on carbon. These particles can interact with the active sites of the carbon to form a species at the metal–carbon interface which is stable against high-temperature reduction. This interaction may occur via oxygen atoms bonding with both the carbon surface and iron atoms contacting the carbon. This oxygen could be provided by dissociation of the CO ligands during decomposition. The remainder of the surface Fe can exist in either a reduced or carburized state, but the small size of these particles results in either case in a superparamagnetically collapsed Mössbauer spectrum. For carbons with fewer active sites, more of the particles

are unbound, and these particles sinter and carburize in a manner more similar to that of Fe particles supported on graphite.

The Missing Term in Effective Pair Potentials[†]

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Effective pair potentials used for simulations of polar liquids include the average effects of polarization. Such potentials are generally adjusted to produce the experimental heat of vaporization. It has not been recognized before that the self-energy term inherent in any polarizable model should be included in effective pair potentials as well. Inclusion of the self-energy correction with a consequent reparametrization of the SPC (simple point charge) model of water yields an improvement of the effective pair potential for water, as exemplified by density, radial distribution functions, and diffusion constant.

Introduction

For the purpose of Monte Carlo and molecular dynamics (MD) simulations of the condensed state, effective pair potentials are widely used. Such potentials incorporate the average many-body interactions into the interaction between pairs. In particular for polar molecules, with water as the most extensively studied example, effective pair potentials deviate significantly from pure pair potentials.[1-4] The main reason that pure pair potentials cannot reproduce condensed-state properties for polar molecules is that such potentials neglect the effect of polarizability beyond the level of pair interactions. In water—and in other polar liquids—there is a considerable average polarization, leading to a cooperative strengthening of intermolecular bonding. Thus effective pair potentials invariably exhibit larger dipole moments than the isolated molecules have and produce second virial coefficients larger (in absolute value) than the experimental ones.[2,5] These dipole moments include the average induced moments in the condensed phase.

It is the purpose of this article to show that in the design of effective pair potentials the self-energy due to polarization has been consistently overlooked. The total Coulombic interaction, normally taken as a representation of the electrical interaction, includes the full interaction of induced dipole moments, instead of only half that term, as should be appropriate if the self-energy were included. This leads to too large heats of vaporization and thus to wrong parametrization if the heat of vaporization is used for parametrization. We will show that the simple point charge (SPC) effective pair model for water[4] is considerably improved by including a self-energy correction.

It is through the pioneering work of A. Rahman and F. H. Stillinger on the simulation of liquid water in the early 1970s[6,7] that the importance of effective pair potentials became clear. The first simulation of liquid water used the Ben Naim–Stillinger (BNS) model that had been derived on the basis of both gas-phase

data (second virial coefficient related to the pure pair potentials) and condensed-phase data (ice). This pair potential appeared too weak for the liquid phase and could be improved by a simple scaling of energy. When a modified version, the ST2 potential,[7] was devised, the notion of an effective pair potential was already developed. In the mean time a CECAM Workshop[8] was held in Orsay in 1972, where polarizability was extensively discussed and the effect of introducing polarizability into a modified BNS model was evaluated.[9] This workshop, with Aneesur Rahman as the leading expert on simulation, has been seminal to many subsequent activities in simulations, including biological systems.[10]

Theory

The basic theory of interactions within a system of polarizable polar molecules is well-known.[11] The contribution of the induced dipoles to the energy corresponds to a self-energy term and hence equals half of the corresponding electrostatic interaction term. This can also be formulated as a positive self-energy necessary to create the induced dipole moments, compensating for half the total electrostatic energy of the induced moments. This formulation has, among others, been used by Wertheim[12,13] in a re-

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normalization theory of polarizable polar liquids and in Monte Carlo simulations of a polarizable dipolar hard-sphere liquid.[14] For the sake of clarity we will summarize the derivation of the relevant formulas.

Let us first consider a system of permanent charges q_i and induced dipoles μ_i. Later we will generalize to a description in which the induced moments are incorporated into the charges.

The potentials V_i at the charges are given by

$$V_i = \sum_{j \neq i} [q_j/(4\pi\epsilon_0 r_{ij}) + G(r_{ij})\mu_j] \tag{1}$$

where $G(r) = r/(4\pi\epsilon_0 r^3)$ and $r_{ij} = r_i - r_j$. The induced dipoles, assuming for simplicity an isotropic scalar polarizability α_i, are

$$\mu_i = \alpha_i E_i \tag{2}$$

where

$$E_i = \sum_{j \neq i} [G(r_{ij})q_j + T(r_{ij})\mu_j] \tag{3}$$

Here

$$T(r) = (3rr - 1r^2)/(4\pi\epsilon_0 r^3) \tag{4}$$

Equations 2–4 represent a system of linear equations in μ_i that can be solved for the induced dipoles.

The energy U of the system is found in the usual way by charging the system from zero to the full charges q_i through a charging parameter λ which is increased from 0 to 1. Since the induced dipole moments, and hence also the potentials V_i, are proportional to the charges, the energy U is given by

$$U = \sum_i \int_0^1 \lambda V_i q_i \, d\lambda = \sum_i \tfrac{1}{2} q_i V_i \tag{5}$$

This expression is not equal to the full electrostatic interaction

$$E_{el} = \tfrac{1}{2}\sum_i q_i V_i - \tfrac{1}{2}\sum_i \mu_i E_i \tag{6}$$

that would be calculated if the induced dipoles were treated in the electrostatic interaction as permanent dipoles.

We can rewrite U as

$$U = E_{el} + E_{pol} \tag{7}$$

with

$$E_{pol} = \tfrac{1}{2}\sum_i \mu_i E_i = \tfrac{1}{2}\sum_i \mu_i^2/\alpha_i \tag{8}$$

This formulation considers the total energy as the sum of the full electrostatic interaction and a positive *self-energy* E_{pol} representing the energy it *costs* to distort a molcule to its polarized state. If polarizability is included explicitly, the induced dipoles will adjust themselves so as to minimize the total energy U, since eq 2 follows from the condition

$$\partial U/\partial \mu_i = 0 \tag{9}$$

when U is written in the form of eq 7. A linear polarizability implies that E_{pol} is quadratic in the induced dipole moment.

An interaction model that includes an average induced dipole moment $\langle \mu_i \rangle$ and computes the energy as E_{el} according to eq 6 disregards the internal polarization energy and should be corrected according to eq 7 and 8 for the *average* value of E_{pol}:

$$\langle E_{pol} \rangle = \tfrac{1}{2}\sum_i \langle \mu_i^2 \rangle/\alpha_i \tag{10}$$

If polarizability is not included explicitly into the Hamiltonian, the induced dipole moment is only taken into account as an average, without allowing it to fluctuate. Thus

$$\langle \mu_i^2 \rangle = \langle \mu_i \rangle^2 \tag{11}$$

and the correction term becomes

$$\langle E_{pol} \rangle = \tfrac{1}{2}\sum_i \langle \mu_i \rangle^2/\alpha_i \tag{12}$$

If an interaction model employs charges *only*, using values q_i that are enhanced compared to the charges q_i^0 which represent the correct dipole moment of the isolated molecule, the excess charges $q_i - q_i^0$ represent induced dipole moments. Following exactly the same arguments as in the description given above, and charging the permanent charges from 0 to q_i^0, we arrive at expressions for the energy:

$$U = \tfrac{1}{2}\sum_i q_i^0 V_i \tag{13}$$

where

$$V_i = \sum_{j=i} q_j/(4\pi\epsilon_0 r_{ij}) \tag{14}$$

Alternatively

$$U = E_{el} + E_{pol} \tag{15}$$

with

$$E_{el} = \tfrac{1}{2}\sum_i q_i V_i \tag{16}$$

and

$$E_{pol} = \tfrac{1}{2}\sum_i (\mu - \mu^0)^2/\alpha_i \tag{17}$$

where μ is the dipole moment of the effective pair model and μ^0 is the dipole moment of the isolated molecule. Equation 17 gives the polarization correction that should be applied to effective pair potentials.

Application to Liquid Water

Many effective pair potentials have been used for liquid water,[2] such as the ST2 model,[7] the SPC model,[4] and the TIPS potential[15] and its variants, among which is TIPS2,[16] and models based on quantum-mechanical calculations, such as the MCY model.[17] The latter is expected to be a pure pair potential, but its parametrization is such that it behaves partly as an effective pair potential. We shall concentrate on the simple, but reasonably successful simple point charge (SPC) model that consists of a tetrahedral water model with an OH distance of 0.1 nm, with point charges on the oxygen and hydrogen positions of -0.82 and $+0.41$ e (electronic charge units), respectively, and a Lennard-Jones interaction on the oxygen positions, given by

$$V_{LJ} = -(A/r)^6 + (B/r)^{12} \tag{18}$$

where $A = 0.37122$ (kJ/mol)$^{1/6}$·nm and $B = 0.3428$ (kJ/mol)$^{1/12}$·nm. The SPC model was derived from a series of MD simulations in the parameter space of the hydrogen charge q_H and the repulsion parameter B, with experimental density and vaporization energy as targets. It turned out that acceptable parameters produced a radial distribution curve with a second neighbor peak characteristic for liquid water but quite near the boundary of parameter values that failed to produce such a peak. The almost equivalent, but slightly differently parametrized TIPS potential does not exhibit the second neighbor peak. The dipole moment of the SPC model is 2.27 D, compared to 1.85 D for the isolated molecule. The second virial coefficient is almost twice the experimental value.[5] The diffusion coefficient of the model is 3.6×10^{-5} cm^2·s^{-1} at 300 K, compared to the experimental value of 2.4×10^{-5}. The potential energy for liquid SPC water[5] at 300 K is -41.7 kJ/mol, and the density at 300 K and atmospheric pressure[5] turns out to be 0.98 g·cm^{-3}. Although the model behaves quite satisfactorily for most purposes, there is room for im-

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TABLE I: Simulations on Polarization-Corrected SPC:Water[a]

model	SPC[b]	1	2	3	4 = SPC/E	exptl
q_H	0.41	0.437	0.422	0.427	0.4238	
B	0.3428	0.34505	0.343	0.3431	0.3428	
$\mu/10^{-30}$ C m	7.585	8.085	7.807	7.900	7.841	6.171 (vac)
μ/D	2.274	2.424	2.341	2.368	2.351	1.85 (vac)
E_{pol}	3.74	6.86	5.01	5.60	5.22	
MD run/ps	20	15	17.5	17.75	27.5	
E_{pot}	−37.7	−42.0	−40.6	−41.9	−41.4	−41.5[c]
T/K	308	306	307	305	306	
press./bar	−1	4	6	9	6	
density/ g·cm^{-3}	0.970	0.981	0.992	0.994	0.998	0.995 (305 K)
diff const	4.3	(2.7)	2.9	2.2	2.5	2.4 (300 K) 2.7 (305 K)
$\partial E_{pot}/\partial q_H$	−236	−271	−259	−266	−262	
$\partial E_{pot}/\partial B$	754	875	835	864	850	
$\partial p/\partial q_H$	−7.9		−8.9	−9.1	−9.1	
$\partial p/\partial B$	8.2		9.2	9.5	9.4	

[a] Units (if not specified): for charges, e (electronic charge); for energies, kJ/mol; for B, (kJ/mol)$^{1/12}$·nm; for diffusion constant, 10^{-5} cm^2·s^{-1}; for pressure, bar. [b] New run under same conditions as models 1–4. [c] Including quantum corrections (ref 5).

provement with respect to density, radial distribution function, and diffusion constant.

With a value[18] of 0.001 445 nm^3 for the polarizability $\alpha/4\pi\epsilon_0$, or 1.608×10^{-40} F m for α, the average induced dipole moment in the SPC model corresponds to 3.74 kJ/mol polarization energy. Hence the corrected potential energy for the SPC model is only −38.0 kJ/mol. In order to increase the potential energy again, the charge on the model should be enhanced.

We have reparametrized the SPC model to obtain the correct density and energy. This was done by performing four trial simulations at different combinations of q_H and B, as given in Table I. Each simulation was performed on a cubic periodic system of 216 rigid water molecules, using a time step of 0.001 ps and a cutoff radius of 0.9 nm. The SHAKE procedure[19] was used to conserve intramolecular constraints. The system was coupled to a bath[20] of constant temperature (300 K) and pressure (1 bar) with time constants of 0.4 ps for the temperature coupling and 0.5 ps for the pressure coupling. Before each analysis an equilibration over 5 ps was carried out; the first run started from a SPC configuration after a 15-ps equilibration. Table I also includes values for the partial derivatives of potential energy and pressure with respect to the two parameters q and B. These values have been determined from the ensemble averages of the derivatives of the Hamiltonian (for the energy) and the virial (for the pressure). Such derivatives are convenient to determine the sensitivity of properties to model parameters and can be accumulated almost without any additional computational effort.

The fourth model gives the best results. We shall denote it by SPC/E, the *extended simple point charge* model. It is characterized by three point masses with OH distance of 0.1 nm and HOH angle equal to the tetrahedral angle, with charges on the oxygen and hydrogen equal to −0.8476 and +0.4238 e, respectively, and with Lennard-Jones parameters of oxygen–oxygen interaction according to eq 18: $A = 0.371\,22$ (kJ/mol)$^{1/6}$·nm and $B = 0.3428$

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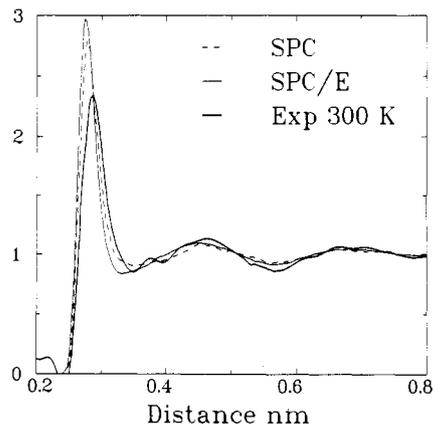

Figure 1. Radial distribution function of oxygen–oxygen distances for SPC and SPC/E water, both at ~306 K, and for real water at 298 K. The latter values are from ref 21.

(kJ/mol)$^{1/12}$·nm. The SPC/E model has a dipole moment of 2.35 D and a polarization correction to the total electrical energy of 5.22 kJ/mol. The energy of a hydrogen-bonded pair in its most favorable configuration was found to be −30.0 kJ/mol (uncorrected for polarization energy), compared to −27.6 kJ/mol for the SPC model.

The *diffusion constant* has improved considerably compared to the SPC model; it is within simulation error equal to the experimental value. The oxygen–oxygen radial distribution curve is given in Figure 1 for the SPC/E and the SPC model, both at 306 K, together with experimental values[21] at 298 K. The agreement with experiment is somewhat better for the SPC/E than for the SPC model. The first peak is too much inward and too sharp and high, as it is for all models employing a repulsive term proportional to r^{12}; another choice of the repulsive shape could possibly remedy this less critical feature.

Conclusions

Application of a polarization correction to the effective pair potential of water brings the model more safely within the region of parameter space that produces well-defined second neighbor peaks in the radial distribution curves, characteristic for liquid water. Also other features of the model improve, in particular the density and diffusion constant. On theoretical grounds the polarization correction should indeed be included, and it seems a general emission in all effective pair potentials used to date that this term is missing! But even with proper correction, effective pair potentials are a surrogate for polarizable potentials. The importance of the polarization correction presented here once more emphasizes the need for a good (but simple) polarization model. We will shortly present such a model that is computationally not very demanding.

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