

# Connecting entropy scaling and density scaling

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## ABSTRACT

It is shown that the residual entropy (entropy minus that of the ideal gas at the same temperature and density) is mostly synonymous with the independent variable of density scaling, identifying a direct link between these two approaches. The residual entropy and the effective hardness of interaction (itself a derivative at constant residual entropy) are studied for the Lennard-Jones monomer and dimer as well as a range of rigid molecular models for carbon dioxide. It is observed that the density scaling exponent appears to be related to the two-body interactions in the dilute-gas limit.

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## I. INTRODUCTION

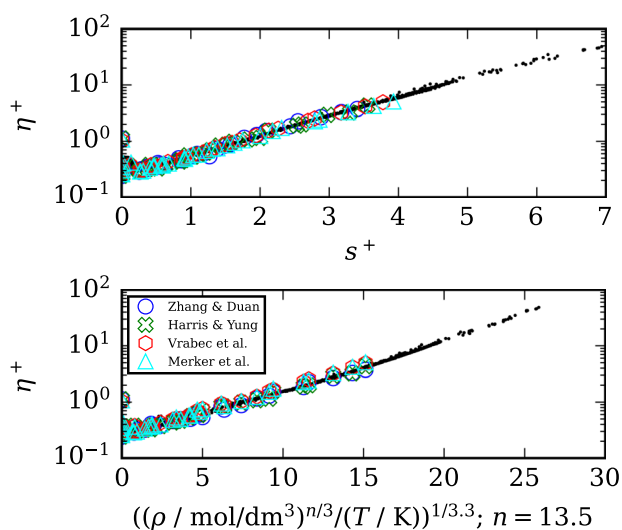
Entropy scaling has been extensively studied in recent years (refer to Ref. 1 for a review) as a means of connecting dynamics and equilibrium thermodynamics. A requirement for applying this approach to the transport properties of real fluids is a reliable model for the residual entropy (the difference between the entropy and the entropy of an ideal gas at the same temperature and density), which is usually obtained from an empirical equation of state (EOS), or more computationally costly molecular simulation methods, limiting the usefulness of entropy scaling. Representing the residual entropy straightforwardly in terms of temperature and density would therefore be appealing and broaden the range of fluids for which entropy scaling might be applied. The goal of this work is to demonstrate that this is possible, and furthermore, it reveals a heretofore unknown link between density scaling<sup>2</sup> and entropy scaling approaches in the entire phase diagram.

As a first demonstration of the motivation of this paper, we overlay shear viscosity data of CO<sub>2</sub> as a function of the independent variable of each approach in Fig. 1. The dependent variable is  $\eta^+ = \eta / (\rho_N^{2/3} \sqrt{mk_B T}) \times (s^+)^{2/3}$ , where  $\eta$  is the shear viscosity,  $\rho_N$  is the number density,  $m$  is the mass of one entity (atom or molecule),  $k_B$  is Boltzmann's constant,  $T$  is the temperature, and  $s^+$  is the reduced residual entropy defined later on. The viscosity data were scaled according to the modified entropy scaling approach introduced in Ref. 3. The density scaling exponent of 13.5 was

taken from Ref. 4. The quantity  $\eta^+$  combines macroscopic scaling (a requirement for isomorph theory, see Sec. 1 C) and the plus-scaling introduced in Ref. 3. We will revisit each of the elements, but for now the key point is that the two approaches yield almost linear relationships in semi-log coordinates.

## A. Entropy scaling

The observation of a correlation between the variation of transport coefficients (e.g., self-diffusion coefficient or shear viscosity) of simple liquids and their residual entropy can be traced back to Rosenfeld in 1977.<sup>5</sup> In Rosenfeld's work, simulation results for different systems were presented and simple exponential relations between dimensionless values of the self-diffusion coefficient or shear viscosity and residual entropy were proposed. A fundamental observation was that in order to observe the correlations between transport coefficients and residual entropy, the physical quantities need to be made dimensionless by using macroscopically reduced units.<sup>6</sup> In macroscopically reduced units, lengths are measured in terms of the average interparticle distance  $\rho_N^{-1/3}$  and energies in terms of  $k_B T$ . A tilde above the quantity of interest will indicate that the quantity is expressed in macroscopically reduced units. Similar results were later found by Dzугutov,<sup>7</sup> which was the start of a growing interest in the entropy scaling approach. While the initial focus was on understanding the nature of the relationship between residual entropy and scaled transport properties, this approach has



**FIG. 1.** Modified entropy scaling applied to shear viscosity data as a function of residual entropy (top panel) and density scaling variable (bottom panel) for CO<sub>2</sub> (open markers: selected simulation results from this work, points: experimental data collection from Ref. 3).

been shown to be applicable to a broad range of fluids (as long as they behave classically and do not form strong directional bonds). The review of Dyre<sup>1</sup> in 2018 summarized the progress in this field up to that date. Since then, additional studies have considered the physical basis of this approach<sup>3,8</sup> and applied the technique to different systems: the Lennard-Jones (LJ) fluid,<sup>9</sup> refrigerants,<sup>10,11</sup> and alkanes.<sup>12,13</sup>

## B. Density scaling

Density scaling is trivially valid for systems interacting via inverse-power-law (IPL) potentials of the form  $V(r) \propto r^{-n}$ , where  $r$  is the molecular center of mass separation. For this family of systems, the dynamic and thermodynamic properties are not functions of  $T$  and  $\rho$  independently but depend on their combination  $\Gamma = \rho^{n/3}/T$ . As a consequence, the phase diagram of these systems is one-dimensional. IPL fluids exhibit a one-to-one mapping between  $\Gamma$  and residual entropy (see the supporting information of Ref. 3) and, indeed, between  $\Gamma$  and all thermodynamic and transport properties with the application of an appropriate scaling.

The density scaling approach takes a fluid of interest governed by a non-IPL potential and expresses its macroscopically scaled transport properties in the form  $\tilde{X} = f(\rho^{n/3}/T)$ , where  $X$  is the shear viscosity, thermal conductivity, or self-diffusion coefficient and  $n$  is in this case a fluid-specific constant for the entire phase diagram.<sup>14</sup> Density scaling is thus predicated on the assumption that the effective interaction potential between molecules can be approximated by  $V \propto r^{-n}$ . Density scaling has been investigated for a wide range of systems, including Lennard-Jones models, modified Buckingham fluids, metals,<sup>15</sup> and flexible molecular analogs,<sup>16</sup> and has also proven to be useful in glass-forming liquids.<sup>17</sup> A major concern for using this approach is the evidence that the density scaling

coefficient  $n$  has been shown to be not constant both in computer simulations<sup>18</sup> and in experiments.<sup>19,20</sup>

Hence, how can entropy scaling and density scaling be reconciled? This work demonstrates that the use of a constant exponent has the effect of making the unique variable of density scaling a monovariate function of residual entropy. In other words, density scaling with a constant effective hardness and entropy scaling are closely related.

## C. Isomorph theory

Both entropy scaling and density scaling indicate that a relationship between the dynamics of fluids and their thermodynamic properties exists (see, for instance, Fig. 1), but they do not provide a satisfying explanation for *why* this is the case. Rosenfeld's reference to the hard sphere system in the dense fluid phase as an explanation for the success of entropy scaling is hard to accept in gas-like phases. The assumption that repulsion, modeled as an IPL interaction, yields density scaling has been challenged, both with simulations and experiments. Simulations showed that  $\tilde{X} = f(\rho^{n/3}/T)$  is too simple an approximation,<sup>18</sup> and experiments<sup>19,20</sup> indicate that, in general, the density scaling exponent depends on the thermodynamic state point. A way to consistently link density scaling and entropy scaling is provided by isomorph theory, briefly introduced below. For a more complete overview of the theory, we refer to Refs. 1, 21, and 22.

According to isomorph theory, it is possible to identify regions in the phase diagram of a given liquid in which its behavior is simpler. These regions can be identified with simulations by evaluating where the correlation coefficient  $R_{\text{Ros}}$ <sup>23</sup> is greater than 0.9,

$$R_{\text{Ros}} = \frac{\langle \Delta U \Delta W \rangle}{\sqrt{\langle (\Delta U)^2 \rangle \langle (\Delta W)^2 \rangle}}. \quad (1)$$

In the definition of  $R_{\text{Ros}}$ ,  $\Delta U$  and  $\Delta W$  are the deviations of the instantaneous values of potential energy and virial from the average value, respectively. The  $\langle \dots \rangle$  syntax indicates the average of the argument over a canonical ensemble. The quantity  $R_{\text{Ros}}$  can also be evaluated with experiments under some approximations, as in Fig. 3 of Ref. 24. In the  $R_{\text{Ros}} > 0.9$  regions, the phase diagram of the system is effectively one-dimensional and the structure and dynamics of the system are invariant when expressed in the macroscopically reduced units introduced earlier, i.e., along curves of constant residual entropy, which are called isomorphs. These invariances have been verified in several works, both with computer simulations<sup>25</sup> and experiments.<sup>26</sup>

This way, isomorph theory provides a clear link between density scaling and entropy scaling, additionally predicting the invariance of the reduced structure. The weak point of this approach is that its validity is limited to some regions of the phase diagram and cannot explain, for example, the validity of entropy scaling at low densities (i.e., below the critical density).

Isomorph theory also predicts that the density scaling exponent  $n/3$  depends on the thermodynamic state, as confirmed by computer simulations and experiments. The density scaling exponent is the slope of the constant residual entropy curves and can be evaluated from simulations in the canonical ensemble using the fluctuation formula<sup>22</sup>

$$n_{\text{eff}} = 3 \frac{\langle \Delta U \Delta W \rangle}{\langle (\Delta U)^2 \rangle} = 3 \left( \frac{\partial \ln(T)}{\partial \ln(\rho)} \right)_s, \quad (2)$$

where  $\Delta U$  and  $\Delta W$  have the same meaning as in Eq. (1). This quantity can also be evaluated at any state point in experiments as shown in Ref. 19.

This work will explore the link between entropy scaling and density scaling in the entire phase diagram of several fluids, i.e., both in the region of the phase diagram where isomorph theory can explain this link and close to the gas–liquid coexistence where this link is not clear. In order to clarify this issue, we consider three families of “simple” systems: the Lennard-Jones monomer, the Lennard-Jones dimer, and a range of molecular models for carbon dioxide. First, we consider the residual entropy calculated for each system, we calculate its density scaling exponent, and finally, we show how residual entropy scaling and density scaling are connected.

## II. METHODS

### A. Thermodynamics

In order to lay out the thermodynamics, we start with the definitions of the relevant quantities. The residual entropy  $s^r$  is defined by

$$s^r \equiv s(T, \rho) - s^{(\text{ig})}(T, \rho), \quad (3)$$

where  $s^{(\text{ig})}$  is the molar entropy of the ideal gas and  $s$  is the total molar entropy. In practice, this difference is not evaluated directly, rather the residual Helmholtz energy and its derivatives are used to obtain the residual entropy  $s^r$  [e.g., see Eq. (6) of Ref. 3]. Furthermore, it is conceptually useful to consider rather than  $s^r$  the non-dimensional term  $s^+$  defined by

$$s^+ \equiv -s^r/R, \quad (4)$$

where  $R$  is the molar gas constant. Other residual properties (residual pressure  $p^r$ , residual molar Helmholtz energy  $a^r$ , and residual isochoric molar heat capacity  $c_v^r$ ) are defined analogously,

$$p^r \equiv p(T, \rho) - p^{(\text{ig})}(T, \rho), \quad (5)$$

$$a^r \equiv a(T, \rho) - a^{(\text{ig})}(T, \rho), \quad (6)$$

$$c_v^r \equiv c_v(T, \rho) - c_v^{(\text{ig})}(T). \quad (7)$$

The quantity  $c_v^{(\text{ig})}$  has only temperature dependence, while the other ideal gas properties depend both on temperature and density.

The effective hardness  $n_{\text{eff}}$  is defined by<sup>22</sup> [identical to Eq. (2)]

$$n_{\text{eff}} \equiv 3 \left( \frac{\partial \ln(T)}{\partial \ln(\rho)} \right)_s = 3 \frac{\rho}{T} \left( \frac{\partial T}{\partial \rho} \right)_s. \quad (8)$$

After some thermodynamic manipulations,<sup>27</sup> the value of  $n_{\text{eff}}$  from Eq. (8) can also be written in the equivalent formulation

$$n_{\text{eff}} = -3 \frac{\rho \left( \frac{\partial s^+}{\partial \rho} \right)_T}{T \left( \frac{\partial s^+}{\partial T} \right)_\rho} = 3 \frac{1}{\rho} \left( \frac{\partial (p^r/R)}{\partial T} \right)_\rho. \quad (9)$$

As will be shown later, the derivative  $(\partial s^+/\partial \rho)_T$  is, in general, positive and  $(\partial s^+/\partial T)_\rho$  is, in general, negative, and thus,  $n_{\text{eff}}$  should be positive for the molecular systems studied here. Other more exotic systems can yield negative values of  $n_{\text{eff}}$ .<sup>28</sup>

With the formalism of Lustig,<sup>29</sup> the residual Helmholtz energy derivatives can be obtained simultaneously in one molecular simulation run. In that framework, the density scaling exponent is defined by

$$n_{\text{eff}} = -3 \frac{\Lambda_{01} - \Lambda_{11}}{\Lambda_{20}}, \quad (10)$$

in which

$$\Lambda_{ij} = (1/T)^i (\rho)^j \left( \frac{\partial^{i+j}(a^r/RT)}{\partial (1/T)^i \partial \rho^j} \right). \quad (11)$$

In the dilute-gas limit, where two-body interactions are quantified by the second virial coefficient  $B_2$ ,  $n_{\text{eff}}$  is given by<sup>30</sup>

$$\lim_{\rho \rightarrow 0} n_{\text{eff}} = -3 \frac{T \frac{dB_2}{dT} + B_2}{T^2 \frac{d^2 B_2}{dT^2} + 2T \frac{dB_2}{dT}}, \quad (12)$$

which has recently been derived in terms of the pair potential for an infinite number of spatial dimensions,<sup>31</sup> where the infinite spatial dimension limit is equivalent to the two-body limit in Eq. (12).

### B. Simulation details

The Lennard-Jones monomer was simulated using the RUMD software package.<sup>32</sup> The potential was cut and shifted at the distance of  $2.5\sigma$  and the potential parameters of  $\sigma$  and  $\epsilon/k_B$  were set to unity. The temperature was controlled with a Nosé–Hoover thermostat using  $\tau = 0.2$  as relaxation time. The time step for the simulation was kept constant in macroscopically reduced units  $d\bar{t} = 0.001$ , and the system size was  $N = 1000$ . The values of  $n_{\text{eff}}$  were obtained from the fluctuation formula in Eq. (2). The dependence of  $n_{\text{eff}}$  on the system size has been studied in Appendix B of Ref. 31.

For the other fluids, molecular dynamics (MD) simulations were performed, solving numerically Newton’s equations of motion with a fifth-order Gear predictor–corrector scheme by using the molecular simulation tool *ms2*.<sup>33–36</sup> All simulations were sampled in the canonical ensemble with the formalism of Lustig<sup>29</sup> to calculate the Helmholtz energy derivatives with respect to density and inverse temperature as well as their combinations. Velocities were isokinetically rescaled to maintain the specified temperature. All CO<sub>2</sub> models given in Table I were simulated with *ms2* as well as the Lennard-Jones (LJ) dimer, which was set to a fixed bond length of  $\sigma$ . The long-range interactions were corrected with the usual analytic mean-field equations.<sup>33–36</sup> Chemical potential data  $\mu_i$  were determined with Widom’s test particle insertion method.<sup>37</sup> The shear viscosity was obtained by applying the Green–Kubo formalism<sup>38,39</sup> and the Einstein relations<sup>36</sup> for the LJ dimer and the selected CO<sub>2</sub> models of Zhang and Duan, Harris and Yung, Vrabec *et al.* Merker *et al.*, and Errington and Hellmann.

The LJ dimer was studied in the temperature range  $k_B T/\epsilon = 0.9–100$  and density range  $\rho\sigma^3 = 0.00017–0.5$  with  $N = 1372$  particles, whereas for transport properties,  $N = 4000$  was used. For

TABLE I. Molecular models for CO<sub>2</sub> considered in this work.

Author	$N_{\text{sites}}$	Site-site	Quadrupole	$Q \times 10^{40} \text{ C}^{-1} \text{ m}^{-2}$
Murthy <i>et al.</i> <sup>47</sup>	3	LJ	Point charges	-12.6
Potoff and Siepmann <sup>48</sup>	3	LJ	Point charges	-15.1
Zhang and Duan <sup>40</sup>	3	LJ	Point charges	-12.8
Harris and Yung <sup>41,a</sup>	3	LJ	Point charges	-13.7
Möller and Fischer <sup>49</sup>	2	LJ	Point quadrupole	-12.2
Vrabec <i>et al.</i> <sup>42</sup>	2	LJ	Point quadrupole	-12.7
Merker <i>et al.</i> <sup>43</sup>	3	LJ	Point quadrupole	-13.6
Errington <sup>44,50</sup>	3	EXP-6	Point charges	-13.5
Hellmann <sup>45</sup>	7	Empirical	Point charges	-14.2

<sup>a</sup>PM2, rigid.

that purpose, simulations were equilibrated by 100 Monte Carlo (MC) cycles and  $10^5$  MD time steps. The production runs were performed for a period of  $4 \times 10^6$  (transport:  $3\text{--}5 \times 10^7$ ) time steps with  $\Delta t/(\sigma\sqrt{m/\epsilon}) = 0.0005$  (respectively, 0.001 near the vapor-liquid equilibrium region). Intermolecular interactions were explicitly calculated up to the cutoff radius  $r_c = 4\sigma$ .

Each CO<sub>2</sub> model listed in Table I was evaluated in the temperature range  $T = 250\text{--}10\,000$  K and density range  $\rho = 0.1\text{--}25$  mol/dm<sup>3</sup> with  $N = 1372$  molecules and a cutoff radius of  $r_c = 14$  Å (transport:  $N = 4000$ ,  $r_c = 17.5$  Å). 200 MC cycles and  $5 \times 10^5$  MD time steps were used for equilibration, and the production run was performed for a period of  $4 \times 10^6$  (for transport at least  $15 \times 10^6$ ) time steps with  $\Delta t = 0.971$  fs (for  $T = 250\text{--}600$  K:  $\Delta t = 1.942$  fs). Besides that, some phase space regions of the Hellmann CO<sub>2</sub> fluid had to be simulated with different settings. At  $T = 10\,000$  K from  $\rho = 9\text{--}25$  mol/dm<sup>3</sup>, an equilibration of 200 MC cycles and  $8 \times 10^5$  MD time steps was performed followed by a production run of  $8 \times 10^6$  time steps with  $\Delta t = 0.104$  fs.

The use of the formalism of Lustig<sup>29</sup> to calculate all thermodynamic properties from the same simulation run yields the  $n_{\text{eff}}$  values directly from its definition in Eq. (10).<sup>46</sup>

The first four CO<sub>2</sub> models are qualitatively similar; they consist of three Lennard-Jones sites and point charges at each site. The next three models use two or three Lennard-Jones sites, along with a point quadrupole at the center of the molecule. The exceptions to this general approach are the models of Hellmann<sup>45</sup> and Errington.<sup>44,50</sup> In these more advanced models, repulsion is roughly exponential in its form, and in the case of Hellmann,<sup>45</sup> empirical potentials have been fitted to each site-site interaction term in order to match first principles calculations of the potential energy surface.

The quadrupole moment of CO<sub>2</sub> is equal to  $(-14.31 \pm 0.74) \times 10^{-40} \text{ C m}^2$ , according to recent measurements of Chetty and Couling,<sup>51</sup> which is consistent with other recent analysis.<sup>52</sup> The quadrupole moment of the molecular models is given in Table I. There is no strong correlation between the quadrupole moment  $Q$  and the representation of the data considered in this work. The details of the evaluation of each potential are covered in the source code of *potter*.<sup>53</sup> All calculations were done in SI units to ensure dimensional consistency.

The second virial coefficient, its temperature derivatives, and values of  $n_{\text{eff}}$  of these models were calculated with the approach described in Ref. 30, with the use of the open-source *potter* library and multicomplex algebra to obtain  $B_2$  and its temperature derivatives simultaneously. The integrator was allowed to evaluate the integrand as many as  $10^7$  times for each temperature.

### III. RESIDUAL ENTROPY

The residual entropy is the independent variable of the macroscopically scaled transport properties in the entropy scaling framework and quantifies the loss of microstates of the system from intermolecular interactions. Residual entropy is a property that is not accessible experimentally, so it is not as well understood as other

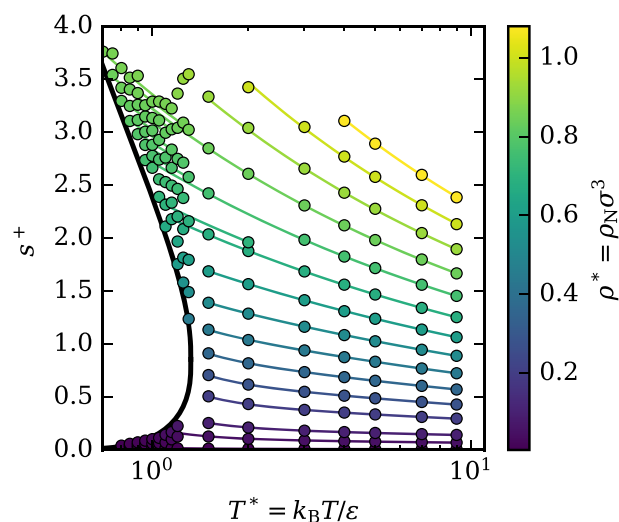
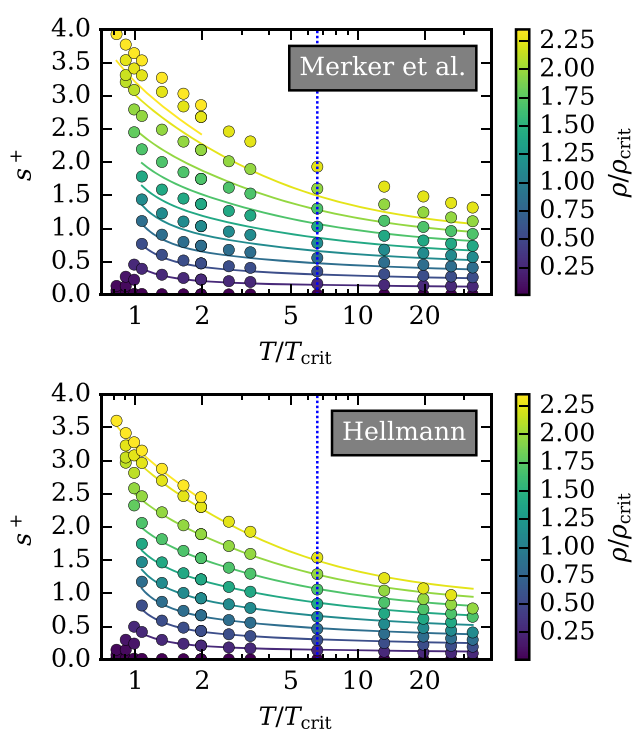


FIG. 2. Values of  $s^+$  for the Lennard-Jones monomer fluid. Markers are corrected simulation results from Ref. 55, and colored curves are from the EOS of Thol *et al.*<sup>55</sup> for isochores with more than two data points. The solid black curve is the vapor-liquid phase boundary.

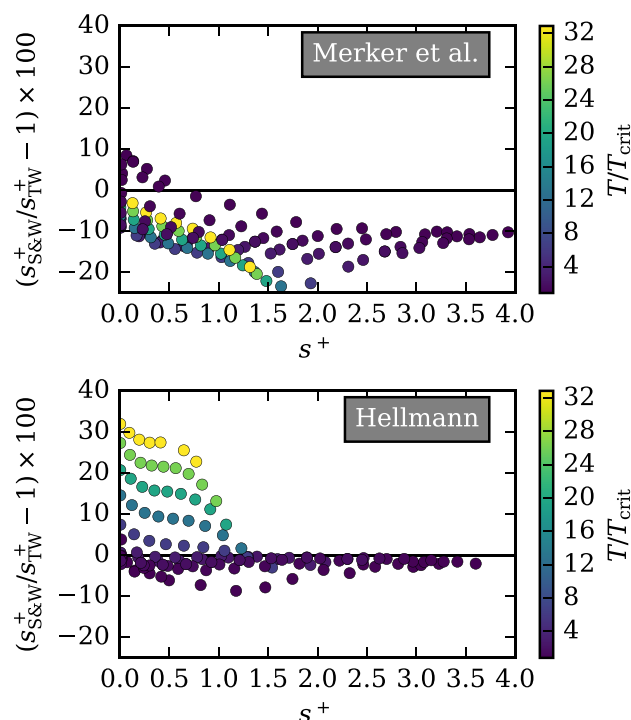
properties, such as pressure, density, or speed of sound. A comprehensive study of the residual entropy obtained from empirical thermodynamic models is called for.

For the Lennard-Jones fluid, the values of  $s^+$  can be obtained by thermodynamic integration<sup>54</sup> or other sampling-based methods, and the EOS of Thol *et al.*<sup>55</sup> gives a faithful representation of this quantity. Figure 2 presents the values of  $s^+$  as a function of temperature and density for the Lennard-Jones fluid.

In this work, we compare the values of  $s^+$  obtained for the thermodynamic models for CO<sub>2</sub> with each other and with the empirical EOS of Span and Wagner.<sup>56</sup> Figure 3 shows the residual entropy calculated with two molecular models, those of Hellmann and Merker *et al.*, with the results from the Span and Wagner EOS overlaid. This result shows that the Hellmann molecular model provides a much closer agreement with the values of  $s^+$  obtained from the EOS of Span and Wagner than those of the molecular model of Merker *et al.* For  $T/T_{\text{crit}} \lesssim 20$ , it is difficult to distinguish the markers (from the molecular model of Hellmann) and the curve (from Span and Wagner). To make the comparison more quantitative, Fig. 4 shows the deviations between the simulation data and the EOS. The other molecular models generally yield similar results to that of Merker *et al.*, showing large deviations in residual entropy relative to the EOS. For the Hellmann model, for temperatures below the limit of the EOS at 2000 K,<sup>57</sup> the mean absolute relative percentage error (MAPE) in  $s^+$  is 2.1%. One distinguishing feature of the Hellmann model is its representation of the effective



**FIG. 3.** Results for  $s^+$  from the CO<sub>2</sub> molecular models of Merker *et al.*<sup>43</sup> and Hellmann.<sup>45</sup> The curve for each isochore is given by the Span and Wagner EOS.<sup>56</sup> The vertical dashed line indicates the temperature limit of the EOS at  $T = 2000$  K.



**FIG. 4.** Deviations of  $s^+$  calculated from the CO<sub>2</sub> molecular models of Merker *et al.*<sup>43</sup> and Hellmann<sup>45</sup> (subscript TW) from the Span and Wagner EOS<sup>56</sup> (subscript SW).

hardness  $n_{\text{eff}}$ , as shown in Sec. V. The differences are already evident at the level of classical calculations based upon the second virial coefficient.

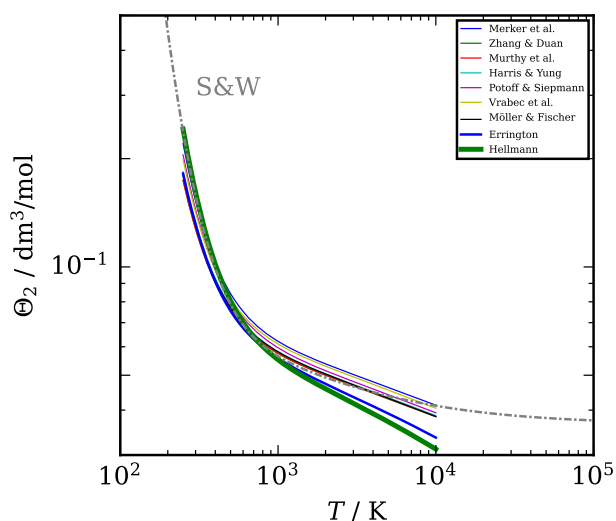
For a state point either above the critical temperature or in the gaseous phase for subcritical temperatures, scaled residual entropy at a given state point can be obtained by an integral taken at constant temperature,

$$s^+ = \int_0^\rho \left( \frac{\partial s^+}{\partial \rho} \right)_T d\rho, \quad (13)$$

where  $s^+$  in the zero density limit (that of the ideal gas) is zero. This is the typical “thermodynamic integration” approach familiar to molecular simulation practitioners, formulated in a different fashion. An alternative (and thermodynamically identical) representation of Eq. (13) is

$$s^+ = \int_0^\rho \frac{1}{\rho^2} \left( \frac{\partial(p^r/R)}{\partial T} \right)_\rho d\rho. \quad (14)$$

The formulation in Eq. (14) highlights the importance of high quality densimetry data (measurements of density  $\rho$  as a function of temperature and pressure) for the representation of residual entropy. If the temperature and density dependence of pressure is well captured by laboratory measurements, the derivative  $(\partial p^r/\partial T)_\rho$  will also be accurate, and the residual entropy obtained from a highly accurate empirical model fitted to these data will also



**FIG. 5.** Values of  $\Theta_2 = B_2 + T(dB_2/dT)$  from molecular models and from the Span and Wagner<sup>56</sup> (SW) EOS for CO<sub>2</sub>.

be accurate. In the case of CO<sub>2</sub>, we may reasonably assume that the residual entropy obtained from the Span and Wagner EOS is probably correct within its range of validity, given the large quantity of high quality densimetry data, and this EOS is in excellent agreement with these data.<sup>56</sup>

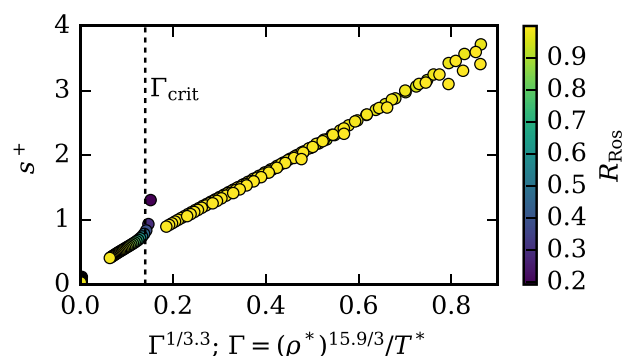
At low density,  $s^+$  is governed by the leading term of the virial expansion, as explained in Sec. S3 in the [supplementary material](#),

$$\lim_{\rho \rightarrow 0} s^+ = \left( B_2 + T \frac{dB_2}{dT} \right) \rho_N, \quad (15)$$

and hence, the behavior of  $\Theta_2 = B_2 + T(dB_2/dT)$  can provide information on the quality of the molecular model and that of the EOS. Figure 5 shows the obtained values of  $B_2 + T(dB_2/dT)$  for each model and the EOS. The model values were obtained classically with *potter*. The quantity  $\Theta_2$  must be positive for all temperatures because the entropy must be less than that of an ideal gas at the same temperature and density (see p. 447 of Ref. 58), a constraint fulfilled by all molecular models and the EOS, but the qualitative behavior of the EOS is incorrect (compared with the Hellmann model) above  $\sim 1000$  K. The reproduction of dilute gas residual entropy values in the low-density gas (considering values of  $\Theta_2$ ) is thus shown to be a sensitive test for the residual entropy.

#### IV. DENSITY SCALING AND ENTROPY SCALING

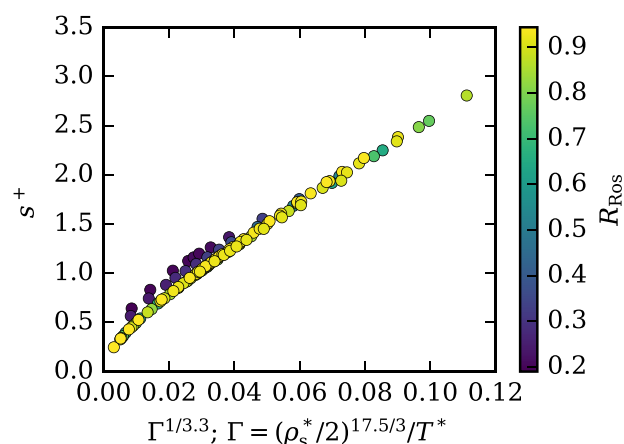
To begin our comparison between density scaling and entropy scaling, we follow the approach taken in density scaling: the use of a constant  $n$  for the entire phase diagram in the definition of  $\Gamma$ . In the case of the Lennard-Jones monomer fluid, there is a particular value of  $n$  that maximizes the correlation between  $(\rho^*)^{n/3}/T^*$  and  $s^+$ . With this optimized value, the Spearman correlation coefficient between  $(\rho^*)^{n/3}/T^*$  and  $s^+$  is greater than 0.999, which represents nearly one-to-one relationship. The MD data also



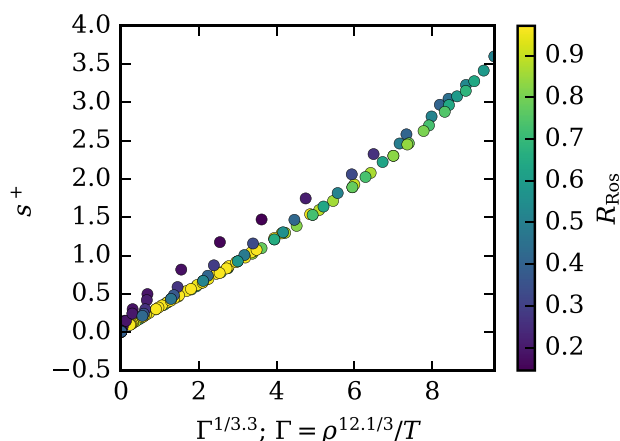
**FIG. 6.** Values of  $s^+$  for the Lennard-Jones monomer as a function of the density scaling variable for  $T^* < 20$ .

consider the gaseous phase and the critical region so that most of the phase diagram is covered. In order to assist with the visualization, the value of  $\Gamma$  was scaled with an exponent to linearize the relationship between  $\Gamma$  and  $s^+$  in Fig. 6. This figure demonstrates that in the case of the Lennard-Jones monomer,  $s^+$  and  $\Gamma$  are directly connected to each other. The particular surprise in this figure is that the relation between  $\Gamma$  and  $s^+$  holds even in parts of the phase diagram where  $R_{Ros} \ll 0.9$ . In the dilute-gas limit, this scaling should break down because the leading term from the virial expansion is defined as in Eq. (15), which does not follow the same scaling.

For the Lennard-Jones dimer, the qualitative picture is similar, as shown in Fig. 7. Again, a constant value of  $n$  was selected, which maximized the Spearman correlation between  $(\rho_s^*/2)^{n/3}/T^*$  and  $s^+$ . The addition of the bond to form a linear molecule does not appear to alter the core conclusion that a fixed value of  $n$  is needed to form a one-to-one relationship between  $(\rho_s^*)^{n/3}/T^*$  and  $s^+$ . For some of the state points with  $R_{Ros} < 0.3$ , indicating a breakdown of isomorph theory, the mapping between the variables is slightly



**FIG. 7.** Values of  $s^+$  for the Lennard-Jones dimer from the present simulations as a function of the density scaling variable. Note that the density  $\rho_s^*$  is the reduced monomer number density.



**FIG. 8.** Values of  $s^+$  from the Hellmann<sup>45</sup> model for CO<sub>2</sub> from the present simulations as a function of the density scaling variable. Density  $\rho$  is in units of mol/dm<sup>3</sup>, and temperature  $T$  is in units of K.

less strong, but aside from these deviating points, the mapping is nearly as one-to-one as for the Lennard-Jones monomer. The values of  $s^+$  for the dimer are approximately two times larger than those of the monomer at the same monomer density and temperature (microstates are removed by the fixed bond, limiting the accessible phase space). The state point dependence is shown in Fig. S1 of the [supplementary material](#).

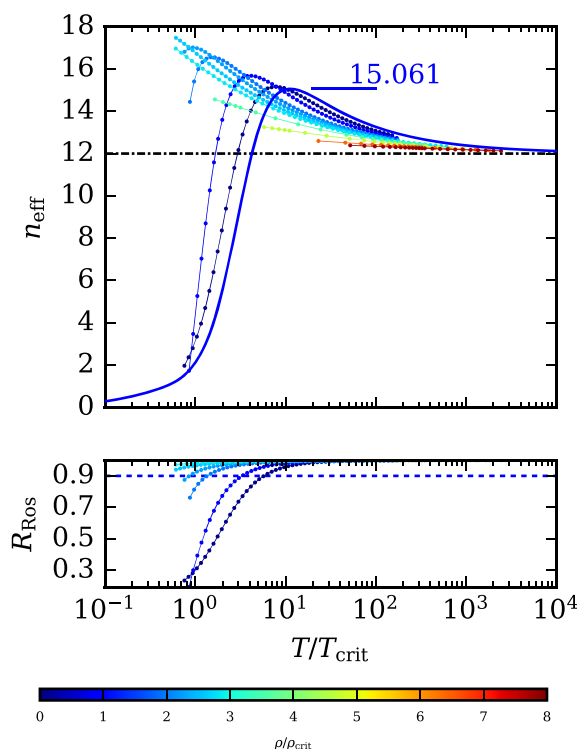
For the CO<sub>2</sub> model of Hellmann,<sup>45</sup> the behavior is much the same as for the Lennard-Jones dimer. Again,  $n$  was selected to maximize the Spearman correlation between  $\rho^{n/3}/T$  and  $s^+$  for the points with  $R_{Ros} > 0.5$ . Figure 8 shows the same type of plot, but with one striking difference. The relationship between  $s^+$  and  $\Gamma^{1/3.3}$  is qualitatively different; the curvature is convex in the case of CO<sub>2</sub> and concave in the case of the Lennard-Jones monomer and dimer.

## V. EFFECTIVE HARDNESS

The analysis above primarily focused on *post hoc* analysis of simulation data in order to determine the optimal value of  $n$  for a particular system. *What if the optimal value of  $n$  is unknown?* A first glimpse of a predictive model for the optimal  $n$  comes from a consideration of the effective hardness of interaction  $n_{eff}$ . The quantity  $n_{eff}$  entered the vocabulary of thermodynamics with the advent of isomorph theory. The effective hardness can be conceptually thought of as the effective repulsiveness of the interactions between molecules.<sup>59</sup>

### A. Lennard-Jones monomer

We first consider the density scaling exponent  $n_{eff}$  obtained from MD simulations for the Lennard-Jones fluid. The results of these simulations are shown in Fig. 9. The calculations extend from the dilute gas up to extremely high temperatures and very dense liquid states. The dilute-gas values obtained from the second virial coefficient<sup>30</sup> are also shown, highlighting that the values approach



**FIG. 9.** Values of  $n_{eff}$  and  $R_{Ros}$  for the Lennard-Jones monomer fluid. The thick curve is the value obtained from the closed form solution for the second virial coefficient published by Sadus,<sup>30,61</sup> and other values were calculated from NVT simulations performed with the RUMD software package.<sup>32</sup>

12 in the infinite temperature limit. In this high-temperature limit, the interactions are entirely governed by the repulsive contribution (which is proportional to  $r^{-12}$  for the Lennard-Jones fluid). For densities and temperatures more aligned with engineering applications,  $n_{eff}$  has both temperature and density dependence. Along the critical isotherm, the values of  $n_{eff}$  vary from  $\sim 16$  to zero (going toward zero at the critical point);  $n_{eff}$  is decidedly not constant for even simple systems, such as the Lennard-Jones fluid.

The integration from Eq. (13) may equivalently be written in terms of  $n_{eff}$  as

$$s^+ = \frac{1}{3} \int_0^\rho \frac{(c_v^t/R) n_{eff}}{\rho} d\rho. \quad (16)$$

This expression provides a useful way of thinking about the relationship between residual entropy and  $n_{eff}$ . The conceptual lesson of Eq. (16) is that if  $n_{eff}$  and  $c_v^t$  obtained from an EOS or molecular model are both correct, the residual entropy will also be correct. Conversely, if the values of  $s^+$  are thought to be correct and the  $n_{eff}$  is correct, the isochoric heat capacity should also be correct. However, experimental measurements of heat capacities for fluids are often characterized by relatively large experimental uncertainties and inconsistency and, in many cases, by a complete lack in the open literature.

At temperatures well above the critical temperature,  $n_{\text{eff}}$  depends only relatively weakly on density,<sup>31</sup> and the representation of the residual entropy is therefore largely governed by the dilute-gas  $n_{\text{eff}}$ . For instance, in Fig. 9, for  $T > 10T_{\text{crit}}$ , the variation of  $n_{\text{eff}}$  is within roughly 30% of the infinite temperature limit of 12. This is why density scaling with a constant  $n$  works reasonably well when studying a narrow region in the liquid region of the phase diagram, but not otherwise. Following Eq. (16), if a model (equally an empirical equation of state or molecular model) correctly predicts the dilute-gas value for  $n_{\text{eff}}$ , the liquid phase residual entropy will be well represented. For liquid states, most of the variation in  $n_{\text{eff}}$  for the Lennard-Jones monomer corresponds to the region close to the critical point.

### B. Lennard-Jones dimer

The authors of Ref. 30 considered the  $n_{\text{eff}}$  in the dilute-gas limit for rigid linear chains with Lennard-Jones sites. The values of  $n_{\text{eff}}$  in this work were obtained by a similar method (integration with *potter* over three angles and center-of-mass separation) and are shown in Fig. 10. The fundamental difference between the Lennard-Jones monomer and dimer is only one of magnitude; the qualitative behavior is similar, and the vertical axis is mostly just scaled. In the infinite-temperature limit, the value of  $n_{\text{eff}}$  also approaches 12 because at sufficiently high temperatures the dominant interaction is the pairwise repulsion of two sites governed by an  $r^{-12}$  interaction.<sup>30</sup>

### C. Carbon dioxide

The molecular models used in this work for CO<sub>2</sub> are linear and rigid and do not allow for vibrational contributions to the energy. The dilute-gas limit of  $n_{\text{eff}}$  can therefore be obtained, as described above, from fourfold integration. Classical values of  $n_{\text{eff}}$  are shown

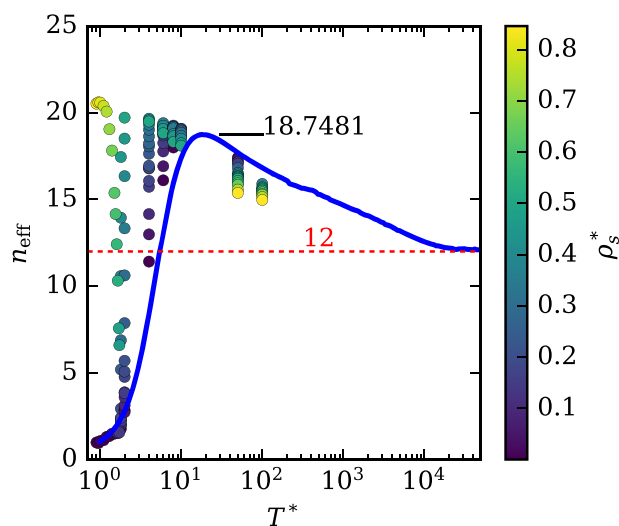


FIG. 10. Values of  $n_{\text{eff}}$  for the Lennard-Jones dimer fluid as a function of temperature and monomer density  $\rho_s^*$  (which is twice the reduced molecular density). The dilute-gas limit (solid curve) was taken from Ref. 30, and the markers are the simulation data from this work.

in Fig. 11 for the considered molecular models as a function of temperature. The *ab initio* potential of Hellmann<sup>45</sup> can yield very accurate predictions of the dilute-gas thermophysical properties (e.g., the second virial coefficient). As such, and especially given the physically sound basis of this model, it is believed that the values of  $n_{\text{eff}}$  from the Hellmann<sup>45</sup> model in the dilute-gas limit are therefore a suitable baseline for comparison with other models. The values of  $n_{\text{eff}}$  calculated from the model of Hellmann are smaller than those of the other models at all temperatures. The model of Errington (which has a more physically sound exponential repulsion as compared with the  $r^{-12}$  repulsion of the other models) is much closer than the other models, which are mostly consistent, but with larger values. The value of  $n$  for CO<sub>2</sub> proposed in the literature for density scaling<sup>4</sup> is 13.5 based upon density scaling of shear viscosity data in the liquid phase, which is near the peak value of 13.24 obtained for  $n_{\text{eff}}$  from the Hellmann<sup>45</sup> model.

Next, the values of  $n_{\text{eff}}$  from the molecular models are plotted as a function of temperature and density in Fig. 12. Given the qualitative similarities, only the results for the Merker *et al.* and Hellmann potentials are shown here; the remainder is provided in the [supplementary material](#). Many qualitative features of these results are similar to those of the Lennard-Jones fluid. At high temperatures ( $T/T_{\text{crit}} \gtrsim 20$ ),  $n_{\text{eff}}$  does not change much as the density is swept through a large range, and the temperature at the maximum of  $n_{\text{eff}}$  along an isochore does not depend strongly on the density; it is close to the maximum obtained from the dilute-gas calculations. The infinite temperature limit for CO<sub>2</sub> (unphysically neglecting dissociation) should be 3/2 (see the Appendix of Ref. 62), which holds for all potentials that are finitely valued at all separations. For the Hellmann model, the contributions to the potentials are divergent at a center-of-mass separation of zero, and a small hard core is required for each site-site interaction, which makes the infinite temperature limit go to infinity (see, for instance, the result for the square-well fluid in Ref. 30).

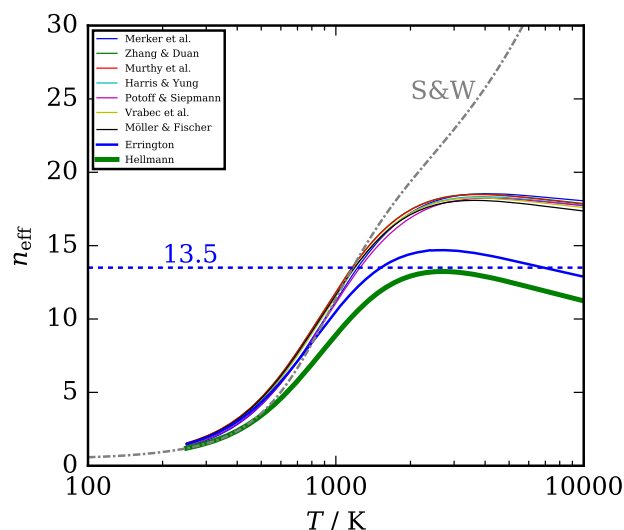


FIG. 11. Values of  $n_{\text{eff}}$  in the dilute-gas limit [from Eq. (12)] obtained by *potter* for the CO<sub>2</sub> molecular models and from the Span and Wagner<sup>56</sup> (SW) EOS.



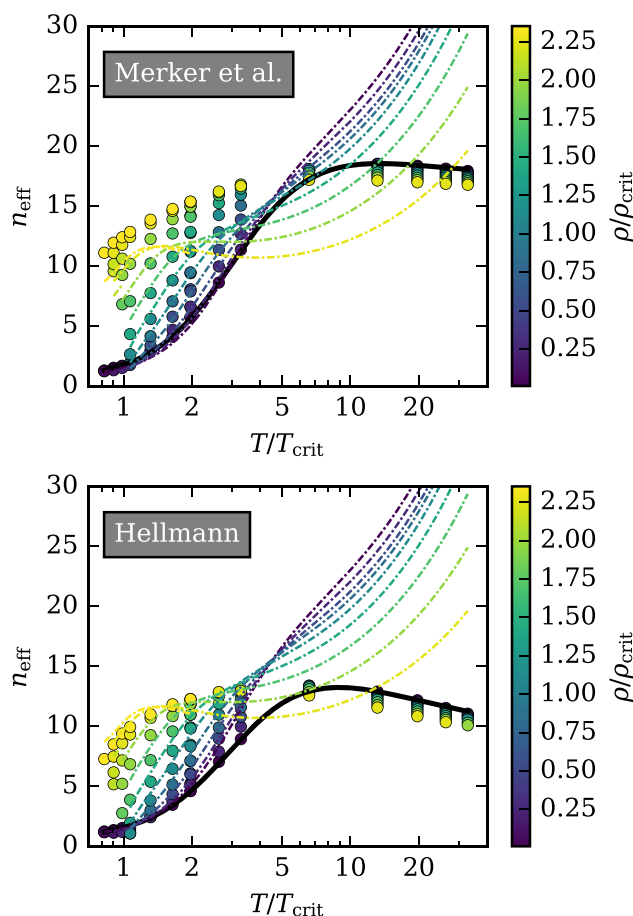


FIG. 12. Results for  $n_{\text{eff}}$  for  $\text{CO}_2$  from the molecular models of Merker *et al.*<sup>43</sup> and Hellmann.<sup>45</sup> The dashed-dotted curve for each isochore is the same quantity given by the Span and Wagner EOS.<sup>56</sup>

## VI. CONCLUSIONS

Density scaling and entropy scaling can be conceptually aligned by considering density scaling as a mapping onto the residual entropy. The optimal value of  $n$  to maximize the correlation between  $\Gamma$  and  $s^+$  appears to be linked to the maximum of  $n_{\text{eff}}$  in the dilute-gas limit. For the Lennard-Jones monomer fluid, the maximum is 15.06 (see Fig. 9), and the optimal scaling value is 15.9. For the Lennard-Jones dimer fluid, the maximum value is 18.7 (see Fig. 10), and the optimal scaling value is 17.5. For the Hellman model for  $\text{CO}_2$ , the maximum value is 13.24 and the optimal scaling value is 12.1. All scaling values are approximately within one unit of the maximum value of  $n_{\text{eff}}$ . This preliminary observation should be further studied in order to understand whether this relationship should be expected to hold in general. If so, it could offer a route to an entirely predictive approach for entropy scaling that does not require an equation of state or molecular simulation methods.

The persistent challenge of both density scaling and entropy scaling is that *a priori* predictions of the functional form of the

relationship between the scaled transport properties and the independent variable remain out of reach. In some cases (e.g., see Ref. 9), entropy scaling yields a very simple functional form (in that case, exponential), but an equation of state is required. The hope is that the observations in this work about the relationship between density scaling and entropy scaling might allow for a new empirical transport property modeling approach that is simpler to apply with a strong theoretical basis. For instance, it was observed for the Lennard-Jones monomer fluid, and indeed for many other fluids, that there is an approximately exponential relationship between macroscopically scaled viscosity times  $s^+$  to the power of 2/3 and the residual entropy.<sup>9</sup>

## SUPPLEMENTARY MATERIAL

The [supplementary material](#) includes additional figures of the other  $\text{CO}_2$  models, results on change of entropy upon dimerization, Python snippet for data processing, and critical region analysis. The complete set of molecular simulation results for  $\text{CO}_2$  and for the Lennard-Jones monomer and Lennard-Jones dimer models are provided in a zip archive.

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## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

### Author Contributions

**Ian H. Bell:** Conceptualization (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (lead). **Robin Fingerhut:** Data curation (equal); Resources (equal); Software (equal). **Jadran Vrabec:** Conceptualization (equal); Project administration (equal); Resources (equal); Supervision (equal); Writing – review & editing (equal). **Lorenzo Costigliola:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Software (equal); Writing – review & editing (equal).

## DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#), and linked code repositories, and from the corresponding author upon reasonable request.

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