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A Drude Polarizable Model for Liquid Hydrogen Sulfide

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Abstract

In this work the, first polarizable model for hydrogen sulfide (H_2S) based on the Drude oscillator has been developed. This model has been design to be analogous to the SWM4–NDP water model; the model is rigid with the point charges assigned to the H and S atoms and a lone pair on the bisector of the $\angle\text{HSH}$ in the molecular plane. The position of the lone pair and its charge have been constrained to produce the experimental gas phase static dipole moment of 0.98 D. Polarizability is incorporated by a charged particle attached to the S atom through a harmonic potential. Intermolecular non-bonded forces are included using a Lennard-Jones potential between S atoms. The model was parameterized to reproduce density, enthalpy of vaporization and dielectric constant of pure H_2S at 212 K and 1 atm. This model accurately reproduces the shear viscosity and self-diffusion coefficient of bulk H_2S along the coexistence curve of hydrogen sulfide within the range of 212–298 K. At 212 K, this model yields a dielectric constant of 8.18 ± 0.13 , a density of $951.4 \pm 0.35 \text{ kg m}^{-3}$ and an enthalpy of vaporization of $17.81 \text{ kJ mol}^{-1}$, self-diffusion coefficient

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of $(3.27 \pm 0.09) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and shear viscosity of $(3.84 \pm 0.29) \times 10^{-4} \text{ Ps}\cdot\text{s}$, which are in good agreement with the experimental values.

Introduction

Hydrogen sulfide (H_2S) is of major importance in industrial chemistry as it is a corrosive and toxic[?] component of natural gas and crude oil. The presence of H_2S complicates the extraction, processing, and transportation of these resources. Desulfurization of natural gas streams via the Claus process is an expensive and complex step in natural gas processing.[?] H_2S is acutely toxic even in low concentration, although it has also recently been discovered to have an intrinsic biological role as an neurotransmitter.[?]

Molecular dynamics (MD) simulations are a valuable tool in developing new chemical processes to manage H_2S , providing valuable data that are difficult to obtain experimentally.^{????} All these studies need a reliable model of H_2S that is able to accurately describe the mechanical, thermodynamic, and transport properties of liquid hydrogen sulfide. Several H_2S models have been developed for this purpose. One early force field for hydrogen sulfide was proposed by Jorgensen.[?] A three point model parameterized to the heat of vaporization and density of pure H_2S . The lack of satisfactory structural properties of this model led Forester et al.[?] to propose a four point model with a lone pair on the bisector of the $\angle\text{HSH}$. Kristóf and Liszi[?] reparameterized the four site Forester model by applying the Gibbs ensemble Monte Carlo method to obtain enthalpy of vaporization and density along coexistence curve within the range of 212–352 K. Recently, Potoff et al.[?] developed new model based on SPC/E water model to study the binary mixture properties of H_2S and *n*-pentane.

While these non-polarizable models are capable of reproducing some of the properties of H_2S , they all neglect induced polarization. Hydrogen sulfide is a highly polarizable molecule with a gas phase molecular polarizability of 3.63 \AA^3 ,[?] more than 2 times that of water. Recently, Drude polarizable force field[?] has been developed for a range of molecular liquids, including water,^{??}

alkanes,[?] amides,[?] and benzene.[?] This model has proven to be able to reproduce mechanical and thermodynamic properties of these liquids without overestimating the dielectric constant and molecular dipole moment. MacKerell and Zhu developed Drude model for series of sulfur containing compounds, although this study did not design a model for H₂S.[?]

In this study we developed a Drude polarizable model by fitting the thermodynamic properties to the experimental value at 212 K, which is the boiling point of H₂S at 1 atm, with method of parameterization analogous to the SWM4-NDP[?] model. We compare the accuracy of this model to the existing non-polarizable models by using a consistent set of simulations parameters, such as the size of the system and the calculation of non-bonded interactions. The S–S radial distribution functions (rdf) of these H₂S models is also compared to ab initio molecular dynamics and neutron diffraction data.[?]

Theory

The Drude Model

A Drude particle is a massless charged particle attached to a central non-hydrogen atom through a harmonic spring and interacts with other particles through electrostatic interactions. In this model, polarizability is expressed as $\alpha = \frac{q_D^2}{k_D}$,[?] where α is the polarizability and k_D is the restraining constant of the Drude oscillator (typically with value of 1000 N/m) and q_D is the charge of the Drude particle. In this model, $q_D + q_A$ represents the total charge of the parent atom. Therefore, given the total charge and polarizability of the parent atom, the associated Drude particle can be specified. Drude particles are typically not added to hydrogen atoms. The inclusion of these Drude particles results in extra expressions in the electrostatic energy function, which accounts for the induced dipole interaction,[?]

$$\begin{aligned}
U_{nonbonded} = & \sum_A^N \sum_{B>A}^N \frac{q_c(A) \cdot q_c(B)}{|r(A) - r(B)|} + \sum_A^N \sum_{B>A}^{N_D} \frac{q_D(A) \cdot q_c(B)}{|r_D(A) - r(B)|} + \\
& \sum_A^N \sum_{B>A}^{N_D} \frac{q_D(A) \cdot q_D(B)}{|r_D(A) - r_D(B)|} + \frac{1}{2} \sum_A^{N_D} k_D (|r_D(A) - r(A)|)^2 + \\
& \sum_A^N \sum_{B>A}^N E_{min,AB} \left[\left(\frac{R_{min,AB}}{|r(A) - r(B)|} \right)^{12} - 2 \left(\frac{R_{min,AB}}{|r(A) - r(B)|} \right)^6 \right]
\end{aligned} \tag{1}$$

In Eqn. (??), the first term is the simple point charge electrostatic interaction between the parent atoms, while the last three expressions result from the interaction of the Drude particles; Drude–point-charge, Drude–Drude, and potential energy of the Drude harmonic restraint. Rigorously, the position of the Drude particles should be energy-minimized in each configuration, so as to adjust in response to the electric field and remain on the self consistent field (SCF) surface. As minimizations are expensive, an extended Lagrangian method was developed to determine the position of the Drude particles by assigning a fictitious mass to the Drude particle and propagating their positions dynamically.[?] A thermostat is applied to these degrees of freedom to ensure the simulation remains close to SCF energy surface.

Parameterization Procedure

For the parameterization of the polarizable H₂S model we applied the same strategy as SWM4-NDP water model.[?] In our model, H₂S molecules have the experimental gas phase geometry and represented as rigid, a point charge, known as lone pair, is located at the bisector of $\angle HSH$ and its distance from the S atom were obtained during parameterization procedure. We make the standard approximation of only having Lennard-Jones interaction between sulfur atoms and not H atoms. Assigning a lone pair to the sulfur and maintaining the H₂S molecule rigid, five free parameters remain, including the polarizability α , charge and position of the lone pair q_m and l_m , and LJ parameters ϵ and σ . During the course of parameterization the constraint of $q_S + q_D = 0$ was applied and other the electrostatic parameters, including the position and charge of the lone pair,

l_m and q_m , were changed to obtain gas phase dipole moment same as experimental value, which is 0.98 D.

First, a very broad scan over parameters of α , l_m , q_m , σ , and ϵ was performed to calculate the dimerization energy, E_{dim} , and S–S distance, R_{SS} , in dimer structure. E_{dim} and R_{SS} were compared to the result of counterpoise corrected CCSD(t)/aug-cc-pVTZ//MP2/aug-cc-pVTZ H₂S–H₂S dimer structure and energy. The parameter space was restricted to the points with $E_{dim} = 1.2 \pm 0.3$ kcal mol^{−1} and $R_{dim} = 3.9 \pm 0.2$ Å. The boundaries of this parameter space were chosen to generate the final designing points of parameterization using the central composite design method, CCD, from the R project[?] package. The generated parameters were then used for MD simulation of bulk system. The density, enthalpy of vaporization and dielectric constant of these trajectories were calculated at 212 K and results were each fitted to the second order (quadratic) polynomial response function with 15 coefficients.

$$\mathcal{F}_{\{\alpha, l_m, q_m, \epsilon, R_{min}\}} = a_1 \alpha^2 + \dots + a_5 R_{min}^2 + b_1 \alpha l_m + \dots + b_{10} \epsilon R_{min}, \quad (2)$$

Where \mathcal{F} can be replaced by any of density, enthalpy of vaporization or dielectric constant. The coefficient a_i and b_i are determined by fitting procedure. The minimum of $\{\mathcal{F}_{expt.} - \mathcal{F}_{\{\alpha, l_m, q_m, \epsilon, R_{min}\}}\}^2$ were obtained for each of three properties. A narrow grid search was performed in the vicinity of the minimum to find the final parameters. This type of optimization is designed to yield the best possible parameters given the constraints imposed on the parameters.

Enthalpy of vaporization was calculated using the formula,

$$\Delta_{vap}H = RT - \langle U \rangle_{liq}, \quad (3)$$

The dielectric constant was calculated using,[?]

$$\epsilon = \epsilon_{\infty} + \frac{4\pi(\langle M^2 \rangle - \langle M \rangle^2)}{3\langle V \rangle k_B T}, \quad (4)$$

where M is the dipole moment of the unit cell and ϵ_∞ is infinite frequency dielectric constant. ϵ_∞ is calculated from the Clausius–Mossotti equation,

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi\alpha}{3v} \quad (5)$$

The diffusion coefficient was calculated using the Einstein relation,[?]

$$D_{PBC} = \frac{1}{6t} \langle |r_i(t) - r_i(0)|^2 \rangle, \quad (6)$$

the PBC indicates that correction from the system size effect has not been applied. The correction for finite size effects of Yeh and Hummer[?] is applied by,

$$D = D_{PBC} + 2.837297 \frac{k_B T}{6\pi\eta L}, \quad (7)$$

where η is the shear viscosity coefficient calculated from the Green–Kubo relation,[?]

$$\eta = \frac{V}{k_B T} \int_0^\infty dt \langle p_{xy}(0) p_{xy}(t) \rangle_0, \quad (8)$$

where p_{xy} is the xy component of the pressure tensor.

Computational Details

Molecular Mechanical Simulations

All the simulations were performed using CHARMM, version c36b2.[?] All the H_2S molecules were made rigid using the SHAKE algorithm. Isobaric–isothermal molecular dynamics simulations were used to calculate all the mechanical and thermodynamics properties, using an extended Lagrangian method implemented within the Velocity–Verlet propagation algorithm. A dual Nosé–Hoover thermostat[?] was applied; the first was coupled to the heavy atoms with a relaxation

time of 0.1 ps and another thermostat with 0.005 ps for the Drude particles. The Andersen–Hoover barostat[?] with a relaxation time of 0.2 ps was used to regulate the pressure. A cubic cell of 560 H₂S molecules was chosen to calculate the bulk properties of each model under periodic boundary conditions. Molecules in the distance of 16 Å were included in pairing list and non-bonded cutoff applied at 12 Å. For electrostatic interactions, the particle mesh Ewald (PME) method with the coupling parameter $\kappa = 0.33$ and sixth order spline function was applied. For all the models, 10 different 1 ns MD simulations with a 1 fs step size were performed to obtain the standard deviation of each property.

Ab Initio Molecular Dynamics Simulations

An ab initio molecular dynamics (AIMD) simulation was also performed for a cubic cell with 16.3 Å box of 64 H₂S molecules. A 50 ps of AIMD simulation was performed using the QUICKSTEP module of CP2K program.[?] The time step of this simulation was 1 fs and PBE functional with TZV2P-MOLOPT-GTH basis set and GTH-PBE-q6 pseudopotential with 80 Ry cutoff density grid were used. The S–H bond length were constrained to 1.34 Å using SHAKE algorithm. Langevin MD with a frictional coefficient (γ) of 1 ps⁻¹ were employed to sample the canonical ensemble of this system.

Results and Discussion

Parameterization

In the calculation of the dimer structure, the majority of parameters could give appropriate R_{SS} , within deviation of 5%, while only a small portion of them could give E_{dim} with values greater than -1.15 kcal mol⁻¹. All of these parameter combinations resulted in very dense liquids with high dielectric constants and heat of vaporizations. Therefore, the acceptance value for dimerization energy was adjusted to the interval between -0.95 to -1.1 kcal mol⁻¹. Those parameter

combinations within this range of dimer properties chosen for the next step. A similar tolerance in the dimerization energy was also necessary in the development of the SWM4-NDP water model.

In the CCD designing process, α were chosen to have only two values 2.5 and 3.0 Å³ and for other parameters these values assigned; l_M between 0.17 to 0.20 Å, E_{min} between 0.40 to 0.65 kcal mol⁻¹, and R_{min} between 2.03 Å to 2.10 Å. MD simulations were performed with these sets of parameters under isobaric–isothermal condition at 212 K.

The final parameters of the Drude polarizable model, along with the all the previous H₂S models, have been presented in the ???. The polarizability of the final Drude model is 2.5 Å³ which is about 69% of the experimental gas phase polarizability 3.631 Å³.[?] This is consistent with the trend in other Drude polarizable models for molecular liquids, ?? where polarizability of 60–70 % of the gas phase also found to be optimal. For example, the polarizability of SWM4-NDP water model is 73% of the experimental gas phase polarizability of water.

The optimized electrostatic parameters used in non-polarizable models tend to have higher dipole moment than the experimental values in orders to achieve satisfactory bulk properties, for instance the TIP3P water model has a dipole moment of 2.35 D while the experimental gas phase dipole moment of water is 1.85 D. The non-polarizable models of H₂S also are also following this rule with dipole moment in the range of 1.4 to 2.1 D compare to the experimental dipole moment 0.98 D (??). However, the current Drude model μ_0 is the same as the experimental gas phase dipole moment and it is able to reproduce for the bulk properties which are in agreement with experiment.

For the Drude polarizable model, only the dielectric constant, enthalpy of vaporization, and density at 212 K and 1 atm were used for parameterization. Other properties within the range of 212 to 298 K along the liquid–vapor coexistence curve obtained in agreement to experimental values without any further adjustment.

Properties

Dimer Properties and Molecular Dipoles

The final Drude model results in the E_{dim} of $-0.98 \text{ kcal mol}^{-1}$, which is $0.5 \text{ kcal mol}^{-1}$ less than CCSD(t)/aug-cc-pVTZ single point calculation and R_{SS} distance is 0.06 \AA larger (??). All the other parameters that generated during the Drude force field parameterization procedure and had better dimerization energy resulted in liquid with high density and heat of vaporization. Among other non-polarizable models, Jorgensen's model overestimates the dimerization energy more than 1 kcal mol^{-1} and predicts a S–S distance that is 0.37 \AA too short. The Potoff and Forester models have very similar dimer properties. Their dimerization energy is $0.4 \text{ kcal mol}^{-1}$ higher. The Kristóf model has a dimerization energy that is within $0.2 \text{ kcal mol}^{-1}$ of the ab initio result, the most accurate dimerization energy predicted by any model.

All the non-polarizable models have higher dimerization energy and shorter sulfur–sulfur distance than those calculated using CCSD(t)/aug-cc-pVTZ//MP2/aug-cc-pVTZ. However, dimerization energy of Drude model is -1 kcal mol^{-1} which shows lower interaction in dimer by about $-0.4 \text{ kcal mol}^{-1}$.

Density

The density of H_2S over the interval of 212–298 K are presented in ??, All the models have a density that is very close to experimental value of 949 kg m^{-3} at 212 K, with exception of the Forester model, which overestimates the density by 67 kg m^{-3} . Jorgensen's model highly deviates from experimental density by increasing the temperature. For instance, at 298 K it calculates the density about 100 kg m^{-3} less than experiment. Forester's model estimates the density larger than the experimental value with same difference within the range of 212–298 K. Kristóf, Potoff, and Drude model are all in good agreement with experiment and show very similar trend in predicting density. Their difference from experiment at 298 K is less than 20 kg m^{-3} .

Enthalpy of Vaporization

The enthalpies of vaporization of the Drude and non-polarizable models are plotted along with the experimental values over the range of 212–298 K in ???. As for the calculated densities, the Forester model has the largest deviation from experiment, significantly overestimating the enthalpy of vaporization across the full range of temperatures. The Potoff model also shows a sizable deviation from experiment, a divergence that increases with temperature; the calculated enthalpy of vaporization is more than 3 kcal mol⁻¹ higher than the experimental value at 298 K. Other models are in acceptable agreement with experimental value and their errors are about 1 kcal mol⁻¹. Kristóf's model starts with exactly the same enthalpy of vaporization as experiment and diverges by increasing the temperature in the way that at 298 K the enthalpy is 1.5 kcal mol⁻¹ more than experimental value. At 212 K, the Drude model begins with the enthalpy of 17.8 kcal mol⁻¹ which is 0.9 kcal mol⁻¹ less than experiment. At increased temperatures, the Drude model approaches the experimental results and at 260 K it gives exactly the same value as experiment. Then it predicts enthalpy larger than experiment and finally at 298 K it gives the enthalpy with less than 1 kcal mol⁻¹ difference from the experiment. Jorgensen's model estimates enthalpy of vaporization in close agreement with the experimental values. It shows better agreement by increasing the temperature. For instance, for temperatures larger than 260 K, the deviation of the calculated enthalpy from experiment is less than 0.2 kcal mol⁻¹. In general, all these models correctly predict a decrease in the enthalpy of vaporization as the temperature increases, but underestimate the rate of decline. As a result, each model is very effective at one particular temperature, but deviates from experiment as the temperature changes.

Dielectric Constant

The dielectric constants calculated using the Drude and non-polarizable models are presented in ???. The non-polarizable models all have significantly larger dielectric constants than the experimental value of 8.04. This can be related to their large gas phase molecular dipole moments, which are all significantly larger than the experimental values. The three point models developed

by Jorgensen and Potoff have considerably larger dielectric constants than the four point models, suggesting that the lone pair site is important for simultaneously describing the mechanical and electric properties of the liquid. The Drude model developed here shows a significant improvement over the non-polarizable models; its calculated dielectric constant of 8.18 ± 0.13 , which matches the experimental value of 8.04 within statistical error. The parameterization of this model to reproduce the experimental gas phase molecular dipole moment, the incorporation of induced polarization effects through the Drude oscillator, and the inclusion of the dielectric constant in the target function account for the improved accuracy. The ability of the Drude model predict accurately the dielectric constants of molecular liquids is one of the most significant successes of this model.???

Self-diffusion and Shear Viscosity

The calculated and experimental self-diffusion coefficients and shear viscosities coefficients are plotted over the range of temperatures between 212–298 K in ?? and ?? respectively. The Jorgensen model yields liquids that are very diffusive, and hence less viscous. The Forester model, on the other hand, yields a less diffusive and more viscous liquid. While its self-diffusion coefficient is closer to the experimental value at lower temperatures, for the shear viscosity by increasing temperature it approaches the experimental value. The Potoff model predicts transport properties in good agreement with experiment. Kristóf and Drude model show very similar trends for both self-diffusion and shear viscosity and their results, considering the standard deviation, are the same and in good agreement with the experiment.

Radial Distribution Function

The radial distribution function ($g_{S-S}(r)$) of a liquid provides the correlation function between the bulk density of a liquid and its radially dependent density as a function of the distance between two atoms in the liquid (r). This provides a rigorous and transferable descriptor of the structure of a liquid. This function can be compared to data derived from experimental neutron and X-

Ray diffraction data or integrated to give the coordination number ($n_c = 4\pi \int_0^r g(r)r^2 dr$). The S–S radial distribution functions ($g_{S-S}(r)$) calculated using for the Drude and non-polarizable models are plotted along with the experimental neutron scattering and AIMD data ?? of liquid H₂S at 298 K and 19.9 atm. With exception of the Jorgensen model, all the models yield similar radial distribution functions that are in good agreement with the experimental and ab initio data, with the maximum of the first peak occurring at a S–S distances of 3.95–4.05 Å. The first peak of the rdf calculated using the Jorgensen model occurs at a distance of 3.75 Å, a significantly shorter inter-atomic distance than the other models predict.

The height of first peak of the rdf's of the force field models are sharper than the height in this peak in the experimentally-derived rdf. This is a common problem in molecular mechanical force fields that use the Lennard-Jones function to describe interatomic Pauli repulsive interactions. The $E \propto r^{-12}$ term in the Lennard-Jones function tends to overestimate of steepness of the short range repulsive interaction, leading to sharper peaks in the rdf.?

Analysis of the rdf provides some insights into the structure of liquid hydrogen sulfide. The ratios of the positions of the second and first peaks are presented in ?. For all the H₂S models, this ratio is near 2, which is the characteristic of a simple fluid.?' In contrast, this ratio is 1.56 for liquid water. Similarly, the integration of the first peak of $g_{S-S}(r)$ gives number of atoms in the first coordination sphere, or the coordination number (n_c). This value is between 11 to 12 for all the H₂S models, reflecting a close-packing arrangement that is typical of simple Lennard-Jones fluids like Ar(l). In contrast, this ratio is typically between 4 to 5 for liquid water, depending on the model. This observation confirms lack of tetrahedral structure in the liquid hydrogen sulfide and shows that it has more characteristics of a simple fluid. This is consistent with the results of previous diffraction experiments.?' ?

Performance of Extended Lagrangian Dynamics

In order to confirm that our use of extended Lagrangian dynamics to propagate the positions of the Drude particles is accurate for these highly polarizable molecules, a 500 ps MD simulation with

SCF method at 212 K was performed. During this simulation, the positions of the Drude particles were adjusted to minimize the potential energy at each step, which ensures that the simulation remains on the SCF surface. The properties derived from this simulation were identical to those calculated using extended Lagrangian dynamics within statistical uncertainty; for the SCF trajectory, the calculated density is 947 kg m^{-3} , the enthalpy of vaporization is $17.66 \text{ kcal mol}^{-1}$ and the dielectric constant is 8.1.

Conclusion

In this study, we developed a polarizable model for liquid hydrogen sulfide based on the Drude model, following the same methodology and constraints on the parameters as was used to develop the SWM4-NDP water model. This model predicts the density, enthalpy of vaporization, self-diffusion coefficient, and shear viscosity coefficients of liquid hydrogen sulfide along the liquid-vapor coexistence curve between 212 and 298 K in good agreement with experiment. Our model also has the correct dipole moment for H_2S in the gas phase and has a dielectric constant that is in good agreement experimental value at 212 K. We have compared this model to existing non-polarizable models for H_2S . While each of these models is effective for modeling some features of liquid hydrogen sulfide, each model has limitations, particularly for the dielectric constant, which all non-polarizable models significantly overestimate. This is likely due the anomalously high static dipole moment in these models, a consequence of the lack of induced polarization in fixed-charge models. Of the non-polarizable models evaluated, the four point model developed by Kristóf and Liszi model shows the best agreement with experiment for most of the properties evaluated, however it overestimates gas phase dipole moment and the liquid dielectric constant. In these two respects, the Drude model we present here shows the best performance of all the models evaluated. The radial distribution function calculated using our Drude model is consistent with the distribution calculated from an AIMD simulation and neutron diffraction data. The analysis of this distribution indicates that although H_2S is an analog of H_2O , hydrogen sulfide forms a simple

liquid that does not have the persistent hydrogen bonding network that is present in liquid water.

Supporting Information Available

CHARMM RTF and parameter files for non-polarizable and Drude models, CHARMM input files for MD simulations, CP2K input file for AIMD simulation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Acknowledgement

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Tables

Table 1: Parameters of the non-polarizable and Drude H₂S models.

	Jorgensen	Potoff et al.	Forester et al.	Kristóf and Liszi	Drude model
d_{SH} (Å)	1.240	1.240	1.240	1.240	1.240
θ_{HSH} (deg)	92	92	92	92	92
d_l (Å)			0.1933	0.1862	0.2020
q_S (e)	−0.470	−0.380	−0.661	0.400	2.7438
q_H (e)	0.235	0.190	0.278	0.250	0.137
q_l (e)			−1.217	−0.900	−0.274
q_D (e)					−2.74381
α (Å ³)					−2.5
ϵ (kcal mol ^{−1})	0.2500	0.4610	0.5345	0.4968	0.4968
σ (Å)	3.70	3.72	3.69	3.73	3.72

Table 2: The structure and interaction energies of the H₂S dimer calculated with the non-polarizable, Drude, and high level ab initio models.

Model	E_{dim} (kcal mol ^{−1})	R_{SS} (Å)
CCSD(t)/aug-cc-pVTZ ^a	−1.40	3.99
Jorgensen	−2.58	3.62
Potoff et al.	−1.76	3.89
Forester et al.	−1.73	3.83
Kristóf and Liszi	−1.56	3.90
Drude model	−0.98	4.06

^a Single-point calculation at MP2/aug-cc-pVTZ optimized structure. NWChem[?] was used for ab initio calculations. The calculations were performed with the Boys–Bernardi correction for Basis Set Superposition Error (BSSE).[?]

Table 3: Calculated physical properties of the non-polarizable and Drude H₂S models at 212 K and 1 atm.

model	density (kg m ⁻³)	$\Delta_{vap}H$ (kJ mol ⁻¹)	ϵ	μ_0^a (D)	μ^b (D)	η (10 ⁻⁴ Ps·s)	Diffusion (10 ⁻⁵ cm ² s ⁻¹)
Jorgensen	959.3 ± 0.5	18.07 ± 0.00	48.60 ± 1.14	2.1	2.1	1.41 ± 0.13	9.25 ± 0.21
Potoff et al.	961.6 ± 1.7	17.98 ± 0.02	25.09 ± 0.75	1.7	1.7	3.04 ± 0.29	4.43 ± 0.15
Forester et al.	1016.5 ± 0.4	20.39 ± 0.01	9.73 ± 0.15	1.4	1.4	4.68 ± 0.46	2.88 ± 0.11
Kristóf and Liszi	958.7 ± 0.4	18.67 ± 0.00	11.59 ± 0.27	1.4	1.4	3.62 ± 0.26	3.73 ± 0.09
Drude model	951.4 ± 0.4	17.81 ± 0.00	8.18 ± 0.13	0.98	1.08	3.84 ± 0.29	3.27 ± 0.09
Expt. ^c	949	18.68	8.04	0.98		3.45	4.00

^a Gas phase dipole moment.

^b Liquid phase dipole moment.

^c Density and enthalpy from Ref. ? , dielectric from Ref. ? , gas phase dipole from Ref. ? , viscosity from Ref. ? , diffusion from Ref. ? .

Table 4: The position of the first and second peak of the rdf and coordination number of first shell calculated from MD simulations at 212 K and 1 atm for the non-polarizable and Drude H₂S models. For comparison, the values for Ar(l) and the SWM4-NDP water model are also included.

model	R_1	R_2	$\frac{R_2}{R_1}$	n_1
Jorgensen	3.75	7.35	1.96	9.0
Potoff et al.	3.95	7.65	1.94	11.1
Forester et al.	3.95	7.55	1.91	11.9
Kristóf and Liszi	4.05	7.65	1.89	12.0
Drude model	4.05	7.65	1.89	12.1
AIMD	3.95	7.75	1.96	12.0
Ar	3.65	7.15	1.96	12.7
SWM4-NDP	2.85	4.45	1.56	4.8

Figures

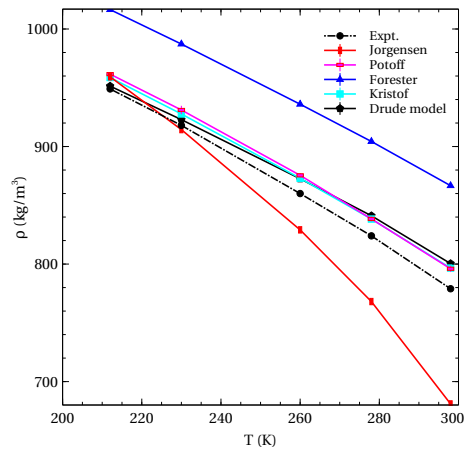


Figure 1: The density of H_2S calculated with the non-polarizable and Drude models over the range 212–298 K along the liquid–vapor coexistence curve. The experimental values are taken from Ref. ? .

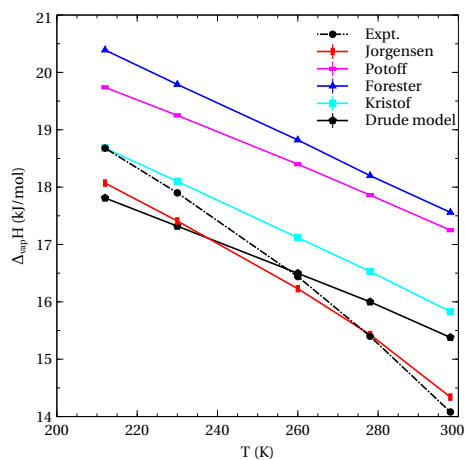


Figure 2: The enthalpy of vaporization of the non-polarizable and Drude models along the liquid–vapor coexistence curve for the temperature range 212–298 K. The experimental values are were from Ref. ? .

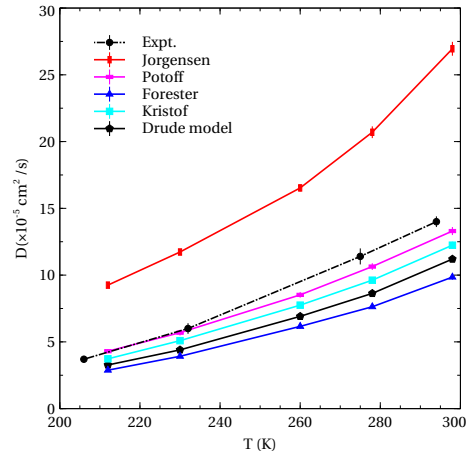


Figure 3: The self-diffusion coefficient of H_2S calculated using the non-polarizable and Drude models along the liquid–vapor coexistence curve for the temperature range 212–298 K. The experimental values were taken from Ref. ? .

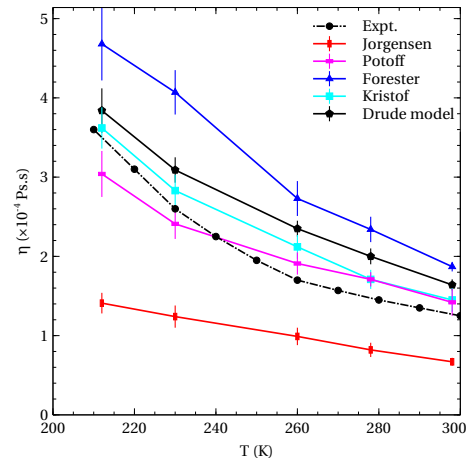


Figure 4: The viscosity coefficient of H_2S calculated using non-polarizable and Drude models along the liquid–vapor coexistence curve for the temperature range 212–298 K. The experimental values were taken from Ref. ? .

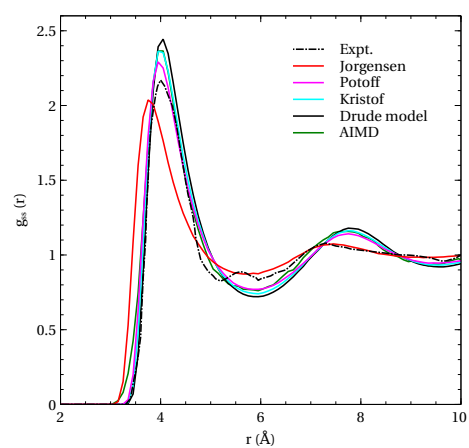


Figure 5: Sulfur–sulfur radial distribution function at 298 K at 19.8 atm. The experimental data was determined by neutron diffraction by Ricci et al.[?].