Understanding correlations in many body systems by computer simulation

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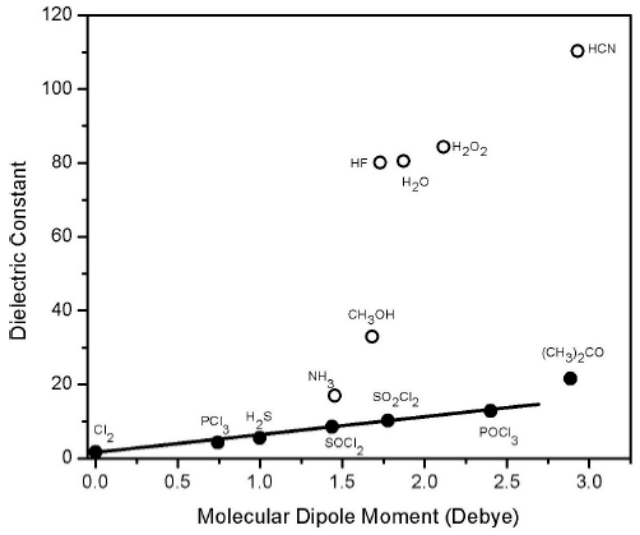
The challenge of correlations

- **Correlated dynamics is crucial in many phenomena in condensed matter physics**
- **A common approximation, the mean field approximation (a particle in the average field of the other particles), is often insufficient**
- **Computer simulation allows us to model many-particle systems “almost” exactly**
- **Here I will focus on two examples: (a) the dielectric constant of water from first principles, (b) the critical coupling in the 2d Ising model**

The RT static dielectric constant of water is ~80: why?



Reproduced from L. Pauling, *General Chemistry* (1970)

Table 14.8 Some physical properties of H_2O, D_2O and T_2O (at 25°C unless otherwise stated)[a]

Property	H_2O	D_2O	T_2O
Molecular weight	18.0151	20.0276	22.0315
MP/°C	0.00	3.81	4.48
BP/°C	100.00	101.42	101.51
Temperature of maximum density/°C	3.98	11.23	13.4
Maximum density/g cm^{-3}	1.0000	1.1059	1.2150
Density(25°)/g cm^{-3}	0.997 01	1.1044	1.2138
Vapour pressure/mmHg	23.75	20.51	~19.8
Viscosity/centipoise	0.8903	1.107	—
Dielectric constant ε	78.39	78.06	—
Electrical conductivity(20°C)/ohm^{-1} cm^{-1}	5.7×10^{-8}	—	—
Ionization constant [H$^+$][OH$^-$]/mol^2 l^{-2}	1.008×10^{-14}	1.95×10^{-15}	$\sim 6 \times 10^{-16}$
Ionic dissociation constant K = [H$^+$][OH$^-$]/[H_2O]/mol l^{-1}	1.821×10^{-16}	3.54×10^{-17}	$\sim 1.1 \times 10^{-17}$
Heat of ionization/kJ mol^{-1}	56.27	60.33	—
ΔH_i°/kJ mol^{-1}	−285.85	−294.6	—
ΔG_i° kJ mol^{-1}	−237.19	−243.5	—

[a] Heavy water (p. 39) is now manufactured on the multikilotonne scale for use both as a coolant and neutron-moderator in nuclear reactors: its absorption cross-section for neutrons is much less than for normal water: σ_H 332, σ_D 0.46 mb (1 millibarn = 10^{-21} cm^2)

Isotope effects on static equilibrium effects indicate that quantum fluctuations on the atomic motions cannot be entirely neglected

$$\varepsilon_0 = 1 + \frac{4\pi}{3}\frac{\langle M^2 \rangle}{V k_B T}$$

M is the electric dipole moment per (super)cell, periodic boundary conditions are assumed. This formula neglects the pure electronic contribution (ε_∞) but the error is very small ($\varepsilon_\infty - 1 = 0.8$).

Phenomenological theory (Onsager, Kirkwood, etc.)

$$\varepsilon_0 = 1 + \frac{4\pi}{3}\frac{\langle M^2 \rangle}{V k_B T}$$

$$\vec{M} = \sum \vec{\mu}$$

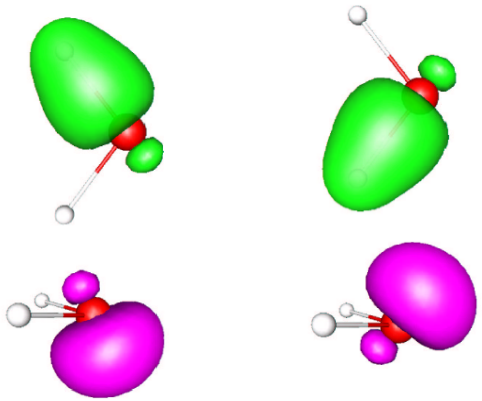
$$\langle M^2 \rangle = N\mu^2(1 + \sum_i N_i \langle \cos\theta_i \rangle) = N\mu^2 G_K$$

μ is the average molecular dipole

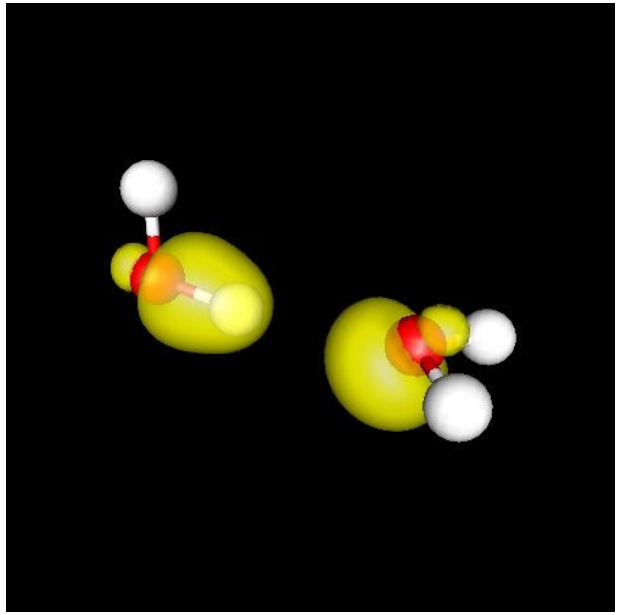
G_K is the correlation factor

In the phenomenological theory μ and G_K are independent parameters. They are not directly accessible from experiment. Can they be derived from first-principles electronic structure theory?

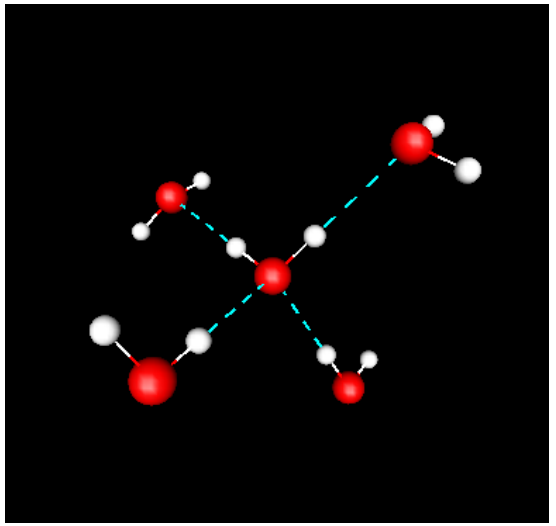
Water molecules: bond and lone pairs



Maximally Localized Wannier Functions (Boys Orbitals) in H_2O: a polar molecule



Hydrogen bond between two molecules in the water dimer



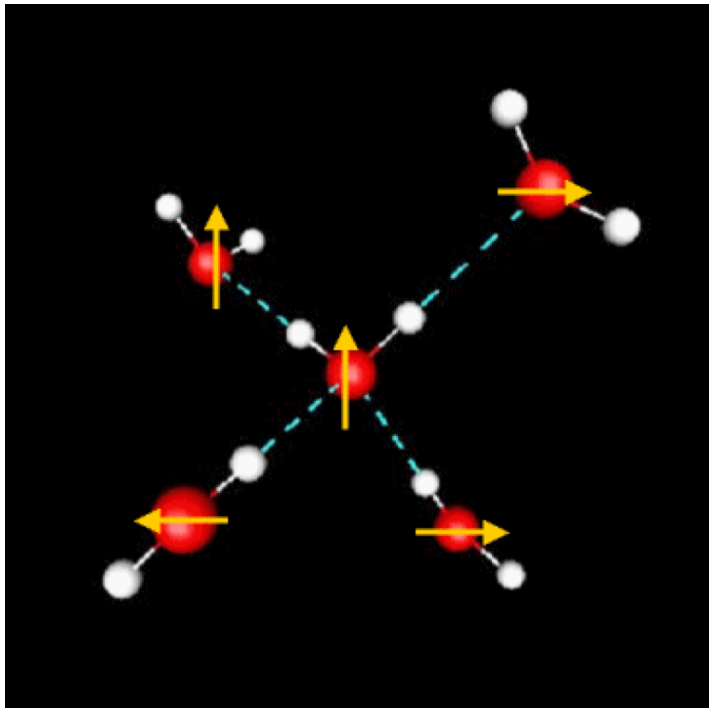
Local tetrahedral order in condensed phase.

Donors (D) and Acceptors (A)

Bernal-Fowler ice rule: 2D + 2A

Proton disorder

Effects of the hydrogen bonds: alignment and polarization

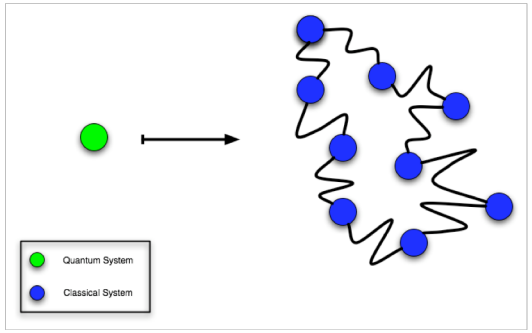


Alignment is consequence of the ice rules

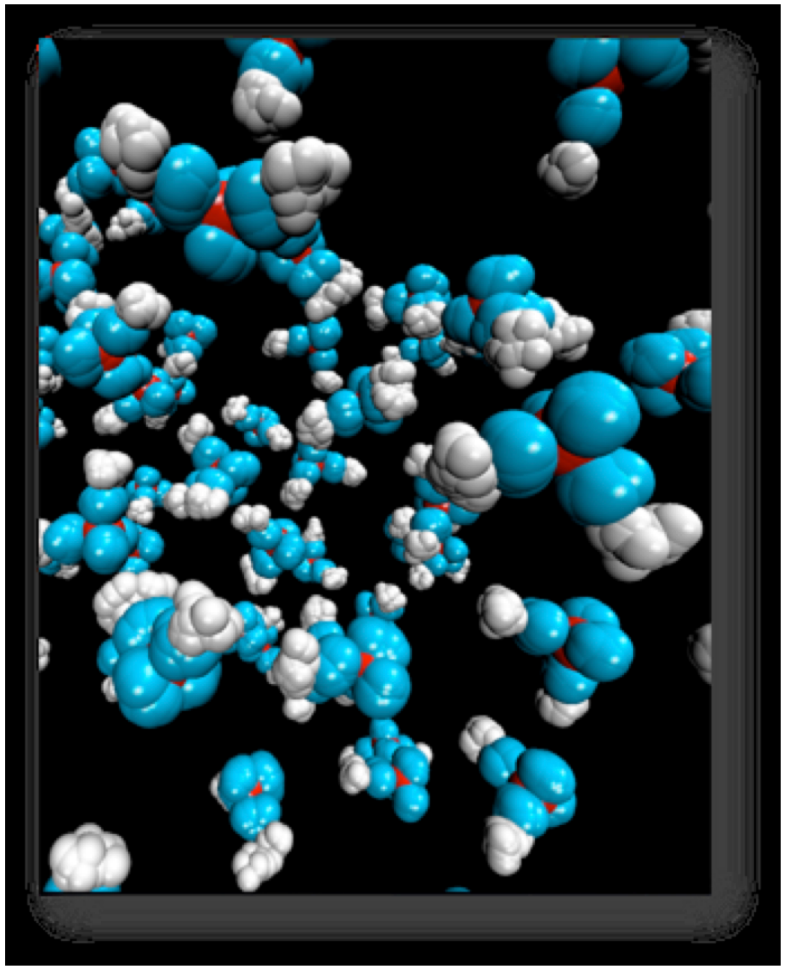
These effects are usually referred to as cooperative effects of the H bonds

Can we predict quantitatively the dielectric constant by molecular dynamics simulations that include nuclear quantum fluctuations ?

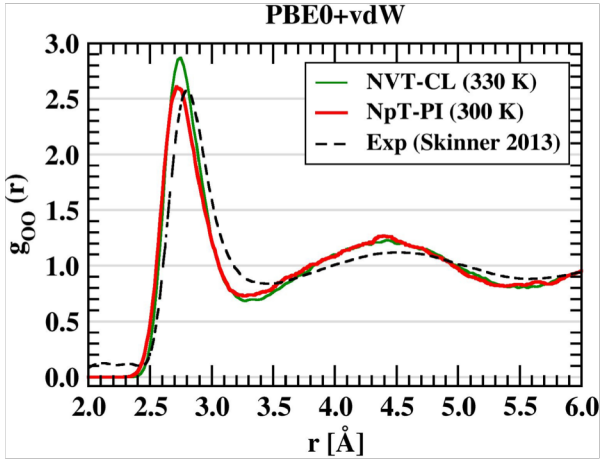
Quantum Statistical Mechanics can be mapped onto Classical Mechanics via discretized Feynman paths

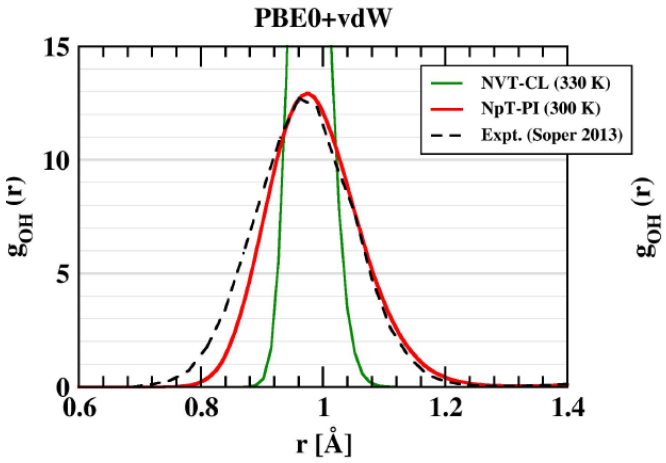


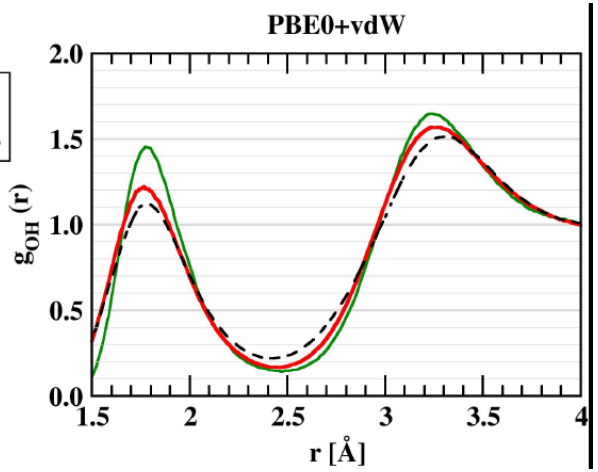
Left: a snapshot of a Path Integral ab-initio MD simulation of liquid water at RT showing oxygens (red), hydrogens (white) and electron MLW centers (blue)

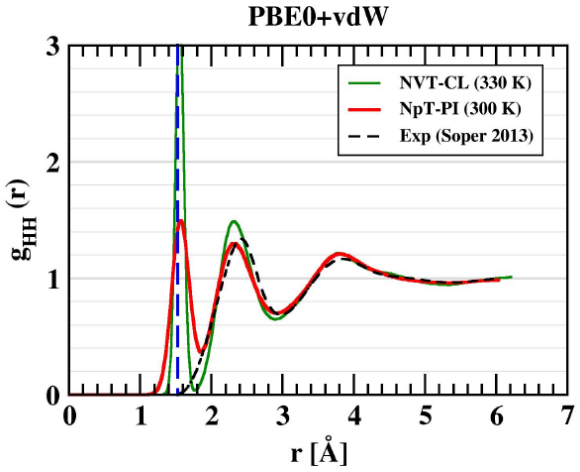


Structural predictions from PI-AIMD (NpT) simulations







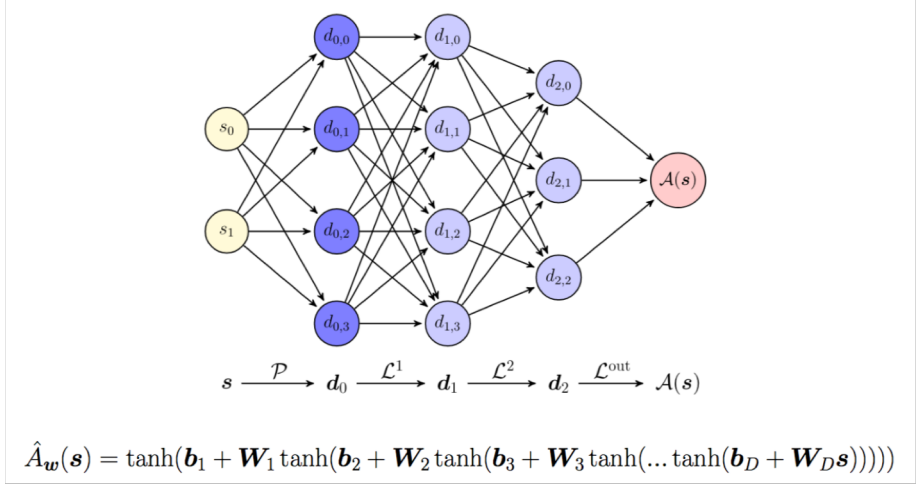


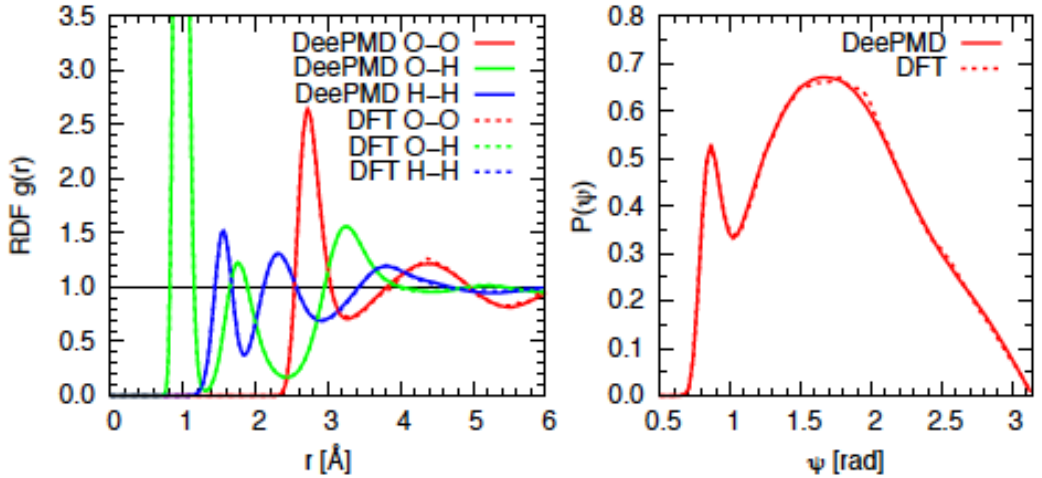
Equilibrium density (g/cm3):

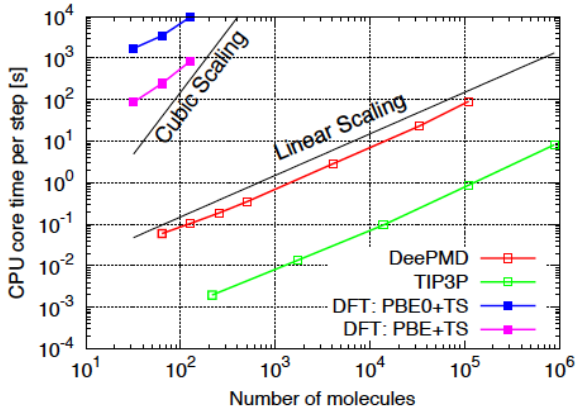
Liquid water (300K): ~1.01 (expt: 1.00)

These are computationally very expensive calculations: they required months on a supercomputer. Yet they are too short to converge the calculation of the dielectric constant. This difficulty can be surmounted with modern machine learning techniques

Deep (Neural Network) Potentials





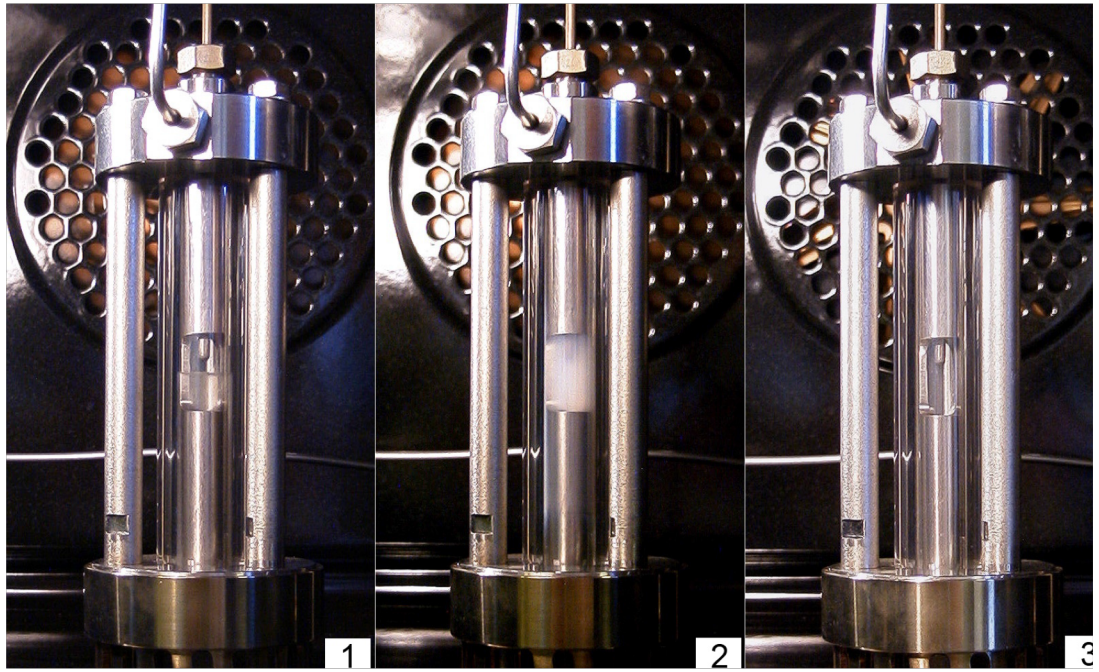


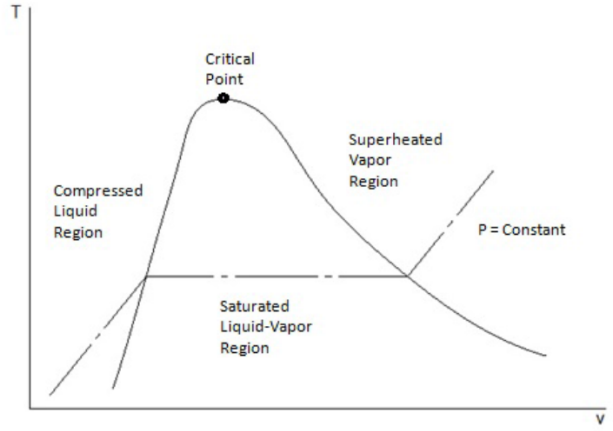
DPMD PI calculations give a dielectric constant of ~82 for liquid water at STP

A Feynman quote (predating the modern era of computer simulations):

*"*Don't forget that the reason a physicist can really calculate from first principles is that he chooses only simple problems. He never solves a problem with 42 or even 6 electrons in it. So far, he has been able to calculate reasonably accurately only the hydrogen atom and the helium atom"
R.P. Feynman, *The Feynman lectures on physics, 3rd printing (1969)*

Diverging correlation length at the critical point

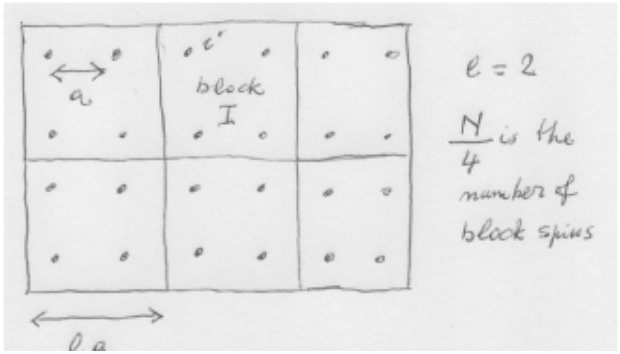




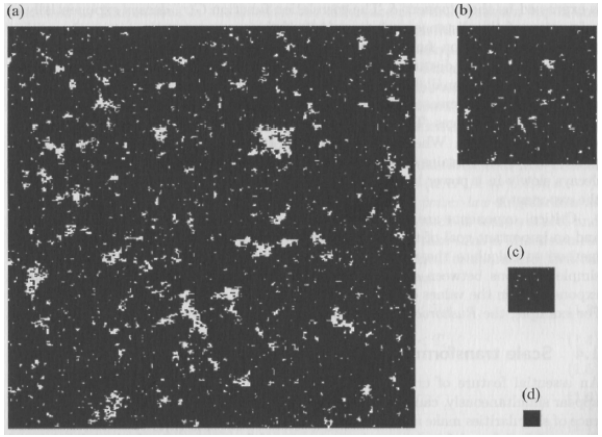
The liquid-vapor transition in a fluid

Scale transformations and coarse graining

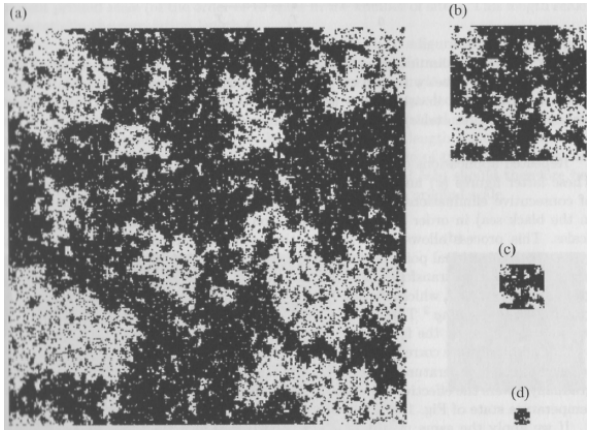
Ising model: $H(\sigma) = -K \sum_{\langle ij \rangle} \sigma_i \sigma_j \qquad (K = J/k_B T > 0)$



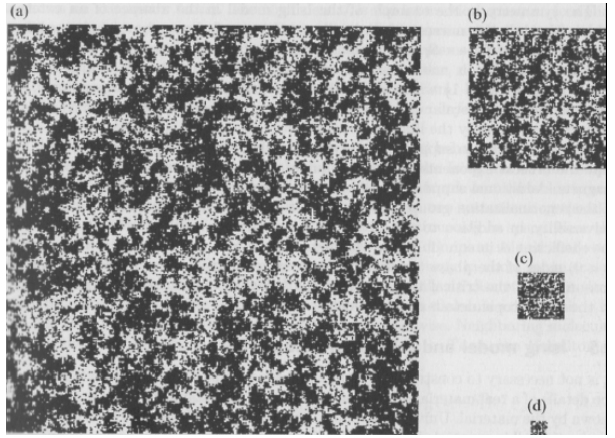
Block spins $\sigma' = \tau(\sigma) \quad N' = \frac{N}{b^d} \quad \xi' = \frac{\xi}{b}$



$K > K_c \ \left(T < T_c\right)$



$K = K_c \ \left(T = T_c\right)$



$K < K_c \ \left(T > T_c\right)$

Scale invariance at the critical point

by Douglas Ashton

www.kineticallyconstrained.com

Onsager (exact) result: $K_c = 0.44069$

Yantao (numerical) result: $K_c = 0.4407 +/- 0.00001$

Why shall we bother to do the simulation if we already know the exact solution?

Well, the 2d Ising model in absence of external field is one of the very few interacting models of which we know the analytical solution. For example, already in 3d we have to resort to numerical solution for a model as simple as Ising. Numerical solutions are very useful in the context of many different models

Some final comments

- 2 examples of numerical simulation: (a) a very realistic model; (b) a very simple model

- Often brute force simulations made possible by the sheer power of modern computers are often not enough

- Physical intuition and theory are necessary to make simulations possible and to gain new insight from them