Influence of repulsion on modified entropy scaling and density scaling of monatomic fluids

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Modified entropy scaling is applied to shear viscosity, self-diffusion coefficient and thermal conductivity of fluids consisting of spherical molecules. An extensive molecular dynamics simulation series is performed to obtain these transport properties and the residual entropy of three potential model classes with variable repulsive exponents: n, 6 Mie (n = 9, 12, 15and 18), Buckingham's exponential-six ($\alpha = 12$, 14, 18 and 30) and Tang-Toennies (α_T = 4.051, 4.275 and 4.600). A wide range of liquid and supercritical gas- and liquid-like states is covered with a total of 1120 state points. Comparisons to equations of state, literature data and transport property correlations are made. Although the absolute transport property values within a given potential model class may strongly depend on the repulsive exponent, it is found that the repulsive steepness plays a negligible role when modified entropy scaling is applied. Hence, the scaled transport properties of n, 6 Mie, exponentialsix and Tang-Toennies fluids lie basically on one master curve, which closely corresponds with entropy scaling correlations for the Lennard-Jones fluid. This trend is confirmed with literature data of n,6 Mie and exponential-six fluids. Further, entropy scaling holds for state points where the Pearson correlation coefficient R is well below 0.9. The condition R > 0.9 for strongly correlating liquids is thus not necessary for the successful application of entropy scaling, pointing out that isomorph theory may be a part of a more general framework that is behind the success of entropy scaling. Density (or thermodynamic) scaling is applied for the transport properties of these potential model classes as well, revealing a strong influence of the repulsive exponent on this scaling approach.

I. INTRODUCTION

The precise knowledge of thermophysical fluid behavior is vital for understanding natural processes and designing engineering applications. Molecular modeling and simulation techniques have become a key tool not only to predict the according properties but also to analyze the microscopic underpinnings giving rise to them. The success of these techniques depends on the underlying models describing the intermolecular interactions.

The most widely used pair potential that implicitly accounts for many-body intermolecular interactions, thus being an effective pair potential, was proposed by John E. Lennard-Jones $(LJ)^1$. It is simple and well suited for describing the interactions of non-polar fluids under moderate temperature and pressure conditions². Molecular models based on the LJ potential reasonably predict the thermophysical properties of many pure fluids and mixtures^{3–11}. For a comprehensive review of thermophysical data of the LJ fluid, see Refs. 12,13. While the attractive term of the LJ potential $\propto r^{-6}$ has a sound theoretical basis, as shown by Fritz Wolfgang London in 1930¹⁴, the repulsive term $\propto r^{-12}$ is predominantly used due to computational convenience, despite the fact that the structural properties of fluids are primarily influenced by the repulsive interactions¹⁵. Under supercritical conditions, those interactions are much softer than modeled with the LJ potential^{2,16}, which underscores the importance of correctly describing repulsion with pair potentials.

The repulsive exponent *n* within the two-parameter LJ potential (n = 12) can be varied, effectively transforming it into the more generalized three-parameter *n*,6 Mie potential. Extensive studies on the phase equilibria and thermodynamic properties of *n*,6 Mie fluids^{17–23} have been carried out, culminating in the development of SAFT-based²⁴, molecular simulation-based²⁵ and physically-based²⁶ equations of state (EoS). Recently, Fischer and Wendland²⁷ delved into the history of key empirical potentials since 1903.

A physically more appropriate alternative is to represent repulsion through an exponential term¹⁶, as known from molecular beam scattering data or quantum chemical studies. This strategy is reflected by Buckingham's exponential-six (exp-6) and the Tang-Toennies (TT) potential. The exp-6 potential may lead to improved vapor pressure²⁸ or shear viscosity²⁹ predictions than the LJ potential so that EoS for exp-6 fluids^{30–32} exist.

The functional form of the TT potential is more complex and similar to the *ab initio* pair potentials for argon³³ or krypton³⁴, which yield very accurate predictions for the thermophysical properties of these noble gases. Next to exponential repulsion, it contains the second-order dipole-

quadrupole contribution to dispersion and damping terms. Consequently, the TT potential was used to accurately predict the equilibrium properties of argon³⁵ or its bulk viscosity³⁶.

The transport properties of fluids that are described with most of these potentials are much less studied than those based on the LJ potential. About 15 years ago, Galliero and co-workers investigated the influence of the repulsive exponent of n,6 Mie and exp-6 fluids on shear viscosity and pressure^{37,38} as well as other thermophysical properties³⁹. Transport properties of n-paraffins modeled with the n,6 Mie potential were also studied¹⁷, but those of TT fluids have yet to undergo similar investigations.

Today, reliable predictive equations for transport properties are in heavy demand. Historically, the development of such equations lags behind those used to obtain time-independent equilibrium properties^{40,41}. Various models are employed to predict transport properties, often lacking a solid physical foundation and sufficient experimental data for parameterization. These include corresponding states approaches⁴², expanded fluid theory⁴³ or scaling models^{44–46}.

In 1977, Rosenfeld proposed that macroscopically reduced transport properties are solely a function of the residual entropy s^r of a given fluid⁴⁴. This semi-quantitative model, now called entropy scaling, was first revealed by molecular simulation of hard spheres, soft spheres and one-component plasma and later confirmed experimentally⁴⁷. Entropy scaling has a theoretical basis in isomorph theory⁴⁸, which indicates its applicability to strongly correlating liquids with a large Pearson correlation coefficient R > 0.9. However, it has been shown that fluids with a Pearson correlation coefficient well below the limiting value of R = 0.9 may still exhibit a univariate relationship between their scaled transport properties and residual entropy⁴⁹.

Recent years have witnessed an increasing interest in entropy scaling. Numerous modifications of the original Rosenfeld approach for liquids⁴⁴ and dilute gases⁴⁵ were proposed. To bridge the gap between these two aggregation states, Bell et al.⁴⁹ introduced the plus-scaled transport variables with an entropy-dependent correction factor using the 2/3 exponent, i.e. $(s^+)^{2/3} = (-s^r/k_B)^{2/3}$, where k_B is the Boltzmann constant. This modified entropy scaling approach was successfully applied to many fluids and mixtures^{49–57}. In other scaling procedures, the residual entropy $-s^r/k_B$ has been exchanged with a dimensionless entropy scaling variable $X_S = f(-s^r/k_B)$ related to the entropy of the fluid at the critical point^{53–55,58,59} or the SAFT-related number of segments^{60–62}.

In 1975, another scaling approach to represent the macroscopically reduced transport properties over the ratio of density to temperature, where the density is raised to an exponent γ , was revealed by a non-equilibrium molecular dynamics study of the LJ fluid by Ashurst and Hoover⁶³. This approach, later known as density (or thermodynamic) scaling⁶⁴, was extensively applied to n,6 Mie model fluids and their mixtures with different repulsive exponents^{22,65}, flexible Lennard-Jones chain models^{66,67} real fluids and ionic liquids^{46,66,68}. In contrast to entropy, temperature and density are properties that can be measured experimentally, and hence, are more accessible than the residual entropy for which elaborate EoS or molecular simulations are required. In this sense, density scaling is more straightforwardly applicable than entropy scaling. However, the density scaling exponent γ , is usually unknown *a priori*, and its suitable choice poses a challenge^{56,69}. Interestingly, a link between residual entropy and the density scaling exponent exists, connecting these two scaling approaches⁵⁶, so that density scaling can also be rationalized within the framework of isomorph theory^{65,70,71}.

The simple numerical handling of entropy scaling equations makes them compelling for the development of predictive equations for transport properties, as proposed e.g. for the LJ fluid⁴⁹. Although not universally applicable, entropy scaling has been broadly applied for the prediction of transport properties of pure fluids, mixtures and even active-matter systems^{51,62,72,73}. Recently, a correlation for the infinite dilution Fick coefficient of supercritical carbon dioxide mixtures was proposed on the basis of the modified entropy scaling approach⁷⁴. However, strongly associating fluids sometimes invalidate the univariate behavior between the macroscopically reduced transport properties and the residual entropy⁷⁵, mostly due to anomalies that are related to hydrogenbonding networks. Still, a reference-quality correlation for the shear viscosity of krypton was developed on the basis of entropy scaling⁵⁷.

Studies on entropy scaling tend to focus on the results generated with it and not on the features of the underlying pair potentials. This paper seeks to remedy this issue by analyzing model fluids with differing repulsive interactions embodied by the repulsive exponent: n,6 Mie (n = 9, 12, 15 and 18), exp-6 ($\alpha = 12$, 14, 18 and 30) and TT ($\alpha_T = 4.051$, 4.275 and 4.600). Monte Carlo (MC) and molecular dynamics (MD) simulations were conducted out to obtain vapor-liquid equilibria, residual entropy and transport properties of those 11 fluids. The latter were sampled over a wide range of the fluid domain, including sub- and supercritical isotherms and low- to high-density states. Subsequently, the modified entropy scaling approach was applied to present simulation and literature data, comparing them to the plus-scaled transport property correlations for the LJ fluid by Bell et al.⁴⁹. Further, density scaling was applied to the present simulation data, highlighting a larger impact of the repulsive exponent, which stands in contrast to the findings obtained for

entropy scaling. Finally, a link between both scaling approaches was established via the residual entropy.

II. METHODS

A. Model fluids

The present work considers spherical molecules with pairwise interactions defined by the n,6 Mie potential

$$u_{Mie}(r) = \frac{\varepsilon}{n-6} \left[6 \left(\frac{r_m}{r}\right)^n - n \left(\frac{r_m}{r}\right)^6 \right],\tag{1}$$

the exp-6 potential

$$u_{exp6}(r) = \frac{\varepsilon}{\alpha - 6} \left[6 \cdot \exp\left(\alpha(1 - \frac{r}{r_m})\right) - \alpha\left(\frac{r_m}{r}\right)^6 \right],$$
(2)

or the TT potential

$$u_{TT}(r) = A \exp\left(-\alpha_T r\right) - f_6(r) \frac{C_6}{r^6} - f_8(r) \frac{C_8}{r^8}.$$
(3)

Therein, ε is the depth of the potential well, r_m the value of the intermolecular distance r where the potential function has its minimum and the steepness of repulsion is determined by n, α or α_T , respectively, cf. Fig 1. Only the TT potential contains damping functions for the dispersive interactions

$$f_n(r) = 1 - \exp(-br) \sum_{k=0}^{l} \frac{(br)^k}{k!}.$$
(4)

A special case of the three-parameter *n*,6 Mie potential is the two-parameter LJ potential (n = 12), whereas the exp-6 potential has three (ε , r_m and α) and the TT potential has five adjustable parameters (A, α_T , b, C_6 and C_8). The reduced form of the intermolecular potentials (1) to (3) is given in Eqs. (S7) to (S9) of the Supporting Information (SI). An almost exact representation of the exp-6 potential with the TT potential is possible (see SI), while the representation of the exp-6 with the Mie potential is approximate^{76,77}.



FIG. 1: Interaction energy u/ε over distance r/r_m of selected *n*,6 Mie (black lines), exp-6 (blue lines) and TT (red lines) fluids with different repulsive exponents.

B. Molecular simulations

Present simulations were carried out in reduced units (see Table S1) with the open-source software $ms2^{78}$ that allows for simultaneous sampling of equilibrium and transport properties. Initially, MC simulations of the vapor-liquid equilibria were conducted with the grand equilibrium method⁷⁹ and the NpT+SVC method⁸⁰ to clarify where the aggregation states are located. MD simulations in the canonical (NVT) ensemble were performed to sample transport properties, residual entropy and Pearson correlation coefficient. At a given pair of temperature T and density ρ , simulation provided the residual, i.e. potential, energy u^r and the residual pressure p^r , while the residual chemical potential μ^r was obtained by Widom's insertion method⁸¹. The residual entropy s^r was calculated from $s^r = -(\mu^r - u^r - p^r/\rho)/T$.

NVT simulations of the *n*,6 Mie and exp-6 fluids with different repulsive exponents were carried out along four isotherms $T/T_c \approx 0.8, 1.1, 2.0$ and 4.0 for up to 36 densities ranging from $\rho/\rho_c \approx 0.083$ to 3. The subcritical isotherm $T/T_c \approx 0.8$ was simulated at about 11 densities rang-

ing from $\rho/\rho_c \approx 2$ to 3. A total of 11 potential models with different repulsive exponents of *n*,6 Mie (*n* = 9, 12, 15 and 18), exp-6 (α = 12, 14, 18 and 30) and TT (α_T = 4.051, 4.275 and 4.600) fluids was considered, cf. Fig. 1. Simulations for the TT fluids were conducted along three supercritical isotherms $k_BT/\varepsilon \approx 1.9$, 3.0 and 6.0 at about 21 densities ranging from $\rho/\rho_c \approx 0.05$ to 3.2. Simulations that turned out to be in the solid state were identified by visual inspection of the mean squared displacement and the non-Gaussian parameter on the basis of the approach given by Mausbach et al.⁸², which is outlined in Fig. S1. Those simulations were discarded from further analyses. Exemplarily, the sampled state points of the exp-6 potential with α = 30 are depicted in Fig. 2.



FIG. 2: Residual entropy of the exp-6 fluid ($\alpha = 30$) from present simulations in the considered state space. The solid line depicts the vapor-liquid equilibrium curve calculated with the EoS from Kataoka³⁰ using the open-source library *teqp*⁸³.

C. Entropy scaling

Rosenfeld⁴⁴ postulated that a univariate relationship between a macroscopically reduced transport property $\tilde{\psi}$ and the dimensionless residual entropy s^r of the form $\tilde{\psi} \propto \exp(-s^r/k_B)$ exists. It should be noted that the term "excess-entropy", which is the difference of mixture behavior from that of an ideal solution, is often used in the physics community instead of the more suitable term residual entropy. The residual entropy s^r is the difference between the total entropy s and the ideal gas contribution s^{id} at the same temperature and density, i.e. $s^r(T,\rho) \equiv s(T,\rho) - s^{id}(T,\rho)$. The residual entropy is negative, characterizes the number of accessible microstates⁸⁴ and is thus a measure for the microscopic structure of the fluid.

Macroscopically reduced shear viscosity $\tilde{\eta}$, self-diffusion coefficient \tilde{D} and thermal conductivity $\tilde{\lambda}$ following Rosenfeld^{44,45} are given by

$$\widetilde{\eta} = \eta \cdot \frac{\rho^{-2/3}}{(mk_B T)^{1/2}},\tag{5}$$

$$\widetilde{D} = (\rho D) \cdot \frac{\rho^{-2/3}}{(k_B T/m)^{1/2}},$$
(6)

$$\widetilde{\lambda} = \lambda \cdot \frac{\rho^{-2/3}}{k_B (k_B T/m)^{1/2}},\tag{7}$$

where ρ is the number density and *m* the mass of one molecule. These macroscopically reduced properties are sometimes referred to as Rosenfeld-scaled properties. However, they diverge in the zero-density limit.

Bell et al.⁴⁹ proposed a modified entropy scaling approach of the form $\psi^+ = \tilde{\psi} \cdot (s^+)^{2/3}$, where $\tilde{\psi}$ is the macroscopically reduced transport property⁴⁴ and $s^+ = -s^r/k_B$. Hence, the following scaled transport properties arise from this approach

$$\eta^+ = \widetilde{\eta} \cdot (s^+)^{2/3},\tag{8}$$

$$D^+ = \widetilde{D} \cdot (s^+)^{2/3},\tag{9}$$

$$\lambda^{+} = \widetilde{\lambda} \cdot (s^{+})^{2/3}.$$
 (10)

These scaled transport properties are commonly referred to as the plus-scaled, novel-scaled or Bell-scaled properties. They were proposed to smoothly connect the distinct gas-phase and liquid-phase entropy scaling approaches proposed by Rosenfeld^{44,45}. For the transport properties of the LJ fluid, Bell et al.⁴⁹ developed correlations on the basis of a fitting procedure for the residual entropy range $1 \le s^+ \le 3$

$$\eta_{IJ}^{+} = 0.2163 \cdot \exp\left(1.068 \cdot s^{+}\right),\tag{11}$$

$$D_{LJ}^{+} = 0.494 \cdot \exp\left(-0.402 \cdot s^{+}\right), \tag{12}$$

$$\lambda_{IJ}^{+} = 1.377 \cdot \exp\left(0.839 \cdot s^{+}\right). \tag{13}$$

Bell's modified entropy scaling approach is suitable for the construction of engineering correlations for transport properties based on the zero-density, residual and critical contribution $\psi^+ = \psi^+_{\rho\to 0}(T) + \psi^{r+}(s^r) + \psi^+_c$, cf. Refs. 49,50,57.

In the zero-density limit, the thermodynamic contribution of the plus-scaled transport properties can be expressed in terms of the second virial coefficient *B* by $\lim_{\rho\to 0} (s^+/\rho) = B + T \cdot dB/dT$ as described in Ref. 50. Making that substitution yields the scaled variables in the zero-density limit of

$$\lim_{\rho \to 0} \eta^{+} = \frac{\eta_{\rho \to 0}}{(mk_{\rm B}T)^{1/2}} \left[B + T\left(\frac{\mathrm{d}B}{\mathrm{d}T}\right) \right]^{2/3} \tag{14}$$

$$\lim_{\rho \to 0} D^{+} = \frac{(\rho D)_{\rho \to 0}}{(k_{\rm B} T/m)^{1/2}} \left[B + T \left(\frac{{\rm d}B}{{\rm d}T} \right) \right]^{2/3}$$
(15)

$$\lim_{\rho \to 0} \lambda^{+} = \frac{\lambda_{\rho \to 0}}{k_{\rm B} (k_{\rm B} T/m)^{1/2}} \left[B + T \left(\frac{\mathrm{d}B}{\mathrm{d}T} \right) \right]^{2/3} \tag{16}$$

The second virial coefficient contribution can either be obtained from integration of the potential⁵⁰ or closed form solutions^{85,86}, while $\eta_{\rho\to 0}$, $(\rho D)_{\rho\to 0}$ and $\lambda_{\rho\to 0}$ with correlations for the collision integrals^{87,88}.

D. Density scaling

Density scaling has the advantage that it does not require the rather elusive entropy⁵⁶ and is based on the observation relaxation times and other dynamic properties of high-density fluids are mainly governed by the repulsive part of the interaction potential⁴⁶. Hence, if the potential is given by an inverse power law (IPL) of the form $u(r) \propto r^{-n}$, its macroscopically reduced transport properties are strictly a function of temperature and density of the form $\tilde{\psi} \propto \rho^{\gamma}/T$, where $\gamma = n_{ds}/3$ is a fluid-specific parameter^{89,90}. Fluids consisting solely of repulsive IPL potentials lead to exact isomorphs, i.e. lines of constant structure and dynamics along which the density scaling variable ρ^{γ}/T , i.e. the density scaling exponent n_{ds} , is constant⁹¹. Density scaling is only approximately obeyed by fluids with both attractive and repulsive molecular interactions, e.g. model fluids and their mixtures^{22,65-67} as well as real fluids and ionic liquids^{46,66,68}. Density scaling suffers from the thermodynamic state-dependence of the density scaling exponent γ , as confirmed by experiments⁹² and molecular simulations⁹³. Further, it was shown that the use of a constant density scaling exponent $\gamma = n_{ds}/3$ can transform the unique variable of density scaling into an univariate function of residual entropy⁵⁶. Nonethless, the determination of this coefficient poses a major challenge for the applicability of density scaling.

Based on molecular simulation data of LJ fluids and nine different CO_2 potential models, the density scaling exponent was found to be related to the maximum of the effective hardness of a fluid in the dilute gas limit⁵⁶. The effective hardness n_{eff} expresses the effective repulsive interaction between molecules and is a function of the ensemble averages that can be sampled with molecular simulation and the Lustig formalism^{78,94,95}

$$\gamma_{\rm eff} = \frac{n_{\rm eff}}{3} = \frac{1}{\rho c_v^{\rm r}} \left(\frac{\partial p^{\rm r}}{\partial T}\right)_{\rho} \tag{17}$$

where p^r is the residual pressure and c_v^r is the residual isochoric capacity. In the zero-density limit, the effective hardness can be calculated with the second virial coefficient $B^{85,96}$

$$\lim_{\rho \to 0} n_{\text{eff}} = -3 \cdot \frac{T \frac{\mathrm{d}B}{\mathrm{d}T} + B}{2T \frac{\mathrm{d}B}{\mathrm{d}T} + T^2 \frac{\mathrm{d}^2B}{\mathrm{d}T^2}}.$$
(18)

III. RESULTS

A. Vapor-liquid equilibria

Fig. 3 depicts the vapor-liquid equilibria of the studied *n*,6 Mie, exp-6 and TT fluids obtained with molecular simulation and literature EoS. Present simulation data are in excellent agreement with the Mie EoS from Pohl et al.²⁵ and Reimer et al.²⁶, where the latter was obtained with the *FeOs* package⁹⁷. More comparisons with literature data are given in the SI, cf. Fig. S2. Guggenheim-type correlations were employed to determine the critical point of the exp-6 and TT fluids. Because the TT fluid with $\alpha_T = 4.2751$ resembles argon³⁵, it agrees excellently with the according reference EoS by Tegeler et al.⁹⁸. Additional representations of these phase equilibria in pressure-temperature diagrams are given in Figs. S3 to S5.

B. Entropy scaling

The modified entropy scaling approach was applied to 1120 state points for which the shear viscosity, self-diffusion coefficient, thermal conductivity and residual entropy were sampled in this work. Fig. 4 shows the plus-scaled shear viscosity over the residual entropy for the entire present dataset for n,6 Mie, exp-6 and TT fluids. Remarkably, the plus-scaled shear viscosity of those fluids with a wide range of repulsive exponents falls onto the same master curve as the LJ correlation.

To further validate this finding, the modified entropy scaling approach was applied to 385 additional shear viscosity data points from non-equilibrium MD for *n*,6 Mie and exp-6 fluids with variable repulsive parameters published by Galliero et al.^{37,38}, see Table S4 and Fig. S6. These data were supplemented with residual entropy values obtained either by present simulations or the EoS of Pohl et al.²⁵. The literature non-equilibrium MD data by Galliero et al.^{37,38} also agree excellently with the plus-scaled shear viscosity correlation for the LJ fluid. This approach was also applied to a very recent and comprehensive database on self-diffusion coefficient (17212 data points), shear viscosity (14288 data points) and thermal conductivity (13099 data points) of *n*,6 Mie fluids (*n* = 7 to 34) by Chaparro and Müller⁹⁹, cf. Figs. S7 to S9. These authors used the Einstein relations to compute the transport properties and studied the *n*,6 Mie fluids over a significantly larger repulsive exponent range. Their data are in excellent agreement with present simulations, confirming that the repulsive exponent plays a negligible role for the modified entropy



FIG. 3: Vapor-liquid equilibria of *n*,6 Mie (top), exp-6 (center) and TT (bottom) fluids. Open circles: present simulation data for different repulsive exponents *n*, α and α_T from blue (*n* = 9, α = 12 and α_T = 4.051) to red (*n* = 18, α = 30 and α_T = 4.600). Solid lines: empirical *n*,6 Mie EoS from Pohl et al.²⁵ and present Guggenheim-type correlations for the exp-6 and TT fluids (see Table S3). Dashed lines: physically-based *n*,6 Mie EoS from Reimer et al.²⁶ obtained with the *FeOs* package⁹⁷ and the reference EoS for argon from Tegeler et al.⁹⁸ for the TT fluid with

scaling approach.



FIG. 4: Plus-scaled shear viscosity η^+ over residual entropy s^+ from the entire present simulation dataset: *n*,6 Mie (triangles), exp-6 (circles) and TT (squares). The blue solid line depicts the correlation for the LJ fluid⁴⁹.

The variation of the repulsive exponent has a strong influence on the absolute value of the shear viscosity of a given fluid class. For a consistent comparison between fluids with different repulsive exponents, the same temperature and density pairs, which are reduced by their critical values, were taken as a reference. For instance, the shear viscosity values of the exp-6 ($\alpha = 12$) fluid and exp-6 ($\alpha = 30$) fluid at these reference pairs differ on average by 32% with a maximum deviation of 167%. This difference largely vanishes when entropy scaling is applied. The absolute average relative deviation between the plus-scaled shear viscosity of those two exp-6 fluids at state points with a similar residual entropy is only 5.5%, which is in the same order of magnitude as statistical uncertainties.

In contrast to the shear viscosity, self-diffusion coefficient and thermal conductivity in their plus-scaled form show more pronounced discrepancies with the LJ correlation ⁴⁹ when the entire

residual entropy range is considered, see Figs. S10 and S11. However, within the residual entropy range $1 \le s^+ \le 3$, the consistency between these scaled properties and the LJ correlations remains strong. It deteriorates in the zero-density limit ($s^+ \rightarrow 0$) and at high density ($s^+ \rightarrow 4$). Both the plus-scaled self-diffusion coefficient and thermal conductivity of the exp-6 and *n*,6 Mie fluids yield absolute average relative deviations that are significantly larger than those of the shear viscosity with about 11.3% and 16.4%, respectively.

For a more accurate description of the present simulation data, new empirical correlations for the plus-scaled self-diffusion coefficient and thermal conductivity were fitted over the residual entropy range $0 \le s^+ \le 4$

$$D^{+} = 0.0602 \cdot (s^{+} + 2)^{2.3901} \cdot \exp(-0.9843 \cdot s^{+}), \tag{19}$$

$$\lambda^{+} = 4 \cdot 10^{-5} \cdot (s^{+} + 4)^{7.1869} \cdot \exp\left(-0.38883 \cdot s^{+}\right).$$
⁽²⁰⁾

Because these correlations have a more complex form, they result in absolute average relative deviations for the plus-scaled self-diffusion coefficient and thermal conductivity that are reduced to 2.3 % and 5.8 %, respectively, in comparison to the LJ correlations. A similar assessment of the simulation database of Chaparro and Müller⁹⁹ indicates a reduction in the absolute average relative deviations for the plus-scaled self-diffusion coefficient are reduced from 14.2% to 5.8% and for plus-scaled thermal conductivity from 12.1% to 9% by using present correlations instead of the LJ correlations.

Fig. 5 depicts the plus-scaled shear viscosity, self-diffusion coefficient and thermal conductivity of *n*,6 Mie fluids with different repulsive exponent α compared with the LJ correlation for η^+ and the present correlations (19) and (20) for D^+ and λ^+ . The plus-scaled transport properties of the *n*,6 Mie fluids agree excellently with the LJ correlation and present correlations, respectively. A similar behavior of the scaled transport properties is observed for the exp-6 and TT fluids, cf. Fig. 6 and Fig. 7. The inclusion of the physically more sound repulsive term in the exp-6 potential and the attractive term in the TT potential does not significantly affect the entropy scaling behavior in comparison to the *n*,6 Mie fluids. A statistical comparison of all sampled transport properties against the LJ and present empirical correlations is given in the SI, cf. Figs. S12 and S17.

The classical Rosenfeld scaling approach was also applied to the present simulation data, cf. Figs. S18 to S20. The main drawback of this approach is the divergence of all three transport properties in the zero-density limit, which does not occur for the plus-scaled transport properties. Further, the modified entropy scaling has a clearly defined limit at zero density and maintains the macroscopic scaling throughout all fluid states. Hence, it can be confirmed that modified entropy scaling is more appropriate.



FIG. 5: Plus-scaled shear viscosity (top), self-diffusion coefficient (center) and thermal conductivity (bottom) of *n*,6 Mie fluids with different repulsive exponents n = 9 (light grey circles), 12 (grey triangles), 15 (dark grey squares) and 18 (black diamonds). Solid lines: plus-scaled shear viscosity correlation for the LJ fluid⁴⁹ (blue) and present correlations for the plus-scaled self-diffusion coefficient and thermal conductivity (red).

To build reference correlations for the shear viscosity, often additional terms, like the zerodensity limit contribution, have to be included. Fig. 8 compares the scaled residual shear viscosity of the sampled *n*,6 Mie fluids to the polynomial correlation for the scaled residual shear viscosity of the LJ fluid⁴⁹. The same comparison was made for the exp-6 fluids with $\alpha = 12$ and 14, cf. Fig. S21. Plus-scaled transport properties in the zero-density limit were obtained from Eqs. (14)



FIG. 6: Plus-scaled shear viscosity (top), self-diffusion coefficient (center) and thermal conductivity (bottom) of exp-6 fluids with different repulsive exponents $\alpha = 12$ (light grey circles), 14 (grey triangles), 18 (dark grey squares) and 30 (black diamonds). Solid lines: plus-scaled shear viscosity correlation for the LJ fluid⁴⁹ (blue) and present correlations for the plus-scaled self-diffusion coefficient and thermal conductivity (red).

to (16), cf. Figs. S22 and S23. An offset value of unity was added to the scaled residual viscosity facilitating semi-log plotting⁴⁹. Here too, an excellent agreement between the scaled simulation data and the correlation is found almost over the entire residual entropy range. Both approaches capture the zero-density limit well, whereas the deviations increase for $s^+ > 3$, because the LJ correlation was not fitted to data in that range.



FIG. 7: Plus-scaled shear viscosity (top), self-diffusion coefficient (center) and thermal conductivity (bottom) of TT fluids with different repulsive exponents $\alpha_T = 4.051$ (light grey circles), 4.275 (grey triangles) and 4.600 (black diamonds). Solid lines: plus-scaled shear viscosity correlation for the LJ fluid⁴⁹ (blue) and present correlations for the plus-scaled self-diffusion coefficient and thermal conductivity (red).

C. Pearson correlation coefficient

Isomorph theory applies to "strongly correlating systems", or "Roskilde (R)-simple fluids". These systems have a large Pearson correlation coefficient R > 0.9 and their phase diagram features isomorphs, representing lines of constant residual entropy. For R-simple fluids along isomorphs, structure and dynamics in macroscopically reduced units are invariant⁹¹. In other words, entropy scaling means that microscopic dynamics at state points with the same residual entropy,



FIG. 8: Plus-scaled residual shear viscosity of *n*,6 Mie fluids with different repulsive exponents n = 9 (circles), 12 (triangles), 15 (squares) and 18 (diamonds). The zero-density contribution to the shear viscosity in first-order approximation was calculated with the approach from Ref. 50. The blue solid line represents the correlation for the LJ fluid⁴⁹.

although at different temperature and density, is approximately the same⁴⁷. This condition was shown to be only sufficient for the applicability of entropy scaling⁴⁹, thus promoting the need to further understand the theoretical basis behind the success of the entropy scaling approach. Density scaling, like entropy scaling, strictly holds for (R)-simple fluids.

The Pearson correlation coefficient *R* is given by 70,100

$$R = \frac{\langle \Delta U \Delta W \rangle}{\sqrt{\langle (\Delta U)^2 \rangle \langle (\Delta W)^2 \rangle}},\tag{21}$$

where ΔU and ΔW are the fluctuations of the instantaneous values of potential energy and virial from their average values, respectively. The Pearson correlation coefficient *R* can also be evaluated from experimental data using some approximations⁷⁰.

Fig. 9 shows the Pearson correlation coefficient *R* over residual entropy s^+ for the considered *n*,6 Mie fluids. Similar plots for the exp-6 and TT fluids are given in the SI, cf. Figs. S24 and S25.



FIG. 9: Pearson correlation coefficient *R* over residual entropy s^+ and varying temperature $k_B T/\varepsilon$ for *n*,6 Mie fluids with different repulsive exponents n = 9 (circles), 12 (triangles), 15 (squares) and 18 (diamonds). The dashed line depicts R = 0.9, above which the potential energy and virial fluctuations are strongly correlated.

As expected, state points at both high temperature and high density exhibit a strong correlation between the potential energy and virial fluctuations, i.e. R > 0.9. The Pearson correlation coefficient increases with temperature, and thus, entropy scaling becomes more successful. Moreover, lower repulsive exponents *n* at the same temperature and density yield a higher Pearson correlation coefficient *R*. Although a total of 568 state points from all 11 fluids exhibit R > 0.9, the number of state points deviating less than 6 % from the shear viscosity correlation for the LJ fluid is notably higher at 824, surpassing the former by about 50 %. Consequently, the condition R > 0.9 from isomorph theory is sufficient, but not indispensable for the successful application of the entropy scaling approach.



FIG. 10: Residual entropy s^+ (top) and plus-scaled shear viscosity (bottom) over density scaling variable $\Gamma^{1/3.3}$ for the entire present simulation dataset of *n*,6 Mie (dark grey), exp-6 (black) and TT (brown) fluids. Symbols: n = 9 (triangles down), n = 12 (triangles right), n = 15 (triangles left), n = 18 (triangles up), $\alpha = 12$ (circles), $\alpha = 14$ (squares), $\alpha = 18$ (pentagons), $\alpha_T = 4.051$ (crosses), $\alpha_T = 4.275$ (pluses) and $\alpha_T = 4.600$ (hexagons). The density scaling exponent γ was chosen to maximize the Spearman correlation between Γ and s^+ for state points with R < 0.5.

D. Density scaling

Fig. 10 shows the residual entropy s^+ and the plus-scaled shear viscosity η over the density scaling variable $\Gamma = (\rho r_m^3)^{\gamma}/(k_B T/\epsilon)$ for the 11 model fluids sampled in this work. Following density scaling, the exponent $\gamma = n_{\rm ds}/3$ was held constant in the entire phase diagram of each fluid⁵⁶. Here, $n_{\rm ds}$ was optimized to increase the Spearman rank correlation coefficient⁵⁶ between $\Gamma = (\rho r_m^3)^{\gamma}/(k_B T/\epsilon)$ and s^+ to a value greater than 0.999 for state points that have R > 0.5, cf. Table S5. Further, following Ref. 56, to achieve a linear relationship between the residual entropy and density scaling variable, the latter was scaled with the exponent 1/3.3.

Fig. 10 shows an almost linear relationship between s^+ and Γ as well as $\log(\eta^+)$ and Γ for each individual fluid. Two plots therein look similar, which is mirrored by a linear relationship between η^+ and s^+ in the semi-log plot of Fig. 4, connecting density scaling and entropy scaling. Hence, as expected, the repulsive exponent plays a major role in density scaling, making it less effective than entropy scaling. For the former approach, the data set of one fluid corresponds to one curve in the diagram, whereas in the latter, all fluids virtually fall onto the same master curve. These trends are further validated by the plus-scaled self-diffusion coefficient and thermal conductivity, cf. Figs. S26 and S27. Further, the nearly linear relationship between s^+ and Γ , as well as $\log(\eta^+)$ and Γ , is valid even for state points with a low Pearson correlation coefficient $R \ll 0.9$.

Density scaling has the major advantage that the variables temperature and density are more accessible than the residual entropy. Still, an *a priori* choice of a constant density scaling exponent remains a challenge, as the effective hardness n_{eff} significantly depends on the state point, cf. Figs. S28 to S30. To address this issue, the effective hardness in the zero-density limit can be used instead. For the studied *n*,6 Mie fluids, the solution of Eq. (18) with second virial coefficient data by Sadus^{85,86} yields $n_{\text{eff}} = 12.25, 15.06, 17.93$ and 20.83, cf. Fig. S28. These values do not differ much from the optimized values of $n_{\text{ds}} = 12.9, 16.15, 18.66$ and 22.03, cf. Table S5.

IV. CONCLUSIONS

This work shows that modified entropy scaling is largerly insensitive to the pair potential type, which accounts for both attractive and repulsive interactions. Hence, the variation of the repulsive exponent has generally a negligible influence on the univariate relationship between the plusscaled transport properties and the residual entropy. This insight result from an extensive molecu-

lar simulation study of 11 model fluids with different repulsive exponent and from the assessment of literature data for the *n*,6 Mie (n = 9 to 34) and exp-6 ($\alpha = 11$ to 22) fluids. Consequently, the correlation developed for the LJ fluid by Bell et al.⁴⁹ captures the plus-scaled shear viscosity of *n*,6 Mie, exp-6 and TT fluids in the residual entropy range $1 \le s^+ \le 3$ excellently. Further, empirical correlations for the plus-scaled self-diffusion coefficient and thermal conductivity of *n*,6 Mie, exp-6 and TT fluids were proposed on the basis of present simulation data for $0 \le s^+ \le 4$, These three correlations can be used as an orientation for the development of practical entropy scaling correlations.

Further, entropy scaling can indeed be applied to state points in the supercritical gas phase, where the Pearson correlation coefficient *R* is well below 0.9. This confirms that R > 0.9 is a sufficient, but not a necessary condition for the successful application of entropy scaling. In other words, there seems to be a more general framework to explain the success of entropy scaling than isomorph theory from which the condition R > 0.9 condition stems.

On the other hand, density scaling is significantly influenced by the repulsive exponent of a given pair potential. The major advantage of density scaling lies in its more accessible parameters temperature and density, but the density scaling exponent is mostly unknown *a priori*. Density scaling and entropy scaling can be connected via the residual entropy for one specific repulsive exponent within a given model class.

These findings are poised to make a significant contribution to the field of entropy and density scaling. In summary, they underscore the necessity for uncovering the underlying reasons behind the remarkable success of the entropy scaling methodology in numerous practical engineering applications. We hope for this research to advance our comprehension in this area and facilitate the development of practical and effective transport property correlations for real fluids and mixtures.

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DATA AVAILABILITY STATEMENT

Excel files containing all the data generated or analyzed during this study are included in the Supporting Information.