# Quantum Nuclei

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# Static and dynamic properties

Physical observables are associated to static and dynamic correlation functions, such as:

$$\langle n(\mathbf{r})n(\mathbf{r}')\rangle \qquad\qquad \langle n(\mathbf{r},t)n(\mathbf{r}',t')\rangle$$

Here I will focus mostly on static properties

Computer simulations such as MD (MC) allow us to compute correlation functions. In these simulations the nuclei are treated as classical particles: is this adequate?

In presence of light atoms (such as H) quantum effects are not negligible even at room temperature and above

# Do nuclei really behave classically?

**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 $\varepsilon$ | 78.39 | 78.06 | — |
| Electrical conductivity(20°C)/ohm$^{-1}$ cm$^{-1}$ | $5.7 \times 10^{-8}$ | — | — |
| Ionization constant $[H^+][OH^{-1}]$/mol$^2$ l$^{-2}$ | $1.008 \times 10^{-14}$ | $1.95 \times 10^{-15}$ | $\sim 6 \times 10^{-16}$ |
| Ionic dissociation constant $K = [H^+][OH^-]/[H_2O]$/mol l$^{-1}$ | $1.821 \times 10^{-16}$ | $3.54 \times 10^{-17}$ | $\sim 1.1 \times 10^{-17}$ |
| Heat of ionization/kJ mol$^{-1}$ | 56.27 | 60.33 | — |
| $\Delta H_f^\circ$/kJ mol$^{-1}$ | −285.85 | −294.6 | — |
| $\Delta G_f^\circ$ 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: $\sigma_H$ 332, $\sigma_D$ 0.46 mb (1 millibarn = $10^{-21}$ cm$^2$)

Isotopic effects on thermodynamic equilibrium properties would not occur in classical water

# Why does QM lead to mass dependence

Configurations are weighted by a Boltzmann factor

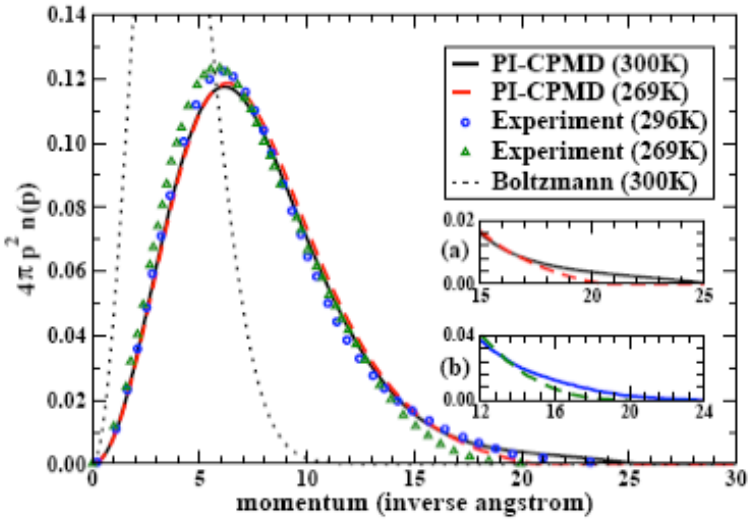
$$\exp\left(-E / k_B T\right)$$

*E* include kinetic (depending on mass and momentum) and potential (depending on position) contributions.

In classical mechanics kinetic and potential contributions to the Boltzmann weight factorize, leading to a partition function that is the product of an *ideal* and an *excess (configurational)* part.

In quantum mechanics kinetic and potential contributions do **not** factorize (uncertainty principle).

# Protons in water and ice: their momentum distribution deviates substantially from the classical Maxwell-Boltzmann distribution




Classical Distribution: $n(p) \propto e^{-p^2/(2mk_BT)}$

Path integral simulations: J. Morrone, RC, *PRL* 2008

Experiment: deep inelastic neutron scattering (DINS), G. Reiter et al., *Braz. J. Phys* 2004

## Quantum statistical averages

$$Z = Tr\left[ e^{-\beta H} \right] \qquad \langle A \rangle = Z^{-1} Tr\left[ A e^{-\beta H} \right]$$

$A$ and $H$ are quantum-mechanical *operators*

$$\langle A \rangle = \sum_n \frac{e^{-\beta E_n}}{Z} \langle \psi_n | A | \psi_n \rangle \qquad \langle A \rangle = Z^{-1} \int dx\, dx' \langle x | A | x' \rangle \rho(x', x)$$

$$\rho(x', x) = \langle x' | e^{-\beta H} | x \rangle \qquad \rho = e^{-\beta H}$$ is the density operator

Can we compute the averages without dealing with *operators*?

# Feynman path integral formulation of quantum statistical mechanics

$$e^{-\beta H} \equiv \left( e^{-\frac{\beta}{P}H} \right)^P \equiv e^{-\frac{\beta}{P}H} e^{-\frac{\beta}{P}H} \ldots e^{-\frac{\beta}{P}H}$$

$$\rho(x',x) = \lim_{P\to\infty} \int dx_1 \ldots dx_{P-1} \left\langle x' \middle| e^{-\frac{\beta}{P}H} \middle| x_{P-1} \right\rangle \left\langle x_{P-1} \middle| e^{-\frac{\beta}{P}H} \middle| x_{P-2} \right\rangle \ldots \left\langle x_1 \middle| e^{-\frac{\beta}{P}H} \middle| x \right\rangle$$

$x, x_1, x_2, \ldots, x_{P-1}, x'$ constitutes a *path* $x(\tau)$ where the *label* $\tau \in (0,\beta)$

The product $\left\langle x' \middle| e^{-\frac{\beta}{P}H} \middle| x_{P-1} \right\rangle \ldots \left\langle x_1 \middle| e^{-\frac{\beta}{P}H} \middle| x \right\rangle$ takes a *value* $W\left[x(\tau)\right]$

$W\left[x(\tau)\right]$ is a *functional* of the *path* $x(\tau)$

$$\rho(x',x) = \int_{x(0)=x;x(\beta)=x'} \mathcal{D}\left[x(\tau)\right] W\left[x(\tau)\right]$$ a sum (integral) over open paths

$$\rho(x,x) = \int_{x(0)=x(\beta)=x} \mathcal{D}\left[x(\tau)\right] W\left[x(\tau)\right]$$ a sum (integral) over close paths

# Computing statistical averages

Let's consider an observable $A$ diagonal in the coordinate representation

and consider *discretized* paths $(x, x_1, ..., x)$. Then:

$$\langle A \rangle = Z^{-1} \int dx_1 \, dx_2 ... dx_{P-1} \, dx_P A(x_P) W(x_1, x_2, ..., x_P) \quad (x_P = x)$$

If $W$ is positive definite: $W(x_1, ..., x_P) = e^{-\Phi(x_1, ..., x_P)}$ where $\Phi$ plays the role of potential energy

Then $\langle A \rangle$ is like a *classical* configuration average

Since all points in a close path are topologically equivalent we can write:

$$\langle A \rangle = Z^{-1} \int dx_1 ... dx_P \left( \frac{1}{P} \sum_{i=1,P} A(x_i) \right) W(x_1, ..., x_P)$$

$\mathcal{E}_A \equiv \frac{1}{P} \sum_{i=1,P} A(x_i)$ is the *estimator* of $A$ $\quad$ $Z^{-1}W$ is the weight of the configuration

All this is correct provided *W* can be assimilated to a classical Boltzmann weight

# Evaluating *W*

$$\Delta \equiv \frac{\beta}{P} \qquad H = T + V \qquad e^{-\Delta H} = e^{-\Delta T} e^{-\Delta V} + O(\Delta^2)$$

$$\left\langle x_i \middle| e^{-\Delta H} \middle| x_{i-1} \right\rangle = \left\langle x_i \middle| e^{-\Delta T} \middle| x_{i-1} \right\rangle e^{-\Delta V(x_{i-1})} + O(\Delta^2)$$

$$\left\langle x_i \middle| e^{-\Delta T} \middle| x_{i-1} \right\rangle = \int dp \left\langle x_i \middle| e^{-\frac{p^2}{2M}\Delta} \middle| p \right\rangle \left\langle p \middle| x_{i-1} \right\rangle = \int dp \left\langle x_i \middle| p \right\rangle \left\langle p \middle| x_{i-1} \right\rangle e^{-\frac{p^2}{2M}\Delta}$$

$$= \frac{1}{2\pi\hbar} \int dp e^{ip(x_i - x_{i-1})/\hbar} e^{-\frac{p^2}{2M}\Delta} = \sqrt{\frac{M}{2\pi\Delta\hbar^2}} \exp\left[ -\frac{M(x_i - x_{i-1})^2}{2\Delta\hbar^2} \right]$$

$$W = \left( \frac{M}{2\pi\Delta\hbar^2} \right)^{P/2} \exp\left[ -\sum_{i=1,P} \left( \frac{M}{\hbar^2} \frac{\left( x(\tau_i) - x(\tau_{i-1}) \right)^2}{2\Delta} + V\left( x(\tau_i) \right) \Delta \right) \right]$$

$$= \left( \frac{M}{2\pi\Delta\hbar^2} \right)^{P/2} \exp\left[ -\Phi(x_1, ..., x_P) \right]$$

Notice: $\frac{1}{2} \frac{M}{\hbar^2 \Delta} \left( x_i - x_{i-1} \right)^2$ is a harmonic interaction between neighboring points (beads) in a path

The spring constant is $k = \frac{M}{\hbar^2 \Delta}$

When $M \to \infty$ or $\beta \to 0$ or $\hbar \to 0$, $k \to \infty$ and one recovers the *classical* limit

# Sampling the paths

$$\langle A\rangle = Z^{-1}\int dx A(x)\langle x|e^{-\beta H}|x\rangle = \frac{\int dx_1 ... dx_p \mathcal{E}_A(x_1,...,x_P)e^{-\Phi(x_1,...,x_P)}}{\int dx_1 ... dx_p e^{-\Phi(x_1,...,x_P)}}$$

Importance sampling can be achieved either by MC or by MD

In the MD case, one introduces (fictitious) sampling masses $\mathcal{M}_i$ :

$$\mathcal{M}_i\ddot{x}_i = -\frac{\partial\Phi}{\partial x_i} \qquad \text{with } \overline{\sum_i \frac{1}{2}\mathcal{M}_i\dot{x}_i^2} = \frac{1}{2} \text{ exploiting ergodicity } (k_B T = 1)$$

Efficacious sampling is also achieved by Langevin dynamics (LD):

$$\dot{x}_i = -\frac{\partial\Phi}{\partial x_i} + \delta F \qquad \langle \delta F(t)\delta F(t')\rangle = 2\delta(t-t')$$

Here $t$ is the sampling time

# Many distinguishable particles (Boltzmannions)

Consider 2 particle for example

$$H = \sum_{I=1,2} \frac{p_I^2}{2M} + V(x_1, x_2)$$

$$\left\langle x_n^1 x_n^2 \right| e^{-\left(\frac{p_1^2}{2M}+\frac{p_2^2}{2M}\right)\Delta} e^{-V(x_1,x_2)\Delta} \left| x_{n-1}^1 x_{n-1}^2 \right\rangle = \left\langle x_n^1 x_n^2 \right| e^{-\left(\frac{p_1^2}{2M}+\frac{p_2^2}{2M}\right)\Delta} \left| x_{n-1}^1 x_{n-1}^2 \right\rangle e^{-V(x_1,x_2)\Delta}$$

$$= \left\langle x_n^1 \right| e^{-\left(\frac{p_1^2}{2M}\right)\Delta} \left| x_{n-1}^1 \right\rangle \left\langle x_n^2 \right| e^{-\left(\frac{p_2^2}{2M}\right)\Delta} \left| x_{n-1}^2 \right\rangle e^{-V(x_1,x_2)\Delta}$$

$$= \left( \frac{M}{2\pi\Delta\hbar^2} \right) \exp\left[ - \sum_{I=1,2;n=1,P} \frac{M}{2\hbar^2\Delta} \left( x_n^I - x_{n-1}^I \right)^2 - \Delta \sum_{n=1,P} V(x_n^1, x_n^2) \right]$$

The required amount of information is linear in $N$ (no. of particles) and also linear in $P$: it is a *classical* simulation of $N$ ring polymers (with $P$ beads each)

# Some (important) formal matter

$$Z = Tr\left[e^{-\beta H}\right] = \int_{x(0)=x(\beta)} \mathcal{D}[x(\tau)] \exp\left\{-\Phi[x(\tau)]\right\}$$

$$\Phi = \lim_{P\to\infty} \sum_{n=1}^{P} \left( \frac{M}{\hbar^2} \frac{\left(x(\tau_n) - x(\tau_{n-1})\right)^2}{2\Delta} + V\left(x(\tau_n)\right)\Delta \right)$$

One can associate a *time* to $\Delta$: $\delta\tau \equiv \hbar\Delta = \frac{\hbar\beta}{P}$ and convert $\tau$ to time units

$$\lim_{\delta\tau\to 0} \frac{x(\tau+\delta\tau) - x(\tau)}{\delta\tau} = \dot{x}(\tau)$$

$$\Phi = \frac{1}{\hbar} \int_0^{\beta\hbar} d\tau \left\{ \frac{1}{2} M\dot{x}(\tau)^2 + V(x(\tau)) \right\} = \frac{1}{\hbar} S_E\left[x(\tau)\right] \qquad S_E \text{ is the Euclidean action}$$

$$Z = \int_{x(0)=x(\beta\hbar)} \mathcal{D}[x(\tau)] \exp\left\{ -\frac{S_E\left[x(\tau)\right]}{\hbar} \right\} \qquad \hbar \text{ sets the scale for the action } S_E$$

Further reading: D.M. Ceperley, Rev Mod Phys **67**, 279 (1995);
D. Landau and K. Binder, A guide to MC methods in statistical physics

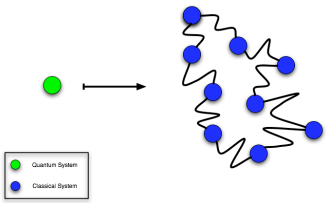
# Path integral simulations

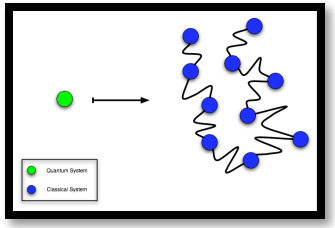
$$\rho_i(\mathbf{r},\mathbf{r}') = \frac{1}{Z}\int \mathrm{d}\mathbf{r}_1 \cdots \mathrm{d}\mathbf{r}_{i-1}\,\mathrm{d}\mathbf{r}_{i+1}\cdots \mathrm{d}\mathbf{r}_M \left\langle \mathbf{R}\left| e^{-\beta\hat{H}} \right| \mathbf{R}' \right\rangle$$

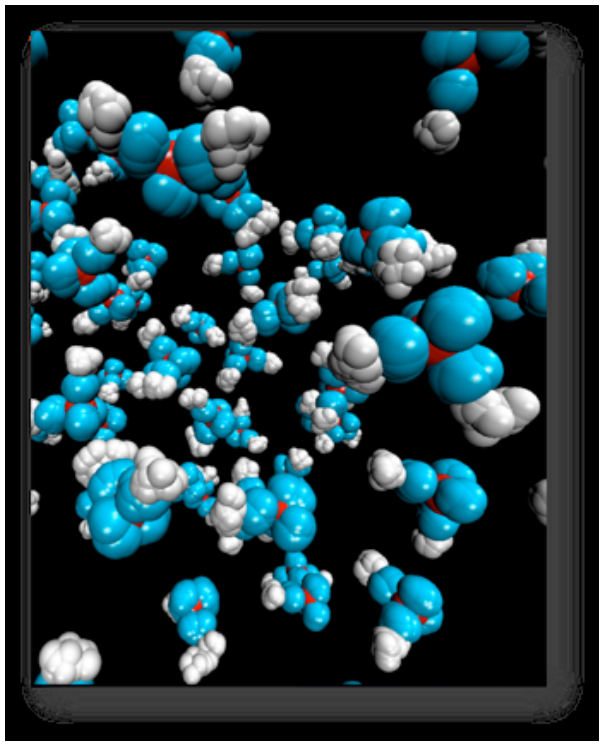
$$\rho_i(\mathbf{r},\mathbf{r}') = \frac{1}{Z}\int_{\mathbf{R}(0)=\mathbf{R},\mathbf{R}(\beta\hbar)=\mathbf{R}'} \mathfrak{D}\mathbf{R}(\tau) e^{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\, \frac{m\dot{\mathbf{R}}^2(\tau)}{2} + V(\mathbf{R}(\tau))}$$

$$Z = \int_{\mathbf{R}(0)=\mathbf{R},\mathbf{R}(\beta\hbar)=\mathbf{R}} \mathfrak{D}\mathbf{R}(\tau) e^{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\, \frac{m\dot{\mathbf{R}}^2(\tau)}{2} + V(\mathbf{R}(\tau))}$$

$$\mathbf{R} = (\mathbf{r}_1,\ldots,\mathbf{r}_{i-1},\mathbf{r},\mathbf{r}_{i+1},\ldots,\mathbf{r}_M),$$
$$\mathbf{R}' = (\mathbf{r}_1,\ldots,\mathbf{r}_{i-1},\mathbf{r}',\mathbf{r}_{i+1},\ldots,\mathbf{r}_M)$$

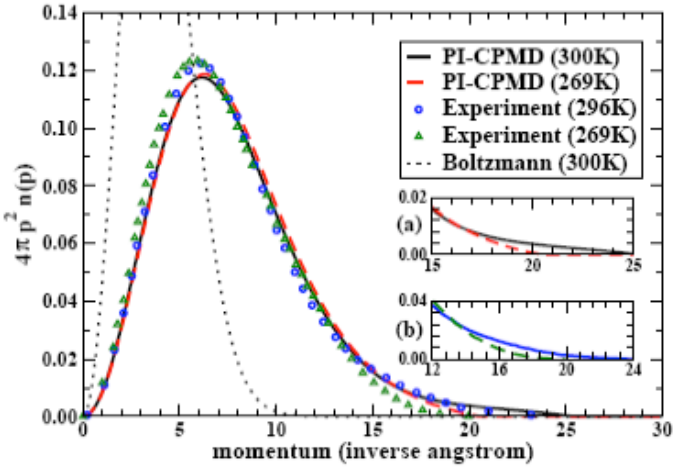


Feynman paths: *closed* and *open*

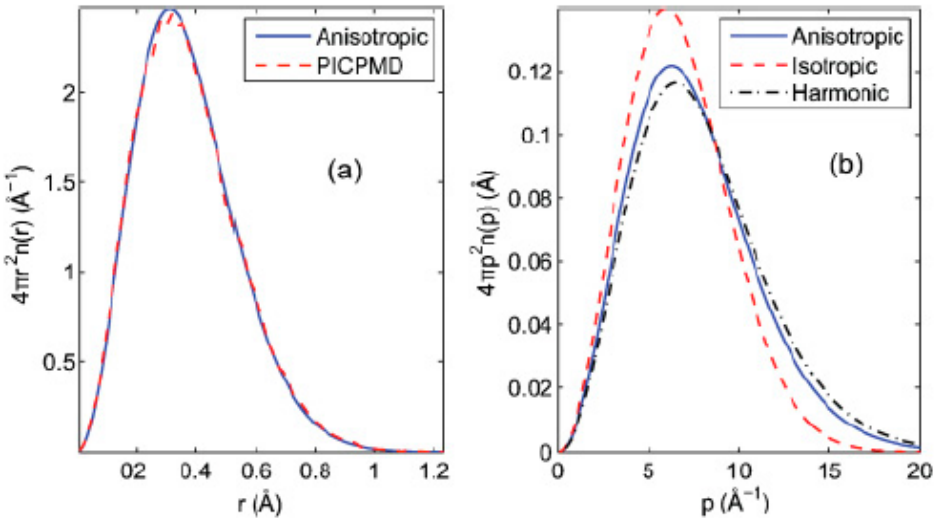
# Quantal protons in water and ice




The momentum distribution differs considerably from the classical equilibrium distribution

Path integral simulations: J. Morrone, RC, *PRL* 2008

Experiment: deep inelastic neutron scattering (DINS), G. Reiter et al., *Braz. J. Phys* 2004

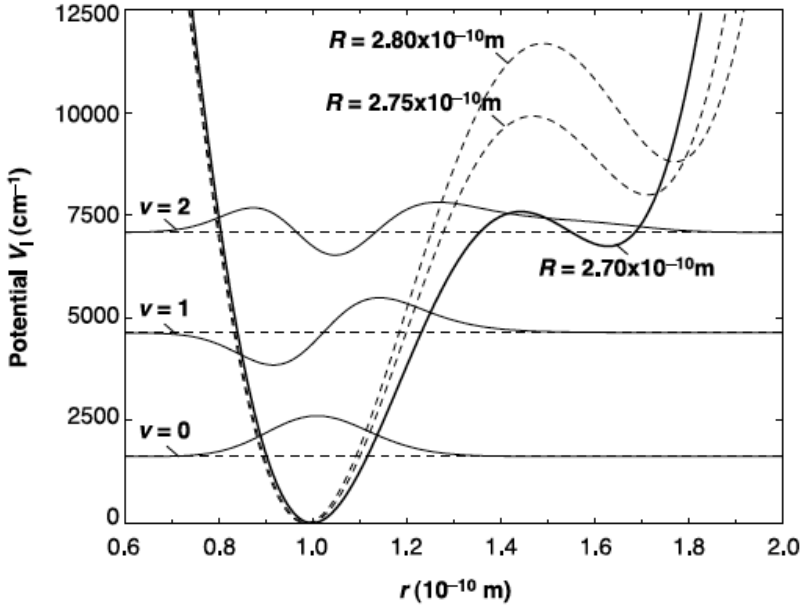


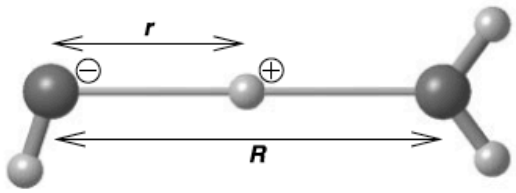

L. Lin, J. Morrone, RC, M. Parrinello, *PRB 2011*

Quasi-harmonic model fits the ice data well: zero-point motion is large but still semi-classical in nature

**How does the potential that the proton experiences look like?**

**Can the potential of mean force be reduced to a 1D potential?**



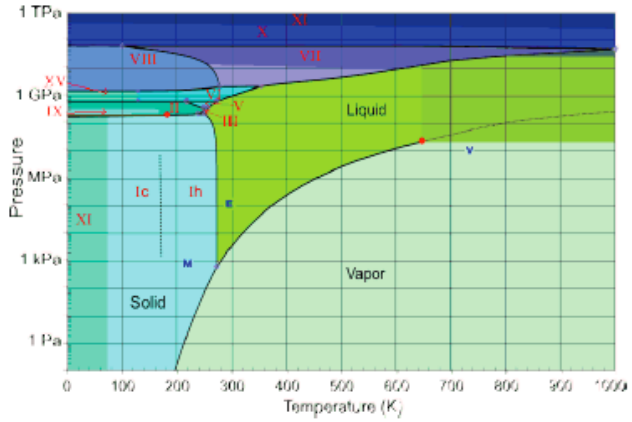




H.J. Bakker and H.K. Nienhuys, *Science* (2002)

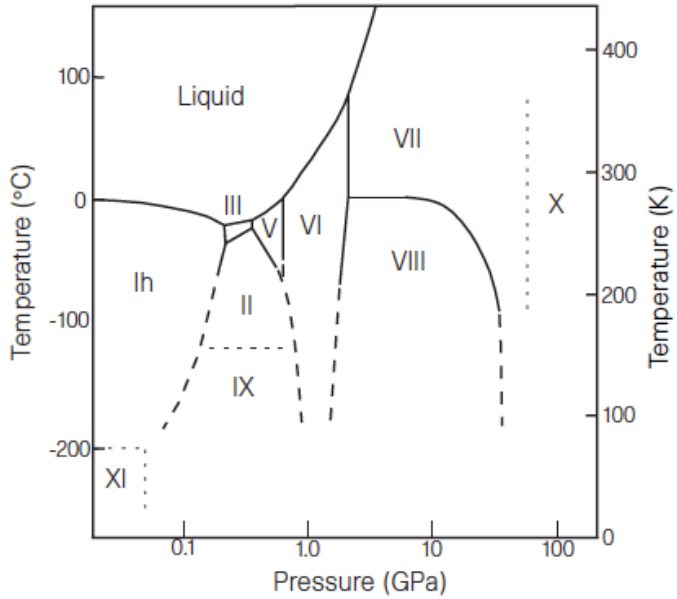
In the cases considered so far, proton motion along a bond (H stretching) reduces to an effective single particle quantum problem, in spite of the many-body nature of the problem.

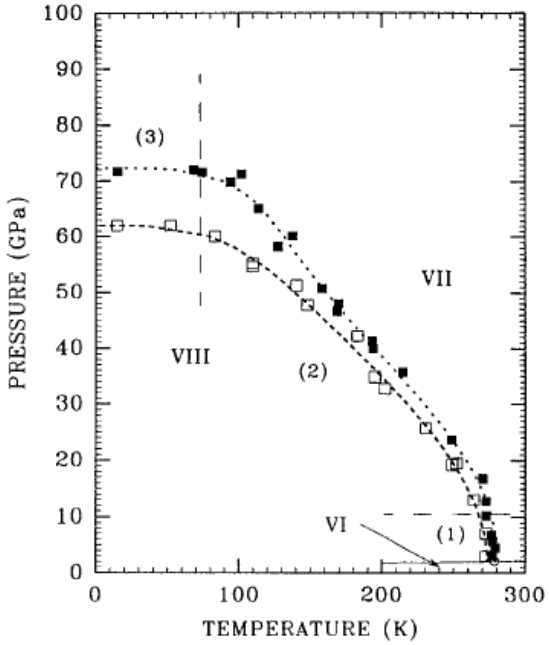
More interesting situations occur when the protons are allowed to tunnel

# Phase Diagram



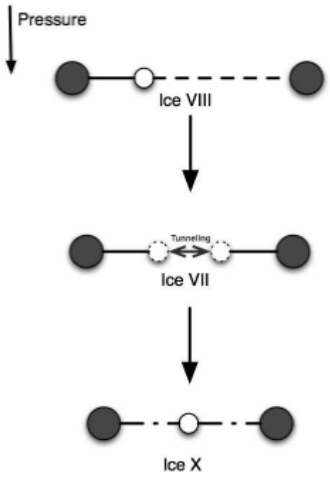

M. Chaplin www.lsbu.ac.uk/water/phase.html




Pruzan et al., *JCP (1993)*

# Tunneling can drive phase transitions



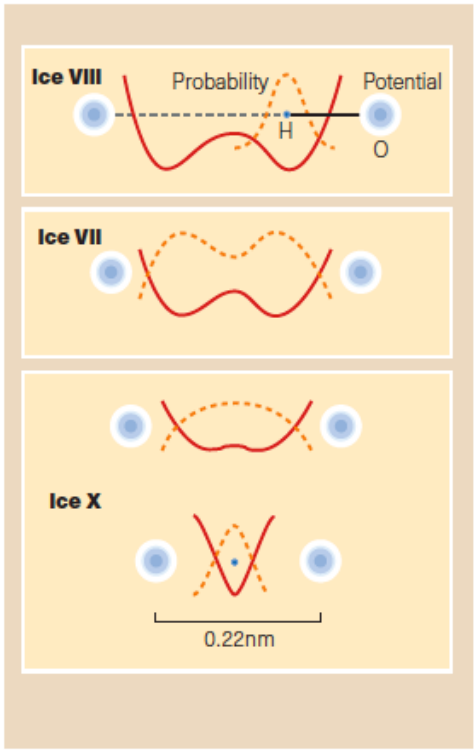




Figure 2 **Proton density in ice under pressure. As the oxygen atoms are forced together, the potential energy changes from a double to a single well; but a new simulation shows that a form of ice with the proton midway between the oxygens occurs even before that happens.**

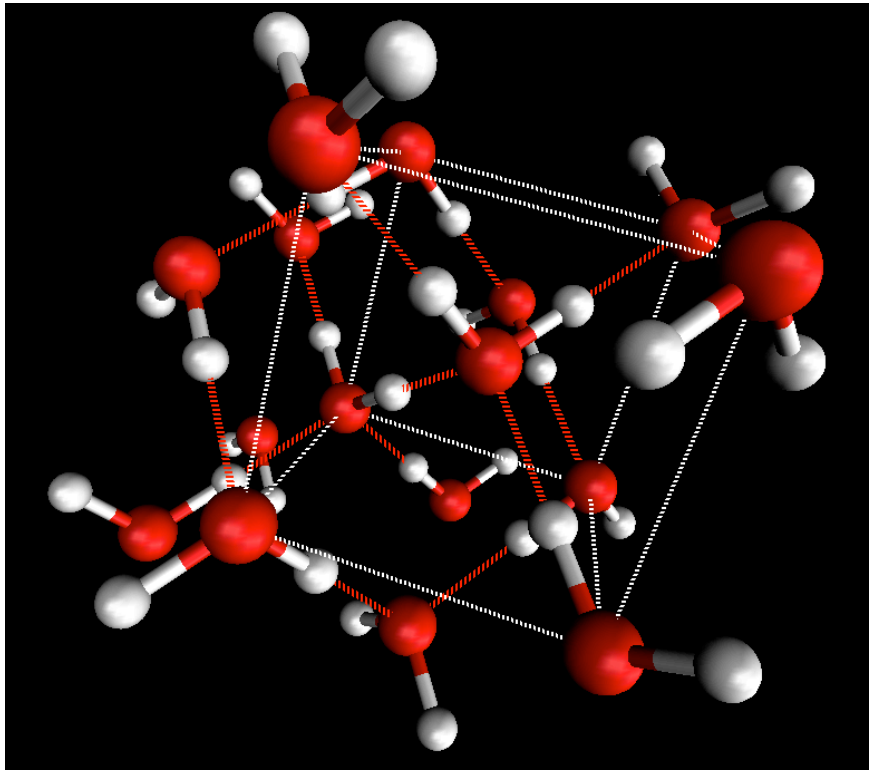
Cartoon from J. Texeira, *Nature N&V* commenting

Benoit, Marx, and Parrinello, *Nature* 1998

Picture is suggestive but rooted in Mean Field Theory

ice VIII -> ice VII: *antiferroelectric* to *disordered* proton sublattice
Another transition driven by quantum fluctuations occurs in KDP: *ferroelectric* to *disordered*

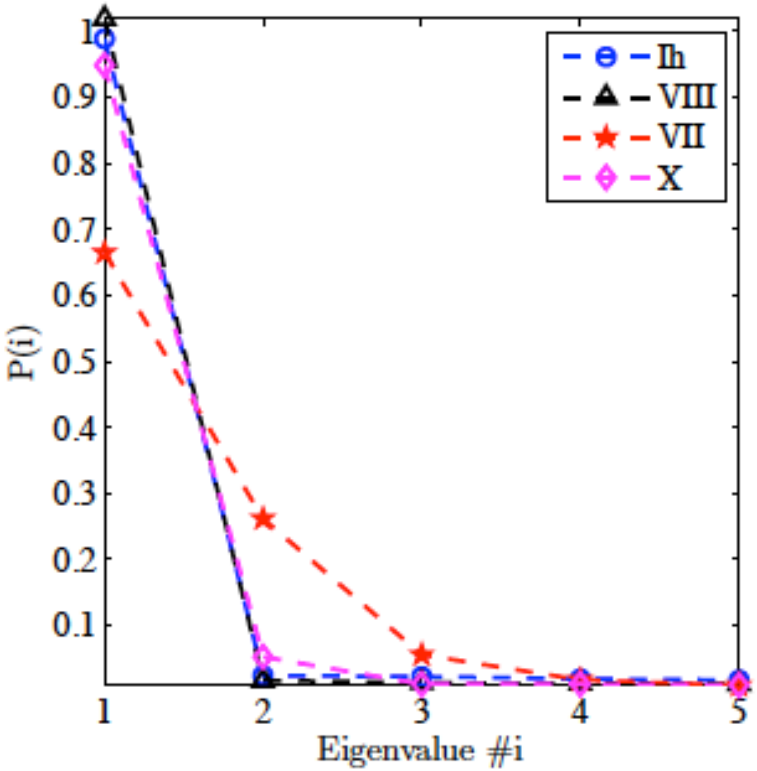
# Reduced longitudinal model



$$\rho(\mathbf{r},\mathbf{r}') \sim \rho(\bar{x},x')\rho(\mathbf{b},\mathbf{b}')$$

L.Lin, J.A.Morrone, RC, *JSP* (2011)

# Entangled protons




$$\rho = \sum_i |\phi(i)\rangle P(i) \langle \phi(i)|$$

von Neumann entanglement entropy

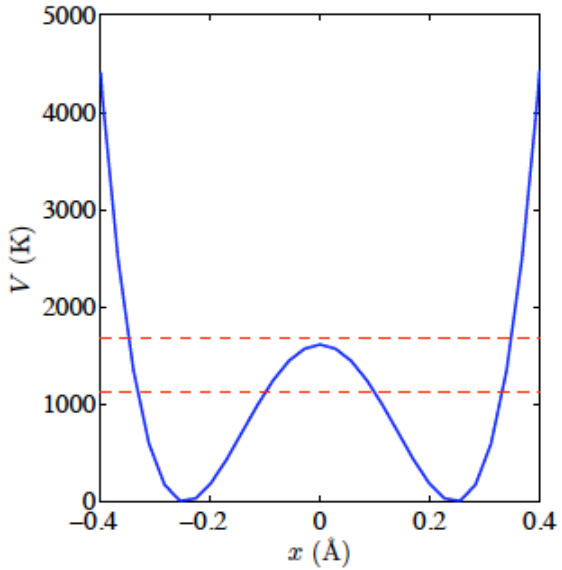
$$S = -\mathrm{Tr}[\rho \log \rho]$$

$S$ is essentially 0 in ice Ih and VIII

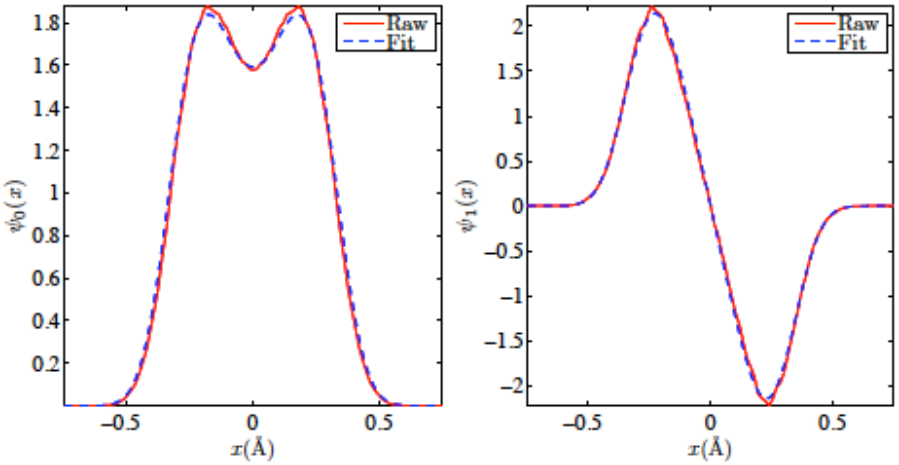
$S = 0.60$ in ice VII and $S = 0.20$ in ice X

What is the origin of the entanglement? Why does it occur in ice VII and X?

# Spectrum of the longitudinal density matrix




Effective potential and tunnel splitting

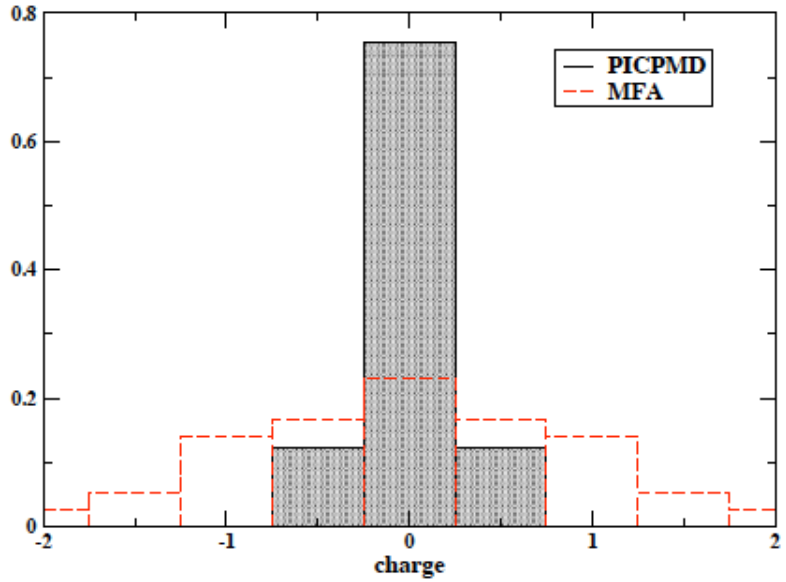



The first 2 eigenstates in ice VII

Tunnel splitting $547K$ *T* of simulation $100K$

Entanglement is mostly due to *correlations*

# Simulation versus Mean Field



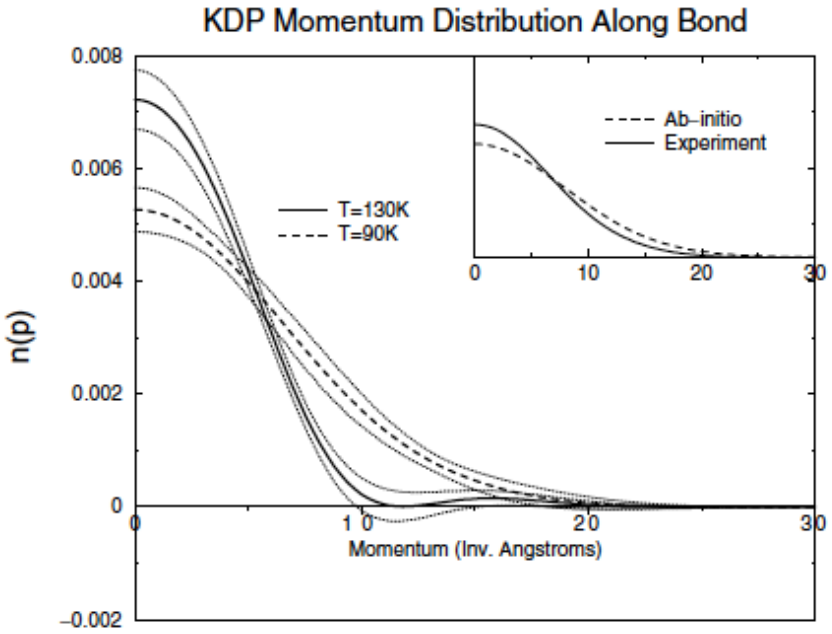

The distribution of local charge fluctuations in a 3-state (spin 1) model with N,C, and F states

MFA would need to a ionization catastrophe that would severely violate local charge neutrality

Ring tunneling does occur but is not the only process as some ionized configurations exist

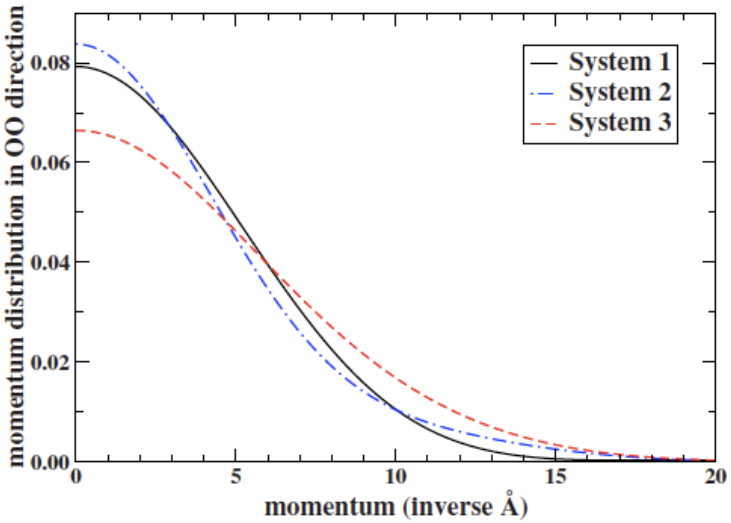
Role of: small cell size, T of the simulation, chosen lattice parameter (applied pressure)

# Tunneling in KDP




(from Reiter, Mayers, Platzman, *PRL (*2002)

Is there a **node** in the proton momentum distribution of KDP in the paraeletric phase?




(from Morrone, Lin, RC, *JPC* (2009)

# Remarks

- ZPE and tunneling (Boltzmannions)
- Faster convergence with the number of beads (*P*): GLE thermostats (M.Ceriotti, G.Bussi, M. Parrinello, *PRL 2009,* M. Ceriotti, D. Manolopoulos, M. Parrinello, *JCP* 2011)
- Quantum statistics: Bosons and Fermions
- Dynamic properties: harmonic approximation, semiclassical approaches (Centroid MD, Ring Polymer MD); analytic continuation from imaginary to real time correlation functions

**Acknowledgement:** RC and collaborators acknowledge support from the DOE and the NSF