About Solubility

Graeme Ackland

https://journals.aps.org/pre/abstract/10.1103/PhysRevE.73.021504

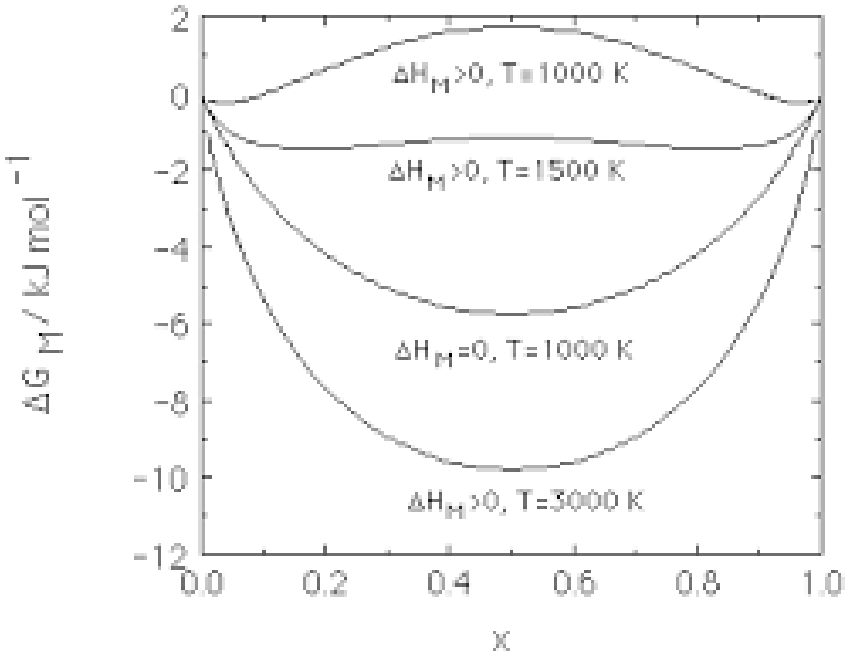
Thermodynamics of solubility

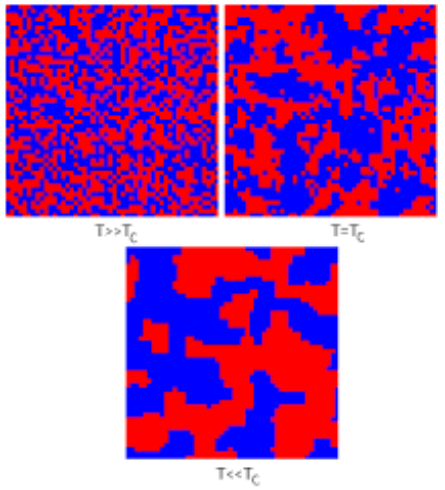
- Minimise the Gibbs free energy of two systems by exchanging particles,
- Or, a single system phase separates into two parts

$G = U + PV - TS + mgz$

(always) gain entropy of mixing.
(may) lose enthalpy of mixing.

$S_{mix} = k_B\, c \log c + (1-c) \log (1-c)$

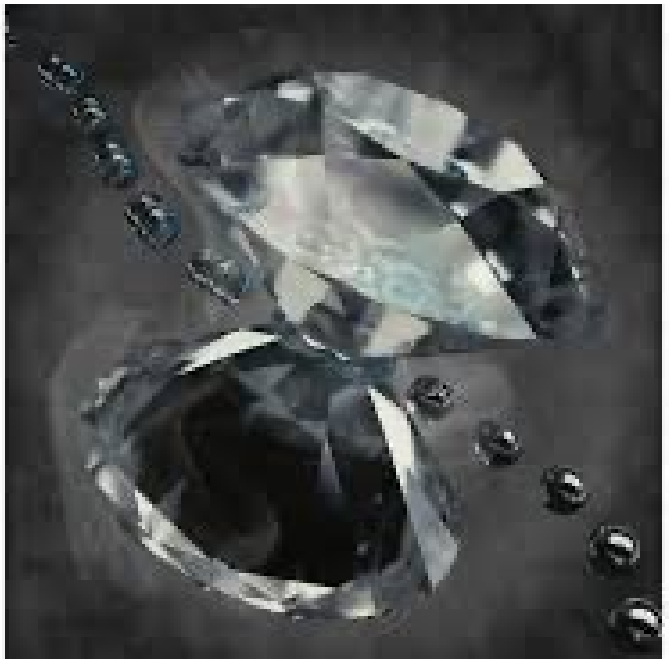




e.g. Ising model with Kawasaki (exchange) dynamics

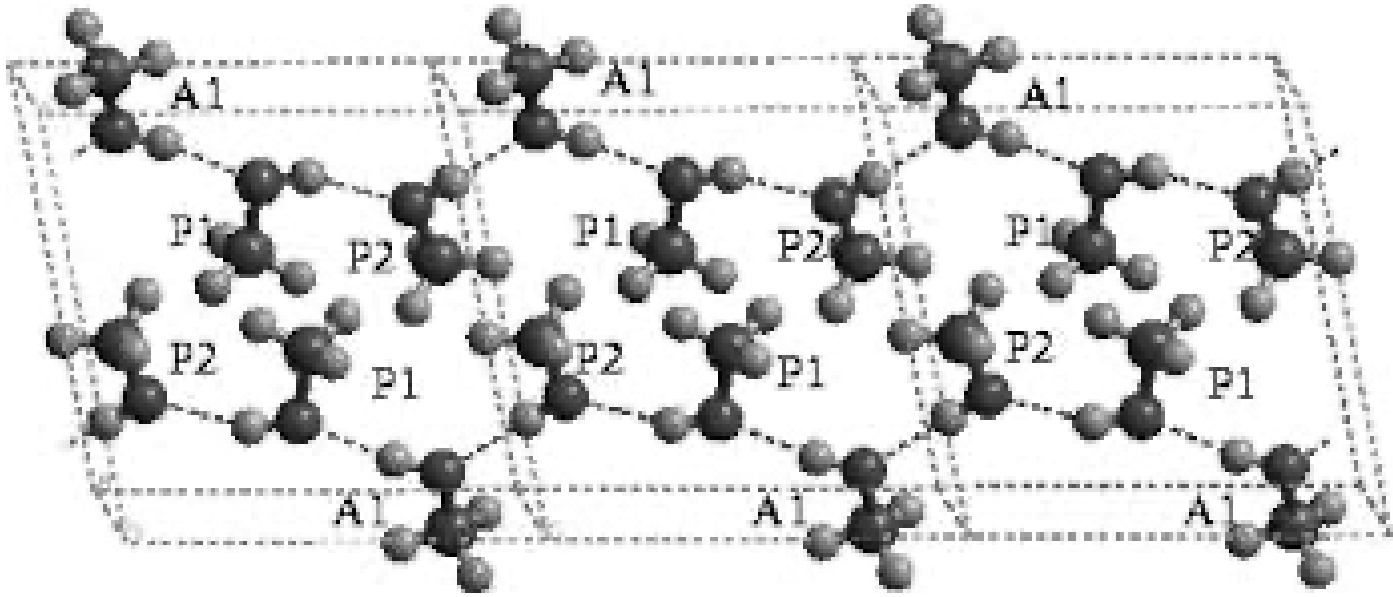
Does carbon dissolve in hydrogen?

- No. We can routinely load hydrogen into a pressure cell
- Yes. Hydrocarbon molecules
- No but yes. Methane and benzene form a two-phase liquid.



Emulsion: Microscopic order, macroscopic mixing.

What is Methanol

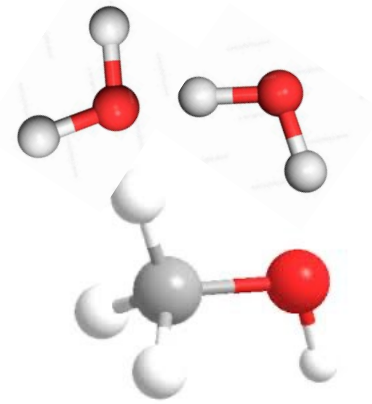


- CH3OH has a polar OH group

at one end, and a non-polar CH3 at the other.

Crystalline methanol makes H-bonded chains, with CH3 groups pointing at each other.

Methanol is, approximately, twice the length of water.



Segue: Ising Model

$$U = \sum_{i=1,N} \sum_{k=1,4} -\sigma_i \sigma_k$$

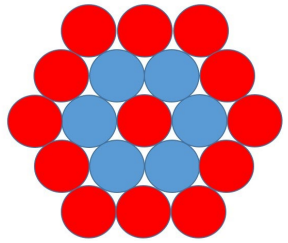
Square lattice

Two species (CH3, OH)

Why square lattice?

No physical reason.
Sociologically: need it for the Onsager analytic solution.

Misses some important physics like antiferromagnetic frustration.



On a triangular lattice. Lowest energy state isn't periodic.

On an fcc lattice. AFM needs second neighbour interactions to avoid degeneracy. Three ordered structures (+paramagnet).

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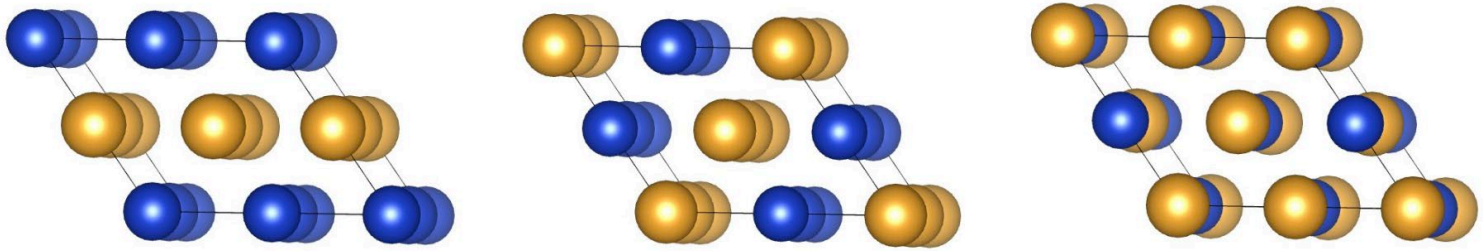
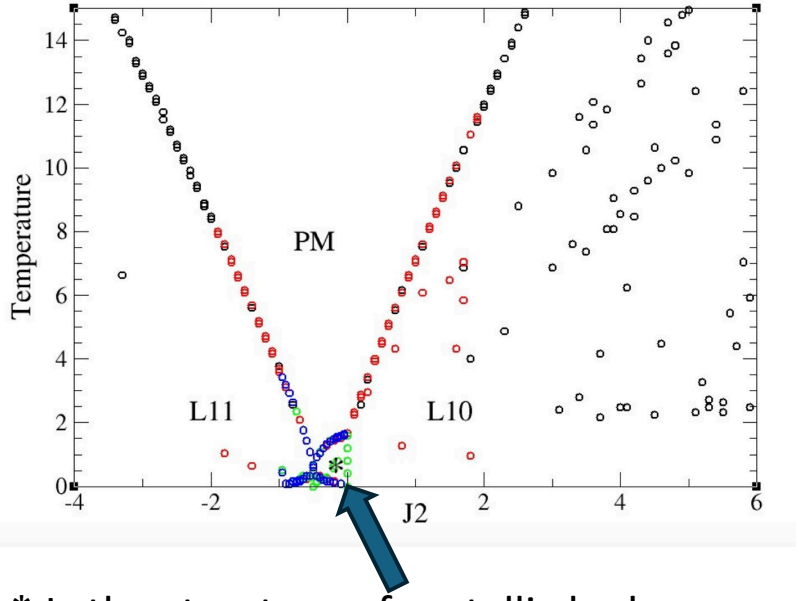


Figure 1: The FCC lattice in the $a = (110), b = (1, \bar{1}, 0), c = (\frac{1}{2}, \frac{1}{2}, 1)$ setting viewed close to the (110) direction. Colouring shows the patterns of the various sublattice spin ordering corresponding to the $L1_0$, $L1_1$ and $I4_1/amd$ structures.



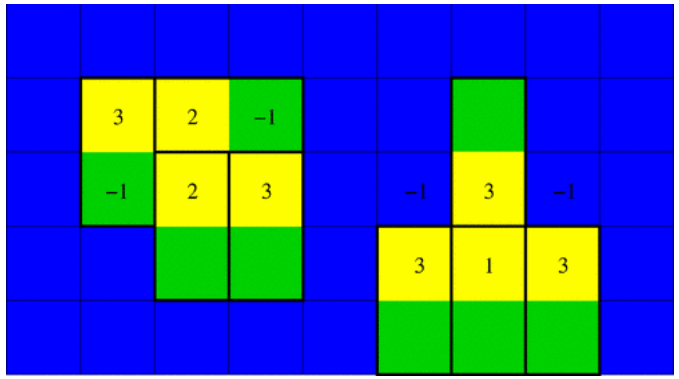
* Is the structure of metallic hydrogen

Water-methanol: when is a bond not a bond?

The bonding energy of water methanol is the number of hydrogen bond.

Hydrogen bonds occur when a polar OH group is near another polar OH

On a lattice model each site can be either OH or Me (CH3)



H2O is blue
CH3OH is green-yellow on adjacent sites

Energy = number of hydrogen bonds
= no of blue/green neighbours

OR number of Me-Me (yellow) neighbours

$$U = \sum_{i=1,N} \sum_{k=1,4} -\sigma_i \sigma_k$$

$$U = -4N + 4N_M - \sum_{i=1,N} \sum_{k=1,4} S_i S_k$$

Because every Me-Me contact enables a, OH-OH elsewhere. (S=1 for Me S=0 for water,OH)

So now its just the Ising model, with a twist!

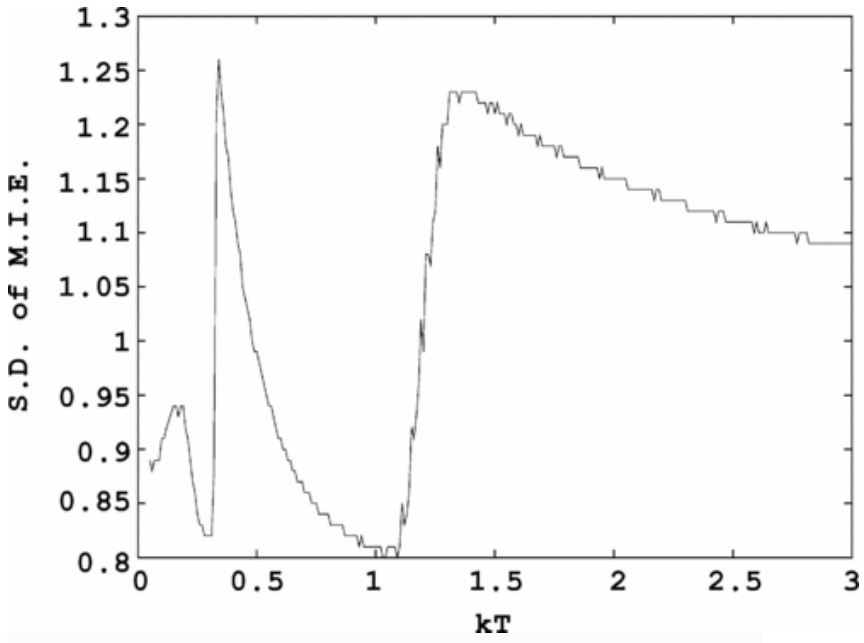
- Hamilitonian – Count the Me-Me neighbours
- Water becomes a neutral background.

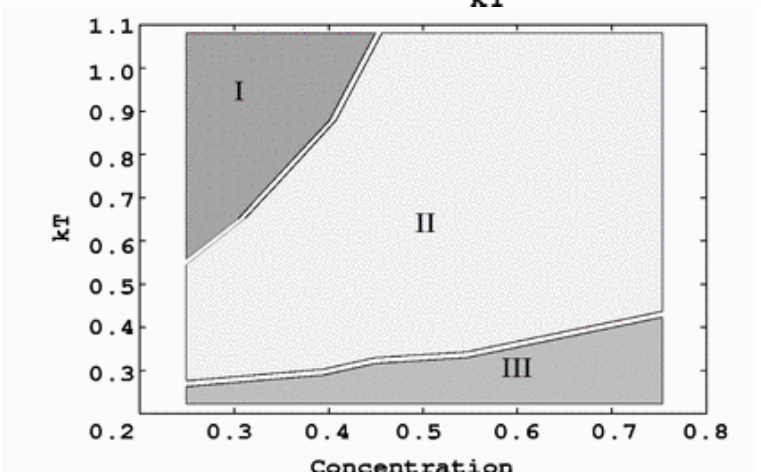
- Dont break the methanol. (must keep track of molecule pairs)

- Move the MeOH pairs to a WW site
- Rotate the MeOH into an adjacent site.

Monitor RMS energy fluctuations (specific heat)

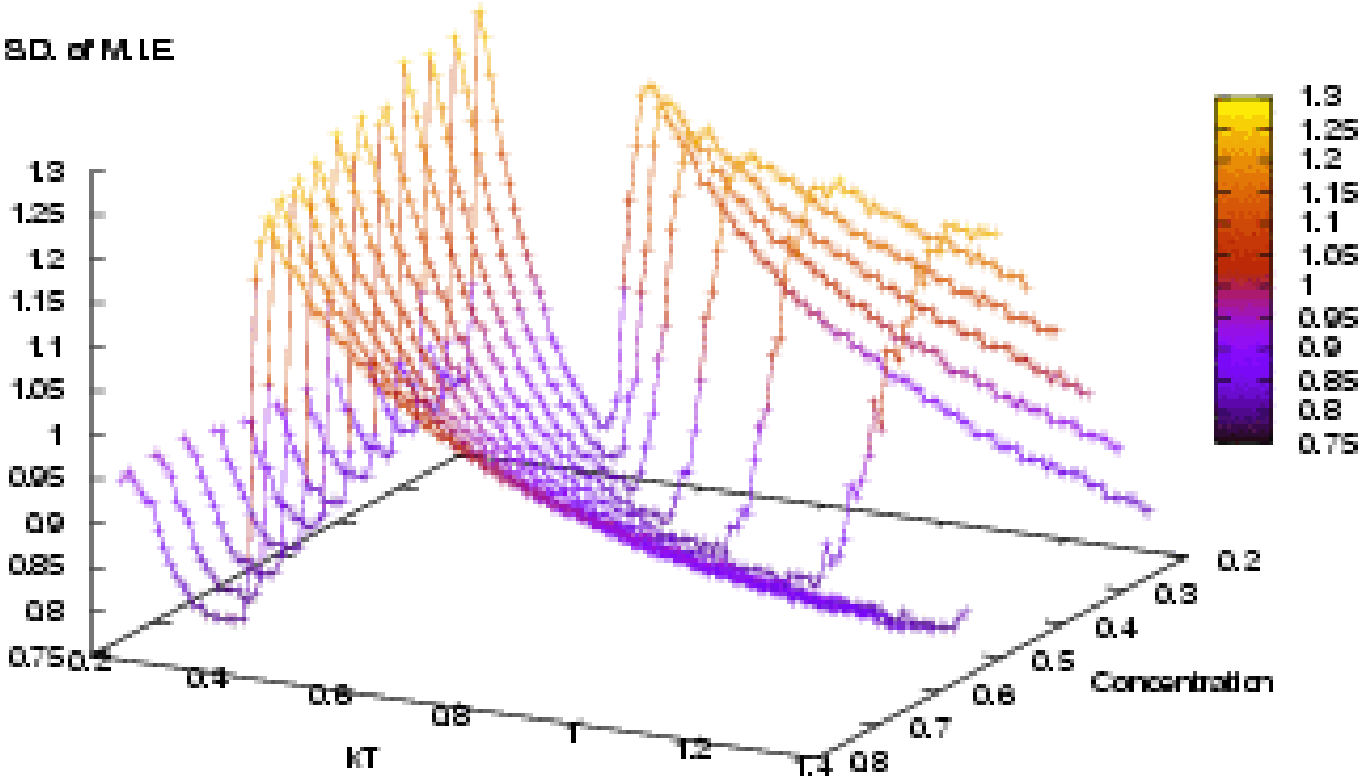
At fixed concentration: Three peaks



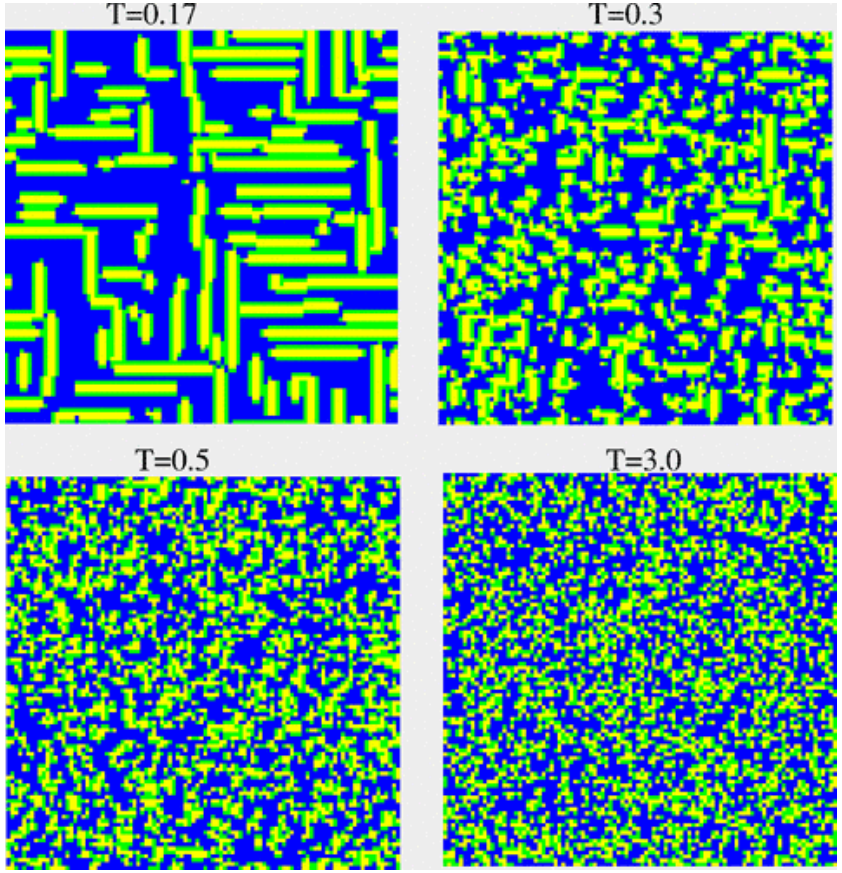


How to find phase boundaries?
Divergent heat capacity … peak in the energy fluctuations.

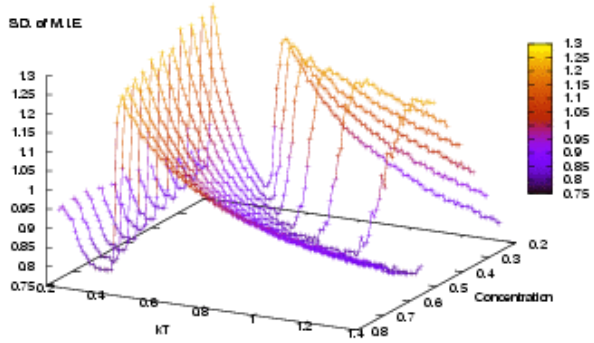
Scan of temperature vs concentration



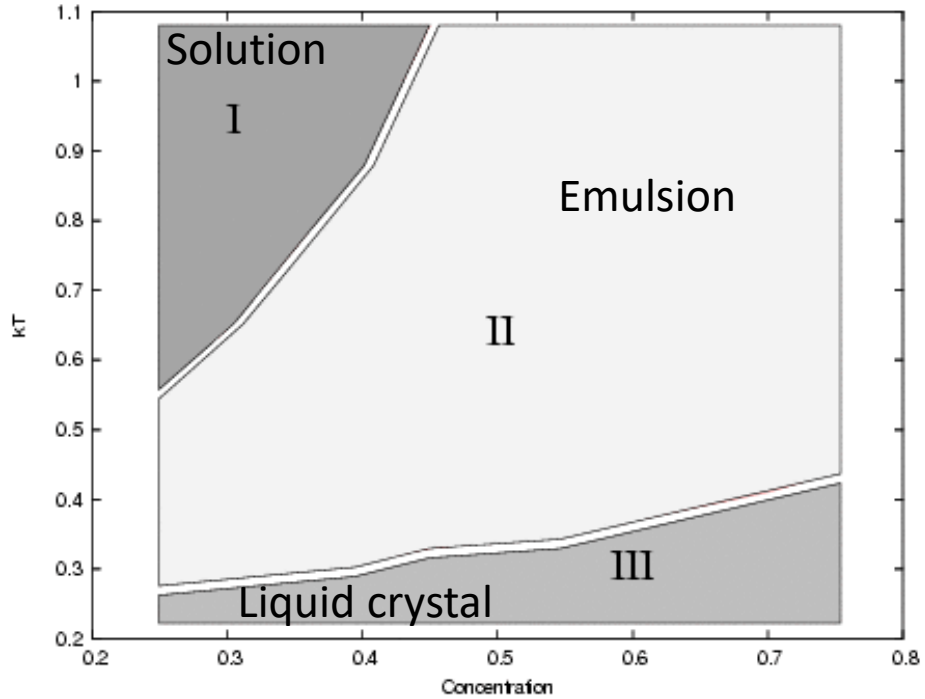
What is going on?



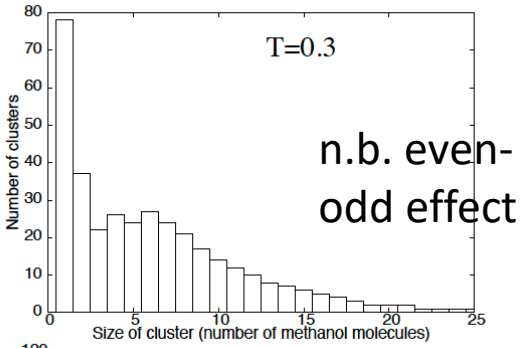
The four phases can be categorized as dis-ordered (I, T=3.0), clustering (II, T=0.5), bilayers (III, T=0.3), bilayer liquid crystal (IV, T=0.17).



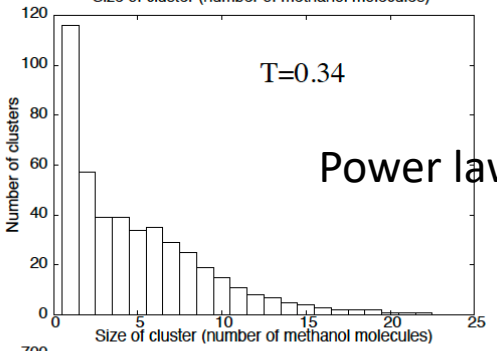
all the phases exist at an appropriate temperature for any concentration (0.5 shown).



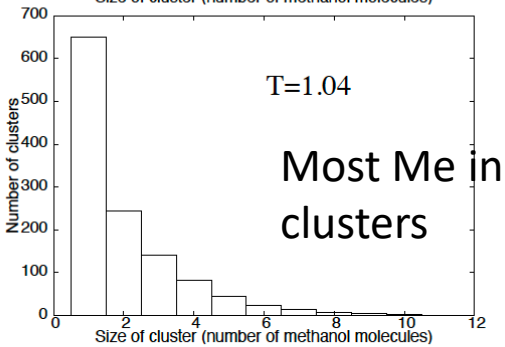
Me Cluster Size Distributions



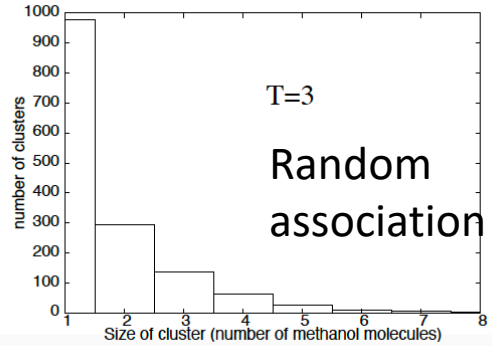
n.b. even-odd effect



Power law tail

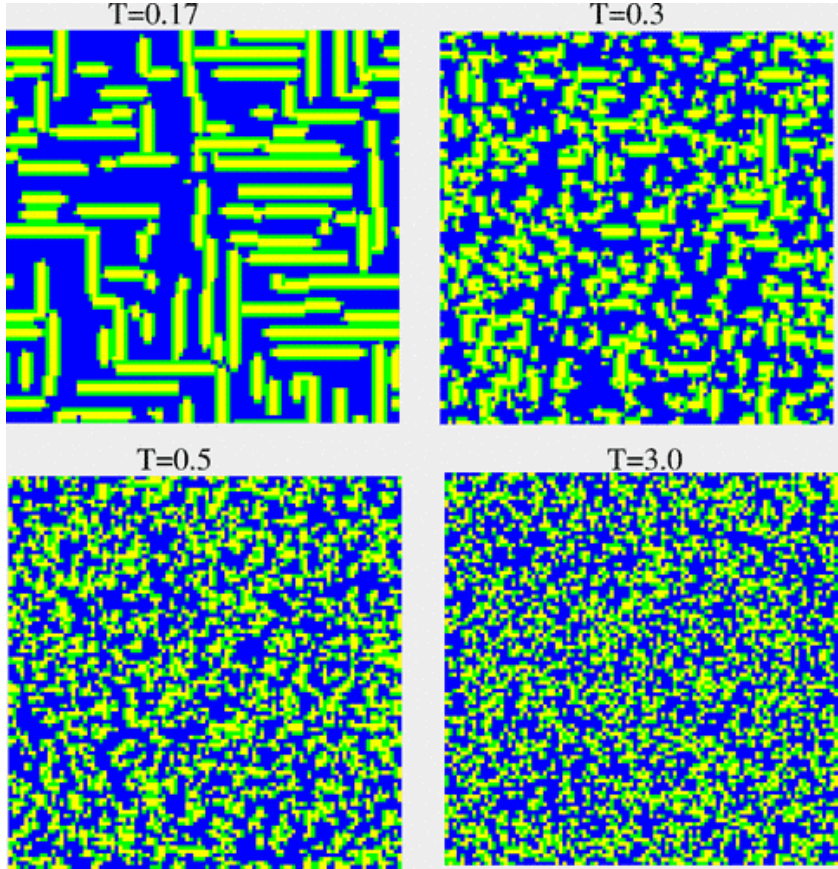


Most Me in clusters



Random association

Phase IV Rods forming
Phase III Water percolating
Phase II clustering
Phase I disordered



Experimental data: Kinks in the Raman

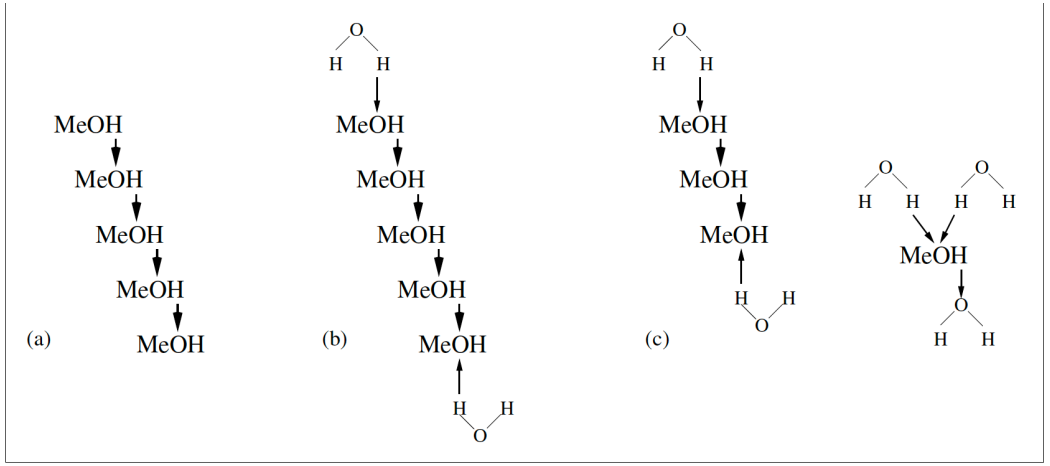


Figure 3. A schematic picture of progressive methanol hydration. (a) An average chain in pure methanol. (b) Water molecules donating hydrogen bonds to chain ends. The proposed mode of hydration in the regime $1 \gtrsim x \gtrsim 0.7$. (c) Water molecules breaking chains; on the right is a single MeOH molecule with 'AAD' hydrogen bonds round its hydroxyl group. The proposed hydration mechanism for $0.7 \gtrsim x \gtrsim 0.25$.

Dixit, Poon et al

Raman: J. Phys. Condens. Matter **12**, 323 (1999)

Neutron *Nature* **416**, 829–832 (2002)

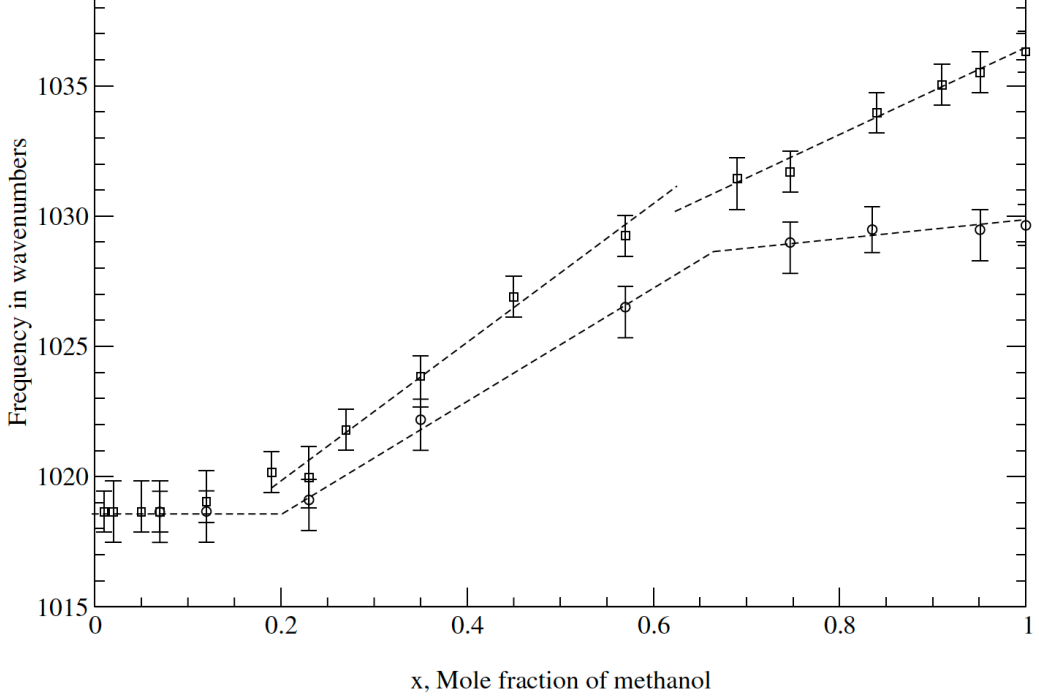


Figure 1. Variation of the C–O symmetric stretch frequencies (□: VV; ○: VH) of methanol as a function of concentration in water. Lines are guides to the eye.

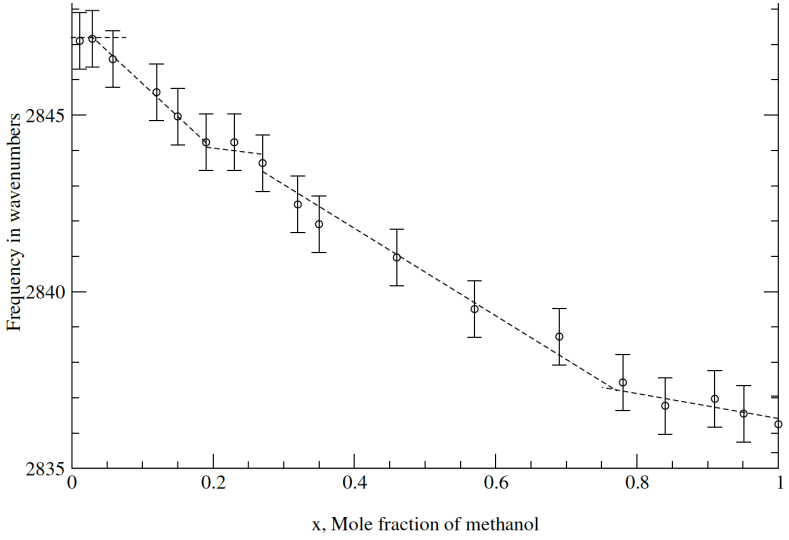


Figure 2. Variation of the C–H stretch frequency (VV) as a function of methanol concentration in water. Lines are guides to the eye

How many, and which type of hydrogen bonds are seen

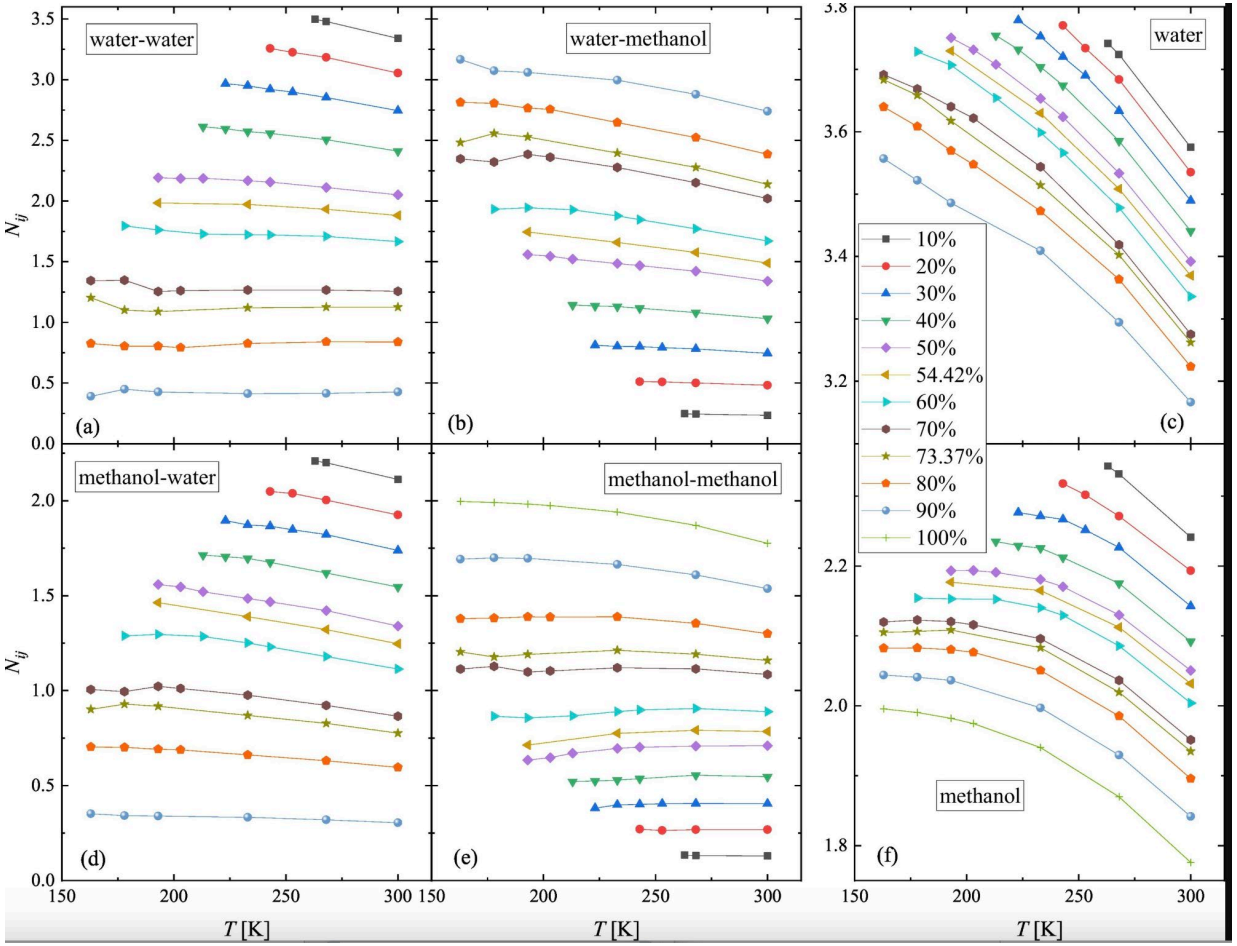


Fig. 8. Temperature dependence of the number of hydrogen bonds at different concentrations, as obtained from MD simulations using the TIP4P/2005 water model: (a) average number of H-bonded water molecules around water, (b) average number of H-bonded methanol molecules around water, (c) average number of H-bonded (water and methanol) molecules around water, (d) average number of H-bonded water molecules around methanol, (e) average number of H-bonded methanol molecules around methanol, (f) average number of H-bonded (water and methanol) molecules around methanol.

Neutron diffraction can give representative molecular structure

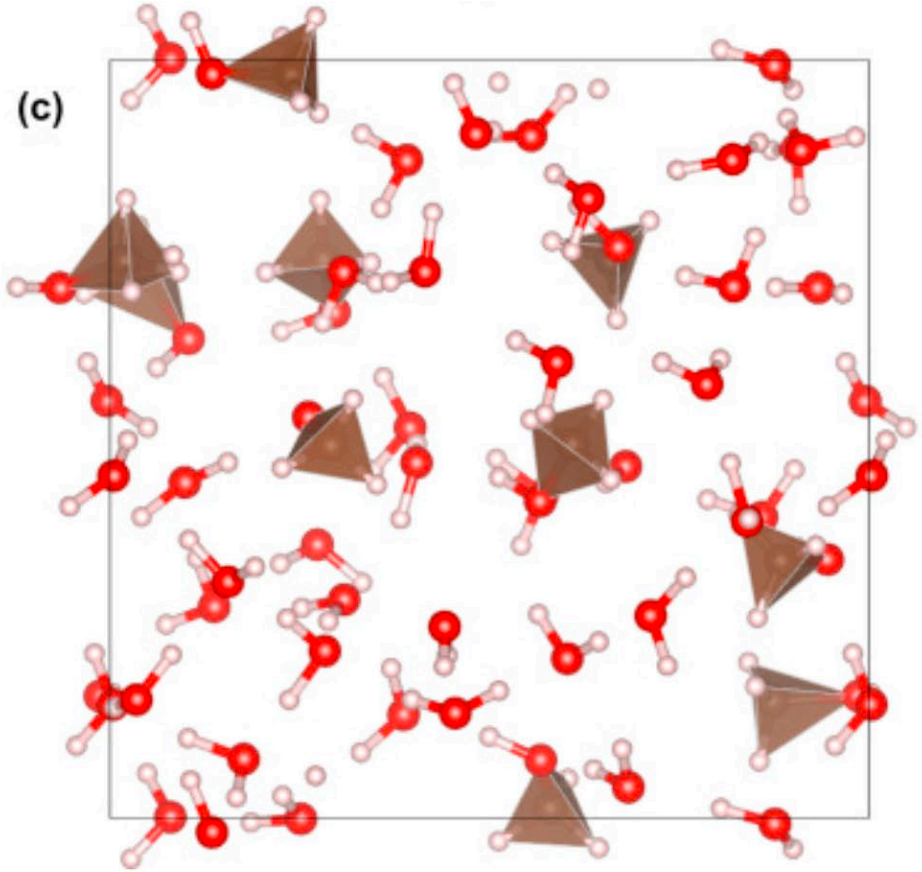
So can DFT molecular dynamics

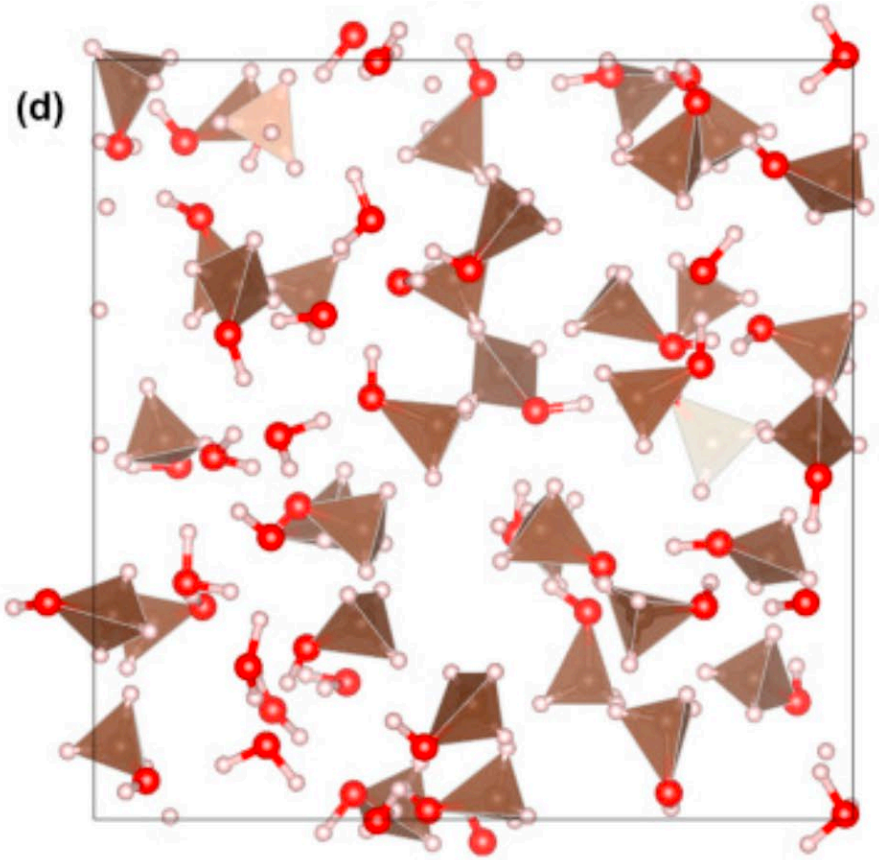
Scanning concentration/temperature space would be heroic work

What are we looking for ?
Focus on H-bond network.

Count number of bonds.
Look for percolation
(0.43 on diamond lattice, so essentially always find it)

Ab initio simulation, low/high concentration 300K





Phase I like random mixing

He et al. Chemical Physics Letters, 635, 2015,

Trabelsi et al Journal of Molecular Liquids 349, 2022, 118131

Identified as “interpenetration of hydrogen bond networks”

So What?

- Concept of “soluble” vs “insoluble” is moot
- Methanol-Water Ising model with one parameter has four phases
- None of these are “insoluble” separation of molecules
- Identify Me-Me contact as a proxy for H-bonding

Now What?

- Need to go to 3D lattice
- Include hydrocarbons to tackle the “ouzo” effect: “spontaneous emulsification”