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**Influence of the repulsive coefficient α and approximate corresponding states in
Mie α -6 and exponential α -6 fluids.**

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Abstract

Nonequilibrium molecular dynamics (NEMD) simulations of the Mie α -6 and the exponential α -6 (exp α -6) fluids have been carried out for 42 thermodynamic states. Various repulsive coefficients have been studied, α ranging from 9 to 14 for the Mie α -6 potentials and from 11 to 16 for the exp α -6 ones, which corresponds to a total of 603 points of simulation of stable phases. The simulations have shown that, for a given set of reduced temperature and density (using an appropriate scaling procedure), the reduced pressure varies linearly with $\sqrt{\alpha-6}$ for the Mie α -6 potentials and with $\sqrt{\alpha-7}$ for the exp α -6 potentials. Concerning the viscosity, it is shown that, for both potential families, the variation is linear with α . Thus, an approximate corresponding states scheme exists on pressure and on viscosity for fluids modelled by both potentials families, but only for each property separately. In addition, it appears that, approximate corresponding states exist between fluids modelled by a Mie α -6 potential and an exp $(\alpha+2)$ -6 one for pressure, and between fluids modelled by a Mie α -6 potential and an

$\exp(\alpha+2.5)^{-6}$ one for viscosity. So, despite obvious similarities, the influence of the shape of the potential on pressure and on viscosity is not strictly the same. Hence, a complete perfect corresponding states scheme (including both the pressure and the viscosity) seems hardly feasible between fluids modelled by the Mie α -6 and the $\exp \alpha$ -6 potential families.

1. Introduction

Usually, when performing molecular simulations of fluid properties, the interactions between particles are modelled with an effective pair potential, the Lennard-Jones 12-6 (LJ) one. This two parameters potential, despite its simplicity, mimics most of the features experimentally found in fluid states. In addition, due its simplicity, this potential is relatively easy to handle and allows a relatively quick computation of the interactions, which is a clear advantage compared to other potentials. However, it represents the decay of the repulsive interaction by an inverse twelve-power dependence on intermolecular separation that is still questionable [1]. This aspect is of importance since the structural properties of a normal fluid are primarily determined by the intermolecular short-range repulsive interactions [2,3]. Therefore, one way to improve the results provided by molecular simulations using simple effective potentials could be the use of different repulsive form as already done for transport properties in low density gases [4] or in modern equation of states [5].

Among the possible simple alternatives to the two parameters LJ potential (energy, ϵ , and size, r_m) are the three parameters Mie α -6 and exponential α -6 potential families (ϵ , r_m and α the repulsive slope). The first one uses a $r^{-\alpha}$ formulation of the repulsive part of potential (where r is the distance between particles) whereas the second one uses an exponential form. Compared to the classical LJ potential, it should be noted that far less attention has been paid to these potential families in molecular simulations. Nevertheless, it should be mentioned that, recently, some interesting results on thermodynamic as well as on transport properties have been found for the Mie α -6 [6-10] and the exp α -6 potentials [10-14].

The purpose of this paper is to study, using molecular dynamics simulation in fluid states, the viscosity and the pressure provided by spherical fluid particles interacting

through Mie α -6 and exp α -6 potentials, testing various slopes (i.e. different values of α) of the repulsive part. Simulations are performed for a wide variety of thermodynamic states ranging from sub to supercritical regimes (42 states). So, by using a much more important database than in a previous paper [10] (603 simulation points of stable phases instead of 72) where these potentials were applied to real simple fluids, and an appropriate scaling procedure (r_m is used as the length parameter instead of σ as usually done [10]), an analysis of the link between the results for various repulsive slopes is performed. Furthermore, the validity of a corresponding states scheme in each family of potentials and between them is discussed (by corresponding states between different potentials, we mean corresponding states between materials described by these different potentials).

2. Theory

2.1. Fluid models

To model interactions between particles two families of three parameters effective potentials have been used, the Mie α -6 and the exponential α -6 ones, which can be written as:

$$U_{Tot} = U_{Repulsive} - \epsilon \left(\frac{\alpha}{\alpha - 6} \right) \left(\frac{r_m}{r} \right)^6 \quad (1)$$

where for the Mie α -6:

$$U_{Repulsive} = \epsilon \left(\frac{6}{\alpha - 6} \right) \left(\frac{r_m}{r} \right)^\alpha \quad (2)$$

and for the exponential α -6:

$$U_{Repulsive} = \epsilon \left(\frac{6}{\alpha - 6} \right) e^{-\alpha \left(\frac{r}{r_m} - 1 \right)} \quad (3)$$

where ε is the potential strength, r_m the distance at which the potential is minimum, α the stiffness of the repulsive slope and r the intermolecular separation.

In this study α varies from 9 to 14 for the Mie α -6 potentials, with a step of 1, and from 11 to 16, with a step of 0.5, for the exp α -6 ones. It should be noted that the larger α , the more repulsive the potential.

2.2. Law of the corresponding states

The law of the corresponding states postulates that, after an adequate scaling (using usually the critical point values), different fluids have superimposed thermodynamic phase diagrams. Furthermore, a similar scaling procedure is possible for transport properties such as for viscosity [15]. The microscopic formulation of the law of the corresponding states is based on the molecular parameters of the potential [16], ε and r_m . This rescaling procedure, when dealing with particles modelled by spheres, means that, for a given potential form, the scaled properties (called reduced properties) will be independent of the molecular parameters (i.e. fluids modelled in such way follow a corresponding states law). It is then possible to deduce the properties of a fluid based on the ones of another fluid.

It should be mentioned that r_m has been used instead of σ (the distance at which the potential is equal to zero) as it is usually done for the LJ potential. In this scheme the reduced thermodynamic variables used to perform the simulations are the reduced temperature:

$$T^* = \frac{k_B T}{\varepsilon} \quad (4)$$

and the reduced density,

$$\rho^* = \frac{N r_m^3}{V} \quad (5)$$

where T is the temperature, N the number of particle, V the volume of the simulation box. The reduced pressure, P^* , which is a universal function of T^* and ρ^* for a given potential, is:

$$P^*(T^*, \rho^*) = P \frac{r_m^3}{\epsilon} \quad (6)$$

where P is the pressure of the system.

The reduced viscosity, which is a universal function of the thermodynamic conditions for a given potential form, is,

$$\eta^*(T^*, \rho^*) = \eta \frac{r_m^2}{\sqrt{m\epsilon}} \quad (7)$$

where m is the molecular weight and η the dynamic viscosity.

2.3. NonEquilibrium Molecular Dynamics

To compute the pressure and the viscosity a homemade molecular dynamics code has been used. The Verlet velocity algorithm has been used to integrate the equation of motion and usual periodic boundary conditions have been applied. To limit finite size effects and to obtain a good accuracy on the value obtained, simulations have been performed on systems composed of 1500 particles. A truncated potential with a cutoff radius r_c equal to $2.5r_m$ has been used. Long range interactions corrections for pressure were included in the computation.

To compute the viscosity, we have chosen to use a boundary driven nonequilibrium scheme developed by F. Müller-Plathe [17], which provides reliable results in a reasonable amount of CPU time [10,18-19]. In this technique, the simulation box is divided in several slabs (in our case 32). Then, the fluid is biperiodically sheared thanks to a net exchange of the momentum between the central part of the simulation box, and the edge layers to conserve the periodic boundary conditions. This exchange is done every 300 timesteps to avoid thermal disturbances and non Newtonian behaviour (this

corresponds to a very weak reduced shear rate always smaller than 0.005) [10,18]. This procedure keeps the overall energy and momentum constant and simply corresponds to a redistribution in the simulation box of a certain amount of momentum. After a transient stage, the system tends towards a stationary state and the viscosity of the system is simply deduced from the Newton's law. To ensure a sufficient statistical precision, simulations have been performed on 10^7 time steps (with a reduced timestep equal to 0.002). It has already been verified that this numerical procedure ensures a better estimation of viscosity and pressure compared to literature [10,19-20]. In addition, to avoid a drift of the temperature during simulations, a Berendsen thermostat has been used [21].

Using these numerical parameters, the statistical errors produced on viscosity are around $\pm 3 \%$ (except in dense phase where errors may reach 5 %) and are around $\pm 1 \%$ on pressure. Error bars have not been included in the figures.

3. Results and discussion

The main point of this work is to perform simulations in various reduced thermodynamic states (and varying also the repulsive stiffness for each state) in order to construct a reduced viscosity and pressure database for each potential. To achieve such a goal, we have sampled the thermodynamic state space to provide values in several conditions including gas, liquid and supercritical phases. Thus, we have performed simulations for T^* ranging from 1 to 2.5 with a step of 0.25 and for ρ^* ranging from 0.3 to 1.3 with a step of 0.2. It should be noted that some of these states correspond to a two-phase region (these points being dependent on the potential), they have been discarded for the analysis. So, 42 different state points were simulated for each potential: the Mie α -6 ones for α going from 9 to 14 with a step of 1, and the exp α -6 ones for α going from 11 to 16 with a step of 0.5, which corresponds to a total of 603

points of simulations of stable phases. The results for both potentials families and both properties are given in tables 1 and 2. It should be noted that the α chosen correspond approximately to the same range of repulsive stiffness for both potential families.

3.1. Results on pressures

The general behavior of the computed reduced pressure found in the stable phases is consistent as P^* increases with T^* and ρ^* in a monotonic way, whatever the potential, see figure 1 for Mie α -6 potentials, figure 2 for exp α -6 ones. Furthermore, as expected, the slope of the repulsive part of the potential strongly affects the amplitude of the pressure; more precisely, the larger α , the higher the pressure for both potential families, which is consistent with previous works [6]. Such increase of the pressure with α is not surprising as long as changing α modifies the position of the critical point in reduced units [6,7] (the phase diagram for both potential families, in the ρ^*, T^* plan, is shifted upwards when α is lowered).

It has been found, for the Mie α -6 potentials, that the increase of reduced pressure with α is not perfectly linear, but is well approximated by a linear function of $\sqrt{\alpha-6}$ as shown in figure 3 along isotherm $T^*=2.0$ over the range of α . Notice that, despite no theoretical foundations, such empirical formulation is consistent with the fact that a geometric law is usually applied as a combining rule for α and the potential is no longer repulsive for $\alpha \leq 6$ (cf. equations (1-2)).

This simple dependence allows to deduce the reduced pressures for a particular value of α from those obtained for two other values of alpha, noted α_i (i.e. a corresponding states scheme on pressure between Mie α -6 potentials). The unique condition is that the values of α_i encompass the one of α . The analysis shows that the following equation have to be used:

$$P^*(\alpha) = \sum_i y_i P^*(\alpha_i) \quad (8)$$

with

$$\alpha = 6 + \left(\sum_i y_i \sqrt{\alpha_i - 6} \right)^2 \quad (9)$$

and

$$\sum_i y_i = 1 \quad (10)$$

where y_i is the weight associated to the result on pressure for α_i . The values of y_i are chosen in order to obtain the desired value of α , from the values of α_i , thanks to eq.(9), while respecting eq. (10) (e.g. to obtain the result for $\alpha=12$ from the values of $\alpha_1=10$ and $\alpha_2=14$, the unique solution is $y_1 = (\sqrt{8} - \sqrt{6})/2(\sqrt{2} - 1)$ and $y_2=1-y_1$).

To test the applicability of this empirical scheme, we have compared the reduced pressures provided by equations (8-10) for $\alpha=10, 11, 12$ and 13 , using the values obtained for $\alpha_1=9$ and $\alpha_2=14$ (the extreme values tested), with those coming from the direct MD simulations for the same values of α .

Table 3 clearly shows that the proposed scheme, equations (8-10), is able to provide results consistent with the simulations whatever the repulsive coefficient. The overall Average Absolute Deviations (AAD) is equal to 1.25 %, and the Maximum absolute Deviation (MxD) is equal to 5.1 %, which is good if we take into account the simplicity of the proposed scheme. Besides, the proposed scheme could serve as a test for modern equation of state based on Mie α -6 potentials [5].

Concerning the exp α -6 potentials, as for the Mie α -6 potentials, it has been noticed that the increase of reduced pressure with α is not perfectly linear. In addition, this increase can be well approximated by a linear function of $\sqrt{\alpha-7}$, for each thermodynamic state, as shown in figure 4 for $T^*=2.0$. Notice that this empirical relation is consistent with the

fact that for $\alpha \leq 7$, the exp α -6 potential is no longer repulsive (cf. equations (1) and (3)) and that a geometric law is usually applied as a combining rule for α .

Using a similar scheme than for the Mie α -6 potential, equations (8) and (10) combined with:

$$\alpha = 7 + \left(\sum_i y_i \sqrt{\alpha_i - 7} \right)^2 \quad (11)$$

allows an estimation of the pressure for a particular value of α from those obtained for two other values of alpha noted α_i (i.e. a corresponding states scheme on pressure between exp α -6 potentials). This empirical scheme has been applied on the exp α -6 potential for α going from 11.5 to 15.5, with a step of 0.5, using the values obtained for $\alpha_1=11$ and $\alpha_2=16$. Comparisons of the results given by this approach with those coming from MD simulations are given in table 4. As for the Mie α -6 potential this simple scheme is able to provide reasonably good results, the overall AAD being equal to 1.73 % with a MxD of 6.18%.

Another interesting point is to investigate similarities between results of both potential families of potentials for the set of reduced variables used, equations (4-6). To do so we have compared the results for all potentials with those given by the usual LJ one. Results for $T^*=2.0$ are shown in figures 5 and 6. It appears that the results on pressure for a Mie α -6 potential are approximately equivalent to those for an exp $(\alpha+2)$ -6 potential, even if non negligible deviations appears. As an example, the AAD on pressures between the exp 14-6 potential and the Mie 12-6 (LJ) one for all the thermodynamic states studied is only equal to 3.96 %, which confirms what observed on figure 6. Such results indicate that, for the set of chosen reduced variables, an approximate corresponding states [3] scheme (but not a “perfect” one) exist between both potentials families for the pressure.

3.2. Results on viscosities

Whatever the potential, the general behavior of the computed viscosity is consistent with what is known for simple non polar systems: i.e. viscosity always increases with density and slightly increases with temperature for low density systems (gas like) and decreases with temperature for high density systems (liquid like). Some results are shown in figures 7 and 8. The change in the slope sign corresponds more or less to a reduced density equal to twice the critical value, this behavior being the classical one in non polar simple fluids [16].

As for the pressure, for both potential families, the slope of the repulsive part strongly affects the amplitude of the viscosity, as shown in figure 7 for the Mie α -6 potentials and figure 8 for the exp α -6 ones. Furthermore, the larger α , the higher the viscosity, except from the low density regime where the viscosities are weakly dependent on α , see figure 9 for the Mie α -6 potentials and figure 10 for the exp α -6 ones .

As shown on figure 9 and 10 for $T^*=2.0$, it has been found that the viscosities for both potential families can be well correlated by a linear relation on α for each thermodynamic state. The analysis of the results shows that it is possible to write that:

$$\eta^*(\alpha) = \sum_i z_i \eta^*(\alpha_i) \quad (12)$$

with

$$\alpha = \sum_i z_i \alpha_i \quad (13)$$

and

$$\sum_i z_i = 1 \quad (14)$$

where z_i is the weight associated to the result on viscosity for α_i .

This scheme has been applied on the Mie α -6 potentials for α ranging from 10 to 13 using the values obtained for $\alpha_1=9$ and $\alpha_2=14$, and on the exp α -6 potentials for α ranging from 11.5 to 15.5 using the values obtained for $\alpha_1=11$ and $\alpha_2=16$. Comparisons with results coming from the MD simulations are given in tables 5 and 6. These tables show that this simple scheme is able to provide excellent results compared to the inherent uncertainties, the overall AAD being equal to 1.96 % (MxD=10.3%) for the Mie α -6 potentials and equal to 1.74% (MxD=11.5%) for the exp α -6 ones. These results indicate that, as for pressure, an approximate corresponding states scheme on viscosity exists for both potential families for the range of α explored.

Figures 11 and 12 show, for $T^*=2.0$, that the relative effects of the repulsive exponent on reduced viscosities, compared to the LJ results, are similar for both potential families. More precisely it appears from these figures that exponential $(\alpha+2.5)$ -6 results are relatively close to those obtained for the Mie α -6 potentials. As an example, the AAD on viscosities between the Mie 12-6 (LJ) potential and the exp 14.5-6 one for all thermodynamics states studied is only equal to 1.95 % which confirms what observed on figure 12. Thus, results exhibit an approximate corresponding states law between both families of potentials for the viscosities in the T^*, ρ^* plan.

Another interesting point is to analyse the relative influence of the repulsive coefficient α on P^* and η^* . To do so, reduced viscosity is drawn versus reduced pressure for the whole range of density and for four different temperatures in figure 13 for the Mie α -6 potentials, and in figure 14 for the exp α -6 potentials. These figures exhibit that, for a given T^* and P^* , η^* is weakly α dependent (i.e. the general trend is similar whatever the symbol for a given T^* on figures 13 and 14). Nevertheless, for both potentials families, this dependence is not negligible for two very different values of α , especially at low temperature. Such result is not surprising as long as the dependence of reduced pressure

and viscosity with α is not the same, see eqs (8-14). This indicates that a complete corresponding states scheme for each potential family, including both pressure and viscosity, cannot be perfectly satisfied.

Concerning a link between both potentials families, a comparison between figures 5 and 6 and figures 11 and 12 clearly shows that the behaviors of pressures and of viscosities differ for a given set of T^* , ρ^* and potential type. This indicates that the influence of the shape of the potential on these two properties is not strictly the same even if similarities exist (see figure 13 and 14). Hence, the relation between η^* and (T^*, P^*) depends on the shape of the repulsive potential part (i.e. there is no perfect corresponding states between the two potentials families). Thus a complete corresponding states scheme (including simultaneously pressure and viscosity), covering the whole range of thermodynamic conditions, seems hardly feasible between the Mie α -6 and the exp α -6 potentials families.

For applications on real fluids, such findings could be of interest because in most cases the optimum molecular parameters of the classical LJ potential are different for a static and a dynamic property [22], which exhibits the intrinsic limitations of such modelling. So, due to the differences found between the behavior of the two potential families (and inside each families) on P^* and η^* , it is suspected that a correct choice of the potential could provide an improvement on this point in some cases [9,10].

4. Conclusion

In this study, an analysis of the general influence of the repulsive slope of the Mie α -6 and exponential α -6 potentials on a static property, the pressure, and on a transport property, the viscosity, has been performed. Values of α ranging from 9 to 14, with a step of 1, for the Mie α -6 potential and from 11 to 16, with a step of 0.5, for the exp α -6 potential have been tested. To conduct this study, nonequilibrium molecular dynamics

simulations have been carried out in various reduced thermodynamic states, T^* varying from 1.0 to 2.5 with a step of 0.25 and ρ^* from 0.3 to 1.3 with a step of 0.2.

These simulations on a large database, 603 points, have shown that the influence of the repulsive coefficient has an expected increasing effect with density on both properties. In addition, for a given set of reduced thermodynamic conditions, simple empirical relations between the properties and the repulsive coefficient have been found (using r_m as the length parameter to scale the properties). For pressure, results have shown that the reduced pressure varies linearly with $\sqrt{\alpha-6}$ for the Mie $\alpha-6$ potentials and with $\sqrt{\alpha-7}$ for the exp $\alpha-6$ potentials. For viscosity, it appears that, for both potential families, its variation is linear with α . Thus, using these dependences, it is possible to deduce pressure and viscosity, for a given α , from the results obtained with other repulsive coefficients, unless the values of these coefficients encompass the one of α . These results indicate that an approximate corresponding states scheme exists on pressure and on viscosity for both potentials families, but only for each property separately. In fact, due to different dependences of pressure and viscosity on α , for a given potentials family, $\eta^*(P^*, T^*)$ depends on α even if this dependence is weak. Hence a complete corresponding states scheme for each potential family, including both the pressure and the viscosity, cannot be perfectly satisfied.

In addition, when results for Mie $\alpha-6$ and exp $\alpha-6$ potentials are compared, it appears that the influence of α on the viscosity differs from the one on pressure, especially at mid densities. A Mie $\alpha-6$ potential provides similar results to those given by an exp $(\alpha+2)-6$ potential for pressure whereas it is an exp $(\alpha+2.5)-6$ one for viscosity. Thus, for each property (pressure and viscosity) separately, an approximate corresponding states law exists between the Mie $\alpha-6$ and the exp $\alpha-6$ potentials families. Nevertheless a

complete corresponding states scheme between both potentials families including together pressure and viscosity seems hardly feasible.

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References

- 1 A. J., Stone, *The theory of Intermolecular Forces*, Clarendon Press, Oxford, 1996.
- 2 I. Nezbeda, *Mol. Phys.* 103 (2005) 59.
- 3 T. Young and H. C. Andersen, *J. Phys. Chem. B.* 109 (2005) 2985.
- 4 S. Chapman and T.G. Cowling, *The mathematical theory of Non-Uniform Gases*, Cambridge Mathematical Library, Cambridge, 1970.
- 5 T. Lafitte, D. Bessières, M.M. Pineiro and J.L. Daridon, *J. Chem. Phys.* 124 (2006) 1.
- 6 A.Z. Panagiotopoulos, *J. Chem. Phys.* 112 (2000) 7132.
- 7 H. Okumura, F. Yonezawa, *J. Chem. Phys.*, 113 (2000) 9162.
- 8 I.I Adamenko, A. N. Grigoriev and Y.I. Kuzovkov, *J. Mol. Liq.* 105 (2003) 261.
- 9 P.A. Gordon, *J. Chem. Phys.*, 125 (2006) 014504.
- 10 G. Galliero, C. Boned, A. Baylaucq and F. Montel, *Phys. Rev. E* 73 (2006) 061201.
- 11 H.L. Vörtler, I. Nezbeda and M. Lisal, *Mol. Phys.* 92 (1997) 813.
- 12 J.R. Errington and A. Z. Panagiotopoulos, *J. Phys. Chem. B.* 103 (1999) 6314.
- 13 G.W. Wu, R.J. Sadus, *Fluid Phase Equi.* 170 (2000) 269.
- 14 H. Zhang and J. F. Ely, *Fluid Phase Equi.*, 217 (2004) 111.
- 15 J.P. Boon and S. Yip, *Molecular Hydrodynamics*, Dover, New-York, 1991.
- 16 B.E. Poling, J. M. Prausnitz and J.P. O'Connell, *The Properties of Gases and Liquids*, McGraw-Hill, New-York, 2001.
- 17 F. Müller-Plathe, *Phys. Rev. E* 59 (1999) 4894.
- 18 P. Bordat and F. Müller-Plathe, *J. Chem. Phys.* 116 (2002) 3362.

- 19 G. Galliero, C. Boned, A. Baylaucq and F. Montel, *Fluid Phase Equi.* 234 (2005) 56.
- 20 G. Galliero, C. Boned and A. Baylaucq, *Ind. Eng. Chem. Res.* 44 (2005) 6963.
- 21 H.J.C Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. di Nola and J.R. Haak, *J. Chem. Phys.* 81 (1984) 3684.
- 22 E. Ruckenstein and H. Liu, *Ind. Eng. Chem. Res.* 36 (1997) 3927.

Tables:

Table 1 Reduced pressures and viscosities of the Mie α -6 potentials.

T^*	ρ^*	$\alpha=9$		$\alpha=10$		$\alpha=11$		$\alpha=12$		$\alpha=13$		$\alpha=14$	
		P^*	η^*	P^*	η^*	P^*	η^*	P^*	η^*	P^*	η^*	P^*	η^*
1.00	1.1					0.548	2.144	0.985	2.238	1.373	2.565	1.718	2.644
1.00	1.3	2.227	3.801	3.470	4.468	4.552	5.320	5.506	6.071	6.402	7.143	7.219	8.448
1.25	0.3							0.149	0.270	0.167	0.272	0.183	0.272
1.25	0.5											0.196	0.435
1.25	0.7									0.205	0.711	0.297	0.726
1.25	0.9					0.300	1.098	0.549	1.153	0.768	1.203	0.962	1.259
1.25	1.1	0.699	1.719	1.408	1.926	2.003	2.074	2.530	2.139	2.979	2.350	3.396	2.520
1.25	1.3	4.160	3.268	5.566	3.771	6.808	4.446	7.913	5.195	8.963	5.884	9.926	7.296
1.50	0.3	0.178	0.307	0.214	0.301	0.242	0.306	0.264	0.308	0.284	0.311	0.300	0.310
1.50	0.5					0.284	0.454	0.343	0.461	0.402	0.477	0.449	0.484
1.50	0.7			0.258	0.686	0.424	0.691	0.560	0.729	0.682	0.731	0.788	0.760
1.50	0.9	0.375	1.045	0.781	1.082	1.115	1.138	1.406	1.177	1.649	1.223	1.873	1.293
1.50	1.1	1.904	1.722	2.689	1.875	3.362	2.025	3.966	2.189	4.485	2.347	4.970	2.450
1.50	1.3	5.951	2.962	7.502	3.471	8.894	4.036	10.133	4.610	11.339	5.222	12.443	6.031
1.75	0.3	0.288	0.344	0.325	0.344	0.354	0.343	0.376	0.346	0.398	0.344	0.415	0.344
1.75	0.5	0.336	0.485	0.440	0.487	0.523	0.487	0.587	0.491	0.650	0.494	0.701	0.508
1.75	0.7	0.465	0.687	0.688	0.712	0.871	0.745	1.020	0.758	1.158	0.783	1.274	0.774
1.75	0.9	1.090	1.048	1.531	1.104	1.902	1.178	2.223	1.206	2.502	1.278	2.754	1.314
1.75	1.1	3.043	1.701	3.906	1.896	4.649	2.014	5.313	2.143	5.911	2.347	6.460	2.429
1.75	1.3	7.630	2.830	9.323	3.274	10.852	3.699	12.262	4.359	13.575	4.928	14.816	5.352
2.00	0.3	0.396	0.375	0.435	0.371	0.465	0.377	0.489	0.377	0.511	0.369	0.529	0.377
2.00	0.5	0.561	0.517	0.671	0.518	0.759	0.514	0.832	0.527	0.896	0.530	0.951	0.530
2.00	0.7	0.874	0.720	1.115	0.742	1.311	0.772	1.475	0.795	1.624	0.798	1.753	0.812
2.00	0.9	1.783	1.051	2.262	1.131	2.663	1.196	3.015	1.241	3.326	1.297	3.608	1.379
2.00	1.1	4.131	1.689	5.065	1.823	5.880	2.006	6.612	2.137	7.274	2.252	7.889	2.487
2.00	1.3	9.225	2.768	11.048	3.096	12.712	3.564	14.220	4.101	15.695	4.600	17.068	5.065
2.25	0.3	0.503	0.407	0.543	0.405	0.574	0.400	0.598	0.407	0.623	0.388	0.642	0.405
2.25	0.5	0.784	0.536	0.900	0.537	0.994	0.549	1.065	0.559	1.140	0.550	1.200	0.560
2.25	0.7	1.277	0.750	1.532	0.757	1.744	0.785	1.920	0.808	2.083	0.812	2.223	0.844
2.25	0.9	2.454	1.051	2.965	1.149	3.404	1.223	3.789	1.276	4.127	1.287	4.438	1.372
2.25	1.1	5.174	1.659	6.178	1.810	7.059	1.963	7.862	2.133	8.589	2.224	9.264	2.376
2.25	1.3	10.747	2.704	12.698	3.054	14.485	3.413	16.113	3.934	17.722	4.340	19.223	4.973
2.50	0.3	0.609	0.439	0.650	0.440	0.683	0.437	0.705	0.427	0.734	0.417	0.754	0.427
2.50	0.5	1.006	0.570	1.128	0.570	1.227	0.606	1.308	0.587	1.382	0.577	1.446	0.590
2.50	0.7	1.674	0.774	1.945	0.804	2.171	0.800	2.360	0.846	2.535	0.862	2.689	0.872
2.50	0.9	3.110	1.100	3.657	1.177	4.124	1.233	4.541	1.324	4.908	1.357	5.250	1.448
2.50	1.1	6.184	1.693	7.255	1.843	8.204	1.988	9.068	2.215	9.858	2.334	10.600	2.497
2.50	1.3	12.211	2.751	14.282	3.182	16.193	3.502	17.959	3.872	19.677	4.134	21.299	4.999

Table 2 Reduced pressures and viscosities of the exp α -6 potentials.

T^*	ρ^*	$\alpha=11$		$\alpha=11.5$		$\alpha=12$		$\alpha=12.5$		$\alpha=13$		$\alpha=13.5$		$\alpha=14$		$\alpha=14.5$		$\alpha=15$		$\alpha=15.5$		$\alpha=16$	
		P^*	η^*	P^*	η^*	P^*	η^*	P^*	η^*	P^*	η^*	P^*	η^*	P^*	η^*	P^*	η^*	P^*	η^*	P^*	η^*	P^*	η^*
1.00	1.1					0.157	1.837	0.416	1.961	0.652	2.016	0.872	2.122	1.074	2.230	1.264	2.229	1.442	2.393	1.612	2.610	1.774	2.501
1.00	1.3	2.050	3.073	2.738	3.555	3.361	3.949	3.935	4.372	4.469	4.689	4.970	5.247	5.450	5.604	5.922	6.337	6.333	6.775	6.747	7.725	7.148	8.367
1.25	0.3							0.135	0.263	0.146	0.268	0.156	0.262	0.165	0.267	0.174	0.269	0.182	0.274	0.189	0.268	0.195	0.275
1.25	0.5																	0.190	0.419	0.208	0.437	0.226	0.434
1.25	0.7													0.173	0.679	0.221	0.680	0.267	0.719	0.309	0.702	0.350	0.717
1.25	0.9							0.274	1.031	0.403	1.070	0.525	1.121	0.639	1.169	0.745	1.188	0.843	1.180	0.937	1.237	1.025	1.242
1.25	1.1	0.739	1.510	1.115	1.692	1.456	1.765	1.763	1.825	2.045	1.910	2.311	2.098	2.554	2.107	2.787	2.287	3.008	2.319	3.215	2.420	3.415	2.384
1.25	1.3	3.771	2.666	4.574	3.113	5.288	3.320	5.958	3.812	6.585	3.921	7.168	4.370	7.739	4.774	8.276	4.968	8.792	5.507	9.279	5.776	9.768	6.286
1.50	0.3	0.204	0.300	0.221	0.303	0.236	0.301	0.249	0.302	0.260	0.306	0.271	0.305	0.280	0.309	0.289	0.305	0.297	0.306	0.304	0.310	0.312	0.310
1.50	0.5	0.177	0.436	0.223	0.443	0.263	0.432	0.298	0.441	0.331	0.449	0.360	0.451	0.388	0.459	0.413	0.463	0.436	0.470	0.457	0.463	0.478	0.471
1.50	0.7	0.161	0.637	0.261	0.652	0.350	0.670	0.429	0.681	0.501	0.691	0.568	0.705	0.629	0.710	0.685	0.725	0.738	0.723	0.789	0.747	0.836	0.744
1.50	0.9	0.477	0.950	0.687	1.006	0.872	1.037	1.039	1.047	1.195	1.106	1.333	1.116	1.466	1.131	1.591	1.204	1.708	1.229	1.818	1.226	1.923	1.282
1.50	1.1	1.840	1.498	2.272	1.633	2.659	1.728	3.015	1.771	3.342	1.891	3.648	1.997	3.936	2.071	4.211	2.207	4.469	2.313	4.713	2.285	4.950	2.355
1.50	1.3	5.350	2.481	6.242	2.896	7.063	3.050	7.818	3.392	8.534	3.655	9.206	4.041	9.853	4.183	10.465	4.657	11.059	5.093	11.637	5.214	12.187	5.603
1.75	0.3	0.313	0.343	0.330	0.337	0.346	0.342	0.359	0.341	0.372	0.343	0.383	0.342	0.392	0.343	0.402	0.339	0.411	0.343	0.419	0.344	0.426	0.346
1.75	0.5	0.396	0.472	0.446	0.469	0.490	0.466	0.529	0.482	0.566	0.481	0.599	0.483	0.627	0.487	0.656	0.492	0.681	0.502	0.706	0.466	0.728	0.494
1.75	0.7	0.554	0.658	0.666	0.659	0.766	0.705	0.856	0.700	0.938	0.720	1.013	0.726	1.082	0.745	1.146	0.738	1.208	0.754	1.263	0.762	1.317	0.778
1.75	0.9	1.143	0.958	1.381	1.021	1.589	1.066	1.778	1.072	1.952	1.094	2.114	1.136	2.265	1.202	2.405	1.197	2.541	1.252	2.665	1.268	2.785	1.274
1.75	1.1	2.878	1.502	3.357	1.609	3.794	1.726	4.196	1.753	4.567	1.903	4.914	1.987	5.239	2.048	5.551	2.169	5.846	2.195	6.129	2.238	6.402	2.366
1.75	1.3	6.821	2.412	7.804	2.805	8.714	2.923	9.555	3.178	10.347	3.398	11.103	3.690	11.824	4.022	12.516	4.196	13.186	4.533	13.828	4.981	14.449	5.201
2.00	0.3	0.419	0.378	0.437	0.374	0.454	0.370	0.469	0.364	0.481	0.373	0.492	0.367	0.504	0.369	0.513	0.375	0.523	0.373	0.531	0.375	0.538	0.381
2.00	0.5	0.614	0.506	0.668	0.505	0.717	0.514	0.759	0.518	0.799	0.511	0.834	0.518	0.868	0.519	0.897	0.524	0.926	0.530	0.952	0.528	0.975	0.530
2.00	0.7	0.943	0.692	1.067	0.705	1.177	0.716	1.275	0.730	1.366	0.735	1.450	0.750	1.526	0.760	1.597	0.786	1.665	0.788	1.729	0.813	1.787	0.825
2.00	0.9	1.786	0.983	2.047	1.012	2.280	1.062	2.491	1.079	2.687	1.119	2.865	1.160	3.032	1.204	3.194	1.227	3.342	1.244	3.484	1.269	3.620	1.305
2.00	1.1	3.858	1.495	4.389	1.573	4.876	1.683	5.315	1.755	5.733	1.842	6.115	1.913	6.481	2.020	6.830	2.095	7.157	2.197	7.481	2.303	7.784	2.350
2.00	1.3	8.211	2.298	9.283	2.614	10.271	2.837	11.197	3.013	12.064	3.302	12.890	3.562	13.690	3.830	14.453	4.060	15.186	4.345	15.906	4.675	16.603	4.984
2.25	0.3	0.523	0.397	0.544	0.395	0.561	0.401	0.575	0.404	0.589	0.404	0.602	0.402	0.612	0.402	0.625	0.398	0.632	0.398	0.643	0.399	0.652	0.402

2.25	0.5	0.829	0.528	0.888	0.518	0.938	0.525	0.987	0.533	1.027	0.540	1.066	0.548	1.103	0.535	1.134	0.548	1.163	0.548	1.193	0.553	1.220	0.549
2.25	0.7	1.325	0.709	1.459	0.712	1.580	0.745	1.688	0.756	1.787	0.756	1.877	0.778	1.962	0.803	2.042	0.799	2.118	0.810	2.184	0.828	2.253	0.831
2.25	0.9	2.411	0.983	2.693	1.041	2.950	1.088	3.182	1.130	3.395	1.133	3.597	1.179	3.778	1.206	3.955	1.257	4.120	1.297	4.278	1.313	4.432	1.392
2.25	1.1	4.796	1.480	5.375	1.543	5.904	1.705	6.391	1.746	6.845	1.793	7.266	1.885	7.670	2.011	8.053	2.126	8.418	2.163	8.770	2.301	9.108	2.283
2.25	1.3	9.530	2.250	10.681	2.536	11.750	2.766	12.745	2.905	13.693	3.215	14.591	3.459	15.459	3.660	16.291	3.842	17.094	4.087	17.888	4.460	18.642	4.532
2.50	0.3	0.627	0.429	0.649	0.433	0.666	0.427	0.682	0.422	0.696	0.425	0.707	0.425	0.725	0.424	0.734	0.428	0.746	0.429	0.752	0.418	0.763	0.421
2.50	0.5	1.045	0.548	1.106	0.551	1.162	0.552	1.211	0.551	1.258	0.561	1.299	0.567	1.339	0.572	1.373	0.570	1.404	0.581	1.433	0.597	1.466	0.601
2.50	0.7	1.700	0.748	1.846	0.754	1.976	0.772	2.092	0.777	2.200	0.773	2.300	0.794	2.391	0.799	2.478	0.826	2.560	0.847	2.636	0.839	2.706	0.854
2.50	0.9	3.014	1.009	3.321	1.041	3.600	1.087	3.849	1.151	4.085	1.179	4.302	1.193	4.505	1.219	4.698	1.266	4.879	1.305	5.052	1.327	5.221	1.364
2.50	1.1	5.700	1.467	6.329	1.553	6.899	1.641	7.426	1.754	7.915	1.828	8.374	1.933	8.818	2.011	9.235	2.113	9.635	2.180	10.020	2.301	10.391	2.424
2.50	1.3	10.790	2.199	12.026	2.437	13.174	2.621	14.242	2.820	15.259	3.122	16.233	3.357	17.163	3.574	18.057	3.739	18.892	4.034	19.801	4.346	20.613	4.533

Table 3 Deviations, for all thermodynamic states studied, between the pressures deduced from equations (8-10), using values for $\alpha=9$ and $\alpha=14$, and those computed by MD simulations for the Mie $\alpha=6$ potentials.

Alpha	10	11	12	13
AAD	1.50	1.63	1.18	0.69
MxD	5.10	4.63	3.61	1.60

Table 4 Deviations, for all thermodynamic states studied, between the pressures deduced from equations (8,10-11), using values for $\alpha=11$ and $\alpha=16$, and those computed by MD simulations for the exp $\alpha=6$ potentials.

Alpha	11.5	12	12.5	13	13.5	14	14.5	15	15.5
AAD	1.67	2.33	2.48	2.40	2.11	1.79	1.40	0.95	0.46
MxD	5.03	6.18	6.07	5.73	4.64	3.77	2.91	1.92	0.97

Table 5 Deviations, for all thermodynamic states studied, between the viscosities deduced from equations (12-14), using values for $\alpha=9$ and $\alpha=14$, and those computed by MD simulations for the Mie $\alpha=6$ potentials.

Alpha	10	11	12	13
AAD	1.72	2.18	1.86	2.09
MxD	8.01	9.74	9.42	10.30

Table 6 Deviations, for all thermodynamic states studied, between the viscosities deduced from equations (8,10-11), using values for $\alpha=11$ and $\alpha=16$, and those computed by MD simulations for the exp $\alpha=6$ potentials.

Alpha	11.5	12	12.5	13	13.5	14	14.5	15	15.5
AAD	1.63	1.79	1.43	1.86	1.66	2.01	1.93	1.76	1.55
MxD	5.60	4.62	6.62	10.70	9.02	11.52	7.23	7.87	5.63

Figure captions:

Fig. 1 Behavior of reduced pressure of some Mie α -6 potentials versus reduced temperature. Circles correspond to $\rho^*=0.9$, up triangles to $\rho^*=1.1$ and squares to $\rho^*=1.3$. Open symbols correspond to $\alpha=9$, grey ones to $\alpha=11$, dark grey ones to $\alpha=12$ and black symbols to $\alpha=14$.

Fig. 2 Behavior of reduced pressure of some exp α -6 potentials versus reduced temperature. Circles correspond to $\rho^*=0.9$, up triangles to $\rho^*=1.1$ and squares to $\rho^*=1.3$. Open symbols correspond to $\alpha=11$, grey ones to $\alpha=13$, dark grey ones to $\alpha=14$ and black symbols to $\alpha=16$.

Fig. 3 Behavior of reduced pressure of Mie α -6 potentials for various reduced densities at $T^*=2.0$ versus $\sqrt{\alpha-6}$. \bullet corresponds to $\rho^*=0.3$, \circ to $\rho^*=0.5$, \blacktriangledown to $\rho^*=0.7$, \triangledown to $\rho^*=0.9$, \blacksquare to $\rho^*=1.1$ and \square to $\rho^*=1.3$.

Fig. 4 Behavior of reduced pressure of exp α -6 potentials for various reduced densities at $T^*=2.0$ versus $\sqrt{\alpha-7}$. \bullet corresponds to $\rho^*=0.3$, \circ to $\rho^*=0.5$, \blacktriangledown to $\rho^*=0.7$, \triangledown to $\rho^*=0.9$, \blacksquare to $\rho^*=1.1$ and \square to $\rho^*=1.3$.

Fig. 5 Deviations between reduced pressures computed for various Mie α -6 potentials and the LJ potential for different reduced densities at $T^*=2.0$. The highest curve (\bullet) corresponds to the values for $\alpha=9$ and the lowest (+) to those for $\alpha=14$, the curves between correspond to values of α ranging from 10 to 13 with a step of 1.

Fig. 6 Deviations between reduced pressures computed for various exp α -6 potentials and the LJ potential for different reduced densities at $T^*=2.0$. The highest curve (\bullet) corresponds to the values for $\alpha=11$ and the lowest (+) to those for $\alpha=16$, the curves between correspond to values of α ranging from 11.5 to 15.5 with a step of 0.5.

Fig. 7 Behavior of reduced viscosity of some Mie α -6 potentials versus reduced temperature. Circles correspond to $\rho^*=0.9$, up triangles to $\rho^*=1.1$ and squares to $\rho^*=1.3$. Open symbols correspond to $\alpha=9$, grey ones to $\alpha=11$, dark grey ones to $\alpha=12$ and black symbols to $\alpha=14$.

Fig. 8 Behavior of reduced viscosity of some exp α -6 potentials versus reduced temperature. Circles correspond to $\rho^*=0.9$, up triangles to $\rho^*=1.1$ and squares to $\rho^*=1.3$. Open symbols correspond to $\alpha=11$, grey ones to $\alpha=13$, dark grey ones to $\alpha=14$ and black symbols to $\alpha=16$.

Fig. 9 Behavior of reduced viscosity of Mie α -6 potentials for various reduced densities at $T^*=2.0$ versus the repulsive slope coefficient α . ● corresponds to $\rho^*=0.3$, ○ to $\rho^*=0.5$, ▼ to $\rho^*=0.7$, ▽ to $\rho^*=0.9$, ■ to $\rho^*=1.1$ and □ to $\rho^*=1.3$.

Fig. 10 Behavior of reduced viscosity of exp α -6 potentials for various reduced densities at $T^*=2.0$ versus the repulsive slope coefficient α . ● corresponds to $\rho^*=0.3$, ○ to $\rho^*=0.5$, ▼ to $\rho^*=0.7$, ▽ to $\rho^*=0.9$, ■ to $\rho^*=1.1$ and □ to $\rho^*=1.3$.

Fig. 11 Deviations between reduced viscosities computed for various Mie α -6 potentials and the LJ potential for different reduced densities at $T^*=2.0$. The highest curve (●) corresponds to the values for $\alpha=9$ and the lowest (+) to those for $\alpha=14$, the curves between correspond to values of α going from 10 to 13 with a step of 1.

Fig. 12 Deviations between reduced viscosities computed for various exp α -6 potentials and the LJ potential for different reduced densities at $T^*=2.0$. The highest curve (●) corresponds to the values for $\alpha=11$ and the lowest (+) to those for $\alpha=16$, the curves between correspond to values of α going from 11.5 to 15.5 with a step of 0.5.

Fig. 13 Mie α -6 reduced viscosities for different reduced temperatures and pressures. Circles correspond to $\alpha=9$, down triangles to $\alpha=10$, squares to $\alpha=11$, diamonds to

$\alpha=12$, up triangles to $\alpha=13$ and hexagons to $\alpha=14$. Black symbols correspond to $T^*=1.0$, dark grey ones to $T^*=1.5$, light grey ones to $T^*=2.0$ and open symbols to $T^*=2.5$.

Fig 14 Exp α -6 reduced viscosities for different reduced temperatures and pressures.

Circles correspond to $\alpha=11$, down triangles to $\alpha=12$, squares to $\alpha=13$, diamonds to $\alpha=14$, up triangles to $\alpha=15$ and hexagons to $\alpha=16$. Black symbols correspond to $T^*=1.0$, dark grey ones to $T^*=1.5$, light grey ones to $T^*=2.0$ and open symbols to $T^*=2.5$.