Published in final edited form as:

Int J Thermophys. 2017 October ; 38: . doi:10.1007/s10765-017-2279-6.

Correlations for the Dielectric Constants of H₂S, SO₂, and SF₆

Allan H. Harvey¹ and Raymond D. Mountain²

¹Applied Chemicals and Materials Division, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305, 303-497-3555

²Chemical Sciences Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899

Abstract

A new method is developed for correlating the static dielectric constant of polar fluids over wide ranges of conditions where few experimental data exist. Molecular dynamics simulations are used to establish the temperature and density dependence of the Kirkwood g -factor, and also the functional form for the increase of the effective dipole moment with density. Most parameters in the model are obtained entirely from simulation; a single proportionality constant is adjusted to obtain agreement with the limited experimental data. The method is applied to hydrogen sulfide (H₂S) and sulfur dioxide (SO₂), both of which are important in geochemistry but have only a few dielectric data available. The resulting correlations agree well with the available liquid data, obey physical boundary conditions at low density and at high temperature, and interpolate in density and temperature in a physically reasonable manner. In addition, we present a more conventional correlation for the dielectric constant of sulfur hexafluoride, SF₆, where more data are available.

Keywords

dielectric constant; hydrogen sulfide; molecular dynamics; relative permittivity; sulfur dioxide; sulfur hexafluoride

1 Introduction

In 2005, Harvey and Lemmon [1] published a model for the static dielectric constant (relative permittivity) of natural gas mixtures. The model used the mixing rule of Harvey and Prausnitz [2], which is appropriate for mixtures of components that differ significantly in volatility. As discussed in [1], the dielectric constant can be useful in estimating the energy content of natural gases. The model included correlations for many pure fluids commonly found in natural gas; use in the mixture model requires correlation of the dielectric constant ϵ as a function of temperature and molar density, $\epsilon(T, \rho)$.

One deficiency of [1] was that it did not contain a correlation for hydrogen sulfide, H₂S, which is present in some natural gases. This omission was partly due to lack of experimental

Correspondence to: Allan H. Harvey.

Contribution of the National Institute of Standards and Technology, not subject to copyright in the United States

data, but primarily because the pure-fluid correlation form in [1] is not applicable to strongly polar fluids.

The dielectric constant is also of interest for geochemistry, where it affects the physics of ion solvation. Recent work has examined the effect of the fluid dielectric constant on specific geochemical problems [3–6], and mixing rules for the dielectric constant of water-gas mixtures at geological conditions have been tested [7]. While a good correlation exists for the dielectric constant of pure water to high temperatures and pressures [8], real geologic fluids may also contain significant amounts of species such as CH₄, CO₂, H₂S, and SO₂. Correlations for CH₄ and CO₂ are given in [1], but geochemists currently have no convenient way to include sulfur-containing compounds in their dielectric modeling.

Since both H₂S and SO₂ are polar and have few experimental dielectric-constant data, our approach for constructing correlations $\epsilon(T, \rho)$ must be different from that of [1]. In this work, we will use knowledge of the molecular dipole moment and polarizability to establish the low-density behavior. We will use molecular dynamics simulation to estimate the shape of the dielectric function over a range of temperatures and densities. Finally, we will use the limited experimental data available (only a few liquid points for both fluids) to normalize the functional form generated from our simulations. The resulting correlations of $\epsilon(T, \rho)$ will have the correct low-density limit, match the available liquid data, and interpolate and extrapolate to other states in a physically realistic way.

Finally, we will produce a dielectric correlation for another sulfur-containing fluid, sulfur hexafluoride. SF₆ is a widely used dielectric in electrical applications. Because SF₆ is nonpolar and a fair number of experimental measurements are available, we will use the methods of [1] to produce its correlation.

2 Background and Correlation Methodology

A standard representation of the dielectric constant of a polar fluid as a function of absolute temperature T and molar density ρ is due to Kirkwood [9]:

$$P_K = \frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} = \rho \left(\frac{4\pi N_A}{3} \alpha + \frac{g A_\mu}{T} \right), \quad (1)$$

where α is the molecular polarizability and N_A is Avogadro's number ($6.022\,140\,857 \times 10^{23} \text{ mol}^{-1}$). P_K is the dielectric polarization per unit volume, which we will call the “polarization” for short. The quantity A_μ is related to the molecular dipole moment μ by $A_\mu = \frac{N_A \mu^2}{9\epsilon_0 k_B}$, where ϵ_0 is the electric constant (permittivity of free space, $8.854\,187\,817 \times 10^{-12} \text{ F m}^{-1}$) and k_B is the Boltzmann constant ($1.380\,648\,52 \times 10^{-23} \text{ J K}^{-1}$). The inverse relationship for converting a calculated value of P_K to ϵ is given by Harvey and Lemmon [1].

The key quantity in Eq. (1) is g , known as the Kirkwood g -factor. If $g = 1$, one simply has the Debye equation for the dielectric constant of a polar gas. At higher densities, interactions cause the dipoles of neighboring molecules to be correlated; the degree of this correlation is expressed by the amount by which g exceeds one.

However, molecular correlations producing $g > 1$ are not the only cause of increased dielectric constants of polar fluids at high densities. The dipole moment becomes higher than its value for the isolated molecule due to polarization from the electric fields of the surrounding molecules. This can be a large effect (especially since the dipole moment is squared in Eq. (1)); for water it has been estimated [10] that the dipole moment in the liquid is on average 50-60 % larger than for the isolated molecule.

Our approach for correlation is to rewrite Eq. (1) as

$$P_K = \frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} = \rho \left(\frac{4\pi N_A}{3} \alpha + \frac{g(T, \rho) A_{\mu, \text{eff}}(\rho)}{T} \right), \quad (2)$$

where $A_{\mu, \text{eff}}(\rho) = \frac{N_A \mu_{\text{eff}}^2(\rho)}{9\epsilon_0 k_B}$, with μ_{eff} an effective dipole moment that depends on density (in principle μ_{eff} also depends on temperature, but we anticipate that the density effect will be dominant because it is the density that mainly determines the strength of the polarizing electric field). The dependence of the effective dipole moment on density is expressed as

$$\mu_{\text{eff}}(\rho) = \mu(1 + f_\mu(\rho)), \quad (3)$$

where μ is the dipole moment of the isolated molecule and a boundary condition is that $f_\mu(\rho)$ must go to zero at $\rho = 0$.

In Eq. (2), we have noted that the g -factor is a function of temperature and density. Physical boundary conditions on the function $g(T, \rho)$ are that $g \rightarrow 1$ in the limit of zero density and also in the limit of infinite temperature. We found it convenient and effective to describe the departure from unity of $g(T, \rho)$ as a product of separate temperature and density functions:

$$g(T, \rho) = 1 + c_g g_1(T) g_2(\rho). \quad (4)$$

A complete correlation therefore requires the functions $f_\mu(\rho)$, $g_1(T)$, and $g_2(\rho)$. These could in principle be determined from experimental data that cover a range of temperature and density, but such data are absent for the species of interest here. We therefore use molecular simulation to provide physically realistic estimates of these functions. While the molecular models available for H_2S and SO_2 cannot be expected to quantitatively predict the dielectric constant over a range of conditions (in part because they are not polarizable, with a fixed dipole moment larger than the single-molecule value), they should give a qualitatively

reasonable representation of the electrostatic forces (especially in the liquid) and of the intermolecular correlations that give rise to the g -factor.

In order to obtain $f_{\mu}(\rho)$ from simulation, we assume that the enhancement of the effective dipole moment is proportional to the average magnitude of the electric field on a molecule due to its neighbors. The function $g(T, \rho)$ is taken as that of the simulated model. The limited experimental data will be used to adjust a proportionality constant in $f_{\mu}(\rho)$, essentially providing a “calibration” for the correlations produced by our simulations.

At various stages of the work, it is necessary to use an equation of state (EOS) for each fluid in order to convert conditions of specified temperature and pressure (T, p) to the variables (T, ρ) used for the correlation. For both H₂S and SO₂, equations developed by Lemmon and Span [11] are used for this purpose.

Equation (2) requires the static polarizability α and the dipole moment μ . For polyatomic species, the static polarizability applicable to the dielectric constant consists not only of the electronic polarizability (often obtained from refractive-index measurements), but also contains a vibrational contribution due to the ability of an electric field to distort the shape of the molecule. We take recommended values of the electronic polarizability from Hohm [12]. The vibrational contribution is taken from Russell and Spackman [13] for H₂S, and from Bishop and Cheung [14] for SO₂. The resulting values of α are $3.66 \times 10^{-24} \text{ cm}^3$ for H₂S and $4.09 \times 10^{-24} \text{ cm}^3$ for SO₂. For the molecular dipole moment μ , accurate measurements are available of 0.978 325 D (1 D $\approx 3.335\,641 \times 10^{-30} \text{ C m}$) for H₂S [15] and 1.633 08 D for SO₂ [16].

3 Molecular Simulation

3.1 Intermolecular Potentials

The intermolecular potentials employed in the simulations are rigid and of the Lennard-Jones plus Coulomb type. For H₂S, the 4-3 model of Shah et al. [17] is used. The model contains three atomic sites and an “X” site located on the bisector of the H-S-H angle. The H- and S-sites are separated by 1.31 Å and the H-S-H angle is 92°. The X-site is located 0.3 Å from the S-site. Charges are located on the X- and H-sites and the Lennard-Jones interactions are located on the atomic sites. For SO₂, the 3-site model of Ketko et al. [18] is used. This model consists of 3 charged atomic sites with Lennard-Jones interactions between all intermolecular sites. The S-O separation is 1.432 Å and the O-S-O angle is 119.3°. The charges and Lennard-Jones parameters are listed in the references [17, 18]. The Lennard-Jones parameters between unlike sites are determined with the Lorentz-Berthelot combining rules [19].

The dipole moments for the models can be computed from the given charges and geometries; they are 1.27 D for H₂S and 2.04 D for SO₂. These are larger than the dipole moments of the real molecules in isolation, reflecting the fact that the models were developed to represent liquid-phase properties where the molecules are further polarized by their neighbors.

We emphasize again that such rigid pairwise potentials cannot be expected to represent quantitatively the dielectric behavior of the fluid, since they will not capture the polarization due to changes in geometry with density, polarization by neighboring molecules, and multibody effects. No models exist that incorporate all of these effects for these fluids, and even if such models did exist the computational requirements would be excessive. We therefore use them only as a tool to estimate the functional form of the physically motivated terms in our correlation. The physical shortcomings of the potentials will lead to some error in the results, but by calibrating with limited experimental data the errors should not be too large.

3.2 Molecular Dynamics Details

The simulations are for 500 molecules confined in a cubic cell with periodic boundary conditions. The equations of motion are solved with a time step of 0.001 ps using a velocity-Verlet type algorithm [20] with quaternions used to describe the orientational degrees of freedom [21]. The simulations generate averages in the NVT ensemble; the temperature is maintained by thermostats of the form described by Martina et al. [22] with separate thermostats tailored to the translational and rotational degrees of freedom. The long-range part of the Coulomb interactions is determined with the Ewald summation method [23]. The simulations are run for a total of 4 ns with block averages recorded every 1 ps for later processing. 4 ns was verified to be sufficiently long by running test simulations also for 1 ns and 2 ns and observing that the relevant averages, already fairly well converged at 2 ns, were very well converged at 4 ns.

The part of the dielectric constant due to the dipoles, ϵ_{pol} , is determined from the long-time average of the square of the total dipole moment $\mathbf{M}$ of the system: [19]

$$\epsilon_{\text{pol}} = 1 + \frac{4\pi(\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2)}{3Vk_{\text{B}}T}. \quad (5)$$

For our simulations, the time average $\langle \mathbf{M} \rangle^2$ was negligible compared to $\langle \mathbf{M}^2 \rangle$. The total dielectric constant ϵ_{tot} corresponding to the model fluid also includes a small “nonpolar” contribution from the molecular polarizability, which was computed according to the first term on the right-hand side of Eq. (1). The nonpolar and polar parts were combined according to their contribution to the polarization [equivalent to adding the two terms on the right side of Eq. (1)], as described previously [7].

The magnitude of the electric field on a molecule was calculated (in most but not all simulations) by adding the vector components of the field on a molecule due to the other molecules and then determining the magnitude of the field. The site at which the electric field is determined is the X site for H₂S and the center of mass for SO₂. The magnitude of the electric field was also saved as 1 ps duration averages for later processing.

The standard uncertainty [24] in $\langle \mathbf{M}^2 \rangle$, determined in the usual way from the statistics of the 1 ps block averages, is on the order of 0.5 % of the average value for H₂S and 1 % of the

average value for SO_2 . The uncertainty in the average electric field magnitude E is less than 0.1 % of the average. The much smaller uncertainty for the electric field is because it is averaged 500 times per time step (once per molecule), while the square of the dipole moment is for a single configuration per time step.

3.3 Results

A number of temperature-density pairs were simulated. To facilitate correlation, a series of simulations was performed at fixed density with varying temperature, and at fixed temperature with varying density. The fixed density and temperature (0.029 mol/cm³ and 380 K for H_2S ; 0.025 mol/cm³ and 450 K for SO_2) were chosen so that all the simulations would be in the single-phase region. A set of high temperatures and densities was also explored corresponding to geologic conditions. In addition, simulations were performed at conditions matching available experimental data, where the density corresponding to the experimental temperature and pressure was determined by the reference equation of state for each fluid [11].

For each simulated point, the Kirkwood g -factor for the model simulation was determined by finding the value of g in Eq. (1) that yielded the simulated dielectric constant. Since the goal in these calculations is to model the effect of orientational correlations, the values of A_μ in this calculation are those corresponding to the dipole moments of the models, given in Sec. 3.1.

Table 1 gives all the simulation results for H_2S , including the calculated g -factors and the total dielectric constants ϵ_{tot} that incorporate the nonpolar contribution. Table 2 provides the same information for SO_2 . The g -factors range up to approximately 1.3 for H_2S , but up to 1.7 for the more polar SO_2 . A few derived values of g are slightly less than 1, which is physically unlikely, but the difference is within the uncertainty of the simulations.

Based on the uncertainty of the dipole moment averages, the relative standard uncertainties of the dielectric constants of H_2S are near 0.5 % for the values in Table 1, while for SO_2 (Table 2) they are near 1 %. The relative standard uncertainties in the computed g -factors are approximately the same as those for the corresponding dielectric constants.

4 Correlations for H_2S and SO_2

We first consider the function $f_\mu(\rho)$, describing the increase in effective dipole moment due to the presence of other molecules. It is reasonable to take this to be proportional to the averaged magnitude of the electric field, as computed in Section 3.2. Physically, one would expect this average field to increase strongly with density at low densities. At higher density, where most molecules are surrounded by near neighbors, it would be expected to increase more slowly. This behavior is seen in the isothermal sections of Tables 1 and 2; the reduced rate of increase at medium and high densities is especially evident for H_2S . This behavior can be approximated by the function

$$f_{\mu}(\rho) = c_{\mu} \left[1 - \exp\left(-a_{\mu} \rho_n^{n_{\mu}}\right) \right], \quad (6)$$

where the decay constant a_{μ} and the exponent n_{μ} are fitted to reproduce the density dependence of the electric field. We use the dimensionless normalized density variable $\rho_n = \rho/\rho^*$, where for convenience the reference density ρ^* is taken as the value at which the temperature dependence was explored in the simulations (0.029 mol/cm³ for H₂S and 0.025 mol/cm³ for SO₂). We will return shortly to the proportionality constant c_{μ} .

For the function $g(T, \rho) - 1 = c_g g_1(T) g_2(\rho)$, we look at the behavior of g as a function of temperature at the reference density ρ^* , and similarly as a function of density along a reference isotherm $T = T^*$, where T^* is 380 K for H₂S and 450 K for SO₂. We find that the temperature dependence of g shows roughly an exponential decay, while the shape of the density dependence can be represented by the same functional form used for $f_{\mu}(\rho)$:

$$g_1(T) = \exp\left(-a_1 T_n^{n_1}\right), \quad (7)$$

$$g_2(\rho) = 1 - \exp\left(-a_2 \rho_n^{n_2}\right), \quad (8)$$

where $T_n = T/T^*$. The proportionality constant c_g in Eq. (4) is adjusted to give the final g -factor the correct magnitude.

Figure 1, comparing the simulated values of g to those from Eq. (4), shows that our correlations for $g(T, \rho)$ agree with the simulation results approximately within their scatter (error bars for the simulated values of g are not shown on Fig. 1 for the sake of clarity, but they would be similar in size to the symbols for H₂S and slightly larger than the symbols for SO₂). As one might expect, the performance is less good for the more strongly polar SO₂, where our relatively simple function must cover a wider range of g and there appears to be a systematic deviation for large values of g . We could have added more complexity to our $g(T, \rho)$ function in order to more closely match the SO₂ results, but it did not seem worthwhile given the limitations of the molecular model and the paucity of experimental data. As shown in the next section, our relatively simple model is still able to reasonably represent the data.

Once we have correlations based on simulations for $g(T, \rho)$ [Eqs. (4), (7), and (8)] and for the functional form of $f_{\mu}(\rho)$ [Eq. (6)], all that remains is to choose the proportionality constant c_{μ} in Eq. (6). It is at this point that we make use of the limited experimental data for both species to calibrate our correlations.

For H₂S, there are five experimental data points for the liquid from four different studies [25–28]. The data are not entirely mutually consistent, with apparent scatter in ϵ on the order of 0.1. We gave lower weight to the two data [25, 26] at the freezing point (which are also

rather old), where experimental difficulty seems more likely. Good overall agreement was obtained by setting the proportionality constant $c_\mu = 0.241$.

Figure 2 compares the correlation developed in this work with the data for liquid H₂S (often the experimental pressure was not reported, so it was assumed to be the saturation pressure at the temperature of the experiment). While the data are sparse, the level of agreement is excellent.

For liquid SO₂, there are three experimental studies [29–31] that are over a century old, and two from the 1950s [32, 33]. We chose to exclude the three older studies from our fitting, considering them only for comparison purposes. We obtained $c_\mu = 0.335$.

Figure 3 compares our correlation to all of the data for liquid SO₂, again assuming the saturated liquid state. At low temperatures, our temperature dependence differs slightly from that obtained by Nickerson and McIntosh [33]; this may reflect deficiencies in the molecular model used in our simulations and/or in our relatively simple correlation. At higher temperatures, the only data come from the 1902 study of Eversheim [31] that was not used in our fit (we have not plotted three points near the critical temperature whose reported dielectric constants are unphysically low). The agreement is fair; again the temperature dependence does not quite match. It is not surprising that the model is less successful for SO₂ than for H₂S, because the former has a larger dipole moment and therefore stronger molecular interactions, and also because our representation of the simulated $g(T, \rho)$ was less good for SO₂.

Table 3 lists the final correlation parameters for both H₂S and SO₂.

5 Correlation for SF₆

Measurements of the dielectric constant of SF₆ have been relatively plentiful, including two studies [34, 35] that covered a wide range of temperatures and densities. Also, SF₆ has no dipole moment. We therefore correlated the dielectric constant of SF₆ with the same equation successfully applied to many nonpolar fluids by Harvey and Lemmon [1]:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \rho(A_\varepsilon + B_\varepsilon\rho + C_\varepsilon\rho^D). \quad (9)$$

A_ε is related to the molecular static polarizability, and in principle can have a slight temperature dependence due to the effect of centrifugal stretching. Hohm [12] lists a number of references in which A_ε was determined, all of which are fairly consistent except for the work of Kita et al. [35], which at low densities produces A_ε about 2 % higher than other sources. We chose a value of A_ε within the range of the scatter of the results that connected smoothly with the wide-ranging data of Obriot et al. [34]; no temperature dependence could be discerned within the scatter of the data.

For nonpolar fluids, A_ε is the primary determinant of the dielectric constant at all densities, but higher-order terms can be determined if suitable data exist. B_ε represents interactions

between pairs of molecules, and can be determined from expansion experiments at moderate densities. We used values of B_e reported by Hosticka and Bose [36] at three temperatures, and fitted them to the form used in [1]:

$$B_e = b_0 + b_1 \left(\frac{T_0}{T} - 1 \right), \quad (10)$$

with $T_0 = 273.16$ K.

The term involving C is fitted to describe the experimental data at higher densities, which come from two studies. The measurements of Kita et al. [35] and of Obriot et al. [34] agree fairly well at high densities, but not at low densities. Because they also disagreed with other low-density data, we discarded the data of Kita et al. at densities below 0.006 mol/cm³. Some points from Obriot et al. near the critical density on the 323 K, 333 K, and 348 K isotherms were also identified as outliers and removed, as were a few near-critical points from Kita et al. on their 320 K, 323 K, and 333 K isotherms. The EOS of Guder and Wagner [37] was used to calculate densities from experimental temperatures and pressures. C was given a temperature dependence as in [1]:

$$C = c_0 + c_1 \left(\frac{T_0}{T} - 1 \right), \quad (11)$$

The final fit gave these parameters: $A_e = 16.5$ cm³ mol⁻¹, $b_0 = 69.2$ cm⁶ mol⁻², $b_1 = 38.8$ cm⁶ mol⁻², $c_0 = -177.9$ cm^{6.6} mol^{-2.2}, $c_1 = -171.9$ cm^{6.6} mol^{-2.2}, $D = 1.2$.

In Fig. 4, we plot deviations of the quantity $\frac{\epsilon - 1}{(\epsilon + 2)\rho}$ between our accepted data and Eq. (9).

While clearly there are some systematic differences between the two data sets, the correlation represents the quantity plotted (which has a magnitude near 16.5, the value of A_e) to within better than 1 %.

6 Check Values for Computer Implementation

In Table 4, we give values (including some intermediate quantities) for H₂S and SO₂, calculated from Eq. (2), at $T = 400$ K and $\rho = 0.03$ mol/cm³. More digits are given than justified by the accuracy of the correlations; this provides the ability to check computer implementations. For checking the SF₆ correlation, we supply a point at $T = 300$ K and $\rho = 0.01$ mol/cm³, where Eq. (9) yields $\frac{\epsilon - 1}{(\epsilon + 2)\rho} = 16.5103$ cm³/mol and $\epsilon = 1.59326$.

7 Discussion and Conclusion

We have developed an approach for describing the dielectric constant of polar fluids for which few experimental data are available (in principle, one liquid data point would suffice). Theory provides the model's low-density behavior, which is determined by the molecular polarizability and dipole moment. The behavior at higher densities, and over a range of

temperatures, is determined by molecular dynamics computer simulation. The model as implemented here contains eight parameters, but seven of them are determined entirely from simulation. The final parameter is chosen to scale the correlation so that it matches the available liquid-phase data.

The approach has been applied to the polar compounds H_2S and SO_2 , providing correlations that can be used over a wide range of conditions, including those encountered in geochemical studies. The agreement with the limited experimental data available is excellent for H_2S (see Fig. 2), and fair for the more polar SO_2 (Fig. 3). In addition, a more conventional correlation was developed for the dielectric constant of the nonpolar fluid SF_6 .

The simulation-aided approach used here for H_2S and SO_2 could be applied for other polar fluids, as long as at least some liquid dielectric data exist and there is a good molecular model to be used in simulations. If more extensive experimental data exist, the data could replace simulation for determining some of the parameters. One possible target for future work would be refrigerants. This would be relatively straightforward for molecules such as substituted methanes that can be modeled as rigid, but the approach would become significantly more complicated for molecules that can adopt different conformations, especially if those conformations have different dipole moments.

Acknowledgments

We are grateful to Dr. Thomas Wagner and especially to Dr. Matthieu Galvez for informing us of the geochemical need for models of the dielectric constants of H_2S and SO_2 .

References

1. Harvey AH, Lemmon EW. *Int J Thermophys.* 2005; 26:31.
2. Harvey AH, Prausnitz JM. *J Solution Chem.* 1987; 16:857.
3. Pan D, Spanu L, Harrison B, Sverjensky DA, Galli G. *Proc Nat Acad Sci.* 2013; 110:6646. [PubMed: 23513225]
4. Sverjensky DA, Harrison B, Azzolini D. *Geochim Cosmochim Acta.* 2014; 129:125.
5. Galvez ME, Manning CE, Connolly JAD, Rumble D. *Earth Planet Sci Lett.* 2015; 430:486.
6. Galvez ME, Connolly JAD, Manning CE. *Nature.* 2016; 539:420. [PubMed: 27853207]
7. Mountain RD, Harvey AH. *J Solution Chem.* 2015; 44:2179. [PubMed: 26664009]
8. Fernández DP, Goodwin ARH, Lemmon EW, Levelt Sengers JMH, Williams RC. *J Phys Chem Ref Data.* 1997; 26:1125.
9. Kirkwood JG. *J Chem Phys.* 1939; 7:911.
10. Liu H, Wang Y, Bowman JM. *J Phys Chem B.* 2016; 120:1735. [PubMed: 26436449]
11. Lemmon EW, Span R. *J Chem Eng Data.* 2006; 51:785.
12. Hohm U. *J Mol Struct.* 2013; 1054–1055:282.
13. Russell AJ, Spackman MA. *Mol Phys.* 1997; 90:251.
14. Bishop DM, Cheung LM. *J Phys Chem Ref Data.* 1982; 11:119.
15. Viswanathan R, Dyke TR. *J Mol Spectrosc.* 1984; 103:231.
16. Patel D, Margolese D, Dyke TR. *J Chem Phys.* 1979; 70:2740.
17. Shah MS, Tsapatsis M, Siepmann JI. *J Phys Chem B.* 2015; 119:7041. [PubMed: 25981731]
18. Ketko MH, Kamath G, Potoff JJ. *J Phys Chem B.* 2011; 115:4949. [PubMed: 21476503]
19. Allen, MP., Tildesley, DJ. *Computer Simulation of Liquids.* Clarendon Press; Oxford: 1987.
20. Martys NS, Mountain RD. *Phys Rev E.* 1999; 59:3733.

21. Evans DJ, Murad S. Mol Phys. 1977; 34:327.
22. Martina GJ, Klein ML, Tuckerman M. J Chem Phys. 1992; 97:2635.
23. Frenkel, D., Smit, B. Understanding Molecular Simulation. 2nd. Academic Press; New York: 2002. p. 292-300.
24. Hogg, RV., McKean, JW., Craig, AT. Introduction to Mathematical Statistics. 6th. Pearson Prentice Hall; Upper Saddle River, NJ: 2005.
25. Kemp JD, Denison GH. J Am Chem Soc. 1933; 55:251.
26. Smyth CP, Hitchcock CS. J Am Chem Soc. 1934; 56:1084.
27. Bickford WG. Iowa State Coll J Sci. 1936; 11:35.
28. Havrillak S, Swenson RW, Cole RH. J Chem Phys. 1955; 23:134.
29. Coolidge WD. Ann Physik. 1899; 305:125.
30. Schlundt H. J Phys Chem. 1901; 5:503.
31. Eversheim P. Ann Physik. 1902; 317:539.
32. Le Fèvre RJW, Ross IG. J Chem Soc. 1950:283.
33. Nickerson JD, McIntosh R. Can J Chem. 1957; 35:1325.
34. Obriot J, Ge J, Bose TK, St-Arnaud JM. Fluid Phase Equilib. 1993; 86:315.
35. Kita T, Uosaki Y, Moriyoshi T. Ber Bunsenges Phys Chem. 1994; 98:112.
36. Hosticka C, Bose TK. J Chem Phys. 1974; 60:1318.
37. Guder C, Wagner W. J Phys Chem Ref Data. 2009; 38:33.

Fig. 1.

Reproduction of simulation data for g by Eq. (4). Standard uncertainties in simulated g -factors are similar in size to the symbols plotted.

Fig. 2.
Comparison of correlation to experimental data for the dielectric constant of saturated liquid H_2S .

Fig. 3.
Comparison of correlation to experimental data for the dielectric constant of saturated liquid SO_2 .

Fig. 4.
Deviations of experimental data for $\frac{\epsilon-1}{(\epsilon+2)\rho}$ from Eq. (9) for SF₆.

Table 1

Simulation results for H₂S. Both here and in Table 2, the electric field E is in units of kJ mol⁻¹ Å⁻¹ C⁻¹.

T (K)	ρ (mol/cm ³)	ϵ_{pol}	ϵ_{tot}	g	E
187.8	0.0291	9.284	10.487	1.274	1.026
194.6	0.0288	8.675	9.863	1.241	1.025
195.6	0.0288	8.636	9.824	1.241	1.028
196.0	0.0286	8.748	9.662	1.228	1.021
200.0	0.0288	8.467	9.655	1.232	1.024
212.0	0.0279	7.573	8.723	1.204	1.018
220.	0.0275	7.188	8.320	1.198	1.016
250.	0.0275	6.254	7.383	1.167	1.022
300.	0.0291	5.377	6.570	1.116	1.044
380.	0.0025	1.203	1.281	0.986	0.626
380.	0.0050	1.423	1.593	0.982	0.846
380.	0.0100	1.909	2.282	0.986	0.991
380.	0.0150	2.477	3.058	1.015	0.988
380.	0.0200	3.084	3.887	1.043	0.986
380.	0.0250	3.719	4.729	1.061	1.013
380.	0.0300	4.426	5.647	1.092	1.066
380.	0.0350	5.051	6.482	1.093	1.141
250.	0.0290	6.595	7.787	1.174	1.036
300.	0.0290	5.423	6.610	1.130	1.045
380.	0.0290	4.268	5.447	1.082	1.058
400.	0.0290	4.065	5.244	1.075	1.058
500.	0.0290	3.320	4.487	1.042	1.068
600.	0.0290	2.856	4.010	1.021	1.081
700.	0.0290	2.541	3.684	1.007	1.092
800.	0.0290	2.314	3.447	0.997	1.098
900.	0.0290	2.153	3.279	0.998	1.106
1000.	0.0290	2.025	3.141	0.996	1.112
673.	0.0250	2.385	3.364	1.021	1.038

T (K)	ρ (mol/cm ³)	ϵ_{pol}	ϵ_{tot}	g	E
673.	0.0293	2.635	3.797	1.012	1.093
673.	0.0340	2.939	4.294	1.014	1.160
673.	0.0388	3.244	4.806	1.016	1.240
773.	0.0237	2.109	3.024	1.014	1.029
773.	0.0284	2.346	3.458	1.006	1.089
773.	0.0331	2.603	3.916	1.011	1.158
773.	0.0381	2.849	4.372	0.998	1.236
873.	0.0227	1.908	2.769	0.996	1.023
873.	0.0273	2.120	3.177	1.002	1.082
873.	0.0323	2.354	3.623	1.005	1.152
873.	0.0375	2.584	4.072	0.996	1.234
973.	0.0216	1.767	2.577	1.004	1.017
973.	0.0266	1.953	2.969	0.989	1.078
973.	0.0316	2.159	3.389	0.995	1.150
973.	0.0370	2.384	3.840	0.995	1.232
1173.	0.0198	1.565	2.289	1.002	1.003
1173.	0.0251	1.730	2.670	0.994	1.069
1173.	0.0305	1.901	3.064	0.986	1.144
1173.	0.0359	2.082	3.477	0.992	1.229

Table 2

Simulation results for SO₂. Where the entry for the electric field E is blank, it was not computed in the simulation.

T (K)	ρ (mol/cm ³)	ϵ_{pol}	ϵ_{tot}	g	E
243.	0.0235	19.08	20.22	1.687	
255.	0.0230	17.31	18.42	1.636	
255.	0.0229	16.07	17.18	1.522	
273.	0.0222	14.76	15.84	1.539	
243.	0.0236	19.164	20.259	1.683	0.911
248.	0.0234	18.059	19.143	1.629	0.906
251.	0.0233	17.790	18.870	1.630	0.903
255.	0.0232	17.259	18.335	1.612	0.900
263.	0.0228	16.091	17.148	1.574	0.890
268.	0.0227	16.078	17.130	1.609	0.886
280.	0.0222	14.196	15.224	1.511	0.873
450.	0.0025	1.488	1.583	1.028	0.305
450.	0.0050	2.083	2.317	1.080	0.434
450.	0.0100	3.537	3.985	1.142	0.582
450.	0.0150	5.276	5.962	1.231	0.691
450.	0.0200	7.225	8.147	1.313	0.804
450.	0.0250	9.238	10.391	1.370	0.927
450.	0.0300	11.640	13.028	1.459	1.057
450.	0.0350	13.877	15.497	1.504	1.193
250.	0.0250	19.569	21.118	1.704	0.943
300.	0.0250	15.568	16.726	1.582	0.937
400.	0.0250	10.794	11.949	1.437	0.929
500.	0.0250	8.272	9.425	1.352	0.926
600.	0.0250	6.651	7.800	1.278	0.926
700.	0.0250	5.696	6.842	1.254	0.928
800.	0.0250	4.930	6.071	1.214	0.932
900.	0.0250	4.406	5.543	1.197	0.936
1000.	0.0250	3.910	5.041	1.151	0.951

T (K)	ρ (mol/cm ³)	ϵ_{pol}	ϵ_{tot}	g	E
1100.	0.0250	3.617	4.744	1.149	0.945
1200.	0.0250	3.373	4.496	1.146	0.950
673.	0.02190	5.193	6.143	1.225	
673.	0.02532	5.942	7.105	1.249	
673.	0.02902	6.964	8.297	1.299	
673.	0.03299	7.818	9.338	1.297	
773.	0.02091	4.331	5.282	1.205	
773.	0.02438	4.975	6.090	1.217	
773.	0.02812	5.709	7.000	1.235	
773.	0.03238	6.628	8.120	1.267	
973.	0.01901	3.185	4.034	1.134	
973.	0.02300	3.749	4.788	1.156	
973.	0.02708	4.369	5.603	1.183	
973.	0.03141	5.030	6.468	1.204	
1173.	0.01752	2.566	3.334	1.098	
1173.	0.02169	3.026	3.994	1.120	
1173.	0.02605	3.528	4.714	1.144	
1173.	0.03058	4.064	5.452	1.157	

Table 3Parameters for the correlation of ϵ with Eq. (2)

Parameter	H ₂ S	SO ₂
α (cm ³)	3.66×10^{-24}	4.09×10^{-24}
μ (D) ^a	0.978 325	1.633 08
T^* (K)	380.	450.
ρ^* (mol/cm ³)	0.029	0.025
c_μ	0.241	0.335
a_μ	2.83	1.018
n_μ	0.5	0.75
c_g	1.18	2.516
a_1	2.546	0.8972
n_1	0.90	0.98
a_2	1.883	0.5264
n_2	3.5	1.2

^a 1 D $\approx 3.335\,641 \times 10^{-30}$ C m

Table 4Calculated results at $T = 400$ K, $\rho = 0.03$ mol/cm³

	H ₂ S	SO ₂
$f_i(\rho)$	0.227 45	0.230 73
$A_{\mu, \text{eff}}(\text{cm}^3 \text{ K mol}^{-1})$	8782.3	24 602.4
$g_1(T)$	0.069 51	0.4496
$g_2(\rho)$	0.8800	0.4806
g	1.0722	1.5437
P_K	0.983 19	3.1579
e	5.0239	14.7445