The van der Waals one-fluid model for viscosity in Lennard-Jones fluids: Influence of size and energy parameters.

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Abstract

This work aims to estimate the limitations of the van der Waals one-fluid (vdW1) approximation in the prediction of the viscosity of Lennard-Jones (LJ) mixtures. To do so, results provided by nonequilibrium molecular dynamics simulations on mixtures have been compared to those deduced from the pure fluids combined with the one-fluid model. Several systems (146 configurations) are studied, which are composed of binary and ternary mixtures in various thermodynamics states and for different combining rules. In a first step, deviations induced separately by LJ molecular parameters (size or energy) have been analyzed. On these synthetic mixtures, it is shown that the vdW1 model is well designed for the energy parameter in every configuration. On the contrary, in dense state and low temperature systems, deviations induced by this one-fluid approach on the size parameter can be large. In a second step, the effect of couplings the LJ size parameter and the LJ energy parameter with the mass is studied. It appears that an “exact” one fluid approximation for viscosity should involve a coupling between the mass and the size parameters in its formulation (which is not the case with the vdW1 model) but not between the mass and the energy.
1. **Introduction**

It seems now possible to accurately estimate with various methods the viscosity for a wide variety of pure compounds on a large range of thermodynamic conditions. But, when dealing with mixtures, the modelling of viscosity is, by far, a more complex problem especially in asymmetric dense systems.

Among the possible approach to tackle this problem, the one-fluid model is one of the most widely used [1]. This model consists in lumping the various components of a mixture into one pseudo-compound representative of this mixture and assumes that the fluid follows the corresponding states principle. This pseudo compound defined as such is then supposed to mimic the thermodynamic and/or transport properties of the given mixture. Nevertheless, in the one-fluid approach the formulation of the pseudo-compound parameters starting from those of pure compounds is not a trivial point and is still an area of active researches.

In such approach, once a fluid model is chosen, results given by a one-fluid approximation are usually compared to experimental data. As a matter of fact, various errors coming from the fluid model itself, the law of the corresponding states, the one-fluid approximation and the combining rules may compensate each other. Hence, one-fluid model results may look acceptable despite some intrinsic errors which limits strongly its correct understanding.

The evaluation of the effectiveness of the one-fluid model alone is in some sense difficult. It is nevertheless sometimes possible to achieve a direct test of the one-fluid model for some peculiar cases where the law of the corresponding states is fulfilled and either an analytical or an approached solution exists as in low density systems [2]. In dense systems, the use of molecular simulations applied on simple conformal spheres may provide new insights on the validity of a one-fluid approach. In fact, molecular
dynamics applied on a molecular model allows a direct comparison between the results on the mixtures and those on the pseudo-compound in the frame of the microscopic formulation of the corresponding states principle. Hence, a direct test of the one-fluid approximation can be achieved [3-6].

In this work, a test of the van der Waals one-fluid approach [7] applied on the viscosity of mixtures of Lennard-Jones has been performed. The viscosities, in pure fluids and in mixtures (binary and ternary), have been evaluated thanks to nonequilibrium molecular dynamics simulations [8].

Following a previous study on mass alone [9], a systematic study of the effects of the molecular parameters ratios between the component (size and energy) has been performed in this work. The effect of the thermodynamic state (covering a large range of conditions), combining rules and molar fraction has been analyzed. Then, the various couplings of the energy and size parameters with the mass have been studied. Such a comparison allows assessing the limitation of such approach for a dynamic property.

2. Models

2.1. Interaction potential

In this work, molecules have been described by simple spheres. In this picture, the fluid particle interactions have been modeled using the well-known Lennard-Jones (LJ) 12-6 potential which is, for a compound $i$ interacting with a compound $j$:

$$U_{ij} = 4\varepsilon_{ij}\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}$$  \hspace{1cm} (1)

where $\varepsilon_{ij}$ is the well depth (energy parameter), $\sigma_{ij}$ the sum of the radii of the compounds $i$ and $j$ (size parameter) and $r$ the intermolecular separation length.

2.2. Combining rules
When dealing with mixtures, the cross molecular parameters $\sigma_{ij}$ and $\varepsilon_{ij}$ should be defined from the pure compounds parameters ($\sigma_{ii}$ and $\varepsilon_{ii}$) through a set of combining rules.

For this study, we have used two different rules for the energy parameter:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \varepsilon_{jj}}$$  \hspace{1cm} (2)

$$\varepsilon_{ij} = \frac{\varepsilon_{ii} + \varepsilon_{jj}}{2}$$  \hspace{1cm} (3)

and three for the size parameter:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}$$  \hspace{1cm} (4)

$$\sigma_{ij} = \sqrt{\sigma_{ii} \sigma_{jj}}$$  \hspace{1cm} (5)

$$\sigma_{ij}^3 = \frac{\sigma_{ii}^3 + \sigma_{jj}^3}{2}$$  \hspace{1cm} (6)

The combination of equations (2) and (4) forms the well known Lorentz-Berthelot (LB) rules.

2.3. **Law of the corresponding states**

The microscopic formulation of the law of the corresponding states postulates that, for a given molecular interaction potential, with an appropriate scaling (reduced properties), different fluids have superimposed thermodynamic phase diagrams [10]. In addition, in this formalism, reduced transport properties are universal function of the reduced thermodynamic conditions.

For the LJ fluid, the reduced thermodynamic variables are simply:

$$T^* = \frac{k_B T}{\varepsilon}, \quad \rho^* = \frac{N \sigma_x^3}{V} \quad \text{and} \quad P^* = \frac{P \sigma_x^3}{\varepsilon}$$  \hspace{1cm} (7)

and the reduced viscosity is defined as [11]:

$$\text{and the reduced viscosity is defined as [11]:}$$
\[ \eta^\ast(R^\ast, \rho^\ast) = \eta \frac{\sigma_x^2}{\sqrt{m_x \epsilon_x}} \]  

where \( k_B \) is the Boltzmann constant, \( N \) the number of particles, \( V \) the volume of the system, \( P \) the pressure and \( \eta \) the dynamic viscosity. The LJ parameters noted with a subscript \( x \) correspond to characteristic quantities of the molecular parameters of the studied fluid.

### 2.4. One-fluid approximation

In pure fluid, \( \sigma_x, \epsilon_x \) and \( m_x \) are simply equal to those of the involved species, but in mixtures a one fluid model is needed to define these parameters starting from those of the components of the mixtures (pure and cross parameters). This procedure consists in the definition of one pseudocompound “equivalent” to the mixture.

Among the alternative, the van der Waals one fluid approximation [7], which provides reasonable results in not too asymmetric systems, is the most widely used. This scheme is defined as:

\[ m_x = \sum_i x_i m_i \]  

\[ \sigma_x^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \]  

\[ \epsilon_x \sigma_x^3 = \sum_i \sum_j x_i x_j \epsilon_{ij} \sigma_{ij}^3 \]  

where the \( x_i \) are the molar fractions.

It should be mentioned that a previous study [9] have shown that the rules for mass, equation (9), is not rigorously appropriate, but no simple theoretical expression for the equivalent mass was found.

Once the parameters of the pseudocompound obtained through the set of equations (9-11), the reduced viscosity of a mixture in the one fluid approximation (\( \eta^\ast_{1\text{-fluid}} \)) may be deduced using the value calculated by molecular dynamics on the mixture and equation
(8). If the one-fluid approximation is “perfect”, $\eta_{1\text{-fluid}}^*$ should be exactly equal to the reduced viscosity of a pure fluid, $\eta_{\text{pure}}^*$, evaluated for the same $T^*$ and $\rho^*$ conditions.

### 2.5. Molecular Dynamics

To compute the viscosity in the LJ fluids, a boundary driven NEMD scheme (called Reverse NEMD), which is simple to handle and provides reliable results [8,12], has been used. Details of the numerical parameters used for this scheme are described in [13].

The Verlet velocity algorithm has been used to integrate the equation of motion. The usual periodic boundary conditions and minimum image convention have been applied. To avoid a temperature drift during the simulation, we have applied a Berendsen thermostat [14] with a time constant $\tau_T=1000\delta t^*$, where $\delta t^*$ is the time step in reduced units ($\delta t^*=\delta t(\varepsilon_x/(m_x\sigma_x^2))^{1/2}$). A constant reduced time step $\delta t^*$ (equal to 0.002) has been used. Simulations have been performed on a 1500 particles system during $10^7$ nonequilibrium time steps. A truncated potential with a 2.5$\sigma$ cutoff radius has been used and long range correction has been introduced [15]. The statistical errors produced on viscosity are around +/- 3%, except in dense phase where errors may reach 5%.

### 3. Results

#### 3.1. Characterization of the studied systems

In order to emphasize the limitations of the vDW1 approach on viscosity for LJ asymmetric fluids, a systematic study of the influence of the molecular parameter ratios between components in various synthetic mixtures has been carried on. In order to be as comprehensive as possible, a large range of thermodynamic states has been explored, $\rho^*$ going from 0.3 to 0.9 with a step of 0.2 and $T^*$ from 1 to 2.5 with a step of 0.5 ($\rho_c^*\approx0.31$ and $T_c^*\approx1.3$ [16]). Unstable states have been discarded for this study (these states corresponding to $\rho^*$ equal to 0.3 and 0.5 when $T^*=1$).
The deviations induced by the one-fluid model have been evaluated using the following relation, for \( N_c \) points:

\[
\text{Dev} = 100 \times \left( 1 - \frac{\eta^*_{\text{fluid}}}{\eta^*_{\text{pure}}} \right) 
\]

(12)

\[
\text{AAD} = \frac{1}{N_c} \sum_{i=1}^{N_c} |\text{Dev}| 
\]

(13)

\[
\text{Max} = \text{Max} |\text{Dev}| 
\]

(14)

\[
\text{Bias} = \frac{1}{N_c} \sum_{i=1}^{N_c} \text{Dev} 
\]

(15)

where, AAD is the Absolute Average Deviation, Max is the Maximum absolute deviation.

In a first step, the influence of the LJ molecular parameters, \( \varepsilon \) and \( \sigma \) uncoupled, has been evaluated (i.e. components having the same \( m \) and \( \varepsilon \) but different \( \sigma \), or the same \( m \) and \( \sigma \) but different \( \varepsilon \)). For these synthetic mixtures, different combining rules (equations (2-6)) have been tested to estimate the sensitivity of the one-fluid model to the definition of the cross interactions. In addition, simulations have been performed on equimolar and nonequimolar binary mixtures, as well as on some ternary systems.

Then, once the separate contributions have been analyzed, the various couplings of the energy and size parameters with the mass have been studied.

Throughout the text, the ratios between component \( i \) and the reference compound (pure fluid) will be noted \( \alpha_i \) for mass, \( \beta_i \) for the energy parameter and \( \chi_i \) for the size parameter. The molar fraction of component \( i \) is noted \( x_i \). In binary systems, for simplicity, the molecular parameters of the first component are taken to be equal to those of the pure fluid (i.e. \( \alpha_1=1, \beta_1=1 \) and \( \chi_1=1 \)) which implies that \( \alpha_2=m_2/m_1, \beta_2=\varepsilon_2/\varepsilon_1 \) and \( \chi_2=\sigma_2/\sigma_1 \). The reduced viscosity of the pure fluid \( \eta^*_{\text{pure}} \), (i.e. \( \alpha_i=1, \beta_i=1 \) and \( \chi_i=1 \))
has been studied previously [13] and is used to calculate the deviations induced by the vDW1 one-fluid approximation, equation (12).

In all cases, the reduced variables, equations (7-8) have been defined through the vDW1 model, equations (9-11).

### 3.2. Influence of the energy parameter

In this section only the energy parameters, \( \varepsilon \), differs between the components of the mixtures (i.e. \( \alpha_i=1, \chi_i=1 \)).

The first test has been done using the most classical combining rule, equation (2), on equimolar binary mixtures (\( x_1=x_2=0.5 \)) for the 14 thermodynamic states given in section 3. Three different well depths values of the second component have been tested: \( \beta_2 \) was taken equal to 1.5, 2 and 3.

For these synthetic equimolar binary mixtures, AAD of the vDW1 model on viscosity is equal to 1.32 %, Max to 4.57% and Bias to 0.56% (see figure 1 for the repartition). It should be mentioned that such deviations lie into the errors bars of the simulation results. This indicates that the vDW1 approach on the energy parameters in equimolar binary mixtures is adequate for viscosity. In addition, no general trends with density, temperature and \( \beta_2 \) values have been noticed, except the fact that deviations are larger in the systems where the simulations uncertainties are the largest (dense systems).

In addition, for some selected thermodynamic conditions (\( T^*=1.5 \) and 2.5 for \( \rho^*=0.3 \) and 0.5, \( T^*=1 \) and 2 for \( \rho^*=0.7 \) and 0.9, i.e. 8 thermodynamic states), simulations have been performed on equimolar binary mixtures (with \( \beta_2=3 \)), using the combining rule given by equation (3).

Table 1 shows clearly that, whatever the combining rule, the pseudocompound defined by the vDW1 approach mimics well the viscosity of the mixtures. It should be
mentioned that the results for these two combining rules are very similar, the denser the system, the larger the deviations.

Then, for $T^*=1.5$ and $\rho^*=0.7$, simulations have been performed on non equimolar binary mixtures (with $\beta_2=3$) for $x_1$ going from 0.1 to 0.9 with a step of 0.1. Equation (2) has been used to define the cross energy parameter.

As shown in Table 2, the vdW1 model provides good results on the nonequimolar mixtures tested, the absolute deviations being always lower than 2%.

Finally, for the same thermodynamic state ($T^*=1.5$ and $\rho^*=0.7$), four ternary mixtures have been investigated. Equation (2) has been used to define the cross energy parameter. In all cases, the molar fraction of each component was chosen equal to 1/3. The characteristic of each component are given in Table 3.

As in the previous cases, results provided by the vdW1 model on the energy parameter does not yield large deviations, see Table 3.

The overall AAD, for the 63 mixtures described in this section, is equal to 1.37%, the Max to 5.3% and the bias to 0.65%. Such results indicate that the vdW1 model is adequate for viscosity in synthetic mixtures where only the energy parameters differ between the compounds.

### 3.3. Influence of the volume parameter

In this section only the volume parameters, $\sigma$, differs between the components of the mixtures (i.e. $\alpha_i=1$, $\beta_i=1$).

First, simulations have been performed on equimolar binary mixtures for the 14 thermodynamics states described in section 3.1, using the most usual combining rule on the size parameter, equation (4). Three different atomic diameter values of the second component have been tested: $\chi_2$ was taken equal to 1.25, 1.5 and 2.
For these systems we have found AAD=11.54%, Max=110.1% and Bias=-11.48%. Such results provided by the vdW1 model for the size parameter, shown on figure 2, are not satisfying. The deviations have the expected trend to increase with the asymmetry of the system. In addition, the lower the temperature and the higher the density, the worse the results.

The fact that Bias≈-AAD indicates that, the deviations are mostly negative (see figure 2). As the reduced viscosity is a monotonous function of ρ*, this trend indicates that σx is underestimated by the vdW1 approach. It is interesting to note that such trend is consistent with the fact that the densest random packing of this kind of mixture (in hard spheres) is different than that of a pure fluid [17-18]. But, as no analytical formulations exists to estimate the value of this dense random packing for this kind of mixtures, an exact formulation of a one-fluid model for volume seems unrealistic (even in hard spheres system).

Additionally, simulations have been performed on equimolar binary mixtures (for χ2=2), but using the two alternative combining rules given by equation (5) and (6). For these simulations, only the extreme temperatures for each reduced densities have been investigated (T*=1.5 and 2.5 for ρ*=0.3 and 0.5, T*=1 and 2 for ρ*=0.7 and 0.9, i.e. 8 thermodynamic states).

Figure 3 shows that the deviations are strongly dependent to the combining rule chosen, and are the largest for the combining rule which yield the smallest σ12, equation (5). In addition, whatever the combining rules, the one-fluid volume parameter, σx, is always underestimated.

Then, to quantify the effect of the concentration, simulations have been performed on nonequimolar binary mixtures at T*=1.5 and ρ*=0.7 (for χ2=2) for x1 going from 0.1 to 0.9 with a step of 0.1. Equation (4) has been used to define the cross volume parameter.
Table 4 shows that the deviations have not a symmetric behavior with the molar fraction, the maximum deviation being located at \( x_1 \approx 0.7 \). This behavior is in agreement with the fact that the dense random fraction of a hard spheres binary mixture (for \( \chi_2 = 2 \)) have a maximum value for \( x_1 = 0.66 \) [18].

The last set of simulation for this kind of mixtures was performed on four ternary systems at \( T^* = 1.5 \) and \( \rho^* = 0.7 \). Equation (4) has been used to define the cross volume parameter and the molar fraction of each component was chosen to be equal to 1/3.

Table 5 exhibits non negligible deviations (always negative) which increase with the asymmetry of the systems. Such results confirm the results found for binary mixtures.

The overall AAD, for the 71 mixtures described in this section, is equal to 20.09 \%, the Max to 171 \% and the bias to -20.06\%.

Hence, these results indicate that the vdW1 formulation for size parameter is clearly inadequate for asymmetric systems, particularly in dense states (\( \rho^* > 0.5 \)) and low temperature.

3.4. Couplings

In the vdW1 model formulation, the one-fluid model for mass is uncoupled from the energy and the size parameters, equation (9), contrary to what proposed by some authors [1,3,5]. So, in this section, some mixtures have been designed to estimate the couplings between the two LJ molecular parameters and the masses of the components (i.e. mixtures with components having the same \( \varepsilon \) but different \( m \) and \( \sigma \), or the same \( \sigma \) but different \( m \) and \( \varepsilon \)).

Simulations have been restricted to binary equimolar mixtures at three thermodynamic states, state 1: \( T^* = 2 \) and \( \rho^* = 0.5 \), state 2: \( T^* = 1.5 \) and \( \rho^* = 0.7 \), state 3: \( T^* = 1 \) and \( \rho^* = 0.9 \).

In all cases the classical LB combining rules have been used.

3.4.1. Couplings between the mass and the energy parameters
To test a possible coupling of mass and energy, simulations have been performed on the two following systems: for the first mixture, $\alpha_2=10$, $\beta_2=3$ and $\chi_2=1$, and for the second one $\alpha_2=1/10$, $\beta_2=3$ and $\chi_2=1$. To complete the comparison, a third mixture for which only the mass differs between the components, studied in a previous paper [9], has been used: $\alpha_2=10$, $\beta_2=1$ and $\chi_2=1$.

The comparison of the results of the first and the second mixture (see Table 6) shows that no coupling exists between mass and energy parameters. Results given in Table 6 indicate that for each of the three tested states, the deviations induced by the various mixtures are very similar. The fact that these deviations are equal to the one for the third mixture indicates that they are only due to the wrong form of the vDW1 model for mass, equation (9) [9]. Furthermore such results prove that no noticeable couplings occurs between mass and energy and therefore a “correct” one-fluid approximation for viscosity should not include such couplings as it is sometimes proposed [1,3,5].

### 3.4.2. Couplings between the mass and the size parameters

As for the energy parameter, in the vDW1 model formulation, the one-fluid approach for mass is uncoupled from the size parameter. So, similarly to the previous section, simulations have been performed in two systems where both ratios (on mass and size) are different from the unity: i.e. for the first mixture $\alpha_2=10$, $\chi_2=2$ and $\beta_2=1$, and for the second mixture $\alpha_2=1/10$, $\chi_2=2$ and $\beta_2=1$.

The comparison of the results of the first and the second mixture (see Table 7) shows that couplings exist between mass and size parameters. Such results imply that the definition of the one-fluid mass should be coupled with the one for the size parameter. Furthermore, this coupling is not simple as the relative results for the two mixtures depend on the state. The viscosity of the first mixture is lower than the one of the second for the state 3 (very dense state) and it is the contrary for the two other sates.
4. Conclusions

In this work, an analysis of the limitation of the van der Waals one-fluid approach applied on the viscosity of Lennard-Jones spheres mixtures has been performed. The viscosities, in pure fluids and in mixtures, have been evaluated thanks to nonequilibrium molecular dynamics simulations. To perform the analysis, several systems have been studied, which are composed of binary and ternary mixtures in various thermodynamics states and for different combining rules.

First, we have analyzed the deviations induced by the separate contributions of the LJ molecular parameters ratios (size and energy) between the components. It has been found, on such synthetic mixtures, that the vdW1 model for the energy parameter leads to negligible deviations. On the contrary, in dense state and low temperature systems, such a one-fluid approach on the size parameter can lead to large deviations when the mixture is asymmetric.

Additionally, the effect of couplings the influence of both LJ molecular parameters with the mass is studied. Results have shown that no coupling should be included between the mass and the energy parameters in a “correct” one fluid formulation for viscosity. In contrast, it appears that a coupling in the formulation of the one-fluid mass and the one-fluid size should be included contrary to what is done in the vdW1 model.

In view of the results obtained on this LJ fluid, the application of a one-fluid approach to predict the viscosity of real mixtures should be probably accurate only in the simplest cases (weakly asymmetric in size and not very dense).

Acknowledgement

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Informatique National de l’Enseignement Supérieur in Montpellier (France) which provided a large part of the molecular dynamic simulation computer time for this study.
Bibliography

**Figure captions:**

- Figure 1: Deviations on viscosity in equimolar binary mixtures, versus reduced density, induced by the vdW1 model on energy, equation (11) for different values of $\beta_2$ (diamonds: 1.5, squares: 2 and circles: 3) and different reduced temperatures (white symbols: $T^*=1$, grey ones: $T^*=1.5$, dark grey ones $T^*=2$ and black ones $T^*=2.5$).

- Figure 2: Deviations on viscosity in equimolar mixtures, versus reduced density, induced by the vdW1 model on volume, eq. (10), for different values of $\chi_2$ (diamonds: 1.25, squares: 1.5 and circles: 2) and different reduced temperatures (white symbols: $T^*=1$, grey ones: $T^*=1.5$, dark grey ones $T^*=2$ and black ones $T^*=2.5$).

- Figure 3: Deviations on viscosity in equimolar mixtures for $\chi_2=2$, $\alpha_2=1$ and $\beta_2=1$, using three different combining rules (equation (4): circles, equation (5): down triangles, equation (6): up triangles) in various thermodynamic states ($T^*=1$: open symbols, $T^*=1.5$: black symbols, $T^*=2.5$: grey symbols).
Tables:

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<th>Bias</th>
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<td>Equation (3)</td>
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Table 1: Deviations on viscosity in binary equimolar mixtures for $\beta_2=3$, $\alpha_2=1$ and $\chi_2=1$, using two different combining rules, equations (2) and (3), in various thermodynamic states ($T^*=1.5$ and 2.5 for $\rho^*=0.3$ and 0.5, $T^*=1$ and 2 for $\rho^*=0.7$ and 0.9).

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<td>0.6</td>
<td>0.9</td>
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<td>1.6</td>
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Table 2: Deviations on viscosity in binary nonequimolar mixtures at $T^*=1.5$ and $\rho^*=0.7$ for $\beta_2=3$, $\alpha_2=1$ and $\chi_2=1$.

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<td>Deviation</td>
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Table 3: Deviations on viscosity in four ternary mixtures at $T^*=1.5$ and $\rho^*=0.7$.

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<th>$x_1$</th>
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<td>-9.7</td>
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<td>-21.9</td>
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Table 4: Deviations on viscosity in nonequimolar mixtures at $T^*=1.5$ and $\rho^*=0.7$ for $\chi_2=2$. 
Table 5: Deviations on viscosity in four ternary mixtures at T*=1.5 and ρ*=0.7.

<table>
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<tr>
<th>Mixture</th>
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Table 6: Deviations induced by different mixtures for various thermodynamic states (see section 3.4) to analyze the couplings of the mass and the energy parameter.

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<th>State 3</th>
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</tr>
<tr>
<td>Second mixture</td>
<td>17.49</td>
<td>25.05</td>
</tr>
<tr>
<td>Third mixture</td>
<td>18.53</td>
<td>22.02</td>
</tr>
</tbody>
</table>

Table 7: Deviations induced by different mixtures for various thermodynamic states (see section 3.4.) to analyze the couplings between the mass and the size parameter.

<table>
<thead>
<tr>
<th>State</th>
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<th>State 3</th>
</tr>
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<td>Second mixture</td>
<td>15.86</td>
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Figures:

Figure 1

![Figure 1](image1)

Figure 2:

![Figure 2](image2)
Figure 3

\[ 100 \ast \frac{1 - \eta_{1\text{-fluid}}^*}{\eta_{\text{pure}}^*} \]

\[ \rho^* \]

\[ 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \quad 0.6 \quad 0.7 \quad 0.8 \quad 0.9 \quad 1.0 \]