Two exchange-correlation functionals compared for first-principles liquid water

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The first-principles description of liquid water using *ab initio* molecular dynamics (AIMD) based on density functional theory (DFT) has recently been found to require long equilibration times, giving too low diffusivities and a clear over-structuring of the liquid. In the light of these findings we compare here the room-temperature description offered by two different exchange correlation functionals: BLYP, the most popular for liquid water so far, and RPBE, a revision of the widely used PBE. We find for RPBE a less structured liquid with radial distribution functions closer to experiment ones than the ones of BLYP. The diffusivity obtained with RPBE for heavy water is still 20% lower than the corresponding experimental value, but it represents a substantial improvement on the BLYP value, one order of magnitude lower than experiment. These characteristics and the hydrogen-bond (HB) network imperfection point to an effective temperature $\sim 3\%$ lower than the actual simulation temperature for the RPBE liquid, as compared with BLYP's $\sim 17\%$ deviation. The too long O—O average nearest-neighbor distance observed points to an excessively weak HB, possibly compensating more fundamental errors in the DFT description.

1. Introduction

The interaction of organic pollutant molecules with the minerals and other components of the soil represents a paradigmatic case within the set of atomic-scale problems of relevance for the environment. It displays the level of complexity that demands a fundamental revision of the way we use computers for the simulation of condensed matter. On one hand the number of adsorption studies to address is enormous (combinations of many different pollutants, minerals, surfaces thereof etc.), on the other, each study displays a large degree of complexity, not least because of the wet character of these systems.

The effect of water in this and other wet systems is crucial in different ways, from the dielectric screening of electrostatic interactions to the active chemical role played in some important wet processes. These different aspects of water can be described at different levels of theory, including the static calculation of the system of interest immersed in an effective dielectric continuum, or the dynamic simulation of the liquid based on empirical potentials of different kinds. Even if simplified descriptions of water can be appropriate for some problems, other problems require the accuracy and transferability provided by first-principles simulation methods. This is not only our case, but it is true for many wet systems throughout geochemistry, biochemistry and wet chemistry. These considerations and the high variety of situations that we encounter in our pollutant problem (see [1] for the combinatorial aspects of the project and the workflow issues it entails) make it extremely important that we can use different simulation methods that involve different computational demands in a seamless fashion and within a single computational environment [2–7]. We need not only to interconnect the different simulations [4] but that each one of them performs at the required level of accuracy.

On the first-principles side of the wet-systems description, *ab initio* molecular dynamics (AIMD) based on density-functional theory (DFT) is the technique that, on one hand, satisfies the needs mentioned above, and, on the other, is efficient enough to allow for the system sizes and time scales needed in the simulations with today's computers. Indeed, the last 10 years have witnessed the success of many DFT-based AIMD simulations of liquid

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water, including work on structural, dynamical, chemical and electronic properties [8–14].

Recent reports [15–17], however, have questioned some of the results of earlier studies, showing that if the simulations are allowed to run for longer times, the diffusivity drops by one order of magnitude and the liquid becomes over-structured. The discrepancy with experiments [18–20] is still unexplained. Prime suspects are the fundamental limitations of present-day AIMD simulations of liquid water: the inability of gradient-corrected (GGA) density functionals to describe dispersion interactions, and the neglect of quantum fluctuations in the classical description of the nuclear dynamics.

The need for long equilibration times and the poor structural and dynamical results have been further assessed in a recent contribution [21], where a relaxation process of a time scale larger than 20 ps was found at room temperature. It was observed to be related to rearrangements of the hydrogen-bond (HB) network in liquid, expressed by the concentration of under-coordinated molecules, including a substantial presence (and relevance) of bi-coordinated ones. Both the radial distribution functions (RDFs) and the diffusivity were found to correlate strongly with the HB network imperfection, in close analogy to what Giovambattista *et al.* [22] found in supercooled water. Furthermore, while the network was slowly evolving, the diffusivity was observed to equilibrate much faster to the instantaneous network state than to the final temperature. The mentioned paper also shows that the structure, diffusivity and network characteristics obtained, would very nicely fit experiment if they corresponded to an effective temperature of ∼240 K, instead of the 300 K actually used in the AIMD simulations.

All those results were obtained for GGA density functionals, specifically for two proposals, BLYP [23,24] and PBE [25]. Both very popular and quite successful, the former comes from the quantum-chemistry community and the latter from the condensed-matter physics community. Even if they were constructed with different criteria, from a fundamental point of view it is good news that both functionals give very similar results [15]. From a more practical view point, however, it would be highly desirable to have a satisfactory and efficient DFT description of liquid water in order to be able to address complex wet systems, especially since the more technical aspects for efficient DFT calculations (including linear scaling) have already been successfully tested for this system [21].

Alternative GGAs are being explored at the moment, and very promising results have been found by VandeVondele *et al.* [26], who tried several functionals finding much more satisfactory results. Since their functionals originate from the chemistry community, where special emphasis is put on accuracy for light elements, and since our interest in wet mineral surfaces involves heavier elements, we think it is worthwhile to complement their work with a similar study with functionals proposed more generally for the whole periodic table. In the following we present results for the structure, diffusivity and equilibration times for RPBE [27]. This GGA functional is a modification of PBE, well within its philosophy and fulfilling all its fundamental criteria. It is also very accessible from the points of view of coding (only a few lines differ from a PBE implementation) and computational demands, remaining at the GGA level. It has already been tested for varied systems, including systems with heavy elements [28,29]. Functionals beyond GGA (meta-GGAs) [30,31], hybrid functionals [32–34] and functionals including Van der Waals interactions [35,36] should also be checked, but their efficiency is lower, and the scope of wet systems that can be addressed at present is much narrower than for GGAs. None of these functionals will be addressed here.

Asthagiri *et al.* [17] tested an alternative GGA, very similar to PBE as well, called revised PBE [37] by Zhang and Yang. Henceforth we call revPBE the one of Zhang and Yang and RPBE the one by Hammer *et al* [27]. The spirit of the PBE modification of this functional is similar to RPBE representing an alternative worth considering. They both modify the functional proposed in PBE for the dependence of the exchange enhancement factor as a function of he reduced gradient of the density. While revPBE simply changes one parameter, RPBE changes the function. In addition, the later was also built in a way that respects the Lieb-Oxford bound locally, which ensures a global fulfilment of the condition for any electronic density. Good revPBE results for liquid water were obtained by those authors [17] before the long time-scale relaxation problem was reported. Under the new circumstances it seems that the equilibration and simulation times used there [17] could have been too short. A revision of those tests would also be useful, but is beyond the scope of the present work.

2. Method

The simulations were performed using the Kohn-Sham approach [38] to DFT [39] in the generalized-gradient approximation (GGA). The BLYP [23,24] and RPBE [27] exchange-correlation functionals were used and are compared in the following. Core electrons were replaced by norm-conserving pseudopotentials [40] in their fully non-local representation [41]. Numerical atomic orbitals (NAO) of finite support were used as basis set, and the calculation of the self-consistent Hamiltonian and overlap matrices was done using the linear-scaling SIESTA method [42,43]. Integrals beyond two-body were performed in a discretized real-space grid, its fineness determined by an energy cutoff of 150 Ry. A double-ζ polarized (DZP) NAO basis set was used, which had been obtained following the method proposed in [44,45] for a confining pressure [45] of 0.2 GPa. The validation of the method, pseudopotentials and basis set can be found in [21], including the approximations required for linear scaling.

Table 1. AIMD simulations performed in this work, all of them with periodic boundary conditions in a cubic cell of size $a = 9.865$Å. DF stands for the particular density functional used, **T** for the final equilibrated temperature, τ_{sim} for the AIMD simulation time after AIMD equilibration, τ_{eq} for the AIMD equilibration time, "Model" for the model used for preparation, T_{pre} for the temperature at which the preparation model had been equilibrated and T_i for the AIMD initial temperature (after the τ_{eq} anneal). Temperatures in K and times in ps.

#	DF	T	τ_{sim}	τ_{eq}	Model	T_{pre}	T_i
1	BLYP	298	20	4	BLYP	315	300
2	BLYP	315	32	6	SPC/E	300	300
3	RPBE	300	17	5	BLYP	315	300
4	BLYP	345	30	4	TIP5P	325	325

We performed AIMD simulations for 32 molecules of heavy water for the BLYP and RPBE density functionals (a detailed comparison between BLYP and PBE for this system can be found in [15]). Details are given in table 1. AIMD equilibration is achieved by means of temperature annealing (velocity re-scaling) [46], while the actual simulations are performed by Verlet's integration [46]. In all the simulations the time step used was 0.5 fs. The observed total-energy drifts corresponded to drifts in the system temperature between 0.26 and 0.36 K/ps. The simulations were performed at constant volume, i.e. for fixed cell size and shape, under periodic boundary conditions. As in [21], the time scale of the HB relaxation process is monitored by following its non-equilibrium behaviour. The "moving time window" used in 21 is used to obtain the time dependence of the variables of interest.

Empirical simulations were performed using different force fields (TIP5P [47] and SPC/E [48]) in order to prepare reasonably equilibrated starting points for AIMD. These simulations were performed with the GROMACS MD package [49,50] under constant volume and temperature conditions using a Berendsen-type thermostat [51]. The empirical simulations were equilibrated during 200 ps.

3. Results and discussion

Figure 1 compares the RDFs obtained with RPBE and BLYP to experiment. Looking mainly at the inter-molecular features, the RDFs for RPBE are considerably less structured than the ones for BLYP, even if still over-structured with respect to experiment. The comparison in [15] between PBE and BLYP gave much closer result. The too large distance for the first peak position of the O—O RDF is worth noting for RPBE, however. It indicates too weak HBs that could account for the more fluid character of the RPBE liquid as compared with BLYP or PBE. The fact that this O—O distance is longer than the experimental value (possibly weaker HBs) but the liquid remains still slightly overstructured otherwise, suggests the presence of a more fundamental error (possibly the same as for BLYP and PBE) that is partly compensated by these weaker HBs.
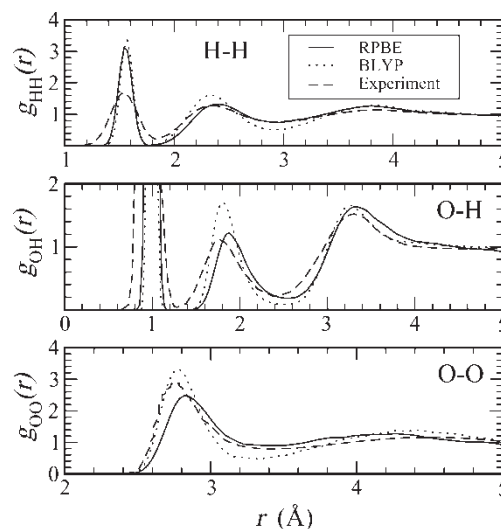

Figure 1. Comparison of the H—H, O—H, and O—O RDFs as obtained in this work for 32 molecules with RPBE (solid line), with BLYP (dotted line) and by experiment [19,20] (dashed line), at a temperature of 300 K.

The values for the corresponding diffusivities are shown in table 2. The table also shows the effective temperatures [21] for the different simulations, i.e. the temperature at which the diffusivity of the real liquid equals the AIMD value. The table shows the effective temperature with respect to both normal and heavy water. In [21] there was no need to refer to the difference between heavy and light water, since the differences in diffusivity between the two ($\sim 25\%$) were negligible when compared with the deviation of AIMD (BLYP) with respect to experiment [21]. In this study, however, the RPBE description is much closer to experiment, and the distinction becomes relevant.

As shown in [21], several results for the room-temperature simulations fairly reproduce results of experiments or empirical models at the effective temperature. Besides the diffusivity, features of the RDFs like the heights of the first minimum and the second maximum of the O—O RDF would conform to this temperature scaling. The HB network also follows this scaling. In figure 2 the distribution of molecular coordinations is compared for RPBE and TIP5P at room temperature and BLYP at 345 K. The RPBE histogram shows a very slightly more over-coordinated liquid than

Table 2. Diffusivity (*D*) obtained in simulations of heavy water for different functionals and in experiment, all at room temperature. Corresponding effective temperatures with respect to light water ($T_{eff}^{H_2O}$) and heavy water ($T_{eff}^{D_2O}$).

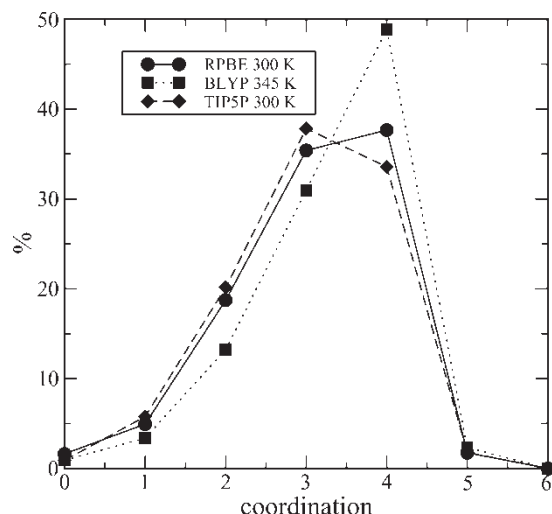|	$D(\times 10^{-5}\,^2/s)$	$T_{eff}^{H_2O}$ (K)	$T_{eff}^{D_2O}$ (K)
BLYP	0.20	240 (− 20%)	250 (− 17%)
BLYP[a]	0.15	237 (− 21%)	245 (− 18%)
PBE[a]	0.16	238 (− 21%)	246 (− 18%)
RPBE	1.50	283 (− 6%)	292 (− 3%)
Exp $(_2)$[b]	1.87		
Exp $(_2)$[b]	2.30		

[a][15] [b][18];

Figure 2. Distribution of molecules with different coordinations. Room-temperature RPBE (circles, solid line) is compared with the TIP5P potential[47] (diamonds, dashed line) at room temperature and with BLYP (squares, dotted line) at 345 K.

the TIP5P one, suggesting a slightly lower effective temperature than 300 K.

Figure 3 shows the evolution of the diffusivity and relates it to the evolution of the liquid structure, as monitored by the heights of the first minimum and of the second maximum of $g_{OO}(r)$. The "moving-window" approach defined in [21] has been used to compute the time averages. In the RPBE simulation windows of 5 ps were considered every 2 ps, whereas in the BLYP simulation the windows were of 7.5 ps every 2.5 ps, given the faster evolution of the former. Even if none of the trajectories has strictly evolved into a stationary situation, the figure reveals that the characteristic time of RPBE is similar the one of BLYP. However, from the tentative assimilation of the experimentally measured

relaxation times [52] to our equilibration times, one would expect for an effective temperature of 292 K a substantially shorted relaxation time. Surprisingly, it does not seem to be the case here.

4. Conclusions

We have performed DFT-based AIMD simulations of room-temperature liquid water, comparing the characteristics of the fluid obtained by BLYP and RPBE. The main conclusions are summarised as follows.

(i) The RDFs for RPBE are closer to experiment than the corresponding ones for BLYP. RPBE water is less structured than BLYP, still slightly over-structured with respect to experiment.

(ii) The diffusivity obtained for RPBE is still low, but much closer to experiment than the value obtained for BLYP, with 20% underestimation instead of one order of magnitude.

(iii) For room-temperature AIMD, the effective temperature (with respect to heavy water experimental results) is ~292 K (−3%) for RPBE, while for BLYP it is ~250 K (−17%). In addition to the quantitative advantage of performing RPBE simulations there is a qualitative advantage in that neither of these RPBE simulations would be for supercooled water.

(iv) The AIMD HB-network at AIMD temperature is extremely similar to the TIP5P network at the effective temperature.

(v) The equilibration time-scale for room-temperature RPBE is similar to BLYP. The fact that it is not substantially shorter is somehow surprising [21].
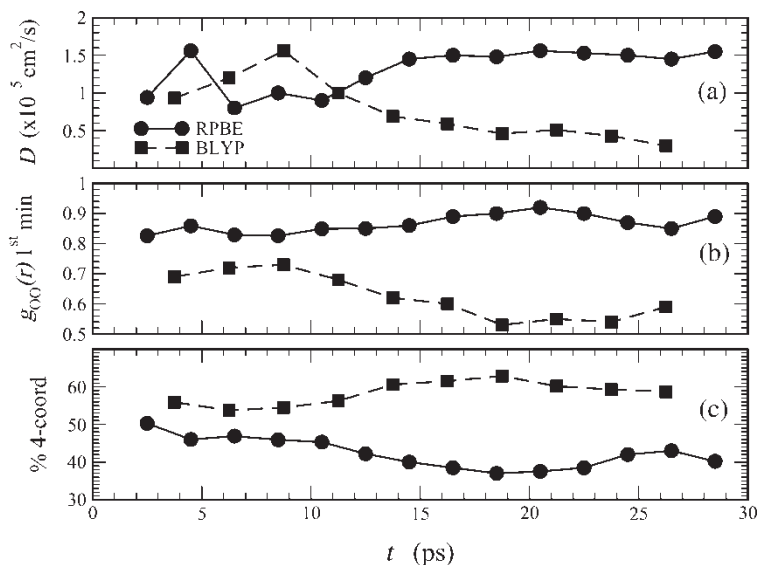

Figure 3. Evolution of the diffusivity (a), the height of the first minimum of $g_{OO}(r)$ (b), and the concentration of coordination defects (c), in simulation 3 (RPBE) calculated in 5-ps-windows every 2 ps (solid line, circles) and in simulation 2 (BLYP) calculated in 7.5-ps-windows every 2.5 ps (dashed line, squares).

Even if there are reasons to believe that the good results found for RPBE are not due to fundamental reasons, but rather to error cancellations, still, the possibility of having a well-behaved GGA water is appealing. We consider that it is worth further exploring the performance of RPBE in other wet systems, possibly starting from well characterised ion hydration shells.

Acknowledgements

References

[1] C. Chapman, W. Emmerich, J. Wakelin, E. Artacho, M. Dove, R. Bruin. (2005). Workflow, Issues in atomistic Simulations. Molecular Simulation. 317−322.

[2] M. Litzkow, M. Livny, M. Mutka. Condor-a hunter of idle workstations. *Proceedings of the 8th International Conference of Distributed Computing Systems*, June (1988).

[3] A. Garcíia, P. Murray-Rust, J. Wakelin. The use of xml and cml in computational chemistry and physics programs. *Proceeding of the UK e-Science All Hands Meeting*, pp. 1111−1114 (2004), ISBN 1-904425-21-6.

[4] J. Wakelin, P. Murray-Rust, S. Tyrrell, Y. Zhang, H.S. Rezpa, A. García. (2005). CML tools and information flow in atomic scale simulations. Molecular Simulation. 309−316.

[5] I. Foster, C. Kesselman (Eds). *The Grid: Blueprint for a New Computing Infrastructure*, Morgan Kaufmann, San Francisco, Calif (1999).

[6] M. Calleja, L. Blanshard, R. Bruin, C. Chapman, A. Thandavan, R. Tyler, P. Wilson, V. Alexandrov, R.J. Allen, J. Brodholt, M.T. Dove, W. Emmerich, K.K. van Dam. Grid tool integration within the eminerals project. *Proceeding of the UK e-Science All Hands Meeting*, pp. 812−817 (2004), ISBN 1-904425-21-6.

[7] M. Calleja, R. Bruin, M. Tucker, M.T. Dove, R.P. Tyler, L.J. Blanshard, K.K. van Dam, R. Allan, C. Chapman, W. Emmerich, P. Wilson, J. Brodholt, A. Thandavan, V. Alexandrov. Collaborative grid infrastructure for molecular simulations: The eMinerals minigrid as a prototype integrated compute and data grid. *Molecular Simulation*, 317−322 (2005).

[8] M. Sprik, J. Hutter, M. Parrinello. *Ab initio* molecular dynamics simulation of liquid water: Comparison of three gradient-corrected density functionals. *J. Chem. Phys.*, **105**, 1142 (1996).

[9] J. Ortega, J.P. Lewis, O. Sankey. First principles simulations of fluid water: The radial distribution functions. *J. Chem. Phys.*, **106**, 3696 (1996).

[10] P.L. Silvestrelli, M. Parrinello. Structural, electronic, and bonding properties of liquid water from first principles. *J. Chem. Phys.*, **111**, 3572 (1999).

[11] P.L. Silvestrelli, M. Parrinello. Water molecule dipole in the gas and in the liquid phase. *Phys. Rev. Lett.*, **82**, 3308 (1999).

[12] P.L. Geissler, C. Dellago, D. Chandler, J. Hutter, M. Parrinello. Autodissociation of a water molecule in liquid water. *Science*, **291**, 2121 (2001).

[13] M. Boero, M. Parrinello, K. Terakura, T. Ikeshoji, C.C. Liew. First-principles molecular-dynamics simulations of a hydrated electron in normal and supercritical water. *Phys. Rev. Lett.*, **90**, 226403 (2003).

[14] S. Izvekov, G.A. Voth. Car-Parrinello molecular dynamics simulation of liquid water: New results. *J. Chem. Phys.*, **116**, 10372 (2002).

[15] J.C. Grossman, E. Schwegler, E.W. Draeger, F. Gygi, G. Galli. Towards an assessment of the accuracy of density functional theory for first principles simulations of water. *J. Chem. Phys.*, **120**, 300 (2004).

[16] E. Schwegler, J.C. Grossman, F. Gygi, G. Galli. Towards an assessment of the accuracy of density functional theory for first principles simulations of water. ii. *J. Chem. Phys.*, **121**(11), 5400−5409 (2004).

[17] D. Asthagiri, L.R. Pratt, J.D. Kress. Free energy of liquid water on the basis of quasichemical theory and *ab initio* molecular dynamics. *Phys. Rev. E*, **68**, 41505 (2003).

[18] R. Mills. Self-diffusion in normal and heavy water in the range 1−45°C. *J. Chem. Phys.*, **77**, 685 (1973).

[19] A.K. Soper. The radial distribution functions of water and ice from 220 K to 673 K and at pressures up to 400 Mpa. *Chem. Phys.*, **258**, 121 (2000).

[20] J.M. Sorenson, G. Hura, R.M. Glaeser, T. Head-Gordon. What can x-ray scattering tell us about the radial distribution functions of water? *J. chem. Phys.*, **113**, 9149 (2000).

[21] M.V. Fernández-Serra, E. Artacho. Network equilibration and first principles liquid water. (2004), in press, preprint in arXiv:cond-mat/0407237 (2004)

[22] N. Giovambattista, F.W. Starr, F. Sciortino, S.V. Buldyrev, H.E. Stanley. Transitions between inherent structures in water. *Phys. Rev. E*, **65**(4), 041502 (2002).

[23] A.D. Becke. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A*, **38**, 3098 (1998).

[24] C. Lee, W. Yang, R.G. Parr. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B*, **37**, 785 (1988).

[25] J.P. Perdew, K. Burke, M. Ernzerhof. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.*, **77**, 3865 (1996).

[26] J. VandeVondele, F. Mohamed, M. Krack, J. Hutter, M. Sprik, M. Parrinello. To be published

[27] B. Hammer, L.B. Hansen, J.K. Norskov. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Phys. Rev. B.*, **59**, 7413 (1999).

[28] A. Eichler, J. Hafner. NO Reduction over Pt(100): Reaction rates from first principles. *Chem. Phys. Lett.*, **343**, 383 (2001).

[29] L.M. Molina, B. Hammer. Active Role of Oxide Support during CO Oxidation at Au/MgO. *Phys. Rev. Lett.*, **90**, 206102 (2003).

[30] J.P. Perdew. Accurate density functional for the energy: Real-space cutoff of the gradient expansion for the exchange hole. *Phys. Rev. Lett.*, **55**, 1665 (1985).

[31] J.P. Perdew, S. Kurth, A. Zupan, P. Blaha. Accurate density functional with correct formal properties: A step beyond the generalized gradient approximation. *Phys. Rev. Lett.*, **82**, 2544 (1999).

[32] A.D. Becke. Density-functional thermochemistry III. The role of exact exchange. *J. Chem. Phys.*, **98**, 5648 (1993).

[33] A.D. Becke. Density-functional thermochemistry IV. A new dynamical correlation functional and implications for exact-exchange mixing. *J. Chem. Phys.*, **104**, 1040 (1996).

[34] A.D. Becke. Density-functional thermochemistry V. Systematic optimization of exchange-correlation functionals. *J. Chem. Phys.*, **107**, 8554 (1997).

[35] W. Kohn, Y. Meir, D.E. Makarov. Van der Waals Energies in Density Functional Theory. *Phys. Rev. Lett.*, **80**, 4153 (1998).

[36] M. Dion, H. Rydberg, E. Schrder, D.C. Langreth, B.I. Lundqvist. Van der Waals density functional for general geometries. *Phys. Rev. Lett.*, **92**, 246401 (2004).

[37] Y. Zhang, W. Yang. Comment on "Generalized Gradient Approximation Made Simple". *Phys. Rev. Lett.*, **80**, 890 (1988).

[38] W. Kohn, L.J. Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, **140**, a1133 (1965).

[39] P. Hohenberg, W. Kohn. Inhomogeneous electron gas. *Phys. Rev.*, **136**, b864 (1964).

[40] N. Troullier, J.L. Martins. Efficient pseudopotentials for plane-wave calculations. *Phys. Rev. B*, **43**, 1993 (1991).

[41] L. Kleinman, D.M. Bylander. Efficacious form for model pseudopotentials. *Phys. Rev. Lett.*, **48**, 1425 (1982).

[42] P. Ordejón, E. Artacho, J.M. Soler. Self-consistent order-N density-functional calculations for very large systems. *Phys. Rev. B*, **53**, 10441 (1996).

[43] J.M. Soler, E. Artacho, J.D. Gale, A. García, J. Junquera, P. Ordejón, D. Sánchez-Portal. The Siesta method for ab initio order-N materials simulation. *J. Phys. Condens. Matter.*, **14**, 2745 (2002).

[44] J. Junquera, O. Paz, D. Sánchez-Portal, E. Artacho. Numerical atomic orbitals for linear-scaling calculations. *Phys. Rev. B*, **64**, 235111 (2001).

[45] E. Anglada, J.M. Soler, J. Junquera, E. Artacho. Systematic generation of finite-range atomic basis sets for linear-scaling calculations. *Phys. Rev. B*, **66**, 205101 (2002).

[46] M.P. Allen, D.J. Tildesley. *Computer simulation of Liquids*, Oxford University Press, (1987).

[47] M.W. Mahoney, W.L. Jorgensen. A five-site model for liquid water and the reproduction of the density anomaly by rigid, nonpolarizable potential functions. *J. Chem. Phys.*, **112**, 8910 (2000).

[48] H.J.C. Berendsen, J.R. Grigera, T.P. Straatsma. The missing term in effective pair potentials. *J. Chem. Phys.*, **91**, 6269 (1987).

[49] H.J.C. Berendsen, D. van der Spoel, R. van Drunen. GROMACS: A message-passing parallel molecular dynamics implementation. *Comp. Phys. Commun.*, **91**, 43 (1995).

[50] E. Lindahl, B. Hess, D. van der Spoel. GROMACS 3.0: A package for molecular simulation and trajectory analysis. *J. Mol. Mod.*, **7**, 306 (2001).

[51] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. DiNola, J.R. Haak. Molecular dynamics with coupling to an external bath. *J. Chem. Phys.*, **81**, 3684 (1984).

[52] C. Masciovecchio, S.C. Santucci, A. Gessini, S.D. Fonzo, G. Ruocco, F. Sette. Structural relaxation in liquid water by inelastic UV scattering. *Phys. Rev. Lett.*, **92**, 255507 (2004).