Diffusion of lithium ions in Lithium-argyrodite solid-state electrolytes

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The use of solid-state electrolytes to provide safer, next-generation rechargeable batteries is becoming more feasible as materials with greater stability and higher ionic diffusion coefficients are designed. However, accurate determination of diffusion coefficients in solids is problematic and reliable calculations are highly sought-after to understand how their structure can be modified to improve their performance. In this paper we compare diffusion coefficients calculated using nonequilibrium and equilibrium ab initio molecular dynamics simulations for highly diffusive solid-state electrolytes, to demonstrate the accuracy that can be obtained. Moreover, we show that ab initio nonequilibrium molecular dynamics can be used to determine diffusion coefficients when the diffusion is too slow for it to be feasible to obtain them using ab initio equilibrium simulations. Thereby, using ab initio nonequilibrium molecular dynamics simulations we are able to obtain accurate estimates of the diffusion coefficients of Li ions in Li₃PS₅Cl and Li₅PS₄Cl₂, two promising electrolytes for all-solid-state batteries. Furthermore, these calculations show that the diffusion coefficient of lithium ions in Li₅PS₄Cl₂ is higher than many other potential all-solid-state electrolytes, making it promising for future technologies. The reasons for variation in conductivities determined using computational and experimental methods are discussed. It is demonstrated that small degrees of disorder and vacancies can result in orders of magnitude differences in diffusivities of Li ions in Li₃PS₅Cl and these factors are likely to contribute to inconsistencies observed in experimentally reported values. Notably, the introduction of Li-vacancies and disorder can enhance the ionic conductivity of Li₅PS₄Cl₂.

A solid-state electrolyte that is comparable with its liquid counterpart in terms of performance should be able to conduct lithium ions from the cathode material to the anode material efficiently. In order to achieve this, the ionic conductivity of the electrolyte should be higher than approximately 10⁻³ S cm⁻¹ at room temperature.

Determination of the conductivity of solid-state electrolytes is complicated in experiments due to the challenges in reproducible synthesis of the materials and the sensitivity of the conductivity on structure. Computational methods provide a resource that can be used to determine conductivity and its dependence on structure and composition of the crystalline materials. In computations, these parameters can be precisely controlled, unlike experimental studies where impurities and defects can be present, which are sensitive to the synthetic conditions and difficult to characterize. In order to avoid difficulties in development of force fields for these systems where charge transfer and polarizability are likely to play a role, ab initio molecule dynamics simulations are attractive and have been widely employed. However, because of the relatively low conductivity of solid-state electrolyte materials (usually lower than 10⁻³ S cm⁻¹), in most cases it is very computationally expensive, and sometimes impossible, to directly calculate an accurate value for conductivity of the materials at room temperature using ab initio molecular dynamics simulations. One way to solve this problem is to calculate the diffusion coefficient at high temperatures and use the Arrhenius relation to predict a value for ionic diffusion at room temperature. However, the relative errors in the final value of the conductivity is likely to be large because statistical errors in the high-temperature data lead to even larger relative errors in the
extrapolated results\textsuperscript{14}. Therefore, alternative computational methods that can give reliable estimates of the diffusion coefficient need to be applied to study these systems. We show that ab initio (AI) nonequilibrium molecular dynamics (NEMD) simulations can be used to this effect. Although AI-NEMD simulations were used to determine the ionic conductivity of LiBH\textsubscript{4} in a previous study\textsuperscript{17}, the results in that study were not compared with results from AI equilibrium molecular dynamics (EMD) simulations. Therefore, one aim of this work is to demonstrate that AI-NEMD simulations enable reliable estimates of the diffusion coefficients to be obtained for materials with diffusivities that are unable to be directly determined using equilibrium calculations. These results can be used to predict materials worthy of consideration as solid-state electrolytes and to identify reasons for variation in experimental measurements.

Among the all-solid-state electrolytes, sulfide-based electrolytes are one of the most promising candidates due to their moderate electrochemical stability, good mechanical properties, and ionic conductivities that are higher than many other potential solid-state electrolytes\textsuperscript{16–21}. The Li-argyrodites are a family of sulfide-base electrolytes based on Li\textsubscript{6}PS\textsubscript{5}X, some of which have relatively high ionic conductivity of \(10^{-5} - 10^{-3}\) S cm\(^{-1}\) at room temperature\textsuperscript{22}. The Li-argyrodites form a high and low-temperature phase and the ionic conductivity is greater in the high-temperature phase. Most of the higher conductivity argyrodite structures, including Li\textsubscript{6}PS\textsubscript{5}X, are not stable at room temperature. However, it has been shown that by making Li vacancies and incorporating halogens into the structure of Li\textsubscript{6}PS\textsubscript{5}X, it is possible to form structures with empirical formula Li\textsubscript{5}PS\textsubscript{4}X (X = Cl, Br and I) that are stable in the higher conductivity phase at room temperature\textsuperscript{23,24}. Experiments show that Li\textsubscript{5}PS\textsubscript{4}X (X = Cl, Br and I) have the same crystallographic structures (space group \(F\overline{4}3m\)) as Li\textsubscript{5}PS\textsubscript{6} and the ionic conductivity of Li\textsubscript{5}PS\textsubscript{5}Cl and Li\textsubscript{5}PS\textsubscript{5}Br at room temperature is high enough to be considered for battery technology\textsuperscript{25,26}. In addition, the effects of halide disorder has been investigated\textsuperscript{27}. Li\textsubscript{5}PS\textsubscript{5}Cl is reported to have a conductivity of \(~10^{-2}\) S cm\(^{-1}\) at room temperature and to be electrochemically stable up to 7 V versus Li/Li\textsuperscript{+}\textsuperscript{26,27}. Calculations have suggested that extra halogens and Li-vacancies result in higher conductivities and it has been proposed that Li\textsubscript{5}PS\textsubscript{5}Cl\textsubscript{2} could be an alternative material, although it has not yet been synthesized\textsuperscript{28}.

Li\textsubscript{5}PS\textsubscript{5}Cl is an argyrodite electrolyte for which there has been much experimental and computational research. However, due to various difficulties mentioned above, the diffusion mechanism in this material is not fully understood and the predictions of the conductivity using computational and experimental results vary over orders of magnitude\textsuperscript{15,16,23,26–29}.

The main aims of this paper are to compare AI-NEMD simulations with standard AI-EMD simulations and show that AI-NEMD methods can be used to determine ionic conductivity in low conductivity materials such as solid-state electrolytes. All our simulations use ab initio molecular dynamics simulations, so we drop ‘AI’ from the acronyms AI-EMD and AI-NEMD from this point on. We firstly consider Li\textsubscript{5}PS\textsubscript{4}Cl\textsubscript{2} because it has a lithium ion self-diffusion coefficient that is sufficiently high that EMD simulations can readily be used for its calculation. Thus, the ionic conductivity of Li\textsubscript{5}PS\textsubscript{5}Cl\textsubscript{2} can be determined at different temperatures and using both EMD and NEMD methods. The results are used to demonstrate the accuracy that can be achieved using both methods, and the statistical errors resulting from extrapolation using the Arrhenius equation. The ionic conductivity of Li\textsubscript{5}PS\textsubscript{5}Cl at room temperature is then determined using NEMD simulations and the results are compared with other computational and experimental results. This material has a much lower diffusion coefficient than Li\textsubscript{5}PS\textsubscript{5}Cl\textsubscript{2} and past results determined using EMD simulations have differed by several orders of magnitude. Finally, the methods are used to study Li\textsubscript{5}PS\textsubscript{5}Cl with vacancies and defects to help identify the reasons for different experimental reports of the conductivity of Li\textsubscript{5}PS\textsubscript{5}Cl\textsubscript{2}\textsuperscript{16,23,26–29}.

### RESULTS

**Argyrodite structures**

The Li\textsubscript{6}PS\textsubscript{5}Cl argyrodite structure is cubic with space group \(F\overline{4}3m\) (space group number 216)\textsuperscript{10}. A supercell based on 2 unit cells each containing 4(Li\textsubscript{6}PS\textsubscript{5}Cl), which has 104 atoms (8 primitive unit cells), was considered for all the calculations on this material. In this work the unit cell lattice parameters were determined by energy minimization and were 10.08 Å \(\times \) 10.08 Å \(\times\) 10.08 Å. Figure 1 shows the crystal structure of Li\textsubscript{6}PS\textsubscript{5}Cl. In this structure the Li ions occupy 48h Wyckoff positions, and S atoms are distributed on 4a and 4c-sites. Sulfurs in the 4a-sites are bound to the phosphorous atoms (4b-sites) forming PS\textsubscript{4}\textsuperscript{3–} (labelled S1), sulfurs as S\textsuperscript{2–} are in 4c-sites and are surrounded by Li ions (labelled S2). The Cl ions are distributed in 4a-sites as well.

The pure and defective structures were formed based on the Li\textsubscript{6}PS\textsubscript{5}Cl crystal structure. Details of the defective Li\textsubscript{6}PS\textsubscript{5}Cl structures are described below. To model the Li\textsubscript{6}PS\textsubscript{5}Cl\textsubscript{2} structure, the S2 sulfur ions were replaced by chloride ions, and to keep the structure charge balanced, one of the Li ions surrounding each S2 was removed from the structure\textsuperscript{28}.

### Ionic conductivity of Li\textsubscript{5}PS\textsubscript{5}Cl\textsubscript{2}

For Li\textsubscript{5}PS\textsubscript{5}Cl\textsubscript{2}, calculation of the diffusion coefficient was feasible using EMD and NEMD simulations at 300 K, 600 K, 800 K and 1000 K. Therefore, this system provides a sample where the accuracy of the EMD and NEMD methods can be compared, and the direct calculation at 300 K can be compared with the result from extrapolation of high temperature-data using the Arrhenius equation (see Methods).
The EMD simulations at 300 K, 600 K, 800 K and 1000 K were run for 45, 40, 20 and 20 ps, respectively. The results of these EMD simulations were used to obtain the average MSD of the Li ions and results for 10 system replicas at each temperature, and the statistical errors at each temperature were obtained. In each case the trajectories were examined to ensure that the simulation times (ranging from $10 \times 45$ ps to $10 \times 20$ ps) were sufficient to observe diffusion of Li ions well away from their initial sites.

Figure 2a–c shows the MSD of the Li ions as a function of time at 300, 600 and 800 K for the 10 independent trajectories. For diffusive motion, the MSD increases linearly with time at long times, and the slope is related to the diffusion coefficient through Eq. (7). Figure 2d–f shows the average MSD of the ten replicas including the error bars (one standard error in the mean) at d 300 K, e 600 K and f 800 K.

Table 1. The self-diffusion coefficient and corresponding conductivity of Li$_5$PS$_4$Cl$_2$ at different temperatures calculated using EMD and NEMD simulations.

| Temperature (K) | EMD | NEMD |
|----------------|-----|------|
|                | $D_s$ (cm$^2$ s$^{-1}$) | $\sigma$ (S cm$^{-1}$) | $D_s$ (cm$^2$ s$^{-1}$) | $\sigma$ (S cm$^{-1}$) |
| 300            | $2.9 (4) \times 10^{-6}$ | 0.35 (5) | $3.3 (4) \times 10^{-6}$ | 0.40 (5) |
| 600            | $2.9 (2) \times 10^{-5}$ | 1.8 (1)  | $2.9 (2) \times 10^{-5}$ | 1.8 (1)  |
| 800            | $5.6 (3) \times 10^{-5}$ | 2.5 (1)  | $5.2 (4) \times 10^{-5}$ | 2.4 (2)  |
| 1000           | $8.9 (4) \times 10^{-5}$ | 3.2 (2)  | $8.9 (5) \times 10^{-5}$ | 2.9 (3)  |

The numbers in brackets refer to error in the last decimal place.

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For solid-state electrolytes that have low conductivity at room temperature ($\sim 10^{-3}$ S cm$^{-1}$ or lower) it is computationally expensive to directly calculate a precise value for the conductivity at room temperature using ab initio simulations. To solve this issue it is common to calculate the conductivity of the material at higher temperatures and extrapolate the data to room temperature to give an estimate of the conductivity$^{16,31}$. An Arrhenius plot of the values of the conductivity calculated from the EMD simulations of the Li ion in Li$_5$PS$_4$Cl$_2$ from the MSDs at different temperatures is shown in Fig. 3 (red data points). Note that plots of the conductivity as a function of temperature in Fig. 3 and subsequent figures show the conductivity multiplied by the temperature versus the reciprocal temperature to enable consistency with Arrhenius behavior.

Table 1.

Fig. 2 Mean square displacement (MSD) of Li ions as a function of time. Results for 10 replicate simulations of Li$_5$PS$_4$Cl$_2$ at a 300 K, b 600 K and c 800 K, and average MSD of the ions as a function of time for 10 replicates with the error bars (one standard error in the mean) at d 300 K, e 600 K and f 800 K.

Fig. 3 Arrhenius plot of the conductivity for Li$_5$PS$_4$Cl$_2$. Results obtained from EMD simulations (red) and NEMD simulations (blue) at various T (data points) are shown. Red lines (EMD) and blue lines (NEMD) show the bounds of error for estimation of extrapolated data at 600 K and 800 K to 300 K assuming Arrhenius behavior.
extrapolation of the 600 and 800 K data are shown. Measurements at many temperatures are normally recommended when an Arrhenius extrapolation is required. Certainly more than two points are required to test if Arrhenius behavior is observed. However, if the purpose is not to test for Arrhenius behavior but to obtain precise diffusion coefficients for a material where this is known to be valid, having many measurements at extreme temperatures (10 measurements at two temperatures in this case) is likely to provide lower statistical error in the extrapolation due to the dependence of the error in the slope on the range of the data.

Based on the MSD calculations, Li$_5$PS$_4$Cl$_2$ has an ionic conductivity of $0.35 \pm 0.05 \text{ S cm}^{-1}$ at 300 K. Figure 3 shows that by considering the data at 600 and 800 K, the calculated conductivity using extrapolation gives an ionic conductivity between 0.17 and 0.37 S cm$^{-1}$ at 300 K. This agrees with the directly calculated value. However, even though the statistical errors for the higher temperature results are small compared to the values, the relative error at lower temperatures is large due to the extrapolation, as can be seen from Fig. 3. Including the result at 1000 K in the extrapolation gave a result of between 0.17 and 0.33 S cm$^{-1}$ at 300 K. Only a small change was observed by adding an extra higher temperature because a large change in temperature is required to obtain a very different value of the reciprocal temperature. Care should be taken that the higher temperature does not result in phase changes or alternative mechanisms of diffusion and consequent non-Arrhenius behavior.

To determine the ionic conductivity of solid-state electrolytes Aeberhard et al. used an alternative approach that has been widely applied in classical simulations, but had not been used in ab initio simulations, and is based on NEMD simulations (see Methods). They determined the self-diffusion coefficient of hexagonal LiBH$_4$ at 535 K. In the present work, to show the accuracy of NEMD simulations this method was used to predict the self-diffusion coefficients and conductivities of Li$_5$PS$_4$Cl$_2$ at 300 K, 600 K, 800 K and 1000 K, and the results are compared with the results determined from the EMD MSD calculations.

In order to calculate the ionic conductivities from NEMD simulations, it is necessary to determine the conductivity at several fields to identify the linear response regime (the region where the color current increases from zero at $F_c = 0$, linearly with the field). The linear response regime cannot be predetermined, and must be tested in each case. To identify the linear regime, at least two points with similar values for the conductivity or the diffusion coefficient are required. At each field in the linear regime, 10 simulations were carried out for 15 ps, 13 ps, 5 ps and 5 ps at 300 K, 600 K, 800 K and 1000 K, respectively. These times were selected to give a total computational effort similar to that required for the EMD simulations. Figure 4a, b shows the time integral of the color current due to a color field of $F_c = 0.04 \text{ eV Å}^{-1}$ for Li$_5$PS$_4$Cl$_2$ at 600 K using the methodology described above. Figure 4c shows the time integral of the color current due to color fields of 0.02 and 0.03 eV Å$^{-1}$ at 300 K. Figure 5 shows the time-averaged color current density of the Li ions as a function of field strength at 300, 600 and 800 K and the linear regime was identified as being between 0 eV Å$^{-1}$ and ~0.03, 0.04 and 0.02 eV Å$^{-1}$, respectively.

The Arrhenius plot for the conductivities calculated using NEMD simulations at different temperatures is presented in Table 1 and shown by the blue data in Fig. 3. The values obtained by the EMD and NEMD methods agree to within the limits of error (within one standard error of the mean). The conductivity of the material at 300 K is also estimated by extrapolating from higher temperatures. Comparing the red and blue lines in Fig. 3, it is clear that using similar total simulation times for NEMD and EMD calculations at 300, 600 and 800 K, the statistical errors in the NEMD simulation results were almost the same as the statistical errors of the results from the EMD method. This was true for the results obtained for direct measurement at 300 K and from extrapolation of the high temperature results to 300 K. These outcomes are consistent with the fact that for this highly diffusive system, the lithium ions are readily able to move between different regions of the sample in all cases and a field is not required to force the ions from one ‘cage’ to the next.

![Fig. 4](image-url)
Collective diffusion coefficient of Li$_5$PS$_4$Cl$_2$

The Nernst-Einstein equation is often used to relate the conductivity to the self-diffusion coefficient. However, if the diffusing atoms or molecules in the studied sample are not moving independently during diffusion then this might not be an adequate approximation and the collective diffusion coefficient should be considered$^{32}$. The self and collective diffusion coefficients will be the same if the diffusing atoms or molecules move independently of each other, but they will differ otherwise (for example, if they move as a cluster). We therefore used Eq. (8) to calculate the collective diffusion coefficient for Li$_5$PS$_4$Cl$_2$ and compare this to the self-diffusion coefficient to check that this approximation is adequate for the systems we consider. The most diffusive pure system we considered in this manuscript was used for this purpose. It was selected because the statistical error is much larger for the collective diffusion calculations than for the self-diffusion calculations and it would be difficult to draw conclusions if the statistical error is too large.

Figure 6 compares the MSD of the ions and their center of mass for Li$_5$PS$_4$Cl$_2$ at 800 K. Note that the ion MSD was determined from 10 independent runs and the ion center of mass MSD from 30 independent runs (each run for 20 ps), yet the error bars for the ion MSD remain much smaller. This is because each of the ions in the sample could provide an independent contribution to the MSD. It is clear that the MSD calculated in both ways agree within the limits of error for this material and therefore the self and collective diffusion coefficients will agree. The agreement is consistent with independent behavior of single Li ions in Li$_5$PS$_4$Cl$_2$ during the diffusion process and therefore gives us confidence that for this system the conductivity can be calculated using the self-diffusion coefficient.

Ionic conductivity of Li$_6$PS$_5$Cl

Since simulation times for diffusive motion scale inversely with the diffusion coefficient$^{33}$, in systems with low conductivity it is expected that EMD simulations would need to be very long to obtain accurate results, and at some stage no movement of ions between regions or cages in the electrolyte will be observed in a feasible time-scale. From the calculations on Li$_6$PS$_5$Cl$_2$, it was found that combining NEMD simulations at high temperatures with extrapolation to low temperatures could give accurate results. Therefore, we propose that this could be a way of extending the range of materials for which the conductivity can be calculated by providing a method when the conductivity is so low that EMD simulations cannot be used. Here we test this proposal by calculating the ionic conductivity of Li$_6$PS$_5$Cl using NEMD simulations.

Both EMD and NEMD simulations were carried out with the aim of calculating the conductivity and understanding the mechanism of diffusion in pure Li$_6$PS$_5$Cl, Li$_6$PS$_5$Cl with S-Cl disorder (S and Cl swapping positions) and Li$_6$PS$_5$Cl with both Li$^+$ vacancies and S-Cl disorder.

We firstly consider pure Li$_6$PS$_5$Cl. There are two distinct types of motion in this system. One where a set of 6 Li ions move in an octahedral region about an S2 sulfur atom and another where the Li ion moves (jumps) between these octahedral regions (or cages). If the timescale for the jumps is longer than the simulation time, then a diffusion coefficient cannot be determined from the simulation. Using EMD simulations of Li$_6$PS$_5$Cl, no jumps between cages were observed in 10 independent trajectories of 100 ps at 300 and 450 K and very few, or no, jumps were observed for the trajectories at 600 K. This suggests a very low diffusion coefficient of the material at 300 K (less than $10^{-4} \text{ S cm}^{-1}$) and demonstrates the difficulty of measuring the value of the conductivity through EMD simulations$^{33}$. However, it was possible to obtain the conductivity values using NEMD simulations at both 600 K and 800 K, where jumps could be observed, and the conductivity at 300 K was estimated using extrapolation of these results, assuming Arrhenius behavior. In Fig. 7, the red unfilled squares show the calculated conductivities at 600 and 800 K (the error bars are smaller than the symbols), and the lines show the bounds of predictions for the conductivity of pure Li$_6$PS$_5$Cl at lower temperatures. As can be seen from Fig. 7, the conductivity of the pure Li$_6$PS$_5$Cl is predicted to be $10^{-5}$–$10^{-4} \text{ S cm}^{-1}$. The simulation time required to obtain similar precision for the conductivity of Li$_6$PS$_5$Cl using the EMD method at 600 and 800 K was prohibitive, and we were not even able to estimate a mean and standard error because jumps did not occur. An alternative would be to consider higher temperatures but the extrapolation errors would be greater if the minimum temperature is higher, and it could lead to a disruption of the structure and non-Arrhenius behavior for the diffusion coefficient. Therefore the NEMD approach is more appropriate in this case.

The Li ion conductivity for pure Li$_6$PS$_5$Cl has previously been determined experimentally$^{29,30,34}$ and computationally$^{16,28}$ at 300 K and these results are also shown in Fig. 7 as circles (experimental data) and crosses (computational data). It can be seen there are differences in the orders of magnitude of results at 300 K. Of particular note is that the computational results from the literature for pure Li$_6$PS$_5$Cl at 300 K differ by 5 orders of magnitude and are between one and four orders of magnitude different from the experimental results. The lower value was obtained by extrapolation of data for simulations at 600 K and higher.
Therefore it seems that there are no reliable computational estimates of the diffusion coefficient for this system prior to the current work. Our computational prediction is similar to the highest experimental result. The statistical error in the computational results from the previous studies were not reported in most cases, but is expected to be high based on the computational time and supercell sizes considered, and the inherent error propagation when extrapolating the data for materials with low conductivity. It is clear that for this system, the low jump frequency of Li ions in Li$_6$P$_5$S$_5$Cl at room temperature ($\sim$10$^{-9}$ s$^{-1}$) according to ref. 37 requires extrapolation of the higher temperature to predict the conductivity at lower temperatures and use of NEMD.

The experimental results differ by a factor of two, and it was proposed in the literature that this could be due to the annealing temperature of the samples which causes different degrees of Cl and S disorder, the level of the crystallinity, existence of extra chlorine in the synthesized structure, Li vacancy in the structure, and existence of impurities of the synthesized samples. The effects of some of these factors are considered in the sections below.

We now consider the effect of disorder in Li$_6$P$_5$S$_5$Cl. It has been proposed that the high conductivity of Li$_6$P$_5$S$_5$Cl observed in some experiments could be due to disorder of Cl and S atoms. To test and understand this, we consider a model of the disordered structure and assume Arrhenius behavior for the diffusion. Other effects are considered in the sections below.

The diffusion pathways of the Li ions in the ordered and disordered structures at 600 K were also determined using EMD simulations and are shown in Fig. 8. Comparing the pathways, it is apparent that introducing disorder by swapping the positions of Cl and S ions significantly changes the motion of the Li ions. As seen in Fig. 8a, b, in the pure systems Li ions move inside the octahedral cages formed by the PS$_x$Cl$_{1−x}$ (see Fig. 1) and the absence of pathways between the cages indicate that the energy barrier for diffusion out of the cages is high compared to the thermal energy available, and consequently the ionic conductivity of the pure crystal is too low to be determined from these EMD simulations.

However, in the disordered structure, a channel between the cages is evident in the right half of the structure (where the ions are swapped) in Fig. 8c, d. This indicates that in the direction of the new channel, the barrier energy for Li ion diffusion to the other cages is much smaller than it was in the pure structure and Li ions move in the disordered part of the structure relatively easily. The presence of a channel with a lower energy barrier explains the increase in the ionic conductivity of the disordered Li$_6$P$_5$S$_5$Cl. Also, variation in the concentration of S2-CI disorder and dispersion of the disordered sites could explain the different experimentally reported conductivities.

It has been proposed that Li vacancies can be present in samples of Li$_6$P$_5$S$_5$Cl which would be expected to increase their Li ion conductivity. In a study considering this, the experimentally synthesized sample was suggested to have experimental formula Li$_{5.8}$P$_{5.8}$S$_{4.8}$Cl$_{1.2}$ after annealing. We note that the charges are not balanced in the proposed empirical formula, Li$_{5.8}$P$_{5.8}$S$_{4.8}$Cl$_{1.2}$. However, a similar formula with charge balance is Li$_{5.8}$P$_{5.8}$S$_{4.8}$Cl$_{2.2}$. To study the effect of the combination of a Li-vacancy, extra Cl ions and fewer S2 ions on the ionic conductivity of the Li$_6$P$_5$S$_5$Cl, we remove Li ions from the Li$_6$P$_5$S$_5$Cl supercell (8 unit cells) and replace two S2 ions with two Cl ions giving a new structure of Li$_{5.7}$S$_{5.7}$P$_{5.7}$Cl$_{1.75}$ which is similar to the empirical formula given in the literature (Li$_{5.8}$P$_{5.8}$S$_{4.8}$Cl$_{2.2}$). The ionic conductivity of this structure at 300 K was calculated to be 0.09 ± 0.03 S cm$^{-1}$, which is several magnitudes higher than the pristine Li$_6$P$_5$S$_5$Cl solid electrolyte (6 × 10$^{-3}$–3 × 10$^{-5}$ S cm$^{-1}$) and higher than the estimated value for Li$_6$P$_5$S$_5$Cl with disorder of the S2 and Cl atoms only (6 × 10$^{-3}$–1 × 10$^{-3}$ S cm$^{-1}$). The estimated value for the ionic conductivity is also higher than that reported in ref. 36 (1.1 × 10$^{-3}$ S cm$^{-1}$), but the sensitivity to vacancies and disorder means that these would not be expected to agree due to the difference in empirical formulas. Clearly, Li vacancies and substitution of an S ion with a Cl ion significantly increase the diffusion in the structure. This increase is expected because the Li vacancies and the smaller size of the Cl ions and the S2 ions will provide more space movement of the Li ions, and the disorder introduced by the replacement of the S2 ions with Cl ions will facilitate diffusion as discussed above (see Supplementary Fig. 2 for the diffusion pathways in Li$_{5.7}$P$_{5.7}$S$_{5.7}$Cl$_{1.75}$, at 450 K).

Table 2 presents a summary of conductivities of the different types of Li$_6$P$_5$S$_5$Cl structures (pure, disordered and structures having both disorder and Li vacancies) from experimental and computational reports. Based on the results from our calculations and previously reports in the literature, it can be concluded that the conductivity of pure Li$_6$P$_5$S$_5$Cl is relatively low (10$^{-5}$–10$^{-4}$ S cm$^{-1}$). However, impurities like Li-vacancies, grain boundaries, and ion disorder introduced during their synthesis would affect the final conductivity of the synthesized argyrodite electrolyte.
In this paper, the diffusion mechanism of Li ions in Li$_6$PS$_5$Cl and Li$_5$PS$_4$Cl$_2$ and the diffusion coefficients/conductivity were studied in detail. Comparison of the EMD and NEMD methods show that both methods can be used to predict the ionic diffusion of these materials when their ionic conductivity is around $10^{-3}$–$10^{-2}$ S cm$^{-1}$. If these materials have much lower ionic conductivity (e.g., at lower temperatures), the EMD simulation times required to get precise and reproducible results are not currently feasible. However, we show that it is feasible to use NEMD to determine diffusion coefficients of solid-state electrolytes with conductivities of around $10^{-6}$–$10^{-4}$ S cm$^{-1}$.

Agreement of the results from these methods showed that they are both able to provide reliable estimates of conductivity when the conductivity is sufficiently high. However, for solid-state electrolyte with low conductivity, which are common at temperatures closer to room temperature, it is necessary to use NEMD simulations. The advantage of NEMD over EMD calculations increases as the diffusivity decreases. This is because the time required to explore a material in equilibrium simulations is inversely proportional to the diffusion coefficient whereas the applied field will also contribute to this in NEMD simulations.

We note, that if the diffusion is not isotropic it will be necessary to carry out several NEMD simulations with fields in different directions in order to obtain the diffusion coefficients. Therefore the efficiency of the NEMD calculations would be reduced in this case. However, it will still be advantageous, or necessary, at sufficiently low fields.

We also studied the conductivity of Li$_6$PS$_5$Cl and Li$_6$PS$_5$Cl$_2$ in detail and the effect of disorder and defects on diffusion of the Li ions in Li$_6$PS$_5$Cl. Based on the results from our calculations, Li$_6$PS$_5$Cl$_2$ is predicted to be a highly conductive solid electrolyte.

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**DISCUSSION**

**Table 2.** The conductivity of Li$_x$PS$_y$Cl and defective materials at 300 K determined in various experiments and computational studies including this work.

| Material                  | Conductivity/S cm$^{-1}$ | Source                          |
|---------------------------|--------------------------|---------------------------------|
| Li$_6$PS$_5$Cl            | $1.4 \times 10^{-5}$     | Experiment$^{29}$               |
|                           | $3.3 \times 10^{-5}$     | Experiment$^{29}$               |
|                           | $6 \times 10^{-5} - 6 \times 10^{-4}$ | This work (NEMD)               |
|                           | $6 \times 10^{-5}$       | Experiment$^{34}$               |
|                           | 0.29                     | Computation (MSD)$^{28}$         |
|                           | 0.05 (0.16)              | Computation (Jump)$^{28}$        |
|                           | $2 \times 10^{-6}$       | Computation (MSD)$^{16}$         |
| Li$_5$PS$_4$Cl$_2$        | $1.1 \times 10^{-3}$     | Experiment$^{36}$               |
| Li$_5$,$P$$_4$S$_7$Cl$_1$ | $6 \times 10^{-2} - 6 \times 10^{-1}$ | This work          |
| Li$_5$PS$_4$Cl$_2$ with Cl and S disorder | $1.9 \times 10^{-3}$ | Experiment$^{35}$               |
|                           | $4.96 \times 10^{-3}$    | Experiment$^{37}$               |
|                           | $3.38 \times 10^{-3}$    | Experiment$^{38}$               |
|                           | 0.26                     | Computation (MSD)$^{16}$         |
|                           | 0.89 (1.29)              | Computation (Jump)$^{28}$        |
|                           | $6 \times 10^{-3} - 6 \times 10^{-1}$ | This work (EMD)               |

$^*$The ranges given are based on extrapolation of data at 800 and 600 K, for which error bars of one standard error are assumed.

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**Fig. 8** Li ion trajectories. Different views of the Li ion trajectories are shown in a, b for pure and c, d for S-Cl disordered Li$_6$PS$_5$Cl at 600 K monitored for 50 ps. The violet, yellow, green and light purple atoms are lithium, sulfur, chlorine and phosphorus, respectively. The small violet dots show the diffusion pathways of the lithium ions. The boxes show one simulation supercell.
although it has not yet been synthesized. For Li$_5$PS$_4$Cl, although the pure material has a relatively low ion conductivity ($6 \times 10^{-5}$ to $3 \times 10^{-4}$ S cm$^{-1}$ at 300 K) we confirmed that by increasing Li vacancies of the structure or introducing disorder in the ionic positions of the Cl and S ions, it is possible to enhance the ion conductivity of this structure. Although these systems had been studied previously, the size of the error bars made it difficult to ascertain the effects. It can be concluded that the higher experimentally reported conductivity of Li$_5$PS$_4$Cl could be due to combinations of Li ion vacancies and Cl-S ion disorder or maybe higher concentration of halogen (Cl) after annealing. We note that our computational results either predict conductivities that are higher than the experimental results, or on the high end of the range of experimental results. There are some systematic errors in the computations that might contribute to this including the system size that can be modelled, the level of theory used in the ab initio molecular dynamics simulations and changes in the lattice parameters during diffusion which is carried out at constant volume conditions. However, the presence of grain boundaries, impurities, disorder and the inhomogeneous distribution of disordered sites in the experimental samples could also explain the differences between the experimental and computational results. Importantly, the computational results are reproducible and the trends due to changes in the structure indicate ways in which a material can be tuned to increase the conductivity which is crucial for the improvement of solid-state-electrolytes.

**METHODS**

**Ab initio molecular dynamics simulations**

Ab initio Born-Oppenheimer molecular dynamics simulations were performed using the CP2K/Quickstep package$^{40,41}$ and a modified version of this that incorporated the NEMD algorithm discussed below. The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA)$^{42}$ was selected for the DFT exchange-correlation functional. To correct for van der Waals interactions the DFT-D3$^{43}$ method was used. Pseudopotentials of Goedecker, Teter and Hutter (GTH) were employed$^{44}$ The D2VP-MOLOPT-SR-GTH$^{45}$ basis set was selected because it is optimized for calculating molecular properties in gas and condensed phases. This is a Gaussian and plane-wave (GPW) basis$^{46}$ and a cutoff energy of 280 Ry was selected. A 1×1×1 1-k point mesh (Γ point) was used in all calculations and preliminary optimization calculations indicated that using grid introduced errors of less than 0.01 Å for lattice parameters and errors of less than 0.06 eV for the energy per unit cell. The optimized lattice constants (10.08 Å) are 2.5% larger than the experimentally reported value for Li$_5$PS$_4$Cl, and similar to results reported in earlier computational work$^{16,48}$

**Equilibrium and nonequilibrium equations of motion**

Both EMD and NEMD simulations were used to calculate the diffusion coefficients of the materials in the NVT ensemble. The equations of motion for the EMD simulations are:

$$\mathbf{q}_i = \frac{\mathbf{p}_i}{m_i}$$  \hspace{1cm} (1)

$$\mathbf{p}_i = \mathbf{F}_i - c_i \mathbf{p}_i$$  \hspace{1cm} (2)

where $\mathbf{q}_i$ is the position, $\mathbf{p}_i$ is the momentum and $m_i$ is mass of atom $i$. $\mathbf{F}_i$ is the interatomic force on atom $i$ and $c_i$ couples the approximations to the Nosé-Hoover thermostat. A chain thermostat with the chain number of 3 (the default for CP2K) was applied for the EMD calculations:

$$\dot{\alpha}_2 = \frac{\alpha_2}{\beta} (\sum_{i=1}^{N} \mathbf{F}_i - g \mathbf{q}_i) - \alpha_1 \alpha_2$$  \hspace{1cm} (3)

$$\dot{\alpha}_3 = \frac{\alpha_3}{\beta} (\sum_{i=1}^{N} \mathbf{F}_i - g \mathbf{q}_i) - \alpha_1 \alpha_2$$  \hspace{1cm} (4)

$$\dot{\alpha}_1 = \frac{\alpha_1}{\beta} (\sum_{i=1}^{N} \mathbf{F}_i - g \mathbf{q}_i) - \alpha_1 \alpha_2$$  \hspace{1cm} (5)

In the above equations $Q$, $Q_1$ and $Q_2$ are the friction coefficients which were all given equal values of 3 in the equilibrium simulations, $k_B$ is Boltzmann’s constant, $T$ is the target temperature and $g$ is the number of degrees of freedom of the system.

The nonequilibrium method used to determine the diffusion coefficients is the color diffusion algorithm (for Li-ions) which has been widely applied in classical molecular dynamics simulations$^{47,48}$. Using this algorithm, the equations of motion for the atoms or ions are given by Eqs. (1) and (2), except for the Li ions where the equation of motion for the momentum Eq. (2) is modified to include a force due to a color field, $\mathbf{F}_i$:

$$\mathbf{p}_i = \mathbf{F}_i + c_i \mathbf{F}_k - c_i \mathbf{p}_i$$  \hspace{1cm} (6)

Here $c_i$ is the color charge (or color label) of each of the Li ions. The sum of the color charge should be zero to ensure there is no drift in the total moment of the system, however the choice of these charges is arbitrary. Usually, half of the Li ions are given a positive color charge (+1) and the other half a negative color charge (−1). The color field does not affect the PS$_3^{3−}$, S$^{2−}$ and Cl$^{−}$ ions and the color charges do not affect the way Li$^+$ ions interact with each other—it just determines their response to the field. For NEMD calculations a chain thermostat was not used as it is inappropriate for the nonequilibrium simulations$^{49}$. The equation of motion for the thermostat for nonequilibrium study is therefore given by Eq. (3) where $\alpha_1$ is equal to zero. For calculations of properties of nonequilibrium systems, the thermostat needs to be applied to the peculiar momentum of the conductive ions. However, because we are extrapolating to zero field, this is not problematic and it is appropriate to use Eq. (6). The color field forces the Li ions to move in response to the field, but as mentioned above, it does not change the interatomic interactions (the electric charge on the Li ions is maintained as +1 and contributes to the Coulomb interactions between atoms that is part of $\mathbf{F}_i$). With a color field applied, Li ions with opposite color charges will experience forces that tend to move them in opposite directions through the diffusion channel. The color field should be strong enough to generate a color current and low enough that the color charge should be zero to ensure there is no drift in the total moment of the system, however the choice of these charges is arbitrary.

The EMD and NEMD equations of motion were integrated using the velocity Verlet algorithm with a time step of 1 fs. Where statistical errors are reported, they are one standard error in the mean (the standard deviation of multiple runs, divided by the square root of the sample size).

**Calculation of diffusion coefficients and conductivity**

The mean square displacement (MSD) of Li ions was used to calculate the diffusion coefficient from EMD simulations. The self-diffusion coefficient is given by the Einstein relation:

$$D_s = \frac{1}{6Nt} \sum_{i=1}^{N} \langle (\Delta r_i(t))^2 \rangle$$  \hspace{1cm} (7)

where $D_s$ is self-diffusion coefficient, $\Delta r_i(t)$ is displacement of the $i$th of Li ion over a period, $t$, and $(...)_{t=0}$ indicates an ensemble average. The collective diffusion coefficient $D_c$ (or Li center of mass diffusion coefficient) is given by:

$$D_c = \frac{1}{6Nt} \sum_{i=1}^{N} \left( \sum_{j=1}^{N} r_{ij}(t) - \sum_{j=1}^{N} r_{ij}(0) \right)^2$$  \hspace{1cm} (8)

where $r_{ij}(t)$ is the position of the $i$th Li ion at time $t$. The self- and collective diffusion coefficients differ if the ions do not move independently. The conductivity experimentally measured from the application of an electric potential will correspond to the collective diffusion coefficient whereas nuclear magnetic resonance experiments give the self-diffusion coefficient. We note that the statistical error in the computations of the self-diffusion coefficient will be lower than the collective diffusion, so if they are expected to have similar values, it is advantageous to consider the self-diffusion coefficient.

From the self-diffusion coefficient, the ionic conductivity of the material, $\sigma$, can be calculated using the Nernst-Einstein equation$^{50}$:

$$\sigma = n e^2 Z^2 \frac{D_i}{k_B T}$$  \hspace{1cm} (9)

where $n$ is the ion density of Li, $e$ is the elementary electron charge and $Z$ is the valence of Li.
Using the NEMD simulations, the self-diffusion coefficient can be determined from the color current produced by the color field. As noted above, this method has previously been used to determine the self-diffusion coefficient of a solid-state electrolyte with low conductivity. The color current is given by:

\[ J_c(t) = \frac{N}{t} \sum_{i=1}^{N} c_i \mathbf{v}_i(t) \]  

(10)

where \( \mathbf{v}_i \) is the velocity of the \( i \)th Li ion. At low fields, the color current in the direction of the field \( \mathbf{E} = \mathbf{F}_c / |\mathbf{F}_c| \) will be linearly proportional to the field, \( \mathbf{F}_c = (\mathbf{F}_c, 0) \), when the system is in a steady state, and then for the color charges used in this work:

\[ D_c = \frac{k_B T}{N} \lim_{t \to \infty} \lim_{t_c \to \infty} J_c / t \]  

(11)

where \( N \) is the number of lithium ions subject to a color field. If a different selection of color charges was used, \( N \) in Eq. (11) should be replaced with \( \sum_i^{N} \epsilon_i \). The value of the field below which there is a linear relationship between the color current and applied field will depend on the system and conditions such as temperature. Therefore to use this expression in practice, simulations need to be carried out to determine that critical field.

Furthermore, although the color current changes with the color field, in the linear regime the statistical error in the color current does not change. Therefore, to obtain results with the lowest statistical error it is best to use the maximum field for which linear response occurs. For ergodic systems, the ensemble average of the color current in Eq. (11) can be replaced with a time-average, giving:

\[ \langle J_c \rangle = \lim_{t \to \infty} \frac{1}{t} \int_{t_c}^{t} J_c(s) ds = \lim_{t \to \infty} \frac{1}{t} \sum_{i=1}^{N} c_i \Delta \mathbf{r}_i(t) \]  

(12)

So if the field is in the \( x \)-direction, the self-diffusion coefficient can also be written as:

\[ D_c = \frac{k_B T}{N} \lim_{t \to \infty} \lim_{t_c \to \infty} \sum_{i=1}^{N} c_i \Delta \mathbf{r}_i(t) / t F_c \]  

(13)

The field adds a force to the particles in the direction of the field, and has a similar effect to reducing the activation energy barrier for diffusion. If the diffusion process can be modelled as a jump process, the expected time for a single jump will increase exponentially with the size of the activation barrier, and therefore application of the field will allow systems with much lower diffusion coefficients to be considered for a given simulation time. In practice, this means that greater advantage for NEMD calculations is expected for systems where the diffusion coefficient is low.

Due to the dependence of the ionic conductivity of solid-state electrolytes on temperature, high-temperature ionic conductivities determined from MD simulations can be used to estimate the diffusion coefficients of the electrolytes at lower temperatures using the Arrhenius relationship:

\[ D = D_0 e^{-E_a / (k_B T)} \]  

(14)

where \( E_a \) is the activation energy and \( D_0 \) is the diffusion pre-exponential factor. Using Eq. (9) this can also be written in terms of the ionic conductivity of the system:

\[ \sigma T = n e^2 Z_i^2 / k_B D_0 e^{-E_a / (k_B T)} \]  

(15)

Note that for our system where only the Li ions are mobile and move independently, the conductivity determined from the Einstein relationship for the self-diffusion, Eq. (7), can also be expressed as a Green-Kubo relationship:

\[ \sigma = n e^2 Z_i^2 / k_B T \int_0^\infty \left\langle \sum_{i=1}^{N} \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \right\rangle dt. \]  

(16)

Furthermore, if the assumption of independency of movement of the Li ions is relaxed, then it can be calculated from the collective diffusion coefficient and the Green-Kubo relationship is:

\[ \sigma = n e^2 Z_i^2 / k_B T \int_0^\infty \left\langle \left( \sum_{i=1}^{N} \mathbf{v}_i(t) \right) \cdot \left( \sum_{j=1}^{N} \mathbf{v}_j(0) \right) \right\rangle dt \]  

(17)

We choose to use the Einstein expressions in this work, which circumvents problems associated with convergence of the time correlation functions in (16) and (17). Of relevance given that this study considers ab initio molecular dynamics simulations of conductivity, it has interestingly been demonstrated that Green-Kubo expression gives the same results using integer charges and velocities of discrete sites (similar to this work), and the mean square dipole displacement obtained using Born charges of each atom.

**DATA AVAILABILITY**

The data that support the findings within this paper are available from the corresponding authors upon reasonable request.

**CODE AVAILABILITY**

The modified CP2K code within this paper are available from the corresponding authors upon reasonable request.

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AUTHOR CONTRIBUTIONS
A.B. performed the calculations and wrote the paper. J.C.R. and D.J.S. extended the simulation code. All authors analyzed the results and revised the paper.

COMPETING INTERESTS
The authors declare no competing interests.

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