

# Derivation of an Optimized Potential Model for Phase Equilibria (OPPE) for Sulfides and Thiols

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An extension of the anisotropic united atoms model is proposed for thiols and sulfides. A complete derivation of the nonbonded parameters is performed with the aim of obtaining a transferable force field. The electrostatic part of the intermolecular potential is represented by a set of atomic charges. These charges are extracted from quantum chemical calculations thanks to a method developed recently. These charges are shown to depend very weakly on the conformation of the molecule. The repulsion–dispersion interactions are described by an anisotropic united atom Lennard-Jones potential: parameters for methyl and methylene groups are directly taken from a previous study on alkanes, whereas parameters for –S and –SH groups are fitted to experimental data. The resulting potential, which we will term OPPE (optimized potential model for phase equilibria), is tested against liquid properties at atmospheric pressure and vapor–liquid-phase equilibria of various sulfides and thiols to prove its transferability. Excellent agreement is obtained with experimental data.

## 1. Introduction

The development of molecular simulation methods has enabled researchers to study more and more complex fluids. The application of these methods to obtain accurate predictions for fluid properties are often limited by an unsatisfactory description of intermolecular interactions. Potential models have been developed for a large range of compounds in the past decade.<sup>1–5</sup> For instance, OPLS models<sup>1</sup> have led to a great stride in the application of molecular simulation to the calculation of liquid properties. The parametrization of the nonbonded part of these models was performed by fitting the liquid properties at ambient conditions of several sets of compounds. By doing so, Jorgensen and co-workers have obtained transferable parameters for atoms and/or united atoms. These parameters can then be straightforwardly applied to the prediction of liquid properties of other molecules containing these atoms or groups. Many models have been parametrized according to this scheme, i.e., by fitting experimental data at one state point. However, with the emergence of new techniques, such as the Gibbs ensemble Monte Carlo or the histogram reweighting technique,<sup>6–8</sup> the field of application of potential models has grown. Thanks to these new methods, it is now possible to estimate the reliability of a model under a wide range of conditions. It has

been shown in several cases<sup>9,10</sup> that it is necessary to reparametrize models fitted to experimental data at one state point to perform a quantitative description of both the coexistence properties and the liquid properties of fluids.

In this work, we focus on the development of a force field for sulfides and thiols. These molecules are important for biological systems—sulfur atoms and SH groups appear in peptide residues—and industrial applications as well. In the petrochemical industry, these compounds are polluting agents which have to be removed from oil. This is of growing importance as refiners will have to process sourer feedstocks (containing more sulfur compounds) in the future.<sup>11</sup> Being able to accurately describe the phase diagram of mixtures containing these compounds, hydrocarbons and various solvents is thus of great interest.

Hydrocarbons and other flexible molecules are often modeled within the united atoms model scheme. In this kind of model, each chemical group is represented by one Lennard-Jones site. Such a scheme allows to divide the number of interaction sites by 3 and thus to reduce the required computational time by an order of magnitude in comparison with an all-atoms model. However, this simplified approach is expected to fail to describe accurately very dense liquids and solids. All-atoms models, thanks to the more detailed definition, yield a more accurate description in this case. Nevertheless, most shortcomings of available united atoms models can be overcome by the introduction of more flexibility in the parametrization. Three approaches have been tried very recently in the case of alkanes. They all yield a quantitative description of coexistence properties of these compounds (coexisting densities, vapor pressures, and vaporiza-

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tion enthalpies as well). Errington et al.<sup>10</sup> have introduced the use of an exp-6 potential (3 parameters per center of force) instead of the Lennard-Jones function (2 parameters). Chen et al. have introduced additional sites on C–H bonds.<sup>12</sup> Ungerer et al.<sup>13</sup> have obtained the AUA 4 model by reparametrizing the Anisotropic United Atom (AUA) model initially proposed by Toxvaerd.<sup>14,15</sup> In the latter, the Lennard-Jones center of force is displaced from the carbon atom toward the hydrogen atoms, the value of this displacement being a third adjustable parameter in addition to the two Lennard-Jones parameters. The AUA 4 model seems promising to us since in addition to accurate predictions for coexistence properties, it also yields results which are in reasonable agreement with experimental data for transport properties.<sup>13</sup>

The aim of this work is to propose an extension of the AUA 4 model in order to obtain a quantitative description of both liquid and coexistence properties of sulfides and thiols. One important criterion while deriving a new model is the transferability of its parameters. This concern has been taken into account in the development of several force fields, such as for instance, OPLS<sup>16</sup> or AMBER.<sup>17</sup> From a practical point of view, transferable parameters allow straightforward extensions to other compounds without any additional fitting. Moreover, physically meaningful parameters should be transferable. We have thus proceeded as follows. We have taken from previous studies on sulfur compounds the parameters and functional forms used to describe the intramolecular part of the force field.<sup>16,17</sup> We have then determined the nonbonded parameters of the force field. According to a procedure proposed by Levy et al.,<sup>18</sup> we derived the electrostatic part by fitting the atomic charges values to the ab initio electrostatic potential (ESP). This method has been recently applied to methylene blue,<sup>18</sup> alanine dipeptide,<sup>19</sup> and also to the case of alkanes.<sup>20</sup> In the same spirit as the restrained electrostatic potential (RESP) method,<sup>21</sup> a specific stabilization process is used in the fitting procedure to obtain atomic charges which are less likely to depend on the chain length and on the conformation of the molecule. For the repulsion–dispersion part, we have taken from Ungerer et al.<sup>13</sup> the Lennard-Jones parameters for the methyl and methylene groups. We have then fitted the Lennard-Jones parameters of the sulfur atom and the SH group to reproduce experimental data of dimethyl sulfide and ethanethiol, respectively. The resulting force field, which we will term OPPE (optimized potential for phase equilibria), has been applied to the calculation of coexistence properties of several compounds in order to estimate its transferability.

This paper is organized as follows. We first give a description of the novel force field developed in this work. We then explain how we deal with the electrostatic part of the model and we present our approach to obtain atomic charges which reproduce accurately the ab initio ESP. These charges are shown to depend weakly on the chain length and on the internal geometry of the molecule. Thereafter, simulation details and the determination of the Lennard-Jones parameters are presented. Thermodynamic properties of several sulfides and thiols at atmospheric conditions are calculated (liquid densities and enthalpies of vaporization) as well as coexisting densities, vapor pressures, and enthalpies of vaporization along the coexistence curve.

## 2. Functional Form of the Force Field

**Intramolecular Interactions.** As in the AUA 4 model, sulfides and thiols are considered as semiflexible chain mol-

**TABLE 1: Bond Lengths, Equilibrium Angles, and Constant Forces<sup>a</sup>**

bond	length (Å)	angle	$\theta_0$ (deg)	$k_\theta$ (K)
C–C	1.535	C–C–S	114.7	50276.6
C–S	1.820	C–S–C	98.9	62343.0
C–H	1.085	C–S–S	103.7	68376.2
S–H	1.340	C–S–H	96	43237.9
S–S	2.100	C–C–H	109.5	

<sup>a</sup> These values are taken from refs 17 and 22.

ecules. This is taken into account by using a harmonic bending potential (functional form taken from ref 13):

$$U^{\text{bend}}(\theta) = \frac{1}{2}k_\theta(\cos \theta - \cos \theta_0)^2 \quad (1)$$

where  $\theta$  is the bond angle ( $\theta_0$  being the equilibrium value), and an united-atom OPLS torsion potential:<sup>22</sup>

$$U^{\text{tors}}(\phi) = c_0 + 0.5c_1(1 + \cos \phi) + 0.5c_2(1 - \cos 2\phi) + 0.5c_3(1 + \cos 3\phi) \quad (2)$$

where  $\phi$  is the dihedral angle.

The positions of the hydrogen atoms (except for the positions of the H atoms and the position of the SH group in thiols) are defined by the remainder of the molecule. There is for instance no bending potential for the angle HCH. The parameters for the bending potential as well as bond lengths are given in Table 1. OPLS torsion potential parameters are given in ref 22. Nonbonded van der Waals interactions between united atoms (see below) belonging to the same molecule and separated by more than three chemical bonds are also included. These interactions are modeled by Lennard-Jones centers of force (these sites are those used to describe intermolecular dispersion–repulsion interactions).

**Intermolecular Interactions.** We have chosen to model the electrostatic interactions by a set of atomic charges. These charges are determined by fitting the ab initio ESP as described in section 3.

Each molecule is also represented by a chain of Lennard-Jones interaction sites standing for each CH<sub>3</sub>, CH<sub>2</sub>, or SH group or for each sulfur atom in order to describe the dispersion–repulsion part of the potential model. These interactions take place between two united atoms,  $i$  and  $j$ , of different molecules according to the following formula:

$$U^{\text{LJ}}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (3)$$

Lorentz–Berthelot combining rules are used to determine the parameters for unlike group interactions:

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad \sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (4)$$

To take into account the excluded volume effect due to the hydrogen atoms, Toxvaerd<sup>14,15</sup> has suggested displacing the position of the interaction site from the carbon atom toward the hydrogen atoms. In the AUA 4 model, the position of the interaction sites for the methylene ( $d_{\text{CH}_2}$ ) and the methyl ( $d_{\text{CH}_3}$ ) groups have been considered as fitting parameters. The parameters for the methyl and the methylene groups are taken from the AUA 4 model for alkanes.<sup>13</sup> In this work, we have only fitted the parameters for the sulfur atom ( $\epsilon_{\text{S}}$  and  $\sigma_{\text{S}}$ ) and for the SH group ( $\epsilon_{\text{SH}}$ ,  $\sigma_{\text{SH}}$  and  $d_{\text{SH}}$ ,  $d_{\text{SH}}$  being the anisotropic displace-

TABLE 2: Atomic Charges for Sulfides in Atomic Units

compound	method	S	C(CH <sub>3</sub> )	C(CH <sub>2</sub> )	H(CH <sub>3</sub> )	H(CH <sub>2</sub> )	accuracy of fit	
							rms (10 <sup>-4</sup> e a <sub>0</sub> <sup>-1</sup> )	rrms (%)
CH <sub>3</sub> SCH <sub>3</sub>	LSQ	0.016	-0.880		0.291		4.21	15.0
	EA	-0.054	-0.673		0.234		4.32	15.4
	Mulliken	0.107	-0.631		0.192			
CH <sub>3</sub> CH <sub>2</sub> SCH <sub>3</sub>	LSQ	-0.086	-0.372	-0.478	0.143	0.224	7.33	18.4
	EA	-0.043	-0.587	-0.454	0.202	0.231	7.49	18.8
	Mulliken	0.111	-0.561	-0.561	0.184	0.182		-
CH <sub>3</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>3</sub>	LSQ	-0.282	-0.165	0.036	0.060	0.045	5.66	15.2
	EA	-0.010	-0.500	-0.496	0.180	0.231	7.84	21.1
	Mulliken	0.116	-0.460	-0.488	0.183	0.175		
CH <sub>3</sub> SSCH <sub>3</sub>	LSQ	-0.165	-0.266		0.144		4.57	21.0
	EA	-0.090	-0.654		0.248		4.88	22.4
	Mulliken	0.013	-0.645		0.211			

<sup>a</sup> LSQ refers to an accurate least-square fit, no eigenvalues discarded; EA to the procedure proposed in this work, one eigenvalue discarded for CH<sub>3</sub>SCH<sub>3</sub> and CH<sub>3</sub>SSCH<sub>3</sub> and two eigenvalues discarded for CH<sub>3</sub>CH<sub>2</sub>SCH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>3</sub>.

ment of the Lennard-Jones site of the SH group from the sulfur atom toward the hydrogen atom).

### 3. Determination of Electrostatic Parameters

**Method.** A least-squares condition is used to determine atomic charges. It consists of minimizing the following quantity:

$$F = \sum_k (V(P_k) - V_{\text{fit}}(P_k))^2 \quad (5)$$

where  $V(P_k)$  is the ab initio ESP at point  $P_k$  and  $V_{\text{fit}}(P_k)$  is the ESP calculated from the fitted distribution of atomic charges at point  $P_k$ :

$$V_{\text{fit}}(P_k) = \sum_{i=1}^N \frac{q_i}{r_{ik}} \quad (6)$$

where  $N$  is the number of atoms,  $q_i$  is the fitted atomic charge, and  $r_{ik}$  is the distance between atom  $i$  and point  $P_k$ .

Minimizing  $F$  with respect to all  $q_i$  leads to a system of linear equations which can be written in matrix notation:

$$\mathbf{A}\mathbf{q} = \mathbf{B} \quad (7)$$

Because of the rank deficiency of  $\mathbf{A}$  (Francl et al.<sup>23</sup>), several sets of electrostatic parameters can accurately fit the ab initio ESP. Levy et al.<sup>18</sup> have suggested taking advantage of this partial undetermination of the solution to obtain a set of parameters close to a set of reference of charges which do not depend too much on the chain length and on the conformation of the molecule. We thus define a threshold  $\epsilon$  and the two following operators:  $\mathbf{P}$  = projection operator on the space spanned by the eigenvectors associated with eigenvalues larger than  $\epsilon$ , and  $\mathbf{Q} = \mathbf{1} - \mathbf{P}$

As shown in ref 18,  $F$  depends on  $\mathbf{P}\mathbf{q}$  but not on  $\mathbf{Q}\mathbf{q}$  (if terms of order  $O(\epsilon)$  are neglected). Hence,  $\mathbf{P}\mathbf{q}$  is determined by the fitting procedure and  $\mathbf{Q}\mathbf{q}$  can be chosen to be equal to  $\mathbf{Q}\mathbf{q}_0$  (where  $\mathbf{q}_0$  stands for a set of reference values).

Finally, the solution is

$$\mathbf{q} = \mathbf{P}[\mathbf{P}\mathbf{A}\mathbf{P} + \mathbf{Q}]^{-1}\mathbf{b} + \mathbf{Q}\mathbf{q}_0 \quad (8)$$

The sum of the  $q_i$  was constrained to be the total molecular charge thanks to a Lagrange multiplier. Some atoms or groups were considered as equivalent: there was only one kind of methyl and methylene group and hydrogen atoms belonging to the same group were assumed to be equivalent.

The ab initio ESP for the molecule was determined at HF/6-31G\* level using the GAMESS package.<sup>24</sup> The fit grids (i.e., the ensemble of points  $P_k$ ) were built using the point selection scheme of Singh and Kollman<sup>25</sup> which consists of shells of points located at  $R$  times the van der Waals radii. Most methods use points located only in the vicinity of the molecule. However, as stated by Sigfridsson et al.,<sup>26</sup> it is also important to reproduce the potential far from the molecule as the number of interactions increases with the third power of the distance.  $R$  has thus been chosen to be equal to 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8, 4.0, 5.0, 6.0, 7.0, and 8.0.

The set of reference charges was obtained from a Mulliken population analysis. The chosen value of the threshold  $\epsilon$  resulted from a compromise between an accurate fit ( $\epsilon$  being low, very few eigenvalues are discarded) and a result close to the transferable reference set for large  $\epsilon$ . Bayly et al.<sup>21</sup> have shown that ill-behaved charges could be associated with "buried atoms", i.e., in our case carbon atoms of methyl and methylene groups. Satisfactory results were obtained when  $\epsilon$  was set so as one eigenvalue was discarded for molecules containing only methyl groups and two for molecules containing both methyl and methylene groups.

The obtained electrostatic distribution was then tested for all fitting points. The root-mean-square (rms) and the relative root-mean-square (rrms) errors were calculated to estimate the accuracy of this procedure. This quantity rrms might not be the best quality criterion because it emphasizes the effect of small ESPs. It is however useful for comparison purpose when various conformations and molecules are involved.

### 3. Results and Discussion

We have applied the fitting procedure described above to several sulfides and thiols. First of all, each compound was considered in the trans conformation which is the lowest energy conformation. The ab initio ESP was then computed at HF/6-31G\* level and fitted by a distribution of atomic charges. Atomic charges obtained for sulfides and thiols, as well as the accuracy of fit of the ab initio electrostatic potential, are presented in Tables 2 and 3. Three sets of partial charges are given: LSQ charges obtained from a normal least-squares fit ( $\epsilon$  is set to 0, no eigenvalue is discarded), EA (an eigenvalue analysis is performed) charges obtained using the method described in this section and Mulliken charges.

The quality of the partial charges obtained by this procedure was tested by calculating the molecular dipole moments and comparing them to the experimental values. Because we included fitting points which were far from the molecule, the

**TABLE 3: Atomic Charges for Thiols in Atomic Units<sup>a</sup>**

compound	method	S	H(SH)	C(CH <sub>3</sub> )	C(CH <sub>2</sub> )	H(CH <sub>3</sub> )	H(CH <sub>2</sub> )	accuracy of fit	
								rms( $10^{-4}e a_0^{-1}$ )	rrms(%)
CH <sub>3</sub> SH	LSQ	-0.341	0.194	-0.272		0.140		5.96	20.2
	EA	-0.281	0.195	-0.641		0.242		6.14	20.8
	Mulliken	-0.088	0.098	-0.621		0.204			
CH <sub>3</sub> CH <sub>2</sub> SH	LSQ	-0.341	0.180	-0.246	0.023	0.091	0.055	3.95	14.6
	EA	-0.208	0.150	-0.495	-0.477	0.189	0.231	4.65	17.2
	Mulliken	-0.063	0.087	-0.488	-0.457	0.179	0.192		
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> SH	LSQ	-0.363	0.198	-0.106	-0.091	0.037	0.086	3.70	14.2
	EA	-0.267	0.162	-0.491	-0.417	0.165	0.233	4.69	18.0
	Mulliken	-0.056	0.088	-0.476	-0.039	0.166	0.181		

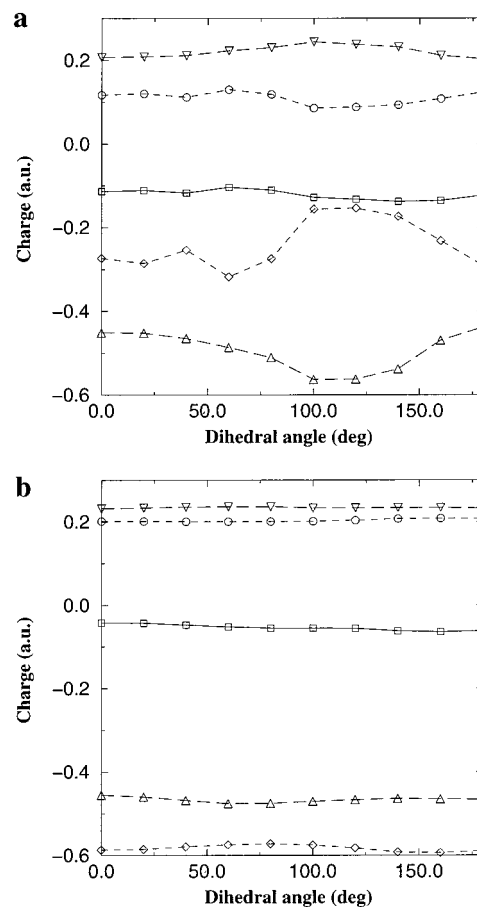
<sup>a</sup> LSQ refers to an accurate least-square fit, no eigenvalues discarded; EA to the procedure proposed in this work, one eigenvalue discarded for CH<sub>3</sub>SH and two eigenvalues discarded for CH<sub>3</sub>CH<sub>2</sub>SH and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>SH.

resulting molecular dipole moment is very close to the ab initio molecular dipole moment. HF/6-31G\* calculations are known to overestimate dipole moments. As a result, the fitting procedure yields molecular dipole moments of 1.86 D for dimethyl sulfide, 1.71 D for diethyl sulfide, 1.92 D for methanethiol, and 1.86 for ethanethiol whereas experimental values are 1.5, 1.54, 1.52, and 1.58 D respectively. Dipole moments are thus 11–27% above the experimental values. This overestimation is likely to implicitly take into account the polarization in the liquid phase in a reasonable way (as stated by Fox et al.,<sup>27</sup> an increase of the dipole moment of 10–20% seems reasonable).

Both LSQ and EA methods of fit yielded rrms between 15 and 20% for all the compounds studied here. As the testing includes many points in the vicinity of the molecule (points of the grids located at distances between 2.0 and 4.0 times the van der Waals radii), it is not surprising to obtain a relatively high value of rrms (in fact, the electrostatic properties of the molecules are well reproduced: for instance, for dimethyl sulfide, the rrms error is of 8.6% at a distance of 4.0 times the van der Waals radii and 4.6% at 8.0 times the van der Waals radii). This relatively high value of rrms is also a limitation induced by the choice of an atomic charge model. Alkane molecules are striking examples of this limitation: Williams<sup>28</sup> has shown that potential-derived atomic charges gave errors of fit of the ab initio ESP ranging from 51 to 62% for *n*-alkanes. This error can be reduced by adding nonatomic sites<sup>28</sup> or by including atomic dipole terms.<sup>20</sup> Though sulfides and thiols include alkyl chains, the error of fit was much lower because of the polarity of these molecules. We also note that the use of the EA method did not lead to errors much higher than a simple least-squares fit. For diethyl sulfide, being the worst case, the rrms increases from 15.2% (LSQ) to 21.1% (EA).

The stability of the atomic charges was remarkably improved when using the EA method. This effect is most pronounced for charges born by “buried atoms”: the charge born by a carbon atom of a methyl group of a sulfide molecule varied between -0.88 and -0.165 (in atomic units) according to LSQ and between -0.673 and -0.5 according to EA. This stabilization also affected the charges born by the other atoms: for instance, the hydrogen of a methyl group of a sulfide bears a charge ranging from 0.06 to 0.291 in a LSQ fit and from 0.18 to 0.248 in a EA fit. The same trend was also observed for thiols: LSQ charges for a carbon atom varied between -0.106 and -0.272 (methyl group) and between 0.023 and -0.091 (methylene group), whereas EA charges ranged from -0.491 to -0.641 (methyl group) and between -0.477 and -0.417 (methylene group).

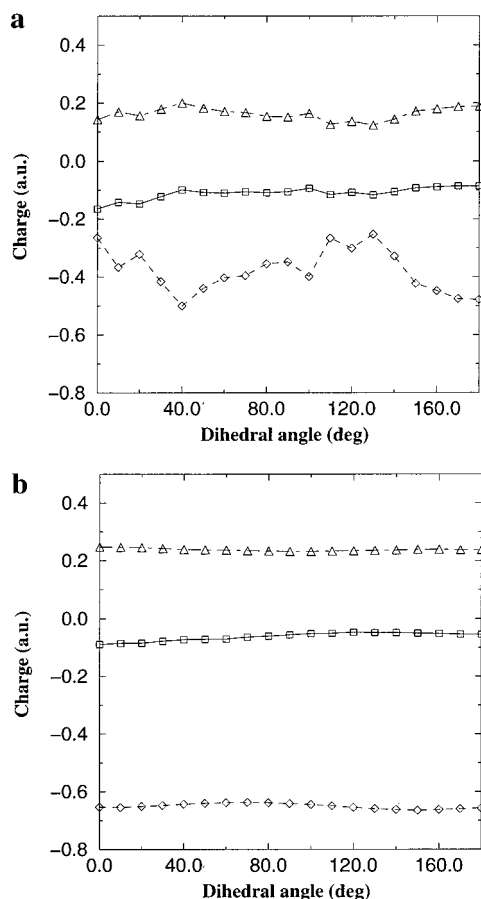
Conformers of higher energy than the trans conformer have to be taken into account in simulations of the liquid state. It is



**Figure 1.** Variation of atomic charges with the conformation of ethylmethyl sulfide (squares correspond to charges born by the sulfur atom, diamonds to the carbon of a methyl group, triangles up to the carbon of a methylene group, circles to the hydrogen of a methyl group, and triangles down to the hydrogen of a methylene group) (a) Normal least-squares fit (no eigenvalues discarded), (b) 2 eigenvalues discarded.

thus important to estimate the variation of the electrostatic parameters with the conformation or to perform the fitting procedure on several conformations.<sup>29</sup> We have studied the conformational dependence of charges obtained by the EA method. We have computed the ab initio ESP for 19 conformations of ethanethiol and dimethyl disulfide (defined by rotations of 10° around the central bond) and 10 conformations of ethylmethyl disulfide (defined by rotations of 20°). For each conformation, we have fitted the ab initio ESP by both LSQ and EA methods. In Figures 1 and 2, the variation of atomic charges, obtained by LSQ and EA fits, are plotted against the dihedral angle for ethylmethyl sulfide and dimethyl sulfide. The





**Figure 2.** Variation of atomic charges with the conformation of dimethyl disulfide (squares correspond to charges born by the sulfur atom, diamonds to the carbon of a methyl group, and triangles up to the hydrogen of a methyl group). (a) Normal least-squares fit (no eigenvalues discarded). (b) 1 eigenvalue discarded.

conformational dependence of atomic charges is also remarkably reduced by using the EA procedure. The charge of a carbon atom of a methyl group of dimethyl sulfide varied from  $-0.25$  to  $-0.50$  in a LSQ fit and from  $-0.638$  to  $-0.664$ , which corresponded to variations of 2% around the average value, in a EA fit. The same improvement was also observed in the case of ethanethiol (not shown) and ethylmethyl sulfide: the extent of variation of EA charges was of 5% for ethanethiol and of 4% for ethylmethyl sulfide. Since EA charges depend very weakly on the conformation of the molecule, we can directly consider the values given in Tables 2 and 3 as constant with regard to the molecular geometry. By doing so, we did not include any additional error in the calculation of the electrostatic contribution to the total energy.

#### 4. Simulation Methods

**Liquid–Vapor Phase Equilibria.** The coexistence curves of sulfides and thiols were determined using the Gibbs ensemble Monte Carlo (GEMC) method<sup>6,7</sup> combined with a configurational bias scheme.<sup>2</sup> An additional bias for the insertion of the first bead of the chain was also included. The selected occurrences for the various types of moves were 0.222 for translation, rotation, and configurational bias regrowth, 0.328 for transfer, and 0.006 for volume change. All simulations were performed on systems containing a total number of 200 molecules. A cutoff radius of 10 Å was used for all nonbonded interactions and analytic long range corrections were applied for the Lennard-Jones part of the potential.<sup>31</sup> As checked in

previous studies conducted by Kristof et al.<sup>9</sup> and our group<sup>32</sup> in the case of  $\text{H}_2\text{S}$ , Coulombic long range corrections have little influence on the coexisting densities. They were therefore not taken into account in this work.

Average coexisting densities, vapor pressures (obtained from the molecular virial), and enthalpies of vaporization (computed as the difference between the average enthalpies of the liquid and the vapor simulation boxes) were calculated in each case.

The critical properties were estimated by fitting the subcritical simulation data to the density scaling law for the critical temperature  $T_c$ :

$$\rho_{\text{liq}} - \rho_{\text{vap}} = B(T - T_c)^\beta \quad (9)$$

and to the law of rectilinear diameters for the critical density  $\rho_c$ :

$$\frac{\rho_{\text{liq}} + \rho_{\text{vap}}}{2} = \rho_c + A(T - T_c) \quad (10)$$

where  $\rho_{\text{liq}}$  and  $\rho_{\text{vap}}$  are the coexisting densities of the liquid phase and the vapor phase,  $T$  and  $P$  are the temperature and the pressure,  $A$  and  $B$  are fitting parameters, and  $\beta = 0.325$  is the critical exponent.

**Liquid properties under Atmospheric Conditions.** Simulations in the isothermal–isobaric (NPT) ensemble were performed on systems of 200 molecules. The external pressure was fixed at 1 atm and the temperature was 298 K for sulfides, 293 K for ethanethiol, and 279.1 K for methanethiol (boiling point of methanethiol). The molar enthalpy of vaporization is given by the following equation:

$$\Delta H_{\text{vap}} = -\langle E_{\text{liq(inter)}} \rangle + RT \quad (11)$$

where  $\langle E_{\text{liq(inter)}} \rangle$  is the average molar intermolecular potential energy in the simulation.

This relationship assumes that (i) the molar volume of the liquid is negligible compared with the vapor, (ii) the vapor is close enough to an ideal gas, and (iii) the difference between the intramolecular energy of the two phases is negligible. The first two assumptions are correct since in all cases except for methanethiol vapor pressures are significantly lower than the atmospheric pressure. The latter is in agreement with results obtained by Jorgensen.<sup>22</sup> It has also been checked in our GEMC calculations.

#### 5. Determination of Lennard-Jones Parameters

The first step in the determination of the Lennard Jones parameters was to choose a set of reference experimental data to be reproduced as accurately as possible. We have chosen dimethyl sulfide as a reference compound to fit the sulfur atom parameters ( $\epsilon_S$  and  $\sigma_S$ ) and ethanethiol for the SH group parameters ( $\epsilon_{\text{SH}}$ ,  $\sigma_{\text{SH}}$ , and  $d_{\text{SH}}$ ). For each reference compound, we have considered the vapor pressure, the vaporization enthalpy and the liquid density at ambient conditions and at a reduced temperature ( $T/T_c$ ) of about 0.8 as reference data. Considering the vaporization enthalpy and the liquid density as reference data allows a reliable extension to lower and higher temperatures since these properties control the temperature dependence of the vapor pressure through the Clapeyron equation. Reference data and their sources are given in Tables 4 and 5. We have used in several cases the correlations provided by the Dortmund Data Bank after having checked their reliability on available measurements at ambient temperature. To estimate the performance of a given set of parameters, we performed two

**TABLE 4: Results of the Optimization of the Lennard-Jones Parameters for Sulfides with All Reference Data**

compound	simulation method	property	statistical uncertainty ( $s_i$ )	this work	experiment
CH <sub>3</sub> SCH <sub>3</sub>	NPT $P = 1$ atm, $T = 298$ K	$\rho_{\text{liq}}$ (g cm <sup>-3</sup> )	0.01	0.838	0.8423 <sup>39</sup>
		$\Delta H_{\text{vap}}$ (kJ mol <sup>-1</sup> )	0.5	27.3	27.8 <sup>37</sup>
	GEMC $T = 375$ K	$\rho_{\text{liq}}$ (g cm <sup>-3</sup> )	0.01	0.734	0.745 <sup>41</sup>
		$\Delta H_{\text{vap}}$ (kJ mol <sup>-1</sup> )	0.5	23.57	23.34 <sup>41</sup>
		$P_{\text{sat}}$ (kPa)	100	706	617 <sup>41</sup>

**TABLE 5: Results of the Optimization of the Lennard-Jones Parameters for Thiols with All Reference Data**

compound	simulation method	property	statistical uncertainty ( $S_i$ )	his work	experiment
CH <sub>3</sub> CH <sub>2</sub> SH	NPT $P = 1$ atm, $T = 273.16$ K	$\rho_{\text{liq}}$ (g cm <sup>-3</sup> )	0.01	0.851	0.86141
		$\Delta H_{\text{vap}}$ (kJ mol <sup>-1</sup> )	0.5	28.3	28.5541
	GEMC $T = 400$ K	$\rho_{\text{liq}}$ (g cm <sup>-3</sup> )	0.01	0.687	0.69441
		$\Delta H_{\text{vap}}$ (kJ mol <sup>-1</sup> )	0.5	21.3	20.9541
		$P_{\text{sat}}$ (kPa)	100	1211	1131

simulations for each compound: one GEMC simulation at a reduced temperature of 0.8 and one NPT monophasic simulation at ambient conditions. These two simulations allowed us then to estimate the performance of a given potential to five independent experimental data.

The second step is the optimization procedure itself. This procedure has already been described in ref 13 and is thus only briefly presented here.

The following dimensionless error criterion was used:

$$F = \sum_{i=1}^n \frac{(X_i^{\text{mod}} - X_i^{\text{exp}})^2}{s_i^2} \quad (12)$$

where  $s_i$  is the estimated statistical uncertainty on the computed variable  $X_i^{\text{mod}}$  (statistical inefficiency estimated from a simulation using the standard block averaging technique<sup>31</sup>), while  $X_i^{\text{exp}}$  is the associated experimental measurement (either  $\ln(P_{\text{sat}})$ ,  $\Delta H_{\text{vap}}$ , or  $\rho_l$ ).  $F$  is considered as a function of two parameters to optimize in the case of sulfides, namely,  $y_1 = \epsilon_S$  and  $y_2 = \sigma_S$  and of three parameters in the case of thiols; namely,  $y_1 = \epsilon_{\text{SH}}$ ,  $y_2 = \sigma_{\text{SH}}$ , and  $y_3 = d_{\text{SH}}$ .

Minimizing  $F$  with respect to all  $y_j$  leads to the following condition:

$$\frac{\partial F}{\partial y_j} = \sum_{i=1}^n \frac{2(X_i^{\text{mod}} - X_i^{\text{exp}}) \frac{\partial X_i^{\text{mod}}}{\partial y_j}}{s_i^2} = 0 \quad (13)$$

This expression was estimated through a first-order Taylor expansion of  $X_i^{\text{mod}}$  around the point  $y^0$  corresponding to an initial set of parameters:

$$X_i^{\text{mod}}(y^0 + \Delta y) = X_i^{\text{mod}}(y^0) + \sum_k \frac{\partial X_i^{\text{mod}}}{\partial y_k} \Delta y_k \quad (14)$$

The minimum condition 13 can thus be expressed as

$$\sum_{i=1}^n \frac{\left( X_i^{\text{mod}}(y^0) - X_i^{\text{exp}} + \sum_k \frac{\partial X_i^{\text{mod}}}{\partial y_k} \Delta y_k \right) \frac{\partial X_i^{\text{mod}}}{\partial y_j}}{s_i^2} = 0 \quad (15)$$

In this expression, the derivatives  $\partial X_i^{\text{mod}} / \partial y_k$  were evaluated by finite difference at the point  $y^0$ . Once these derivatives were known, the  $\Delta y_k$  were obtained by solving a linear system of

**TABLE 6: Lennard-Jones Parameters for Liquid Sulfur Compounds**

chemical group	$\sigma$ (Å)	$\epsilon$ (K)	$d_{\text{AUA}}$ (Å)
CH <sub>3</sub>	3.6072	120.15	0.21584
CH <sub>2</sub>	3.4612	86.291	0.38405
SH	3.6547	220.62	0.0588
S	3.60	190.0	

**TABLE 7: Densities and Enthalpies of Vaporization for Liquid Sulfur Compounds at Atmospheric Pressure<sup>a</sup>**

compound	$T$ (°C)	density (g cm <sup>-3</sup> )		enthalpy of vaporization (kJ mol <sup>-1</sup> )	
		exptl	simulation	exptl	simulation
CH <sub>3</sub> SCH <sub>3</sub>	25	0.842339	0.8389	27.837	27.35
CH <sub>3</sub> CH <sub>2</sub> SCH <sub>3</sub>	25	0.8368 <sup>37</sup>	0.827 <sub>10</sub>	31.8 <sup>39</sup>	31.8 <sub>5</sub>
CH <sub>3</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>3</sub>	25	0.8312 <sup>37</sup>	0.824 <sub>9</sub>	35.7 <sup>40</sup>	35.5 <sub>5</sub>
CH <sub>3</sub> SSCH <sub>3</sub>	25	1.0569 <sup>37</sup>	1.070 <sub>10</sub>	38.4 <sup>37</sup>	42.0 <sub>6</sub>
CH <sub>3</sub> SH	5.95	0.888 <sup>38</sup>	0.877 <sub>9</sub>	24.53 <sup>38</sup>	26.5 <sub>5</sub>
CH <sub>3</sub> CH <sub>2</sub> SH	0	0.861 <sup>41</sup>	0.851 <sub>10</sub>	28.55 <sup>41</sup>	28.3 <sub>5</sub>

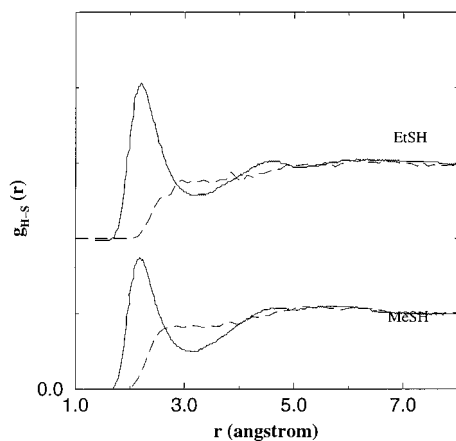
<sup>a</sup> The subscripts give the accuracy of the last decimal(s), i.e., 0.8389 stands for  $0.838 \pm 0.009$ .

two equations and two unknowns for sulfides (three for thiols). The optimized parameters are given by  $y_k = y_k^0 + \Delta y_k$ .

The first task was to find a suitable set of initial values  $y^0$ . We had to proceed iteratively. We started with the set of OPLS-UA parameters ( $\epsilon = 125.7$  K and  $\sigma = 3.55$  Å for both S and SH group). This set yields reasonable results for liquid densities at ambient conditions but poor agreement with experiment for coexistence properties at the reduced temperature of 0.8. A second set of initial values, with the same value for  $\sigma$  but an increased value for  $\epsilon$ , was thus used when applying the optimization procedure. The results for the optimization procedure are given in Table 4 for sulfides and Table 5 for thiols. All fitting properties were reproduced within the statistical error bar. The corresponding parameters are listed in Table 6. The final values taken by the parameters  $\sigma$  in OPPE model are rather close to the one used in OPLS-UA model: this could be expected as OPLS parameters were fitted so as to reproduce liquid densities at ambient temperature. However, values taken by  $\epsilon$  in OPPE are very different from those of OPLS: this may be accounted for by the fact that the molecular dipole moment is somewhat less overestimated in OPPE than in OPLS.

## 6. Performance of the OPPE Force Field

**Liquid Properties.** The performance of OPPE force field to reproduce thermodynamic properties at ambient conditions has been tested on several sulfides and thiols (Table 7). The OPPE

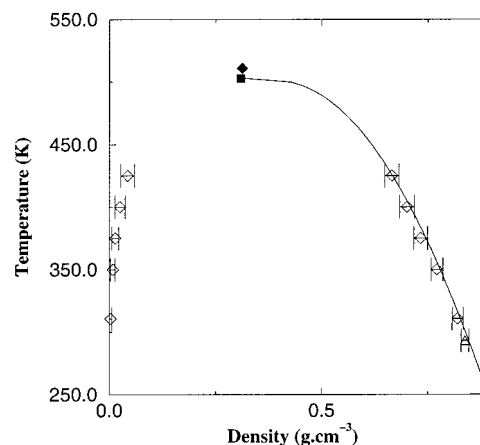


**Figure 3.** H-S radial distribution function in methanethiol and ethanethiol (straight lines are OPLS-UA results and dashed lines are OPPE results).

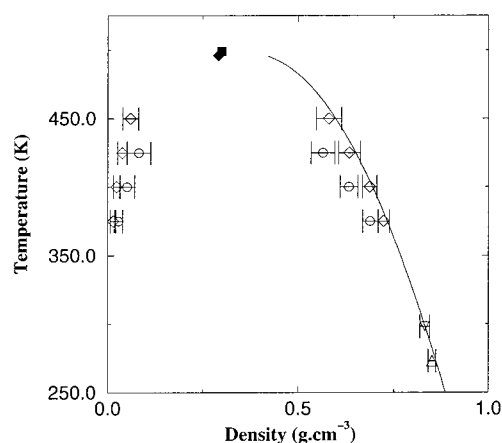
force field seems to perform better than the OPLS-UA model<sup>22</sup> and OPLS-AA model.<sup>16</sup>

The OPPE force field yields a relative deviation with experimental data for sulfides of 0.8% for densities and 0.8% for enthalpies of vaporization compared with 5.5 and 9.6%, respectively, for the OPLS-UA model. The OPLS-AA model leads to an improvement of the OPLS-UA since deviations are of 1.5% and 6% respectively. OPLS models describe thiols more accurately than sulfides. Again, our model yields quantitative results for the density (deviation of 1.3% compared with 1.2% for OPLS-UA and 1.5% for OPLS-AA). Enthalpies of vaporization are not improved: OPLS-UA gives a deviation of 1%, OPLS-AA 3.1%, and this model 4.2%. This is mainly due to the deviation observed for methanethiol. This deviation might be induced by the fact that the partial charges do not treat polarization in the same way for methanethiol and ethanethiol: the molecular dipole moment of methanethiol was overestimated by 27% (18% in the case of ethanethiol which is a more polarizable molecule). The dipole moment of methanethiol might thus be too high, resulting in an overestimation of enthalpies. For dimethyl disulfide, our force field yields better results for density (deviation of 1% compared with 2.5% for both OPLS models) and worse for enthalpy (9% compared with 1.1% for OPLS-UA and 3.5% for OPLS-AA). The lack of experimental data for dimethyl disulfide prevents us from drawing a conclusion on the ability of this model to describe disulfides.

We have also computed radial distribution functions. They exhibit the same features as those obtained by Jorgensen et al. for sulfides.<sup>1,16</sup> However, regarding thiols, the H-S radial distribution function differs from the one obtained in ref 16. According to OPPE force field, there is little structure whereas OPLS leads to a strong first peak associated with extensive hydrogen bonding. Both of these radial distribution functions are plotted for methanethiol and ethanethiol in Figure 3. No neutron diffraction data is available on liquid thiols so it is not possible at present to discard any of these results. Nevertheless, we want to underline the following point: though OPPE and OPLS force fields yield a good agreement with thermodynamic data, they are associated with rather different structural features. This difference between OPPE and OPLS results can be accounted for by the fact that OPLS charges are higher in magnitude ( $-0.45$  on sulfur and  $+0.27$  on the hydrogen of the SH bond) than the charges proposed here ( $-0.21$  for S and  $+0.15$  for H (SH)). This result points out the importance of the method used in the parametrization of the force field.



**Figure 4.** Coexistence curve of dimethyl sulfide (straight lines are experimental data,<sup>41</sup> the filled square is the experimental critical point, open triangle (NPT simulation), open diamonds (GEMC simulations), and the filled diamond (estimated critical point) are OPPE results).

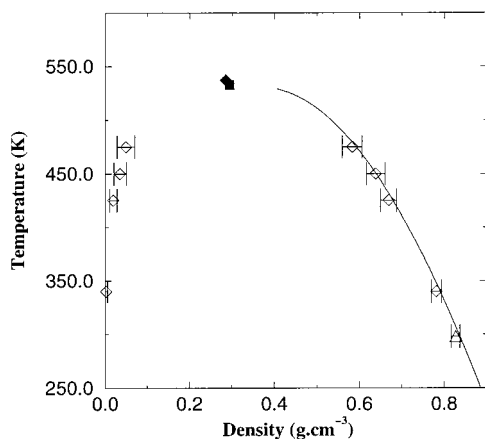


**Figure 5.** Coexistence curve of ethanethiol (straight lines are experimental data,<sup>41</sup> the filled square is the experimental critical point, open triangle up (NPT simulation), open diamonds (GEMC simulations), and the filled diamond (estimated critical point) are OPPE results; open triangle down (NPT simulation) and open circles (GEMC simulations) are OPLS results).

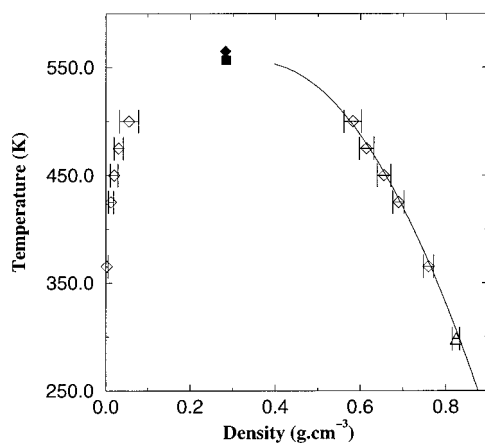
**TABLE 8: Estimated Critical Point for Various Sulfides and Thiols (experimental data are taken from Ref 41) (the subscripts give the accuracy of the last decimal(s))**

compound	critical density (g cm <sup>-3</sup> )		critical temperature (K)	
	exptl	simulation	exptl	simulation
CH <sub>3</sub> SCH <sub>3</sub>	0.309	0.312 <sub>9</sub>	503.0	511 <sub>6</sub>
CH <sub>3</sub> CH <sub>2</sub> SCH <sub>3</sub>	0.294	0.285 <sub>8</sub>	533.0	537 <sub>4</sub>
CH <sub>3</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>3</sub>	0.284	0.283 <sub>9</sub>	557.0	565 <sub>5</sub>
CH <sub>3</sub> SH	0.332	0.320 <sub>9</sub>	470.0	477 <sub>6</sub>
CH <sub>3</sub> CH <sub>2</sub> SH	0.300	0.291 <sub>9</sub>	499.0	496 <sub>4</sub>

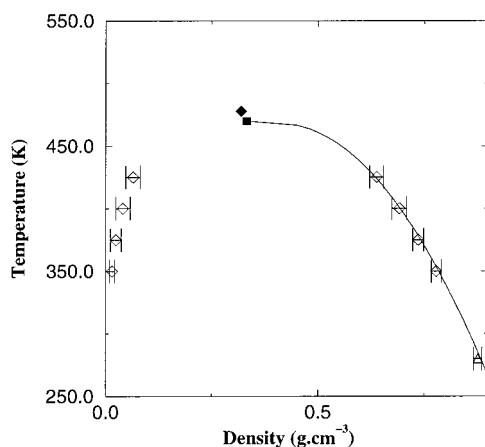
**Liquid-Vapor Phase Equilibria.** The coexistence curves of dimethyl sulfide and ethanethiol, obtained with the OPPE force field, are presented in Figures 4 and 5. Some simulations with the OPLS-UA model were also performed for ethanethiol and are plotted in Figure 5. Very good agreement is obtained for the whole coexistence curve for OPPE. The estimated critical points are given in Table 8: they are very close to experiment for these two compounds. On the other hand, as can be seen in Figure 5, the OPLS-UA model yields good results at ambient temperature. However, at higher temperatures, a deviation between experiment and simulation results obtained with the OPLS-UA model, was observed. Fitting the parameters of a model on one state point as it is done in OPLS-UA model,



**Figure 6.** Coexistence curve of ethylmethyl sulfide (same legend as Figure 5).



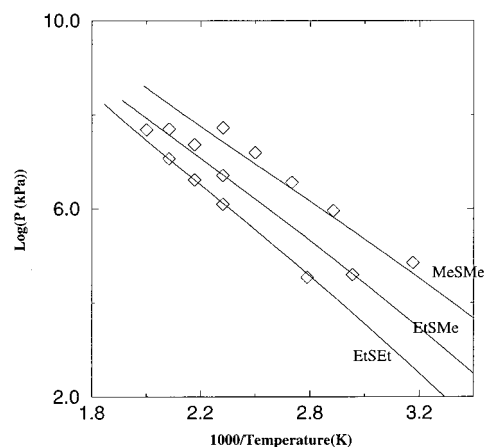
**Figure 7.** Coexistence curve of diethyl sulfide (same legend as Figure 5).



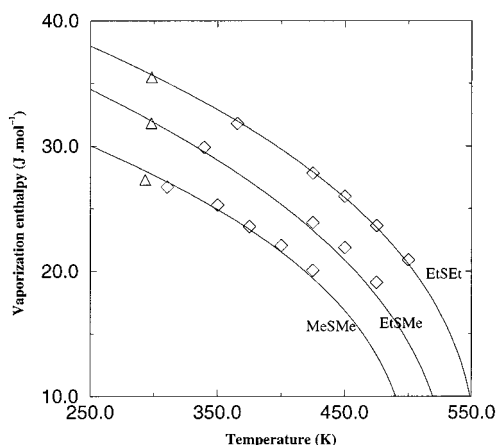
**Figure 8.** Coexistence curve of methanethiol (same legend as Figure 5).

only ensures that good agreement with experiment is obtained in the vicinity of the state point where the fitting procedure was performed. This brings us to the conclusion that the fitting procedure used in this work enables to obtain a good description of the whole coexistence curve: the coexistence curve was reasonably described by fitting only two state points, one at ambient conditions and one at a reduced temperature of 0.8.

We have then computed the coexistence curves of several other compounds to test the transferability of the Lennard-Jones parameters for S and SH groups. Coexistence curves for ethylmethyl sulfide, diethyl sulfide and methanethiol are plotted



**Figure 9.** Clausius-Clapeyron plots of the saturated vapor pressure against the inverse temperature for dimethyl sulfide, ethylmethyl sulfide, and diethyl sulfide (straight lines are experimental data<sup>41</sup> and open diamonds (GEMC simulations) are OPPE results).



**Figure 10.** Enthalpy of vaporization of sulfides (straight lines are experimental data,<sup>41</sup> open triangle (NPT simulation), and open diamonds (GEMC simulations) are OPPE results).

in Figures 6–8 as well as the variation of the vapor pressure (Figure 9) and of the enthalpy of vaporization (Figure 10) with temperature for the three sulfides studied in this work. Very good agreement was obtained for all these properties. Critical properties were estimated within a deviation of 2.2% for the critical density and 1.2% for the critical temperature from experimental results (Table 8). The Lennard-Jones parameters for S and SH groups were thus proven to be transferable as their extension to ethylmethyl sulfide and diethyl sulfide and to methanethiol yields good results. We also want to underline the following point: the parameters determined for alkanes in the AUA 4 model<sup>13</sup> have proven to stay valid in a more general context. The good performance of the OPPE force field for sulfides and thiols provides an additional evidence of the soundness of parameters of the AUA 4 model.

## 7. Conclusion

A methodology to derive and to optimize the parameters of a transferable potential was described in this paper and applied to the case of sulfides and thiols. The electrostatic part of the potential was modeled by a set of atomic charges. These charges were obtained by fitting the ab initio electrostatic potential. Similar to the RESP method,<sup>21</sup> a stabilization process was used to deal with ill-defined charges in the fitting procedure. Atomic charges obtained thanks to this method reproduce accurately



the ab initio ESP, exhibit more stability than charges obtained from a simple least-squares fit, and almost do not depend on the conformation of the molecule. This has been shown here on various sulfides and thiols. The repulsion-dispersion part was modeled by anisotropic Lennard-Jones sites. Parameters for methyl and methylene groups were taken from a previous study on alkanes,<sup>13</sup> and parameters for S and SH groups were fitted to experimental data. These parameters were proven to be transferable as they yield good agreement with experiment for several sulfides and thiols. The novel OPPE force field yields an excellent agreement between experimental data and simulation results at ambient conditions and along the coexistence curve as well. However, due to the lack of experimental data, we have not been able to test the performance of the OPPE model regarding the structural properties.

A future application of OPPE force field is to compute the thermodynamic properties of mixtures of alkanes, modeled by the AUA 4 force field,<sup>13</sup> with sulfur compounds. This approach has already been used in the case of CO<sub>2</sub>–alkane and H<sub>2</sub>S or H<sub>2</sub>O–alkane mixtures. The results were most often in good agreement with experiment,<sup>13,32,34</sup> provided that the force field used for pure components yields accurate results. (Cui et al.<sup>35</sup> have found results only in qualitative agreement for CO<sub>2</sub>–alkanes using the SKS force field. We attribute this effect to errors in the parametrization of the SKS force field as explained by Smit et al.<sup>36</sup>) When computing the properties of sulfide–alkane mixtures, the use of united atoms to model the repulsion-dispersion part in OPPE force field will lead to savings of computer time: as there is no point charge on alkane molecules in the AUA 4 model, only repulsion–dispersion interactions between united atoms will take place between unlike molecules. However, performing accurate calculations on these mixtures might require to include polarizability effects as suggested by Errington and Panagiotopoulos.<sup>34</sup> We plan to test the effect of including polarizability on the coexistence curves of those mixtures.

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