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Cross-Plane and In-Plane Heat Conductions in Layer-by-Layer Membrane: Molecular Dynamics Study

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an electrostatic assembly of polyelectrolyte multilayers and are expected to have different heat conduction characteristics between cross-plane and in-plane directions. We constructed models of a poly(acrylic acid)/polyethylenimine (PAA/PEI) LbL membrane sandwiched by charged solid walls and investigated their anisotropic heat conduction using molecular dynamics simulations. In the cross-plane direction, the thermal boundary resistance between the solid wall and the LbL membrane and that between the constituent PAA and PEI layers decrease with increasing degree



of ionization (solid surface charge density and the number of electric charges per PAA/PEI molecule). When the degree of ionization is low, the cross-plane thermal conductivity of a constituent layer is higher than that of the bulk state. As the degree of ionization increases, however, the cross-plane thermal conductivity of PAA, a linear polymer, decreases because of the increase in the number of in-plane oriented polymer chains. In the in-plane direction, we investigated the heat conduction of each layer and found the enhancement of effective in-plane thermal conductivity again due to the in-plane oriented chain alignment. The heat conduction in the LbL membrane is three-dimensionally enhanced compared to those in the bulk states of the constituent polymers because of the electrostatic interactions in the cross-plane direction and the molecular alignment in the in-plane direction.

INTRODUCTION

Advanced thermal management is a common and unavoidable challenge in industrial fields. Thermal interface material (TIM) is often inserted between two components such as heat source and sink for effective heat transfer from one to the other, i.e., for reduction of thermal resistance. Further improvement of TIMs has been required with an increase in the heat generation density of high-performance devices such as power modules. Generally, various types of thermal grease, elastomers, gels, or phase-change materials are commercially used for TIMs, which consist of polymers, with high-thermal-conductivity fillers such as metals, ceramics, and carbon materials occasionally added.¹ The thermal conductivity of polymeric matrices is not high,² and the performance of TIMs is mainly determined from the fillers. Although numerous studies³⁻⁵ of such polymer composites have been conducted to improve thermal conductivity, problems still remain, e.g., high cost, decreasing softness due to high filler content, and insufficient thermal percolation.

On the other hand, Shen et al. reported that the thermal conductivity of highly drawn polyethylene nanofiber achieved 104 W/(m·K) in the fiber direction, i.e., in the direction of intramolecular chains.⁶ Even in the case of heat conduction in a bulk liquid of alkane, energy transfer via intramolecular

chains is the dominant factor that determines its thermal conductivity, and thus, the molecular structure oriented in a specific direction induces an anisotropic thermal conductivity. Alkane chains with 12–18 C atoms have a single-chain thermal conductance of ~100 pW/K.8 Therefore, we can estimate that thermal conductivity in the direction of intermolecular chains is ~100 W/(m·K) if the packing density is $10^{19}\ m^{-2}$ and the ballistic phonon mean free path is ~100 nm, which is consistent with Shen's result. In fact, self-assembled monolayers (SAMs), in which alkane chains align along the heat flow, exhibit a significantly high thermal conductivity compared to the bulk liquid of the same alkane molecules. These results indicate that depending on the aggregation structure of chains, even polymers without fillers can be sufficiently performant as a TIM. In the present study, we focus on layer-by-layer (LbL) membranes¹⁰ as promising base

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materials for TIMs. In general, LbL membranes are fabricated by successively depositing positively and negatively charged materials onto a charged surface. This is a simple and versatile approach to fabricate thin films on a substrate with various surface structures and can give various features¹¹ to LbL membranes depending on the deposited materials, e.g., polymer,^{12,13} protein,¹⁴ carbon nanotube,¹⁵ and graphene.¹⁶

Successive depositions in the LbL fabrication approach enable us to control the thickness of a membrane because the thickness linearly increases with the number of lavers.^{17–19} In general, thickness is a major factor for the intrinsic thermal resistance of a bulk material, through the relationship $R = L/\lambda$, where R, L, and λ are the intrinsic thermal resistance, thickness, and thermal conductivity of the material, respectively. This controllable nature of thickness is a great advantage of LbL. In addition, LbL membranes are soft and flexible materials, and in principle, there is no restriction about substrate size and topology because polymers can fill gaps realized by the surface roughness on a substrate during the deposition process.²⁰ As for the point of thermal energy transfer, it is expected that the LbL membrane has two characteristic heat transfer paths in the in-plane and cross-plane directions. Because a constituent layer is an ultrathin film, the polymer chains are mostly oriented in the in-plane direction. Lussetti et al. created an oriented bulk polymer by stretching a molecular dynamics (MD) simulation system of an amorphous polyamide-6,6 in one direction and found that the thermal conductivity parallel to the stretching direction increases, while that perpendicular to the stretching direction decreases compared to that of the isotropic system.² Liu et al. also reported a similar result for bulk polyethylene subjected to mechanical strain.²² Therefore, LbL membranes are expected to have a high thermal conductivity in the inplane direction. Even in the case of heat dissipation in the cross-plane direction, the high in-plane thermal conductivity induces the heat spreading effect, in which a concentration of heat is dispersed in the in-plane direction and effective heat transfer area is expanded, and contributes to the overall crossplane heat transfer through the TIM. However, this in-plane oriented structure does not help the cross-plane thermal conductivity, as shown by Lussetti et al. However, in the case of the LbL structure, the electrostatic interaction between positively and negatively charged membranes may play an important role in the heat transfer in the cross-plane direction. Although not strictly a case of an LbL membrane, Kim et al. reported that a blend of poly(acrylic acid) (PAA) and poly-Nacryloyl piperidine (PAP) has a thermal conductivity about 7 times higher than that of each component.²³ This is caused by a structure where the hydrogen bonds between PAA, a donating polymer, and PAP, an accepting polymer, are homogeneously distributed inside the blend. This fact implies that the electrostatic interaction between composed membranes in an LbL membrane may improve the heat transport in the cross-plane direction. Therefore, such an LbL membrane with three-dimensional heat transfer paths due to the two characteristic thermal transport mechanisms has a high potential to exhibit a high three-dimensional thermal conductivity required for high-performance TIMs. Experimentally, the enhancement of heat transfer coefficient in pool boiling by polyethylenimine (PEI)/multiwalled carbon nanotube LbL coating¹⁵ and the measurement of the thermal conductivity of LbL membranes consisting of nanofibrillated cellulose/graphene nanosheets¹⁶ and PAA/polyallyamine hydrochloride²⁴ were reported. Although several promising results have been reported, heat conduction properties of LbL membranes and their molecular mechanisms have not yet been sufficiently analyzed. To evaluate the applicability of an LbL membrane to TIM, it is necessary to clarify the mechanism of thermal energy transport in LbL membranes and to find the dominant factor that determines their heat conduction property.

In this work, the heat conduction properties in the two directions of the poly(acrylic acid)/polyethylenimine (PAA/ PEI) LbL membrane were investigated using MD simulation, which has been widely used to explore the polymer thermal conductivity.^{21,22,25–29} Two types of nonequilibrium molecular dynamics (NEMD) simulations, where one of them was newly developed by us, were conducted for the calculation of the cross-plane and in-plane heat conduction properties, respectively.

MOLECULAR DYNAMICS SIMULATIONS

Figure 1 shows the flowchart of the present MD simulations. There are three main parts: construction of simulation systems



Figure 1. Flowchart of the present simulations.

from step (1) to (3), cross-plane NEMD simulations from step (C-4) to (C-6), and in-plane NEMD simulations from step (I-4) to (I-6). Each part is described in detail in later sections.

In our present systems, an LbL membrane consisting of two types of ionized polymers is sandwiched between two parallel solid walls, as shown in Figure 2c. Detailed explanations for the LbL membrane and the solid walls are given in the following sections. The CHARMM General Force Field (CGenFF),^{30–34} an all-atom force field, was used for all polymer molecules. The CHARMM potential energy function is expressed as a



Figure 2. Molecular structures of (a) ionized PAA with a charge of -4 e and (b) ionized PEI with a charge of +4 e, and computational domains of (c) cross-plane NEMD and (d) in-plane NEMD simulations.

superposition of bonded interactions (bonds, angles, and dihedrals) and nonbonded interactions (van der Waals (vdW) and electrostatic interactions). The vdW interactions are treated as the 12–6 Lennard-Jones (LJ) potential. The force-field parameters for the polymer molecules were determined by *Ligand Reader & Modeler* in CHARMM-GUI,^{35–37} a web-based CGenFF input generator. The solid wall was modeled by platinum atoms with the LJ potential, and the potential well depth and equilibrium nonbond distance parameters were set at 7.80 kcal/mol and 2.845 Å, respectively.³⁸ The LJ potential parameters between the solid and polymer atoms were calculated using the Lorentz–Berthelot mixing rules as usual in the CHARMM force field.

LAMMPS package³⁹ was used to conduct all of the MD simulations. Unless otherwise specified, the simulation settings described below were used. For the LJ potential, a smooth cutoff^{40,41} was applied from 10 to 12 Å. In the *x* and *y* directions, periodic boundary conditions were applied in the *z* direction. Corresponding to these boundary conditions, to calculate the electrostatic interactions in a two-dimensional periodic system, the particle–particle particle–mesh (PPPM) method⁴² with the EW3DC method⁴³ was used. Here, the real-space cutoff of 9 Å, accuracy of 10⁻⁶, and extending factor of 3.0 for the EW3DC were used. For the time integrator, the reversible reference system propagator algorithm (r-RESPA)⁴⁴ was used, and two-level time steps, 0.2 fs for bond and angle and 1.0 fs for the other interactions, were used.

LbL Membranes. Figure 2a,b shows examples of molecular structures of the ionized PAA and PEI molecules, respectively. Isotactic PAA with a degree of polymerization of 10 was selected as the polyanion. In the ionized PAA molecules, negatively ionized monomers, in which the COOH group is

replaced by the COO⁻ form, were assigned as uniformly as possible among 10 monomers, as shown in Figure 2a. As the polycation, hyperbranched PEI with a degree of polymerization of 13 was selected and its molecular structure was determined according to previous works.^{29,45} Positively ionized monomers were assigned on the primary amines, i.e., the terminal NH₂ group was replaced by the NH_3^+ form, because the primary amines are more nucleophilic.^{45,46} These polymers were selected for the present simulation as they are often used for LbL membranes.^{15,17–19,47} In addition, both polymers have almost the same radius of gyration, i.e., molecular size,^{27,29} and the effect of either linear or branching structure can be examined systematically. The heat conduction properties of bulk PAA and PEI were investigated in our previous works.^{27,4} In the present simulations, the number of ionized monomers, i.e., degree of ionization, was varied from 1 to 4, which hereinafter are denoted by ± 1 to ± 4 *e*, respectively, where *e* is the elementary charge. For example, the degree of ionization of $\pm 4 e$ indicates that the membrane is composed of ionized PAA with an electric charge of -4 e and ionized PEI with that of +4e.

PAA and PEI layers, three for each, were interlaminated so that each layer is parallel to the solid surfaces, as shown in Figure 2c. The leftmost polymer layer is PAA, and the rightmost one is PEI, and for convenience, each layer is named as PAA₁, PEI₁, PAA₂, PEI₂, PAA₃, and PEI₃ from the leftmost layer. The number of molecules in each layer is 48; therefore, the LbL membrane is neutral for all degrees of ionization.

Solid Walls with Surface Charge. Each solid wall consisted of 15 atomic layers with a face-centered cubic (FCC) (111) crystal plane perpendicular to the z axis. The sizes of the solid wall in the x and y directions were 143.84 and 33.54 Å, respectively, and one layer consisted of 728 atoms,

where the lattice constant is 3.912 Å.48 To realize polymer adsorption on a substrate by electrostatic interaction in an LbL system, an electric charge was given to each atom in the solid surface layers adjacent to the LbL membrane. The left-handside surface layer was positively charged to be opposite to the adjacent negatively ionized PAA layer, and the right-hand-side surface layer was negatively charged against the adjacent positively ionized PEI layer. The total charge of each surface layer was determined to cancel one-half of the total charge of the adjacent polymer layer, and this total charge was distributed to 728 surface atoms equally. This is because it was reported in previous experimental research that surface charge determines the amount of deposited polymer, and its value is one-half of the total charge in a single deposited polymer layer.49 The absolute values of the surface charge density of each surface layer are 4.97×10^{-3} , 9.95×10^{-3} , 1.49 $\times 10^{-2}$, and 1.99×10^{-2} e/Å² for the cases of $\pm 1, \pm 2, \pm 3$, and ± 4 e, respectively, and they fall within a reasonable range compared to those of silica, mica, and TiO2.50-53 In preliminary simulations, it was confirmed that the solid structure is maintained even when the solid wall has surface atomic charges in vacuum. Although this model surface cannot represent an actual charged solid surface perfectly, such a model has been often used to provide an electrostatic field and to capture primary features of polymer on a charged surface.^{51,54-}

Construction of Simulation System. In this section, we provide the construction procedures of the present simulation system, which correspond to steps (1)-(3) in Figure 1. The procedure of step (1) is given in the Supporting Information in detail and is only briefly described here. The MD box with a size of $143.84 \times 33.54 \times 129.80$ Å³ was divided into six small slabs in the z direction. Ionized PAA molecules were placed in the first, third, and fifth slabs, and ionized PEI molecules were placed in the second, fourth, and sixth slabs. The number of molecules in each slab was 48. The widths of the slabs in the zdirection for PAA and PEI were 9.6 and 10 Å, respectively. At this time, each slab was partitioned by imaginary walls to keep PAA and PEI immiscible. The solid walls were positioned on both sides. In the present simulations, there were no counterions because in an actual LbL membrane, counterions are excluded from polymer layers during film growth.^{49,5}

In step (2), the system equilibration was conducted under a uniform temperature and constant pressure for 20 ns. From step (2), the slab partitions were removed, and PAA and PEI were allowed to interdiffuse. From the second to fifth outermost layers of both solid walls, Langevin thermostats⁵⁹ with a damping coefficient of 100 fs were applied and the control temperature was set at 300 K. The outermost layers were subjected to a constant inward force. Here, the relative positions of the atoms in the outermost layers were fixed, and they were only able to move in the *z* direction an identical amount and acted as a piston to maintain the constant system pressure. The control pressure was set at 1 atm. The total translational momentum of the system was set to zero by subtracting the momentary center-of-mass velocity from each atom every 10 ps to avoid system drift during the simulation.

In step (3), for further equilibration, an annealing process for structure relaxation described below was conducted: (a) Warming up the whole system from 300 to 500 K in 50 ps under a constant volume. (b) Equilibration for 100 ps at 500 K under the constant volume. (c) Cooling the whole system from 500 to 300 K in 50 ps under the constant volume. (d) Equilibration for 300 ps at 300 K and 1 atm. This annealing cycle from (a) to (d) was repeated eight times, and then further equilibration was conducted for 5 ns. The system temperature in (a)–(c) was controlled by a Nosé–Hoover thermostat⁶⁰ with a damping coefficient of 100 fs, and the simulation procedures of (d) and the final equilibration were the same as step (2). The final density of the LbL membrane of approximately 1.155 g/cm³ was obtained for all ionization conditions (see Figure S3).

Methodology of Cross-Plane NEMD Simulations. In this section, we provide the procedures of the present crossplane NEMD simulation, steps (C-4)-(C-6) in Figure 1. Following step (3), the relaxation run of the cross-plane NEMD simulation under a constant pressure was conducted for 15 ns in step (C-4). The simulation procedure is the same as that of step (2) except for the temperature setting. The control temperatures were set to 330 and 270 K for the left (heat source) and right (heat sink) thermostats, respectively, to induce a steady temperature gradient in the z direction, i.e., in the cross-plane direction. In step (C-5), the outermost layers were fixed and the relaxation run under a constant volume was conducted for 5 ns. The positions of the outermost layers were determined from their mean coordinates during the last 5 ns of step (C-4), while the zeroing out of the system translational momentum was turned off.

Following the relaxation runs, the production run was carried out for 10 ns in step (C-6) using the system shown in Figure 2c. The heat flux, J_{\perp} , in the cross-plane direction was obtained from the following equation:

$$J_{\perp} = \frac{E_{\rm left} - E_{\rm right}}{2A_{\perp}t} \tag{1}$$

where E_{left} and E_{right} are the total kinetic energies added to the simulation system by the left and right thermostats over time *t*, respectively, and A_{\perp} is the *xy* cross section of the MD box. For each ionization condition, 10 simulations starting from the same state after step (C-5) with different random forces, i.e., using a different pseudorandom number sequence for the Langevin thermostats, were carried out to enhance statistical accuracy. Therefore, the total combined length of production runs of each condition was 100 ns.

Methodology of In-Plane NEMD Simulations. In this section, we provide the procedures of the present in-plane NEMD simulation, steps (I-4)-(I-6) in Figure 1. Following step (3), the system equilibration under constant temperature and constant volume was conducted for 5 ns in step (I-4). During the present in-plane MD simulations, Pt atoms of the solid walls were fixed at perfect FCC crystal positions to investigate only heat flow in the *x* direction, i.e., in the in-plane direction (see the Supporting Information for details). This technique has been often used in the previous works to prevent heat exchange with the surrounding walls.⁶¹⁻⁶³ The positions of the innermost surface layers adjacent to the LbL membrane were determined from the mean position during the last 5 ns of step (3). Two Langevin thermostats with a damping coefficient of 1000 fs were set at both edges and the center of the MD box along the x direction, and the widths in the x direction of the ends and center thermostats are 1/14 and 2/14 of the domain length in the *x* direction, respectively. The control temperature was set at 300 K.

In step (I-5), the relaxation of the in-plane NEMD simulation was conducted for 20 ns. The edge (heat source)

and center (heat sink) thermostats were set at 330 and 270 K, respectively. In the present in-plane NEMD simulation, the heat source and sink consisted of six independent small Langevin thermostats, respectively, aligned in the z direction, as shown in Figure 2d. Hereinafter, these small thermostats are referred to "arrayed thermostats". The z positions of the arrayed thermostat borders correspond to the intersections of the density profiles of PAA and PEI obtained in step (I-4), and thus, each layer in the LbL membrane has an individual heat source and sink. Using this system, we can obtain the heat flux through a single layer in the in-plane direction from computing the kinetic energy that was added to the single layer by the corresponding arrayed thermostats as follows

$$J_{\parallel}^{i} = \frac{E_{\text{edges}}^{i} - E_{\text{center}}^{i}}{4A_{\parallel}^{i}t}$$
(2)

where J^i_{\parallel} is the in-plane heat flux through the *i*th layer; E^i_{edges} and E^i_{center} are the total kinetic energies added by the edges and center arrayed thermostats at the *i*th layer over time *t*, respectively; and A^i_{\parallel} is the *yz* cross section of the *i*th layer. The constant in the denominator of eq 2 is 4 rather than 2 found in eq 1 because the number of thermostat interfaces is doubled. This arrayed thermostat system was developed by referring to Liang's system.⁶²

Following the relaxation run in step (I-5), the production run of the in-plane NEMD simulation was carried out for 5 ns in step (I-6) using the system shown in Figure 2d. Two control volumes with a width of 3/14 of the domain length in the *x* direction were placed between the edge and center thermostats. As with the cross-plane NEMD simulation, the total combined length of production runs of each condition was 5 ns \times 10 cases.

RESULTS AND DISCUSSION

Structure of LbL Membrane. Before the analysis of heat conduction, we discuss the structure of the LbL membranes constructed in the present study. Figure 3 shows the electric charge density and mass density profiles in the z direction



Figure 3. Profiles of electric charge density (solid lines, left axis), and mass density (transparent lines, right axis) in the *z* direction for the degrees of ionization of (a) $\pm 1 e$ and (b) $\pm 4 e$. The total charge is the sum of Pt, PAA, and PEI charges. The mass density for Pt is displayed at a scale of 0.017 compared to that of the polymers.

obtained in the cross-plane NEMD simulation, step (C-6), where the degrees of ionization are ± 1 and ± 4 *e*. The MD box was divided into slabs with a width of 1.0 and 0.5 Å in the zdirection for the calculation of charge and mass densities, respectively, and the local charge and mass densities for each slab were calculated. We note that almost the same profiles were obtained for the equilibrium state (step (3)) and the state under in-plane thermal gradient (I-6). In the polymer density profiles, no significant difference between the profiles of ± 1 and $\pm 4 e$ was observed. Although broad density peaks of PAA and PEI alternate, no well-defined interface between the PAA and PEI layers can be seen, which suggests interdiffusion. Hereinafter, such fuzzy interfaces between the polymer layers are called "interlayers". Such interpenetration between the adjacent polymer layers agrees well with structural properties of an LbL membranes reported in the previous experimental^{20,49,58,64} and simulation⁵⁴ research. Except for layers adjacent to the solid walls, there is a plateau regime, and this indicates that these layers have a bulk-like region. In the charge density profiles, the total charge is almost neutral at any zposition except near the solid walls. On the other hand, the PAA and PEI components of the charge density are negatively and positively overcharged only at the interlayer, respectively, and the degree of the overcharging increases as the degree of ionization increases. The integral of each overcharged peak is almost equal to one-half of total charge in the respective single layer. Therefore, the charges of the PAA and PEI layers balance each other out at the interlayers. Similarly, the integral of each charge density profile in the first layer adsorbed on the solid surface balances out that of the respective adjacent wall. These properties of the charge distribution such as neutralizing each other and the existence of the overcharging at the interlayers agree well with those reported in the literature.⁴⁹ From the above results, we conclude that our simulation systems appropriately reproduce actual LbL membranes and are reasonable to clarify heat conduction through LbL membranes.

Cross-Plane Heat Conduction. Figure 4a-d shows temperature and density profiles in the cross-plane NEMD for the degrees of ionization of $\pm 1-4$ e, respectively. The profiles were calculated with the slab widths of 0.5 Å for PAA and PEI and 0.1 Å for Pt. Using density profiles, the LbL membrane regions are divided into two types: a bulk-layer region and an interlayer region. Here, the bulk-layer region is defined as a region where the density ratio of a nondominant polymer to a dominant polymer is less than 20%. For example, at z = 60.25 Å in Figure 4a, the density ratio is 0.053/1.139 =4.7%, where the dominant polymer is PAA and the nondominant polymer is PEI; hence, this point belongs to the PAA₂ bulk-layer region. Note that the left and right edges of the bulk-layer regions of PAA₁ and PEI₃, respectively, are defined as the highest-density peak positions because their positions cannot be determined using the density ratio. The region between two bulk-layer regions is defined as the interlayer region, e.g., the PAA₂/PEI₂ interlayer region is located between the bulk-layer regions of PAA₂ and PEI₂. In Figure 4, the bulk-layer regions are colored gray, while interlayer regions are kept white. In the bulk-layer regions of both PAA and PEI, linear temperature profiles were formed for all cases. The black solid lines in the LbL membrane graphs in Figure 4 represent linear fittings to the temperature profiles inside each bulk-layer region. The black solid lines in the wall represent similar linear fittings for the Pt crystal, where the temperature profiles over the 8th to 12th layers counting from

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Figure 4. Temperature (points) and mass density (transparent lines) profiles in the cross-plane NEMD for the degree of ionization of (a) $\pm 1 e_i$ (b) $\pm 2 e_i$ (c) $\pm 3 e_i$ and (d) $\pm 4 e_i$ (e, f) Close-up views of the temperature profiles enclosed by a dashed rectangle in (a) and (d), respectively.

the outermost layer were used to avoid the effect of thermostats and interfaces. There is a temperature difference at not only the solid/polymer interface but also the polymer/ polymer interlayer when we compute respective polymer temperatures. The temperature jump, $\Delta T^i_{
m interface}$, at the solid/ polymer interface is defined as the difference between the extrapolated values of the linear fittings of the wall and adjacent polymer bulk-layer region at the midpoint between the innermost solid layer and the highest-density peak position, as shown in Figure 4b. Similarly, we define the temperature jump, $\Delta T^{i}_{interlayer}$ at the polymer/polymer interlayer as the difference between the extrapolated values of the fitted lines in the polymer bulk-layer regions at the center of the interlayer region, as shown in Figure 4e. Using these temperature jumps and linear fittings with extrapolation, the temperature profile of the system can be modeled as a step-like profile consisting of the black solid (linear fittings) and dashed (temperature jumps) lines. As shown in Figure 4e, even though the actual temperature profile of all components (purple line) differs from such a step-like profile, this model is useful to investigate the microscopic heat conduction properties in our LbL membrane systems.

The overall thermal resistance, *R*_{overall}, between the two solid surfaces sandwiching the LbL membrane is given by

$$R_{\text{overall}} = \frac{\Delta T_{\text{overall}}}{J_{\perp}}$$
(3)

where $\Delta T_{\text{overall}}$ is calculated from the difference between the extrapolated values of the linear fittings of the wall temperature at the solid/polymer interfaces, as shown in Figure 4b. The cross-plane heat flux, J_{\perp} , was computed by eq 1 and was on average $J_{\perp} \sim 1.9 \text{ GW/m}^2$. Figure 5 shows the overall thermal resistance as a function of the degree of ionization. The error bars represent the 95% confidence interval for the error of the



Figure 5. Overall thermal resistance, $R_{overalb}$ as a function of degree of ionization.

mean. The lowest overall thermal resistance $R_{overall}$ is in the case of $\pm 3 \ e$, i.e., the highest degree of ionization does not produce the lowest thermal resistance. To clarify this tendency, $R_{overall}$ is divided into three types of resistances as follows

$$R_{\text{overall}} = \sum_{i}^{2} R_{\text{interface}}^{i} + \sum_{i}^{5} R_{\text{interlayer}}^{i} + \sum_{i}^{6} R_{\text{bulk-layer}}^{i}$$
$$= \sum_{i}^{2} \frac{\Delta T_{\text{interface}}^{i}}{J_{\perp}} + \sum_{i}^{5} \frac{\Delta T_{\text{interlayer}}^{i}}{J_{\perp}} + \sum_{i}^{6} \frac{L^{i}}{\lambda_{\perp}^{i}} \qquad (4)$$

where $R_{interface}^{i}$ is the thermal boundary resistance (TBR) at the solid/polymer interface, $R_{interlayer}^{i}$ is the TBR at the polymer/ polymer interlayer, and $R_{bulk-layer}^{i}$ is the thermal resistance of a polymer bulk-layer. The macroscopic thermal resistance of a material with thickness L and thermal conductivity λ is given by L/λ , and hence, $R_{bulk-layer}^{i}$ is given by $L^{i}/\lambda_{\perp}^{i}$. Here, λ_{\perp}^{i} is the cross-plane thermal conductivity of a bulk-layer region *i* and is calculated from Fourier's law using the temperature gradient obtained from the linear fitting for each bulk-layer region in Figure 4 and J_{\perp} . The thickness L^{i} is the distance between pubs.acs.org/Langmuir

points at which temperature jumps were defined, i.e., not the width of the bulk-layer region. Each thermal resistance type is analyzed separately in the following paragraphs.

First, we investigate the TBR at the solid/polymer interface. Figure 6 shows the TBRs, $R_{interface}^{i}$ and mean values of the



Figure 6. Thermal boundary resistances, $R_{interface}^{i}$, and interfacial potential energies per unit area at solid/polymer interfaces as functions of degree of ionization.

interfacial potential energy per unit area, which is the total energy between the solid wall and remaining atoms, at the Pt/ PAA and Pt/PEI interfaces as functions of the degree of ionization. The TBR at the solid/polymer interface decreases with increasing absolute value of the interfacial potential energy due to the higher degree of ionization, and a similar tendency was reported in the previous works for solid/simple liquid interfaces. 65-69 For TBR at a solid/liquid interface in general, the amount of adsorbed molecules is also an important factor. However, as shown in Figure 4, the density profiles are almost the same for various ionization conditions. Therefore, the reduction of TBR at the solid/polymer interface is caused not by an increase in the amount of adsorbed polymer but only by the improved affinity due to the enhancement of electrostatic interaction between the charged surface and the adsorbed polymer. Similar results have been reported for gold-SAM-water system.⁷⁰⁻⁷² In such a system, the interfacial thermal conductance across the SAM/water interface improved with increasing polarity of the SAM because more polar functionalized surface can lead to stronger electrostatic interaction across the SAM/water interface.

Second, we describe the interpolymer TBR. Figure 7 shows the TBRs, $R_{interlayer}^{i}$, at the polymer/polymer interlayers as



Figure 7. Thermal boundary resistances, $R_{interlayer}^{i}$, at polymer/polymer interlayers as functions of degree of ionization.

functions of the degree of ionization. All TBRs at the interlayers have a similar tendency to the solid/polymer interface observed in Figure 6, and they decrease with increasing degree of ionization. As shown in Figure 3, the degree of overcharging at the interlayer increases with the degree of ionization, and hence, it is expected that higher

overcharging enables the stronger electrostatic interaction between ionized PAA and PEI at the interlayers, reducing their TBR. To confirm this, we calculated radial distribution functions (RDFs) between atom pairs in the interlayer regions. The interlayer regions have a finite width in the *z* direction, as shown in Figure 4, and hence, the RDF for a limited region⁷³ was used. A detailed description can be found in the Supporting Information.

Figure 8a shows the total RDF and its components in the PAA_2/PEI_2 interlayer region for the degree of ionization of ± 4



Figure 8. Slab geometry-based radial distribution functions (RDFs) in the PAA₂/PEI₂ interlayer region. (a) RDFs for ± 4 *e* and its component based on the combination of polymer types of selected atoms. (b) RDFs of PAA...PEI pairs, $g_{PAA...PEI}(r)$, for various ionization conditions. (c) The inset graph in (b): RDFs of PAA... PEI pairs for ± 4 *e* and its component based on the combination of atom types of selected atoms. In (a)–(c), the green solid lines are the same plots for $g_{PAA...PEI}(r)$ for ± 4 *e*.

e. In this RDF, only C, O, and N atoms were considered to capture the backbone of polymers and only intermolecular pairs were considered. The total RDF was decomposed into three components based on polymer types, PAA…PAA, PEI… PEI, and PAA…PEI, where $g_{PAA...PAA}(r) + g_{PEI...PEI}(r) +$ $g_{\text{PAA}\dots\text{PEI}}(r) = g_{\text{Total}}(r) \rightarrow 1$ as $r \rightarrow \infty$. In the interlayer region, the component of the heterogeneous pair PAA…PEI is dominant, and hence, the intermolecular interaction between PAA and PEI molecules plays an important role in determining heat conduction at the interlayer. In the other interlayer regions, similar distributions were obtained, while the component of homogeneous pairs is dominant in the bulklayer region (not shown). Figure 8b shows a comparison of $g_{\text{PAA} \dots \text{PEI}}(r)$ in the PAA₂/PEI₂ interlayer region for various ionization conditions. The first peak becomes higher as the degree of ionization increases. In Figure 8c (inset), $g_{\text{PAA}\dots\text{PEI}}(r)$ for $\pm 4 e$ was decomposed into three components based on the combination of atom types. The first peak corresponds to N-H…O hydrogen bonds, where hydrogen bonds between NH³⁺ and COO⁻ are dominant.

Using Figure 8b,c, the coordination numbers within the range of r < 3 Å and its components were calculated as shown in Figure 9 by integrating over the sphere with radius r (i.e., we assume that the RDF in the z direction is the same as



Figure 9. Coordination numbers within the range of r < 3 Å calculated from RDFs of PAA…PEI pairs, $g_{PAA…PEI}(r)$, in the PAA₂/ PEI₂ interlayer region and its component based on the combination of atom types of selected atoms.

 $g_{\text{PAA}\dots\text{PEI}}(r)$). Figure 9 also provides an illustration of the hydrogen bonds of (a) NH³⁺...COO⁻ and (b) NH³⁺...COOH. The coordination number increases with the degree of ionization, and the component of NH³⁺...COO⁻ becomes dominant, as was observed from RDF in Figure 8. Such hydrogen bonds in which both donor and acceptor atoms are ionized are called salt bridges and have a significantly higher bonding energy than hydrogen bonds between unionized atoms or between ionized and unionized atoms.⁷⁴ Salt bridges can be often seen in proteins and have an important role in protein stability.⁷⁵⁻⁷⁸ The number of salt bridges in the interlayer region increases with the degree of ionization. Wei et al.^{79,80} reported that in the system of ionized polymer with counterions, the electrostatic interaction between oppositely charged atoms does not improve the thermal conductivity directly but leads to shifting the vdW force to the stronger repulsive regime by attracting atoms closer together, and this repulsive vdW force enhances the heat conduction. Therefore, in the LbL system, it is likely that salt bridges, i.e., stiff noncovalent bonds via the electrostatic interaction, lead to the stronger repulsive vdW force and enhance heat conduction, i.e., reduce TBR, at the interlayers.

Third, we investigate bulk-layer thermal conductivity. Figure 10 shows the cross-plane thermal conductivity, λ_{\perp}^{i} , of each



Figure 10. Cross-plane thermal conductivities, λ_{\perp}^{i} of each bulk-layer region as functions of degree of ionization.

bulk-layer region as functions of the degree of ionization. Compared to the thermal conductivities of the bulk PAA²⁷ and PEI,²⁹ 0.339 and 0.219 W/(m·K), respectively, the cross-plane thermal conductivities of PAA and PEI in the case of $\pm 1 e$ are unexpectedly higher in spite of the in-plane oriented structure. Although the average mass densities of the PAA₁ and PEI₃ bulk-layer regions that are adjacent to solid surfaces are higher than the respective bulk densities of PAA and PEI due to the interfacial adsorption, the average densities of the other layers are almost the same as each bulk density (see Figure S4). A

possible reason for the higher thermal conductivities is that the thermal conductivity of the ionized polymer is higher than that of the neutral polymer because of chain extension and increase of elastic modulus.⁸¹ The cross-plane thermal conductivity of PAA decreases with increasing degree of ionization, while that of PEI is almost constant regardless of the degree of ionization. To clarify this different tendency, we considered the gyration tensor R for each molecule and defined the order parameter as $2\langle R_{zz} \rangle / \langle R_{xx} + R_{yy} \rangle$,²¹ where $\langle \rangle$ denotes an ensemble average. This quantity is unity for a completely random and isotropic system, whereas it is less than unity for a system oriented in the in-plane direction (inside the *xy* plane). Figure 11 shows the



Figure 11. Order parameters, $2\langle R_{xx} \rangle / \langle R_{xx} + R_{yy} \rangle$, in each bulk-layer region as functions of degree of ionization.

order parameters of each bulk-layer region as functions of the degree of ionization, and a similar tendency with the crossplane thermal conductivity was obtained. PAA, a linear polymer, is more oriented in the in-plane direction as the degree of ionization increases because ionized PAA was attracted by positively charged layers and a linear structure is easy to align in the in-plane direction. Therefore, the crossplane thermal conductivity of PAA decreases. On the other hand, PEI, a hyperbranched polymer, is difficult to align in the in-plane direction due to its steric hindrance, resulting in the almost constant cross-plane thermal conductivity of PEI. Among the various ionization conditions, the thickness L^{i} is almost the same, and hence, the thermal resistance, $R_{\text{bulk-layer}}^{i}$, has a reciprocal tendency of the cross-plane thermal conductivity, λ_{\perp}^{i} , when the degree of ionization changes. In fact, the thermal resistance of the PAA bulk-layer increases with the degree of ionization, whereas that of the PEI bulklayer is almost constant (see Figure S5).

The reason for the overall thermal resistance to have the minimum value at $\pm 3 e_1$ as shown in Figure 5, is the trade-off relationship in which the TBRs at the solid/polymer interface and at the polymer/polymer interlayer decrease with the degree of ionization, whereas the thermal resistance of the PAA bulk-layer increases with the degree of ionization because of decreasing the cross-plane thermal conductivity. The different tendency of the cross-plane thermal conductivity depending on the molecular structures suggests that the trade-off relationship between TBRs and cross-plane thermal conductivity might be overcome if hyperbranched polymers are used for both positively and negatively charged layers. In such an LbL membrane, the overall thermal resistance might decrease with increasing degree of ionization. In the present study, it was found that the electrostatic interaction has an important role in forming effective heat transfer paths at the solid/polymer interface and at the polymer/polymer interlayer in the crossplane heat conduction through the LbL membrane.

Actual LbL membranes in practical applications generally have more layers compared to our model. Under the same ionization condition, Figure 7 shows that the TBRs at each interlayer have almost the same value and Figure 10 shows that the respective cross-plane thermal conductivities for the PAA and PEI layers also have almost the same values. Therefore, the overall thermal resistance of practical LbL membranes with a larger number of layers can be estimated by considering that these values of interlayer and thermal resistance per layer are maintained as long as the polymer layers are interlaminated orderly. In addition, although in the present MD simulation the thickness of each laver is almost the same, the thickness might change with the number of layers in actual LbL membranes. The influence of changing the thickness on the overall thermal resistance can be estimated as dependent only on the thickness L^i using eq 4 if we assume that the cross-plane thermal conductivity does not change significantly with the thickness.

In-Plane Heat Conduction. Figure 12 shows the temperature profiles in each layer along the x direction, i.e., the in-



Figure 12. Temperature profiles for each layer along the *x* direction in the in-plane NEMD for the degree of ionization of $\pm 1 e$. The red and blue parts represent the heat source and sink, respectively, and the green parts represent the control volumes.

plane direction, in the in-plane NEMD simulation for the degree of ionization of $\pm 1 e$. Although the heat source and sink were independently set for each layer, almost the same temperature profiles were formed in each layer, indicating that the temperature gradient, i.e., net heat flux, in the z direction is almost zero. On the basis of this result, heat fluxes through each layer can be computed individually from the added kinetic energies in each arrayed thermostat using eq 2. For each ionization condition, the temperature gradient, $\partial T/\partial x_i$ was given as the average of those calculated from linear fittings in the 12 control volumes. The in-plane thermal conductivity, λ_{\parallel}^{i} , for each layer was calculated using this average temperature gradient, and the respective in-plane heat flux, J_{\parallel} , is displayed in Figure 13. For reference, the same protocol was performed for the neutral systems in which neutral PAA or PEI was sandwiched by uncharged Pt walls, and λ^i_{\parallel} is also plotted in Figure 13. Here, the total number of polymer molecules in the neutral systems is the same as that of the LbL systems, and the layer positions, i.e., the arrayed thermostat positions, were determined from each density profile, as described in Figure S6.

The in-plane thermal conductivities of each PAA and PEI layer were around 0.28–0.35 and 0.26–0.34 W/(m·K), respectively, and the corresponding mean values were 0.328 and 0.305 W/(m·K). The PAA layers have a -19 to 5% enhancement and the PEI layers have a 19-54% enhancement from the respective bulk thermal conductivities. Strictly



Figure 13. In-plane thermal conductivity, λ_{\parallel}^{i} , distributions in the *z* direction for each polymer layer in an LbL membrane for different degrees of ionization (from ±1 to ±4 *e*). The filled and open symbols represent the results of PAA and PEI layers, respectively. The abscissa represents the center position of each polymer layer. The results for the single-component neutral membranes are also included.

speaking, although the bulk-layer regions in the cross-plane NEMD simulations were considered as mostly pure, the layers in these in-plane simulations should be considered as PAA-rich or PEI-rich due to interdiffusion, as is seen in Figure 2d. The PEI layers contain a small amount of PAA with higher thermal conductivity, and also the in-plane oriented structure induces a large enhancement in thermal conductivity, whereas it seems that for the PAA layer, the significant enhancement was not obtained because of the conflicting effect between the inclusion of the lower thermal conductivity polymer and the oriented structure.

In Figure 13, the neutral PEI in the vicinity of the walls has a higher in-plane thermal conductivity than that of bulk PEI because of the in-plane oriented structure and high density due to the existence of solid surface, whereas in the middle region, it is almost the same as the bulk thermal conductivity. This is because the in-plane oriented structure of the neutral PEI disappears in the middle region and it behaves as a bulk (see Figure S6). On the other hand, the results in Figure 13 indicate that the in-plane thermal conductivities of the LbL membrane maintains relatively high values in the whole region because the highly oriented structure in the in-plane direction is sustained at all regions due to the thinned layer structure which is a characteristic property of LbL membranes. The neutral PAA also maintains a higher in-plane thermal conductivity in the whole region. This is because the highly oriented structure of linear polymers due to the existence of solid surfaces extends over a longer distance than PEI. However, it is believed that the in-plane thermal conductivity of the neutral PAA will also decrease to the bulk value as seen for that of the neutral PEI in Figure 13 when the thickness of the PAA film increases enough for the oriented structure to disappear.

If we apply the macroscopic heat conduction model for a multilayered flat plate, the effective thermal conductivity of this layered structure is calculated as the volume average thermal conductivity. With this model, the effective in-plane thermal conductivities of the LbL membranes are calculated as 0.333, 0.321, 0.298, and 0.313 W/(m·K) for the conditions of ± 1 , ± 2 , ± 3 , and ± 4 *e*, respectively. Using the bulk thermal conductivities and the volume ratio of PAA and PEI calculated from the bulk densities, the volume average thermal

conductivity would be 0.283 W/($m\cdot K$). Compared to this value, the effective in-plane thermal conductivity in the LbL membranes was higher for all ionization conditions. Lussetti et al.²¹ and Liu et al.²² reported over 30% enhancement of polymer thermal conductivity in the oriented direction. Comparing with these past works, the enhancement obtained in the present LbL membrane is small. This is because the heat flow direction coincides with the oriented direction in their cases, whereas in our LbL systems, the axis of molecular alignment in the xy plane deviated from the heat flow direction, the x direction. We defined another orientation order parameter, $\langle R_{xx}/R_{yy}\rangle$, for each layer using the gyration tensor. This quantity represents a degree of molecular alignment in the x direction, and it is unity for isotropic alignment on the xy plane. For PAA layers, $\langle R_{xx}/R_{yy} \rangle$ falls within the range of 0.67-1.38, showing varying deviation of the axis of molecular alignment from the heat flow direction. The present in-plane NEMD simulation can only capture the enhancement of the x direction thermal conductivity, and hence, the enhancement of the in-plane thermal conductivity by the in-plane oriented structure might not be evaluated accurately. This fact may also explain why the in-plane thermal conductivity of PAA does not increase with the degree of ionization although the cross-plane thermal conductivity decreases with decreasing order parameter. This feature may be more pronounced in linear polymers than branched polymers.

CONCLUSIONS

In this work, we constructed models of a poly(acrylic acid) (PAA)/polyethylenimine (PEI) layer-by-layer (LbL) membrane sandwiched by charged solid walls for various ionization conditions represented by different charge densities of the solid walls and degrees of ionization of each polymer and investigated the heat conduction properties in the crossplane and in-plane directions using NEMD simulations. LbL membranes can transfer heat efficiently in both the cross- and in-plane directions using different mechanisms, and this suggests a new strategy to enhance heat conduction of polymeric materials in three-dimensional directions using LbL membranes. Each heat conduction mechanism is summarized below.

In the cross-plane NEMD simulations, the overall thermal resistance is divided into three types of resistances: TBR at solid/polymer interfaces, TBR at polymer/polymer interlayers, and thermal resistance in bulk-layers. The TBRs at interfaces and interlayers decreased with increasing degree of ionization, and hence, we concluded that efficient heat transfer paths are formed by electrostatic interaction. The tendency of the thermal resistance in bulk-layers with increasing degree of ionization depended on the molecular structure.

In the in-plane NEMD simulations, each polymer layer in the LbL membranes showed a high in-plane thermal conductivity due to the thinned layer structure. As a result, the effective in-plane thermal conductivity of the LbL membranes was higher than the volume average of bulk thermal conductivity of the constituent polymers.

Although we dealt with the LbL membrane that has a welldefined structure, actual LbL membranes would be more complicated. The boundaries between constituent layers may be ambiguous and the degree of ionization may be distributed nonuniformly. Nevertheless, the picture of the in-plane and cross-plane heat conductions obtained here for an ideal LbL membrane is still helpful as a basis when one investigates heat conduction in such realistic membranes.

Although the heat conduction properties obtained here are not high enough to replace existing TIMs, our work presents a proper understanding of the different mechanisms of the crossplane and in-plane heat conductions in LbL membranes and provides important knowledge for the development of a highperformance LbL-based TIM.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c00845.

Construction of initial system, reason for fixed wall in inplane NEMD simulation, radial distribution function for a limited region, time changing of membrane densities during the annealing process, average densities of each bulk-layer region, thermal resistances in each bulk-layer, and profiles of density and order parameter in neutral systems (PDF)

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Notes

The authors declare no competing financial interest.

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