



**The Abdus Salam
International Centre for Theoretical Physics**



2054-2

Structure and Dynamics of Hydrogen-Bonded Systems

26 - 27 October 2009

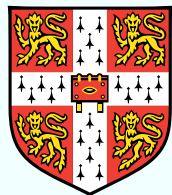
Hydrogen Bonds and Liquid Water

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Hydrogen Bonds and Liquid Water

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1. Collaborators

1

- Teresa Head-Gordon, University of California, Berkeley
- Pablo Debenedetti, Princeton University
- Dan Bergman, Stockholm
- T. Youngs, Belfast
- José Alejandro, Mexico
- Swaroop Chatterjee, formerly Princeton

2. Water is an unusual liquid.

2

Water is both unusual and essential for life.

- It is liquid under ambient conditions although the water molecule is small.
- It dissolves polar and charged species readily.
- It dissolves non-polar species reluctantly.
- It shows anomalies in various equilibrium and dynamic quantities.
- It self-ionises and so supports acid and base chemistry.

The properties of liquid water depend on the intermolecular potentials (or force fields) between water molecules.

3. Intermolecular forces in liquid water

3

Unusual aspects of the intermolecular interactions between water molecules include:

- Water acts as a hydrogen bond donor and a hydrogen bond acceptor;
- It has two hydrogens which can form hydrogen bonds;
- Its molecular volume is small compared to most liquids at ambient conditions;
- Its bond angle is nearly tetrahedral which promotes the tetrahedral network structure.

How important are the hydrogen bonds relative to other properties of the intermolecular potential?

4. How important are hydrogen bonds?

4

The answer to this question depends on which property of liquid water is being considered.

How important are the hydrogen bonds:

- for the formation of the liquid phase under ambient conditions,
- for the tetrahedral structure of the liquid,
- for the existence of various anomalies,
- for the existence of a high dielectric constant,
- for the various effects described by hydrophobicity?

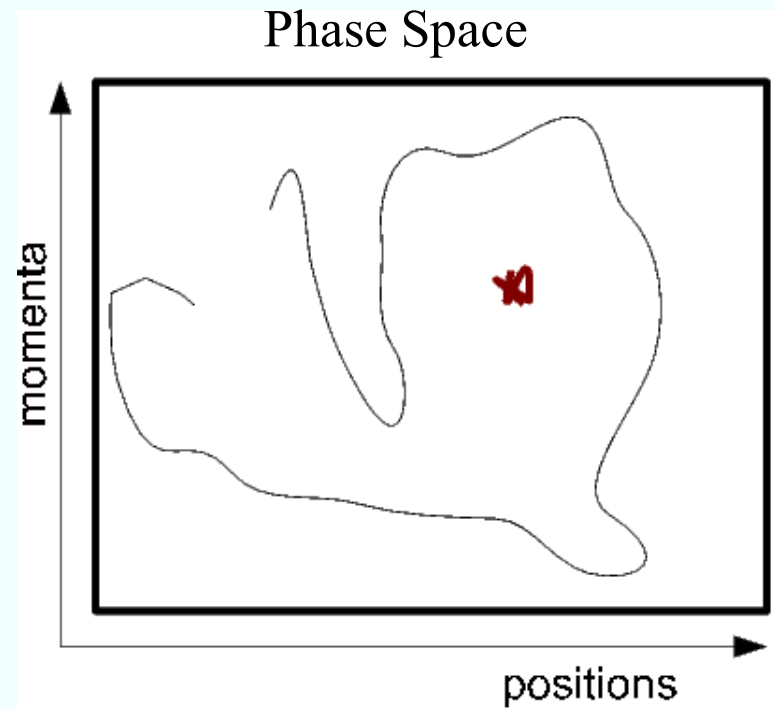
Although quantum mechanics does not allow properties such as hydrogen bonds, bond angle and molecular size to be separated, a simple classical model does.

Computer simulation allows one to perform impossible experiments.

5. Modelling liquids

The main characteristic of liquids are

- they only exist at non-zero temperatures,
- molecules interact with several other molecules at the same time,
- molecules move significant distances relative to each other.



This makes theory and modelling more difficult than gases or solids.

Phase Space is the space of all $3N$ possible positions and $3N$ momenta of the N atoms in the liquid (or solid or gas). It is a concept used in statistical mechanics.

A solid corresponds to a small volume of phase space.

A liquid corresponds to a large volume of phase space.

6. Atomistic simulation

6

In **computer simulation** one tries to explore the phase space of the liquid by generating many configurations of molecules typical of the liquid. From these one can generate average properties such as energetics or local structures.

There are two main methods of atomistic simulation: **Molecular Dynamics** and **Monte Carlo**. For these methods one needs to know either the intermolecular forces or energies.

This can be done either with a **quantum method** where the energy and forces are calculated on the fly or with a **classical method** with an empirical force field.

We shall consider the method of classical Molecular Dynamics with simple empirical force fields.

7. Minimal molecular models for water

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How simple is simple?

Molecular models for simulating liquid water must include:

- Molecular size
- Molecular shape
- Hydrogen bonds
- Cohesive forces

8. Models for simulating liquid water

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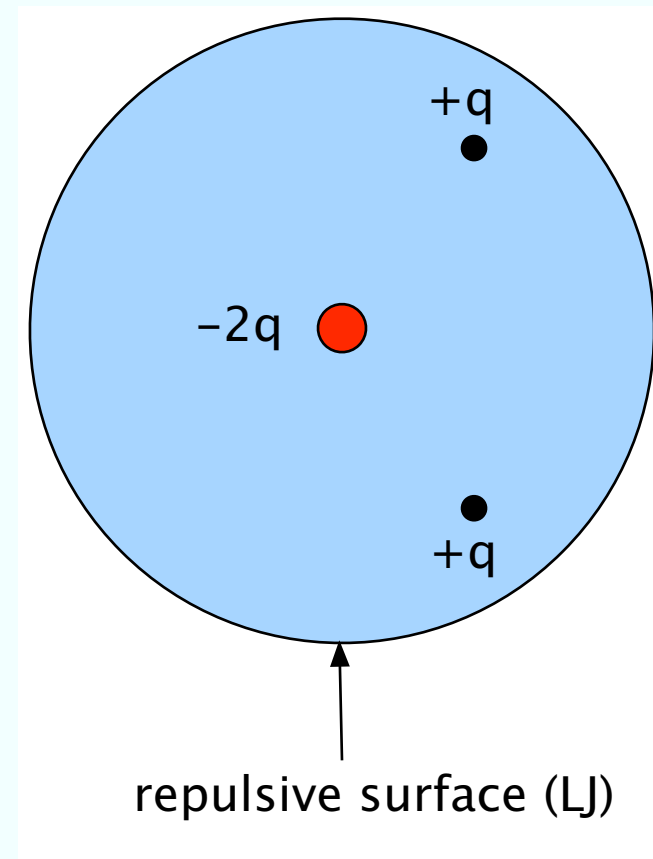
‘Simple point charge’ models for water are surprisingly successful. (e.g. SPC, SPC/E, TIP4P, TIP3P)

The electrostatic interaction between molecules (including hydrogen bonds) comes from 3 (or 4) point charges. These may be on oxygen and hydrogen sites.

The size of the molecule is determined by a spherical Lennard-Jones interaction based on the central oxygen site.

This Lennard-Jones interaction also gives an isotropic attraction at greater distances.

Such models are cheap to simulate and the basic physics is straightforward.



9. Where are the hydrogen bonds?

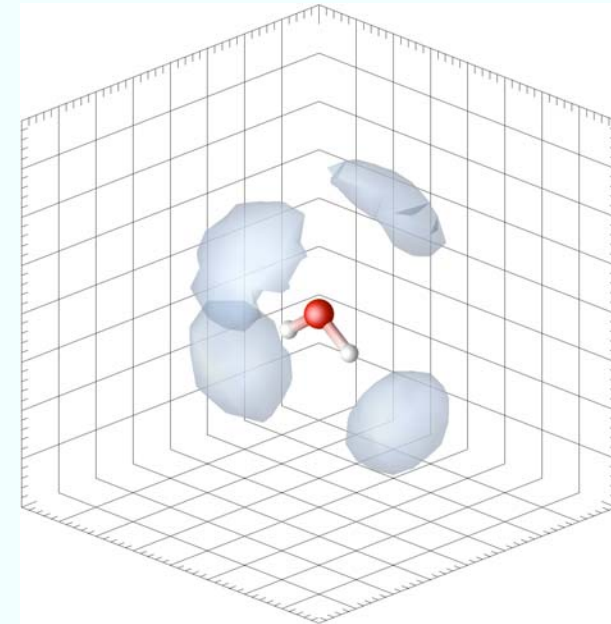
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In these models the hydrogen bonds are described by the electrostatic interaction between the positive charges on the hydrogen atoms which are near the surface and the negative charges at the 'back' of the molecule.

In ice Ih each molecule donates two hydrogen bonds, so must accept two hydrogen bonds. This gives a tetrahedral structure with 4 nearest neighbours.

In liquid water the local structure is still mainly tetrahedral.

There are four hydrogen-bonded nearest neighbours which are hydrogen bonded.



Oxygen probability distribution function around an spc/e water molecule at 300K.

10. Modified water models

10

We have compared the properties of the liquid formed by a water model (SPC/E) with liquids formed from models with altered intermolecular potentials designed to change the **hydrogen bond strength**. We also considered models designed to change the network structure, but with hydrogen bonds.

In the reference **SPC/E model** H₂O molecule the HOH angle is tetrahedral (109.5°) and the OH bond lengths 0.1 nm. The pair energy is

$$U(r) = 4\gamma\epsilon \left[(\sigma/r_{OO})^{12} - (\sigma/r_{OO})^6 \right] + q_{\alpha}q_{\beta}/4\pi\epsilon_0 r_{\alpha\beta}.$$

with $\gamma = 1$. We have two families of modified water models:

- In the **hybrid** family the Lennard-Jones energy is increased by γ and as a result the **hydrogen bond strength is reduced**. These liquids are hybrids between tetrahedral liquids and Lennard-Jones or normal organic liquids.
- In the **bent** family the **bond angle is changed from tetrahedral**, but the site charges remain constant. Such liquids do not have a local tetrahedral network although they still have strong hydrogen bonds.

11. Purpose

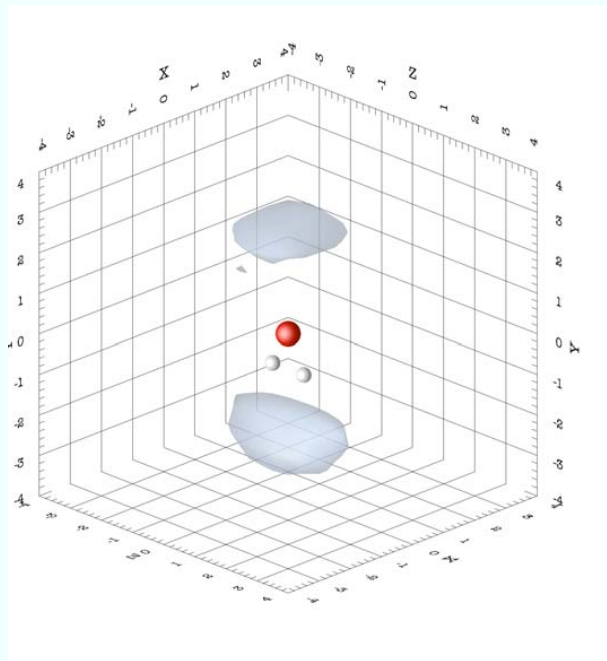
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We are NOT trying to make realistic models for particular liquids.

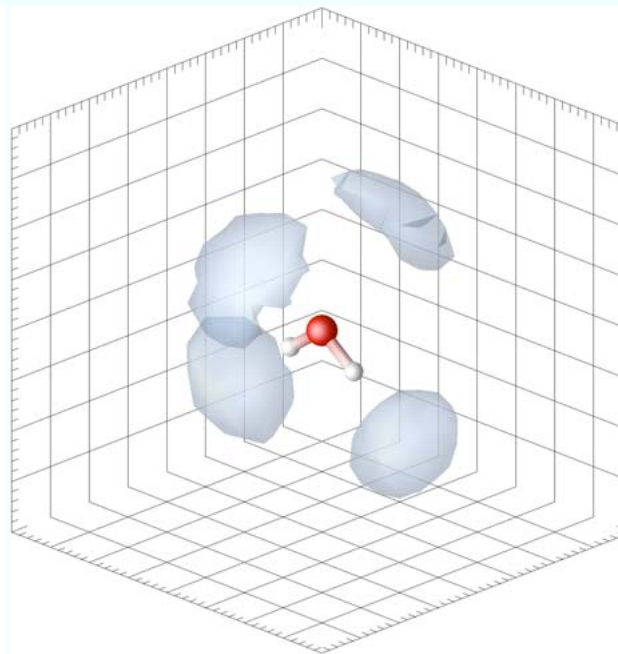
We are trying to UNDERSTAND the properties of liquid water by comparing it to model liquids where the intermolecular potential has been altered in a controlled way.

In the first part of the work all the liquids are constructed to have approximately the same number density at 298K and 1 atmosphere pressure by varying the Lennard-Jones σ parameter. The molecular dipole moment is also unchanged.

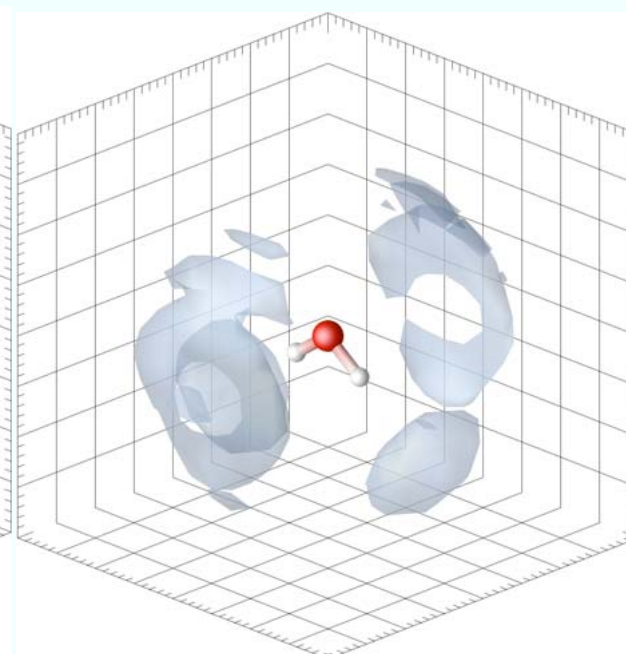
Thus we are changing the hydrogen bond strength or the network structure but keeping the small molecular size.



Bent B60



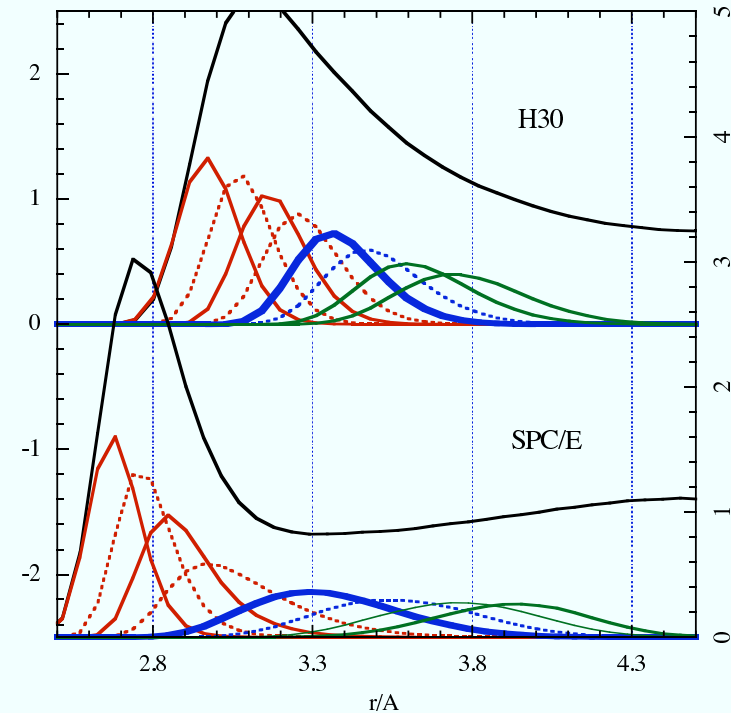
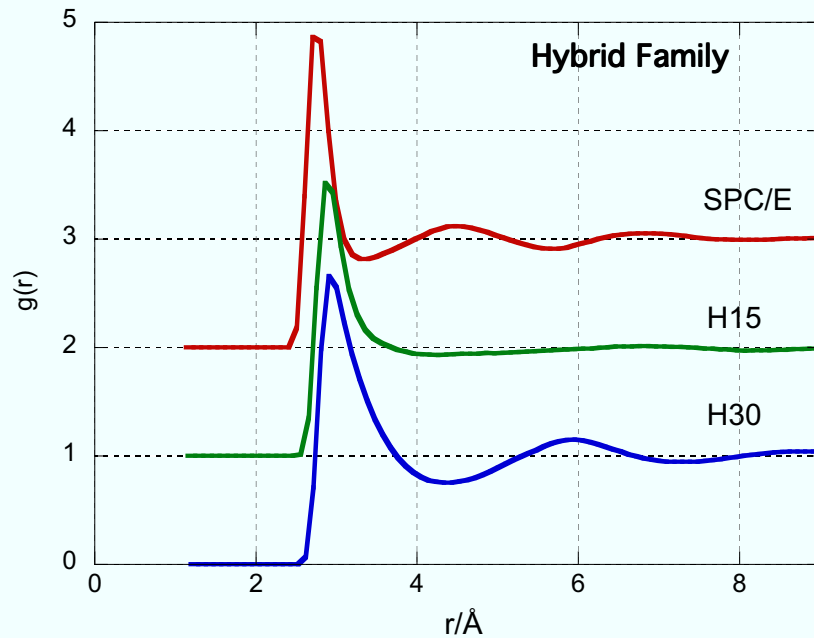
SPC/E



Hybrid H30

The blue regions are volumes where there is a high probability of finding another water molecule. Note the changes in local structure and coordination.

13. Radial distribution functions



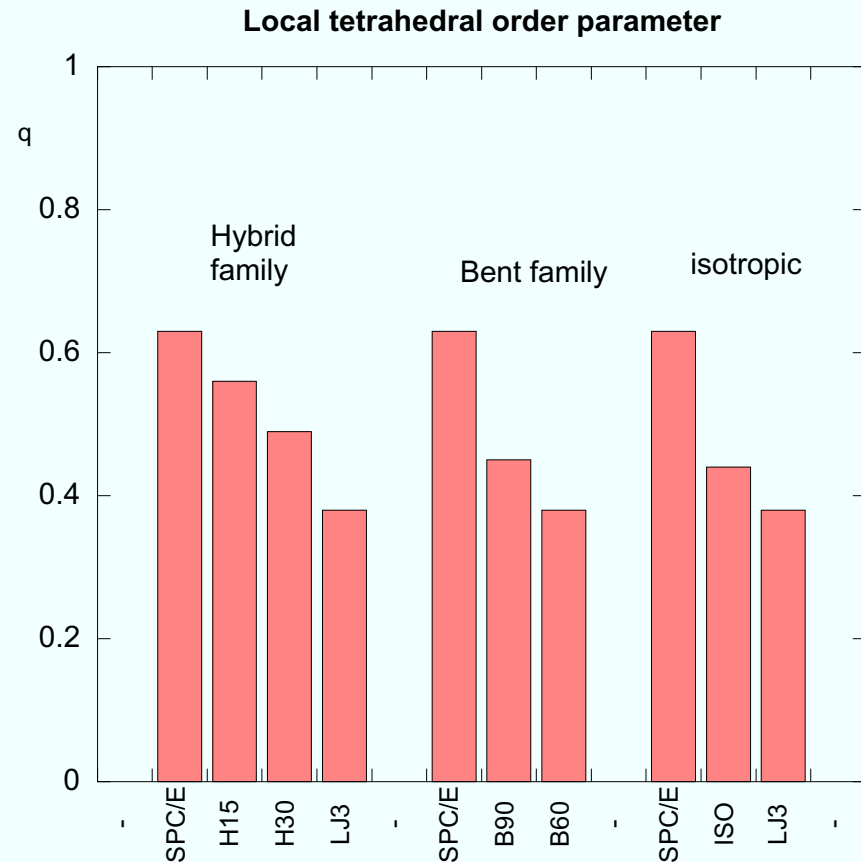
The hybrid model H30 has a radial distribution function typical of an atomic Lennard-Jones Liquid. In the hybrid model H15 there is essentially no second shell.

In spc/e water the first four neighbours (red) contribute to the first peak of $g(r)$. The fifth neighbour has a much broader distribution. In hybrid H30 the fifth neighbour contributes to the broader first peak.

14. Local tetrahedral order

The local environment of a water molecule in ice is tetrahedral. The tetrahedrality can be measured by an order parameter q . In liquid water much tetrahedral character remains which gives a value of the tetrahedral order parameter q greater than 0.6.

In all the families the local tetrahedral order parameter decreases as the modifications go further from water.



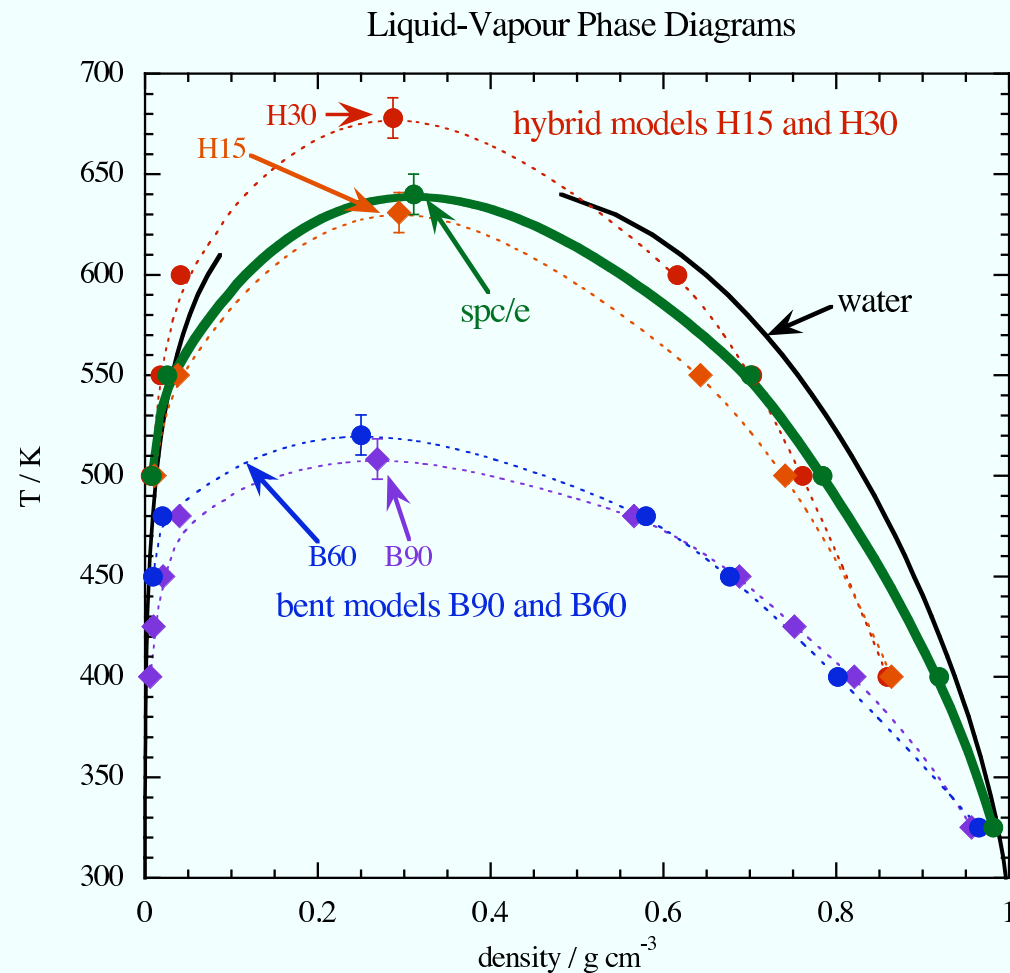
15. Phase Diagrams

José Alejandre found that there is a big difference between the families.

Compared to spc/e water (green), the **bent** models (shades of blue) have lower critical temperatures. These models have altered liquid networks.

In the **hybrid** family (shades of red), the model with weaker hydrogen bonds (H30) has a higher critical point. These models have more nearest neighbours.

Destroying the network structure has a greater effect on the critical temperature than does reducing the hydrogen bond strength.

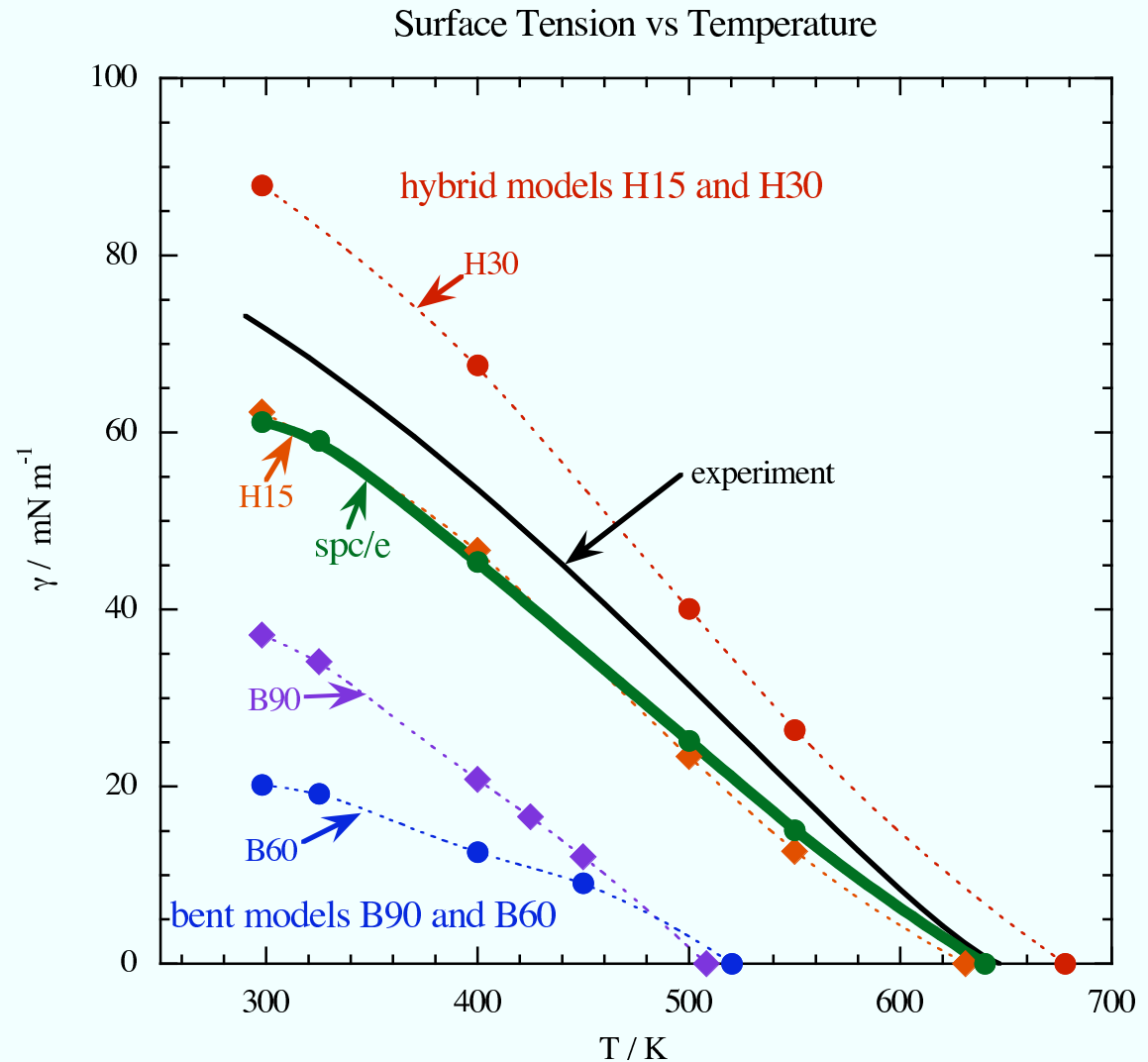


16. Surface properties

High surface tensions imply high critical points and correlate with close packing.

Destroying the network structure lowers the surface tension and critical temperature.

The slope gives minus the surface entropy. This is much the same for all models except the extreme bent one - B60

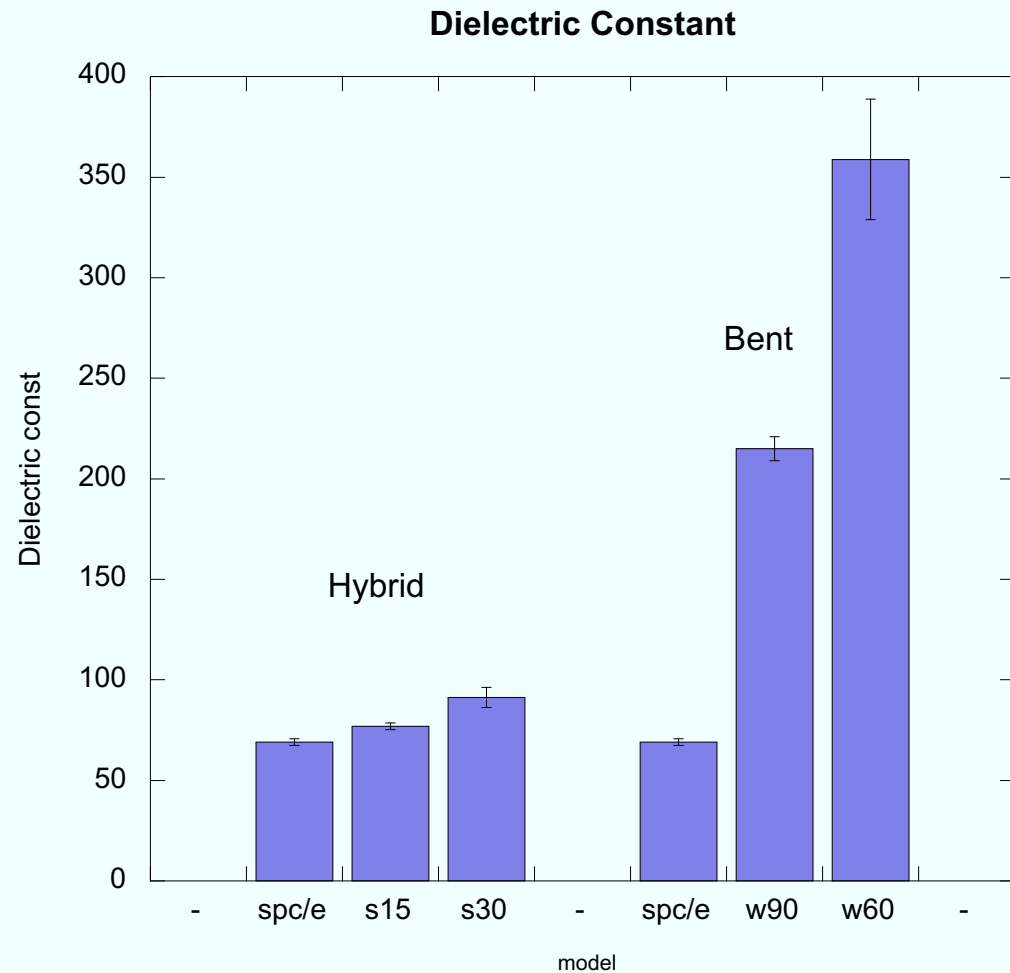


Surface tension as a function of temperature.

17. Permittivity

The relative permittivity increases enormously in the bent family, probably due to the formation of chains in model B60.

The relative permittivity increases slightly in the hybrid family although the hydrogen bonds get weaker.



Hydrogen-bonded chains (rather than a tetrahedral network) enhance permittivity (cf liquid HF).

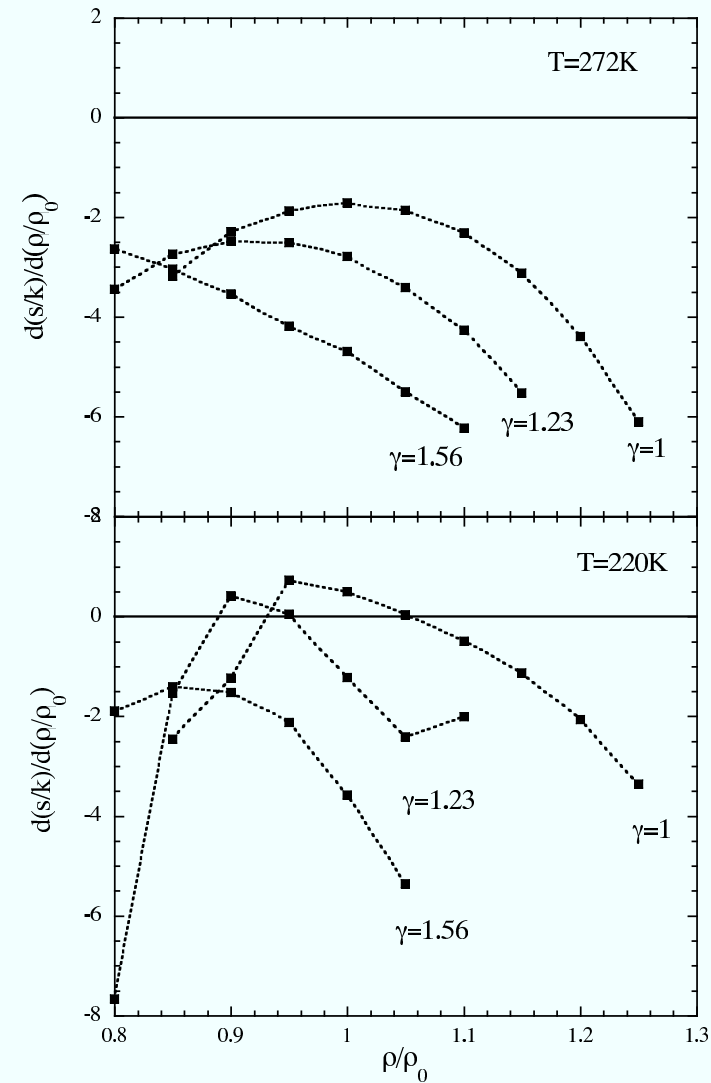
Pablo Debenedetti and I showed that in the hybrid family various anomalies such as

- Region of density increasing with temperature
- Region of entropy increasing with density
- Region of translation diffusion increasing with density
- Region of reorientational diffusion increasing with density

all decrease and eventually disappear as the hydrogen bond strength decreases and the liquid becomes more like a Lennard-Jones liquid.

19. Density anomalies

The density increases with T at constant p if the entropy increases with density at constant T . The region where this is true decreases and disappears when the hydrogen bond strength is decreased (γ increases).



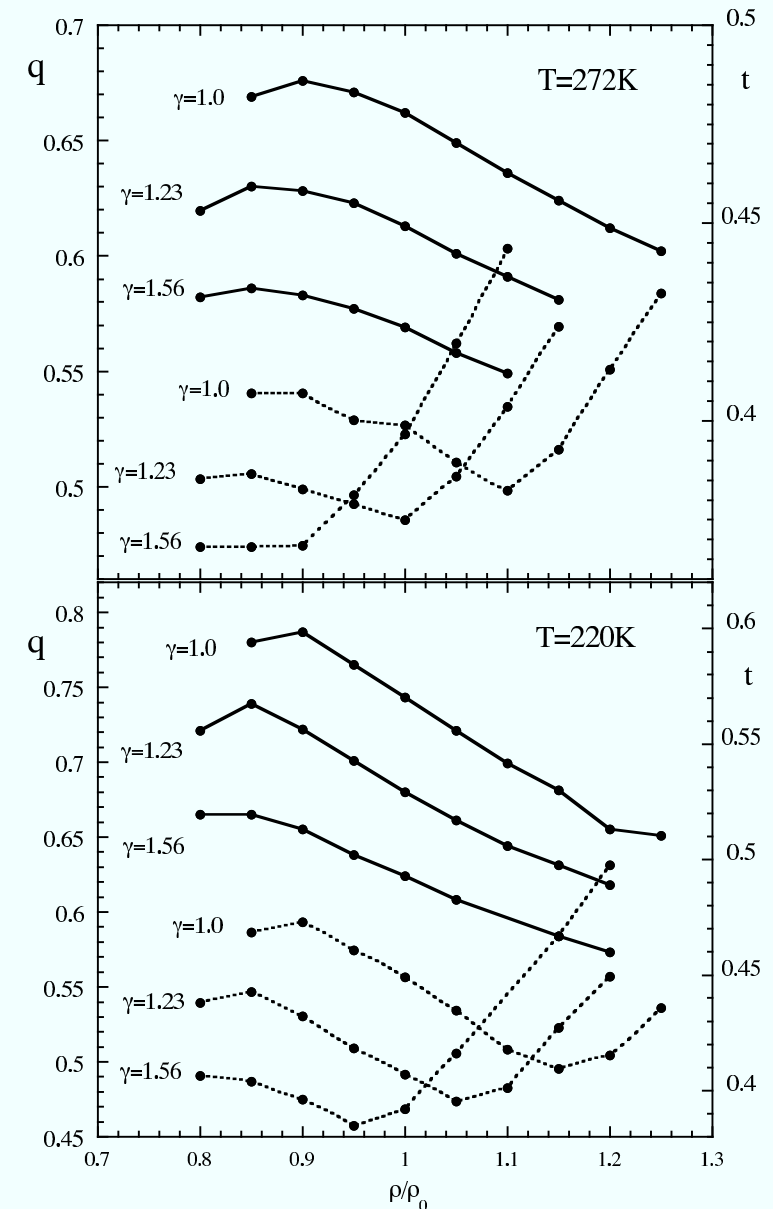
20. Order Parameters

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The tetrahedral order parameter q (solid lines) decreases with density although the ‘translational’ order parameter, t , (dashed lines) goes through a minimum.

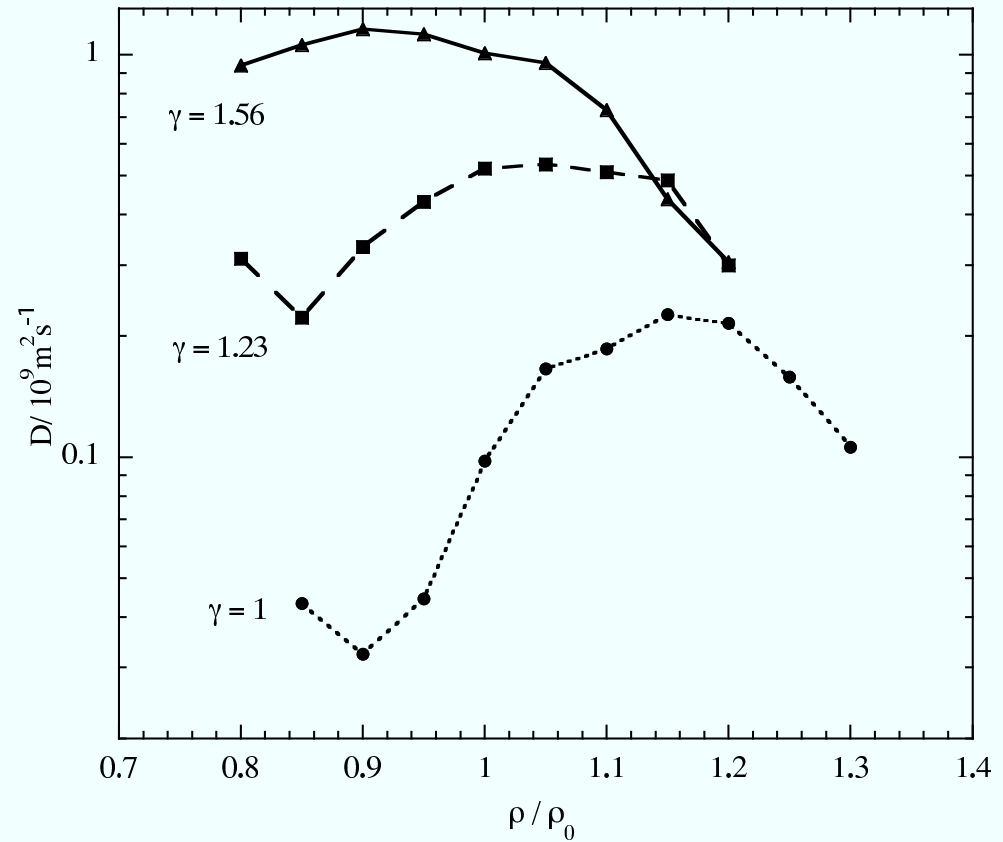
This shows that increasing the density destroys the tetrahedral network but increases the close packing.

This behaviour persists as γ , the ratio of the Lennard-Jones to the electrostatic term, increases.



21. Diffusion Anomalies

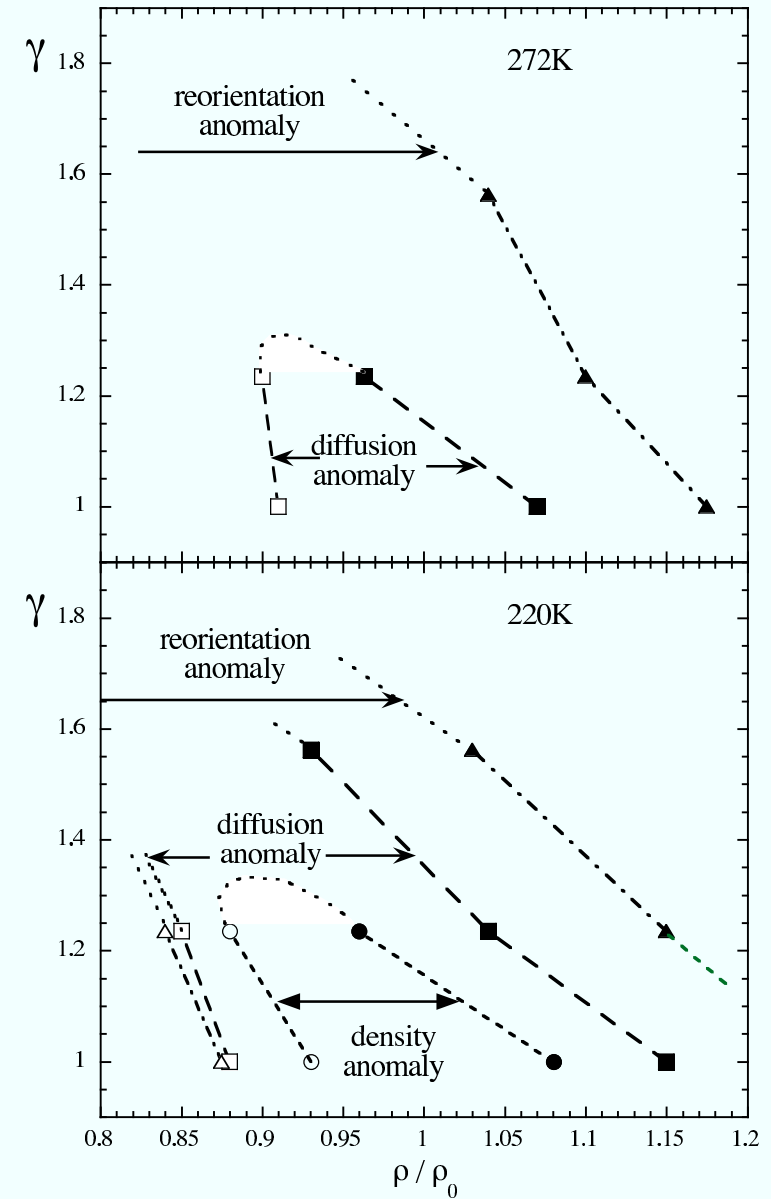
The anomalous region where the diffusion constant increases with density disappears as the hydrogen bonds get weaker. (increased γ).



22. Anomalous regions

22

As the hydrogen bond strength decreases the anomalous regions become smaller and shift to higher densities.



23. Hydrogen bonds in the pure liquid

23

Microscopic properties

The bent family has strong hydrogen bonds but the tetrahedral network is destroyed, to be replaced by chains in model B60. The coordination number decreases and the structure becomes 'looser'.

The hybrid family has progressively weaker hydrogen bonds; the local coordination number increases so that the liquid becomes more close packed.

Macroscopic properties

The **critical temperature and surface tension** are increased by closer packing and decreased by destroying the tetrahedral network. Hydrogen bonding has little direct effect.

The anomalous properties decrease and disappear as the hydrogen bond strength is reduced.

24. Water as a solvent

24

How do the properties of water considered as a solvent depend on hydrogen bonding?

It is generally found that hydrophobic effects on the Ångstrom scale are different to those on the nanometre scale.

Teresa Head-Gordon and I studied two aspects of the hydrophobic effect in our models:

- Contrasts in solubility of small hydrophobic particles (hard spheres 0.1-0.5nm)
- Drying between plates 1.3nm radius.

- Water dissolves small hydrophobic solutes *better* than the hybrid models which are more Lennard-Jones like. Do hybrid model liquids show more ‘hydrophobicity’ than water?
- Water dries hydrophobic plates less well than the bent models and better than hybrid models. Do hybrid model liquids show less ‘hydrophobicity’ than water?

Small scale hydrophobicity

Hard Spheres are the ultimate hydrophobic particles. We measured the excess chemical potential of hard spheres of different sizes by Widom’s particle insertion method.

26. Chemical Potential of dissolved hard spheres — 26

As the blue curve for hybrid model H30 (top) lies above the corresponding red curve for spc/e water.

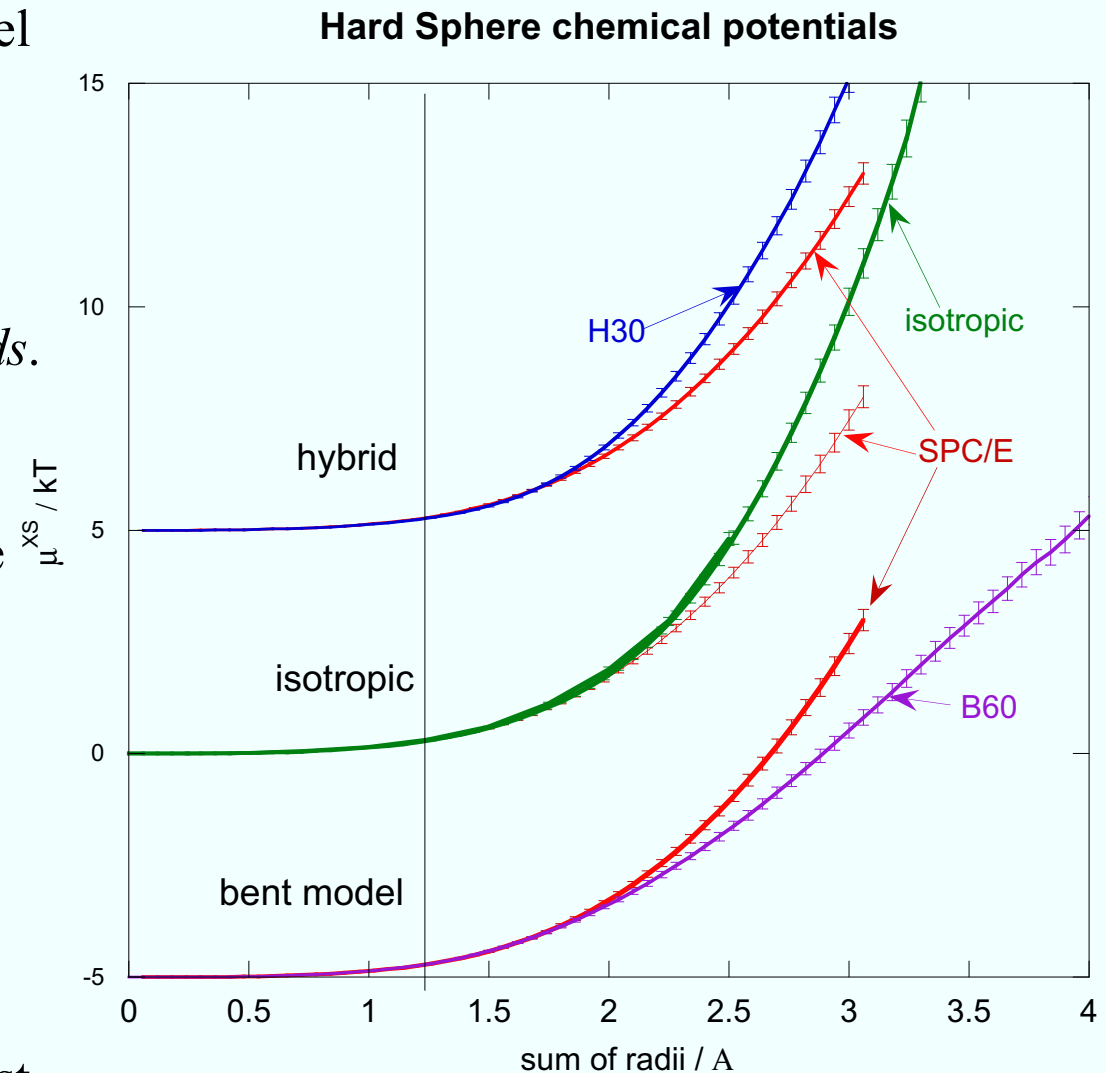
Hard spheres are more 'hydrophobic' in the hybrid liquids.

As the mauve curves for bent model B60 (bottom) lie below the corresponding red curve for spc/e water.

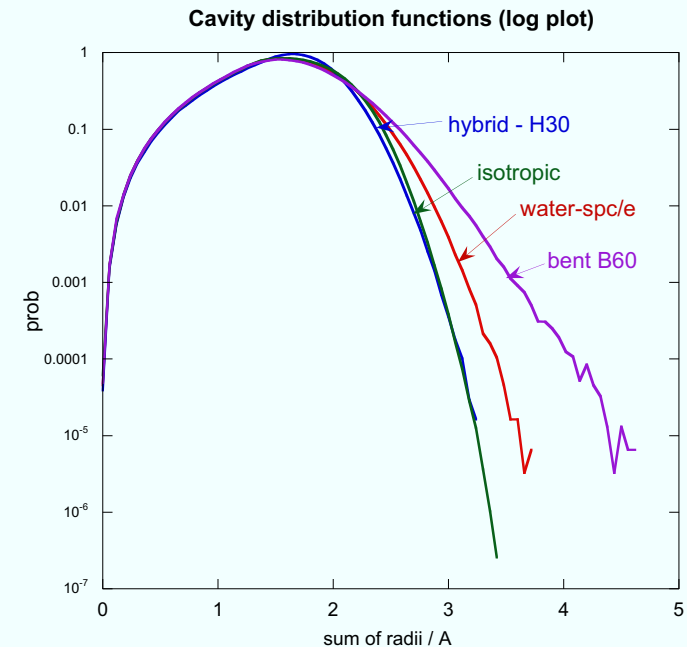
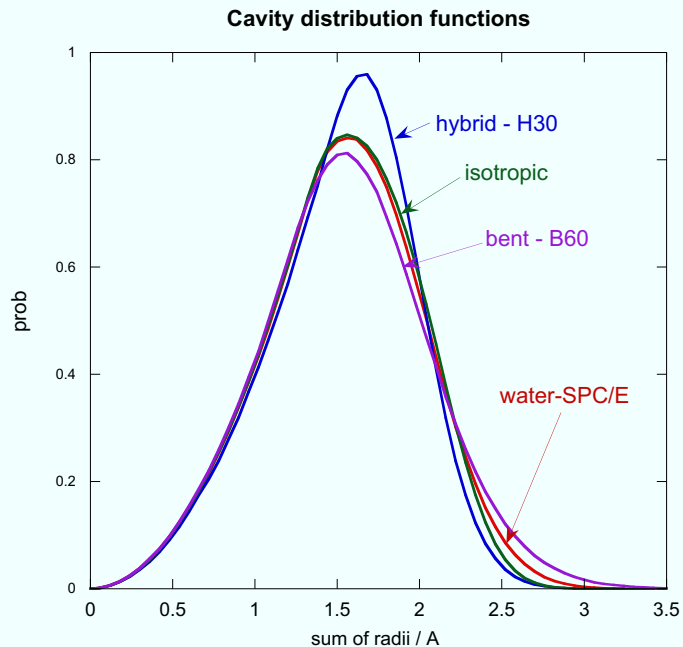
Hard spheres are less 'hydrophobic' in the bent liquids.

WHY?

Why doesn't water with its tetrahedral structure show the most hydrophobicity?



27. Cavity distribution functions



The solubility of small hydrophobic solutes is determined by the distribution of cavities in the liquid.

In a close packed liquid such as hybrid H30 there are fewer large cavities than in an open tetrahedral structure *with the same number density*.

The 60° B60 ‘water’ has an even more open structure and more large cavities than spc/e water due to its lack of a three dimensional network and preference for chain formation.

Water is a more favourable solvent for hydrophobic solutes than more close-packed liquids - such as the hybrid liquids

Why do methane, alkanes and other hydrophobic solutes dissolve better in organic liquids than in water?

Why doesn't water with its tetrahedral structure show the greatest hydrophobicity?

We have seen that a Lennard-Jones solute ('methane') is less soluble in water than in a water-Lennard-Jones hybrid, which one might think is more like a normal organic liquid.

But

- Normal organic liquids have larger molecules and so the cavities are larger.
- The magnitude of the dispersion interaction may be larger in organic liquids.
We have used the same Lennard-Jones ϵ for all solute-solvent interactions.

We conclude that it is the small molecular size which is the most important factor in the hydrophobic effect, although the bent family shows that the network structure is also important.

29. Longer length scale hydrophobicity

29

On a longer length scale a typical result of hydrophobicity is that the water will not wet a hydrophobic surface.

Hydrophobic behaviour around nano-sized and larger particles is due to competition between the surface tension of the vapour-liquid and solid-liquid interfaces.

If the solid-liquid surface tension is low, then the surface will not wet - typical hydrophobic behaviour.

This leads to drying between nanometre sized plates at nanoscale separations.

This was studied by Huang, Margulis and Berne for pairs of ellipsoidal Gay-Berne particles in spc water at different separations.

Teresa Head-Gordon and I have extended this to a comparison of our different model liquids.

30. Gay-Berne plates

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We have studied a similar set of thin ellipsoidal Gay-Berne particles in our model liquids.

They are 13\AA in radius and 3.7\AA thick.

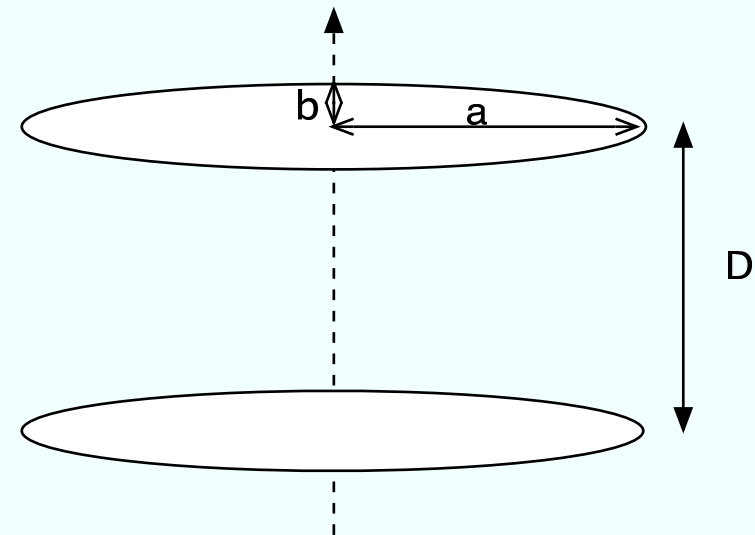
We have two types of particle -

- attractive ellipsoidal Lennard-Jones

$$V = 4\epsilon \left[\left(\frac{\sigma(\varphi)}{r} \right)^{12} - \left(\frac{\sigma(\varphi)}{r} \right)^6 \right]$$

with $\epsilon = kT$.

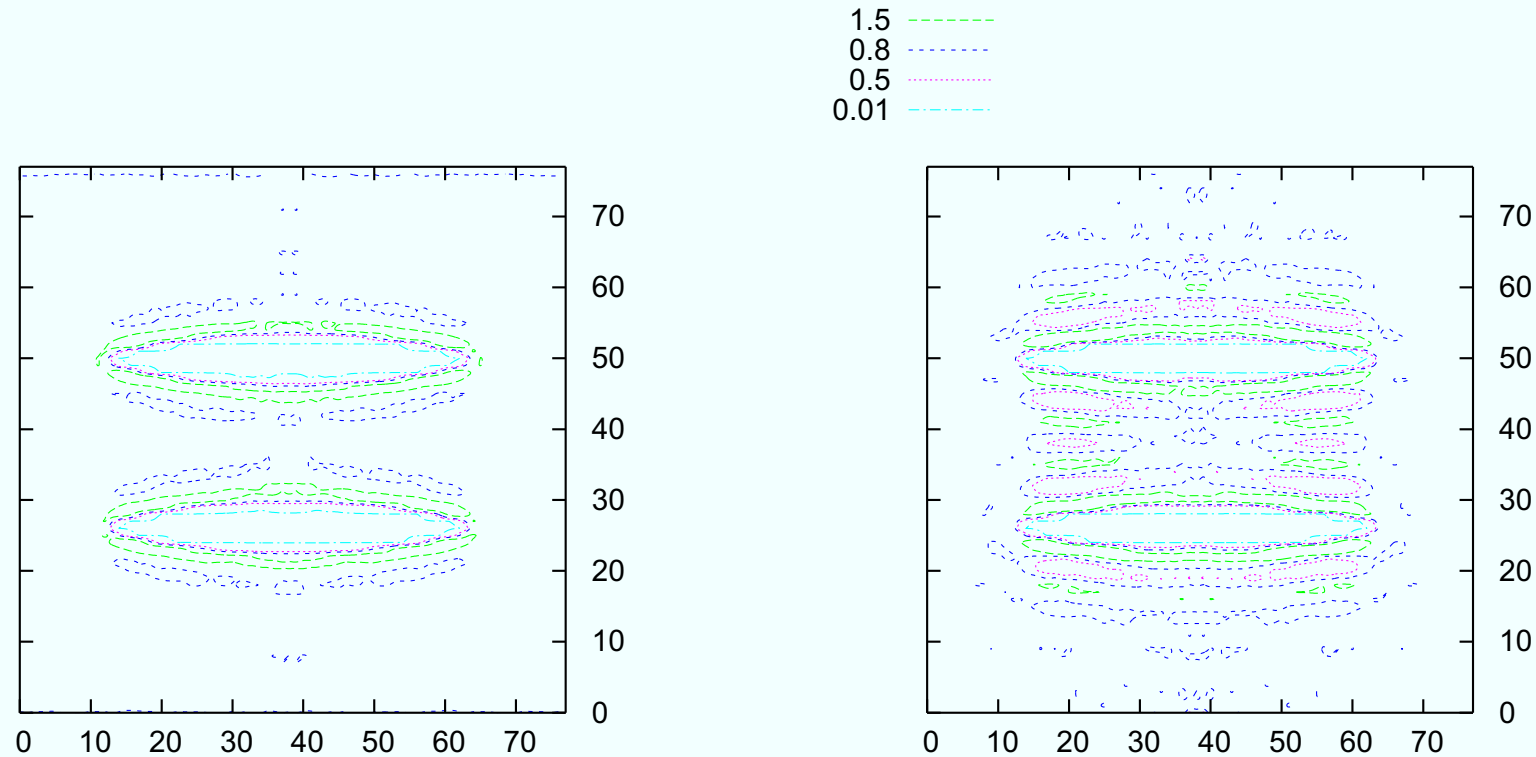
- purely repulsive with the r^{-12} term only.



We study the density between the plates as a function of separation, D .

The hydrophobic effect is expected to lead to drying between the plates.

31. Differences between liquids



Contour plots of average densities with attractive Gay-Berne particles separated by 12Å.

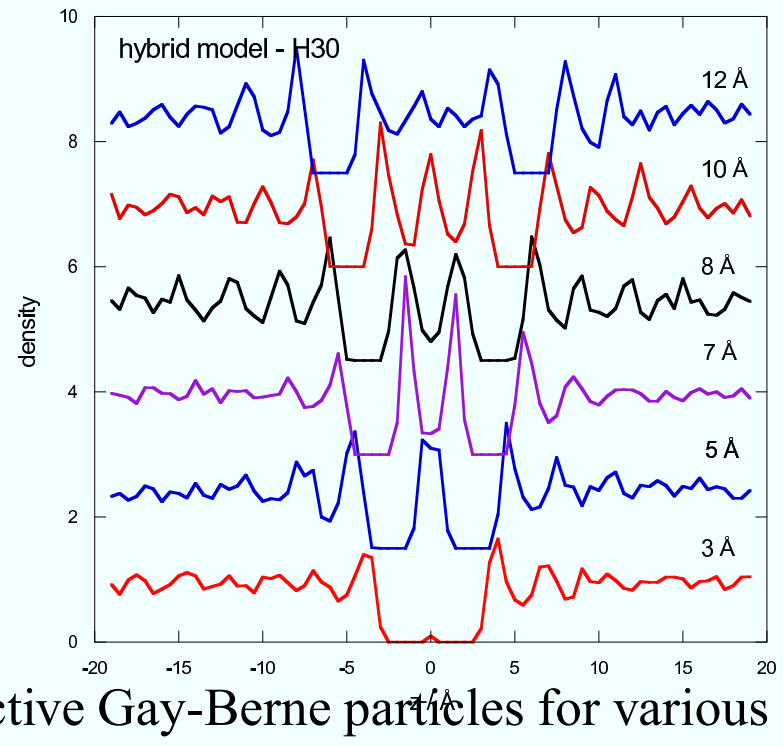
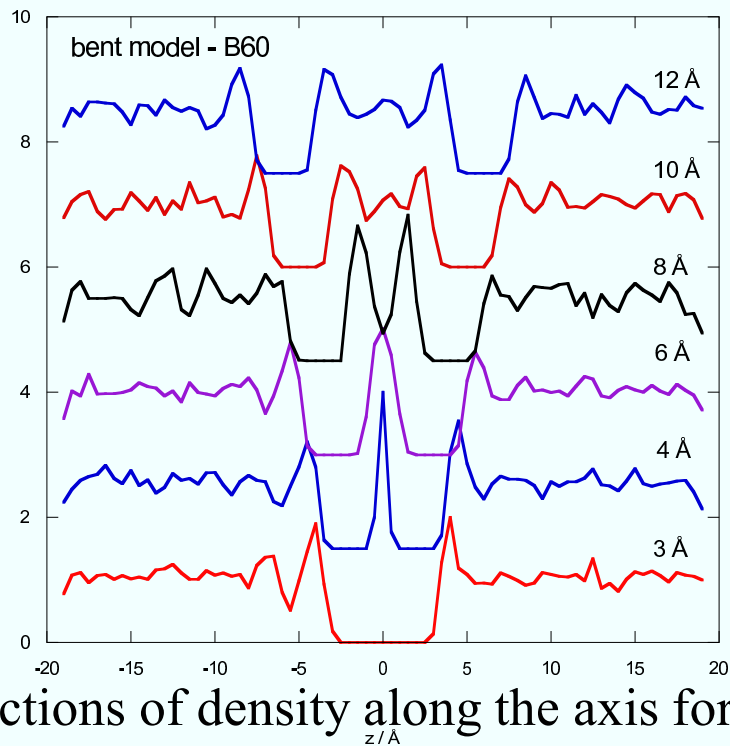
LEFT: bent model B60;

RIGHT: hybrid model H30

More structure and layering is induced in the hybrid liquid than in the bent liquid.
Both liquids wet the plates.

32. Attractive Gay-Berne particles

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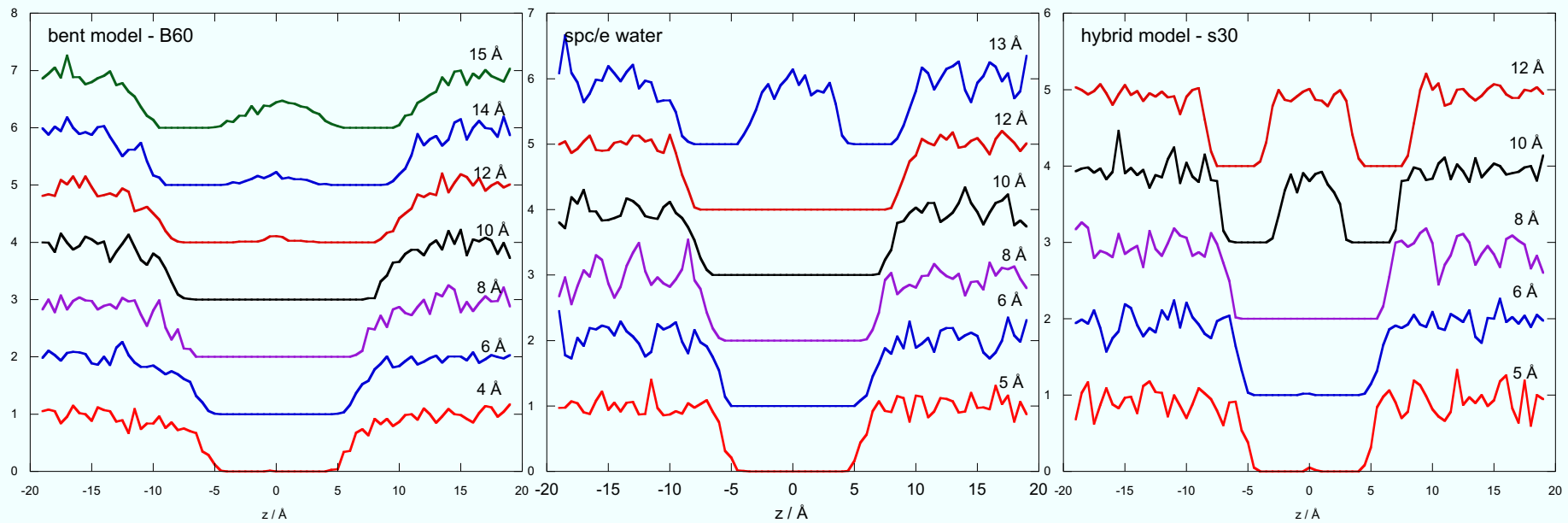
Cross sections of density along the axis for attractive Gay-Berne particles for various spacings.

LEFT: bent model B60;

RIGHT: hybrid model H30

The gap is filled by all liquids if the spacing between the Gay-Berne centres $> 3\text{\AA}$. There is no sign of drying even in the hybrid model H30. As all the liquids wet the particles, Gay Berne particles with attractive potentials show no hydrophobic effects.

33. Repulsive Gay-Berne particles



Cross sections of density perpendicular to repulsive Gay-Berne particles at the Gay Berne centres for various spacings.

LEFT: bent model B60;

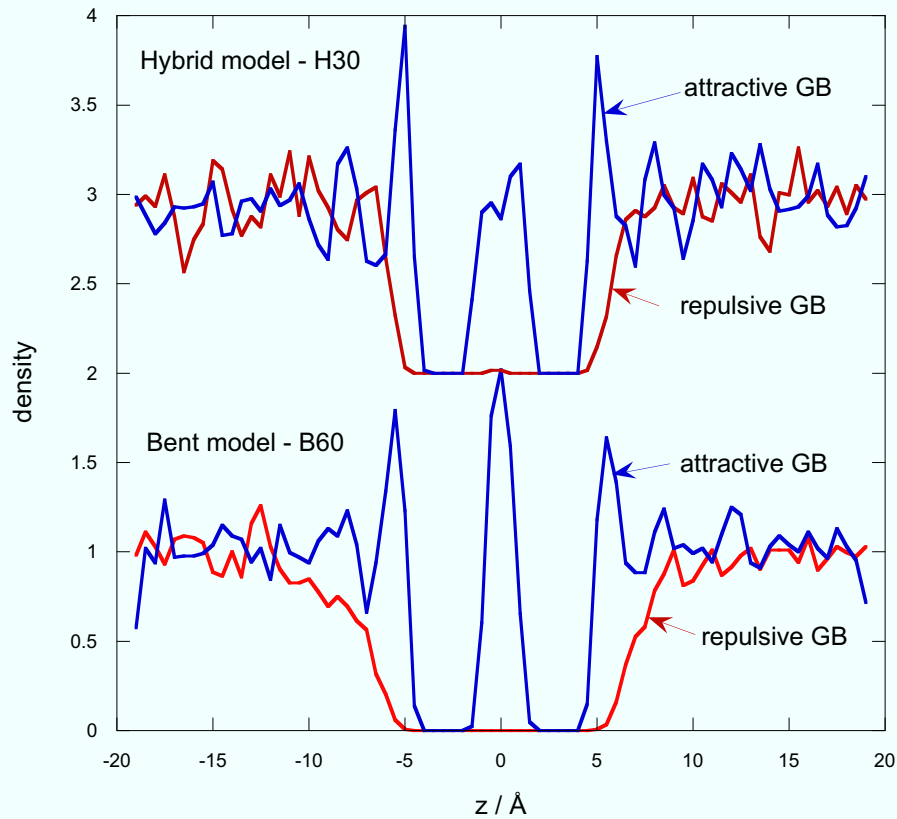
MIDDLE: spc/e

RIGHT: hybrid model H30

The gap is empty in all liquids below a critical spacing. This is a sign of the hydrophobic effect.

This critical spacing is least in hybrid H30 water and greatest in bent B60 water.

34. Comparison of model liquids



The liquids move away from the repulsive GB particles.

The bent molecules move further.

35. What determines the critical separation?

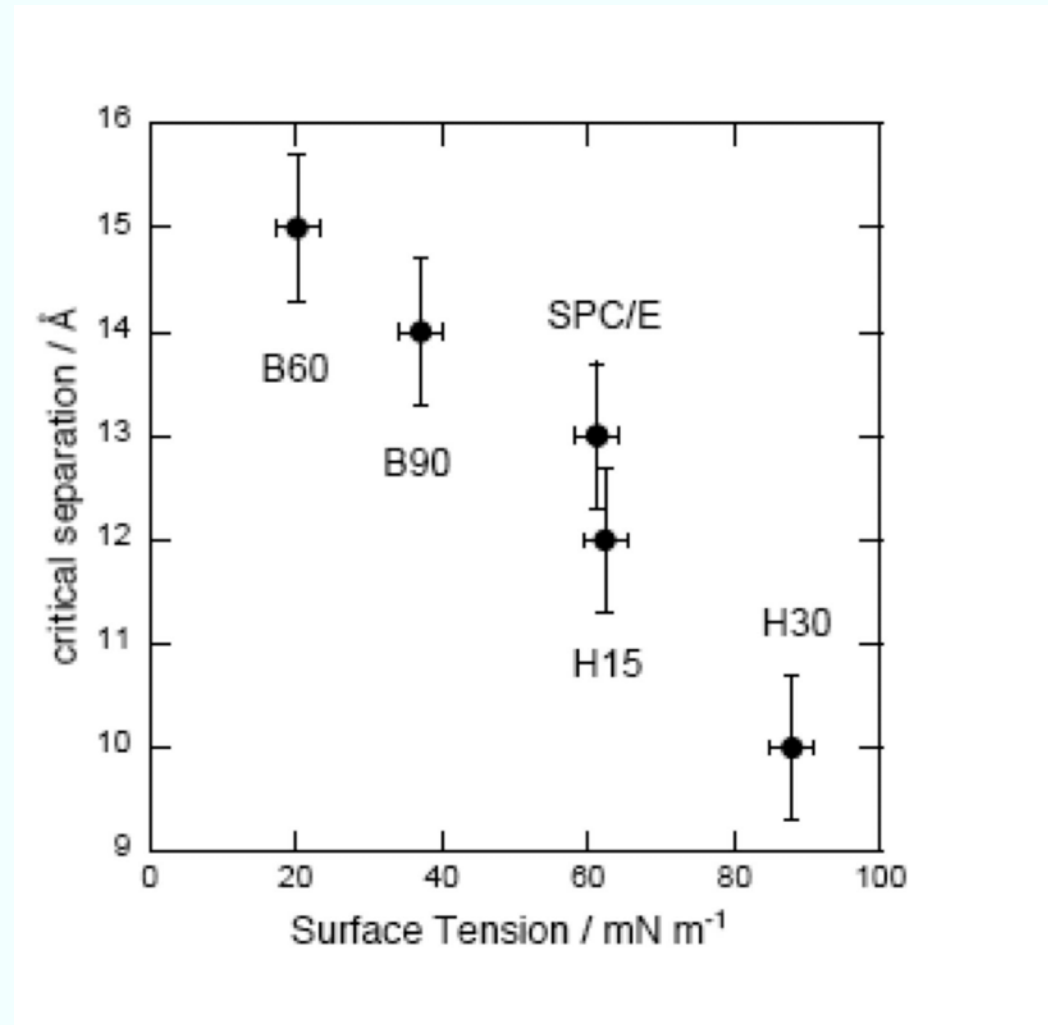
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In a continuum model the critical separation D_c is given by

$$D_c/a = (\gamma_{ls} - \gamma_{vs})/\gamma_{lv} \approx \gamma_{ls}/\gamma_{lv}$$

where a is the radius of the plate, γ_{lv} , γ_{ls} are the liquid-vapour and liquid-solid surface tensions. We find an inverse correlation of the critical separation with γ_{lv} .

The lower the value of γ_{lv} the greater the nanoscale hydrophobicity.



36. Temperature dependence

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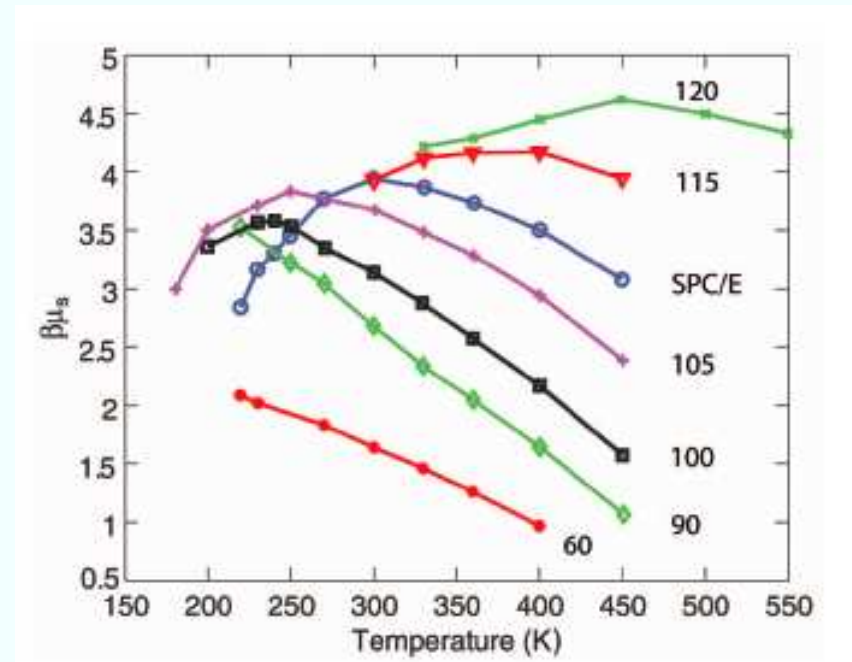
Swaroop Chatterjee (together with Pablo Debenedetti, Frank Stillinger and myself) looked at the temperature dependence of the solubility of 3.16Å Lennard-Jones particles in Bent models of water.

The slopes of these curves are equal to $-\Delta H/T^2$

The cross-over from negative heats of solution at low temperatures to positive heats of solution at high temperatures is characteristic of bent models with angles greater than 100°

This temperature dependence is characteristic of hydrophobicity.

The negative heat of solution at low temperatures can be ascribed to network breakup.



37. So why IS water unusual?

37

- Anomalous properties such as its increase of density with temperature and increase of translational and rotational diffusion with pressure are due to the tetrahedral structure which can be broken down by pressure or temperature. Reducing the hydrogen bond strength reduces the range of the existence of these anomalies. The point of minimum structure in $g(r)$ (model H15) does not seem to lead to particular properties.
- The bent models have lower critical temperatures and lower surface tensions than spc/e water. The relative permittivity is particularly high for the 'looser' bent models.
- Water's reluctance to dissolve Ångstrom-sized hydrophobic solutes is primarily due to the small size of the water molecule (and so high number density) which leads to small cavities. Its network structure gives a sharp cavity distribution. But a Lennard-Jones liquid has an even sharper distribution so hydrogen bonding is not uniquely important.
- Although the hybrid and bent liquids both de-wet hydrophobic Gay-Berne particles, the critical separation is smallest for the hybrid model and largest for the bent B60 model.

D.L.Bergman and R.M.Lynden-Bell *Is the hydrophobic effect unique to water? The relation between solvation properties and network structure in water and modified water models.* Mol. Phys. 99 (2001) 1011-21

R.M.Lynden-Bell and P.G. Debenedetti *Computational investigation of Order, Structure and Dynamics in Modified Water Models.* J.Phys.Chem B. 109 (2005) 6527-6534.

R.M.Lynden-Bell and T.Head-Gordon *Solvation in modified water models: towards understanding hydrophobic effects.* Mol.Phys. 104 (2006) 3593.

T.Head-Gordon and R.M.Lynden-Bell *Hydrophobic solvation of Gay-Berne particles in modified water models* J. Chem. Phys. 128 (2008) 104506

J.Alejandre and R.M.Lynden-Bell *Phase diagrams and surface properties of modified water models.* Mol. Phys. 105 (2007) 3029-3033

S Chaterjee, P.G.Debenedetti, F.H.Stillinger and R.M.Lynden-Bell *A computational investigation of thermodynamics, structure and solvation behaviour in modified water models.* J. Chem. Phys. 128 (2008) 124511