Molecular insights into the physics of poly(amidoamine)-dendrimer-based supercapacitors

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Increasing the energy density in electric double-layer capacitors (EDLCs), also known as supercapacitors, remains an active area of research. Specifically, there is a need to design and discover electrode and electrolyte materials with enhanced electrochemical storage capacity. Here, using fully atomistic molecular dynamics (MD) simulations, we investigate the performance of hyper-branched ‘poly(amidoamine) (PAMAM)’ dendrimer as an electrolyte and an electrode coating material in a graphene-based supercapacitor. We investigate the performance of the capacitor using two different modeling approaches, namely the constant charge method (CCM) and the constant potential method (CPM). These simulations facilitated the direct calculation of the charge density, electrostatic potential and field, and hence the differential capacitance. We found that the presence of the dendrimer in the electrodes and the electrolyte increased the capacitance by about 65.25% and 99.15% respectively, compared to the bare graphene electrode-based aqueous EDLCs. Further analysis revealed that these increases were due to the enhanced electrostatic screening and reorganization of the double layer structure of the dendrimer based electrolyte.

I. INTRODUCTION

Improving the energy densities of electric double layer capacitor (EDLC), also known as supercapacitor based energy devices, is of great practical interest [1–3], as these devices have higher power densities compared to conventional energy storage devices such as fuel cells, electrochemical batteries and even dry/moist electrolytic capacitors. The improved energy density, in turn, would increase the commercial viability of EDLCs, thus spurring large scale, mainstream adoption [4]. To this end, recent work has focused on engineering advanced electrode and electrolytes materials. Porous materials, with high specific surface areas and good electronic conductivity, have traditionally been used as electrode materials in these devices [5–6]. Room temperature ionic liquids (RTILs) are typically chosen as the electrolyte, owing to their superior electrochemical properties, including high operating voltage windows and non-flammability, compared to aqueous and organic based electrolytes [7]. Yet, despite progress over the years in electrode and electrolyte optimization, further advances demand direct knowledge of the interfacial structure and dynamics, and design principles for unique nanoscale physics therein.

In this work, we consider dendrimers: hyper-branched synthetic polymers as intriguing potential candidates as electrolytes in these devices [8]. Dendrimers have well-defined molecular structure, are flexible in size and shape, and are responsive to controllable stimuli such as pH [9–11]. They are also known to undergo structural deformations at interfaces [12–13] and their charge densities are comparable to that of ionic liquids [14]. Moreover, the pore size of a typical microporous electrode ranges from 0.5 to 5 nm, which matches well with the sizes of poly
amidoamine (PAMAM) dendrimers, which vary from 0.6 nm for generation 0 (G0) to 6 nm (G10). Experiments and theory have shown that the capacitance in EDLCs is significantly enhanced when the pore size of the electrode material matches the size of the electrolyte ions [16, 17]. Interfacial adsorption of dendrimers on electrodes dynamically exposes their charge groups to the electrolyte, which facilitates the formation of unique electric double layer structures. This has been demonstrated by experiments by Guo et al. [18], who reported that hyper-branched polymers, like dendrimers, exhibit very low losses in the dielectric response function, even at high operational frequencies (∼1 MHz). Freire et al. also showed that the presence of dendrimer can screen repulsive contacts between different counter ion molecules and favored ionic conductivity [19]. These interesting properties of dendrimers make them potentially excellent candidates as electrolytes in EDLCs, however, a thorough microscopic examination of the interfacial behaviour, and the resulting effect on electrochemical performance, have not yet been elaborated.

Computer simulations employing molecular dynamics (MD) based quantum mechanically derived accurate potentials (force-fields) is a common tool for elucidating the microscopic nature of interfacial systems, and would be well suited for exploring the role of dendrimers in modulating the EDL structure and ultimately the performance of EDLCs. The key here is an accurate description of the interaction parameters, coarse-grained simulations revealed significant force-field dependence in the binding strength of dendrimers to graphene electrodes, as the system’s pH [11] is varied [20]. To more clearly understand the nature of the interaction of the dendrimer-graphene composites requires us to go beyond coarse-grained force-fields and perform fully atomistic simulations. Yet, fully atomistic simulations of dendrimers at interfaces, where the dendrimer is being used as an electrolyte, are relatively rare to the best of our knowledge. In contrast, there have been several experimental [21, 22] and simulation studies [23, 24] that reported carbon-based electrode materials and studied the capacitance values with ionic liquids being the electrolytes [24]. For example, Triguero et al. [21] reported that the dendrimer functionalised carbon nanotubes can improve the nanotube’s performance as an electrode. Another study by Chandra et al. [20] reported that dendrimer functionalised nanoparticles coated on an electrode surface can enhance the surface area available to the electrolyte atoms, thereby achieving efficient charge transfer and low contact resistances. In another experimental work, Liu et al. [27] used dendrimer functionalized graphene-oxide sheet as a coating on the sulfur electrode of a Li-S battery and achieved long cycle life (up to 500 cycles). When considering common electrolytes in EDLCs, various computational studies on RTILs have been reported, including work by Yeh et al. [28] which discussed the effect of periodic boundary conditions (BCs) in EDLC simulations.

Recently, we used atomistic MD simulations to study the structural deformations [13] and the free-energy of the binding [29] of PAMAM dendrimers at a charge neutral graphene/water interface, as a function of the protonation state of the dendrimer. We found that the van der Waals interactions play a pivotal role in driving dendrimer adsorption. We also found that moderately charged (neutral pH) dendrimers achieve maximum surface wetting as compared to the non-protonated (high pH) and fully protonated (low pH) dendrimers. We showed that lower generation dendrimers tended to deform and form flat, disk-like architectures, with good surface accessibility, at the graphene/water interface [13]. These observations suggest that the lower generation PAMAM at neutral pH condition as an ideal choice for achieving maximum charge densities in PAMAM-based supercapacitors. Therefore, in this work, we considered a G2 PAMAM dendrimer at neutral pH, and eludiate the electrochemical performance in graphene/water based EDLCs. Beyond accurate simulations of dendrimer based systems, we are also concerned with modelling biased nanoscale interfaces, as a means of probing electrochemical effects in EDLCs. Here, there are two main computation methods commonly employed for doing this: 1) the constant charge method (CCM) – the charges of the electrode atoms are fixed, and 2) the constant potential method (CPM) – a grand canonical statistical mechanical ensemble is defined by means of a fictitious bath that exchanges electrons with the electrodes to maintain a constant electrode potential (the number of electrons and chemical potential are conjugate pairs) [30, 31]. The CPM approach is generally preferred as it enables simulations that are more directly comparable to experiments. However, it is somewhat restricted in its applicability due to significant additional computational demands. To this end, Wang et al. [32] compared both approaches for a LiClO4-acetonitrile/graphite EDLC and showed that both the approaches lead to similar ion and solvent density profiles for voltages less than 2V. Comparing the performance of both approaches for a more complicated electrode/electrolyte morphology is one of the aims of this study. Moreover, to address the computational challenges, Reed and coworkers et al. [32] have developed an efficient approach for simulating cells within CPM [30] in the LAMMPS simulation engine, which we employ here.

The manuscript is organized as follows. In section II, we provide the model building and the simulation methodologies adopted in this work. In section III, we present our results on the electrostatic potential, charge density profiles and the capacitance values, obtained from the CCM and the CPM approaches. Finally, in section IV, we summarize our findings and conclude with the key insights from our study to provide future research directions.
We aim to understand how the presence of the dendrimer modifies the electrochemical charge storage and the capacitance values of the aqueous supercapacitor with a graphene electrode. Hence, we performed the simulations for a system with two bare graphene electrode encapsulating a box of TIP3P waters, denoted BAREGP, as a control. To test the potential of using the dendrimer as an electrolyte and as an electrode, two additional systems, namely G2PEL and GPDEN respectively, were considered. G2PEL comprised a G2 PAMAM dendrimer at neutral pH, immersed in a pre-equilibrated box of 10,118 TIP3P water molecules and placed between two graphene electrodes. We neutralize the system by adding 16 Cl\(^-\) counter ions (the charge of the G2 PAMAM at neutral pH is +16\(\epsilon\)). For the GPDEN system, we covalently grafted the G2 dendrimer onto the graphene electrode, using a "top-binding and grafting-to" approach, as detailed in our previous work [41]. Here, a dendrimer grafted graphene was used as a positive electrode while a pristine graphene was used as a negative electrode. 10,775 TIP3P water molecules were added in between the two electrodes.

### II. MODEL AND SIMULATION DETAILS

In this work we focus on an aqueous supercapacitor simulation cell based on water/water+dendrimer electrolyte and graphene/dendrimer coated graphene electrode (Table 1). The initial structure of the PAMAM dendrimer was built using the Dendrimer Builder Toolkit (DBT) [15], while VMD [33] was used to build the graphene sheet. The aromatic carbon atoms of graphene were described using the AMBER FF10 force field (atom-type CA), as in our earlier works [34,35], which we showed captures the water-graphene interactions accurately. Inter-molecular interactions involving dendrimer atoms were described by GAFF force field [36], the water molecules were modelled using TIP3P [37,38] water model, and the Joung-Cheatham [39] parameters were used to model the Cl\(^-\) counter ions. Using the xLEaP module of AMBER 14 [40], the equilibrated electrolyte solution was placed in-between two graphene sheets with dimensions of 32.63 Å × 62.50 Å and separated by 150 Å.

| System | Positive Electrode (+15\(\epsilon\)) | Negative Electrode (-15\(\epsilon\)) | Electrolyte |
|--------|-----------------------------------|-----------------------------------|-------------|
| BAREGP | Graphene                          | Graphene                          | H\(_2\)O     |
| G2PEL  | Graphene                          | Graphene                          | H\(_2\)O + G2 PAMAM + Cl\(^-\) ions |
| GPDEN  | Dendrimer coated graphene         | Graphene                          | H\(_2\)O     |

#### A. Constant Charge Method (CCM)

We employed two different computational schemes for simulating applied bias in our systems. First, we used the PMEMD module of the AMBER14 [40] MD simulation suite to perform supercapacitor simulations with the CCM method. As mentioned above, in the GPDEN case, the net charge of the dendrimer coated graphene electrode was +15\(\epsilon\), where charge of grafted dendrimer atom was adapted from Gosika et al. [41]. Thus, a charge of 0.01875\(\epsilon\) was distributed on each of the carbon atom comprising the graphene electrode. In these studies, we minimized spurious electrode-electrostatic interactions by inserting large 15 nm vacuum slab buffer in z-direction between the simulation cell, as shown in Fig. 1.

For the BAREGP and G2PEL cases, we performed two sets of simulations, where the electrodes are i) discharged (charge on every electrode atom is set to 0\(\epsilon\)) ii) oppositely charged (charge on each electrode atom was set to 0.01875\(\epsilon\), to be consistent with the GPDEN system). We initiated each simulation with 1000 steps of the steepest descent energy minimization, followed by further 1000 steps of conjugate gradient minimization, to remove the initial bad contacts. We then gradually heated the system from 0 K to 300 K using a Langevin thermostat with random friction collision frequency 1 ps\(^{-1}\) in the constant temperature-constant volume (canonical or NVT) ensemble for 5 ns. During heating, we restrained the solute (electrode) atoms with a harmonic spring, with a force constant of 20 kcal mol\(^{-1}\) Å\(^{-2}\). Equilibrium MD simulations were then performed under the constant pressure-constant temperature (isothermal-isobaric or NPT) ensemble, with a weaker restraint (10 kcal mol\(^{-1}\) Å\(^{-2}\)) on graphene atoms (no restraint on dendrimer).
The Langevin thermostat and Berendsen barostat were used to control the temperature at 300 K and pressure at 1 bar, respectively, with a collision frequency of 1 ps\(^{-1}\) and pressure coupling constant of 0.5 ps. Finally, we performed 50 ns long NVT production dynamics at 300 K, using a Langevin thermostat. The electrostatic interactions were evaluated using the particle mesh Ewald (PME) method \[42\] with a real space cut off of 9 Å and a reciprocal space convergence tolerance of 5 \times 10^{-4}. The SHAKE algorithm \[43\] with a tolerance of 0.005 Å was used to constrain all bonds involving hydrogen atoms, as well as the H-O-H angle in water, to their equilibrium positions. This allowed us to use larger integration time steps of 2 fs. The trajectory from the final 10 ns of the MD simulations was used for statistical data analysis.

We obtained the electrostatic potential across the cell by solving the 2D Poisson’s equation with \(xy\)-symmetry. We set the field to be zero at both the ends of the box (i.e., Neumann BC) \[44\], and set the potential to be zero at the middle of the simulation cell. With these two BCs, one can formulate the expression for the potential as,

\[
\psi(z) = -\frac{1}{\varepsilon_0} \int_{-D}^{D} dz' \int_{-D}^{D} \rho(z'') dz'' - \psi(0). \quad (1)
\]

where, \(\rho(z)\) is the charge density along the sheet’s normal and \(\psi(0)\) is the potential at the mid-point of the simulation box. The positive and negative electrodes are located at \(-D\) and \(+D\), respectively. Once the potential profiles were obtained, one can define the capacitance as: \[45\]

\[
C_s = \frac{|\sigma_s|}{\Delta \Delta \psi_{cell}}, \quad C_M = C_s \frac{A_0}{2M}. \quad (2)
\]

Here,

\[
\Delta \Delta \psi_{cell} = \Delta \psi_{cell}(charged) - \Delta \psi_{cell}(discharged) \quad (3)
\]

and,

\[
\Delta \psi_{cell} = \psi(z = -D) - \psi(z = +D)
\]

where \(\sigma_s\), \(A_0\) and \(M\) are the charge density, area, and mass of the electrode, respectively; \(C_s\) is the area-specific capacitance with units of \(\mu\text{F cm}^{-2}\) and \(C_M\) is the mass-specific capacitance with units of \(\text{F g}^{-1}\) \[2\].

**B. Constant Potential Method (CPM)**

The CCM approach neglects the charge fluctuations on the electrode induced by local density fluctuations in the electrolyte solution. To explicitly take into account such physics, we also considered the CPM method which allows the charges on the electrode atoms to vary while maintaining a constant potential. We follow the implementation of the CPM method developed by Reed \textit{et al.} and later further improved by Gingrich \textit{et al.} \[16\], based on earlier work of Siepmann \textit{et al.} \[47\]. Here, the electric potential (\(\psi_i\)) on each electrode atom is constrained at each simulation step to be equal to a preset applied external potential \(V_{ext}\), which is held constant. The charge on each electrode atom \(q_i\) (where \(i\) is the atom index of the electrode), is calculated self-consistently to satisfy the constraint condition: \[42\]

\[
\psi_i = \frac{\partial U}{\partial q_i} = V_{ext} \quad (4)
\]

where \(U\) is the total coulomb energy of the system. The starting structures for the CPM simulations were the equilibrated structures of the CCM simulations (discharge cases). All CPM simulations were performed using the LAMMPS \[30\] MD package. 20 ns NVT production simulations were performed using Nosé-Hoover thermostat at 300 K with a relaxation time of 100 fs, which was long enough to achieve the total charge equilibration of the electrodes. The cutoff used for the non-bonded interactions was 9 Å. The long-range electrostatic interactions were calculated by the particle-particle-particle-mesh Ewald summation method with a tolerance of \(10^{-4}\). Instead of using 2d-periodic Ewald sums, we have used 3d-periodic Ewald sums with shape corrections in this work to enhance the calculation speed, with a volume factor set to 3 \[28\]. Parameter of Gaussian charge distribution for electrode atom was 19.79 nm\(^{-1}\) \[42\]. All the result are reported here are the last 10 ns statistical averages.

The electrodes are maintained at a constant potential \(\pm V_{ext}\) using the constant potential method (conp) module in LAMMPS \[30\]. To calculate the differential capacitance, we first calculated the averaged equilibrated charge density of the electrodes (which is a direct output from the CPM simulations) and applied the following equation:

\[
C_{diff} = \langle \sigma \rangle \frac{d}{dV_{ext}} \quad (5)
\]

where, \(\langle \sigma \rangle\) is the equilibrated average surface charge density on the electrode. The mass-specific capacitance can be calculated from Eq. \(2\). Note that, one can employ constant pH method \[48\] \[49\] also to simulate dendrimer and dendrimer coated graphene electrodes to investigate their behaviour. However, constant pH method is best suited for systems where protonation state of the system is not very well known and has been used for some protein simulations. The situation is different in case of dendrimer where titration experiments give the protonation state of dendrimer as a function of pH very accurately \[50\]. That is why in the literature dendrimer simulations are done taking into account the protonation states corresponding to a pH as has been done in the present study. It is worth mentioning here that constant pH simulation for dendrimer also \[51\] has shown to produce similar results like
pH dependent swelling using the same protocol used in our work. But constant pH calculations take significantly large computational cost.

III. RESULTS AND DISCUSSIONS

A. CCM method

1. EDL structure

The structure of the electrode/electrolyte interface is an important property that gauges the performance of a supercapacitor. Hence, to understand the nature of the EDL structure and the distribution of the positive and the negatively charged entities of the system, we calculated their number densities across the cell. In Fig. 2, we plot the normalized density profiles ($\rho_N(z)$) of the relevant charged species of the system, defined as,

$$\rho_N(z)_{\text{species}} = \frac{1}{N_{\text{species}}} \frac{n(z, z + dz)}{L_x L_y dz},$$

where $N_{\text{species}}$ is the total number of a given species in the system, and $n(z, z + dz)$ is the number of the atoms of the species located between $z$ and $z + dz$. $L_x$ and $L_y$ are the box dimensions in the $x$ and $y$ directions, respectively. By definition $\int_{-D}^{D} \rho_N(z) L_x L_y dz = 1$.

In the case of BAREGP and GPDEN, there are no mobile anions or cations that would adsorb at the electrode’s interface, thus electrostatic screening of the charged interface is only achieved by reorientation of the dipole of the water molecules. This fact, coupled with the nature of the electrode charge distribution leads to notable changes in the interfacial water structure. For BAREGP, we find in (a) and (b), significant densification of the 1st layer waters compared to the bulk. While density fluctuations are commonly observed in fluids next to a hard wall (due to the reduction in dimensionality), we find that the 1st shell water density and layer thickness on the left (positively charged) BAREGP electrode is larger than on the right (negatively charged), reflecting the directionality of the hydrogen bonding in water, which competes with the electrostatic screening effect that requires the water dipole point into the negative electrode (i.e., both hydrogens closer to the surface). The net effect is more disordered 1st layer at the negative electrode.

Turning our attention to the systems with the dendrimer, we find that the 1st layer water structure at the positively charged electrode of GPDEN (Fig. 2 (e)) differs significantly from that of BAREGP and G2PEL (Fig. 2 (a)). This reflects the inhomogenous charge distribution in GPDEN, where we have the dendrimer coated graphene as the positively charged electrode (Fig. 2 (e)). In GPDEN, the water molecules can penetrate deeper into to the electrode (i.e., dendrimer), so that the effective surface charge of the positively charged electrode is well compensated. By contrast, in the G2PEL system, the adsorption of the positively charged dendrimer at the right electrode (negatively charged) leads to best possible screening of the electrode’s charge. (Fig. 2 (d)). Similarly, the mobile Cl$^-$ anions compensate the positive charge of the left electrode (Fig. 2 (c)). Overall these microscopic EDL reorganization effects have a significant impact on the cell capacitance, as will be discussed in section III-B.

2. Potential profiles and capacitance values

The total charge densities of the systems at the left and the right electrodes are presented in Fig. 3 (a) and (b), respectively, and encapsulates the results of the EDL structure in section III-A. For example, at the left electrode, the charge density for GPDEN is significantly less than BAREGP (Fig. 3 (a)), due to the better penetration of the water molecules in to the electrode in the latter case. Similarly, we find that the charge density of G2PEL at the right electrode is less than that of BAREGP and
we found a modulation of the potential as evidenced by the reduced slope in the G2PEL system. Nevertheless, we do find a modulation of the potential difference across the electrodes for G2PEL and GPDEN cases for CCM case. Presumably, the increased screening of the dendrimer as an electrolyte and electrode reduces the potential difference across the simulation cell.

Further, we obtained the electrostatic potential (\(\psi\)) using, integrating the charge density across each sub-box, as illustrated in Fig. 3. (c) sub-boxes. We consider a virtual parallel plate capacitor whose electrodes are now represented by these left and right regions, indicated by the two parallel line separators in Fig. 3.

To test this hypothesis and quantify the effect, we calculated the cell capacitance using Eq. 2 for all three systems and tabulated the values in Table II. This required us to perform both charged and discharged simulations in order compute the potential difference across the cell (Eq. 3). While we performed these two sets of simulations for BAREGP and G2PEL, for GPDEN case we performed only charged simulations, since we considered the discharged GPDEN case to be the same as the BAREGP system.

We found significantly higher capacitance in the two systems with the dendrimer, compared to BAREGP, with an increase of 65.25% and 99.15% for the dendrimer in electrode (GPDEN) and electrolyte (G2PEL) systems, respectively. To further understand the molecular origins of this effect, we divided our simulation cells into left (\(z = -100\) Å to \(z = -25\) Å) and right (\(z = 25\) Å to \(z = 100\) Å) sub-boxes. We consider a virtual parallel plate capacitor whose electrodes are now represented by these left and right regions, indicated by the two parallel line separators in Fig. 3.

| System  | \(\Delta \psi_{cell}(ch)(V)\) | \(\Delta \psi_{cell}(dis)(V)\) | \(C_s\) (\(\mu F/cm\)) | \(C_M\) (\(\mu F/cm\)) |
|---------|--------------------------|--------------------------|----------------------|----------------------|
| BAREGP  | 0.12                     | 9.53                     | 1.18                 | 6.58                 |
| GPDEN   | 0.12                     | 5.86                     | 1.95                 | 11.03                |
| G2PEL   | 0.04                     | 4.75                     | 2.35                 | 13.14                |

The surface charge density \(\sigma_L\) was then calculated by integrating the charge density across each sub-box, as below:

\[
\sigma_L(z) = \int_{-25}^{-55} \rho(z)dz, \quad z \in [-55, -25] \tag{7}
\]

\[
\sigma_R(z) = \int_{25}^{55} \rho(z)dz, \quad z \in [25, 55] \tag{8}
\]

This allows us to reduce the fluctuations in a given bin during the simulation. The average values for \(\sigma\) are obtained using,

\[
\sigma_{L,R} = \langle \sigma_{L,R}(z) \rangle
\]
and are presented in the Table III.

For both the G2PEL and GPDEN cases, the net surface charge on the virtual parallel plate capacitor was found to be smaller than in BAREGP, again suggesting that the electrode’s charge is better compensated in the presence of the dendrimer. Here, in G2PEL, the solvated G2 PAMAM dendrimer behaves as a dielectric screening medium that decreases the strength of electric field, thus decreasing the potential and increasing the capacitance. Indeed, the dendrimer in GPDEN can be thought of as a porous electrode, where the availability of the charged groups accessible to the water molecules gives rise to the lowered potential difference.

B. Capacitance values: CPM method

![Fig. 4. Time evolution of the charge per unit area deposited on the (a) positive and (b) negative electrodes for BAREGP and G2PEL cases. The electrodes are maintained at fixed constant potentials \( \pm 1V \), using CPM algorithm. Presence of dendrimers accumulates more charge at electrodes to maintain \( 1V \). (c) Surface charge density on the positive electrode as a function of applied potential across the cell. The lines represent linear fits of the data. The corresponding slopes give the capacitance 5.84 \( \mu \text{F cm}^{-2} \) and 4.18 \( \mu \text{F cm}^{-2} \) for G2PEL and BAREGP cases, respectively.](image)

Fig. 4(a),(b) show the accumulation of positive and negative charges density on the two electrodes in order to maintain \( \pm 1V \), obtained using the CPM method. Equilibrium surface charge densities for all the voltage are included in Fig. 5 in Appendix.

Convergence was typically observed after \( \sim 10 \) ns of MD and we found that the presence of protonated G2 PAMAM dendrimer significantly affected the charge distributions, compared to BAREGP. In Fig. 5(c) we depict the charge density \( \sigma \) of the positive electrode as a function of applied voltage for the BAREGP and G2PEL systems (the negative electrode acquired an opposite charge density). In both the cases, we found that the surface charge density of the electrode scaled linearly with applied potential, which implies a constant value of the differential capacitance over the potential range.

| System     | \( C_s (\mu \text{F cm}^{-2}) \) | \( C_M (\text{F g}^{-1}) \) |
|------------|-------------------------------|-----------------------------|
| BAREGP     | 4.18                          | 23.35                       |
| G2PEL      | 5.84                          | 32.62                       |

The values of the capacitance were then computed through a linear regression of the charge density data, shown in Fig. 4, with the results being 4.18 \( \mu \text{F cm}^{-2} \) and 5.84 \( \mu \text{F cm}^{-2} \) for BAREGP and G2PEL cases respectively (Table IV). These capacitance and the surface charge density data are consistent with those reported in literature for BAREGP case. Notably, we found a 39% increase in capacitance in G2PEL, compared to BAREGP.

Further insights into the origin of the increased capacitance was obtained by computing the potential profile of the cell using the Poisson equation [44]:

\[
\Delta \psi(z) = -\frac{1}{\epsilon_0} \int_{-L}^{z} dz' \int_{-L}^{z'} \rho(z'')dz'' + C_1(x - L) + V_{\text{ext}},
\]

\[
C_1 = \frac{1}{L_2 - L_1} \left[ \Delta V_{\text{ext}} + \frac{1}{\epsilon_0} \int_{-L}^{L} dz' \int_{-L}^{z'} \rho(z'')dz'' \right].
\]

Here we use Dirichlet BC, \( \psi(L_1 = -D) = V \) and \( \psi(L_2 = D) = -V \). Fig. 6 shows that the potential maintained a constant value within the electrode, oscillates in a region of 15 \( \text{Å} \) near the electrode interface, before exhibiting a linear profile in the bulk region. The oscillation of the potential close to the electrode is due to water layering, resulting from intrinsic entropy-dominated forces at low voltage and stronger graphene-water interactions and electrostatic binding at larger potentials [64].

To understand how dendrimer affects the potential profile we calculated the electric field inside the bulk region (Table V). Here, we used the negative gradient of the potential in the bulk, from \(-L' \) to \( L' \), where \( L' = \frac{D}{2} \to \frac{D}{3} \). We found that as the voltage increases, so does the electric field in the bulk region (Table V). Fig. 6 shows that for G2PEL, the strength of the electric field was reduced in the bulk region, as compared to BAREGP, due to electrostatic screening of the dendrimer at all voltages.
FIG. 5. Poisson potential ($\psi$) across the cell computed using Eq. (9) for different values of the applied voltage $\Delta V$. Different colors represent different voltage. Solid line and dash represent BAREGP and G2PEL case respectively. The inset of Fig. depicts electric field inside the bulk region as a function of the applied potential difference in a cell.

### TABLE V. Electric field in bulk region of electrolyte of BAREGP and G2PEL at different voltage

| $\Delta V$ (V) | $E(10^{-3} V/Å)$ in BAREGP | $E(10^{-3} V/Å)$ in G2PEL |
|---------------|----------------------------|---------------------------|
| 0.5           | 3.2 ± 0.2                  | 1.2 ± 0.1                 |
| 1.0           | 6.4 ± 0.1                  | 1.1 ± 0.2                 |
| 2.0           | 9.7 ± 0.1                  | 8.4 ± 0.1                 |
| 3.0           | 11.8 ± 0.1                 | 9.1 ± 0.2                 |

In other words, in order to maintain the required voltage, the G2PEL system has to store more charge than BAREGP.

### C. Comparison between CCM and CPM approaches

To compare the CCM and CPM method, we performed additional simulations using the CCM method, where total charge on each electrode was taken as the average equilibrated charge in the CPM method at ±1V, distributed evenly on each carbon atom of the graphene sheet.

Fig. 6 reports the Poisson’s potential across the simulation cell for both methods. The solid curves are the results obtained from CPM method using Dirichlet BCs and dashed curved are the potential profile correspond to the CCM method using Newman’s BCs.

### TABLE VI. Comparison of capacitance computed using CPM and CCM respectively.

| System  | $\Delta \psi$ (V) | $C_s$ (µF cm$^{-2}$) |
|---------|-------------------|----------------------|
|         | CPM              | CCM                  | CPM              | CCM              |
| BAREGP  | 2.0              | 3.14                 | 2.08             | 1.32             |
| G2PEL   | 2.0              | 2.85                 | 2.59             | 1.89             |

The corresponding data is shown in Table VI. Our results using the CPM method compares well to reported values in the literature. We found that the although the CCM method predicted consistant capacitive enhancements in the G2PEL system compared to BAREGP, it generally overestimated the value of the potential in both cases. Thus, we conclude that while CCM method may be adequate to obtain qualitatively insights into the electrochemical behaviour of these systems, more detailed, quantitative results will require the CPM method.

### IV. CONCLUSIONS AND FUTURE OUTLOOK

To summarize, we have used extensive MD simulations to show that the presence of a protonated G2 PA-MAM dendrimer, in aqueous solutions or grafted on the electrode, enhances the capacitance and reduces the potential across the cell significantly compared to pristine graphene electrodes. The EDL structure and overall cell performance was shown to be a dramatic function of the
dendrimer morphology (free or grafted) and chemistry (charged or neutral), suggesting two different ways to utilize dendrimers with the aim of improving the capacitances of the graphene-based aqueous supercapacitors. Further, these results advance our understanding of the role of macro-molecules in modifying the properties of electrochemical systems and suggest important avenues for predictive design for improved efficiencies.

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Appendix A: Charge density profiles as a function of the applied voltage

FIG. 7. (a),(b) equilibrium charge densities in positive electrode and negative electrode respectively. Solid and dashed line represent G2PEL and BAREGP case respectively. Different color represent different voltage. For all the voltage G2PEL case required more charge on electrode to maintain a fixed voltage compared to BAREGP.

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