

Towards an analytical model of water: The octupolar model

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NOTES

Towards an analytical model of water: The octupolar model

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Analytic models with explicit, closed form expressions for thermodynamic and structural properties can be very useful in understanding the nature of some important processes such as solvation and solvation dynamics.

In particular, due to its important role in many physical, chemical and biological processes, water has been the subject of numerous works and a number of excellent studies of effective intermolecular potential models exist.¹⁻⁷ In these models, the water molecule is represented as a sphere with Lennard-Jones interaction containing a number of charges or force centers, which create directional forces to emulate the hydrogen bonding of water. An important recent addition has been the polarizability.⁸

A simple model potential that can be solved in the invariant expansion formalism⁹ was proposed by Bratko, Blum and Luzar (BBL).¹⁰ It consists of hard spheres with an embedded dipole and a tetrahedral octupolar attractive well with an angular part of the form

$$v(\theta, \phi) = A(r) \cos \theta \sin^2 \theta \cos 2\phi$$

and an electrostatic dipole-dipole interaction term. Analytic methods that we use are, of course, suitable for treatment of quite general potentials including an arbitrary number of angular components and possibly a soft spherical repulsion. The model system consists of N hard spheres of diameter σ and number density $\rho = N/V$ in a volume V . Each sphere has an embedded point dipole of moment μ . The center of sphere i is at position $\mathbf{R}_i = (\mathbf{x}, \mathbf{y}, \mathbf{z})$ and its orientation $\mathbf{\Omega}_i = (\phi, \theta, \psi)$.

The interaction between particles has a core contribution, a dipolar part and sticky terms of octupolar symmetry:

$$u(\mathbf{1}, \mathbf{2}) = u^{\text{SPHER}}(\mathbf{1}, \mathbf{2}) + u^D(\mathbf{1}, \mathbf{2}) + u^S(\mathbf{1}, \mathbf{2}), \quad (1)$$

where

$$u^{\text{SPHER}}(\mathbf{1}, \mathbf{2}) = \begin{cases} \infty & R_{12} < \sigma \\ K \exp[-zR_{12}]/R_{12} & R_{12} > \sigma, \quad z = \text{complex} \end{cases} \quad (2)$$

$$u^D(\mathbf{1}, \mathbf{2}) = \sqrt{\frac{10}{3}} \frac{\mu^2}{R_{12}^3} \hat{\Phi}^{112}(\mathbf{\Omega}_1, \mathbf{\Omega}_2, \mathbf{\Omega}_R), \quad (3)$$

and $u^S(\mathbf{1}, \mathbf{2})$ is the angular dependent surface adhesion that is a generalization of Baxter's sticky potential.¹¹ In these equations, R_{12} and $\mathbf{\Omega}_R$ denote the magnitude and orientation of the vector $\mathbf{R}_{12} = \mathbf{R}_1 - \mathbf{R}_2$, respectively, and we use the rotational invariants $\hat{\Phi}^{mnl}(\mathbf{\Omega}_1, \mathbf{\Omega}_2, \mathbf{\Omega}_R)$.⁹

The simplest sticky interaction model requires that the correlation function $h(\mathbf{1}, \mathbf{2})$ be of the form

$$\begin{aligned} h(\mathbf{1}, \mathbf{2}) = & -1 + \lambda^{000} \delta(R_{12} - \sigma) \\ & + [\lambda^{033} \hat{\Phi}_{22}^{033} + \lambda^{303} \hat{\Phi}_{22}^{303}] \xi_3(R_{12} - \sigma^-) \\ & + [\lambda^{312} \hat{\Phi}_{20}^{312} + \lambda^{132} \hat{\Phi}_{02}^{132}] \xi_2(R_{12} - \sigma^-) \\ & + [\lambda^{112} \hat{\Phi}^{112}] \xi_2'(R_{12} - \sigma^-), \quad R_{12} < \sigma, \end{aligned} \quad (4)$$

where $\delta(x)$ is Dirac's delta and $\xi_2(x)$, $\xi_2'(x)$, and $\xi_3(x)$ are also singular functions, related to $\delta(x)$. The explicit angular dependence of the rotational invariants has been omitted for simplicity. This model is solved analytically in the sticky limit of an infinitely narrow tetrahedral well.¹² A new solution of the factored Ornstein-Zernike equation for the sticky multipole model, as a set of coupled nonlinear equations in the sticky parameters was recently found. The sticky parameters of the pair correlations are treated as free parameters for the time being. The actual value depends on the closure that is chosen. A detailed discussion of this point is left for a future publication. The solution depends on the inversion of a 9 by 9 matrix, but the inverses are expressed in terms of the inverses of 3 by 3 matrices.¹³

One of the important questions for the usefulness of such an analytical approach is how many harmonics in the invariant expansion are needed for a proper representation of the properties of water. We know from symmetry⁹ that the lowest harmonic to be able to generate a tetrahedral geometry is the Y_2^3 spherical harmonic, so that the lowest term in the invariant expansion must be the octupolar one.

To establish this point the model was studied in 1985 by Monte Carlo simulation.¹⁰ However, in spite of considerable efforts, we were never able to reproduce the $g_{\text{OH}}(r)$ and $g_{\text{HH}}(r)$ functions to the then existing ones by Narten *et al.*¹⁴ It is now agreed that these functions are not correct. How-

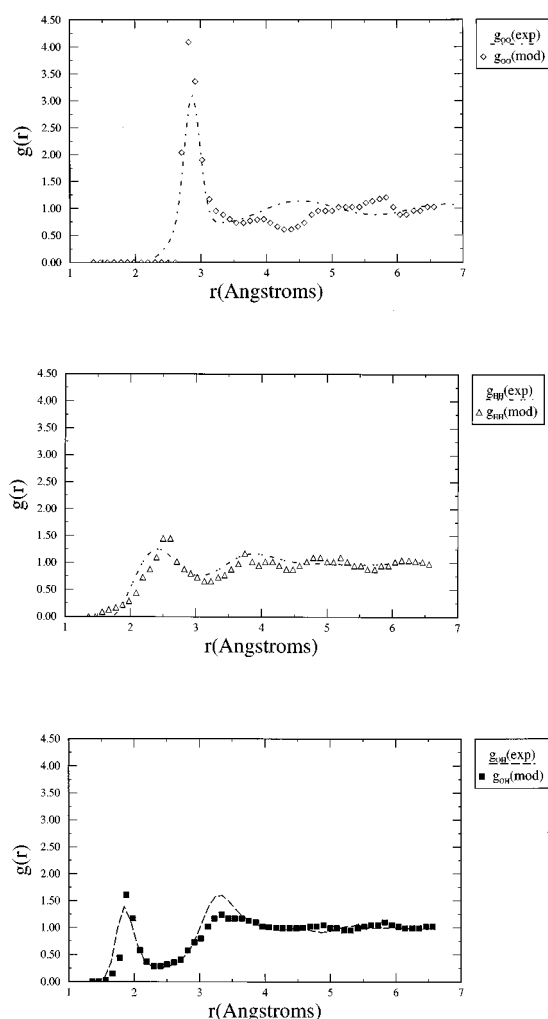


FIG. 1. Comparison of the pair correlation functions of Soper and Phillips to the BBL model. A slight shift of -0.1 Å was made to account for the fact that in BBL the core and not the center of the attractive well was adapted to the diameter of water.

ever, the agreement with the neutron diffraction data of Soper and Phillips¹⁵ is excellent for $g_{OH}(r)$ and $g_{HH}(r)$ (considering the simplicity of the model) as shown in Figs. 1(a), 1(b), 1(c). In these figures we see a comparison of the SP1 potential of this work to the correlation functions.

The agreement is not so good for $g_{OO}(r)$, but this has to do with the fact that a hard core potential is used for the spherical part of the simulation, which is a convenient but not essential part of the analytically solvable potential.

We show that our model can reproduce the nonspherical correlation functions of water quite well. The model has been found equally successful in describing solvation of simple ions in solution.¹⁶ In previous work we have shown that an exceedingly simple model of polar-polarizable with directional stickiness gives excellent dielectric constants in the MSA with little parameter adjustment.¹⁷ We believe that this is a clear indication that at least for the thermodynamic properties of water the invariant expansion up to octupoles is sufficient and that the coupling of the octupoles to the dipoles is relatively weak. The main discrepancies arise in the $g_{OO}(r)$, where an extra bump appears at the distance twice the hard core diameter, rather than at a shorter distance. This is a (mathematical) consequence of the use of hard core sticky potentials. The proper treatment should therefore include a soft spherical part, which however will include non-linear contributions due to octupole-octupole interactions. Higher multipole terms will sharpen the geometry and soft core repulsion should improve the model in terms of its agreement with diffraction pair distribution functions. Both will be our projects for the future.

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