Process Models of the Equilibrium Size and State of Organic/Inorganic Aerosols

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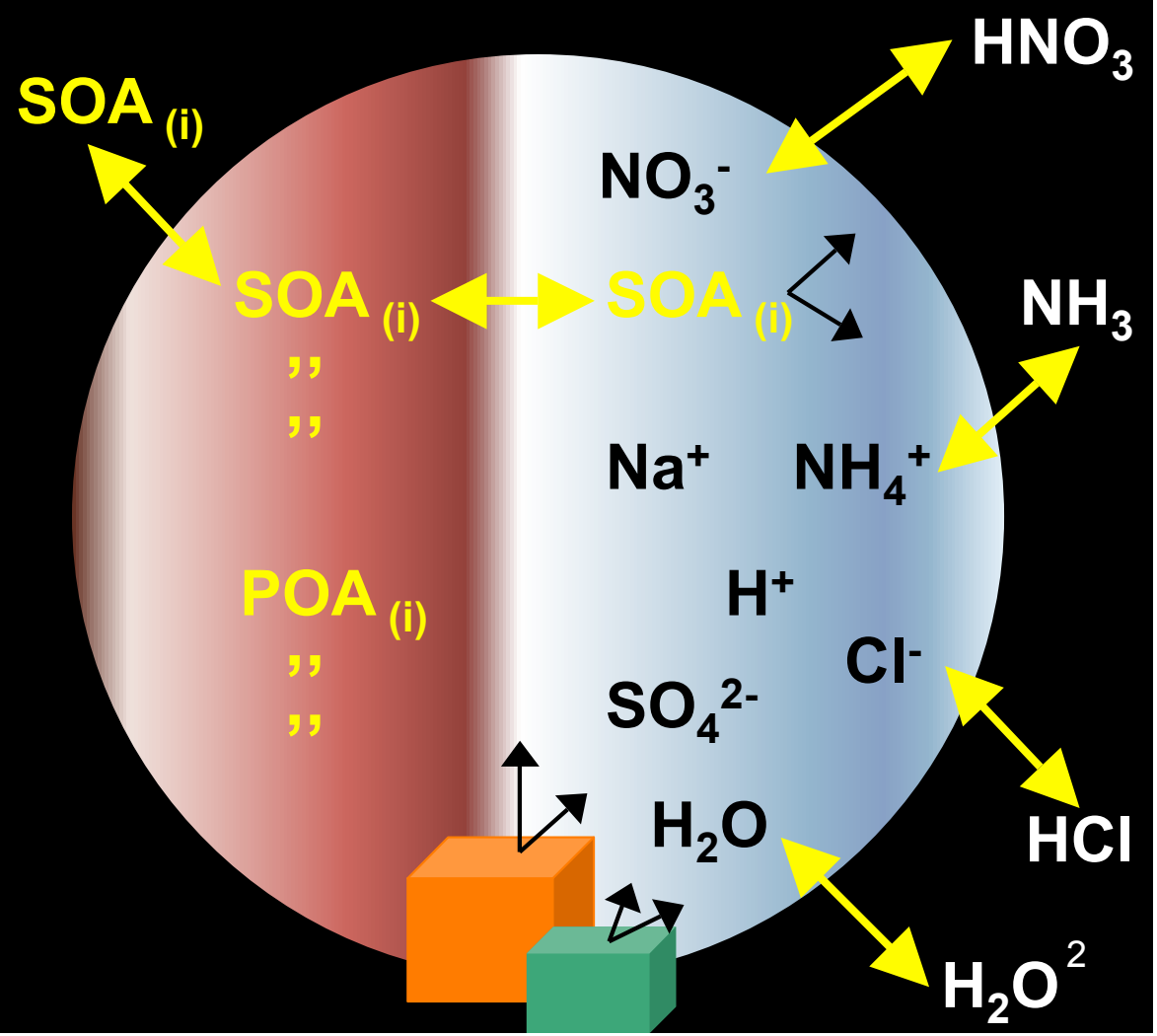
Extended Aerosol Inorganics Model

Organic Properties

1. Molar mass
2. p^0 (or K_H) and ΔH.
3. K_d **and ΔH** (≤ 2).
4. Activity treatment in each phase (Raoult, UNIFAC, fitted).
5. K_s of organic solids.



Progress in 2008

1. Added organics to the web-based model, so they can be defined and used in calculations (www.aim.uea.ac.uk/aim/aim.php).

2. Completed a quantitative treatment of salt effects on NH_3 gas/aerosol partitioning.

3. Partially completed a treatment of solution density.

Salt Effects on NH_3 Gas/ Aerosol Partitioning

1. In common acid sulphate/seasalt aerosols the effect is to increase the equilibrium pNH_3.

2. Magnitude of the effect: in an $(NH_4)_2SO_4$ aerosol at 80% RH, pNH_3 is increased by 60%.

3. The effect on partitioning is likely to be greatest near NH_3 sources where comparable amounts are present in both phases.

Densities of Aqueous Aerosols

(Needed to calculate particle size and CCN activation)

- Practical problems:

1. Extrapolation to supersaturated concentrations.
2. Extrapolation to low temperatures.
3. Estimates for mixtures.

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Melt densities for $NaHSO_4$, $NaNO_3$, NH_4HSO_4, NH_4NO_3 (Zelenyuk).

Densities of supersaturated aqueous solutions (Tang).

Densities of molten salts (extrapolated to 25 ºC)

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$\Delta\rho$ (crystal-melt) at 25°C

Differences, as percentages:

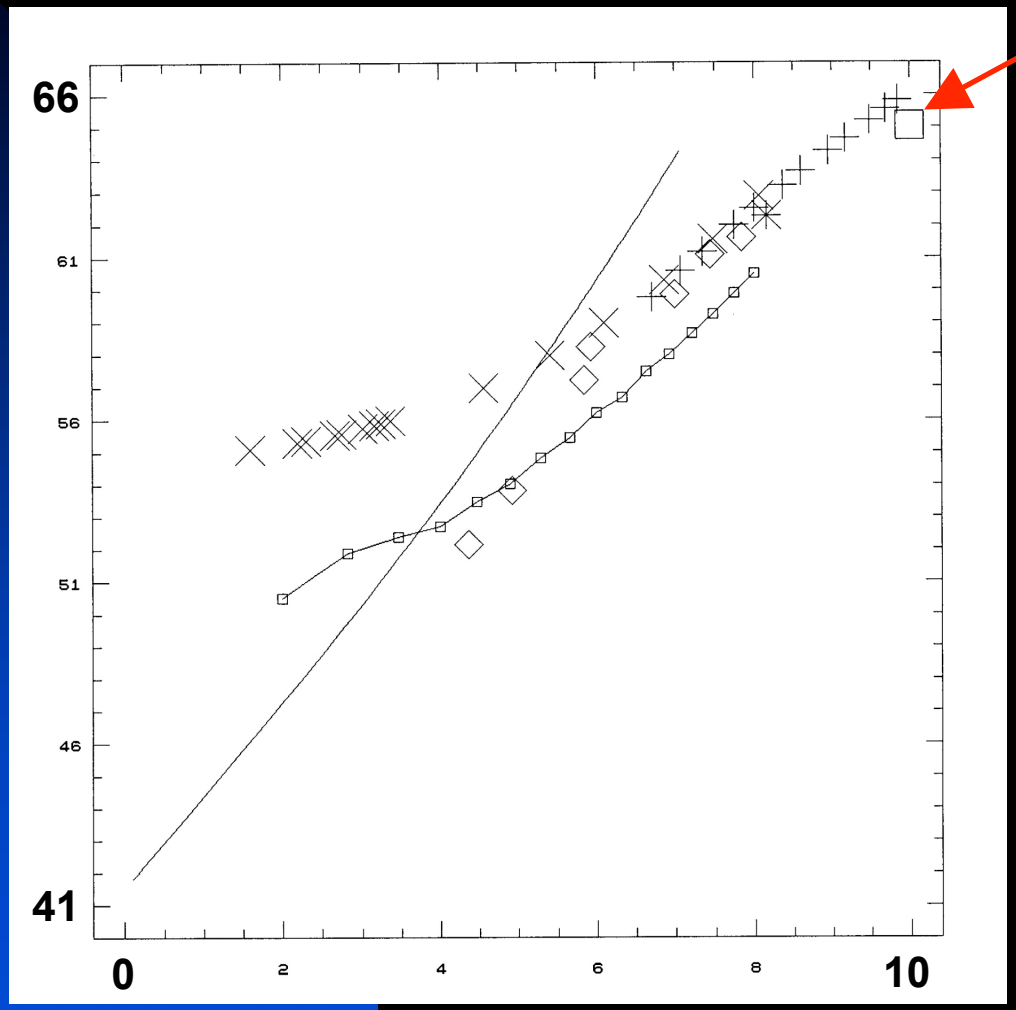
	Zelenyuk	Tang (extrapolated)	Molten salt (extrapolated)
$NaHSO_4$	11.0	9.5	3.6
$NaNO_3$	7.6	8.1	8.9
NH_4HSO_4	1.1	2.9	2.3
NH_4NO_3	8.1	*	10.6

Densities at 25 °C

0 – 100 wt% for combinations of the following cations and anions:

	H	NH_4	Na
HSO_4		Y	Y
SO_4	Y	Y	Y
Cl	Y	Y	Y
NO_3	Y	Y	Y

ρ of NH_4HSO_4 (1)

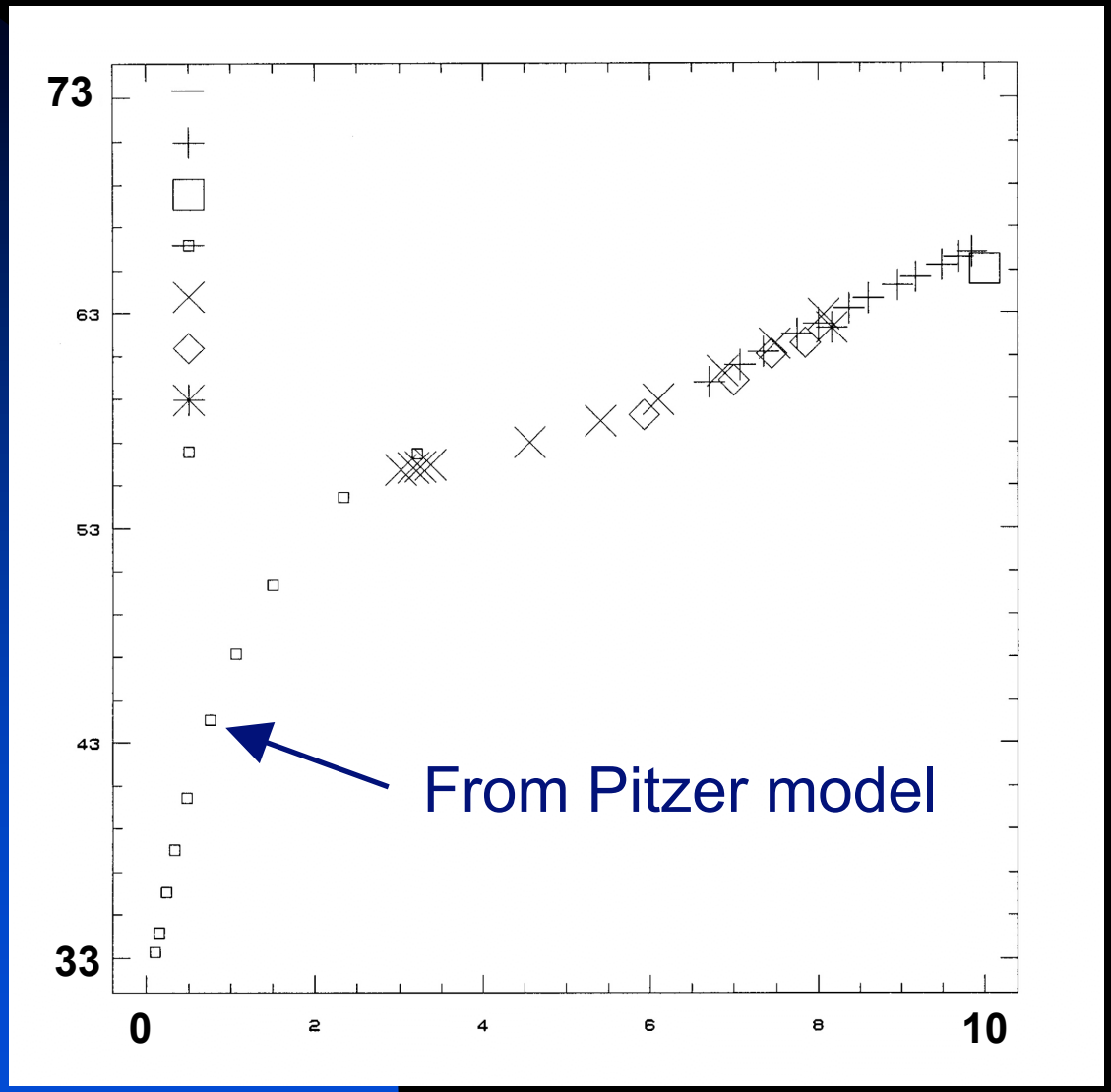


liquid NH_4HSO_4

V^{φ}

$\sqrt{\text{wt\%}}$

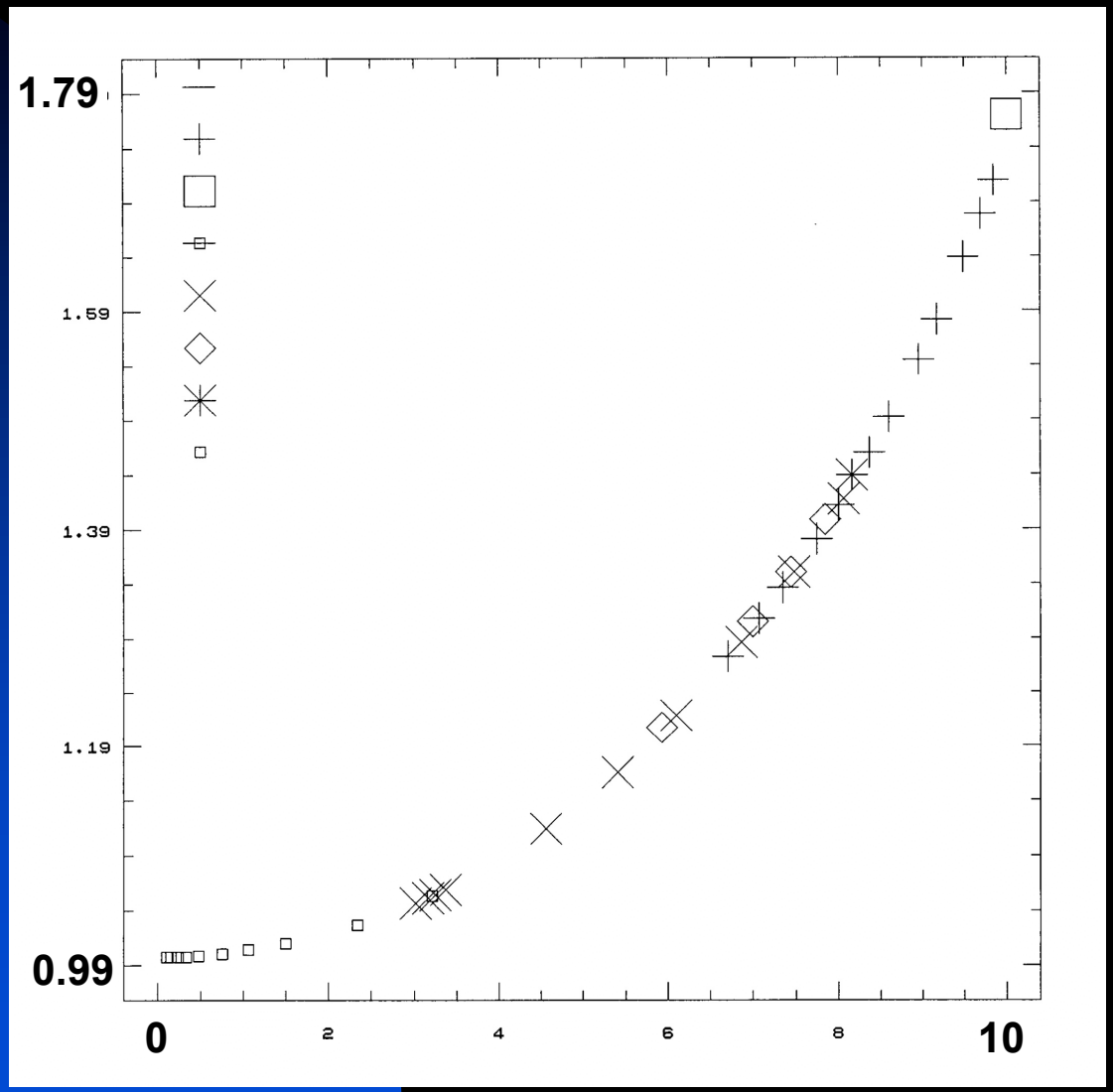
ρ of NH_4HSO_4 (2)



V^{φ}

√ wt%

ρ of NH_4HSO_4 (3)



ρ

√ wt%

Densities of Aqueous Aerosols

(Needed to calculate particle size and CCN activation)

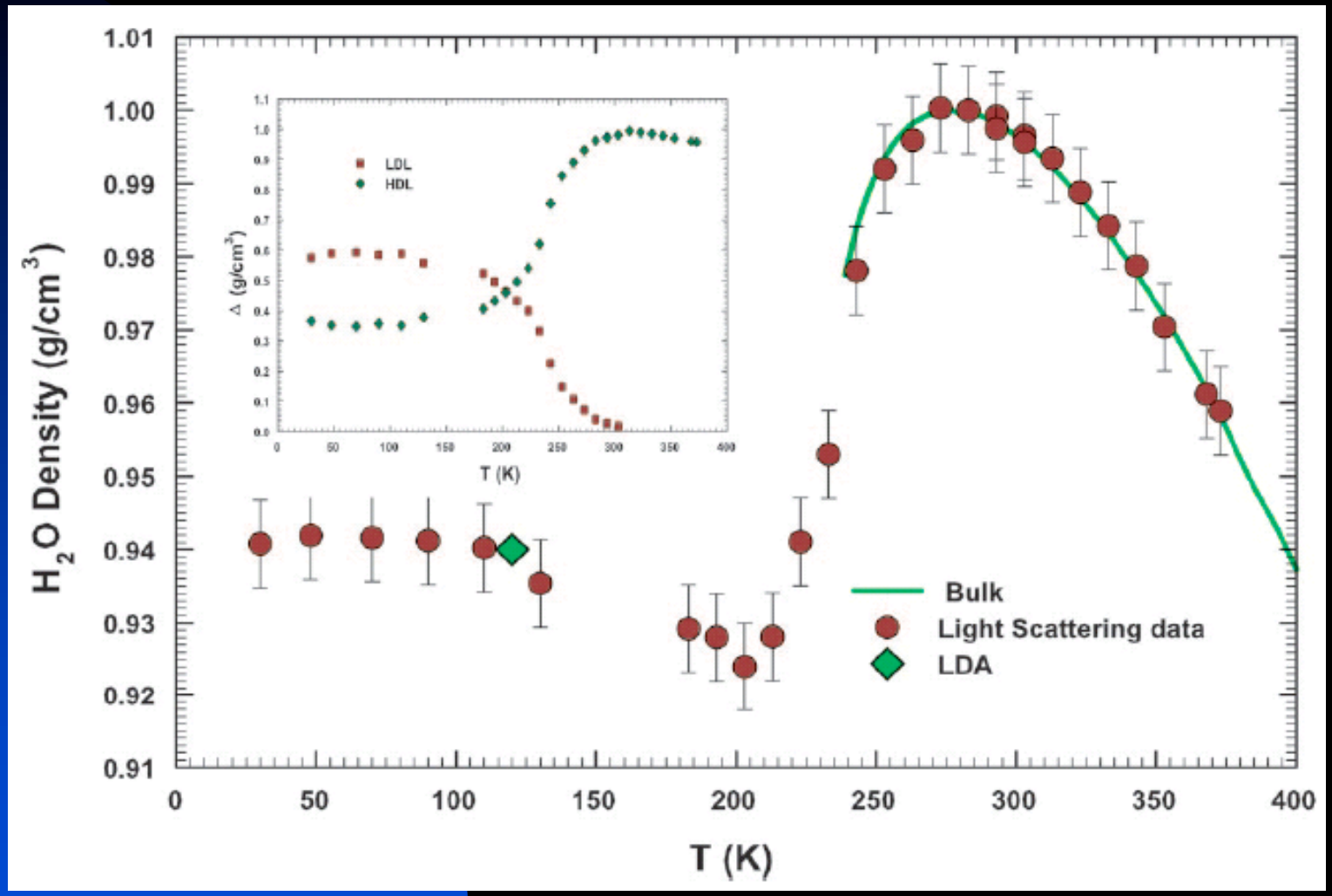
- Practical problems:

2. Extrapolation to very low temperature (~200 K).

➡ Above about 6 mol kg^{-1} solution density is quite linear wrt T, and unlike that of water.

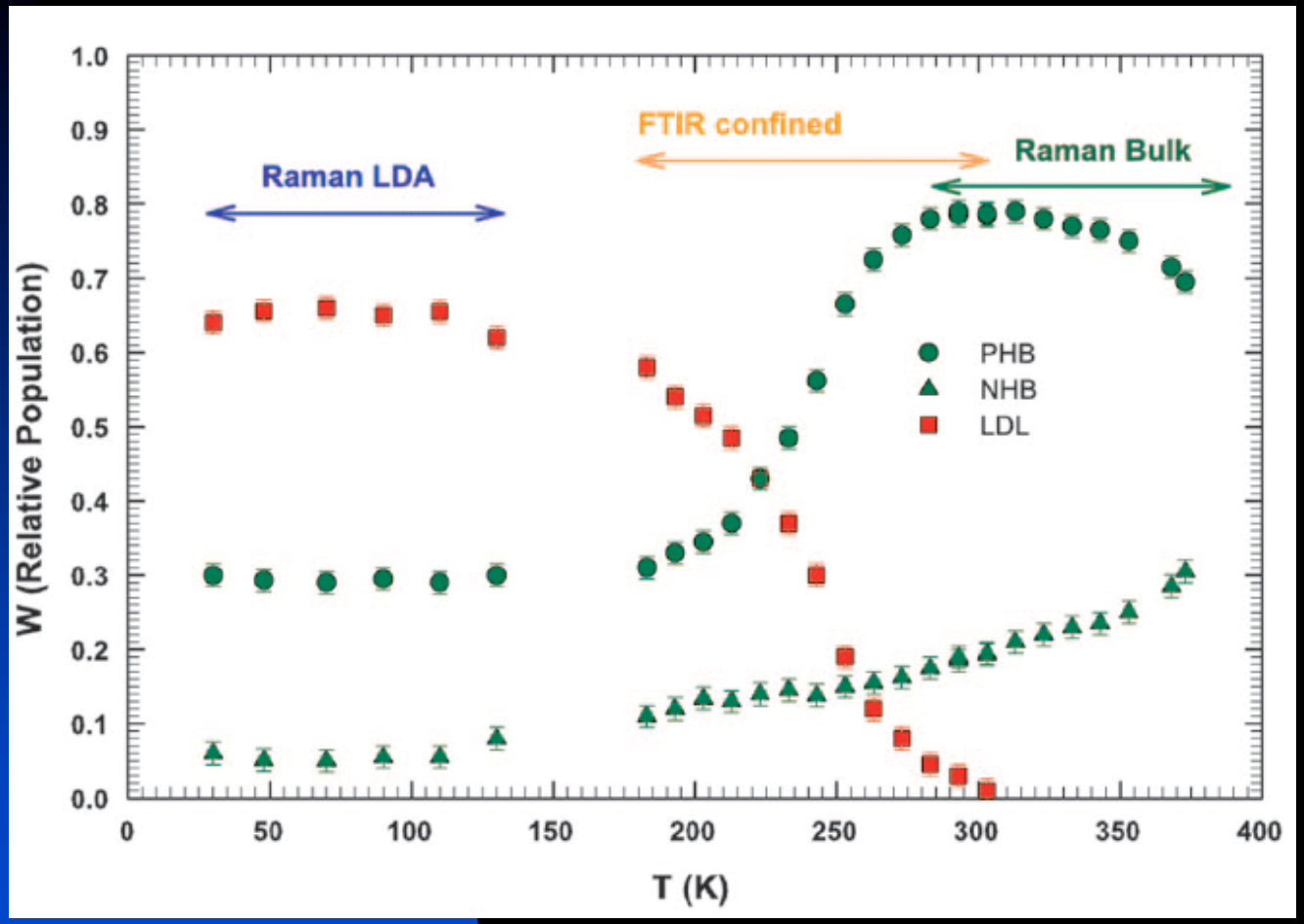
➡ In more dilute solutions, ρ(soln.) → ρ(water)

Density of Liquid Water



Source: Mallamace et al., *PNAS* **104**, 18387 (2007)

Why That Shape?

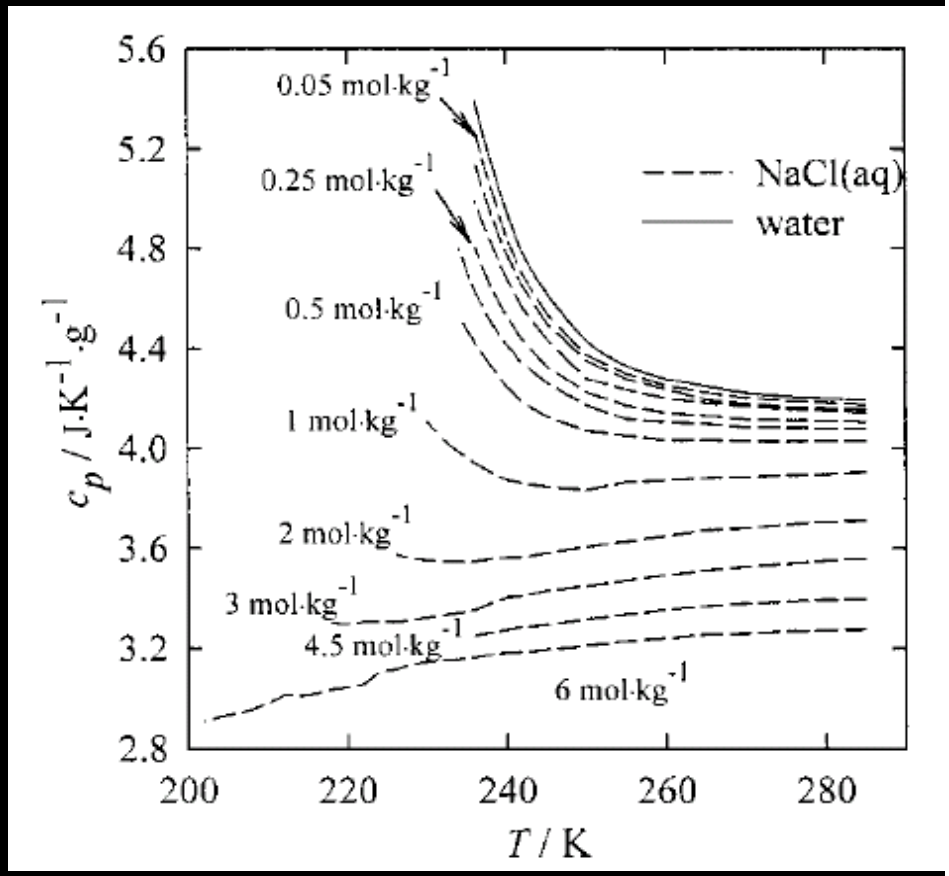


There are three different (transient) hydrogen bonded structures in liquid water – each with a characteristic density – and the relative proportions change with T.

Implications: C_p of liquid water

Improved estimates of the heat capacity of pure water at very low T, needed for calculations of equilibrium uptake of water by liquid aerosols at very low T (ΔC_p, for the reaction:

$$H_2O_{(g)} \leftrightarrow H_2O_{(l)}$$



Source: Archer and Carter, *J. Phys. Chem. B*, **104**, 8563 (2000)

Current and Future Work

- Complete the treatment of densities, extending it over a range of *T*, and to mixtures.
- Plan (with PNNL) further additions to the organic systems modelled by *E-AIM*.
- (Improved low *T* thermodynamics)