Ionic Clustering in Polymer Electrolytes

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Computer simulation techniques reveal key features of the distribution of ions in polymer electrolytes.

It is well known that polymers containing polar atoms, for example polyethylene oxide (PEO) may dissolve ionic solids (*e.g.*, NaI) to give useful and effective solid electrolytes with high ionic conductivities.[1] Such materials have found important applications in solid state batteries.[2] There is far less understanding of the structural properties of these intriguing solid solutions, particularly the behaviour of the amorphous phases in which it has been established that the high conductivity occur.[3]

Crystal structures of ionically doped polymer electrolytes are only avaialble in a limited number of cases.[4–6] Little is available for the highly conductive amorphous phases, although EXAFS studies have shown that the cations are solvated by the oxygen atoms giving a reasonably well defined first co-ordination shell,[7] but there is little detailed information on the extent of ionic association, knowledge of which is essential for the formulation of accurate transport models based on either weak or strong electrolyte theories. Indeed there is considerable debate about the degree of ionic clustering as a function of both temperature and salt concentration with various experimental studies giving conflicting results and conclusions.[8–11]

In view of the well-known difficulty in obtaining structural information relating to the problems in the intermediate range order of an amorphous material (of which the extent of ion aggregation is a good example) we have investigated the structural and dynamic properties of these systems using molecular dynamics (MD) computer simulation techniques. These methods have been extensively and successfully applied to the study of ionic transport in ionically conducting solids,[12–17] with some recent applications to polymer electrolytes.[18,19] Our work focuses on the extent of ionic clustering in these solids and its variation with temperature. We take as a typical example the case of PEO–NaI which has been the subject of detailed experimental investigations.[20]

The molecular dynamics technique models the time evolution at the atomic level of an ensemble of particles acting under specified interatomic forces by numerically solving the equations of motion in an iterative manner. A detailed description of this technique is given in ref. 21. In the present case standard microcanonical (NVE) simulation methods were used with a parallelised version of the recently rewritten FUNGUS[22] code implemented on the Intel IPSC/860 at the SERC Daresbury Laboratory, UK. This allowed simulations to be performed routinely for periods typically of between 100 and 250 ps using an interation time step of 10^{-3} ps. Periodic boundary conditions (PBC) were applied to remove surface effects, the minimum image convention was utilised to evaluate short-range interactions and the Ewald summation[23] used to compute the longer ranged coulombic forces. The potential parameters for both the chain (including bond bending and torsional terms) and chain···ion interactions were taken from the established constant valence force field (CVFF),[24,25] while those for ionic interactions ($Na^+\cdots I^-$, $Na^+\cdots Na^+$ *etc.*) originated from Catlow *et al.*[26] As suitable iodide potentials were not available in CVFF, these were derived from the known chloride and bromide parameters by extrapolation with subsequent fitting to the crystal structure. Using energy minimization techniques it was found that the potentials reproduced the crystal structures of both pure PEO[27] and PEO–NaI[5] well. In the subsequent simulations, the boxes contained *ca.* 1000 atoms, and in every case an equilibration period of 50 ps, in which the system attains thermal equilibrium, was followed by a production run of up to 250 ps, where data were collected for subsequent analysis. In the case of the MD simulations of the amorphous material

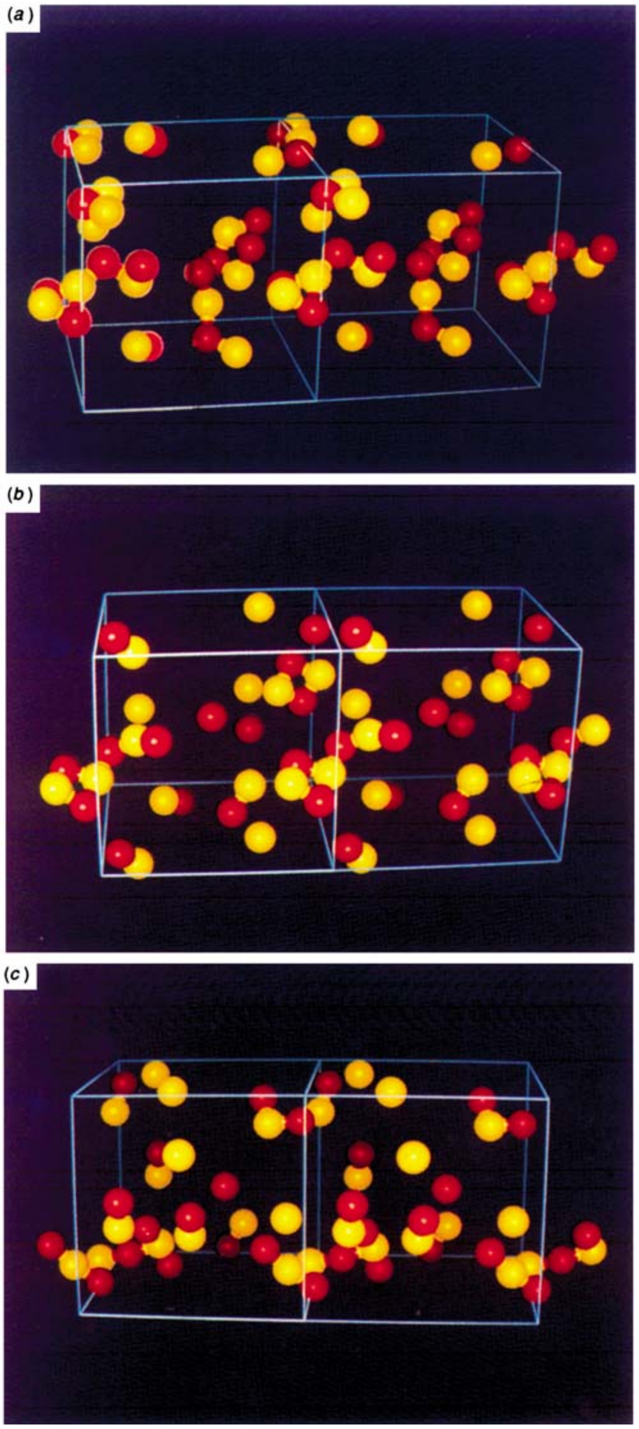

Fig. 1 A snapshot of the simulation showing the positions of the sodium and iodide ions at temperatures of (*a*) 323, (*b*) 370 and (*c*) 400 K. Note that several unit cells are displayed in each case.

the starting structures were generated using a combination of RIS theory,[28] energy minimization and molecular dynamics[29] to yield configurations in which the distribution of backbone conformers was statistically similar to that of the bulk material.

An initial set of MD simulations performed on the crystalline phase of PEO–NaI using a spherical short-range potential cut-off of 7.15 Å showed that our forcefield was able to reproduce accurately the experimental structure of Chatani.[5] During the period of the simulation no ionic diffusion was observed, a result which is in line with the observed low conductivity of this phase.

Simulations of the amorphous phase were performed, using a potential cut-off of 9.65 Å, with salt concentrations of 3:1, 10:1 and 30:1 (PEO:NaI) and at temperatures of 323, 370 and 400 K, although at present we will focus on the studies carried at the mid-range concentration. It should be noted that although the 323 K study is performed below the melting temperature of PEO, where physically the doped material would not be fully amorphous, our initial configurations are generated artificially to yield completely amorphous systems which may be used over a range of temperatures.

The results have important implications for the understanding of the structure of the material, as is apparent from the radial distribution functions (RDF) calculated during the last 5 ps of each run. In Fig. 1(*a*) it is immediately clear from the Na···O correlation that at all temperatures the cations, as expected, are co-ordinated to *ca.* 4 oxygens in the chain, a similar result to that obtained in simulations of the crystalline material. The ion···ion functions shown in Fig. 1(*b*)–(*d*) are particularly interesting, a notable feature being the well-defined peak at 2.7 Å in the Na···I RDF. Taken overall, the peaks in these functions can only be interpreted in terms of the formation of clusters involving several ions, although the life times of such clusters may be short. At the lowest temperature (323 K) we appear to have extensive formation of chains and rings of oppositely charged ions (consistent with the coordination number of 2 for Na apparent in Fig. 1(*b*). With increasing temperature it can be seen that although clustering still occurs, it is present to a lower degree with the primary, secondary and tertiary peaks in the Na···Na and I···I functions [Fig. 1(*c*) and (*d*)] lying at larger distances with smaller intensities. This point is amplified by the graphical representation of these results in Fig. 2(*a*)–(*c*), which reveals extensive ring and chain forma-

Table 1. Calculated diffusion coefficients for PEO:NaI (10:1)[a]

T/K	D(Na)/10^8 cm^2 s^{-1}	D(I)/10^8 cm^2 s^{-1}
323	3.55	2.10
370	4.00	6.25
400	9.07	10.71

[a] Calculated using a sliding average of the mean square displacement $\langle r_i^2(t) - r_i^2(0)\rangle$, where $r_i(t)$ is the atom position, and the Einstein relation, $2tD = \frac{1}{3}\langle r_i^2(t)\rangle$

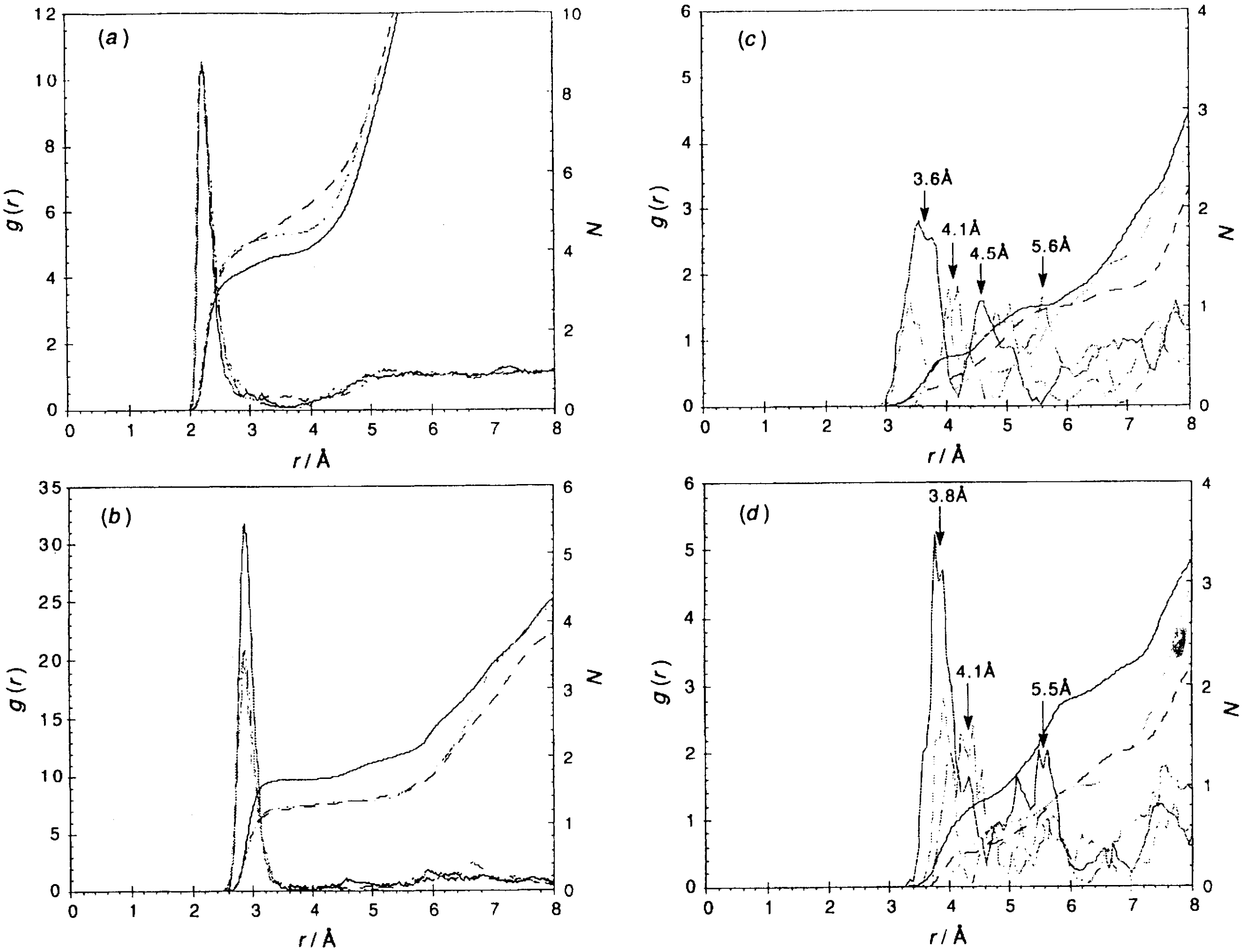

Fig. 2 Calculated radial distribution functions, $g(r)$ and integrated function, N, for PEO:NaI (10:1) averaged over the last 5 ps of simulation at temperatures of 323 (——), 370 (– – –) and 400 (–·–·–) K. (*a*) Na···O Note that the curve with peak refers to $g(r)$ and that with the plateau to N; the latter was calculated by integration of the $g(r)$; (*b*) Na···I; (*c*) Na···Na; (*d*) I···I.

tion, at 323 K, with dissociation into triplets, pairs and isolated ions at the higher temperatures. We note that in this key respect our results differ from earlier simulations,[18,19] which found increases in ionic association with temperature.

Preliminary investigations on ion diffusivity over the temperature range studied indicate the appreciable ionic motion occurs in the amorphous phase. Diffusion coefficients obtained from the mean square displacements (MSD) taken over 100 ps of simulation are summarised in Table 1. They are of the same order as those measured experimentally by Hamner and Chadwick.[20] More accurate values and the subsequent determination of activation energies will, however, require longer simulations runs *e.g.* 500–1000 ps.

In line with earlier work,[18,19] this work confirms the 'weak' electrolyte model for polymer electrolytes, with the presence of extensive ionic clustering that decreases with increasing temperature. Moreover is clearly demonstrates that MD is a powerful tool for probing the structure and dynamics of this important class of materials.

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