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# Fluctuation solution theory of pure fluids

Elizabeth A. Ploetz,<sup>a)</sup> Gayani N. Pallewela,<sup>b)</sup> and Paul E. Smith

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Fluctuation Solution Theory (FST) provides an alternative view of fluid thermodynamics in terms of pair fluctuations in the particle number and excess energy observed for an equivalent open system. Here we extend the FST approach to provide a series of triplet and quadruplet particle and excess energy fluctuations that can also be used to help understand the behavior of fluids. The fluctuations for the gas, liquid, and supercritical regions of three fluids ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{SF}_6$ ) are then determined from accurate equations of state. Many of the fluctuating quantities change sign on moving from the gas to liquid phase and, therefore, we argue that the fluctuations can be used to characterize gas and liquid behavior. Further analysis provides an approach to isolate contributions to the excess energy fluctuations arising from just the intermolecular interactions and also indicates that the triplet and quadruplet particle fluctuations are related to the pair particle fluctuations by a simple power law for large regions of the phase diagram away from the critical point. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4977040>]

## I. INTRODUCTION

Fluctuation Solution Theory (FST) represents a valuable tool to help understand and rationalize the widely studied closed system behavior of pure liquids and solution mixtures.<sup>1</sup> The theory provides an alternative view of these systems in terms of the fluctuations in excess energy and particle number for an equivalent open system in the Grand Canonical Ensemble (GCE). The closely related Kirkwood-Buff (KB) theory represents a subset of FST where one is restricted to the study of (typically) only pair particle number fluctuations.<sup>2,3</sup> The KB theory has proven very successful in interpreting the properties of solution mixtures as it relates the particle number fluctuations to a set of thermodynamic properties (isothermal compressibility, partial molar volumes, and activity composition derivatives). Alternatively, when the corresponding thermodynamic data are available, one can invert the whole approach and obtain the particle number fluctuations.<sup>4</sup> This is particularly useful to help test and modify the results of computer simulation studies.<sup>5</sup> Hence, the FST/KB theory provides a direct link between thermodynamic properties and the corresponding fluctuations for an equivalent open system. Furthermore, the particle number fluctuations can also be expressed in terms of integrals over a set of pair correlation functions and thereby provide a measure of the fluid structure.<sup>2</sup> One could argue that FST is not as powerful as the Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy of distribution functions.<sup>6</sup> However, the fluctuations inherent to FST are directly available from experimental or simulation data. Hence, they can be used to interpret the properties of fluids and their mixtures without invoking approximations.

The main applications of FST have simply involved the particle-particle, particle-excess energy, and excess energy-excess energy pair fluctuations.<sup>1,3,7-10</sup> These pair fluctuations quantify the covariance of the corresponding bivariate particle-excess energy joint probability distribution for the equivalent open system. However, as this distribution is not Gaussian (or symmetric) in nature, the higher central moments of the distribution are non-trivial.<sup>11,12</sup> Recently, we investigated the triplet and quadruplet particle number fluctuations for pure liquids and liquid mixtures.<sup>13-15</sup> These higher order fluctuations are related to higher derivatives of the free energy for the system of interest and, therefore, can also be used to probe the nature of the solution. The role of pair, triplet, and quadruplet correlations in osmotic pressure expansions has also been investigated using the KB and FST approaches.<sup>2,16,17</sup> Most recently, FST has provided expressions for the determination of thermodynamic properties of biomolecules by computer simulation.<sup>5,15</sup>

In this study, we extend the theory by including bivariate particle-excess energy triplet and quadruplet fluctuations for pure fluids and then relate these quantities to common thermodynamic derivatives. The complete set of pair, triplet, and quadruplet fluctuations are then extracted from available Equations of State (EOS) for three example systems. Furthermore, we provide the relationships that enable one to separate intramolecular from intermolecular contributions to the energy fluctuations for classical systems. Finally, we argue that a FST analysis uncovers characteristic features of fluids that are not apparent from the corresponding thermodynamic data alone.

## II. THEORY

### A. General background

In this section, we describe and extend FST to provide equations relating closed system thermodynamic derivatives to

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a series of pair, triplet, and quadruplet fluctuating particle number and excess energy quantities characterizing an equivalent open system at the same temperature, pressure, and density. Some of the relationships presented here have appeared before; however, many are new. In particular, the working equations that illustrate exactly how to extract the triplet and quadruplet fluctuations from experimental data are presented. Here we provide a complete set of useable equations and an approach to obtain all three pair fluctuations, all four triplet fluctuations, and all five possible quadruplet fluctuations for a pure fluid. We also provide new FST based expressions for many additional thermodynamic quantities that may be of interest across the phase diagram.

For simplicity, all the pressure derivatives are inferred to be isothermal, and all the temperature derivatives are inferred to be isobaric, unless stated otherwise. All angular brackets signify a GCE average unless stated otherwise. We have expressed the fluctuations and thermodynamic derivatives in terms of dimensionless quantities as far as possible, thereby reducing the number of required unit conversions. All expressions are considered exact unless specifically noted otherwise.

The fluctuation densities of primary interest include the particle number ( $N_1$ ) and excess energy ( $\varepsilon$ ) fluctuations described by the quantities,<sup>5,13</sup>

$$\begin{aligned} B_{YZ} &\equiv \langle \delta Y \delta Z \rangle / V, \\ C_{XYZ} &\equiv \langle \delta X \delta Y \delta Z \rangle / V, \\ D_{WXYZ} &\equiv \left[ \frac{\langle \delta W \delta X \delta Y \delta Z \rangle - \langle \delta W \delta X \rangle \langle \delta Y \delta Z \rangle}{-\langle \delta W \delta Y \rangle \langle \delta X \delta Z \rangle - \langle \delta W \delta Z \rangle \langle \delta X \delta Y \rangle} \right] / V, \end{aligned} \quad (1)$$

where  $\delta X = X - \langle X \rangle$  denotes a fluctuation in the value of  $X = N_1$  or  $\varepsilon$ ,  $V$  is the volume of the system, and the angular brackets denote a GCE average at a fixed temperature  $T$  and chemical potential  $\mu_1$  of interest giving rise to an average density ( $\rho_1 = \langle N_1 \rangle / V$ ) and pressure  $p$ . The excess energy is defined by  $\varepsilon \equiv E - N_1 H_1$ , where  $E$  is the instantaneous internal energy of the system or the energy of a single member of the ensemble, and  $H_1$  is the average molar enthalpy. The molar enthalpy can also be written in terms of the average molar internal energy ( $E_1$ ) and the molar volume ( $V_1 = 1/\rho_1$ ) of the pure fluid,  $H_1 = E_1 + pV_1$ . The use of this specific form of excess energy is discussed later. The above quantities represent the cumulants of the bivariate particle number-excess energy distribution for the system in the GCE.

The following dimensionless fluctuating pair particle-particle, particle-excess energy, and excess energy-excess energy quantities will prove useful,<sup>7,13,18,19</sup>

$$\begin{aligned} b_{11} &\equiv B_{11} / \rho_1, \\ b_{1\varepsilon} &\equiv \beta B_{1\varepsilon} / \rho_1, \\ b_{\varepsilon\varepsilon} &\equiv \beta^2 B_{\varepsilon\varepsilon} / \rho_1, \end{aligned} \quad (2)$$

where  $\beta = (RT)^{-1}$  and  $R$  is the Gas constant. Similar reduced quantities can also be written for  $C$ 's and  $D$ 's—incorporating as many  $\beta$ 's as there are  $\varepsilon$  terms in the expression—and will be signified by using lower case letters. The above fluctuations can be used to quantify the pair, triplet, and quadruplet fluctuations for the equivalent open system.<sup>15</sup> The pair fluctuations provide information concerning the covariance of the particle-

excess energy distribution, while the triplet and quadruplet fluctuations quantify the coskewness and (excess) cokurtosis of the distribution in terms of the corresponding cumulants.

All the relationships described here are based upon the fact that the differential of an ensemble average density in the GCE can be written as<sup>5</sup>

$$d \left[ \frac{\langle X \rangle}{V} \right] = \frac{\langle \delta X \delta N_1 \rangle}{V} d\beta\mu_1 - \frac{\langle \delta X \delta E \rangle}{V} d\beta, \quad (3)$$

$X = E, N_1, EN_1, N_1^2$ , etc. Hence, derivatives of the above expression, together with the following thermodynamic relationships:<sup>20</sup>

$$\begin{aligned} p \left( \frac{\partial \beta\mu_1}{\partial p} \right)_T &= Z, & \beta \left( \frac{\partial \beta\mu_1}{\partial \beta} \right)_p &= \beta H_1, \\ p\beta \left( \frac{\partial H_1}{\partial p} \right)_T &= Z(1 - T\alpha_p), & \beta^2 \left( \frac{\partial H_1}{\partial \beta} \right)_p &= -\frac{C_{p,m}}{R}, \end{aligned} \quad (4)$$

where  $Z = \beta p V_1$  is the compressibility factor,  $\alpha_p$  is the thermal expansion coefficient, and  $C_{p,m}$  is the constant pressure heat capacity, can be used to relate higher order fluctuations in the particle and excess energy distribution to additional thermodynamic derivatives. In attempting to obtain the required temperature derivatives, it is usually simpler to evaluate the corresponding  $\beta$  derivatives and then obtain the final temperature derivative from the fact that  $d \ln \beta = -d \ln T$ .

## B. Pair fluctuations

Most of the second derivatives of any thermodynamic potential are fluctuating quantities. In the GCE, they provide information concerning the covariance of the particle-excess energy probability distribution. Using  $X = E + pV$  and  $X = N_1$  in Equation (3), one finds that the pair fluctuations are related to the experimental data according to<sup>5,7</sup>

$$\begin{aligned} \frac{p\kappa_T}{Z} &\equiv \frac{p}{\rho_1 Z} \left( \frac{\partial \rho_1}{\partial p} \right)_T = b_{11}, \\ T\alpha_p &\equiv -\frac{T}{\rho_1} \left( \frac{\partial \rho_1}{\partial T} \right)_p = -b_{1\varepsilon}, \\ \frac{C_{p,m}}{R} &\equiv \frac{1}{R} \left( \frac{\partial H_1}{\partial T} \right)_p = b_{\varepsilon\varepsilon}, \end{aligned} \quad (5)$$

where  $\kappa_T$  is the isothermal compressibility. The first relationship is the well-known compressibility equation.<sup>19</sup> The thermal expansion and heat capacity relationships are also known but their use is less common.<sup>7,21</sup> These established relationships provide the starting point for the derivation and subsequent study of derivatives of the above quantities. However, before proceeding we provide a variety of thermodynamic quantities of interest for the study of fluids that can also be expressed in terms of the pair fluctuations. These are obtained via standard thermodynamic transformations.

A series of quantities related to the fluid compressibility can be expressed in terms of the pair fluctuations. The bulk modulus ( $K$ ), the isentropic/adiabatic compressibility ( $\kappa_S$ ), and the speed of sound ( $w$ ) are given by<sup>20</sup>

$$\begin{aligned}\frac{ZK}{p} &\equiv \frac{Z\rho_1}{p} \left( \frac{\partial p}{\partial \rho_1} \right)_T = \frac{1}{b_{11}}, \\ \frac{p\kappa_S}{Z} &\equiv \frac{p}{\rho_1 Z} \left( \frac{\partial \rho_1}{\partial p} \right)_S = \frac{p\kappa_T}{Z} \frac{C_{V,m}}{C_{p,m}} = b_{11} - \frac{b_{1\varepsilon}^2}{b_{\varepsilon\varepsilon}}, \\ \beta M_1 w^2 &= \frac{Z}{p\kappa_S} = \frac{b_{\varepsilon\varepsilon}}{b_{\varepsilon\varepsilon}b_{11} - b_{1\varepsilon}^2},\end{aligned}\quad (6)$$

where the speed of sound is in m/s when the molar mass  $M_1$  is in kg/mol and  $RT$  is in J/mol. This can be extended to include the isentropic/adiabatic thermal expansion ( $\alpha_S$ ), the Gruneisen parameter ( $\gamma$ ), and the internal pressure ( $p_{\text{int}}$ ) according to<sup>20</sup>

$$\begin{aligned}T\alpha_S &\equiv -\frac{T}{\rho_1} \left( \frac{\partial \rho_1}{\partial T} \right)_S = -\frac{p\kappa_T}{Z} \frac{C_{V,m}/R}{T\alpha_p} = \frac{b_{\varepsilon\varepsilon}b_{11} - b_{1\varepsilon}^2}{b_{1\varepsilon}}, \\ \gamma &\equiv \frac{ZRT}{p} \left( \frac{\partial p}{\partial E_1} \right)_{\rho_1} = \frac{Z}{p\kappa_T} \frac{T\alpha_p}{C_{V,m}/R} \\ &= -\frac{1}{T\alpha_S} = -\frac{b_{1\varepsilon}}{b_{\varepsilon\varepsilon}b_{11} - b_{1\varepsilon}^2}, \\ \frac{Z}{p}p_{\text{int}} &\equiv \frac{V_1}{RT} \left( \frac{\partial E_1}{\partial V_1} \right)_T = -Z \left[ 1 - \frac{T}{p} \left( \frac{\partial p}{\partial T} \right)_{\rho_1} \right] \\ &= -\frac{b_{1\varepsilon} + b_{11}Z}{b_{11}}.\end{aligned}\quad (7)$$

A variety of properties relevant for gases are also then available. The Joule-Thomson coefficient ( $\mu_{JT}$ ), the Joule coefficient ( $\mu_J$ ), and the isothermal throttling coefficient ( $\delta_T$ ) are given by<sup>20</sup>

$$\begin{aligned}\frac{p}{ZT}\mu_{JT} &\equiv \frac{p}{ZT} \left( \frac{\partial T}{\partial p} \right)_H = -\frac{1 - T\alpha_p}{C_{p,m}/R} = -\frac{1 + b_{1\varepsilon}}{b_{\varepsilon\varepsilon}}, \\ \frac{V_1}{T}\mu_J &\equiv \frac{V_1}{T} \left( \frac{\partial T}{\partial V_1} \right)_{E_1} = \frac{ZR}{C_{V,m}} \left[ 1 - \frac{T}{p} \left( \frac{\partial p}{\partial T} \right)_{\rho_1} \right] \\ &= \frac{b_{1\varepsilon} + b_{11}Z}{b_{\varepsilon\varepsilon}b_{11} - b_{1\varepsilon}^2}, \\ \frac{p}{ZRT}\delta_T &\equiv \frac{p}{ZRT} \left( \frac{\partial H_1}{\partial p} \right)_T = -\frac{C_{p,m}}{R} \frac{p}{ZT}\mu_{JT} = 1 + b_{1\varepsilon}.\end{aligned}\quad (8)$$

All twelve of these properties, together with the isochoric heat capacity and thermal pressure coefficient given below, can be expressed in terms of just three pair fluctuation densities corresponding to the equivalent open system.

### C. Triplet fluctuations

The triplet fluctuations are related to the third derivatives of the thermodynamic potentials. In the GCE, they provide information concerning the coskewness of the bivariate particle-excess energy probability distribution. To obtain expressions for higher thermodynamic derivatives in terms of the triplet (and pair) fluctuations, one can first expand the far right terms of Equation (5) to provide a series of combinations, where  $\langle X \rangle = \langle E \rangle$ ,  $\langle N_1 \rangle$ ,  $\langle EN_1 \rangle$ ,  $\langle N_1^2 \rangle$ , and/or  $\langle E^2 \rangle$ , take derivatives of the expanded terms using Equation (3), and then contract back to the pair and triplet fluctuations. Doing so provides

$$\begin{aligned}\frac{p^2}{\rho_1 Z^2} \frac{\partial^2 \rho_1}{\partial p^2} &= c_{111} - b_{11}^2, \\ \frac{Tp}{\rho_1 Z} \frac{\partial^2 \rho_1}{\partial T \partial p} &= c_{11\varepsilon} - b_{11}(1 + b_{1\varepsilon}), \\ \frac{T^2}{\rho_1} \frac{\partial^2 \rho_1}{\partial T^2} &= c_{1\varepsilon\varepsilon} - 2b_{1\varepsilon} - b_{11}b_{\varepsilon\varepsilon}, \\ \frac{T}{R} \frac{\partial C_{p,m}}{\partial T} &= c_{\varepsilon\varepsilon\varepsilon} - 3b_{\varepsilon\varepsilon}b_{1\varepsilon} - 2b_{\varepsilon\varepsilon}.\end{aligned}\quad (9)$$

Some intermediate results that facilitate these transformations are presented in [Appendix A](#). The above relationships correspond to the FST based equations for the thermodynamic properties listed on the left hand side. Alternatively, one can use the relationships in Equation (5) to isolate the triplet fluctuations in terms of thermodynamic derivatives. This is analogous to the traditional KB inversion approach for pair fluctuations.<sup>4</sup> We will see that some of the triplet fluctuations take on different signs for specific regions of the phase diagram and can therefore be used to help characterize the liquid and gas behavior.

### D. Quadruplet fluctuations

The quadruplet fluctuations are related to the fourth derivatives of the thermodynamic potentials. In the GCE, they provide information concerning the excess cokurtosis of the bivariate particle-excess energy probability distribution. Continuing the process outlined in Sec. II C by taking derivatives of the relationships in Equation (9), and then using Equation (3), provides the required quadruplet fluctuations via

$$\begin{aligned}\frac{p^3}{\rho_1 Z^3} \frac{\partial^3 \rho_1}{\partial p^3} &= d_{1111} - 4c_{111}b_{11} + 3b_{11}^3, \\ \frac{Tp^2}{\rho_1 Z^2} \frac{\partial^3 \rho_1}{\partial T \partial p^2} &= d_{111\varepsilon} - 2c_{11\varepsilon}b_{11} + b_{1\varepsilon}b_{11}^2 \\ &\quad - 2(1 + b_{1\varepsilon})(c_{111} - b_{11}^2), \\ \frac{T^2p}{\rho_1 Z} \frac{\partial^3 \rho_1}{\partial T^2 \partial p} &= d_{11\varepsilon\varepsilon} + 2b_{11}(1 + b_{1\varepsilon})^2 - 2c_{11\varepsilon}(2 + b_{1\varepsilon}) \\ &\quad - b_{11}(c_{1\varepsilon\varepsilon} - b_{11}b_{\varepsilon\varepsilon}) - c_{111}b_{\varepsilon\varepsilon}, \\ \frac{T^3}{\rho_1} \frac{\partial^3 \rho_1}{\partial T^3} &= d_{1\varepsilon\varepsilon\varepsilon} - 6c_{1\varepsilon\varepsilon} - 3c_{11\varepsilon}b_{\varepsilon\varepsilon} - c_{\varepsilon\varepsilon\varepsilon}b_{11} \\ &\quad + 6b_{11}b_{\varepsilon\varepsilon} + 3b_{11}b_{1\varepsilon}b_{\varepsilon\varepsilon} + 6b_{1\varepsilon}^3, \\ \frac{T^2}{R} \frac{\partial^2 C_{p,m}}{\partial T^2} &= d_{\varepsilon\varepsilon\varepsilon\varepsilon} - 2c_{\varepsilon\varepsilon\varepsilon}(3 + 2b_{1\varepsilon}) - 6c_{1\varepsilon\varepsilon}b_{\varepsilon\varepsilon} \\ &\quad + 6b_{\varepsilon\varepsilon}(1 + b_{1\varepsilon})(1 + 2b_{1\varepsilon}) + 3b_{11}b_{\varepsilon\varepsilon}^2.\end{aligned}\quad (10)$$

The relationships outlined in Equations (5)–(10) provide expressions for thermodynamic quantities in terms of fluctuations in the GCE and, upon rearrangement, for the fluctuating quantities in terms of thermodynamic derivatives.

### E. Isochoric derivatives

Secs. II C and II D have focused on providing expressions containing isothermal and/or isobaric derivatives in terms of fluctuating quantities. In addition, there are several isochoric derivatives that are also of common interest. To evaluate these



quantities, we require the following standard thermodynamic relationships:<sup>20</sup>

$$\begin{aligned}\beta \left( \frac{\partial \beta \mu_1}{\partial \beta} \right)_{\rho_1} &= \beta H_1 - Z \frac{T \alpha_p}{p \kappa_T}, \\ \beta^2 \left( \frac{\partial H_1}{\partial \beta} \right)_{\rho_1} &= -\frac{C_{V,m}}{R} - Z \frac{T \alpha_p}{p \kappa_T}, \\ \frac{T}{p} \left( \frac{\partial p}{\partial T} \right)_{\rho_1} &= \frac{T \alpha_p}{p \kappa_T}, \\ \frac{C_{V,m}}{R} &\equiv \frac{1}{R} \left( \frac{\partial E_1^0}{\partial T} \right)_{\rho_1} = \frac{C_{p,m}}{R} - Z \frac{(T \alpha_p)^2}{p \kappa_T}.\end{aligned}\quad (11)$$

Using the above thermodynamic relationships, one finds that the pair fluctuations provide the thermal pressure coefficient, the isochoric molar heat capacity ( $C_{V,m}$ ), and the heat capacity ratio according to

$$\begin{aligned}Z \frac{T}{p} \left( \frac{\partial p}{\partial T} \right)_{\rho_1} &= -\frac{b_{1\varepsilon}}{b_{11}}, \\ \frac{C_{V,m}}{R} &= b_{\varepsilon\varepsilon} - \frac{b_{1\varepsilon}^2}{b_{11}}, \\ \frac{C_{p,m}}{C_{V,m}} &= \left[ 1 - b_{1\varepsilon}^2 / (b_{\varepsilon\varepsilon} b_{11}) \right]^{-1}.\end{aligned}\quad (12)$$

Taking derivatives of the left and right hand side of the first two relationships in Equation (12), and then using Equations (3) and (11), leads to expressions involving the triplet fluctuations,

$$\begin{aligned}Z \frac{T^2}{p} \left( \frac{\partial^2 p}{\partial T^2} \right)_{\rho_1} &= \frac{b_{\varepsilon\varepsilon} b_{11} - b_{1\varepsilon}^2}{b_{11}} \\ &\quad - \frac{1}{b_{11}} \left[ c_{1\varepsilon\varepsilon} - 2c_{11\varepsilon} \frac{b_{1\varepsilon}}{b_{11}} + c_{111} \left( \frac{b_{1\varepsilon}}{b_{11}} \right)^2 \right], \\ \frac{T}{R} \left( \frac{\partial C_{V,m}}{\partial T} \right)_{\rho_1} &= -2 \frac{b_{\varepsilon\varepsilon} b_{11} - b_{1\varepsilon}^2}{b_{11}} + \left[ c_{\varepsilon\varepsilon\varepsilon} - 3c_{1\varepsilon\varepsilon} \left( \frac{b_{1\varepsilon}}{b_{11}} \right) \right. \\ &\quad \left. + 3c_{11\varepsilon} \left( \frac{b_{1\varepsilon}}{b_{11}} \right)^2 - c_{111} \left( \frac{b_{1\varepsilon}}{b_{11}} \right)^3 \right].\end{aligned}\quad (13)$$

These latter relationships provide an alternative route to both  $c_{1\varepsilon\varepsilon}$  and  $c_{\varepsilon\varepsilon\varepsilon}$  using experimental derivatives. We will not investigate higher derivatives of these quantities.

Interestingly, the isochoric derivatives can be further condensed by making a simple transformation such that

$$\begin{aligned}\frac{C_{V,m}}{R} &= [b_{\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_V}, \\ Z \frac{T^2}{p} \left( \frac{\partial^2 p}{\partial T^2} \right)_{\rho_1} &= [b_{\varepsilon\varepsilon} - c_{1\varepsilon\varepsilon}/b_{11}]_{\varepsilon=\varepsilon_V}, \\ \frac{T}{R} \left( \frac{\partial C_{V,m}}{\partial T} \right)_{\rho_1} &= [c_{\varepsilon\varepsilon\varepsilon} - 2b_{\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_V},\end{aligned}\quad (14)$$

where  $\varepsilon_V = E - N_1(B_{1E}/B_{11}) = \varepsilon - N_1(B_{1\varepsilon}/B_{11})$ . Here, the square bracket notation is used to imply a fluctuating quantity, as defined in Equation (2), but where  $\varepsilon$  is substituted by (in this case)  $\varepsilon_V$ . We did attempt to find similar transformations for the isobaric and isothermal derivatives presented previously but were unsuccessful.

## F. Distribution functions

The results presented in the main text focus on a variety of fluctuating quantities. However, the particle number fluctuations can also be expressed in terms of two, three, and four body correlation functions and their integrals.<sup>2</sup> The pair, triplet, and quadruplet integrals are given by<sup>13</sup>

$$\begin{aligned}G_{11} &\equiv V^{-1} \int [g_{11}^{(2)} - 1] dr_1 dr_2, \\ G_{111} &\equiv V^{-1} \int [g_{111}^{(3)} - 1 - 3(g_{11}^{(2)} - 1)] dr_1 dr_2 dr_3, \\ G_{1111} &\equiv V^{-1} \int [g_{1111}^{(4)} - 1 - 4(g_{111}^{(3)} - 1) \\ &\quad - 3(g_{11}^{(2)} - 1)(g_{11}^{(2)} - 1) + 6(g_{11}^{(2)} - 1)] dr_1 dr_2 dr_3 dr_4,\end{aligned}\quad (15)$$

in terms of a series of  $n$ -body spatial (center of mass) probability distribution functions,  $g_{\alpha\beta\dots}^{(n)}(r_1, r_2, \dots)$ , defined in the GCE. The spatial dependencies are implied in Equation (15). An in depth discussion of the properties of these integrals, and a comparison to the corresponding closed system integrals, is provided elsewhere.<sup>3,15</sup> The particle number fluctuations can then be expressed as<sup>2,13</sup>

$$\begin{aligned}b_{11} &= 1 + \rho_1 G_{11}, \\ c_{111} &= 1 + 3\rho_1 G_{11} + \rho_1^2 G_{111}, \\ d_{1111} &= 1 + 7\rho_1 G_{11} + 6\rho_1^2 G_{111} + \rho_1^3 G_{1111}.\end{aligned}\quad (16)$$

Hence, once one has the particle number fluctuations then the  $G$ 's can be extracted from the experimental data using Equation (16). The above integrals involve distribution functions defined in the GCE.<sup>2</sup> The corresponding integrals for a closed system are given by  $\rho_1 G_{11}(\text{closed}) = -1$ ,  $\rho_1^2 G_{111}(\text{closed}) = 2$ , and  $\rho_1^3 G_{1111}(\text{closed}) = -6$ <sup>14</sup> and provide zero fluctuations. Unfortunately, despite some efforts in this direction,<sup>7,22</sup> we know of no similar general formulation for the energy fluctuations. Furthermore, the correlations and behavior outlined later in Section III appear to be less obvious using the above integrals.

## G. Intermolecular excess energy fluctuations

The pair, triplet, and quadruplet fluctuations help to quantify the behavior of the molecules and then relate this behavior to the fluid thermodynamics. We envision that this will be important to understand fluid properties in terms of intermolecular interactions and to compare and contrast with existing models used for simulation studies of fluids. The current formulation has focused on the internal energy. However, for classical systems, it is often more useful to separate the intramolecular and kinetic contributions from the intermolecular contributions to the energy terms. If we factor according to  $E = E_m + E_{ij}$ , where  $E_m$  represents the instantaneous contribution from all the molecular based energy terms and  $E_{ij}$  corresponds to the remaining instantaneous intermolecular interaction energy, then we can write

$$\begin{aligned}\beta \varepsilon_m &\equiv \beta E_m - N_1 \beta E_{1,m}, \\ \beta \varepsilon_{ij} &\equiv \beta E_{ij} - N_1 (\beta E_{1,ij} + Z).\end{aligned}\quad (17)$$

In this case,  $\beta E_{1,m} = \frac{n}{2}$  is the average molecular based energy per molecule, where  $n$  is the number of molecular degrees of

freedom per molecule. If there are  $n_1$  atoms in the molecule, then  $n = 6n_1 - 3$ . Of course, this assumes all the non-intermolecular degrees of freedom can be written as simple harmonic terms in the momenta and some set of (normal) coordinates, and thereby each contributes the classical equipartition value.<sup>23</sup> This may not always be true, especially for high frequency vibrations,<sup>24</sup> but corrections can be made to this approximation. Alternatively, one could simply separate the internal energy into kinetic (molecular) and potential energy contributions and use  $n = 3n_1$ .

The factorization of the energy fluctuations into molecular and intermolecular contributions is somewhat involved. While it is relatively simple for fluctuations that include only one or two energy terms, the fluctuations involving three or more energy terms are more complicated. The details are provided in [Appendix B](#). The final results for the pair energy fluctuations are given by

$$\begin{aligned} b_{1\epsilon} &= [b_{1\epsilon}]_{\epsilon=\epsilon_{ij}}, \\ b_{\epsilon\epsilon} &= \frac{n}{2} + [b_{\epsilon\epsilon}]_{\epsilon=\epsilon_{ij}}, \end{aligned} \quad (18)$$

while the triplet energy fluctuations are given by

$$\begin{aligned} c_{11\epsilon} &= [c_{11\epsilon}]_{\epsilon=\epsilon_{ij}}, \\ c_{1\epsilon\epsilon} &= \frac{n}{2}b_{11} + [c_{1\epsilon\epsilon}]_{\epsilon=\epsilon_{ij}}, \\ c_{\epsilon\epsilon\epsilon} &= 2\frac{n}{2} + 3\frac{n}{2}[b_{1\epsilon}]_{\epsilon=\epsilon_{ij}} + [c_{\epsilon\epsilon\epsilon}]_{\epsilon=\epsilon_{ij}}, \end{aligned} \quad (19)$$

and the quadruplet energy fluctuations factor according to

$$\begin{aligned} d_{111\epsilon} &= [d_{111\epsilon}]_{\epsilon=\epsilon_{ij}}, \\ d_{11\epsilon\epsilon} &= \frac{n}{2}c_{111} + [d_{11\epsilon\epsilon}]_{\epsilon=\epsilon_{ij}}, \\ d_{1\epsilon\epsilon\epsilon} &= 2\frac{n}{2}b_{11} + 3\frac{n}{2}[c_{11\epsilon}]_{\epsilon=\epsilon_{ij}} + [d_{1\epsilon\epsilon\epsilon}]_{\epsilon=\epsilon_{ij}}, \\ d_{\epsilon\epsilon\epsilon\epsilon} &= 6\frac{n}{2} + 3\left(\frac{n}{2}\right)^2 b_{11} + 8\frac{n}{2}[b_{1\epsilon}]_{\epsilon=\epsilon_{ij}} \\ &\quad + 6\frac{n}{2}[c_{1\epsilon\epsilon}]_{\epsilon=\epsilon_{ij}} + [d_{\epsilon\epsilon\epsilon\epsilon}]_{\epsilon=\epsilon_{ij}}. \end{aligned} \quad (20)$$

Use of the above relationships in Equations (9), (10), and (13) indicates (as expected) that only terms involving intermolecular contributions survive as all the molecular based terms cancel. Finally, we note that  $Z$  can often be safely dropped from the definition in Equation (17) for liquids under ambient conditions as it is typically quite small ( $\approx 0.01$ ) due to the relatively high densities observed for liquids. Alternatively, one can remove the  $Z$  based terms using the relationships provided in [Appendix B](#).

## H. Ideal gas results

The results obtained for ideal gases represent useful reference values for real systems, especially in the gas and/or supercritical phase. Ideal gases follow the ideal gas equation and therefore  $Z = 1$ . The particle number fluctuation densities then follow a Poisson distribution for a unit volume of fluid.<sup>25</sup> Corresponding values for the excess energy fluctuations can be determined by noting that the terms in Equation (5) adopt values of 1, 1, and  $1 + C_{V,m}/R$ , respectively, for ideal gases. Here,  $C_{V,m}/R$  represents the contribution to the heat capacity

from the translational kinetic energy, rotational kinetic energy, and (active) intramolecular vibrational degrees of freedom of the specific gas and is assumed to be independent of temperature. This leads to values of 0, -1, 2, and 0, respectively, for the quantities displayed in Equation (9), together with values of 0, 0, 2, -6, and 0, respectively, for the derivatives in Equation (10), and finally values of 1,  $C_{V,m}/R$ ,  $C_p/C_V$ , 0, and 0, respectively, for the isochoric derivatives displayed in Equations (12) and (13). The following values for the fluctuations are then obtained:

$$\begin{aligned} b_{11} &= -b_{1\epsilon} = c_{111} = -c_{11\epsilon} = d_{1111} = -d_{111\epsilon} = 1, \\ b_{\epsilon\epsilon} &= c_{1\epsilon\epsilon} = -c_{\epsilon\epsilon\epsilon} = d_{11\epsilon\epsilon} = -d_{1\epsilon\epsilon\epsilon} = 1 + C_{V,m}/R, \\ d_{\epsilon\epsilon\epsilon\epsilon} &= -2(1 + C_{V,m}/R) + 3(1 + C_{V,m}/R)^2, \end{aligned} \quad (21)$$

$$G_{11} = G_{111} = G_{1111} = 0.$$

While the intermolecular interactions are clearly zero for an ideal gas, the fluctuations involving the intermolecular excess energy adopted here are actually finite. They are given by

$$\begin{aligned} [-b_{1\epsilon} &= -c_{11\epsilon} = -d_{111\epsilon} = b_{\epsilon\epsilon} = c_{1\epsilon\epsilon} = d_{11\epsilon\epsilon} \\ &= -c_{\epsilon\epsilon\epsilon} = -d_{1\epsilon\epsilon\epsilon} = d_{\epsilon\epsilon\epsilon\epsilon}]_{\epsilon=\epsilon_{ij}} = 1, \end{aligned} \quad (22)$$

where  $\beta\epsilon_{ij} = -N_1$ . The relationships provided in Equation (22) can be used in Equations (18)–(20) and provide the same results as described in Equation (21) with  $C_{V,m}/R = \frac{n}{2}$ .

## III. METHODS

The fluctuating quantities of interest here were obtained from the relationships outlined in Equations (5), (9), and (10). The equations were solved sequentially. The required derivatives were obtained from the recommended EOS as implemented in REFPROP v. 9.1.<sup>26</sup> Existing EOSs for fluid water,<sup>27</sup> carbon dioxide,<sup>28</sup> and sulfur hexafluoride<sup>29</sup> were used. The last expression in Equation (9) required a thermodynamic derivative not provided by the EOSs. Hence, we have used a simple finite difference approximation for the left hand side. This should be reasonable for all state points except those very close to the critical point.<sup>13</sup> Again, the expressions in Equation (10) required thermodynamic derivatives not provided by the EOSs. Furthermore, the last derivative in Equation (10) required a double finite difference approach. The single and double finite difference (temperature) derivatives were determined according to

$$\begin{aligned} \frac{\partial X}{\partial T} &\approx \frac{X(T + \Delta T) - X(T - \Delta T)}{2\Delta T}, \\ \frac{\partial^2 X}{\partial T^2} &\approx \frac{X(T + \Delta T) - 2X(T) + X(T - \Delta T)}{(\Delta T)^2}, \end{aligned} \quad (23)$$

using a  $\Delta T$  of 1 mK and a  $\Delta p$  of  $10^{-10}$  bar and employing double precision arithmetic. Alternatively, one could use finite difference derivatives of the actual fluctuating quantities, as indicated in Equations (A2)–(A4) of [Appendix A](#).

## IV. RESULTS AND DISCUSSION

### A. General

The particle number fluctuations ( $b_{11}$ ) and excess energy fluctuations ( $b_{\epsilon\epsilon}$ ) have to be positive, as do the

corresponding thermodynamic properties in the form of the isothermal compressibility and the isobaric heat capacity. The value of  $b_{1\epsilon}$  is determined by the coefficient of thermal expansion and can therefore be positive, negative, or zero. It is negative over the vast majority of the liquid and gas regions of the phase diagram of most fluids, corresponding to a positive thermal expansion. From Equation (12), it is apparent that a positive isochoric heat capacity implies that  $b_{11}b_{\epsilon\epsilon} > b_{1\epsilon}^2$  always holds. The signs associated with the triplet and higher fluctuations are more complicated in nature and are discussed in Section IV B.

A number of thermodynamic properties are related to the particle number-excess energy cross fluctuations. These include the presence of a density maximum with temperature, leading to a zero thermal expansion and  $b_{1\epsilon} = 0$ , together with a change in sign for the Joule and Joule-Thomson coefficients, the isothermal throttling coefficient, and the internal pressure. If we expand the expression for  $b_{1\epsilon}$ , we find  $b_{1\epsilon} = b_{1E} - b_{11}(\beta E_1 + Z)$  and, according to Equation (18), this quantity relies on just the intermolecular interactions. As  $Z \approx 0$  for liquids, and  $b_{11} \approx Z \approx 1$  for gases, we find that the change in sign for all the above properties occurs when

$$\langle \delta N_1 \delta E_{ij} \rangle \approx \langle \delta N_1 \delta N_1 \rangle E_{1,ij}, \quad (24)$$

which is equivalent to a perfect correlation between  $N_1$  and the total instantaneous intermolecular energy  $E_{ij}$ , i.e.,  $E_{ij} = N_1 E_{1,ij}$ . This can be written as an equality in the case of the Joule coefficient and the internal pressure, while it represents a good approximation for the thermal expansion, the Joule-Thomson coefficient, and the isothermal throttling coefficient.

In our previous work, we noted that the corresponding, ensemble specific, fluctuation based formulas for many thermodynamic properties could be obtained from the FST results via suitable transformations.<sup>10</sup> For instance, starting with the GCE expression for the isochoric heat capacity, a simple transformation  $\delta E - \delta N_1 B_{1E}/B_{11} \rightarrow \delta E$  generates the corresponding energy fluctuation formula for the heat capacity in the Canonical ensemble. Indeed, this can be extended to include the triplet based properties outlined in Equation (14)—presumably because the GCE and Canonical ensembles are both isochoric in nature. However, while using the transformations  $\delta \epsilon \rightarrow \delta H$  and  $\delta N_1 V_1 \rightarrow -\delta V$  in Equation (5) generates the corresponding fluctuation based expressions for the heat capacity, thermal expansion, and compressibility in the isothermal-isobaric (Gibbs) ensemble,<sup>18</sup> apparently this is not true for the relationships provided in Equations (9) and (10).

The use of an excess energy ( $\epsilon$ ) greatly simplifies many of the previous relationships. One can expand the relationships containing the excess energy to generate multiple terms that isolate the energy fluctuations themselves. However, while these terms can be obtained from molecular simulation, these quantities cannot be isolated from experimental data. The primary reason for this is that the energy fluctuations in the GCE depend on the zero of energy. For example, if one adds a simple constant of energy for each molecule ( $e_o$ )—representing the electronic partition function, for instance—then the resulting pair energy fluctuation corresponding to the molecular terms

is given by the approach presented in Appendix B and leads to

$$[b_{EE}]_{E=E_m} = \frac{n}{2} + \left(\frac{n}{2} + \beta e_o\right)^2 b_{11}. \quad (25)$$

Hence, while the closed system result ( $b_{11} = 0$ ) for the energy fluctuations is independent of  $e_o$ , the GCE result is not. Consequently, the energy fluctuations themselves are unavailable. The form of the excess energy fluctuations adopted here eliminates this problem and the quantities then become experimentally available.

It is envisioned that isolation of the energy fluctuations corresponding to just the intermolecular interactions may provide deeper insight into the nature of many phase diagrams as it is the intermolecular interactions that give rise to phase transitions, etc. It is also clear that the direct rationalization of the energy fluctuations, or the thermodynamic derivatives they are associated with, is complicated by the presence of the molecular terms and, possibly, the  $Z$  factor also included with the intermolecular term in Equation (17)—even though it is actually molecular in nature. Unfortunately, the number of molecular degrees of freedom that contribute to these terms is dependent on the temperature and pressure.<sup>24</sup> While the gas phase results for the intermolecular based energy fluctuations should be relatively easy to obtain given some knowledge of the corresponding vibrational frequencies, the results for the condensed phase will remain problematic. Hence, we have not pursued this issue further at the present time.

## B. Phase diagrams

The previous relationships allow one to express the fluid thermodynamics in terms of fluctuating quantities or to express the fluctuating quantities in terms of fluid thermodynamics. Using the latter approach, one can extract the fluctuating quantities from experimental data covering large parts of the phase diagram. The full pair, triplet, and quadruplet FST analysis of water, sulfur hexafluoride, and carbon dioxide is presented in Figures 1–3 for the gas, liquid, and supercritical regions. As expected, the fluctuations increase dramatically in magnitude as one approaches the critical point. Away from the critical point, however, there are several consistent trends in the fluctuating quantities displayed by all three systems. In particular,  $c_{111}$  is consistent within a phase and is negative for liquids and positive for gases. The crossover in behavior can be directly related to the thermodynamic derivatives leading to the triplet particle number fluctuation. The first relationship in Equation (9) can be written as

$$c_{111} = Z^{-2} p^2 [V_1 \partial^2 \rho_1 / \partial p^2 + (V_1 \partial \rho_1 / \partial p)^2]. \quad (26)$$

The last derivative is related to the compressibility and is therefore positive for both liquids and gases. The first derivative must therefore be negative for liquids. Further examination reveals that this derivative is positive for real gases (it is zero for ideal gases). The quadruplet particle fluctuations ( $d_{1111}$ ) are positive for both liquids and gases and only change sign in the supercritical region.

The observed signs for all the fluctuation densities obtained from an analysis of the data in Figures 1–3 are summarized in Table I. It is clear that, in most cases, the

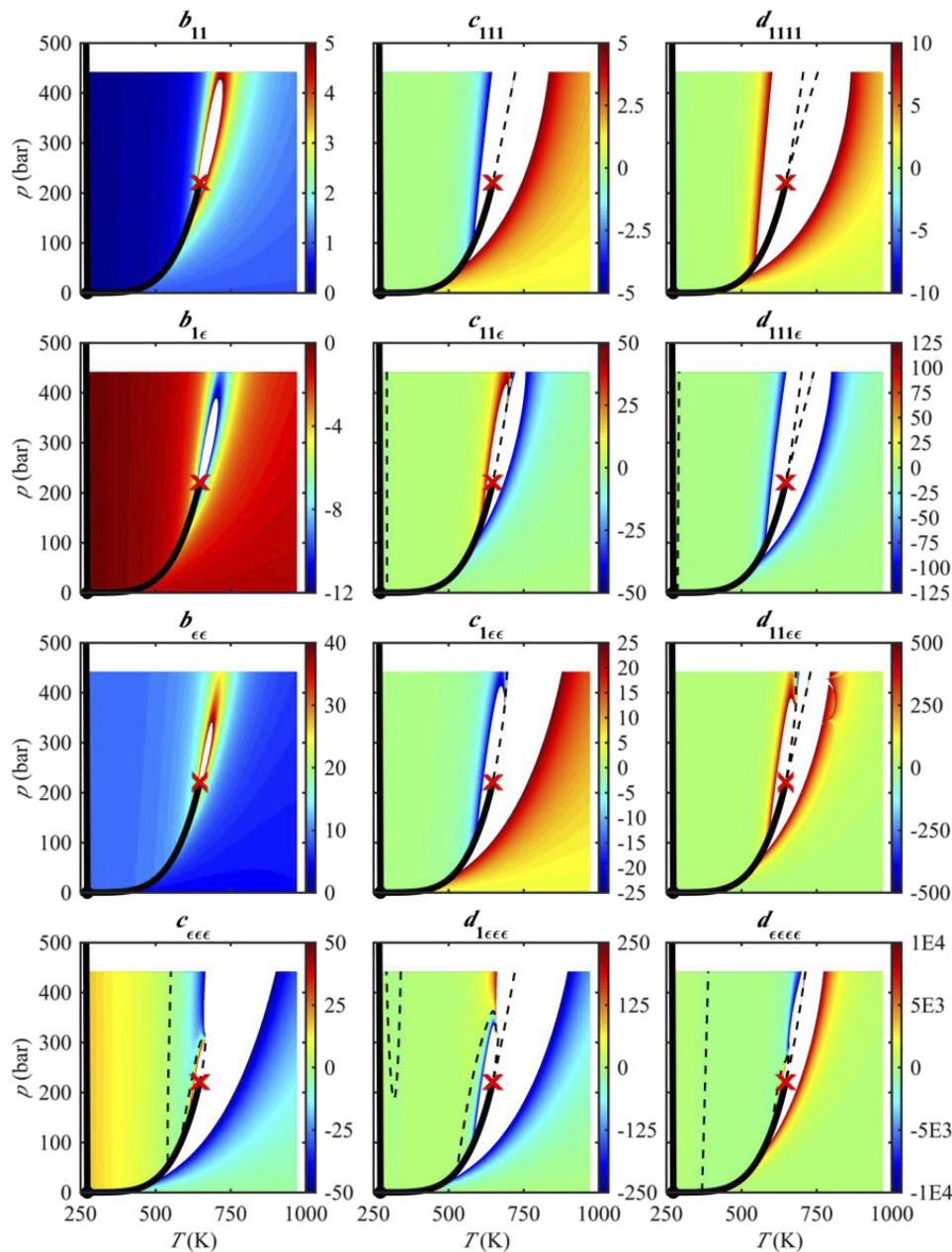


FIG. 1. A FST analysis of fluid water using the IAPWS-95 EOS.<sup>27</sup> Zero contours are indicated by dashed lines. The thick solid line indicates the phase boundaries and the critical point is indicated with a red cross. Data outside the ranges depicted on the color bars were removed and those state points appear white. Data were only contoured from the solid-liquid coexistence temperature to  $1.5T_c$  and from 1 bar to  $2p_c$ .

sign associated with a particular fluctuation density is determined by the phase, while in the supercritical region one can observe both possibilities. The signs of  $B$ 's and  $D$ 's are the same in a single (subcritical) phase as long as the number of  $\varepsilon$ 's associated with the fluctuation is the same. The sign observed for a phase changes each time one increases the number of  $\varepsilon$  terms associated with the same order fluctuation, e.g.,  $D_{1111} > 0$ ,  $D_{111\varepsilon} < 0$ ,  $D_{11\varepsilon\varepsilon} > 0$ ,  $D_{1\varepsilon\varepsilon\varepsilon} < 0$ , and  $D_{\varepsilon\varepsilon\varepsilon\varepsilon} > 0$  for gases. The appearance of a single sign for the liquid region is absent for fluctuations containing three or more  $\varepsilon$  terms. Here, the appearance of both signs in the liquid phase may be due to contributions from the molecular terms which complicate the issue. Preliminary studies attempting to remove the molecular terms, using the expressions in Equations (18)–(20), suggest this may be so (data not shown), but a more thorough analysis is required before this can be considered conclusive. Nevertheless, the fluctuation densities appear to reveal specific

characteristics of different regions. This is one of the main reasons we have argued that a thorough FST based analysis of fluids is potentially very beneficial to our understanding of their behavior.

### C. Relationships between the fluctuations

Examination of the particle fluctuations reveals that the pair, triplet, and quadruplet fluctuations appear to be related. In particular, the particle fluctuations along an isotherm display simple power law relationships. The behavior in the gas phase region is relatively simple. Here, the relationships in Equation (16) are dominated by the pair correlations ( $G_{11}$ ) and hence the fluctuations are related according to

$$\begin{aligned} c_{111} &\approx 1 + 3\rho_1 G_{11} \approx b_{11}^3, \\ d_{1111} &\approx 1 + 7\rho_1 G_{11} \approx b_{11}^7, \end{aligned} \quad (27)$$



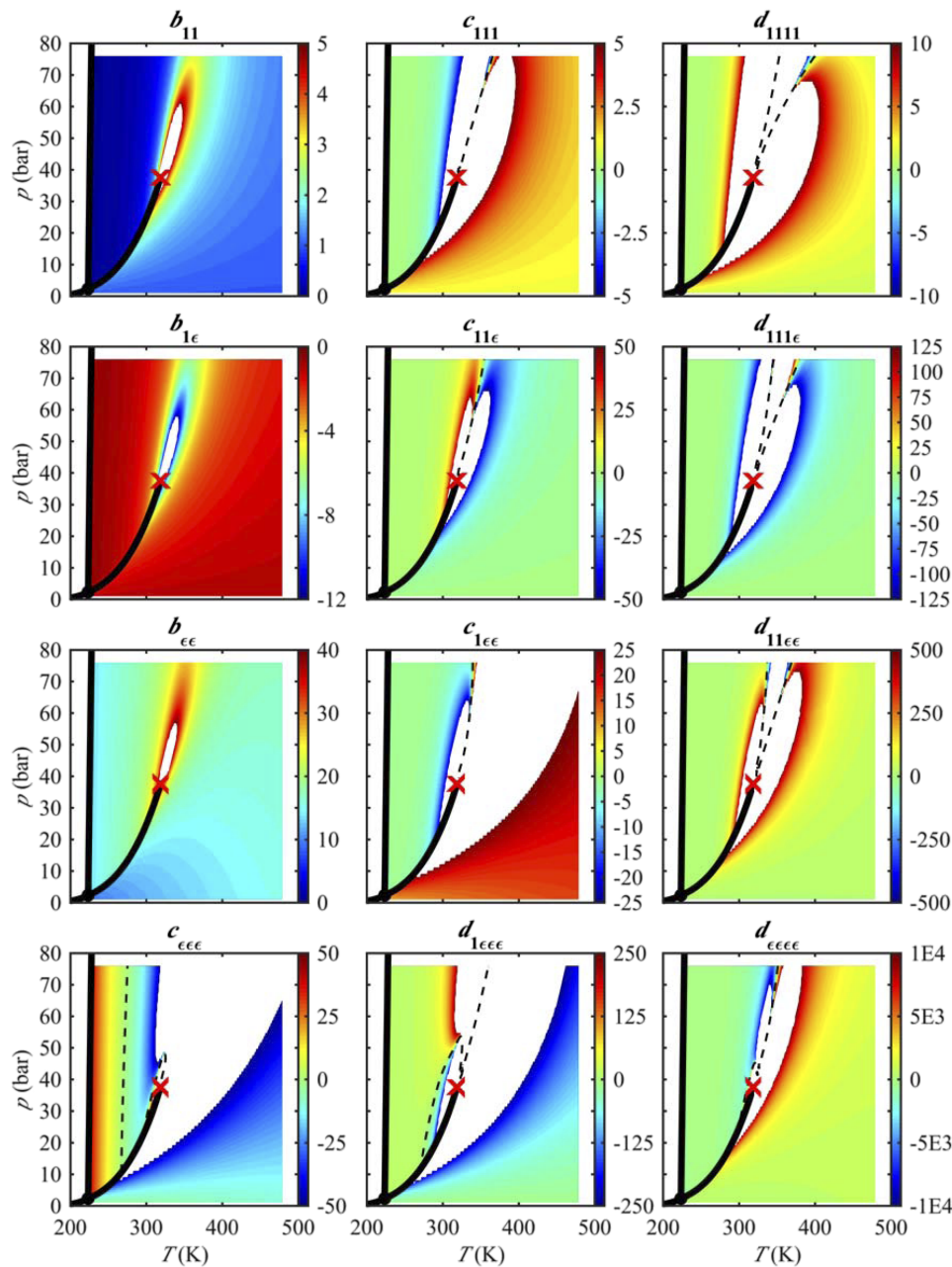


FIG. 2. A FST analysis of fluid sulfur hexafluoride using the Guder and Wagner EOS.<sup>29</sup> Zero contours are indicated by dashed lines. The thick solid line indicates the phase boundaries and the critical point is indicated with a red cross. Data outside the ranges depicted on the color bars were removed and those state points appear white. Data were only contoured from the solid-liquid coexistence temperature to  $1.5T_c$  and from 1 bar to  $2p_c$ .

when the density is low. This behavior is illustrated in Figure 4 where the non-ideal, low density, approach to the ideal limiting behavior gives rise to a slope of three and seven for the triplet and quadruplet fluctuations, respectively.

The behavior in the liquid region is less obvious. A simple power law relationship does appear to hold for large regions of the phase diagram, especially for higher temperature isotherms. The behavior for liquid water is displayed in Figure 5. The data can be represented by relationships of the form

$$\begin{aligned} c_{111} &= -yb_{11}^m, \\ d_{1111} &= yb_{11}^{m+1} [myb_{11}^{m-2} + m - 1], \end{aligned} \quad (28)$$

where the second relationship was derived from the first using the equations in Appendix A. Here,  $y$  and  $m$  are constants for a particular isotherm but do vary slightly with

temperature. Unfortunately, the variation in the excess energy fluctuations, and the behavior of the particle fluctuations along an isobar, does not appear to be so simple (data not shown). Using the above relationships—together with the hierarchy of equations in (5), (A1), and (A4) that relate the singlet-pair, pair-triplet, and triplet-quadruplet fluctuations—it is possible that the above observations may prove useful in the development of improved (isothermal) EOSs for liquids.

#### D. Excess energy fluctuations

As mentioned previously, the fluctuating quantities described here represent the cumulants of the bivariate particle-excess energy joint probability distribution for an equivalent GCE. The particle number density and the corresponding particle number fluctuations simply correspond to derivatives of the thermodynamic potential for the GCE for a



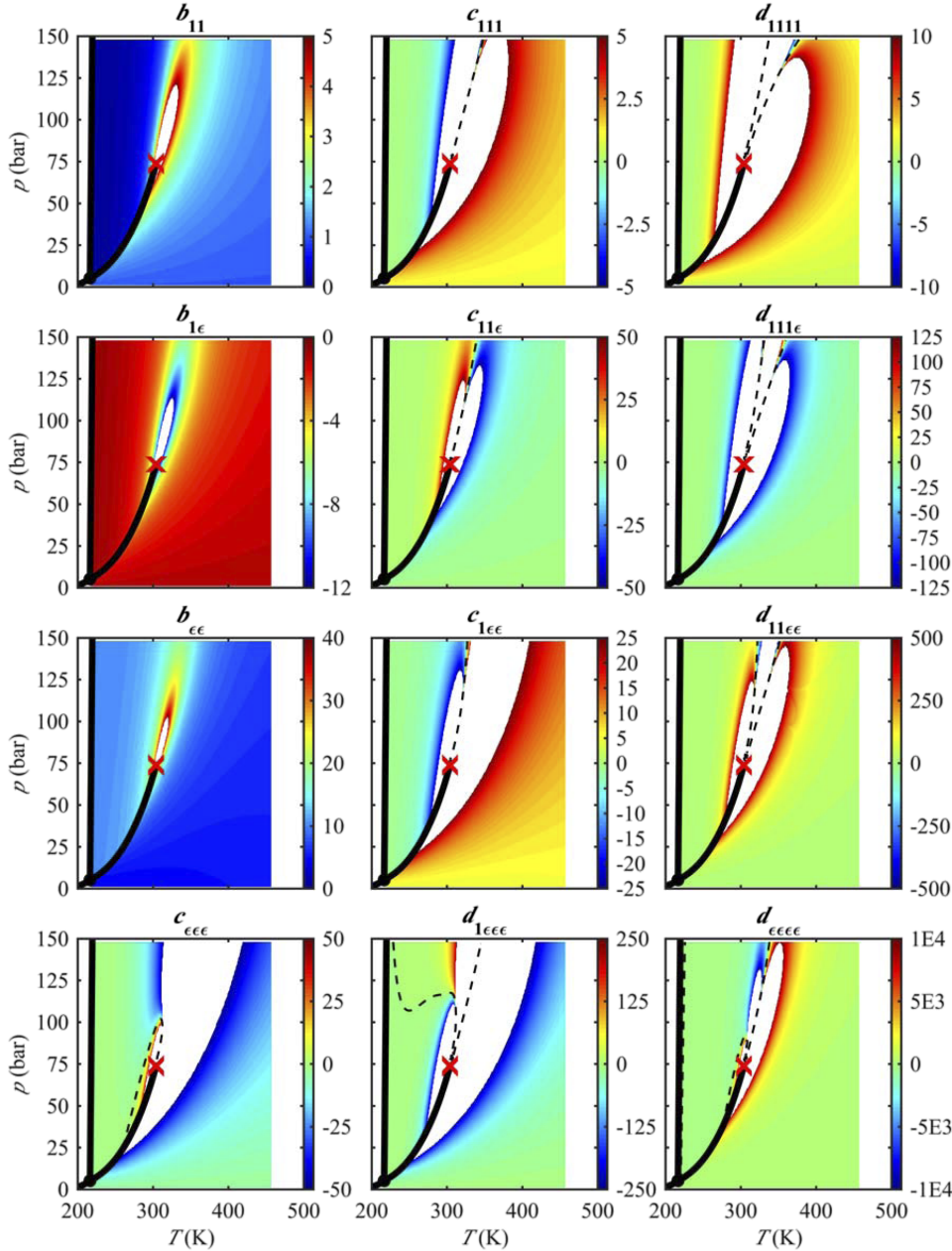


FIG. 3. A FST analysis of fluid carbon dioxide using the Span and Wagner EOS.<sup>28</sup> Zero contours are indicated by dashed lines. The thick solid line indicates the phase boundaries and the critical point is indicated with a red cross. Data outside the ranges depicted on the color bars were removed and those state points appear white. Data were only contoured from the solid-liquid coexistence temperature to  $1.5T_c$  and from 1 bar to  $2p_c$ .

single component fluid,<sup>30</sup>

$$\begin{aligned} Vd\beta p &= -Ed\beta + N_1d\beta\mu_1, \\ \beta pV &= \ln \Xi, \end{aligned} \quad (29)$$

where  $\Xi$  is the GCE partition function. The derivatives,

$$V \left( \frac{\partial^n \beta p}{\partial \beta \mu_1^n} \right)_\beta, \quad (30)$$

then provide  $\langle N_1 \rangle$ ,  $\langle \delta N_1 \delta N_1 \rangle$ , etc. The derivatives with respect to  $\beta$ ,

$$V \left( \frac{\partial^n \beta p}{\partial \beta^n} \right)_{\beta\mu_1}, \quad (31)$$

provide the average internal energy and the corresponding energy fluctuations  $\langle E \rangle$ ,  $\langle \delta E \delta E \rangle$ , etc. The cross derivatives

provide a series of particle and energy fluctuations. Unfortunately, the above energy fluctuations cannot be isolated from experimental data for the reasons outlined in Section IV A and Appendix B. Clearly, the fluctuations in the excess energy  $\varepsilon$  can be obtained from experiment. However, while the response functions are directly related to the pair fluctuations, the variances and higher cumulants are not simple derivatives of the GCE potential. Hence, we examine the meaning of the excess energy fluctuations.

First, we note that  $\langle \varepsilon \rangle = -pV$  and so it is tempting to associate the corresponding fluctuations in  $\varepsilon$  with the fluctuation in the pressure. This latter quantity is provided by Hill,<sup>30</sup>

$$\beta \langle \delta p \delta p \rangle = \left\langle \partial^2 E / \partial V^2 \right\rangle. \quad (32)$$

However, the pressure appearing in the excess energy expression is actually  $p = \langle p \rangle$ , and hence it does not contribute to the

TABLE I. Signs of the pair, triplet, and quadruplet fluctuation densities in different phases. As provided by the EOSs for water,<sup>27</sup> sulfur hexafluoride,<sup>29</sup> and carbon dioxide.<sup>28</sup>  $B_{1\varepsilon}$  can be positive or zero in the liquid phase of water, but it is negative across the vast majority of the phase diagram.

Quantity	Gas	Liquid	Supercritical	I.G.
$B_{11}$	+	+	+	+
$C_{111}$	+	-	+/-	+
$D_{1111}$	+	+	+/-	+
$B_{1\varepsilon}$	-	-	-	-
$C_{11\varepsilon}$	-	+	+/-	-
$D_{111\varepsilon}$	-	-	+/-	-
$B_{\varepsilon\varepsilon}$	+	+	+	+
$C_{1\varepsilon\varepsilon}$	+	-	+/-	+
$D_{11\varepsilon\varepsilon}$	+	+	+/-	+
$C_{\varepsilon\varepsilon\varepsilon}$	-	+/-	+/-	-
$D_{1\varepsilon\varepsilon\varepsilon}$	-	+/-	+/-	-
$D_{\varepsilon\varepsilon\varepsilon\varepsilon}$	+	+/-	+/-	+

fluctuations. In contrast, the manipulation of the GCE partition function is more informative. The probability that a member of the GCE contains  $N_1$  particles and is in a microscopic state  $k$  with energy  $E_k$  is given by<sup>30</sup>

$$P(N_1, E_k) = \frac{e^{\beta(\mu_1 N_1 - E_k)}}{\Xi}. \quad (33)$$

The corresponding probability that a member of the GCE contains  $N_1$  particles and has an energy  $E$  is given by the

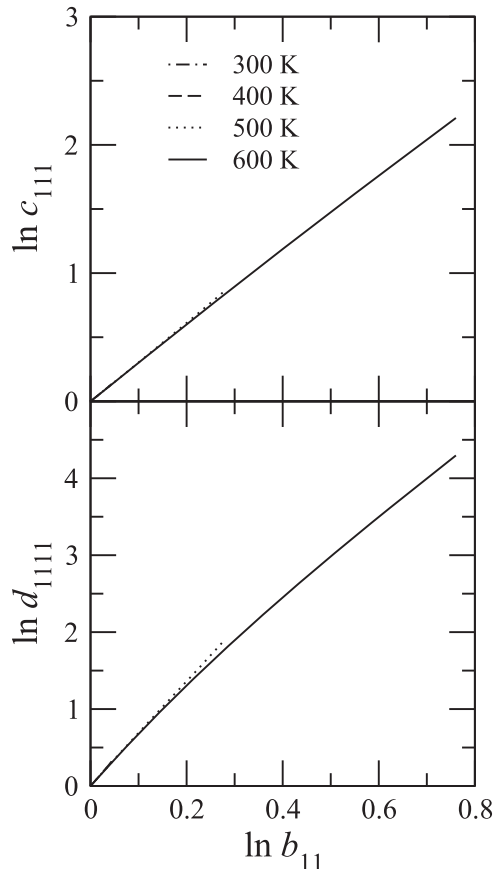


FIG. 4. The correlation between the pair, triplet, and quadruplet particle number fluctuations for gaseous water along different isotherms obtained using the IAPWS-95 EOS.<sup>27</sup>

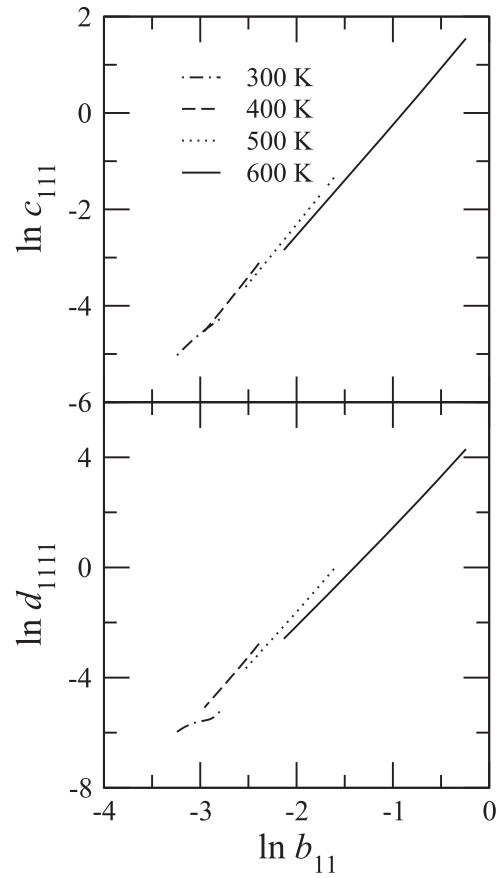


FIG. 5. The correlation between the pair, triplet, and quadruplet particle number fluctuations for liquid water along different isotherms obtained using the IAPWS-95 EOS.<sup>27</sup>

above equation, and the fact that the degeneracy of the energy levels can be written as  $\Omega = e^{S/R}$ , and using  $\mu_1 = H_1 - TS_1$  to give

$$\ln P(N_1, E) = -\beta(\varepsilon - \langle \varepsilon \rangle) + (\varepsilon_S - \langle \varepsilon_S \rangle)/R, \quad (34)$$

where we have also used Equation (29) and defined  $\varepsilon_S \equiv S - N_1 S_1$ . Hence, it is the excess energy, in combination with the variation in entropy, that determines the particle number and energy distribution. The above expression can be manipulated further using a Taylor expansion of the entropy and eventually provides the Gaussian result<sup>31</sup>

$$\ln P(N_1, E) = -\frac{1}{2} \frac{C_{p,m}}{C_V} \left[ \frac{(\delta N_1)^2}{p\kappa_T/Z} + 2T\alpha_p \frac{\delta N_1}{p\kappa_T/Z} \frac{\beta\delta\varepsilon}{C_{p,m}/R} + \frac{(\beta\delta\varepsilon)^2}{C_{p,m}/R} \right]. \quad (35)$$

This clearly illustrates the relationship between the particle and energy fluctuations and the thermodynamic quantities of common interest. In particular, the excess energy plays an integral role in this relationship and leads to the simplest expressions for the thermodynamic derivatives in terms of fluctuations in the GCE. The Gaussian result is an approximation. This can be improved using the higher thermodynamic derivatives presented here and will be described in a separate publication.<sup>31</sup>

## V. CONCLUSIONS

A complete FST analysis of pure fluids up to and including quadruplet particle and excess energy fluctuations has been outlined and performed on three fluids. The approach provides an alternative viewpoint of fluid thermodynamics using an equivalent GCE picture of the corresponding particle number and (excess) energy fluctuations. Interesting features of these fluctuating quantities are observed as a function of pressure and temperature. The possibility to isolate contributions from the intermolecular based energy terms is outlined and holds the potential to reveal other additional features of the phase diagram. Furthermore, simple power law relationships appear to hold between the particle number fluctuations for large regions of the phase diagram. We envision that this type of analysis will help in the development of more accurate force fields for molecular simulation, lead to the generation of improved EOSs, and can be used to strengthen our understanding of fluid behavior and phase equilibria.

## ACKNOWLEDGMENTS

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## APPENDIX A: RELATIONSHIPS BETWEEN DERIVATIVES OF THE GCE FLUCTUATIONS AND HIGHER MOMENTS OF THE PARTICLE-EXCESS ENERGY DISTRIBUTION

The relationships provided in Equations (9), (10), and (13) were obtained from derivatives of the pair (and triplet) fluctuations. These derivatives provide higher moments of the particle-excess energy probability distribution. Here, we present the derivatives required for the manipulations described in the main text. The derivatives are obtained from Equation (3) using values of  $X = N_1, N_1^2, E$ , etc. Again, the temperature derivatives are most easily obtained from the derivatives with respect to  $\beta$  followed by a simple transformation.

The pressure derivatives of the pair fluctuation densities are given by

$$\begin{aligned} \frac{p}{\rho_1 Z} \frac{\partial B_{11}}{\partial p} &= c_{111}, \\ \frac{\beta p}{\rho_1 Z} \frac{\partial B_{1\varepsilon}}{\partial p} &= c_{11\varepsilon} - b_{11}(1 + b_{1\varepsilon}), \\ \frac{\beta^2 p}{\rho_1 Z} \frac{\partial B_{\varepsilon\varepsilon}}{\partial p} &= c_{1\varepsilon\varepsilon} - 2b_{1\varepsilon}(1 + b_{1\varepsilon}), \end{aligned} \quad (\text{A1})$$

where we have used the derivatives in Equation (4). The quantities in Equation (A1) adopt values of 1, -1, and  $1 + C_{V,m}/R$ , respectively, for ideal gases. The first two derivatives in Equation (A1) have appeared before.<sup>13</sup> The temperature derivatives

of the pair fluctuation densities are provided by

$$\begin{aligned} \frac{T}{\rho_1} \frac{\partial B_{11}}{\partial T} &= c_{11\varepsilon}, \\ \beta \frac{T}{\rho_1} \frac{\partial B_{1\varepsilon}}{\partial T} &= c_{1\varepsilon\varepsilon} - b_{11}b_{\varepsilon\varepsilon}, \\ \beta^2 \frac{T}{\rho_1} \frac{\partial B_{\varepsilon\varepsilon}}{\partial T} &= c_{\varepsilon\varepsilon\varepsilon} - 2b_{1\varepsilon}b_{\varepsilon\varepsilon}. \end{aligned} \quad (\text{A2})$$

The quantities in Equation (A2) adopt values of -1, 0, and  $1 + C_{V,m}/R$ , respectively, for ideal gases. The first derivative in Equation (A2) has appeared before.<sup>13</sup>

The derivatives along an isochore are slightly more involved but can be obtained by the use of the derivatives in Equation (11) to give

$$\begin{aligned} \frac{T}{\rho_1} \left( \frac{\partial B_{11}}{\partial T} \right)_{\rho_1} &= c_{11\varepsilon} - c_{111}b_{1\varepsilon}/b_{11}, \\ \beta \frac{T}{\rho_1} \left( \frac{\partial B_{1\varepsilon}}{\partial T} \right)_{\rho_1} &= c_{1\varepsilon\varepsilon} - c_{11\varepsilon}b_{1\varepsilon}/b_{11} \\ &\quad + b_{1\varepsilon} - (b_{\varepsilon\varepsilon}b_{11} - b_{1\varepsilon}^2), \\ \beta^2 \frac{T}{\rho_1} \left( \frac{\partial B_{\varepsilon\varepsilon}}{\partial T} \right)_{\rho_1} &= c_{\varepsilon\varepsilon\varepsilon} - c_{1\varepsilon\varepsilon}b_{1\varepsilon}/b_{11} \\ &\quad + 2b_{1\varepsilon}^2/b_{11} - 2(b_{\varepsilon\varepsilon}b_{11} - b_{1\varepsilon}^2)b_{1\varepsilon}/b_{11}. \end{aligned} \quad (\text{A3})$$

The quantities in Equation (A3) adopt values of 0, -1, and  $2(1 + C_{V,m}/R)$ , respectively, for ideal gases. The first derivative in Equation (A3) has appeared before.<sup>13</sup> The corresponding pressure derivatives are then provided by the use of the thermal pressure coefficient provided in Equation (12).

Derivatives of the triplet fluctuations involve the quadruplet fluctuations. The pressure derivatives are given by

$$\begin{aligned} \frac{p}{\rho_1 Z} \frac{\partial C_{111}}{\partial p} &= d_{1111}, \\ \frac{\beta p}{\rho_1 Z} \frac{\partial C_{11\varepsilon}}{\partial p} &= d_{111\varepsilon} - c_{111}(1 + b_{1\varepsilon}), \\ \frac{\beta^2 p}{\rho_1 Z} \frac{\partial C_{1\varepsilon\varepsilon}}{\partial p} &= d_{11\varepsilon\varepsilon} - 2c_{11\varepsilon}(1 + b_{1\varepsilon}), \\ \frac{\beta^3 p}{\rho_1 Z} \frac{\partial C_{\varepsilon\varepsilon\varepsilon}}{\partial p} &= d_{1\varepsilon\varepsilon\varepsilon} - 3c_{1\varepsilon\varepsilon}(1 + b_{1\varepsilon}), \end{aligned} \quad (\text{A4})$$

where the quantities in Equation (A4) adopt values of 1, -1,  $1 + C_{V,m}/R$ , and  $-(1 + C_{V,m}/R)$ , respectively, for ideal gases. The first derivative in Equation (A4) has appeared before.<sup>13</sup> In addition, the temperature derivatives are given by

$$\begin{aligned} \frac{T}{\rho_1} \frac{\partial C_{111}}{\partial T} &= d_{111\varepsilon}, \\ \beta \frac{T}{\rho_1} \frac{\partial C_{11\varepsilon}}{\partial T} &= d_{11\varepsilon\varepsilon} - c_{111}b_{\varepsilon\varepsilon}, \\ \beta^2 \frac{T}{\rho_1} \frac{\partial C_{1\varepsilon\varepsilon}}{\partial T} &= d_{1\varepsilon\varepsilon\varepsilon} - 2c_{11\varepsilon}b_{\varepsilon\varepsilon}, \\ \beta^3 \frac{T}{\rho_1} \frac{\partial C_{\varepsilon\varepsilon\varepsilon}}{\partial T} &= d_{\varepsilon\varepsilon\varepsilon\varepsilon} - 3c_{1\varepsilon\varepsilon}b_{\varepsilon\varepsilon}, \end{aligned} \quad (\text{A5})$$

and the quantities in Equation (A5) adopt values of -1, 0,  $1 + C_{V,m}/R$ , and  $-2(1 + C_{V,m}/R)$ , respectively, for ideal gases.

## APPENDIX B: MOLECULAR BASED CONTRIBUTIONS TO THE GCE EXCESS ENERGY FLUCTUATIONS

In this section, we provide a decomposition of the energy fluctuations into molecular and intermolecular contributions. The molecular contributions are then obtained analytically. The same results are obtained by writing the classical partition function in a form suitable for molecules, and this may (at first sight) seem simpler.<sup>21</sup> However, this apparent initial simplicity is lost after performing multiple temperature derivatives. Here we will simply factor the established relationships from the main text.

We factor the excess energy fluctuations into two terms  $\varepsilon = \varepsilon_m + \varepsilon_{ij}$  using the definitions given in Equation (17). First, we focus on the molecular based terms that contribute to  $\varepsilon_m$ . We require the GCE values of the molecular energy  $E_m$  and various powers and products of  $E_m$  with  $N_1$ . The average energy due to these molecular based terms in the Canonical ensemble can be written as

$$\beta \langle E_m \rangle_{NVT} = \left\langle \sum_i a_i \right\rangle_{NVT} = N \langle a \rangle_{NVT}, \quad (\text{B1})$$

where  $a_i = \beta p_i^2 / (2m_i)$ , with  $p_i$  being the momentum (in one direction) and  $m_i$  being the mass of a single molecule. The sum is over  $N$  ( $\neq N_1$ ) equivalent molecular terms. Here, we assume a form corresponding to the molecular kinetic energies, but this can be extended to include any contributions that provide the equipartition values (quadratic in either the momenta or coordinates). If we extend this to include the square of the molecular based energy, we find

$$\begin{aligned} \beta^2 \langle E_m^2 \rangle_{NVT} &= \left\langle \sum_i a_i \sum_j a_j \right\rangle_{NVT} \\ &= N \langle a^2 \rangle_{NVT} + N(N-1) \langle a \rangle_{NVT}^2. \end{aligned} \quad (\text{B2})$$

The factorization assumes that the molecular terms are independent, i.e.,  $\langle a_i a_j \rangle_{NVT} = \langle a_i \rangle_{NVT} \langle a_j \rangle_{NVT}$  for  $i \neq j$ . In the Canonical ensemble, the energy fluctuations are then simply given by  $\beta^2 \langle \delta E_m \delta E_m \rangle_{NVT} = N[\langle a^2 \rangle_{NVT} - \langle a \rangle_{NVT}^2]$ , as the  $N^2$  terms cancel, but this will not be the case in the GCE as we will see below. The higher powers of the energy are provided by the fact that

$$\begin{aligned} \beta^3 \langle E_m^3 \rangle_{NVT} &= \left\langle \sum_i a_i \sum_j a_j \sum_k a_k \right\rangle_{NVT} \\ &= N \langle a^3 \rangle_{NVT} + 3N(N-1) \langle a^2 \rangle_{NVT} \langle a \rangle_{NVT} \\ &\quad + N(N-1)(N-2) \langle a \rangle_{NVT}^3, \end{aligned} \quad (\text{B3})$$

and after using the multinomial coefficients,

$$\begin{aligned} \beta^4 \langle E_m^4 \rangle_{NVT} &= \left\langle \sum_i a_i \sum_j a_j \sum_k a_k \sum_l a_l \right\rangle_{NVT} \\ &= N \langle a^4 \rangle_{NVT} + 4N(N-1) \langle a^3 \rangle_{NVT} \langle a \rangle_{NVT} \\ &\quad + 3N(N-1) \langle a^2 \rangle_{NVT}^2 \\ &\quad + 6N(N-1)(N-2) \langle a^2 \rangle_{NVT} \langle a \rangle_{NVT}^2 \\ &\quad + N(N-1)(N-2)(N-3) \langle a \rangle_{NVT}^4. \end{aligned} \quad (\text{B4})$$

This completes the set of energy terms required here.

The required ensemble averages can be evaluated using standard integrals to provide the general result

$$\langle a^r \rangle_{NVT} = \left\langle \left( \frac{\beta p^2}{2m} \right)^r \right\rangle_{NVT} = \frac{(2r)!}{r! 2^r}, \quad (\text{B5})$$

for any power  $r$ . If  $n$  is the number of molecular based terms (degrees of freedom) per molecule then  $N = nN_1$  and the above averages can be written as

$$\begin{aligned} \beta \langle E_m \rangle_{NVT} &= N_1 \frac{n}{2}, \\ \beta^2 \langle E_m^2 \rangle_{NVT} &= N_1 \frac{n}{2} + N_1^2 \left( \frac{n}{2} \right)^2, \\ \beta^3 \langle E_m^3 \rangle_{NVT} &= 2N_1 \frac{n}{2} + 3N_1^2 \left( \frac{n}{2} \right)^2 + N_1^3 \left( \frac{n}{2} \right)^3, \\ \beta^4 \langle E_m^4 \rangle_{NVT} &= 6N_1 \frac{n}{2} + 11N_1^2 \left( \frac{n}{2} \right)^2 + 6N_1^3 \left( \frac{n}{2} \right)^3 + N_1^4 \left( \frac{n}{2} \right)^4, \end{aligned} \quad (\text{B6})$$

and hence,  $\beta E_{1,m} = \frac{n}{2}$ . The relationships in Equation (B6) can then be used to evaluate the GCE fluctuations originating from the molecular based terms by noting that  $\langle E_m \rangle = \langle \langle E_m \rangle_{NVT} \rangle$  and  $\langle N_1 E_m \rangle = \langle N_1 \langle E_m \rangle_{NVT} \rangle$ , etc., obtained by a simple manipulation of the GCE partition function. The results for the pair fluctuations are then

$$\begin{aligned} [b_{1E}]_{E=E_m} &= \frac{n}{2} b_{11}, \\ [b_{EE}]_{E=E_m} &= \frac{n}{2} + \left( \frac{n}{2} \right)^2 b_{11}, \end{aligned} \quad (\text{B7})$$

while the results for the triplet fluctuations are given by

$$\begin{aligned} [c_{11E}]_{E=E_m} &= \frac{n}{2} c_{111}, \\ [c_{1EE}]_{E=E_m} &= \frac{n}{2} b_{11} + \left( \frac{n}{2} \right)^2 c_{111}, \\ [c_{EEE}]_{E=E_m} &= 2\frac{n}{2} + 3 \left( \frac{n}{2} \right)^2 b_{11} + \left( \frac{n}{2} \right)^3 c_{111}, \end{aligned} \quad (\text{B8})$$

and finally the quadruplet fluctuations provide

$$\begin{aligned} [d_{111E}]_{E=E_m} &= \frac{n}{2} d_{1111}, \\ [d_{11EE}]_{E=E_m} &= \frac{n}{2} c_{111} + \left( \frac{n}{2} \right)^2 d_{1111}, \\ [d_{1EEE}]_{E=E_m} &= 2\frac{n}{2} b_{11} + 3 \left( \frac{n}{2} \right)^2 c_{111} + \left( \frac{n}{2} \right)^3 d_{1111}, \\ [d_{EEEE}]_{E=E_m} &= 6\frac{n}{2} + 11 \left( \frac{n}{2} \right)^2 b_{11} + 6 \left( \frac{n}{2} \right)^3 c_{111} + \left( \frac{n}{2} \right)^4 d_{1111}. \end{aligned} \quad (\text{B9})$$

These can then be used to give the molecular based fluctuations  $[b_{\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_m}$ , etc. On doing this, many (but not all) of the terms on the right hand side of the above equations cancel. The equivalent closed system (NVT) results can be obtained by setting  $b_{11} = c_{111} = d_{1111} = 0$ , and then the only finite quantities that remain are those that involve just the energy fluctuations.

The final step is to factor the total fluctuations into molecular and intermolecular contributions. This can be achieved by expanding each term, applying the fact that  $\langle \varepsilon_m \rangle = 0$ ,  $\langle \delta \varepsilon_m \delta \varepsilon_{ij} \rangle = 0$ , and  $\langle \varepsilon_m \varepsilon_{ij}^r \rangle = 0$ , and then simplifying. Most of the required fluctuations simply factor to give  $b_{\varepsilon\varepsilon} = [b_{\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_m} + [b_{\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}}$ , etc. However, fluctuations

containing more than two energy terms are more complicated and result in the following relationships:

$$\begin{aligned} c_{\varepsilon\varepsilon\varepsilon} &= [c_{\varepsilon\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_m} + \frac{n}{2} [b_{1\varepsilon}]_{\varepsilon=\varepsilon_{ij}} + [c_{\varepsilon\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}}, \\ d_{1\varepsilon\varepsilon\varepsilon} &= [d_{1\varepsilon\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_m} + 3\frac{n}{2} [c_{11\varepsilon}]_{\varepsilon=\varepsilon_{ij}} + [d_{1\varepsilon\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}}, \\ d_{\varepsilon\varepsilon\varepsilon\varepsilon} &= [d_{\varepsilon\varepsilon\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_m} + 8\frac{n}{2} [b_{1\varepsilon}]_{\varepsilon=\varepsilon_{ij}} + 6\frac{n}{2} [c_{1\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}} \\ &\quad + [d_{\varepsilon\varepsilon\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}}. \end{aligned} \quad (\text{B10})$$

The combination of Equations (B7)–(B10) gives rise to the relationships in Equations (18)–(20). They are consistent with the results obtained for ideal gases.

Should one want to remove the  $Z$  terms from the fluctuations to focus solely on the non-molecular intermolecular energy term then these can be obtained by a simple expansion to give

$$\begin{aligned} [b_{1\varepsilon}]_{\varepsilon=\varepsilon'_{ij}} &= [b_{1\varepsilon}]_{\varepsilon=\varepsilon_{ij}} + b_{11}Z, \\ [b_{\varepsilon\varepsilon}]_{\varepsilon=\varepsilon'_{ij}} &= [b_{\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}} + 2[b_{1\varepsilon}]_{\varepsilon=\varepsilon_{ij}}Z + b_{11}Z^2, \end{aligned} \quad (\text{B11})$$

for the pair fluctuations with

$$\begin{aligned} [c_{11\varepsilon}]_{\varepsilon=\varepsilon'_{ij}} &= [c_{11\varepsilon}]_{\varepsilon=\varepsilon_{ij}} + c_{111}Z, \\ [c_{1\varepsilon\varepsilon}]_{\varepsilon=\varepsilon'_{ij}} &= [c_{1\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}} + 2[c_{11\varepsilon}]_{\varepsilon=\varepsilon_{ij}}Z + c_{111}Z^2, \\ [c_{\varepsilon\varepsilon\varepsilon}]_{\varepsilon=\varepsilon'_{ij}} &= [c_{\varepsilon\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}} + 3[c_{1\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}}Z \\ &\quad + 3[c_{11\varepsilon}]_{\varepsilon=\varepsilon_{ij}}Z^2 + c_{111}Z^3, \end{aligned} \quad (\text{B12})$$

for the triplet fluctuations, and

$$\begin{aligned} [d_{111\varepsilon}]_{\varepsilon=\varepsilon'_{ij}} &= [d_{111\varepsilon}]_{\varepsilon=\varepsilon_{ij}} + d_{1111}Z, \\ [d_{11\varepsilon\varepsilon}]_{\varepsilon=\varepsilon'_{ij}} &= [d_{11\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}} + 2[d_{111\varepsilon}]_{\varepsilon=\varepsilon_{ij}}Z + d_{1111}Z^2, \\ [d_{1\varepsilon\varepsilon\varepsilon}]_{\varepsilon=\varepsilon'_{ij}} &= [d_{1\varepsilon\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}} \\ &\quad + 3[d_{11\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}}Z + 3[d_{111\varepsilon}]_{\varepsilon=\varepsilon_{ij}}Z^2 + d_{1111}Z^3, \\ [d_{\varepsilon\varepsilon\varepsilon\varepsilon}]_{\varepsilon=\varepsilon'_{ij}} &= [d_{\varepsilon\varepsilon\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}} + 4[d_{1\varepsilon\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}}Z + 6[d_{11\varepsilon\varepsilon}]_{\varepsilon=\varepsilon_{ij}}Z^2 \\ &\quad + 4[d_{111\varepsilon}]_{\varepsilon=\varepsilon_{ij}}Z^3 + d_{1111}Z^4, \end{aligned} \quad (\text{B13})$$

for the quadruplet fluctuations. Here,  $\varepsilon'_{ij} = E_{ij} - N_1 E_{1,ij} = \varepsilon_{ij} + N_1 Z$ .

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