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Computer simulation of chemical equilibria

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Abstract. The chemical potential is a key quantity in the theory of chemical equilibria and solvation processes in the liquid phase. Several approaches, all equivalent in principle, were proposed in the literature to evaluate this quantity by computer simulation. It will be shown for some examples that these methods converge to the same values for molecular liquids but yield different values for ionic solutions. This discrepancy is discussed in detail.

1. Introduction

The investigation, by computer simulation, of chemical equilibria in solution is a field in full development. The key quantity to evaluate is the equilibrium constant $K(T, p)$; its calculation can be reduced to that of the chemical potentials. There are two methods of obtaining these quantities: one of them is the test particle method (Byckling 1961, Widom 1963) and the other is the free energy perturbation method (Zwanzig 1954). Unfortunately, although they are both exact and equivalent in principle, they are not so in practice. What is worse, no internal convergence test exists which permits an estimate of the quality of the results, a source of a considerable controversy. A way out of the impasse is to compare the two methods. The coincidence of the results can be considered as an external convergence test. The purpose of the present paper is to investigate a number of representative systems from this point of view. It will be shown that, for molecular liquids and for sufficiently long simulation runs, both methods converge. This is not the case for ionic solutions. The role of the polarizability in these systems is also discussed.

2. Methods of calculation

The basic formula for the excess chemical potential in the test particle method has the following form

$$\mu^{\text{ex}} = -k_{\text{B}} T \ln \langle \exp(-\beta\Phi) \rangle_N \quad (1)$$

where Φ is the energy difference between a system composed of $N + 1$ particles and one of N particles. The test, or solute, particle is thrown randomly into the computer generated solvent configurations and the contribution of each event to the average in equation (1) is evaluated. The main difficulty is that at liquid densities only a very small

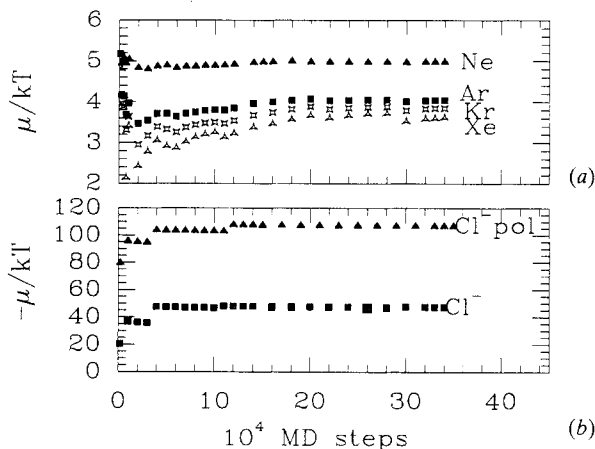


Figure 1. (a) Cumulated average of the excess chemical potential for noble gases in water. (b) Cumulated average of the excess chemical potential of Cl^- in water where the upper curve corresponds to the calculation with the polarization energy included, and the lower curve without it. The pressure correction is not reproduced in these figures.

number of events contribute to μ^{ex} since in this case the test particle overlaps the solvent particles too frequently. Important efforts were thus made to improve the accuracy of the calculation (Powles *et al* 1982, Shing and Gubbins 1982) but it is only in the last few years that, by introducing the excluded volume mapping (Guissani *et al* 1985, Heinbuch and Fisher 1987, Deitrick *et al* 1989) and with the help of supercomputers such as CRAY 1, CRAY 2 and CYBER 205, the accuracy of the method has been drastically increased.

In the perturbation method, the difference ΔF^{ex} in free energies between the states A and B is calculated by introducing a series of M intermediate states, where $U_{\lambda_i} = U_A + \lambda_i(U_B - U_A)$ and U_A and U_B are internal energies of A and B, respectively. One has:

$$\Delta F^{\text{ex}} = -K_B T \sum_{i=1}^M \ln \langle \exp[-\beta(U_{\lambda_{i+1}} - U_{\lambda_i})] \rangle_{\lambda_i} \quad (2)$$

$$\Delta F^{\text{ex}} = \sum_{i=1}^M \langle U_{\lambda_{i+1}} - U_{\lambda_i} \rangle_{\lambda_i} \quad (3)$$

Equation (3), valid only if the energy difference between successive states is much smaller than $K_B T$, is called the 'slow growth' formula.

Each of these two methods has its advantages and disadvantages. The main weakness of the test particle method is the absence of an internal test of convergence. The well known f-g convergence test is not easily applicable to diluted solutions (Powles *et al* 1982). The internal convergence test is also absent in the perturbation method. In fact, the reversibility of the transformation process, from state A to state B, which is the basic assumption underlying this method, is not easily realized. The closure of the hysteresis loop is by no means a sufficient condition. Even in the 'slow growth' method where the energy changes very little between the two states ($\delta\lambda \sim 10^{-4}$), the system always 'lags' the Hamiltonian and is never in equilibrium (Pearlman and Kollman 1989). However,

Table 1. Excess chemical potentials of noble gases in water (kcal mol⁻¹).

Solute	Test particle (our values)	Slow growth (Straatsma and Berendsen 1986)	Slow growth (Pearlman and Kollman 1989a)	Dynamically modified windows (Pearlman and Kollman 1989a)
Neon	2.70	2.41 ± 0.20	2.60 ± 0.77	2.51 ± 0.19
Argon	2.08	1.98 ± 0.57	—	—
Krypton	1.94	1.60 ± 0.55	2.79 ± 0.63	1.65 ± 0.39
Xenon	1.75	1.17 ± 0.05	3.41 ± 0.74	1.05 ± 0.28

comparing the results of the test particle and perturbation methods may represent a useful external convergence test and will be employed in the subsequent analysis.

3. Hydrophobic hydration of rare gases

The first element of comparison refers to the rare gas–water systems which have recently been studied in the frame of the perturbation method by Straatsma *et al* (1986), and by Pearlman and Kollman (1989a). These authors have evaluated, by the slow growth procedure, the excess chemical potential of the noble gases Ne, Ar, Kr and Xe in water. The molecular configurations of the systems were generated by molecular dynamics simulations. Although there are small differences in the potentials (TIP3P or SPC for the water–water interactions) the results are fully comparable. Straatsma *et al* have performed a long simulation run of roughly 110 ps whereas Pearlman and Kollman have realized, first, a short run of roughly 20 ps in which the coupling parameter λ was linearly modified, and then another run of similar computer time where the variation of λ was modified during the run in order to improve the sampling ('dynamically modified windows'). Our contribution to this problem was to take the same potential as Straatsma *et al* and to calculate the excess chemical potential in the framework of the test particle method. Considering a system of 256 water molecules, we first realized a molecular dynamics simulation run of 160 ps, or equivalently of 320 000 steps, and then sampled each 10th step 4000 times to evaluate μ^{ex} (figure 1(a) and table 1).

It is evident that our results and those of Straatsma *et al* are in good agreement for Ne, Ar and Kr. The short runs of Pearlman and Kollman gave bad results, but using the dynamically modified windows permitted them to re-establish good agreement between the calculations. Xenon poses some problems since it is a large solute and difficult to treat by either of these methods. We obtain a different value from that of Straatsma *et al* and Pearlman and Kollman (1.75 instead of 1.17, 3.41 or 1.05) but we believe that our result is correct. In spite of this uncertainty, we conclude that, in the case of rare gas–water systems and, more generally, in the case of molecular solutions, the test particle and perturbation methods converge to the same values. However, the simulation runs must be long enough, and the 'slow growth' method should be used with caution.

4. Ionic hydration

The second part of our comparison is the Cl⁻–water system. We chose to check whether the presently available computer simulation techniques could be applied to the unfavourable case of the structure breaking ions. This system has already been studied carefully

by applying the perturbation method (Straatsma and Berendsen 1988). These authors started with a system containing one neon atom plus 216 water molecules and then gradually mutated the neon atom into an ion. The spc potential was used for the water–water interactions and a pair potential without polarizability for the ion–water interactions. A long range correction due to Born was employed, but a dependence of the results on the cut-off radius of interaction was observed.

Our contribution in this domain was to recalculate μ^{ex} of Cl^- with the help of the test particle method by using the same interaction potentials as Straatsma and Berendsen. In practice, a molecular dynamics run of 160 ps, including an Ewald summation, was generated with 256 water molecules. Each 10th step was sampled by throwing at random the solute particle (Cl^-) in the basic box N times, where $4 \times 10^4 < N < 2 \times 10^5$. This very long calculation, involving 10^9 – 10^{10} events, was performed to find configurations in which the water molecules of the first hydration shell are conveniently oriented. In spite of this effort, and contrary to the case of rare gases in water, the test particle result differs considerably from that obtained using the perturbation method: we obtain $\mu_{\text{Cl}^-} = -28.4 \text{ kcal mol}^{-1}$ whereas Straatsma and Berendsen find $-75.4 \text{ kcal mol}^{-1}$, which is close to the experimental value. Still, the evolution of the cumulated average for μ_{Cl^-} with the length of the simulation run seems to indicate that, after 100 000 molecular dynamic steps, the calculation has converged (figure 1(b)). Of course, the ability of the ‘slow growth’ procedure to maintain the equilibrium, uncertain even in the case of a rare gas atom interacting with water, makes the reliability of the method questionable when the strong ion–water interactions are involved. Recent calculations by Caillol *et al* (1990) reinforce this belief. It may even be that the periodic boundary conditions, introducing spurious interactions between the water molecules of the basic cell and the replicates of the ion, make the results of the two methods intrinsically different. A further study would be necessary to settle this point.

Another aspect of the problem concerns the role of the polarizability of water in the hydration process. Thus we have performed a new calculation of μ_{Cl^-} with the help of the test particle method by including the water and ionic polarizabilities explicitly; the latter are known *a priori* (Guillot *et al* 1989). This new calculation gives $\mu_{\text{Cl}^-} = -63.9 \text{ kcal mol}^{-1}$, a value in much better agreement with the experiment where $\mu_{\text{Cl}^-} \sim 75 \text{ kcal mol}^{-1}$. The contribution of the water polarizability to the ionic solvation is essentially energetic and has virtually no entropic counterpart. In fact, the entropy of solvation, ΔS , can also be evaluated in the framework of the test particle method and turns out to be almost unaffected by the polarization effect. We find $T\Delta S_{\text{Cl}^-} = -9.4 \text{ kcal mol}^{-1}$ with polarizability, $-8.8 \text{ kcal mol}^{-1}$ without it, whereas $T\Delta S_{\text{exp}} \sim -5.5 \text{ kcal mol}^{-1}$. Our results thus permit us to understand the puzzling fact, known for many years in thermochemistry, that the solvation entropies of Cl^- and Ar in water are comparable in magnitude whereas their solvation enthalpies differ by more than one order of magnitude.

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