is all evaporated from the crucible. This time progression is illustrated by spectra (d) and (e).

None of the spectra obtained in this study gave any definite indication for the presence of features which could be associated with KOH, $(KOH)_2$, O_2, or oxides of potassium. If such species were present in the beam, their energy-loss features were strongly overshadowed by H_2O and H_2. Although, in principle, the contributions to the elastic scattering from K, H_2, and H_2O could be subtracted out on the basis of the known inelastic-to-elastic scattering intensity ratios, these contributions are so dominant that the resulting data would be meaningless.

This study yielded a negative result as far as electron scattering by KOH is concerned, but at the same time demonstrated the progression of potassium hydroxide vaporization as followed through the observation of energy loss spectra. This study has also shown that electron scattering data on KOH cannot be obtained by the present technique because of the strong disturbing effects of the dissociation products. One will have to come up with a more clever way to be able to attack this problem.

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[b] NRC/NASA Senior Resident Research Associate: permanent address: Institute of Physics, P. O. Box 57, Belgrade, Yugoslavia.

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Radial correlations in associated liquids[a]

M. L. Klein

Division of Chemistry, National Research Council of Canada, Ottawa, Canada, K1A 0R6

I. R. McDonald

Physical Chemistry Department, University of Cambridge, Cambridge CB2 1EP, U. K.

B. J. Berne and M. Rao

Chemistry Department, Columbia University, New York, N. Y. 10027

D. L. Beveridge and P. K. Mehrotra

Chemistry Department, Hunter College, City University of New York, N. Y. 10021

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The problem of the choice of summation method for long range forces is a recurrent one in computer simulation calculations for strongly polar and, in particular, associated liquids. The most common procedure is to use periodic boundary conditions and the so-called spherical cut-off (SC) convention, which includes only those interactions due to molecules in a sphere of fixed radius centers on a given molecule. This method was adopted in the pioneering Monte Carlo (MC) calculations on water by Barker and Watts,[1] in the subsequent molecular dynamics (MD) studies of Rahman and Stillinger,[2] and in the most recent MC investigations.[3–6] MD calculations carried out for a variety of models of H_2O, NH_3 and HF have used the Ewald (EW) technique.[7–12] While neither of these approaches is entirely satisfactory, it is of interest to ask whether or not the liquid structure, as described, for example, by the atomic radial distribution functions $g_{\alpha\beta}(R)$, depends on the summation method used. A number of contradictory claims have been made. The MC(SC) calculations of Clementi and his co-workers,[3,4] and those of Swaminathan and Beveridge,[5] show little dependence of $g_{\alpha\beta}$ on system size (from 64 to 343 molecules) in simulations of H_2O based on intermolecular force models derived from quantum calculations. By contrast, in the work of Ladd[13] based on a variant of the EW method, there

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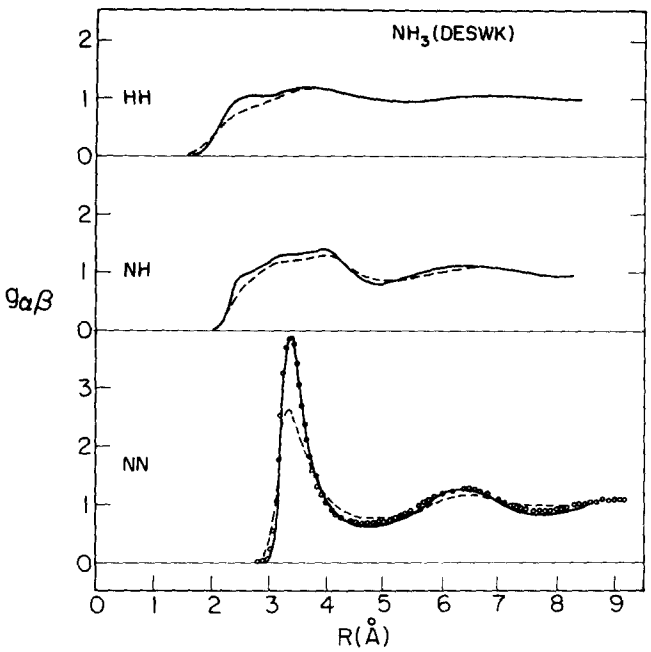

FIG. 1. Atomic pair distribution functions for liquid NH_3. The full (dashed) curves are the MD(EW) results for $T = 272$ (547) K and $V = 26.5$ cm^3 mol^{-1}. The circles are the MC(SC) results for 277 K.

is not only a discernible size dependence but, more seriously, significant disagreement with earlier results of Rahman and Stillinger[2] based on SC. Klein and McDonald[12] have employed both SC and EW in their MD calculations for models of liquid HF. For what are believed to be the more realistic models which were studied, little difference was found between the various $g_{\alpha\beta}$; the largest differences arose for the most dipolar model. These findings can be rationalized in part in terms of the known behavior of systems of hard spheres with embedded dipoles and quadrupoles, for which Patey and his co-workers[14] have demonstrated the importance of the quadrupole moment in breaking long range dipolar correlations. One consequence of this is that for models with reasonably large quadrupole moments, which includes most strongly polar systems, the choice of summation method is of minor importance and hence a matter of personal convenience. The reverse argument may be used to explain the severe dependence on system size seen in recent MC(SC) calculations[15] on a dipolar model of HF.

In the course of our separate researches into the properties of molecular liquids we have had cause to compute, independently, the $g_{\alpha\beta}$ for intermolecular force models proposed for NH_3 and H_2O on the basis of gas phase data.[16,17] Unfortunately, neither of these models yields liquid structures that resemble at all closely those of the real systems. However, this point is secondary here, since our main purpose is to use these models as representative associated liquids for which we may compare the results of MC(SC) and MD(EW) calculations.

The MD(EW) calculations for liquid NH_3 were carried out for a cubic system of 108 molecules with $V = 26.5$ cm^3 mol^{-1}. The calculations ran for approximately 2000 time steps of 0.5×10^{-14} s, all atoms being given the same mass; the method of calculation is described elsewhere.[12] The $g_{\alpha\beta}(R)$ for $T = 272$ K are shown in Fig. 1 as solid lines and for $T = 547$ K as dashed lines, the average potential energy $\langle U\rangle$ being, respectively, -24.7 and -20.4 kJ mol^{-1}.

The MD(EW) calculations of $g_{\alpha\beta}(R)$ for liquid H_2O are shown in Fig. 2. For these a cubic ($V = 18.0$ cm^3 mol^{-1}) system of 216 molecules was employed and the runs (again with equal masses) were of approximately 1500 time steps of 1.0×10^{-14} s. The solid lines show the $g_{\alpha\beta}(R)$ for $T = 278$ K ($\langle U\rangle = -39.1$ kJ mol^{-1}) dashed lines for $T = 410$ K ($\langle U\rangle = -33.0$ kJ mol^{-1}). It should be noted that our previously published results[9] for this model, which we inadvertently attributed to 0 °C, corresponded in fact to $T = 410$ K. The present results thus serve as a revision of these data, but the conclusions drawn previously concerning the adequacy of the model are unaltered.

The MC(SC) results for liquid NH_3 were carried out for 100 molecules confined to a Wigner–Seitz cell of the face-centered cubic lattice with appropriate periodic boundary conditions. The MC "experiment" was run for 200 000 moves starting from a previously equilibrated configuration (for another potential) and utilized a 7 Å cut off. The resulting g_{NN} ($T = 277$ K) is shown by the circles in Fig. 1 and is virtually indistinguishable

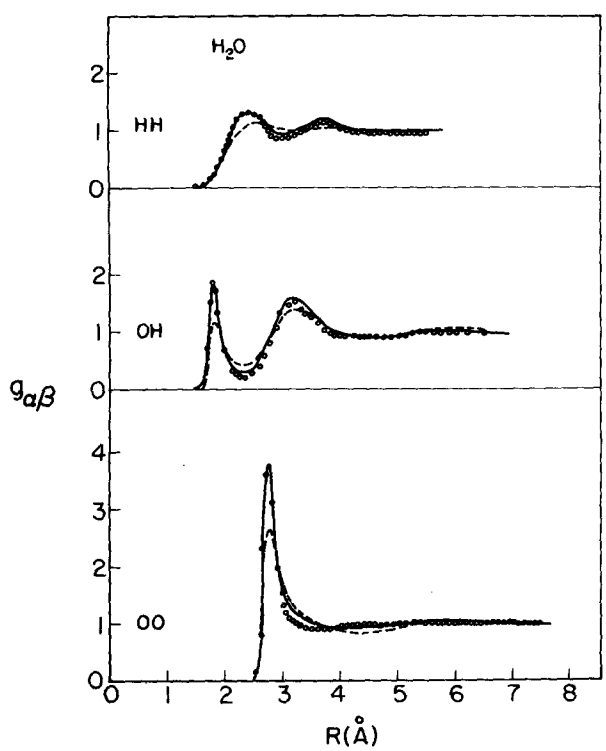

FIG. 2. Atomic pair distribution functions for liquid H_2O. The full (dashed) curves are the MD(EW) results for $T = 277$ (410) K and $V = 18.0$ cm^3 mol^{-1}. The circles are the force-bias MC(SC) results for 273 K.

from the MD(EW) result; the average potential energy was -26.0 kJ mol^{-1}.

The MC(SC) results for liquid H_2O at 273 K are shown by the circles in Fig. 2. These were obtained by the force-bias method recently introduced by Rao *et al.*[6] The simulation run for 2.16×10^6 moves. A cubic system of 216 molecules was used, with a cut off radius of 8.2 Å, and the average potential energy was found to be -39.3 kJ mol^{-1}. The agreement with the EW calculation is remarkable. There are some small differences between SC and EW, but these are insignificant in comparison with previously reported[13] discrepancies.

In summary, we find that there is little difference between the SC and EW methods of computing $g_{\alpha\beta}(R)$. The implication of this is that computer simulation calculations of $g_{\alpha\beta}$ by either SC or EW can be used with confidence in testing intermolecular force models for liquids consisting of molecules with appreciable quadrupole moments. However, the same cannot be said for dielectric properties, which pose different and as yet unresolved problems,[14,18] or for the structural properties of those rather unrealistic models of strongly polar fluids in which no account is taken of quadrupole interactions.

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Branching ratio determination in the $O_2^+(b\,^4\Sigma_g^-)$ predissociation

Mireille Tadjeddine

Laboratoire des Collisions Atomiques et Moléculaires,[a] *Université de Paris-Sud, 91405 Orsay, France*
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Photodissociation processes have been recently investigated with a high resolution. One of the main reasons is that photodissociation experiments yield one of the best ways of studying the dynamics of molecular collisions since from the theoretical point of view[1] the dissociation step can be described as a "half collision" scattering. A central question is the internal energy distributions of fragments resulting from photodissociation. When different dissociation channels are allowed one can experimentally determine the branching ratio if the resolution is good enough.

The photodissociation of the O_2^+ molecular ion is now very well known.[2–8] In a previous paper[5] we have analyzed in detail the photopredissociation of O_2^+.[5a] In that work the O_2^+ molecular ion beam was studied both coaxially and transversely with respect to the polarized light of a cw dye laser and the O^+ photofragments were recorded as a function of laser wavelength. Different spectra have been obtained for different locations of the spectrometer analysis window of the kinetic energy W of photofragments in the center-of-mass system. The knowledge of the dependence of the spectra on photofragment energy allowed us to make an unambiguous assignment of the individual lines in the transition:

$$O_2^+(a\,^4\Pi_u, v''=4 \text{ or } 5, J'', \Omega''=|\Lambda|+\Sigma) + h\nu \rightarrow O_2^+(b\,^4\Sigma_g^-, v'=4 \text{ or } 5, N', F') \rightarrow O(^3P)+O^+(^4S^0)\,. \quad (1)$$

Moreover from the kinetic energy spectra we had determined (5) the energy of the first predissociated levels of $O_2^+(b\,^4\Sigma_g^-, v'=4)$. Such a determination for the

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