Diffusion within α-CuI studied using *ab initio* molecular dynamics simulations

Diffusion within α-CuI studied using *ab initio* molecular dynamics simulations

Chris E Mohn[1,2], **Svein Stølen**[2] and **Stephen Hull**[3]

[1] Laboratoire des Colloïdes, Verres et Nanomatériaux, UMR 5587, Université Montpellier II-CNRS, 34095 Montpellier, France
[2] Department of Chemistry and Centre for Materials Science and Nanotechnology, University of Oslo, PO Box 1033 Blindern, N-0315 Oslo, Norway
[3] The ISIS Facility, STFC Rutherford Appleton Laboratory, Didcot, Oxfordshire 0X11 0QX, UK

E-mail: chrism@kjemi.uio.no

Abstract

The structure and dynamics of superionic α-CuI are studied in detail by means of *ab initio* Born–Oppenheimer molecular dynamics simulations. The extreme cation disorder and a soft immobile face centred cubic sublattice are evident from the highly diffuse atomic density profiles. The Cu–Cu pair distribution function and distribution of Cu–I–Cu bond angles possess distinct peaks at 2.6 Å and 60° respectively, which are markedly lower than the values expected from the average cationic density, pointing to the presence of pronounced short-range copper–copper correlations. Comparison with lattice static calculations shows that these correlations and the marked shift in the cationic density profile in the $\langle 111 \rangle$ directions are associated with a locally distorted cation sublattice, and that the movements within the tetrahedral cavities involve rapid jumps into and out of shallow basins on the system potential energy surface. On average, the iodines are surrounded by three coppers within their first coordination shell, with the fourth copper being located in a transition zone between two neighbouring iodine cavities. However, time-resolved analysis reveals that the local structure actually involves a mixture of threefold-, fourfold- and fivefold-coordinated iodines. Examination of the ionic trajectories shows that the copper ions jump rapidly to nearest neighbouring tetrahedral cavities (aligned in the $\langle 100 \rangle$ directions) following a markedly curved trajectory and often involving short-lived ($\sim$1 ps) interstitial positions. The nature of the correlated diffusion underlying the unusually high fraction of coppers with short residence time can be attributed to the presence of a large number of 'unsuccessful' jumps and the likelihood of cooperative motion of pairs of coppers. The calculated diffusion coefficient at 750 K, $D^{Cu} = 2.8 \times 10^{-5}$ cm^2 s^{-1}, is in excellent agreement with that found experimentally.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Disordered solids based on the copper and silver halides have attracted considerable interest due to their exceptionally high values of ionic conductivity ($\sim$1 Ω^{-1} cm^{-1}) [1, 2]. However, the extensive disorder within the cationic sublattice continues to present challenges both to theoretical and experimental methods and progress is often hampered by a lack of agreement within the literature. Nevertheless, identifying the underlying factors responsible for the exceptionally high ionic conductivity, including the influence of the atomistic times and the local structure on the macroscopic properties (e.g. the conductivity itself) is an essential aspect in the search for improved materials for future energy device applications.

Superionic CuI, α-CuI, which adopts an anion deficient-fluorite structure, has been the subject of a number of computational and experimental studies, with many focusing on the mean location of the mobile coppers. Whereas extended x-ray absorption fine structure (EXAFS) experiments [2] and molecular dynamics (MD) simulations [3] suggest that the
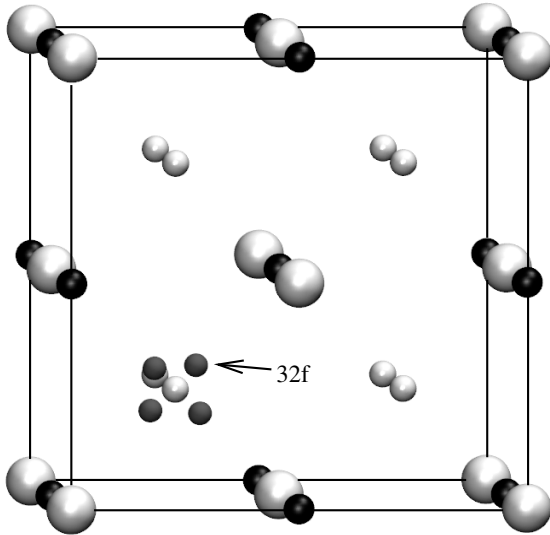
Figure 1. Different sites/cavities within an fcc lattice, representing possible positions of the coppers within α-CuI, as suggested within the literature. The iodines are shown as large white spheres and the octahedral 4b sites are shown by black spheres. The small white spheres represent the (ideal) tetrahedral 8c sites whereas the 32f sites (which are the site on a straight line connecting the tetrahedral 8c and the nearest octahedral 4b position (i.e. at the positions (x, x, x) etc with $x \sim 0.30$ [4, 5]) are the grey spheres (only plotted in the one of the tetrahedral cavities for clarity)).

coppers occupy *both* the octahedral (4b) and the tetrahedral (8c) sites of the space group $Fm\bar{3}m$ (see figure 1), results from neutron diffraction [4, 5], Raman spectroscopy [6], MD simulations [7] and structural optimizations using density functional theory [8] find very little evidence for a population of the octahedral site. However, the refined positions reported in [4, 5] indicate that the coppers are significantly displaced away from the ideal tetrahedral 8c site of $Fm\bar{3}m$, toward the octahedral positions, into the 32f site [4, 5] (see figure 1). The cation displacements in the $\langle 111 \rangle$ directions are clearly seen in the highly diffuse cationic density distribution found in previous computational and experimental work [8–11]. These profiles show that the density maximum of the coppers is located at the tetrahedral 8c site and that the cationic density has a marked tetrahedral distortion in the $\langle 111 \rangle$ directions. Interestingly, a significant fraction of the cationic density is located *within* the octahedral cavity although the octahedral site itself appears to be a density minimum. The average density profiles [8, 10, 11] are, therefore, consistent with all EXAFS [2], different ND [4, 5, 10, 12] and x-ray [11] refinements but do not provide an atomistic picture of the underlying copper dynamics that give rise to this average. A time-resolved inspection of the MD trajectories [9, 13] show that the coppers basically reside within the tetrahedral cavity, but undergo large amplitude of vibrations and often venture into an octahedral cage.

Further information beyond that of the average is contained in the atom correlation functions. Results from MD [13], ND (together with reverse Monte Carlo modelling (RMC)) [10], EXAFS [14] and extensive lattice static simulations [8] all show that the coppers are strongly correlated. The positions of the dominant peaks in the Cu–Cu pair distribution function (PDF) at $\sim$2.6 Å are at a markedly shorter distance than those expected from the average alone. Similarly, deviations from an average structure are also seen in the $A_{\text{CuICu}}(\theta)$ and $A_{\text{CuCuCu}}(\theta)$ angular distribution functions (ADFs) [8], where distinct peaks are found at around 60° which are at substantially lower angles than those expected from the mean cationic density profile.

The diffusion process within α-CuI has been subject to some debate within the literature. Results from MD simulations carried out using pair potentials [3] and *ab initio* MD simulations [13] both suggest that the coppers diffuse from a tetrahedral cavity to a vacant tetrahedral cavity via an octahedral site along the $\langle 111 \rangle$ directions, whereas results from EXAFS [2] suggest that jumps may involve tetrahedral cavities aligned in both $\langle 111 \rangle$ and $\langle 110 \rangle$ directions. By contrast, ND [10], x-ray diffraction [11] and MD simulations using pair potentials [7, 15] have put forward a different model where the coppers are diffusing to a neighbouring vacant tetrahedral cage along the $\langle 100 \rangle$ directions. This is surprising, bearing in mind the large amplitudes of vibrations in the $\langle 111 \rangle$ directions and suggests that atomic correlations between the mobile and immobile species may have a strong influence on the cation diffusion process.

In this work we perform a detailed investigation of the local structure and the dynamical properties of superionic CuI using *ab initio* MD simulations. The advantages of atomistic analyses from fully equilibrated atomic trajectories using MD and pair potentials have previously been demonstrated for binary superionic solids such as CaF_2 [16] and AgI [17], enabling a detailed atomistic insight into the superionic state which would normally elude experimental investigations. However, results from ND-RMC [10] and recent *ab initio* MD [13, 18] have shown that the use of pair potentials may be hampered by the presence of some artificial features. In particular, they appear to lack the ability to capture certain structural and thermodynamic features of the disordering process. For example [13, 10], the pair potentials are unable to reproduce the pronounced first peak in the Cu–Cu PDF of α-CuI at $\sim$2.6 Å. In addition, the diffusion coefficient of α-CuI is highly sensitive to the choice of the functional form (parametrization) of the potential. Indeed, the calculated diffusion coefficient from different MD simulations differ by an order of magnitude [7, 3, 19].

To validate the use of *ab initio* MD for modelling highly disordered superionic conductors, we shall compare our results with those obtained by previously reported experimental and computational work. We also take the opportunity to link this work to previously reported configurational (Boltzmann) averaging (CA) results (using density functional theory (DFT)) [8]. CA is a direct (brute force) Monte Carlo technique [20–22], where randomly chosen configurations are optimized and Boltzmann weighted. The comparison with CA [23] is of particular interest here since the optimized configurations represent snapshots of rapidly quenched-in disordered (inherent) structures, which allows one to identify the extent of 'static' configurational disorder (the nature of the distinct local minima on the potential energy) and vibrations (excitations out of these local minima).

2. Computational details

We carry out *ab initio* Born–Oppenheimer MD simulations of α-CuI within a simulation cell constructed of $2 \times 2 \times 2$ crystallographic unit cells (64-ions). The generalized gradient approximation (specifically, the Perdew–Wang 91 functional [24]) was used for the calculation of the exchange–correlation contribution to the total energy as implemented in the Vienna *ab initio* simulation package (VASP) [25, 26]. The MD runs were carried out in the NVT ensemble, where the lattice parameter, $a = 6.15$ Å is the thermodynamic (Boltzmann) average value calculated at 750 K using 25 optimized 64-ion configurations [8]. This value is in very good agreement with that of experiment ($a = 6.158$ Å) reported in [4] at 718 K. A Nosé–Hoover thermostat was used, and the equations of motion were integrated using a Verlet algorithm with a time-step of 2 fs. With this choice of step length, the drift in the total energy is less than 0.4 meV ps^{-1} atom^{-1}. Results from test-calculations where the properties of interest were examined by systematically changing the energy cut-off, E_{cut}, indicate that $E_{cut} = 200$ eV is sufficient for the present purpose. A somewhat higher value ($E_{cut} = 400$ eV) was chosen in the structural optimizations carried out in [8], to minimize the errors associated with the distortions of the basis set due to the changes in the cell volume. The Brillouin zone was sampled at the gamma point. No notable drift in the potential energy or the structural and dynamical properties were found after a few pico seconds of equilibration. Eight individual MD simulations were allowed to equilibrate for a few pico seconds, followed by a production time of $\sim$30 ps each, giving a total $\sim$0.25 ns (nanoseconds) of statistics[4]. This is sufficient for extracting well converged ionic density profiles, correlation functions and residence time distributions.

3. Results and discussion

3.1. Structure: average structure

The average ionic density profile from MD simulations carried out at 750 K is shown as a slice through the $(1\bar{1}0)$ plane in figure 2. The highly diffuse average density profile of the coppers is striking! The cation density maximum is located at the 8c site and the marked tetrahedral distortions in the $\langle 111 \rangle$ directions is consistent with previous experimental refinements [4, 5, 11]. A small, but notable, local maximum is found at the octahedral (4b) site. Interestingly, in contrast to results from DFT calculations carried out in the static limit [8], no visible density maxima are seen in the cationic profile at the 32f positions. Thus, although the results from CA indicate that the coppers reside near the 32f site, the peak is smeared out due to thermal vibrations. The distribution of the iodines form broad and roughly spherical thermal clouds centred at the regular fcc lattice site, pointing to a highly flexible immobile sublattice.

The cationic density suggests that the coppers can migrate in all $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions. However, in contrast
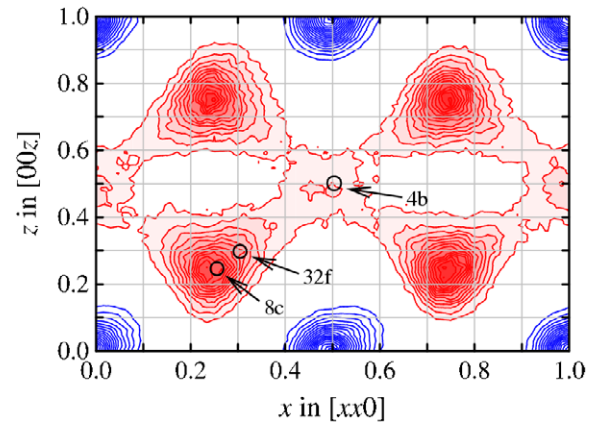
---

[4] With these settings a 1 ps (500 steps) simulation took about 1 CPU hour on a Sun Fire X2200 64-core cluster.

Figure 2. Density plot of coppers (grey) (red online) and iodines (black) (blue online) within the $(1\bar{1}0)$-plane of α-CuI from MD simulation at 750 K.

to MD simulations carried out using pair potentials [27], where the coppers where found to migrate along $\langle 100 \rangle$ (i.e. through the midpoint of the edge shared by two neighbouring tetrahedral cavities), the density profile in figure 2 indicates that the possible migration trajectories, involving tetrahedral cavities aligned in $\langle 100 \rangle$ and $\langle 110 \rangle$ directions, are markedly *curved*. This model is in good agreement with ND results reported in [10]. We discuss this issue further below.

3.2. Structure: local structure

To investigate the local motifs underlying the average ionic densities in further detail, we plot the I–I, Cu–I and Cu–Cu pair distribution functions, $g_{II}(r)$, $g_{CuI}(r)$ and $g_{CuCu}(r)$ respectively, in figure 3. All results are extracted from the MD trajectories at 750 K. The overall shape of the peaks and the positions of the peak maxima are in good agreement with previous EXAFS [14], ND-RMC [10] and *ab initio* MD results [13], although a detailed comparison reveals notable differences. For instance, the marked left shoulders of $g_{CuI}(r)$ and $g_{II}(r)$ reported in [10] are not found in this work, and neither are I–I separations as short as 3.0 Å. This supports a recent structural reinvestigation [14] of the ND-RMC results [10] suggesting that the left shoulders in $g_{CuI}(r)$ and $g_{II}(r)$ reported in [10] are possibly due to some spurious effects in the RMC analysis of the ND data associated with a low sensitivity of the apparatus. Indeed, the shapes of $g_{CuI}(r)$ and $g_{CuCu}(r)$ reported in this work are in better agreement with those of EXAFS [14] and *ab initio* MD [13], although it should be noted that $g_{CuCu}(r)$ calculated in this work involves shorter Cu–Cu bonds ($<$2.4 Å) compared to that of EXAFS [14].

The first peak position of $g_{CuI}(r)$ at $\sim$2.6 Å is consistent with the occupation of the ideal 8c tetrahedral site within a rigid fcc lattice of iodines. By contrast, the position of the first peak in $g_{CuCu}(r)$, at $\sim$2.6 Å, is located at significantly shorter distance than that expected from the density profile shown in figure 2 (the distance between the peak maxima in figure 2 is $\sim$3.1 Å). This emphasizes the presence of pronounced short-range copper–copper correlations. A tendency towards

Figure 4. Distribution of the instantaneous coordination numbers (in per cent) of the iodines calculated by integrating the first peak in the Cu–I PDF to 3.5 Å.
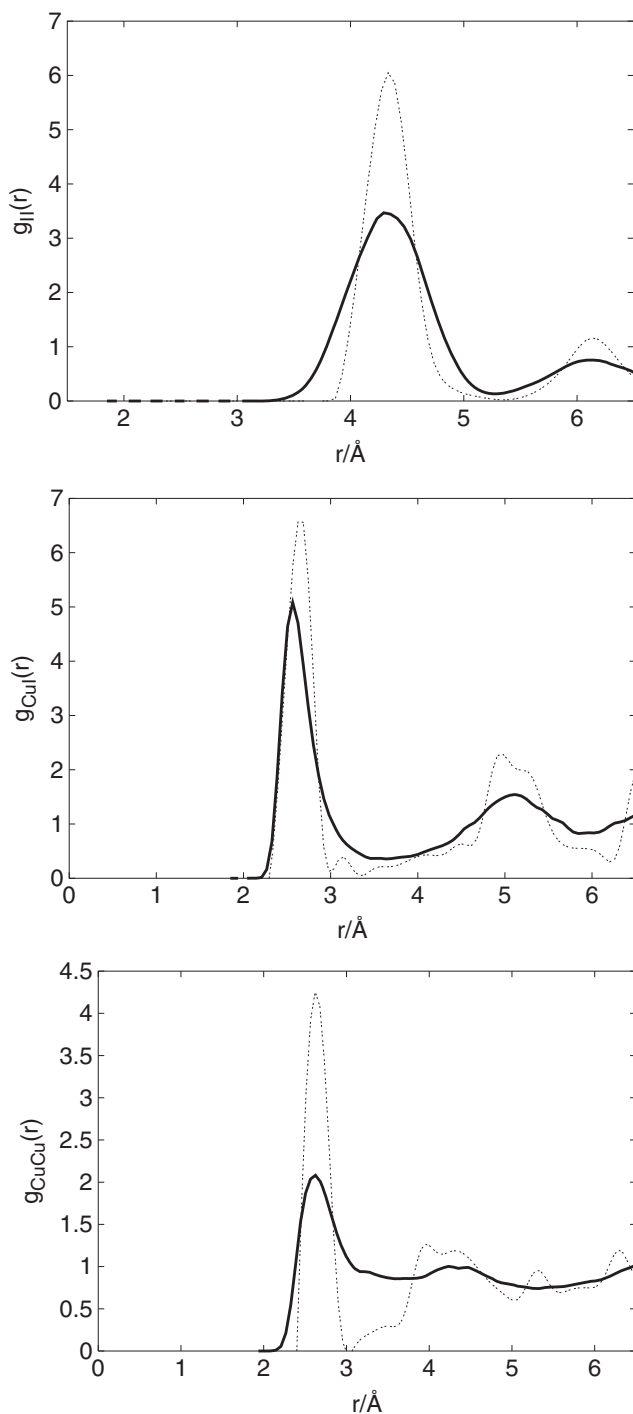
Figure 3. Partial PDFs from MD simulations (thick full lines) and from CA [8] (thin dashed lines) at 750 K.

intermediate-range order, associated with a broad peak at ~4.3 Å in $g_{CuI}(r)$, is in good agreement with that of ND [10]. This is consistent with alignments along ⟨110⟩, as expected from the average cationic density profile, emphasizing that the marked copper–copper correlations involve only the nearest neighbour contacts.

The I–I PDF confirms that the iodines remain at their regular fcc lattice site, although the average coordination number of the iodi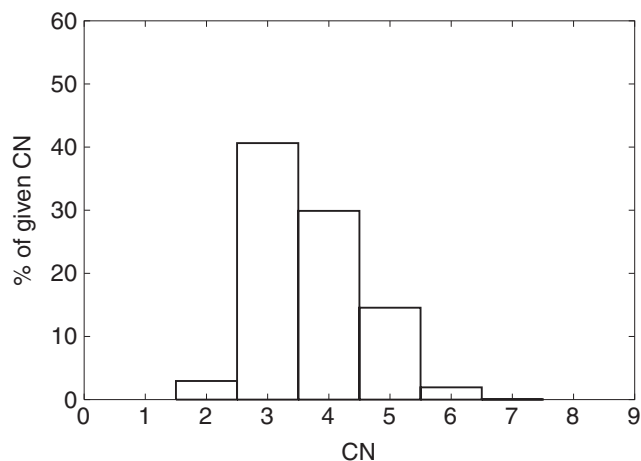nes (calculated by integrating the first peak in $g_{CuI}(r)$ up to 3.5 Å) is lower than that expected by distributing the coppers at random over the tetrahedral positions. We find that, on average, three coppers are located within a distance of 3.0 Å from the central iodine, whereas the fourth copper is located in a transition zone i.e. 3.0 Å $< r_{Cu-I} < 4.0$ Å from the central iodine. However, this average local structure does not capture the variation in the coordination number (CN) as is seen in a time-resolved picture by decomposing the nearest neighbouring environments of the iodines into distinct CNs (see figure 4).

These time-snapshots show that the iodines are surrounded by three, four, and five coppers within their first coordination shells. Furthermore, few iodines are found with less than two nearest neighbours and few iodines are instantaneously surrounded by six coppers within a distance of 3.5 Å. The latter implies no significant occupation of the octahedral sites, consistent with the average cationic density profile shown in figure 2.

It is worth bearing in mind that the large amplitudes of vibrations of the coppers are manifested in rapid fluctuations of the CNs. However, the distribution of CNs from an additional analysis where the trajectories were resolved in times consistent with the average residential times of the coppers, rather than being dumped at every time-step along the trajectory, are in good agreement with that shown in figure 4. Furthermore, the distribution of coordination numbers from lattice static simulation using CA [8] (which represent a frozen-in picture of the interbasin movements) is in excellent agreement with that of figure 4. These findings confirm that the iodines take a range of coordination numbers. It is of note that the variation in coordination number stands in some contrast to results from a recent MD study of superionic AgI [18] where the iodines are most commonly surrounded by three silvers whereas a fourth silver was most commonly found regularly located in a transition zone between neighbouring tetrahedral cavities.

The ADFs displayed in figure 5, calculated by integrating the first peak of the relevant PDF to its first minimum, provide
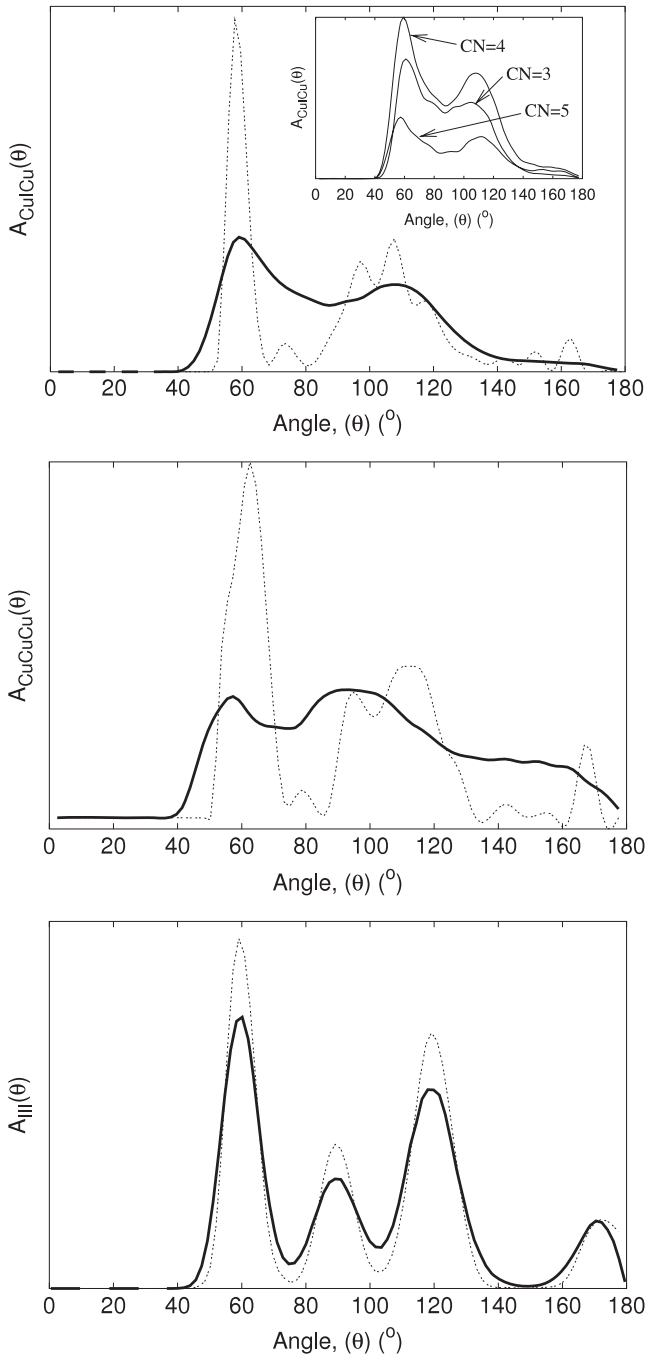
Figure 5. Partial and decomposed partial bond angle distribution functions from MD (thick full lines) and from CA [8] (thin dashed line).

a further detailed picture of the local neighbourhood of the iodines and the coppers. The Cu–I–Cu ADF, A_{CuICu}, possesses a distinct peak at approximately 60° and one broader feature at around 110°. The first peak is located at lower angles than that expected from the average ionic densities (at 70°) and is consistent with the peak at ∼2.6 Å in $g_{CuCu}(r)$. The peak at 110° confirms the presence of intermediate-range as is seen in $g_{CuI}(r)$ at 4.3 Å possibly due to alignments along the ⟨110⟩ directions. Resolving the partial Cu–I–Cu ADF into contributions with different coordination numbers (see

figure 5) shows that the angular preferences are independent of the number of nearest neighbours located near an iodine.

The PDFs and ADFs from MD (figures 3 and 5 respectively) are in good agreement with those extracted in the static limit using CA [8] (plotted as a thin dashed line). In particular, the first peak in $g_{CuCu}(r)$ and A_{CuICu} are located at the same positions. This indicates that the presence of pronounced short-range copper–copper correlations is associated with a markedly distorted cationic sublattice. The movements of the copper *within* a given tetrahedral cavity (metabasin) therefore involve rapid 'jumps' into and out of shallow potential energy basins with characteristic times comparable to an optical phonon mode. Thus, the pronounced displacement in the ⟨111⟩ directions visualized in the ionic density profile is probably associated with both a 'static', locally distorted, sublattice, and the presence of thermal excitations out of these shallow basins. This points to an unusual and pronounced coupling between configurations and vibrational degrees of freedom, as is seen in the shape and widths of the peaks as well as a small peak shift in $g_{CuI}(r)$. A locally distorted sublattice (i.e. the presence of several shallow local minima associated with movements within a tetrahedral cage) *and* vibrations (i.e. the thermal excitations out of these shallow wells) both underlie the extreme disorder within the mobile sublattice of α-CuI. The rapid excitations out of these shallow basins and the extreme disorder within the mobile lattice is also evident by the comparison of the Cu–Cu–Cu angular distribution functions, A_{CuCuCu}, from CA and MD. Indeed, these are quite different although both show a weak angular preferences for 60° and 90°. By contrast, the I–I–I angular distribution functions, A_{III}, from CA and MD are strikingly similar. This points to the presence of a locally distorted immobile sublattice.

Although we are not aware of any reported results of ADFs from superionic CuI, the Cu–I–Cu ADF is very similar to those measured by ND-RMC and high energy x-ray diffraction of CuI melts [28] and to the Ag–I–Ag ADF extracted from MD simulations of superionic AgI [18]. This indicates that 'distorted' tetrahedral environments are characteristic of superionic conductors of late-transition metal halides and their liquids.

3.3. Dynamical properties: calculation of diffusion coefficient

The mean square displacements (MSDs) plotted in figure 6 are characteristic of solid electrolytes; whereas the iodines show no tendency for diffusion, the MSD of the coppers increases roughly linearly with time. The presence of small 'steps' or 'plateaus' should be noted in the MSD of the coppers which *may* indicate the presence of cooperative events involving two or more coppers [7]. We will discuss this in further detail below. From the asymptotic value of the MSD of the iodines we estimate the extent of the Debye–Waller thermal cloud, B_{iodine}, for the iodines: $B_{iodine} \sim 0.6$ Å^2, and the self-diffusion coefficient, D^{Cu}, of the coppers is calculated from the slope of MSD of the coppers using the Einstein relation

$$D^{Cu} = \lim_{t \to \infty} \frac{1}{6N_{Cu}t} \left\langle \sum_{i=1}^{N_{Cu}} |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \right\rangle. \quad (3.1)$$
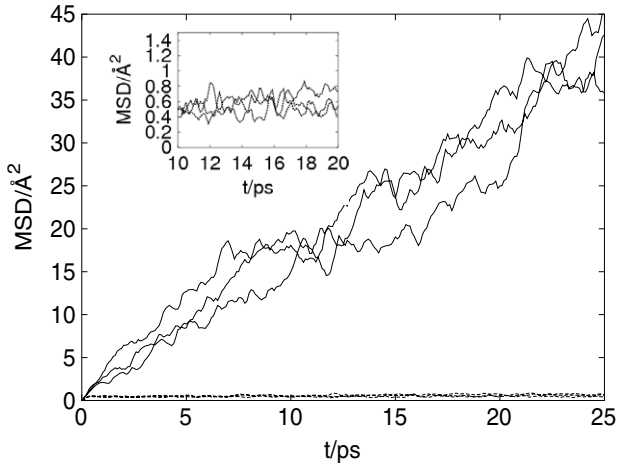
Figure 6. MSDs of coppers (full lines) and iodines (dashed lines and inset) of α-CuI at 750 K. Results from three MD simulations are displayed.

Here, the $\langle \cdots \rangle$ denotes a time-average over the trajectory, N_{Cu} is the number of coppers in the simulation box, and $r_i(t)$ and $r_i(0)$ are positions of the ith copper at times t and 0 respectively. The calculated value, $D^{Cu} = 2.8 \times 10^{-5}$ cm^2 s^{-1}, is in quantitative agreement with that of experiment ($2.2 \pm 0.4 \times 10^{-5}$ cm^2 s^{-1}) measured at 763 K [29]. The good agreement with experiment is particularly satisfactory bearing in mind the large discrepancy between the calculated diffusion coefficient from previously reported MD simulations using different parametrizations of the pair potentials [7, 3, 19].

3.4. Dynamical properties: characteristic times and diffusion

Analysis of interbasin movements (i.e. the diffusion process) within α-CuI has been carried out by dividing the simulation cell into distinct space-filling cubes (sub-cells) [16, 30] with the cube-centre located at the cationic density peak (i.e. the tetrahedral 8c site) and the octahedral site located at alternate cube-corner positions. This choice is convenient for the interpretations of the ionic trajectories since most of the cationic density associated with a given tetrahedral cavity is encapsulated within a given sub-unit (see figure 2). Jumps can be identified when a copper 'escapes' a given sub-cell and 'enters' a new sub-cell. However, to distinguish jumps and vibrations with amplitudes stretching into a neighbouring cavity, a copper is assumed to undergo diffusion if it has 'left' its original cavity and carried out at least one vibrational period, $\tilde{\tau}_{vibr}$, within a new cavity. Thus, a reasonable choice of $\tilde{\tau}_{vibr}$ for the analysis of diffusion within α-CuI, would be within the low frequency domain of the partial vibrational density of states (vDOS). However, since an inspection of the trajectories clearly shows that the 'jumps' are rapid, the possibility of a sequence of rapid successive jumps cannot be ruled out if $\tilde{\tau}_{vibr}$ is set too low. By Fourier transforming the velocity autocorrelation function we find that the vDOS of the coppers possesses a peak at ~ 10 ps^{-1}, which is consistent with a vibrational period of $\tau_{vibr} \sim 0.1$ ps, whereas an inspection of the trajectories shows that the typical flight-time τ_{flight} is

~ 0.5 ps. We therefore choose $\tilde{\tau}_{vibr} \sim 0.25$ ps, which is within the low frequency domain of vDOS and is markedly lower than a typical jump-time. Using this value of $\tilde{\tau}_{vibr}$, the average residence time, $\tau_{residence}$, is ~ 6 ps, which is between one and two orders of magnitude higher than the average vibrational period $\tau_{vibr} \sim 0.1$ ps and roughly an order of magnitude higher than the average flight-time.

The analysis of the trajectories shows that the majority of the coppers are migrating in $\langle 100 \rangle$ directions. Compared to that expected from a simple random diffusion model, where jumps in the $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions would occur in the ratio 3:6:2 (i.e. a tetrahedral cavity has 6, 12 and 4 available migration pathways along a straight line in the three directions respectively), we find that $\sim 85\%$, $\sim 10\%$ and $\sim 5\%$ were migrating in the $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions respectively. The marked bulges in the $\langle 111 \rangle$ directions in the cationic density profile therefore show that the trajectories along the $\langle 100 \rangle$ directions are markedly *curved*, in good agreement with the average density profiles (see figure 2). This is visualized in figure 7 showing different stages of a migrating copper.

3.5. Dynamical properties; correlated diffusion

In our previous discussion, the analysis of the trajectories has been carried out in terms of single-particle events. That is, we have ignored the influence of the neighbouring iodines and the coppers on the jumps of a given copper. However, the presence of highly curved trajectories, the pronounced short-ranged copper–copper correlations and the breakdown in the well established jump diffusion model of Chudley and Elliott [31] at low temperature [7] raises the question of whether atomic correlations may play an important role in the diffusion process within α-CuI.

To investigate this further, we compare the distribution of residence times, $f(\tau)$, with that expected for random (uncorrelated) interbasin jumps [32]. If their diffusion process follows that of random migration one would expect

$$\overline{f}(\tau) = \frac{1}{\langle \tau_{residence} \rangle} \exp(-\langle \tau_{residence} \rangle) \qquad (3.2)$$

whereas any correlated diffusion would be seen as a deviation from this behaviour.

Indeed, as is shown in figure 8, a marked deviation from random diffusion is evident at times $t < 2$ ps, showing an unusually high number of short residential coppers. By contrast, the distribution of residence times at $t > 2$ ps follows that expected for random uncorrelated diffusion. The deviation from random diffusion at $t < 2$ ps can either be (1) attributable to the presence of correlations among the coppers (cooperative migrations), (2) associated with a pronounced coupling of the migrating copper and the low frequency lattice resolved vibrational modes of neighbouring iodines, or (3) both.

The influence of the immobile lattice on the diffusion of the coppers can be calculated by comparing the number of short residence time coppers which are returning to their previous cavity with that expected if they were jumping to a random neighbouring cavity (i.e. the relative number of 'unsuccessful' jumps). We find that a higher fraction, $\sim 25\%$,
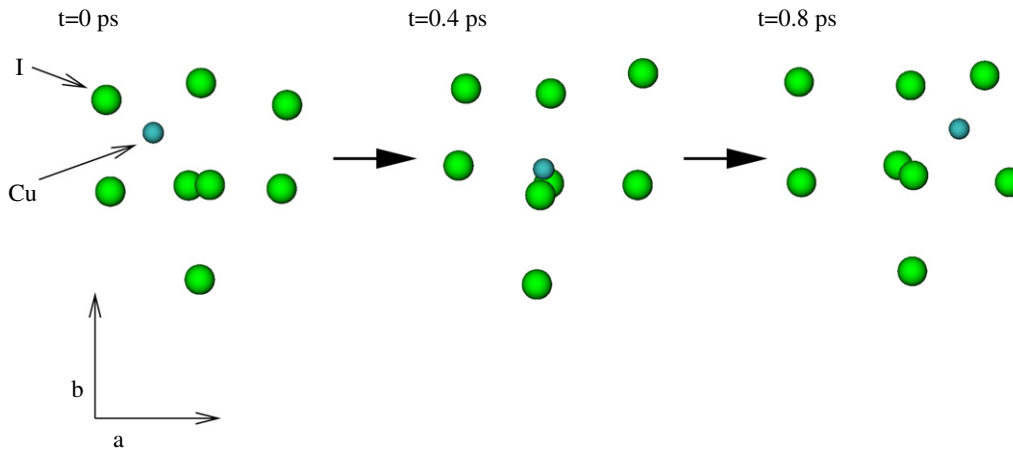
Figure 7. A typical example of a diffusing copper (small sphere) along the $\langle 100 \rangle$ direction. The nearest iodine neighbours (large spheres) during the diffusion are shown.
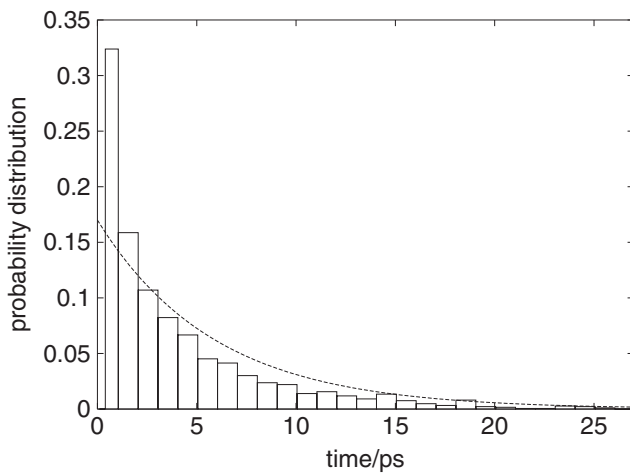

Figure 8. Distribution of the estimated residence times, $\tau_{\text{residence}}$, between jumps. The full line represents the distribution expected for random events.

of the short residence time coppers did return to their original cavities compared to that expected for random diffusion. Such effects have been discussed previously in the context of silver ion conductors, to explain the behaviour of the ionic conductivity measured at GHz frequencies and quasielastic neutron scattering results in terms of the relaxations of the surrounding lattice and their role in determining the success of individual hops [33]. However this does not fully account for all cooperative events, so we carry out an additional analysis investigating the possibility of cooperative diffusion.

Assuming that cooperative diffusion involves only the nearest neighbouring basins (tetrahedral cavities) of a given copper, we can estimate the fraction of cooperative events from the self-part of the van Hove correlation function localized in time and space. If a copper jumps from cavity 'A' to a neighbouring cavity 'B' at time t, we calculate the number of nearest neighbouring (short residential) coppers of 'A' and 'B' that jump at $[t - \Delta t, t + \Delta t]$ (where $\Delta t = 1$ ps), and compare this number with that expected for a random uncorrelated diffusion process. This analysis shows that significant correlations between the migrating coppers take place and that these events basically involve pairs of cooperatively migrating coppers. We estimate that more than 50% of all simultaneously migrating pairs of coppers are of cooperative origin. A very few incidences of simultaneously migrating coppers involving three and four species have been identified, although more statistics is needed to quantify these events. Investigating the nature of these 'cooperative pairs' indicate that the collective diffusion process typically involves a copper jumping from cavity 'A' to 'B' whereas a second copper jumps, shortly after, from cavities 'C' to 'D' (where 'C' and 'B' are neighbours). We find very few events where a given copper enters an already occupied cavity and 'pushes' the copper out of that cavity.

The high occurrence of short residence times can therefore be attributed to both collective diffusion of pairs of coppers and a distinct coupling between the jumping coppers and the nearest neighbouring iodines. It is important to bear in mind that although we find evidence for correlated motion within α-CuI at 750 K, this only accounts for about 10% of all jumps (see figure 8). Thus, we can use a simple jump diffusion model for describing diffusion within α-CuI at $T = 750$ K. Assuming that all jumps occur in the $\langle 100 \rangle$ direction we calculate the diffusion coefficient using $D'^{\text{Cu}} = \frac{1}{6} \nu_{\text{j}} b_{\text{Cu}}^2$, where $\nu_{\text{j}} = 1/\tau_{\text{residence}}$ is the jump frequency, and b_{Cu} is the average jump distance between the nearest neighbouring copper positions. Inserting $\nu_{\text{j}} = \frac{1}{6}$ ps^{-1} above, we find $D'^{\text{Cu}} = 2.6 \times 10^{-5}$ cm^2 s^{-1} which is in good agreement with that found via the Einstein relation above.

4. Concluding remarks

We have examined in detail the structural and dynamical properties of superionic CuI by means of *ab initio* (Born–Oppenheimer) MD simulations. The calculated average ionic density profiles are broadly consistent with previous experimental and computational work and illustrates the extreme disorder of the coppers and a highly flexible immobile

sublattice. The Cu profile has a maximum at the tetrahedral 8c site of space group $Fm\overline{3}m$, contains a marked distortion in the $\langle 111 \rangle$ directions and has a low density in the vicinity of the octahedral 4b site.

Investigations of the local structure within α-CuI have been carried out by calculating the distributions of ion–ion pairs and bond angles. The PDFs are in good agreement with EXAFS [14], ND [10] and CA [8], providing strong evidence for a flexible immobile lattice and pronounced short-range copper–copper correlations. The latter is evident from marked first peaks in the Cu–Cu PDF at 2.6 Å and in the Cu–I–Cu ADF at 60°, since these are located at lower distances and angles compared to those expected from the average cationic density distributions. These shifts have been investigated by the detailed comparison with previously reported lattice static simulations using configurational averaging [8], which enables us to visualize the extent of static disorder (the inherent structures), and thermal excitations out of these inherent structures. The overall good agreement between CA and MD shows that the pronounced short-range copper–copper correlations are due to a locally distorted lattice of mobile ions. The dynamics of the coppers *within* a given cavity therefore involve rapid jumps into and out of shallow basins on the potential energy surface, consistent with the view that the copper undergo extensive anharmonic vibrations along the $\langle 111 \rangle$ directions [5]. Investigations of the local neighbourhood of the iodines show that the iodines are *on average* surrounded by three coppers, whereas a fourth copper is located in a transition zone between the first and second coordination shells of a given iodine. However, a time-resolved analysis indicates that the iodines actually possess a *range* of coordination numbers. This emphasizes the important role played by the immobile lattice in accommodating the coppers under various 'local structural conditions'.

The time-resolved picture of the diffusion of coppers shows that the dynamics of the coppers involves distinct timescales. The coppers are vibrating with a typical period of $\tau_{\text{vibr}} = 0.1$ ps within a tetrahedral cavity for $\sim$6 ps. Inspection of the trajectories emphasizes that the coppers possess extensive anharmonic vibrations along the $\langle 111 \rangle$ directions but are migrating rapidly in the $\langle 100 \rangle$ directions following a highly curved pathway. An investigation of cooperative events underlying the unexpected high number of short residence times was performed by considering (1) the influence of the immobile lattice on the diffusion of coppers and (2) cooperative diffusion of coppers. Firstly, we find an unusually high fraction of 'unsuccessful jumps'. The coppers appear to migrate to a neighbouring cavity but, if the neighbouring iodines do not possess the required degrees of freedom to accommodate a migrating copper, the copper returns to its original cavity. Secondly, investigation of the self-part of the van Hove correlation function provides strong evidence for cooperative movements of pairs of coppers within α-CuI at 750 K. It is important to bear in mind that although we find evidence for correlated motion within α-CuI at 750 K, this only accounts for about 10% of all jumps (see figure 8).

References

[1] Tubandt C and Lorenz E 1914 *Z. Phys. Chem.* **87** 513
[2] Boyce J B, Hayes T M and Mikkelsen J C Jr 1981 *Phys. Rev.* B **23** 2876
[3] Ihata K and Okazaki H 1997 *J. Phys.: Condens. Matter* **9** 1477
[4] Bührer W and Hälg W 1977 *Electrochim. Acta* **22** 701
[5] Keen D A and Hull S 1995 *J. Phys.: Condens. Matter* **7** 5793
[6] Burns G, Dacol F H, Shafer M W and Alben R 1977 *Solid State Commun.* **24** 753
[7] Zheng-Johansson J X M, Ebbsjö I and McGreevy R L 1995 *Solid State Ion.* **82** 115
[8] Mohn C E and Stølen S 2007 *J. Phys.: Condens. Matter* **19** 466208
[9] Zheng-Johansson J X M and McGreevy R L 1996 *Solid State Ion.* **83** 35
[10] Chahid A and McGreevy R L 1998 *J. Phys.: Condens. Matter* **10** 2597
[11] Yashima M, Xu Q, Yoshiasa A and Wada S 2006 *J. Mater. Chem.* **16** 4393
[12] Krug J and Sieg L 1952 *Z. Naturf.* a **7** 369
[13] Shimojo F and Aniya M 2003 *J. Phys. Soc. Japan* **72** 2702
[14] Trapananti A, Di Cicco A and Minicucci M 2002 *Phys. Rev.* B **66** 014202
[15] Keen D A, Hull S, Barnes A C, Berastegui P, Crichton W A, Madden P A, Tucker M G and Wilson M 2003 *Phys. Rev.* B **68** 014117
[16] Jacucci G and Rahman A 1978 *J. Chem. Phys.* **69** 4117
[17] Vashishta P and Rahman A 1978 *Phys. Rev. Lett.* **40** 1337
[18] Wood B C and Marzari N 2006 *Phys. Rev. Lett.* **97** 166401
[19] Vashishta P, Mundy J N and Shenoy G K (ed) 1979 *Fast Ion Transport in Solids* (New York: North-Holland)
[20] Allan N L, Barrera G D, Fracchia R M, Lavrentiev M Yu, Taylor M B, Todorov I T and Purton J A 2001 *Phys. Rev.* B **63** 094203
[21] Todorov I T, Allan N L, Lavrentiev M Yu, Freeman C L, Mohn C E and Purton J A 2004 *J. Phys.: Condens. Matter* **16** S2751
[22] Mohn C E, Allan N L, Freeman C L, Ravindran P and Stølen S 2005 *J. Solid State Chem.* **178** 346
[23] Mohn C E, Stølen S, Norberg S T and Hull S 2009 *Phys. Rev. Lett.* **102** 155502
[24] Perdew J P and Wang W 1992 *Phys. Rev.* B **45** 13244
[25] Kresse G and Hafner J 1993 *Phys. Rev.* B **47** 558
[26] Kresse G and Hafner J 1994 *Phys. Rev.* B **49** 14251
[27] Chahid A and McGreevy R L 1997 *Physica* B **234** 87
[28] Kawakita Y, Tahara S, Fujii H, Kohara S and Takeda S 2007 *J. Phys.: Condens. Matter* **19** 335201
[29] Dejus R, Sköld K and Granéli 1980 *Solid State Ion.* **1** 327
[30] Wengert S, Nesper R, Andreoni W and Parrinello M 1996 *Phys. Rev. Lett.* **77** 5083
[31] Chudley C T and Elliott R J 1961 *Proc. Phys. Soc. Lond.* **77** 353
[32] Da Fano A and Jacucci G 1977 *Phys. Rev. Lett.* **39** 50
[33] Funke K 1993 *Prog. Solid State Chem.* **22** 111