

Ab initio Nonequilibrium Molecular Dynamics in the Solid Superionic Conductor LiBH₄Philippe C. Aeberhard,^{1,*} Stephen R. Williams,² Denis J. Evans,² Keith Refson,³ and William I. F. David^{1,4}¹*Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, United Kingdom*²*Research School of Chemistry, The Australian National University, Canberra ACT 0200, Australia*³*Computational Science and Engineering Department, Rutherford Appleton Laboratory, Chilton, Oxfordshire, OX11 0QX, United Kingdom*⁴*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Oxfordshire, OX11 0QX, United Kingdom*

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The color-diffusion algorithm is applied to *ab initio* molecular dynamics simulation of hexagonal LiBH₄ to determine the lithium diffusion coefficient and diffusion mechanisms. Even in the best solid lithium ion conductors, the time scale of ion diffusion is too long to be readily accessible by *ab initio* molecular dynamics at a reasonable computational cost. In our nonequilibrium method, rare events are accelerated by the application of an artificial external field acting on the mobile species; the system response to this perturbation is accurately described in the framework of linear response theory and is directly related to the diffusion coefficient, thus resulting in a controllable approximation. The calculated lithium ionic conductivity of LiBH₄ closely matches published measurements, and the diffusion mechanism can be elucidated directly from the generated trajectory.

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Understanding the mechanisms and kinetics of fast ion diffusion in solids is fundamental in the development of materials with high ionic conductivity; lithium, oxide, and proton conductors are of particular technological relevance. *Ab initio* computational treatments of diffusion in solids typically proceed by calculating all the variables entering a simple Arrhenius description of the diffusion coefficient based on a known or hypothetical diffusion pathway [1], or by *ab initio* molecular dynamics (AIMD), using the Einstein-Sutherland equation to determine diffusion coefficients from calculated mean-squared displacements [2]. The latter approach has the potential to give the most accurate results as well as direct insight into the transport mechanisms; however, it is practically limited to liquids in which the time scale of diffusion is similar to the time scale accessible by simulation at an acceptable computational cost; for example, Farrell *et al.* [3] were able to determine the lithium diffusion coefficient in liquid Li₄(BH₄)(NH₂)₃ by AIMD, but not in the solid state, even though this material has a similarly high lithium ionic conductivity as LiBH₄ [4].

A number of AIMD approaches to address the problem of mismatching time scales exist, such as increasing the simulation temperature to accelerate all thermal processes in the system including diffusion [3], selectively heating up only the mobile species, scaling the atomic masses to reduce the time scale mismatch [5], or the metadynamics technique [6]. However, the former three approaches are uncontrolled approximations with respect to dynamical properties of the system, and the metadynamics approach requires the not straightforward determination of a large number of parameters, often requiring a trial-and-error

approach or prior knowledge of the mechanism under study.

Here we propose to combine the color-diffusion algorithm by Evans *et al.* [7] to the AIMD simulation of the solid state lithium ion conductor LiBH₄ in its hexagonal phase. This nonequilibrium molecular dynamics (NEMD) algorithm is conceptually simple and has so far mostly been applied to classical model systems of liquids [2,8]; here we apply it within the framework of AIMD to present an efficient, controlled, and systematically improvable approach to determine both the diffusion coefficient and the diffusion mechanisms in a solid ion conductor.

The color-diffusion algorithm is an extension of the tagged-particle algorithm [9] and improves the efficiency of the method by making every particle a tagged particle, thus quantitative results can be obtained from a single NEMD simulation. By having half the particles move in the opposite direction, self-diffusion of the particles is in effect simulated; the theoretical background of the algorithm is described in more detail elsewhere [7,8].

The equations of motion governing the dynamics of the atoms in the system are the following in our simulations:

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m_i}, \quad (1)$$

$$\dot{\mathbf{p}}_i = \begin{cases} \mathbf{F}_i - \alpha \mathbf{p}_i + \mathbf{F}_c & \forall i \in \{\text{B, H}\} \\ \mathbf{F}_i + c_i \mathbf{F}_e & \forall i \in \{\text{Li}\}, \end{cases} \quad (2)$$

where the coefficient α couples the B and H atoms to a Gaussian isokinetic thermostat [7,8] to extract the energy introduced into the system by the external field. The thermostat is not applied to the mobile atoms to avoid having to

determine the streaming velocity; the temperature of the lithium ions is efficiently controlled by heat exchange with the B and H atoms and does not affect the linear response of the system. \mathbf{F}_c is a constraint force that keeps the total momentum of the thermostatted atoms at zero. \mathbf{F}_e is a (fictitious) constant external field and c_i are the “color charges,” set to +1 for half of the lithium atoms in the system and -1 for the other half and zero for all other atoms, making the overall color charge of the system zero.

After equilibration at zero field for 20 ps at 535 K, the field is switched on, defining $t = 0$. The response of the system is a color flux in the direction of the external field, defined as

$$J_c(t) = \frac{1}{V} \sum_{i=1}^N c_i v_i(t), \quad (3)$$

where $v_i(t)$ is the velocity of atom i in the direction of the external field. The work done on the system by the dissipative field is extracted by the thermostat, and after a short transient period, the system reaches a steady state that is out of thermodynamic equilibrium, but that is characterized by a constant temperature and a constant color flux. In the steady state, linear response theory relates the time-averaged response to the diffusion coefficient of the color-charged particles:

$$D = \frac{k_B T}{\rho_c} \lim_{t \rightarrow \infty} \lim_{F_e \rightarrow 0} \frac{\langle J_c(t) \rangle}{F_e}, \quad (4)$$

where ρ_c is the number density of color-charged particles, i.e., the lithium atom number density in the present case. The ionic conductivity and the diffusion coefficient of the charge carrier are related by the generalized Nernst-Einstein equation [7]:

$$\sigma = \frac{(Ze)^2 \rho_c}{k_B T} D = (Ze)^2 \lim_{t \rightarrow \infty} \lim_{F_e \rightarrow 0} \frac{\langle J_c(t) \rangle}{F_e}, \quad (5)$$

where Ze is the electric charge of the mobile ions, in the case of Li^+ ions equal to +1 elementary charge. It is interesting to note the correspondence between the experimental electric conductivity, defined by $\sigma = I/E$ where I is the current density and E is the electric field, and the color conductivity expressed by $\langle J_c(t) \rangle / F_e$ in the above relation determined from nonequilibrium statistical mechanics. Thus, the present NEMD method is a simulation that directly mimics a conductivity experiment.

The NEMD calculations were performed using a model consisting of 48 f.u. (288 atoms) in an orthorhombic simulation cell with dimensions $12.968518 \text{ \AA} \times 14.974664 \text{ \AA} \times 14.073600 \text{ \AA}$ and periodic boundary conditions. The simulation cell was constructed from the experimental crystal structure and lattice parameters of hexagonal LiBH_4 at 535 K, space group $P6_3mc$, taken from the literature [10]. The forces \mathbf{F}_i in Eq. (2) are calculated by density functional theory using the QUICKSTEP method [11] as

implemented in the package CP2K [12]. The Perdew-Burke-Ernzerhof functional for exchange and correlation was used [13]; valence electrons were expanded in a dual basis set consisting of double-zeta Gaussian functions [14] and plane waves with a cutoff energy of 280 Ry; core electrons were represented by Goedecker-Teter-Hutter pseudopotentials [15]. The equations of motion were integrated by a velocity-Verlet scheme with a time step of $\Delta t = 1$ fs. The CP2K package had to be modified to implement the equations of motion, Eqs. (1) and (2).

Two series of short NEMD simulations were carried out with varying values of the field strength in order to determine the linear response domain: one series with the field applied along the (110) direction in the ab plane of the primitive hexagonal unit cell, and one series along the (001) direction perpendicular to the ab plane (see Fig. 1), thus probing diffusion in different directions in this anisotropic environment separately. Table I summarizes the calculations at different directions and magnitudes of the external field. In the linear response domain, the ionic conductivity determined according to Eq. (5) is independent of field strength. These series of NEMD runs were run for relatively few time steps, and the average responses shown in Fig. 2 have a rather large margin of error. Nevertheless, for both series of calculations, the precision is sufficient to judge that fields stronger than 0.05 eV \AA^{-1} lead to a strongly nonlinear response; below this value the response appears to be largely linear. As the energy barriers for lithium hopping are relatively high, about 0.3 eV according to *ab initio* calculations [16], it is expected that for solid ionic conductors the linear response domain is narrow, and the response becomes sharply nonlinear, as is the case for glassy systems. As a supercooled liquid is cooled toward the glass transition, the maximum field strength F_{em} , for which the response appears linear, shrinks towards zero, apparently scaling like $F_{em} \sim \sqrt{D}$ [9].

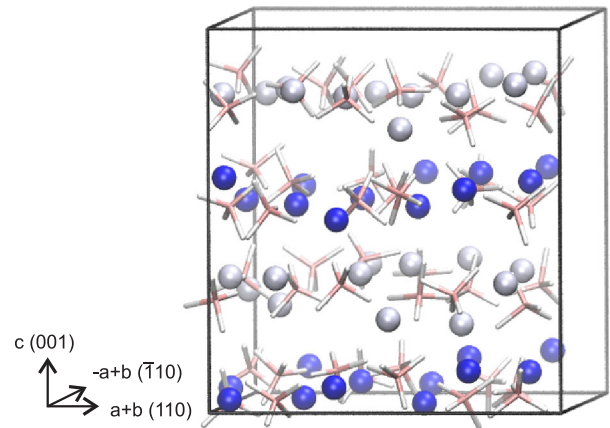


FIG. 1 (color online). A snapshot of the model after equilibration at 535 K using the Gaussian isokinetic thermostat. Light and dark spheres: lithium atoms with +1 and -1 color charge, respectively.

TABLE I. The ionic conductivity σ calculated according to Eq. (5) from series of NEMD simulations of length t .

F_e direction	$\ F_e\ $ (eV/Å)	t (ps)	σ (S/cm)
(110)	0.04	20.8	0.4588
(110)	0.05	18.7	0.6072
(110)	0.0625	13.8	1.1789
(110)	0.08	5.3	4.0701
(110)	0.125	8.1	6.3359
(001)	0.04	72.1	0.10898
(001)	0.05	100.9	0.08183
(001)	0.08	13.9	1.50356

From these preliminary results, a field strength of 0.05 eV \AA^{-1} is assumed to be the highest field at which the response remains predominantly linear. Two simulations of 100 ps are run each with the external field at 0.05 eV \AA^{-1} in the (110) and in the (001) directions, respectively, to determine the diffusion coefficients with more precision. The response is shown in Fig. 3, represented as the time integrated dissipative flux conjugate to the external field:

$$\int_0^t \langle J_c(t) \rangle V F_e = F_e \sum_{i=1}^N c_i \Delta x_i(t), \quad (6)$$

where $\Delta x_i(t)$ is the displacement in the direction of the external field of atom i , calculated from the NEMD trajectory.

The resulting ionic conductivity is 0.356 S cm^{-1} in (110) and 0.082 S cm^{-1} in (001) (Table II). These results suggest that lithium diffusion is effectively two-dimensional: diffusion is fast in the ab plane [the hopping mechanism in the (110) direction applies to diffusion in any direction in the ab plane], but it is more than 4 times slower in the (001) direction, perpendicular to the ab -plane. This is consistent with experiments where it

has been found that a 2-dimensional hopping model results in the best agreement of NMR measurements with the more direct impedance measurements [17]. Since the experiment was carried out with a powdered sample, it is expected that a diffusion coefficient lower than the calculated value for the (110) direction but higher than for (001) is measured. The reported experimental value at 535 K, calculated according to a simple hopping model from Li motion correlation times measured by $^7\text{Li-NMR}$ [17], is 0.139 S cm^{-1} . The agreement between the NEMD result and the experiment is remarkably good. The two main sources of error are the nonlinearity of the response and the evaluation of the time average of the response. The nonlinear effects will bias the result toward higher values; the time averaging error decreases proportionally to the square root of simulation time. Even though a linear fit to a stepped curve as in Fig. 3 can be expected to have a rather large error margin, we obtain a good estimate of the diffusion coefficient and a better precision than other MD-based methods mentioned above, which achieve at best an estimate of the order of magnitude.

Finally, we note that the trajectory thus generated is following realistic dynamics (as opposed to, e.g., the mass scaling method) and contains a large number of ion hopping events. The details of the diffusion mechanism can therefore be directly deduced by inspecting an NEMD trajectory. Figure 4 shows a trace of one such hopping event induced by an external field applied in the (110) direction, and the ion follows the same pathway that has previously been suggested [16].

While the direction in which the induced ion jumps occur is certainly biased by the field, the details of the mechanism are not influenced by the presence of the field. In the weak field limit, the external field only increases the frequency of ion jumps, but they remain rare events and are the same processes that are occurring in equilibrium (zero field) but less frequently; in the limit of zero field strength, the time between two events corresponds to the

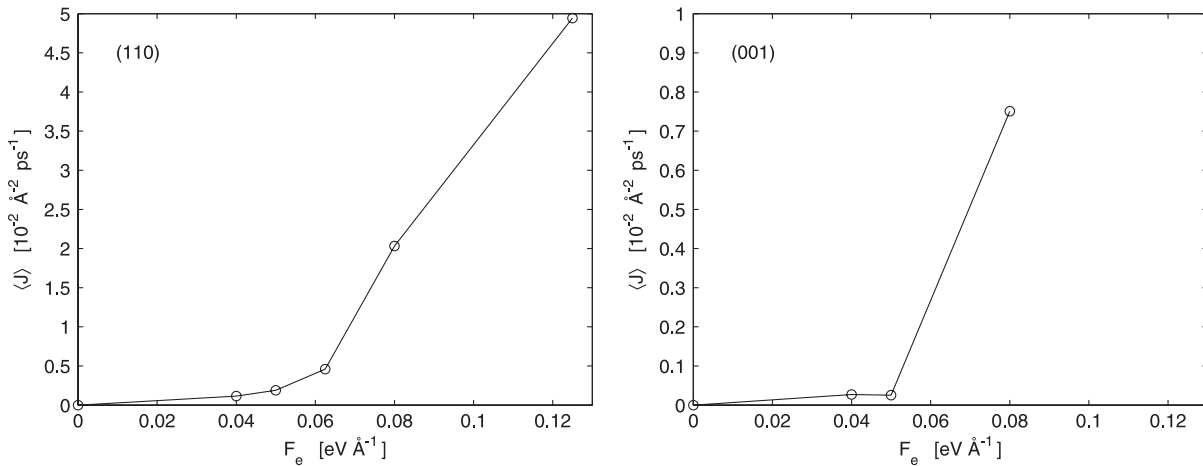


FIG. 2. The time-averaged response versus the external field strength (circles) from Table I; the black lines are guides for the eye.

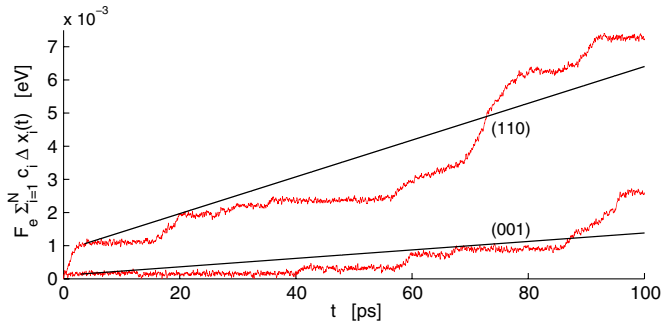


FIG. 3 (color online). The time integrated dissipative flux versus simulation time with the external field $F_e = 0.05 \text{ eV \AA}^{-1}$ in the (110) and (001) directions. A straight line without intercept is fitted to the steady state (from 3.5 ps onwards) to obtain the steady-state average flux $\langle J_c(t) \rangle$.

equilibrium value. As the ion jumps remain rare events, the probability of spurious effects caused by the opposing fluxes of the same species is proportional to the square of the jump rate, which in turn is proportional to the external field.

In conclusion, we have successfully applied an NEMD method to AIMD simulations of ionic diffusion in solid state materials. The basic problem of mismatching time scales when simulating atomic or molecular diffusion in solids is addressed by introducing a constant external field acting on the mobile species to increase the number of ion jumps observed during the molecular dynamics time frame. The trajectories generated by this method follow realistic dynamics, provided that the applied field is sufficiently weak so that the system response is linear, and thus can provide direct insight into the microscopic mechanism of the ion jump events. Moreover, by applying the field in a specific direction, diffusion in anisotropic environments can be studied for any spatial direction separately; in the presented case study, diffusion coefficients in the ab plane and perpendicular to the ab plane of hexagonal LiBH_4 could be determined separately and revealed that diffusion preferentially occurs in the ab plane.

The algorithm is conceptually simple and can be combined with any molecular dynamics method, with little coding effort. The preliminary series of NEMD simulations to establish the linear response domain is necessary as there is no mathematical diagnostic that is currently known; however, these preliminary simulations are

TABLE II. Ionic conductivity and diffusion coefficient calculated from long NEMD trajectories with an external field strength of 0.05 eV \AA^{-1} .

F_e direction	(110)	(001)	Experiment ^a
t_s	100.0	100.0	
σ (S cm^{-1})	0.355 49	0.0818	0.139
D_{Li} ($\text{cm}^2 \text{ s}^{-1}$)	$5.824 48 \times 10^{-6}$	1.3407×10^{-6}	2.28×10^{-6}

^aLi-NMR results at 535 K from Ref [17].

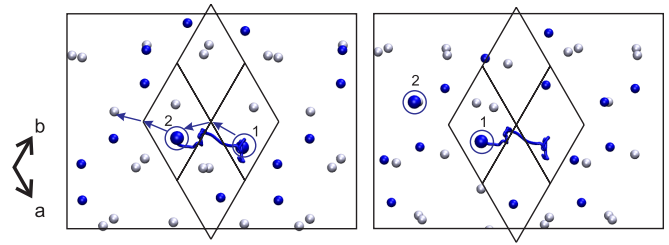


FIG. 4 (color online). The hopping sequence of two lithium atoms (labeled 1 and 2) observed in an NEMD trajectory [field along (110)]; only lithium atoms are shown as light and dark spheres. Lithium atoms jump into an empty hexagonal site (situated on the origins of the primitive cells) and from there jump into a free lattice site.

straightforward to carry out, and their computational cost can be kept at a minimum by carrying out short runs with successively increasing field strength until strongly non-linear behavior is observed. Compared to other schemes for accelerating rare events (except for metadynamics), such as increasing temperature or scaling masses, no uncontrolled approximations are made, and the effects of the perturbation are accurately described by linear response theory, provided that a linear response regime can be identified. The quality of the result obtained can thus be straightforwardly improved by decreasing the external field strength and increasing the simulation time, thereby shifting the system more and more into the linear response domain.

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