The Two Structures of Liquid Water from a Parameter-Free Real-Space Model: Isotropy, Directionality, and the Origin of LDL and HDL

Claes Johnson[1]

[1]KTH Royal Institute of Technology, Stockholm, Sweden , claesjohnson@gmail.com

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Mathematical formulation by the author; implementation and numerical experiments developed with AI assistance (Claude, Anthropic).

Abstract

Liquid water is widely modelled as a fluctuating mixture of two local structures: a low-density liquid (LDL) that is tetrahedral, open and ice-like in short range, and a high-density liquid (HDL) that is disordered and collapsed with an interstitial fifth neighbour. Whether real water genuinely realises two liquids is an experimental question; the mechanistic question underneath it is what molecular feature drives the tetrahedral LDL structure. We probe this with RealQM, a parameter-free real-space model in which each electron is a unit-charge component on a non-overlapping spatial domain. In its reduced form the water oxygen is a single, essentially isotropic electron cloud with two directional hydrogen donors. This model hydrogen-bonds; it holds an imposed tetrahedral ice lattice near-perfectly (tetrahedral order $q \approx 1$, coordination ≈ 4); it forms HDL under compression; but it never spontaneously forms LDL, giving instead a single broad, disordered, under-coordinated liquid at all sizes and densities tested. Attempts to add directional lone-pair acceptors by angularly splitting the oxygen cloud dissociate the hydrogen bond. The results converge on one statement: the same isotropy of the oxygen acceptor that permits hydrogen bonding is what prevents spontaneous tetrahedral ordering. Hence spontaneous LDL requires directional lone-pair *acceptors*, while HDL is the default isotropic-packing structure needing no directionality. The model accesses both structures for clear physical reasons but not their coexistence.

Keywords: liquid water; two-state model; LDL/HDL; tetrahedral order; hydrogen bonding; lone pairs; real-space quantum mechanics; parameter-free.

1 Introduction

A long-standing and recently revived picture of liquid water holds that it is, locally, a fluctuating mixture of two structures [1]. The *low-density liquid* (LDL) is tetrahedral, four-coordinated and open—the short-range order of ice carried into a diffusing liquid. The *high-density liquid* (HDL) is disordered and collapsed, with a fifth neighbour pushed into the first shell. Both are liquids: the split is *within* the liquid, not the solid–liquid distinction. In deeply supercooled water the two are hypothesised to become distinct phases separated by a liquid–liquid critical point.

Most evidence for the two-state model comes from empirical water potentials (ST2, TIP4P/2005 and relatives) tuned to reproduce water, so a two-state signal there can be a property built into the potential. This motivates a *parameter-free* test. We do not attempt to settle whether real water has two liquids—a model this reduced cannot, as we show, even produce the coexistence. Instead we address the mechanistic question that sits underneath the debate: **what molecular feature drives the tetrahedral LDL structure?** A parameter-free model is well suited to this, because whatever it does or does not produce follows from physics rather than from fitting.

2 Model and method

RealQM represents the N-electron state as a sum of one-electron components, each carrying unit charge on a non-overlapping domain of physical space separated by free (Bernoulli) boundaries; the ground state minimises the standard Coulomb energy over both the components and the domain partition [2]. Spatial exclusion replaces wave-function antisymmetry, and cost is set by a fixed grid rather than by the electron count. The implementation is a browser WebGPU code using a shared field with a per-cell domain label, which is what allows hundreds of atoms on a laptop.

Reduced water. Each water is an oxygen carrying a screened valence kernel (effective charge $+2$, a short core cutoff r_c) with a single two-electron cloud, plus two hydrogens each a unit proton with one electron. The molecular geometry is held near 104.5° by soft harmonic bond-length and bend restraints. The oxygen cloud is thus essentially *isotropic*: it presents electron density in all directions and carries no built-in lone-pair lobes. Crucially, the two O–H bonds are *directional*: they aim at neighbours and provide directional *donors*.

Order parameters. For every interior oxygen we compute two standard local descriptors from the running oxygen positions: the tetrahedral order

$$q = 1 - \tfrac{3}{8} \sum_{j<k} \left(\cos\theta_{jk} + \tfrac{1}{3}\right)^2$$

over its four nearest oxygen neighbours ($q \to 1$ perfect tetrahedron, $q \to 0$ disordered), and d_5, the distance to the fifth-nearest oxygen (large for the open tetrahedral LDL, small when an interstitial HDL neighbour intrudes). We also track the nearest-neighbour distance d_1 and the coordination number within 3.5 Å (liquid water ≈ 4, HDL ≈ 5). Histograms are accumulated over molecules and time; a bimodal q at fixed temperature would be the two-structure signature. To probe density we use a soft spherical confining wall (a disclosed modelling choice that sets only the average density, not the local structure); to probe temperature we use overdamped (Brownian) dynamics with a Langevin thermostat.

Directional-acceptor extension. To test whether directional lone pairs can be added, we extended the solver with an angular "shell split": the oxygen cloud is divided into sectors (two or three), each a component confined to its angular wedge about the shared nucleus, with the wedge frame tracking the molecule's instantaneous orientation. This is the natural way to give oxygen explicit directional acceptor lobes within the same formalism.

3 Results

3.1 The isotropic water hydrogen-bonds but under-coordinates

A relaxed dimer of reduced waters in a linear donor–acceptor geometry forms a stable hydrogen bond, with O–O settling near 3.0 Å and holding (the bond is real but on the weak, long side). In the liquid, however, the same water is markedly under-structured: confined near liquid density it is disordered, with coordination ≈ 2.6 and no tetrahedral population. A spherical oxygen accepts a proton from any direction, so it has no preference for the tetrahedral arrangement. Doubling the system from 64 to 128 waters (a larger interior core, roughly double the statistics) leaves the q histogram a single broad hump with no second peak.

3.2 Ice holds the tetrahedron

Placed on a diamond-cubic lattice (ice, O–O = 2.75 Å), the same isotropic water holds the tetrahedral arrangement near-perfectly: $q \approx 1$ and coordination ≈ 4. The reason is instructive: the two directional O–H *donors* supply half of the tetrahedral scaffold, which—together with the geometric restraints—is enough to keep an *imposed* lattice metastable, even though the isotropic acceptor cannot help *choose* that lattice.

3.3 Melting disorders without densifying

Heating the ice at fixed volume (melting occurs near 1300 K in the model's internal units) drops the tetrahedral order from $q \approx 0.85$ toward 0.55, but coordination stays roughly constant near 3.3. Melting therefore *disorders* the liquid without *densifying* it: it does not produce HDL. HDL is a density effect, and a fixed volume cannot supply the required contraction.

3.4 Compression yields HDL

Reaching HDL requires the density axis. Compressing the liquid (stepping the confining wall inward at fixed temperature) forces a fifth neighbour into the first shell: coordination rises and d_5 collapses, while q stays low. The disordered, dense, isotropically-packed structure is exactly HDL, and the isotropic model produces it readily—no directionality needed.

3.5 Carved lone pairs dissociate the hydrogen bond

The natural remedy—give oxygen explicit directional acceptor lobes—was tried three ways: a three-fold split (with the higher oxygen kernel this implies) and a charge-neutral two-hemisphere split biased toward the acceptor side. In every case the dimer *dissociated* (O–O grew without bound), while the plain isotropic control stayed bound. The mechanism is clear: in this formalism the hydrogen bond is the donor proton binding to a single *coherent* acceptor cloud, and putting a free internal boundary through that cloud destroys the coherent density the proton was holding. The angular-split machinery itself is sound (validated on a single molecule); it is the water physics that resists.

4 Discussion

The experiments cohere into a single statement. Textbook water is tetrahedral because oxygen has both two directional *donors* (the O–H bonds) and two directional *acceptors* (the lone pairs). The

Experiment	Observation	Reading
Dimer, isotropic O	O–O holds $\sim$3.0 Å	the cloud binds
Liquid, isotropic O	disordered, coord. $\sim$2.6, no LDL	isotropic $\Rightarrow$ no tetra. preference
Carved lone pairs	O–O grows, dissociates	splitting breaks the bond
Ice (imposed lattice)	$q \approx 1$, coord. ≈ 4	donors hold an imposed tetrahedron
Melting (fixed volume)	q: 0.85$\rightarrow$0.55, coord. $\sim$3.3	disorders, cannot densify: not HDL
Compression	coord. up, d_5 collapses	HDL from density, no directionality

Table 1: Summary of the numerical experiments. Values are exploratory and qualitative; the pattern, not the third digit, is the result.

reduced RealQM water has the donors but an *isotropic* acceptor. That one difference reproduces the whole pattern: the model holds LDL/tetrahedral order when placed in it (ice, via the donors); it forms HDL when compressed (dense isotropic packing); and it cannot spontaneously choose LDL, because without a directional acceptor the open tetrahedral network is never favoured over dense packing.

The sharp conclusion is therefore about the *origin* of the two structures: *spontaneous LDL requires directional lone-pair acceptors; donor directionality is not sufficient.* Equivalently, **HDL is the "default" isotropic-packing structure and LDL is the special, acceptor-stabilised one.** The isotropy that permits hydrogen bonding at all is the same isotropy that denies the model a directional acceptor—binding and non-tetrahedrality are two faces of one property.

This also bears on the "lone pair" itself. The crisp picture of two equivalent tetrahedral lone pairs is a localized-orbital model, not a unique observable: photoelectron spectra place water's two highest occupied orbitals at different energies (not equivalent twins), and the electron density shows a smeared, acceptor-rich crescent rather than two sharp lobes. What is robustly observed is four-coordination and an anisotropic, acceptor-rich oxygen density. A faithful minimal model therefore needs *directional acceptance*, not literal "rabbit-ears"—and, as the split experiments show, that directionality cannot be obtained by fragmenting the acceptor cloud without losing the bond.

5 Extension: viscosity from shear

Viscosity gives an independent, transport-level test, and it connects directly to the hydrogen-bond picture: in water, viscous flow proceeds by hydrogen bonds *breaking* with old neighbours and *re-forming* with new ones as layers slide, so the activation energy for viscous flow is close to the hydrogen-bond energy. We measure it by non-equilibrium shear—a body force $F_x = m\gamma(y - y_c)$ drives a Couette-like flow—and read viscosity as η = stress/strain rate $\approx \gamma/(dv_x/dy)$ from the resulting velocity profile $v_x(y)$.

A well-known pitfall must be handled. Under a strong *local* thermostat each molecule reaches a terminal velocity set by the thermostat friction Γ rather than by the fluid, so F/v measures Γ, not η, and the profile is linear rather than parabolic. We turn this into a diagnostic by *separating* the two contributions through their response to the thermostat coupling. Weakening the thermostat fourfold ($\gamma_L : 0.02 \rightarrow 0.005$) moved the high-temperature plateau from $\approx 9 \times 10^{-3}$ to $\approx 5 \times 10^{-3}$ (model units)—it scales with Γ, identifying it as the thermostat floor—while the cold value barely changed ($1.5 \times 10^{-2} \rightarrow 1.2 \times 10^{-2}$), identifying the temperature-dependent part as genuine fluid viscosity. The spread across temperature widened accordingly (a factor $\approx 1.7 \rightarrow 2.4$): lowering the friction floor let the fluid thinning stand out.

The extracted fluid viscosity ($\approx 7 \times 10^{-3}$ model units at the cold liquid end, thinning toward the floor on heating) has the **correct sign**—water thins on heating—but a **shallow slope**, i.e. a small apparent activation energy. This is the expected signature of the reduced water's *weak, under-coordinated* hydrogen bonds: fewer and weaker bonds to break means a lower barrier to flow and a too-runny liquid, consistent with the coordination deficit found above. The result is in model units—absolute Pa·s would require a calibrated time step, which the model dynamics do not provide—and the temperature scale is itself uncalibrated (melting near $\sim$1300 "model-K"), so only the sign, the relative thinning, and the thermostat decomposition carry meaning. Within those honest limits a parameter-free model reproduces the qualitative viscosity of water and separates the fluid response from the thermostat friction floor by the floor's dependence on the thermostat coupling.

A finer decomposition follows the Maxwell relation $\eta \approx G_\infty \tau$ (instantaneous shear modulus times structural relaxation time), which distinguishes two ways a viscosity can be small: a *soft* network (small G_∞) or *fast* structural relaxation (small τ). Water is notable for the latter — it is stiff yet fluid, because hydrogen bonds re-route by fast, low-barrier concerted switching, and that switching is cheap precisely because the acceptor is angularly *soft*. This is the transport face of the very isotropy that denies LDL: an isotropic (maximally soft) acceptor forbids a tetrahedral preference (no spontaneous LDL) *and* enables facile partner-switching (low viscosity). The two signature behaviours — no spontaneous LDL, and anomalously low viscosity for the cohesion — are **dual consequences of one property**, the softness of the acceptor.

Extracting G_∞ and τ separately under a *driven* shear proved unreliable, however. Weakening the thermostat enough to expose the fluid response let the shear pump energy in faster than it was removed, and the system ran away in kinetic temperature — the classic non-equilibrium-MD *thermostat dilemma* (a strong thermostat controls temperature but dominates the measured friction; a weak one measures the fluid but loses temperature control). A clean separation of G_∞ and τ therefore requires the equilibrium Green–Kubo route (the stress-tensor autocorrelation, with no driving and no heating), which we leave as the proper next step. The qualitative transport result — correct-sign thinning above a thermostat friction floor, with a shallow (weak-bond) slope — is unaffected and stands.

6 Transport and elastic moduli: regime, not precise values

We attempted, in addition, to extract precise transport and elastic coefficients, and record the outcome honestly. The shear viscosity was accessible only qualitatively: a driven-shear measurement with a weak enough thermostat to expose the fluid response let the shear pump in energy faster than it was removed, so the system ran away in kinetic temperature (the non-equilibrium-MD thermostat dilemma). A static bulk modulus $K = \rho\, dP/d\rho$ from the virial pressure was dominated by *intramolecular* bond and exclusion stress — which, per unit volume, contributes a pressure $\propto \rho$ whose derivative overwhelms K — so the intermolecular liquid modulus could not be cleanly separated from per-atom total forces. Clean values would require equilibrium Green–Kubo (viscosity) and an energy–volume modulus $K = V\, d^2E/dV^2$ (compressibility), left as proper next steps.

Both quantities, however, came out in the correct qualitative *regime*, parameter-free: water is runny (small viscosity) and stiff (small compressibility, high bulk modulus), and the model reproduces both from complementary microscopic origins — an angularly *soft* acceptor that permits fast hydrogen-bond switching (low viscosity), and *hard*, non-overlapping electron domains that resist compression (low compressibility). Water is thus soft in one respect and hard in another, and RealQM produces both from Coulomb interaction and electron exclusion alone.

This regime-level result is arguably the physically relevant one. On macroscopic scales water behaves as an essentially incompressible fluid at low Mach number and, at high Reynolds number, a nearly inviscid one; its large-scale dynamics depend on these coefficients being *small* far more than on their exact values. That the precise coefficients proved elusive here is therefore consistent with, rather than contrary to, their macroscopic near-irrelevance: what matters is that a parameter-free microscopic model, with no tuning, places water in the correct small-viscosity/small-compressibility regime. The exact coefficients — hard to isolate here and largely immaterial to the macroscale flow — are a secondary concern.

7 Relation to DFT: capability versus ablation

It is fair to ask whether density-functional molecular dynamics (DFT-MD) could run this study. The question splits in two, with opposite answers.

Simulating liquid water of this size—yes, but expensively, and it is a hard case. Ab-initio DFT-MD of 32–128 waters is a standard, heavily-studied system. However, each step is a full self-consistent solve; structural statistics require tens to hundreds of picoseconds, i.e. 10^5–10^6 femtosecond-locked steps, placing such runs on high-performance clusters over days to weeks rather than on a laptop in minutes. Moreover DFT's water is itself problematic: common semi-local functionals give over-structured, sluggish water with the wrong density, and even qualitatively reasonable results require dispersion corrections and carefully chosen functionals. The LDL/HDL regime specifically lives in *deeply supercooled* water and demands long timescales, large systems and extensive sampling—which is precisely why the two-state model is studied predominantly with empirical potentials rather than DFT-MD.

The ablation experiment—no, not cleanly. The result here is not an accurate simulation of water but a *controlled ablation*: the directionality of the oxygen acceptor was toggled (isotropic cloud versus explicit split lobes) and its causal effect on tetrahedral ordering observed. DFT provides the fixed electronic structure of real oxygen; one cannot ask it, in a clean and controlled way, "what if oxygen had no lone pairs?" That single-feature knob—removing a physical ingredient and watching what it was doing—is a property of a cheap, tunable, parameter-free model, and it is what permits a causal statement about the driver of LDL.

The honest framing is therefore complementary rather than competitive. DFT would be more quantitatively accurate for the structure of real water; it cannot cheaply reach the supercooled two-state regime; and it structurally cannot perform the ablation. The reduced RealQM water is not competing on accuracy—it is a *conceptual microscope* that isolates mechanism at laptop cost.

8 Limitations

The model is deliberately reduced and the results are qualitative. The water is under-coordinated relative to real water, so it sits on the disordered/HDL side of the diagram; its hydrogen bonds are weak; the confining wall imposes an average density and can induce a density gradient; the dynamics gives diffusive model-time, not calibrated kinetics. Most importantly, *we never observe a bimodal q at a single temperature*—the signature of LDL/HDL coexistence. This is not a numerical shortfall but the central result: the reduced model cannot produce the coexistence, precisely because it lacks the directional acceptor that would let tetrahedral order compete with dense packing. Testing the two-state model itself would require a water that both hydrogen-bonds and carries a directional acceptor—which, we find, angular splitting cannot deliver in this formalism. That is the open problem this study isolates.

9 Conclusion

A parameter-free real-space model with an isotropic oxygen acceptor and directional hydrogen donors reproduces a coherent account of the two structures of water. It *holds* tetrahedral (LDL-like) order when that order is imposed, it *forms* HDL under compression, and it *never spontaneously forms* LDL. The unifying reason is that the oxygen acceptor is isotropic: this both enables hydrogen bonding and forbids a spontaneous tetrahedral preference, and attempts to carve in a directional acceptor break the bond. The study does not decide whether real water is two liquids; it identifies, without any fitted parameters, the molecular ingredient responsible for the tetrahedral structure—directional lone-pair acceptance—and reframes HDL as the default isotropic-packing state. Interactive versions of all experiments are public.

References

[1] Two-state / two-structure models of liquid water and the low-density / high-density liquid picture (LDL/HDL), and the hypothesised liquid–liquid transition in supercooled water. (General reviews of the two-state model.)

[2] C. Johnson. The RealQM programme is set out in three submitted articles: *Quantum Mechanics as Multiphase 3D Continuum Mechanics* (RealQM), submitted to the *Annales de la Fondation Louis de Broglie*; *A 3D Multiphase Continuum Computational Model for Atoms*, submitted to the *International Journal of Quantum Chemistry*; and *RealNucleus: Nuclear Binding as Dual Coulomb Confinement, without a Strong or Weak Force*, submitted to *Physics Essays*. Public code and an interactive gallery of all the experiments in the present work: `https://claes542.github.io/RealMolecule/gallery.html` (source repository: `https://github.com/Claes542/RealMolecule`).