Scaling of the viscosity of the Lennard-Jones chain fluid model, argon, and some normal alkanes

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Scaling of the viscosity of the Lennard-Jones chain fluid model, argon, and some normal alkanes

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In this work, we have tested the efficiency of two scaling approaches aiming at relating shear viscosity to a single thermodynamic quantity in dense fluids, namely the excess entropy and the thermodynamic scaling methods. Using accurate databases, we have applied these approaches first to a model fluid, the flexible Lennard-Jones chain fluid (from the monomer to the hexadecamer), then to real fluids, such as argon and normal alkanes. To enlarge noticeably the range of thermodynamics conditions for which these scaling methods are applicable, we have shown that the use of the residual viscosity instead of the total viscosity is preferable in the scaling procedures. It has been found that both approaches, using the adequate scaling, are suitable for the Lennard-Jones chain fluid model for a wide range of thermodynamic conditions whatever the chain length when scaling law exponents and prefactors are adjusted for each chain length. Furthermore, these results were found to be well respected by the corresponding real fluids. © *2011 American Institute of Physics*. [doi:10.1063/1.3553262]

I. INTRODUCTION

Accurate estimations of transport properties of monoatomic fluids in the low density regime are now accessible thanks to extended kinetic theories.[1–3] However, the situation is more complex when dealing with polyatomic fluids and dense states for which no rigorous theory is yet available for an exact representation of transport properties in terms of the parameters of a molecular model, i.e., interaction parameters + description of the molecule structure and thermodynamic conditions.

Nevertheless, there exist promising scaling approaches to describe transport properties in dense fluids.[4–10] In such approaches it is generally assumed that it is possible to relate transport properties to a single thermodynamic quantity. Among them, we have studied in this work the method based on the excess entropy[7,11] and the approach based on a quantity defined by the density, ρ, raised at a given exponent γ divided by the temperature,[4,9] T (i.e., the ratio ρ^γ/T) named "Thermodynamic Scaling" in the following. Both methods have been initially motivated by molecular dynamics (MD) results on very simple fluids such as soft sphere fluids.[4,11,12] More recently several researchers have analyzed the thermodynamic scaling using MD simulations on various model fluids,[13–16] including Lennard-Jones Liquid[13,14] and a Lennard-Jones dumbbell model.[16] As regards to the entropy scaling a large amount of work has been achieved recently using molecular simulation on model fluids[17–24] including the square well fluid,[19] Lennard-Jones fluid,[20] a Lennard-Jones dumbbell model[23] and the Lennard-Jones Chain (LJC)

model.[21] Interestingly it seems that these scaling approaches are applicable to a certain extent to real fluids but fail for some hydrogen bonding fluids such as water[9,25–28] Additionally, it is interesting to point out that, recently, Gnan *et al.*[29] have introduced the concept of "isomorphs" which embodies the two scaling approaches described previously in a more general frame.

Among the various model fluids of interest, the Lennard-Jones Chain is a three parameters molecular model for which there exists accurate Equations of State[30,31] and transport properties[21,32–34] data coming from molecular dynamics simulations. In this fluid model, the molecule is described as a flexible chain of freely jointed spheres with nonbonded interactions represented by a Lennard-Jones potential.[30] It is worth to point out that, to the best of our knowledge, except the work of Goel *et al.*[21] using the excess entropy scaling, this LJC fluid model (for chain length of more than two segments) has not been studied previously in the literature in the frame of both scaling approaches. In addition, apart from its fundamental interest, such a model fluid is interesting from an engineering point of view as long as it has been shown that it can be used to represent rather accurately many thermophysical properties of some real fluids.[31,33,35–40]

So, in this work, we have applied both excess entropy and thermodynamic scaling approaches to the LJC fluid (from the monomer to the hexadecamer) from the shear viscosity point of view for which there is less studies available on model fluids than those using diffusivities. In addition, we have evaluated the advantage of using the reduced residual viscosity instead of the reduced total viscosity in the scaling procedure. Furthermore, following the results obtained on the LJC fluid, we have applied the two scaling schemes using the reduced residual viscosity on some simple real fluids (argon and nor-

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mal alkanes) for a wide range of thermodynamic conditions covering not only the liquid but also the gas and supercritical states.

In a first part, a brief presentation of the two scaling approaches dealt with in this work together with a description of the LJC fluid model is provided. Then, in a second part, the results on model and real fluids are presented and analyzed through the two scaling approaches.

II. THEORY AND MODELS

A. Excess entropy

Among the attempts to link transport properties to an equilibrium thermodynamic property, Rosenfeld[7,11] has shown that, for simple atomic model fluids, the viscosity (and more generally transport properties) of dense pure fluids can be correlated with the excess entropy. This last is defined as the difference between the thermodynamics entropy and the entropy of the ideal gas at the same conditions[7] and is so a configurational quantity. It is interesting to notice that, in this approach, it is implicitly assumed that there is a simple relation between the viscosity and the number of accessible configurations.[25,26]

To obtain a "universal" link (i.e., a corresponding states behavior[3]) between the viscosity, η, and the excess entropy, S^e, the starting point is the definition of the corresponding reduced quantities using the adequate macroscopic reduction parameters.[4,11] The reduction of the viscosity, originally defined for inverse power-law (IPL) potential,[4,12] is based on a time scale defined by $(k_B T/M)^{1/2}$, where k_B is the Boltzmann constant, T the temperature, and M the mass of the molecule and on a length scale defined by $(V/N_m)^{1/3}$, where N_m is the number of molecules in a volume V. In that frame, the reduced shear viscosity is defined as

$$\eta^r = \eta \frac{\rho_n^{-2/3}}{(Mk_BT)^{1/2}}, \qquad (1)$$

where ρ_n is the number density ($=N_m/V$). The reduced excess entropy is expressed by

$$S^r = \frac{S^e}{k_B N_m}. \qquad (2)$$

In that frame, Rosenfeld[4,11] has found that the universal link that exists between the two reduced properties defined above can be written as

$$\eta^r = a e^{-bS^r}, \qquad (3)$$

where a and b are two numerical parameters. Using various results of MD simulations on spheres interacting with various pair potentials, Rosenfeld[11] has found that reasonable results can be obtained in dense fluids using $a = 0.2$ and $b = 0.8$.

It should be noticed that such scaling approach, through Eq. (3), has been tested recently with a relative success on some experimental data[25,26] of small real molecules (N_2 and CO_2) up to very high pressure (few GPa). Among other, it has been confirmed that the parameter b is decreasing with the nonsphericity of the molecule.

B. Thermodynamic scaling

Another approach, named thermodynamic scaling, assumes that it is possible to express a relaxation time/dynamic property as a unique function of the thermodynamics quantity ρ^γ/T, where ρ is the mass density and γ a constant specific of the material.[4,9] In this approach, γ quantifies the relative influence of the volume and temperature in the dynamic behavior of the studied compound. As for the excess entropy approach, it is useful to work with the reduced viscosity which leads to assume that:

$$\eta^r = F\left(\frac{\rho^\gamma}{T}\right), \qquad (4)$$

where F is an unknown function.

For inverse power-law fluids the thermodynamic scaling approach and the excess entropy scaling are closely related and are both embodied in a more general frame, the "isomorphs" concept.[29] For such simple spherical molecules interacting through an IPL potential, γ is simply equal to $n/3$, where n is the repulsive exponent,[4,12] whereas the excess entropy of dense fluids which interact through an IPL potential is[41] a function of $\rho^{n/3}/T$.

C. Extension to low/moderate density conditions

Excess entropy and thermodynamic scaling methods described previously have been developed to deal with dense fluids only. In fact, both approaches exhibit deficiencies when going toward low densities conditions when the reduced viscosity is employed. More precisely, at extremely low density conditions, the viscosity should tend to its "zero-density" contribution, η_0, which is a non-null quantity accurately provided by kinetic theories[1–3] for simple fluid models and which is independent of density.[1–3] So, as the reduced viscosity defined by Eq. (1) is diverging when $\rho_n \to 0$ (i.e., when S^r and $\rho^\gamma/T \to 0$), that leads to an inconsistency of the two scaling approaches described previously for low density fluids.

It should be noticed that this inconsistency in the excess entropy scaling approach has already been pointed out by Rosenfeld[7] and discussed for thermal conductivity[26] and mass diffusion[22,42] and has led to a "generalized" Rosenfeld scaling scheme for diffusion.[22] Concerning the shear viscosity of IPL fluids, Rosenfeld[7] has argued that in the dilute gas limit the reduced viscosity should be proportional to the reduced excess entropy at the power −2/3.

To avoid this unphysical divergence while keeping a single scaling relation of the type of Eqs. (3) and (4), we propose, as initially used by Ashurst et al.,[4] to employ the residual (sometimes called excess) contribution to the viscosity, η_{res}, defined as

$$\eta_{res} = \eta - \eta_0, \qquad (5)$$

instead of using the total viscosity in the scaling procedure, i.e., in Eq. (1). In the case of excess entropy scaling, this choice is guided by the fact that it seems more consistent to link excess entropy to the residual viscosity (sometimes called excess viscosity) and not the total viscosity as long as both quantities are defined relatively to an "ideal" contribution.

By doing so, we ensure that the reduced residual viscosity, η_{res}^r, defined by the combination of Eqs. (1) and (5) is not diverging in the low density limit where S^r and $\rho^\gamma/T \to 0$. In that frame, Eq. (3) becomes

$$\eta_{\text{res}}^r = \alpha e^{-\beta S^r}, \tag{6}$$

where α and β are numerical parameters, and Eq. (4) becomes

$$\eta_{\text{res}}^r = G\left(\frac{\rho^\gamma}{T}\right), \tag{7}$$

where G is a unknown function.

D. The Lennard-Jones flexible chain model

In this fluid model, each molecule is described as a set of N tangent spheres/segments which are freely jointed. In addition, all segments of a molecule possess the same mass, size, and energy (homonuclear). The intermolecular and non-bonded intramolecular interactions (corresponding to nonadjacent segments) are described by the Lennard-Jones 12-6 potential[43]:

$$U_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{8}$$

where ε is the potential strength, σ, the segment diameter, which is the distance at which the potential is null, r the center to center distance between the two considered segments. The bond between two adjacent spheres is described by a constrained bond of a length of σ or by a stiff spring with an equilibrium distance equal to σ, both methods leading generally to similar results.[30,33]

In the following, the LJC data have been sometimes expressed in Lennard-Jones (LJ) dimensionless units, noted with a star as superscript, using the monomer parameters (σ, ε, and m, where $m = M/N$ is the mass of the monomer) as characteristic length, energy, and mass. This dimensionless procedure leads to $T^* = k_B T/\varepsilon$, $\rho^* = N_S \sigma^3/V$ and $\eta^* = \eta(\sigma^2/\sqrt{m\varepsilon})$, where N_S is the total number of spheres/segments ($N_S = N \times N_m$) inside a volume V containing N_m molecules.

III. RESULTS AND DISCUSSION

A. Excess entropy

1. LJ fluid

In a first step, we have applied the excess entropy approach to the simple Lennard Jones fluid ($N = 1$, monomer) for a wider range of thermodynamic conditions than done previously for viscosity.[4,7] To do so, we have employed a large database of LJ shear viscosity values coming from accurate MD simulations (error bars of a few percents) performed by Meier et al.[44] and Galliero et al.[45] which covers gas, liquid and supercritical states ($0.6 \leq T^* \leq 6$ and $0 \leq \rho^* \leq 1.275$). The zero-density limit of the LJ fluid viscosity has been estimated using the classical Chapman–Enskog relation for the LJ fluid.[1,3] Excess entropies have been deduced from the LJ equation of state (EoS) of Kolafa and Nezbeda.[46]

As shown in Fig. 1(a), the excess entropy scaling using the reduced viscosity, Eq. (3) is consistent for not too low density conditions (i.e., when S^r is roughly smaller than -1.5) even if the scattering of the data is non-negligible and is by far larger than the uncertainties. Interestingly, a and b values (respectively, 0.2 and 0.8) proposed by Rosenfeld[7] are consistent with these recent MD results which covers a wider range of thermodynamic states than previously tested.

When η_{res}^r is used instead of η^r, the applicability of the excess entropy scaling is extended to a wider range of thermodynamic conditions, as clearly shown when looking at Fig. 1(b) compared to Fig. 1(a). More precisely the scaling using η_{res}^r seems to be valid up to $S^r \approx -0.5$ whereas using η^r, the scaling is valid only up to $S^r \approx -1.5$. A consistent fit of the data with Eq. (6) can be obtained using $\beta = 1$ (and $\alpha = 0.09$), see Fig. 1(b). The average absolute deviation (AAD) between the viscosity deduced from this scaling procedure and the large MD database is equal to 9% with a maximum (MxD) equal to 45.1%, the deviations being larger at very low density.

It should be noticed that when $S^r \to 0$ (i.e., the low density limit), η_{res}^r should tend toward zero whereas Eq. (6) implies that $\eta_{\text{res}}^r \to \alpha$ and is so not applicable below $S^r \approx -0.5$, see Fig. 1(b). In addition, concerning this low density limit, it is interesting to notice that the relation proposed by
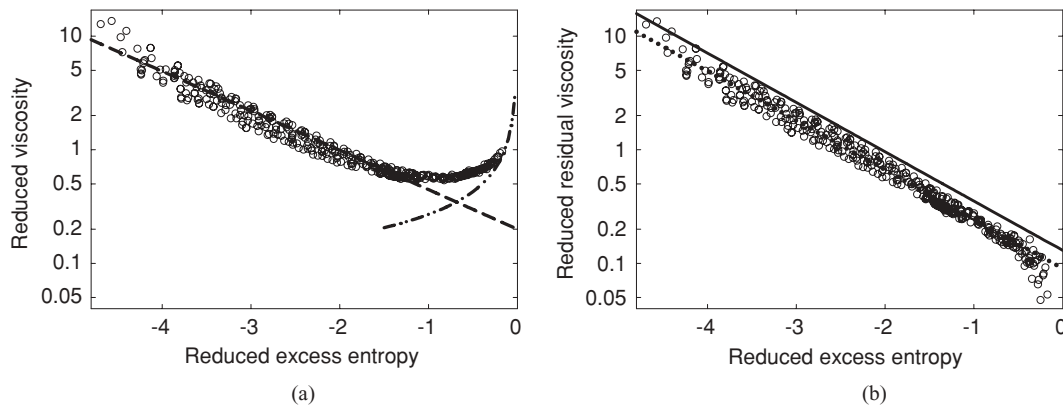

FIG. 1. (a) Reduced viscosity η^r and (b) reduced residual viscosity η_{res}^r of the LJ fluid (monomer) vs reduced excess entropy S^r. Symbols correspond to MD simulations results (Refs. 44 and 45). In (a) dashed line to Eq. (3) with $a = 0.2$ and $b = 0.8$ and dashed-dotted line to $0.27(-S^r)^{-2/3}$ as proposed by Rosenfeld (Ref. 7). In (b) full line to Eq. (6) with $\alpha = 0.13$ and $\beta = 1$ and dotted line to Eq. (6) with $\alpha = 0.09$ and $\beta = 1$.
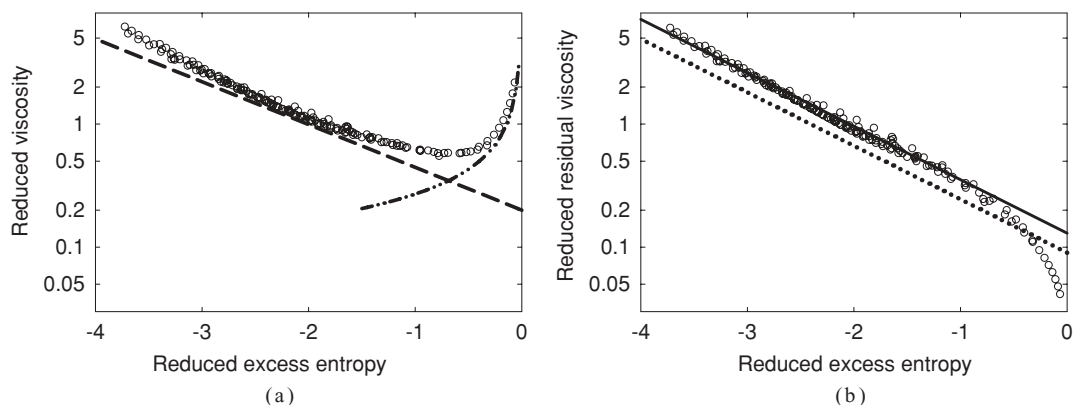
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FIG. 2. Reduced viscosity (a) and reduced residual viscosity (b) vs reduced excess entropy of argon (over $T = 100–600$ K and $p = 0.1–1000$ MPa). Symbols correspond to Tegeler *et al*. (Ref. [47]) and Lemmond *et al*. (Ref. [48]) data. In (a) dashed line to Eq. (3) with $a = 0.2$ and $b = 0.8$ and dashed-dotted line to $0.27(-S^r)^{-2/3}$ as proposed by Rosenfeld (Ref. [7]). In (b) full line to Eq. (6) with $\alpha = 0.13$ and $\beta = 1$ and dotted line to Eq. (6) with $\alpha = 0.09$ and $\beta = 1$.

Rosenfeld,[7] $\eta^r = 0.27(-S^r)^{-2/3}$, seems to be rather consistent with the MD results, see Fig. 1(a).

2. Argon

Argon, which is often represented by a LJ fluid model, is a monoatomic compound for which it exists very accurate relations that describe its thermophysical properties for a very wide range of fluid states. So, as done for the LJ fluid, we have tested the excess entropy approach on the argon for T varying between 100 and 600 K and p ranging from 0.1 to 1000 MPa. Excess entropies have been obtained using the equation of state of Tegeler *et al*.[47] and viscosity data have been computed using the correlation provided by Lemmon and Jacobsen.[48]

As shown in Fig. 2, results on argon are similar to those obtained with the LJ fluid, in particular it is obvious that the use of the reduced residual viscosity increases the range of applicability of the excess entropy scaling compared to what is obtained with reduced viscosity. Furthermore the direct use of the relations proposed by Rosenfeld,[7] see Fig. 2(a), provides reasonable results but not as good as for the LJ fluid, see Fig. 1(a).

It is worth to notice that the optimal slope ($\beta = 1$) for the argon in Eq. (6) is the same as for that of the LJ fluid when the residual viscosity is employed. However, rather surprisingly, the optimal value of α for the argon (0.13) is somewhat larger than for the LJ fluid (0.09), see Figs. 1(b) and 2(b), which may indicate some intrinsic limitations of the LJ potential to describe very precisely and simultaneously excess entropy and shear viscosity of Argon.

Another interesting point is that the scattering of the data for argon is by far smaller than for the LJ fluid for a similar range of thermodynamic states, see Figs. 1 and 2. This is probably due to the fact that both viscosity and excess entropy are more accurately determined for argon than for the LJ fluid. More precisely, the AAD between the viscosity deduced from this scaling procedure and the experimental database is equal to 5.1% with a MxD equal to 12.3%, the deviations being larger at very low density.

3. LJC fluid

An interesting point, as already pointed out in the literature,[21,23] is to analyze to which extent the excess entropy scaling based on Eq. (6) is consistent when dealing with nonspherical molecules such as short LJ chains (up to 16 segments in this work). One can expect that internal degrees of freedom would have an impact on this scaling. More precisely, because of possible rotational motions, a decrease of β with the chain length is expected.[25,26]

So, as previously done for the LJ fluid, we have tested the excess entropy scaling for the LJC fluid model for various N (from 2 to 16, i.e., for lengths below the entanglement[33,49]) and for a wide range of thermodynamic states ($0.7 \leq T^* \leq 6$ and $0 \leq \rho^* \leq 1.1$) covering gas, liquid, and supercritical states. MD data of the viscosity of the LJC fluid model have been taken from Galliero and Boned.[33] The "zero-density" of the LJC fluid viscosity has been estimated using the modified Chapman–Enskog relation for the LJC fluid proposed in Galliero and Boned.[33] Excess entropies of the LJC model have been estimated using the LJ-SAFT EoS,[31] i.e., a reference LJ term modeled by the Kolafa and Nezbeda EoS[46] combined with the chain term of Johnson *et al*.[30]
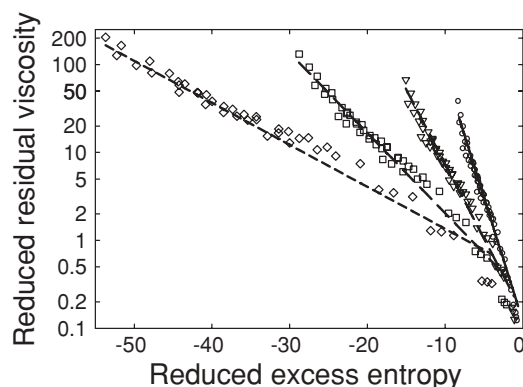

FIG. 3. Reduced residual viscosity of the LJC fluid for various chain lengths vs reduced excess entropy. Symbols correspond to MD simulations results (Ref. [33]), $N = 2$: circles, $N = 4$: down triangles, $N = 8$: squares and $N = 16$: diamonds. Lines correspond to Eq. (6) with parameters given in Table I.

TABLE I. Parameters in Eq. (6) adjusted on MD simulations data for various chain lengths.

N	1	2	4	8	16
α	0.09	0.12	0.15	0.25	0.45
β	1	0.65	0.39	0.21	0.11

TABLE II. Parameters in Eq. (6) obtained for three *n*-alkanes.

	Methane	*n*-Butane	*n*-Decane
α	0.13	0.25	0.27
β	0.88	0.56	0.40

The excess entropy scaling based on the reduced residual viscosity seems to be consistent for all (short) LJ chains tested in this work, see Fig. 3, for a wide range of thermodynamics conditions except in the dilute regime. From a quantitative point of view, using this scaling the AADs on the total viscosity compared to direct MD results are equal (with MxD in parenthesis) to 15.7% (72.6%), 28% (99%), 40% (99%), and 50.6% (171%), respectively for $N = 2$, 4, 8, and 16.

In addition $\beta \approx 2/(1 + N)$ which corresponds, as expected,[25,26] to a strong decrease of β with N whereas α increases roughly linearly with N, see Table I. It is worth it to point out that in the work of Goel *et al.*[21] it has been found that β was increasing with chain length in LJC fluids using the total reduced viscosity contrary to what we obtained. This difference can be simply explained by the fact that, rather surprisingly, instead of the using the reduced excess entropy per molecule they have employed the reduced excess entropy per segment of molecule.

4. Normal alkanes

Normal alkanes are sometimes modeled by the LJC fluid model.[33,35–37,40] So, to apply the excess entropy scaling to such fluids using the reduced residual viscosity, we have selected three of them, methane, *n*-butane, and *n*-decane that corresponds usually to a LJC fluid with respectively 1, 2, and 4 segments in a SAFT representation[40,50] and for which it exits accurate relations to estimate their excess entropy and viscosity. For methane ($T = 150–400$ K, $p = 0–100$ MPa) we have employed the EoS of Setzmann and Wagner[51] and the viscosity data[52] provided by the NIST (REFPROP8). For *n*-butane ($T = 200–500$ K, $p = 0–65$ MPa), we have used the EoS of Bücker and Wagner[53] and the viscosity correlation of Vogel *et al.*[54] For *n*-decane ($T = 250–650$ K, $p = 0–200$

MPa) we have employed the EoS of Lemmon and Span[55] and the viscosity correlation of Huber *et al.*[56]

As shown in Fig. 4, the excess entropy scaling seems to work well for the three normal alkanes tested in this work in agreement with the findings on the LJC fluid. The optimal β is strongly decreasing with the number of carbons, see Table II. Furthermore, the β values obtained for these *n*-alkanes are consistent with what obtained on the corresponding LJC fluids. From a quantitative point of view, using this scaling the AADs are equal (with MxD in parenthesis) to 5% (11%), 3.6% (39.4%), and 3.9% (46%), respectively for C_1, C_4, and C_{12}, with deviations being larger at very low density.

Thus, despite not being a way to construct a reference correlation (i.e., deviations within a few percent at maximum for all states) for viscosity, the excess entropy approach using the residual viscosity can be employed to yield a very reasonable estimation of the shear viscosity of some model and real fluids for a wide range of thermodynamics states provided an accurate equation of state. Furthermore, this approach can be used as a straightforward way to test the consistency of the data provided by some EoS and viscosity correlation out of their range of fitting.

B. Thermodynamic scaling

1. LJ fluid

As previously done with the excess entropy scaling, we have applied the thermodynamic scaling approach to the reduced residual viscosity of the LJ fluid model using the same database. For sake of generality LJ dimensionless units have been employed, i.e., the quantity $\rho^{*\gamma}/T^*$ has been used instead of ρ^γ/T to apply the thermodynamic scaling approach on the LJ fluid.
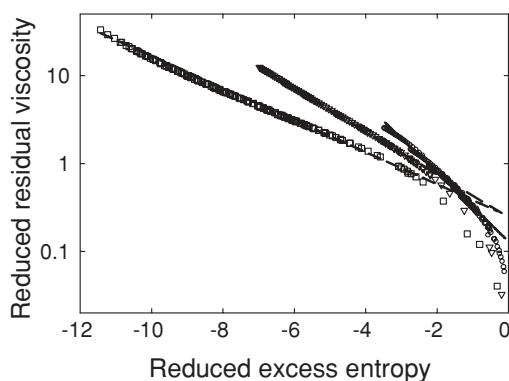

FIG. 4. Reduced residual viscosity of some *n*-alkane vs reduced excess entropy. Circles correspond to methane (Refs. 51 and 52), down triangles to *n*-butane (Refs. 53 and 54), and squares to *n*-decane (Refs. 55 and 56). Lines correspond to Eq. (6) with optimal parameters given in Table II.
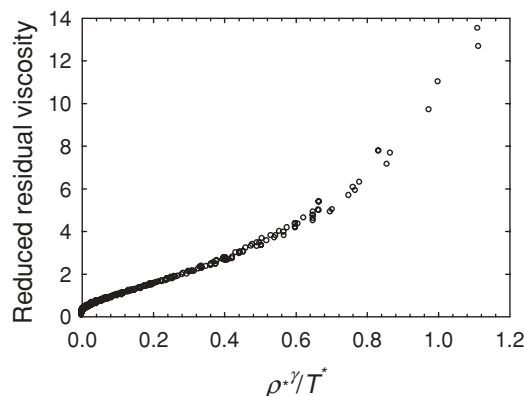

FIG. 5. Reduced residual viscosity of the LJ fluid (monomer) vs $\rho^{*\gamma}/T^*$ for $\gamma = 4.9$. Symbols correspond to MD simulations results (Refs. 44 and 45).
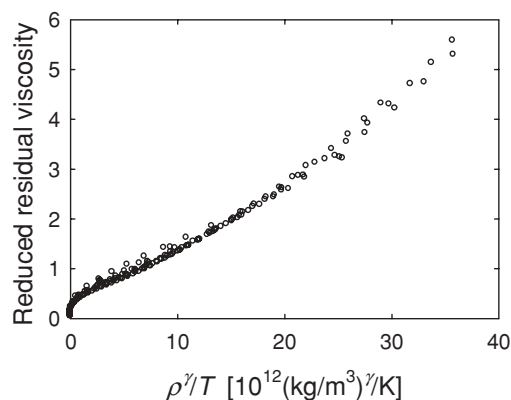
FIG. 6. Reduced residual viscosity of argon (Refs. 47 and 48) vs ρ^γ / T using $\gamma = 4.9$.

As clearly shown in Fig. 5, using this approach on the LJ fluid, it is possible to find a value for γ (equal to 4.9) which leads to a single curve with a very limited scattering over all thermodynamics conditions tested even in the dilute regime. Such a value for γ is consistent with the fact that the viscosity of the LJ fluid is mainly influenced by the density (relatively to temperature) as usually for nonpolar fluids.[9, 27]

Interestingly the value obtained for γ is close to the one found by Coslovich and Roland[14] for the diffusion coefficients of a dense mixture of LJ particles for which they obtained $\gamma = 5$. Furthermore, as in a LJ fluid model the repulsive exponent n is equal to 12, one can expect a value of γ around 4 (i.e., $n/3$) from a rough extrapolation of the IPL results to the LJ fluid.[4] However, it should be noticed that, very recently, Paluch et al.[28] and Grzybowsky et al.[57] have modified the scaling temperature–volume version of the Avramov entropic model[58, 59] concluding that γ *is* not straightforwardly related to the exponent n of the IPL potential or of the repulsive term of the LJ potential.

2. Argon

In order to check to which extent the results on the LJ fluid are consistent with those obtained for a real spherical molecule, we have applied this scheme (with $\gamma = 4.9$ as for the LJ fluid) to the Argon using the same dataset than in the excess entropy section.
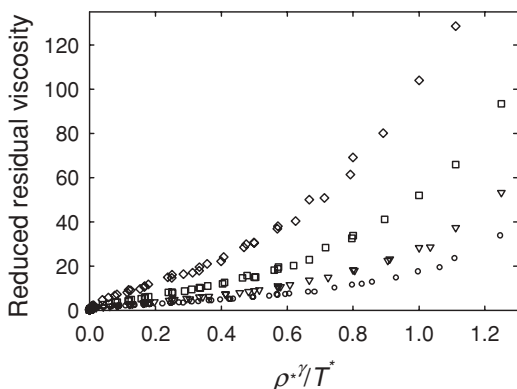
As it appears clearly from Fig. 6, the thermodynamic scaling approach is rather efficient for the Argon over the full range of thermodynamics conditions using the γ value deduced from the LJ fluid. This result is consistent with the literature as long as the LJ fluid is generally able to represent correctly the viscosity of argon over a wide range of thermodynamics conditions using temperature and density as inputs.[45, 60]

3. LJC fluid

Using the database employed for the excess entropy method, we have applied the thermodynamic scaling approach to the LJC fluid using the reduced residual viscosity.

As noted for the LJ fluid, this scaling approach is efficient when applied to the LJC reduced residual viscosity whatever the chain length and the thermodynamic state are, see Fig. 7. An interesting point is that, as shown in Table III, γ is increasing noticeably and monotonously with the chain length of this fully flexible chain fluid model. Such a behavior of γ with N indicates that, for the LJC model, the longer the chain the larger the effect of density on the reduced residual viscosity relatively to that of the temperature. In addition, the optimized value of γ obtained for the dimer (dumbbell models) case is similar to what found in the recent literature.[16, 23]

4. Normal alkanes

As done for the excess entropy approach, using the same database, we have employed the thermodynamic scaling scheme to study the reduced residual viscosity behavior of three normal alkanes (methane, n-butane, and n-decane).

As shown in Fig. 8, if the γ corresponding to $N = 1$ ($\gamma = 4.9$), $N = 2$ ($\gamma = 5.7$), and $N = 4$ ($\gamma = 6.3$) are employed
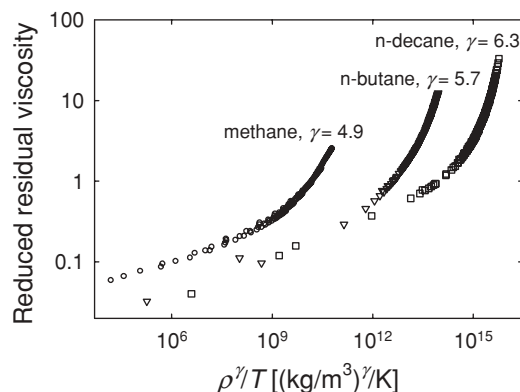
TABLE III. Optimal γ adjusted on MD data for various chain lengths of the LJC fluid.

N	1	2	4	8	16
γ	4.9	5.7	6.3	6.5	6.6

FIG. 7. Reduced residual viscosity of the LJC fluid vs $\rho^{*\gamma} / T^*$ for different chain lengths, $N = 2$: circles, $N = 4$: down triangles, $N = 8$: squares, and $N = 16$: diamonds. Values of γ are provided in Table III.

FIG. 8. Reduced residual viscosity of methane (Refs. 49 and 50), n-butane (Refs. 51 and 52), and n-decane (Refs. 53 and 54) vs ρ^γ / T.

respectively for methane, n-butane, and n-decane, the thermodynamic scaling approach yields a consistent scaling for the full range of thermodynamics conditions. This confirms that the behavior noted on the LJC fluid seems to be transposable to normal alkanes (at least up to n-decane) in a rather straightforward way. However, care should be taken when trying to generalize this result to longer n-alkanes in particular because of the intrinsic limitations of this fluid model which is based on a fully flexible representation of the molecules whereas real n-alkanes are not fully flexible molecules (bending and torsion).

IV. CONCLUSIONS

On the flexible Lennard-Jones chain fluid and some real simple fluids, we have tested two scaling approaches aiming at relating shear viscosity to a single thermodynamic quantity in dense liquids, namely the excess entropy and the thermodynamic scaling approaches. To noticeably enlarge the range of thermodynamics conditions for which these schemes can be applied, we have shown that the use of the residual viscosity instead of the total viscosity is obviously preferable in the scaling procedure.

Using the reduced residual viscosity, it has been found that both excess entropy and thermodynamic scaling schemes are well respected by the Lennard-Jones Chain fluid model over a wide range of thermodynamics conditions and for all the chain lengths tested in this work (from 1 to 16 segments) when scaling law exponents and prefactors are adjusted for each chain length. In addition, this result has been shown to hold as well for simple real nonpolar fluids, such as argon, methane, n-butane, and n-decane, provided accurate viscosity database and equation of state are available.

Using the excess entropy approach, it has been observed on the LJC fluid model that the coefficient, β (in the relation $\eta_{res}^r = \alpha e^{-\beta S^r}$), was equal to 1 for the LJ fluid using the reduced residual viscosity and was decreasing with the nonsphericity (i.e., chain length). Additionally, using the thermodynamic scaling approach, it has been observed that the longer the chain the larger the influence of density on the residual reduced viscosity relatively to that of the temperature, i.e., the parameter γ (in the relation $\eta_{res}^r = G(\rho^\gamma/T)$) was increasing with the chain length.

Finally, it has been found that these features obtained on the LJC fluid model are rather well exhibited by some corresponding simple real fluids (argon, methane, n-butane, and n-decane) tested in this work. This confirms that the LJC fluid model, despite its simplicity, is able to represent reasonably the main dynamic characteristics of a large variety of simple real fluids.

ACKNOWLEDGMENTS

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