

MONTE CARLO SIMULATION OF THE AVERAGE FORCE BETWEEN TWO IONS IN A STOCKMAYER SOLVENT

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Received 21 April 1975

The average force between two ions in a Stockmayer fluid has been computed as a function of interionic distance by Monte Carlo simulation. The ion-solvent energy has also been calculated for each ionic configuration.

1. Introduction

This report is on a Monte Carlo calculation of the average force between a pair of ions in a polar solvent. The latter is assumed to be a Stockmayer fluid at a reduced density $\rho^* = 0.74$ with the reduced temperature set at 1.0. The dipole moment μ of each solvent molecule is 1.36 debye and the Lennard-Jones parameters σ and ϵ/k have been taken as 3.405 Å and 119.8 K respectively. The dielectric constant D of this fluid is approximately 30 according to the mean spherical approximation for point dipoles [1]; it is nearly 12 when the Onsager theory is employed [2]. To complete the description of our model system of two ions in a polar solvent, we must also specify the ion-ion and ion-solvent interactions. We have, of course, the usual Coulomb potential (e_+e_-/r) between the ions, and the ion-dipole potential ($e_i\mu\cos\theta/r^2$) between an ion of charge e_i and a solvent molecule of dipole moment μ , but in addition to these, we also suppose that there are Lennard-Jones interactions between all species (ions and solvent molecules) in solution. The molecular parameters, σ and ϵ/k , for these additional forces are taken to be precisely the same as those assumed for the solvent-solvent potential, so that if the charges on the ions and on the di-

poles are turned off, there would be no way of distinguishing the two molecules which were ions before discharge from the sea of solvent molecules which surround them.

An important conclusion of our work is the demonstration of the feasibility (in terms of computer techniques and running time) of a Monte Carlo calculation of the potential of average force between two ions at infinite dilution. Apart from this some interesting features are already apparent in our results with the simple Stockmayer solvent. For example, the "hump" which appears in the average force as a function of interionic separation (fig. 1) seems to be related, at least partly, to the granularity of the solvent. Much more extensive (and costly) computer runs will have to be done to confirm this effect, and its interpretation, but the results obtained so far seem to be statistically significant. We have also calculated the energy of interaction between an ion and the surrounding solvent medium as a function of the distance of separation between two ions (fig. 2). These results have a bearing on our understanding of how the solvation energy of one ion is influenced by the presence of another nearby.

To extend these studies to aqueous systems, we would require a more sophisticated model for the

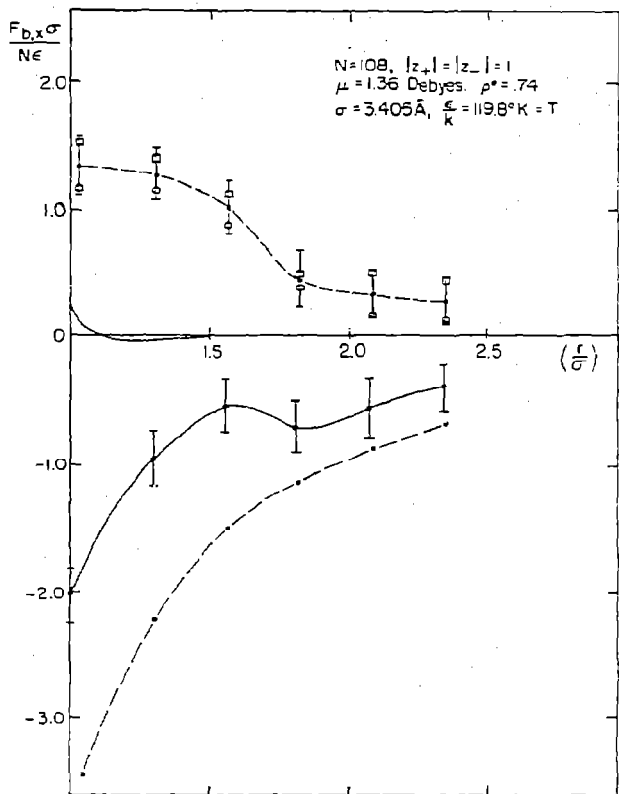


Fig. 1. The average force (in reduced units) on an ion b as a function of the distance r from an ion of opposite sign. The curves from top to bottom represent $\langle F_{b,x}^{\text{sol}} \rangle \sigma / N\epsilon$, $F_{b,x}^{\text{LJ}} \sigma / N\epsilon$, $\langle F_{b,x}^{\text{Coul}} \rangle \sigma / N\epsilon$ and $F_{b,x}^{\text{Coul}} \sigma / N\epsilon$. The points \square and \circ are the magnitudes of the mean ion-solvent forces computed for each ion; the averages of these, shown as dark circles on the same curve, are our best estimates, used to calculate the total average force $\langle F_{b,x} \rangle \sigma / N\epsilon$ shown in the same figure.

solvent, such as the one employed in recent molecular dynamic studies of liquid water by Rahman and Stillinger [3]. With more complicated potentials it may be also necessary to study a larger system, with an attendant increase in computer time and work, but our preliminary work here shows that efforts in this direction are likely to be rewarding.

2. Theoretical background

A clue to the resolution of the electrolyte problem comes from the realisation that the reduced ionic density ρa^3 in a simple aqueous ionic solution at a concentration typical of the usual preparative range (e.g.,

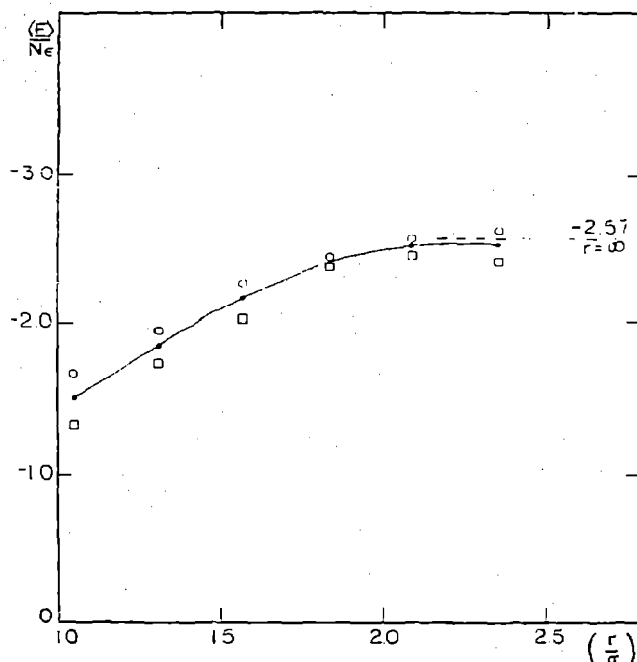
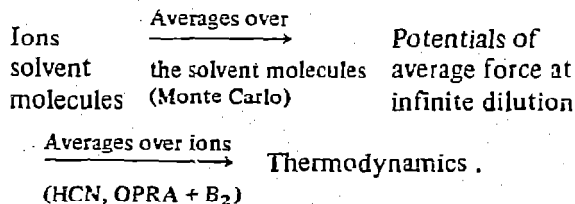


Fig. 2. The average ion-solvent energy (in reduced units) of an ion as a function of the distance from an ion of opposite sign. The limiting value at $r = \infty$ is the energy calculated for a single ion in the solvent medium. The points \square and \circ are the individual mean ion-solvent energies for each ion, while the dark circles represent the average of these two energies which are our best estimates of $\langle E \rangle / N\epsilon$.

2 molar NaCl solution) is nearly an order of magnitude lower than the reduced solvent density ρa_s^3 . Typical values for a 2 molar 1-1 electrolyte such as sodium chloride would be ≈ 0.05 for the reduced ionic density and nearly 0.7 for the reduced solvent density. The ion-ion interactions are also very different from the ion-solvent and solvent-solvent potentials, so that it is useful to separate the statistical mechanical calculation into two parts by averaging successively over the solvent molecules and then over the solute (ionic) particles [4]. It is the first of these averaging processes which interests us here, a problem which has been treated theoretically elsewhere [5,6].



We assume that the potential of average force at infinite dilution among n ions is pairwise additive,

$$W_n^0(1, 2, \dots, n) = \sum_{1 < a < b < n} W_2^0(a, b), \quad (1)$$

so that it is really the determination of the solvent averaged pair-potential $W_2^0(a, b)$ which concerns us here. When this is known, the second problem of averaging over the coordinates of the ions can be tackled by a variety of methods which have been developed recently, e.g., the hypernetted chain or ORPA + B₂ approximations [6].

Suppose two ions a and b are held fixed at a distance r_{ab} apart in a box of volume V containing N solvent molecules whose coordinates (position and orientation) are denoted by $\{N\}$. Then the expression for $W_2^0(a, b)$ is

$$\exp[-\beta W_2^0(a, b)] = (V^2/Z) \int \exp(-\beta U_{N+2}) d\{N\}, \quad (2)$$

where Z is the canonical ensemble partition function for the whole system of $N+2$ particles, and U_{N+2} is the configuration energy of this system. We can split U_{N+2} into two parts: the direct ion-ion interaction u_{ab} and the rest U'_{N+2} which includes ion-solvent and solvent-solvent terms.

$$U_{N+2} = u_{ab} + U'_{N+2}. \quad (3)$$

The ion-ion potential u_{ab} is the sum of a Lennard-Jones term and a bare Coulomb term:

$$u_{ab} = u_{ab}^{\text{LJ}} + e_a e_b / r_{ab}. \quad (4)$$

Since it does not enter into the averaging process implicit in (2) we may write

$$\exp(-\beta W_2^0) = (V^2/Z) \exp(-\beta u_{ab}) \int \exp(-\beta U'_{N+2}) d\{N\}, \quad (5)$$

or taking the logarithm of both sides

$$-\beta W_2^0 = -\beta u_{ab} + \ln \left[(V^2/Z) \int \exp(-\beta U'_{N+2}) d\{N\} \right]. \quad (6)$$

The interionic potential u_{ab} is of course known completely, which reduces the problem of determining W_2^0 to the problem of calculating the second term in (6). A Monte Carlo calculation of this term is difficult,

and it becomes convenient instead to compute the average force on each ion by taking the appropriate gradient of (6). The average force on ion b for example is

$$\begin{aligned} \langle F_b \rangle &\equiv -\nabla_b W_2^0 \\ &= -\nabla_b u_{ab} + \frac{\int \nabla_b U'_{N+2} \exp(-\beta U'_{N+2}) d\{N\}}{\int \exp(-\beta U'_{N+2}) d\{N\}}. \end{aligned} \quad (7)$$

The first term in (7) is simply the direct force on ion b due to ion a ; it is the sum of a Lennard-Jones force and a Coulomb force.

$$-\nabla_b u_{ab} = F_b^{\text{LJ}} + F_b^{\text{Coul}}. \quad (8)$$

The next term in (7), which we have calculated here by Monte-Carlo simulation, is the average force which the solvent molecules exert on ion b . Writing this as $\langle F_b^{\text{solv}} \rangle$, we have

$$\langle F_b \rangle = F_b^{\text{LJ}} + F_b^{\text{Coul}} + \langle F_b^{\text{solv}} \rangle, \quad (9)$$

where

$$\langle F_b^{\text{solv}} \rangle = \frac{\int F_b^{\text{solv}} \exp(-\beta U'_{N+2}) d\{N\}}{\int \exp(-\beta U'_{N+2}) d\{N\}} \quad (10)$$

and

$$\begin{aligned} F_b^{\text{solv}} &= -\nabla_b U'_{N+2} \\ &= \sum_s F_{sb}^{\text{LJ}} - \sum_s \left(\frac{e_b \mu_s}{r_{sb}^3} - 3e_b \frac{(\mu_s \cdot r_{sb}) r_{sb}}{r_{sb}^5} \right). \end{aligned} \quad (11)$$

By resolving this force into three mutually perpendicular components, one finds, by symmetry, that the only non-vanishing solvent-averaged force on ion b is $\langle F_{b,x}^{\text{solv}} \rangle$, where the x direction is along the line joining the two ions a and b . Our Monte-Carlo simulation monitored the six components of the forces on the two ions. In an exact calculation, four of these components (along the y and z directions) would be expected to be zero, while the other two (along the x direction) should be equal but opposite in sign, since the two ions are identical except for the signs of the ionic charges. The average ion-solvent energy

$$\langle E_b \rangle = \frac{\int E_{sb} \exp(-\beta U'_{N+2}) d\{N\}}{\int \exp(-\beta U'_{N+2}) d\{N\}}, \quad (12)$$

where

$$E_{sb} = u_{sb}^{LJ} + (e_b \mu_s \cdot r_{sb}) / r_{sb}^3. \quad (13)$$

We wish to emphasize again that there are only two ions in our system. They are placed at a distance r_{ab} apart, and the averages that we calculate are averages over the positions and orientations of the solvent molecules, which are, of course, influenced by the presence of the two ions.

3. Monte-Carlo calculations

The Monte-Carlo method used was essentially a modification of the procedure described by McDonald [5] for a Stockmayer fluid, so we will discuss only those features that were peculiar to this calculation. The first novelty was that there were two particles, namely the ions, which were always held fixed during each run. One of these ions was a positive ion and the other was negatively charged. They were placed symmetrically about the center of a cube on a line passing through the middle and parallel to four edges. The solvent molecules were 108 other particles in the same cube of volume V maintained at temperature T . Each side of cube was approximately 5.24σ in length, and calculations were done for six interionic distances ranging from 1.048σ to 2.353σ at intervals of 0.261σ .

A chain of configurations was generated by choosing, displacing and rotating solvent molecules randomly in precisely the way described by McDonald in his study of Stockmayer molecules [7]. The change in energy of the whole system was calculated after each move, which was accepted or rejected by applying the criterion suggested by Metropolis et al. [8]. The initial configuration of the N solvent molecules was either the equilibrium state of a Stockmayer fluid obtained in an earlier study or it was the final state determined by us (usually in the previous run) for the interionic distance closest to the one under consideration. In either case, the first 50 000 configurations were not used in calculating the configurational averages. An additional 800 000 configurations were generated for this purpose, and the average force on each ion and its energy of interaction with the solvent molecules were computed as mean values over these configurations. Periodic boundary conditions were used throughout, but the interactions between ions in neighboring cells

were suppressed. Since the line joining the ions is an axis of symmetry for the system, some errors in computing the interactions between the ions and solvent molecules in the primary cell with solvent particles in neighboring cells were unavoidable. We have also not allowed for the effect of the reaction field, a necessary correction if our results are to reflect the behavior of an infinitely large system. By ignoring it, the absolute magnitude of the energy and the large r_{ab} -dependence of the average force may have been altered, but it is less likely that the behavior of the forces at small r_{ab} would have been radically changed. Important chemical effects are included in the latter, since it reflects, in the language of solution chemists, the net effect due to solvent granularity, co-sphere overlap and dielectric saturation and repulsion [4,6].

Our main results are summarized in table 1. The average forces and energies are given in reduced units ($F_{b,x} \sigma / Ne$ and E / Ne), but the magnitudes are in fact the average of the magnitudes of the Monte Carlo results for each ion. We are able to do this, and incidentally improve the accuracy of our calculations, because, as we have remarked earlier, the average force on a positive ion is equal in magnitude but opposite in sign to the corresponding force on a negative ion while the solvation energies of both ions are equal in magnitude and sign. These, of course, follow from the symmetry of our model system. In fig. 1 (upper part) and in fig. 2 we have displayed the individual as well as the average forces and energies for each ion. The error bars in fig. 1 (also table 1) equal twice

$$\max \{ \langle F_y^{\text{soliv}} \rangle \sigma / Ne, \langle F_z^{\text{soliv}} \rangle \sigma / Ne \},$$

which should be zero since there are no solvent-averaged forces in the y and z directions. The discrepancies between the magnitudes of the forces on the two ions in the x direction, which is along r_{ab} , are also within these error bars.

Figs. 1 and 2 also show how strongly the average forces and energies are influenced by the proximity of the two oppositely charged ions. When r_{ab} is very large, the average force on each ion should tend to zero as $e_a e_b / Dr_{ab}^2$, and the ion-solvent interaction energy of either ion must approach the energy of a single ion in the solvent medium. We have found by a Monte-Carlo calculation of the interaction energy of one ion placed at the center of the cube, that this limiting energy is approached rapidly at first when r_{ab}

Table 1

Monte-Carlo calculation of the average force on an ion and its average energy in a Stockmayer solvent containing just two ions. The separation between the ions is r , the temperature $T = 119.8$ K and the dipole moment of the solvent is 1.36 debye. The Lennard-Jones parameters are $\sigma = 3.405$ Å and $\epsilon/k = 119.8$ K. The x direction is along the line joining the two ions

$\frac{r}{\sigma}$	$\frac{F_{b,x}^{LJ}\sigma}{N\epsilon}$	$\frac{F_{b,x}^{Coul}\sigma}{N\epsilon}$	$\frac{\langle F_{b,x}^{solv} \rangle \sigma}{N\epsilon}$	$\frac{\langle F_{b,x} \rangle \sigma}{N\epsilon}$	$\frac{\langle E \rangle}{N\epsilon}$
1.048	0.082	-3.449	1.353 ± 0.2	-2.014 ± 0.2	-1.502
1.309	-0.020	-2.211	1.290 ± 0.3	-0.941 ± 0.3	-1.847
1.571	-0.001	-1.535	1.014 ± 0.2	-0.522 ± 0.2	-2.152
1.834	-0.000	-1.126	0.427 ± 0.16	-0.699 ± 0.16	-2.430
2.090	-0.000	-0.861	0.327 ± 0.15	-0.540 ± 0.15	-2.528
2.353	-0.000	-0.687	0.282 ± 0.20	-0.402 ± 0.20	-2.540
∞	0	0	0	0	-2.569

changes from 1.0σ to 2.0σ and then perhaps more slowly beyond $r_{ab} = 2.0 \sigma$. That is to say, our results do not exclude the possibility of a second region beyond $r_{ab} = 2.0 \sigma$ where the average energy changes much more slowly with the interionic distance until it reaches the limiting energy of single ion at $r_{ab} = \infty$. An independent calculation of the potential of average force of two ions in a hard-sphere dipolar solvent has been completed recently by Patey [9].

Acknowledgement

We wish to thank Dr. Aneesur Rahman, Professor Harold Friedman and Professor K. Singer for their encouragement and advice. We also thank Dr. Carl Moser for inviting us to attend the CECAM workshop on ionic liquids held at Orsay (France) in June 1974, where this work was done. Finally, we are indebted to

Professor George Stell for helpful comments on the manuscript.

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