Normal Mode Analysis of Low-frequency Collective Vibrations of Solid Polymer Electrolytes

9.1 Introduction

Solid Polymer Electrolytes (SPEs) consisting of alkali salts dissolved in a solid polymer matrix are of intense research interest due to their unique property of ionic conductivity with mechanical flexibility. Poly(ethylene oxide), PEO, is the most widely used polymer host in SPEs due to its low toxicity and high electrochemical stability. PEO exhibits unusual conformational adaptability in response to different salts and compositions thus giving rise to a variety of crystalline PEO:salt complexes with diverse crystal structures. PEO-based SPEs find their applications in solid-state electrochemical devices such as thin-film batteries, electrochromic devices, and fuel cells due to their advantages over liquid electrolytes. SPEs can exist in crystalline or amorphous state. Crystalline SPEs are formed at certain discrete compositions while the amorphous SPEs are obtained over a wide range of compositions and temperature.

Ion conduction mechanism in SPEs is complex and unclear. The cation transport in amorphous SPEs above their glass transition temperature \( T_g \) is believed to be coupled to the dynamical relaxation modes of polymer due to strong ion-dipole interactions between the cation and polymer. The role of low-frequency collective vibrational modes of polymer in ion transport and the nature of transport-promoting polymer vibrations and salt-induced perturba-
9.2. Simulation details

It is believed that the conduction pathways of ions in SPEs may follow the trajectories of one or a few low-frequency normal modes. A comparison of the vibrational modes of PEO in crystalline PEO and PEO-salt complexes can help us understand salt-induced changes in the low-frequency vibrational modes of PEO in SPEs. A detailed characterization of the VDOS of different crystalline PEO:salt complexes provides clues on the vibrational response of PEO to different salts and on the relationship between polymer dynamics and ion transport in these systems. In this chapter, we have used normal mode analysis (NMA) and MD simulations to characterize the nature of low-frequency vibrational modes of different PEO-based SPEs and pristine PEO in the crystalline and amorphous state.

9.2 Simulation details

MD simulations and NMA were performed on crystalline and amorphous PEO, PEO$_3$:NaI, PEO$_3$:LiBF$_4$, and PEO$_6$:LiPF$_6$. The experimental crystal structures were used as the starting structures for the crystalline phase simulations. The simulated crystals consisted of 64 unit cells with 16 PEO chains in PEO, PEO$_3$:NaI, PEO$_3$:LiBF$_4$ and 32 PEO chains in PEO$_6$:LiPF$_6$ system. The amorphous SPEs were generated by randomly packing PEO chains (same number and chain length as in the crystalline model) and randomly placing the cations and anions in a cubic box of suitable volume corresponding to the experimental density. The amorphous samples were subjected to energy minimization followed by a 50 ns NVT and a 100 ns NPT equilibration runs to ensure that they are relaxed prior to the production runs.

The MD simulations and NMA were carried out using GROMACS-4.5.5 with the polymer and NaI force field parameters taken from the work of Neyertz et al. and the parameters for LiBF$_4$ and LiPF$_6$ were taken from the work of Borodin et al. The MD runs were performed in NPT-ensemble using the isotropic and anisotropic pressure couplings for the amorphous and crystalline phases, respectively. The pressure control in NPT simulations was achieved using the Parrinello-Rahman method with a time constant of 1 ps. The temperature was controlled using the Nosé-Hoover thermostat with a time constant of 0.1 ps. Three dimensional periodic boundary conditions consistent with the symmetry
9.2. Simulation details

Figure 9.1: Vibrational density of states obtained from NMA of crystalline (black) and amorphous (red) (a) PEO and (b) PEO$_3$:NaI are shown with the VACF-based power spectrum (green (a) amorphous PEO and (b) crystalline PEO$_3$:NaI).

of the simulation boxes were applied. The long-range electrostatic interactions were treated using the particle-mesh ewald (PME) method with a real space cut-off of 12 Å. A time step of 1 fs was used in all simulations. During 1 ns production runs on all equilibrated systems, the velocities of each particle were stored at regular time intervals. The atomic velocities were dumped every time step to obtain the power spectrum from the velocity autocorrelation functions. The velocity autocorrelation functions (VACF) calculated from the atomic velocities for a given system were Fourier transformed to obtain the power spectra. The VACF-derived power spectra were compared with the vibrational density of states (VDOS) obtained from the NMA. The calculated spectra were convoluted with a Gaussian function of width 2 cm$^{-1}$ to account for the spectral broadening due to the instrumental resolution function. The spatial extent of the modes of vibration was characterized by a quantity called the local character, which is defined as

\[ L_j = \sum_{i=1}^{3N} u_{ij}^4 \]  \hspace{1cm} (9.1)
9.3 Results and discussion

A comparison of the vibrational spectra of crystalline and amorphous systems investigated here provides insights into the role of disorder and intermolecular interactions in determining the features of the vibrational density of states of these systems. The vibrational spectra of crystalline and amorphous PEO and PEO<sub>3</sub>:NaI are shown in Figure 9.1. The polymer alone VDOS of PEO<sub>3</sub>:NaI are extracted from the total Hessian by using the methodology discussed

where $u_{ij}$ is the $i^{th}$ component of the $j^{th}$ eigenvector. The value of $L_j$ for a given vibrational mode $j$ can vary from 0 (extended) to 1 (localized) depending on the degree of localization of the vibrational mode of interest.

Figure 9.2: Comparison of polymer alone VDOS of PEO<sub>3</sub>:NaI with the pristine PEO (a) crystalline PEO (black) and PEO<sub>3</sub>:NaI (red), (b) amorphous PEO (black) and PEO<sub>3</sub>:NaI (red), and (c) crystalline (black) and amorphous (red) PEO<sub>3</sub>:NaI.
9.3. Results and discussion

Figure 9.3: Local character indicator, $L_j$, for normal modes of crystalline phases PEO (black) and PEO$_3$:NaI (red)

in the section 2.6.1 and the results are presented in the Figure 9.2. From the results it is evident that the vibrational states of amorphous systems differ from that of the crystalline counterpart for example, the population of VDOS in the regions around 600-750 and 850-920 cm$^{-1}$ are observed for amorphous PEO and PEO$_3$:NaI and such modes are absent in the crystalline PEO and PEO$_3$:NaI (Figure 9.1 and Figure 9.2(c)). The softening of low-frequency vibrational modes is observed in the crystalline PEO$_3$:NaI when compared to the crystalline PEO (Figure 9.2(a)), which can be attributed to weakening of intermolecular forces in the PEO$_3$:NaI when compared to the pristine PEO. The shape of low-frequency modes of amorphous PEO and PEO$_3$:NaI are similar (Figure 9.2(b)) indicating that they are insensitive to the local interactions and are dependent on the entire structure or architecture. This is consistent with the earlier studies that the overall shape of low-frequency VDOS depends on the overall shape, form, or native contact topology of the system under investigation.

The absence of unstable vibrational modes with imaginary frequencies indicates that the systems are in stable equilibrium on the corresponding potential energy surface (PES). The vibrational spectrum obtained by Fourier transformation of the velocity autocorrelation function of the atoms is also compared with the NMA-derived VDOS in Figure 9.1. The agreement
between the VACF-derived and NMA-derived spectra is excellent, despite the fact that NMA is only a harmonic approximation to the potential energy surface. The calculated $L_j$ values are very small for low-frequency vibrational modes ($< 200 \text{ cm}^{-1}$) due to the participation of a large number of atoms in these modes.

We have characterized the transport promoting modes in crystalline PEO$_3$:NaI by calculating the maximum value of a quantity pertaining to the transport of ions, here the helical pitch ($P_h$), $D_{13}$, and $D_{24}$ (see Figure 6.1(d) for definitions), along each normal mode. The frequency evolution of the maximum values of $P_h$, $D_{13}$, and $D_{24}$ is shown in Figure 9.4. Form the results it is evident that the maximum values are fluctuating more in the low-frequency region ($< 200 \text{ cm}^{-1}$) and fluctuations are almost zero beyond the frequency $600 \text{ cm}^{-1}$. This indicates that the transport promoting modes are highly populated in the low-frequency region. We have further carried out the visual inspection of some of these vibrational modes and identified that backbone twisting of PEO helical chains about their long axes is the prominent mode in the
Figure 9.5: Atomic displacements of low-frequency (< 200 cm$^{-1}$) vibrational modes of the PEO$_3$:NaI crystal. For each mode, one of the chains that exhibit significant atomic displacement is shown. Green spheres denote carbon atoms and red spheres denote oxygens. Sodium and Iodide ions and Hydrogen atoms are not shown for clarity. Arrows denote the directions of atomic displacements and their lengths are scaled up for better visualization. The mode at (a) 50 cm$^{-1}$, (b) 100 cm$^{-1}$, and (c) 150 cm$^{-1}$ are shown.
Figure 9.6: Vibrational density of states obtained from NMA of crystalline (black) and amorphous (red) (a) PEO$_3$:LiBF$_4$ and (b) PEO$_6$:LiPF$_6$. 
low-frequency region. The pictorial representation of the atomic displacements along a few representative transport promoting modes is shown in Figure 9.5.

We have also characterised the vibrational density of states for the crystalline and amorphous phases of PEO\textsubscript{3}:LiBF\textsubscript{4} and PEO\textsubscript{6}:LiPF\textsubscript{6} using NMA and results are shown in Figure 9.6

### 9.4 Conclusions

The vibrational density of states for crystalline and amorphous phases of PEO and PEO\textsubscript{3}:NaI have been calculated using the normal mode analysis (NMA) and the power spectral analysis of MD-derived velocity autocorrelation function (VACF) to characterize the transport-promoting low-frequency collective vibrational modes of polymers. The VDOS derived from NMA and VACF are consistent with experimental IR and Raman spectra of the sample. Based on the local character metric, $P_{h\text{--}max}$, $D_{13\text{--}max}$, and $D_{24\text{--}max}$ we have identified low-frequency collective modes involving the participation of large number of atoms that drive ion transport in these systems. In particular, the backbone twisting of PEO helical chains about their long axes and softening of a few other low-frequency collective modes are found to be important for ion transport in SPEs.