Experimental triplet and quadruplet fluctuation densities and spatial distribution function integrals for pure liquids

Elizabeth A. Ploetz, Sadish Karunaweera, and Paul E. Smith

Experimental triplet and quadruplet fluctuation densities and spatial distribution function integrals for pure liquids

Elizabeth A. Ploetz, Sadish Karunaweera, and Paul E. Smith
Department of Chemistry, Kansas State University, 213 CBC Building, Manhattan, Kansas 66506, USA

Fluctuation solution theory has provided an alternative view of many liquid mixture properties in terms of particle number fluctuations. The particle number fluctuations can also be related to integrals of the corresponding two body distribution functions between molecular pairs in order to provide a more physical picture of solution behavior and molecule affinities. Here, we extend this type of approach to provide expressions for higher order triplet and quadruplet fluctuations, and thereby integrals over the corresponding distribution functions, all of which can be obtained from available experimental thermodynamic data. The fluctuations and integrals are then determined using the International Association for the Properties of Water and Steam Formulation 1995 (IAPWS-95) equation of state for the liquid phase of pure water. The results indicate small, but significant, deviations from a Gaussian distribution for the molecules in this system. The pressure and temperature dependence of the fluctuations and integrals, as well as the limiting behavior as one approaches both the triple point and the critical point, are also examined. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4905562]

I. INTRODUCTION

From a theoretical point of view, liquids and liquid mixtures are commonly characterized in terms of probability distribution functions. These distribution functions provide a way to describe liquid structure and can be further used to relate this structure to the corresponding thermodynamics.[1] The Kirkwood-Buff (KB) theory of solutions provides such a link between integrals over the spatial pair distribution functions and the thermodynamic properties of any stable multicomponent system.[2] These integrals can also be expressed in terms of particle fluctuation densities and both quantities can be considered to characterize a liquid or liquid mixtures.[3] Consequently, KB theory, also more generally known as Fluctuation Solution Theory (FST), has provided an alternative view of many solution properties in terms of particle number fluctuations and distributions.[2,4,5]

Many theoretical approaches also employ distribution functions beyond the simple pair distribution. The role of triplet and higher distribution functions in liquids is well established.[6–9] However, quantitative information concerning these distributions remains quite limited, especially from experimental sources.[7–10] In particular, there are no systematic studies of triplet correlations over a wide range of temperature and pressure for complex liquids using experimental data. Previous work has been primarily restricted to scattering studies that provide the pair distribution function, and thereby partial information concerning triplet distributions, via studies of the pressure and temperature dependence of the pair distribution. Unfortunately, scattering studies are usually limited to molecules of low complexity.

Here, we describe an extension of traditional FST to generate triplet and quadruplet particle number fluctuations, together with the corresponding integrals over the triplet and quadruplet spatial distribution functions, in an effort to provide experimental data concerning higher distributions in pure liquids at any density. The new expressions are then combined with existing relationships to systematically investigate these higher correlations in pure water over a range of pressure and temperature. Finally, we compare and contrast this approach with currently available experimental methods that attempt to access similar liquid state correlations. The results can therefore be used to provide rigorous tests of current theories of solutions, to guide the development of accurate models for computer simulation, and to further relate solution structure to solution thermodynamics.

II. THEORY

As is traditional with Fluctuation Solution Theory, one starts with the equations of the Grand Canonical Ensemble (GCE) and then uses various thermodynamic transformations to provide properties corresponding to either semi-open osmotic systems or fully closed isothermal isobaric systems.[11] Hence, all ensemble averages and distribution functions in this type of approach correspond to the GCE. The fluctuating quantities are then related to integrals over distribution functions. Usually the application is to liquids, but there is no reason the same approach cannot be applied to pure gases or even solids.

The thermodynamic potential and partition function in the GCE—where the set of chemical potentials ($\{\mu\}$), the volume (V), and the absolute temperature (T) are the independent variables—can be written as[1]

$$\beta p = V^{-1} \ln \Xi,$$
$$\Xi = \sum_{\{N\}=0}^{\infty} Q(\{N\}, V, T) e^{\beta \mathbf{\mu} \cdot \mathbf{N}}, \tag{1}$$

where $\beta = (k_B T)^{-1}$, p is the pressure, $\boldsymbol{\mu} \cdot \mathbf{N} = \mu_1 N_1 + \mu_2 N_2 \cdots$, and N_α is the number of molecules of species α. The sum is over the full permutation of molecule numbers, and Q $(\{N\}, V, T)$ is the canonical partition function for each system of $\{N\}$ molecules in the same fixed volume. The most useful value for the Boltzmann constant (k_B) in this work is 0.083 143 714 bar L mol^{-1} K^{-1}. The above partition function applies for any system where Boltzmann statistics are obeyed. Our main focus will be single component liquids. We will, however, retain the full multicomponent expressions during the initial derivation and then simplify to a single component later.

The corresponding differential for the GCE can be written in terms of just the intensive variables,

$$d\beta p = -\frac{U}{V} d\beta + \sum_\alpha \frac{N_\alpha}{V} d\beta \mu_\alpha, \tag{2}$$

where U is the internal energy. The ensemble average of a property (X) in the GCE is given by

$$\langle X \rangle = e^{-\beta p V} \sum_{\{N\}} \sum_i X e^{-\beta E_i} e^{\beta \boldsymbol{\mu} \cdot \mathbf{N}}, \tag{3}$$

and Eqs. (1) and (2) lead directly to the following relationships for the internal energy density and the particle number densities of each species:

$$\frac{U}{V} = -\left(\frac{\partial V^{-1}\ln\Xi}{\partial\beta}\right)_{\{\beta\mu\}} = \frac{\langle E \rangle}{V},$$
$$\frac{N_\alpha}{V} = \left(\frac{\partial V^{-1}\ln\Xi}{\partial\beta\mu_\alpha}\right)_{\beta,\{\beta\mu\}'} = \frac{\langle N_\alpha \rangle}{V} = \rho_\alpha \tag{4}$$

for any multicomponent system.[1] Here, the prime indicates that all chemical potentials except for the one of interest are held constant.

One can continue to take derivatives with respect to the chemical potentials in the GCE to provide,[6]

$$\left(\frac{\partial\rho_\alpha}{\partial\beta\mu_\beta}\right)_{\beta,\{\beta\mu\}'} = V^{-1}[\langle\delta N_\alpha \delta N_\beta\rangle] \equiv B_{\alpha\beta},$$
$$\left(\frac{\partial B_{\alpha\beta}}{\partial\beta\mu_\gamma}\right)_{\beta,\{\beta\mu\}'} = V^{-1}[\langle\delta N_\alpha \delta N_\beta \delta N_\gamma\rangle] \equiv C_{\alpha\beta\gamma}, \tag{5}$$
$$\left(\frac{\partial C_{\alpha\beta\gamma}}{\partial\beta\mu_\delta}\right)_{\beta,\{\beta\mu\}'}$$
$$= V^{-1}\begin{bmatrix}\langle\delta N_\alpha \delta N_\beta \delta N_\gamma \delta N_\delta\rangle - \langle\delta N_\alpha \delta N_\beta\rangle\langle\delta N_\gamma \delta N_\delta\rangle - \\ \langle\delta N_\alpha \delta N_\gamma\rangle\langle\delta N_\beta \delta N_\delta\rangle - \langle\delta N_\alpha \delta N_\delta\rangle\langle\delta N_\beta \delta N_\gamma\rangle\end{bmatrix}$$
$$\equiv D_{\alpha\beta\gamma\delta},$$

where $\delta X = X - \langle X \rangle$ denotes a fluctuation in the value of X. The particle number fluctuations can also be expressed in terms of density fluctuations, but this becomes increasingly more awkward for the higher moments of the distribution. The most appropriate intensive properties are the fluctuations per unit volume, or fluctuation densities, as displayed above. The fluctuation densities provide quantitative measures of the correlation between particles in an open system.

The above expressions are restricted to open systems. The next step is to provide a connection to equivalent closed

systems, which are of more common interest. The intensive GCE averages are a function of the intensive thermodynamic variables associated with the GCE, and therefore, one can write the following general differential:

$$d\langle X \rangle = \left(\frac{\partial\langle X\rangle}{\partial\beta}\right)_{\{\beta\mu\}} d\beta + \sum_\alpha \left(\frac{\partial\langle X\rangle}{\partial\beta\mu_\alpha}\right)_{\beta,\{\beta\mu\}'} d\beta\mu_\alpha, \tag{6}$$

where X is an intensive property. It should be noted that there is no volume derivative in the above expressions as it can be shown that this derivative is zero when X is intensive, i.e., intensive properties only depend on the intensive variables.[6] If we restrict ourselves to the study of isothermal changes, the results relate to particle number fluctuations only. Energy fluctuations will be included fully at a later date. However, some preliminary results are invoked in Secs. III F and III G.

Taking derivatives of Eq. (6) with respect to pressure provides a series of useful relationships. When $X = \beta p = V^{-1}\ln\Xi$, one obtains the common relationship between the partial molar volumes ($\bar{V}_\alpha$),

$$\left(\frac{\partial V^{-1}\ln\Xi}{\partial p}\right)_{\beta,\{N\}} = \beta\sum_\alpha \rho_\alpha \bar{V}_\alpha = \beta. \tag{7}$$

Using $\langle X \rangle = \rho_\alpha$ in Eq. (6) provides

$$\left(\frac{\partial\rho_\alpha}{\partial p}\right)_{\beta,\{N\}} = \beta\sum_\beta B_{\alpha\beta}\bar{V}_\beta = \rho_\alpha \kappa_T \tag{8}$$

and corresponds to the Kirkwood-Buff theory of solutions expression for the isothermal compressibility,[2]

$$\kappa_T \equiv -\left(\frac{\partial\ln V}{\partial p}\right)_{\beta,\{N\}}. \tag{9}$$

This well-known relationship can be used to extract particle-particle number (or density) fluctuations in pure liquids. Here, we wish to go beyond these pair correlations to examine the triplet and higher fluctuations (correlations). Finally, using $\langle X \rangle = B_{\alpha\beta}$ and $\langle X \rangle = C_{\alpha\beta\gamma}$ in Eq. (6) provides

$$\left(\frac{\partial B_{\alpha\beta}}{\partial p}\right)_{\beta,\{N\}} = \beta\sum_\gamma C_{\alpha\beta\gamma}\bar{V}_\gamma,$$
$$\left(\frac{\partial C_{\alpha\beta\gamma}}{\partial p}\right)_{\beta,\{N\}} = \beta\sum_\delta D_{\alpha\beta\gamma\delta}\bar{V}_\delta. \tag{10}$$

The above expressions describe the pressure dependence of the two and three body particle number fluctuations. Obviously, one could continue indefinitely. However, it is unclear if reliable estimates for higher distributions can be obtained from experiment. This represents a particular aim of the current work.

It is clear from the above expressions that if the multivariate particle number probability distribution for the liquid was simply Gaussian in nature, the C's and D's would then be zero and the B's would therefore be independent of pressure. This is clearly not the case, as noted previously.[12] The expressions in Eq. (5) correspond to the cumulants of the multivariate particle number probability distribution expressed in terms of the central moments. Alternatively, they can be viewed as the mean, covariance, coskewness, and excess cokurtosis of the same distribution. We note that there are several different

definitions of skewness and excess kurtosis in the literature. The definition of skewness and excess kurtosis referred to here are those provided by $VC_{\alpha\beta\gamma}$ and $VD_{\alpha\beta\gamma\delta}$ expressions, respectively.

Before discussing a real system of common interest, we note that the fluctuating quantities can be related to a series of corresponding distribution functions (see Appendix A). For single component systems, the relationships between the fluctuating quantities and the corresponding distribution functions are provided by

$$
\begin{aligned}
B_{11} &= \frac{\langle(\delta N_1)^2\rangle}{V} = \rho_1(1+\rho_1 G_{11}),\\[4pt]
C_{111} &= \frac{\langle(\delta N_1)^3\rangle}{V} = \rho_1(1+3\rho_1 G_{11}+\rho_1^2 G_{111}),\\[4pt]
D_{1111} &= \frac{\langle(\delta N_1)^4\rangle-3\langle(\delta N_1)^2\rangle^2}{V}\\[4pt]
&= \rho_1(1+7\rho_1 G_{11}+6\rho_1^2 G_{111}+\rho_1^3 G_{1111}),
\end{aligned}
\tag{11}
$$

which involve integrals over the n-body spatial distribution functions $g^{(n)}_{\alpha\beta\ldots}(r_1,r_2,\ldots)$ that are similar in form to the integrals appearing in the theory of imperfect gases or the McMillan-Mayer theory of (osmotic) solutions,[1]

$$
\begin{aligned}
G_{11} &= V^{-1}\int\left[g^{(2)}_{11}-1\right]dr_1 dr_2,\\[4pt]
G_{111} &= V^{-1}\int\left[g^{(3)}_{111}-1-3(g^{(2)}_{11}-1)\right]dr_1 dr_2 dr_3,\\[4pt]
G_{1111} &= V^{-1}\int\left[g^{(4)}_{1111}-1-4(g^{(3)}_{111}-1)-3(g^{(2)}_{11}-1)(g^{(2)}_{11}-1)\right.\\
&\left.\quad +6(g^{(2)}_{11}-1)\right]dr_1 dr_2 dr_3 dr_4.
\end{aligned}
\tag{12}
$$

The integrals can also be expressed in terms of particle number fluctuations,

$$
\begin{aligned}
\rho_1^2 V G_{11} &= \langle(\delta N_1)^2\rangle-\langle N_1\rangle,\\[4pt]
\rho_1^3 V G_{111} &= \langle(\delta N_1)^3\rangle-3\langle(\delta N_1)^2\rangle+2\langle N_1\rangle,\\[4pt]
\rho_1^4 V G_{1111} &= \langle(\delta N_1)^4\rangle-3\langle(\delta N_1)^2\rangle^2-6\langle(\delta N_1)^3\rangle\\
&\quad +11\langle(\delta N_1)^2\rangle-6\langle N_1\rangle,
\end{aligned}
\tag{13}
$$

if desired. Hence, if one can obtain the fluctuating quantities in terms of experimental data, then the corresponding integrals over the center of mass based two, three, and four body distribution functions can also be obtained.

The integrals over the spatial distribution functions are valid for any liquid density and are obtained after averaging over the positions (and orientations) of all the other molecules in the system. Hence, they can be used for regions of the phase diagram where many expansions do not usually apply. Furthermore, any orientational effects of the molecules do not appear (directly) in the associated integrals. This means the integrals for molecular systems adopt a much simpler form than observed for many low density expansions. They cannot be used to probe the detailed nature of the interaction energy between molecules, as required in many integral equation theories, but they are valid for both pairwise additive and non-additive potentials.

The fluctuation densities and corresponding integrals provide alternative, but complimentary, descriptions of the correlation between particles within the system. The above integrals

and probability distributions are often used to provide insight into the "structure" of liquids and liquid mixtures.[4] It should be noted that, because the distribution functions are defined for the GCE, the corresponding integrals are not those expected for closed systems (where $\rho_\beta G_{\alpha\beta}=-\delta_{\alpha\beta}$), and the distribution functions tend towards unity in an exact manner when all molecules become widely separated.

The pressure dependence of the G's can be obtained by taking derivatives of Eq. (11) and comparing with Eq. (10). One finds

$$
\begin{aligned}
G'_{11} &= \beta(G_{111}-2G_{11}^2),\\[4pt]
G'_{111} &= \beta(G_{1111}-3G_{111}G_{11}),
\end{aligned}
\tag{14}
$$

where the prime indicates an isothermal derivative with respect to pressure (a notation that will be used throughout this article). The first relationship in Eq. (14) is the integrated form of the well-known expression for the pressure dependence of the pair correlation function.[13,14]

In summary, we have provided an extension of the traditional FST approach to investigate the fluctuations and distribution integrals for real solutions using experimental data. In doing so, we are not attempting to provide a low density expansion valid for solutions. Furthermore, no attempt is made to link the results to the underlying pair interactions from which they came. We are providing access to the experimental fluctuations and integrals over distribution functions that characterize the liquid and give rise to the thermodynamic properties at a particular state point, regardless of the density. The relationship between the present approach and existing previous studies of higher distribution functions will be discussed further in Sec. IV.

III. RESULTS

Some of the expressions presented here for pure systems have appeared previously. For instance, the expression for the compressibility given by Eqs. (8) and (11) is well known.[2] It is also known that the pressure dependence of the pair or radial distribution function (rdf) is related to the triplet distribution.[13] However, we have found no relevant quantitative experimental data in the literature concerning the fluctuations (beyond the compressibility) for molecular liquids over a range of pressures and temperatures.

Using the results from Eqs. (8) and (10), the fluctuating quantities for pure gases and liquids can be expressed in terms of pressure derivatives of the density and are given by

$$
\begin{aligned}
B_{11} &= \beta^{-1}\rho_1\rho'_1,\\[4pt]
C_{111} &= \beta^{-2}\rho_1[\rho_1\rho''_1+(\rho'_1)^2],\\[4pt]
D_{1111} &= \beta^{-3}\rho_1[\rho_1^2\rho'''_1+4\rho_1\rho'_1\rho''_1+(\rho'_1)^3].
\end{aligned}
\tag{15}
$$

Expressions for the fluctuations in terms of derivatives of the molar volume or the isothermal compressibility are given in Appendix B. The above expressions essentially correspond to the familiar Kirkwood-Buff inversion procedure[15] that provides fluctuating quantities in terms of experimental observables. Once the fluctuating quantities have been obtained, the integrals over the distribution functions can also be extracted

using the relationships outlined in Eq. (11). However, to obtain reliable values for the derivatives, an accurate equation of state (EOS) is required.

The results obtained for pure water as a function of pressure and temperature are determined here using the IAPWS-95 EOS as implemented in the National Institutes of Standards and Technology (NIST) Standard Reference Database 10: NIST/American Society of Mechanical Engineers Steam Properties Database version 2.22.[16,17] The source code provides a series of thermodynamic properties as a function of pressure (or density) and temperature via a subroutine call. First and second derivatives of the density are provided directly by the EOS. The third derivatives were obtained numerically via a finite difference approach using the second derivatives and a value of $dp = \pm 10^{-20}$ bars. Calculations were performed in quadruple precision.

A. Density and pressure expansions

Before presenting the results for water, it is informative to clarify the uses and exact meaning of the integrals presented here, especially as similar quantities are also found in the literature. In Sec. II, we provided expressions that relate a series of fluctuating quantities to a series of corresponding pressure derivatives. Consequently, one of the most obvious uses for the fluctuations is to rationalize changes in the density as a function of pressure along a particular isotherm. A simple Taylor series expansion provides

$$\rho_1(p) = \rho_1(p_o) + \rho_1'(p_o)\Delta p + \frac{1}{2}\rho_1''(p_o)\Delta p^2 + \frac{1}{6}\rho_1'''(p_o)\Delta p^3 + O(\Delta p^4) \tag{16}$$

in terms of the pressure change $\Delta p = p - p_o$ from a reference pressure p_o. The pressure derivatives appearing in the above expression are given by the fluctuating quantities appearing in Eq. (15),

$$
\begin{aligned}
\rho_1' &= \frac{\beta B_{11}}{\rho_1}, \\
\rho_1'' &= \frac{\beta^2}{\rho_1^3}\left[\rho_1 C_{111} - B_{11}^2\right], \\
\rho_1''' &= \frac{\beta^3}{\rho_1^5}\left[\rho_1^2 D_{1111} - 4\rho_1 C_{111}B_{11} + 3B_{11}^3\right],
\end{aligned} \tag{17}
$$

or via integrals over the distribution function according to

$$
\begin{aligned}
\rho_1' &= \beta[1 + \rho_1 G_{11}], \\
\rho_1'' &= \beta^2\left[G_{11} + \rho_1(G_{111} - G_{11}^2)\right], \\
\rho_1''' &= \beta^3\left[2G_{111} - 3G_{11}^2 + \rho_1(G_{1111} - 4G_{111}G_{11} + 3G_{11}^3)\right].
\end{aligned} \tag{18}
$$

The above derivative expressions are valid at any liquid or gas density but should be evaluated at the reference pressure/density for use in Eq. (16). In the case of gases, where ρ_1 will be very small, the derivatives may simplify further. Expressions for the equivalent virial coefficients (B_n) can also be obtained from Eq. (16) using a series reversion approach—although to obtain the fourth virial coefficient, one requires an additional density derivative. This provides the following

expansion:

$$\beta\Delta p = \Delta\rho_1\left[B_1 + B_2\Delta\rho_1 + B_3\Delta\rho_1^2 + \cdots\right] \tag{19}$$

for which the B's are given by

$$
\begin{aligned}
B_1(T,p_o) &= [1 + \rho_1 G_{11}]^{-1}, \\
B_2(T,p_o) &= -\frac{1}{2}[1 + \rho_1 G_{11}]^{-3}\left[G_{11} + \rho_1(G_{111} - G_{11}^2)\right], \\
B_3(T,p_o) &= -\frac{1}{6}[1 + \rho_1 G_{11}]^{-5} \\
&\quad \times \left[\begin{array}{l} 2G_{111} - 6G_{11}^2 + \rho_1(G_{1111} + 6G_{11}^3 - 8G_{111}G_{11}) \\ + \rho_1^2(G_{1111}G_{11} + 2G_{111}G_{11}^2 - 3G_{111}^2) \end{array}\right].
\end{aligned} \tag{20}
$$

Again, the virial coefficient expressions in Eq. (20) appear more complicated than the traditional expressions as they are valid for any reference pressure (away from a first order transition). The traditional virial EOS is provided when p_o and ρ_1 are zero. Hence, the more common virial EOS is actually a limiting case of FST. Clearly, the expansion provided in Eqs. (16) and (18) is simpler in form for finite reference pressures (densities).

One can also develop expansions for G_{11} using Eq. (14). This further illustrates how the structure of the liquid or gas changes with pressure or density. The pressure derivatives are then

$$
\begin{aligned}
G_{11}' &= \beta(G_{111} - 2G_{11}^2), \\
G_{11}'' &= \beta^2(G_{1111} - 7G_{111}G_{11} + 8G_{11}^3),
\end{aligned} \tag{21}
$$

while the corresponding density derivatives are given by

$$
\begin{aligned}
\left(\frac{\partial G_{11}}{\partial \rho_1}\right)_\beta &= [1 + \rho_1 G_{11}]^{-1}[G_{111} - 2G_{11}^2], \\
\left(\frac{\partial^2 G_{11}}{\partial \rho_1^2}\right)_\beta &= [1 + \rho_1 G_{11}]^{-3} \\
&\quad \times \left[\begin{array}{l} G_{1111} - 8G_{111}G_{11} + 10G_{11}^3 \\ + \rho_1(G_{1111}G_{11} - G_{111}^2 - 4G_{111}G_{11}^2 + 6G_{11}^4) \end{array}\right],
\end{aligned} \tag{22}
$$

where we have used the chain rule to write $\partial G_{11}/\partial \rho_1 = G_{11}'/\rho_1'$, etc.

B. Gas phase fluctuations and distribution function integrals

While our primary focus is the liquid phase, as this has traditionally been the more difficult system to study, a brief discussion of the results for the gas phase region is in order (the gas phase diagrams containing results up to 1250 K are provided in the supplementary material[68]). The two body fluctuations (B_{11}/ρ_1) generally increase with decreasing temperature and increasing pressure. The skewness of the distributions (C_{111}/ρ_1) is always positive (an excess of particles in the volume is favored over a depletion) and the excess kurtosis (D_{1111}/ρ_1) is always positive (the actual distribution is more peaked than a normal distribution). The magnitude of C_{111}/ρ_1 and D_{1111}/ρ_1 follows the same pressure and temperature trends as B_{11}/ρ_1. The pair distribution integral $\rho_1 G_{11}$ is positive and generally increases with decreasing temperature and increasing pressure, while the triplet distribution integral $\rho_1^2 G_{111}$ is positive over most of the gas phase region investigated here, but

can take on negative values at high pressure and high temperature near the supercritical region. The quadruplet distribution integral $\rho_1^3 G_{1111}$ can adopt either positive (as one approaches the critical point) or negative (for low pressures and higher temperature) values. As expected, the gas phase approaches ideal behavior at low pressure and high temperature, where $B_{11} = C_{111} = D_{1111} = \rho_1$, which corresponds to the known Poisson distribution for the particle number fluctuations.[18] All the G's would be zero for a perfect gas but are finite for real gases even at low pressures.

Figure 1 displays the two virial coefficient forms described above as obtained at 298.15 K. In addition, we have included the following related virial coefficients:

$$B_1^* = 1,$$
$$B_2^* = -\frac{1}{2}G_{11}, \qquad (23)$$
$$B_3^* = -\frac{1}{3}\left[G_{111} - 3G_{11}^2\right].$$

These correspond to the traditional (low density) forms of the virial coefficients. However, the integrals used in Eq. (23) can be applied to finite densities and do not form part of an expansion. They are, however, useful as integrals that correspond to particle correlations at a finite density, after averaging over all other molecules in the system, where one can apply the Kirkwood Superposition Approximation to the (orientationally averaged) potential of mean force between the molecules

at that particular finite density. The first three virial coefficients decrease with an increase in pressure (or density). This is in agreement with the fact that G_{11} and G_{111} are positive over the pressures studied. The data for B_i^* also indicate that the presence of additional water molecules in the gas phase serves to decrease the effective pair and triplet correlations—as would be expected.

C. Liquid phase fluctuations and distribution function integrals

The results for liquid water are displayed in Figures 2 and 3 as dimensionless quantities. In the supplementary material, we also provide Figures 2 and 3 as the raw quantities, but they essentially exhibit the same overall trends. Figure 2 indicates that the fluctuation cumulants alternate in sign for the liquid region. As expected, the two body fluctuations (B_{11}/ρ_1) generally increase with increasing temperature and decreasing pressure.[68] The skewness of the distributions (C_{111}/ρ_1) is always negative (a depletion of particles in the volume is favored over an excess) and the excess kurtosis (D_{1111}/ρ_1) is always positive (the actual distribution is more peaked than a normal distribution). The underlying distributions tend to a normal distribution (B_{11} is constant, $C_{111} = D_{1111} = 0$) as the pressure increases and the temperature decreases. Figure 3 indicates that the integrals $(G_{\alpha\beta..})$ alternate in sign and increase in magnitude as the pressure decreases and/or temperature increases. As expected, B_{11}/ρ_1 and $\rho_1 G_{11}$ tend to large positive values as the critical point is approached, as do the values of D_{1111}/ρ_1 and $\rho_1^3 G_{1111}$, whereas the values of C_{111}/ρ_1 and $\rho_1^2 G_{111}$ become very large and negative in this region.

The alternating signs of the fluctuation quantities appear to be an inherent characteristic of liquids and are determined by the expressions found in Eqs. (8) and (10). Hence, one observes $\rho_1' > 0$ as $B_{11} > 0$, $B_{11}' < 0$ as $C_{111} < 0$, and $C_{111}' > 0$ as $D_{1111} > 0$. These patterns indicate that all the fluctuating quantities decrease in magnitude as the pressure increases. The fluctuating quantities and corresponding integrals are displayed in Figure 4 and Table I for selected isobars, isotherms, and state points.

D. Moelwyn-Hughes isotherms

The IAPWS-95 EOS for water, while very accurate, is quite complicated and similar quality expressions for other liquids are relatively few in number. In an effort to provide a more accessible analysis of pure liquids, while maintaining a significant degree of accuracy, we have investigated a simple relationship accredited to Moelwyn-Hughes.[19] The Moelwyn-Hughes isotherm can be developed from the semi-empirical observation that the bulk modulus is proportional to pressure for a variety of substances. Hence,

$$\left(\frac{\partial \kappa_T^{-1}}{\partial p}\right)_T \equiv \mu(T), \qquad (24)$$

where μ is a constant for a fixed temperature. The relationship holds over a reasonable range of temperatures and pressures.
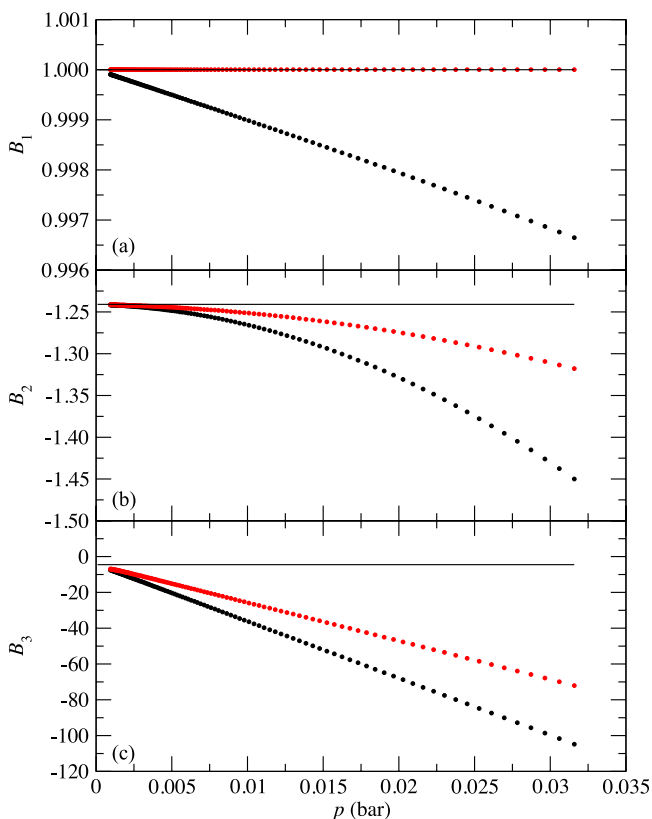

FIG. 1. The (a) first, (b) second, and (c) third virial coefficients for water vapor at 298.15 K for pressures up to the saturation pressure. Black dotted lines: B_i from Eq. (20). Red dotted lines: B_i^* from Eq. (23). Black solid lines: the traditional (zero pressure and density) virial coefficient values provided by the IAPWS-95 EOS. Units for the B_2 coefficients are in M^{-1} while the B_3 coefficients are in M^{-2}.
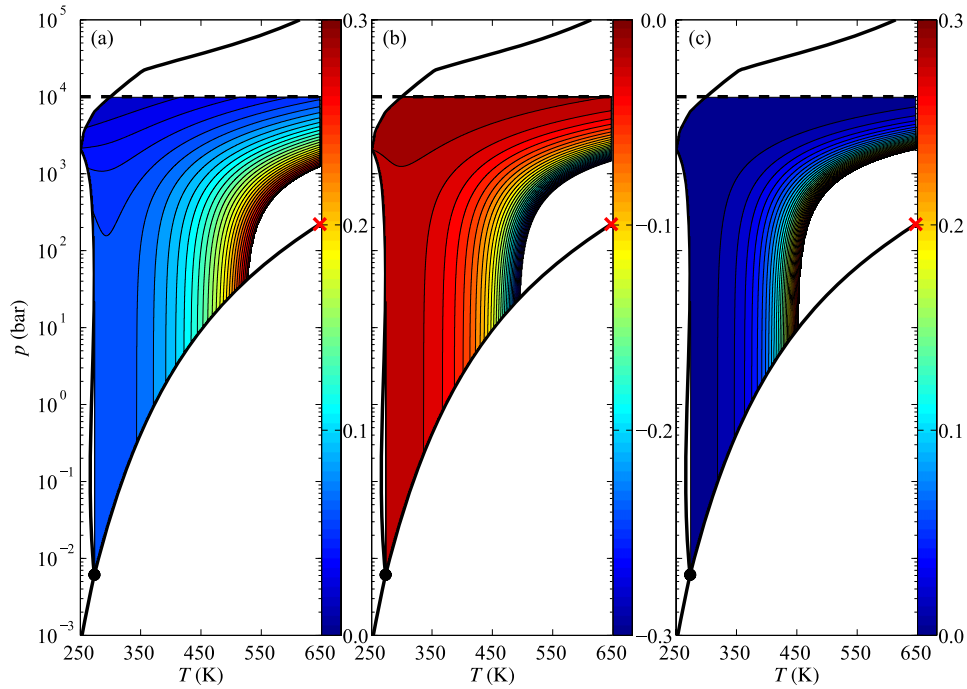
FIG. 2. Liquid phase fluctuation cumulants (a) B_{11}/ρ_1, (b) C_{111}/ρ_1, and (c) D_{1111}/ρ_1. The triple point is indicated by a black dot and the critical point by a red "×." The horizontal dashed line is the maximum valid pressure for the IAPWS-95 equation of state. Only the liquid phase was contoured. Data outside of the ranges depicted on the color bars were removed, due to the divergence of these properties at the critical point.

The value of μ can also provide details regarding the intermolecular potential. For instance, it can be shown that $\mu = 1$ for ideal gases, $\mu = 8$ for a Lennard-Jones 6–12 potential, and $\mu = 6$–11 for typical real liquids.[19,20]

Assuming the Moelwyn-Hughes isotherm is obeyed, one can integrate to obtain an expression for the compressibility as a function of a pressure change,

$$\frac{\kappa_T(p,T)}{\kappa_T(p_o,T)} = [1 + \Delta p \mu(T) \kappa_T(p_o,T)]^{-1}, \quad (25)$$

and integrate again to obtain the density as a function of a pressure change,
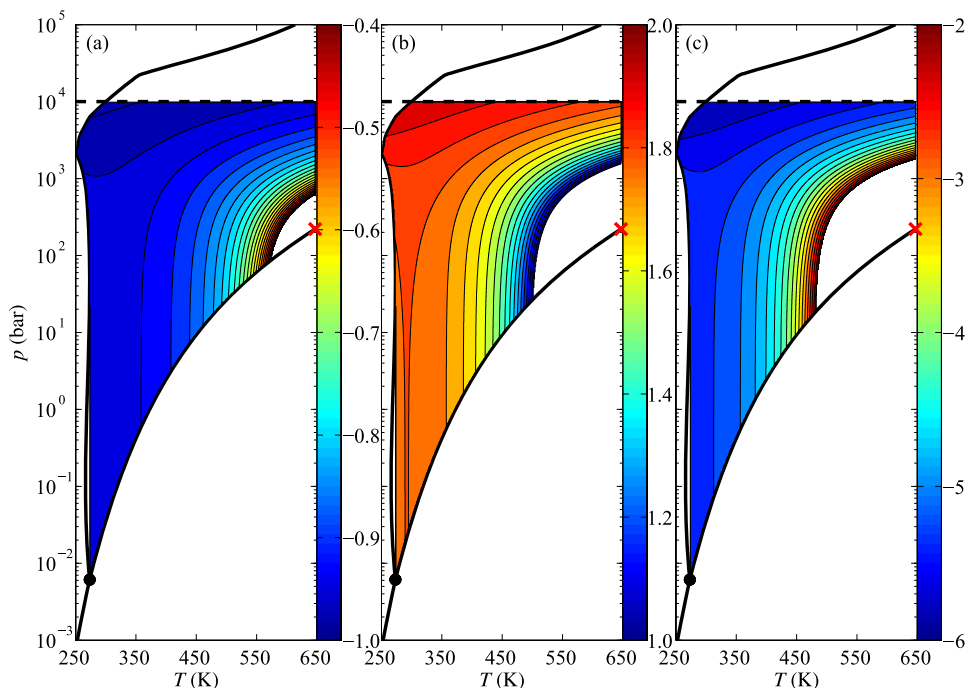
FIG. 3. Liquid phase distribution function integrals (a) $\rho_1 G_{11}$, (b) $\rho_1^2 G_{111}$, and (c) $\rho_1^3 G_{1111}$. The triple point is indicated by a black dot and the critical point by a red "×." The horizontal dashed line is the maximum valid pressure for the IAPWS-95 equation of state. Only the liquid phase was contoured. Data outside of the ranges depicted on the color bars were removed, due to the divergence of these properties at the critical point.

FIG. 4. Liquid phase (a) fluctuation cumulants and (b) distribution function integrals for selected isotherms [left column of panels (a) and (b)] and isobars [right column of panels (a) and (b)].

$$\frac{\rho_1(p,T)}{\rho_1(p_o,T)} = [1 + \Delta p \mu(T) \kappa_T(p_o,T)]^{1/\mu(T)}. \quad (26)$$
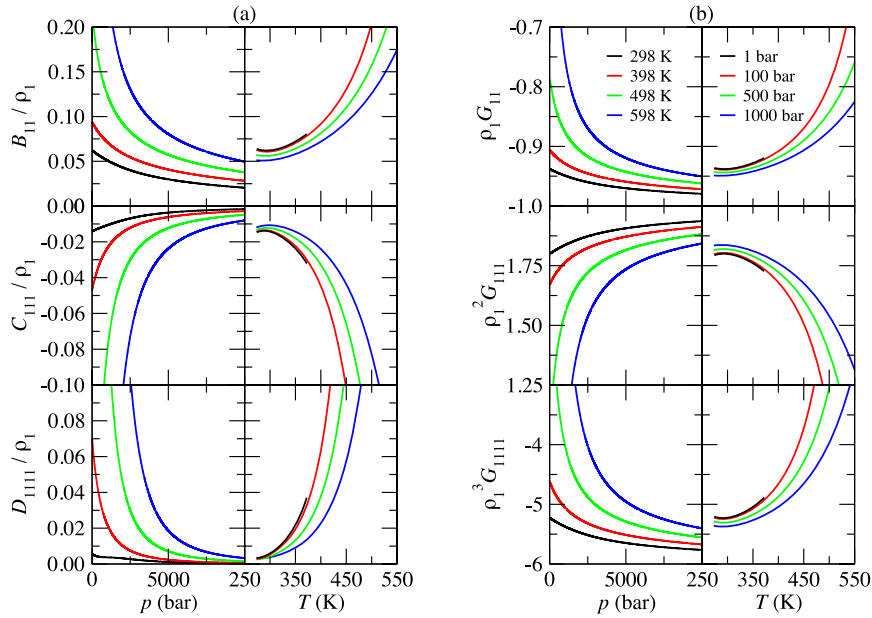
A further integration provides the change in chemical potential as a function of a pressure change, but that is not needed in the present study. Here, we use the above expressions to provide the fluctuating quantities and integrals. First, we note that Eq. (8) implies

$$B_{11}(p,T) = \beta^{-1} \rho_1(p,T)^2 \kappa_T(p,T), \quad (27)$$

and hence, Eqs. (25) and (26) provide the value of B_{11} and G_{11} anywhere along the isotherm. Using the expression provided in Eq. (24) and then comparing with the derivative of Eq. (27) obtained using the expressions given in Eqs. (8) and (10) provides

$$C_{111} = (2 - \mu) \frac{B_{11}^2}{\rho_1},$$
$$\rho_1^2 G_{111} = (1 - \mu) + (1 - 2\mu)\rho_1 G_{11} + (2 - \mu)\rho_1^2 G_{11}^2, \quad (28)$$

where we have dropped the explicit dependencies on pressure and temperature for clarity. A further pressure derivative, assuming μ is constant, then provides

$$D_{1111} = (2 - \mu)(3 - 2\mu)\frac{B_{11}^3}{\rho_1^2},$$
$$\rho_1^3 G_{1111} = -(1 - \mu)(1 + 2\mu) + (5 - 9\mu + 6\mu^2)\rho_1 G_{11}$$
$$+ 3(2 - \mu)(1 - 2\mu)\rho_1^2 G_{11}^2 + (2 - \mu)(3 - 2\mu)\rho_1^3 G_{11}^3. \quad (29)$$

Hence, using this approach, all the cumulants and integrals over distribution functions can be related to B_{11} and/or G_{11} through a single constant, μ.

The relatively simple forms for the fluctuations shown above allow us to characterize a series of possible situations. First, when $\mu = 1$, we obtain results consistent with the Poisson distribution observed for ideal gases. When $\mu = 2$, the moments describe a Gaussian distribution for the particle number fluctuations where B_{11} is independent of pressure and

TABLE I. Fluctuations and integrals for water at various state points.[a,b,c,d]

Property	Ambient T = 298.15 K p = 1 bar	Triple point [(l) approach, along T_{tp}]	Triple point [(g) approach, along p_{tp}]	Triple point [(g) approach, along T_{tp}]
ρ_1	55.344 56	55.496 95	$2.694\,692 \times 10^{-4}$	$2.694\,697 \times 10^{-4}$
B_{11}/ρ_1	0.062 076	0.064 150	1.001 2	1.001 2
C_{111}/ρ_1	−0.014 19	−0.014 83	1.004	1.004
D_{1111}/ρ_1	0.005 61	0.003 27	1.01	1.01
$\rho_1 G_{11}$	−0.937 924	−0.935 850	0.001 218	0.001 218
$\rho_1^2 G_{111}$	1.799 6	1.792 7	0.000 252	0.000 252
$\rho_1^3 G_{1111}$	−5.226	−5.202	0.000 25	0.000 25

[a] According to the IAPWS-95 EOS.
[b] Triple point (tp) values are estimated by approaching the tp from three directions.
[c] Units: ρ_1 is in M and all other properties are dimensionless.
[d] Triple point: = 273.16 K, 0.00 611 655 bar, 0.0 180 190 M^{-1} (liquid), 3710.98 M^{-1} (vapor).
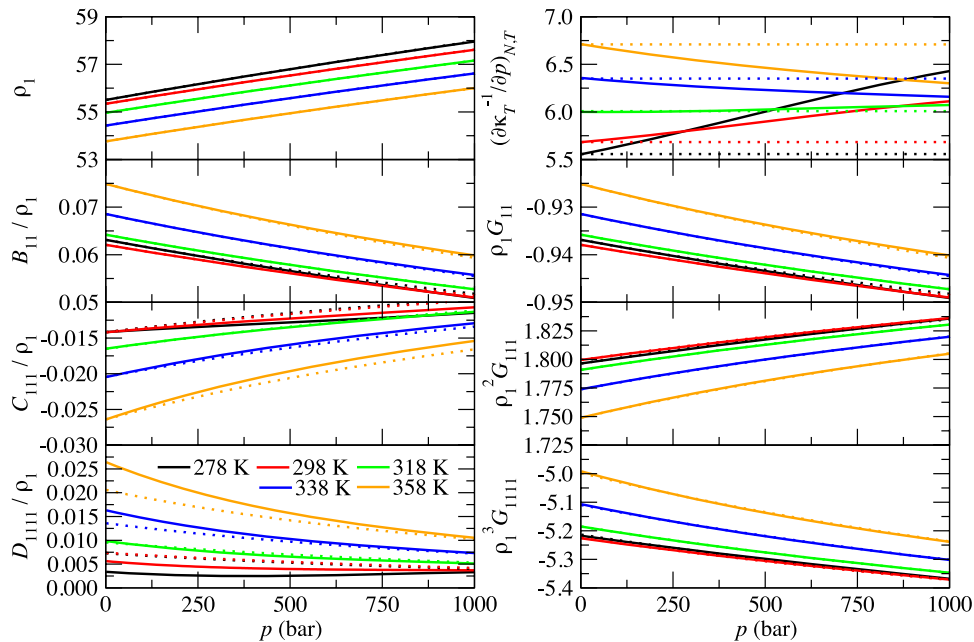
FIG. 5. Properties of liquid water according to the Moelwyn-Hughes isotherms (dotted lines) provided by Eqs. (24)–(30) compared to the values given by the IAPWS-95 EOS (solid lines). The density (ρ_1) is displayed in units of M.

$C_{111} = D_{1111} = 0$—the G's being non zero. An intermediate case where $\mu = 3/2$ would result in $B_{11} > 0$, $C_{111} < 0$, and $D_{1111} = 0$. For real liquids, where $\mu = 6$–11,[20] we find that $B_{11} > 0$, $C_{111} < 0$, and $D_{1111} > 0$. This is the pattern observed in Figure 2. Unfortunately, a clear pattern does not emerge for the G's from the above equations, although one is observed experimentally (see Figure 3).

The optimal value of μ does depend slightly on temperature. Therefore, to account for isothermal changes at temperatures greater ($^+$) or less ($^-$) than $T_o = 298.15$ K, we have fitted the dependence of μ on temperature according to the relationship

$$\begin{aligned}
\mu(T^+) &= \mu(T_o) + a^+ \Delta T + b^+ \Delta T^2, \\
\mu(T^-) &= \mu(T_o) + a^- \Delta T + b^- \Delta T^2 + c^- \Delta T^3,
\end{aligned} \quad (30)$$

where $\Delta T = T - T_o$. The parameters for Eq. (30) were obtained from the IAPWS-95 EOS by first fitting a series of bulk modulus versus pressure ($p_{sat} < p \leq 5$ bars) isotherms using Eq. (25) with $p_o = 1$ bar, and then fitting the resulting $\mu(T)$ values to Eq. (30). The parameters are then $\mu(T_o) = 5.68$, $a^+ = 1.58 \times 10^{-2}$, $b^+ = 2.1 \times 10^{-5}$, $a^- = 1.27 \times 10^{-2}$, $b^- = 7.3 \times 10^{-5}$, and $c^- = -1.2 \times 10^{-5}$. The results from this approach are compared to the more exact results provided by the IAPWS-95 EOS in Figure 5. The results at 298.15 K and 1 bar are in very good agreement with those reported in Table I, with the exception of the value for D_{1111}/ρ_1.

Figure 5 indicates that the distribution function integrals are very well reproduced by the Moelwyn-Hughes approximation over a range of pressures and isotherms, even though the slope of the bulk modulus vs pressure (μ) is changing over this range. The fluctuation cumulants are more problematic. The pair fluctuations are well reproduced, while the triplet fluctuations are well reproduced at low pressures and start to deviate from reality as the pressure increases. The quadruplet

fluctuations are poorly reproduced at low pressures, primarily due to the assumption that μ is independent of pressure, but are very well reproduced at higher pressures. All the data are well reproduced for the 318 K isotherm as the value of μ is independent of pressure for this temperature. Interestingly, this isotherm is very close to the compressibility minimum observed for liquid water at relatively low pressures.

E. Linear density approximation

A further simplification can be achieved when the density varies linearly with pressure. This is often observed or assumed. For instance, the simulated compressibility of a solution often involves a simple finite difference density calculation.[21] In this case, one can use Eq. (26) with $\mu = 1$. However, linear behavior of any kind (slope) will satisfy Eq. (24) with $\mu = 1$. To distinguish these possibilities, and to simplify the resulting expressions, we define a new positive constant μ_L by

$$\beta \mu_L(T) \equiv \rho_1(p_o, T) \kappa_T(p_o, T) \mu(T) \quad (31)$$

such that $\rho_1(p) = \rho_1(p_o) + \beta \mu_L \Delta p$ for linear behavior. Hence, $\mu_L = \mu = 1$ for an ideal gas ($\rho_1 = \beta p$ and $\kappa_T = p^{-1}$ for any p and T), but not necessarily for a liquid where μ_L will typically be much smaller than unity (0.06 for water at 298 K and 1 bar). It is relatively easy to show, using Eq. (15) with $\rho_1'' = \rho_1''' = 0$, that the fluctuating quantities are then given by

$$\begin{aligned}
B_{11} &= \rho_1 \mu_L, \\
C_{111} &= \rho_1 \mu_L^2, \\
D_{1111} &= \rho_1 \mu_L^3
\end{aligned} \quad (32)$$

which are all positive quantities. The corresponding integrals are provided by

$$\rho_1 G_{11} = \mu_L - 1,$$
$$\rho_1^2 G_{111} = (\mu_L - 1)(\mu_L - 2), \qquad (33)$$
$$\rho_1^3 G_{1111} = (\mu_L - 1)(\mu_L - 2)(\mu_L - 3)$$

and will alternate in sign if $\mu_L < 1$. Both of these expressions suggest the general relationships

$$\kappa_{n+1} = \mu_L^n \kappa_1,$$
$$\rho_1^n G_{1(n+1)} = \prod_{k=1}^{n} (\mu_L - k), \qquad (34)$$

where κ_i is the ith cumulant of the particle number distribution.

Unfortunately, it is immediately clear that this is a poor approximation for the fluctuating quantities. The value of B_{11} is reasonably well reproduced for small deviations from the reference state. However, this provides the wrong sign and magnitude for C_{111} indicating that the higher fluctuations are sensitive probes of the density variations. Thus, a linear density approximation, while adequate for obtaining the compressibility (B_{11}), is probably insufficient to obtain the higher order fluctuations in most cases.

F. Temperature related effects

The previous discussion has focused on pressure effects at constant T. However, many interesting observations occur as a function of T. FST can also be extended to include derivatives with respect to T.[11,22–24] Temperature effects naturally introduce energy fluctuations. The density maximum observed for water indicates a value of zero for the thermal expansion. FST provides the following expression for the thermal expansion coefficient (α_P) of a pure liquid:[24]

$$T\alpha_P = T\left(\frac{\partial \ln V}{\partial T}\right)_p = -\beta \frac{\langle \delta N_1 \delta \varepsilon \rangle}{\langle N_1 \rangle} = -\beta \frac{B_{1\varepsilon}}{\rho_1} \qquad (35)$$

in terms of the fluctuations in an excess energy $\varepsilon = E - N_1 H_1$, where E is the instantaneous internal energy of the volume of interest and H_1 is the average molar enthalpy of the solution. The subscript ε indicates a substitution of N_1 by ε in the previous expressions for B_{11} (and later C_{111}). When the thermal expansion is zero, the following condition must hold:

$$\langle \delta N_1 \delta E \rangle = \langle \delta N_1 \delta N_1 \rangle H_1 \approx \langle \delta N_1 \delta N_1 \rangle U_1, \qquad (36)$$

where the approximation should be reasonable for liquids under ambient conditions. Hence, the density maximum is characterized by the absence of a correlation between the particle number and the internal energy, i.e., $E = N_1 H_1 \approx N_1 U_1$.

The condition for the well-known minimum in the compressibility of water, located at 315 ± 5 K between 1 and 8 bars,[25–30] can also be phrased in terms of fluctuations. This requires the temperature derivatives developed in our previous work and provided in Appendix C.[11] The simplest result obtained from Eq. (8) is

$$T\left(\frac{\partial [\rho_1 \kappa_T / \beta]}{\partial T}\right)_p = \frac{\beta}{\rho_1^2}[\rho_1 C_{11\varepsilon} - B_{11} B_{1\varepsilon}]. \qquad (37)$$

Therefore, a minimum in the compressibility term is characterized by

$$\langle N_1 \rangle \langle \delta N_1 \delta N_1 \delta \varepsilon \rangle = \langle \delta N_1 \delta N_1 \rangle \langle \delta N_1 \delta \varepsilon \rangle \qquad (38)$$

which indicates that the triplet correlation is then simply related to the corresponding pair correlations. This can also be expressed in terms of density and energy fluctuations by dividing throughout by V^3.

G. Behavior of the fluctuations approaching the critical point

As mentioned previously, the fluctuation densities tend to $\pm\infty$ at the critical point for this second order transition. The critical point is characterized by the fact that[31]

$$\frac{\partial p}{\partial V} \to 0, \qquad \frac{\partial^2 p}{\partial V^2} \to 0. \qquad (39)$$

Hence, many of the derivatives required in order to obtain the fluctuations from Eq. (15) become very large in this region. The correlation length is therefore very long and the integrals described here also become large. However, pressure varies smoothly as a function of T along the critical isochore. Using the thermodynamic identity,

$$\left(\frac{\partial p}{\partial T}\right)_{\rho_1}\left(\frac{\partial T}{\partial \rho_1}\right)_p\left(\frac{\partial \rho_1}{\partial p}\right)_T = -1,$$
$$\left(\frac{\partial p}{\partial T}\right)_{\rho_1} = \frac{\alpha_P}{\kappa_T} = -\frac{\rho_1 B_{1\varepsilon}}{T B_{11}}, \qquad (40)$$

the above expressions indicate that while the thermal expansion and compressibility diverge as one approaches the critical point, their ratio remains finite. It also indicates that the same behavior with respect to T or p will be exhibited along the critical isochore. Furthermore, the approach to the critical point along the critical isotherm or isobar will also be the same.

Even though the fluctuations appear to diverge at the critical point, one can still investigate this divergence in terms of the traditional scaling laws and also obtain relationships between the triplet and pair correlations under these circumstances. To do this, we examine the behavior of B_{11}, which is closely related to the isothermal compressibility and bulk modulus and tends to infinity at the critical point. Analysis of the derivative of B_{11} with respect to either T or p provides expressions in terms of both the particle-particle and particle-energy fluctuations (see Appendix C for the isochoric expressions),

$$\left(\frac{\partial \ln B_{11}}{\partial \ln T}\right)_{\rho_1} = \beta\left[\frac{C_{11\varepsilon}}{B_{11}} - \frac{C_{111} B_{1\varepsilon}}{B_{11}^2}\right],$$
$$\left(\frac{\partial \ln B_{11}}{\partial \ln p}\right)_T = \frac{\beta p}{\rho_1}\frac{C_{111}}{B_{11}}, \qquad (41)$$
$$\left(\frac{\partial \ln B_{11}}{\partial \ln T}\right)_p = \beta\frac{C_{11\varepsilon}}{B_{11}}.$$

The expressions found in Eqs. (41) are valid anywhere away from a first order phase boundary. These derivatives tend to infinity at the critical point, but they do so in a well-defined manner. To see this, we need to examine the critical exponent associated with the limiting behavior of B_{11}. A series of related critical exponents can be defined by

$$\left(\frac{\partial \ln B_{11}}{\partial \ln |\Delta T|}\right)_{\rho_{1,c}, \Delta T \to 0} \equiv \gamma,$$

$$\left(\frac{\partial \ln B_{11}}{\partial \ln |\Delta T|}\right)_{p_c, \Delta T \to 0} \equiv \gamma_p, \qquad (42)$$

$$\left(\frac{\partial \ln B_{11}}{\partial \ln |\Delta p|}\right)_{T_c, \Delta p \to 0} \equiv \gamma_T,$$

where $\Delta T = T - T_c$ and $\Delta p = p - p_c$. We note that γ is the traditional exponent describing the divergence of the compressibility along the critical isochore.[32] Then, we can relate the two sets of derivatives via

$$\left(\frac{\partial \ln B_{11}}{\partial \ln T}\right)_{\rho_{1,c}, \Delta T \to 0} = -\frac{\gamma T}{|\Delta T|},$$

$$\left(\frac{\partial \ln B_{11}}{\partial \ln T}\right)_{p_c, \Delta T \to 0} = -\frac{\gamma_p T}{|\Delta T|}, \qquad (43)$$

$$\left(\frac{\partial \ln B_{11}}{\partial \ln p}\right)_{T_c, \Delta p \to 0} = -\frac{\gamma_T p}{|\Delta p|}.$$

This strongly suggests that the divergence of the fluctuating quantities is related in a simple manner—as one moves from the pair fluctuations to the triplet and quadruplet, the divergence increases by a factor of ΔT^{-1} or Δp^{-1} each time. Hence, the ratio of C_{111}/B_{11} and D_{1111}/C_{111} quantities diverges in the same manner, as do the ratios of integrals G_{111}/G_{11} and G_{1111}/G_{111}. The following limiting behavior is therefore observed along the critical isochore,

$$G_{11}, B_{11}, B_{1\varepsilon} \propto (p - p_c)^{-\gamma} \propto (T_c - T)^{-\gamma},$$
$$G_{111}, C_{111}, C_{11\varepsilon} \propto (p - p_c)^{-\gamma-1} \propto (T_c - T)^{-\gamma-1}, \qquad (44)$$
$$G_{1111}, D_{1111} \propto (p - p_c)^{-\gamma-2} \propto (T_c - T)^{-\gamma-2},$$

while along the critical isotherm or isobar, one finds

$$G_{11}, B_{11}, B_{1\varepsilon} \propto (p - p_c)^{-\gamma_T} \propto (T_c - T)^{-\gamma_P},$$
$$G_{111}, C_{111}, C_{11\varepsilon} \propto (p - p_c)^{-\gamma_T-1} \propto (T_c - T)^{-\gamma_P-1}, \qquad (45)$$
$$G_{1111}, D_{1111} \propto (p - p_c)^{-\gamma_T-2} \propto (T_c - T)^{-\gamma_P-2}.$$

From the relationship provided in Eq. (40), it is clear that $\gamma_T = \gamma_p$. The value of both constants can be obtained from the Taylor expansion provided in Eq. (16). If we rewrite the expansion for the critical isotherm using $p_o = p_c$ as

$$\Delta \rho_1 = \rho_1'(p_c)\Delta p \left[1 + \frac{\frac{1}{2}\rho_1''(p_c)\Delta p}{\rho_1'(p_c)} + \frac{\frac{1}{6}\rho_1'''(p_c)\Delta p^2}{\rho_1'(p_c)} + O(\Delta p^3)\right], \qquad (46)$$

then the relationships provided in Eqs. (17) and (45) indicate that all the terms in the square brackets are finite and constant when approaching the critical point. In fact, the general relationship

$$\left(\frac{\partial^n \rho_1}{\partial p^n}\right)_\beta \left(\frac{\partial p}{\partial \rho_1}\right)_\beta^{-1} \propto \Delta p^{1-n} \qquad (47)$$

would then hold where the derivatives are dominated by the first term in the square brackets of Eq. (17). It is known that $|\Delta \rho_1|^\delta \propto |\Delta p|$ as one approaches the critical point and so $\rho_1'(p_c) \propto \Delta p^{\delta^{-1}-1}$ and consequently $B_{11} \propto \Delta p^{\delta^{-1}-1}$, or γ_T

$= \gamma_p = 1 - \delta^{-1}$. The IAPWS-95 EOS state is a classical EOS for water that provides a value of $\gamma = 1$. The IAPWS-95 EOS has nonanalytic terms and the value of β is set at 0.3,[17] close to the renormalization group theory value (0.326),[32] and hence, a value of δ close to the renormalization group theory value $(4.8)^{32}$ would be expected. We have examined the limiting behavior of the fluctuations in Table II. The results are in agreement with the EOS and a value of $\delta \approx 5$. It should be noted that the analysis of critical exponents provided in Table II does not shed any new light on the experimental data, as these exponents result from the EOS, but they do provide support for the results presented in Eqs. (41) and (43)–(45). It should also be noted that the uncertainties in the properties generally increase as the critical region is approached and that the IAPWS-95 isothermal compressibility has an unphysical indentation in a region from T_c to $T_c + 2$ K for densities $\pm 0.5\%$ from ρ_c. Hence, the properties in Table II may not be entirely representative of real experimental data in this region.[17]

The scaling relations illustrated in Eqs. (44) and (45) also suggest quantities for which limiting fluctuation ratio values can be obtained at the critical point and can therefore be used to characterize the distribution. Specifically, these quantities are ratios of particle and/or energy fluctuations of the same order (pair/pair, triplet/triplet, etc.). It should also be noted that the terms preceded by delta functions in Eq. (A5) become negligible as we approach the critical point, and hence, the behavior of B_{11}, C_{111}, and D_{1111} is determined by the behavior of G_{11}, G_{111}, and G_{1111}, respectively. The estimated values for these quantities are provided in Table II. Examination of the critical exponents in Table II also suggests that the following ratio of moments should be constant at the critical point:

$$\frac{B_{11}D_{1111}}{C_{111}^2} = \frac{G_{11}G_{1111}}{G_{111}^2} = \frac{\langle(\delta\rho)^2\rangle\left[\langle(\delta\rho)^4\rangle - 3\langle(\delta\rho)^2\rangle^2\right]}{\langle(\delta\rho)^3\rangle^2}, \qquad (48)$$

where $\rho = N_1/V$ is an instantaneous density. The above ratio is also the ratio of the fourth standardized central moment to the square of the third standardized central moment.

IV. DISCUSSION

The fluctuations investigated here using FST are the same properties that cause radiation to scatter when it impinges on a liquid.[33] The measured distribution of scattered radiation intensity, $I(Q)$, provides information on the distribution of the atomic positions in the liquid.[34,35] Several steps and corrections must be taken to go from $I(Q)$ to the structure factor, $S(Q)$.[36–38] The resulting $S(Q)$ is a sum of weighted averages of $m(m+1)/2$ partial structure factors, $S_{\alpha\beta}(Q)$, where m is the number of distinct atomic species.[36,39] For water, there are three partial structure factors, $S_{OO}(Q)$, $S_{OH}(Q)$, and $S_{HH}(Q)$.[36,38] If each $S_{\alpha\beta}(Q)$ can be de-convoluted, the site-site rdfs can be obtained by Fourier transformation.[36,38,40,41] So far, it has only been possible to obtain the complete set of site-site rdfs for a very small set of all the molecules that make up chemical space.[10,37,39,42]

Even knowing $g_{\alpha\beta}^{(2)}$ for a liquid does not "close the book" on its structure.[43] The structure of monatomic liquids is fully defined by the relative probability of finding $n = 1, 2, \ldots, N$, of the N molecules in the system at various separation radii.[8,43–50] These relative probabilities are trivial for $n = 1$, $g_\alpha^{(1)} = 1$, and obtainable for $n = 2$, $g_{\alpha\beta}^{(2)}$, for monatomic liquids as described above. For molecular systems, a complete description of the structure would additionally require knowledge of the relative probability of finding triplets, etc., of the molecules' constituent atoms at various separation radii and the angular relative probability distributions that describe the molecular orientations.[39,41,43,51] Experimental studies that provide $g_{\alpha\beta}^{(2)}$ do not provide the complete angular distributions.[41,43,52,53] As a workaround, Soper and coworkers obtained angular distributions from computer simulations.[41,51,54] Indeed, the full set of site-site and angular dependent distribution functions are required for integral equation studies of molecules, but FST does not require this exhaustive level of detail regardless of the type of molecule under study. All that is needed in the FST approach is the center of mass based, not the site-site and/or the angular dependent distributions for any type of molecule. From this input information, a thermodynamic and microstructural description of the system can be obtained.

In addition to the sequence of positional distribution functions, the sequence of interatomic potentials is also relevant to this discussion.[7] In most studies, all that is considered is the two-body correlations and/or potential.[13,43,46,50] Largely, this is because there has been no experimental determination of three-body distribution functions for (three-dimensional) fluids.[8,39,42,47–49,55] However, several examples where knowledge of the triplet correlations are important have been discussed by von Grunberg,[47,48] Abascal,[56] Winter,[49] and Rice.[42] Higher-order potential terms are included in some atomic and homonuclear diatomic fluid theories, where accurate pair potentials can be obtained.[13,43,53,57] In contrast, molecular potentials are generally "effective" potentials, meaning that a pair potential is adjusted to reproduce target data to circumvent the need for the correct combinations of pair plus higher potentials.[43]

Attempts to measure higher distribution functions directly, despite the experimental limitations with conventional scattering methods, have led to interesting video microscopy studies of quasi two-dimensional, colloidal systems.[42,47,48] Additionally, indirect experimental measurements of integrals over the triplet distribution function may be obtained for fluids for which $g_{\alpha\beta}^{(2)}$ is known. However, this approach is not applicable to molecular fluids without making approximations.[8] The isothermal pressure derivative of $S(Q)$ involves the pressure or density derivative of $g_{\alpha\beta}^{(2)}$, which can be written as an integral over $g_{\alpha\beta\gamma}^{(3)}$.[14] For example, the pressure derivative of $g_{11}^{(2)}$ is given by[8]

$$\rho_1 k_\mathrm{B} T \left(\frac{\partial \rho_1^2 g_{11}^{(2)}(r)}{\partial p} \right)_T = \rho_1^3 \int \left[g_{111}^{(3)}(\mathbf{r},\mathbf{s}) - g_{11}^{(2)}(r) \right] d\mathbf{s} + 2\rho_1^2 g_{11}^{(2)}(r), \tag{49}$$

where $\mathbf{r}$ and $\mathbf{s}$ are interatomic vectors connecting atoms at positions 1 and 2 and positions 1 and 3, respectively. The above expression is consistent with Eq. (14). It should be noted that neither $g_{111}^{(3)}$ itself nor an integral over $g_{111}^{(3)}$ by itself is obtained, but instead an integral over $g_{111}^{(3)} - g_{11}^{(2)}$. Nevertheless, the integral has been useful for the few systems for which the rdfs are obtainable. These relationships, first provided by Buff and coworkers and by Schofield,[22,58–61] have been used extensively by Egelstaff and others to test theories and models for $g_{\alpha\beta\gamma}^{(3)}$ [8,9,13,14,22,49,55,58–62] and are described below.

Our work is similar to the $S(Q \to 0)$ limit of Egelstaff's (and others') work, which is focused on $S(Q)$ and therefore only technically valid for monatomic liquids.[8] Egelstaff did make a very brief mention of this $S(0)$ limit. For example, most similar to our work, he compared the pressure derivative of the bulk modulus for argon at its triple point from experiment with various models for $g^{(3)}$.[13] Similar analysis was performed for gaseous krypton at a state point near its critical point.[9] Ram and Egelstaff assessed the pressure of room temperature krypton versus density.[53,63] They compared experiment and simulation using an accurate pair potential and attributed deviations in the agreement to higher order interactions.[53,63]

TABLE II. Critical point behavior.[a,b]

	$\dfrac{\beta B_{1\varepsilon}}{B_{11}}$	$\dfrac{C_{111}}{B_{11}^2}$ M^{-1}	$\dfrac{D_{1111}}{B_{11}^3}$ M^{-2}	$\dfrac{\beta C_{11\varepsilon}}{C_{111}}$	$\dfrac{B_{11}D_{1111}}{C_{111}^2}$
		Estimated finite critical point quantities for water			
$\rho_{1,\mathrm{c}}, \partial p/\partial T$	−1.80				
$\rho_{1,\mathrm{c}}, T > T_\mathrm{c}$	−1.8	0.149	ND	−2.0	ND
$T_\mathrm{c}, p > p_\mathrm{c}$	−1.7			−1.7	2.2
$p_\mathrm{c}, T < T_\mathrm{c}$	−1.7			−1.7	2.2
	Critical exponents from the IAPWS-95 EOS				
	B_{11}^{-1}	$|C_{111}|^{-1}$	D_{1111}^{-1}	$|B_{1\varepsilon}|^{-1}$	$|C_{11\varepsilon}|^{-1}$
$\rho_{1,\mathrm{c}}, T > T_\mathrm{c}$	1.01	2.02	ND	1.00	2.00
$T_\mathrm{c}, p > p_\mathrm{c}$	0.81	1.81	2.80	0.81	1.83
$p_\mathrm{c}, T < T_\mathrm{c}$	0.83	1.84	2.83	0.84	1.85

[a]$T_\mathrm{c} = 647.096$ K, $p_\mathrm{c} = 220.64$ bars, $\rho_{1,\mathrm{c}} = 17.87\ M$, $\beta_\mathrm{c} = 0.186$ mol/kJ, and $\beta_\mathrm{c} p_\mathrm{c}/\rho_{1,\mathrm{c}} = 0.229$.
[b]Values of $\Delta p \approx$ m bar and $\Delta T \approx$ m K were used to determine the critical exponents. ND, could not be determined accurately.

Gray, Gubbins, and Egelstaff have derived general expressions for thermodynamic derivatives of properties that are a function of the phase variables averaged over the GCE to derive the thermodynamic derivatives of dynamic correlation functions in a systematic fashion.[14] They discussed using derivatives of radiation scattering functions to study higher-order correlations and to test models or theories of fluids and used examples taken from other studies of the derivative of the Van Hove self-scattering function for hydrogen gas at 85 K and 120 atm and of the pressure derivative of the distinct Van Hove scattering function for nitrogen gas at room temperature and 200 atm.[14] They briefly noted that their equations could also be extended to mixtures and would then be considered generalizations of KB theory.[14]

Several other works are also directly dependent upon scattering data. Buff and Brout[22] and Schofield[58] developed recursion relationships between the density derivatives of correlation functions of all orders and integrals over higher order correlation functions, but no real applications were provided. In a later study, Buff and Brout used the concentration derivative of the rdf for argon at 91.8 K and 2 atm to assess the quality of the superposition approximation and also obtained G_{111} from a similar route to that described here.[59] Egelstaff, Page, and Heard assessed the isothermal pressure derivative of $S(Q)$ for liquid rubidium near its triple point and argon near its critical point and also assessed the isothermal pressure derivative of the centers-$S(Q)$ for liquid carbon tetrachloride (reliant upon approximations since this is polyatomic) at an intermediate state point at 296 K.[8] They compared their findings to integral equation theory results using various models for $g^{(3)}$.[8] Gläser and coworkers presented a neutron diffraction investigation of the $S(Q)$ of liquid cesium close to its liquid-vapor critical point to obtain the isothermal density derivative of $S(Q)$.[62] Soper and coworkers measured the isothermal density derivative of $S(Q)$ of dense fluid helium by neutron diffraction to test a model for $g^{(3)}$.[55] Finally, Egelstaff[64] additionally assessed the second derivative of $S(Q)$ with respect to pressure for liquid neon at 35 K and $\rho = 1.119$ g/cm^3, which is related to integrals over the quadruplet correlation function, and Ballentine[65] has further considered the long wavelength limit.

Most notably, Gorbaty and coworkers determined the pair correlation function of liquid water at pressures up to 7.7 kilobars.[66] No attempt to connect to three body correlations was reported. Soper also measured the rdf in water and ice over a range of temperatures and pressures, but connections to the integrals over the three body correlation function were, again, not reported.[37]

V. CONCLUSIONS

We have illustrated how triplet and quadruplet fluctuation densities, or integrals over triplet and quadruplet distribution functions, can be obtained from existing experimental data for pure liquids. The results should help to provide a deeper understanding of liquids and liquid mixtures. The only other experimental technique that we know of which provides such data for solutions is that of solution scattering studies.[13] However, these are limited to triplet correlations and to

relatively simple pure liquids and very simple mixtures. No such limitation is found with the current approach. It appears that the experimental extraction of these correlations is viable for the triplet distributions, while the quadruplet distributions are somewhat more problematic, but also seem obtainable. Fortunately, while the current approach does not provide the experimental values of $g^{(3)}_{\alpha\beta\gamma}$ or $g^{(4)}_{\alpha\beta\gamma\delta}$ as a function of intermolecular distance (no currently available approach does), the thermodynamics of the solution is directly related to integrals over these distribution functions, which are provided by the current approach. For simple liquids, it has already been shown that this type of integral is useful.[8,9,13,14,22,49,55,58–62] Using FST, integrals over $g^{(3)}_{\alpha\beta\gamma}$ and $g^{(4)}_{\alpha\beta\gamma\delta}$ may now be obtained without the need for scattering experiments, albeit with a loss of spatial resolution. They may be obtained for any liquid (or solution) where the required bulk thermodynamic data have been determined. Thus, we believe the field may now begin to assess how important the $g^{(3)}_{\alpha\beta\gamma}$ and $g^{(4)}_{\alpha\beta\gamma\delta}$ distributions are for describing the thermodynamic properties of any system of interest.

APPENDIX A: DISTRIBUTION FUNCTIONS AND FLUCTUATION DENSITIES

In the grand canonical ensemble, the probability that any n_α molecules of species α, n_β molecules of species β, etc. are within $d\{r\}$ at $\{r\}$ is given by $\rho^{(n)}(\{r\})d\{r\}$ where[1]

$$\int \rho^{(n)}(\{r\})d\{r\} = \left\langle \prod_s \frac{N_s!}{(N_s - n_s)!} \right\rangle. \tag{A1}$$

Here, the product involves the different species (s) present in the solution, while n_s is the number of molecules of each species in the (n) particle distribution. We require integrals up to and including the four body distribution for a general mixture of any number of components. These involve integrals over the following spatial probability density distributions:

$$\int \rho^{(1)}_\alpha(r_1)dr_1 = \langle N_\alpha \rangle,$$

$$\int \rho^{(2)}_{\alpha\beta}(r_1,r_2)dr_1dr_2 = \langle N_\alpha(N_\beta - \delta_{\alpha\beta}) \rangle,$$

$$\int \rho^{(3)}_{\alpha\beta\gamma}(r_1,r_2,r_3)dr_1dr_2dr_3$$
$$= \langle N_\alpha(N_\beta - \delta_{\alpha\beta})(N_\gamma - \delta_{\alpha\gamma} - \delta_{\beta\gamma}) \rangle, \tag{A2}$$

$$\int \rho^{(4)}_{\alpha\beta\gamma\delta}(r_1,r_2,r_3,r_4)dr_1dr_2dr_3dr_4$$
$$= \langle N_\alpha(N_\beta - \delta_{\alpha\beta})(N_\gamma - \delta_{\alpha\gamma} - \delta_{\beta\gamma})(N_\delta - \delta_{\alpha\delta} - \delta_{\beta\delta} - \delta_{\gamma\delta}) \rangle.$$

By analogy with the theory of imperfect gases, we define the following integrals:[1,2]

$$\rho_\alpha \rho_\beta V G_{\alpha\beta} \equiv \int \left[\rho^{(2)}_{\alpha\beta} - \rho^{(1)}_\alpha \rho^{(1)}_\beta \right] dr_1 dr_2,$$

$$\rho_\alpha \rho_\beta \rho_\gamma V G_{\alpha\beta\gamma} \equiv \int \left[\rho^{(3)}_{\alpha\beta\gamma} - \rho^{(2)}_{\alpha\beta}\rho^{(1)}_\gamma - \rho^{(2)}_{\alpha\gamma}\rho^{(1)}_\beta - \rho^{(2)}_{\beta\gamma}\rho^{(1)}_\alpha + 2\rho^{(1)}_\alpha \rho^{(1)}_\beta \rho^{(1)}_\gamma \right] dr_1 dr_2 dr_3, \tag{A3}$$

$$\rho_\alpha \rho_\beta \rho_\gamma \rho_\delta V G_{\alpha\beta\gamma\delta} \equiv \int \begin{bmatrix} \rho^{(4)}_{\alpha\beta\gamma\delta} - \rho^{(3)}_{\alpha\beta\gamma}\rho^{(1)}_\delta - \rho^{(3)}_{\alpha\beta\delta}\rho^{(1)}_\gamma - \rho^{(3)}_{\alpha\gamma\delta}\rho^{(1)}_\beta - \rho^{(3)}_{\beta\gamma\delta}\rho^{(1)}_\alpha \\ -\rho^{(2)}_{\alpha\beta}\rho^{(2)}_{\gamma\delta} - \rho^{(2)}_{\alpha\gamma}\rho^{(2)}_{\beta\delta} - \rho^{(2)}_{\alpha\delta}\rho^{(2)}_{\beta\gamma} \\ +2\rho^{(2)}_{\alpha\beta}\rho^{(1)}_\gamma\rho^{(1)}_\delta + 2\rho^{(2)}_{\alpha\gamma}\rho^{(1)}_\gamma\rho^{(1)}_\delta + 2\rho^{(2)}_{\alpha\delta}\rho^{(1)}_\beta\rho^{(1)}_\gamma \\ +2\rho^{(2)}_{\beta\gamma}\rho^{(1)}_\alpha\rho^{(1)}_\delta + 2\rho^{(2)}_{\beta\delta}\rho^{(1)}_\alpha\rho^{(1)}_\gamma + 2\rho^{(2)}_{\gamma\delta}\rho^{(1)}_\alpha\rho^{(1)}_\beta \\ -6\rho^{(1)}_\alpha\rho^{(1)}_\beta\rho^{(1)}_\gamma\rho^{(1)}_\delta \end{bmatrix} dr_1 dr_2 dr_3 dr_4,$$

where we have removed the spatial dependencies for clarity. Similar integrals arise during the expansion of the partition function (see Eq. (1)) employed in gas and solution theory. The first two integrals also appeared in the original KB paper.[2] The above integrals can be expressed in terms of spatial probability distributions via their definitions

$$g^{(1)}_\alpha(r_1) \equiv \frac{\rho^{(1)}_\alpha(r_1)}{\rho_\alpha} = 1, \qquad g^{(2)}_{\alpha\beta}(r_1,r_2) \equiv \frac{\rho^{(2)}_{\alpha\beta}(r_1,r_2)}{\rho_\alpha\rho_\beta},$$

$$g^{(3)}_{\alpha\beta\gamma}(r_1,r_2,r_3) \equiv \frac{\rho^{(3)}_{\alpha\beta\gamma}(r_1,r_2,r_3)}{\rho_\alpha\rho_\beta\rho_\gamma}, \qquad g^{(4)}_{\alpha\beta\gamma\delta}(r_1,r_2,r_3,r_4) \equiv \frac{\rho^{(4)}_{\alpha\beta\gamma\delta}(r_1,r_2,r_3,r_4)}{\rho_\alpha\rho_\beta\rho_\gamma\rho_\delta}. \tag{A4}$$

A combination of Eqs. (A3) and (A4), followed by some minor rearrangement, provides the integrals given in the main text as Eq. (12). Furthermore, a combination of Eqs. (A2) and (A3) provides the G's in terms of fluctuating quantities

$$\rho_\alpha\rho_\beta V G_{\alpha\beta} = \langle \delta N_\alpha \delta N_\beta \rangle - \delta_{\alpha\beta}\langle N_\alpha \rangle,$$

$$\rho_\alpha\rho_\beta\rho_\gamma V G_{\alpha\beta\gamma} = \langle \delta N_\alpha \delta N_\beta \delta N_\gamma \rangle - \delta_{\beta\gamma}\langle \delta N_\alpha \delta N_\beta \rangle - \delta_{\alpha\beta}\langle \delta N_\alpha \delta N_\gamma \rangle$$

$$- \delta_{\alpha\gamma}\langle \delta N_\beta \delta N_\gamma \rangle + 2\delta_{\alpha\beta}\delta_{\alpha\gamma}\langle N_\alpha \rangle, \tag{A5}$$

$$\rho_\alpha\rho_\beta\rho_\gamma\rho_\delta V G_{\alpha\beta\gamma\delta} = \langle \delta N_\alpha \delta N_\beta \delta N_\gamma \delta N_\delta \rangle - \langle \delta N_\alpha \delta N_\beta \rangle\langle \delta N_\gamma \delta N_\delta \rangle$$

$$- \langle \delta N_\alpha \delta N_\gamma \rangle\langle \delta N_\beta \delta N_\delta \rangle - \langle \delta N_\alpha \delta N_\delta \rangle\langle \delta N_\beta \delta N_\gamma \rangle$$

$$- (\delta_{\alpha\delta} + \delta_{\gamma\delta})\langle \delta N_\alpha \delta N_\beta \delta N_\gamma \rangle - (\delta_{\alpha\gamma} + \delta_{\beta\gamma})\langle \delta N_\alpha \delta N_\beta \delta N_\delta \rangle$$

$$- (\delta_{\alpha\beta} + \delta_{\beta\delta})\langle \delta N_\alpha \delta N_\gamma \delta N_\delta \rangle$$

$$+ (\delta_{\alpha\gamma}\delta_{\alpha\delta} + \delta_{\alpha\delta}\delta_{\gamma\delta} + \delta_{\beta\delta}\delta_{\gamma\delta} + \delta_{\beta\gamma}\delta_{\gamma\delta})\langle \delta N_\alpha \delta N_\beta \rangle$$

$$+ (\delta_{\alpha\beta}\delta_{\alpha\gamma} + \delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\gamma} + \delta_{\alpha\gamma}\delta_{\beta\delta})\langle \delta N_\alpha \delta N_\delta \rangle$$

$$+ (\delta_{\alpha\beta}\delta_{\alpha\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma} + \delta_{\alpha\delta}\delta_{\beta\delta})\langle \delta N_\alpha \delta N_\gamma \rangle - 6\delta_{\alpha\beta}\delta_{\alpha\gamma}\delta_{\alpha\delta}\langle N_\alpha \rangle.$$

These expressions can then be rearranged to provide the equivalent fluctuating quantities given in the main text. It should be noted that when all the particles are of a different type (all delta functions are zero) then the integrals are simply the cumulants of the multivariate particle distribution.

APPENDIX B: FLUCTUATING QUANTITIES AND DISTRIBUTION FUNCTION INTEGRALS FROM EXPERIMENTAL DATA

The fluctuating quantities were expressed in terms of density derivatives in the main text. They can also be expressed in terms of derivatives of the molar volume ($V_1 = 1/\rho_1$) and are then given by

$$B_{11} = -\frac{1}{\beta V_1^3} V_1',$$

$$C_{111} = -\frac{1}{\beta^2 V_1^5}[V_1 V_1'' - 3(V_1')^2], \tag{B1}$$

$$D_{1111} = -\frac{1}{\beta^3 V_1^7}[V_1^2 V_1''' - 10 V_1 V_1' V_1'' + 15(V_1')^3],$$

where the prime again indicates an isothermal derivative with respect to pressure. The corresponding fluctuations can also be expressed in terms of pressure derivatives of the compressibility and are then given by the expressions

$$B_{11} = \beta^{-1}\rho_1^2 \kappa_T,$$

$$C_{111} = \beta^{-2}\rho_1^3[\kappa_T' + 2\kappa_T^2], \tag{B2}$$

$$D_{1111} = \beta^{-3}\rho_1^4[\kappa_T'' + 7\kappa_T \kappa_T' + 6\kappa_T^3].$$

The most convenient choice will depend on the EOS used to fit the experimental or simulated data.

APPENDIX C: ENERGY FLUCTUATIONS

Here, we provide expressions for the triplet fluctuations involving the excess energy of the region of interest. Previously we have shown that[11,67]

$$C_{11\varepsilon} = -\left(\frac{\partial B_{11}}{\partial \beta}\right)_P \tag{C1}$$

which is also evident from Eq. (6). Using the expression for B_{11} provided in Eq. (15) allows one to derive an expression for the particle-particle-excess energy triplet fluctuation density in terms of experimental data for pure components. The result is

$$\frac{\beta C_{11\varepsilon}}{\rho_1} = \frac{\rho_1 \kappa_T}{\beta}(1 - T\alpha_P) + \frac{T}{\beta}\left(\frac{\partial^2 \rho_1}{\partial p \partial T}\right), \qquad \text{(C2)}$$

whereas the FST expression for the second density derivative is

$$\frac{T}{\beta}\left(\frac{\partial^2 \rho_1}{\partial p \partial T}\right) = \frac{\beta C_{11\varepsilon}}{\rho_1} - \frac{B_{11}}{\rho_1}\left[1 + \frac{\beta B_{1\varepsilon}}{\rho_1}\right]. \qquad \text{(C3)}$$

These expressions are used to obtain $C_{11\varepsilon}$ from the EOS.

The same type of approach can also be used to provide derivatives along a particular isochore. From Eq. (6) with $\langle X \rangle = B_{11}$, we find

$$\left(\frac{\partial B_{11}}{\partial \beta}\right)_{\rho_1} = -C_{11E} + C_{111}\left(\frac{\partial \beta \mu_1}{\partial \beta}\right)_{\rho_1}. \qquad \text{(C4)}$$

Using the fact that

$$\left(\frac{\partial \beta \mu_1}{\partial \beta}\right)_{\rho_1} = \left(\frac{\partial \beta \mu_1}{\partial \beta}\right)_P + \left(\frac{\partial \beta \mu_1}{\partial p}\right)_\beta \left(\frac{\partial p}{\partial \beta}\right)_{\rho_1} = H_1 - \frac{T\alpha_P}{\rho_1 \kappa_T}, \qquad \text{(C5)}$$

where we have also used Eq. (40) leads to

$$\left(\frac{\partial B_{11}}{\partial \beta}\right)_{\rho_1} = -C_{11\varepsilon} + C_{111}\frac{B_{1\varepsilon}}{B_{11}}, \qquad \text{(C6)}$$

which provides the first expression in Eq. (41).

[1] T. L. Hill, *Statistical Mechanics: Principles and Selected Applications* (McGraw-Hill Book Company Inc., New York, 1956).
[2] J. G. Kirkwood and F. P. Buff, J. Chem. Phys. **19**, 774 (1951).
[3] A. Ben-Naim, in *Fluctuation Theory of Solutions: Applications in Chemistry Chemical Engineering Biophysics*, edited by P. E. Smith, E. Matteoli, and J. P. O'Connell (Taylor & Francis, Boca Raton, 2013), pp. 35–63.
[4] A. Ben-Naim, *Molecular Theory of Solutions* (Oxford University Press, New York, 2006).
[5] P. E. Smith, E. Matteoli, and J. P. O'Connell, *Fluctuation Theory of Solutions: Applications in Chemistry, Chemical Engineering and Biophysics* (Taylor & Francis, Boca Raton, 2013).
[6] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids. Vol. 1: Fundamentals* (Oxford University Press, New York, 1984).
[7] P. A. Egelstaff, J. Phys. (Paris) **46**, 1 (1985).
[8] P. A. Egelstaff, D. I. Page, and C. R. T. Heard, J. Phys. C: Solid State Phys. **4**, 1453 (1971).
[9] D. J. Winfield and P. A. Egelstaff, Can. J. Phys. **51**, 1965 (1973).
[10] P. A. Egelstaff, in *Molecular Liquids: New Perspectives in Physics and Chemistry*, edited by J. J. C. Teixeira-Dias (Springer, Netherlands, 1992), Vol. 379, pp. 29–44.
[11] E. A. Ploetz and P. E. Smith, in *Adv. Chem. Phys.* (John Wiley & Sons Inc., 2013), pp. 311–372.
[12] R. F. Greene and H. B. Callen, Phys. Rev. **83**, 1231 (1951).
[13] P. A. Egelstaff, Annu. Rev. Phys. Chem. **24**, 159 (1973).
[14] E. Gubbins, C. G. Gray, and P. A. Egelstaff, Mol. Phys. **35**, 315 (1978).
[15] A. Ben-Naim, J. Chem. Phys. **67**, 4884 (1977).
[16] A. H. Harvey, A. P. Peskin, and S. A. Klein, NIST Standard Reference Database 10: NIST/ASME Steam Properties, version 2.22, U.S. Department of Commerce, Gaithersburg, 2008.
[17] W. Wagner and A. Pruss, J. Phys. Chem. Ref. Data **31**, 387 (2002).
[18] L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part I, Vol. 5 of Course of Theoretical Physics*, 3rd ed. (Pergamon Press, Oxford, 1980), [Translated from the Russian by J. B. Sykes and M. J. Kearsley].
[19] E. A. Moelwyn-Hughes, *Physical Chemistry*, 2nd ed. (Pergamon Press, Oxford, 1961).
[20] D. P. Kharakoz, Biophys. J. **79**, 511 (2000).
[21] H. B. Yu and W. F. van Gunsteren, J. Chem. Phys. **121**, 9549 (2004).
[22] F. P. Buff and R. Brout, J. Chem. Phys. **23**, 458 (1955).
[23] P. G. Debenedetti, J. Chem. Phys. **86**, 7126 (1987).
[24] E. A. Ploetz and P. E. Smith, J. Chem. Phys. **135**, 044506 (2011).
[25] H. L. Pi, J. L. Aragones, C. Vega, E. G. Noya, J. L. F. Abascal, M. A. Gonzalez, and C. McBride, Mol. Phys. **107**, 365 (2009).
[26] G. S. Kell, J. Chem. Eng. Data **20**, 97 (1975).
[27] R. J. Speedy and C. A. Angell, J. Chem. Phys. **65**, 851 (1976).
[28] T. S. Carlton, J. Phys. Chem. B **111**, 13398 (2007).
[29] F. Mallamace, C. Corsaro, and H. E. Stanley, Sci. Rep. **2**, 993 (2012).
[30] M. Vedamuthu, S. Singh, and G. W. Robinson, J. Phys. Chem. **99**, 9263 (1995).
[31] A. Munster, *Classical Thermodynamics* (Stonebridge Press, Bristol, 1970).
[32] W. Wagner, "From the beginning to this day: My first naive ideas and the research results achieved (Gibbs Award Lecture)," in *15th International Conference on the Properties of Water and Steam* edited by R. Span and I. Weber (VDI - The Association of German Engineers and GET—Society for Energy Technology, Berlin, 2008).
[33] P. A. Egelstaff, "Inelastic-scattering of neutrons and possible biological applications," in *Brookhaven Symposia in Biology Number 27: Neutron Scattering for the Analysis of Biological Structures (BNL: 50453)*, edited by B. P. Schoenborn (Brookhaven National Laboratory Associated Universities, Inc.: Upton, NY, 1976), pp. I26–I39.
[34] G. Allen and J. S. Higgins, Rep. Prog. Phys. **36**, 1073 (1973).
[35] P. A. Egelstaff, in *Molecular Liquids: New Perspectives in Physics and Chemistry*, edited by J. J. C. Teixeira-Dias (Springer, Netherlands, 1992), Vol. 379, pp. 1–27.
[36] B. Tomberli, C. J. Benmore, P. A. Egelstaff, J. Neuefeind, and V. Honkimaki, J. Phys.: Condens. Matter **12**, 2597 (2000).
[37] A. K. Soper, Chem. Phys. **258**, 121 (2000).
[38] P. A. Egelstaff, Phys. Chem. Liq. **40**, 203 (2002).
[39] G. W. Neilson and A. K. Adya, Annu. Rep. Prog. Chem., Sect. C: Phys. Chem. **93**, 101 (1997).
[40] P. A. Egelstaff, in *Methods in the Determination of Partial Structure Factors of Disordered Matter by Neutron and Anomalous X-ray Diffraction*, edited by J. B. Suck, P. Chieux, D. Raoux, and C. Riekel (World Scientific Publishing Co, Singapore, Singapore, 1993), pp. 1–15.
[41] A. K. Soper, J. Chem. Phys. **101**, 6888 (1994).
[42] H. M. Ho, B. H. Lin, and S. A. Rice, J. Chem. Phys. **125**, 184715 (2006).
[43] P. A. Egelstaff, Adv. Chem. Phys. **53**, 1 (1983).
[44] P. Linse, J. Chem. Phys. **94**, 8227 (1991).
[45] W. J. McNeil, W. G. Madden, A. D. J. Haymet, and S. A. Rice, J. Chem. Phys. **78**, 388 (1983).
[46] J. A. Krumhansl and S. S. Wang, J. Chem. Phys. **56**, 2034 (1972).
[47] K. Zahn, G. Maret, C. Russ, and H. H. von Grunberg, Phys. Rev. Lett. **91**, 115502 (2003).
[48] C. Russ, K. Zahn, and H.-H. von Grunberg, J. Phys.: Condens. Matter **15**, S3509 (2003).
[49] M. A. Schroer, M. Tolan, and R. Winter, Phys. Chem. Chem. Phys. **14**, 9486 (2012).
[50] P. A. Egelstaff, Pure Appl. Chem. **51**, 2131 (1979).
[51] A. K. Soper, J. Mol. Liq. **78**, 179 (1998).
[52] L. Van Hove, Phys. Rev. **95**, 249 (1954).
[53] P. A. Egelstaff, Methods Exp. Phys. **23**, 405 (1987).
[54] A. K. Soper and C. J. Benmore, Phys. Rev. Lett. **101**, 065502 (2008).
[55] W. Montfrooij, L.A. de Graaf, P. J. van den Bosch, A. K. Soper, and W. S. Howells, J. Phys.: Condens. Matter **3**, 4089 (1991).
[56] S. Jorge, E. Lomba, and J. L. F. Abascal, J. Chem. Phys. **116**, 730 (2002).
[57] J. A. Barker, R. A. Fisher, and R. O. Watts, Mol. Phys. **21**, 657 (1971).
[58] P. Schofield, Proc. Phys. Soc. **88**, 149 (1966).
[59] F. P. Buff and R. Brout, J. Chem. Phys. **33**, 1417 (1960).
[60] F. P. Buff and F. M. Schindler, J. Chem. Phys. **29**, 1075 (1958).
[61] F. P. Buff, J. Chem. Phys. **23**, 419 (1955).
[62] R. Winter, F. Hensel, T. Bodensteiner, and W. Glaser, J. Phys. Chem. **92**, 7171 (1988).
[63] J. Ram and P. A. Egelstaff, Phys. Chem. Liq. **14**, 29 (1984).
[64] P. A. Egelstaff and S. S. Wang, Can. J. Phys. **50**, 684 (1972).
[65] L. E. Ballentine and A. Lakshmi, Can. J. Phys. **53**, 372 (1975).
[66] A. V. Okhulkov, Y. N. Demianets, and Y. E. Gorbaty, J. Chem. Phys. **100**, 1578 (1994).
[67] Y. F. Jiao and P. E. Smith, J. Chem. Phys. **135**, 014502 (2011).
[68] See supplementary material at http://dx.doi.org/10.1063/1.4905562 for four additional contour plots of the gas and liquid phase fluctuation cumulants and distribution function integrals.