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Experimental Investigation of Triplet Correlation Approximations for Fluid Water

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Abstract

Triplet correlations play a central role in our understanding of fluids and their properties. Of particular interest is the relationship between the pair and triplet correlations. Here we use a combination of Fluctuation Solution Theory and experimental pair radial distribution functions to investigate the accuracy of the Kirkwood Superposition Approximation (KSA), as given by integrals over the relevant pair and triplet correlation functions, at a series of state points for pure water using only experimental quantities. The KSA performs poorly, in agreement with a variety of other studies. Several additional approximate relationships between the pair and triplet correlations in fluids are also investigated and generally provide good agreement for the fluid thermodynamics for regions of the phase diagram where the compressibility is small. A simple power law relationship between the pair and triplet fluctuations is particularly successful for state points displaying low to moderately high compressibilities.

Keywords

Triplet Correlations; Fluctuation Solution Theory; Kirkwood Superposition Approximation; radial distribution function; fluid thermodynamics

1. Introduction

Our current understanding of fluids generally involves a series of n -body correlation functions, $g_{\alpha\beta\dots}^{(n)}(r_1, r_2, \dots, r_n)$, which quantify the relative probability of observing particle 1 of type α at position r_1 , etc., as obtained after appropriate averaging over all other particles in the system [1–3]. While it is well known that knowledge of the pair correlation function (and a pairwise potential) is sufficient to provide the thermodynamic properties of a fluid at a particular state point [3], the true pair correlation function for fluids is generally unavailable using current theoretical approaches. However, a series of hierarchies – the

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Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy being one example [4] – have demonstrated that the n -body correlations in fluids are related to integrals over the $n+1$ -body correlations. Hence, if the triplet correlations can be expressed in terms of the pair correlations, then one can solve for the pair correlations, and thereby the thermodynamic properties of the fluid. This type of approach lies at the heart of many theories of fluids [3]. Triplet correlations are therefore central to our understanding of fluids. Furthermore, triplet correlations also play a crucial role in the pressure and temperature derivatives characterizing fluid thermodynamics and scattering behavior [5–8], the development of accurate Equations of State [9], the phase behavior of fluids [10, 11], and in common expansions of the density, the pair correlation function, and the fluid entropy [3, 12–14].

Unfortunately, our ability to determine triplet (and higher) correlations from experiment is quite limited [10, 15]. Hence, the exact relationship between the triplet and pair distributions, if there is one, is still the subject of some debate. By far the most common approximation in this regard is that of Kirkwood [16]. However, its frequent use does not necessarily reflect the accuracy of the approximation, but merely the simple nature of the approach and the historical significance. The Kirkwood superposition approximation (KSA) for the triplet correlation function in terms of the pair correlation functions is given by [3, 16],

$$g_{111}^{(3)}(r_1, r_2, r_3) = g_{11}^{(2)}(r_1, r_2)g_{11}^{(2)}(r_1, r_3)g_{11}^{(2)}(r_2, r_3) \quad (1)$$

for a pure fluid (1). Alternatively, the KSA expressed in terms of the n -body potentials of mean force (pmf), $W_{\alpha\beta\dots}^{(n)}(r_1, r_2, \dots, r_n)$, is given by [3],

$$W_{111}^{(3)}(r_1, r_2, r_3) = W_{11}^{(2)}(r_1, r_2) + W_{11}^{(2)}(r_1, r_3) + W_{11}^{(2)}(r_2, r_3) \quad (2)$$

where $W_{\alpha\beta\dots}^{(n)}(r_1, r_2, \dots, r_n) = -k_B T \ln g_{\alpha\beta\dots}^{(n)}(r_1, r_2, \dots, r_n)$, k_B is the Boltzmann constant, and T the absolute temperature. The KSA has been derived using a variety of approaches [17, 18], and its validity has been extensively reviewed [19, 20]. Clearly, the KSA assumes the triplet pmf is pairwise additive. While this is (usually) a good approximation for the potential energy, pairwise additivity for the pmf is more debatable [21]. Indeed, the general consensus is that the KSA represents a rather poor approximation for the triplet distribution [20], especially for short molecular distances [22–24], and there have been many attempts to improve upon it [19, 20]. However, due to the absence of substantial experimental data concerning the triplet correlations, these conclusions have primarily relied on theoretical and simulation data for simple model fluids, such as hard sphere virial coefficients, or the comparison between simulated pair and triplet correlation functions.

There is some experimental data concerning triplet correlations provided by diffraction studies. Here, the variation of the fluid structure factor with pressure is investigated and related to a single integral over the corresponding triplet correlation function [7, 25–27]. More recently, this analysis has involved a combination of experimental and simulation

based approaches [28, 29]. The triplet correlations displayed by the simulations can then be examined further to provide additional detail. This has the advantage that more complex fluids can be studied using real experimental data. However, the difficulty of obtaining scattering data, and the requirement of finite difference pressure derivatives of the structure factor, has limited the number of systems and state points that have been studied.

Some time ago, Buff and Brout presented a simple method to test the KSA using just experimental data [30]. Their approach focused upon relationships between integrals over the pair and triplet correlation functions and thermodynamic pressure derivatives of the fluid density. Using the pair correlation function from experimental scattering data one can then determine the effect of the KSA while avoiding the need for numerical derivatives. Unfortunately, to our knowledge, this was only applied to one system at one state point – liquid Argon at 92 K and 2 atm. The main advantages of this type of approach are that one obtains a single integrated measure of the quality of the KSA as judged by the fluid thermodynamics using just experimental data (see below for more details). The major disadvantage is that no spatial information is provided. It is well known that the thermodynamics are sensitive to the long range behavior of the pair correlation function [5, 6]. Hence, even when significant differences are observed in the KSA for the triplet distribution at close distances, the overall effect on the fluid thermodynamics may actually be negligible if the long range behavior of the correlation function is correct.

In a series of recent studies, we have been investigating triplet correlations in fluids and liquid mixtures as characterized by the triplet fluctuations observed for an open system [14, 31–34]. This has involved the use of Fluctuation Solution Theory (FST) [35], an extension of the Kirkwood-Buff (KB) theory of solutions [36], to relate the thermodynamic properties of fluids to the fluctuations expected for an equivalent system in the Grand Canonical Ensemble (GCE). This parallels the approach used by Buff and Brout [30]. Here, we extend this approach to investigate the validity of the KSA for a complex fluid (water) at a series of state points. In addition, we investigate a variety of alternative approximations relating the pair to the triplet (and quadruplet) integrals and fluctuations in order to determine their validity. All of these approaches require only experimental data and help to provide a deeper understanding of the role of triplet correlations in fluid thermodynamics.

2. Theory

In the FST approach, a series of thermodynamic properties (derivatives) characterizing a fluid are expressed in terms of the particle fluctuations for an equivalent system open to matter exchange. The main fluctuating quantities of interest here are provided by [14],

$$b_{11} \equiv \frac{\langle (\delta N_1)^2 \rangle}{\langle N_1 \rangle} = 1 + \rho_1 G_{11}$$

$$c_{111} \equiv \frac{\langle (\delta N_1)^3 \rangle}{\langle N_1 \rangle} = 1 + 3\rho_1 G_{11} + \rho_1^2 G_{111} \quad (3)$$

$$d_{1111} \equiv \frac{\langle (\delta N_1)^4 \rangle - 3\langle (\delta N_1)^2 \rangle^2}{\langle N_1 \rangle} = 1 + 7\rho_1 G_{11} + 6\rho_1^2 G_{111} + \rho_1^3 G_{1111}$$

where $\rho_1 = \langle N_1 \rangle / V$ is the average number density, V is volume, $\delta N_1 = N_1 - \langle N_1 \rangle$ denotes a fluctuation in the number of molecules N_1 for each member of the ensemble, and the angular brackets denote an ensemble average for the GCE. The above fluctuating quantities are essentially the cumulants of the particle probability distribution for the equivalent GCE. The second equalities in Eq. (3) express these fluctuations in terms of integrals over a series of GCE n -body correlation functions defined according to [14],

$$G_{11} \equiv V^{-1} \int [g_{11}^{(2)} - 1] dr_1 dr_2$$

$$G_{111} \equiv V^{-1} \int [g_{111}^{(3)} - 1 - 3(g_{11}^{(2)} - 1)] dr_1 dr_2 dr_3 \quad (4)$$

$$G_{1111} \equiv V^{-1} \int [g_{1111}^{(4)} - 1 - 4(g_{111}^{(3)} - 1) - 3(g_{11}^{(2)} - 1)(g_{11}^{(2)} - 1) + 6(g_{11}^{(2)} - 1)] dr_1 dr_2 dr_3 dr_4$$

where the integrations are over molecule positions and, for simplicity, the molecule position indices have been omitted from the correlation function notation. Note that the molecular orientations do not appear in these integrals as the correlation functions correspond to those between the molecular centers of mass after averaging over their molecular orientations, and after averaging over the positions and orientations of all other molecules in the system.

The above fluctuations can be expressed in terms of pressure derivatives of the density according to [14],

$$b_{11} = k_B T \rho_1' = \rho_1 k_B T \kappa_T$$

$$c_{111} = (k_B T)^2 [\rho_1 \rho_1'' + (\rho_1')^2] \quad (5)$$

$$d_{1111} = (k_B T)^3 [\rho_1^2 \rho_1''' + 4\rho_1 \rho_1' \rho_1'' + (\rho_1')^3]$$

where the prime indicates an isothermal derivative with respect to pressure (p), and κ_T is the isothermal compressibility. Consequently, if the density derivatives are known – usually from an accurate Equation of State – then experimental values for the fluctuations can be determined and subsequently provide the integrals described in Eq. (4).

Hence, the above equations relate the thermodynamics of the fluid to integrals over the corresponding correlation functions that describe the structure of the fluid. The integrals in Eq. (4) take the same form as the integrals in McMillan-Mayer (MM) theory and the theory of imperfect gases [37, 38]. However, while the integrals in these theories are only applicable at low solute and gas densities, respectively, the integrals described here can also be used in pressure or density expansions for high density fluids. The pressure derivatives of the above integrals are given by [14],

$$k_B T G'_{11} = G_{111} - 2G_{11}^2$$

$$(k_B T)^2 G''_{11} = G_{1111} - 7G_{111}G_{11} + 8G_{11}^3 \quad (6)$$

$$k_B T G'_{111} = G_{1111} - 3G_{111}G_{11}$$

The pressure derivatives are clearly related to integrals over higher correlation functions for the fluid. The above expressions correspond to the (fully) integrated versions of the well-known recursive relationships between the probability density distribution functions [5, 7, 39, 40],

$$k_B T \left(\frac{\partial [\rho_1^n g^{(n)}]}{\partial p} \right)_T = \rho_1 k_B T \kappa_T \left(\frac{\partial [\rho_1^n g^{(n)}]}{\partial p_1} \right)_T = n \rho_1^{n-1} g^{(n)} + \rho_1^n \int [g^{(n+1)} - g^{(n)}] dr_{n+1} \quad (7)$$

which can also be written in terms of just the spatial correlation functions,

$$k_B T \left(\frac{\partial g^{(n)}}{\partial p} \right)_T = \rho_1 k_B T \kappa_T \left(\frac{\partial g^{(n)}}{\partial p_1} \right)_T = \int [g^{(n+1)} - g^{(n)}(n g^{(2)} - n + 1)] dr_{n+1} \quad (8)$$

where the integration is over the molecular positions.

The expressions in the previous sections indicate that integrals over the pair, triplet and quadruplet distributions can be obtained from experiment. This provides a route for testing

approximations for $g_{111}^{(3)}$, such as the KSA, using purely experimental data for real liquids, both simple and complex. This type of approach was established by Buff and Brout [30], and is extended here. The accuracy of the KSA can be quantified by the difference between the triplet or quadruplet correlations and their pairwise analogues. Hence, we define,

$$\Delta g_{111}^{(3)} \equiv g_{11}^{(2)}(r_1, r_2)g_{11}^{(2)}(r_1, r_3)g_{11}^{(2)}(r_2, r_3) - g_{111}^{(3)}(r_1, r_2, r_3)$$

$$\Delta g_{1111}^{(4)} \equiv g_{11}^{(2)}(r_1, r_2)g_{11}^{(2)}(r_1, r_3)g_{11}^{(2)}(r_1, r_4)g_{11}^{(2)}(r_2, r_3)g_{11}^{(2)}(r_2, r_4)g_{11}^{(2)}(r_3, r_4) - g_{1111}^{(4)}(r_1, r_2, r_3, r_4) \quad (9)$$

where the expressions would be zero when the KSA and the analogous four-body approximations hold, respectively. It should be noted that this particular approximation for $g_{1111}^{(4)}$ only involves the pair correlations and is the logical extension of Eq. (2) to represent the four body pmf. However, there are many alternative approximations relating the quadruplet distributions to various combinations of the triplet and pair distributions, which are typically more useful in traditional integral equation approaches [17, 18, 20].

A comparison of the approximate and real distributions is facilitated by using the same functional form for the virial coefficients used to describe imperfect gases or osmotic solutions [3, 38]. The first few virial coefficients we require are given by the expressions [38],

$$B_2^* = -\frac{1}{2}G_{11}$$

$$B_3^* = -\frac{1}{3}[G_{111} - 3G_{11}^2] \quad (10)$$

$$B_4^* = -\frac{1}{8}[G_{1111} - 12G_{111}G_{11} + 20G_{11}^3]$$

where we have used an asterisk to indicate these expressions are valid for any density and are therefore different from the usual low density (gas or solute) forms. Using the same manipulations as performed for the traditional virial coefficients, the third virial coefficient using the KSA can then be written [3],

$$B_{3, KSA}^* = -\frac{1}{3}I_0 = -\frac{1}{3}V^{-1} \int [h_{11}^{(2)}(r_1, r_2)h_{11}^{(2)}(r_1, r_3)h_{11}^{(2)}(r_2, r_3)]dr_1dr_2dr_3 \quad (11)$$

in terms of the total correlation function $h_{11}^{(2)} = g_{11}^{(2)} - 1$. Hence, we can evaluate the difference between the real triplet correlations and the KSA via,

$$\Delta G_{111} \equiv G_{111}^{\text{KSA}} - G_{111} = V^{-1} \int \Delta g_{111}^{(3)} dr_1 dr_2 dr_3 = -3(B_{3,\text{KSA}}^* - B_3^*) \quad (12)$$

The above (integrated) quantity provides a single measure of the accuracy of the KSA. If $G_{111} > 0$ then the KSA results in a net increase in the triplet correlations compared to the real distribution, and *vice versa*. The integral does not provide information concerning the accuracy as a function of distance, and clearly there may be some cancellation upon integration. Nevertheless, this approach eliminates the necessity for theoretical or simulation data and therefore avoids the assumption that these approaches are sufficiently accurate for analysis.

To evaluate the third virial coefficient using the KSA one requires additional experimental data. Specifically, the experimental pair correlation as a function of distance, or radial distribution function (rdf), is needed. This can be obtained from the experimental structure factor, $S(k) = 1 + \rho_1 H_{11}(k)$, or the total correlation function, via Fourier transforms valid for isotropic liquids [41],

$$H_{11}(k) = \int_0^\infty h_{11}^{(2)}(r) \sin(kr) (kr)^{-1} 4\pi r^2 dr$$

$$h_{11}^{(2)}(r) = (2\pi)^{-3} \int_0^\infty H_{11}(k) \sin(kr) (kr)^{-1} 4\pi k^2 dk \quad (13)$$

where k is the corresponding wavevector. The KSA expression for the third virial coefficient is then given by the fact that [30],

$$I_0 = (2\pi)^{-3} \int_0^\infty [H_{11}(k)]^3 4\pi k^2 dk \quad (14)$$

via the convolution-correlation theorem [42]. Hence, one can compare the third virial coefficient obtained experimentally from the thermodynamic data to that obtained via the KSA using only pair correlations to determine the integrated difference indicated in Eq. (12). This avoids the need to determine finite difference approximations for derivatives corresponding to changes in the structure factor with pressure, as required by other experimental approaches.

We can also investigate the severity of the KSA for four body correlations. A simple way to evaluate this is to determine the pressure dependence of the KSA for the three body correlations. To achieve this we define,

$$\Delta G_{1111} \equiv G_{1111}^{\text{KSA}} - G_{1111} = V^{-1} \int [\Delta g_{1111}^{(4)} - 4\Delta g_{1111}^{(3)}] dr_1 dr_2 dr_3 dr_4 \quad (15)$$

Then, if we take pressure derivatives of G_{111} for the experimental and KSA approach given by the expressions provided in Eq. (6) one finds,

$$\Delta G_{1111} = k_B T \left(\frac{\partial \Delta G_{111}}{\partial p} \right)_T + 3\Delta G_{111} G_{11} \quad (16)$$

which provides access to G_{1111} . The difference between the real and KSA for the four (and three) body correlations is related to the difference in the fourth virial coefficients via,

$$\Delta G_{1111} - 12\Delta G_{111} G_{11} = -8(B_{4,KSA}^* - B_4^*) \quad (17)$$

Unfortunately, the fourth virial coefficient under the KSA does not simplify as easily as the third virial coefficient. Indeed, the fourth virial coefficient involves several terms [38],

$$B_{4,KSA}^* = -\frac{1}{8}(3I_1 + 6I_2 + I_3)$$

$$I_1 = V^{-1} \int [h_{11}^{(2)}(r_1, r_2) h_{11}^{(2)}(r_2, r_3) h_{11}^{(2)}(r_3, r_4) h_{11}^{(2)}(r_1, r_4)] dr_1 dr_2 dr_3 dr_4$$

$$I_2 = V^{-1} \int [h_{11}^{(2)}(r_1, r_2) h_{11}^{(2)}(r_2, r_3) h_{11}^{(2)}(r_3, r_4) h_{11}^{(2)}(r_1, r_4) h_{11}^{(2)}(r_1, r_3)] dr_1 dr_2 dr_3 dr_4 \quad (18)$$

$$I_3 = V^{-1} \int [h_{11}^{(2)}(r_1, r_2) h_{11}^{(2)}(r_2, r_3) h_{11}^{(2)}(r_3, r_4) h_{11}^{(2)}(r_1, r_4) h_{11}^{(2)}(r_1, r_3) h_{11}^{(2)}(r_2, r_4)] dr_1 dr_2 dr_3 dr_4$$

only one of which can be easily obtained from the experimental structure factor,

$$I_1 = (2\pi)^{-3} \int_0^\infty [H_{11}(k)]^4 4\pi k^2 dk \quad (19)$$

via the convolution-correlation theorem.

The fluid fluctuations can also be expressed in terms of integrals over the analogous direct correlation functions [43], and relationships between the pair and higher order direct

correlation functions also exist [44]. Furthermore, approximations for the direct correlation function, such as the Percus-Yevick (PY) and Hypernetted Chain (HNC), lead to a variety of integral equations that can be solved numerically [3]. However, there are several reasons we have not pursued that approach here. Primarily, the PY and HNC approaches also require a suitable (pair) potential between molecules. In general, this potential is unknown and would therefore introduce an element of uncertainty that is avoided in the present approach.

3. Methods

The experimental thermodynamic data for pure water as a function of pressure and temperature were determined using the IAPWS-95 Equation of State, developed by Wagner and Pruss [45], as implemented in the National Institute of Standards and Technology (NIST) Standard Reference Database 10: NIST/American Society of Mechanical Engineers Steam Properties Database version 2.22 [46]. The source code provides the required first and second density derivatives as a function of pressure and temperature via a simple subroutine call. Third density derivatives were obtained numerically via a finite difference approach using the second derivatives and a value of $dp = \pm 10^{-20}$ bar. Calculations were performed in quadruple precision.

There are many experimental scattering studies of liquid water in the literature and these have been reviewed by Head-Gordon and Hura [47]. Here, the rdf data for liquid and supercritical water were taken from the neutron scattering studies of Soper and coworkers [48]. The rdfs for a variety of pressures and temperatures are provided, after refinement using computer simulation data in an iterative procedure. In addition, raw X-ray scattering data were also used to provide an indication of the effects of possible experimental errors [49]. The exact state points considered here are indicated in Fig. 1, where we also include the values of b_{11} for the gas, liquid and supercritical regions.

Experimental scattering data suffer from technical issues at low and high scattering amplitudes [50, 51]. Scattering at high amplitudes represents a relatively unimportant contribution to the thermodynamic properties, however scattering at low amplitudes plays a significant role. Fortunately, the limiting value of $H_{11}(k)$ can be checked for consistency by noting that $S(0) = 1 + r_1 H_{11}(0) = 1 + r_1 G_{11} = r_1 k_B T k T = b_{11}$ for simple molecules such as water [52]. To ensure consistency between the thermodynamic and scattering data we have modified the low scattering behavior to obey the Ornstein-Zernike approximation – which has been demonstrated to hold even close to the critical point [53] – as given by,

$$S(k)/S(0) = 1 + ak^2 + bk^4 \quad (20)$$

for small k values. The a and b parameters were obtained after fitting k values between 10–20 nm⁻¹. Other approaches are available to ensure correct behavior of the structure factors and/or rdfs [51, 54–56], although many of these require a knowledge of the intermolecular potential. As the above equation resulted in good fits to the experimental structure factors for all but the $T = 673$ K and $p = 500$ bar state point, which lies closest to the critical point ($T = 647.096$ K and $p = 220.64$ bar) [45], we adopted the simple approach provided by Eq. (20).

We will refer to these modified structure factors as being thermodynamically consistent, *i.e.* they provide the correct values of G_{11} . The integrals described in Eqs. (13), (14) and (19) were determined using discrete numerical Fourier transforms. The rdFs extend to 1.5 nm using 500 observations (n_{pt}) with intervals (dr) of 0.003 nm which provides a maximum k value of 333 nm^{-1} and intermediate k values that satisfy $n_{pt} dr dk = 1$.

To determine the value of G_{1111} we need to evaluate the derivative indicated in Eq. (16). This was achieved by fitting the G_{111} values to a simple low order polynomial,

$$\Delta G_{111} = c_0 + c_1 p + c_2 p^2 \quad (21)$$

where the last term was dropped for the limited data available for the $T = 298$ and 423 K isotherms. This provides reasonable derivatives for points not too close to the critical point. The state points located at $T = 673 \text{ K}$ and $p = 500 \text{ bar}$ and $T = 573 \text{ K}$ and $p = 100 \text{ bar}$ were also dropped to ensure reasonable fits were obtained using the above low order polynomial.

4. Results

The behavior of the pair fluctuations, b_{11} , in the liquid and supercritical regions of the water p - T phase diagram is illustrated in Fig. 1. Also included are the state points corresponding to the rdFs used here. The magnitude of b_{11} increases as one approaches the critical point, whereas b_{11} decreases with increasing pressure along the isotherms for the state points considered here. For comparison, $b_{11} = 1$ for an ideal gas and is approximately 0.01 for ice [14, 57, 58]. A detailed FST analysis of the fluid thermodynamics is provided in Tables 1 and 2. The values of c_{111} indicate a negative skewness for the particle number distribution in the equivalent GCE, and therefore particle deletion is more favorable than addition on the average. For comparison, c_{111} is positive for gaseous water. Positive values for d_{1111} (the excess kurtosis) indicate the distribution is more peaked than a normal distribution and so smaller net deletions or insertions are favored over larger deletions or insertions. Both of these quantities decrease in magnitude as the pressure increases, *i.e.* the particle number distribution tends towards a normal distribution as T decreases and p increases. Indeed, the low temperature, high pressure, region of the phase diagram tends to the incompressible limit (IL), where $b_{11} = c_{111} = d_{1111} = 0$ (see Table 2), and the fluctuations correspond to that of a closed system. All the integrals contained in Eq. (3) contribute significantly to the corresponding fluctuating quantities for the state points considered here.

The experimental water oxygen-oxygen radial distribution functions used in this study are displayed in Fig. 2 as a function of temperature and pressure. As expected, they indicate reduced structure as the temperature increases. However, the pressure dependence is less straightforward. What is clear is that pressure changes lead to relatively small changes in the rdFs, even for the states closest to the critical point. The rdFs displayed in Fig. 2 were used to determine the corresponding structure factors, and the small k behavior of the structure factor was modified using Eq. (20) to ensure thermodynamic consistency at each state point. These modified structure factors were then used to determine the integrals in Eqs. (14) and (19). The results of this process are displayed in Figs. 3 and 4 for two of the state points. At

298 K and 1 bar the difference between the original and modified structure factors and rdfs is completely negligible. The differences at 423 K and 1900 bar are more significant. However, even here changes to the low k behavior of the structure factor have only small effects on the recalculated rdf. The effect on the third virial coefficient is sizable (not shown), but we consider the thermodynamically consistent structure factors to be more reasonable. Also shown in Figs. 3 and 4 are the partially integrated analogues of Eq. (14) where the integration is performed over all k values up to K . This plot illustrates the known large contributions to the third virial coefficient from the small k (or long r) behavior of the structure factor (or rdfs) [59], typically providing 110–120% of the total contribution, as obtained using the KSA.

The results of using the KSA for fluid water are summarized in Table 3. The experimental $G_{111} - 3G_{11}^2$ values are always negative and vary systematically with pressure along each isotherm. The corresponding KSA values are also generally negative, but display significantly less variation with temperature and pressure, especially closer to the critical point. The G_{111} values are typically negative – indicating an overall underestimation of the triplet correlations by the KSA – for state points away from the critical point. As we approach the critical point the errors become positive and significantly larger in magnitude suggesting the real triplet correlations are increasing much slower than the pair correlations. The (signed) percentage errors for the triplet KSA suggest that this is a poor approximation for the majority of state points investigated here, with similar errors to other studies of the KSA using alternative approaches [22, 60]. The errors indicated by G_{1111} generally display the opposite sign to that observed for G_{111} suggesting that either the quadruplet correlations were overestimated for state points away from the critical point, or G_{1111} is dominated by the error in the triplet correlations. The contribution of I_1 , as obtained from Eq. (19), to the fourth virial coefficient was typically of the same order of magnitude as the virial coefficient (data not shown), although this contribution dropped to essentially zero as one approached the critical point.

It is noticeable that the KSA values for $G_{111} - 3G_{11}^2$ do not always vary systematically with pressure, although the subsequent values for G_{111} are systematic. In an effort to determine how the above results may differ between different experimental determinations of the pair correlation function, we have compared a variety of results obtained for water at 298 K and 1 bar. These are presented in Fig. 5 and include the experimental Neutron diffraction rdf data currently used here (denoted by 2000) [48], together with a series of refinement results for the structure factor also obtained from the Soper group but via X-ray scattering (denoted by 2013a–c) [49]. All data were made thermodynamically consistent by fitting to Eq. (20). The data shown in Fig. 5 indicate that, while there were some differences between the structure factor datasets, the final integrated values of I_0 provided consistent results with one notable exception, 2013b. This exception corresponded to a data analysis procedure that was known to produce spurious results [49]. Hence, reasonable estimates for the structure factors produce consistent results for the KSA, yet the results are not so insensitive to the structure factors that there is no information. We conclude that the KSA estimates for I_0 are sufficiently accurate, although the exact degree of accuracy might vary between state points, and therefore the results displayed in Table 3 are meaningful.

The results for the KSA are not particularly encouraging. This conclusion is in agreement with a series of other studies using a variety of approaches [20, 30, 61]. The goal of the KSA was to relate the triplet and pair correlations in fluids. Here, we investigate a series of alternative approaches that can be used to achieve a similar goal. The first is based on an observation by Moelwyn-Hughes (MH) that the change in the bulk modulus with pressure along an isotherm is essentially a constant for many liquids over a wide range of state points [62]. While this is clearly an approximation, it provides a useful framework for a variety of treatments. Hence, one can write [14],

$$\mu \equiv \left(\frac{\partial \kappa_T^{-1}}{\partial p} \right)_T = 1 - \frac{\rho_1 \rho_1''}{(\rho_1')^2}$$

$$\mu' \equiv \frac{p}{Z} \left(\frac{\partial \mu}{\partial p} \right)_T = \frac{p}{Z} \frac{\rho_1''}{\rho_1'} \left[1 - 2\mu - \frac{\rho_1 \rho_1'''}{\rho_1' \rho_1''} \right] \quad (22)$$

where $Z = p/(\rho_1 k_B T)$ is the fluid compressibility factor, and the pressure derivatives μ and μ' are sufficient to relate the pair fluctuations and integrals to higher fluctuations and integrals (see below). The value of μ does vary with temperature (and pressure) for real fluids, but only slightly (see Table 1). The MH approach performs better at high pressures. However, not surprisingly, it is a poor approximation close to the critical point.

Using the above definitions in Eq. (5) provides [14, 33],

$$c_{111} = (2 - \mu) b_{11}^2$$

$$d_{1111} = (2 - \mu)(3 - 2\mu) b_{11}^3 - \mu' b_{11}^2 \quad (23)$$

Both expressions are exact if μ and μ' are evaluated at the state point of interest. Consequently, the triplet and quadruplet fluctuations (correlations) are then simply proportional to powers of the pair fluctuations. The corresponding relationships between the integrals are given by,

$$\rho_1^2 G_{111} = (1 - \mu) + (1 - 2\mu) \rho_1 G_{11} + (2 - \mu) \rho_1^2 G_{11}^2$$

$$\begin{aligned} \rho_1^3 G_{1111} = & - (1 - \mu)(1 + 2\mu) - \mu' + [3(1 - \mu)(1 - 2\mu) + 2(1 - \mu')] \rho_1 G_{11} \\ & + [3(2 - \mu)(1 - 2\mu) - \mu'] \rho_1^2 G_{11}^2 + (2 - \mu)(3 - 2\mu) \rho_1^3 G_{11}^3 \end{aligned} \quad (24)$$

They represent (un-truncated) power series in terms of the pair integrals. An additional advantage of the MH approach is that the value of μ can be related to the nature of the intermolecular potential [62, 63]. For instance, $\mu = \mu' = b_{11} = 0$ for an incompressible fluid, $\mu = b_{11} = 1$ and $\mu' = 0$ for an ideal gas resulting in a Poisson particle number distribution, $\mu = 2$ and $\mu' = 0$ corresponds to a Gaussian particle number distribution, $\mu = 8$ and $\mu' = 0$ for a 6–12 Lennard-Jones potential, while $\mu = 5$ –11 and $\mu' \approx 0$ for common liquids [63]. All terms in Eq. (24) appear to contribute significantly to the above expressions for pure water, as shown in Tables 1 and 2.

The above relationship for G_{111} in Eq. (24) suggests the following form for the triplet correlation function,

$$g_{111}^3(r_1, r_2, r_3) - 1 \approx \left[h_{11}^{(2)}(r_1, r_2) + h_{11}^{(2)}(r_1, r_3) + h_{11}^{(2)}(r_2, r_3) \right] \left[1 + \frac{1}{3}(1 - 2\mu)/\langle N_1 \rangle \right] + \frac{1}{3}(2 - \mu) \left[h_{11}^{(2)}(r_1, r_2)h_{11}^{(2)}(r_1, r_3) + h_{11}^{(2)}(r_2, r_1)h_{11}^{(2)}(r_2, r_3) + h_{11}^{(2)}(r_3, r_1)h_{11}^{(2)}(r_3, r_2) \right] + (1 - \mu)/\langle N_1 \rangle^2 \quad (25)$$

The use of Eq. (25) in Eq. (4) followed by a triple integration generates the exact relationship for G_{111} provided in Eq. (24). Unfortunately, this does not guarantee that the spatial dependence is also correct. Indeed, our initial investigations of simulated water systems (data not shown) indicate significant deviations between the real triplet correlation function and that predicted by Eq. (25) using an appropriate value for μ . The above form, however, does allow one to gain some additional insight. The $O(h)$ and $O(h^2)$ terms, ignoring the $O(N_1^{-1})$ contribution, resemble previous expansions suggested in the literature [7, 25, 64].

This includes the limiting asymptotic form given by just the $O(h)$ term, albeit with different coefficients, and also some of the terms appearing in an expansion of the fluid entropy through third order. Interestingly, there is no $O(h^3)$ term as would be expected according to Eqs. (1) and (11). The $O(N_1^{-1})$ and $O(N_1^{-2})$ terms do not affect the triplet distribution for large (macroscopic) systems, but lead to significant contributions to the fluid thermodynamics upon integration. Whether this type of behavior can be reproduced using just the pair correlations remains unknown. However, it seems clear that these types of differences will be extremely difficult to study using traditional simulation approaches.

The original MH approach assumes μ is indeed independent of pressure and so $\mu' = 0$. In Table 4 we investigate the accuracy of this approximation for water as provided when adopting a single value of $\mu = 5.68$ (obtained at 298 K and 1 bar) for all temperatures and pressures. It should be noted that, from here on, G_{111} and G_{1111} simply refer to the difference between the predicted and observed G 's. The results represent a substantial improvement over the KSA, although neither approach performs well closer to the critical point. By definition, the results for the triplet correlations are exact at 298 K and 1 bar. This

also provides a good description of the corresponding quadruplet correlations even though a value of $\mu' = 0$ is assumed. In Table 5 we provide the results for the related Gaussian ($\mu = 2$ and $\mu' = 0$) approximation ($c_{111} = d_{1111} = 0$) for the particle number fluctuations. The Gaussian limit is approached, but never reached, at low temperatures and high pressures. Again, the results appear to be very reasonable for the liquid state away from the critical point, although the results for the supercritical fluid region are significantly worse than for the original MH approach shown in Table 4. Both approaches overestimate the magnitude of the triplet correlations as one nears the critical point.

An alternative approach is to assume that the rdfs are independent of pressure. This is clearly an approximation as indicated in Fig. 2. Nevertheless, some of the observed increases and decreases in the rdfs may cancel on integration leading to a reasonable overall approximation for the fluid thermodynamics. Under these conditions the derivatives in Eqs. (6) and (8) are zero and we find,

$$G_{111} = 2G_{11}^2$$

$$G_{1111} = 6G_{11}^3 \quad (26)$$

and therefore,

$$c_{111} = 1 + 3\rho_1 G_{11} + 2\rho_1^2 G_{11}^2$$

$$d_{1111} = 1 + 7\rho_1 G_{11} + 12\rho_1^2 G_{11}^2 + 6\rho_1^3 G_{11}^3 \quad (27)$$

This corresponds to a situation where $\mu = 1/b_{11}$ and $\mu' = \mu - 1$. Hence, the value of μ is not constant but is related to the fluid thermodynamics in a simple manner.

Assuming the rdfs are independent of pressure one can use the pair integrals at each state point to predict the corresponding triplet and higher integrals using Eq. (26). The results obtained from such an approximation are provided in Table 6. Again, the results are very good for the liquid region away from the critical point, with a small general underestimation of the triplet correlations. This corresponds to regions where the G_{111}/G_{11}^2 and G_{1111}/G_{11}^3 ratios approach the values predicted by Eq. (26), and also the IL. However, the approximation in the supercritical region is unsatisfactory and the triplet correlations are again overestimated on approaching the critical point.

The previous non-KSA approaches appear to work well for regions not too close to the critical point. We can make this statement more quantitative by analysis of the results in Tables 2, 4–6 and the data shown in Fig. 1. While there is not a perfect correlation between b_{11} and the accuracy of the various approximations, using the pair fluctuations to correlate

the observed accuracy is (in our opinion) more revealing than relying on the fluid density. It appears that reasonable results are obtained when $b_{11} = \rho_1 k_B T \kappa_T = S(0) < 0.2$, *i.e.* low to moderate compressibility. This covers a large portion of the liquid and supercritical regions of the phase diagram of water. Unfortunately, we do not know if this condition holds true for other fluids. The observed performance of each approach for both G_{111} and G_{1111} is also shown graphically in Fig. 6. All the methods perform well for $b_{11} < 0.2$, while the KSA underestimates the three body correlations for low compressibilities but overestimates the correlations at moderate compressibilities. The reason for the success of the non-KSA approaches for lower compressibilities appears to lie in the fact that c_{111} and d_{1111} are also small when b_{11} is small. Hence, it does not matter whether one uses $\mu = 2$ (Gaussian), $\mu = 5.68$ (water at 298 K and 1 bar), or $\mu = 1/b_{11} = 16.1$ (water at 298 K and 1 bar), one always has $\rho_1 G_{11} \approx -1$ and the expressions in Eq. (24) are then essentially independent of μ as they are close to the IL, or closed system, values.

The final approximation investigated here involves a simple power law dependence between the triplet and pair fluctuations along a particular isotherm [33]. A plot of $\ln |c_{111}|$ vs $\ln b_{11}$ is displayed in Fig. 7 corresponding to state points in the liquid and supercritical regions. Almost perfect linear behavior is observed, especially at higher temperatures, for variations in the pair and triplet fluctuations that cover two orders of magnitude. This suggests that the following simple functional form,

$$c_{111} = -y b_{11}^m$$

$$d_{1111} = y b_{11}^{m+1} [m y b_{11}^{m-2} + m - 1] \quad (28)$$

holds for the liquid and supercritical regions, where the second expression has been obtained from the isothermal pressure derivative of c_{111} using previous relationships [14]. Here, y and m are positive constants for a particular isotherm, and correspond to values of $\mu = 2 + y b_{11}^m$ and $\mu' = (2-m)(\mu-2)(\mu-1)b_{11}$ using the MH approach. The resulting fits provided in Fig. 7 are excellent for all the isotherms and pressures considered here, although the fit for the lowest isotherm (298 K) does display deviations from simple linearity on closer examination using additional data points not shown here [33]. This may be due to the increased role of hydrogen bonding at lower temperatures. Further analysis presented in Table 7 also suggests that almost perfect agreement with experiment for the triplet and quadruplet correlations is observed for all the current state points, *i.e.* for $b_{11} < 1.25$. Additional examination of states along the $T = 673$ K isotherm suggests that reasonable results ($< 5\%$ error) can be obtained for the triplet correlations up to $b_{11} \approx 2.0$ (results not shown), corresponding to changes in compressibility of almost two orders of magnitude.

The exact reason for an observed power law relationship between the triplet and pair fluctuations along an isotherm is not clear. We can explain such relationships for the limiting (non-ideal) low density behavior in the gas phase where G_{11} dominates [33], but not for liquids and the supercritical region where all the G 's contribute significantly to the particle

number fluctuations (see Table 2). We are currently investigating the relationships for other fluids to determine if this is a general result. Previous work by Huang and O'Connell suggests that similar correlations of the reduced bulk modulus ($1/b_{11}$) and the fluid density exist for a large number of fluids, and hence the power law dependence observed here may also hold for fluids other than water [65]. Unfortunately, the power law relationship does not immediately suggest a useful closure relationship relating the pair and triplet correlation functions. Nevertheless, it does at least provide a simple consistency test for any proposed forms of the triplet correlations. Finally, it should be noted that no similar correlation is observed between the pair and triplet integrals themselves, suggesting that the fluctuating quantities are more informative.

5. Conclusions

We have investigated the applicability of the KSA, together with several other approximations relating the pair and triplet correlations, for fluid water over a range of temperatures and pressures. The KSA does not perform well, with a general underestimation of the three body correlations at low compressibilities (low b_{11}), and a general overestimation of the correlations at moderate to high compressibilities. A series of other relationships between the pair and triplet correlations that do not require scattering data, and can be applied to any system at any state point (excluding phase transitions), were also investigated. All provided good results for values of $b_{11} < 0.2$. In particular, an observed power law relationship between the pair and triplet fluctuations accurately reproduced the triplet and quadruplet correlations up to values of $b_{11} \approx 2.0$, which covers most of the fluid region except for states close to the critical point. We are currently investigating if the power law relationships can be used to develop improved equations of state for simple fluids. While this latter, FST based, approach does not immediately solve the original problem of expressing the triplet correlation function in terms of the pair correlations, it does provide a different perspective regarding this issue that may prove fruitful in the future.

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Nomenclature

a, b	Fitting parameters obtained after fitting low k values of the structure factor (unitless), Eq. (20)
B_n^*	n -body virial coefficient, but valid for any density and therefore different from the usual low density (gas or solute) forms $(\text{cm}^3/\text{mol})^{n-1}$, Eq. (10)

$B_{n,KSA}^*$	B_n^* , but under the KSA (or KSA analog) (cm^3/mol) $^{n-1}$, Eq. (11)
$b_{11}, c_{111}, d_{1111}$	Particle number fluctuations (unitless), Eq. (3)
C_n	Coefficients of a low order polynomial, $n = 0 - 2$, (cm^3/mol) $^2\text{bar}^{-n}$, Eq. (21)
dk	Wavevector interval (nm^{-1}), Eq. (13)
dp	Pressure difference used in finite difference calculations (bar), see Methods
dr	Distance interval (nm), Eq. (4)
$G_{11}, G_{111}, G_{1111}$	Integrals over a series of GCE 2-body (cm^3/mol), 3-body (cm^3/mol) 2 , and 4-body (cm^3/mol) 3 , respectively, correlation functions, Eq. (4)
(g)	Gas phase
$g_{\alpha\beta\dots}^{(n)}(r_1, r_2, \dots, r_n)$	n -body correlation function between particles of type $\alpha, \beta, \dots$ located at position $r_1, r_2, \dots, r_n$ (unitless), above Eq. (1)
$g_{11}(r)$	Radial distribution function (unitless), Eq. (1)
$H_{11}(k)$	Fourier transform of the total correlation function (cm^3/mol), Eq. (13)
$h_{11}^{(2)}$	Total correlation function (unitless), below Eq. (11)
I_n	Integral terms used in the calculation of $B_{4,KSA}^*$, $n = 1 - 3$ (cm^3/mol) 3 , Eq. (18)
I_0	Integral used in the calculation of $B_{3,KSA}^*$ (cm^3/mol) 2 , Eq. (11)
K	Total integration wavevector (nm^{-1}), Fig. (3)
k	Wavevector (nm^{-1}), below Eq. (13)
k_B	Boltzmann constant (energy/temperature), below Eq. (2)
(l)	Liquid phase
N_1	Number of molecules of species 1 (unitless), below Eq. (3)
n_{pt}	Number of observations (unitless), see Methods
$O(X)$	On the order of X
p	Pressure (bar), below Eq. (5)

r	Distance (nm), above Eq. (1)
$S(k)$	Structure factor (unitless), above Eq. (13)
(s.c.)	Supercritical region
T	Absolute temperature (Kelvin), below Eq. (2)
V	Volume (cm ³ /mol), below Eq. (3)
$W_{\alpha\beta\ldots}^{(n)}(r_1, r_2, \ldots, r_n)$	n -body potential of mean force between particles of type α , β , ... located at position $r_1, r_2, \ldots, r_n$ (energy), Eq. (2)
X', X'', X'''	First, second, and third, respectively, isothermal derivative of X with respect to pressure (units depend on X), Eq. (5)
$\langle X \rangle$	Ensemble average of X in the GCE (units of X), below Eq. (3)
y, m	Positive constants for a particular isotherm (unitless), Eq. (28)
Z	Fluid compressibility factor (unitless), below Eq. (22)
%err	(Signed) percentage error (percent), see Table 3
α, β	Molecular type indices
G_{111}	Initial use: Difference between the integrated real triplet correlations and the integrated KSA triplet correlations (provides a single measure of the accuracy of the KSA); Later use: difference between the predicted and observed G_{111} (cm ³ /mol) ² , Eq. (12)
G_{1111}	Initial use: Difference between the integrated real quadruplet correlations and the integrated KSA-analog quadruplet correlations (provides a single measure of the accuracy of the four-body analog of the KSA); Later use: difference between the predicted and observed G_{1111} (cm ³ /mol) ³ , Eq. (15)
$\Delta g_{111}^{(3)}$	Difference between the true three-body correlation function and the KSA (unitless), Eq. (9)
$\Delta g_{1111}^{(4)}$	Difference between the true four-body correlation function and the four-body KSA analog (unitless), Eq. (9)
δX	Denotes a fluctuation in X (instantaneous value of X minus ensemble average of X) for each member of the ensemble (units of X), below Eq. (3)
κ_T	Isothermal compressibility (bar ⁻¹), below Eq. (5)
μ	Isothermal derivative of the bulk modulus with respect to pressure; Observed by MH to be essentially a constant for many liquids over a wide range of state points (unitless), Eq. (22)

π	3.14159...
ρ_1	Average number density of species 1 (mol/cm ³), below Eq. (3)
B	Boltzmann
KSA	Kirkwood Superposition Approximation
pt	Observations
T	Isothermal
α, β	Molecular type indices
1	Species 1 or particle 1
(n)	n -body
*	Used to indicate validity at any density
', ', ''	First, second, and third, respectively, isothermal derivative with respect to pressure
BBGKY	Bogolyubov-Born-Green-Kirkwood-Yvon
FST	Fluctuation Solution Theory
GCE	Grand Canonical Ensemble
HNC	Hypernetted Chain
IAPWS-95	International Association for the Properties of Water and Steam Formulation 1995 (Equation of State for water)
IL	Incompressible Limit
KB	Kirkwood-Buff
KSA	Kirkwood Superposition Approximation
MH	Moelwyn-Hughes
MM	McMillan-Mayer
NIST	National Institute of Standards and Technology
PMF	Potential of Mean Force
PY	Percus-Yevick
RDF	Radial Distribution Function

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Fig. 1.

Contour plot of b_{11} as a function of temperature and pressure for the liquid (l), gas (g) and supercritical ($s.c.$) regions of pure water as given by the IAPWS-95 equation of state [45]. The gray-filled regions were not contoured. Crosses indicate the state points considered here. Unlabeled contour values are as follows: 0.1, 0.2, 0.3, 0.425, 1.05, 1.15, 1.25, 1.35, 1.45. Contours above 1.5 were omitted for clarity, because b_{11} is increasing rapidly as the critical point is approached from any phase. The phase coexistence curves are shown as bold lines. The triple point ($T = 273.16$ K and $p = 0.006$ bar) and critical point ($T = 647.096$ K and $p = 220.64$ bar) are shown as filled black circles. 1 column width.

Fig. 2. Oxygen-oxygen radial distribution functions, $g_{11}(r)$, as a function of temperature and pressure (bar) obtained by Soper and coworkers [48]. 2 column width.

Fig. 3.

Radial distribution functions, $g_{11}(r)$ (top), structure factors, $S(k)$ (center), and integrals, $I_0(K)$ (bottom), for liquid water at 298 K and 1 bar. In the top two panels the original rdf and structure factor are shown in thin solid black lines, while the thermodynamically consistent rdf and structure factor are shown in thick dotted black lines. The bottom panel displays the integral containing the thermodynamically consistent structure factor as a function of total integration wavevector, K . 1 column width.

Fig. 4. Radial distribution functions, $g_{11}(r)$ (top), structure factors, $S(k)$ (center), and integrals, $I_0(K)$ (bottom), for liquid water at 423 K and 1900 bar. In the top two panels the original rdf and structure factor are shown in thin solid black lines, while the thermodynamically consistent rdf and structure factor are shown in thick dotted black lines. The bottom panel displays the integral containing the thermodynamically consistent structure factor as a function of total integration wavevector, K . 1 column width.

Fig. 5. Radial distribution functions, $g_{11}(r)$ (top), structure factors, $S(k)$ (center), and integrals, $I_o(K)$ (bottom), for liquid water at 298 K and 1 bar. The rdfs were taken from the Soper data published in 2000 [48], and a series of refinements by Soper in 2013 [49]. The bottom panel displays the integrals containing the thermodynamically consistent structure factors as a function of total integration wavevector, K . 1 column width.

Fig. 6. Observed (signed) errors obtained for the triplet and quadruplet integrals as obtained from the KSA and a series of approximate relationships between the pair and triplet fluctuations (see text for details) as a function of the reduced pair fluctuations, b_{11} . 1 column width.

Fig. 7.

The correlation between triplet (c_{111}) and pair (b_{11}) fluctuations for different isotherms. The symbols represent the experimental data. The lines represent fits to the data using Eq. (28). The MH isotherm would result in a slope of $m = 2$ and $y = \mu - 2$. Fitted values of m were: 1.58 (298 K), 2.53 (423 K), 2.39 (573 K) and 2.12 (673 K). Fitted values of y were: 1.14 (298 K), 18.57 (423 K), 9.81 (573 K) and 4.81 (673 K). 1 column width.

Table 1

Experimental Thermodynamic Properties of Fluid Water at Selected State Points.

<i>T</i>	<i>P</i>	<i>1</i>	<i>Z</i>	$10^5 \kappa_T$	μ	μ'
K	bar	<i>M</i>		Bar⁻¹		
298	1	55.35	0.0007	4.53	5.68	0.46
298	2100	59.68	1.42	2.87	6.32	0.06
423	100	51.20	0.06	5.93	7.63	-2.44
423	1900	55.44	0.98	3.42	6.37	-0.76
573	100	39.72	0.05	30.5	9.98	-20.60
573	500	43.11	0.24	14.7	8.03	-4.90
573	1100	46.12	0.50	8.85	7.15	-2.07
573	1970	49.06	0.84	5.80	6.56	-1.17
573	2800	51.16	1.15	4.44	6.22	-0.83
673	500	32.10	0.28	71.3	6.93	-1.99
673	800	36.62	0.39	29.2	6.61	-1.72
673	1300	40.58	0.57	15.0	6.30	-1.00
673	3400	48.38	1.26	5.20	5.77	-0.50

See text for definitions. Experimental properties as provided by the IAPWS-95 equation of state [45].

Table 2

Fluctuation Solution Theory Based Analysis of Fluid Water.

T	p	ρ_l	$\rho_l^2 G_{ll}$	$\rho_l^3 G_{lll}$	b_{ll}	c_{lll}	d_{llll}	$\rho_l^2 B_2^*$	$\rho_l^3 B_3^*$	$\rho_l^4 B_4^*$
K	bar									
298	1	-0.94	1.80	-5.23	0.062	-0.014	0.006	0.469	0.280	0.184
298	2100	-0.96	1.86	-5.48	0.042	-0.008	0.003	0.479	0.295	0.202
423	100	-0.89	1.62	-4.33	0.107	-0.064	0.112	0.447	0.259	0.158
423	1900	-0.93	1.78	-5.13	0.067	-0.019	0.016	0.467	0.278	0.182
573	100	-0.42	-2.39	49.12	0.577	-2.656	32.84	0.212	0.974	-4.436
573	500	-0.70	0.54	3.28	0.303	-0.552	2.632	0.349	0.306	-0.126
573	1100	-0.81	1.22	-2.19	0.195	-0.195	0.506	0.403	0.242	0.104
573	1970	-0.86	1.51	-3.87	0.136	-0.084	0.137	0.432	0.244	0.141
573	2800	-0.89	1.63	-4.45	0.108	-0.049	0.060	0.446	0.253	0.155
673	500	0.28	-9.93	172.38	1.281	-8.088	115.8	-0.141	3.390	-25.792
673	800	-0.40	-1.44	21.12	0.598	-1.646	10.67	0.201	0.642	-1.609
673	1300	-0.66	0.47	2.53	0.342	-0.502	1.762	0.329	0.276	-0.070
673	3400	-0.86	1.50	-3.91	0.141	-0.075	0.099	0.430	0.237	0.137
IL		-1	2	-6	0	0	0	1/2	1/3	1/4

Using Eqs. (3), (5) and (10) with experimental thermodynamic derivatives obtained using the IAWPS-95 equation of state [45]. IL: incompressible limit.

Table 3

Triplet and Quadruplet Integrals Provided by the KSA.

<i>T</i>	<i>p</i>	$G_{111}-3G_{11}^2$		G_{111}	%err	G_{1111}	%err
		KSA	exp				
298	1	-324	-274	-50	-9	1313	4
298	2100	-403	-249	-155	-30	6210	24
423	100	-394	-297	-97	-16	4407	14
423	1900	-403	-271	-132	-23	6002	20
573	100	-443	-1853	1410	93		
573	500	-408	-494	86	30	-19907	-49
573	1100	-390	-341	-49	-9	-5967	-27
573	1970	-438	-304	-133	-21	8851	27
573	2800	-291	-290	-1	0	11774	35
673	500	78	-9872	9950	103		
673	800	-186	-1435	1250	116	-164655	-38
673	1300	-190	-502	312	109	-101687	-268
673	3400	-321	-304	-18	-3	69825	202

Units: *T* in K, *p* in bar, G_{11} in cm³/mol, G_{111} in (cm³/mol)² and G_{1111} in (cm³/mol)³. G_{111} and G_{1111} obtained using Eqs. (12) and (16). The (signed) percentage error (%err) is given by 100 $|G_{111}/G_{111}|$, etc.

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Table 4

Triplet and Quadruplet Integrals Provided by Moelwyn-Hughes Isotherms.

T	p	G_{111}	%err	G_{1111}	%err
298	1	0	0	28	0
298	2100	0	0	-8	0
423	100	9	1	-1554	-5
423	1900	1	0	-148	0
573	100	908	60	-566950	-72
573	500	116	40	-38360	-94
573	1100	26	5	-6275	-28
573	1970	7	1	-1337	-4
573	2800	2	0	-444	-1
673	500	1992	21	-1918704	-37
673	800	249	23	-124602	-29
673	1300	44	15	-14624	-39
673	3400	0	0	-189	-1

Units: T in K, p in bar, G_{111} in $(\text{cm}^3/\text{mol})^2$ and G_{1111} in $(\text{cm}^3/\text{mol})^3$. G_{111} and G_{1111} obtained using Eqs. (23) and (24) with $\mu = 5.68$ and $\mu' = 0$.

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Table 5

Triplet and Quadruplet Integrals Provided by the Gaussian Approximation.

T	p	G_{111}	%err	G_{1111}	%err
298	1	5	1	474	2
298	2100	2	0	213	1
423	100	25	4	1425	4
423	1900	6	1	500	2
573	100	1683	111	-563027	-72
573	500	297	102	-16525	-40
573	1100	92	16	2117	10
573	1970	35	6	1950	6
573	2800	19	3	1285	4
673	500	7852	81	-5794278	-111
673	800	1228	114	-256521	-60
673	1300	305	106	-12095	-32
673	3400	32	5	1932	6

Units: T in K, p in bar, G_{111} in $(\text{cm}^3/\text{mol})^2$ and G_{1111} in $(\text{cm}^3/\text{mol})^3$. G_{1111} and G_{11111} obtained using Eqs. (23) and (24) with $\mu' = 2$ and $\mu' = 0$.

Table 6

Triplet and Quadruplet Integrals Provided by Pressure Independent Rdfs.

T	p	G_{111}/G_{11}^2	G_{1111}/G_{11}^3	G_{111}	%err	G_{1111}	%err
298	1	2.05	6.34	-13	-2	166	5
298	2100	2.03	6.25	-9	-2	1040	4
423	100	2.02	6.07	-8	-1	388	1
423	1900	2.04	6.31	-12	-2	1502	5
573	100	-13.33	-648.69	1739	115	-790896	-101
573	500	1.11	-9.66	233	80	-66257	-162
573	1100	1.88	4.18	36	6	-9687	-43
573	1970	2.02	5.99	-6	-1	-59	0
573	2800	2.04	6.28	-14	-2	1476	4
673	500	-125.55	7747.67	9795	102	-5209463	-100
673	800	-8.89	-324.29	1315	122	-438005	-102
673	1300	1.09	-8.86	239	83	-63514	-168
673	3400	2.04	6.16	-12	-2	891	3

Units: T in K, p in bar, G_{11} in cm^3/mol , G_{111} in $(\text{cm}^3/\text{mol})^2$ and G_{1111} in $(\text{cm}^3/\text{mol})^3$. G_{111} and G_{1111} obtained using Eq. (26) and the values of G_{11} at each state point.

Table 7

Triplet and Quadruplet Integrals Provided by a Power Law Dependence.

T	p	G_{111}	%err	G_{1111}	%err
298	1	0	0	35	0
298	2100	0	0	24	0
		0			
423	100	0	0	-23	0
423	1900	0	0	3	0
573	100	11	1	-30647	-4
573	500	-8	-3	1694	4
573	1100	-1	0	240	1
573	1970	0	0	12	0
573	2800	0	0	-5	0
673	500	-49	-1	173483	3
673	800	26	2	-7285	-2
673	1300	6	2	-1065	-3
673	3400	0	0	-37	0

Units: T in K, p in bar, G in $(\text{cm}^3/\text{mol})^2$ and G_{1111} in $(\text{cm}^3/\text{mol})^3$. G_{111} and G_{1111} obtained using Eqs. (3) and (28) together with the fitting parameters provided in Fig. 7.