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Comparison of Hypernetted Chain Equation and Monte Carlo Results for a System of Charged Hard Spheres

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Extensive calculations have been made by the Monte Carlo method[1,2] and by the HNC integral equation method[3,4] of the observable properties of a model system in which the N-body potential is a sum of pair contributions of the form

$$u_{ab}(r) = u_{ab}^*(r) + e_a e_b/\epsilon r, \qquad (1)$$

$$u_{ab}^* = \infty \qquad \text{if } r < r_a^* + r_b^*,$$

$$= 0 \qquad \text{if } r_a^* + r_b^* < r. \qquad (2)$$

This is the primitive model for an electrolyte solution in a solvent of dielectric constant ϵ, a system of charged hard spheres in a dielectric medium.

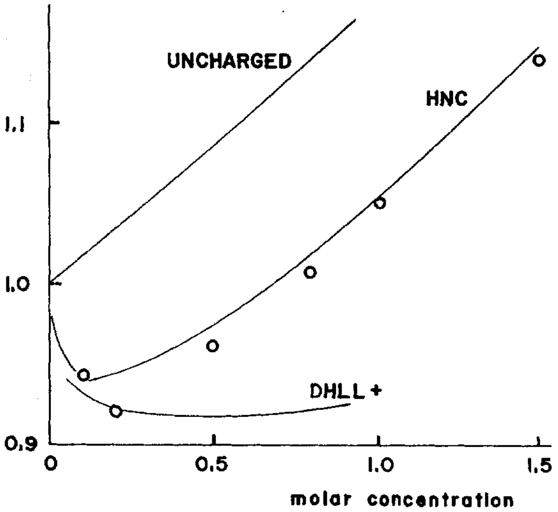

FIG. 1. Comparison of HNC and Monte Carlo results. The circles are the Monte Carlo results. The MC computations at 0.2 and 0.8M are for fewer ions or shorter chains than the others and are less reliable.

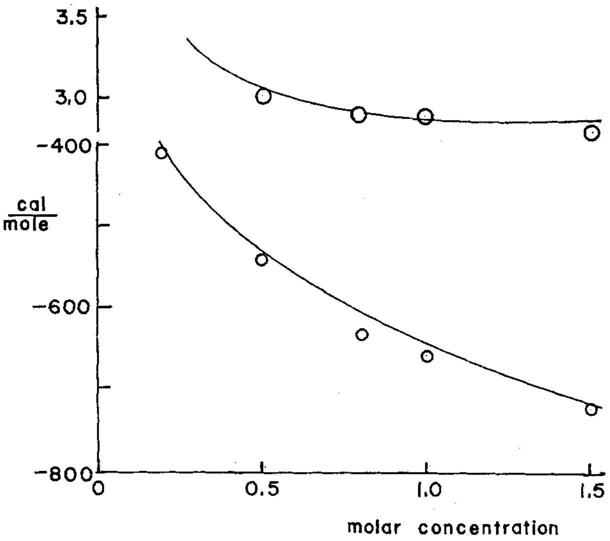

FIG. 2. Upper figure g^0 for the HNC computation and the Monte Carlo computation. Lower figure, Excess energy per mole of electrolyte for the two computations. In both cases the circles are the Monte Carlo results.

The purpose of this note is to report a comparison of the results of the two methods which exhibits their substantial agreement. Because the sources of error in the two methods of calculation are so different, the agreement is compelling evidence that both are accurate over the range of model parameters for which agreement is found. The studies reported here are for model parameters corresponding to 1:1 electrolytes in water at 25°C: $\epsilon = 80$ and $e_+ = -e_- = 1$ electronic charge.

For models in which $r_+^* = r_-^* = 2$ Å, the osmotic coefficient ϕ is given in Fig. 1 as a function of ion concentration.[5,6] The HNC computations are easy and precise enough so that their results may be given as a continuous curve. The MC results cited are those for the largest systems studied, 64 cations and 64 anions in most cases. Consistent MC results were also obtained for systems with only a half or a quarter as many ions in many cases.[2]

In comparing these results it is of interest to do so with reference to the equation of state for uncharged hard spheres of the same size, also given in Fig. 1.[7] This provides an important measure of the consistency of the HNC and MC results, namely

$$\Delta\phi = (\phi_{\mathrm{HNC}} - \phi_{\mathrm{MC}})/(\phi_{\mathrm{uncharged}} - \phi_{\mathrm{MC}}), \qquad (3)$$

which is the error in assessing the Coulomb contribution to ϕ. Apparently $\Delta\phi$ is less than 10% and it is especially satisfactory that it is much smaller at high concentrations where the truncation error in the derivation of the HNC equation is expected to be most serious.

Another interesting comparison is with the DHLL+ curve in Fig. 1, which is typical of the equation of state obtained from various extended forms of the Debye-

Hückel limiting law as well as of the cluster expansion for ionic solutions truncated after the B_2 term, the approximation studied by Poirier.[8] It is now clear that these approximations greatly underestimate the positive (repulsive) contribution to ϕ from the hard-sphere cores.

The computed excess energies per mole of electrolyte, roughly the heats of dilution, computed for the same model with the additional restraint that $d\epsilon/dT=0$, are shown in Fig. 2. The measure of the error, analogous to Eq. (3), is just the difference divided by the MC value since $E^{\text{ex}}{}_{\text{uncharged}}=0$. The agreement is even more satisfactory than for the osmotic coefficients.

On a separate scale in Fig. 2 we compare the quantity

$$g^0=\tfrac{1}{2}(g_{+-}+g_{-+}+g_{++}+g_{--}), \qquad (4)$$

where g_{ab} is the correlation function $g_{ab}(r)$ for r just larger than $r_a{}^*+r_b{}^*$. Again the agreement is satisfactory. Less extensive Monte Carlo computations for systems with $r_+{}^*=1.50$ Å and $r_-{}^*=2.50$ Å are in equally good agreement with the HNC results for the same model.[9]

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[5] ϕ for the solution is the same function as PV/NkT for a gas (plasma) at the same ionic concentration.

[6] A 1M solution of ions of this size has a reduced particle number density $\rho[r_+{}^{*3}+r_-{}^{*3}]4\pi/3=0.04$.

[7] From the PY equation with the compressibility equation.

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[9] *Note added in proof*: The conclusions reported here are supported by independent Monte Carlo studies by J. P. Valleau and S. Card (to be published).

Comments

Ammonia Decomposition on Tungsten Surfaces

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The first applications of a modern technique, namely field electron emission microscopy (FEM), to this classical problem have been reported by one of the present authors.[1,2] Several papers have subsequently appeared describing flash desorption[3–5] and low energy electron diffraction (LEED)[3,4] studies of this system. Since these papers place the interpretation of the original field emission work in contention and are in disagreement amongst themselves, some comment is appropriate at this time.

The FEM study[2] showed that chemisorbed ammonia adsorbed on W at $T\leq200$°K remained undissociated on the smooth (100) and (211) planes up to 350°K but was, at least partially, dissociated on rougher planes at 300°K. These observations have now been confirmed by flash desorption measurements.[3–6] However the claim[3,4] that the residue has the stoichiometry NH_2 does not agree with the FEM results nor with flash desorption measurements on polycrystalline samples.[5,6] The FEM results[2] did predict that N_2 and H_2 would desorb simultaneously at $T\sim900$°K, i.e., much higher than H_2 alone would desorb, but only when NH_3 interacted with W *above* room temperature. Since the flash desorption/LEED[3,4] experiments were carried out in a continuous NH_3 ambient, some NH_3/W interaction inevitably occurs above room temperature, and one is tempted to consider the results confirmation of the FEM predictions. Unfortunately, this is at best only partly true, since (a) the high-temperature H_2 peak is at 1200°K which is too high, and more important, (b) we have observed such high-temperature H_2 peaks at 1200–1300°K which can be ascribed to decomposition of ambient NH_3. The peak occurs when the pumping of H_2 by the hot sample surface at $T>1100$°K exceeds the rate of H_2 production by NH_3 decomposition. The excellent agreement as to the N_2/H_2 stoichiometry between the results from independent though admittedly very similar measurements makes one reticent to interpret the results as due to decomposition of ambient NH_3. Closer inspection shows that the agreement is fortuitous. First, the high-temperature nitrogen and hydrogen peaks are in complete disagreement in the raw data presented in the two papers; comparison is difficult because the data are presented in a qualitative manner, and one must be highly critical of the presentation of flash desorption spectra with no scales on either axis.[3] However, in one paper[3] the mass-2 peak is much smaller than that for mass 14, whereas the other[4] has a mass-2 peak greater than that for mass 30 (N.B. sensitivity of mass 30 is $\sim$23 times *greater* than mass 15). Second, one must criticise the use of H_2 pumping speeds determined at low temperature in the integration of H_2 desorption peaks in the temperature range where the sample itself acts as an efficient additional hydrogen pump of variable efficiency; we have tried many different ways to analyze such high-temperature H_2 peaks with widely varying results. Third, experiments carried out in the absence of an ammonia ambient[5,6] show a negligible high-temperature H_2 peak. Finally, if the high-temperature H_2 peaks can be dismissed in this way many of the problems associated with the interpretation of the several *direct* observations of the surface can be resolved. Thus, in the FEM the field emission patterns, measured work functions ϕ, and Fowler–Nordheim pre-exponentials at $T\sim1100$°K for NH_3 adsorption at 300°K were identical to those