Finite-size Effects on the Molecular Dynamics Simulation of Fast-ion Conductors: a case study of lithium garnet oxide $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

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ABSTRACT

A useful tool to study ionic conduction mechanisms in fast-ion conductors is the molecular dynamics (MD) simulation performed on finite simulation cells with periodic boundary conditions. While there have been many studies of the effect of cell size on the thermodynamics and kinetics of simple liquids, the finite-size effect in fast-ion conductors remains elusive. This work presents a case study to investigate the finite-size effect on the phase transition, self-diffusivity, ionic conductivity, Haven ratio, thermodynamic factor, and Fickian diffusivity using lithium garnet oxide $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ as a model material. It was found that cell sizes influence extracted thermodynamic and kinetic characteristics in different ways with magnitude ranging from weak to strong. For $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, reliable properties can be obtained with a $3\times 3\times 3$ (5184 atoms) cell.

Keywords: finite-size effect, thermodynamic factor, Haven ratio, fast-ion conductors, molecular dynamics

INTRODUCTION

The changing landscape of energy production and consumption has spurred interest in the development of new energy generation or storage materials that can meet a wide variety of applications. Fast-ion conductors, also called solid electrolytes, superionic conductors, or ionic solids, capable of transporting H^+ , Li^+ , Na^+ , and O^{2-} are of particular interest for their use in electrochemical applications such as batteries, fuel cells, and sensors.¹⁻⁵ Solid electrolytes for Li-ion batteries for instance offer promises of higher potential redox chemistry, safety improvements through the removal of volatile solvents, and mechanical blocking of dendrites that can lead to cell failure.⁵⁻¹¹ These enhancements are due to the unique nature of fast-ion conductors, in which a rigid network of framework atoms support interconnecting structural cages allowing for the transport of ions. Understanding the fine details of ion conducting mechanisms in these materials is of great importance, as this can lead to insights on how to improve current solid electrolyte technology or develop novel materials with enhanced properties.

A useful tool for examining the aforementioned conduction mechanisms is the molecular dynamics (MD) simulation, generally performed within a finite simulation cell with periodic boundary conditions. In many MD simulation studies, it was observed that structural and dynamical properties obtained from MD results varied with the size of the simulation box. For example, the self-diffusivity of liquid atoms was often found to increase with increasing system size.¹²⁻¹⁵ In addition, small subsystems are usually carved out from the cell to simulate the grand canonical ensemble and extract thermodynamic properties. These thermodynamic properties were found to depend strongly on the size of subsystems.^{16,17} However, most investigations into

these finite-size effects have been centered on simulating water or Lenard-Jones fluids while leaving fast-ion conductors largely unexplored.

The purpose of this work is to present a case study investigating the role of cell sizes on the calculated properties of fast-ion conducting $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ), from force-field based MD simulations. First, LLZ is a model material in the lithium garnet oxide family touted with potential to replace conventional liquid electrolytes for the next-generation Li-ion batteries.¹⁸⁻²¹ Ions of La, Zr, and O form the framework while lithium ions are able to move between tetrahedral and octahedral cages. Second, LLZ exhibits a classic superionic transition going from a low-temperature/low-conductivity tetragonal phase ($I4_1/acd$) to a high-temperature/high-conductivity cubic phase ($Ia-3d$), giving easily identifiable metrics for comparisons.²²⁻²⁴ In this paper, we will individually investigate the finite-size effect on the thermodynamic and kinetic characteristics of LLZ such as phase transition (section 1), self-diffusivity, ionic conductivity, and Haven ratio (section 2), thermodynamic factor and Fickian diffusivity (section 3). The relevant equations on different types of diffusivities, thermodynamic factor, Haven ratio, and ionic conductivity are presented in the Appendix.

EXPERIMENTAL

Force-field parameters

The force-field model employed in the present work includes a long-range Coulombic interaction and a short-range Buckingham interaction, as is commonly done for ionic solids.^{25,26} For the atomic charges, instead of the core-shell model reported in our previous work,²³ we employed a partial charge model that is based on first-principles density functional theory (DFT)

calculations. Specifically, we obtained the partial charges of atoms in the DDEC (Density Derived Electrostatic and Chemical charge) scheme²⁷, from results of DFT calculation with the VASP package^{28,29,30,31} employing the Projector Augmented-Wave (PAW) method.^{32,33} The simulation cell was a 1×1×1 cell of Li₇La₃Zr₂O₁₂ with 192 atoms with P1 symmetry. Structural parameters were taken from experimental values in literature.²⁴ A self-consistent calculation was performed with the Generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof parametrization (PBE)^{34,35} as the exchange-correlation functional, a 600 eV cut-off energy, and at the Gamma point. Valence electron configurations for La, Li, O, and Zr atoms are 5s²5p⁶5d¹6s², 1s²2s¹, 2s²2p⁴ and 4s²4p⁶4d²5s², respectively. The DDEC charges of all atoms in the same species were averaged to yield values of 2.53 (La), 1.01 (Li), -1.70 (O), and 2.86 (Zr). In order to facilitate the investigation of Li₇La₃Zr₂O₁₂-Li₅La₃Ta₂O₁₂ composition series in a forthcoming article, we slightly offset these DDEC charges to values reported in Table 1. The interaction parameters were refined against the experimental structure²⁴ by the GULP package^{36,37}, with initial values taken from the reference.³⁸ The force-field parameters are listed in Table 1.

Table 1: Force-field Parameters

Species	z (e)	Buckingham Pair Interaction with Oxygen		
		A (eV)	ρ (Å)	C (eV Å ⁶)
Li	1.00	1087.29	0.260	0.00
La	2.50	2075.26	0.326	23.25
Zr	2.65	1650.32	0.311	5.10
O	-1.65	4870.00	0.267	77.00

Molecular Dynamic Simulations

Molecular dynamic simulations were performed using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)³⁹. Initial tetragonal LLZ simulation cells consisting of 1×1×1 (192

atoms), $2 \times 2 \times 2$ (1536 atoms), $3 \times 3 \times 3$ (5184 atoms), and $4 \times 4 \times 4$ unit cells (12288 atoms) were generated using the same structure as the DFT calculation. The Ewald summation of long-range interactions was calculated using a cutoff radius of 6 Å for $1 \times 1 \times 1$ cells and 12 Å for $2 \times 2 \times 2$ and larger cells. Anisotropic constant number/pressure/temperature (NPT) simulations were carried out by heating the initial tetragonal structure to 1400 K and sequentially cooling the simulation cells in 100 K decrements until 300 K was achieved. For the $3 \times 3 \times 3$ and $4 \times 4 \times 4$ cells, we implemented additional sequential heating and cooling from 800-1000 K in 25 K increments to study the hysteresis. NPT simulations ran for 75 ps with a 1.0 fs time-step employing the Nose-Hoover thermostat and barostat⁴⁰⁻⁴³ with relaxation time constants of 0.05 ps and 0.25 ps respectively. Lattice parameters were extracted from the last 50 ps. Once average lattice parameters were determined, constant number/volume/energy (NVE) simulations were performed for 1 ns utilizing the same 1.0 fs time-step. The atomic trajectories are saved every 10 fs. Mean square displacements (MSD) of lithium atoms were generated using the DL_POLY GUI⁴⁴ interface. The self-diffusivity of Li was determined by taking the slope of a MSD vs time plot between 500 and 700 ps. The velocity correlation functions were sampled for 70 ps. A more detailed explanation of our methods for calculating diffusivity, thermodynamic factor, Haven ratio, and conductivity can be found in the Appendix.

RESULTS & DISCUSSION

Phase characterization

An important aspect in determining the validity of our simulations is to ensure that they accurately reproduce lattice parameters and phase transition characteristics represented

experimentally. In the literature, a wide variety of transition temperatures ranging from 373 to 923 K was reported.⁴⁵⁻⁴⁹ Literature results and our previous work suggest that such variation could be attributed to intentional or inadvertent impurity (e.g. Al)/dopant incorporation, H₂O or CO₂ exposure, all of which reduces the transition temperature.^{45,49,50} Thus we chose experimental data with the highest transition temperatures, i.e. works of Larraz et al⁴⁷ and Matsuda et al⁴⁹, as the benchmark. Figure 1(a) shows the lattice parameters (normalized to 1×1×1 cell) for different cell sizes resulting from the sequential cooling from 1400 K, along with experimental measurements. Overall, our simulation results match closely to experimental ones in terms of change of lattice parameters and phase transition temperature (~900 K), with the exception of 2×2×2 cells indicating a transition temperature of 1000 K. The only major deviation in average lattice parameter shown is for the 1×1×1 simulation at low temperatures, where it consistently has larger lattice parameters.

Figure 1: Finite-size effects on the phase transition. (a) Average lattice parameters as a function of temperature for 1×1×1 – 4×4×4 simulations. Solid lines are guide to the eye. Experimental data from Matsuda et al⁴⁹ and Larraz et al⁴⁷ are shown for comparison. (b) Fluctuation of lattice parameters as a function of number of atoms for selected temperatures. Solid lines are the linear fit (slopes close to -0.5). (c) Time evolution of lattice parameters for different cell sizes at 900 K.

The standard deviation of lattice parameters decreases with the increase of cell sizes in Figure 1(a). These values are plotted in Figure 1(b) as a function of number of particles to further investigate the size effects. For simplicity, we only plotted data for 800, 1100, and 1400 K. For the ideal gas with N number of particles and L cubic length, the fluctuation of L in a NPT ensemble takes the form of $\delta L/L \propto 1/\sqrt{N}$. The linear fit of the log-log plot in Figure 1(b) yields slopes varying from -0.49 to -0.50, consistent with the dependence of ideal gas.

Another way to study size effects is to examine the fluctuation of lattice parameters around the phase transition when cells are volatile. Lattice parameters (as orthogonal a , b , c) are shown as a function of time at 900 K in Figure 1(c). Larger $3 \times 3 \times 3$ and $4 \times 4 \times 4$ simulations both show very small variation in lattice parameter and maintain a mostly cubic phase throughout the simulation. The $2 \times 2 \times 2$ simulation shows a more complicated situation where a slightly tetragonal unit cell undergoes reorientation of its lattice vectors as the simulation completes. We treated $2 \times 2 \times 2$ simulation as a tetragonal phase and extracted the average lattice parameters from 25-60 ps. The $1 \times 1 \times 1$ simulation shows larger fluctuations with more frequent tetragonal reorientation, making an accurate description of phase difficult. To simplify the extraction of lattice parameters, we characterized it as being cubic.

After determining that $3 \times 3 \times 3$ and $4 \times 4 \times 4$ cells were large enough for the phase characterization, we further explored the hysteresis of phase transition in LLZ by sequentially cooling from 1000 K and heating from 800 K, respectively, in 25 K steps. Figure 2 plots the lattice parameters in a heating or cooling cycle. For $3 \times 3 \times 3$ cells, we see that starting at 800 K and heating, the tetragonal to cubic transition occurs at around 950 K, but during cooling we

did not observe a tetragonal phase until below 875 K. For $4 \times 4 \times 4$ cells, the hysteresis region was slightly reduced to within around 25 K. Similar hysteresis behavior was also observed in our previous ionic conductivity measurements.⁵⁰ We think $4 \times 4 \times 4$ cells capture the hysteresis more accurately but $3 \times 3 \times 3$ cells offer a good balance of accuracy and efficiency.

Figure 2: Phase transition hysteresis plot for $3 \times 3 \times 3$ and $4 \times 4 \times 4$ simulations between 800-1000 K. Solid lines are guide to the eye.

Self-diffusivity, ionic conductivity, and Haven ratio

Figure 3: Self-diffusivity as a function of temperature for four different simulation sizes. Literature data from the FPMD simulation ($1 \times 1 \times 1$) by Jalem et al⁵¹ are shown for comparison. The inset shows details at high temperatures. Solid lines are guide to the eye.

Self-diffusivity represents the ability of an individual atom to move. The self-diffusivity values of Li ions for the four cell sizes are shown in Figure 3. Our calculated values are slightly higher than those from Jalem et al⁵¹ employing first-principles molecular dynamics (FPMD) simulation with 1×1×1 cell sizes. The difference could be caused by the difference in lattice parameters employed. Experimental measurement of Li self-diffusivity by the spin-lattice relaxation Nuclear Magnetic Resonance (NMR) studies yielded diffusivities on the order of 10⁻¹⁴ cm²s⁻¹ at ~300 K.⁴⁶ Our simulations were unable to calculate diffusivity at such a low temperatures due to the low mobility of Li, but extrapolating from 800-700 K for the 3×3×3 and 4×4×4 simulations yields a diffusivity on the order of 10⁻¹⁷ cm²s⁻¹. However, it is worth noting that two relaxation times that differ by around 3 orders of magnitude were reported in the NMR study and the faster relaxation time was employed to calculate the diffusivity. If the slower relaxation time was used instead, the result would be closer to the value obtained in the present computational work.

Previous MD simulations have shown that self-diffusivity of simple liquids such as water¹² and silica¹³ increases with increasing cell size in the form of $D(L) = D_{\infty} - \frac{2.837k_B T}{6\pi\eta L}$, where $D(L)$ is the diffusivity at cell size L , D_{∞} the diffusivity at the thermodynamic limit, k_B the Boltzmann constant, T the temperature, and η the shear viscosity. While the present study indicates that 1×1×1 structures maintain a consistently higher diffusivity than that in larger simulation cells, overall we observe no size-determining trend for 2×2×2, 3×3×3, and 4×4×4 simulations in Figure 3 and the inset. Such a lack of clear size effects could be due to different interaction potentials in LLZ compared with those in simple liquids. With respect to the appropriate

simulation size, the $2 \times 2 \times 2$ simulations allow for a reasonable calculation of diffusivity at higher temperatures, but as we approach the transition temperature the increased stability of the larger $3 \times 3 \times 3$ and $4 \times 4 \times 4$ cells allows for a more reasonable diffusivity calculation.

Figure 4: Finite-size effects on the ionic conductivity for $3 \times 3 \times 3$ and $4 \times 4 \times 4$ cells. Values calculated from both (A18) (named “ideal”) and (A9) are presented. Literature data from experimental measurements by Wang et al⁵⁰ and Matsui et al⁴⁸, along with FPMD simulations by Miara et al⁵² (also “ideal”), are shown for comparison.

Next we will study the size effect on the ionic conductivity, one of the most important properties of fast-ion conductors. The ionic conductivity σ of both cubic and tetragonal LLZ has been widely studied, and is commonly used to draw comparisons between experimental and simulation properties.¹⁸⁻²¹ For the reason discussed earlier, we selected the experimental conductivity results with high transition temperatures (~ 900 K), e.g. from Wang et al⁵⁰ and Matsui et al⁴⁸. For the computational results, we first applied the Nernst-Einstein relation for ideal solutions, i.e. (A18), to convert self-diffusivity D^* to conductivity, as commonly done in the literature, e.g. in the classical MD simulation by Adams et al⁵³ and FPMD simulation by Jalem et al⁵¹ and Miara et al.⁵² The computed conductivities for $3 \times 3 \times 3$ cells are similar to those from Miara et al⁵² ($1 \times 1 \times 1$ cell) in Figure 4. For nonideal solutions such as LLZ, we plot the ionic

conductivity calculated from (A9) in Figure 4 for cell sizes. Similar to what was observed for self-diffusivity, ionic conductivity shows small variations from $2 \times 2 \times 2$ to $4 \times 4 \times 4$ cells. The difference between calculated and experimental values could be due to impurity incorporation of the experimental samples, e.g. Al. Such impurity effect will be reported in a future publication.

Figure 5: Finite-size effects on the Haven ratio for four simulation cell sizes. Solid lines are guide to the eye.

As discussed in the Appendix, the Haven ratio characterizes the ratio of self-diffusion vs collective diffusion (ionic conductivity). Its value is commonly assumed to be 1, i.e. no correlation of motion of different atoms. This allows the use of self-diffusivity and Nernst-Einstein equation to calculate the ionic conductivity, named as “ideal” in the previous discussion. However, for complex materials such as fast-ion conductors, the Haven ratio is expected to deviate from 1. Finite-size effects on the Haven ratio are shown in Figure 5. At high temperatures, Haven ratios are around 0.3 and size dependence is weak. At lower temperatures, the ratios dropped to lower values signifying strong collective motion.

Thermodynamic factor and Fickian diffusivity

In fast-ion conductors, the thermodynamic factor reveals the effective fraction of mobile charge carriers, as discussed in the Appendix. There are three methods in obtaining the thermodynamic factor Γ from the trajectory of MD simulation: fluctuation, KBI, and static structure factor. The fluctuation method involves dividing a simulation cell into subsystems that are large enough compared with the microscopic volume $V_{sub} \gg V_{micro}$ but small enough compared with the cell volume ($V_{sub} \ll V_{cell}$ to achieve grand canonical ensemble).^{16,54} We applied this method in our previous study of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ by averaging values corresponding to V_{sub}/V_{cell} of 1/8 and 8/125 for $2 \times 2 \times 2$ cells.²³ However, the guideline to choose the right size of subsystem remains unclear. The KBI method involves evaluating the Kirkwood-Buff integral of the Li-Li pair distribution function¹⁷. For simple liquids in which the pair distribution function decays to the value of one quickly, this method allows reliable estimation of Γ^{-1} . For complex materials such as fast-ion conductors, such KB integrals are more susceptible to finite size truncation errors. An alternative is the static structure factor method which is the KBI method in the Fourier space. This is the method employed in the present study.

Figure 6: Finite-size effects on the inverse thermodynamic factor Γ^{-1} at different temperatures. Solid lines are guide to the eye.

The plot of the inverse thermodynamic factor Γ^{-1} from different cell sizes at different temperatures are shown in Figure 6. Overall, with increasing temperature we see a corresponding increase in Γ^{-1} suggesting that Li diffusion is becoming less coordinated at higher temperatures. A kink at 900 K was identified for all cell sizes, corresponding to the tetragonal to cubic phase transition. Since the thermodynamic factor is related to the number fluctuation reflecting interatomic interaction, the two regions above and below 900 K imply different Li-Li interaction in the cubic and tetragonal phases, respectively. In addition, the Γ^{-1} values are decreasing with the increasing cell sizes and they start to converge above $3 \times 3 \times 3$ cells. The values of Γ^{-1} in both $3 \times 3 \times 3$ and $4 \times 4 \times 4$ cells are on the order of a few permille which suggest that only a small fraction of Li ions contribute to the conduction. A value of $\sim 6\%$ was reported in the literature based on the muon-spin relaxation and conductivity measurement for LLZ at 300 K, although the reported conductivity is similar to our calculated value at around 800 K.⁵⁵ Such difference in effective concentration is likely caused by the impurity incorporation discussed earlier for the ionic conductivity.

Figure 7: Finite-size effects on the Fickian diffusivity for four simulation sizes.

Finite-size effects on the Fickian diffusivity are shown in Figure 7. According to (A15), the Fickian diffusivity is related to the ionic conductivity (Figure 4) through the thermodynamic factor (Figure 6). While the ionic conductivity has weak dependence on the cell size, the Fickian diffusivity increases with increasing cell sizes due to the opposite trend in thermodynamic factors.

CONCLUSIONS

In this work, we performed the molecular dynamics simulation and investigated the effect of simulation cell sizes on the phase transition, self-diffusivity, ionic conductivity, Haven ratio, thermodynamic factor, and Fickian diffusivity of a model fast-ion conductor: $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. In terms of phase transition, even the smallest cell size ($1 \times 1 \times 1$ with 192 atoms) was able to capture the tetragonal to cubic phase transition. Increasing the cell size reduces the fluctuation of lattice parameters in the form of $\delta L/L \propto 1/\sqrt{N}$ and increases the accuracy in estimating the phase transition hysteresis. No obvious size effect was detected for the self-diffusivity of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, as opposed to the observation of increasing diffusivity with increasing cell size for simple liquids. The ionic conductivity and Haven ratio also shows similar weak size dependence as the self-diffusivity. In terms of thermodynamics, the inverse thermodynamic factor decreases with the increasing cell sizes, with values on the order of a few permille suggesting only a small fraction of all lithium ions are responsible for the electrical conduction. On the contrary, Fickian diffusivity increases with increasing cell sizes since it is inversely related to the inverse thermodynamic factor. Overall, a cell size of $3 \times 3 \times 3$ (5184 atoms) offers the best balance

between accuracy and efficiency for $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. The methods and consideration employed in this study can be extended to other fast-ion conductors.

APPENDIX

In this Appendix, we will summarize both the thermodynamic/structural (thermodynamic factor, Haven ratio) and kinetic/dynamic (different types of diffusivities, electrical conductivity) properties commonly used to study fast-ion conductors.

1. Phenomenological parameters of diffusion and thermodynamics

The Onsager's phenomenological flux equations state that the mass flux of species α , J_α , is proportional to the driving forces from all the species as the following:

$$\mathbf{J}_\alpha = - \sum_{\beta} L_{\alpha\beta} \nabla \mu_\beta \quad (\text{A1})$$

where μ_β is the chemical potential of species β and $L_{\alpha\beta}$ acts as the kinetic coefficient. If species α has a charge of $z_\alpha e$ where e is the electron charge, the equilibrium of electrochemical potential $\nabla \mu_\beta = -z_\beta e \nabla \phi$ leads to the following current flux:

$$z_\alpha e \mathbf{J}_\alpha = \sum_{\beta} z_\alpha z_\beta e^2 L_{\alpha\beta} \nabla \phi = \sum_{\beta} \sigma_{\alpha\beta} \nabla \phi \quad (\text{A2})$$

where $\sigma_{\alpha\beta} = z_\alpha z_\beta e^2 L_{\alpha\beta}$ is the species-species electrical conductivity. The conductivity of species α can be defined as $\sigma_\alpha = \sum_{\beta} \sigma_{\alpha\beta}$. In terms of concentration (number-density) gradient ∇c_γ ,

(A1) can be rewritten as:

$$\mathbf{J}_\alpha = - \sum_{\beta} k_B T L_{\alpha\beta} \sum_{\gamma} \frac{\partial (\mu_\beta / (k_B T))}{c_\gamma \partial \ln c_\gamma} \nabla c_\gamma \quad (\text{A3})$$

where k_B the Boltzmann constant, and T the temperature. The partial derivative in (A3) has been called the thermodynamic factor:

$$\Gamma_{\gamma\beta} = \frac{\partial(\mu_\beta / (k_B T))}{\partial \ln c_\gamma} \quad (\text{A4})$$

2. Atomistic parameters of diffusion and thermodynamics

The thermodynamic and kinetic parameters such as $\Gamma_{\alpha\beta}$ and $L_{\alpha\beta}$ can be obtained from the trajectory of molecular dynamics (MD) simulation. First, in the grand canonical ensemble, the thermodynamic factor takes the following form⁵⁶:

$$\Gamma_{\alpha\beta}^{-1} = \left[\frac{\partial \ln \langle N_\alpha \rangle}{\partial(\mu_\beta / (k_B T))} \right]_{T,V,\mu_{\gamma \neq \beta}} = \frac{\langle N_\alpha N_\beta \rangle - \langle N_\alpha \rangle \langle N_\beta \rangle}{\langle N_\alpha \rangle} = \frac{\langle (N_\alpha - \langle N_\alpha \rangle)(N_\beta - \langle N_\beta \rangle) \rangle}{\langle N_\alpha \rangle} \quad (\text{A5})$$

where N is the number of particles. The angle bracket represents the ensemble average. The right-hand side of (A5) can also be evaluated from the number-density correlation function in the form of pair distribution function as the following^{17,57}:

$$\frac{\langle N_\alpha N_\beta \rangle - \langle N_\alpha \rangle \langle N_\beta \rangle}{\langle N_\alpha \rangle \langle N_\beta \rangle} = \frac{1}{V} \int [g(\mathbf{r}_{\alpha\beta}) - 1] d\mathbf{r}_{\alpha\beta} + \delta_{\alpha\beta} \frac{1}{\langle N_\alpha \rangle} = G_{\alpha\beta}^V + \delta_{\alpha\beta} \frac{1}{\langle N_\alpha \rangle} \quad (\text{A6})$$

where δ is the Kronecker delta function, V the volume, $\mathbf{r}_{\alpha\beta}$ the position difference between an atom in species α and β , and $g(\mathbf{r}_{\alpha\beta})$ the pair distribution function. The first term in the right hand side, $G_{\alpha\beta}^V$, has been called the Kirkwood-Buff Integrals (KBI). Alternatively, the number-density fluctuation can be evaluated in the form of static structure factor as the following⁵⁸:

$$\frac{\langle N_\alpha N_\beta \rangle - \langle N_\alpha \rangle \langle N_\beta \rangle}{\langle N_\alpha \rangle \langle N_\beta \rangle} = \lim_{\mathbf{Q} \rightarrow 0} S_{\alpha\beta}(\mathbf{Q}, 0) \quad (\text{A7})$$

The static structure factor $S_{\alpha\beta}(\mathbf{Q},0)$ is the number-density correlation in the Fourier space:

$$S_{\alpha\beta}(\mathbf{Q},0) = \frac{1}{N_\alpha N_\beta} \left\langle \sum_{\alpha=1}^{N_\alpha} e^{i\mathbf{Q} \cdot \mathbf{r}_\alpha(0)} \sum_{\beta=1}^{N_\beta} e^{-i\mathbf{Q} \cdot \mathbf{r}_\beta(0)} \right\rangle \quad (\text{A8})$$

The forms of (A7) and (A8) include the cases of both $\alpha \neq \beta$ and $\alpha = \beta$. For orthogonal cells with periodic boundary conditions, the allowed $\mathbf{Q}$ values are $n_x 2\pi / L_x \hat{x} + n_y 2\pi / L_y \hat{y} + n_z 2\pi / L_z \hat{z}$ where L is the size along each Cartesian direction, $n_x / n_y / n_z$ the integers, and $\hat{x} / \hat{y} / \hat{z}$ the unit vectors. $\mathbf{Q} \rightarrow 0$ corresponds to the long-wavelength limit.

In summary, there are three methods, i.e. the fluctuation method (A5), KBI method (A6), and the static structure factor method (A7), to evaluate the thermodynamic factor $\Gamma_{\alpha\beta}$.

Second, the kinetic coefficient $L_{\alpha\beta}$ can be obtained from the hydrodynamic limit (long-wavelength and long-time as $\mathbf{Q} \rightarrow 0, \omega \rightarrow 0$) of the dynamic structure factor based on the collective velocity correlation function^{59,60}:

$$L_{\alpha\beta} = \lim_{\substack{\mathbf{Q} \rightarrow 0 \\ \omega \rightarrow 0}} \frac{1}{3Vk_B T} \int_0^\infty \langle \mathbf{J}_\alpha(\mathbf{Q},0) \cdot \mathbf{J}_\beta(-\mathbf{Q},t) \rangle e^{i\omega t} dt, \quad \mathbf{J}_\alpha(\mathbf{Q},t) = \sum_{k=1}^{N_\alpha} \mathbf{v}_\alpha^k(t) e^{-i\mathbf{Q} \cdot \mathbf{r}_\alpha^k(t)} \quad (\text{A9})$$

where $\mathbf{Q}$ is the wavevector, ω the angular frequency, $\mathbf{v}_\alpha^k$ the velocity of the k th atom in species α , and $\mathbf{J}_\alpha(\mathbf{Q},t)$ the collective velocity. This is essentially the Kubo formula in the Fourier space⁶¹. The correlation of the collective velocity can be separated into the longitudinal and transverse components:

$$\begin{aligned}
C_{\alpha\beta}^L(Q,t) &= \frac{1}{Q^2} \left\langle (\mathbf{Q} \cdot \mathbf{J}_\alpha(Q,0)) (\mathbf{Q} \cdot \mathbf{J}_\beta(-Q,t)) \right\rangle \\
C_{\alpha\beta}^T(Q,t) &= \frac{1}{2Q^2} \left\langle (\mathbf{Q} \times \mathbf{J}_\alpha(Q,0)) \cdot (\mathbf{Q} \times \mathbf{J}_\beta(-Q,t)) \right\rangle
\end{aligned} \tag{A10}$$

While the hydrodynamic limit due to the longitudinal component tends to zero, the kinetic coefficient can be obtained from the transverse component⁵⁶. Third, the tracer^{58,62} or self-diffusivity⁶³ can be obtained from velocity autocorrelation function (VAF) or mean square displacement (MSD) of individual particles:

$$D_\alpha^* = \frac{1}{3} \int_0^\infty \frac{1}{N_\alpha} \sum_{k=1}^{N_\alpha} \langle \mathbf{v}_\alpha^k(0) \cdot \mathbf{v}_\alpha^k(t) \rangle dt = \frac{1}{6t} \lim_{t \rightarrow \infty} \frac{1}{N_\alpha} \sum_{\alpha=1}^{N_\alpha} \left\langle |\mathbf{r}_\alpha^k(t) - \mathbf{r}_\alpha^k(0)|^2 \right\rangle \tag{A11}$$

where $\mathbf{r}_\alpha^k(t)$ is the position of the k th atom in species α .

3. Practical consideration for fast-ion conductors

Fast-ion conductors commonly contain one mobile species α and a few other non-diffusing framework species. If we assume the kinetic coefficients of different species are negligible, i.e.

$L_{\alpha\beta} = 0$ ($\alpha \neq \beta$), (A3) leads to the diffusion of species α in the form of Fick's 1st law:

$$\mathbf{J}_\alpha = - \sum_\gamma \frac{k_B T L_{\alpha\alpha} \Gamma_{\gamma\alpha}}{c_\gamma} \nabla c_\gamma \tag{A12}$$

The term in front of the concentration gradient can be denoted as the Fickian diffusivity:

$$D_{\gamma\alpha} = \frac{k_B T L_{\alpha\alpha} \Gamma_{\gamma\alpha}}{c_\gamma} \tag{A13}$$

In addition, the electrical conductivity of species α becomes the following:

$$\sigma_\alpha = (z_\alpha e)^2 L_{\alpha\alpha} \tag{A14}$$

If we recast (A14) in the form of the Nernst-Einstein equation with the help of $D_{\alpha\alpha}$, it becomes:

$$\sigma_{\alpha} = (z_{\alpha} e)^2 \left(\frac{D_{\alpha\alpha}}{k_B T} \right) (c_{\alpha} \Gamma_{\alpha\alpha}^{-1}) \quad (\text{A15})$$

where $\Gamma_{\alpha\alpha}^{-1}$ can be considered as the effective fraction of mobile charge carriers out of the total concentration c_{α} . $\frac{D_{\alpha\alpha}}{k_B T}$ is the mobility. Alternatively, we can keep c_{α} unchanged and define a conduction diffusivity from the Nernst-Einstein equation as:

$$\sigma_{\alpha} = (z_{\alpha} e)^2 \left(\frac{D_{\alpha}^{\sigma}}{k_B T} \right) (c_{\alpha}) \quad (\text{A16})$$

The combination of (A15) and (A16) yields $D_{\alpha}^{\sigma} = D_{\alpha\alpha} \Gamma_{\alpha\alpha}^{-1}$ that was found in a few reports^{61,64}.

In the solid-state ionics community, the ratio of D_{α}^* to D_{α}^{σ} has been commonly called the Haven ratio⁶⁵ H_R , although the original paper by Compaan and Haven only focused on the correlation among successive jumps⁶⁶:

$$H_R = \frac{D_{\alpha}^*}{D_{\alpha}^{\sigma}} \quad (\text{A17})$$

From (A9) and (A11), it can be seen that the Haven ratio characterizes the ratio of self-diffusion vs collective diffusion. It is worth noting sometimes the ratio of D_{α}^{σ} to D_{α}^* , instead of D_{α}^* to D_{α}^{σ} , was named as the Haven ratio instead.⁶⁷ In addition, D_{α}^{σ} in (A16) is often replaced by the self-diffusivity D_{α}^* to obtain σ as:

$$\sigma_{\alpha} = (z_{\alpha} e)^2 \left(\frac{D_{\alpha}^*}{k_B T} \right) (c_{\alpha}) \quad (\text{A18})$$

Obviously, this corresponds to the case of H_R being 1, which only applies to ideal solutions.

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