

Use of NMR Imaging to Determine Asphalt Surface Energy

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Scope

- **Imaging preliminaries**
- **Measurements of contact angles using NMR imaging**
- **Solution to Young's equation for surface tension**
- **Calculation of surface tensions from imaging data**
- **Images of water drops on PPA modified asphalts**
- **Some additional images of interest**
- **Conclusions**

Nuclear Magnetic Resonance Imaging

~~Nuclear~~ Magnetic Resonance Imaging

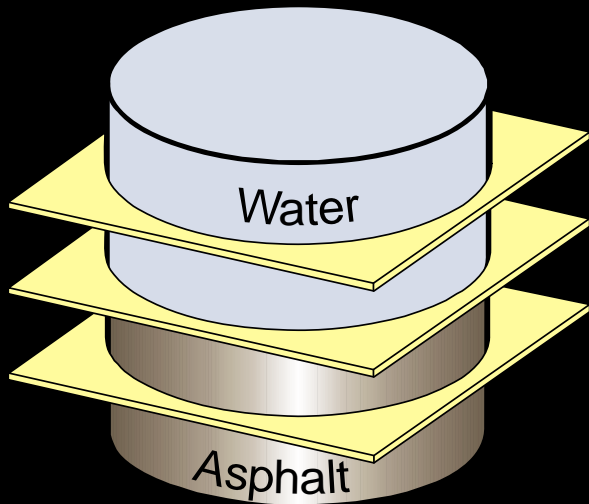
- **Provides spatial information in three dimensions about the hydrogen distribution in a sample.**
- **In medical applications, images are acquired mainly of the water in tissues and organs. Sometimes protons in fats and lipids are also imaged.**
- **Mostly used in medicine, but more non-medical applications starting to appear.**

Sample in Probe

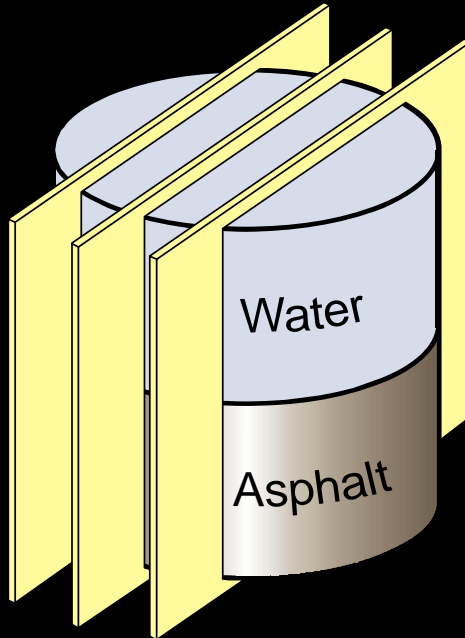


Imaging Configurations

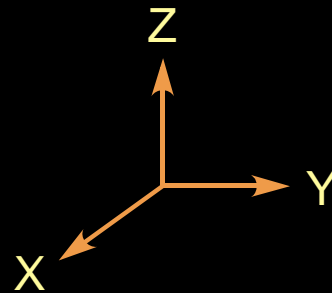
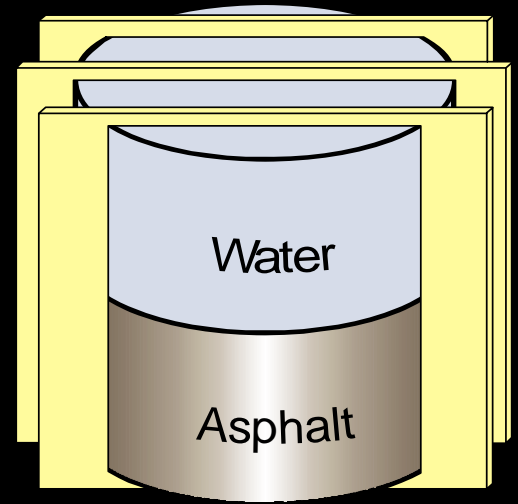
XY



XZ



YZ



Water Drop on Asphalt

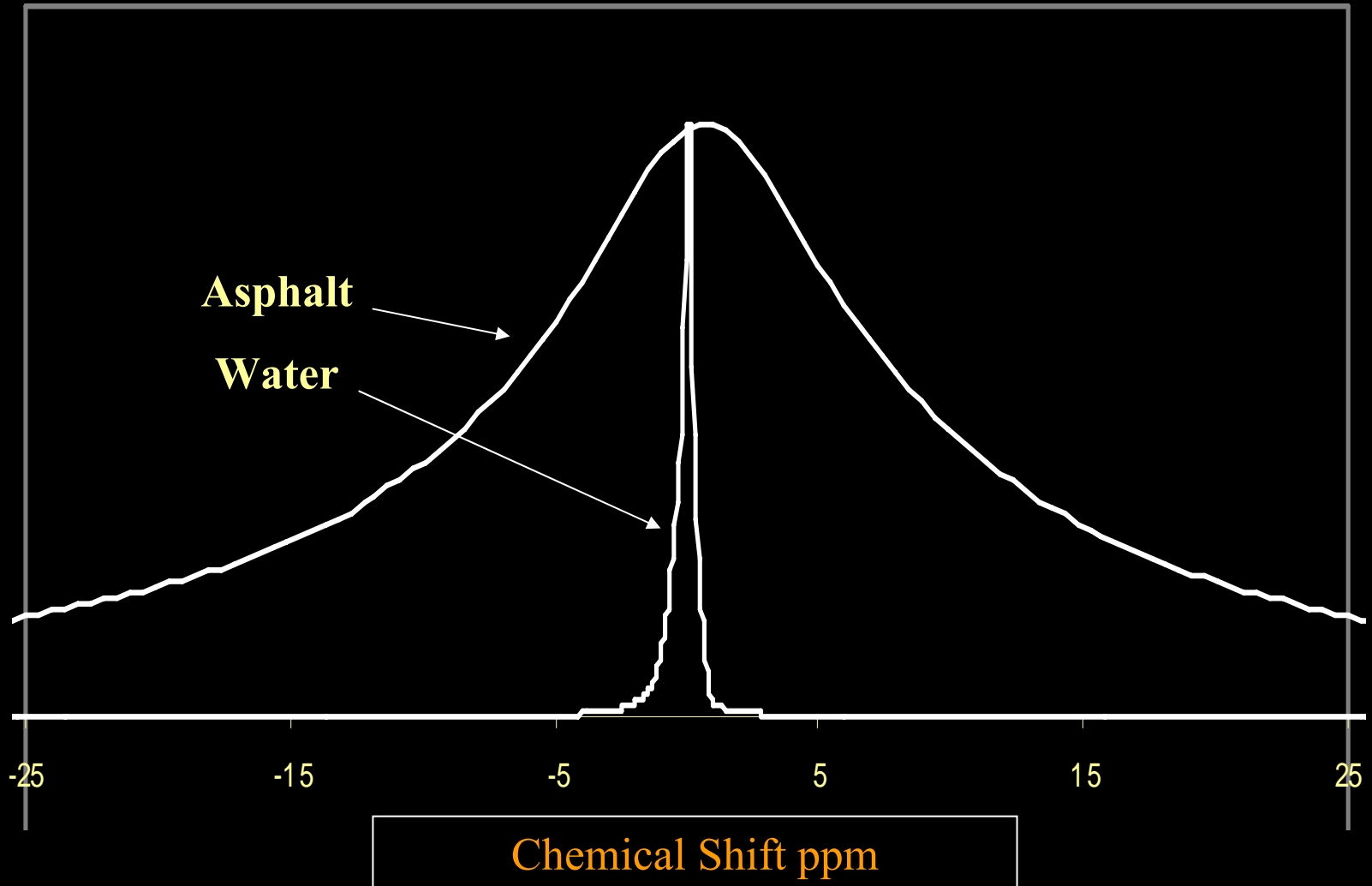


Image of Water Drop on Asphalt

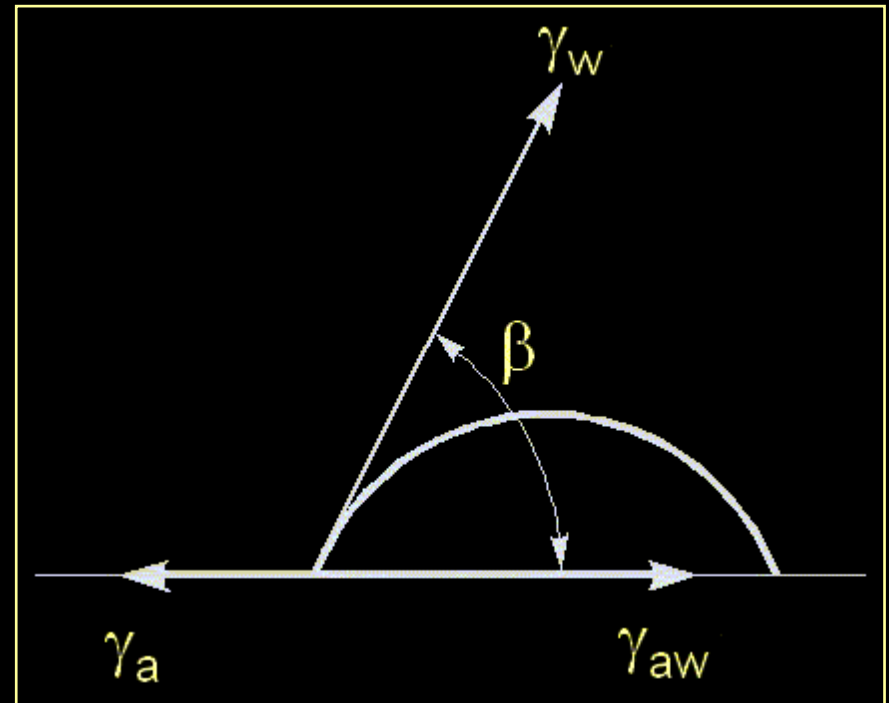


F. P. Miknis, A. T. Pauli, A. Beemer, B. Wilde, Use of NMR Imaging to Measure Interfacial Properties of Asphalts, Fuel, 84, 1041-1051(2005).

NMR Lineshapes



Young's Equation

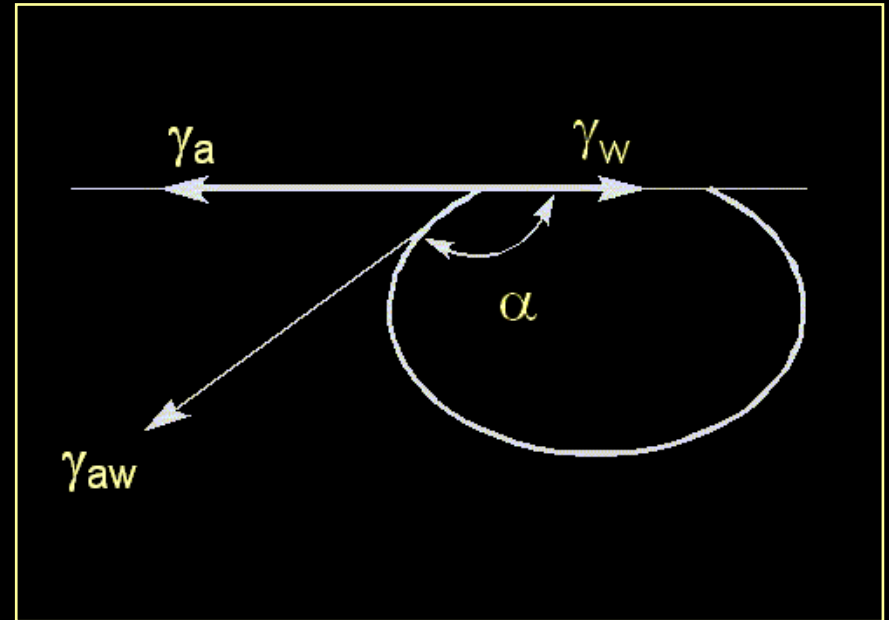
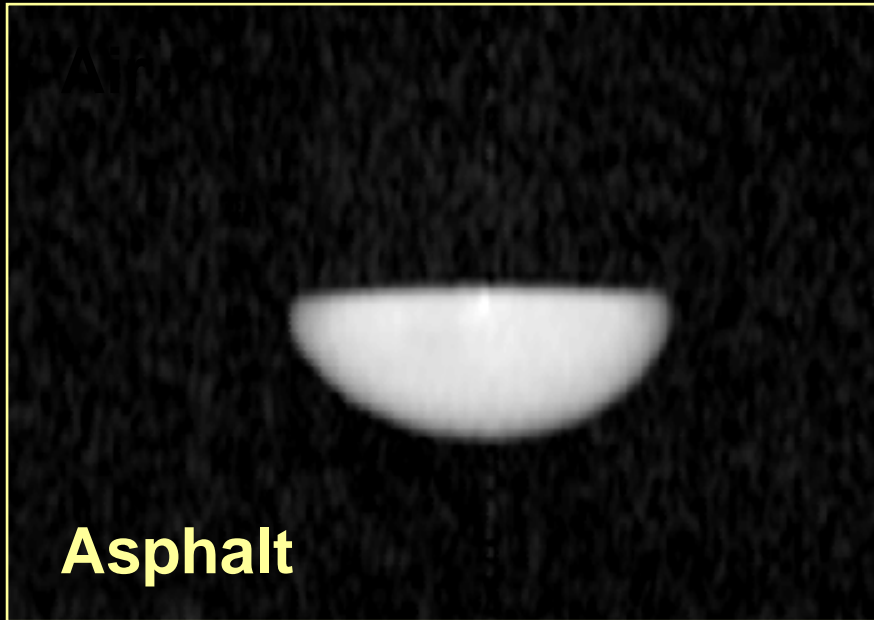


$$\gamma_a = \gamma_{aw} + \gamma_w \cos\beta$$

Water Drop In Asphalt

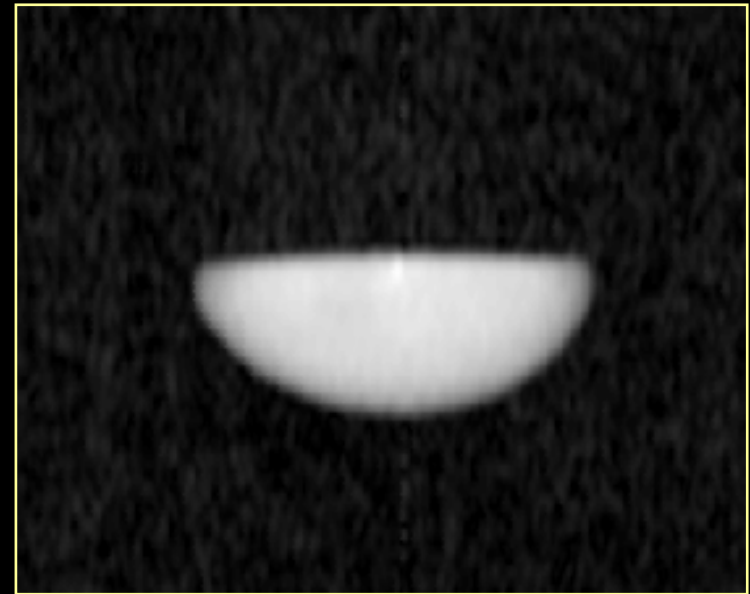
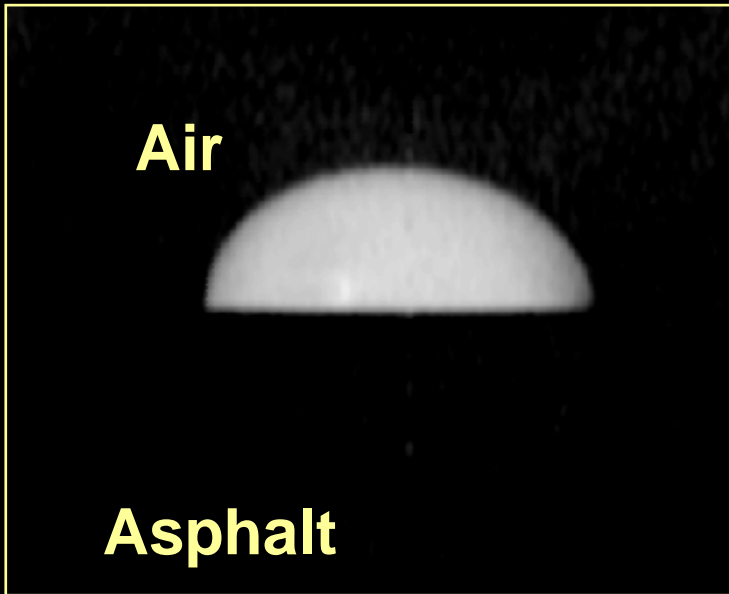


Young's Equation for Inverted Drop



$$\gamma_a = \gamma_w + \gamma_{aw} \cos \alpha$$

Water Drop on AAD Young's Eq.



$$\gamma_a = \gamma_{aw} + \gamma_w \cos \beta$$

$$\gamma_a = \gamma_w + \gamma_{aw} \cos \alpha$$

$$\gamma_{aw} = \gamma_w (1 - \cos \beta) / (1 - \cos \alpha)$$

Other Models

- **Zisman critical wetting tension (2)**
- **Girifalco, Good, Fowkes, Young combining rule (1)**
- **Owens, Wendt geometric mean (2)**
- **Wu harmonic mean (2)**
- **Lewis acid/base theory (3)**

Water Drops on Asphalt

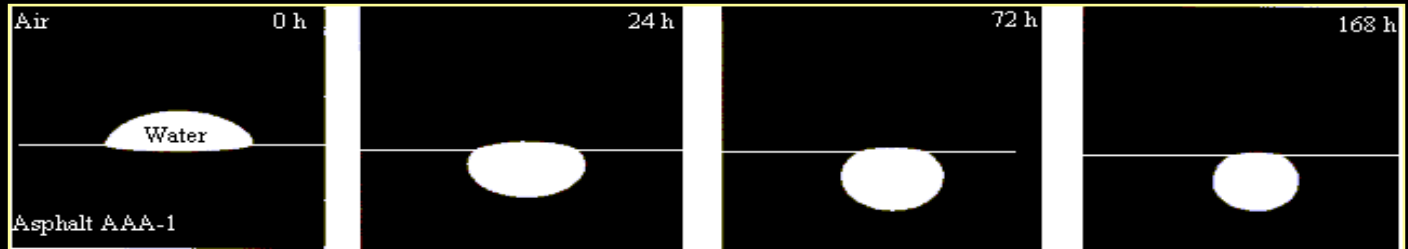
0 h

24 h

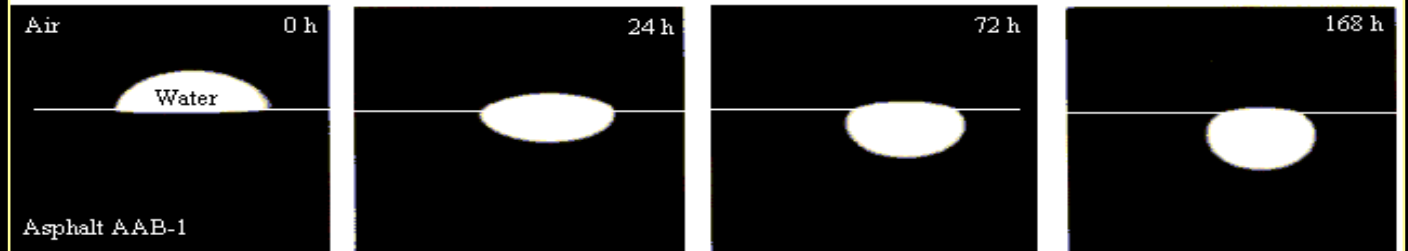
72 h

168 h

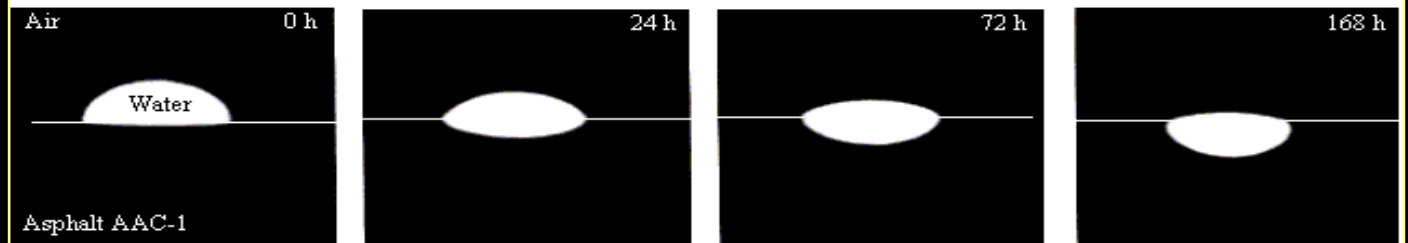
AAA-1



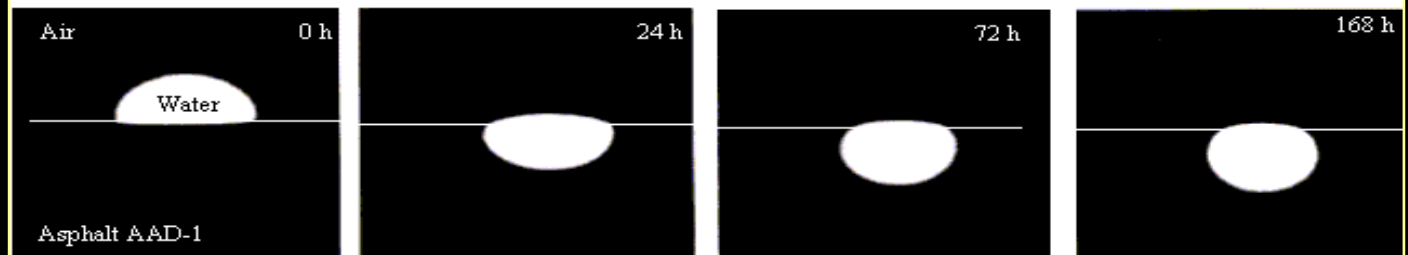
AAB-1



AAC-1

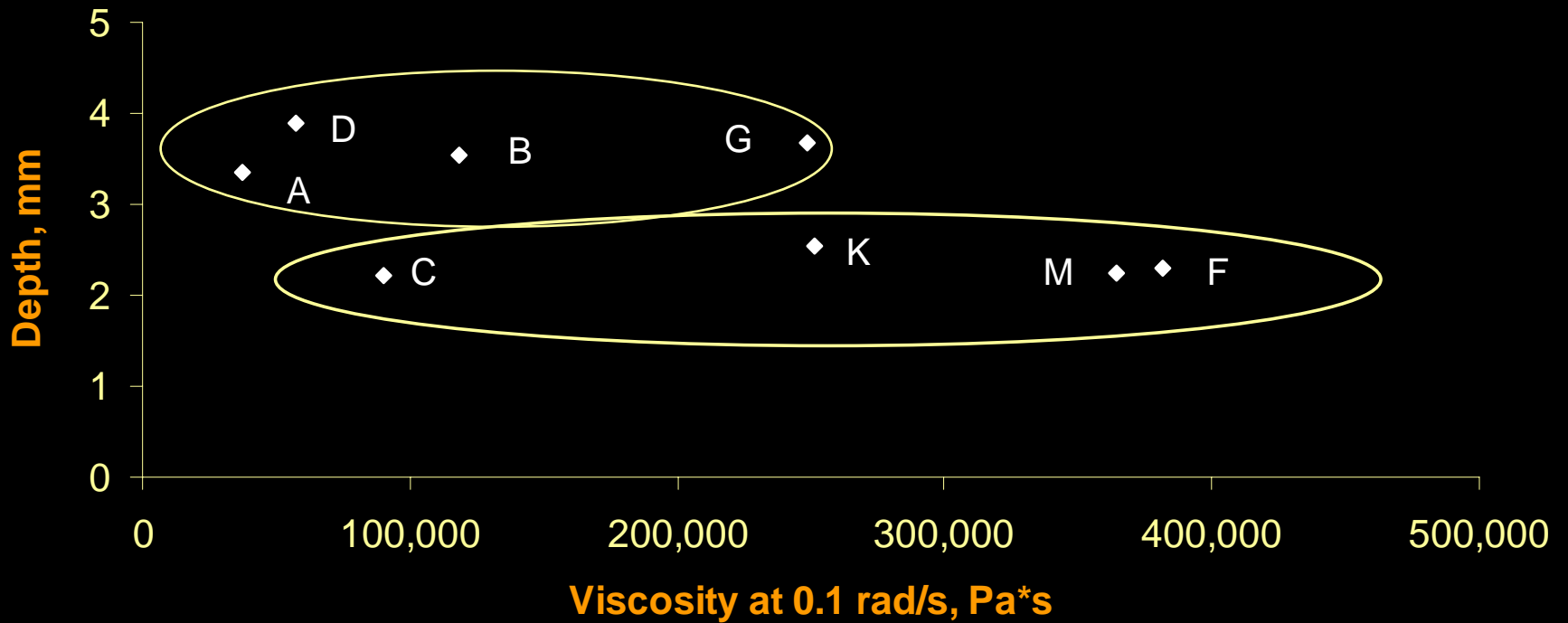


AAD-1

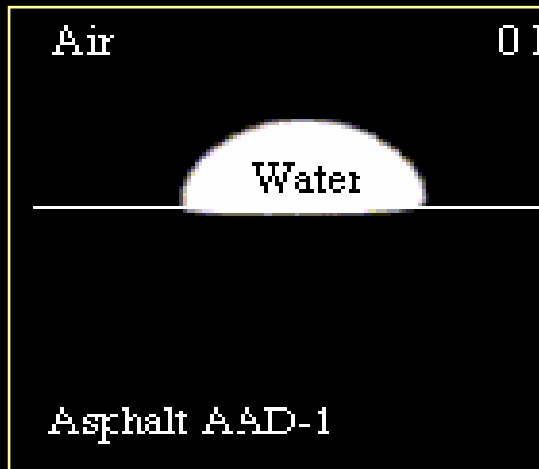


Water Drop Depth vs Viscosity

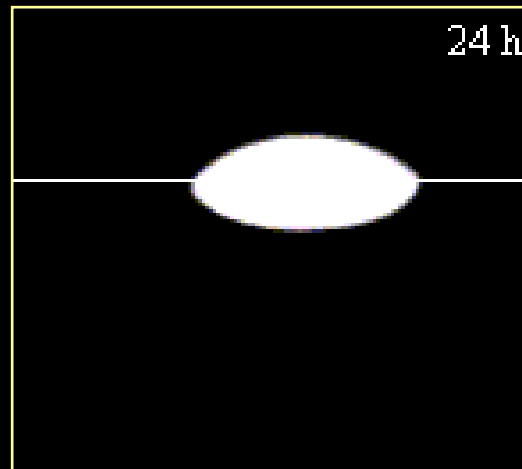
Water Droplet Depth Below Asphalt Surface after One Week vs. Viscosity



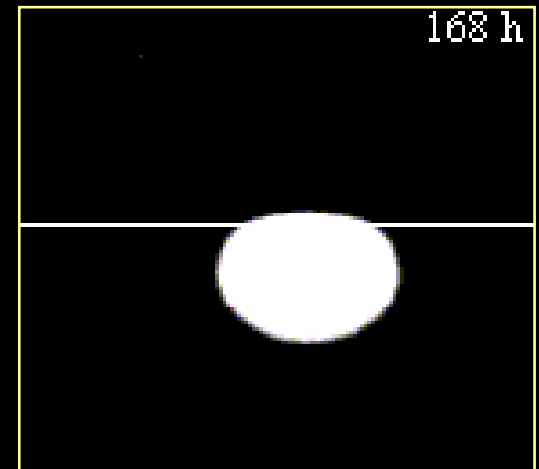
How Does the Drop Become Inverted?



0 h

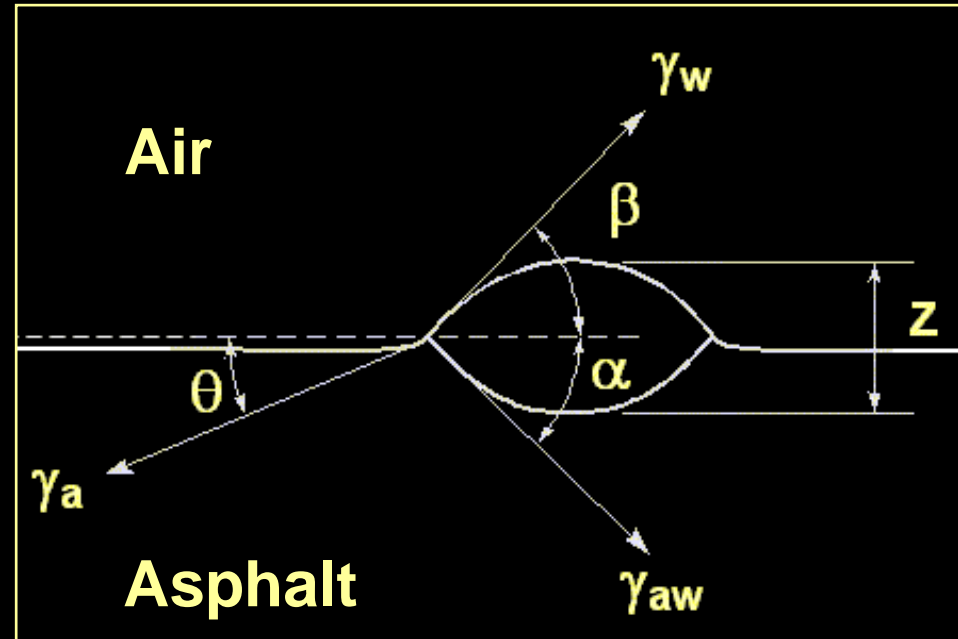
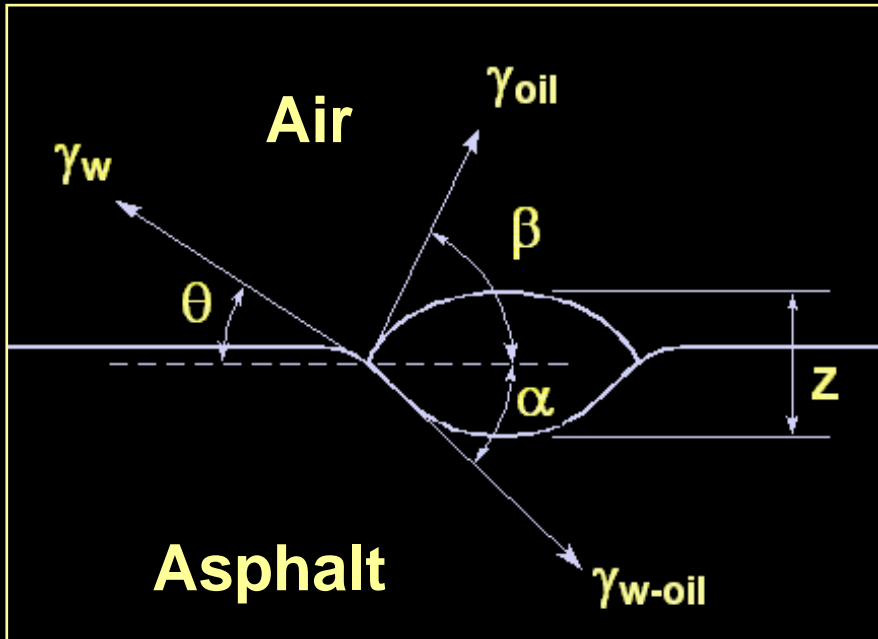


24 h



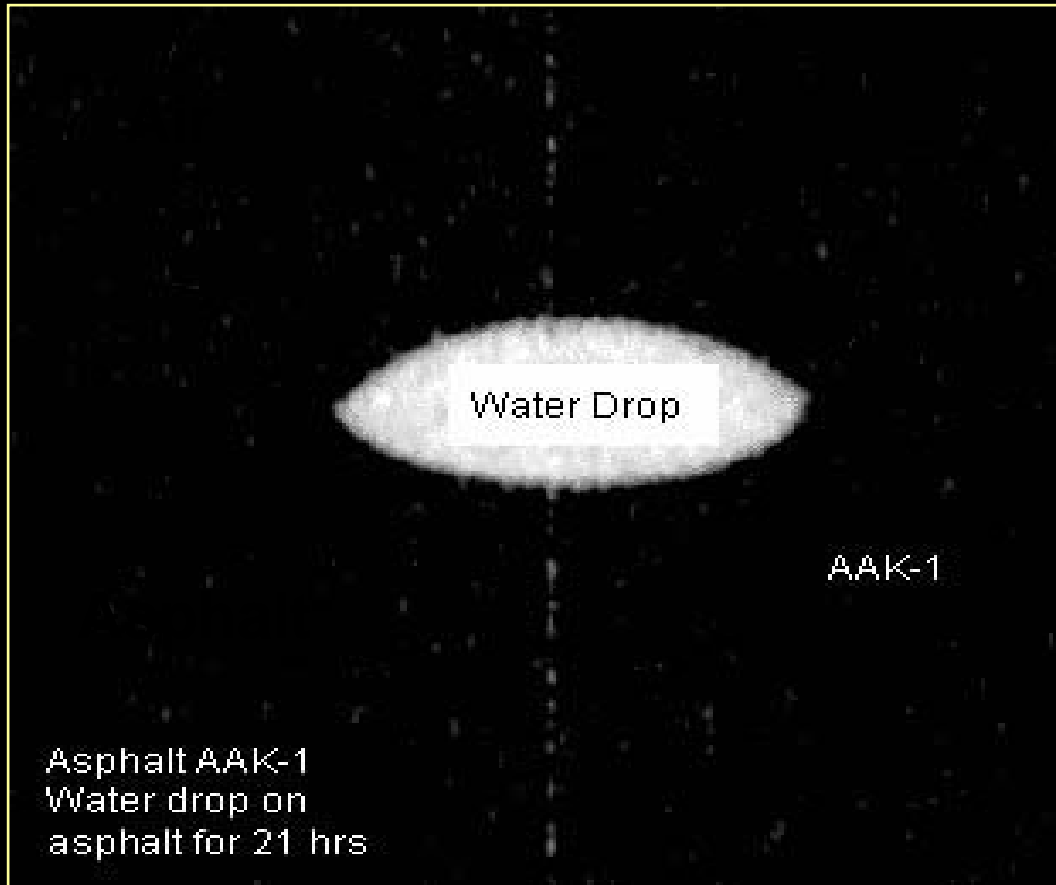
168 h

Equations for Lenses



$$\gamma_a \cos \theta = \gamma_w \cos \beta + \gamma_{aw} \cos \alpha$$

Water Lens on AAK-1



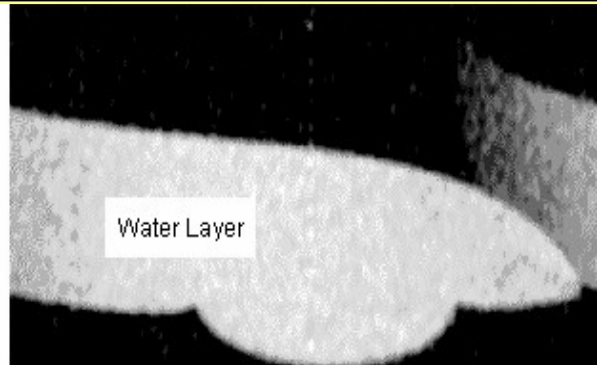
Water Lens Cusping



Water Drop

AAK-1

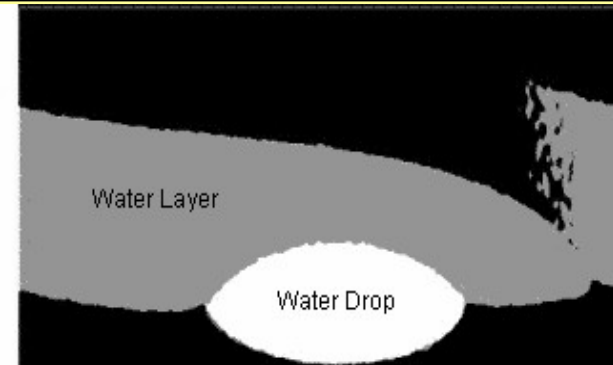
Asphalt AAK-1
Water drop on
asphalt for 21 hrs



Water Layer

AAK-1

Asphalt AAK-1
Water layer on
asphalt for 0 hrs



Water Layer

Water Drop

AAK-1

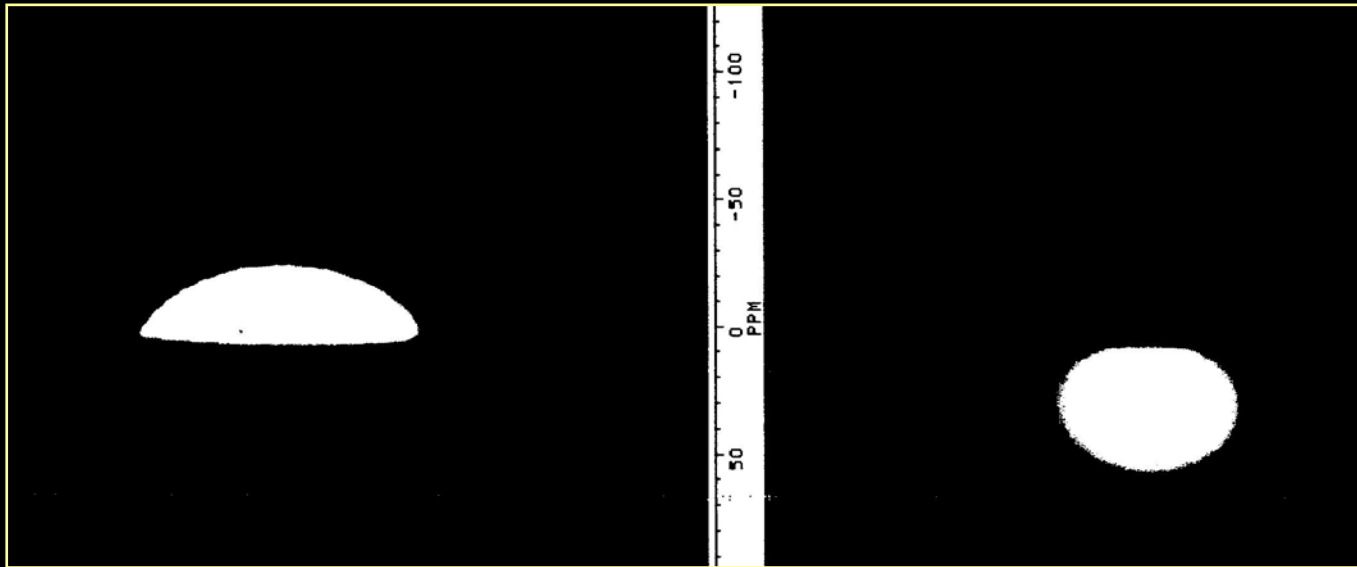
Overlay of water
drop at 21 hrs and
water layer at 0 hrs

Surface Tensions Calculated from NMR Imaging Measurements

Solutions to Equations

Sessile Drop

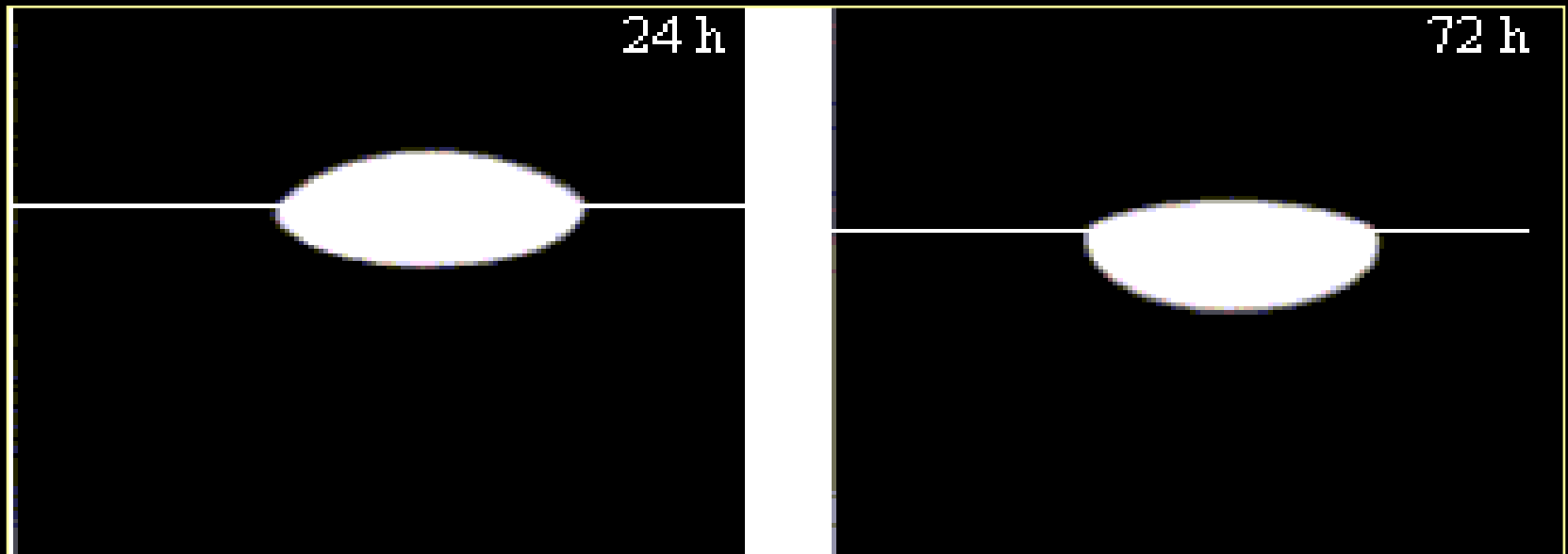
$$\gamma_{aw} = \gamma_w \frac{1 - \cos \beta(t_1)}{1 - \cos \alpha(t_2)}$$



Solutions to Equations

Lens Equation

$$\gamma_{aw} = \gamma_w \left(\frac{\cos \beta(t_1) - \cos \beta(t_2)}{\cos \alpha(t_2) - \cos \alpha(t_1)} \right)$$

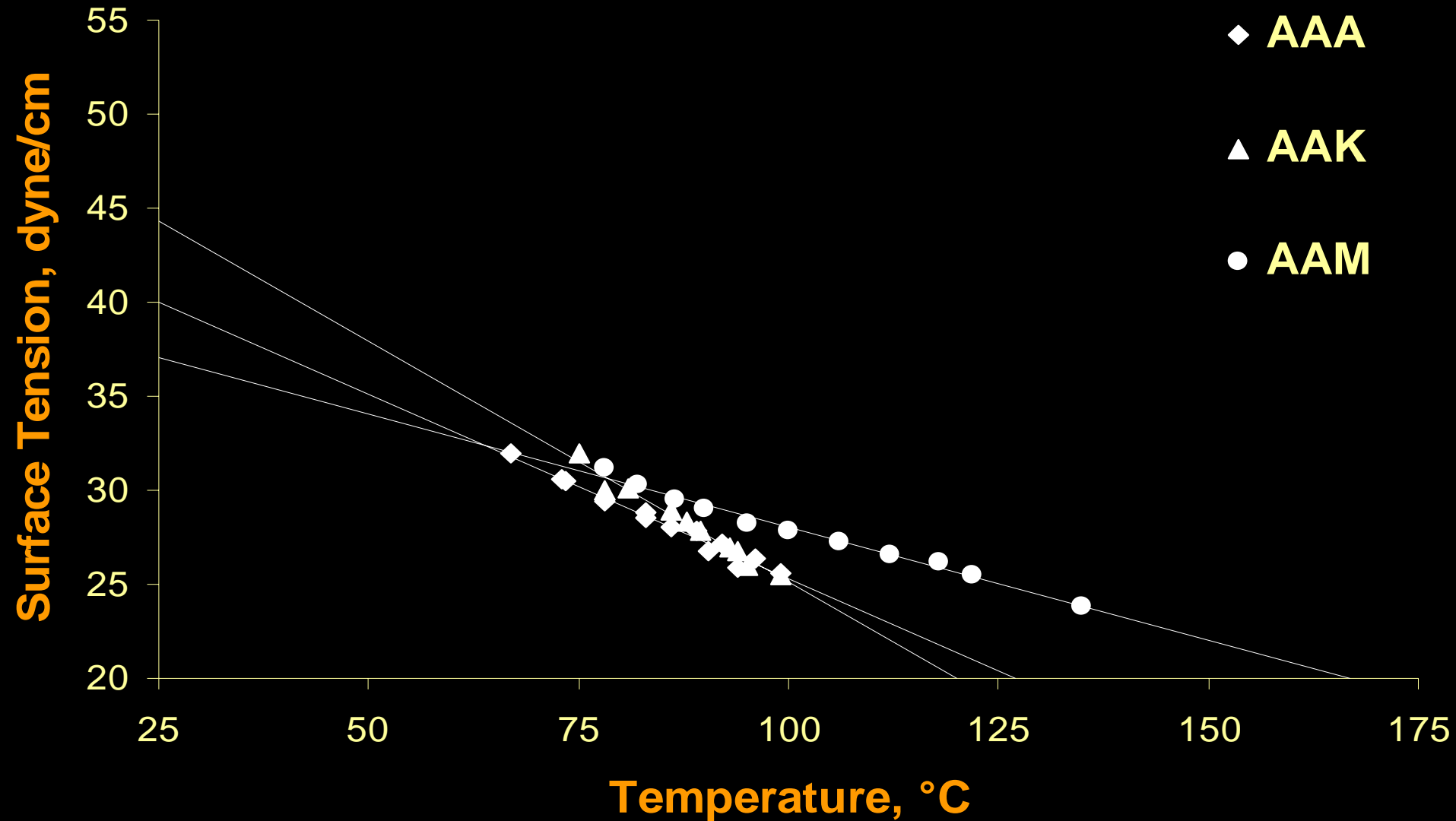


NMRI Surface Tension Results

Asphalt	NMRI^a	NMRI^a
	dynes/cm	dynes/cm
	Asphalt-Water	Asphalt-Air
AAA	26.0 ± 0.8	47.2 ± 0.7
AAB	26.0 ± 0.5	48.4 ± 0.5
AAC	28.3 ± 2.1	45.9 ± 2.0
AAD	38.3 ± 2.0	38.2 ± 1.8
AAF	39.2 ± 5.8	47.5 ± 4.5
AAG	27.7 ± 1.6	46.7 ± 1.5
AAK	37.2 ± 3.5	43.0 ± 3.4
AAM	30.8 ± 5.3	50.4 ± 4.9

^a at 25°C

du Noüy Tensiometer Extrapolation



Comparison with du Noüy Results

	NMRI ^a dynes/cm	NMRI ^a dynes/cm	du Noüy ^b dynes/cm
Asphalt	Asphalt-Water	Asphalt-Air	Asphalt-Air
AAA	26.0	47.2	40.0
AAB	26.0	48.4	37.6
AAC	28.3	45.9	36.1
AAD	38.3	38.2	35.9
AAF	39.2	47.5	41.1
AAG	27.7	46.7	35.7
AAK	37.2	43.0	44.3
AAM	30.8	50.4	37.0
	^a at 25°C	^b extrapolated to 25°C	

Comparison With TAMU Results

	NMRI ^a dynes/cm	NMRI ^a dynes/cm	du Noüy ^b dynes/cm	Wilhelmy Plate ^{a,c} dynes/cm
Asphalt	Asphalt-Water	Asphalt-Air	Asphalt-Air	Asphalt-Air
AAA	26.0	47.2	40.0	54.4
AAB	26.0	48.4	37.6	
AAC	28.3	45.9	36.1	
AAD	38.3	38.2	35.9	27.1
AAF	39.2	47.5	41.1	
AAG	27.7	46.7	35.7	
AAK	37.2	43.0	44.3	
AAM	30.8	50.4	37.0	48.3
	^a at 25°C	^b extrapolated to 25°C		^c receding angle

Other Interfacial Properties

Work of Adhesion is the resistance that two surfaces stuck together have to coming apart. Higher work of adhesion means the two materials are “more stuck.”

Spreading coefficient is the tendency to wet the surface. More negative spreading coefficient means more hydrophobic or less wetting.

Capillary number is the deformation of the drop. At the lens, which is where our numbers were calculated, the capillary number shows the deformation from a sphere. 0.3-0.5 are a good range for a lens.

Other Interfacial Properties

	Work of Adhesion	Spreading Coefficient	Capillary Number
AAA	93.2	-50.8	
AAB	94.4	-49.6	
AAC	89.6	-54.4	
AAD	71.9	-68.5	0.29
AAF	80.4	-63.6	
AAG	90.9	-53.1	
AAK	77.8	-66.2	0.34
AAM	91.6	-52.4	0.33

$$\text{Work of Adhesion} = \gamma_a + \gamma_w - \gamma_{aw} = \gamma_w (1 + \cos(\beta))$$

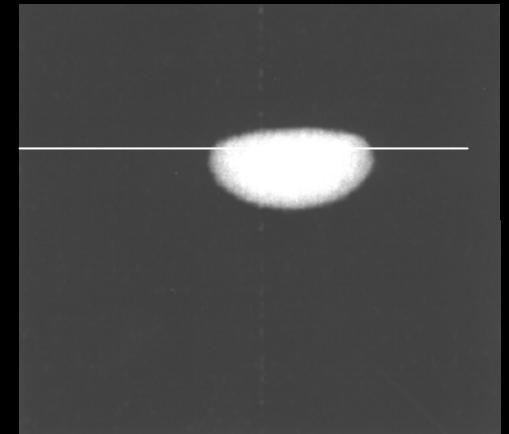
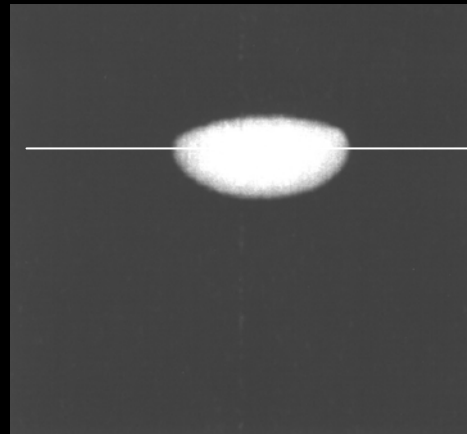
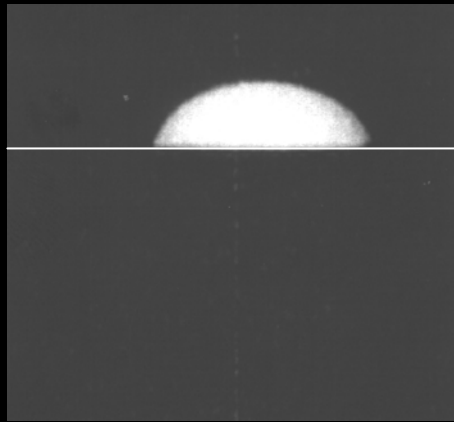
$$\text{Spreading Coefficient} = S = \gamma_a - \gamma_w - \gamma_{aw}$$

$$\text{Capillary Number} = \frac{v\eta_a}{S} \quad v = \text{velocity, } \eta_a' \text{ is } \sim 3\eta_a$$

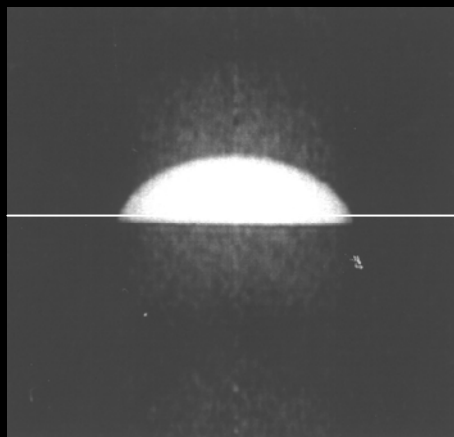
NMR Images of Water Drops on PPA Modified Asphalts

Water Drop on ABD

**Neat
ABD**



**1.5 % PPA
in ABD**



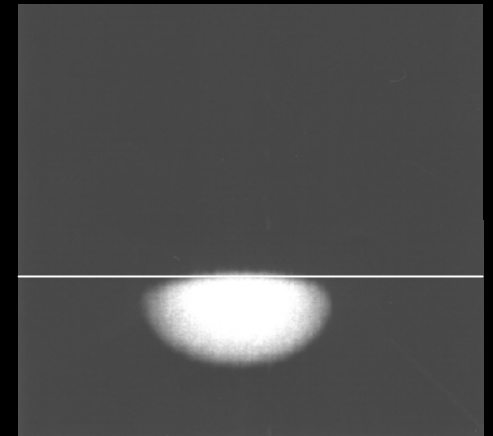
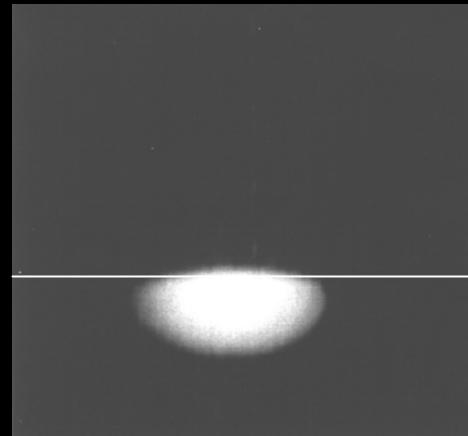
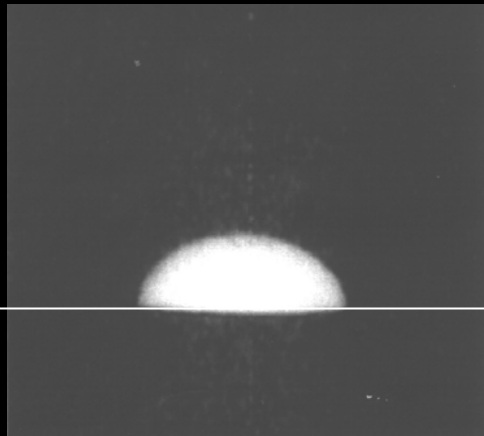
@ 0 h

24 h

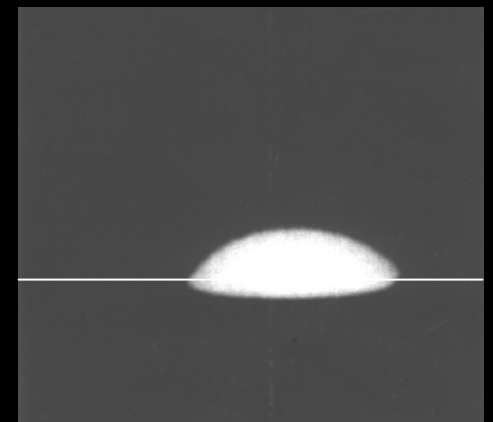
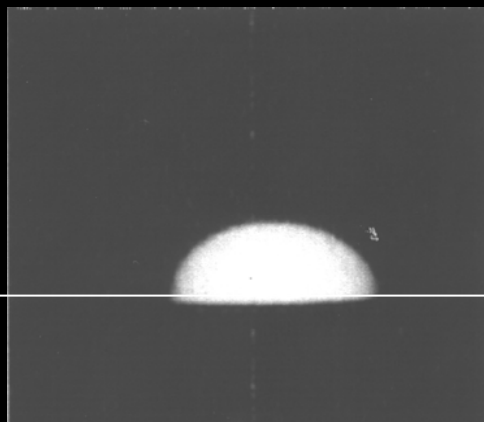
48 h

Water Drop on AAD

Neat AAD



1.5 % PPA
in AAD



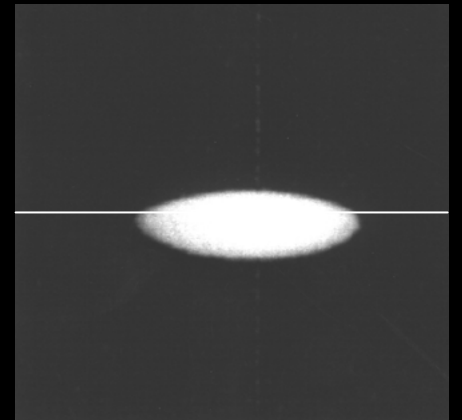
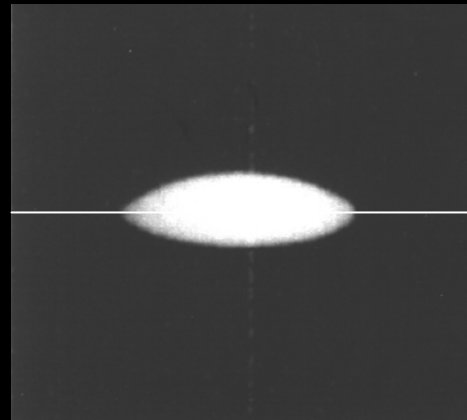
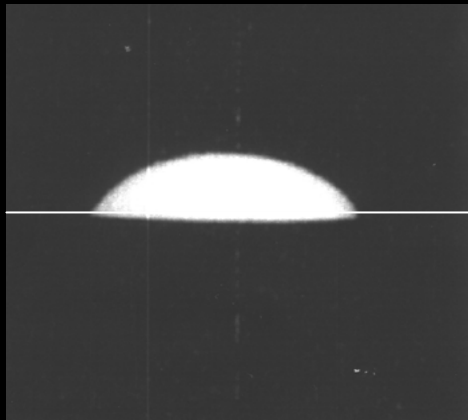
@ 0 h

24 h

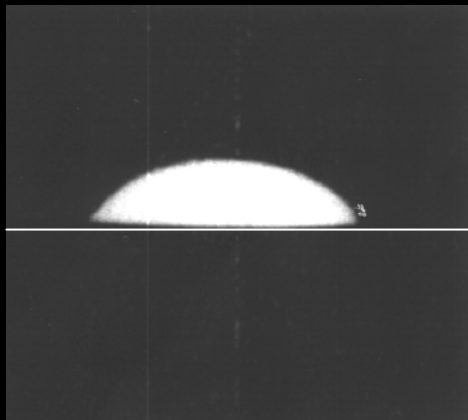
48

Water Drop on AAM

Neat AAM



1.5 % PPA
in AAM



@ 0 h

24 h

48 h

Some more images

Deforming Water Cylinders

AAA-1



0 h

96 h

120 h

AAM-1

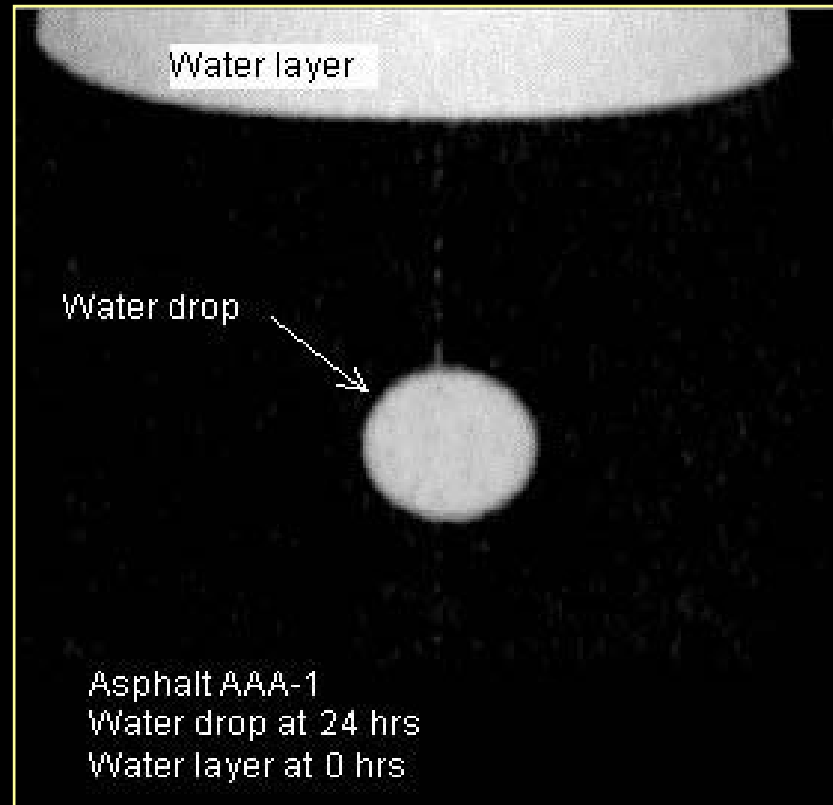


0 h

1080 h

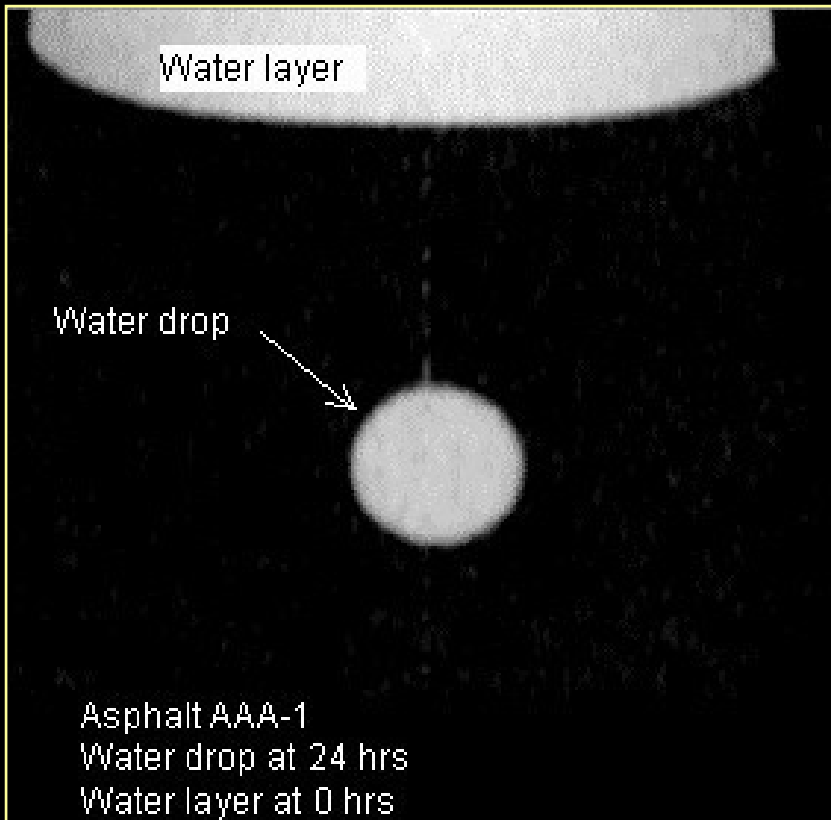
1896 h

Water Drop in AAA-1

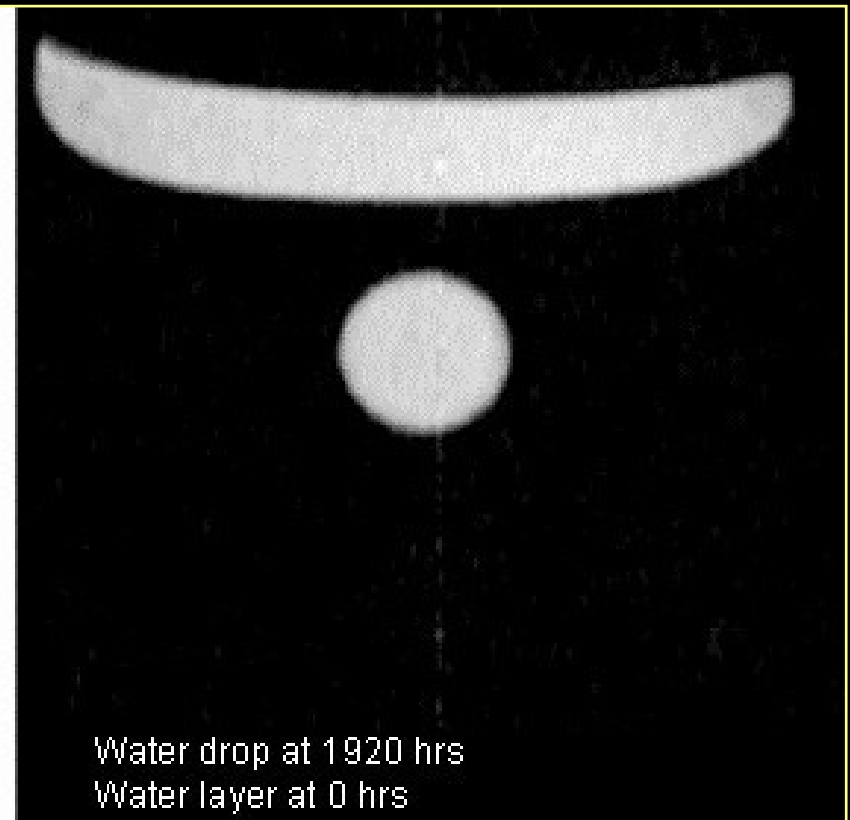


Water Drop at 24 h
Water layer at 0 h

Rising Drop in AAA-1



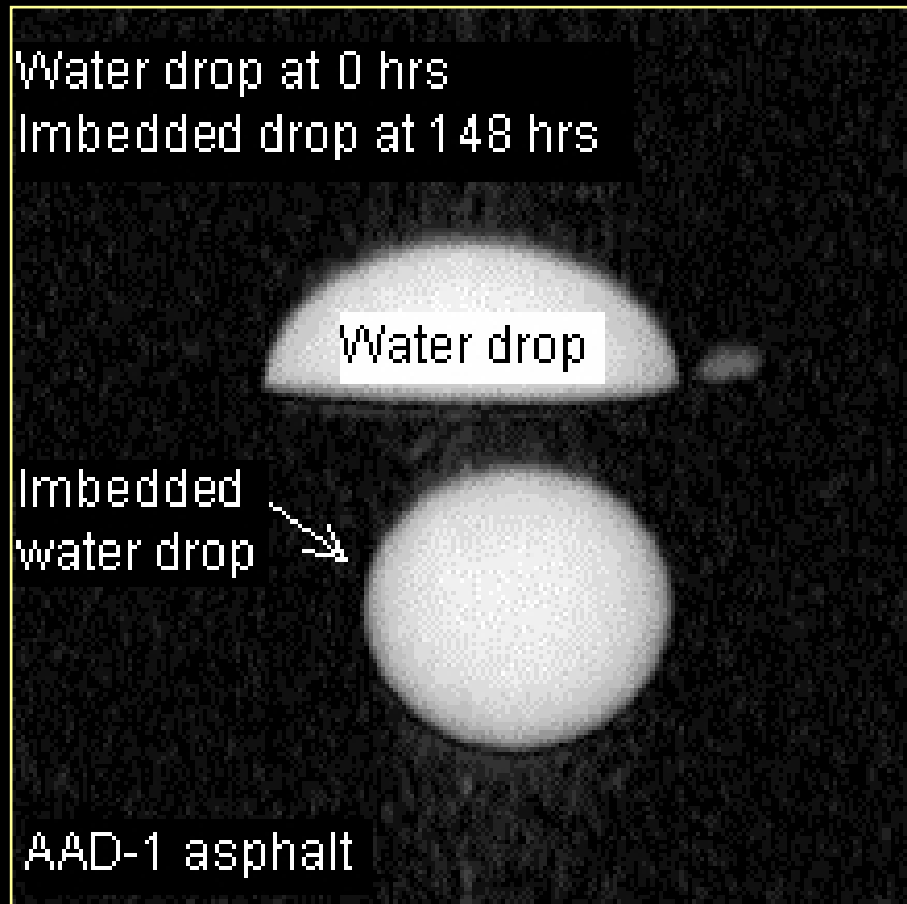
Water Drop at 24 h
Water layer at 0 h



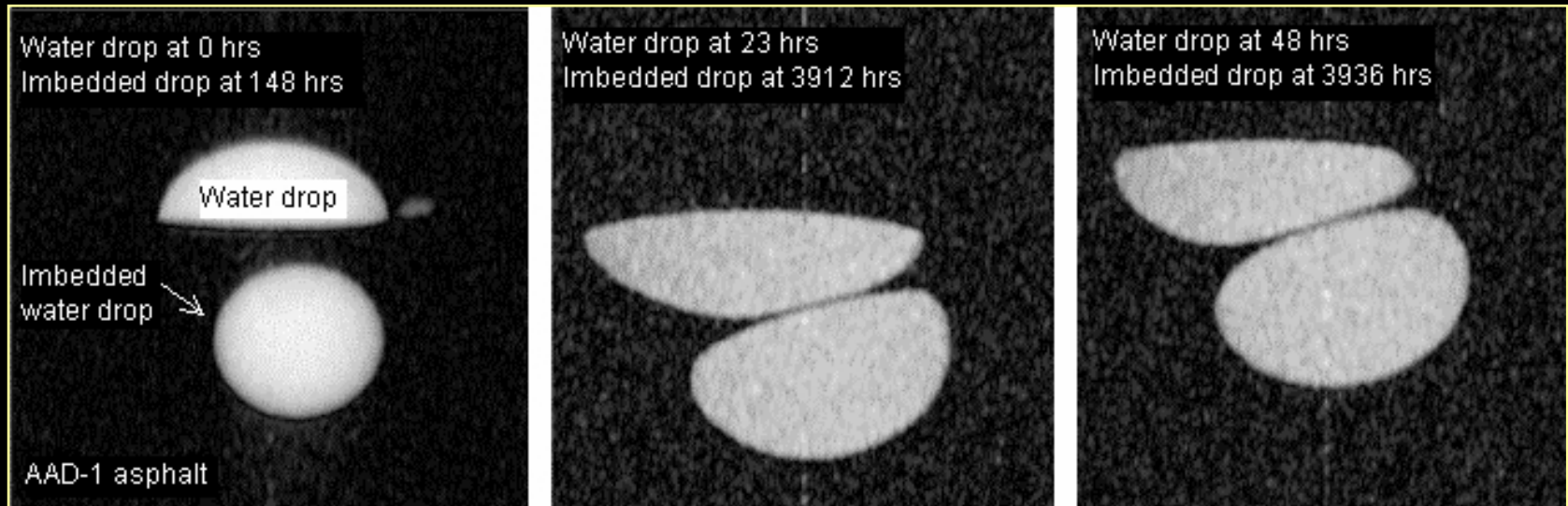
Water drop at 1920 h
Water layer at 0 h

Will the Drops Coalesce?

AAD-1 Asphalt



Non Coalescence of Drops in Asphalt AAD-1



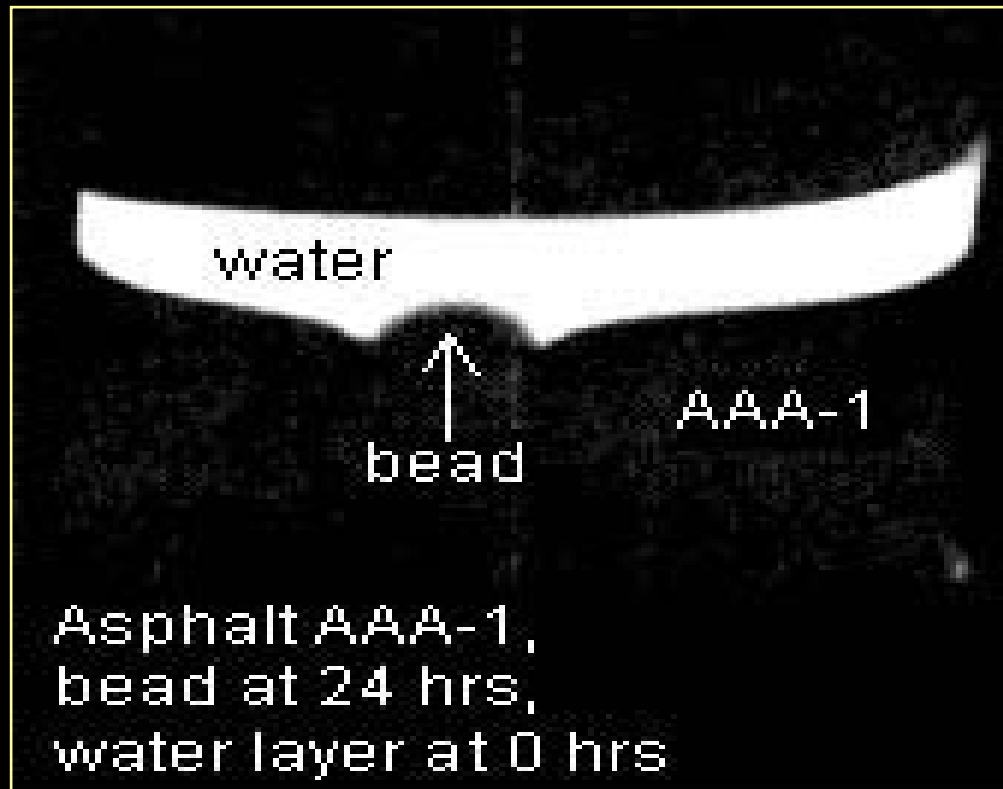
Water Drop at 0 h

24 h

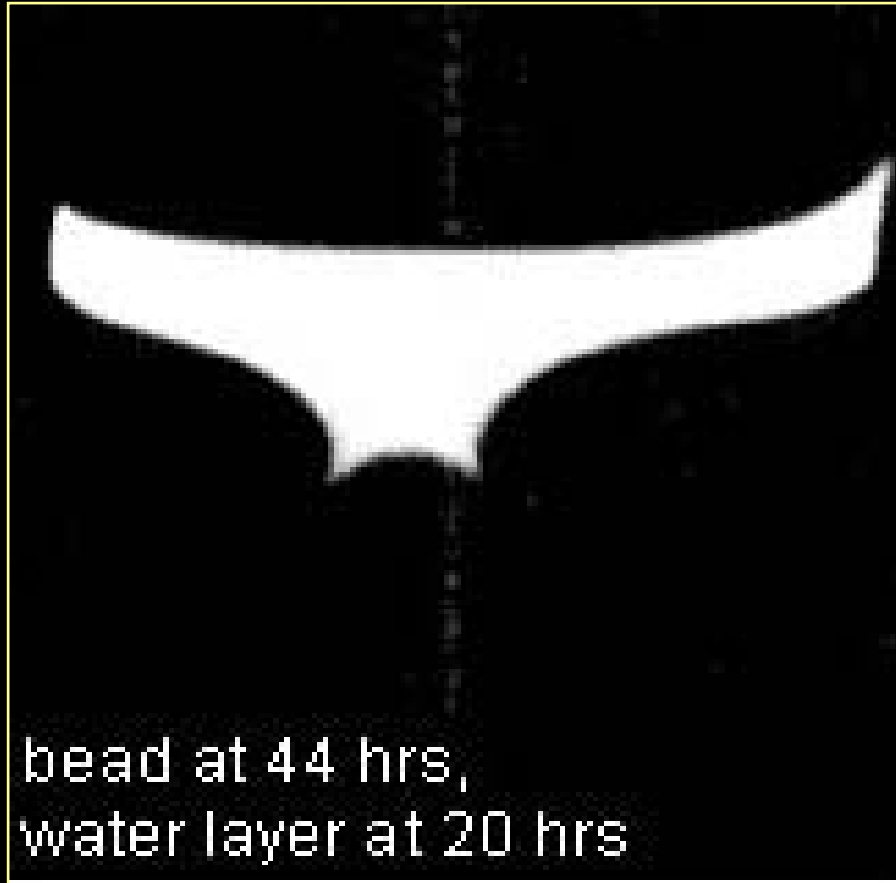
48 h

The “Moses” Experiment

4 mm Glass Bead on AAA

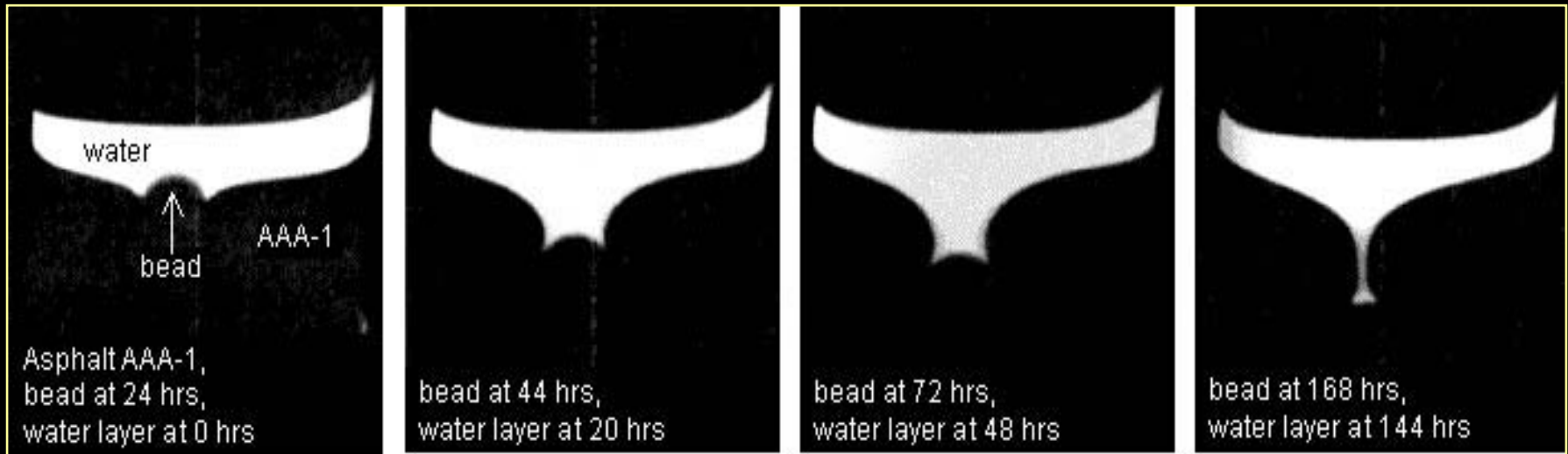


4 mm Glass Bead on AAA



20 h

4 mm Glass Bead on AAA



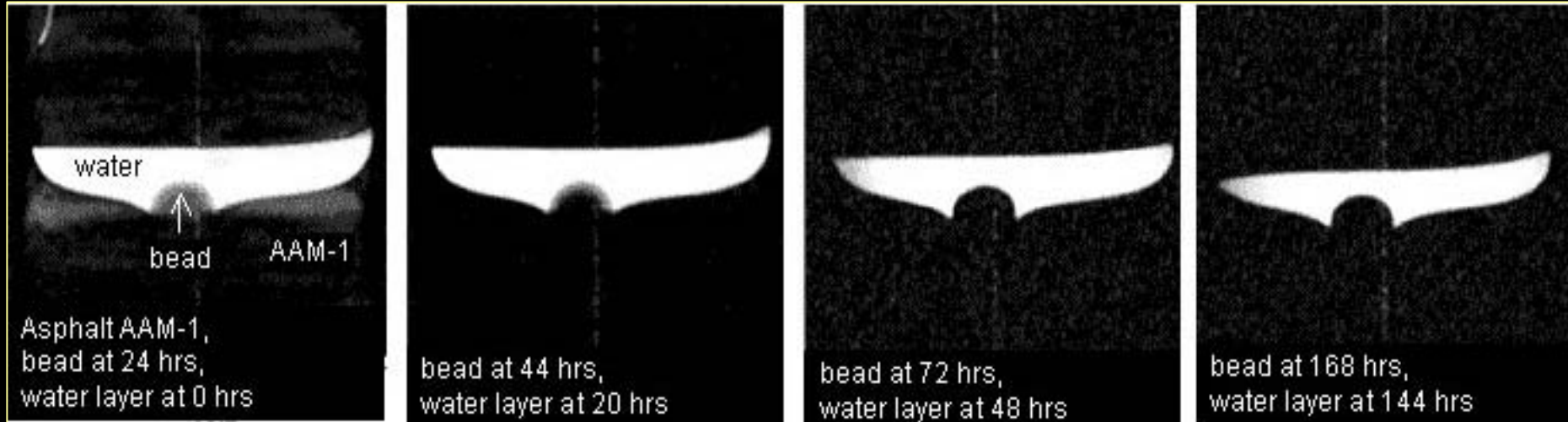
0 h

20 h

48 h

144 h

4 mm Glass Bead on AAM



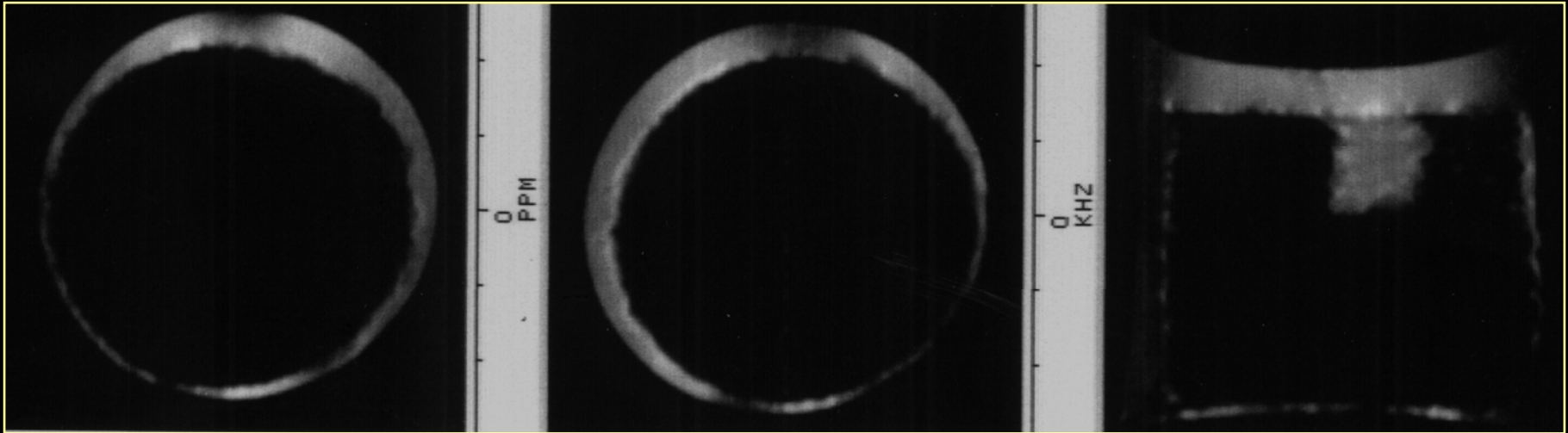
0 h

20 h

48 h

144 h

Asphalt Core in Water



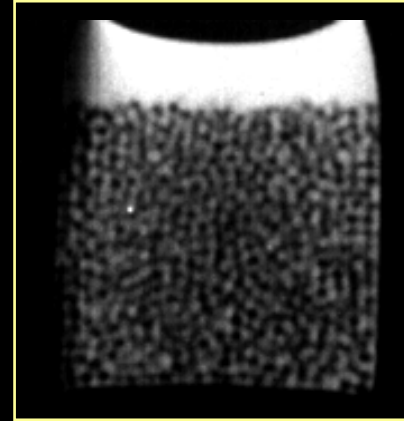
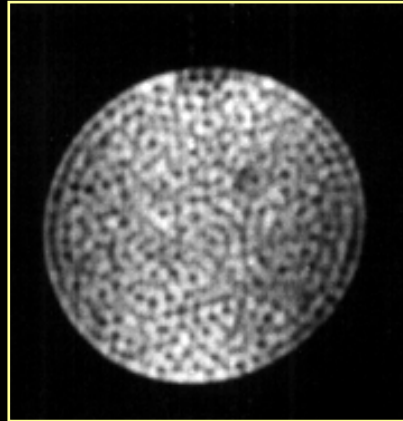
**XY image
0 hrs**

**XY Image
794 hrs**

**XZ Image
795 hrs**

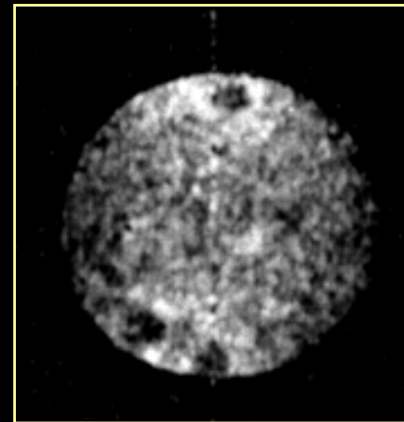
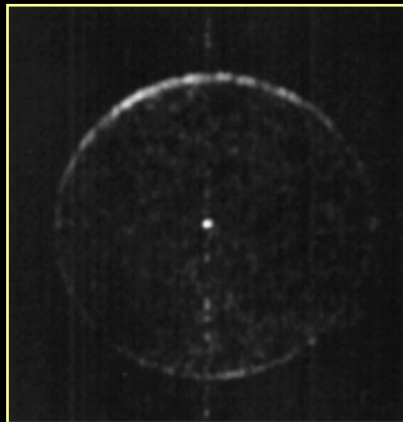
Glass Beads in Water

- 1 mm beads,
- no vacuum,
- XY plane



- 1 mm beads
- no vacuum,
- XZ plane,

- -60+ 80 mesh
- beads in water,
- 140 hours
- no vacuum
- XY plane



- -60+ 80 mesh
- beads in water
- under vacuum,
- XY plane

Conclusions

The behavior of a water drop on an asphalt surface has been studied as a function of time using NMR imaging techniques.

Conclusions

The study showed that:

- 1. By measuring the contact angles of a water drop on an asphalt surface at two different times, and using Young's equation or the liquid lens equation, surface tensions of asphalt-air and asphalt-water at room temperature can be calculated directly.**
- 2. The results obtained by this method are in reasonably good agreement with surface tensions obtained by other methods, i.e., extrapolation from higher temperatures, or Wilhelmy plate measurements in different solvents.**
- 3. Other interfacial parameters of interest such as work of adhesion, spreading coefficients and capillary numbers can be calculated using the surface tension data.**

Acknowledgements

The authors gratefully acknowledge the Federal Highway Administration, U. S. Department of Transportation for financial support of this work under contract no. DTFH61-99C-00022.