

Thermodynamic response functions of fluids with repulsive inverse power pair potentials

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The repulsive inverse power (IP) pair potential, $\phi(r) \sim r^{-n}$, where r is the particle pair separation and the exponent n determines the steepness of the potential, is widely used as a reference model for real fluid and solid systems. Some aspects of the density ρ , temperature T , pressure P , and n dependence of IP fluid systems are derived and explored analytically and numerically using accurate IP equations of state derived from molecular-dynamics simulations. The focus of the work is on deriving analytic expressions for the derivatives or response functions of the total and excess entropies of the IP system with respect to these independent variables. The analytic expressions assist in navigating through the $[\rho, T, P]$ and n multidimensional equation-of-state space of the IP system. Statistical mechanical expressions are derived for the derivatives of the potential energy, Helmholtz free energy, and excess entropy with respect to n , which were implemented in molecular-dynamics simulations for the excess entropy case. The relationships between the hard sphere, IP, and Lennard-Jones potential response functions as a function of temperature, density, and pressure, particularly at high temperature are investigated, in the latter case using an approximate statistical mechanical analysis.

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I. INTRODUCTION

The inverse power (IP) pair potential is defined through the expression [1,2]

$$\phi(r) = \epsilon \left(\frac{\sigma}{r} \right)^n, \quad (1)$$

where the exponent n controls the stiffness, and σ and ϵ , respectively, set the characteristic length and energy scales of the IP particle. The IP potential used here is purely repulsive; otherwise, if it were a negative quantity, its intensive thermodynamic properties would not achieve constant values in the large system size limit [3,4]. Also, $n > 3^+$ is required to produce a definable thermodynamic state.

The inverse power potential, also often referred to as the “soft sphere” potential, has been widely used in theory and molecular simulations to represent a diverse range of fluid and solid systems. Its simple analytic form and scale invariance make it useful in these applications. The variable n in its definition can be tuned to adjust the effective softness of the particle and therefore represent in a mean-field sense different chemical systems, from small molecules [5], polymer-colloid systems [6], granular assemblies [7], and even metals [8]. These applications have been employed despite there being no liquid-vapor coexistence region in the IP phase diagram because of the absence of an attractive part in the IP potential.

More recently, IP systems have been at the center of the isomorph theory of fluids and solids [9,10].

In the $n \rightarrow \infty$ limit, the IP potential tends to that of the hard sphere (HS), which has been employed extensively in its own right to represent the thermophysical properties of real and model fluid systems [11–13]. If the diameter of the HS particle is σ_{HS} , the HS potential is, $\phi(r) = \infty$ for $r < \sigma_{\text{HS}}$, and $=0$ for $r > \sigma_{\text{HS}}$.

The advantage of the IP potential is that it can, in principle, account for the thermophysical properties of real molecular liquids of variable “softness,” although many small- and medium-sized molecules can also be treated as effective hard spheres to a very good approximation, particularly for the transport coefficients [12,14–16]. This is because the effective n value is large, typically greater than 12 (the Lennard-Jones potential repulsive exponent) [12]. The thermodynamic and transport coefficients of the HS fluid and solid have been determined by molecular dynamics (MD) over many decades, particularly recently in Refs. [17–19].

The thermophysical properties of the HS system are either independent of temperature T or simply related through a multiplicative factor of powers of temperature. In contrast, for the IP system, properties are trivially related along $[\rho, T]$ lines when $\rho/T^{3/n}$ is constant [20,21], where T is the temperature in units of ϵ/k_B (k_B is Boltzmann’s constant), and the number density $\rho = N\sigma^3/V$ (for N particles in volume V). The value of a property at any $[\rho, T]$ state point can be obtained by suitable density and temperature scaling from its value at a point along a single isotherm or isochore which crosses that constant $\rho/T^{3/n}$ line on the phase diagram. Expressed alternatively, along the line defined by a constant value of $\rho/T^{3/n}$, the value of a quantity multiplied by appropriate powers of ρ and T is itself constant. These scaled quantities are referred to as being expressed in so-called macroscopic

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units (MUs), which are usually denoted by $\tilde{X}$ for the quantity X [22].

The thermodynamic, mechanical, and transport coefficient properties of the IP fluid system for variable n have been determined by molecular-dynamics (MD) simulations in, for example, Refs. [23–26]. The equation of state and the excess entropy, which is the contribution to the total entropy in excess of that from the ideal gas at the same temperature and density, were the main focus of Ref. [26].

The dependence of various thermodynamic properties with respect to temperature, density, and pressure is of considerable experimental interest. The derivatives of these thermodynamic quantities with respect to the independent variables (e.g., expansivity and compressibility) are often measured in experiment and are often of considerable practical importance. These derivatives are the focus of attention in the present study. Their connection to thermodynamic response functions makes them potentially valuable, particularly for the entropy derivatives, which are related to experimentally measurable quantities such as the heat capacities and compressibility.

The present investigation is mainly built on the results found in Ref. [26]. Analytic expressions for the slope of s_{ex} with respect to density, temperature, pressure, and n are derived in this work. The characteristic features of these functions are explored here. The pressure derivative expressions could be particularly useful as pressure is often more readily and accurately determined than density under experimental conditions, for example in the field of tribology. In addition, fluctuation-type formulas for the n dependence of the potential energy and excess entropy of IP fluids at a given $[\rho, T]$ state point are derived here and computed using MD simulations.

Section II gives the necessary theoretical background concerning the IP compressibility factor and entropy expressions of relevance to this work. In Sec. III formulas for the entropy derivatives with respect to volume (density), temperature, and pressure are derived. Their behavior as a function of these variables is explored. In Sec. IV exact formulas for the derivative or response function of s_{ex} and other thermodynamic quantities with respect to the IP potential parameter n are derived. Pair potentials between model molecules take on a wide range of analytic forms, and it is of interest to also derive expressions for the response functions involving the excess entropy for these systems. Section VB discusses from a statistical mechanics perspective the relationship between the properties of the IP $n = 12$ system and those of the Lennard-Jones (LJ) fluid system, which has an $\approx r^{-6}$ attractive term and is a more realistic representation of molecular liquids. A summary of the main conclusions of this work and their practical relevance is given in Sec. VI.

II. THEORETICAL BACKGROUND

The total entropy, S , of an N -particle system is a state function which is independent of the ensemble in the thermodynamic (large- N) limit. It can be written as the sum of an ideal-gas term S_{id} and an excess contribution S_{ex} ,

$$S(\rho, T, N) = S_{\text{id}}(\rho, T, N) + S_{\text{ex}}(\rho, T, N). \quad (2)$$

The excess entropy is in its own right a state function, which can be expressed as the sum of the m -body relative positional

distribution functions [27]. The entropy per particle is $s = S/N$, and its two components per particle are correspondingly $s_{\text{ex}} = S_{\text{ex}}/N$ and $s_{\text{id}} = S_{\text{id}}/N$.

The excess entropy is not a simple ensemble average of a readily determined quantity in molecular simulation and has been determined by more indirect molecular simulation procedures, for example, from the mean particle displacement on Monte Carlo [28–30]. In this work, routes to the total entropy and its ideal and excess components are chosen that follow the statistical mechanics and thermodynamics of the system, forming a self-consistent and coherent treatment of the related quantities.

The entropy and its two components have thermodynamic definitions in terms of more basic quantities. Considering a monatomic particle, let u and a_{ex} be the average potential energy and excess Helmholtz free energy per particle, respectively. If $Z = P/\rho k_B T$ is the compressibility factor and $\beta = 1/k_B T$,

$$\begin{aligned} \frac{s_{\text{ex}}(\xi, T)}{k_B} &= \beta u - \beta a_{\text{ex}} \\ &= \frac{3}{n}(Z - 1) - \int_0^\xi \frac{(Z(x) - 1)}{x} dx, \end{aligned} \quad (3)$$

where, for an IP system, $Z - 1 = \beta n u / 3$ [31], which is used widely in this work. The integral in Eq. (3) is performed along an isotherm. In this work, both T and β will be used, depending partly on what is most convenient in a particular context.

Hard spheres. In the HS or $n \rightarrow \infty$ limit, $u = 0$, and s_{ex} is then just equal to the integral term in Eq. (3), which can be evaluated analytically using a simple approximate HS equations of state, for example, the Carnahan-Starling (cs) [32] and Kolafa (kol) formulas [33–35]. They give for the compressibility factor,

$$\begin{aligned} Z_{\text{cs}} &= \frac{1 + \xi_{\text{HS}} + \xi_{\text{HS}}^2 - \xi_{\text{HS}}^3}{(1 - \xi_{\text{HS}})^3}, \\ Z_{\text{cs}} - 1 &= \xi_{\text{HS}} \frac{(4 - 2\xi_{\text{HS}})}{(1 - \xi_{\text{HS}})^3}, \\ Z_{\text{kol}} &= \frac{1 + \xi_{\text{HS}} + \xi_{\text{HS}}^2 - \frac{2}{3}\xi_{\text{HS}}^3(1 + \xi_{\text{HS}})}{(1 - \xi_{\text{HS}})^3}, \end{aligned} \quad (4)$$

where the HS volume or packing fraction is, $\xi_{\text{HS}} = \pi \rho \sigma_{\text{HS}}^3 / 6$.

The Carnahan-Starling and Kolafa compressibility factors given in Eq. (4) substituted in Eq. (3) lead to

$$\begin{aligned} \frac{s_{\text{ex,cs}}(\xi, T)}{k_B} &= -\xi_{\text{HS}} \frac{(4 - 3\xi_{\text{HS}})}{(1 - \xi_{\text{HS}})^2}, \\ \frac{s_{\text{ex,kol}}(\xi, T)}{k_B} &= -\frac{5}{3} \ln(1 - \xi_{\text{HS}}) \\ &\quad - \frac{\xi_{\text{HS}}(34 - 33\xi_{\text{HS}} + 4\xi_{\text{HS}}^2)}{6(1 - \xi_{\text{HS}})^2}. \end{aligned} \quad (5)$$

Inverse power particles. Explicit expressions for the excess entropy of the IP fluid using Eq. (3) require an analytic expression for Z . The IP equation of state for specific values of n between 4 and the HS limit based on a least squares parametrization of MD simulation data was given in Ref. [26],

which is in the form of an m -term series expansion of powers of the nominal IP volume fraction,

$$\xi = \frac{\pi}{6} \frac{\rho}{(k_B T / \epsilon)^{3/n}}, \quad (6)$$

which for the IP system is dependent on temperature. For notational compactness, $k_B T / \epsilon$ is replaced by T in most of the expressions in the rest of this work. The compressibility factor, Z and its derivatives are functions of ρ and T . The IP state point derivatives presented here are therefore generally functions of ρ and T , and are presented for $T = 1$. This formulation for Z and its first density derivative, Z' , are expressed using the following formulas:

$$Z(\xi) = 1 + \sum_{i=1}^m C_i \xi^i, \quad (7)$$

$$Z'(\xi) \equiv dZ/d\xi = \sum_{i=1}^m i C_i \xi^{i-1}.$$

The constant C_1 is the second virial coefficient, $b_2 = 4\Gamma(1 - 3/n)/T^{3/n}$, for all $n > 3^+$, where $\Gamma(x)$ is the gamma function of x . The constant C_2 was assigned to the exact third virial coefficient, where known; otherwise, it was treated as a parameter to be fitted to the MD Z data.

Equations (3) and (7) give the IP fluid excess entropy (in units of k_B)

$$s_{\text{ex}}(\xi, T) = \sum_{i=1}^m \left(\frac{3}{n} - \frac{1}{i} \right) C_i \xi^i, \quad (8)$$

making use of the series expansion formulation. Details of the constants C_i used in this work, for a range of n and how they were obtained are presented in Ref. [26].

For notational convenience, the quantity

$$R(\xi) = \frac{Z'(\xi)}{Z(\xi)}, \quad (9)$$

is used extensively in subsequent equations.

In this work, the calculated quantities and other variables are expressed in IP reduced units of ϵ for energy, σ for length, and m , the mass of the particle, for mass. The entropy per particle and its ideal and excess components are given in units of k_B . To assist interpretation of any trends with density or ξ and pressure, these quantities are typically normalized by their freezing points, i.e., ρ_{fr} , ξ_{fr} , and P_{fr} , respectively, whose values are obtained from the data of Agrawal and Kofke [36,37] fitted to a low-order polynomial in powers of n^{-1} :

$$\kappa = \frac{\rho}{\rho_{fr}(T)} = \frac{\xi}{\xi_{fr}}, \quad (10)$$

where note along the constant $\rho/T^{3/n}$ or isomorph curve, ξ and ξ_{fr} are independent of temperature. Also Z is an explicit or unique function of ξ and not ρ , as there is a temperature dependence to Z for the IP system (unlike for hard spheres).

Details of the IP freezing point density and pressure values and their parametrization as a function of n are presented and discussed in Ref. [26]. The Agrawal and Kofke fluid-fcc fluid coexistence density used for all n values was given in Table I of Ref. [37]. Agrawal and Kofke showed that the small- n fluid-bcc coexistence values obtained by a single occupancy

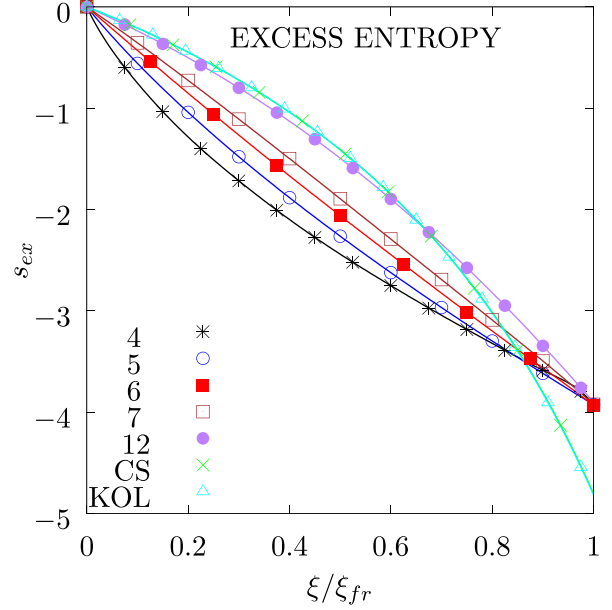


FIG. 1. The density dependence of the IP excess entropy s_{ex} , from Eqs. (3) and (8). The normalized density ξ/ξ_{fr} is used on the abscissa. The values of n are given in the figure. The Carnahan-Starling (CS) and Kolafa (KOL) HS (i.e., $n \rightarrow \infty$) analytic formulas of Eq. (5) for s_{ex} are also shown.

model were nearly the same as the fcc-MD values for $n < 6$ and of sufficient accuracy for the purposes of the present work. These values were also used by Agrawal and Kofke in further analysis and interpretation of their simulation-derived coexistence data.

Figure 1 shows s_{ex} as a function of κ up to the freezing volume fraction for n values of 4, 5, 6, 7, and 12. These curves were generated using Eq. (8). Figure 1 reveals that the curves change from being convex to concave with increasing n at $ca. n = 6$, as was also discussed in Ref. [26]. In the $\kappa \rightarrow 1$ limit, it is seen that $s_{\text{ex}} \rightarrow -3.9$, independent of n , at least in the presented range. Khrapak also showed that close to freezing, the limiting excess entropy was relatively independent of the parameter controlling the degree of repulsiveness in the Yukawa pair potential fluid [38]. Figure 1 illustrates that the $s_{\text{ex}}(\xi/\xi_{fr})$ curve is *not* universal at any density, i.e., independent of n . The spread of $s_{\text{ex}}(\xi/\xi_{fr})$ reaches a maximum for values of $\xi/\xi_{fr} \simeq 0.5$.

Figure 2 shows the excess entropy as a function of pressure for the same values of n as in Fig. 1. At each temperature, the pressure is normalized by the value of P at freezing, P_{fr} . The figure shows that s_{ex} becomes more negative with increasing pressure, as it does with increasing density (see Fig. 1). As $Z(\xi)$ is convex for all valid n , the figure accentuates the s_{ex} data points close to freezing compared with the plot of s_{ex} as a function of ξ/ξ_{fr} shown in Fig. 1.

III. STATE POINT DERIVATIVE FORMULAS OF THE EXCESS ENTROPY

The $Z(\xi, 1/n)$ surface of the IP fluid derived from extensive MD simulations, for $n > 12$, was presented in Ref. [23]. This was extended to a wider n range in Refs. [25,26]. The

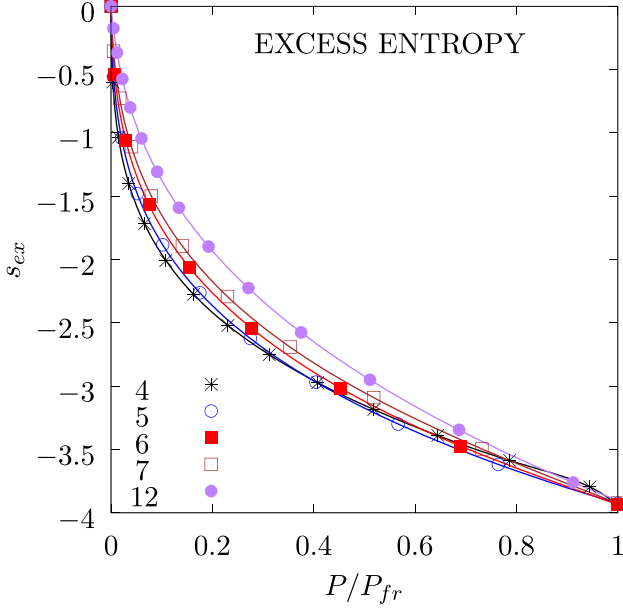


FIG. 2. As for Fig. 1, except that the normalized pressure P/P_{fr} is employed. The pressure at freezing is P_{fr} .

ability to navigate on such a surface in directions where certain independent variables are kept constant or vary subject to a specified relationship between two of them will facilitate exploration and characterization of the global physical property landscape. These directions are not restricted to isotherms, isochores, and isobars.

Expressions for various second-order thermodynamic and related properties of the inverse power fluid were derived in Ref. [25]. These were expressed in terms of the potential exponent, n , Z , and Z' . This section is built on the data and formulas found in Ref. [26] in deriving and portraying graphically expressions for the gradient dependence of s_{ex} with respect to the thermodynamic independent variables.

These derivative functions can be derived using a purely thermodynamic procedure or from one based on statistical mechanics and partition functions. The latter will be considered first as it forms the basis for some of the steps in the thermodynamic route derivations. Both approaches are employed below.

A. Statistical mechanics

Some of the statistical mechanical fundamentals which can be used to derive the three entropy terms (i.e., ideal, excess, and total) are given in Ref. [39], in particular the expression in Eq. (4) of that work, which is reproduced here with slightly different notation. The Helmholtz free energy of the N -particle system of monatomic particles A is linked to the partition function of the total system, Q , through $A\beta = -\ln Q$. For the IP fluid system, the following simplification of Q forms the foundations of the rest of this work,

$$Q = \left(\frac{(V/N\Lambda^3)^N}{N!} \right) \int \exp \left[- \left(\frac{\rho^{n/3}\epsilon}{k_B T} \right) \sum_{i<j} \tilde{r}_{ij}^{-n} \right] d\tilde{r}^{3N} \\ = Q_{id} Q_{ex}, \quad (11)$$

where the de Broglie wavelength $\Lambda = h/(2\pi m k_B T)^{1/2}$ (h is Planck's constant). The pair separation in dimensionless MUs, $\tilde{r}_{ij} = \rho^{1/3} r_{ij}$, and the $3N$ -dimensional volume element is $d\tilde{r}^{3N}$ in MUs. The ideal and excess parts of Q are Q_{id} and Q_{ex} , respectively. It follows from Eq. (11) that as the integrand is a function of $\rho^{n/3}\epsilon/k_B T$ only, and the limits of integration are independent of ρ and T , the excess thermodynamic properties (with respect to the ideal gas at ρ and T) are functions of $\rho^{n/3}/T$ (in IP reduced units) only. The consequence of this is that a single isotherm or isochore is sufficient to determine the entire equation of state and the physical properties for the IP system. This is a unique feature of the IP and hard-sphere potential, and the scaling is not so simple for other pair-potential analytic forms, where aspects of isomorphic behavior are more hidden [40].

Using Eq. (11) applied to the ideal term gives

$$\beta U = -\beta \left(\frac{\ln Q}{\beta} \right)_\rho, \quad S = \beta U - \beta A,$$

$$S = -\beta \left(\frac{\ln Q}{\beta} \right)_\rho + \ln Q,$$

$$S_{id} = \ln Q_{id} \quad (U_{id} = 0),$$

$$s_{id}(\rho, T) = S_{id}/N = -\ln \rho + \frac{3}{2} \ln T + C(m),$$

$$C(m) = 1 + 3 \ln[(2\pi m)^{1/2}/h],$$

$$\rho \left(\frac{\partial s_{id}}{\partial \rho} \right)_\beta = -1, \quad (12)$$

where $C(m)$ is independent of ρ and T . See the further discussion of these relationships which is given in Ref. [41]. The corresponding excess entropy term is

$$\beta U = \frac{3N}{n} (Z - 1),$$

$$S_{ex} = -\beta \left(\frac{\partial \ln Q_{ex}}{\partial \beta} \right)_\rho + \ln Q_{ex},$$

$$\left(\frac{\partial s_{ex}}{\partial \rho} \right)_\beta = \left(\frac{\partial}{\partial \rho} \right)_\beta \left(\frac{3}{n} (Z - 1) + \frac{1}{N} \ln Q_{ex} \right),$$

$$\rho \left(\frac{\partial s_{ex}}{\partial \rho} \right)_\beta = - \left[(Z - 1) - \frac{3}{n} \xi Z' \right]. \quad (13)$$

Combining the last lines of Eqs. (12) and (13) give

$$\rho \left(\frac{\partial s}{\partial \rho} \right)_\beta = \rho \left(\frac{\partial s_{id}}{\partial \rho} \right)_\beta + \rho \left(\frac{\partial s_{ex}}{\partial \rho} \right)_\beta = -Z \left(1 - \frac{3}{n} \xi R \right). \quad (14)$$

Note that both the total, ideal, and excess parts of the entropy, and their density derivatives are evaluated at the same state point ρ , T (or, equivalently, ξ , T).

Another class of entropy derivative involves the pressure P as the variable or constraint of the partial derivative. Consider, for example, $(\partial s / \partial P)_\beta$. As $(\partial P / \partial \rho)_\beta = TZ[1 + \xi R]$, this partial derivative is given by

$$(\partial s / \partial P)_\beta = \frac{(\partial s / \partial \rho)_\beta}{(\partial P / \partial \rho)_\beta},$$

$$P(\partial s/\partial P)_\beta = -Z \left[\frac{(1 - \frac{3}{n}\xi R)}{(1 + \xi R)} \right]. \quad (15)$$

In splitting the total entropy into excess and ideal parts, the excess entropy is not an arbitrary quantity. It has a unique definition and is the entropy of a system minus the entropy of an ideal gas at the same temperature and density [42,43]. The excess entropy s_{ex} is physically meaningful, reflecting the deviation of a system's structure from that of an ideal gas, due to the intermolecular interactions.

B. Thermodynamics

The six partial derivatives of interest for the IP fluid state can be derived independently for the total value, and for its ideal and excess entropies using partial differentiation and Maxwell's thermodynamic relations [44–46]. Density, ρ or ξ , rather than volume ($\equiv v = V/N$), is usually a more useful quantity in liquid or dense fluid state treatments, especially where the state is close to the freezing line.

The basis of the following analysis is that the total entropy, and its ideal and excess components, are all explicit functions of ρ and T (or, equivalently, of ξ). This can be seen from the statistical mechanics derivations above. Expressions for $s_{\text{id}}(\rho, T)$ and $s_{\text{ex}}(\rho, T)$ are given in Eqs. (12) and (13), respectively. The pressure dependence of these quantities can be obtained from $P = Z(\rho, T)\rho T = Z(\xi)\rho T$. This includes their state point derivatives involving P , where the partial derivative chain rule can be employed. The pressure dependence of s_{ex} along an isotherm is already known, in fact, as is evident in Fig. 2, from which its partial derivative automatically follows.

1. Total entropy s

The total entropy formulas can be expressed in terms of second-order thermodynamic quantities (e.g., see Refs. [45,46]),

$$\begin{aligned} P(\partial s/\partial P)_T &= ZT\alpha_P, \\ T(\partial s/\partial T)_\rho &= c_v, \\ T(\partial s/\partial T)_P &= c_P, \\ \rho(\partial s/\partial \rho)_T &= -\alpha_P B_T/\rho, \\ \rho(\partial s/\partial \rho)_P &= -\frac{c_P}{T\alpha_P}, \\ P(\partial s/\partial P)_\rho &= Z\rho \frac{c_v}{\alpha_P B_T}, \end{aligned} \quad (16)$$

where the heat capacity per particle at constant volume is c_v and at constant pressure is c_P (both in units of k_B), the isothermal bulk modulus is B_T , and the volume thermal expansivity at constant pressure is α_P . These quantities are defined explicitly for the IP fluid as follows:

$$\begin{aligned} \alpha_P &= -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P = \frac{1}{T} \left(\frac{1 - \frac{3}{n}\xi R}{1 + \xi R} \right), \\ B_T &= \rho \left(\frac{\partial P}{\partial \rho} \right)_T = P(1 + \xi R), \\ c_v &= T \left(\frac{\partial s}{\partial T} \right)_v = \frac{3}{2} + \frac{3}{n} \left[(Z - 1) - \frac{3}{n}\xi Z' \right], \end{aligned}$$

$$c_P = T \left(\frac{\partial s}{\partial T} \right)_P = c_v + \frac{T}{\rho} (\alpha_P^2 B_T). \quad (17)$$

For the IP fluid, both α_P and B_T are greater than or equal to zero. The limiting values of these thermodynamic quantities in the low-density (ideal-gas) limit are $\alpha_P = T^{-1}$, $B_T = \rho T$, $c_v = 3/2$, $c_P = 5/2$, and $\alpha_P B_T = \rho$.

The explicit expressions for the partial derivatives in terms of Z and its density derivative are from Eqs. (16) and (17),

$$\begin{aligned} P \left(\frac{\partial s}{\partial P} \right)_T &= -Z \left(\frac{1 - \frac{3}{n}\xi R}{1 + \xi R} \right), \\ T \left(\frac{\partial s}{\partial T} \right)_\rho &= c_v = \frac{3}{2} + \frac{3}{n} \left(Z - 1 - \frac{3}{n}\xi Z' \right), \\ T \left(\frac{\partial s}{\partial T} \right)_P &= c_P = c_v + Z \left(\frac{(1 - \frac{3}{n}\xi R)^2}{1 + \xi R} \right), \\ \rho \left(\frac{\partial s}{\partial \rho} \right)_T &= -Z \left(1 - \frac{3}{n}\xi R \right), \\ \rho \left(\frac{\partial s}{\partial \rho} \right)_P &= -c_P \left(\frac{1 + \xi R}{1 - \frac{3}{n}\xi R} \right), \\ P \left(\frac{\partial s}{\partial P} \right)_\rho &= \frac{\frac{3}{2} + \frac{3}{n} (Z - 1 - \frac{3}{n}\xi Z')}{1 - \frac{3}{n}\xi R}. \end{aligned} \quad (18)$$

In deriving the expressions in Eq. (18), use has been made of the relationships $u = [3/n](Z - 1)T$ for the potential energy, $d\xi/dT = -3\xi/nT$, and $dZ/dT = [d\xi/dT][dZ/d\xi] = -3\xi Z'/nT$.

The partial derivatives in Eq. (18) can be written as the sum of the contributions from the s_{ex} and s_{id} parts, which are derived by independent procedures specified below.

2. Excess entropy s_{ex}

The six derivatives of s_{ex} can be derived using the following expressions:

$$\begin{aligned} (\partial A/\partial B)_C &= -\frac{(\partial C/\partial B)_A}{(\partial C/\partial A)_B}, \quad (\partial P/\partial \rho)_T = TZ(1 + \xi R), \\ (\partial P/\partial T)_\rho &= \rho Z \left(1 - \frac{3}{n}\xi R \right), \quad (\partial \rho/\partial T)_{s_{\text{ex}}} = \frac{n}{3} \frac{\rho}{T}, \\ (\partial P/\partial T)_{s_{\text{ex}}} &= \rho Z \left(1 + \frac{3}{n} \right). \end{aligned} \quad (19)$$

Expressions for the six excess entropy partial derivatives can then be derived from Eqs. (3) and (19),

$$\begin{aligned} (\partial s_{\text{ex}}/\partial \rho)_T &= \frac{3}{n} \left(\frac{\partial Z}{\partial \rho} \right)_T - \frac{Z - 1}{\rho}, \\ \rho(\partial s_{\text{ex}}/\partial \rho)_T &= -\left([Z - 1] - \frac{3}{n}\xi Z' \right). \end{aligned} \quad (20)$$

The following identities:

$$\begin{aligned} T(\partial s_{\text{ex}}/\partial T)_\rho &= -T(\partial s_{\text{ex}}/\partial \rho)_T (\partial \rho/\partial T)_{s_{\text{ex}}}, \\ P(\partial s_{\text{ex}}/\partial P)_T &= P \frac{(\partial s_{\text{ex}}/\partial \rho)_T}{(\partial P/\partial \rho)_T}, \end{aligned}$$

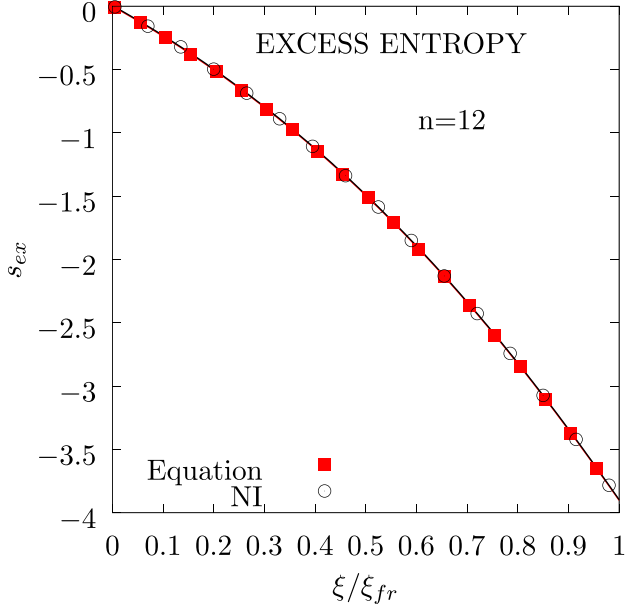


FIG. 3. The excess entropy from Eq. (8) (Equation) compared with numerical integration (NI) $(\partial s_{\text{ex}}/\partial P)_T$ from Eq. (22) with respect to pressure. The IP exponent is $n = 12$. The Z and Z' were obtained using Eq. (7), taking the C_i parameters from Ref. [26].

$$\begin{aligned} P(\partial s_{\text{ex}}/\partial P)_\rho &= P \frac{(\partial s_{\text{ex}}/\partial T)_\rho}{(\partial P/\partial T)_\rho}, \\ T(\partial s_{\text{ex}}/\partial T)_P &= -T(\partial s_{\text{ex}}/\partial P)_T (\partial P/\partial T)_{s_{\text{ex}}}, \\ \rho(\partial s_{\text{ex}}/\partial \rho)_P &= -\rho(\partial s_{\text{ex}}/\partial P)_\rho (\partial P/\partial \rho)_{s_{\text{ex}}}, \end{aligned} \quad (21)$$

combined with Eq. (20) gives explicit expressions for the six excess entropy partial derivatives,

$$\begin{aligned} P(\partial s_{\text{ex}}/\partial P)_T &= -\left(\frac{Z-1-\frac{3}{n}\xi Z'}{1+\xi R} \right), \\ T(\partial s_{\text{ex}}/\partial T)_\rho &= \frac{3}{n} \left(Z-1-\frac{3}{n}\xi Z' \right), \\ T(\partial s_{\text{ex}}/\partial T)_P &= \left[1 + \frac{3}{n} \right] \left(\frac{Z-1-\frac{3}{n}\xi Z'}{1+\xi R} \right), \\ \rho(\partial s_{\text{ex}}/\partial \rho)_T &= -\left(Z-1-\frac{3}{n}\xi Z' \right), \\ \rho(\partial s_{\text{ex}}/\partial \rho)_P &= -\left[1 + \frac{3}{n} \right] \left(\frac{Z-1-\frac{3}{n}\xi Z'}{1-\frac{3}{n}\xi R} \right), \\ P(\partial s_{\text{ex}}/\partial P)_\rho &= \frac{3}{n} \left(\frac{Z-1-\frac{3}{n}\xi Z'}{1-\frac{3}{n}\xi R} \right). \end{aligned} \quad (22)$$

A comparison between the excess entropy from Eq. (8) compared with numerical integration $(\partial s_{\text{ex}}/\partial P)_T$ from Eq. (22) with respect to pressure at $T = 1$ for $n = 12$ is given in Fig. 3. The two routes agree within machine precision over the complete fluid density range. Figures 2 and 3 demonstrate that the density and pressure derivatives of the excess entropy along an isotherm are monotonic and qualitatively similar.

For the $n \rightarrow \infty$ or hard-sphere limiting case, the expressions in Eq. (22) reduce to

$$\begin{aligned} \rho \left(\frac{\partial s_{\text{ex}}}{\partial \rho} \right)_T &= -(Z-1), & \left(\frac{\partial s_{\text{ex}}}{\partial T} \right)_\rho &= 0, \\ T \left(\frac{\partial s_{\text{ex}}}{\partial T} \right)_P &= \frac{(Z-1)}{(1+\rho R)}, \\ \rho \left(\frac{\partial s_{\text{ex}}}{\partial \rho} \right)_P &= -(Z-1), \\ P \left(\frac{\partial s_{\text{ex}}}{\partial P} \right)_T &= -\frac{(Z-1)}{(1+\rho R)}, \\ P \left(\frac{\partial s_{\text{ex}}}{\partial P} \right)_\rho &= 0, \end{aligned} \quad (23)$$

using Eq. (22).

3. Ideal gas entropy s_{id}

By differentiating the definition of the ideal gas expression for the entropy from Eq. (12) and using the chain rule, the following derivatives of the ideal part of the entropy are

$$\begin{aligned} P \left(\frac{\partial s_{\text{id}}}{\partial P} \right)_T &= P \frac{(\partial s_{\text{id}}/\partial \rho)_T}{(\partial P/\partial \rho)_T}, \\ T \left(\frac{\partial s_{\text{id}}}{\partial T} \right)_P &= T \left(\frac{\partial s_{\text{id}}}{\partial T} \right)_\rho - T \left(\frac{\partial s_{\text{id}}}{\partial \rho} \right)_T \frac{(\partial P/\partial T)_\rho}{(\partial P/\partial \rho)_T}, \\ \rho \left(\frac{\partial s_{\text{id}}}{\partial \rho} \right)_P &= \rho \left(\frac{\partial s_{\text{id}}}{\partial \rho} \right)_T - \rho \left(\frac{\partial s_{\text{id}}}{\partial T} \right)_\rho \frac{(\partial P/\partial T)_T}{(\partial P/\partial T)_\rho}, \\ P \left(\frac{\partial s_{\text{id}}}{\partial P} \right)_\rho &= P \frac{(\partial s_{\text{id}}/\partial T)_\rho}{(\partial P/\partial T)_\rho}, \end{aligned} \quad (24)$$

which gives

$$\begin{aligned} P(\partial s_{\text{id}}/\partial P)_T &= -\frac{1}{(1+\xi R)}, \\ T(\partial s_{\text{id}}/\partial T)_\rho &= \frac{3}{2}, \\ T(\partial s_{\text{id}}/\partial T)_P &= \frac{3}{2} + \left(\frac{1-\frac{3}{n}\xi R}{1+\xi R} \right), \\ \rho(\partial s_{\text{id}}/\partial \rho)_T &= -1, \\ \rho(\partial s_{\text{id}}/\partial \rho)_P &= -\left(1 + \frac{3}{2} \frac{(1+\xi R)}{(1-\frac{3}{n}\xi R)} \right), \\ P(\partial s_{\text{id}}/\partial P)_\rho &= \frac{3}{2} \left(\frac{1}{1-\frac{3}{n}\xi R} \right). \end{aligned} \quad (25)$$

Equations (16) and (17) can also be used to estimate an effective IP exponent for an arbitrary system just from

second-order thermodynamic data using

$$n = 3 \frac{\rho}{T} \left(\frac{\partial T}{\partial \rho} \right)_{s_{\text{ex}}} = -3 \frac{\rho}{T} \frac{(\partial s_{\text{ex}} \partial \rho)_T}{(\partial s_{\text{ex}} \partial T)_\rho} = \frac{3}{\rho} \left(\frac{\alpha_P B_T - \rho}{c_v - \frac{3}{2}} \right), \quad (26)$$

which follows from the condition that $\rho^{n/3}/T$ is a constant along a configurational adiabat (i.e., the constant excess entropy line). This was also recognized previously by Kamayashi and Hiwatari [47]. Equation (26) is exact for IP systems and it might be considered as a possible way of attaching an effective n value (or “ n_{eff} ”) for real molecular liquids, as was performed using experimental shear viscosity data in Ref. [12]. A potential problem with using Eq. (26) for real molecules is that they may have many internal degrees of freedom which would contribute to c_v and possibly α_P and B_T , which one might not expect should influence n_{eff} . Equation (26) might be useful in treating model (“monatomic”) purely repulsive potential systems, such as the Yukawa form.

There are some basic relationships between the various partial derivatives of s_{ex} which are exact and analytic for the IP system. The interaction part of the pressure, $P_{\text{ex}} = (Z - 1)\rho T$, when expressed in macroscopic units, $\tilde{P}_{\text{ex}} = P_{\text{ex}}/\rho T = Z - 1$ is (like s_{ex}) constant along the configurational adiabat line on the ρ, T plane defined by a constant value of $\rho/T^{3/n}$. Making use of these relationships, the expressions below follow:

$$\begin{aligned} \frac{(\partial s_{\text{ex}}/\partial T)_{P_{\text{ex}}}}{(\partial s_{\text{ex}} \partial P_{\text{ex}})_T} &= - \left(\frac{\partial P_{\text{ex}}}{\partial T} \right)_{s_{\text{ex}}} = -(Z - 1)\rho \left(1 + \frac{3}{n} \right), \\ \frac{(\partial s_{\text{ex}} \partial T)_\rho}{(\partial s_{\text{ex}} \partial \rho)_T} &= - \left(\frac{\partial \rho}{\partial T} \right)_{s_{\text{ex}}} = - \frac{3}{n} \frac{\rho}{T}, \\ \frac{(\partial s_{\text{ex}} \partial \rho)_{P_{\text{ex}}}}{(\partial s_{\text{ex}} \partial P_{\text{ex}})_\rho} &= - \left(\frac{\partial P_{\text{ex}}}{\partial \rho} \right)_{s_{\text{ex}}} = -T(Z - 1) \left(1 + \frac{n}{3} \right). \end{aligned} \quad (27)$$

Two quantities that are frequently involved in these formulas are the ratios $\xi R \equiv \xi Z'/Z$ and $1 - 3\xi R/n$, which are plotted as a function of κ in Figs. 4 and 5, respectively. Data for several representative values of n in the soft ($n = 5$), intermediate (12), and hard ($n = 72$) potential regimes are shown. Using $Z = 1 + \xi b_2 + O(\xi^2)$ in the low-density limit, it is evident that $\xi R \rightarrow 0$ as $\xi \rightarrow 0$ for all n (see Fig. 4), and also $[1 - 3\xi R/n] \rightarrow 1$ in Fig. 5, in the same limit. Both ξR and $1 - 3\xi R/n$ are seen in Figs. 4 and 5, respectively, to be non-negative in the equilibrium fluid part of the phase diagram.

The density dependencies of the dimensionless excess entropy partial derivative expressions are compared graphically. First, the trends for the hard-sphere limiting cases given in Eq. (23) are presented in Fig. 6. As may be discerned from Eq. (23), only $\rho(\partial s_{\text{ex}}/\partial \rho)_T$, $T(\partial s_{\text{ex}}/\partial T)_P$, $\rho(\partial s_{\text{ex}}/\partial \rho)_P$, and $P(\partial s_{\text{ex}}/\partial P)_T$ are nonzero for hard spheres. Note that, in the HS limit, $\rho(\partial s_{\text{ex}}/\partial \rho)_T$ and $\rho(\partial s_{\text{ex}}/\partial \rho)_P$ are the same functions of κ .

The density dependence of the dimensionless excess entropy partial derivative expressions defined in Eq. (22) for $n = 12$ are presented in Fig. 7. As indicated in these equations, the derivatives $(\partial s_{\text{ex}}/\partial P)_\rho$, $(\partial s_{\text{ex}}/\partial T)_P$, and $(\partial s_{\text{ex}}/\partial T)_\rho$ are pos-

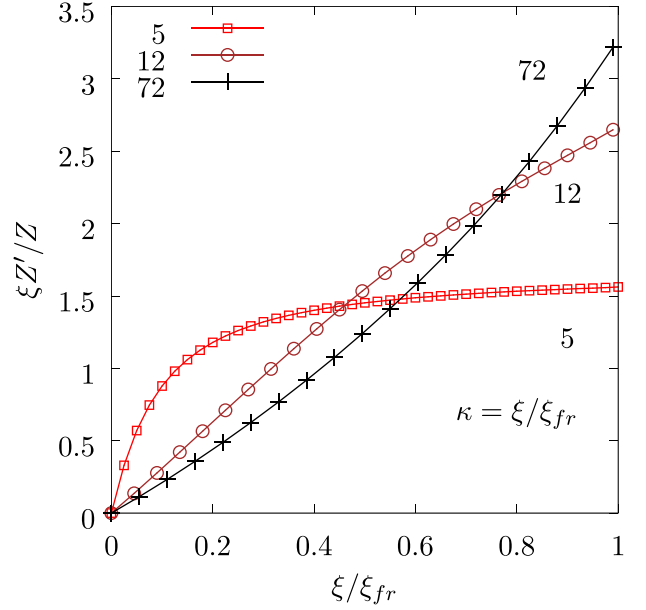


FIG. 4. The dependence of $\xi R \equiv \xi Z'/Z$ on ξ/ξ_{fr} for $T = 1$ and n values given in the figure. The data points were obtained from the multiparameter series of Eq. (7) fitted to the MD simulation Z values as a function of ξ .

itive and increase with density. The derivatives $(\partial s_{\text{ex}}/\partial P)_T$, $(\partial s_{\text{ex}}/\partial \rho)_T$, and $(\partial s_{\text{ex}}/\partial \rho)_P$ are negative and also increase in magnitude with density. All six partial derivatives are nonzero apart from in the $\xi \rightarrow 0$ limit, whereas for HS, $\rho(\partial s_{\text{ex}}/\partial T)_\rho$ and $\rho(\partial s_{\text{ex}}/\partial P)_\rho$ are zero at all densities in both cases because the excess entropy does not depend on temperature for hard spheres.

The six partial derivatives of $s_{\text{ex}}(\rho, T)$ with respect to ρ , T , and P can also be obtained by numerical differentiation

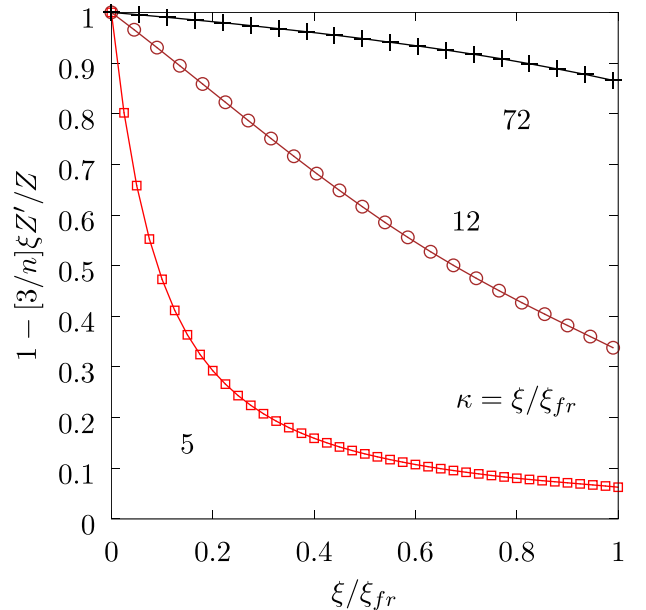


FIG. 5. As for Fig. 4, except the dependence of $(1 - [3/n]\xi R) \equiv (1 - [3/n]\xi Z'/Z)$ on ξ/ξ_{fr} for three n values is presented in the figure.

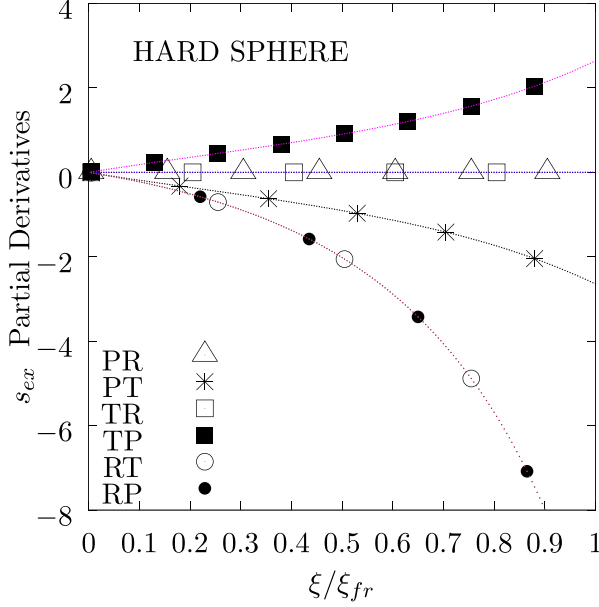


FIG. 6. The dimensionless excess entropy partial derivatives from the analytic formulas defined in Eq. (23) for the hard-sphere fluid as a function of density. Key: The figure annotation XY refers to the letters in the plotted term, $X(\partial s_{\text{ex}}/\partial X)_Y$, where X and Y can be density ρ (R), temperature (T), and pressure (P).

of $s_{\text{ex}}(\rho, T)$ with respect to these independent variables. Both P and $s_{\text{ex}}(\rho, T)$ are obtained from the multiparameter equation of state from Eqs. (7) and (8), respectively. On choosing

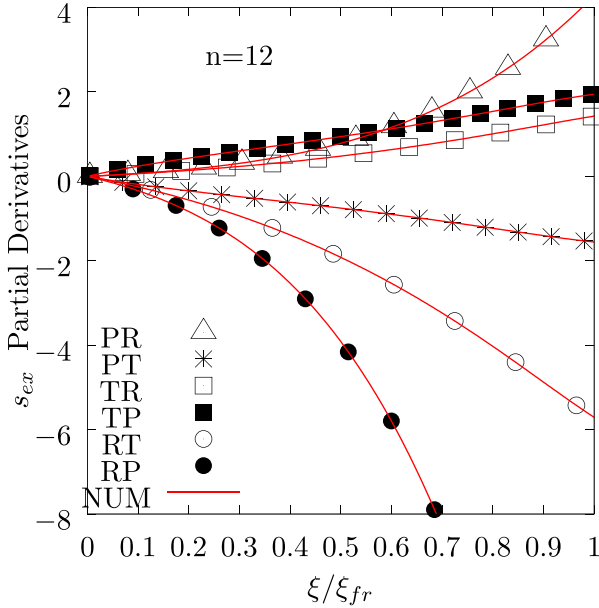


FIG. 7. The dimensionless excess entropy partial derivatives from the analytic formulas defined in Eq. (22) for the IP exponent $n = 12$ and $T = 1$ as a function of κ . Key: The figure annotation XY refers to the letters in the plotted term, $X(\partial s_{\text{ex}}/\partial X)_Y$, where X and Y can be density ρ (R), temperature (T), and pressure (P). The continuous curves (NUM) were obtained by numerical differentiation of the $s_{\text{ex}}(T, \rho, P)$ values obtained from Eqs. (28)–(31).

the density and temperature increments, $\Delta\rho$ and ΔT ,

$$\begin{aligned} \left(\frac{\partial s_{\text{ex}}}{\partial T}\right)_\rho &= \lim_{\Delta T \rightarrow 0} \left(\frac{s_{\text{ex}}(\rho, T + \Delta T) - s_{\text{ex}}(\rho, T - \Delta T)}{2\Delta T} \right), \\ \left(\frac{\partial s_{\text{ex}}}{\partial \rho}\right)_T &= \lim_{\Delta \rho \rightarrow 0} \left(\frac{s_{\text{ex}}(\rho + \Delta \rho, T) - s_{\text{ex}}(\rho - \Delta \rho, T)}{2\Delta \rho} \right), \\ \left(\frac{\partial s_{\text{ex}}}{\partial P}\right)_\rho &= \lim_{\Delta T \rightarrow 0} \left(\frac{s_{\text{ex}}(\rho, T + \Delta T) - s_{\text{ex}}(\rho, T - \Delta T)}{P(\rho, T + \Delta T) - P(\rho, T - \Delta T)} \right), \\ \left(\frac{\partial s_{\text{ex}}}{\partial P}\right)_T &= \lim_{\Delta \rho \rightarrow 0} \left(\frac{s_{\text{ex}}(\rho + \Delta \rho, T) - s_{\text{ex}}(\rho - \Delta \rho, T)}{P(\rho + \Delta \rho, T) - P(\rho - \Delta \rho, T)} \right), \end{aligned} \quad (28)$$

where $P(\rho, T + \Delta T) = Z(\rho, T + \Delta T)\rho(T + \Delta T)$. The density and temperature derivatives of s_{ex} at constant pressure are obtained numerically by computing the temperature change, $\Delta T'$ for a given $\Delta\rho$, which causes no change in P , employing the following expansion:

$$\begin{aligned} \Delta P &= \Delta\rho(\partial P/\partial \rho)_T + \Delta T'(\partial P/\partial T)_\rho = 0, \\ \Delta T' &= -\Delta\rho \frac{(\partial P/\partial \rho)_T}{(\partial P/\partial T)_\rho} = -\Delta\rho \frac{T(1 + \xi R)}{\rho(1 - \frac{3}{n}\xi R)}, \end{aligned} \quad (29)$$

and on defining

$$\begin{aligned} \Delta s'_{\text{ex}}(\rho, T) &= s_{\text{ex}}(\rho, T + \Delta T') - s_{\text{ex}}(\rho, T - \Delta T') \\ &\quad + s_{\text{ex}}(\rho + \Delta \rho, T) - s_{\text{ex}}(\rho - \Delta \rho, T), \end{aligned} \quad (30)$$

gives

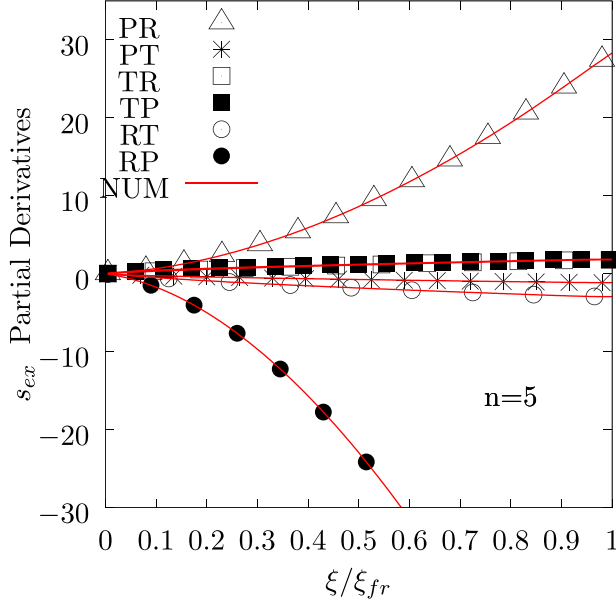
$$\begin{aligned} \left(\frac{\partial s_{\text{ex}}}{\partial T}\right)_\rho &= \lim_{\Delta T' \rightarrow 0} \left(\frac{\Delta s'_{\text{ex}}(\rho, T)}{2\Delta T'} \right), \\ \left(\frac{\partial s_{\text{ex}}}{\partial \rho}\right)_P &= \lim_{\Delta \rho \rightarrow 0} \left(\frac{\Delta s'_{\text{ex}}(\rho, T)}{2\Delta \rho} \right). \end{aligned} \quad (31)$$

Figure 7 also shows the excess entropy derivatives obtained by numerical differentiation according to Eqs. (28)–(31). The two approaches are in excellent agreement for all six excess entropy derivatives (to within machine precision). When the s_{ex} and s_{id} derivative formulas given in Eqs. (22) and (25), respectively, are added, they give those in Eq. (18). The data produced by these formulas are self-consistent and give the exact results obtained by numerical differentiation.

Figure 8, which gives the corresponding quantities for $n = 5$, reveals that $(\partial s_{\text{ex}}/\partial P)_\rho$ and $(\partial s_{\text{ex}}/\partial \rho)_P$ increase the most in magnitude with density as n decreases.

4. Phase diagram traversal along arbitrary directions

In the equations above in Sec. III expressions for the dependence of the slope of s_{ex} with respect to lines parallel to the ρ (or, equivalently, ξ), T and P axes are derived. Combinations of these quantities can be used to derive expressions for the rate of excess entropy change along arbitrary directions on the independent variable landscape. For a quantity $y(x)$ the slope of the $y(x)$ can be generalized and implemented in such a multidimensional surface as follows [48]: Consider the specific example $g = dT/d\rho$ (i.e., where locally the relationship $T = g\rho + \text{const}$ is taken) and therefore $(\partial T/\partial \rho)_g = g$ as defining a direction along the ρ - T plane at a particular value of T and ρ . Using the rules of partial

FIG. 8. As for Fig. 7, except $n = 5$.

derivatives [44],

$$\begin{aligned} \left(\frac{\partial s_{\text{ex}}}{\partial T}\right)_g &= \left(\frac{\partial s_{\text{ex}}}{\partial T}\right)_\rho + \left(\frac{\partial s_{\text{ex}}}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial T}\right)_g \\ &= \left(\frac{\partial s_{\text{ex}}}{\partial T}\right)_\rho + \left(\frac{\partial s_{\text{ex}}}{\partial \rho}\right)_T / g, \\ \left(\frac{\partial s_{\text{ex}}}{\partial \rho}\right)_g &= \left(\frac{\partial s_{\text{ex}}}{\partial \rho}\right)_T + g \left(\frac{\partial s_{\text{ex}}}{\partial T}\right)_\rho, \end{aligned} \quad (32)$$

taking the T - P plane, where $h = dP/dT$,

$$\begin{aligned} \left(\frac{\partial s_{\text{ex}}}{\partial P}\right)_h &= \left(\frac{\partial s_{\text{ex}}}{\partial P}\right)_T + \left(\frac{\partial s_{\text{ex}}}{\partial T}\right)_P / h, \\ \left(\frac{\partial s_{\text{ex}}}{\partial T}\right)_h &= \left(\frac{\partial s_{\text{ex}}}{\partial T}\right)_P + h \left(\frac{\partial s_{\text{ex}}}{\partial P}\right)_T, \end{aligned} \quad (33)$$

and for the ρ - P plane, where $e = dP/d\rho$,

$$\begin{aligned} \left(\frac{\partial s_{\text{ex}}}{\partial P}\right)_e &= \left(\frac{\partial s_{\text{ex}}}{\partial P}\right)_\rho + \left(\frac{\partial s_{\text{ex}}}{\partial \rho}\right)_P / e, \\ \left(\frac{\partial s_{\text{ex}}}{\partial \rho}\right)_e &= \left(\frac{\partial s_{\text{ex}}}{\partial \rho}\right)_P + e \left(\frac{\partial s_{\text{ex}}}{\partial P}\right)_\rho. \end{aligned} \quad (34)$$

The IP exponent n is held constant during these operations.

To summarize Sec. III, for the IP system, exact analytic expressions involving the equation of state are derived for the derivatives or response functions of the excess entropy with respect to the independent variables of ρ (or, equivalently, v), P , and T . These provide the necessary foundation to map out s_{ex} along an arbitrary path in ρ , T , and P space.

In the next section, fluctuation-based expressions for the n -dependence of the excess entropy and related thermodynamic quantities, i.e., where the system's Hamiltonian changes, are derived. These can be evaluated by molecular-dynamics and Monte Carlo molecular simulation techniques.

IV. RELATION BETWEEN THERMODYNAMICS OF SYSTEMS WITH DIFFERENT n VALUES

Exact expressions for the derivatives of the thermodynamic variables u , P , a_{ex} , and s_{ex} as a function of n are derived in this section. Each of these derivative quantities is determined at an arbitrary ρ , T fluid state point. This provides the analytic expressions to traverse from one n thermodynamic system to another with a slightly different value of n , at the same value of ρ and T . The Hamiltonian of the fluid is changed in this step. Once on the potential-energy surface of the new n , the properties at another ρ , T state point on that surface can be calculated using the partial derivatives presented in Sec. III.

Agrawal and Kofke [37] considered taking n or n^{-1} as another “thermodynamic” quantity for IP systems. They mapped out the freezing-melting point boundary thermodynamic parameters as a function of n^{-1} based on a generalization of the Gibbs–Duhem method [49], which takes the form

$$d\left(\frac{\mu}{T}\right) = \rho^{-1} d\left(\frac{P}{T}\right) + X_n d(n^{-1}), \quad (35)$$

where μ is the chemical potential, and an isothermal system was assumed. This approach can be developed further. Let X_n in Eq. (35) be a thermodynamic quantity that is n and $[\rho, T, P]$ state-point dependent. The exponent n rather than n^{-1} is (ultimately) employed in this treatment, but the two descriptions can be readily related using $\partial n = -n^2 \partial n^{-1}$.

To make the derivation procedure more generally applicable, assume that the pair potential is also a function of a parameter λ or $\phi(r, \lambda)$. For a dependent thermodynamic quantity X ,

$$X(\lambda + \delta\lambda) = X(\lambda) + \left(\frac{\partial X}{\partial \lambda}\right)_{\rho, T} \delta\lambda + O(\delta\lambda^2), \quad (36)$$

where $\delta\lambda$ is a small increment in λ . Formal statistical mechanical expressions for $(\partial X/\partial \lambda)_{\rho, T}$ are derived below.

For conciseness of notation let

$$\omega_\lambda(r) = \left(\frac{\partial \phi(r, \lambda)}{\partial \lambda}\right)_r, \quad (37)$$

and as $\lambda = n^{-1}$ here,

$$\omega_\lambda(r) = n^2 \frac{\ln r}{r_{ij}^n} = n^2 \phi(r) \ln r, \quad (38)$$

from Eq. (15.28) of Ref. [50]. The quantity of relevance suitable for evaluation in a molecular simulation is

$$\begin{aligned} \Omega_\lambda &= \frac{1}{N} \sum_i \sum_{j < i}^{N-1} \omega_\lambda(r_{ij} < r_c) + \Omega_{\lambda, lrc}, \\ \Omega_{\lambda, lrc} &= 2\pi \frac{\rho n^2}{n-3} \left(\ln r_c + \frac{1}{n-3} \right) \frac{1}{r_c^{n-3}}, \end{aligned} \quad (39)$$

where r_{ij} is the pair separation between particles, r_c is the pair interaction truncation distance, and $\Omega_{\lambda, lrc}$ is the long-range correction assuming that the radial distribution function is equal to 1 for $r > r_c$.

The partial derivative of property X with respect to n^{-1} is converted to the derivative with respect to n using

$$\left(\frac{\partial X}{\partial n}\right)_{\rho,T} = -\frac{1}{n^2} \left(\frac{\partial X}{\partial \lambda}\right)_{\rho,T}, \quad (40)$$

which will be employed in the analysis below.

For example, for the excess Helmholtz free energy per particle a_{ex} , then $X = \beta a_{\text{ex}}$ and

$$\left(\frac{\partial \beta a_{\text{ex}}}{\partial n}\right)_{\rho,T} = -\left(\frac{\partial \ln Q_{\text{ex}}}{\partial n}\right)_{\rho,T} = -\frac{\beta}{n^2} \langle \Omega_{\lambda} \rangle, \quad (41)$$

where the angular brackets indicate an ensemble or time average for a system consisting of particles interacting with the IP potential with exponent n . The quantity Q_{ex} is again the configurational part of the partition function. Note that the Helmholtz free-energy derivative in Eq. (41) is a simple ensemble average of Ω_{λ} .

From Ref. [37], the inverse- n derivative is $(\partial \beta a_{\text{ex}} / \partial n^{-1})_{\rho,T} = \Pi$ which gives $\Pi_{\text{HS}} = 3\beta\epsilon\gamma(Z_{\text{HS}} - 1)$ in the hard-sphere limit, where γ is Euler's constant. (In Ref. [37] Π was denoted by the symbol λ .) In the soft-particle limit, as $n \rightarrow 3^+$ then $(\partial \beta a_{\text{ex}} / \partial n)_{\rho,T} \rightarrow \infty$ because the defining integral of u_n is slower to converge than the potential energy if $u = (\sum_i^N \sum_{j<i}^{N-1} r_{ij}^{-n})/N$ (which itself diverges in this limit).

The corresponding partial derivative of u is

$$\begin{aligned} \left(\frac{\partial \beta u}{\partial n}\right)_{\rho,T} &= -\frac{\beta}{n^2} \frac{\partial}{\partial n} \left(\frac{1}{Q_{\text{ex}}} \int d\mathbf{R}^N u e^{-\beta u} \right) = -\frac{\beta}{n^2} \langle \Omega_{\lambda} \rangle \\ &+ N \frac{\beta^2}{n^2} (\langle u \Omega_{\lambda} \rangle - \langle u \rangle \langle \Omega_{\lambda} \rangle), \end{aligned} \quad (42)$$

where $\mathbf{R}^N$ is the phase-space configurational space volume element, and $u \equiv u(\mathbf{R}^N)$. As $s_{\text{ex}}/k_B = \beta u - \beta a_{\text{ex}}$ then,

$$\left(\frac{\partial s_{\text{ex}}}{\partial n}\right)_{\rho,T} = N \frac{\beta^2}{n^2} (\langle u \Omega_{\lambda} \rangle - \langle u \rangle \langle \Omega_{\lambda} \rangle), \quad (43)$$

from Eqs. (41) and (42), and again $\langle \dots \rangle$ averages are generated from IP states with exponent n . The potential-energy and excess entropy derivatives with respect to n derived in Eqs. (42) and (43), respectively, are in the form of a standard deviation fluctuation expression.

As u and Ω_{λ} tend to zero in the $n \rightarrow \infty$ limit, then $(\partial s_{\text{ex}} / \partial n)_{\rho,T} \rightarrow 0$ in that limit. The hard-sphere approximation, using an n -dependent effective hard-sphere diameter, is applicable down to about $n \simeq 20$ [26]. For much smaller n (i.e., less than about $n = 12$) it would probably be necessary to use molecular simulation to evaluate $(\partial s_{\text{ex}} / \partial n)_{\rho,T}$ because $\langle u_n \rangle$ is not obviously a quantity that could be approximated by exact or approximate liquid-state theory treatments. It is noteworthy that the expression in the final line of Eq. (43) is a fluctuation expression of the same generic response function form found in the statistical mechanics definition of many second-order thermodynamic quantities, such as the constant-volume heat capacity [51,52].

Figure 9 compares the $\omega(r)$ function with the IP potential $\phi(r)$. The function $\omega(r)$ has a weaker dependence on r than ϕ_r for $r \approx 1$ [i.e., $\omega(r) < \phi(r)$ in the strongly repulsive region of

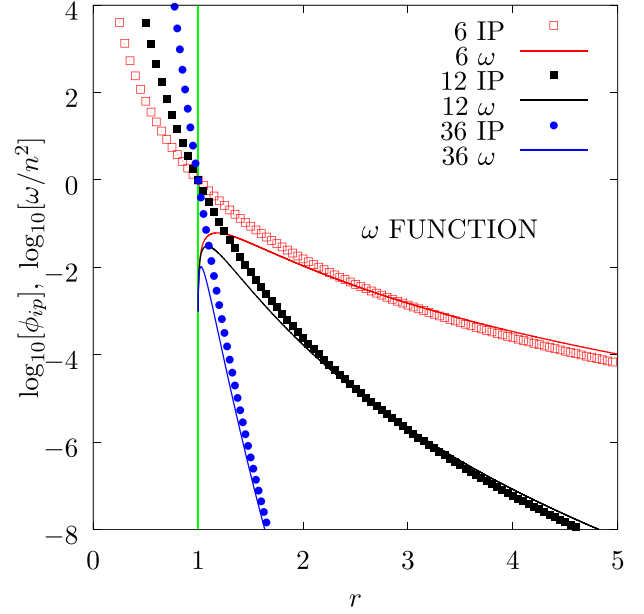


FIG. 9. The function $\omega(r)/n^2$ defined in Eq. (38) compared with the IP potential $\phi(r)$ specified in Eq. (1) for the three values of $n = 6, 12$, and 36 .

the IP potential], and decays more slowly than $\phi(r)$ at large r . It is negative for r less than unity.

Equation (42) can be employed to express the derivative of Z with respect to n . As $Z - 1 = n[\beta u]/3$,

$$\left(\frac{\partial Z}{\partial n}\right)_{\rho,T} = \frac{1}{3}(\beta u) + \frac{n}{3} \left(\frac{\partial(\beta u)}{\partial n}\right)_{\rho,T}, \quad (44)$$

where $(\partial \beta u / \partial n)_{\rho,T}$ is defined in Eq. (42). As the ρ, T state point values are fixed, it follows that $(\partial P / \partial n)_{\rho,T} = \rho T (\partial Z / \partial n)_{\rho,T}$.

As for the excess entropy given in Fig. 1, it is convenient to normalize the density (volume fraction) by its value at freezing to help establish the origin of trends observed across the n range. The expressions in Eqs. (41), (43), and (44) can be employed to achieve the constraint of fixed κ . For a generic quantity X under isothermal conditions, the following relationships apply:

$$\begin{aligned} \left(\frac{\partial X}{\partial n}\right)_{\kappa} &= \left(\frac{\partial X}{\partial n}\right)_{\xi} + \left(\frac{\partial X}{\partial \xi}\right)_n \left(\frac{\partial \xi}{\partial n}\right)_{\kappa}, \\ \left(\frac{\partial \xi}{\partial n}\right)_{\kappa} &= \left(\frac{\partial \kappa \xi_{fr}}{\partial n}\right)_{\kappa} = \kappa \left(\frac{\partial \xi_{fr}}{\partial n}\right)_{\kappa}. \end{aligned} \quad (45)$$

Hence, from Eq. (45),

$$\left(\frac{\partial X}{\partial n}\right)_{\kappa} = \left(\frac{\partial X}{\partial n}\right)_{\xi} + \kappa \left(\frac{\partial X}{\partial \xi}\right)_n \left(\frac{\partial \xi_{fr}}{\partial n}\right)_{\kappa}, \quad (46)$$

where $(\partial \xi_{fr} / \partial n)_{\kappa} \equiv d\xi_{fr} / dn$ is independent of κ . An analytic expression for the freezing line density, $\xi_{fr}(n)$, is from Ref. [26]

$$\xi_{fr}(x) = f_1 + f_2 x + f_3 x^2 + f_4 x^3 + f_5 x^4, \quad (47)$$

TABLE I. The excess entropies calculated using Eq. (8) as a function of normalized density κ and IP exponent n . The value of each n is given at the head of each column.

κ	3.5	4.0	5.0	6.0	7.0	8.0	12.0	36.0	72.0	∞
0.05	-0.52	-0.43	-0.29	-0.22	-0.18	-0.15	-0.12	-0.10	-0.10	-0.10
0.15	-1.24	-1.03	-0.81	-0.64	-0.54	-0.47	-0.37	-0.31	-0.32	-0.32
0.25	-1.66	-1.51	-1.27	-1.06	-0.92	-0.82	-0.65	-0.56	-0.56	-0.58
0.35	-2.06	-1.91	-1.69	-1.47	-1.30	-1.18	-0.96	-0.84	-0.85	-0.88
0.45	-2.39	-2.28	-2.08	-1.87	-1.70	-1.56	-1.31	-1.17	-1.18	-1.22
0.55	-2.68	-2.60	-2.45	-2.25	-2.09	-1.96	-1.69	-1.54	-1.56	-1.62
0.65	-2.94	-2.90	-2.80	-2.64	-2.49	-2.37	-2.11	-1.98	-2.02	-2.10
0.75	-3.13	-3.18	-3.13	-3.01	-2.89	-2.79	-2.58	-2.50	-2.56	-2.69
0.85	-3.26	-3.46	-3.46	-3.38	-3.29	-3.23	-3.08	-3.12	-3.22	-3.40
0.95	-3.47	-3.71	-3.77	-3.75	-3.70	-3.67	-3.62	-3.86	-4.03	-4.29
1.00	-3.60	-3.94	-3.92	-3.94	-3.92	-3.87	-3.90	-4.28	-4.51	-4.82

where $x \equiv n^{-1}$, and the constants f_k from $k = 1$ to 5 are 0.4918, -0.502978, 22.8108, -36.4360, and 450.079, respectively.

First, consider the excess Helmholtz free energy per particle, a_{ex} . From $\beta a_{\text{ex}} = -\ln Q_{\text{ex}}$, from Eq. (3) that $(\partial[\beta a_{\text{ex}}]/\partial\xi)_{\beta,n} = (Z-1)/\xi$ and, consequently,

$$\begin{aligned} \left(\frac{\partial\beta a_{\text{ex}}}{\partial n}\right)_{\kappa} &= \left(\frac{\partial\beta a_{\text{ex}}}{\partial n}\right)_{\xi} + \kappa \frac{(Z-1)}{\xi} \left(\frac{\partial\xi_{fr}}{\partial n}\right)_{\kappa} \\ &= \left(\frac{\partial\beta a_{\text{ex}}}{\partial n}\right)_{\xi} + \frac{(Z-1)}{\xi_{fr}} \left(\frac{\partial\xi_{fr}}{\partial n}\right)_{\kappa}. \end{aligned} \quad (48)$$

The corresponding derivative formula for βu can be obtained using $\beta u = 3(Z-1)/n$:

$$\left(\frac{\partial\beta u}{\partial n}\right)_{\kappa} = \left(\frac{\partial\beta u}{\partial n}\right)_{\xi} + \kappa \frac{3}{n} \left(\frac{\partial Z}{\partial\xi}\right)_n \left(\frac{\partial\xi_{fr}}{\partial n}\right)_{\kappa}, \quad (49)$$

where $(\partial Z/\partial\xi)_n \equiv Z'$, and for the excess entropy,

$$\left(\frac{\partial s_{\text{ex}}}{\partial n}\right)_{\kappa} = \left(\frac{\partial s_{\text{ex}}}{\partial n}\right)_{\xi} + \kappa \left(\frac{\partial s_{\text{ex}}}{\partial\xi}\right)_n \left(\frac{\partial\xi_{fr}}{\partial n}\right)_{\kappa}. \quad (50)$$

Therefore, for the derivative quantities given in Eqs. (48), (49), and (50) the partial derivatives of the thermodynamic quantities with respect to n involve an extra term at constant κ , as opposed to at constant ξ . This additional expression can be computed from already known terms in each case.

Table I presents the values of s_{ex} as a function of n and κ for representative values of these parameters. There is for all n a consistent decrease in s_{ex} with increasing density normalized by the freezing value. The general trend is for s_{ex} to increase with n (i.e., become less negative) for low values of κ for all n , but s_{ex} decreases with n for high values of κ in the large- κ regime.

These features are brought out in more detail and resolution in Fig. 10, which shows $(\partial s_{\text{ex}}/\partial n)_{\kappa}$ and $(\partial s_{\text{ex}}/\partial n)_{\xi}$ as a function of κ for $n = 4$ and 12. It is noteworthy that $(\partial s_{\text{ex}}/\partial n)_{\xi}$ is consistently negative while $(\partial s_{\text{ex}}/\partial n)_{\kappa}$ is typically positive except for large κ (the range increases with decreasing n). This is presumably because at constant ξ the main effect of increasing n is to increase κ . It has already been established in Fig. 1 and Table I that this results in a decrease in s_{ex} (i.e., go more negative). The origin of these trends is highlighted in

Fig. 11, which is a replot of Fig. 1 where the data are presented as a function of ξ rather than the freezing density normalized density κ . It may be seen that there is no crossover of the curves in Fig. 11, even close to freezing.

Figure 10 also compares three methods proposed here to calculate, $(\partial s_{\text{ex}}/\partial n)_{\xi}$, for the $n = 12$ case. In the first approach, simple formulas for the excess entropy optimized for small n given in Eqs. (19) and (20) of Ref. [26] are used at two closely separated n values to determine this derivative. The second approach employed was the fluctuation formula of Eq. (43) within MD simulations. The values for the particle number in the MD simulation cell, $216 \leq N \leq 1331$, were used, and a $1/N$ extrapolation to the thermodynamic limit was

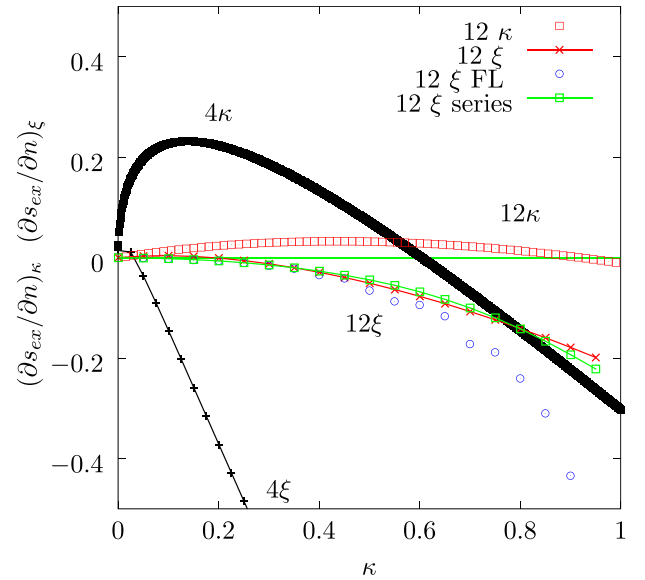


FIG. 10. The excess entropy density derivatives $(\partial s_{\text{ex}}/\partial n)_{\kappa}$ and $(\partial s_{\text{ex}}/\partial n)_{\xi}$ as a function of $\kappa = \xi/\xi_{fr}$ for $n = 4$ and 12. For example, 4ξ in the figure refers to the partial derivative where ξ is held constant and $n = 4$. These partial derivatives were obtained using (a) the prescriptions for s_{ex} found in Eqs. (19) and (20) of Ref. [26] at two closely separated n values (red asterisk symbols and line), (b) the fluctuation formula of Eq. (43) (FL) (further details are given in the main text), and (c) from a local n -parabolic fit to the series multiparameter expansion of Eq. (8) for s_{ex} at distinct n values (series).

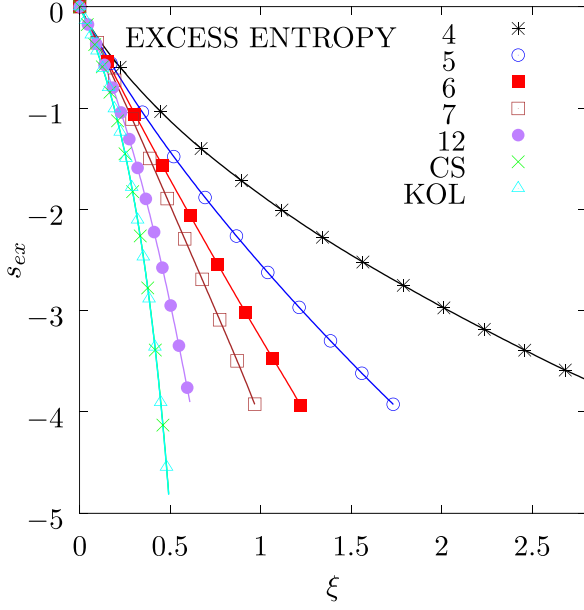


FIG. 11. As for Fig. 1, except that the data are presented as a function of ξ for $\xi \leq \xi_{fr}$. The density dependence of the IP excess entropy s_{ex} from Eqs. (3) and (8) are shown. Data for different n are given, as indicated in the figure. The Carnahan-Starling (CS) and Kolafa (KOL) HS (i.e., $n \rightarrow \infty$) analytic formulas of Eq. (5) are also shown.

employed to obtain the partial derivative shown in the figure. The third method took the multiparameter series expression given in Eq. (8) for the s_{ex} data as a function of density for $n = 10, 12$, and 18 . The value of $(\partial s_{ex}/\partial n)_{\xi}$ was obtained by fitting a parabola to these values at each constant value of ξ .

The three routes agree quite well within their statistical uncertainties up to about $\kappa = 0.6$, as may be seen in Fig. 10. Systematic differences are seen for greater κ , where they become more negative at a given ξ (or κ) value in the sequence of the first, third, and second approaches. Bearing in mind that the quantity in Fig. 10 is a partial derivative of a complex function of the fitted equation of the equation of state Z , it might be expected that there would be some systematic differences between the three methods, particularly close to freezing. The N dependence of $(\partial s_{ex}/\partial n)_{\xi}$ using the direct MD fluctuation formula was found to be relatively small. This suggests that this approach might be the most accurate as a routine tool, especially close to freezing, where the density derivatives of Z are more difficult to determine accurately from a fitted analytic equation of state.

The configurational part of the partition function depends on several variables, which can be expressed as

$$d(\ln Q_{ex}) = \left(\frac{\partial \ln Q_{ex}}{\partial \beta} \right)_{\rho, n} \delta \beta + \left(\frac{\partial \ln Q_{ex}}{\partial V} \right)_{\beta, n} \delta V + \left(\frac{\partial \ln Q_{ex}}{\partial n} \right)_{\beta, \rho} \delta n, \quad (51)$$

$$\frac{1}{N} d(\ln Q_{ex}) = -u \delta \beta - (Z - 1) \delta \ln \rho - \frac{\beta}{n^2} \langle \Omega_{\lambda} \rangle \delta n, \quad (51)$$

which can be used to trace out lines of constant Q_{ex} from MD data or an analytic expression for the equation of state.

It has been demonstrated in this Sec. IV that the response functions of several key thermodynamic quantities involving increments of the IP exponent n can be computed as fluctuation expressions in molecular simulations.

In the next section, the response functions of model fluids where the pair potential is the sum of two IP terms are considered.

V. RELATIONSHIP BETWEEN THE IP AND LJ SYSTEMS

This section considers the relationships between the thermodynamics and response functions of inverse power and Lennard-Jones fluid systems, in the latter case where the assembly of particles interacts with a pair potential composed of the sum of two IP terms, one of which is negative. The basic statistical mechanics is considered first in Sec. VA and then some response function formulas are derived, which apply to the high-temperature LJ part of its phase diagram, and are reported in Sec. VB.

A. LJ thermodynamics and statistical mechanics

Relatively small molecules have been represented by the Lennard-Jones (LJ) potential, $\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, which tends toward the $n = 12$ IP system at high temperature. Some of the thermodynamic properties of the LJ system converge extremely slowly with temperature to the IP $n = 12$ limit [53]. In fact, this limit is hardly achievable in practice by simulation and would be in a temperature range where the molecule or atom would be unstable to dissociation into ions anyway. Nevertheless, knowledge of the functional form of the convergence will enable values of properties in the infinite temperature limit to be estimated by extrapolation. An isomorph is a curve of constant excess entropy on the phase diagram where the assembly structure and derived thermophysical properties can be collapsed to the same value when appropriately scaled by combinations of density and temperature (i.e., when expressed in so-called macroscopic units (MUs) [54]).

The LJ freezing and melting phase boundary lines have often been represented by the analytic form

$$T = A\rho^4 - B\rho^2, \quad (52)$$

where A and B are positive constants using molecular-simulation data, since it was proposed by Rosenfeld as an approximation [55,56]. If the A and B are fitted using high-temperature data, it does not reproduce the exact LJ phase boundaries below $T \simeq 2$ [40,57], and only converges to an $n = 12$ IP system in the extremely-high- T limit. The approximate nature of this analytic form is because the configurational part of the partition function of the LJ system is not the product of the two separate partition functions of the IP systems with $n = 6$ and 12 . There are cross terms which cannot be ignored at low temperatures, but gradually these two contributions become more decoupled in the high-temperature and -density limit, when this product approximation becomes more accurate.

The high-temperature ($\sim T^{-1/2}$) limiting behavior of thermodynamic properties along a configurational adiabat was established in Ref. [53]. The exception to this slow convergence is that of the excess entropy, which is essentially constant along certain $\rho(T)$ lines (notably the freezing and melting curves) above about the critical temperature on the phase diagram, signifying a remarkable degree of cancellation between the potential energy and Helmholtz free energy. This was demonstrated for the LJ freezing and melting curves in Ref. [53]. We think it is fair to state that the origin of this noteworthy feature is still not well understood, which could hold the key to further advances in this field.

These trends can be explained qualitatively by making use of the concepts of liquid state perturbation theory, in which, in its most basic form, states that the structure of the liquid is determined entirely by the repulsive part of the potential [58]. Assuming LJ units for conciseness, the following quantities are defined:

$$\Phi_{12} = \sum_i \sum_{<j} \frac{4}{r_{ij}^{12}} = \rho^4 \sum_i \sum_{<j} \frac{4}{\tilde{r}_{ij}^{12}} \equiv \rho^4 \tilde{\Phi}_{12},$$

$$\Phi_6 = - \sum_i \sum_{<j} \frac{4}{r_{ij}^6} = -\rho^2 \sum_i \sum_{<j} \frac{4}{\tilde{r}_{ij}^6} \equiv \rho^2 \tilde{\Phi}_6, \quad (53)$$

where the tilde again denotes macroscopic units. The two excess configurational partition functions of relevance here are that for the IP $n = 12$ system (Q_{12}) and that for the LJ system (Q_{LJ}), where the ex subscript has been dropped for notational convenience):

$$\begin{aligned} Q_{12} &= \int d\mathbf{r}^N e^{-\beta\Phi_{12}}, \\ Q_{LJ} &= \int d\mathbf{r}^N e^{-\beta(\Phi_{12} + \Phi_6)} \\ &\simeq \int d\mathbf{r}^N e^{-\beta\Phi_{12}} (1 - \beta\Phi_6) \\ &= \int d\mathbf{r}^N e^{-\beta\Phi_{12}} (1 - \beta\rho^2 \tilde{\Phi}_6) \\ &= \int d\mathbf{r}^N e^{-\beta\Phi_{12}} (1 - \sqrt{\beta}X^{1/2} \tilde{\Phi}_6) \\ &= Q_{12} - \sqrt{\beta}X^{1/2} \int d\mathbf{r}^N \tilde{\Phi}_6 e^{-\beta\Phi_{12}} \\ &= Q_{12} (1 - \sqrt{\beta}X^{1/2} \langle \tilde{\Phi}_6 \rangle_{12}), \end{aligned} \quad (54)$$

where $d\mathbf{r}^N$ is the N -particle configurational volume element, $\beta = 1/T$, and $X = \rho^4/T$. The term $\langle \tilde{\Phi}_6 \rangle_{12}$ is the average total r^{-6} potential energy computed for a system generated by the $n = 12$ IP system. A first-order expansion of $\exp[-\beta\Phi_6]$ was used in the derivation in Eq. (54). In Eq. (54), it has been assumed that the assembly structure is dominated by the repulsive part of the potential, and the attractive contribution can be included in the form of a first-order expansion. In the last line, the correction term is expressed in terms of the mean attractive part of potential energy. Following this procedure, it was derived in Ref. [53] that along a particular LJ isomorph

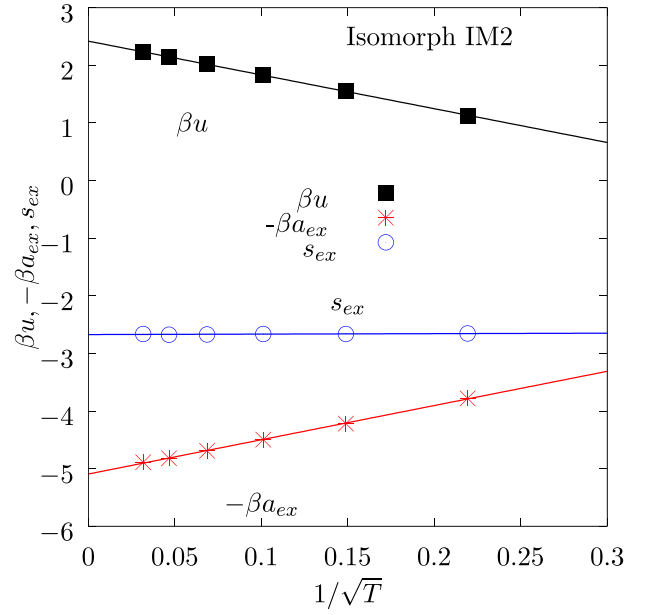


FIG. 12. The high-temperature behavior along the IM2 Lennard-Jones isomorph considered in Refs. [53,59]. The symbols are the values computed directly by MD, and the solid lines are linear regression fits. The intercepts and slopes for βu , $-\beta a_{ex}$, and s_{ex} are [2.42, -5.09, -2.67] and [-5.86, 5.94, 0.08], respectively.

ρ , T curve, in the high-temperature limit,

$$\begin{aligned} \beta u_{12,LJ} &\simeq \beta u_{12,12} + \sqrt{\beta} A_{12}, & \beta u_{6,LJ} &\simeq -\sqrt{\beta} A_6, \\ \beta a_{12,LJ}^{ex} &\simeq \beta a_{12,12}^{ex} + \sqrt{\beta} B_{12}, & \beta a_{6,LJ}^{ex} &\simeq -\sqrt{\beta} B_6, \end{aligned} \quad (55)$$

where A_{12} , A_6 , B_{12} , and B_6 are positive constants whose numerical value depends on the given isomorph. The behavior indicated by the expressions in Eq. (55) is evident in the MD results found in Fig. 13 of Ref. [53].

The notation $X_{6,12}$, for example, means the value of the r^{-6} component of quantity X calculated from a simulation where the particle dynamics (for MD) are generated using the $n = 12$ IP potential. Along a configurational adiabat, $A_{12} - B_{12} - A_6 + B_6 = 0$, which was confirmed to be the case using MD-generated values for the potential energy and excess Helmholtz free energy for the LJ fluid [53].

Figure 12 presents the $T^{-1/2}$ dependence of βu , $-\beta a_{ex}$, and s_{ex} for the IM2 LJ isomorph considered in Refs. [53,59]. Within the simulation statistics, the slopes of the three quantities are consistent with the condition $A_{12} - B_{12} - A_6 + B_6 = 0$, which follows from Eq. (55). The figure on this model system suggests that for real small molecule experimental systems the convergence of the thermodynamic quantities, other than for the excess entropy, to that of the purely repulsive part of the potential would be extremely slow with temperature.

Figure 12 shows that, along an isomorph line, the Lennard-Jones, βu , and βa_{ex} vary significantly as $T^{-1/2}$ to a very good approximation in the high-temperature limit, even at extremely high temperatures (e.g., $T \approx 5000$). The slopes are finite, while, in contrast, s_{ex} is essentially constant over the temperature range considered. The excess entropy is central in determining the behavior of other thermodynamic properties.

B. LJ thermodynamic response functions

The LJ thermodynamic and s_{ex} response functions are more complicated to specify and evaluate than those derived for the pure IP systems given in Eq. (18) for the total entropy, and Eq. (22) for s_{ex} . The LJ potential is the sum of two IP terms, one repulsive and one attractive, whose effects are to varying degrees coupled to different extents in various regions of the phase diagram. Consequently, the LJ equation of state is more complicated than that of the IP system because the phase diagram has more distinct regions and phases (e.g., liquid-vapor coexistence). There are a number of accurate LJ equations of state in the literature obtained by fitting assumed analytic forms to extensive molecular simulation data (see, for example, Ref. [60]). However, these EoS are still not accurate enough to explore excess entropy related response functions because s_{ex} is the difference between two large numbers involving the potential energy per molecule and (integral of the) pressure, as evident in the expression in Eq. (3). These two quantities increase in magnitude with temperature and density.

The LJ fluid at high temperature can be represented to a good approximation as an effective IP system with a value of n a little higher than 12. It was demonstrated by Bailey *et al.* [61] that the single-component LJ fluid thermophysical properties can be reproduced by an effective power-law fluid where $n \simeq 18$, with an additional term linear in r . Later, Pieprzyk *et al.* [60] derived an expression based on LJ MD data for the $T > 35$ fluid region in terms of the IP isomorph variable, $\rho/T^{3/n}$, with the optimum $n = 14$. These observations suggest that, at least in the high-temperature regime, the response functions of the LJ fluid may take on a more manageable analytic form than in the liquid region or the supercritical fluid close to the critical point.

The strong linear $1/\sqrt{T}$ behavior in the first-order thermodynamic quantities evident in Fig. 12 can be exploited to derive approximate expressions for the LJ thermodynamic response functions, which become more accurate with increasing ρ and T .

Along an LJ isomorph, the quantities in Eq. (55) involve the potential energy per particle component. Let u_{12} and u_6 be the average repulsive and attractive components, respectively, of the average potential energy per particle of an LJ system. The excess pressure $P_{\text{ex}} = P - \rho T$ can be expressed as follows:

$$\begin{aligned} P_{\text{ex}} &= \rho(4u_{12} + 2u_6), \\ \beta P_{\text{ex}} &= \rho(4U_{12} + \sqrt{\beta}[4A_{12} - 2A_6]), \end{aligned} \quad (56)$$

where $U_{12} = \beta u_{12}$, which is a constant along the $n = 12$ IP isomorph. From Eq. (52),

$$\begin{aligned} \rho &= \left(\frac{B + \sqrt{B^2 + 4AT}}{2A} \right)^{1/2} \\ &\simeq \left(\frac{B}{2A} + \sqrt{\frac{T}{A}} \right)^{1/2} \text{ for large } T \gg B^2/4A. \end{aligned} \quad (57)$$

For $T \rightarrow \infty$, then, $\rho \rightarrow (T/A)^{1/4}$. It is convenient to express the constant A in terms of state point parameters ρ_0 , T_0 which is any point on the limiting $n = 12$ IP isomorph line, i.e., where ρ^4/T is constant along it. The following relations and

constants relating to the LJ isomorph are defined:

$$\begin{aligned} T &= A\rho^4, \quad T_0 = A\rho_0^4, \quad A = T_0/\rho_0^4, \\ \rho &= \rho_0[T/T_0]^{1/4}, \quad \sqrt{\beta} \equiv \frac{1}{\sqrt{T}} = \frac{\rho_0^2}{\rho^2 T_0^{1/2}}. \end{aligned} \quad (58)$$

Combining the terms in Eqs. (57) and (58) in the excess pressure final expression in Eq. (56) gives

$$P_{\text{ex}}(T) = \frac{\rho_0}{T_0^{1/4}}(4U_{12}T^{5/4} + [4A_{12} - 2A_6]T^{3/4}), \quad (59)$$

along a high- T LJ isomorph, where the excess pressure is expressed in terms of the temperature. The temperature derivative response functions is

$$\left(\frac{\partial P_{\text{ex}}}{\partial T} \right)_{s_{\text{ex}}} = \rho \left(5U_{12} + 3 \frac{[A_{12} - A_6/2]}{T^{1/2}} \right). \quad (60)$$

The alternative formulas for the excess pressure and its density derivative along the LJ isomorph in the high-density limit are

$$\begin{aligned} P_{\text{ex}}(\rho) &= A(4U_{12}\rho^5 + C\rho^3), \\ C &= \frac{(4A_{12} - 2A_6)}{T_0^{1/2}}\rho_0^2, \end{aligned} \quad (61)$$

where C is a constant along the high-temperature part of the LJ isomorph, and

$$\left(\frac{\partial P_{\text{ex}}}{\partial \rho} \right)_{s_{\text{ex}}} = A(20U_{12}\rho^4 + 3C\rho^2). \quad (62)$$

The temperature and density derivatives of the excess pressure have the same T and ρ dependencies as those of the potential energy and Helmholtz free energy.

VI. CONCLUSIONS

This work builds on previous theoretical and molecular simulation studies of the model purely repulsive inverse power (IP) potential fluid, $\approx r^{-n}$ [23–25], and particularly Ref. [26]. The focus is on the excess entropy s_{ex} , which has been found in recent decades to be a key property in collapsing fluid thermophysical property data, including the transport properties of fluids. Previous studies (e.g., Refs. [11, 12]) of the thermophysical properties of certain complex molecular liquids have shown that they can be represented at an effective or mean field level by an IP fluid.

Any thermodynamic property of the IP fluid is a function of density ρ , temperature T , pressure, and the value of the IP repulsive exponent n . Analytic expressions are derived that specify the second-order (i.e., ‘derivative’) thermodynamic response functions of IP fluids. Formulas for the derivatives of s_{ex} with respect to temperature, density, and pressure are derived by statistical mechanics and thermodynamic routes and are displayed graphically as a function of density for representative values of n . They are confirmed by comparison with numerical differentiation of $s_{\text{ex}}(\rho, T, n)$ with respect to these independent variables. These second-order quantities could be used to map out the multidimensional thermodynamic surface of the IP fluid. They can be positive or negative and all increase in magnitude along isotherms as density increases. These expressions depend solely on the density and

temperature dependence of the compressibility factor and its first density derivative, which are both functions of n .

Expressions are also derived for the derivatives of the potential energy u and s_{ex} with respect to n as fluctuation formulas, in Eqs. (42) and (43), respectively. Close to freezing, the fluctuation formula for the derivative of s_{ex} with respect to n shows possible advantages over an equation-of-state route, as the equation of state and especially its partial derivative with respect to density are less accurately known in that region of the phase diagram.

Relatively simple expressions are derived for the excess pressure and its temperature and density response functions along a Lennard-Jones fluid isomorph at high temperature.

The combination of these excess entropy derivative response functions provides perspectives on and ways of characterizing the thermodynamic behavior of inverse power potential fluids as a function of state point and the system's Hamiltonian through the potential exponent n . These theoretical developments could be exploited to predict and interpret

trends in the thermophysical properties of real experimental low- and high-density fluids by representing them as effective inverse power potential systems.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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