT



Example

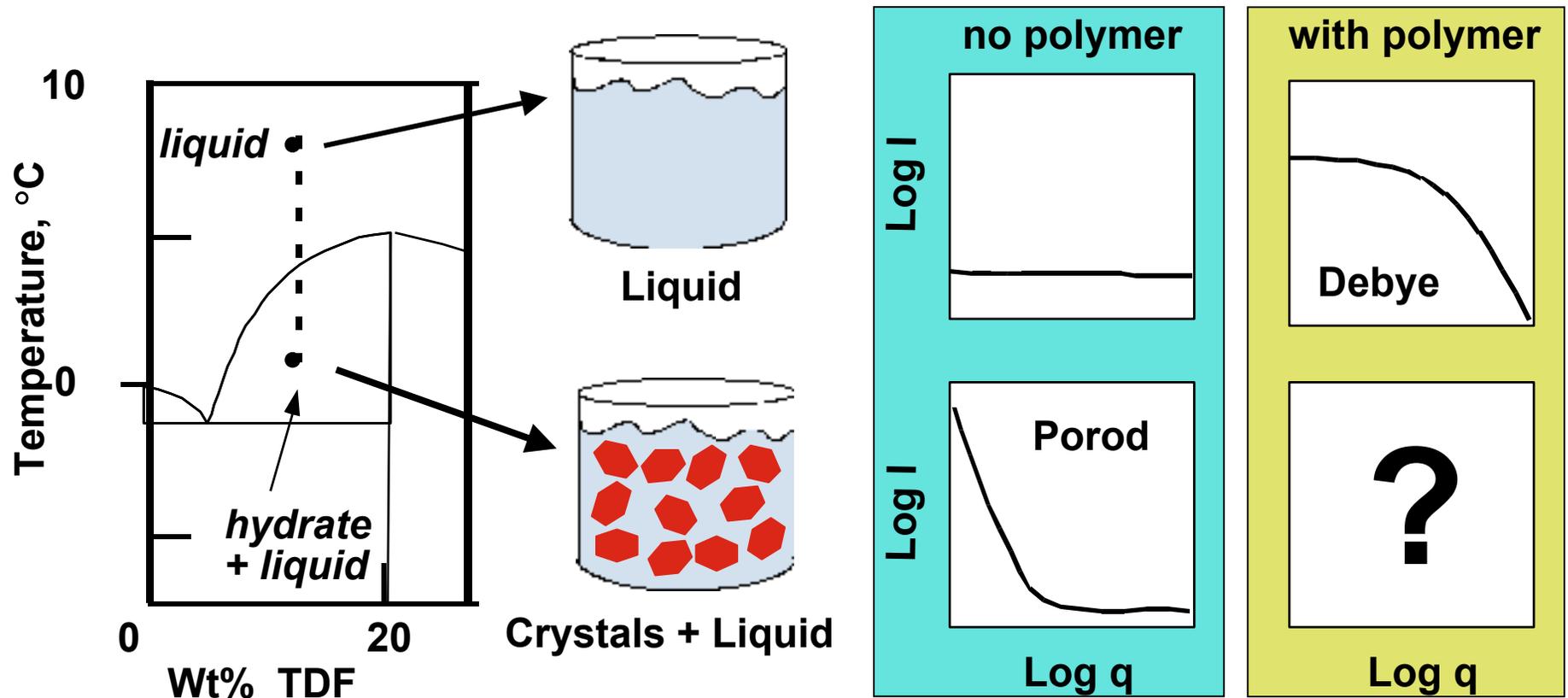


PVP

How do kinetic inhibitors work?

Liquid and [Crystals + Liquid] Investigated By Changing T

Small Angle Neutron Scattering



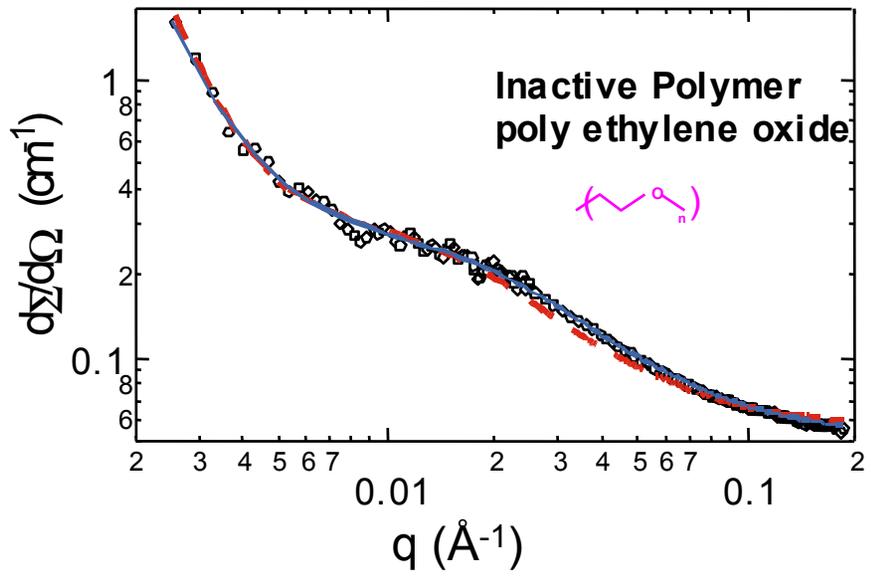
- Experimental method:

- Solutions of TDF and D₂O/H₂O water
- Partially frozen while stirring (~50% vol. frac., simulates crystal-liquid mixture in pipeline)

SANS from Crystals + Liquid + Polymer

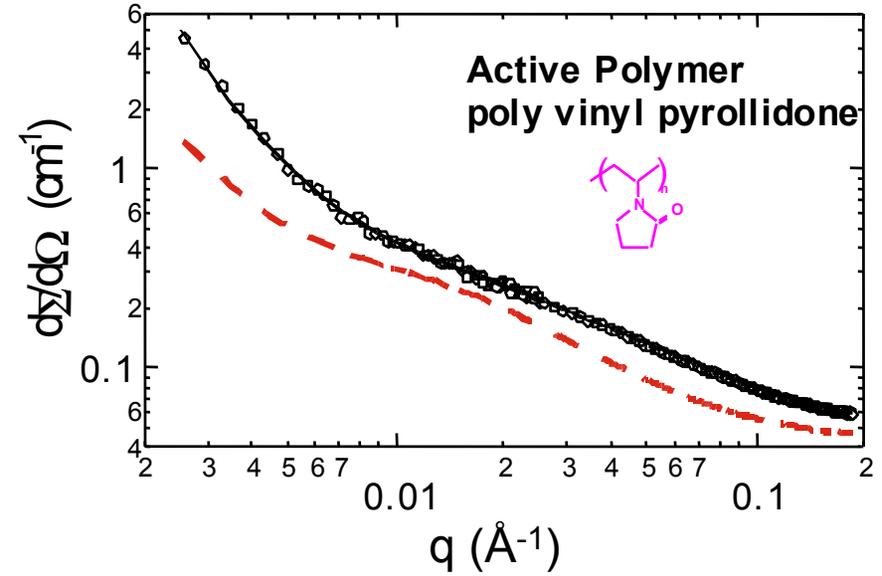
Non-Inhibitor

Intensity equal to
Porod + Debye scattering (---)



Inhibitor (PVP)

Intensity not equal to
Porod + Debye scattering (---)



Excess scattering due to polymer layer

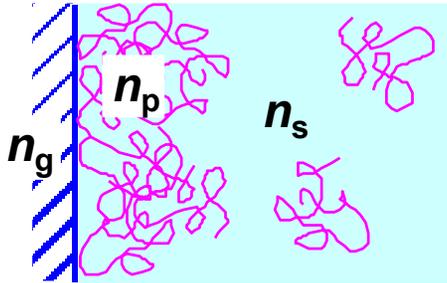
$$I(q) = (n_g - n_s)^2 S_{gg}(q) - 2(n_p - n_s)(n_g - n_s) S_{pg}(q) + (n_p - n_s)^2 S_{pp}(q)$$

Porod
(surfaces)

Polymer Layer

Solvated Polymer
+ Polymer Layer

Use Contrast Variation to Extract Structure Factors



- **Total scattering intensity depends on:**
 - Hydrate-solution contrast
 - Polymer-solution contrast

$$I(q) = (n_g - n_s)^2 S_{gg}(q) - 2(n_p - n_s)(n_g - n_s) S_{pg}(q) + (n_p - n_s)^2 S_{pp}(q) + B$$

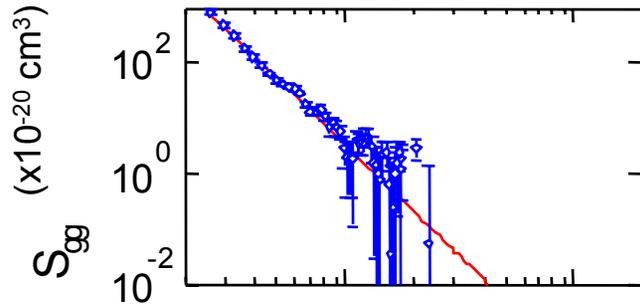
Porod (surfaces)
Polymer Layer
Solvated Polymer + Polymer Layer

- **Contrast factors, $\Delta\rho=(n_1-n_2)$, changed by varying H₂O/D₂O ratios**

	Measured Intensity	Contrast Matrix	Structure Factors	Background	
5 H₂O/ D₂O ratios 	$\begin{bmatrix} I^{(1)}(q) \\ \vdots \\ I^{(i)}(q) \\ \vdots \\ I^{(N)}(q) \end{bmatrix}$	$= \begin{bmatrix} (\Delta\rho_{gg}^{(1)})^2 & (\Delta\rho_{gp}^{(1)})^2 & (\Delta\rho_{pp}^{(1)})^2 \\ \vdots & \vdots & \vdots \\ (\Delta\rho_{gg}^{(i)})^2 & (\Delta\rho_{gp}^{(i)})^2 & (\Delta\rho_{pp}^{(i)})^2 \\ \vdots & \vdots & \vdots \\ (\Delta\rho_{gg}^{(N)})^2 & (\Delta\rho_{gp}^{(N)})^2 & (\Delta\rho_{pp}^{(N)})^2 \end{bmatrix}$	$\begin{bmatrix} S_{gg}(q) \\ \vdots \\ S_{gp}(q) \\ \vdots \\ S_{pp}(q) \end{bmatrix}$	$+ \begin{bmatrix} b^{(1)} \\ \vdots \\ b^{(i)} \\ \vdots \\ b^{(N)} \end{bmatrix}$	<p>5 data 3 unknowns at each scattering vector, q</p>

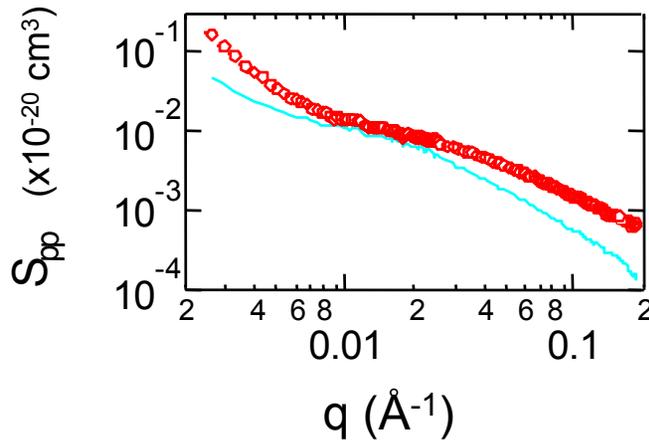
Structure Factors for Crystal + Liquid + Polymer

$$I(q) = (n_g - n_s)^2 S_{gg}(q) - 2(n_p - n_s)(n_g - n_s) S_{pg}(q) + (n_p - n_s)^2 S_{pp}(q) + B$$



Porod scattering (surfaces)

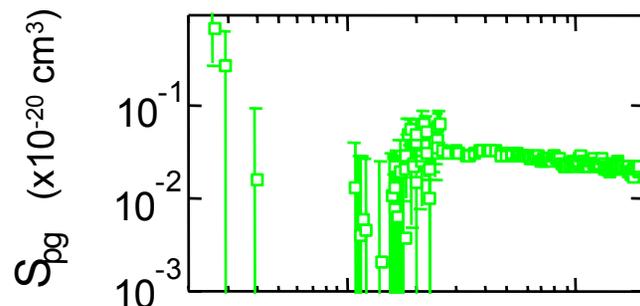
- $\sim q^{-4}$
- Surface area increased 7 fold over no inhibitor case, as expected from change to flat plate shapes from octahedra



Polymer in solution and layer

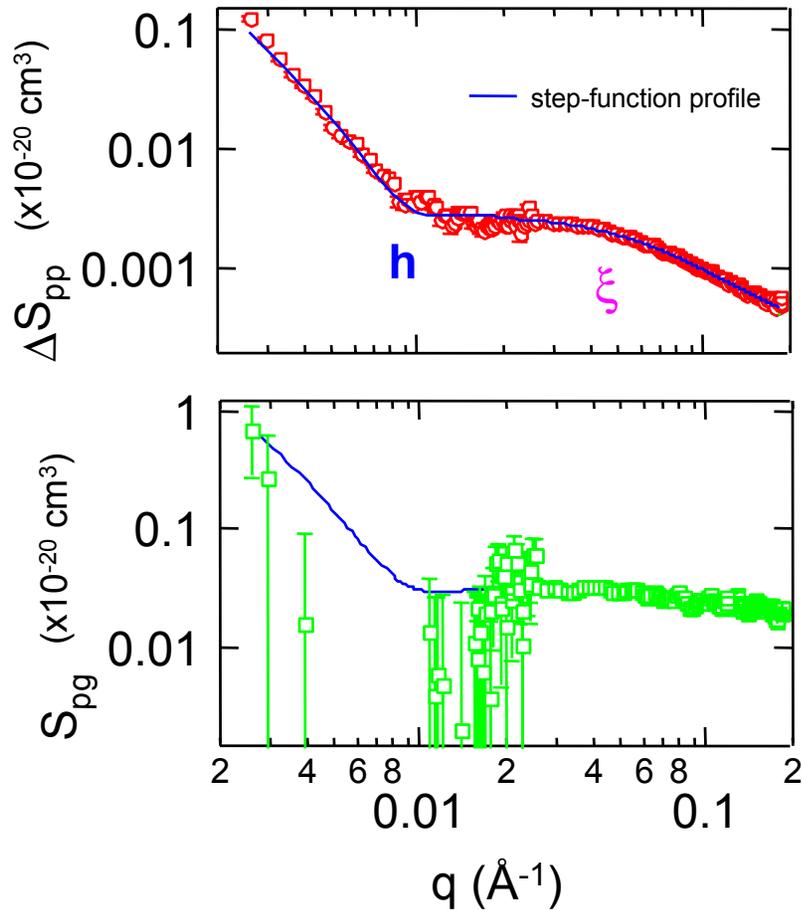
- $S_{pp} >$ solution scattering
- => polymer in surface layer contributes extra scattering intensity

S_{pp} @ 7 °C
(no crystals)



Cross term(adsorbed polymer layer)

Structure of Polymer Layer from ΔS_{pp} and S_{pg}



Excess scattering in ΔS_{pp}

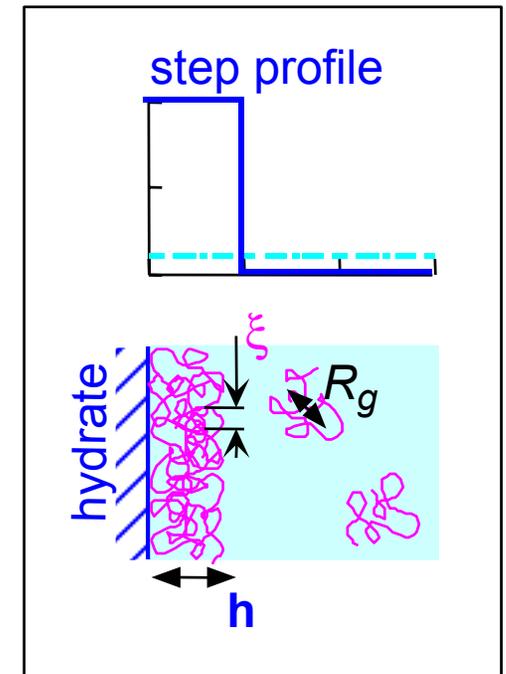
Length scales:

$h \sim 550 \pm 8 \text{ \AA}$

$\xi \sim 25 \pm 1 \text{ \AA}$

$\neq R_g (\sim 80 \text{ \AA})$

Profile model



• Layer covers $\sim 2\%$ of surface, e.g. S-polymer/S-total

$$S_{pp} \sim (S) \phi^2$$

$$S_{pg} \sim (S) \phi$$

} solve for $S, \phi \Rightarrow$

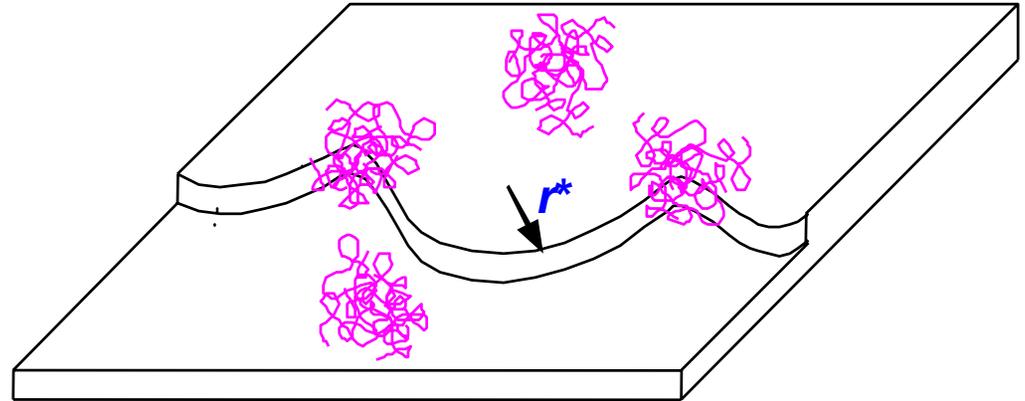
$$S\text{-polymer} = 80 \text{ cm}^{-1}$$

$$\phi = 0.07$$

Unusual Adsorbed Layer is Characteristic of Polymeric Hydrate Inhibitors

PVP

- Layer is 550 Å thick
 - Surprising that layer $> R_g$
 - Self-aggregation implied
- Layer covers only 2% of crystal surface
 - Adsorption to specific sites?
- Other inhibitor polymers show similar behavior



Is enough polymer adsorbed to slow the growth?...YES!

- Distribution into 550 Å clumps \Rightarrow ~ 2000 Å spacing
- This spacing is same order of magnitude as critical radius for hydrate nucleation on surface (r^*)

Summary: Neutron Scattering Studies at ExxonMobil

- Length scale for SANS appropriate to molecular and supra-molecular problems typical of our industry
- Time scale for Neutron Spin Echo appropriate for dynamics of complex systems of interest
- Variable scattering length density through changing H/D ratios is key to study of complex hydrocarbons
- Penetration through light-adsorbing materials such as crude oils
- Examples from this study:
 - Self-assembled, diblock "hairy" plate structure key to wax crystal modifier development for diesel fuels
 - Surface adsorption and aggregation of polymer on gas hydrate surface key to understanding and design of kinetic hydrate inhibitors