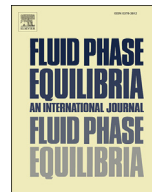




Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Experimental investigation of triplet correlation approximations for fluid water

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ARTICLE INFO

Article history:

Received 21 August 2017

Received in revised form

26 October 2017

Accepted 27 October 2017

Available online xxx

Keywords:

Triplet correlations

Fluctuation solution theory

Kirkwood superposition approximation

Radial distribution function

Fluid thermodynamics

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.

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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 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

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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],

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

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],

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

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],

$$\begin{aligned} b_{11} &= k_B T \rho_1' = \rho_1 k_B T \kappa_T \\ c_{111} &= (k_B T)^2 [\rho_1 \rho_1'' + (\rho_1')^2] \\ d_{1111} &= (k_B T)^3 [\rho_1^2 \rho_1''' + 4\rho_1 \rho_1' \rho_1'' + (\rho_1')^3] \end{aligned} \quad (5)$$

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],

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