



HAL
open science

Molecular dynamics simulation of acid gas mixtures: a comparison between several approximations.

Guillaume Galliero, C. Nieto-Draghi, Christian Boned, J.B. Avalos, A.D. Mackie, Antoine Baylaucq, François Montel

► To cite this version:

Guillaume Galliero, C. Nieto-Draghi, Christian Boned, J.B. Avalos, A.D. Mackie, et al.. Molecular dynamics simulation of acid gas mixtures: a comparison between several approximations.. Industrial and engineering chemistry research, 2007, 46 (15), pp.5238-5244. 10.1021/ie061616l . hal-00322172

HAL Id: hal-00322172

<https://hal.science/hal-00322172>

Submitted on 16 Sep 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Molecular dynamics simulation of acid gas mixtures: a comparison between several approximations.

Guillaume Galliero^{1}, Carlos Nieto-Draghi², Christian Boned³, Josep B. Avalos⁴, Allan D. Mackie⁴,
Antoine Baylaucq³ and François Montel⁵.*

¹Université de Marne-la-Vallée, Laboratoire d'Etude des Transferts d'Energie et de Matière (EA 2546),
Cité Descartes, Champs-sur-Marne, 77454 Marne-la-Vallée Cedex 2, France.

²Institut Français du Pétrole, 1-4 Avenue de Bois Préau, 92852 Rueil-Malmaison Cedex, France

³Université de Pau et des Pays de l'Adour, Laboratoire des Fluides Complexes (UMR-5150), BP 1155,
F-64013 Pau Cedex, France.

⁴Departament d'Enginyeria Química, Escola Técnica Superior d'Enginyeria Química (ETSEQ),
Universitat Rovira i Virgili, Avda. dels Països Catalans 26, 43007 Tarragona, Spain

⁵TOTAL, CSTJF, Avenue Larribau, F-64018 Pau, France.

*guillaume.galliero@univ-mlv.fr

ABSTRACT

Molecular dynamics simulations of CH₄, CO₂, H₂S and their mixtures, chosen as representative of acid gas mixtures, have been performed. Static properties (pressure or density) and dynamic properties (shear viscosity) have been computed. A comparison has been performed between results from three different models: a simple Lennard-Jones (LJ) model, an isotropic multipolar (IMP) one and the usual Lennard-Jones plus point charge (LJP). For pure fluids, a reasonable agreement is found between all three models and experiments except for CO₂, for which the LJ model suffers from its lack of electrostatic contributions. Concerning CH₄-H₂S mixtures, results obtained using the three molecular models are consistent with each other for static and dynamic properties. In addition, no significant differences between the results obtained using both, Lorentz-Berthelot and Kong combining rules were noticed. For the CH₄-H₂S-CO₂ mixture, the situation is different: a strong dependence of the pressure on the molecular models as well as on the combining rules, in the case of the LJP model, has been noted. Shear viscosity was found to be less dependent on the choice of models and combining rules. Thanks to simulations on H₂S-CO₂ mixtures, it has been found that the way cross interactions are treated between these two compounds explains the discrepancies for CH₄-H₂S-CO₂ mixtures. For the systems studied, the IMP approximation seems to be the best option for engineering calculations of physical properties since it is quick to compute, ensures accuracy and is weakly dependent on the combining rules employed. In addition, it is shown that a van der Waals one fluid model combined with an accurate LJ Equation of State together with a correlation on viscosity is able to provide results consistent with simulations (on both LJ and IMP models). Such a result makes this correlative scheme a good alternative for industrial applications.

KEYWORDS

Acid gas mixture, hydrogen sulfide, isotropic multipolar potential, molecular dynamics, one fluid model, viscosity.

1 Introduction

Although acid gas mixtures (i.e. natural gases containing carbon dioxide and/or hydrogen sulphide) are often encountered in the petroleum industry¹, experiments on thermophysical properties are scarce due to the high toxicity of the hydrogen sulphide. This is especially true for the high pressures and temperatures of petroleum reservoir conditions. This lack of knowledge is particularly apparent concerning transport properties of such systems. As an example, to the best of our knowledge, only one set of measurement of the viscosity of pure H₂S under high pressure has ever been performed² and none are available concerning its mixture with methane or carbon dioxide. As experiments are difficult to perform on such systems, alternatives are highly encouraged.

Among the possible alternatives to experiments to gather information on acid gas mixtures is molecular simulation, which can be considered as “numerical experiments” on a model fluid. But, when using such an approach, a question arises concerning the choice of the model to describe the molecule. The appropriate choice is guided by a compromise between accuracy of the predictions of the model and CPU needs.

In this work, we are interested in the main compounds of natural acid gas mixtures, i.e. methane (non polar), hydrogen sulphide (dipolar) and carbon dioxide (quadrupolar). For these compounds, a large number of force fields exists in the literature and among them, the model of Möller et al.³ for CH₄, of Kristof and Liszi⁴ for H₂S, and of Harris and Yung⁵ for CO₂ have shown to provide good results for thermodynamic properties from Monte-Carlo simulations⁶. They are based on effective two body Lennard-Jones potentials (one or three centres) combined with an explicit treatment of partial charges to represent the dipolar moment of H₂S and the quadrupolar moment of CO₂. The number of different interactions that are involved in these models thus implies important CPU needs. Hence, when dealing with transport properties, which required Molecular Dynamics (MD) simulations (usually more CPU time consuming than Monte Carlo simulations) with relatively long runs, the needs in computation can become unreasonable for a systematic study. Therefore, it is interesting to see to which extent the molecular description can be simplified while keeping a good estimation of two kinds of properties, a

static one, the density or the pressure, on the one hand, and a dynamic one, the viscosity, on the other. A particular emphasis will be placed on an analysis of the influence, on both properties, of the way that polar interactions are taken into account.

In this work, the usual United Atom model of Möller et al.³ is used to describe CH₄, while for CO₂ and H₂S, three levels of modelling are tested. The first one is the simple Lennard-Jones sphere approach (LJ); the second one is a description using Lennard-Jones spheres augmented with an isotropic multipolar (IMP) contribution⁷ and, the last one, using Lennard-Jones interactions combined with point charges to describe electrostatic interactions. It should be noted that the first two models require approximately one order of magnitude less computational time than the third one.

In the results section, the ability of the various models to mimic pure fluid properties (density and viscosity) is first of all studied. Then, a comparison of the results provided by the different models on CH₄-H₂S, CO₂-H₂S and CH₄-CO₂-H₂S mixtures is performed. In addition, an analysis of the influence of the combining rules is carried out.

2 Theory and Models

2.1 Intermolecular potential

The general formulation of the intermolecular interaction potentials, U_{Tot} , used in this work can be written as:

$$U_{Tot} = U_{LJ} + U_{pol} \quad (1)$$

U_{LJ} represent the non polar interaction part which is modelled by a classical Lennard-Jones 12-6 potential:

$$U_{LJ} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2)$$

where ϵ_{ij} and σ_{ij} are respectively the energy and the size parameters between a site i and a site j and r_{ij} is the distance between the corresponding sites.

For the polar contribution occurring in H₂S and CO₂ modelling, U_{pol} , three approaches are tested. The first one is to consider the crude assumption that with an adequate modification of the values of the LJ parameters (σ and ϵ), the polar effects may be embodied, which leads to:

$$U_{pol} = 0 \quad (3)$$

The second one, corresponding to a combination of a centrally located multipole expansion combined with an averaging over molecular orientations which yields (combined with the non polar potential) what is called an isotropic multipolar potential. The isotropic assumption implies that such an approach remains valid only as long as structural effects are not large, i.e. when the energy involved by the polar interaction is low as compared with the thermal energy $k_B T$. This implies that the accuracy of this assumption is not favoured by very polar molecules, high densities, and low temperatures. A clear example of failure of the assumption would be liquid water at room temperature. When limited to dipolar and quadrupolar interactions such a formulation yields:

$$U_{pol} = -\frac{1}{k_B T} \left[\frac{\mu_i^2 \mu_j^2}{3r_{ij}^6} + \frac{\mu_i^2 Q_j^2 + Q_i^2 \mu_j^2}{2r_{ij}^8} + \frac{7Q_i^2 Q_j^2}{5r_{ij}^{10}} \right] \quad (4)$$

where μ is the dipole moment, Q the quadrupole moment and T the temperature. It is important to notice that the temperature enters in the definition of this effective contribution due to its average character. In particular, when dealing with pure dipolar fluids (Keesom potential), the total potential can be rewritten as a LJ potential with rescaled temperature dependent parameters:

$$U_{LJ} = 4\epsilon_{ij}^{pol} \left[\left(\frac{\sigma_{ij}^{pol}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}^{pol}}{r_{ij}} \right)^6 \right] \quad (5)$$

where σ_{ij}^{pol} and ϵ_{ij}^{pol} are given by:

$$\left(\sigma_{ij}^{pol} \right)^6 = \frac{\sigma_{ij}^6}{F} \quad (6)$$

$$\epsilon_{ij}^{pol} = \epsilon_{ij} F^2 \quad (7)$$

$$F = 1 + \frac{\mu_i^2 \mu_j^2}{12k_B T \epsilon_{ij} \sigma_{ij}^6} \quad (8)$$

The third approach consists of an explicit treatment of the electronic interactions by means of a coulombic potential between adequately distributed partial charges, q :

$$U_{pol} = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \quad (9)$$

	σ (Å)	ϵ (J.mol ⁻¹)	μ (D)	Q (D.Å)
CH ₄	3.7327	1246.5	0	0
H ₂ S LJ	3.667	2355	0	0
H ₂ S IMP	3.688	2320	0.9	0
CO ₂ LJ	3.627	1919	0	0
CO ₂ IMP	3.758	1619	0	4.0982

Table I: H₂S, CO₂ and CH₄ molecular parameters used for the LJ and IMP models.

Compound (site)	Position (Å)		σ (Å)	ϵ (J.mol ⁻¹)	Charge (e)
	X	Y			
H ₂ S (S)	0	0	3.73	2078.5	0.4
H ₂ S (H1)	0.9639	0.9308	0.0	0.0	0.25
H ₂ S (H2)	-0.9639	0.9308	0.0	0.0	0.25
H ₂ S (M)	0	0.1862	0.0	0.0	-0.9
CO ₂ (C)	0	0	2.757	233.9	+0.6512
CO ₂ (O1)	1.149	0	3.033	669.4	-0.3256
CO ₂ (O2)	-1.149	0	3.033	669.4	-0.3256

Table II: H₂S⁴ and CO₂⁵ molecular parameters used for the LJP model.

Using the previous formulations, three models are used to describe H₂S and CO₂ compounds since we recall that methane is modelled by a LJ sphere in all cases. The first one, the simple LJ model, consists

of a LJ sphere to describe the molecules, i.e. eqs. (2) and (3) are used. The second one, the IMP model, is based on an IMP sphere and thus eqs. (2) and (4) apply. Finally the third one, the LJP model, combines partial charges with either one (H_2S) or three LJ centres (CO_2) description, corresponding to eqs. (2) and (9). All molecular parameters are given in table I-II. The way the LJ and IMP parameters were chosen is described in the results section.

2.2 Mixtures

2.2.1 Combining rules

The choice of the combining rules is a crucial point when dealing with the thermodynamic behaviour of mixtures^{1,8-10}, but less is known concerning their influence on the dynamic properties of mixtures. In this work, two types of combining rules are used, the usual Lorentz-Berthelot ones:

$$\sigma_{ij} = \left(\frac{\sigma_i + \sigma_j}{2} \right) \quad (10)$$

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2} \quad (11)$$

and the Kong ones:

$$\varepsilon_{ij} \sigma_{ij}^6 = (\varepsilon_{ii} \sigma_{ii}^6 \varepsilon_{jj} \sigma_{jj}^6)^{1/2} \quad (12)$$

$$\varepsilon_{ij} \sigma_{ij}^{12} = \frac{\varepsilon_{ii} \sigma_{ii}^{12}}{2^{13}} \left[1 + \left(\frac{\varepsilon_{jj} \sigma_{jj}^{12}}{\varepsilon_{ii} \sigma_{ii}^{12}} \right)^{1/13} \right]^{13} \quad (13)$$

Our study has been restricted to these two set of combining rules but it should be mentioned that many alternatives exist, such as the Waldman-Hagler¹¹ one or the Sadus¹⁰ one, which has shown to be efficient in mixtures involving water and methane⁹.

2.2.2 One fluid approximation

When using LJ spheres, it is possible to lump different compounds of a mixture into one equivalent pseudocomponent, which is supposed to mimic the behaviour of the given mixture. To achieve such a goal, the van der Waals one fluid approximation (vdW1) is used¹²:

$$m_x = \sum_i x_i m_i \quad (14)$$

$$\sigma_x^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \quad (15)$$

$$\epsilon_x \sigma_x^3 = \sum_i \sum_j x_i x_j \epsilon_{ij} \sigma_{ij}^3 \quad (16)$$

where x is the molar fraction and m is the mass of component i .

2.3 Simulation details

Depending on the fluid model, two different approaches are used to compute viscosity. For the LJ and the IMP models a Boundary Driven Non-Equilibrium Molecular Dynamics (NEMD) scheme has been applied whereas an Equilibrium Molecular Dynamics (EMD) approach has been used for the simulations of the LJP model. The NEMD scheme is called Reverse NEMD and is due to Müller-Plathe¹³ whereas the EMD scheme is based on the Einstein relation and is described in Smith and Gunsteren¹⁴. Further details can be found in Galliero et al.¹⁵ and Nieto-Draghi et al.¹⁶.

Simulations are performed for 1500 to 3000 particles when using LJ and IMP models, and for 300 to 500 molecules when using the LJP model. For the latter, we have employed the intermolecular potential parameters set of Möller et al.³ for CH₄, Kristof and Liszi⁴ for H₂S and Harris and Yung⁵ for CO₂. In particular, these H₂S and CO₂ models have shown an excellent ability to reproduce shear viscosity at different thermodynamic conditions^{16,17}. All simulations are performed using periodic boundary conditions. A cutoff radius of 2.5σ is used for pure LJ and IMP interactions, whereas a cutoff going from 2.5σ to 7σ , combined with the reaction field methodology is chosen for simulations on the LJP model. Long-range corrections for the energy and the pressure are also included. To perform NVT and NPT simulations, the Berendsen Thermostat and Barostat are used¹⁸. A timestep of 2fs is used for LJP model simulations and a reduced timestep of 0.002 is taken for the LJ and IMP model simulations. For the viscosity computation, after equilibration, $2.5 \cdot 10^6$ timesteps are used when the LJP model is involved and 10^7 timesteps for simulations on the LJ and IMP models.

3 Results

3.1 Pure fluids

3.1.1 Molecular parameter adjustment of H₂S and CO₂

In order to adjust the molecular parameters of the LJ and IMP models for both polar compounds H₂S and CO₂, three different state points are considered, one on the saturated curve and two at high temperature/high pressures. The adjustment of the parameters is done using MD NPT simulations and minimizing the density difference between the MD results and the corresponding experimental data:

$$\sum_i |\rho_{i,MD} - \rho_{i,exp}| \quad (17)$$

For each system, the Average Absolute Deviation (AAD) and the Maximum Deviation (MxD) are estimated.

Concerning the IMP model, in order to limit the number of adjustable parameters, the dipole and quadrupole moment are fixed to values consistent with experimental ones i.e. $\mu=0.9$ D for H₂S¹⁹ and $Q=1.367 \cdot 10^{-39}$ C.m² for CO₂⁷.

For H₂S, the data of Goodwin²⁰ for the point at $T=273$ K and $P=1.028$ MPa and those of Ihmels and Gmehling²¹ for the points at $T=498.2$ K, $P=10.02$ and 39.993 MPa, are used for the fitting procedure. For the density of CO₂, values are taken from Span and Wagner²² for $T=270$ K, $P=3.203$ MPa, $T=500$ K and $P=10$ MPa and 100 MPa.

The molecular parameter sets obtained using this procedure are given in table I. The AAD and MxD between simulations and experimental data are given in table III.

	H ₂ S LJ	H ₂ S IMP	CO ₂ LJ	CO ₂ IMP
AAD (%)	1.19	0.79	3.62	0.31
MxD (%)	1.5	0.83	5.85	0.39

Table III: H₂S and CO₂ deviations for density obtained after fitting.

From this fit, it appears that the LJ model is able to provide reasonable results for H₂S but not for CO₂. Concerning the IMP model, the results are satisfying given the simplicity of the approach,

especially for CO₂ where a strong improvement over the simple LJ model results appears (with the same number of adjustable parameters).

It should be commented that for the three states mentioned above, the NPT simulations on CO₂, using both LJ and IMP models, have shown to provide a reasonable estimation of viscosity as compared to reference values²³. For the LJ model AAD=11.8 % and MxD of 16.6 % and for the IMP model, AAD=4.1 % and MxD=6.6 %, which shows a clear advantage of the IMP model over the simple LJ one being these deviations consistent with those for density.

3.1.2 Viscosity and density of H₂S: A comparison between models

To compare the ability of the three different models to mimic the behaviour of H₂S, NPT simulations are performed for various points on the vapour-liquid equilibrium curve for which experimental results on density and viscosity exist. Results for the LJP model come from Nieto-Draghi et al.¹⁶. All the results are summarized in tables IV and V.

<i>T</i> (K)	<i>P</i> (MPa)	ρ (kg.m ⁻³)				η (10 ⁻⁶ Pa.s)			
		Exp.	LJ	IMP	LJP	Exp.	LJ	IMP	LJP
217.15 (L)	0.124	943.0	936.9	937.5	939.3	414	274.3	294.4	271
240 (L)	0.337	899.0	894.5	895	899	229	209.5	222.6	229
243 (V)	0.379	6.6	6.6	6.6	6.7	10.6	9.17	9.12	8.3
273 (L)	1.028	835.2	827.9	828.5	833.6	159	146.1	156.1	159
273.15 (V)	1.028	16.9	16.8	16.85	17.25	11.7	10.93	10.73	10
300 (L)	2.11	778.4	765.5	769	774.8	118	113.9	115.2	114
310 (V)	2.67	46.5	43.2	43.6	43.94	13.4	13.37	13.3	13.1
333.15 (V)	4.342	73.0	71.6	71.8	73	14.4	14.87	14.85	14.4
333.15 (L)	4.342	680.3	672.8	677.5	680.3	93	80.9	83.9	93

Table IV: Comparisons between H₂S experimental results (density and viscosity) and MD results along the vapour-liquid equilibrium curve using three different models. (L) stands for liquid and (V) for vapour.

	ρ			η		
	LJ	IMP	LJP	LJ	IMP	LJP
AAD (%)	1.60	1.29	1.13	10.05	7.98	8.49
MxD (%)	7.10	6.24	5.51	33.74	28.89	34.54

Table V: Deviations on densities and viscosities between experimental data and MD results for the three H₂S models tested.

Concerning density, apart from the unexpected deviation at $T=310$ K, all models are able to provide a good evaluation, see table V, with a MxD<2.1% if this point is omitted. As shown by table V, generally the LJP model performs better on densities than the IMP one, which in turn, is better than the simple LJ one.

In addition, tables IV and V show that all models yield reasonable predictions for viscosity, apart from an unexplained deviation at the lowest temperature ($T=217.15$ K). In the liquid state, the LJP model is generally the most accurate, whereas the LJ model generally tends to underestimate viscosity (which is consistent with the underestimation of density). It should be mentioned that we have noticed finite size effects for low-density states, which would partly explain the overall underestimation of the viscosity.

The fact that the IMP performs nearly as well as the LJP is not so surprising. It has been shown that, for a state of lower temperature than those analysed here, for which polar effects should be enhanced, H₂S fluid does not exhibit a strong structure¹⁶. This is confirmed by a simple estimation of the reduced dipole moment $\mu^* = (\mu^2 / \epsilon \sigma^3)^{1/2}$ that yields a value close to 0.65, which is relatively low²⁴ (approximately five times smaller than the value for water) and indicates that the use of the IMP approach is reasonable for this system.

Although the ultimate goal of the molecular simulation approach is to use one set of molecular parameters for each molecule but transferable to different thermodynamic conditions, from the point of view of practical applications, one of the most interesting features of the IMP model for dipolar fluids is

that it can be formulated as a LJ model with temperature dependent molecular parameters, eq (5). Therefore, correlations found for the LJ potential can be applied with conveniently scaled parameters. So, for thermodynamic properties prediction, it is possible to use an efficient LJ Equation of State (EOS) such as the one from Kolafa and Nezbeda²⁵ or Mecke et al.²⁶. The same remark is valid even for dynamic properties for which correlations exist, such as for mass diffusion²⁷⁻²⁹ and viscosity^{30,31}.

As an example, we have applied for the EOS of Kolafa and Nezbeda²⁵ combined with both LJ and IMP models in order to estimate the density, using the molecular parameters of table I, on the subcritical data of Ihmels and Gmehling²¹ (in a temperature and pressure range between 273 K to 363 K and from 3 MPa to 40 MPa, 206 points). When T and P are fixed, AAD on ρ is equal to 0.51 % for the IMP model (with a MxD of 0.97 %) and 0.57 % for the LJ one (with MxD of 5.36 %). This result indicates that such a correlative scheme can be applied with reasonable success.

3.1.2 Viscosity and density of CO₂: Comparison between models

Similarly to what has previously been done for pure H₂S, a comparison between the results provided by the three models is performed. NPT simulations are performed for various points on the vapour-liquid equilibrium curve as well as NVT simulations along one isotherm ($T=328.15$ K) for various densities. Results for the LJP model come from the work of Nieto-Draghi et al.¹⁷ where Lorentz-Berthelot mixing rules have been used as was done in the original work of Harris and Yung⁵.

Concerning density, tables VI and VII show that, somewhat surprisingly, the IMP model is the one that performs best. In fact, as shown in table VI, the LJP model is inadequate for the vapour phase whereas it performs extremely well for the liquid phase. Concerning the LJ model, it generally tends to underestimate densities for all states.

As for viscosity, tables VI and VII show that the LJP model and especially the IMP model provide a good estimation of viscosity, whereas the LJ model tends to underestimate it (which is linked to the underestimation of densities).

These results, confirming those noticed in section 3.1.1., obviously indicate that the IMP model is a good compromise to provide both densities and viscosities of CO₂ whereas the LJ model suffers from its intrinsic limitations to do so.

T (K)	P (MPa)	ρ (kg.m ⁻³)				η (10 ⁻⁶ Pa.s)			
		Exp.	LJ	IMP	LJP	Exp.	LJ	IMP	LJP
216.6 (L)	0.518	1178	1124	1202	1168.6	257	172	243	219
216.6 (V)	0.518	13.8	13.2	13.5	16.57	11	10.1	10.2	10
240 (L)	1.283	1089	1038	1100	1080.6	173	124	163	160
240 (V)	1.283	33.3	30.8	32.2	38.75	12.3	11.7	11.5	12.8
260 (V)	2.419	64.4	58.7	59.7	80.9	13.6	13.9	13.5	12.9
270 (L)	3.203	946	902	949	937.1	105	88.2	102	96
280 (V)	4.161	121.7	101.7	107.1	149	15.6	16.8	16.1	13.9
285 (L)	4.712	847	804	856	838.7	79.5	70.2	83	79

Table VI: Comparisons between CO₂ experimental results (density and viscosity) and MD results using three different models along the vapour-liquid equilibrium curve using three different models. (L) stands for liquid, (V) for vapour.

	ρ			η		
	LJ	IMP	LJP	LJ	IMP	LJP
AAD (%)	7.02	3.65	11.00	14.01	4.53	7.59
MxD (%)	16.43	12.00	25.62	33.07	7.27	14.79

Table VII: Deviations on densities and viscosities between experimental data and MD results for the three CO₂ models tested.

3.2 Mixtures

For pure fluids, the IMP approach has shown to be a good and simple alternative, but, when dealing with mixtures, there is a need for combining rules which have proven to be of importance in acid gas

simulations¹. Therefore, a comparison, for CH₄-H₂S, H₂S-CO₂ and CH₄-H₂S-CO₂ mixtures, is performed between the different models using both the LB and KG combining rules, eqs. (10-13).

3.2.1 CH₄-H₂S mixtures

NVT simulations on CH₄-H₂S liquid mixtures are performed at $T=350$ K and $\rho=500$ kg.m⁻³. Results for pressures and viscosities for the different models combined with the two combining rules sets are given in tables (VI–VIII). In addition, for the same conditions, Kolafa and Nezbeda²⁵ EOS and Galliero et al.³¹ correlation combined with a vdW1 approximation, eqs. (14-16), are applied (this scheme will be denoted Corr in the following) for the LJ and IMP models to predict the pressure and the viscosity of the mixtures.

	ρ (kg.m ⁻³)			η (10 ⁻⁶ Pa.s)		
	LJ	IMP	LJP	LJ	IMP	LJP
H ₂ S	3.45	2.6	1.6	49.3	50.1	49.1
CH ₄	620.3	620.3	619.7	224.5	224.5	220

Table VIII: Pure fluid properties for the three models at $T=350$ K and $\rho=500$ kg.m⁻³

x_{CH_4}	LB combining rules					KG combining rules				
	LJ MD	LJ Corr.	IMP	IMP Corr	LJP	LJ MD	LJ Corr	IMP	IMP Corr	LJP
0.4	42.9	44.0	43.1	44.7	45.5	43.1	44.1	43.4	44.6	45.7
0.6	98	99.8	99.2	101.7	104.7	98.3	100.0	99.5	101.6	104.7

Table IX: Pressures (in MPa) in two liquid CH₄-H₂S mixtures at $T=350$ K and $\rho=500$ kg.m⁻³, for the three models tested (+Corr results for two of them) and two combining rules.

Tables VIII to X show that, the IMP model provides results that are closer to those given by the LJP approach than in the case of the simple LJ, although differences between both are very small. Hence, it appears that, for this thermodynamic condition, the polar contributions are small, or at least could be embodied in an “effective” potential. In addition, tables V and VI indicate that the combining rules do not affect the results, whatever the potential is. This result is certainly linked to the fact that, the sigma parameters of CH₄ and H₂S are very similar which lead to similar cross molecular parameters whatever

the combining rules. So, for such mixtures and thermodynamic conditions, the choice of the models and combining rules does not seem to be of great importance.

x_{CH_4}	LB combining rules					KG combining rules				
	LJ MD	LJ Corr.	IMP	IMP Corr	LJP	LJ MD	LJ Corr	IMP	IMP Corr.	LJP
0.4	60.9	63.8	61.3	64.5	60	60.7	63.8	61.1	64.6	60.5
0.6	75.8	79.3	76.4	80.1	75.7	76.1	79.4	76.3	80.2	79.2

Table X: Viscosity (in microPa.s) in two liquid CH_4 - H_2S mixtures at $T=350$ K and $\rho=500$ $kg.m^{-3}$, for the three models tested (+Corr results for two of them) and two combining rules.

Besides, pressure and viscosity values provided by the vdW1 scheme combined with correlations are consistent with MD results, even if they are slightly overestimated (from 2 to 6 % which may be attributed to the vdW1 limitations^{32,33}). Thus, for industrial applications, using the vdW1 approach, the combination of the simple LJ model or preferentially the IMP model with the correlation scheme proposed can provide reasonable results on such mixtures without molecular simulations.

3.2.2 CH_4 - H_2S - CO_2 and H_2S - CO_2 mixtures

As for CH_4 - H_2S mixtures, NVT simulations using the three models tested in this work are performed on CH_4 - H_2S - CO_2 mixtures under thermodynamic conditions typical of petroleum reservoirs. The mixture studied is composed of 63 % CO_2 , 27 % H_2S and 10 % CH_4 (in mole percent). Results on pressure and viscosity are given in tables IX and X.

It should be noted for such mixtures that, due to quadrupolar interactions, the IMP model cannot be “reduced” to a simple LJ with temperature dependent parameters as in the dipolar case. Hence, for these mixtures, the correlation scheme is only applicable to the LJ model.

The results, see tables XI and XII, show that pressure is strongly affected by both the model used and the combination rules for the LJP model, whereas viscosity is not or only weakly so. Thus, for such mixtures, if T and ρ are known, viscosity can be reasonably predicted (within 10 %) by a simple LJ approach combined with the LB rules as shown in tables XI and XII. Such a result is in agreement with previous findings³¹. In addition, the correlations combined with the vdW1 scheme provide results

consistent with simulations on the LJ model, even if the results are slightly overestimated. Thus, for industrial applications, the use of a LJ correlation combined with a one-fluid model is an interesting and simple alternative for estimating the viscosity of such mixtures without molecular simulations.

T (K)	ρ (kg.m ³)	LB combining rules				KG combining rules			
		LJ	LJ Corr	IMP	LJP	LJ	LJ Corr	IMP	LJP
290	810	16.8	18.1	23.4	13.6	16.85	18.2	23.5	30.28
320	810	35.7	36.9	45.6	36.38	35.8	37	45.7	53.05
350	810	54.25	55.4	62.7	59.43	54.35	55.5	62.9	76.57
290	953	65.4	66.5	83	68.15	65.6	66.7	83.2	96.41
320	953	94.3	95.5	117.8	104.84	94.5	95.7	118	134.18
335	953	108.5	109.7	143.2	122.45	108.65	109.9	143.4	151.52

Table XI: Pressure (in MPa) for CH₄-H₂S-CO₂ mixtures, for the three models tested (+ Corr on the LJ model) and two combining rules.

T (K)	ρ (kg.m ³)	LB combining rules				KG combining rules			
		LJ	LJ Corr	IMP	LJP	LJ	LJ Corr.	IMP	LJP
290	810	89.91	93	95.76	91.28	89.88	93	94.57	94.5
320	810	90.07	94.1	96.24	99.71	90.73	94.2	96.86	86.84
350	810	91.76	95.3	97.2	90.53	92.12	95.4	97.45	87.3
290	953	144.61	144.8	154.09	155.02	144	144.8	155.49	151.18
320	953	142.23	144.8	156.45	147.5	143.16	144.8	155.27	158.99
335	953	143.1	144.9	157.2	147.52	141.48	144.9	155.35	150

Table XII: Viscosity (in microPa.s) for CH₄-H₂S-CO₂ mixtures, for the three models tested (+ Corr on the LJ model) and two combining rules.

Concerning the pressure, the strong dependence of the results of the LJP model to the set of combining rules is in agreement with findings on CH₄-CO₂ mixtures¹ but raises the problem of its choice which is not an easy task and should be consistent with that used for optimisation in pure fluids (LB rules for the CO₂). This dependence is probably linked to the fact that the LJP model has quite different sigma that makes the results very sensitive to the combining rules.

In addition, from a comparison of the results of simple LJ and IMP models with those of the LJP one, we can deduce that the differences come from the way cross interactions between CO₂ with both H₂S and CH₄ are treated. As a test, NPT simulations have been performed on H₂S-CO₂ mixtures for which experimental results exist³⁴. Results for the LJP model come from Monte Carlo simulations¹ which uses a slightly modified version of the Harris and Yung⁵ potential for CO₂. Concerning this mixture, a recent work³⁵ using Monte Carlo simulations has shown that this system is hard to describe correctly.

$x_{\text{H}_2\text{S}}$	T (K)	P (MPa)	ρ Exp.	LB rules			KG rules		
				LJ	IMP	LJP	LJ	IMP	LJP
0.095	273	15	951.9	970.9	975.5	1003.1	970.5	975.3	964.5
0.293	273	15	913.8	956	937.5	987.6	955.7	937.3	926
0.5	273	2.7	846	891.1	865.7	931.4	890.6	865.5	853.8
0.095	400	7.5	113.9	112.6	111.7	113	112.5	111.6	111.2
0.293	400	7.5	111	110	108.7	110	110	108.6	107.5
0.5	400	7.5	107.9	106.6	105.6	109	106.5	105.6	105

Table XIII: Comparison between experimental values and molecular simulations of density (in kg/m³) for H₂S-CO₂ mixtures, for the three models tested and two combining rules.

As expected, due to the similarity of the sigma, the results given in tables XIII and XIV confirm that for the simple LJ and the IMP models, results are weakly dependent on the combining rules for the mixtures studied. On the contrary, combining rules play an important role for the LJP model. In addition it appears that, on average, as shown in table XIII, the best results are obtained with the LJP+KG approach and the IMP model (for both combining rules), and the worst with the LJP+LB approach. Quite surprisingly the simple LJ yields a reasonable estimation of density for the cases studied which is certainly due to a compensation of errors.

	LB rules			KG rules		
	LJ	IMP	LJP	LJ	IMP	LJP

AAD (%)	2.53	2.26	4.38	2.54	2.27	1.97
MxD (%)	5.33	2.59	10.09	5.27	2.57	3.15

Table XIV: Deviations on H₂S-CO₂ densities between experimental data and MD results for the three models tested and two combining rules.

4 Conclusions

In this paper, we have used a simple Lennard-Jones intermolecular potential and the Isotropic Multipolar Potential to perform molecular dynamic simulations of pure CH₄, CO₂, H₂S and their mixtures as a model for real acid gas mixtures. Density, or pressure, as well as viscosities have been evaluated for each system. These results have been compared with experimental data, when available, and with the results provided by standard Lennard-Jones plus point charge potentials which is approximately one order of magnitude more CPU demanding than the LJ and the IMP models.

Concerning pure H₂S, all three models are able to provide reasonable results, but we have observed a slightly better agreement with respect to experimental data using the LJP model and the IMP approximation than using the simple LJ model. For pure CO₂, the IMP model performs well whereas the LJP model is excellent for the liquid phase but inadequate for the vapour phase and the LJ model is unable to provide accurately both density and viscosity. In general, the simple LJ model tends to underestimate shear viscosity, particularly at low temperatures, due to the lack of electrostatic contributions.

For the case of mixtures, we have noticed that, due to weak polar effects, MD results obtained for liquid CH₄-H₂S systems using the three molecular models (LJ, IMP and LJP) are close to each other. In addition, the influence of the combining rules was also analysed in this system and no significant differences were found between the obtained results using both Lorentz-Berthelot and Kong rules (certainly due to the similarity of the sigma of CH₄ and H₂S).

The situation is completely different for the case of the CH₄-H₂S-CO₂ mixture, where a strong dependence with respect to the combining rules, in the LJP case, and molecular model employed was

observed for the pressure. Shear viscosity was found to be less dependent on the choice of models and methods. Unfortunately, there is no experimental data available in the literature to confirm our findings. It seems, however, that the key to understand this behaviour is on the CO₂-H₂S interactions. In order to clarify this situation, we have performed simulations of this mixture for which experimental data are available. As expected, for this system, the LJP is strongly affected by the choice of combining rules whereas the LJ and IMP models are not. In addition, it appears that the LJP+KG and the IMP approaches provide the best whereas the LJP+LB scheme yields the worst.

Regarding all the previous results, the IMP approximation seems to be the best choice to obtain reasonable predictions without an exhaustive CPU time used, since it ensures sufficient accuracy and independency with respect to the combining rules employed.

In addition, we have tested the predictive capability of a one fluid approximation (vdW1) combined with an accurate LJ Equation of State and correlation on viscosity. Due to its formulation, such a scheme is applicable to the LJ model for all systems as well as for the IMP model except when CO₂ is involved. We have observed equivalent results between this method and standard MD simulations (on both LJ and IMP models) for all the cases tested which could make this correlative scheme a good alternative for industrial applications.

ACKNOWLEDGMENT

This work is a part of the ReGaSeq project managed by TOTAL and the Institut Français du Pétrole. ADM and JBA wish to thank the Ministerio de Educación y Ciencia of the Spanish Government for financial support under the grant CTQ2004-03346/PPQ. We thank the Centre Informatique National de l'Enseignement Supérieur (Montpellier, France) and the pôle de Simulation et MOdélisation en Aquitaine in Bordeaux (France) which provided a large part of the computer time used for this study.

REFERENCES

- (1) Ungerer, P.; Tavitian, B.; Boutin, A. *Applications of molecular simulation in the oil and gas industry*, Technip, Paris, 2005.
- (2) Monteil, J.M.; Lazare, F.; Salviniene, J.; Viallet, P. *Journal de Chimie Physique* **1969**, 66.
- (3) Möller, D.; Oprzynski, J.; Müller, A.; Fischer, J. Prediction of thermodynamic properties of fluid mixtures by molecular dynamics simulations: methane-ethane, *Mol. Phys.* **1992**, 75, 363.
- (4) Kristof, T.; Liszi, J. Effective Intermolecular potential for fluid hydrogen sulfide, *J. Phys. Chem. B* **1997**, 101, 5480-5483.
- (5) Harris, J.G.; Yung, K.H. Carbon dioxide's liquid-vapor coexistence curve and critical properties as predicted by a simple molecular model, *J. Chem. Phys.* **1995**, 99, 12021-12024.
- (6) Ungerer, P.; Wender, A.; Demoulin, G.; Bourasseau, E.; Mougin, P. Thermodynamic properties of H₂S-rich systems by Monte Carlo simulation, *Mol. Sim.* **2004**, 30, 631-648.
- (7) Muller, E.A.; Gelb, L.D. Molecular modeling of fluid-phase equilibria using an isotropic multipolar potential, *Ind. Eng. Chem. Res.* **2003**, 42, 4123-4131.
- (8) Delhomelle, J.; Millié, P. Inadequacy of the Lorentz-Berthelot combining rules for accurate predictions of equilibrium properties by molecular simulation, *Mol. Phys.* **2001**, 99, 619-625.
- (9) Lenart P.J., Panagiotopoulos A.Z., Tracing the Critical loci of binary fluid mixtures using molecular simulation. *J. Phys. Chem. B*, **2006**, 110, 17200.
- (10) Sadus R.J., Influence of combining rules and molecular shape on the high-pressure phase-equilibria of binary fluid mixtures. *J. Phys. Chem.*, **1993**, 97, 1985.
- (11) Waldman M., Hagler A.T., New combining rules for rare-gas van-der-waals parameters. *J. Comp. Chem.*, **1993**, 14, 1077.

- (12) Prausnitz, J.M.; *Molecular thermodynamics of fluid phase equilibrium*, Prentice Hall, Englewood Cliffs, 1969.
- (13) Müller-Plathe, F. Reversing the perturbation in non-equilibrium molecular dynamics: An easy way to calculate the shear viscosity of fluids. *Phys. Rev. E.*, **1999**, *59*, 4894.
- (14) Smith, P.E.; van Gunsteren, W.F., The viscosity of SPC and SPC/E water at 277 K and 300K. *Chem. Phys. Lett.* **1993**, *215*, 315-318.
- (15) Galliero, G.; Boned, C.; Baylaucq, A.; Montel, F. Molecular dynamics comparative study of Lennard-Jones a-6 and Exponential a-6 potentials. Application to real simple fluids (viscosity and pressure), *Phys. Rev. E.* **2006**, *73*, 0612201-1/9.
- (16) Nieto-Draghi, C.; Mackie, A.D.; Avalos, J.B. Transport coefficients and dynamic properties of hydrogen sulfide from molecular simulation, *J. Chem. Phys.* **2005**, *123*, 014505.
- (17) Nieto-Draghi, C.; de Bruin, T.J.M.; Pérez-Pellitero, J.; Mackie, A.D.; Avalos, J.B. *J. Chem. Phys.* (submitted).
- (18) Berendsen, H.J.C.; Postma, J.P.M.; van Gunsteren, W.F.; di Nola, A.; Haak, J.R. Molecular dynamics with coupling to an external bath. *J. Chem. Phys.* **1984**, *81*, 3684.
- (19) Poling, B.E.; Prausnitz, J.M.; O'Connell, J.P. *The properties of Gases and Liquids*; McGraw-Hill: New York, 2001.
- (20) Goodwin; R.D. Hydrogen sulfide provisional thermophysical properties from 188 to 700 K at pressure to 75MPa, NBSIR 83-1694, Nat. Bureau Stds, Boulder, Colorado, 1983.
- (21) Ihmels, E.C.; Gmehling, J. Densities of toluene, carbon dioxide, carbonyl sulfide, and hydrogen sulfide over a wide temperature and pressure range in the sub- and supercritical state, *Ind. Eng. Chem. Res.* **2001**, *40*, 4470-4477.

- (22) Span, R.; Wagner, W.; A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa, *J. of Phys. And Chem. Ref. Data* **1996**, 25, 1509-1596.
- (23) Fenghour, A.; Wakeham, W.A.; Vesovic, V. The viscosity of carbon dioxide. *J. Phys. Chem. Ref. Data*. **1999**, 27, 31.
- (24) Sadus, R.J.; Molecular simulation of the vapour-liquid equilibria of pure fluids and binary mixtures containing dipolar components: the effect of Keesom interactions, *Mol. Phys.* **1996**, 87, 979-990.
- (25) Kolafa, J.; Nezbeda, I. Lennard-Jones fluid: An accurate analytic and theoretically-based equation of state, *Fluid Phase Equi.* **1994**, 100, 1-34.
- (26) Mecke, M.; Müller, A.; Winkelmann, J.; Vrabc, J.; Fischer, J.; Span, R.; Wagner, W. An accurate van der waals-type equation of state for the Lennard-Jones fluid *Int. J. of Thermophys.* **1996**, 17, 391-404.
- (27) Ruckenstein, E.; Liu, H. Self-Diffusion in Gases and Liquids. *Ind. Eng. Chem. Res.* **1997**, 36, 3927.
- (28) Zabaloy, M.S.; Machado, J.M.V. Macedo, E.A. A study of Lennard-Jones equivalent analytical relationships for modelling viscosities. *Int J. of Thermophys.* **2001**, 22, 829-858.
- (29) Zhu, Y.; Lu, X.; Zhou, J.; Wang, Y.; Shi, J. Prediction of diffusion coefficients for gas, liquid and supercritical fluid: application to pure real fluids and infinite dilute binary solutions based on the simulation of Lennard-Jones fluid. *Fluid Phase Equi* **2002**, 194, 1141-1159.
- (30) Laghaei, R.; Nasrabad, A.E.; Eu, B.C. Generic van der waals equation of state, modified free volume theory of diffusion and viscosity of simple liquids *J. Phys. Chem. B* **2005**, 109, 5873-5883.

- (31) Galliero, G.; Boned, C.; Baylaucq, A.; Montel, F. Influence of the mass ratio on viscosity in Lennard-Jones mixtures: The one-fluid model revisited using nonequilibrium molecular dynamics, *Fluid Phase Equi.*, **2005**, 234, 56-63.
- (32) Galliero, G.; Boned, C.; Baylaucq, A. Molecular dynamic study of the viscosity of the Lennard-Jones fluid. Application to real fluids, *Ind. Eng. Chem. Res.* **2005**, 44, 6963-6972.
- (33) Galliero, G.; Boned, C.; Baylaucq, A.; Montel, F. The van der Waals one-fluid model for viscosity in Lennard-Jones fluids: Influence of size and energy parameters, *Fluid Phase Equi.* **2006** 245, 20-25.
- (34) Kellerman, S.J.; Stouffer, C.E.; Eubank, P.T.; Holste, J.C.; Hall, K.R.; Gammon, B.E.; Marsh K.N. Thermodynamic properties of CO₂+H₂S mixtures, Gas processors Association, Tulsa, Research Report RR-141, 1995.
- (35) Kamat, G.; Potoff, J.J. Monte Carlo predictions for the phase behavior of H₂S+n-alkane, H₂S+CO₂, CO₂+CH₄ and H₂S+CO₂+CH₄ mixtures, *Fluid Phase Equi.* **2006**, 246, 71-78.