Computer Simulations of Dense Polar Fluids: Hydrogen Chloride

S. Murad
Department of Chemical Engineering
University of Illinois
Chicago, IL 60680

Introduction

Computer simulation techniques have now reached a level of development where it is possible to investigate moderately complex polar substances such as hydrogen chloride, ammonia, sulfur dioxide, and others. These substances are of obvious practical interest to the chemical industry; they are also of considerable fundamental interest, since despite their small size, many interesting orientation-dependent molecular forces are present in such compounds. In this note we present a computer simulation study of hydrogen chloride to demonstrate the possibilities such techniques now offer.

Computer simulations can be carried out using two methods. In molecular dynamics one studies the time evolution of many-body systems using Newton-Euler equations of motion. The second method, Monte Carlo simulation, is based on Markov chain ensemble averaging. Detailed descriptions of these two techniques have been given in several excellent reviews (Evans and Morris, 1984; Gubbins et al., 1983; Streett and Gubbins, 1977; among others). We will, therefore, concentrate primarily on the results we have obtained.

The primary input in a computer simulation study is the intermolecular force potential. Ideally, quantum chemistry can provide such intermolecular potential models. At present this has been done only for simple nonpolar compounds. Consequently, it is necessary to use semiempirical models with some adjustable parameters that can be fitted to available data (e.g., dilute gas or crystal lattice properties that are usually available). The model we have used for HCl has the form

$$u(\underline{r}w_1w_2) \equiv u(12) = u_o(12) + u_{DD}(12) + u_{DQ}(12) + u_{QQ}(12) + u_{\text{ind}}(12) \quad (1)$$

where $\underline{r}$ is the vector joining the two molecules, and w_i the orientations of the molecules. u_o is the nonpolar force contribution, which we modeled using the Lennard-Jones potential

$$u_o = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \quad (2)$$

where ϵ and σ are the Lennard-Jones parameters. u_{DD}, u_{DQ}, and u_{QQ} represent the forces due to the permanent dipoles and quadrupoles, while u_{ind} represents induction forces, which in our study also included many-body effects. Expressions for these forces are given elsewhere (Buckingham, 1978). The parame-

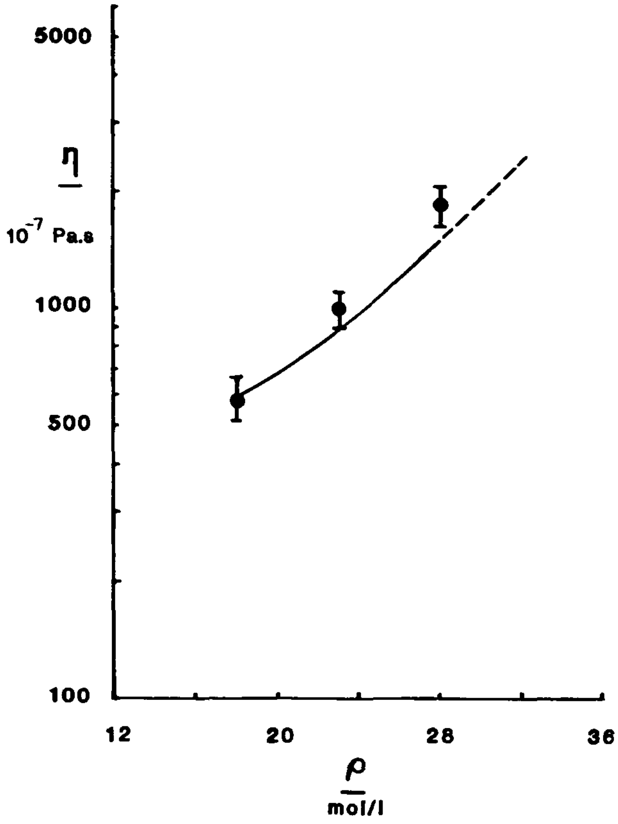

Figure 1. Calculated viscosity of HCl (points) compared with experimental data (solid lines) of Krynicki and Hennel (1963).

ters of the Lennard-Jones potential were obtained from experimental data on the virial coefficients and dimer structure and energy as described in more detail by Murad (1984). Experimental values of the dipole and quadrupole moments, and the polarizability were used for the polar forces. These are well known for HCl and are for example given in Gray and Gubbins (1984). This intermolecular potential model for HCl was then used in molecular dynamics (both equilibrium and nonequilibrium) and Monte Carlo studies. In the following section, we briefly discuss the results obtained. We focus on properties that are difficult to estimate *a priori* using other techniques.

Results

Transport properties of dense fluids (liquids or gases) are particularly difficult to investigate for polar fluids, as discussed by Reid et al. (1977). Computer simulations using the method of molecular dynamics (Monte Carlo cannot be used as it does not treat time as a variable) therefore provide an attractive alternative. Figure 1 shows the results obtained for viscosity compared with the experimental data of Krynicki and Hennel (1963). Figure 2 shows results for the self-diffusion coefficients obtained compared with experimental measurements of Krynicki et al. (1980). As can be seen from these two figures the results are rather satisfactory.

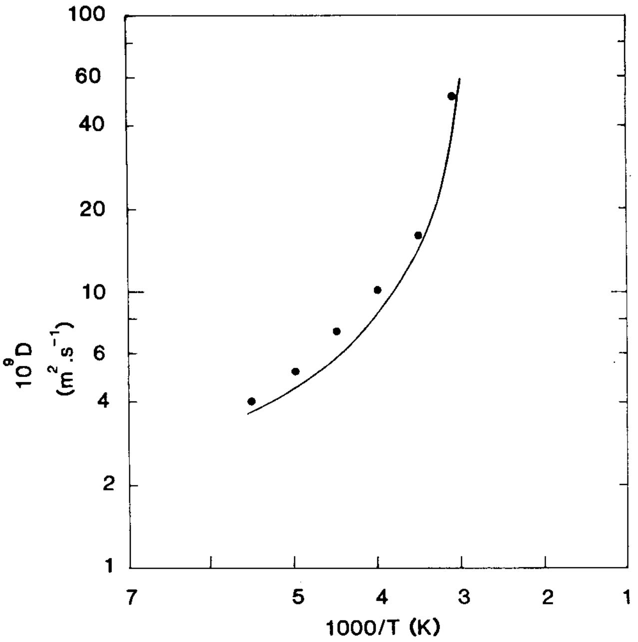

Figure 2. Calculated self-diffusion coefficient of HCl (points) compared with experimental data (solid line) of Krynicki et al. (1981).

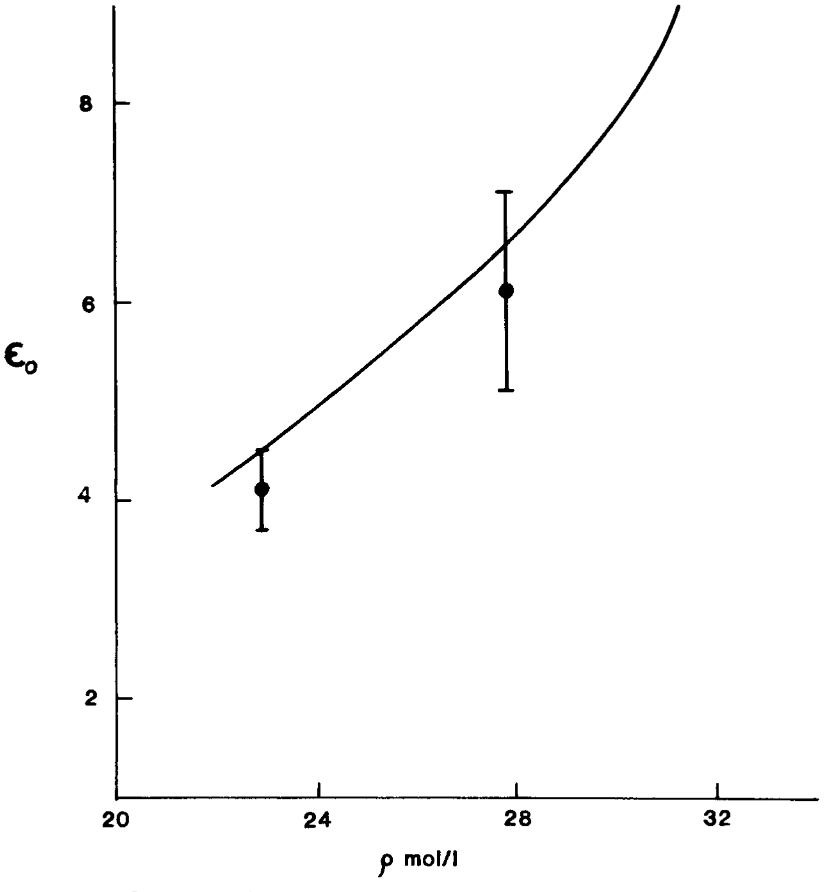

Figure 3. Dielectric constant of HCl obtained from computer simulation (points) compared with experimental data (solid lines).

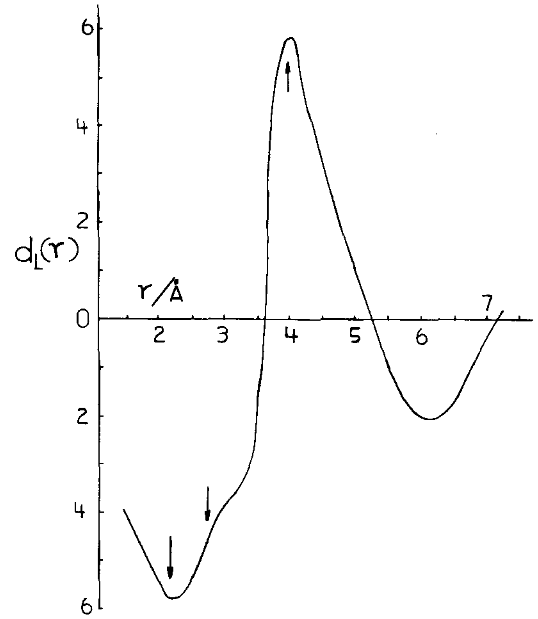

Figure 4. Composite pair correlation function for liquid structure of HCl.
Arrows show features discussed in text.

Dielectric constant is another property that is usually difficult to study. Both molecular dynamics and Monte Carlo can be used to estimate it. Results obtained for HCl are shown in Figure 3, where they are also compared with experimental data given in the *Handbook of Chemistry and Physics* (Chemical Rubber Co., 1984). Good agreement is obtained with experimental data.

Finally, hydrogen bonding, a phenomenon of considerable fundamental and practical interest, can also be investigated using computer simulations. One method of doing this is by examining the composite pair correlation function, d_L (r), which can be calculated quite easily in a simulation described by Powles et al. (1981). Results for d_L(r) for liquid HCl at 293 K are shown in Figure 4. There are three distinct features. The valley at 2.2 Å represents the distance of closest approach of the molecules; the shoulder at 2.7 Å is due to hydrogen bonding, since such shoulders are not present in nonhydrogen bonding liquids. Experimental measurements of Powles et al. (1981), also point to the liquid hydrogen bond to be at approximately this distance. The peak at 4.0 Å is the packing distance of the liquid, which also corresponds quite well with the experimental measurements of Powles et al. It is therefore possible to investigate the presence of hydrogen bonding using computer simulations.

Conclusion

Using the computer simulation technique, we have shown that it is possible to study properties for polar fluids that are considered difficult to predict otherwise. The results, we believe, clearly show the potential of such methods.

Acknowledgment

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Notation

$\underline{r}$ = intermolecular distance
u = intermolecular energy
w = molecular orientation

Subscripts

DD = dipole-dipole contribution
DQ = dipole-quadrupole contribution
ind = induction (including multibody) contribution
o = nonpolar contribution
QQ = quadrupole-quadrupole contribution

Greek letters

ϵ = Lennard-Jones energy parameter
σ = Lennard-Jones distance parameter

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