Supporting Information: Molecular Modeling of Interfacial Layer-by-Layer Assembly Towards Functionalized Capsule Materials

Andrew W. Ruttinger † and Paulette Clancy *,‡

[†]Robert F. Smith School of Chemical and Biomolecular Engineering, Cornell University [‡]Department of Chemical and Biomolecular Engineering, The Johns Hopkins University

E-mail: pclancy3@jhu.edu

Detailed Review of Background Literature

Previous Computational Work

Computational studies of the LbL assembly of capsules formed at interfaces are scarce. However, related studies have used MD to investigate oil/water interfaces,¹⁻³ surfactants,⁴⁻⁶ and polylectrolyte solutions.⁷ There have also been studies of assembly on surfaces: LbL assembly onto a surface using polymer "bead" models^{8,9} and LbL assembly onto a surface using explicit, all-atom models.^{10–13} Simulation studies of surfactants at an oil-water interface reveal significant hydrogen-bonding between the water and the surfactant's head group, along with an increased interfacial thickness due to a vertical orientation of the hydrophobic tail.⁶ Polarity of the surfactant was found to significantly influence interfacial thickness, interaction energy between the surfactants using different functional groups like oxygen, benzene, and oxyethyl groups.⁵ The effect of surface area per molecule (SAPM) on the IFE also reveals the nature of the relationship between selected surfactants and the resulting surface charge,⁶ which has implications on capsule assembly.

A "coarse-grained" model of LbL assembly provides insight into the electrostatic behaviour of polyelectrolytes during assembly.⁹ While this study is limited to consideration of a solid surface rather than the fluid interface considered here, it reveals that the behavior of the deposited monolayers varies between the first monolayer and subsequent layers,⁹ highlighting the role played by the charged surface. Additionally, significant surface roughness and layer overlap is observed, leading to non-uniform multilayers.⁹ Finally, previous all-atom simulations revealed important structural insight into LbL assembly that could not have been obtained otherwise.^{10,12,13} This includes absorption dynamics,¹⁰ the density profiles of resulting polyelectrolyte layers,^{10,12} and the role of water content on electrostatic behavior.¹³ In all cases, these studies are limited to a single polycation/polyanion pair.

Layer-by-Layer Assembly

Encapsulation of materials begins with formation of an oil-in-water emulsion using surfactants to form oil droplets. These droplets can be reduced in size through an external energy input in order to improve the surface area to volume ratio.¹⁴ Once formed, the capsule material can be added to the emulsified solution for encapsulation. Polymer capsules are the most common, since they offer a good balance of strength and flexibility, despite their low thermal conductivity. Inorganic capsules have also been used; they have high thermal conductivity but are brittle.¹⁴ In this regard, layer-by-layer (LbL) assembly offers a unique method to incorporate the benefits of both capsule materials through synthesis of multifunctional shells.¹⁵⁻¹⁷

The LbL assembly technique is based on the iterative assembly of oppositely charged molecules, allowing for different combinations of polymers and particles leading to high tunability of capsule properties.¹⁶

Experimentally, LbL assembly is carried out by consecutive steps of "dipping and wash-

ing." An oil-in-water emulsion is generated using a charged surfactant, creating a net charge around the oil. Next, the emulsified oil is "dipped" in an oppositely charged polyelectrolyte, leading to the electrostatically driven deposition of the first monolayer. The solution is then "washed," meaning the excess polyelectrolyte is removed from solution to ensure they do not interact with the oppositely charged polyelectrolytes used for the impending second layer formation. Once the excess polyelectrolyte has been successfully removed, the process is repeated, with a second dipping step.¹⁸ While the primary driver of LbL assembly involves harnessing electrostatic interactions, other interactions play a role, such as hydrogenbonding, covalent bonding, base-pair interactions, guest-host interactions and hydrophobic interactions.¹⁹ As a result, insight into improved properties of capsule materials could help steer future research and development of functionalized encapsulated nanomaterials.

To date, a number of experimental studies have investigated LbL assembly for encapsulation using a diverse range of surfactants, polyelectrolytes, and encapsulated materials.^{18,20–22} While selection of these materials, as well as system conditions, including pH, salt content, and solvent, have an effect of the resulting capsule properties, more research is needed to establish the fundamental factors that lead to specific functional attributes in multi-layered emulsions.²³ In particular, research should focus on the design of multi-functional capsules with enhanced thermal conductivity through methods such as LbL assembly.¹⁴ In this regard, computational approaches have been described in literature as an important player in prediction of properties and performance of capsules based on the materials used during LbL assembly.^{16,19,24}

Justification for Computational Details

Force Field Parameters

While we used the Optimized Potential for Liquid Simulations (OPLS) as our force field, some parameters for sulfonate and benzesulfonate groups were not natively included in OPLS and were drawn instead from the literature.^{25–29} All bonds, angles, dihedrals, and Van der Waals parameters taken from literature were reported, in their original sources, to be consistent with the OPLS force field. While charges for the benzenesulfonate group were originally derived for use with the CHARMM force field, they were developed in a manner consistent with charge parameterization in OPLS^{25,30} and are similar in magnitude to OPLS charges of related groups.^{26,31}

Long-Range Interactions Solver

In our study, we used a long-range Coulombic potential coupled to a Particle-Particle Particle-Mesh (PPPM) solver to describe longer-ranged interaction beyond 10 Å.³² Use of a solver like PPPM helps capture long-ranged electrostatic behavior in the system. While similar studies used the smooth Particle Mesh Ewald (PME) method,^{10,12,13,31} this method is not native to LAMMPS, which guided our choice. The PPPM method is computationally less intensive³³⁻³⁵ and more similar to PME than the alternatives.³⁶ An accuracy in the relative root mean square error per-atom forces of 1.0E-4 was specified. Grid size is set automatically within LAMMPS, consistent with the accuracy and pairwise cutoff.

Ionic Concentration

Salt concentration has a significant effect on layer growth behavior, with high salt concentrations resulting in reduced effective polyelectrolyte charge and, consequently, non-linear growth with respect to layer number.³⁷ This screening of charges causes the polyelectrolytes to coil in solution, leading to thicker layers.^{38,39} Moderate salt concentrations may bias polyelectrolytes against forming free solvated complexes in favor of forming polyelectrolyte multilayers.⁴⁰ A transition from exponential to linear growth has been observed at a salt concentration of 0.5 M, below which linear growth, with respect to layer number, occurs.⁴¹ Importantly, adding salt during LbL assembly of low molecular weight polyelectrolytes, such as those used in the present study, was shown to reduce mass loss during assembly.⁴²

We used a salt concentration of 0.15 M NaCl as additional ionic concentration in the polyelectrolyte solution. Its role was to facilitate a more linear LbL assembly, and its value fell within the range typically used in the literature.^{12,21} A salt concentration of 0.15 M NaCl has been demonstrated successfully for PSS/PAH and PAA/PAH pairings, showing its applicability to our studied systems.⁴³ Near 0.1 M NaCl, polyelectrolyte growth is neither linear nor exponential, but instead can be fitted reasonably well by a parabolic curve.⁴¹ More linear growth is desirable for the controlled growth of capsules. Water was used as the solvent for the polyelectrolyte solution and washing step. Structures for the surfactants and polyelectrolytes used in the study are provided in Figure S1.

System Setup Methods and Results

Interface Verification

Prior to any of the main LbL assembly simulations, we perform preliminary analyses to validate the system's behavior, define simulation parameters, and characterize molecular properties. To validate system behavior, an interface between hexadecane and water is generated to compare bulk densities and interface width with experimental observations. We generated a box of size 40 Å by 40 Å by 100 Å and packed it with hexadecane and water phases of size 40 Å³, side-by-side. Since we only desire one interface and fixed x and y dimensions, a 40 Å by 40 Å by 20 Å slab is left empty at the outside of the system. This leaves a vacuum buffer between the phases in a periodic system, while also allowing for corrections in the density of the phases.

The system undergoes a short energy minimization for up to 1 ps, followed by a 2 ns system relaxation period using an NVT ensemble. An additional 5 ns simulation in an NVT ensemble was then used to gather data and calculate properties. Bulk densities were calculated by finding the average density of the water and hexadecane phases at positions far removed from the interface. The interface width has been calculated in the past for liquid-vapor interfaces using the "10-90" thickness rule which aims to define the distance between the positions where the density varies from 10% to 90% of its bulk density.⁴⁴ In the case of an interface featuring two different bulk liquids, this approach can be modified to the "90-90" thickness rule where the interface thickness is defined as the distance between the positions where each liquid is 90% of its bulk density.⁴ The interfacial density profile for each phase can be fitted using a hyperbolic tangent function.^{4,44}

$$\rho_i(z) = \frac{1}{2}\rho_{bulk,i} - \frac{1}{2}\rho_{bulk,i} tanh\left(\frac{(z-z_0)}{d}\right)$$
(1)

Here, $\rho_{bulk,i}$ is the bulk density for the liquid *i*, *z* is the axial position, z_0 is the Gibb's dividing surface, and *d* is related to the interface thickness (*t*) of the liquid. The two-phase interface thickness can be calculated using these density profiles:

$$t_{1,2} = z(\rho_1 = 0.9) - z(\rho_2 = 0.9) \tag{2}$$

Experimental and theoretical values are provided in Table S1. Deviation between the experimental and theoretical bulk densities are 1.7% and 0.2% for hexadecane and water, respectively, indicating the dynamics are well modeled by our MD system. While the deviation for the interface width is larger, the calculated interface width is sensitive to the selected boundaries of the interface. For example, increasing the interface boundary to the position where 95% of the bulk density is achieved, the calculated interface width changes to 6.1 Å which sits in the range of the measured width. Based on this observation, we deem the interface width to be in fair agreement with experimental values and feel that the validation is sufficiently encouraging to proceed with the MD simulations as modeled.

For density profiles that involve surfactant or polyelectrolyte molecules, the thickness of those layers are determined by again modifying the "10-90" thickness rule and using a "10-10" thickness rule to demarcate the layer boundaries.

Observable	MD Simulation	Experimental
Water Bulk Density (g/cm ³)	0.995	0.997
Hexadecane Bulk Density (g/cm ³)	0.760	0.773
Interface Width (Å)	4.8	5.55 (calc.), 6.0 \pm 0.2 (meas.) ⁴⁵

Table S1: Comparison of experimental and MD-derived bulk densities and interface width for a water/hexadecane interface.

Surfactant and Polyelectrolyte Structures



Figure S1: Structures of the polyelectrolytes and surfactants studied in the LbL assembly of nanomaterial capsules. Surfactant polarities and polyelectrolyte radii of gyration are provided; their calculation is described below in the SI. Each molecule is paired with a counter-ion that is the opposite charge of its head-group. This counter-ion is exchanged with depositing polyelectrolyte during LbL assembly, also the opposite charge of the surfactant head-group.

Interface Formation Energy

Determination of the requisite number of surfactants at the interface was important because it defines the surface charge, which influences the overall LbL assembly. The number of surfactants at an interface is often defined using the surface area per molecule (SAPM). Surfactants act as a intermediary at an oil/water interface, modifying the interfacial properties such as decreasing interfacial tension.⁴ The average intermolecular interactions arising from adding a surfactant to an interface can be characterizing using the interface formation energy (IFE).^{4–6} This can be interpreted as the energetic stability provided by a surfactant that bridges between immiscible liquids:

$$IFE = \frac{E_{total} - (n \times E_{surfactant} + E_{interface})}{n}$$
(3)

Here *n* is the number of surfactant, while E_{total} , $E_{surfactant}$, and $E_{interface}$ are the total system energy, energy of one surfactant, and energy of the interface without surfactants, respectively. We specify the number of surfactants at our surfactant-mediated interface by determining the most favorable IFE resulting from optimized SAPM.⁶

IFEs were evaluated at SAPMs between 20-80 Å² at an average interval of 4 Å². For each SAPM, three simulations were required: (1) the interface with surfactants, (2) the interface with no surfactants, and (3) the surfactant alone.⁵ For the interface with surfactants, the surfactant layer was generated by first optimizing the surfactant molecule in Density Functional Theory (DFT). Then, a 7×7 lattice of surfactants was generated based on the required SAPM, defining the required cross-sectional area of the simulation box. We used an axial dimension of 120 Å with the surfactant layer placed at the centre of the box. The hexadecane phase was packed into a 40 Å slab with the hydrophobic tail of the surfactant. The water phase was packed into a 40 Å slab with the hydrophobic tail of the surfactant and included a 0.15 M ionic concentration of NaCl, important for the ion exchange during the LbL assembly. For both systems, a slab of 40 Å was left empty at the outside of the box to ensure that a second interface does not form.

The interfacial system without surfactants was set up similarly, based on the crosssectional area required by the SAPM. For the surfactant, the DFT-optimized molecule was placed in the center of a 100 Å³ box. The surfactant-mediated interface was simulated following methodology adapted from the literature.⁵ After a short minimization period of no more than 1 ps, the system was run under an isothermal NVT ensemble for 0.2 ns, constraining the molecules constituting the water phase and the head-groups of the surfactants. Initial packing of the hexadecane phase is high-energy due to the long molecules, so fixing the polar phase allows the hexadecane molecules to relax faster. The constraints were then removed and the simulation was performed for 30 ns in an NVT ensemble. The interfacial systems without surfactants were simulated with a 1 ps minimization period followed by a 30 ns NVT ensemble MD simulation. For the surfactant system, due to the small system size, we used a 1 ps minimization period, followed by a 100 ns simulation in an NVT ensemble. For the IFE calculations, we discarded data for the first 15 ns of the NVT MD simulation to allow the system to relax in the surfactant-mediated interfacial system. Uncertainties in the data were taken into account using standard error estimations.⁴⁶

Results from our evaluation of the IFE at different SAPMs for each surfactant corroborated previous studies, showing that increased surfactant head-group polarity leads to a higher IFE.⁵ Polarity was determined from DFT calculations, providing the dipole moment of the surfactant. The most polar surfactant, SDBS, has a minimum IFE of -96.9 kcal/mol, while the least polar surfactant, DTAC, has a minimum IFE of -75.8 kcal/mol (Table S2). Moreover, this trend in IFE persisted regardless of SAPM. However, we found that the relationship between polarity and interface width did not hold. Instead, we found that the water/hexadecane interface width was related to the length of the surfactant, determined using DFT, and the size of the counter-ion (Na = 1.02 Å, Cl = 1.81 Å).⁴⁷

Table S2: Calculated properties for the three surfactants studied in the LbL assembly. In the case of DTAC, three SAPMs were noted since they are statistically indistinguishable.

Property	SDBS	SDSn	DTAC
Minimum IFE (kcal/mol)	$-96.91 \pm 0.72,$	-86.15 ± 0.65	-75.84 ± 0.50
	$-96.46 \pm 0.56,$		
	-96.40 ± 0.62		
Corresponding SAPM (Å ² /surfactant)	37.8, 52.0,	64.0	64.0
	64.0		
Polarity (a.u.)	13.50	10.99	3.00
Interface Width (Å)	18.25	14.0	17.75
Surfactant Length (Å)	21.327	17.595	18.281

The relationship between IFE and SAPM is provided in Figure S2. For smaller SAPMs, steric hindrance caused surfactants to be ejected from the interface into the water phase.



Figure S2: IFE versus SAPM for the three surfactants studied. For each surfactant, a dashed horizontal line indicates the minimum IFE along the curve, indicating the most energy-favorable SAPM. We show both the average and standard error are and provide a legend.

In those cases, estimates for the IFE were based on data prior to this occurence (2-5 ns). For all stable interfaces, data was taken from 15-30 ns, giving sufficient time for the system to relax. Both SDSn and DTAC show a single minimum IFE exists at an SAPM of 64.0 Å²/surfactant. At lower SAPMs, repulsion between surfactants leads to a bulging of the interface. At higher SAPMs, holes begin to develop in the interface, leading to unfavorable interactions between the oil and water phases. An example of this behavior for the SDBS system is provided in Fig. S3. The analogous curve for SDBS, however, exhibits three statistically significant minima at SAPMs of 37.8, 52.0, and 64.0 Å²/surfactant. Here, the benzene ring in the head-group allows the surfactants to pack together more closely under higher concentrations of surfactants. While not within the scope of this study, this unique ability of SDBS to adjust to surfactant concentration has important implications for tuning charge density and, ultimately, layer thickness in the synthesis of capsules. To maintain consistency in the subsequent simulations, a SAPM of 64.0 Å²/surfactant is used for all surfactants since each surfactant exhibited a minimum at this concentration. The density profile of each surfactant system at a SAPM value of 64.0 Å²/surfactant is provided in Figs. S4-S6, with the interface widths from each system provided in Table S2.



Figure S3: Snapshots of the SDBS-mediated interface at different SAPMs: **A.** SAPM = 24 Å² (front); **B.** SAPM = 64 Å² (front); **C.** SAPM = 24 Å² (side); **D.** SAPM = 64 Å² (side). A SAPM of 24 Å² results in significant deformation of the interface that would inhibit LbL assembly. Color key provided in the top left hand corner of the figure.



Figure S4: Density profile for a water/hexadecane interface with SDBS. The surfactants lie inbetween the water and hexadecane phases, helping to bridge the two distinct liquid phases. The counter-ions accumulate in the water phase near the head-groups of the SDBS molecules. Color key as shown in the inset.

Polyelectrolyte Properties

Preliminary simulations of the polyelectrolyte solutions were used to characterize their diffusivity and radius of gyration (R_g) for comparative purposes, as well as to define the number of repeating units that was necessary to use. Due to the large conformational space occupied by the polyelectrolytes, five replicates were performed to capture deviations in the calculated properties. Starting conformations for the polyelectrolytes were determined by placing the polyelectrolyte molecule in the centre of a 150 Å³ box, performing a 1 ps minimization, running for 10 ns in an NVT ensemble, and then taking the instantaneous conformation every 2 ns starting at the 2 ns mark. We evaluated polyelectrolytes with a degree of polymerization between 4 and 32. Starting seeds were placed in the center of a simulation box ranging from 50 - 100 Å³, depending on the length of the polyelectrolyte, and packed with water at an ionic concentration of 0.15 M NaCl. Each simulation was run for a 1 ps minimization



Figure S5: Density profile for a water/hexadecane interface with SDSn. The surfactants lie inbetween the water and hexadecane phases, helping to bridge the two distinct liquid phases. The counter-ions accumulate in the water phase near the head-groups of the SDSn molecules. Color key as shown in the inset.

period, followed by a 30 ns NVT simulation. R_g was computed using the native function in LAMMPS; it is the root mean squared distance of each atom from the molecule's center of mass:

$$R_g^2 = \frac{1}{M} \sum_i m_i (r_i - r_{cm})^2 \tag{4}$$

Here, r_i is the position of each atom *i*, r_{cm} is the position of the centre of mass, and *M* is the total mass of the polyelectrolyte. Diffusivity was calculated by relating Fick's law of diffusion to the microscopic movements of the molecules through their mean squared displacement (MSD), which describes the motion of atoms in space over time.⁴⁸

$$MSD = 2dDt \tag{5}$$

Here, d is the number of dimensions, D is the diffusivity, t is the time period, and the



Figure S6: Density profile for a water/hexadecane interface with DTAC. The surfactants lie inbetween the water and hexadecane phases, helping to bridge the two distinct liquid phases. The counter-ions accumulate in the water phase near the head-groups of the DTAC molecules. Color key as shown in the inset.

MSD is given as:

$$MSD = \langle (r - r_0)^2 \rangle = \frac{1}{N} \sum_{n}^{N} \left((r_n(t) - r_n(0))^2 \right)$$
(6)

N is the number of the number of atoms and r_n denotes the atomic position of atom n. For our systems, we track the position of the center of mass of the polyelectrolyte to characterize the diffusivity. Furthermore, we use multiple time origins that combine and average samples throughout the simulation to help smooth the trajectory.⁴⁹ This is recognized as the most accurate way to determine the diffusivity. Then, Equation 6 can be rewritten as follows:

$$MSD(t) = \frac{1}{N_t} \sum_{t_0=0}^{N_t} \left((r_{com}(t_0+t) - r_{com}(t_0))^2 \right)$$
(7)

Here, N_t is the number of time origins for a given simulation length and t_0 is the time origin. Pragmatically, the diffusivity, D, can be determined by finding the slope of the plot

of MSD versus time.

In polyelectrolyte solutions, R_g has been shown to be influenced by the salt concentration and the degree of polymerization, which, in turn can affect the deposited polyelectrolyte layers.¹² Moreover, in cases where the polyelectrolytes adopt an extended conformation in solution, the polyelectrolytes tend to absorb flat to the absorbing surface, meaning that the thickness of the interface depends on the thickness of the molecule.²³ For those reasons, we calculate the R_g to relate the polyelectrolytes to layer thickness. Further, we also use the R_g to select the degree of polymerization for the polyelectrolytes. Similar studies have used a degree of polymerization ranging from 12-30.^{10,12,13} However, justification for selection of these values is typically not provided. We select our degree of polymerization by minimizing computational expense, while ensuring that the polyelectrolyte was long enough to exhibit flexibility.



Figure S7: R_g values for each polyelectrolyte as a function of degree of polymerization. Both the average and standard error are shown; legend provided in the inset.

 R_g values for each polyelectrolyte studied here are provided in Figure S7. In each case, R_g increases with the degree of polymerization. Although there is slight overlap in R_g for different polyelectrolytes due to uncertainty, in general, R_g follows the trend: PSS > PAH > PA. A noticeable increase in the error from a degree of polymerization of 12 to 16 can be explained by the increased flexibility of the polyelectrolyte in solution for the larger length. That is, at a degree of polymerization of 16, the polyelectrolytes are able to sample a larger conformational space and therefore behave more similarly to the higher molecular weight polyelectrolytes that are used in experimental systems. Thereafter, we used a degree of polymerization of 16 throughout our study.

The diffusivity of each polyelectrolyte in solution indicates the ability of the polyelectrolyte to effectively diffuse through the solution to the interface for assembly. Due to large uncertainties we observed in the calculated diffusivities, we provide estimates of these values by fitting an exponential curve to a plot of diffusivity versus degree of polymerization. This fit was found to represent the data reasonably well (Fig. S8-S10). Diffusivity values for each polyelectrolyte reveal an inverse relationship with R_g , where diffusivity increases with decreasing R_g , following the trend: PA > PAH > PSS. Table S3 shows the calculated properties for each polyelectrolyte at a degree of polymerization of 16.

Table S3: R_g and diffusivities calculated for the three polyelectrolytes studied in the LbL assembly.

Property	PSS	PAH	PA
R_{g} (Å)	9.63 ± 0.51	8.86 ± 0.33	7.14 ± 0.43
Diffusivity $(10^{-6} \text{ cm}^2/\text{s})$	2.85	3.21	3.93



Figure S8: Estimation of the diffusivity of PSS, comparing linear and exponential fits to the raw data. The exponential fit was used to estimate diffusivity as a function of polyelectrolyte length. Legend as in the inset.



Figure S9: Estimation of the diffusivity of PA, comparing linear and exponential fits with the raw data. The exponential fit was used to estimate diffusivity as a function of polyelectrolyte length. Legend as in the inset.



Figure S10: Estimation of the diffusivity of PAH, comparing linear and exponential fits with the raw data. The exponential fit was used to estimate diffusivity as a function of polyelectrolyte length. Legend as in the inset.

Detailed Methods for Dipping and Washing Simulations

To model the deposition of a polyelectrolyte bilayer at an oil-water interface stabilized by surfactant emulsifiers, we equilibrated the systems representing the individual interface system, the polyelectrolyte solutions for dipping, and the water solution for washing. Details on the setup and simulation of these systems can be found here.

System Set-up

In all cases, the oil-water interface was oriented in the xy-plane. The x- and y-directions in the simulation box are periodic. To ensure only one interface formed between the oil and water phases, we provided a vacuum at the edges of the simulation boxes in the z-direction. The faces of the box in the xy-plane are treated as two structureless, reflective walls, using a Lennard-Jones 12-6 surface potential with parameters given as the oxygen in water or the carbon in hexadecane, depending on the phase interacting with it. For all simulations involving surfactants, we used 49 surfactants, seeded initially as a 7×7 lattice. The crosssectional area (56 Å x 56 Å) was determined by combining this number of surfactants with a surface area per molecule (SAPM) of 64 Å²/surfactant, which we calculated was the most favorable IFE with respect to SAPM; see SI, Table S2, Fig. S1. In order to keep the SAPM constant throughout the simulation, we chose a constant-volume NVT ensemble. However, the vacuum at the edges of the box allowed the system to regulate the pressure appropriately and ensure no lateral extrusion occurred at the interface. A similar approach has been used in the literature for polyelectrolyte multilayer assembly.¹⁰ We verified appropriate system behavior and pressure (1 atm) in each system *via* density profiles, which exhibited bulk densities for water and hexadecane phase that corresponded well to experimental densities at ambient pressure (SI, Figs. S3-S5). Bulk densities were verified for all systems both before and after each deposition step.

Interface Set-up

We prepared the three surfactant systems by placing the 7×7 lattice of surfactants at the center of a simulation box and packing a slab of 20 Å thick hexadecane at the hydrophobic tail and a slab of 40 Å 0.15 M NaCl water solution at the hydrophilic head. Since assembly did not occur in the oil phase, the size of the hexadecane solution was selected to minimize computational expense while preserving system physics. That is, we ensured that (1) the edge of the hexadecane phase was at least 10 Å - equivalent to the cut-off for Lennard-Jones interactions - from the edge of the surfactant layer and (2) the hexadecane phase was at least twice as large as the average C1-to-C16 distance of hexadecane molecules (12.9 Å from 8 sampled molecules in a relaxed system). From Fig. S16, we find the average distance from the edge of the surfactant layer to the edge of the hexadecane phase to be 18.6 Å and resulting length of the hexadecane phase to be 29.1 Å, meeting both criteria. A size of 40 Å for the water phase was deemed to be more than sufficient based on the justification of the

size of the hexadecane phase. After a short 1 ps minimization period, the system was run in an iosothermal, NVT, ensemble for 200 ps, fixing the water phase and hydrophilic head groups of the surfactant molecules. Then, the constraints are released and the system was simulated for a further 20 ns to allow the system to relax.

Polyelectrolyte Solution Set-up

Separately, the three polyelectrolyte solutions were each packed into a slab 120 Å-thick with 10 polyelectrolyte molecules in a 0.15 M NaCl water solution. The required number of polyelectrolytes for monolayer formation was estimated by approximating the surface area of coverage per polyelectrolyte as πR_g^2 and assuming that the water content was similar to experimental observations, near 66% for PAH.⁵⁰ This estimated water content is verified by similar water contents calculated in our study (Tables 2 and 4). For the three studied polyelectrolytes, use of 10 molecules was deemed to be more than sufficient for monolayer formation. The system was relaxed through a 1 ps minimization period followed by a 20 ns NVT simulation.

Washing Solution Setup

The final 0.15 NaCl water solution used for washing was packed into a 60 Å-thick slab, allowed to minimize for 1 ps, and run in an NVT ensemble for a further 30 ns.

Dipping and Washing Procedure

For the "dipping" step, the interfacial system and polyelectrolyte solution system were combined using data files produced at the end of the individual relaxation simulations. The polyelectrolyte has the opposite charge to the surfactant layer. The bulk water phase of the interfacial system was removed, leaving a small "buffer" of water near the interface to avoid disruption of the surfactants' conformations. The z-dimension of the cut-off was determined based on a position that maintained charge-neutrality, typically in the range of 10-20 Å from the interface. Then, the polyelectrolyte solution was inserted near the boundary of the water phase. A minimization period of up to 100 ps was performed, followed by a NVT simulation of 100 ns to allow the polyelectrolytes to assemble at the interface. Data on the dynamics of the LbL assembly were gathered during this time. To balance assembly extent and computational cost, we selected 100 ns, based on a previous study that showed 100 ns to be sufficient for approximately 90% of absorption events to occur.¹⁰ This proved sufficient for juxtaposition of the kinetics and structure of each system. There is a MD study of similar length polyelectrolytes in the literature that observed assembly over 200 ns, ¹² but the large number of systems studied in this work made consideration of longer time scales too resource-intensive. The number of atoms in these systems ranged from 58,860 to 59,818 atoms.

For the "washing" step, the combined interface/polyelectrolyte solution system resulting from the end of the dipping step was combined with the water solution using data files from the end of their respective simulations. Similar to the dipping step, the polyelectrolyte solution was removed, leaving a buffer ranging in extent from 10-20 Å from the deposited polyelectrolytes, with the position chosen based on maintaining charge-neutrality in the system. Then, the water solution was inserted at the edge of the polyelectrolyte solution that remained from the previous simulation and minimized for up to 100 ps to fully combine the systems. The newly combined system was run for a further 50 ns. To ensure the combined system was given some time to relax, the first 10 ns were discarded prior to analysis. Structural data of the polyelectrolyte layer were gathered during the remaining 40 ns. The approach to equilibrium was verified through comparison of the density profiles of the bulk phases with experimental densities (Fig. S16, Fig. 8) and by ensuring that the total system energy remained constant within a tolerance of typical fluctuations (Fig. S15).

For the second dipping step and washing step, this process is repeated using an oppositely charged polyelectrolyte. In total, six different combinations of surfactants and polyelectrolytes were evaluated to juxtapose their characteristic behaviors. The number of atoms for the second dipping step ranged from 62,953 to 65,404 atoms.



Additional Ion Distribution Plots

Figure S11: Ion density profiles for SDBS/PAH throughout the LbL assembly at A. 1-4 ns, B. 10-13 ns, C. 50-53 ns, and D. 97-100 ns. Ionic concentrations were averaged over the 3 ns window. A legend is provided in each sub-figure.



Figure S12: Ion density profiles for DTAC/PSS throughout the LbL assembly at A. 1-4 ns, B. 10-13 ns, C. 50-53 ns, and D. 97-100 ns. Ionic concentrations were averaged over the 3 ns window. A legend is provided in each subfigure.



Figure S13: Ion density profiles for DTAC/PA throughout the LbL assembly at A. 1-4 ns, B. 10-13 ns, C. 50-53 ns, and D. 97-100 ns. Ionic concentrations were averaged over the 3 ns window. A legend is provided in each subfigure.

Minimum Ion Separation and Absorption Profiles

To estimate the cutoff for determining paired surfactant-polyelectrolyte pairs, we use Density Functional Theory to determine the ground-state separation between the ion groups. All simulations are performed using the B97-D3 electron density functional⁵¹ and the def2-TZVP basis set.^{52–54} All calculations were performed in implicit water solvent using the CPCM implicit solvation model.⁵⁵ Distances between ion groups were measured between the central atoms of the groups (*e.g.*, the sulfur atom of SDBS, the nitrogen atom of PAH). To minimize computational expense, the surfactant and polyelectrolyte were truncated beyond the ionic groups since these groups were non-polar and would have negligible effect on the electrostatic interactions between charged headgroups.

We assume ion groups within some value greater than these ground-state distances are considered interacting. We test two cutoff values - 5 Å and 6 Å - roughly 1 Å and 2Å greater than the ground-state distances. The results are shown in Fig. S14, comparing both cutoffs for each system. As expected, the larger cutoff leads to a higher number of interacting groups. However, the trend across the systems is the same. We ultimately select the 6 Å cutoff since it provides at least a 1 Å buffer beyond the ground-state distance for all surfactant-polyelectrolyte pairs.

Similar to the DFT simulations, distances between atoms in MD are measured between the central atom of the interacting group (e.g., the sulfur of SDSn to the nitrogen of PAH). In the case of PA, the average position of the two oxygen atoms in the head group was used. A rolling average was used to smooth out fluctuations in the data. The value from the end of the 100 ns dipping step was reported as the final number of interacting groups.

Surfactant-	Separation (Å)	Interacting Group	s Interacting Groups
Polyelectrolyte Pairing		with 6 Å cutoff	with 5 Å cutoff
SDSn/PAH	3.475	104	82
SDBS/PAH	3.456	99	69
DTAC/PSS	4.280	78	30
DTAC/PA	3.914	34	13

Table S4: Minimum separation of surfactant-polyelectrolyte ion pairs derived from Density Functional Theory simulations.



Figure S14: Number of interacting groups between the surfactants and polyelectrolytes of each system and comparing different cutoffs for interaction distance: A. SDSn/PAH with a 6 Å cutoff, B. SDSn/PAH with a 5 Å cutoff, C. SDBS/PAH with a 6 Å cutoff, D. SDBS/PAH with a 5 Å cutoff. The blue line represents the raw data, while the green line represents a smoothed average over 2000 data points. Figures continued on the next page.



Figure S14: Continued from previous page. Number of interacting groups between the surfactants and polyelectrolytes of each system and comparing different cutoffs for interaction distance: E. DTAC/PSS with a 6 Å cutoff, F. DTAC/PSS with a 5 Å cutoff, G. DTAC/PA with a 6 Å cutoff, H. DTAC/PA with a 5 Å cutoff. The blue line represents the raw data, while the green line represents a smoothed average over 2000 data points.



Energy Profiles for the First Dipping Step

Figure S15: Interaction energy profiles for each polyelectrolyte/surfactant system studied for the first monolayer deposition: **A.** SDSn/PAH, **B.** SDBS/PAH, **C.** DTAC/PA, and **D.** DTAC/PSS. A legend is provided delineating the different interaction energies evaluated.

Example Total System Energy Profile

Prior to data analysis of the polyelectrolyte layers, we ensure the system is sufficiently relaxed by (1) ensuring the bulk densities of the water and hexadecane agree with experimental values and (2) ensuring the total system energy is constant throughout the simulation. Density profiles are provided in Fig. S17 for layer 1. An example of the total system energy profile is provided in Fig. S16 for the SDBS/PAH system. This example shows that the system energy quickly relaxes to an equilibrium value within 1 ns where it remains throughout the simulation.



Figure S16: Example of the total system energy profile during the washing step of the SDBS/PAH system. An inset is provided (bottom), showing the behavior of the energy close to the start of the simulation.

Density Profiles for the First Layer



Figure S17: Density profiles for each polyelectrolyte/surfactant system studied for the first monolayer deposition: A. SDSn/PAH, B. SDBS/PAH, C. DTAC/PA, and D. DTAC/PSS. A legend is provided delineating the different species.

Table S5: Comparison of the properties of deposited polyelectrolyte layers for layer n=1.

System	Layer Thick-	Max Layer Den-	Water	Number of Polyelec-
	ness~(Å)	sity (g/cm^3)	Content	trolytes in Layer
SDSn/PAH	11.73	0.358	61.0%	5
SDBS/PAH	11.60	0.282	57.3%	4
DTAC/PSS	19.48	0.532	45.7%	4
DTAC/PA	17.37	0.311	69.7%	5

Derived Correlations for the First Polyelectrolyte Layer

For Fig. S18A:

$$\rho(t_{layer}) = \frac{N_{poly} \times MW}{10^6} (-3.928 t_{layer} + 122.14)$$
(8)

For Fig. S18B:

$$t_{layer}(E_{interact}) = R_g \left(-0.4017 \frac{E_{interact}}{N_{poly}} + 2.6639 \right)$$
(9)



Figure S18: Correlations for layer n=1 across systems, showing A. the relationship between layer density and layer thickness, and B. the relationship between layer thickness and polyelectrolyte/surfactant interaction energy. A trendline is fitted to each set of data; R^2 values are provided.

Derived Correlation for the Second Polyelectrolyte Layer

For Fig. S19:

 $t_{layer,2}(E_{interact,1}, E_{interact,2}) = R_{g,2} \left(-0.3533 \left[\frac{E_{interact,1}}{N_{poly,1}} + \frac{E_{interact,2}}{N_{poly,2}} \right] + 5.4679 - \left(\frac{t_{layer,1}}{R_{g,1}} \right) \right)$ (10)



Figure S19: Correlation for layer n=2 across systems, showing the relationship between layer thickness and polyelectrolyte/polyelectrolyte + polyelectrolyte/surfactant interaction energy. A trendline is fitted to the data; R^2 value is provided.

Energy Profiles for the Second Dipping Step



Figure S20: Interaction energy profiles for each polyelectrolyte/surfactant system studied for the second monolayer deposition: A. SDSn/PAH/PA, B. SDSn/PAH/PSS, C. SDBS/PAH/PA, D. SDBS/PAH/PSS, E. DTAC/PA/PAH, and F. DTAC/PSS/PAH. A legend is provided delineating the different interaction energies evaluated.





Figure S21: Density profiles for each polyelectrolyte/surfactant system studied for the second monolayer deposition: A. SDSn/PAH/PA, B. SDSn/PAH/PSS, C. SDBS/PAH/PA, D. SDBS/PAH/PSS, E. DTAC/PA/PAH, and F. DTAC/PSS/PAH. An unanticipated issue arose for the SDBS/PAH/PSS system (D.) where the simulation box was too small and led to a higher than expected density in the oil phase. However, this had no effect on the interface and water phase, allowing the LbL assembly to behave appropriately. A legend is provided delineating the different species.

System	Layer Thick- ness (Å)	Max Layer Den- sity (g/cm ³)	Water Content	Number of Polyelec- trolytes in Layer
SDSn/PAH/PA	12.57	0.248	76.4%	3
SDSn/PAH/PSS	21.46	0.357	71.9%	3
SDBS/PAH/PA	15.32	0.204	79.3%	3
SDBS/PAH/PSS	24.52	0.363	74.8%	3
DTAC/PA/PAH	16.59	0.256	70.5%	5
DTAC/PSS/PAH	19.64	0.181	74.0%	4

Table S6: Comparison of the properties of deposited polyelectrolyte layers for layer n=2.

Second Layer Structure



Figure S22: Orientation of layer n=2 in relation to the interface for each system studied. A legend is provided to identify the different systems.



Figure S23: Void fraction at the interface for each system after the LbL assembly of layer n=2, showing the distribution of void fraction in each system. A legend is provided for each sub-figure.

References

- Bresme, F.; Chacón, E.; Tarazona, P.; Tay, K. Intrinsic Structure of Hydrophobic Surfaces: The Oil-Water Interface. *Physical review letters* 2008, 101, 056102.
- (2) Xiao, H. Y.; Zhen, Z.; Sun, H. Q.; Cao, X. L.; Li, Z. Q.; Song, X. W.; Cui, X. H.; Liu, X. H. Molecular Dynamics Study of the Water/n-Alkane Interface. *Science China Chemistry* 2010, 53, 945–949.
- (3) Wick, C. D.; Chang, T.-M.; Slocum, J. A.; Cummings, O. T. Computational Investigation of the n-Alkane/Water Interface with Many-Body Potentials: The Effect of Chain Length and Ion Distributions. *The Journal of Physical Chemistry C* 2012, 116, 783–790.
- (4) Jang, S. S.; Lin, S.-T.; Maiti, P. K.; Blanco, M.; Goddard, W. A.; Shuler, P.; Tang, Y. Molecular Dynamics Study of a Surfactant-Mediated Decane-Water Interface: Effect of Molecular Architecture of Alkyl Benzene Sulfonate. *The Journal of Physical Chemistry B* 2004, 108, 12130–12140.
- (5) Xu, J.; Zhang, Y.; Chen, H.; Wang, P.; Xie, Z.; Yao, Y.; Yan, Y.; Zhang, J. Effect of Surfactant Headgroups on the Oil/Water Interface: An Interfacial Tension Measurement and Simulation Study. *Journal of Molecular Structure* **2013**, *1052*, 50–56.
- (6) Munusamy, E.; Luft, C. M.; Pemberton, J. E.; Schwartz, S. D. Unraveling the Differential Aggregation of Anionic and Nonionic Monorhamnolipids at Air-Water and Oil-Water Interfaces: A Classical Molecular Dynamics Simulation Study. *The Journal of Physical Chemistry B* 2018, *122*, 6403–6416.
- (7) Smiatek, J.; Holm, C. From the Atomistic to the Macromolecular Scale: Distinct Simulation Approaches for Polyelectrolyte Solutions. *Handbook of Materials Modeling, eds Andreoni W., Yip S., editors.(Heidelberg* **2018**, 1–15.

- (8) Panchagnula, V.; Jeon, J.; Dobrynin, A. V. Molecular Dynamics Simulations of Electrostatic Layer-by-Layer Self-Assembly. *Physical review letters* 2004, 93, 037801.
- (9) Patel, P. A.; Jeon, J.; Mather, P. T.; Dobrynin, A. V. Molecular Dynamics Simulations of Layer-by-Layer Assembly of Polyelectrolytes at Charged Surfaces: Effects of Chain Degree of Polymerization and Fraction of Charged Monomers. *Langmuir* 2005, 21, 6113–6122.
- (10) Qiao, B.; Sega, M.; Holm, C. An Atomistic Study of a Poly (Styrene Sulfonate)/Poly (Diallyldimethylammonium) Bilayer: The Role of Surface Properties and Charge Reversal. *Physical Chemistry Chemical Physics* 2011, 13, 16336–16342.
- (11) Micciulla, S.; Sánchez, P. A.; Smiatek, J.; Qiao, B.; Sega, M.; Laschewsky, A.; Holm, C.; Von Klitzing, R. Layer-by-Layer Formation of Oligoelectrolyte Multilayers: A Combined Experimental and Computational Study. *Soft Materials* **2014**, *12*, S14–S21.
- (12) Sánchez, P. A.; Vögele, M.; Smiatek, J.; Qiao, B.; Sega, M.; Holm, C. Atomistic Simulation of PDADMAC/PSS Oligoelectrolyte Multilayers: Overall Comparison of Triand Tetra-Layer Systems. *Soft matter* **2019**, *15*, 9437–9451.
- (13) Sánchez, P. A.; Vögele, M.; Smiatek, J.; Qiao, B.; Sega, M.; Holm, C. PDADMAC/PSS Oligoelectrolyte Multilayers: Internal Structure and Hydration Properties at Early Growth Stages from Atomistic Simulations. *Molecules* **2020**, *25*, 1848.
- (14) Shchukina, E.; Graham, M.; Zheng, Z.; Shchukin, D. Nanoencapsulation of Phase Change Materials for Advanced Thermal Energy Storage Systems. *Chemical Society Reviews* 2018, 47, 4156–4175.
- (15) Sukhorukov, G. B.; Donath, E.; Lichtenfeld, H.; Knippel, E.; Knippel, M.; Budde, A.;
 Möhwald, H. Layer-by-Layer Self Assembly of Polyelectrolytes on Colloidal Particles.
 Colloids and Surfaces A: physicochemical and engineering aspects 1998, 137, 253–266.

- (16) Richardson, J. J.; Cui, J.; Bjoörnmalm, M.; Braunger, J. A.; Ejima, H.; Caruso, F.
 Innovation in Layer-by-Layer Assembly. *Chemical Reviews* 2016, *116*, 14828–14867.
- (17) Bédard, M. F.; Munoz-Javier, A.; Mueller, R.; Del Pino, P.; Fery, A.; Parak, W. J.; Skirtach, A. G.; Sukhorukov, G. B. On the Mechanical Stability of Polymeric Microcontainers Functionalized with Nanoparticles. *Soft Matter* **2009**, *5*, 148–155.
- (18) Grigoriev, D.; Bukreeva, T.; Möhwald, H.; Shchukin, D. New Method for Fabrication of Loaded Micro- and Nanocontainers: Emulsion Encapsulation by Polyelectrolyte Layerby-Layer Deposition on the Liquid Core. *Langmuir* 2008, 24, 999–1004.
- (19) Borges, J.; Mano, J. F. Molecular Interactions Driving the Layer-by-Layer Assembly of Multilayers. *Chemical reviews* **2014**, *114*, 8883–8942.
- (20) Szczepanowicz, K.; Dronka-Góra, D.; Para, G.; Warszyński, P. Encapsulation of Liquid Cores by Layer-by-Layer Adsorption of Polyelectrolytes. *Journal of microencapsulation* 2010, 27, 198–204.
- (21) Yi, Q.; Sukhorokov, G. B.; Ma, J.; Yang, X.; Gu, Z. Encapsulation of Phase Change Materials using Layer-by-Layer Assembled Polyelectrolytes. *International Journal of Polymer Science* **2015**, 2015, 756237.
- (22) Seitz, S.; Ajiro, H. Self-Assembling Weak Polyelectrolytes for the Layer-by-Layer Encapsulation of Paraffin-Type Phase Change Material Icosane. *Solar Energy Materials* and Solar Cells **2019**, 190, 57–64.
- (23) Guzey, D.; McClements, D. J. Formation, Stability and Properties of Multilayer Emulsions for Application in the Food Industry. Advances in colloid and interface science 2006, 128, 227–248.
- (24) Zhao, S.; Caruso, F.; Dahne, L.; Decher, G.; De Geest, B. G.; Fan, J.; Feliu, N.;Gogotsi, Y.; Hammond, P. T.; Hersam, M. C.; Khademhosseini, A.; Kotov, N.; Lepo-

ratti, S.; Li, Y.; Lisdat, F.; Liz-Marzán, L. M.; Moya, S.; Mulvaney, P.; Rogach, A. L.; Roy, S.; Shchukin, D. G.; Skirtach, A. G.; Stevens, M. M.; Sukhorukov, G. B.; Weiss, P. S.; Yue, X.; Zhu, D.; Parak, W. J. The Future of Layer-by-Layer Assembly: A Tribute to ACS Nano Associate Editor Helmuth Möhwald. *ACS nano* **2019**, *13*, 6151–6169.

- (25) He, X.; Guvench, O.; MacKerell Jr, A. D.; Klein, M. L. Atomistic Simulation Study of Linear Alkylbenzene Sulfonates at the Water/Air Interface. *The Journal of Physical Chemistry B* 2010, 114, 9787–9794.
- (26) Sunda, A. P.; Venkatnathan, A. Molecular Dynamics Simulations of Triflic Acid and Triflate Ion/Water Mixtures: A Proton Conducting Electrolytic Component in Fuel Cells. J. Comput. Chem. 2011, 32, 3319–3328.
- (27) Jorgensen, W. L.; Tirado-Rives, J. Potential Energy Functions for Atomic-Level Simulations of Water and Organic and Biomolecular Systems. *Proceedings of the National Academy of Sciences* 2005, 102, 6665–6670.
- (28) Dodda, L. S.; Vilseck, J. Z.; Tirado-Rives, J.; Jorgensen, W. L. 1.14* CM1A-LBCC: Localized Bond-Charge Corrected CM1A Charges for Condensed-Phase Simulations. *The Journal of Physical Chemistry B* 2017, 121, 3864–3870.
- (29) Dodda, L. S.; Cabeza de Vaca, I.; Tirado-Rives, J.; Jorgensen, W. L. LigParGen Web Server: An Automatic OPLS-AA Parameter Generator for Organic Ligands. *Nucleic acids research* 2017, 45, W331–W336.
- (30) Klauda, J. B.; Brooks, B. R.; MacKerell, A. D.; Venable, R. M.; Pastor, R. W. An ab initio study on the torsional surface of alkanes and its effect on molecular simulations of alkanes and a DPPC bilayer. *The journal of physical chemistry B* 2005, *109*, 5300–5311.
- (31) Qiao, B.; Cerda, J. J.; Holm, C. Poly (styrenesulfonate)- Poly (diallyldimethylammo-

nium) Mixtures: Toward the Understanding of Polyelectrolyte Complexes and Multilayers via Atomistic Simulations. *Macromolecules* **2010**, *43*, 7828–7838.

- (32) Hockney, R.; Eastwood, J. The Particle-Mesh Force Calculation. Computer Simulation Using Particles, Adam Hilger, Bristol and New York, NY, USA 1989, 120–165.
- (33) Luty, B. A.; Davis, M. E.; Tironi, I. G.; Van Gunsteren, W. F. A comparison of particleparticle, particle-mesh and Ewald methods for calculating electrostatic interactions in periodic molecular systems. *Molecular Simulation* **1994**, *14*, 11–20.
- (34) Pollock, E.; Glosli, J. Comments on P3M, FMM, and the Ewald method for large periodic Coulombic systems. *Computer Physics Communications* **1996**, *95*, 93–110.
- (35) Moore, S. G.; Crozier, P. S. Extension and evaluation of the multilevel summation method for fast long-range electrostatics calculations. *The Journal of chemical physics* 2014, 140, 06B619_1.
- (36) Thompson, D. L. Modern methods for multidimensional dynamics computations in chemistry; World Scientific, 1998.
- (37) Guzman, E.; Rubio, R. G.; Ortega, F. A closer physico-chemical look to the Layerby-Layer electrostatic self-assembly of polyelectrolyte multilayers. Advances in Colloid and Interface Science 2020, 282, 102197.
- (38) Klitzing, R. v. Internal Structure of Polyelectrolyte Multilayer Assemblies. Physical Chemistry Chemical Physics 2006, 8, 5012–5033.
- (39) Dubas, S. T.; Schlenoff, J. B. Factors controlling the growth of polyelectrolyte multilayers. *Macromolecules* **1999**, *32*, 8153–8160.
- (40) Cerda, J. J.; Qiao, B.; Holm, C. Understanding polyelectrolyte multilayers: an open challenge for simulations. *Soft Matter* 2009, 5, 4412–4425.

- (41) Tang, K.; Besseling, N. A. Formation of Polyelectrolyte Multilayers: Ionic Strengths and Growth Regimes. Soft Matter 2016, 12, 1032–1040.
- (42) Micciulla, S.; Dodoo, S.; Chevigny, C.; Laschewsky, A.; von Klitzing, R. Short Versus Long Chain Polyelectrolyte Multilayers: A Direct Comparison of Self-Assembly and Structural Properties. *Physical Chemistry Chemical Physics* **2014**, *16*, 21988–21998.
- (43) Elzbieciak, M.; Kolasinska, M.; Warszynski, P. Characteristics of polyelectrolyte multilayers: The effect of polyion charge on thickness and wetting properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2008**, *321*, 258–261.
- (44) Dang, L. X.; Chang, T.-M. Molecular Dynamics Study of Water Clusters, Liquid, and Liquid-Vapor Interface of Water with Many-Body Potentials. *The Journal of chemical physics* **1997**, *106*, 8149–8159.
- (45) Mitrinović, D. M.; Tikhonov, A. M.; Li, M.; Huang, Z.; Schlossman, M. L. Noncapillary-Wave Structure at the Water-Alkane Interface. *Physical review letters* 2000, 85, 582.
- (46) Chipot, C.; Pohorille, A. Free Energy Calculations. Springer series in chemical physics 2007, 86, 159–184.
- (47) Barbalace, K. Periodic Table of Elements—Sorted by Ionic Radius. Environmental-Chemistry.com. 1995-2008. 2008.
- (48) Wang, J.; Hou, T. Application of Molecular Dynamics Simulations in Molecular Property Prediction II: Diffusion Coefficient. *Journal of computational chemistry* 2011, 32, 3505–3519.
- (49) Haile, J. M.; Johnston, I.; Mallinckrodt, A. J.; McKay, S. Molecular Dynamics Simulation: Elementary Methods. *Computers in Physics* **1993**, *7*, 625–625.
- (50) Iturri Ramos, J. J.; Stahl, S.; Richter, R. P.; Moya, S. E. Water Content and Buildup of Poly (Diallyldimethylammonium Chloride)/Poly (Sodium 4-styrenesulfonate) and Poly

(Allylamine Hydrochloride)/Poly (Sodium 4-styrenesulfonate) Polyelectrolyte Multilayers Studied by an In Situ Combination of a Quartz Crystal Microbalance with Dissipation Monitoring and Spectroscopic Ellipsometry. *Macromolecules* **2010**, *43*, 9063–9070.

- (51) Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *Journal of computational chemistry* **2006**, *27*, 1787–1799.
- (52) Schäfer, A.; Horn, H.; Ahlrichs, R. Fully optimized contracted Gaussian basis sets for atoms Li to Kr. The Journal of Chemical Physics 1992, 97, 2571–2577.
- (53) Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. RI-MP2: optimized auxiliary basis sets and demonstration of efficiency. *Chemical physics letters* **1998**, *294*, 143–152.
- (54) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Physical Chemistry Chemical Physics* 2005, 7, 3297–3305.
- (55) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *Journal of computational chemistry* 2003, 24, 669–681.