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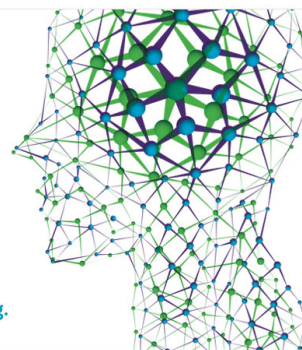
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# Thermodynamic scaling of the shear viscosity of Mie $n$ -6 fluids and their binary mixtures

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In this work, we have evaluated the applicability of the so-called thermodynamic scaling and the isomorph frame to describe the shear viscosity of Mie  $n$ -6 fluids of varying repulsive exponents ( $n = 8, 12, 18, 24$ , and  $36$ ). Furthermore, the effectiveness of the thermodynamic scaling to deal with binary mixtures of Mie  $n$ -6 fluids has been explored as well. To generate the viscosity database of these fluids, extensive non-equilibrium molecular dynamics simulations have been performed for various thermodynamic conditions. Then, a systematic approach has been used to determine the gamma exponent value ( $\gamma$ ) characteristic of the thermodynamic scaling approach for each system. In addition, the applicability of the isomorph theory with a density dependent gamma has been confirmed in pure fluids. In both pure fluids and mixtures, it has been found that the thermodynamic scaling with a constant gamma is sufficient to correlate the viscosity data on a large range of thermodynamic conditions covering liquid and supercritical states as long as the density is not too high. Interestingly, it has been obtained that, in pure fluids, the value of  $\gamma$  is directly proportional to the repulsive exponent of the Mie potential. Finally, it has been found that the value of  $\gamma$  in mixtures can be deduced from those of the pure component using a simple logarithmic mixing rule. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4919296>]

## I. INTRODUCTION

Accurate transport properties of fluids in both dilute and dense phases, and in particular shear viscosity, are often required in many industrial domains.<sup>1</sup> However, the appropriate modeling of these properties over a wide range of thermodynamic conditions still remains a challenge.<sup>2,3</sup> This is largely due to the lack of a rigorous molecular based theory to describe transport properties applicable to all fluid states, despite noticeable recent progresses<sup>3</sup> such as the Assael and Dymond approach and its extensions based on the hard-sphere framework.<sup>4,5</sup>

Among the most promising approaches to describe shear viscosity in dense phases are those based on scaling and isomorph concepts.<sup>6–10</sup> In particular, the model based on the so-called thermodynamic scaling has proven to be useful in describing shear viscosity of a large variety of species in the dense states.<sup>11,12</sup> Furthermore, this approach can be extended to deal with moderately dense fluid thermodynamic conditions.<sup>13</sup> This model relies on the assumption that the shear viscosity of simple fluids scales with the ratio of the density, raised at an exponent  $\gamma$ , divided by the temperature, i.e., this ratio forms isomorphs on which viscosity is invariant.<sup>9</sup>

The parameter  $\gamma$  is material dependent<sup>14</sup> but can be deduced from the equilibrium fluctuations in the canonical ensemble of the potential energy,  $U$ , and the virial,  $W$ .<sup>9</sup> It should be noticed that this frame has been extended recently to deal with large variations in density.<sup>9,15</sup>

An additional problem, when trying to model shear viscosity, is linked to the difficulty in defining a molecular model (molecular structure + effective interaction potential) adapted to deal with both equilibrium and transport properties.<sup>16–21</sup> Since the 1960s, a lot of progress has been performed towards that goal, thanks to molecular dynamics (MD) simulations.<sup>17,19,22,23</sup> This is due to the fact that these numerical methods allow generating “exact” thermophysical properties (including viscosity) of a given molecular model for a set of thermodynamic conditions. In that frame, the most popular interaction potential is certainly the Lennard-Jones (LJ) one.<sup>24</sup> However, recent works on thermodynamic properties<sup>25–27</sup> and on viscosity<sup>16,28</sup> of fluids in various thermodynamic states have shown that the Mie  $n$ -6 potential<sup>29</sup> can lead to noticeable improvements relatively to the LJ potential. Compared to the Lennard-Jones potential, the Mie potential provides one extra degree of freedom associated to a possible modulation of the steepness of the repulsion contribution of the potential. This feature is interesting because the structure of not too complex fluids is primarily guided by short range interactions<sup>30,31</sup> and the viscosity varies noticeably with repulsion steepness.<sup>28,32,33</sup>

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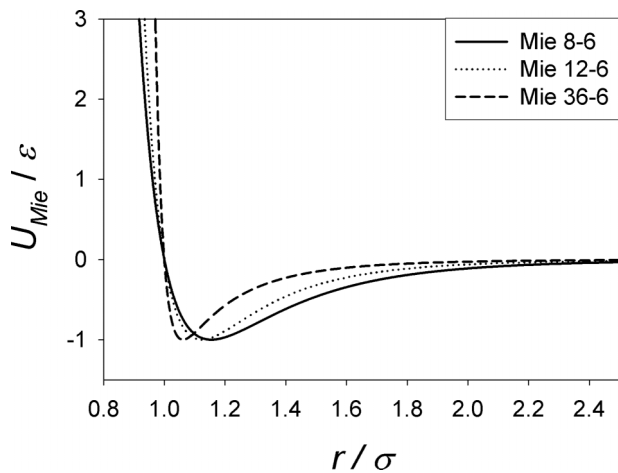


FIG. 1. Mie potentials shape for three different repulsive exponents tested in this work ( $n = 8, 12,$  and  $36$ ).

Furthermore, allowing variable repulsion steepness makes it suitable in a coarse grained frame, as long as bottom-up coarse graining leads to softer potential than the usual one.<sup>34</sup>

Thus, this work aims at checking the ability of the thermodynamic scaling/isomorph frame to deal with the shear viscosity of fluids composed of Mie spheres of various repulsive exponents. For that purpose, extensive Non-Equilibrium Molecular Dynamics (NEMD) simulations have been performed over a wide range of fluid thermodynamic conditions and for repulsive exponents varying between 8 and 36. In addition, the limits of this approach to deal with binary mixtures of Mie fluids have been considered.

The article is structured as follows. In Sec. II the fluid model and the simulation methodology are described. Then, the main results are presented and discussed in Sec. III. Finally, the conclusions are drawn in Sec. IV.

## II. MODELS AND THEORY

### A. The Mie fluid model

In this work, we consider fluids composed of spheres whose inter-particle interactions are described by the so-called Mie  $n$ -6 potential.<sup>35</sup> This potential is characterized by

TABLE I. Exponents deduced from thermodynamic scaling of viscosity ( $\gamma$ ) and from  $W$ - $U$  correlations ( $\Gamma$ ) for different Mie  $n$ -6 pure fluids.  $R$  is the virial-potential energy correlation coefficient.  $\Gamma$  and  $R$  have been computed at  $\rho^* = 1$  and  $T^* = 2$ .

$n$	$\gamma$	$\gamma$ from diffusion data <sup>59</sup>	$\Gamma$	$R$
8	3.65	3.5	3.75	0.988
12	5.05	5.0	5.05	0.989
18	7.15		7.1	0.989
24	9.3	9.1	9.1	0.990
36	13.7	13.4	13.3	0.989

a repulsive term in  $r^{-n}$  and an attractive term in  $r^{-6}$ , where  $r$  is the centre to centre distance between the two interacting spheres considered and  $n$  is the stiffness of the repulsion. It can be expressed as

$$U_{Mie}(r) = \begin{cases} \frac{n}{n-6} \left(\frac{n}{6}\right)^{\frac{6}{n-6}} \varepsilon \left[ \left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^6 \right] & \text{if } r \leq r_c, \\ 0 & \text{if } r > r_c \end{cases}, \quad (1)$$

where  $\varepsilon$  is the potential strength,  $\sigma$  is the sphere ‘‘diameter,’’ and  $r_c$  is the cutoff radius (taken equal to  $2.5\sigma$  in this work). In mixtures composed of Mie fluids of different repulsion exponents, a simple arithmetic combining rule has been employed on the  $n$  exponent.<sup>36</sup>

In this work,  $n$  was chosen to vary between 8 and 36, which yields very different potential shapes (see Fig. 1). This range of  $n$  covers the values that are usually employed to describe real fluids.<sup>27,28</sup> It should be noticed that this potential reduces to the well known Lennard-Jones potential when  $n = 12$ .

The Mie  $n$ -6 fluids are strongly non-conformal as exhibited by their van der Waals constant that varies from 1.26 to 0.52, respectively.<sup>27</sup> However, as shown in Fig. 2, they exhibit a strong correlation between the virial,  $W$ , and the potential energy,  $U$ , during canonical (NVT) molecular dynamics simulations. The values of the correlation coefficient  $R = \langle \Delta W \Delta U \rangle / \sqrt{\langle (\Delta U)^2 \rangle \langle (\Delta W)^2 \rangle}$  are provided in Table I and confirms quantitatively that a strong correlation exists between the virial and potential energy fluctuations ( $R \approx 0.99$ ).

This result supports the use of the thermodynamic scaling, and more generally the concept of isomorph, for such fluids.<sup>9</sup>

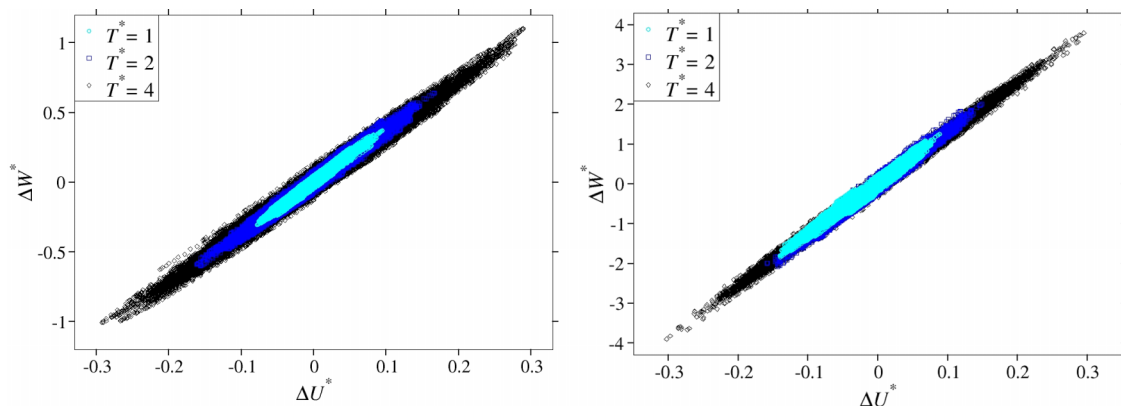


FIG. 2. Fluctuations, per particle, of virial,  $\Delta W^*$ , versus fluctuations of potential energy,  $\Delta U^*$ , for the Mie 8-6 fluid (left figure) and the Mie 36-6 fluid (right figure). The results correspond to NVT simulations at  $\rho^* = 1$  for three different  $T^*$ .

In the following sections dimensionless units are used,<sup>22</sup>

$$T^* = \frac{k_B T}{\varepsilon}, \rho^* = \frac{N \sigma^3}{V}, P^* = \frac{P \sigma^3}{\varepsilon}, \text{ and } \eta^* = \eta \frac{\sigma^2}{\sqrt{M \varepsilon}} \quad (2)$$

as well as the reduced viscosity given by<sup>6</sup>

$$\eta^r = \eta \frac{\rho_n^{-2/3}}{(M k_B T)^{1/2}}, \quad (3)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $N$  is the total number of particles in the simulation box,  $V$  is the volume of the simulation box,  $P$  is the pressure,  $M$  is the mass of one particle,  $\eta$  is the shear viscosity, and  $\rho_n$  is the number density ( $= \frac{N}{V}$ ).

## B. Molecular dynamics simulations

### 1. Computation of shear viscosity

Non-equilibrium molecular dynamics simulations have been performed to compute the shear viscosity of Mie fluids for various thermodynamic states. To do so, the boundary driven NEMD scheme of Müller-Plathe<sup>37</sup> is used. This approach is based on a momentum exchange between the central and the edge parts of the simulations box and is compatible with periodic boundary conditions. This exchange generates a biperiodical shear stress, which combined with the computation of the shear rate allows a direct estimation of the shear viscosity of the studied system at the stationary state.<sup>37</sup> This approach has shown to be efficient to compute the shear viscosity of simple fluids including Mie fluids.<sup>28,32,36</sup>

### 2. Numerical details

The simulations have been performed using a homemade code already validated on various fluid types including the Mie ones.<sup>32,36,38–40</sup> The equations of motion are integrated by using the velocity Verlet algorithm and a reduced time step  $\delta t^* = 0.002$ . Classical periodic boundaries with Verlet neighbor's lists are employed.<sup>22</sup> The targeted temperature is maintained by applying a Berendsen thermostat.<sup>41</sup> The sub-block method is used to compute error bars. The NEMD scheme is applied with a subdivision of the simulation box in 24 slabs. An exchange frequency equal to 500 has been chosen to avoid shear thinning,<sup>40,42,43</sup> a point that has been verified during simulations. The slabs where the exchanges are performed, as well as their first neighbors, have been discarded to compute the shear rate. Simulations have been performed on 1500 particles during at least  $1.5 \times 10^7$  non-equilibrium time steps at the steady state to compute shear viscosity of the Mie fluid. Using these parameters, the error bars on viscosity are lower than 5% in most cases. They are omitted in the figures for sake of clarity.

## C. Viscosity modeling

### 1. Thermodynamic scaling of viscosity

In simple dense fluids,<sup>6</sup> the reduced shear viscosity, as well as other dynamic properties,<sup>14</sup> is invariant when  $\frac{\rho^\gamma}{T}$  is constant (so-called an isomorph<sup>9</sup>), i.e.,  $\eta^r = f\left(\frac{\rho^\gamma}{T}\right)$ . In this

frame,  $f$  is an unknown function and  $\gamma$  is a parameter specific of the considered fluid that is closely related to the steepness of the repulsion between the molecules of the considered fluid.<sup>11,15</sup> Recently, this approach has been modified to be applicable to a wider range of thermodynamic conditions, towards low to moderate density conditions<sup>13</sup> and towards very high densities.<sup>44</sup>

To deal with low to moderate density conditions, one has to use the reduced residual viscosity,  $\eta_{res}^r$ , instead of the total reduced shear viscosity.<sup>6,13</sup> The residual viscosity is defined as  $\eta_{res} = \eta - \eta_0$ , where  $\eta_0$  is the zero-density viscosity that can be evaluated from the kinetic theory<sup>46,47</sup> for the Mie fluids. The rationale for that choice relies on the fact that linear momentum transfer is composed of two contributions at the microscopic scale, one due to particle translation from one place to another (“ideal” part) and one due to interaction/collisions (“configurational” part).<sup>13,40</sup> Thus, shear viscosity can be decomposed into a sum of two contributions. The first contribution, due to translations and equal to the zero-density viscosity,<sup>40–43</sup> is dominant at low density (gas state) and the second contribution, due to collisions, is dominant at high density (liquid state). As thermodynamic scaling describes the behavior of the fluid due to interactions and not the “ideal” part, it is physically sensible to employ the reduced residual viscosity instead of the reduced total viscosity. Indeed, in the seminal article of Ashurst and Hoover on thermodynamic scaling,<sup>6</sup> it is already proposed to do so. Another practical reason is that when using reduced total viscosity instead of the residual reduced one, the former diverges at zero density.<sup>13</sup> In this frame, the thermodynamic scaling leads to the following relation:

$$\eta_{res}^r = g\left(\frac{\rho^\gamma}{T}\right), \quad (4)$$

where  $g$  is an unknown function.

To deal with very dense states, it has been shown recently that  $\gamma$  should be taken as density dependent, and so,  $\rho^\gamma$  should be replaced by a function  $h(\rho)$ .<sup>9,44,45</sup> In this frame, for a Mie  $n$ -6 fluid,

$$h(\rho) = \alpha \rho^{n/3} + (1 - \alpha) \rho^2, \quad (5)$$

where  $\alpha = 3(\Gamma - 2)/(n - 6)$  and  $\Gamma$  is deduced during NVT simulations from the potential energy and virial fluctuations thanks to the relation  $\Gamma = \langle \Delta W \Delta U \rangle / \langle (\Delta U)^2 \rangle$ .<sup>44,45</sup> It should be noticed that  $\Gamma$  corresponds to the slopes of the  $WU$  plots in the least squares frame.

### 2. Viscosity correlation

Starting from the shear viscosity values computed using NEMD simulations, the knowledge of the zero density viscosity is required in order to compute the residual viscosity, cf. Eq. (4). To do so, for the Mie fluids studied in this work, the Chapman-Enskog solution of the Boltzmann equation is employed.<sup>46</sup> The zero density viscosity writes in dimensionless units,

$$\eta_0^* = \frac{5}{16\Omega_v} \sqrt{\frac{\rho^*}{\pi}}, \quad (6)$$

where  $\Omega_v$  is the collision integral that is temperature and potential dependent. To compute  $\Omega_v$ , we have used the accurate correlation proposed by Fokin *et al.*,<sup>47</sup> which applies to the Mie  $n$ -6 fluid,

$$\ln(\Omega_v) = -\frac{2}{n} \ln(T^*) + \ln\left(1 - \frac{2}{3n}\right) + \sum_{i=1}^4 a_i(n) \left(\frac{1}{T^*}\right)^{\frac{i-1}{2}}, \quad (7)$$

where  $a_i(n) = a_{i1} + \frac{a_{i2}}{n} + \frac{a_{i3}}{n^2} + \frac{a_{i4}}{n^3}$ . The constants  $a_{i1}$ ,  $a_{i2}$ ,  $a_{i3}$ , and  $a_{i4}$  are provided in Fokin *et al.*<sup>47</sup>

As it will be shown in Sec. III, for the thermodynamic range studied in this work, the  $\gamma$  parameter in the thermodynamic scaling approach can be considered as a constant. However, the function  $g$  in Eq. (4) is not theoretically known even if recent progress has been recently achieved.<sup>14,48–50</sup> So, in this work, we have employed an empirical relation<sup>51</sup> to describe the reduced residual viscosity,

$$\eta_{res}^r = b_1 \left[ e^{b_2 X^{b_3}} - 1 + b_4 X^{b_5} \right], \quad (8)$$

where  $b_1$ ,  $b_2$ ,  $b_3$ , and  $b_4$  are adjusted numerical parameters and  $X = \frac{\rho^{*\gamma}}{T^*}$ . The first term in the bracket of Eq. (8) is a modified Avramov's model.<sup>14</sup> The last term is an empirical term used to describe  $\eta_{res}^r$  in the low density (and/or high temperatures) regime, i.e., when  $X$  is small. It should be noticed that Eq. (8) ensures that  $\eta_{res}^r$  tends to zero when the density tends to zero. The fitting to determine all the  $b_i$  and  $\gamma$  for each Mie fluid has been performed so as to minimize the Average Absolute Deviation (AAD) between the estimated total viscosity and the molecular dynamics simulation results.

### III. RESULTS

#### A. Pure Mie fluids

In this section, we aim at testing the applicability of the thermodynamic scaling/isomorph theory on Mie fluids. To do so, we have performed extensive NEMD simulations on the Mie  $n$ -6 fluid ( $n = 8, 12, 18, 24$ , and  $36$ ) to compute its viscosity for various thermodynamic conditions covering liquid and supercritical states. More precisely,  $T^*$  ranges from 0.8 to 6 and  $\rho^*$  varies from 0.6 to 1.1. Then, we have deduced the residual reduced viscosity for each Mie  $n$ -6 fluid by using the procedure described in Sec. II.

##### 1. Classical thermodynamic scaling

In this subsection, we aim at showing that the reduced residual  $\eta_{res}^r$  of Mie fluids is a function of  $\frac{\rho^{*\gamma}}{T^*}$  (with  $T^*$  varying from 0.8 to 6 and  $\rho^*$  varying from 0.6 to 1.1), in which the coefficient  $\gamma$  is taken as a constant and is a function of  $n$  only. Equation (8) was used to determine the optimal values of  $\gamma$  for each  $n$  with the procedure described in Subsection II C 2. The values are provided in Table I.

As clearly exhibited in Fig. 3, the thermodynamic scaling with  $\gamma$  taken as a constant is well adapted to describe the reduced residual shear viscosity of Mie  $n$ -6 fluids for all systems studied here. As expected,  $\eta_{res}^r$  increases monotonously with  $\frac{\rho^{*\gamma}}{T^*}$  on the thermodynamic range studied and tends to zero

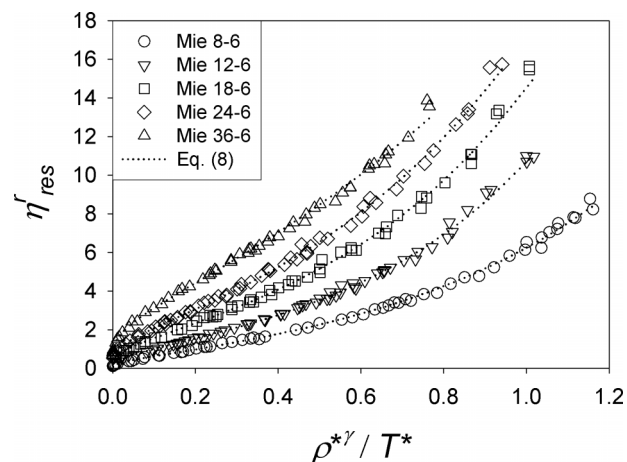


FIG. 3. Reduced residual viscosity for different Mie  $n$ -6 fluids versus  $\rho^{*\gamma}/T^*$  for the  $\gamma$  values indicated in Table I. Symbols correspond to MD simulation results and dotted lines to the correlations.

when  $\frac{\rho^{*\gamma}}{T^*}$  tends to zero. Furthermore, empirical Eq. (8) is able to correlate accurately the simulation results for all Mie  $n$ -6 fluids over the full range of thermodynamic conditions tested, see Table II. Quantitatively, Eq. (8) combined with Eq. (6) allows an estimation of the total viscosity with AAD between 1.9% and 2.3% and Maximum absolute Deviations (MxD) between 6.9% and 7.6% compared to NEMD simulation results. Such deviations are as good as those obtained using the most accurate empirical correlations dedicated to deal with model fluids<sup>38,52</sup> and real fluids.<sup>53–56</sup>

Concerning the behavior of  $\gamma$  with the repulsion exponent  $n$ , the results are consistent with the literature on similar model fluids,<sup>57–59</sup> see Table I. In particular,  $\gamma$  increases noticeably with the repulsion exponent  $n$ . Interestingly, this increase is linear on the studied range of  $n$  and is well described by

$$\gamma = \frac{n}{2.78} + 0.68. \quad (9)$$

This behavior is consistent with the fact that  $\gamma = n/3$  when dealing with a purely repulsive model fluid (soft spheres) interacting through an  $r^{-n}$  potential.<sup>6</sup> Qualitatively, the difference between the Mie and the soft sphere models is due to the attractive term which leads to an effective repulsive part of the potential noticeably steeper than the  $r^{-n}$  term alone.<sup>57–59</sup>

These findings can be used to shed light on the modeling of thermophysical properties of real simple fluids using the Mie potential. As an example, Avendaño *et al.*<sup>60</sup> have shown that the SF<sub>6</sub> is adequately modeled by a Mie 19.02-8.8 sphere

TABLE II. Deviations between the viscosity correlation, Eq. (8), and MD simulation results for different Mie  $n$ -6 pure fluids.

$n$	Number of data points	AAD (in %)	MxD (in %)
8	54	2.1	7.4
12	55	2.0	7.1
18	57	2.3	6.9
24	61	2.2	7.6
36	54	1.9	7.4

when dealing with thermodynamic properties. This potential corresponds to a relatively high repulsive exponent compared to the usual values for spherical fluids (typically around 12). This is fully consistent with the value  $\gamma = 8$  obtained when Boned *et al.*<sup>51</sup> applied the thermodynamic scaling to the reduced residual viscosity of SF<sub>6</sub>, a value that was noticed as particularly high for a spherical fluid ( $\gamma$  of argon is approximately equal to 5 as shown in Ref. 13).

It should be noticed that when dealing with non-spherical fluids, usually the larger the non-sphericity, the higher the repulsive exponent of the spherical potential.<sup>13</sup> For example, this effect has been noted for chain molecules interacting through a Lennard-Jones site-site potential both at low densities<sup>61</sup> and in the dense regime.<sup>13</sup>

## 2. Thermodynamic scaling with a density dependent parameter

As shown recently,<sup>9,44,45</sup> when dealing with a large range of densities, in the dense regime,  $\gamma$  cannot be taken as density independent, and so,  $\rho^\gamma$  should be replaced by a function  $h(\rho)$  to define the isomorphs. In Mie  $n$ -6 fluids,  $h(\rho)$  can be fully determined using Eq. (5) which only requires the computation of  $\Gamma = \langle \Delta W \Delta U \rangle / \langle (\Delta U)^2 \rangle$  at a given state point, i.e., the slope of the  $WU$  plot. This has been done during NVT simulations at  $\rho^* = 1$  and  $T^* = 2$  for all Mie  $n$ -6 studied in this work. Results are provided in Table I and shown in Fig. 4.

Results provided in Fig. 4 clearly exhibit that the reduced residual viscosity scales very well with  $h(\rho)/T$ , confirming the applicability of the approach without any fitting procedure. One can however note a non-monotonous behavior when  $h(\rho)/T$  becomes small and negative. Thus, the improvement over the approach considering  $\gamma$  as a constant (see Sec. III A 1) is not obvious for the studied systems. This is mainly because we have not performed simulation in very dense systems ( $\rho^* \leq 1.1$ ) and probably because of the non-negligible error bars of the computed shear viscosity for the densest systems (up to 5%).

In addition, as already shown in Ref. 59 for similar model fluids, it is interesting to note that  $\gamma$  deduced from the whole

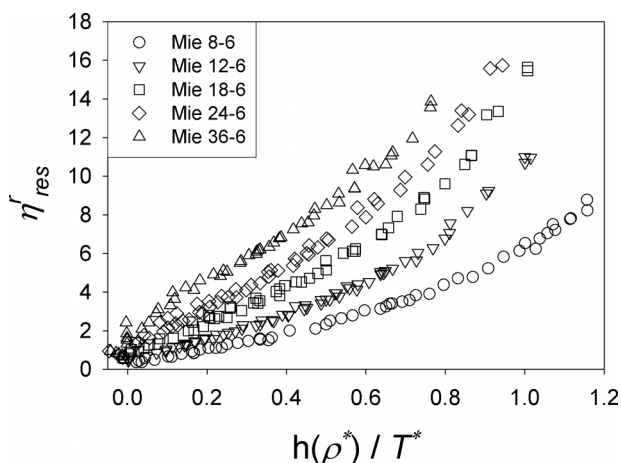


FIG. 4. Reduced residual viscosity for different Mie  $n$ -6 fluids versus  $h(\rho^*)/T^*$ . Symbols correspond to MD simulation results.

set of viscosity data and  $\Gamma$  computed from the  $\Delta U - \Delta W$  correlation at one state point ( $\rho^* = 1$  and  $T^* = 2$ ) are very close to each other, see Table I.

## B. Thermodynamic scaling of binary mixtures

In the literature, some studies were dedicated to mixtures, e.g., Refs. 44 and 62, but to the best of our knowledge, none were dedicated to make a link (thanks to a mixing rule) between the  $\gamma$  values obtained in pure fluids and in mixtures. This is the purpose of this subsection while considering  $\gamma$  as density independent. The Mie  $n$ -6 fluid is relevant for such a study since it is based on a simple molecular model (spherical molecules, only repulsive/dispersive interactions) and the associated value of  $\gamma$  varies strongly with  $n$ , see Subsection III A 1. Thus, we have studied a binary mixture composed of Mie 8-6 and Mie 36-6 particles (having the same size, energy and mass parameters) in various proportions: 0.125, 0.25, 0.5, 0.75, and 0.875 in mole fraction. This choice allows working on a mixture composed of species corresponding to very different values of  $\gamma$ , 3.65 and 13.7, respectively.

Extensive NEMD simulations have been performed to compute the viscosities of these mixtures for the same thermodynamic conditions as in pure fluids, i.e.,  $T^*$  ranges from 0.8 to 6 and  $\rho^*$  varies from 0.6 to 1.1. To deduce the residual reduced viscosity of the mixtures and to apply the thermodynamic scaling approach, a scheme similar to that used to deal with pure fluids has been applied, see Sec. II C 2. Wilke's method<sup>63</sup> combined with the correlation method of Fokin *et al.*<sup>47</sup> has been used to estimate the zero-density shear viscosity of these mixtures. It should be noted that, despite the limitations of the Wilke's method, this approach leads to errors which are lower than the error bars of the simulation results for the systems studied here (relatively dense and not very asymmetric mixtures). Finally, Eq. (8) has been applied to determine the optimal value of  $\gamma$  for each composition of the mixture. Results are provided in Table III and shown in Fig. 5.

Interestingly, as exhibited in Fig. 5, the thermodynamic scaling applies well to the studied mixtures. Furthermore, the empirical relation given in Eq. (8) is able to correlate well the results, the deviations being similar to that on pure fluids, see Table III. The values of  $\gamma$  computed from the simulation results on the mixtures are shown in Fig. 6. As expected, they vary smoothly and monotonously with concentration between those obtained on pure fluids.

TABLE III. Results on the thermodynamic scaling of viscosity for different mixtures composed of Mie 8-6 and Mie 36-6 species.

Mole fraction of Mie 36-6	$\gamma$	Number of data points	AAD (in %) using Eq. (8)	MxD (in %) using Eq. (8)
0	3.65	59	2.3	7.1
0.125	4.2	96	1.5	4.4
0.25	5.05	28	1.3	4.9
0.5	7.1	51	1.3	4.8
0.75	9.7	27	1.4	4.2
0.875	11.65	90	1.5	5.7
1	13.7	54	1.9	7.4

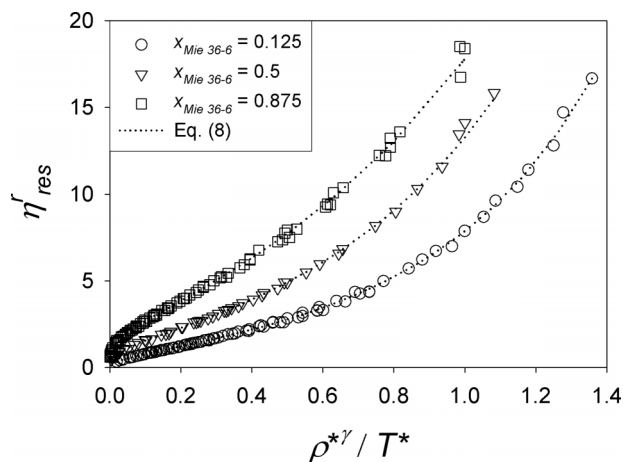


FIG. 5. Reduced residual viscosity for different binary mixtures composed of Mie 36-6 and Mie 8-6 fluids versus  $\rho^* \gamma / T^*$  for the  $\gamma$  values indicated in Table III.

An interesting point is to check whether it is possible to deduce these values of  $\gamma$  in mixtures from those of the pure components. For that purpose, we have first tested a one-fluid approximation developed for the Mie fluid thermodynamic properties.<sup>36</sup> Such an approach consists in defining the repulsive exponent,  $n_{1\text{-fluid}}$ , of the pseudo-compound “equivalent” to the mixture by

$$\left(\frac{n_{1\text{-fluid}} - 6}{n_{1\text{-fluid}}}\right)^{1/2} = \sum_i \sum_j x_i x_j \left(\frac{n_{ij} - 6}{n_{ij}}\right)^{1/2}, \quad (10)$$

where  $x_i$  is the mole fraction of component  $i$  and  $n_{ij}$  is the repulsive exponent between particles  $i$  and  $j$ . Fig. 6 indicates that such an approximation combined with Eq. (9) yields a reasonable estimate of the values of  $\gamma$  in Mie mixtures, despite a systematic underestimation that is maximum at equimolar composition.

In addition to the one-fluid approximation approach, we have tested several empirical mixing rules on  $\gamma$ . It has been found that the one based on the following relation:

$$\ln(\gamma_{Mix}) = x_1 \ln(\gamma_1) + (1 - x_1) \ln(\gamma_2) \quad (11)$$

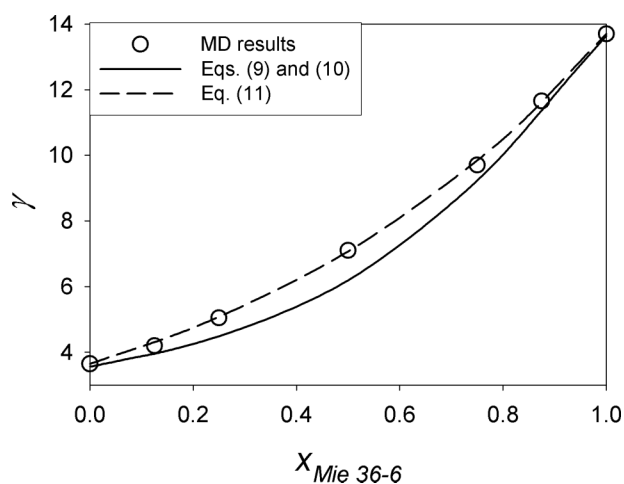


FIG. 6.  $\gamma$  values for binary mixtures composed of Mie 36-6 and Mie 8-6 fluids against the Mie 36-6 mole fractions,  $x_{Mie\ 36-6}$ .

is the most accurate one as clearly shown in Fig. 6, the deviation from the simulation results being at most 2.5%. In addition, when using Eq. (11) to estimate gamma in mixtures, the correlation of the MD viscosity using Eq. (8) is as good as those obtained with a full fit, AAD and MxD being within 0.2% of those provided in Table III. Eq. (11) is so very interesting as it allows yielding an estimate of  $\gamma$  in mixture directly from the pure component values and the composition.

#### IV. CONCLUSIONS

We have tested the applicability of the so-called thermodynamic scaling and isomorph theory to model the reduced residual shear viscosity of Mie  $n$ -6 fluids and binary mixtures of Mie  $n$ -6 fluids,  $n$  varying from 8 to 36. To do so, a viscosity database of these model fluids has been created using NEMD simulations for various thermodynamic conditions ( $0.8 \leq T^* \leq 6$  and  $0.6 \leq \rho^* \leq 1.1$ ).

It has been found that the thermodynamic scaling with a constant gamma parameter is well respected in such model fluids both in pure fluids and mixtures in the studied density range. In addition, the applicability of the isomorph theory with a density dependent gamma has been confirmed in pure fluids. However, this approach does not show noticeable improvements over the assumption of a constant gamma when density is not too high (i.e.,  $\rho^* \leq 1.1$ ) as in the systems studied in this work. When combined with an empirical equation, the thermodynamic scaling frame can be used efficiently to correlate the viscosity results with deviations below 8% in all cases.

Rather interestingly, it has been found that  $\gamma$  increases noticeably with the repulsion exponent  $n$  in a linear manner, consistently with what known for soft spheres. Such a result could be interesting to estimate the effective repulsion exponent from viscosity data of coarse grained molecular model of simple real fluids.

In mixtures, the values of  $\gamma$  computed from the simulation results vary smoothly and monotonously between those obtained on pure fluids. Hence, it has been found that a simple logarithmic mixing rule allows to estimate accurately  $\gamma$  in mixture directly from the pure component values and the composition.

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