Computer simulations of liquids and solvation using density functional theory-based molecular dynamics: Liquid water

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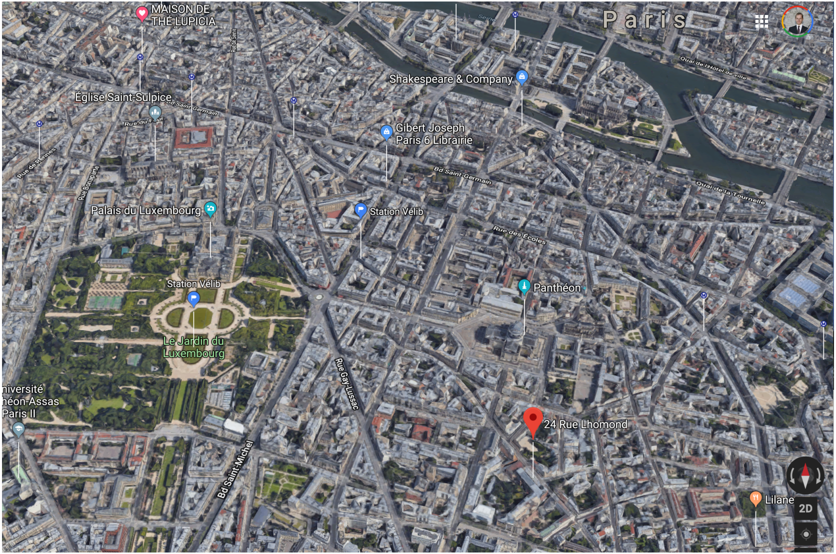
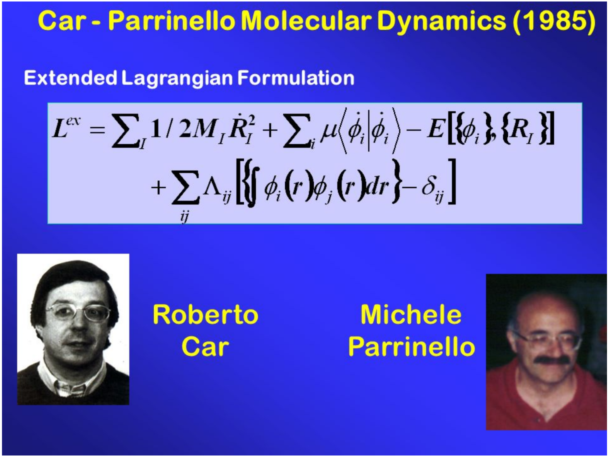


Water — computer simulations

- Water is everywhere
- Benchmark liquid — solvent
- Despite huge effort, no overall satisfying description
- Explicit electronic structure: Attempt for complete description, including dissociation, polarisability, …
- “Ab initio”, “first principles” molecular dynamics — and Monte Carlo

Method — Car-Parrinello molecular dynamics

- Extended Lagrangean: Electronic degrees of freedom introduced as *fictitious* variables



Car - Parrinello Molecular Dynamics (1985)

Extended Lagrangian Formulation

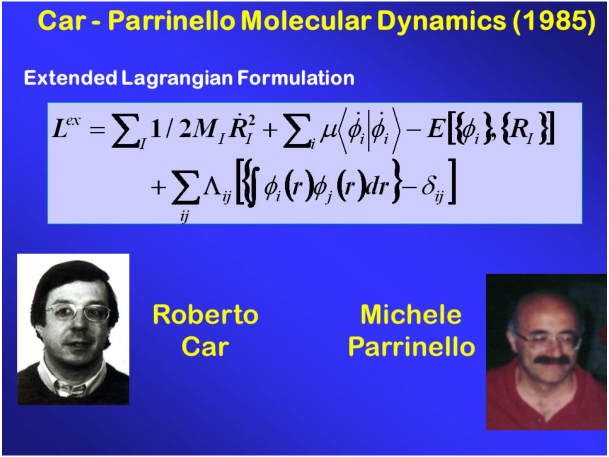
$$L^{ex} = \sum_I 1/2 M_I \dot{R}_I^2 + \sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle - E[\{\phi_i\},\{R_I\}] + \sum_{ij} \Lambda_{ij} \left[\left\{ \int \phi_i(r) \phi_j(r) dr \right\} - \delta_{ij} \right]$$

Roberto Car

Michele Parrinello

Method — Car-Parrinello molecular dynamics

- Extended Lagrangian: Electronic degrees of freedom introduced as *fictitious* variables



Car - Parrinello Molecular Dynamics (1985)

Extended Lagrangian Formulation

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Roberto Car

Michele Parrinello

Method — Born-Oppenheimer molecular dynamics

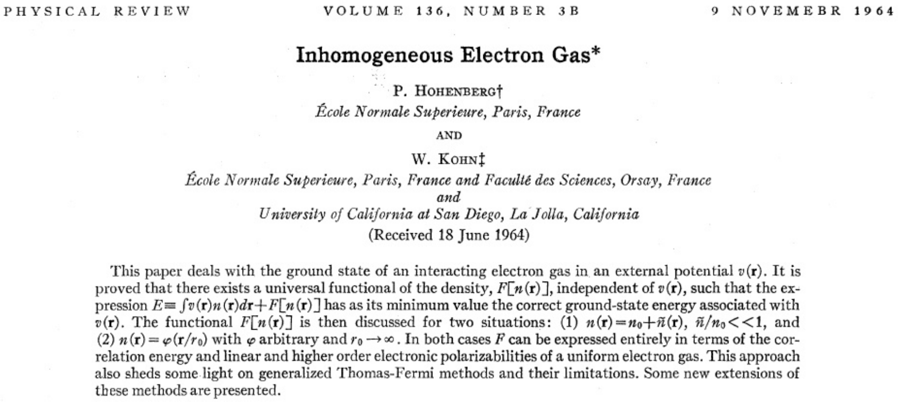
- $\mathbf{a}_I = \mathbf{F}_I / m_I$ like in “classical” molecular dynamics (MD)
- How to obtain **m**?
- Simple self-consistent electronic structure optimisation before calculating forces on the ions, propagation of time
- Drift due to inaccuracy in forces due to incompleteness of self-consistency, basis set

Method — Monte Carlo

- Useful for example when atomic forces are not available or too tedious to evaluate
- Several applications on liquid water and ice (`CP2K` code)

Method — electronic structure method

- Almost exclusively: Density functional theory (DFT)



PHYSICAL REVIEW VOLUME 136, NUMBER 3B 9 NOVEMEBR 1964

Inhomogeneous Electron Gas*

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AND
W. Kohn‡
École Normale Superieure, Paris, France and Faculté des Sciences, Orsay, France
and
University of California at San Diego, La Jolla, California

(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E\equiv\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r})=n_0+\tilde{n}(\mathbf{r})$, $\tilde{n}/n_0<<1$, and (2) $n(\mathbf{r})=\varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0\rightarrow\infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

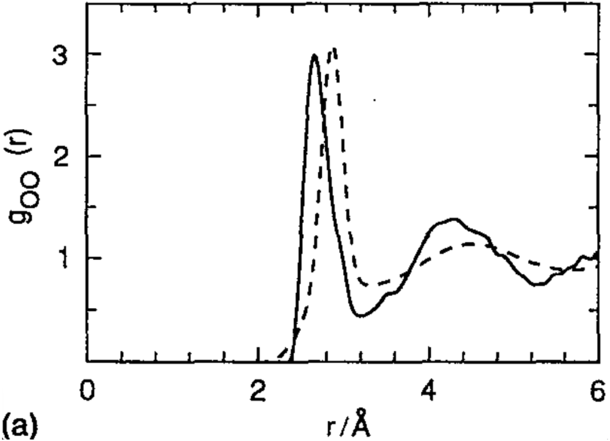
Method — density functional theory

- Formally exact (within Born-Oppenheimer approximation, non-relativistic, . . .)
- Usual formalism: Kohn-Sham single-particle orbitals, non-interacting electrons
- Many-body interactions (difficulties) are collected into the *exchange-correlation* term:
  Analytic form of correlation unknown
- Preferable scaling over wave function-based methods
- Typical size: $10^2 - 10^3$ atoms, up to 1 ns

Liquid water — early simulations

Laasonen, Sprik, Parrinello, Car; *JCP* 1993: *“Ab Initio”* liquid water

- GGA-exchange; 0.5+1.5 ps; deuterated



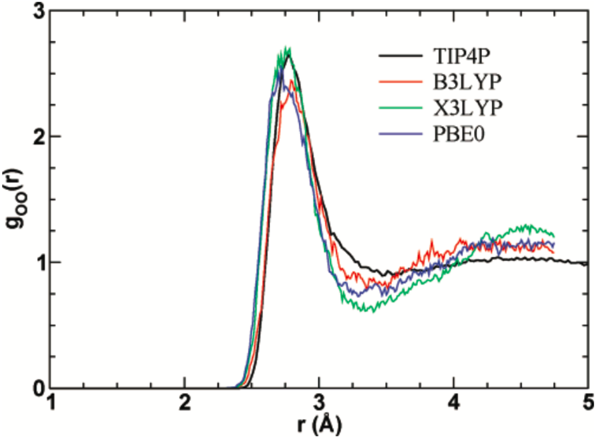
Liquid water — 1990's and early 2000's

- Slow progress in length of simulations
- Observation of effect of effective mass
- Elevated temperature (empirism)
- Applications to solvated electron, hydronium, hydroxyl, Grotthus mechanism, …
- But still over-structuring, slow diffusion, …

DFTb-MD on liquid water — exchange-correlation

Todorova, Seitsonen, Hutter, Kuo and Mundy, *J Phys Chem B* 2006

- Hybrid functional-exchange; 5+5 ps



DFTb-MD on liquid water — exchange-correlation

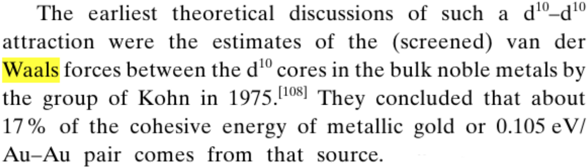
Todorova, Seitsonen, Hutter, Kuo and Mundy, *J Phys Chem B* 2006

- Hybrid functional-exchange; 5+5 ps

functional	D (Å^2/ps)	functional	D (Å^2/ps)
LDA	0.013	B3LYP	0.30
BLYP	0.048	X3LYP	0.17
XLYP	0.028	PBE0	0.28
PBE	0.047	HF	0.47
rPBE	0.180		
TPSS	0.032		
experiment (45°C) 0.2979			

van der Waals interactions

- van der Waals interactions important in several cases
    - Rare gases
    - Non-polar molecular systems with closed-shell consituents
    - Biology
    - …
- Even in bulk Au the van der Waals interactions significant!



The earliest theoretical discussions of such a d^{10}–d^{10} attraction were the estimates of the (screened) van der Waals forces between the d^{10} cores in the bulk noble metals by the group of Kohn in 1975.[108] They concluded that about 17 % of the cohesive energy of metallic gold or 0.105 eV/ Au–Au pair comes from that source.

[Pyykkö, 2004]

- (Semi-)local approximations like LDA, GGA cannot reproduce it

van der Waals interactions

- Arise from instantaneous fluctations in electron densities
- Fluctuation-dissipation theory:

$$E_c = -\frac{1}{2\pi} \int\limits_{\alpha=0}^{1} \int\limits_{\omega=0}^{\infty} \int\limits_{\mathbf{r}} \left[\alpha \chi_0 (\mathbf{r}_1, \mathbf{r}_3, \omega)\, W(\mathbf{r}_3, \mathbf{r}_4, \omega)\, \chi_0 (\mathbf{r}_4, \mathbf{r}_2, \omega) \right.$$
$$+\alpha^2 \chi_0 (\mathbf{r}_1, \mathbf{r}_3, \omega)\, W(\mathbf{r}_3, \mathbf{r}_4, \omega)\, \chi_0 (\mathbf{r}_4, \mathbf{r}_5, \omega)\, W(\mathbf{r}_5, \mathbf{r}_6, \omega)\, \chi_0 (\mathbf{r}_6, \mathbf{r}_2, \omega)$$
$$\left. + \mathcal{O}(\alpha^3) + \ldots \right] \prod_i d\mathbf{r}_i$$

- After some approximations:

$$E_{\mathrm{disp}}^{\mathrm{asymp}} = -\frac{3}{\pi} \frac{1}{R^6} \int\limits_0^{\infty} \alpha^A_{\alpha\beta} \alpha^B_{\gamma\delta}\, d\omega$$

vdW — semi-empirical treatments

- Most popular now:
  - Grimme 2006 “DFT+D2”
  - Grimme *et alia* 2010 “DFT+D3”
  - Tkatchenko-Scheffler
- General properties:
  - Usually do not depend on electron densities, only on atomic coordinates
  - Usually pair-wise
  - Energy of electronic system no longer minimimised in equilibrium structure

vdW — “real” functionals

- Langreth-Lundqvist *et alia*, “vdW-DF” or “vdW-LL”
- Truly non-local: $E_c^{nl}[n] = \int_{\mathbf{r}} \int_{\mathbf{r}'} n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}'$
- Usually accompanied with revPBE-GGA functional (reproduces “best” Hartree-Fock-exchange)
- One edition:

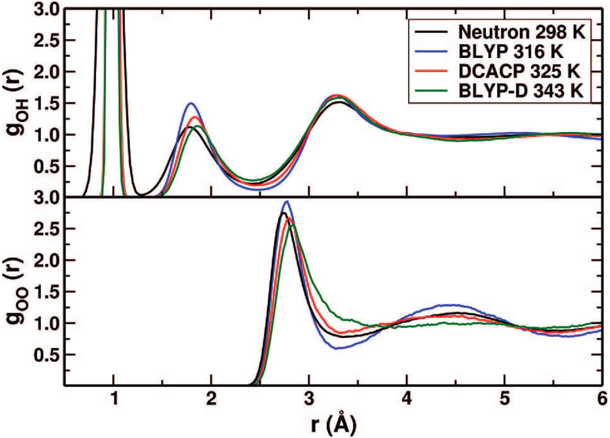
  Lee, Murray, Kong, Lundqvist *&* Langreth; *PRB* 2010
- Yet results depend strongly on choice of *exchange* term

Liquid water — vdW

Lin, Seitsonen, Coutinho-Neto, Tavernelli & Röthlisberger; *JPCB*, 2009

(Received: February 13, 2008)

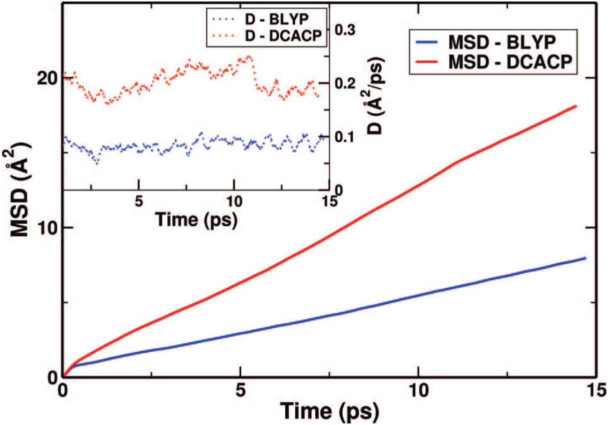
- Softening of structure when vdW-treatment included



Liquid water — vdW

Lin, Seitsonen, Coutinho-Neto, Tavernelli & Röthlisberger; *JPCB*, 2009

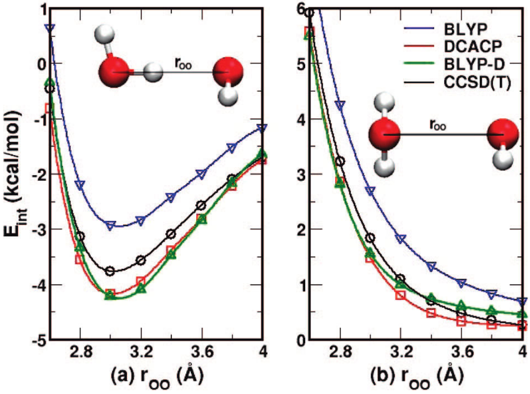
- Faster diffusion



Liquid water — vdW

Lin, Seitsonen, Coutinho-Neto, Tavernelli & Röthlisberger; *JPCB*, 2009

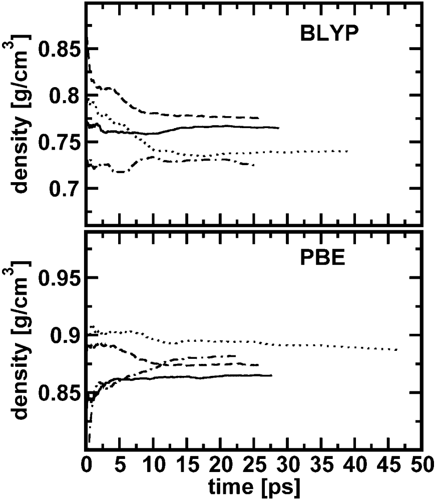
- Reduced directionality

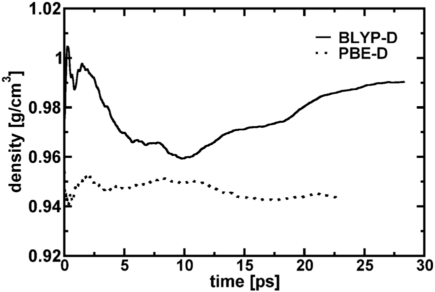


Liquid water — vdW

Schmidt, VandeVondele, Kuo, Sebastiani, Siepmann, Hutter & Mundy; *JPCB*, 2009

- Density greatly improved upon employing DFT+D2

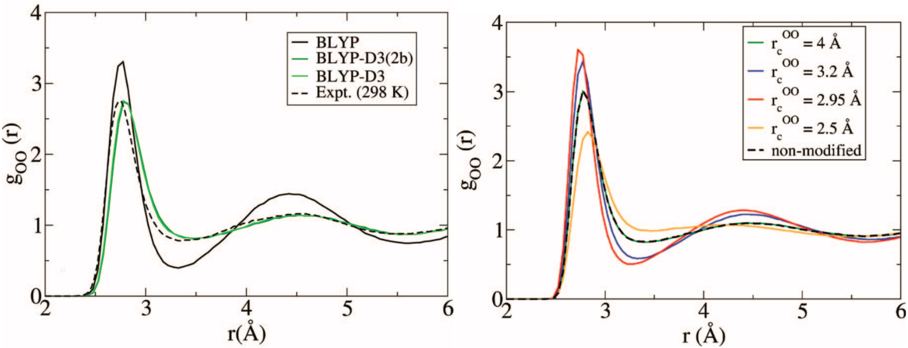




Liquid water — vdW

Jonchiere, Seitsonen, Ferlat, Saitta & Vuilleumier; *JCP*, 2011

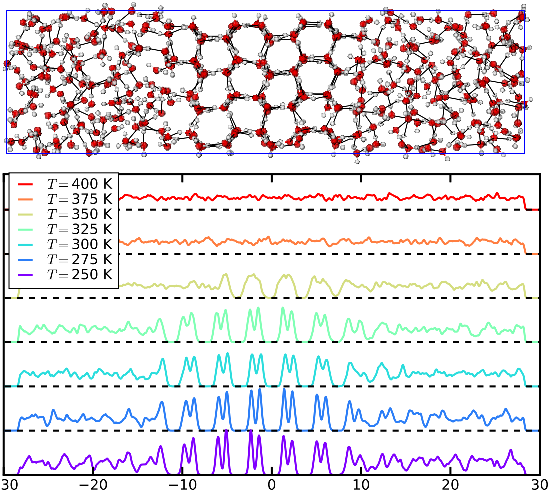
- Removing R^{-6} tail leads to same effect as GGA dropping vdW



Liquid water — vdW

Ari P Seitsonen & Taras Bryk; *PRB*, 2016

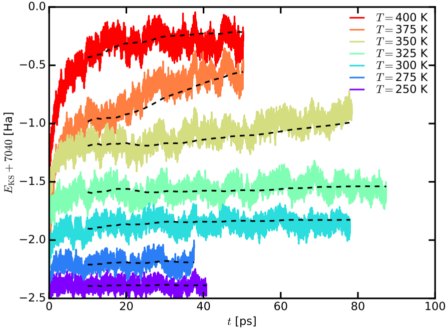
- BLYP+D3: Melting temperature of water: $T_m^{\mathrm{BLYP+D3}} \approx 325$ K



Liquid water — vdW

Ari P Seitsonen & Taras Bryk; *PRB*, 2016

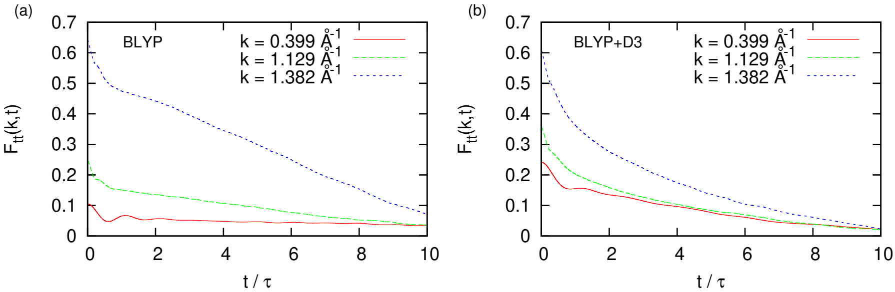
- BLYP+D3: Melting temperature of water: $T_m^{\mathrm{BLYP+D3}} \approx$ 325 K
- Earlier simulations (Xantheas *et alia*): $T_m^{\mathrm{BLYP}} \approx$ 400 K, $T_m^{\mathrm{BLYP+D2}} \approx$ 360 K
- Nuclear quantum effects: $\Delta T_m^{\mathrm{q-TIP4P/F}} \approx$ 10 K



Liquid water — vdW

Taras Bryk & Ari P Seitsonen; *CMP*, 2016

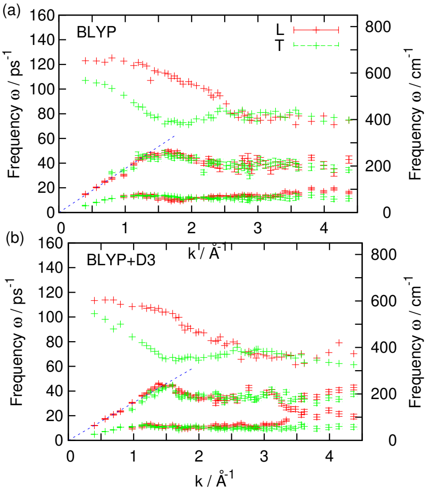
- BLYP+D3: Collective excitations in H_2O, D_2O
- Stretched exponential in BLYP-D_2O at 50 K, exponential decay in BLYP+D3-D_2O

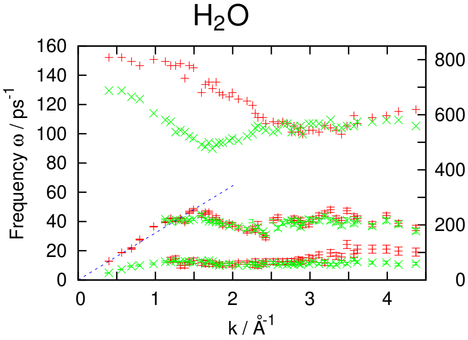


Liquid water — vdW

Taras Bryk & Ari P Seitsonen; *CMP*, 2016

- BLYP+D3: Collective excitations in H_2O, D_2O



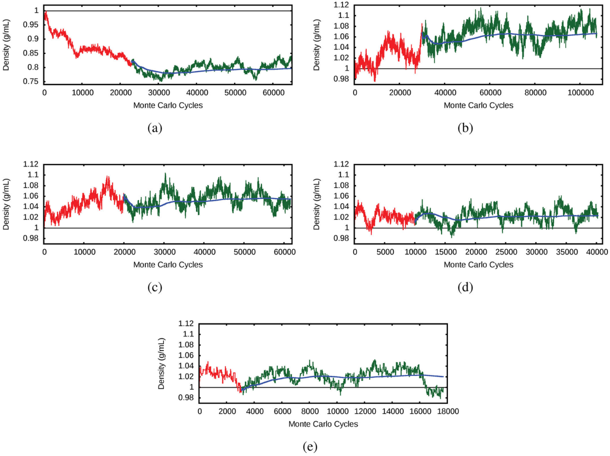


LO and TO gap $\sim$ 24 ps, or 127 cm^{-1}
Apparent high-frequency speed of sound 3223 m/s; expr $\approx$ 3100 m/s (XRS), $\approx$ 3200 m/s

Liquid water — *ab initio*

Mauro Del Ben, Mandes Schönherr, Jürg Hutter & Joost VandeVondele; JPCL, 2013

- Going up to MP2; Monte Carlo-*NpT*

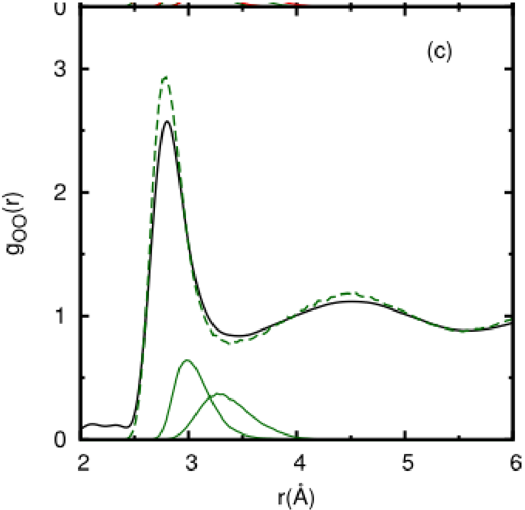


(a) (b) (c) (d) (e)

Liquid water — more *ab initio*

Mauro Del Ben, Mandes Schönherr, Jürg Hutter & Joost VandeVondele; JCP, 2015

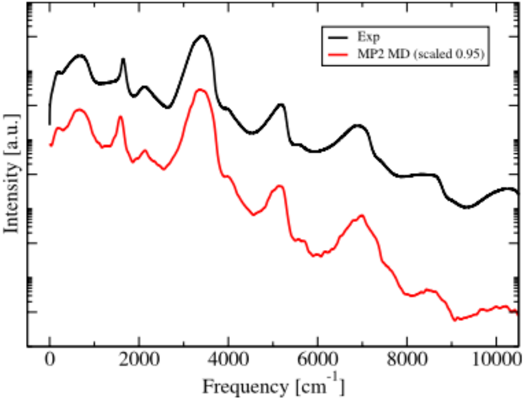
- MP2, RPA



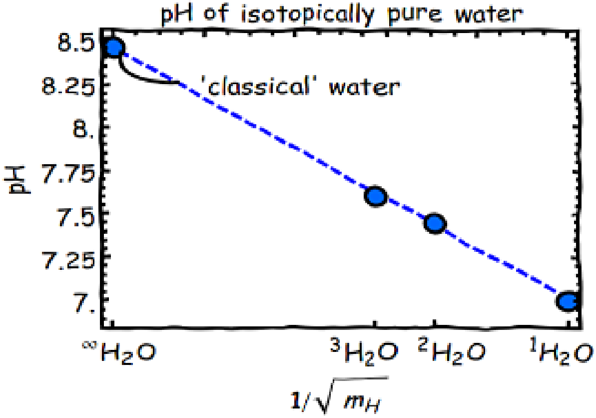
Liquid water — more *ab initio*

Mauro Del Ben, Mandes Schönherr, Jürg Hutter & Joost VandeVondele; JCP, 2015

- More quantities: Nuclear quantum effects (DFT/hybrid functionals), volume of ice



Liquid water — nuclear quantum effects



- Nuclear quantum effects *do* matter

Liquid water — nuclear quantum effects

Path integral molecular dynamics

- *Equilibrium* properties
- Several (32-64) replicas, or *beads*: Increase of computing cost
- *Ad hoc* approach for dynamics: Ring polymer MD

M Ceriotti *&* D E Manolopoulos; *PRL*, 2012

Thermostatting:

- Path integral generalised Langevin equation thermostat (PIGLET)
- GLE: *coloured* noise, frequency-dependent temperature
- Reduces number of beads

T E Markland *&* D E Manolopoulos; *JCP*, 2008

Ring-polymer contraction

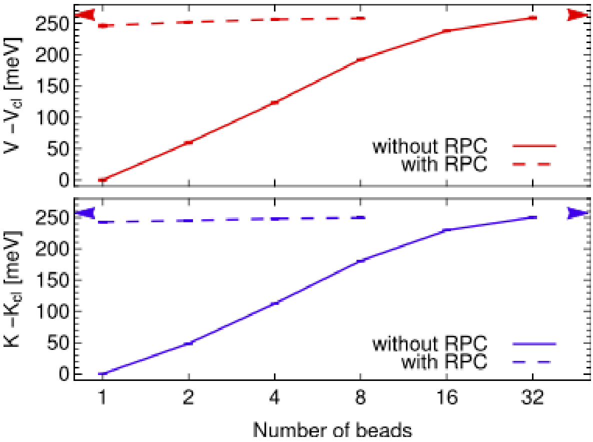
- RPMD-level accurady at the cost of the *accurate* method

Liquid water — nuclear quantum effects

V Kapil, J VandeVondele & M Ceriotti; *JCP*, 2016

RPC-example

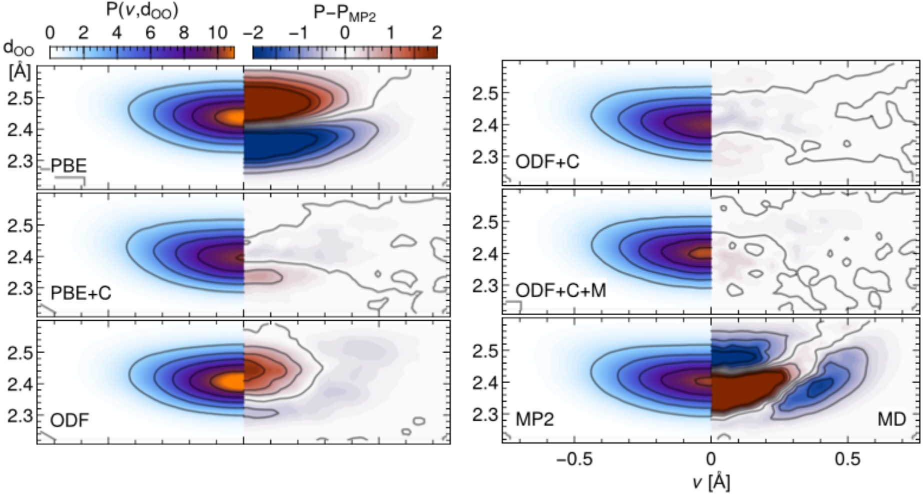
- Division bonded *versus* non-bonded in q-TIP4P/F-H_2O



Liquid water — nuclear quantum effects

V Kapil, J VandeVondele & M Ceriotti; *JCP*, 2016

RPC-example: Zundel cation



Water — *quo vadis?*

Improved *ab initio* molecular dynamics by minimally biasing with experimental data; JCP, 2017

Added potential:

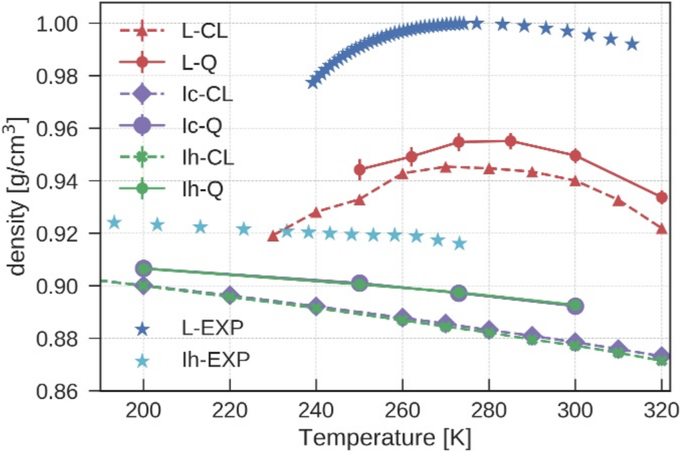
$$V(r_i) = \sum_{k=0}^{3} \frac{\alpha}{\hat{f}_k} \sum_{j\neq i}^{N} r_{ij}^k \left[1 - u(r_0 - r_{ij})\right]$$

> *Biased AIMD simulations of water and an excess proton in water are shown to give significantly improved properties both for observables which were biased to match experimental data and for unbiased observables. This approach also yields new physical insight into inaccuracies in the underlying density functional theory as utilized in the unbiased AIMD.*

Water — *quo vadis?*

Bingqing Cheng, Edgar A Engel, Jörg Behler, Christoph Dellago & Michele Ceriotti; *PNAS*, 2019

Neural Networks / Machine Learning



Electronic structure-based MD — summary

- “Predictable” over-all accuracy
- Reactions, dynamics, free-energy surfaces, …
- Liquid water *via* DFTb-MD still a challenge
- *Ab initio* huge effort, but appearing