

Excess-entropy-based anomalies for a waterlike fluid

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Many thermodynamic and dynamic properties of water display unusual behavior at low enough temperatures. In a recent study, Yan *et al.* [Phys. Rev. Lett. **95**, 130604 (2005)] identified a spherically symmetric two-scale potential that displays many of the same anomalous properties as water. More specifically, for select parametrizations of the potential, one finds that the regions where isothermal compression anomalously (i) decreases the fluid's structural order, (ii) increases its translational self-diffusivity, and (iii) increases its entropy form nested domes in the temperature-density plane. These property relationships are similar to those found for more realistic models of water. In this work, the authors provide evidence that suggests that the anomalous regions specified above can all be linked through knowledge of the excess entropy. Specifically, the authors show how entropy scaling relationships developed by Rosenfeld [Phys. Rev. A **15**, 2545 (1977)] can be used to describe the region of diffusivity anomalies and to predict the state conditions for which anomalous viscosity and thermal conductivity behavior might be found. © 2006 American Institute of Physics. [DOI: 10.1063/1.2409932]

INTRODUCTION

It has been known for some time that there exists a class of fluids that display anomalous thermodynamic and kinetic behaviors. Examples of these atypical behaviors include fluid expansion upon isobaric cooling and an increase in fluid mobility upon isothermal compression. The identities of the fluids that display this behavior are also notable, with tetrahedral network-forming fluids, such as water, silica, and silicon being prominent members of the class. Recent studies have focused on understanding the quantitative link between the various structural, thermodynamic, and kinetic anomalies that these fluids display. We continue this effort here by demonstrating how a select group of anomalies can be connected through the excess entropy.

In an earlier study of the extended simple point charge (SPC/E) model of water,¹ Errington and Debenedetti found a relationship between regions in the temperature-density plane characterized by anomalous trends in translational self-diffusivity (where single-particle mobility increases upon isothermal compression) and density (where the thermal expansion coefficient is negative).² They found that both of these anomalous regions fell entirely within a broader structurally anomalous region (see Fig. 1), wherein the structural order of the system decreases upon isothermal compression, in contrast to what is observed for simple fluids.^{3,4} The struc-

tural order was characterized using a combination of translational^{3,5} and orientational⁶ (tetrahedral) order metrics. The regions of anomalous diffusivity and density behavior also exhibited a subset relationship, with the envelope of density anomalies lying entirely within the corresponding diffusivity region. Overall, the study depicted a scenario in which water displays a cascade of anomalies, whereby structural anomalies trigger diffusivity anomalies, and later density anomalies.

Although it is tempting to attribute water's anomalous behavior to its highly directional interactions, a number of studies⁷⁻¹⁹ have documented waterlike anomalous behavior in fluids that interact through spherically symmetric potentials. More specifically, this behavior has been found in so-called core-softened models, in which the "hard" repulsive interaction that typifies normal fluids is preceded by a softer "ramp" repulsion. This interaction is similar to the effective intermolecular potential for water in that it provides two characteristic length scales that bias particles to adopt either locally open or close-packed structures, depending on the temperature and density of the system. Yan *et al.*^{20,21} recently characterized the structural, thermodynamic, and kinetic properties of a family of discontinuous core-softened potentials that vary in the length scale of the soft repulsion region. In each case, they found the same relationship between anomalous regions as observed for SPC/E water: structural anomalies (characterized by a decrease in translational order upon isothermal compression) preceded diffusivity anomalies, which preceded density anomalies.

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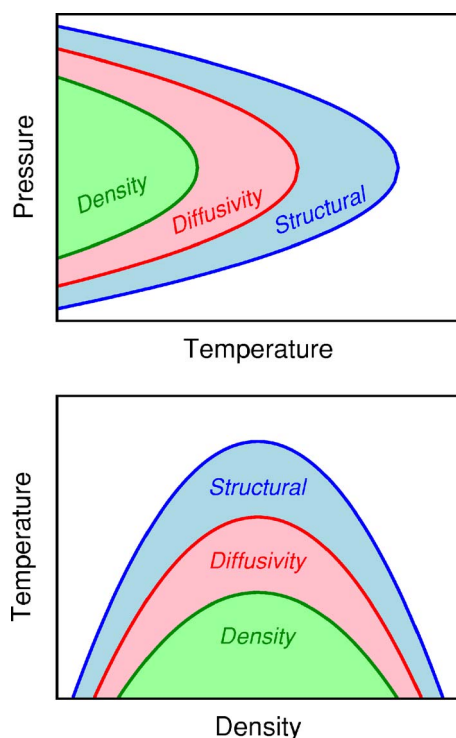


FIG. 1. Schematic of the regions wherein structural, diffusivity, and density anomalies are found within the temperature-density (bottom panel) and pressure-temperature (top panel) planes. Structural, diffusivity, and density anomalies are found within the outermost, intermediate, and innermost envelopes, respectively. Regions of anomalous diffusivity and density behavior appear as nested domes within the structurally anomalous envelope. The behavior depicted here is consistent with simulation results obtained with the SPC/E water model (Ref. 2) and the core-softened Jagla model (Ref. 11).

The observation of an identical ordering of structural, diffusivity, and density anomalies in systems as seemingly dissimilar as SPC/E water and a core-softened fluid suggests that this behavior can be characterized by a set of general underlying principles. In this work, we illustrate how the anomalous behaviors a fluid exhibits can be described in terms of how its excess entropy varies with temperature and density. To make this connection, we recall basic thermodynamic relations to link density and excess entropy and employ empirical scaling relationships to connect transport properties to the excess entropy. We show that such an approach is capable of qualitatively describing the anomalous density and diffusivity behavior exhibited by the core-softened fluid studied by Yan *et al.*

Kinetic scaling relationships have been employed to predict transport properties for some time. Here, we focus on so-called entropy scaling relationships in which transport properties are expressed as a function of the excess entropy. In particular, we utilize a series of empirical relationships introduced by Rosenfeld,^{22–24} and later supported by calculations performed by Grover *et al.*,²⁵ in which diffusivities, viscosities, and thermal conductivities, reduced by macroscopic thermodynamic properties (e.g., temperature, density), scale with the exponential of the excess entropy. We note that an alternative scaling approach has been proposed by Dzugotov,²⁶ which has recently been employed to probe the connection between excess entropy and self-diffusivity of waterlike fluids.²⁷ Although the Dzugotov approach has also

yielded interesting results, we refrain from implementing it here because its scope is limited to diffusivities and it requires the use of microscopic structural information for property reduction, which inherently limits its predictive power.

Application of Rosenfeld's scaling relationships has been restricted primarily to the description of atomistic fluids. In such simplified cases, the excess entropy has a straightforward interpretation. It quantifies the reduction in the number of states (relative to an ideal gas) accessible to a system due to translational interparticle correlations, which arise from strong couplings between center-of-mass positions of neighboring particles in a liquid. These translational correlations between particles act to reduce a single particle's ability to perform translational self-diffusion relative to its neighbors. Thus, it is intuitive that thermodynamic conditions which make the excess entropy more negative also reduce translational self-diffusivity. In molecular systems, however, the total excess entropy contains translational contributions as well as contributions due to the correlations between the orientations of neighboring particles. We suspect that the transport property of a molecular fluid associated with a particular type of motion will scale with the component of the excess entropy related to the intermolecular correlations associated with those degrees of freedom. For example, we expect the translational self-diffusivity of molecular fluids to scale with the component of the excess entropy related to the translational intermolecular correlations, and so forth. Exploration of this question in future work should provide important new insights. In the analysis that follows, we restrict our attention to atomistic fluids and circumvent these subtle issues. This enables us to provide a clear demonstration of the use of entropy scaling relationships to describe anomalous diffusivity behavior under circumstances where the role of the excess entropy is clearly understood. Before concluding, however, we briefly return to mention how the ideas generated here might be extended to describe molecular fluids.

Our motivation for pursuing an excess-entropy-based strategy also stems from our recent work^{28–30} in which we have found robust relationships between diffusion coefficients and excess entropies. More specifically, we have shown that the bulk relationship between diffusivity and excess entropy for the hard-sphere fluid is maintained upon severe confinement,²⁸ suggesting that one can use knowledge of how confinement modifies thermodynamics to infer its effect on dynamics. We have also demonstrated that for a number of model supercooled fluids with very different thermodynamic and dynamic behaviors, one observes a linear relationship between the logarithm of the self-diffusivity and the excess entropy.^{29,30} This relationship can be compared to Adam-Gibbs theory,^{31,32} which links the dynamics of a supercooled fluid to the configurational entropy—a measure of the number of distinct, mechanically stable packing arrangements³³ that its molecules can adopt. From a practical perspective, the excess entropy is more readily accessible than configurational entropy because the former entropy is a standard thermodynamic quantity that is obtainable from both experiment and simulation. The latter entropy, on the other hand, requires an approximate model for the free en-

ergy associated with the vibrational excitations of a liquid about its mechanically stable packing arrangements.³⁴

To illustrate the ideas generated here we use recently developed grand canonical transition matrix simulation methods^{35,36} to accurately calculate excess entropies of the discontinuous core-softened model¹¹ studied by Yan *et al.*^{20,21} over a wide range of temperatures and densities. This information is then used to predict the state conditions in which various thermodynamic and transport properties display anomalous behavior. We then examine the quality of these predictions through comparison with the simulated anomalous density and transport regions identified by Yan *et al.*

In what follows, we first develop the mathematical relationships that enable one to connect structural, thermodynamic, and kinetic anomalies to the excess entropy. We then introduce the core-softened model examined in this work and describe the computational tools employed to obtain properties of interest. Finally, we examine the ability of Rosenfeld's scaling relationships to accurately predict regions of anomalous transport behavior.

THERMODYNAMIC, KINETIC, AND STRUCTURAL RELATIONSHIPS

We now describe how one can predict the thermodynamic conditions under which an atomistic fluid exhibits density and/or kinetic anomalies through knowledge of the excess entropy. In the discussion that follows, all properties are made dimensionless using appropriate combinations of a characteristic energy ε , length scale σ , mass m , and the Boltzmann constant k_B . For example, temperature T , pressure P , time t , and entropy S are reduced by ε/k_B , ε/σ^3 , $\sigma\sqrt{m/k_B T}$, and k_B , respectively. The characteristic energy and length scale will be explicitly linked to the interparticle interactions studied in this work below. The relationships we develop for density anomalies stem from rigorous thermodynamic identities and are generally applicable. In contrast, our analysis of transport properties relies on empirical scaling relationships, and is therefore limited by the validity of the scaling model employed. To be specific, regions of anomalous density behavior are those in which the density ρ increases with increasing temperature at constant pressure, $(\partial\rho/\partial T)_P > 0$. Kinetic anomalies are defined by an increase in diffusivity D with increasing density at constant temperature, $(\partial D/\partial\rho)_T > 0$, a decrease in shear viscosity η with increasing density at constant temperature, $(\partial\eta/\partial\rho)_T < 0$, or a decrease in thermal conductivity κ with increasing density at constant temperature, $(\partial\kappa/\partial\rho)_T < 0$. In what follows we describe how to identify density ranges in which anomalous behavior is observed at a given temperature, when provided the density dependence of the excess entropy at the temperature of interest.

Density anomalies are rigorously linked to the molar entropy s through the thermodynamic identity³⁷

$$\left(\frac{\partial\rho}{\partial T}\right)_P = \rho^2 \left(\frac{\partial\rho}{\partial P}\right)_T \left(\frac{\partial s}{\partial\rho}\right)_T. \quad (1)$$

Mechanical stability requires that $(\partial\rho/\partial P)_T > 0$. Therefore, density anomalies occur when $(\partial s/\partial\rho)_T > 0$. To obtain the link between density anomalies and the excess entropy s^{ex} , recall that excess entropies are defined as the difference between the entropy of a real fluid and that of an ideal gas at the same temperature and density, $s^{\text{ex}} = s - s^{\text{ig}}$, where the ideal gas entropy $s^{\text{ig}} = -\ln\rho + c(T)$ is given in terms of the logarithm of the density and a temperature-specific constant $c(T)$. Using these relationships enables one to recast the conditional statement for density anomalies in terms of the excess entropy,

$$\left(\frac{\partial s^{\text{ex}}}{\partial \ln\rho}\right)_T > 1. \quad (2)$$

For a "normal" fluid, the excess entropy decreases with density at constant temperature.³⁸ Therefore, one could describe a condition in which $(\partial s^{\text{ex}}/\partial \ln\rho)_T > 0$ as an excess entropy anomaly. The condition provided by Eq. (2) indicates that the strength of the excess entropy anomaly needs to grow beyond a specified magnitude before a density anomaly is observed.

We now turn our attention to understanding the relationship between excess entropy and translational order. In doing so, it is helpful to recall the physical meaning of the former: it characterizes the reduction in the number of states (relative to an ideal gas) accessible to a system due to translational interparticle correlations. In other words, while s^{ex} is indeed a standard thermodynamic quantity, the negative of the excess entropy can also be thought of as a metric for translational order. As a result, regions on the phase diagram where the excess entropy anomalously increases upon isothermal compression are also regions where translational structural order anomalously decreases upon isothermal compression. In this sense, the thermodynamic relationship of Eq. (2) is qualitatively consistent with the subset relationship between regions of anomalous structural order and of anomalous density behavior observed earlier by Yan *et al.*^{20,21} The caveat that should be mentioned here is that instead of using $-s^{\text{ex}}$, Yan *et al.* employed an empirical order metric that uses an integral measure of the radial distribution function to quantify the "two-body" translational order in their simulations. However, as was shown by Truskett *et al.*,³ this empirical order metric displays behavior similar to the negative of the two-body approximation for the excess entropy for simple fluids and glasses. For the discontinuous core-softened model studied here and by Yan *et al.*, one finds that the two measures of translational structural order capture the same qualitative behavior, with the empirical order metric indicating that the structurally anomalous region spans a broader range of state conditions. For the purposes of this study, we choose to focus on excess entropy because of its aforementioned connection to density anomalies and its ability to capture translational order for all n -body correlations in the fluid. Furthermore, as we discuss in this paper, it has a potentially intimate connection with transport anomalies.

We now turn our attention to transport properties. While general rigorous relationships connecting thermodynamic and transport properties do not currently exist, a number of empirical scaling relationships^{22,24,26} have been developed to provide this link. These expressions enable one to predict transport properties of a system through knowledge of its thermodynamic behavior. Previous studies²²⁻³⁰ have demonstrated that entropy scaling relationships, in which a transport property is expressed as a function of the excess entropy, often provide a means to predict transport properties of simple fluids with quantitative accuracy over a wide range of state conditions. In this work, we assess the ability of entropy scaling relationships developed by Rosenfeld²⁴ to predict the conditions under which transport anomalies are observed.

Rosenfeld asserts that a reduced transport property X^* is related to the excess entropy per particle as

$$X^* \approx a_X \exp(b_X s^{\text{ex}}), \quad (3)$$

where a_X and b_X are property-specific constants, with $a_X = 0.6, 0.2,$ and 1.5 and $b_X = 0.8, -0.8,$ and -0.5 for the diffusivity, shear viscosity, and thermal conductivity, respectively. Rosenfeld assigned these constants by regressing simulation data from systems interacting through disparate, spherically symmetric pair potentials, such as the hard-sphere, soft-sphere, Lennard-Jones, and one-component plasma systems.²⁴ He found that while, undoubtedly, the description of each fluid's transport properties could be optimally described with its own set of scaling parameters, the properties of all fluids could be estimated to within about 30% by using the "corresponding-states" values given above. It is these quasiuniversal values that we employ in this work.

The three transport properties are reduced with respect to the mass, temperature, and density as follows:

$$\begin{aligned} D^* &= D \frac{\rho^{1/3}}{T^{1/2}}, \\ \eta^* &= \eta \frac{\rho^{-2/3}}{T^{1/2}}, \\ \kappa^* &= \kappa \frac{\rho^{-2/3}}{T^{1/2}}. \end{aligned} \quad (4)$$

Combination of the expressions above leads to the following criterion for the existence of transport anomalies:

$$\left(\frac{\partial s^{\text{ex}}}{\partial \ln \rho} \right)_T > \frac{\gamma}{3|b_X|}, \quad (5)$$

where γ is related to the exponent of the density used in Eq. (4) above, with $\gamma=1$ for the diffusivity and $\gamma=2$ for the shear viscosity and thermal conductivity. The conditional statements for both density and transport anomalies have the same mathematical form, $(\partial s^{\text{ex}} / \partial \ln \rho)_T > c$, where c is a property-specific constant. For each of the properties examined here, c is a positive value, from which it follows that the set of state points where a given transport anomaly is found represents a subset of the region in which excess entropy behavior is anomalous. This relationship is identical to that

found for the density anomaly above. This analysis indicates that anomalous behavior of the excess entropy can be viewed as a precursor to anomalous behavior with respect to other properties. In other words, the excess entropy anomaly "announces" the approach of density and transport anomalies. The magnitude of c indicates the strength of the excess entropy anomaly required to observe anomalous behavior in a given property. Based on Rosenfeld's scaling parameters, anomalous behavior occurs in the following order: excess entropy ($c=0$), diffusivity ($c=0.42$), viscosity ($c=0.83$), density ($c=1.00$), and thermal conductivity ($c=1.33$). This sequence of anomalies is consistent with the studies of Yan *et al.*,^{20,21} where structural anomalies are found to precede diffusivity anomalies, which in turn precede density anomalies.

MODELING AND SIMULATION

We investigate the behavior of a fluid interacting through a two-scale potential introduced by Jagla.¹¹ The energy of interaction u between any two particles separated by a distance r is given by

$$u(r) = \begin{cases} \infty, & r < \sigma_0 \\ \varepsilon(\sigma_1 - r)/\sigma_1, & \sigma_0 < r < \sigma_1 \\ 0, & r > \sigma_1, \end{cases} \quad (6)$$

where ε sets the energy scale, σ_0 represents the hard-core distance, and σ_1 provides the outer boundary of a region of soft repulsion in which the potential decreases linearly from ε to zero between the distances of σ_0 and σ_1 . From this point forward, all quantities are made dimensionless using ε and σ_1 as characteristic energy and length scales, respectively.

We examine the condition in which the ratio of the two characteristic length scales $\lambda = \sigma_0/\sigma_1$ is set to $4/7$. Yan *et al.*^{20,21} found that fluids described by this value of λ display qualitative trends in their thermodynamic and kinetic properties that are similar to those of supercooled water. For example, this fluid is known to exhibit density anomalies, kinetic anomalies, and structural anomalies.

As is readily apparent from the above discussion, the excess entropy plays a central role in this investigation. Two approaches are used to calculate this quantity. In the first, we estimate the value of the excess entropy through its two-body contribution $s^{(2)}$, defined as

$$s^{(2)} = -2\pi\rho \int \{g(r)\ln[g(r)] - [g(r) - 1]\}r^2 dr, \quad (7)$$

where $g(r)$ is the pair correlation function. This expression stems from an expansion of the entropy in terms of the partial N -body distribution functions.³⁹ The definition above was originally introduced by Nettleton and Green⁵ (and later developed by Raveche⁴⁰ using an alternative approach) as an expression for the pair entropy appropriate for use with the grand canonical ensemble. This restriction was later lifted by Baranyai and Evans, who showed that the expression is ensemble invariant.³⁸ Several studies^{38,41,42} involving model atomistic liquids have suggested that truncating the entropy

expansion after the two-body term provides a reasonable estimate for the total excess entropy. Below, we also describe an approach for evaluating the total excess entropy. Comparison of predictions based on the two-body excess entropy and the total excess entropy provides us with the means to evaluate the extent to which three- and higher-body terms contribute to the excess entropy.

We calculate the total excess entropy using grand canonical transition matrix Monte Carlo simulation (GC-TMMC).^{35,36} At each temperature of interest, a GC-TMMC simulation is conducted with a specified value of the activity $\xi = q \exp(\beta\mu)$ and volume V , where $\beta = 1/T$, μ is the chemical potential, and q is the molecular partition function. The key quantities extracted from each simulation are the particle number (density) probability distribution $\Pi(N)$ and the particle-number-specific configurational energy $U(N)$. Biased sampling methods⁴³ are used to evaluate these quantities over a range of particle numbers spanning from N_{\min} to N_{\max} .

The probability distribution provides a direct link to the canonical partition function $Q(N, V, \beta)$ through the expression⁴⁴

$$\Pi(N) = \exp(\beta\mu N) Q(N, V, \beta) / \Xi(\mu, V, \beta), \quad (8)$$

where $\Xi(\mu, V, \beta)$ is the grand canonical partition function. Evaluation of the above expression in the zero-particle limit provides the relationship $\Xi(\mu, V, \beta) = 1/\Pi(0)$.⁴⁵ One obtains the Helmholtz free energy $A(N)$ through the bridge equation

$$\begin{aligned} \beta A(N) = & -\ln Q(N, V, \beta) = -\ln[\Pi(N)/\Pi(0)] \\ & + N \ln \xi - N \ln q, \end{aligned} \quad (9)$$

and the entropy naturally follows from the expression

$$S(N) = \beta U(N) - \beta A(N). \quad (10)$$

Excess entropies are defined as the difference between the entropy of the real fluid and that of an ideal gas at the same density and temperature. The Helmholtz free energy of the ideal gas is provided by the analytical expression⁴⁶

$$\beta A^{\text{ig}}(N) = \ln N! - N \ln V - N \ln q. \quad (11)$$

After taking the intramolecular energy of a molecule in the ideal gas phase to be u^{ig} , the excess entropy evaluates to

$$\begin{aligned} S^{\text{ex}}(N) = & \beta[U(N) - Nu^{\text{ig}}] + \ln[\Pi(N)/\Pi(0)] \\ & - N \ln \xi V + \ln N!. \end{aligned} \quad (12)$$

In this work, we examine a simple monatomic fluid with no intramolecular degrees of freedom, and therefore $u^{\text{ig}} = 0$. Equation (12) provides the extensive excess entropy, with the intensive quantity given by $s^{\text{ex}} = S^{\text{ex}}/N$.

To collect the thermodynamic and structural properties of interest, a series of GC-TMMC simulations was conducted over a range of temperatures. In each simulation, a particle number range spanning from $N_{\min} = 0$ to $N_{\max} = 455$ was sampled using a cubic simulation cell with a volume of $V = 216$. A pair correlation function was compiled for each particle number. Data from a given simulation provided

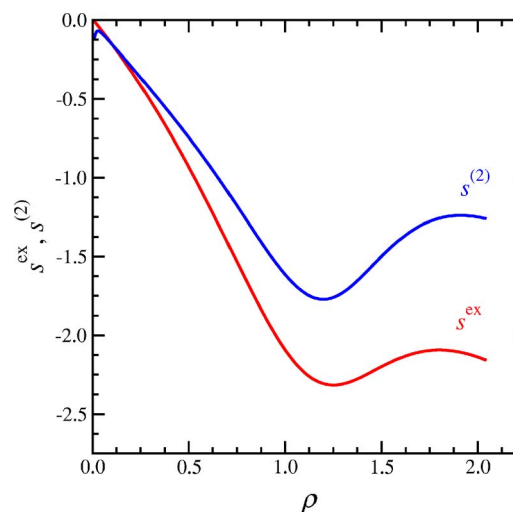


FIG. 2. The two-body excess entropy $s^{(2)}$ and the total excess entropy s^{ex} as a function of density at $T=0.055$.

properties along a selected isotherm up to a density of $\rho_{\max} = 2.106$. Statistical uncertainties were determined by performing four independent sets of simulations. The standard deviation of the results from the four simulation sets was taken as an estimate of the statistical uncertainty.

RESULTS AND DISCUSSION

We now examine the behavior of the Jagla model¹¹ through analysis of the excess entropy. The grand canonical simulations performed in this work provide both the two-body approximation to the excess entropy $s^{(2)}$, through collection of the density-specific pair correlation function, and the total excess entropy s^{ex} from basic thermodynamic arguments. Figure 2 provides an example of these quantities for the two-scale potential along the $T=0.055$ isotherm. At this temperature, it is clear that a region exists in which the excess entropy displays anomalous behavior, $(\partial s^{\text{ex}} / \partial \ln \rho)_T > 0$, with $s^{(2)}$ and s^{ex} reaching local minima at $\rho \approx 1.2$ and local maxima at $\rho \approx 1.85$. The results also indicate clear differences between $s^{(2)}$ and s^{ex} , with $s^{(2)}$ providing estimates for the excess entropy that are consistently smaller in magnitude than s^{ex} . In a previous study³⁸ involving the Lennard-Jones fluid, a similar relation was found regarding the magnitudes of $s^{(2)}$ and s^{ex} , i.e., $|s^{\text{ex}}| > |s^{(2)}|$. However, three- and higher-body contributions were found to account for at most 15% of the total excess entropy of the Lennard-Jones fluid. Here, we find that such contributions total approximately 35% of the excess entropy at $\rho = 1.85$.

Given that values for $s^{(2)}$ are calculated through an integration involving the pair correlation function, we were concerned that system size may have a noticeable influence on this property. To check the sensitivity of $s^{(2)}$ on system size, we calculated this quantity using $g(r)$ data produced from simulations with cell volumes of 216 and 1000 at densities corresponding to the local extrema noted above. In each case, estimates from the two system sizes deviated by less than 0.5%. Similar concerns regarding the system-size dependence of s^{ex} were examined in a previous study²⁸ and were also found to be negligible.

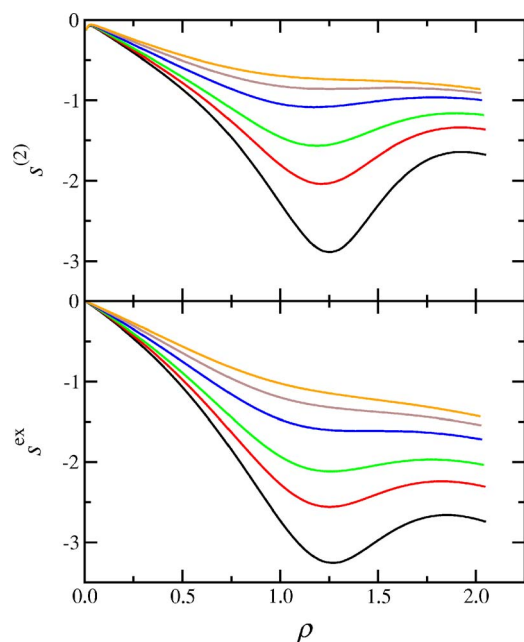


FIG. 3. Density dependence of $s^{(2)}$ (top panel) and s^{ex} (bottom panel) along a series of isotherms. Curves from bottom to top are for $T=0.04, 0.05, 0.06, 0.08, 0.10,$ and 0.12 .

Figure 3 shows the density dependence of $s^{(2)}$ and s^{ex} along a series of isotherms spanning from $T=0.04$ to $T=0.12$. The $s^{(2)}$ data suggest that anomalous behavior of the excess entropy occurs at temperatures of $T \approx 0.105$ and lower, whereas s^{ex} values indicate that this anomaly begins at a temperature of $T \approx 0.080$. Close inspection of the data also reveals that $s^{(2)}$ consistently predicts a stronger excess entropy anomaly [larger values of $(\partial s^{\text{ex}} / \partial \ln \rho)_T$] than s^{ex} . Based on the discussion above, the practical consequence of this relation is that $s^{(2)}$ will predict the onset of anomalous behavior in a given property at a higher temperature than s^{ex} .

Once anomalous behavior in the excess entropy has been established at a given temperature, the existence of anomalous behavior in other properties can be ascertained by examining the magnitude of $(\partial s^{\text{ex}} / \partial \ln \rho)_T$. Figure 4 contains this quantity as a function of density at $T=0.055$. These curves were obtained through simple numerical differentiation of the data found in Fig. 2. As expected, $s^{(2)}$ predicts a stronger excess entropy anomaly than s^{ex} . In fact, $s^{(2)}$ predicts that all properties examined in this work display anomalous behavior over some range of densities at $T=0.055$. In contrast, s^{ex} indicates that only the diffusivity and viscosity show anomalous behavior at this temperature. Similar discrepancies related to $s^{(2)}$ - and s^{ex} -based predictions have been found in earlier studies.⁴⁷

Figures 5 and 6 show where the various anomalous regions lie on P - T and T - ρ diagrams, respectively, based on the analysis of $s^{(2)}$ or s^{ex} data. As expected, the anomalous regions for the thermodynamic and transport properties examined here appear as nested domes within the P - T and T - ρ planes. The stronger anomalous behavior of the excess entropy predicted by $s^{(2)}$ leads to an overall shift in the location of $s^{(2)}$ -based anomalous regions to higher temperatures when contrasted with the corresponding s^{ex} -based envelopes. Our predictions are compared to regions of diffusivity and den-

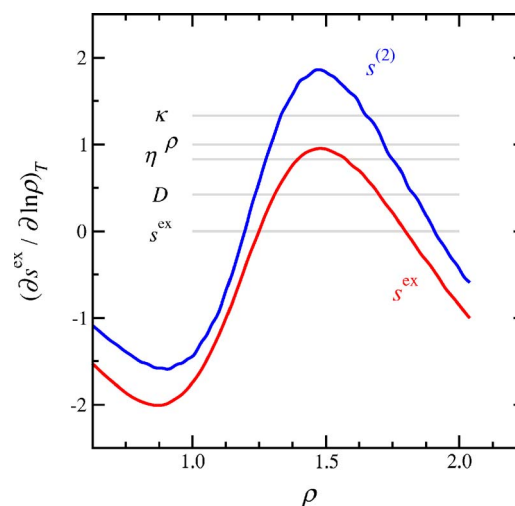


FIG. 4. Strength of the excess entropy anomaly based upon $s^{(2)}$ and s^{ex} as a function of density at $T=0.055$. The horizontal lines indicate the value $(\partial s^{\text{ex}} / \partial \ln \rho)_T$ must reach for one to observe anomalous behavior in the denoted property.

sity anomalies located by Yan *et al.*^{20,21} using molecular dynamics simulations. In their study, diffusivities were calculated from a mean-squared displacement analysis and regions of anomalous density behavior were obtained through examination of P - ρ - T data. Therefore, these can be considered true markers of anomalous diffusivity and density behavior.

We begin by considering the region of density anomalies. Note that our location of this region through analysis of

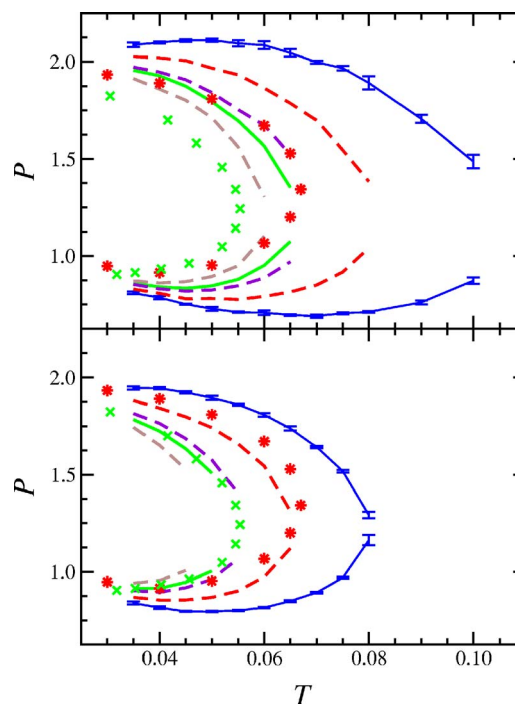


FIG. 5. Boundaries of anomalous regions within the P - T plane based on $s^{(2)}$ (top panel) and s^{ex} (bottom panel). The outer and inner solid lines represent the excess entropy and density, respectively. The dashed lines denote transport anomalies, with the outermost, intermediate, and innermost envelopes corresponding to diffusivity, viscosity, and thermal conductivity, respectively. The asterisk and cross symbols denote the boundary of the simulated diffusivity and density anomalies, respectively, obtained through molecular dynamics simulations performed by Yan *et al.*

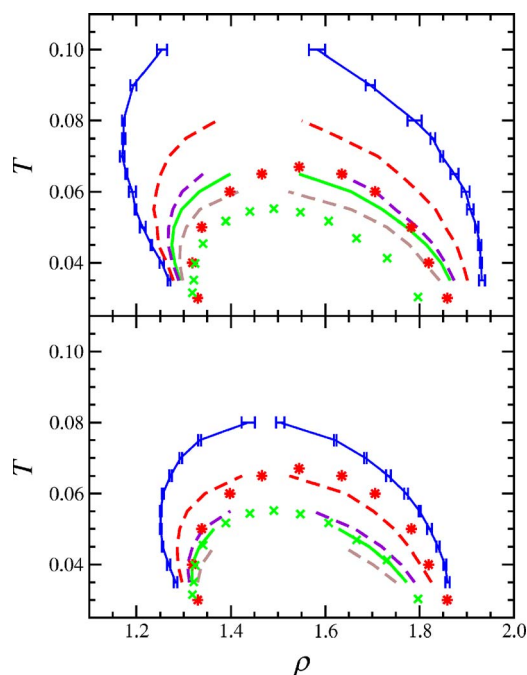


FIG. 6. Boundaries of anomalous regions within the T - ρ plane based on $s^{(2)}$ (top panel) and s^{ex} (bottom panel). The symbols are the same as for Fig. 5.

s^{ex} is in excellent agreement with the data of Yan *et al.* This finding is to be expected given that s^{ex} represents the total excess entropy, and the relationship between excess entropy and density anomalies arises through a rigorous thermodynamic identity. Failure to observe this agreement would represent an inconsistency between our work and the study of Yan *et al.* On the other hand, $s^{(2)}$ provides only an approximation to the excess entropy, and the location of the region of density anomalies based on this quantity is generally not expected to provide quantitative agreement with the simulated region. Indeed, this is what we observe here, where the use of $s^{(2)}$ data predicts density anomalies over a wider range of state conditions than actually observed.

We now examine the ability of Rosenfeld's entropy scaling to predict the region of diffusivity anomalies. When Rosenfeld's scaling is combined with s^{ex} , a reasonable description of anomalous diffusivity behavior is obtained. This combination correctly locates the upper temperature limit ($T \approx 0.067$) of the anomalous region and provides a decent estimate of the width of this area. However, the scaling approximation suggests that the envelope of diffusivity anomalies lies at lower densities than actually observed. The region of anomalous behavior obtained from $s^{(2)}$ extends to temperatures approximately 25% above the region obtained by Yan *et al.*

Also included in Figs. 5 and 6 are predictions for the anomalous regions for shear viscosity and thermal conductivity. At present, data for these two transport properties, which are difficult to determine accurately via molecular simulation, are not yet available for this model. However, we are currently exploring efficient means for calculating these properties, and we plan to make comparisons to the scaling predictions in a future study.

We now return briefly to the application of entropy scal-

ing relationships to molecular fluids. As noted in the Introduction, we feel that the basic principles encapsulated in these relationships can be extended to molecular fluids, but one must relate a given transport property to a specific contribution to the total excess entropy. One can find evidence to support this reasoning by examining investigations of SPC/E water. For example, data from the study of Errington and Debenedetti² reveal that a region of anomalous translational structural order encloses the region of anomalous translational diffusivity behavior within the temperature-density plane (see Fig. 1). In a more recent study, Mittal *et al.*³⁰ showed that the translational diffusivity of SPC/E water scales linearly with the exponential of the translational component of the two-body excess entropy along an isochore. Clearly, these two examples do not provide sufficient evidence to validate the general tenet argued above, and further investigation is needed to better understand how entropy scaling ideas can be utilized to describe molecular fluids.

CONCLUSIONS

We have used empirical scaling relationships introduced by Rosenfeld to develop mathematical relationships that enable one to utilize excess entropy information to predict the state conditions where anomalous transport behavior is observed. Thermodynamic identities were also used to establish the criterion for density anomalies in terms of the excess entropy. Our analysis indicates that all regions of anomalous density and transport behavior reside within an envelope of excess entropy anomalies. A given property exhibits anomalous behavior when the strength of the excess entropy anomaly exceeds a property-specific threshold. The conditions formulated here for the density anomaly are completely general, whereas those developed for the transport properties are limited by the validity of Rosenfeld's scaling relations.

To illustrate the potential of these ideas, we performed simulations to determine thermodynamic properties of a discontinuous core-softened model introduced by Jagla. Total excess entropies and the two-body approximation were used to predict regions of anomalous transport behavior, which were then compared to the actual region of anomalous diffusivity behavior determined by Yan *et al.* Comparison of the two approaches pursued for determining excess entropies revealed that the two-body approximation predicts anomalous behavior over a broader region of state conditions than obtained with the total excess entropies. Overall, Rosenfeld's scaling relations provided a quite reasonable description of the anomalous diffusivity region.

The results presented here show promise for using thermodynamic data coupled with empirical scaling laws to predict anomalous transport behavior. We are currently examining the extent to which these ideas can be employed to describe the behavior of a broader array of fluids. Of particular interest is the application of these ideas to molecular fluids. We are also extending our calculations to measure a broader set of kinetic properties, including the viscosity and thermal conductivity.

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