

Entropy Scaling of Viscosity – II: Predictive Scheme for Normal Alkanes [†]

Ian H. Bell*

*Applied Chemicals and Materials Division, National Institute of Standards and Technology,
Boulder, CO 80305*

E-mail: ian.bell@nist.gov

Abstract

In this work, a residual entropy value $6/10$ of the way between the critical point and a value of $-2/3$ of Boltzmann’s constant is shown to collapse the scaled viscosity for the family of normal alkanes. Based on this approach, a nearly universal correlation is proposed that can reproduce 95% of the experimental data for normal alkanes within $\pm 18\%$ (without removal of clearly erroneous data). This universal correlation has no new fluid-specific empirical parameters and is based on experimentally accessible values. This collapse is shown to be valid to a residual entropy half way between the critical point and the triple point, beyond which the macroscopically-scaled viscosity has a super-exponential dependence on residual entropy, terminating at the triple point.

A key outcome of this study is a better understanding of entropy scaling for fluids with intramolecular degrees of freedom. A study of the transport and thermodynamic properties at the triple point rounds out the analysis.

1 Introduction

The viscosity of hydrocarbons have been intensively studied over the years due to their importance to the petroleum industry and other allied fields. Hydrocarbons range between gases,

liquids, and even solids at room temperature depending on their carbon number and branching. In this work the focus is on the homologous series of normal alkanes, and in particular the focus rests on the viscosity in the liquid phase; the analysis connects to the gaseous phase. This family is sufficiently well-studied by high-quality measurements that the physics can be investigated in some detail.

Empirical models for the viscosity of normal alkanes have been developed over the years, and the Properties of Gases and Liquids¹ provides a summary of the modeling efforts up to the year 2000, including the TRAPP method, the Chung method, etc. A more modern review is that of Ref. 2. The previous paper in this series³ highlights that many of the previously considered approaches for empirical viscosity model development have strong links to the residual entropy.

An important question that this work investigates empirically is how the dynamics of molecular fluids change as a function of residual entropy, and in particular the chain length dependence. A conclusive answer to this question will hopefully open the door to a new generation of empirical models with a strong link to equilibrium thermodynamics.

1.1 Entropy Scaling

The work of Rosenfeld⁴ ambitiously posited, based on the minimal molecular dynamics data available at the time, a universal relationship

[†]Contribution of the National Institute of Standards and Technology, not subject to copyright in the US

between the macroscopically scaled viscosity (a transport property) and the residual entropy (an equilibrium thermodynamic property) for atomic liquids; this universal relationship does not hold for molecular fluids.⁵ The macroscopically reduced viscosity is defined by

$$\tilde{\eta} \equiv \frac{\eta}{\rho_N^{2/3} \sqrt{m k_B T}} \quad (1)$$

in which η is the shear viscosity, ρ_N is the number density (the number of particles per unit volume), m is the mass of one particle, k_B is Boltzmann’s constant, and T is the temperature. In the case of atomic fluids (Rosenfeld’s focus), the dimensional scales are those of the liquid phase (length: $\rho_N^{-1/3}$, energy: $k_B T$, time: $\rho_N^{-1/3} \sqrt{m/(k_B T)}$),⁶ yielding a scaling term of $\rho_N^{2/3} \sqrt{m k_B T}$ for viscosity (with dimensions of mass/(length $\times$ time)). The “correct” dimensional scales for polyatomic molecules are not as straightforwardly defined, but it is common practice⁷ to use m as the mass of one molecule, and ρ_N the number of molecules per volume, as will be done here.

The independent variable of entropy scaling is the residual entropy, which is defined as the entropy minus that of the ideal gas at the same temperature and density

$$s^r \equiv s(T, \rho_N) - s^{(\text{ig})}(T, \rho_N) \quad (2)$$

where s is the entropy per molecule, and $s^{(\text{ig})}$ is the ideal-gas entropy per molecule. The ideal gas entropy has both temperature and density dependence; see for instance Eq. 6 of Ref. 8. In the physics community, s^r is referred to as the excess entropy, but “excess” properties have a particular meaning in chemical thermodynamics.⁹ In order to avoid circumlocutions like “the negative of the residual entropy is increasing”, to simplify the conceptual model, and to simplify the nomenclature, the scaled residual entropy term is therefore defined by

$$s^+ \equiv -s^r/k_B \quad (3)$$

The recent years have seen a groundswell of interest in entropy scaling, as indicated by a recent review on the topic.¹⁰ The research group

of Jeppe Dyre has built a theoretical basis to entropy scaling from their isomorph theory,^{11–15} which makes a link between reduced structure in the fluid, residual entropy, and scaled transport properties.

The most clear precursor of the present study is the Novak scaling approach^{16–19} in which the viscosity was divided by the dilute gas viscosity, and this quantity then expressed as a function of the residual entropy. In the same lineage, this approach was further extended by the wide-ranging group-contribution methods developed by the group of Joachim Gross using as their basis the PCP-SAFT equation of state, and also then considering self-diffusion and thermal conductivity in a similar empirical framework.^{20–25}

The divergence of the scaled viscosity as the density approaches zero in Eq. (1) is a nuisance for practical applications.^{20,22,26} The most popular solution to the divergence problem is to divide by the dilute-gas viscosity rather than $\rho_N^{2/3} \sqrt{m k_B T}$. This approach cannot be recommended because it does not employ the correct dimensional scales; the transport properties should be divided by the appropriate length, energy, and time scales of the liquid phase. Otherwise, significant non-monovariability is found in the liquid phase for small molecules (e.g., see Fig. S5 from the SI of Ref. 5).

1.2 Modified Entropy scaling

Later work of Rosenfeld²⁷ provided the path to follow. He noted that $\tilde{\eta}$ is proportional to $(s^+)^{-2/3}$ for dilute gases of finite density modeled by inverse-power-law potentials (sometimes called the soft sphere model). This theme has been further explored in detail for other “simple” potentials.²⁸ In order to reconcile the results with the liquid phase, the term

$$\eta^+ \equiv \tilde{\eta} \times (s^+)^{2/3} \quad (4)$$

is therefore defined^{5,26} with the characteristic that it a) retains the correct scaling in the liquid phase for small molecules and b) does not diverge at zero density. This scaling approach was explored in detail in Ref. 26 for the Lennard-Jones fluid, and first used with-

out further study in Ref. 5. While the modified entropy scaling approach does not have a theoretical basis in the liquid phase, when $\tilde{\eta}$ is a monovariate function of s^+ , η^+ should also be.

The dilute gas limit of this scaling is^{26,28}

$$\eta_{\rho_N \rightarrow 0}^+ \equiv \frac{\eta}{\sqrt{mk_B T}} \left[B_2 + \left(\frac{dB_2}{d \ln(T)} \right) \right]^{2/3} \quad (5)$$

in which B_2 is the second virial coefficient of the virial expansion for the compressibility factor as a function of number density.

In order to ensure the formulation matches the ideal gas limit, $\eta_{\rho_N \rightarrow 0}^+$ is subtracted from η^+ , rather than dividing the viscosity by the dilute-gas viscosity. While this approach will subtly shift the liquid phase scaled viscosities, and therefore no longer strictly follows the requirements of isomorph theory,^{11–15} the effect is very small,³ likely smaller than the liquid-phase uncertainties.

There is now a growing body of work that has utilized this modified entropy scaling framework for building empirical viscosity models^{3,26,29} and successfully applied it to mixtures.^{29,30}

2 Data & Thermodynamic Models

The experimental data utilized in this study were obtained from the SOURCE database of NIST, and made available through an internal version of the ThermoDataEngine. The Thermodynamics Research Center of NIST has agreed to make the viscosity data for this study available in tabular form. The complete dataset considered in this work includes more than 16 thousand unique data points (including bibliographic information for each dataset) and is contained in comma-separated-value format at <https://doi.org/10.18434/mds2-2289>

Like the previous paper in this series³ for propane, the present paper focuses on the normal alkanes $n\text{-C}_N\text{H}_{2N+2}$ in the set of “REFPROP compounds”, that is, fluids that are included in the NIST REFPROP library.³¹ These represent well-measured fluids with accurate

multiparameter equations of state. We can generally assume that the residual entropy obtained from these models is a faithful representation of the residual entropy of the actual species, aside from some issues identified below. The residual entropy is not a directly measurable quantity, but a means of assessing the residual entropy reliability at the triple point is proposed below.

2.1 Data Screening

Large collections of experimental data for transport properties are frequently riddled with data capture errors, not the least because of the plethora of units that have been historically used for dynamic viscosity and the ease with which unit conversion errors can be made. For dynamic viscosity, the SI unit is the Pascal-second, but many others have been used when the range is expanded to kinematic viscosity and fluidity (the reciprocal of viscosity): poise, centipoise, reyn, stokes, to name only a few. A method that can quickly screen data to flag outliers polluting the database (likely caused by unit conversion) is very useful.

The results below show that the experimental transport property data for all fluids demonstrate a qualitatively similar behavior when the s^+ is divided by the appropriate value. *What readily-calculated value of s^+ should be used to scale the residual entropy?* There are a number of options: the triple point, critical point, a point along the vapor-liquid equilibrium curve, etc. For rough screening, Fig. 1 shows an overview of the data with their entropies scaled by the value $F_{\text{screen}} = (6s_{\text{PR,crit}}^+ + 8/3)/10$; the motivation for this choice will be made clear later on. The quantity $s_{\text{PR,crit}}^+$ is the critical residual entropy term evaluated from the Peng-Robinson equation of state (EOS). The derivations in the SI of Ref. 3 show that this quantity is a linear function of the acentric factor. The scaled viscosities in the ordinate contain the term $(s^+)^{2/3}$ (see Eq. (4)), therefore the scaled viscosity terms need to be divided by $F_{\text{screen}}^{2/3}$ in order to scale both axes appropriately. The dilute contribution $\eta_{\rho \rightarrow 0}^+$ comes from the model of Chung.³² All thermodynamic properties are

calculated from the Peng-Robinson EOS³³ with the Twu alpha function³⁴ as implemented in CoolProp version 6.4.1.³⁵ Although the Peng-Robinson EoS is known to provide erroneous values for a variety of thermodynamic properties (especially so for associating fluids and fluids with strong quantum effects), it is at least consistently erroneous, allowing for a reliable screening method.

Many of the erroneously captured (or reported) data are visually straightforward to pick out because they do not match the bulk of the data. Measurement errors on the order of 20% are not uncommon, but errors of 1000% are almost certainly a unit conversion problem, and an erroneous multiplicative factor of 10 is common with the conversion between Poise and Pa·s. Screening curves were sketched onto the data coordinates, indicated by the solid curves, that were used to determine whether a point seemed reliable or not; the curves are conservative. Data points within the band were deemed to be at least reasonable, but that determination still represents no guarantee that the data points are correct, only that they are not *very* erroneous.

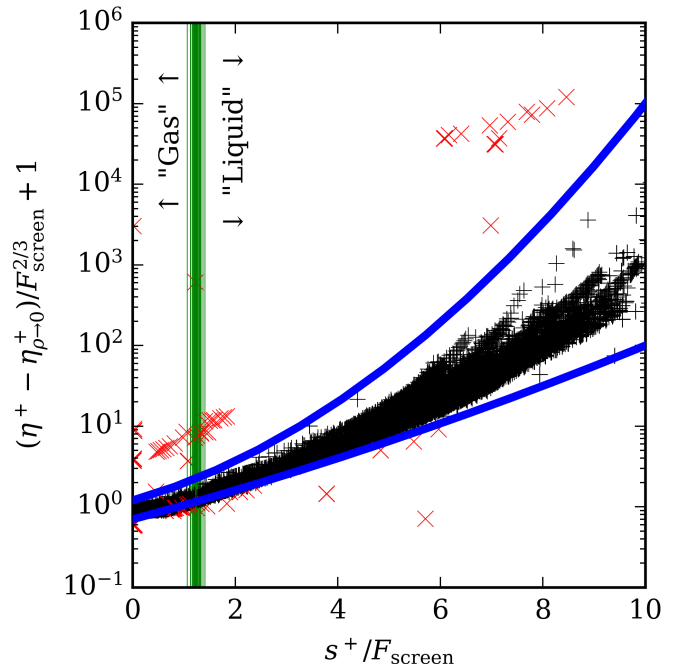


Figure 1: Experimental data from the SOURCE database for the fluids listed in Table 1, scaled by the values of F_{screen} , evaluated from the Peng-Robinson equation of state. An x marker is rejected according to the coarse screening, and a + marker is retained. The thick blue curves are the screening curves. The values of s^+ at the critical points (according to the Peng-Robinson EOS) are shown as thin vertical lines

2.2 Models

The Peng-Robinson EOS is suitable for screening experimental data as a consequence of the minimal information needed for the fluid (critical temperature, critical pressure, and acentric factor, parameters that are frequently tabulated) and its generally reasonable (if not accurate) qualitative behavior. However, it is not suitable for accurate entropy scaling approaches. Figure 2 shows a histogram of the deviations between three thermodynamic models for *n*-octane: the EOS as implemented in REFPROP 10.0, the PC-SAFT model from Gross and Sadowski³⁶ as implemented in CoolProp 6.4.1 and the Peng-Robinson EOS, as implemented in CoolProp 6.4.1. From these results it is clear that PC-SAFT and the reference model from REFPROP 10.0 yield similar residual entropy values, deviating by less than 4% in most

cases, while those of the Peng-Robinson EOS are significantly different.

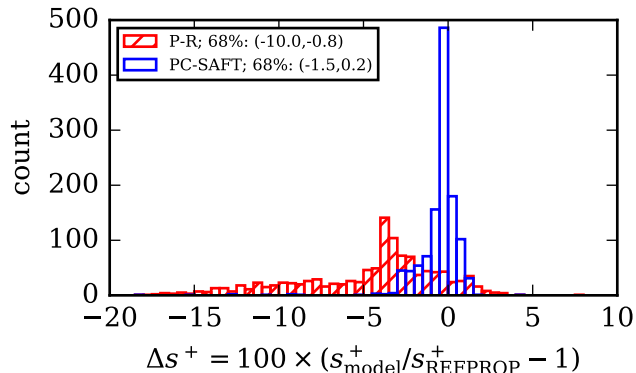


Figure 2: Histograms of deviations between the calculated values for s^+ for n -octane for each available experimental data point with Peng-Robinson (P-R) and PC-SAFT models, with the REFPROP 10.0 model as the baseline. The central 68 percentiles of the deviations are shown in the legend entries

A full accounting of the uncertainty in residual entropy values from equations of state is an important topic for future research. A rudimentary means of assessing the residual entropy uncertainty is to consider vapor-liquid equilibrium at very low pressure. Here, the residual entropy of the gas phase is very close to zero. For instance, for propane at its triple point, the vapor phase s^+ is on the order of 10^{-9} . The change in residual entropy between the vapor (v) and liquid (l) phases can be related to the latent heat of vaporization and the logarithm of the density ratio via

$$s_{l,3\varphi}^+ \approx \frac{-s_l^r}{R} \quad (6)$$

$$= \frac{h_v - h_l}{RT} + \ln \left(\frac{\rho_v}{\rho_l} \right) \quad (7)$$

where h is the molar enthalpy, and R is the universal gas constant. If the uncertainties in densities and latent heat are known, the uncertainty in the residual entropy can be straightforwardly calculated. The derivation of this result is in the supporting information (See Section ??)

2.3 Phenomena

As was described in the first paper in this series,³ the “liquid” region roughly defined by $s^+ > s_{\text{crit}}^+$ is approximately characterized by an “Arrhenius” region with a linear dependence of the logarithm of the “residual viscosity” on s^+ , followed, at larger values of s^+ , by a super-exponential dependence. For the normal alkanes, these trends are shown in Fig. 3, where these results demonstrate that this general trend also holds for the normal alkanes.

The breakpoint between the “Arrhenius” behavior and the super-Arrhenius behavior must still be defined. An empirical observation, tantalizing in its simplicity, is that for normal alkanes containing at least two carbons, the dynamics seems to changeover at the residual entropy half way between the value of s^+ at the critical point and that of the liquid at the crystal-liquid-vapor triple point. The physical explanation for this changeover in dynamics appears to be within grasp, given its uniformity, but is left to further study. The breakpoint residual entropy value is therefore defined by

$$s_b^+ \equiv \frac{s_{\text{crit}}^+ + s_{\text{liq},3\varphi}^+}{2} \quad (8)$$

Among the normal alkanes, the change in the sign of the curvature given by $d^2 \ln(\eta^+)/d(s^+)^2$ seems to consistently occur in the vicinity of s_b^+ , but it does not occur at precisely this value, as shown graphically in Fig. 4. The changeover in dynamics is indicated by a change in curvature in Fig. 4, or in Fig. 3, by a change in slope. For small molecules and atomic fluids (see also Ref. 26 for Lennard-Jones), there does not appear to be any inflection point, indicating that the location of s_b^+ must be somehow related to the internal degrees of freedom.

A potentially useful application of this observation about the breakpoint entropy is that if viscosity data are available, but the triple point is unknown, the triple-point temperature could be estimated from the viscosity data.

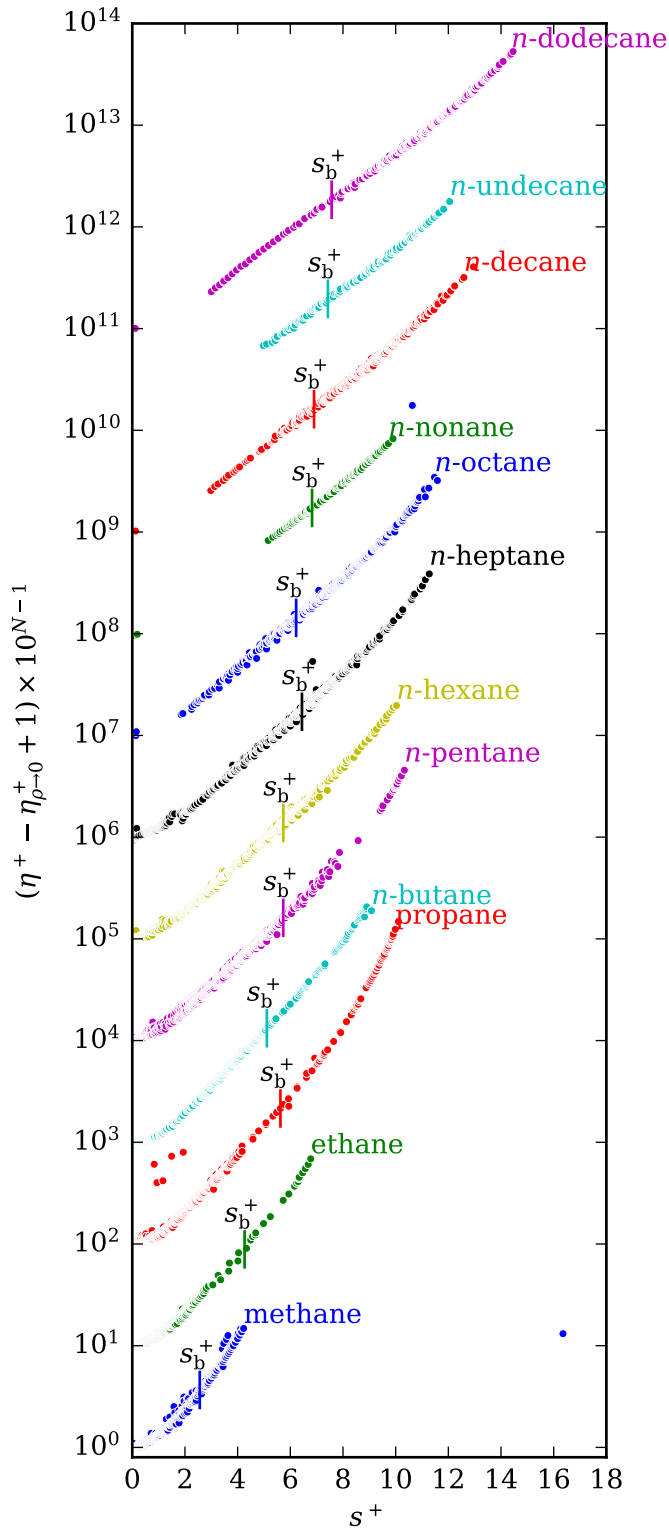


Figure 3: Residual scaled viscosities of the normal alkanes $n\text{-C}_N\text{H}_{2N+2}$ as a function of s^+ and their breakpoint residual entropies calculated from Eq. (8), indicated by the line labeled s_b^+ . Data points have been scaled by increasing factors of 10 to avoid overlap.

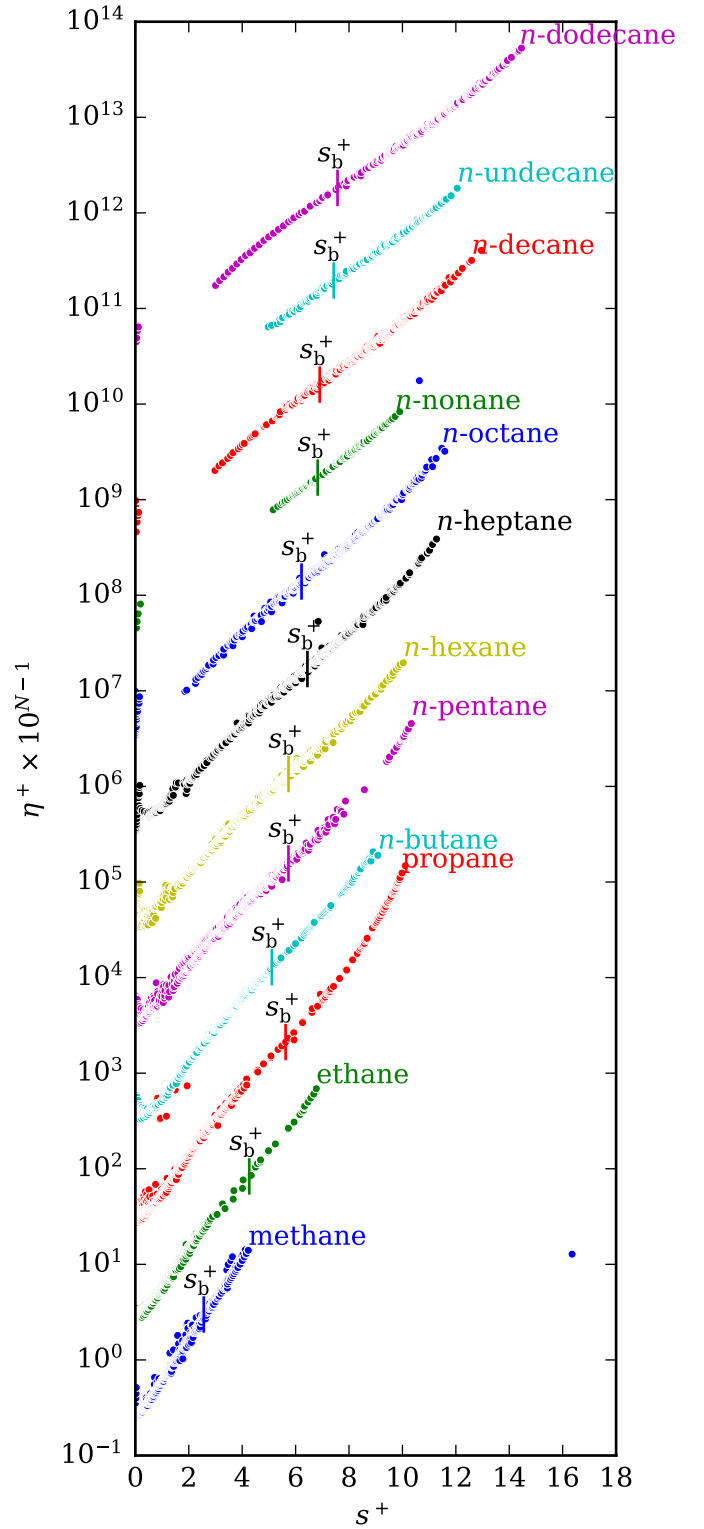


Figure 4: Normal alkanes $n\text{-C}_N\text{H}_{2N+2}$ and their breakpoint residual entropies calculated from Eq. (8), indicated by the line labeled s_b^+ . Data points have been scaled by increasing factors of 10 to avoid overlap.

3 Three-Phase Equilibria

In order to pin the high-density limit of the correlations of scaled transport properties, it was desirable to develop an understanding of the scaled viscosity at the crystal-liquid-vapor (CLV) triple point. Taking inspiration from the work of Fragiadakis and Roland,³⁷ with origins in da Andrade’s work³⁸ from the 1930s, it was hypothesized that $\tilde{\eta}$ should be roughly constant at the CLV triple point. While that proposed relationship does not hold in general, a slight rethinking of the question provides a potential path forwards. The CLV triple point appears to play an important role in understanding the dynamics in the liquid phase. This notion was explored in the work of Laesecke and Muzny,³⁹ in which they used estimated values of the liquid at the CLV triple point as a scaling parameter of the viscosity.

It has been known since the 19th century^{40,41} that the triple point *temperatures* of normal alkanes above methane demonstrate an even-odd oscillating behavior, with the relative magnitude of the oscillation decaying as the molecules increase in mass. Phase equilibrium between liquid and gas phases *above* the triple-point temperature are associated with equal Gibbs energy in each of the co-existing phases. When the Gibbs energy of the liquid phase (which is the same as the gas phase) becomes the same as the solid phase at the given temperature and saturation pressure, the incipient solid phase appears, and the CLV triple point is reached. *Ergo*, the crystal Gibbs energy controls the triple point, and explains why the triple point temperatures demonstrate oscillations not present in the normal boiling point temperature or critical point, for which classical corresponding states applies (at least approximately), see Fig. 5. The long-chain limit of critical temperatures has also been the subject of study.⁴²

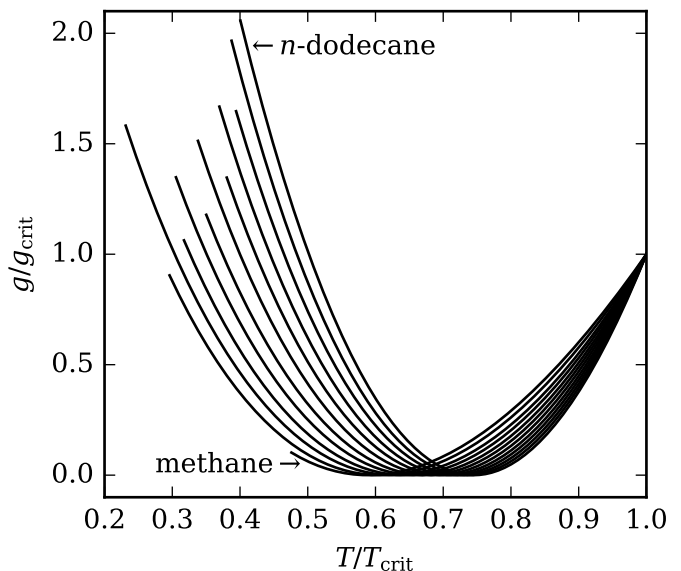


Figure 5: Saturated liquid Gibbs energy for all the normal alkanes from methane to *n*-dodecane (first and last members of the set are labeled). Reference state for the equation of state for all fluids has been set to yield entropy and enthalpy of saturated liquid equal to zero at a pressure of one atmosphere

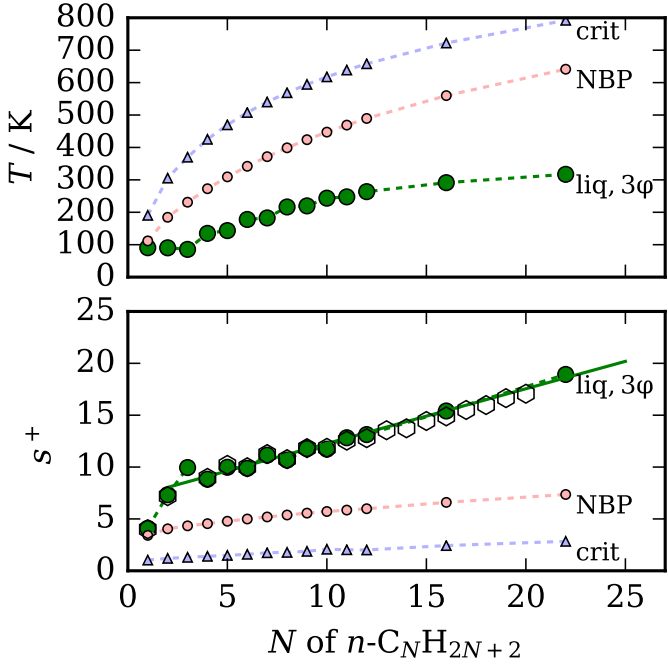


Figure 6: Values of temperature (upper) and s^+ (lower) of the liquid phase at the crystal-liquid-vapor triple point (liq, 3φ), the normal boiling point (NBP), and the critical point (crit). Values are according to the default thermophysical property models in NIST REFPROP 10.0.³¹ Open hexagons are values calculated from the PC-SAFT EOS as implemented in CoolProp 6.4.1 with the triple point temperatures estimated from TDE.⁴³ Solid curve is the long-chain limit from Eq. (9).

The trend in residual entropy of the liquid phase at the CLV triple point mirrors that of the temperature, showing strong oscillatory behavior diminishing in magnitude for carbon numbers greater than 10. Figure 6 shows the values calculated from the reference EOS for the liquid at the triple point, and also shown are the values from the PC-SAFT EOS evaluated at the triple-point temperature. The asymptotic long chain limit in residual entropy is approximately a linear relationship between residual entropy of the liquid at the CLV triple point and carbon number

$$s_{N \rightarrow \infty}^+ = 0.53N + 7.0 \quad (9)$$

Experimental measurements of the liquid phase viscosity at precisely the triple point are essentially non-existent, though they are in principle possible to measure directly. One

must therefore presently resort to interpolation (or possibly extrapolation) of empirical models to obtain estimated values at the triple point. Where fluid-specific correlations of wide-ranging applicability exist, the values should be considered as a suitable reference. Figure 7 shows estimated values of the liquid viscosity at the triple-point. Like the residual entropy, the viscosity shows a strongly oscillatory behavior as a function of carbon number, in which the magnitude of the oscillations decay for carbon numbers greater than 10, and are governed more or less by a linear relationship for longer chain lengths. Propane seems very anomalous at first glance, given that its residual entropy at the triple point is not so much above the $s_{N \rightarrow \infty}^+$ curve in Fig. 6. The derivative $d\tilde{\eta}/ds^+$ is very large in magnitude approaching the melting curve, so a modest increase in s^+ corresponds to a large increase in $\tilde{\eta}$.

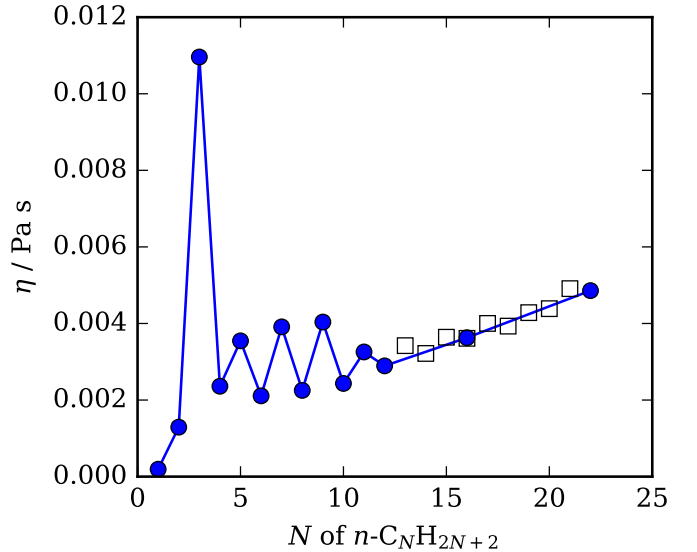


Figure 7: Values of η of the liquid phase at the CLV triple point according to the default thermophysical property models in NIST REFPROP 10.0³¹ (filled circles) and from the empirical models of NIST ThermoDataEngine (open squares) where no model is available in REFPROP 10.0.

The estimated values of $\tilde{\eta}$ and η^+ at the triple point are shown in Figure 8 as a function of carbon number, for which the trend mirrors that of the shear viscosity. The similarity in long-chain behavior is a consequence of the long-chain scal-

ing, in which both s^+ and ρ_N show linear dependence on N at the CLV triple point. The scaled thermal conductivity (see Fig. ?? in the SI) also shows an even-odd oscillatory behavior for smaller alkanes, decaying to a long-chain asymptotic behavior.

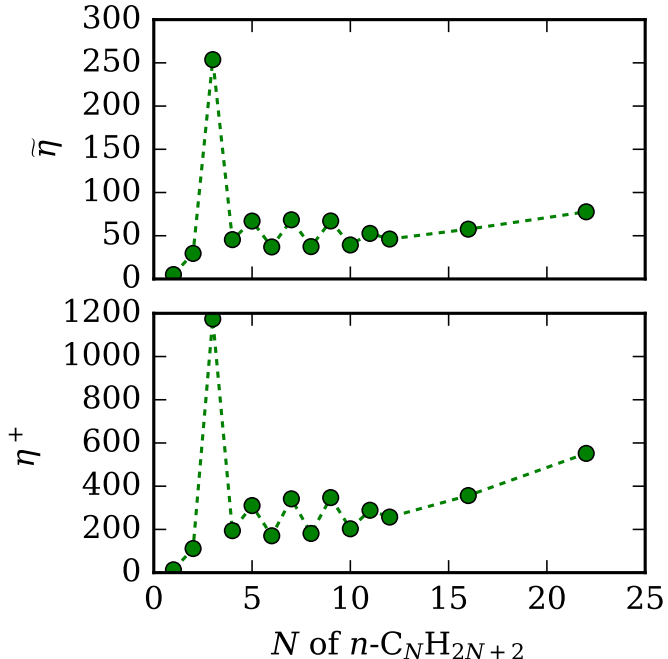


Figure 8: Values of $\tilde{\eta}$ (upper) and η^+ (lower) of the liquid phase at the crystal-liquid-vapor triple point according to the default thermo-physical property models in NIST REFPROP 10.0.³¹

4 Model Development

The key insight of this work is that when the appropriate scaling parameter is selected, the “Arrhenius” portions of the curves overlay very closely, which represents a significant portion of the liquid phase behavior. The super-exponential increase in the dense liquid phase is handled as a separate power-law correction term after the scaling has been applied.

4.1 Arrhenius Region

Taking inspiration from Ref. 44, a value of s^+ equal to that of the critical point intuitively feels like it might be the right choice for scaling s^+ as it seems to generally correspond to

the minima of the kinematic viscosity and the thermal diffusivity.⁴⁴ On the other hand, the minima of $\tilde{\eta}$ for simple fluids all occur around $s^+ = 2/3$.^{5,44} *Perhaps a scaling value in between these two values would be best?*

In order to test that hypothesis, the scaling parameter F was defined by

$$F = \chi s_{\text{crit}}^+ + (1 - \chi) \frac{2}{3} \quad (10)$$

linearly weighting s_{crit}^+ and the value of $2/3$ by the weighting parameter χ .

The experimental data for each fluid were downselected to the Arrhenius region defined by (s_1^+, s_b^+) , with $s_1^+ = 3s_{\text{crit}}^+/2$. The value of s_1^+ was selected to ensure that the fluid was well into its Arrhenius region. The values of F from Eq. (10) were used to scale both s^+ and Υ for the given value of χ . The value of Υ is defined by

$$\Upsilon \equiv (\eta^+ - \eta_{\rho \rightarrow 0}^+)/F^{2/3} + 1 \quad (11)$$

For each point cloud given by a value of χ , a linear function of $\ln(\Upsilon)$ as a function of s^+/F was obtained, and the average absolute relative deviation (AAD) for the Arrhenius portion is plotted against χ in Fig. 9. The minimum occurs at a value of 0.5875, or approximately $6/10$, and clearly neither s_{crit}^+ (for $\chi = 1$) or $2/3$ (for $\chi = 0$) are superior scaling schemes. The fully predictive scaling value for F is therefore defined by

$$F_{\text{pred}} \equiv \frac{6}{10} s_{\text{crit}}^+ + \left(1 - \frac{6}{10}\right) \frac{2}{3} \quad (12)$$

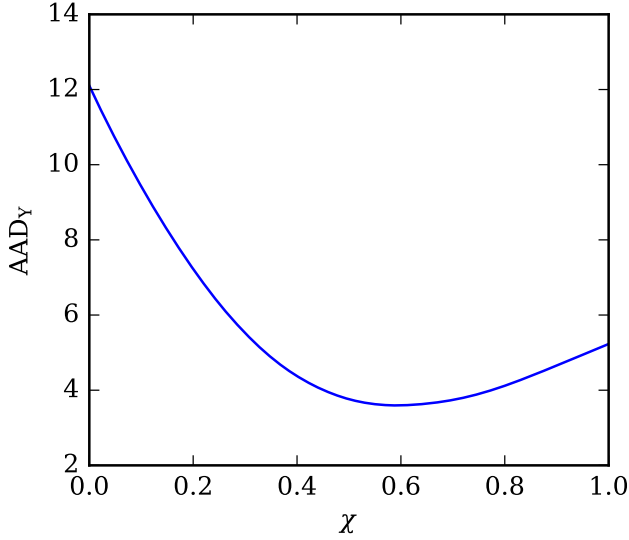


Figure 9: AAD in Υ for the Arrhenius portion of the phase diagram for all the data for the normal alkanes given in Table 1.

The best-fit correlation associated with all the Arrhenius data scaled by the value from Eq. (12) is then given by

$$\ln(\Upsilon) = m_{\text{Ar}} \left(\frac{s^+}{F_{\text{pred}}} \right) + b_{\text{Ar}} \quad (13)$$

with $m_{\text{Ar}} = 0.64639504$ and $b_{\text{Ar}} = -0.5318307$. The numerical coefficients are not so different than those for propane,³ largely because by pure happenstance, the value of F_{pred} for propane (1.045) calculated from Eq. (12) is very close to 1.0. A very similar empirical approach was used by Ref. 29.

4.2 Super-Arrhenius Region

Paralleling the approach for propane,³ the super-Arrhenius term is defined by

$$\ln(\ln(\Upsilon)) = \sum_{i=0}^2 c_i \left(\ln \left(\frac{s^+}{F_{\text{pred}}} \right) \right)^i, \quad (14)$$

motivated by a consideration of the behavior near the melting line.

For this “quadratic” equation, three constraints are needed, the first two being the value and derivative constraints at s_b^+ . One adjustable parameter remains for the super-Arrhenius curve to fully define the quadratic.

The 3x3 system of equations to be solved for the coefficients c_i is therefore:

$$\mathbf{A} \begin{bmatrix} c_0 \\ c_1 \\ c_2 \end{bmatrix} = \mathbf{b} \quad (15)$$

with

$$\mathbf{A} = \begin{bmatrix} 1 & \ln \left(\frac{s_b^+}{F} \right) & \ln^2 \left(\frac{s_b^+}{F} \right) \\ 0 & 1 & 2 \ln \left(\frac{s_b^+}{F} \right) \\ 1 & \ln \left(\frac{s_{\text{liq},3\varphi}^+}{F} \right) & \ln^2 \left(\frac{s_{\text{liq},3\varphi}^+}{F} \right) \end{bmatrix} \quad (16)$$

$$\mathbf{b} = \begin{bmatrix} \ln \left(m_{\text{Ar}} \frac{s_b^+}{F} + b_{\text{Ar}} \right) \\ \frac{m_{\text{Ar}} \frac{s_b^+}{F}}{m_{\text{Ar}} \frac{s_b^+}{F} + b_{\text{Ar}}} \\ \ln(\ln(\Upsilon_{\text{liq},3\varphi})) \end{bmatrix} \quad (17)$$

The values of $s_{\text{liq},3\varphi}^+$ and $\Upsilon_{\text{liq},3\varphi}$ are taken from the triple point analysis shown above. This system of equations is particular to the given fluid, and has no statepoint dependence, so may be pre-calculated and cached.

4.3 Gas Region

The Chung approach^{32,45} models molecular fluids as though they were spherically symmetric Lennard-Jones 12-6 particles, plus an empirical correction term. Length and energy scales are obtained from the critical point. This approach is detailed, along with some further remarks, in the supporting information (see Section ??). More accurate collision integrals are now available for the Lennard-Jones 12-6 potential,⁴⁶ but for consistency with existing literature, the Chung model has been used. The overall value for $\eta_{\rho \rightarrow 0}^+$ from Eq. (5) also invokes the second virial coefficients.

Unlike propane, in which case the initial density term was considered³ in the gaseous region, this work takes a simpler approach for the crossover from dilute-gas to Arrhenius regions due to a more limited amount of low-density ex-

perimental data for other normal alkanes. The gas portion is therefore modeled with no additional adjustable parameters, simply a smooth transition from the Arrhenius region to the zero-density limit with the function constrained to match the dilute-gas limit, and smoothly transition into the Arrhenius curve. The value of Υ in this region is defined by

$$\ln(\Upsilon) = \sum_{i=0}^3 a_i (s^+/F)^i \quad (18)$$

The first value constraint at the dilute-gas limit ($\ln(\Upsilon) = 0$, $\Upsilon = 1$, for $s^+ = 0$) yields $a_0 = 0$. The second constraint of a negligible initial density contribution yields $a_1 = 0$, and the remaining coefficients a_2 and a_3 are obtained by solving the 2x2 linear system for a_2 and a_3 , yielding

$$a_2 = \frac{-m_{\text{Ar}} \left(\frac{s_1^+}{F} \right) + 3 \ln(\Upsilon_1)}{\left(\frac{s_1^+}{F} \right)^2} \quad (19)$$

$$a_3 = \frac{m_{\text{Ar}} \left(\frac{s_1^+}{F} \right) - 2 \ln(\Upsilon_1)}{\left(\frac{s_1^+}{F} \right)^3} \quad (20)$$

with

$$\ln(\Upsilon_1) = m_{\text{Ar}}(s_1^+/F) + b_{\text{Ar}} \quad (21)$$

Therefore all the coefficients of Eq. (18) are constants for a given fluid, and can be pre-calculated and cached.

4.4 Overall

The model for a particular fluid is defined, piecewise, in terms of s^+ . For $s^+ < s_1^+$ the contribution of Eq. (18) is used, for $s_1^+ \leq s^+ \leq s_b^+$, the Arrhenius model of Eq. (13) is used, and for $s^+ > s_b^+$, the super Arrhenius contribution of Eq. (14) is used.

4.5 Implementation

In order to avoid any confusion about the proposed model, an implementation in the Python

programming language is provided in the supporting information. This implementation includes the described models as well as some calculated values from the implementation. Table 1 summarizes the fixed points according to the pure fluid models in REFPROP 10.0.³¹

5 Model Results

In this section the fully predictive approach is used, in which case the scaling parameter F is given by Eq. (12). To begin, all of the experimental results are scaled with the appropriate predictive value of F , as shown in Fig. 10. The results in the super-Arrhenius region begin to fan out in order to reach the correct triple point values (which do not follow the same scaling), but the Arrhenius region is well-modeled by a linear curve in these coordinates. In short, this scaling approach successfully collapses (even if not perfectly) more than 15,000 data points for viscosity for some of the most important chemical species.

Recalling the results for the liquid phase at the triple point, propane stood out for having an anomalously large value of viscosity relative to the other normal alkanes. Figure 10 shows that propane stands atop the scaled data in the liquid phase too. In other words, the molecular interactions resulting in anomalous solid phase behavior result in anomalous liquid phase behavior.

The last question then is how well the model represents the experimental data. Figure 11 shows the deviations between the model and the experiments. The model implementation file described above is used directly to calculate the viscosity. It should be noted that the work of carefully screening data to remove outliers has not been carried out, and with additional effort, further improvements in the statistics would be possible. For the fluids ethane to *n*-nonane, 94% of the data are predicted within 10%, and with outliers removed the deviations should be far smaller. For the longer alkanes, there is more variability, with systematic offsets present. It seems likely that much of the variability can be attributed to erroneous behavior

Table 1: Characteristic values as obtained from the default thermodynamic models in NIST REFPROP 10.0.³¹ Quantities with subscript 3φ correspond to the saturated liquid phase at the triple point. The value N is the carbon number of normal alkane $n\text{-C}_N\text{H}_{2N+2}$

N	Name	T_{crit}/K	$\rho_{\text{crit}}/\text{mol dm}^{-3}$	s_{crit}^+	$T_{3\varphi}/\text{K}$	$\rho_{3\varphi}/\text{mol dm}^{-3}$	$s_{3\varphi}^+$	$\eta_{3\varphi}/\text{mPa s}$	F_{pred}
1	methane ⁴⁷	190.564	10.139128	1.03	90.69	28.14	4.09	0.194	0.89
2	ethane ⁴⁸	305.322	6.856887	1.20	90.37	21.67	7.33	1.292	0.99
3	propane ⁴⁹	369.890	5.000000	1.30	85.53	16.63	9.95	10.960	1.05
4	<i>n</i> -butane ⁵⁰	425.125	3.922770	1.40	134.90	12.65	8.83	2.360	1.10
5	<i>n</i> -pentane	469.700	3.210000	1.49	143.47	10.58	9.98	3.546	1.16
6	<i>n</i> -hexane	507.820	2.706000	1.59	177.83	8.80	9.88	2.110	1.22
7	<i>n</i> -heptane	540.200	2.330000	1.74	182.55	7.74	11.15	3.911	1.31
8	<i>n</i> -octane	568.740	2.031000	1.77	216.37	6.68	10.67	2.252	1.33
9	<i>n</i> -nonane ⁵¹	594.550	1.810000	1.87	219.70	6.05	11.78	4.037	1.39
10	<i>n</i> -decane ⁵¹	617.700	1.640000	2.08	243.50	5.41	11.73	2.434	1.51
11	<i>n</i> -undecane ⁵²	638.800	1.514900	2.03	247.54	4.96	12.83	3.256	1.48
12	<i>n</i> -dodecane ⁵³	658.100	1.330000	2.01	263.60	4.53	13.13	2.893	1.47
16	<i>n</i> -hexadecane	722.100	1.000000	2.43	291.33	3.42	15.41	3.628	1.72
22	<i>n</i> -docosane	792.200	0.723000	2.84	317.04	2.51	18.93	4.858	1.97

in the equation of state.

The values of residual entropy at the respective critical points provide insight to some of the deviations seen in the Arrhenius region. The scaling approach in this work is based on the assumption that the EOS provides a faithful representation of the residual entropy at the critical point. Figure 12 shows in more detail than in Fig. 6 the values of residual entropy at the critical points. The fluids showing strong deviations from the best-fit curve are strongly correlated with the fluids demonstrating an offset in the scaling in the Arrhenius region: *n*-heptane, *n*-decane, and *n*-dodecane. For *n*-decane, the values of η are consistently under-predicted, while those for *n*-dodecane are consistently overpredicted. Thus the defects in the representation of the residual entropy seem to infect the outputs of the model as well. Thinking about the problem from the other direction, high quality transport property data seem to be helpful in ensuring the correct behavior of the equation of state.

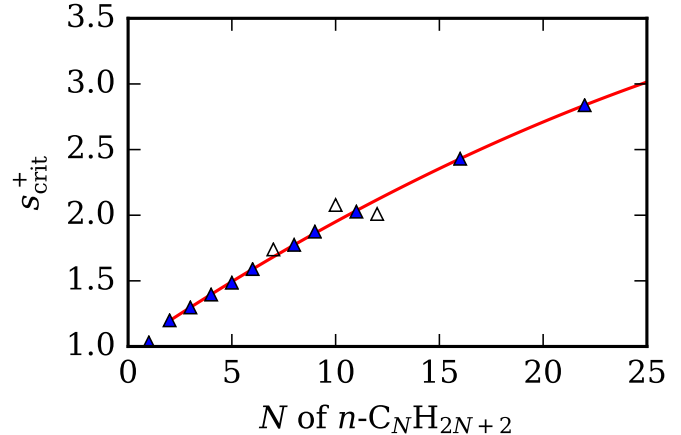


Figure 12: Values of the residual entropy s_{crit}^+ at the critical points according to the default thermophysical property models in NIST REFPROP 10.0.³¹ The deviating fluids from the curve $s_{\text{crit}}^+ = 0.9881N^2 + 0.1067N - 0.0010$ are shown with open markers.

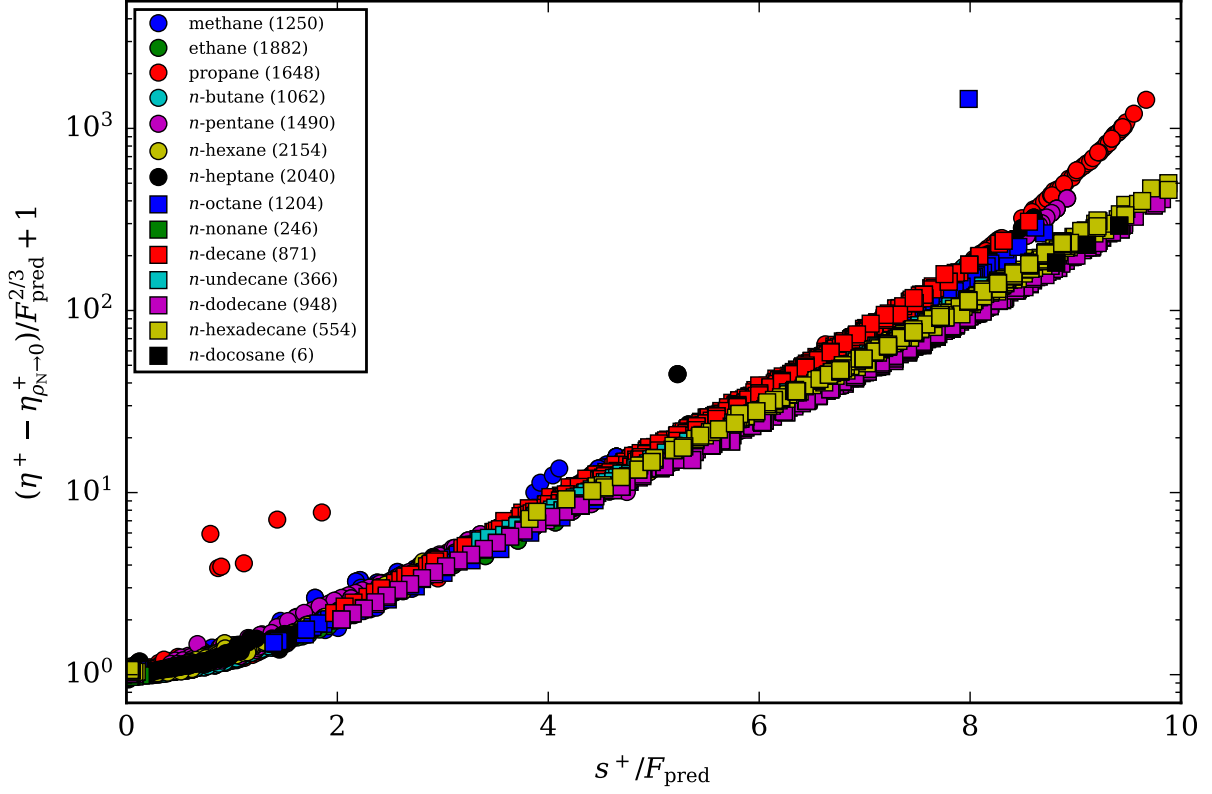


Figure 10: Scaled values of η^+ with the fully predictive scheme from Eq. (12). The outliers were retained to highlight how easily they can be identified. The label for each fluid gives the number of data points in parentheses.

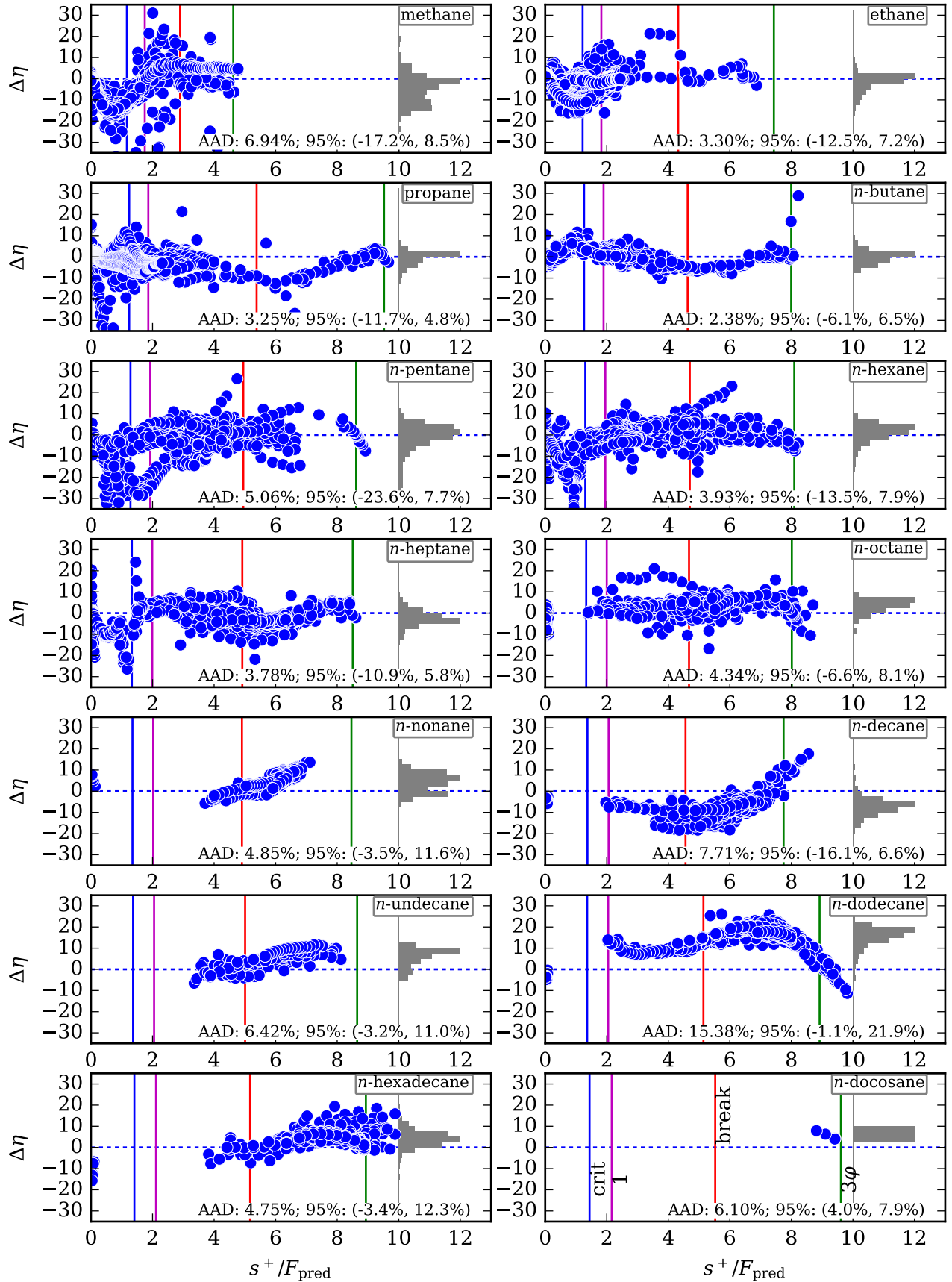


Figure 11: Deviations in η ($\Delta\eta = 100 \times (\eta_{\text{model}}/\eta_{\text{exp}} - 1)$) for the normal alkanes. The markers represent the deviations for each data point, the four vertical lines represent the critical, onset of Arrhenius, break, and CLV triple point values, respectively (as labeled in bottom right axes) and the histogram in each figure shows a graphical representation of the deviations, useful for fluids with many overlapping points. The AAD (average absolute relative deviation) and central 95 percentiles of the error distribution are shown in each panel.⁴

6 Concluding Remarks

At first glance the scaling in this paper might appear to not be very successful. The statistics of the correlations are similar to existing models from entropy scaling,²² and much worse than reference correlations for which only the best data were considered.^{54–61} On the other hand, extremely accurate correlations are not the goal of this work, which is to introduce new notions about entropy scaling. The target is to remove as much empiricism as possible in order to be able to investigate more deeply the relationship between transport properties and residual entropy for fluids with intramolecular degrees of freedom. Only a very cursory data screening was carried out. The scaling approach proposed here has zero (or, one might argue, one) empirical parameters per fluid. Certainly one could do much better with even a little bit more flexibility, as was the case for propane³ when only the best data were considered.

One key outcome of this work is that the value

F_{pred} from Eq. (12) appears, even if not exactly, to represent the value of residual entropy that controls the crossover from gas-like behavior to liquid-like behavior for normal alkanes. This conclusion represents an important modification of crossover proposed for model fluids in a recent study.⁴⁴

The consistency of the relative location of the breakpoint s_b^+ changes the conceptual model for liquid-phase viscosity. It shows that the residual entropy, and in particular s_b^+ , is largely controlling the transition between two different behaviors, which seem to be roughly cage-rattling and cooperative dynamics.^{10,62} In the case of Lennard-Jones, the same change in slope, even if subtle, can be seen,²⁶ though the transition occurs nearer the triple point than the breakpoint coming from Eq. (8). While the idea of a liquid having also solid-like behavior is perhaps an unpopular concept, it is at the heart of two-phase approaches to thermodynamics,^{63,64} and has also recently been investigated for some simple systems.⁶⁵ In confined liquids under shear, solid-like structures can be seen in simulations.^{66–69}

Considering the viscosity at the triple point (or its scaled counterparts) represents a new way of thinking about transport properties in deeply compressed states, and adds more physics to the entropy scaling approach for real fluids. This approach connects the solid phase with the discussion of fluid phase behavior, which might feel uncomfortable, but the solid phase is also shown to obey isomorph theory under the right conditions, and some scaling approaches appear to also work for solid-liquid phase equilibria.³⁷

This paper also highlights that an EOS which faithfully represents the most accurate thermodynamic experimental data for density, vapor pressure, speed of sound, etc., does not necessarily guarantee an accurate representation of the residual entropy. It is for that reason recommended that EOS developers carefully consider the representation of the residual entropy at key points (triple point, critical point) and compare it with similar fluids. Furthermore, the PC-SAFT equation of state is shown to yield consistent values of s^+ with

those of the multiparameter EOS, perhaps clarifying the success of the PC-SAFT approach more generally.

Supporting Information Available

In order to ensure reproducibility of the results, all of the considered experimental data are deposited at data.nist.gov: <https://doi.org/10.18434/mds2-2289>. The supporting information further includes:

- The Python implementation of the proposed model in the file `implementation.py`
- Additional derivations and discussion not appropriate for inclusion in the main manuscript.

Readers are invited to contact the author for clarification of any aspect of the paper, or if any errors are identified.

Acknowledgement The author thanks Zach Baird (of Aalto University) for adding PC-SAFT to CoolProp, Guillaume Galliero (of Université de Pau, France) for energizing collaboration, Allan Harvey (of NIST) and Ulrich Deiters (of University of Cologne) for discussions of phase equilibria, and Velisa Vesovic (of Imperial College London) for asking insightful questions.

References

- (1) Poling, B. E.; Prausnitz, J. M.; O’Connell, J. P. *The Properties of Gases and Liquids, 5th edition*; McGraw Hill, 2001.
- (2) Baled, H. O.; Gamwo, I. K.; Enick, R. M.; McHugh, M. A. Viscosity models for pure hydrocarbons at extreme conditions: A review and comparative study. *Fuel* **2018**, *218*, 89–111, DOI: 10.1016/j.fuel.2018.01.002.
- (3) Bell, I. H. Entropy Scaling of Viscosity – I: A Case Study of Propane. *J. Chem. Eng. Data* **2020**, 3203–3215, DOI: 10.1021/acs.jced.0c00209.
- (4) Rosenfeld, Y. Relation between the transport coefficients and the internal entropy of simple systems. *Phys. Rev. A* **1977**, *15*, 2545–2549, DOI: 10.1103/PhysRevA.15.2545.
- (5) Bell, I. H. Probing the link between residual entropy and viscosity of molecular fluids and model potentials. *Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 4070–4079, DOI: 10.1073/pnas.1815943116.
- (6) Dyre, J. C. Simple liquids’ quasiuniversality and the hard-sphere paradigm. *J. Phys.: Condens. Matter* **2016**, *28*, 323001, DOI: 10.1088/0953-8984/28/32/323001.
- (7) Voyatzis, E.; Müller-Plathe, F.; Böhm, M. C. Excess entropy scaling for the segmental and global dynamics of polyethylene melts. *Phys. Chem. Chem. Phys.* **2014**, *16*, 24301–24311, DOI: 10.1039/c4cp03559c.
- (8) Lemmon, E. W.; Jacobsen, R. T. A New Functional Form and New Fitting Techniques for Equations of State with Application to Pentafluoroethane (HFC-125). *J. Phys. Chem. Ref. Data* **2005**, *34*, 69–108, DOI: 10.1063/1.1797813.
- (9) Marsh, K. N. Editorial. *J. Chem. Eng. Data* **1997**, *42*, 1, DOI: 10.1021/je9604996.
- (10) Dyre, J. C. Perspective: Excess-entropy scaling. *J. Chem. Phys.* **2018**, *149*, 210901, DOI: 10.1063/1.5055064.
- (11) Bailey, N. P.; Pedersen, U. R.; Gnan, N.; Schröder, T. B.; Dyre, J. C. Pressure-energy correlations in liquids. I. Results from computer simulations. *J. Chem. Phys.* **2008**, *129*, 184507, DOI: 10.1063/1.2982247.

- (12) Bailey, N. P.; Pedersen, U. R.; Gnan, N.; Schröder, T. B.; Dyre, J. C. Pressure-energy correlations in liquids. II. Analysis and consequences. *J. Chem. Phys.* **2008**, *129*, 184508, DOI: 10.1063/1.2982249.
- (13) Gnan, N.; Schröder, T. B.; Pedersen, U. R.; Bailey, N. P.; Dyre, J. C. Pressure-energy correlations in liquids. IV. “Isomorphs” in liquid phase diagrams. *J. Chem. Phys.* **2009**, *131*, 234504, DOI: 10.1063/1.3265957.
- (14) Schröder, T. B.; Bailey, N. P.; Pedersen, U. R.; Gnan, N.; Dyre, J. C. Pressure-energy correlations in liquids. III. Statistical mechanics and thermodynamics of liquids with hidden scale invariance. *J. Chem. Phys.* **2009**, *131*, 234503, DOI: 10.1063/1.3265955.
- (15) Schröder, T. B.; Gnan, N.; Pedersen, U. R.; Bailey, N. P.; Dyre, J. C. Pressure-energy correlations in liquids. V. Isomorphs in generalized Lennard-Jones systems. *J. Chem. Phys.* **2011**, *134*, 164505, DOI: 10.1063/1.3582900.
- (16) Novak, L. T. Predictive Corresponding-States Viscosity Model for the Entire Fluid Region: n-Alkanes. *Ind. Eng. Chem. Res.* **2013**, *52*, 6841–6847, DOI: 10.1021/ie400654p.
- (17) Novak, L. T. Predicting Natural Gas Viscosity with a Mixture Viscosity Model for the Entire Fluid Region. *Ind. Eng. Chem. Res.* **2013**, *52*, 16014–16018, DOI: 10.1021/ie402245e.
- (18) Novak, L. T. Predicting Fluid Viscosity of Nonassociating Molecules. *Ind. Eng. Chem. Res.* **2015**, *54*, 5830–5835, DOI: 10.1021/acs.iecr.5b01526.
- (19) Novak, L. T. Fluid Viscosity-Residual Entropy Correlation. *Int. J. Chem. React. Eng.* **2011**, *9*, A107.
- (20) Lötgering-Lin, O.; Gross, J. Group Contribution Method for Viscosities Based on Entropy Scaling Using the Perturbed-Chain Polar Statistical Associating Fluid Theory. *Ind. Eng. Chem. Res.* **2015**, *54*, 7942–7952, DOI: 10.1021/acs.iecr.5b01698.
- (21) Hopp, M.; Gross, J. Thermal Conductivity of Real Substances from Excess Entropy Scaling Using PCP-SAFT. *Ind. Eng. Chem. Res.* **2017**, *56*, 4527–4538, DOI: 10.1021/acs.iecr.6b04289.
- (22) Lötgering-Lin, O.; Fischer, M.; Hopp, M.; Gross, J. Pure Substance and Mixture Viscosities Based on Entropy Scaling and an Analytic Equation of State. *Ind. Eng. Chem. Res.* **2018**, *57*, 4095–4114, DOI: 10.1021/acs.iecr.7b04871.
- (23) Hopp, M.; Mele, J.; Gross, J. Self-Diffusion Coefficients from Entropy Scaling using the PCP-SAFT equation of state. *Ind. Eng. Chem. Res.* **2018**, *57*, 12942–12950, DOI: 10.1021/acs.iecr.8b02406.
- (24) Hopp, M.; Gross, J. Thermal Conductivity from Entropy Scaling: A Group-Contribution Method. *Ind. Eng. Chem. Res.* **2019**, *58*, 20441–20449, DOI: 10.1021/acs.iecr.9b04289.
- (25) Hopp, M.; Mele, J.; Hellmann, R.; Gross, J. Thermal Conductivity via Entropy Scaling: An Approach That Captures the Effect of Intramolecular Degrees of Freedom. *Ind. Eng. Chem. Res.* **2019**, *58*, 18432–18438, DOI: 10.1021/acs.iecr.9b03998.
- (26) Bell, I. H.; Messerly, R.; Thol, M.; Costigliola, L.; Dyre, J. Modified Entropy Scaling of the Transport Properties of the Lennard-Jones Fluid. *J. Phys. Chem. B* **2019**, *123*, 6345–6363, DOI: 10.1021/acs.jpcc.9b05808.
- (27) Rosenfeld, Y. A quasi-universal scaling law for atomic transport in simple fluids. *J. Phys.: Condens. Matter* **1999**, *11*, 5415–5427, DOI: 10.1088/0953-8984/11/28/303.

- (28) Bell, I. H.; Hellmann, R.; Harvey, A. H. Zero-Density Limit of the Residual Entropy Scaling of Transport Properties. *J. Chem. Eng. Data* **2019**, *65*, 1038–1050, DOI: 10.1021/acs.jced.9b00455.
- (29) Taib, M. B. M.; Trusler, J. P. M. Residual entropy model for predicting the viscosities of dense fluid mixtures. *J. Chem. Phys.* **2020**, *152*, 164104, DOI: 10.1063/5.0002242.
- (30) Liu, H.; Yang, F.; Yang, Z.; Duan, Y. Modeling the viscosity of hydrofluorocarbons, hydrofluoroolefins and their binary mixtures using residual entropy scaling and cubic-plus-association equation of state. *J. Mol. Liq.* **2020**, *308*, 113027, DOI: 10.1016/j.molliq.2020.113027.
- (31) Lemmon, E. W.; Bell, I. H.; Huber, M. L.; McLinden, M. O. NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 10.0, National Institute of Standards and Technology. <http://www.nist.gov/srd/nist23.cfm>, 2018.
- (32) Chung, T. H.; Ajlan, M.; Lee, L. L.; Starling, K. E. Generalized multiparameter correlation for nonpolar and polar fluid transport properties. *Ind. Eng. Chem. Res.* **1988**, *27*, 671–679, DOI: 10.1021/ie00076a024.
- (33) Bell, I. H.; Jäger, A. Helmholtz Energy Transformations of Common Cubic Equations of State for Use with Pure Fluids and Mixtures. *J. Res. Nat. Inst. Stand. Technol.* **2016**, *121*, 238, DOI: 10.6028/jres.121.011.
- (34) Bell, I. H.; Satyro, M.; Lemmon, E. W. Consistent Two Parameters for More than 2500 Pure Fluids from Critically Evaluated Experimental Data. *J. Chem. Eng. Data* **2018**, *63*, 2402–2409, DOI: 10.1021/acs.jced.7b00967.
- (35) Bell, I. H.; Wronski, J.; Quoilin, S.; Lemort, V. Pure and Pseudo-pure Fluid Thermophysical Property Evaluation and the Open-Source Thermophysical Property Library CoolProp. *Ind. Eng. Chem. Res.* **2014**, *53*, 2498–2508, DOI: 10.1021/ie4033999.
- (36) Gross, J.; Sadowski, G. Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules. *Ind. Eng. Chem. Res.* **2001**, *40*, 1244–1260, DOI: 10.1021/ie0003887.
- (37) Fragiadakis, D.; Roland, C. M. Connection between dynamics and thermodynamics of liquids on the melting line. *Physical Review E* **2011**, *83*, 031504, DOI: 10.1103/physreve.83.031504.
- (38) da C. Andrade, E. N. Viscosity of Liquids. *Nature* **1931**, *128*, 835–835, DOI: 10.1038/128835a0.
- (39) Laesecke, A.; Muzny, C. D. Reference Correlation for the Viscosity of Carbon Dioxide. *J. Phys. Chem. Ref. Data* **2017**, *46*, 013107, DOI: 10.1063/1.4977429.
- (40) Baeyer, A. Ueber Regelmässigkeiten im Schmelzpunkt homologer Verbindungen. *Ber. Dtsch. Chem. Ges.* **1877**, *10*, 1286–1288, DOI: 10.1002/cber.18770100204.
- (41) Boese, R.; Weiss, H.-C.; Bläser, D. The Melting Point Alternation in the Short-Chain n-Alkanes: Single-Crystal X-Ray Analyses of Propane at 30 K and of n-Butane to n-Nonane at 90 K. *Angew. Chem. Int. Ed.* **1999**, *38*, 988–992, DOI: 10.1002/(sici)1521-3773(19990401)38:7<988::aid-anie988>3.0.co;2-0.
- (42) Vega, C.; MacDowell, L. G. Critical temperature of infinitely long chains from Wertheim's perturbation theory. *Molecular Physics* **2000**, *98*, 1295–1308, DOI: 10.1080/002689700413550.
- (43) Diky, V.; Chirico, R. D.; Frenkel, M.; Bazyleva, A.; Magee, J. W.; Paulechka, E.; Kazakov, A.; Lemmon, E. W.; Muzny, C. D.; Smolyanitsky, A. Y.; Townsend, S.; Kroenlein, K.

- NIST Standard Reference Database 103b: ThermoData Engine (Version 10.1). 2017; <https://www.nist.gov/srd/nist-standard-reference-database-103b>.
- (44) Bell, I. H.; Galliero, G.; Delage Santacreu, S.; Costigliola, L. Communication: An Entropy Scaling Demarcation of Gas- and Liquid-like Fluid Behaviors. *J. Chem. Phys.* **2020**, *152*, 191102, DOI: 10.1063/1.5143854.
 - (45) Chung, T.-H.; Lee, L. L.; Starling, K. E. Applications of Kinetic Gas Theories and Multiparameter Correlation for Prediction of Dilute Gas Viscosity and Thermal Conductivity. *Ind. Eng. Chem. Fundam.* **1984**, *23*, 8–13, DOI: 10.1021/i100013a002.
 - (46) Kim, S. U.; Monroe, C. W. High-accuracy calculations of sixteen collision integrals for Lennard-Jones (12–6) gases and their interpolation to parameterize neon, argon, and krypton. *J. Comput. Phys.* **2014**, *273*, 358–373, DOI: 10.1016/j.jcp.2014.05.018.
 - (47) Setzmann, U.; Wagner, W. A New Equation of State and Tables of Thermodynamic Properties for Methane Covering the Range from the Melting Line to 625 K at Pressures up to 100 MPa. *J. Phys. Chem. Ref. Data* **1991**, *20*, 1061–1155, DOI: 10.1063/1.555898.
 - (48) Bücker, D.; Wagner, W. A Reference Equation of State for the Thermodynamic Properties of Ethane for Temperatures from the Melting Line to 675 K and Pressures up to 900 MPa. *J. Phys. Chem. Ref. Data* **2006**, *35*, 205–266, DOI: 10.1063/1.1859286.
 - (49) Lemmon, E. W.; McLinden, M. O.; Wagner, W. Thermodynamic Properties of Propane. III. A Reference Equation of State for Temperatures from the Melting Line to 650 K and Pressures up to 1000 MPa. *J. Chem. Eng. Data* **2009**, *54*, 3141–3180, DOI: 10.1021/je900217v.
 - (50) Bücker, D.; Wagner, W. Reference Equations of State for the Thermodynamic Properties of Fluid Phase n-Butane and Isobutane. *J. Phys. Chem. Ref. Data* **2006**, *35*, 929–1019, DOI: 10.1063/1.1901687.
 - (51) Lemmon, E. W.; Span, R. Short Fundamental Equations of State for 20 Industrial Fluids. *J. Chem. Eng. Data* **2006**, *51*, 785–850, DOI: 10.1021/je050186n.
 - (52) Aleksandrov, I. S.; Gerasimov, A. A.; Grigor’ev, B. A. Using fundamental equations of state for calculating the thermodynamic properties of normal undecane. *Therm. Eng.* **2011**, *58*, 691–698, DOI: 10.1134/s0040601511080027.
 - (53) Lemmon, E. W.; Huber, M. L. Thermodynamic Properties of n-Dodecane. *Energy & Fuels* **2004**, *18*, 960–967, DOI: 10.1021/ef0341062.
 - (54) Vogel, E.; Herrmann, S. New Formulation for the Viscosity of Propane. *J. Phys. Chem. Ref. Data* **2016**, *45*, 043103, DOI: 10.1063/1.4966928.
 - (55) Michailidou, E. K.; Assael, M. J.; Huber, M. L.; Abdulagatov, I. M.; Perkins, R. A. Reference Correlation of the Viscosity of n-Heptane from the Triple Point to 600 K and up to 248 MPa. *J. Phys. Chem. Ref. Data* **2014**, *43*, 023103, DOI: 10.1063/1.4875930.
 - (56) Huber, M. L.; Laesecke, A.; Xiang, H. W. Viscosity correlations for minor constituent fluids in natural gas: n-octane, n-nonane and n-decane. *Fluid Phase Equilib.* **2005**, *228-229*, 401–408, DOI: 10.1016/j.fluid.2005.03.008.
 - (57) Vogel, E.; Span, R.; Herrmann, S. Reference Correlation for the Viscosity of Ethane. *J. Phys. Chem. Ref. Data* **2015**, *44*, 043101, DOI: 10.1063/1.4930838.
 - (58) Huber, M. L.; Laesecke, A.; Perkins, R. Transport Properties of n-Dodecane. *En-*

ergy & Fuels **2004**, *18*, 968–975, DOI: 10.1021/ef034109e.

- (59) Michailidou, E. K.; Assael, M. J.; Huber, M. L.; Perkins, R. A. Reference Correlation of the Viscosity of n-Hexane from the Triple Point to 600 K and up to 100 MPa. *J. Phys. Chem. Ref. Data* **2013**, *42*, 033104, DOI: 10.1063/1.4818980.
- (60) Assael, M. J.; Papalas, T. B.; Huber, M. L. Reference Correlations for the Viscosity and Thermal Conductivity of n-Undecane. *J. Phys. Chem. Ref. Data* **2017**, *46*, 033103, DOI: 10.1063/1.4996885.
- (61) Herrmann, S.; Vogel, E. New Formulation for the Viscosity of n-Butane. *J. Phys. Chem. Ref. Data* **2018**, *47*, 013104, DOI: 10.1063/1.5020802.
- (62) Agarwal, M.; Singh, M.; Jabes, B. S.; Chakravarty, C. Excess entropy scaling of transport properties in network-forming ionic melts (SiO₂ and BeF₂). *J. Chem. Phys.* **2011**, *134*, 014502, DOI: 10.1063/1.3521488.
- (63) Yoon, T. J.; Patel, L. A.; Ju, T.; Vigil, M. J.; Findikoglu, A. T.; Currier, R. P.; Maerzke, K. A. Thermodynamics, dynamics, and structure of supercritical water at extreme conditions. *Phys. Chem. Chem. Phys.* **2020**, DOI: 10.1039/d0cp02288h.
- (64) Sun, T.; Xian, J.; Zhang, H.; Zhang, Z.; Zhang, Y. Two-phase thermodynamic model for computing entropies of liquids reanalyzed. *J. Chem. Phys.* **2017**, *147*, 194505, DOI: 10.1063/1.5001798.
- (65) Schröder, T. B.; Dyre, J. C. Solid-like mean-square displacement in glass-forming liquids. *J. Chem. Phys.* **2020**, *152*, 141101, DOI: 10.1063/5.0004093.
- (66) Heyes, D. M.; Smith, E. R.; Dini, D.; Spikes, H. A.; Zaki, T. A. Pressure dependence of confined liquid behavior subjected to boundary-driven shear. *The Journal of Chemical Physics* **2012**, *136*, 134705, DOI: 10.1063/1.3698601.
- (67) Gattinoni, C.; Heyes, D. M.; Lorenz, C. D.; Dini, D. Traction and nonequilibrium phase behavior of confined sheared liquids at high pressure. *Physical Review E* **2013**, *88*, 052406, DOI: 10.1103/physreve.88.052406.
- (68) Ewen, J. P.; Heyes, D. M.; Dini, D. Advances in nonequilibrium molecular dynamics simulations of lubricants and additives. *Friction* **2018**, *6*, 349–386, DOI: 10.1007/s40544-018-0207-9.
- (69) Ewen, J. P.; Gattinoni, C.; Zhang, J.; Heyes, D. M.; Spikes, H. A.; Dini, D. On the effect of confined fluid molecular structure on nonequilibrium phase behaviour and friction. *Phys. Chem. Chem. Phys.* **2017**, *19*, 17883–17894, DOI: 10.1039/c7cp01895a.

Graphical TOC Entry

