Single Ion Transport with a Single-Layer Graphene Nanopore

Vishal V. R. Nandigana, Mohammad Heiranian, Narayana R. Aluru

Abstract—Graphene material has found tremendous applications in water desalination, DNA sequencing and energy storage. Multiple nanopores are etched to create opening for water desalination and energy storage applications. The nanopores created are of the order of 3-5 nm allowing multiple ions to transport through the pore. In this paper, we present for the first time, molecular dynamics study of single ion transport, where only one ion passes through the graphene nanopore. The diameter of the graphene nanopore is of the same order as the hydration layers formed around each ion. Analogous to single electron transport resulting from ionic transport is observed for the first time. The current-voltage characteristics of such a device are similar to single electron transport in quantum dots. The current is blocked until a critical voltage, as the ions are trapped inside a hydration shell. The trapped ions have a high energy barrier compared to the applied input electrical voltage, preventing the ion to break free from the hydration shell. This region is called "Coulomb blockade region". In this region, we observe zero transport of ions inside the nanopore. However, when the electrical voltage is beyond the critical voltage, the ion has sufficient energy to break free from the energy barrier created by the hydration shell to enter into the pore. Thus, the input voltage can control the transport of the ion inside the nanopore. The device therefore acts as a binary storage unit, storing 0 when no ion passes through the pore and storing 1 when a single ion passes through the pore. We therefore postulate that the device can be used for fluidic computing applications in chemistry and biology, mimicking a computer. Furthermore, the trapped ion stores a finite charge in the Coulomb blockade region; hence the device also acts a super capacitor.

Keywords—Graphene, single ion transport, Coulomb blockade, fluidic computer, super capacitor.

I. INTRODUCTION

ELECTRICAL transport through single molecules have garnered significant attention [1] owing to the possibility of using single molecules as electronic components. Single molecule transport was first realized in electronic devices like quantum dots [2] later on in carbon nanotubes [3] and C60 molecules [4]. Such miniature devices offer us a possibility to analyze properties of a single electron one at a time and obtain a fundamental understanding of the quantum physics in these devices. The understanding can cater ways to novel and advanced quantum devices for quantum computing and cryptographic applications.

Analogous to the single electron transport in quantum dots, experiments have been carried out recently in 2D materials to investigate single ion transport in nanopores [5],

V. V. R. Nandigana is with the Department of Mechanical Engineering, Indian Institute of Technology, Madras, Chennai 600036 (e-mail: nandiga@iitm.ac.in).

M. Heiranian and N. R. Aluru are with Department of Mechanical Science and Engineering, University of Illinois at Urbana Champaign, Urbana 61801, USA.

[6]. In the nanometer scale pores, analogous single-electron phenomenon, such as Coulomb blockade and Coulomb oscillations have been observed in Graphene and MoS_2 based 2D material nanopores. Such phenomenon are observed for narrow channels when the channel diameter approaches the dimensions of the hydration layers formed around each ion [7], [8]. This translates to pores of sub-nm size. Fabrication of such small-sized pores have been a challenge until experimental groups of Karnik and Aleksandra showed that such miniature sized pores could be fabricated using controlled electrochemical reaction or by electron irradiation [5], [6]. The observation of Coulomb blockade currents were postulated to the hydration effects of ions trapped inside a water cage. The postulations were made based on semi-analytical modeling and modifications to continuum based models. An exact prediction of the single ion transport is not illustrated in their experimental findings.

In this article, we report why Coulomb blockade happens in a nanopore under single ion transport regime using molecular dynamics simulation. We consider 2D material like graphene to showcase the current-voltage characteristics and present the physics behind the blockade currents. We observe that until a critical voltage, current is blocked from flowing inside the nanopore. In other words, ions do not transport through the nanopore until a critical voltage. Beyond the critical voltage, current flows through the nanopore, illustrating ion transport through the nanopore. The flux recorded from the MD simulation shows that at a given time either a single potassium or chloride ion transports through the pore illustrating single ion transport physics inside the nanopore. The ion is prevented from traveling through the pore at low voltage due to the hydration shell formed around the ion. At low voltage, the ion does not have enough energy to break free from the hydration shell. Our potential of mean force (pmf) calculations show the high energy barrier created by the hydration shell around the ion is beyond the input voltage. However, at high electrical voltage beyond the threshold voltage, the pmf of the hydration shell is less than the applied electrical voltage allowing the ion to break free from the shell to enter into the pore. The size of the nanopore however allows the transport of single ion inside the nanopore. The transport of single ion can be applied in venues like biology, chemistry for fluidic computing applications.

II. THEORY

A. VN Oscillator Model

We discuss a simple oscillator model to understand the notion of ionic current. The oscillator is called as "variational

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non-equilibrium potential oscillator", VN oscillator. In this model, we assume that the graphene membrane allows only one ion to transport through the pore. The model states that, the mass transfer of each ion $(\vec{n_i})$ in retrospection to the charge of the ion (q_i) constitutes the equation of motion of the charged particle, manifesting current, $\vec{I} = \sum_i^N \vec{n_i} q_i$. The mass transfer rate is mapped to the charge transfer rate $\left(\dot{q}_n^{\delta V} = \frac{(q_n^{\delta V}(t+\Delta t) - q_n^{\delta V}(t))}{\Delta t} \right)$ which is again mapped to the Eulerian space inferring in the net ion motion, $\vec{I} = \left[\frac{(q_n^{\delta V}(t+\Delta t) - q_n^{\delta V}(t))}{\Delta t} \right] = q_n^{\delta V}(t+\Delta t) \frac{1}{\delta l} \lim_{\delta \vec{l} \to \vec{L}_{nano}} \frac{\delta \vec{x_n}}{\delta t}$, where $q_n^{\delta V}$ is the charge of the ionic particle. Δt is the time step. δl is the length of the membrane accounting for either micro or nanomembrane. We propose a theorem called "potential charge-momentum theorem (PCM)" to rationalize the displacement of charged particle, $\vec{x}_n$. The theorem solves the Newton's law of motion for the coarse grained charged particle given by, $m_{\delta V} \frac{\partial^2 \vec{x}_n}{\partial t^2} + \dot{\lambda} \frac{\partial \vec{x}_n}{\partial t} = F|_{t_n}$, where $m_{\delta V}$ is the mass of the coarse grained charged particle, $\dot{\lambda}$, is the mass transfer rate of the particle given as $\left(\frac{K_B T}{D_b} \right)$, D_b is the bulk diffusion coefficient of the particle, $(K_B T)$ is the thermal energy of the particle, and $F|_{t_n}$ is the mean force harnessed at time t_n by the particle. The mean interaction potential force formulated by electrostatic interaction is, $F|_{t_n} = \frac{q_s q_n^{\delta V}}{4 \pi \epsilon_0 \epsilon_r |\vec{x}_n - \vec{x}_0|^2} + \frac{q_n^{\delta V} V_0}{|\vec{x}_{b2} - \vec{x}_{b1}|}$, where $q_s = \sigma_s \delta S$ is the charge constituted by the surface of the nano and micro membrane with δS is the surface area of the membrane. σ_s is the surface charge density of the micro or nanomembrane. An electrostatic potential, V_0 is applied across the micro-nanoporous architecture within a distance of $|\vec{x}_{b2} - \vec{x}_{b1}|$. $\vec{x}_0$ is the position of the charged nano-membrane. The model is marched in time by Δt amount using a well know velocity-verlet algorithm [9]. $\vec{x}^n(t+\Delta t) = \vec{x}^n(t) + \dot{\vec{x}}(t)\Delta t + \frac{1}{2}\ddot{\vec{x}}(t)(\Delta t)^2$. The ionic particle acceleration at $(t+\Delta t)$ is configured using the interaction potential force at $\vec{x}^n(t+\Delta t)$. Finally, the velocity is, $\dot{\vec{x}}(t+\Delta t) = \dot{\vec{x}}(t) + \frac{1}{2}\left(\ddot{\vec{x}}(t) + \ddot{\vec{x}}(t+\Delta t) \right)(\Delta t)$. Note, while calculating the velocity $(\dot{\vec{x}}(t))$ and acceleration $(\ddot{\vec{x}}(t))$ we have to substitute the right length δl and surface charge σ_s accounting for micro-reservoir and nanopore membranes.

III. SIMULATION DETAILS

Molecular Dynamics simulations (MD) have been carried out using the LAMMPS package [10]. A small nanopore with a diameter of $9.45°A$ (center to center) is created in the graphene by deleting the unwanted carbon atoms. The system dimensions are $4nm \times 4nm \times 6nm$ in x, y and z, respectively. The membrane lies in the xy plane. The box contains about 11,000 atoms in which the concentration of ions is $1.0M$. The whole simulation box was generated by the Visual Molecular Dynamics [11]. Periodic boundary conditions were imposed in x, y and z directions. The SPC/E water model was employed with a SHAKE algorithm to ensure the rigidity of each water molecule. The ion-ion interactions were described by the force-field (Lennard-Jones (LJ) parameters) developed in ref [12]. For carbon-water interactions, the force-field parameters given in ref [13] were used. For the rest of the

non-bonded interactions, the combination rule was applied to obtain the LJ parameters. The LJ cutoff distance was $12°A$. The long range electrostatic interactions were computed by the Particle Particle Particle Mesh (PPPM) [14]. The energy of the system was first minimized using the steepest descent algorithm for 10000 steps in each simulation. Next, the system was simulated for 1 ns in NPT ensemble at a pressure of 1 atm and a temperature of 300 K to reach the equilibrium density of water $(1g/cm^3)$. Then, the system was further equilibrated in NVT ensemble for 1 ns. Temperature was kept at 300 K by using the Nose-Hoover thermostat with a time constant of 0.1 ps [15], [16]. In all the simulations, the carbon atoms of the graphene were held fixed in space. Different voltages were applied across the simulation box (in the z direction) in the form of a constant electric field in the final production simulations which were performed in NVT ensemble. The external voltages are enforced according to V = ELz, where E is the constant electric field and Lz is the length of the simulation box in the z direction. For the energy barrier calculations, the constant velocity pulling method was used to pull an ion through the nanopore along the z direction with a velocity of $10^{-5}nm/ps$.

IV. RESULTS AND DISCUSSION

A. Coulomb Blockade

A typical graphene nanopore and reservoir system is shown in Fig. 1. The bulk reservoir is filled with KCl salt solution and its concentration is considered as 1 M. The diameter of the nanopore is chosen in such a way that only one ion transports through the nanopore at a given period of time. A schematic illustration of single ion transporting through the nanopore is shown in Fig. 1. Fig. 2(a) shows the ion flux illustrating that only a single potassium or a chloride ion transports through the nanopore at a given instant of time. Typical current-voltage characteristics of the single ion transport system is shown in Fig. 2(b) where the current does not mimic the traditional Ohmic characteristics but mimics nonlinear characteristics. At low voltage, the current is blocked in the system as no ion travels into the nanopore at this voltage regime. The region is known as the Coulomb blockade region similar to the Coulomb blockade physics observed in single electron transport systems in quantum dots. The physics behind the current-blockade levels can be explained from the potential of mean force (pmf) calculation. Fig. 3(a) shows that the pmf experienced by the ion at different voltage. From the figure we see that at $0.5V$ the pmf is nearly 5.7 kcal/mol. This energy is higher than the input electrical voltage. The reason we see a high pmf experienced by the ion is because the ion is trapped inside a cage (hydration shell) of water molecules. The ion does not have enough input energy to break free from the cage of water molecules and hence, stays near the entrance of the nanopore (see Fig. 1). Thus, there is no transport of ion inside the nanopore. At high electrical voltage, i.e., at $6V$, the pmf experienced by the ion is 0.5 kcal/mol which is much lower than the input electrical energy. Hence, the ion has enough energy to break free from the hydration shell and transport through the pore. Thus, we see a single ion transporting through the pore at

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high electrical voltage. This is evident from the current in the Fig. 2(b). The region beyond the critical voltage where there is a net current in the system is called as single ion transport regime. Apart from the MD simulations, the VN oscillator model also matches the current-voltage characteristics. In the oscillator model, we use an empirical mass to match the MD simulation. $m_{\delta V} = 6 \times 10^{-11} kg$ is used to fit one of the MD simulation for a given voltage. The same mass is used for all the other voltages. A surface charge of $-30 mC/m^2$ is assumed on the graphene nanopore to match the MD simulation results. Analytical models have also been derived to predict the current-voltage characteristics. Considering the hydration energy barrier acting on the ion at low input voltage, the current for single ion transport is given as,

$$I = (n_{dV} q_n A \mu E) exp \left(\frac{-F_p}{K_B T} \right) \qquad (1)$$

where, n_{dV} is the number of ions per unit volume. Here a single ion transports through the pore, so, $n_{dV} = 1/\delta V$, with δV being the volume of the graphene nanopore. q_n is the charge on the coarse grained ion. The charge is empirically obtained by matching the I-V characteristics. A is the area of the nanopore, the diameter of the graphene nanopore $d = 0.88 nm$ is considered. E is the electric field applied. The mobility μ is obtained from MD simulations. F_p is the pmf experienced by the ion due to the hydration shell. The pmf is obtained from MD simulation. The model is different from the current calculation for bulk reservoir system, which does not account for the hydration energy term. Thus, we are able to predict both numerically (using MD simulation and Oscillator model simulation) and analytically the current voltage characteristics. We observe that owing to the blockade of ions and the narrow channel opening, the mobility of both potassium and chloride ion is less than the bulk mobility of the ion (see Fig. 3(b)). The bulk mobility of K^+ and Cl^- are $7.62 \times 10^{-8} m^2/Vs$ and $7.91 \times 10^{-8} m^2/Vs$, respectively. We observe at least 50% reduction in the mobility of the ion for voltages below the critical voltage. The interaction of the ion with the narrow pore diameter is responsible for such low mobility. Also, a reduced concentration distribution inside the nanopore is shown in Fig. 3(c). Owing to the thin graphene membrane thickness the concentration polarization effects are minimal at this voltage near the interfaces of the membrane. Hence, we do not account for these effects in our analysis.

Further, the ion inside the nanopore stores charge and a finite capacitance. The capacitance of the ion inside the nanopore is given as,

$$C = e^2 / (2F_p) \qquad (2)$$

where e is the charge of a single ion stored inside the nanopore. Substituting for the pmf at the critical voltage, we obtain the capacitance $C = 0.3214 aF$. This capacitance is for a single pore. Now, if we have a quadrillion (10^{15}) pores in parallel, we can achieve a capacitance of $C_p = 0.3214 mF$, which can be used as a super capacitor. Further, the resistance of a single nanopore at the threshold voltage can be obtained from the I-V characteristics. The resistance R is $15.33 G\Omega$. Now, if we have a quadrillion nanopores in parallel the
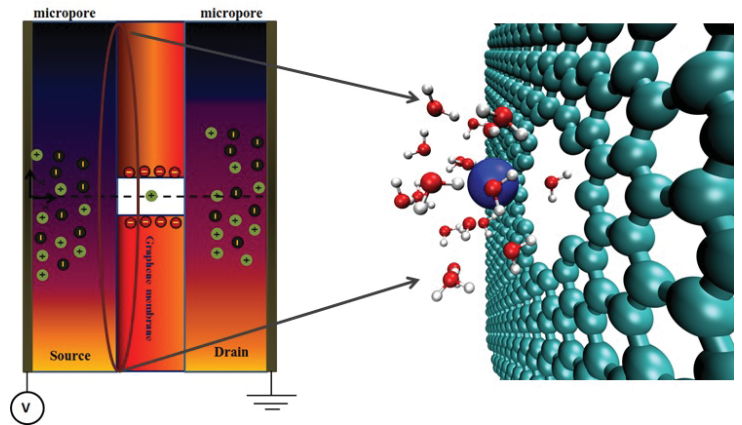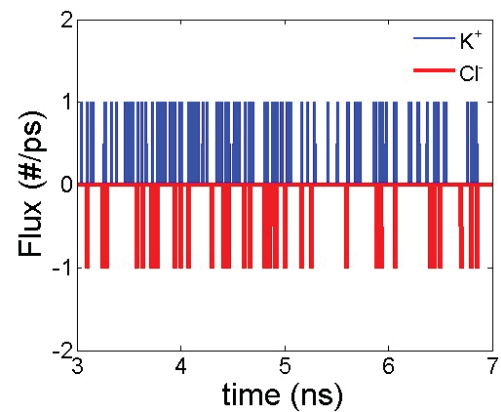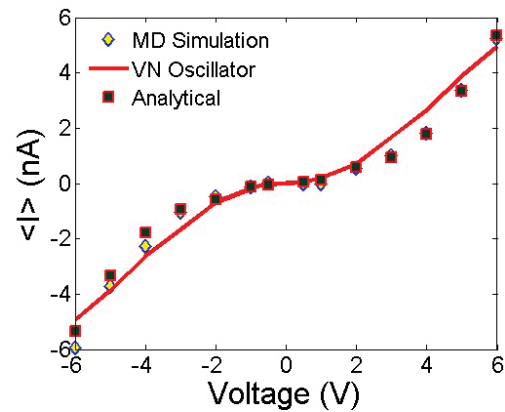

Fig. 1 Schematic illustration of Graphene nanopore system. The schematic on the right illustrates the ion trapped inside a hydration shell near a graphene nanopore
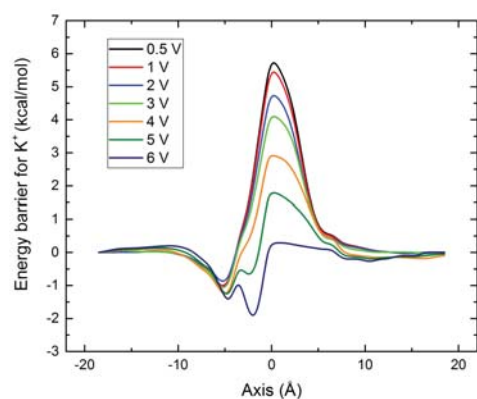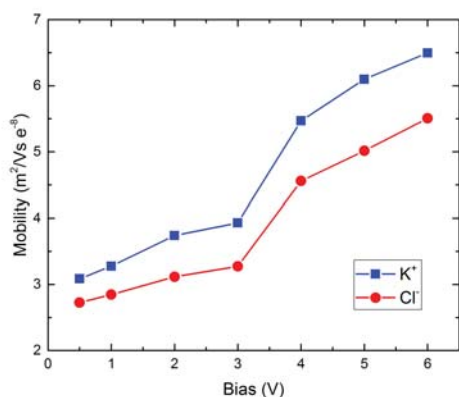

(a)

(b)

Fig. 2 (a)Flux of single ion transport inside graphene nanopore. Either one Potassium or Chloride ion transports through the pore at a given time. (b)Current-Voltage characteristics of single ion transport. The region where the current is blocked is called Coulomb blockade region and region where current flows is called single ion transport region. Comparison of MD (diamond symbols), VN oscillator model (solid line) and analytical (filled squares) results
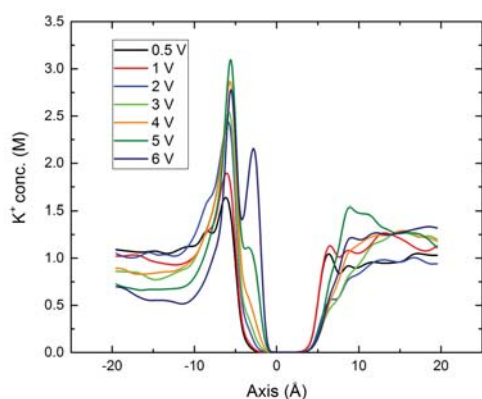
resistance of the entire system is $R_p = 65.2 k\Omega$. Considering the resistance and capacitance, the RC relaxation time constant for quadrillion pores is given as $\tau_{RC} = 20.98 s$. Thus, if we can

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(a)

(b)

(c)

Fig. 3 (a) Potential of Mean Force of single ion trapped inside a hydration shell at different voltages. (b) Ionic mobility of Potassium and Chloride inside graphene nanopore. (c) Potassium ion concentration distribution inside the reservoir-graphene nanopore system at different voltages

fabricate a quadrillion pores over $1\ cm^2$ area, we can achieve a super capacitor which can charge in 20 seconds. This super capacitor can be used to replace a battery in smart phones.

This single ion super-capacitor is much better than a multi-ion bulk transport capacitor. As the capacitance for a quadrillion multi-ion bulk capacitor for the same pore dimension and for $1M$ concentration is $C_m = 0.4896mF$. The capacitance is obtained using the classical formula, $C = \frac{\epsilon_0 \epsilon_r A}{d}$. Even though the capacitance is high, the resistance for quadrillion multi-ion transport pores is $R_m = 29.67 M\Omega$, which is three orders higher than the single ion transport resistance for quadrillion pores. The resistance is obtained from multi-ion bulk current, given as, $I = (2n_{bulk}q_n A\mu_{bulk}E)$, where $n_{bulk} = c_0/\delta V$, with c_0 being the bulk concentration of the ion and μ_{bulk} is the bulk mobility of the ion. The factor 2 accounts for both positive and negative monovalent ion. The RC relaxation time constant for the multi-ion quadrillion pores is $\tau_{RC_m} = 14,527s$ or $\tau_{RC_m} = 4.035h$. The time constant is almost 700 times slower than a single ion transport device. Thus, we see that a single ion offers a superior advantage as a super-capacitor. Furthermore, we noticed that the mobility of the ion is reduced 50% inside the nanopore for single ion transport device. Thus, the ion stays longer inside the pore giving it time for charging.

V. CONCLUSION

The observation of single ion transport in nanopores from MD simulation perspective is to our knowledge the first time. The single ion transport mimics quantum-like mesoscopic effect. We show using our MD and VN oscillator model the nonlinear current-voltage characteristics. The current showcases Coulomb blockade regimes owing to the ions trapped inside the hydration shell. Potential of mean force calculation of the ion at different voltage illustrate the energy barrier acting on the ion from entering into the nanopore. Analytical models were developed to calculate the capacitance and resistance along with the relaxation time constant of the system consisting of quadrillion pores. The RC time constant illustrates that the system can act as a super-capacitor to charge a cell phone in 20 seconds compared to 4-5 hours a Li-ion battery takes. Further, the single ion transport device is superior in fast charging compared to an equivalent multi-ion transport device. The voltage controlled transport of single ion can be used for fluidic computing applications, mimicking a computer for biology and chemistry applications along with smart phone charger device. We believe atomically thin and small (sub-nm) pores offer a new platform to explore in the areas of nanofluidics along with biology and chemistry.

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REFERENCES

[1] M. L. Perrin, E. Burzuri, and H. S. J. van der Zant, "Single-molecule transistors," *Chem. Soc. Rev.*, vol. 44, pp. 902–919, 2015.

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[2]   J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruna, P. L. McEuen, and D. C. Ralph, "Coulomb blockade and the kondo effect in single-atom transistors," *Nature*, vol. 417, pp. 722–725, 2002.

[3]   P. J. Herrero, J. Kong, H. S. J. van der Zant, C. Dekker, L. P. Kouwenhoven, and S. D. Franceschi, "Orbital kondo effect in carbon nanotubes," *Nature*, vol. 434, pp. 484–488, 2005.

[4]   L. H. Yu and D. Natelson, "The kondo effect in c60 single-molecule transistors," *Nano Lett.*, vol. 4, pp. 79–83, 2004.

[5]   T. Jain, B. C. Rasera, R. J. S. Guerrero, M. S. H. Boutilier, S. C. O'Hern, J. C. Idrobo, and R. Karnik, "Heterogeneous sub-continuum ionic transport in statically isolated graphene nanopores," *Nat. Nanotech.*, vol. 10, pp. 1053–1057, 2015.

[6]   J. Feng, K. Liu, M. Graf, D. Dumcenco, A. Kis, M. D. Ventra, and A. Radenovic, "Observation of ionic coulomb blockade in nanopores," *Nat. Mat.*, vol. 15, pp. 850–855, 2016.

[7]   M. Krems and M. D. Ventra, "Ionic coulomb blockade in nanopores," *J. Phys. Condens. Matter*, vol. 25, p. 065101, 2013.

[8]   M. Zwolak, J. Lagerqvist, and M. D. Ventra, "Quantized ionic conductance in nanopores," *Phys. Rev. Lett.*, vol. 103, p. 128102, 2009.

[9]   L. Verlet, "Computer experiments on classical fluids. i. thermodynamical properties of lennardjones molecules," *Phys. Rev.*, vol. 159, pp. 98–103, 1967.

[10] S. Plimpton, "Fast parallel algorithms for short-range molecular-dynamics," *J. Comput. Phys.*, vol. 117, pp. 1–19, 1995.

[11] W. Humphrey, A. Dalke, and K. Schulten, "Vmd: visual molecular dynamics," *J. Mol. Graph.*, vol. 14, pp. 33–38, 1996.

[12] I. S. Joung and T. E. CheathamIII, "Determination of alkali and halide monovalent ion parameters for use in explicitly solvated biomolecular simulations," *J. Phys. Chem. B*, vol. 112, p. 90209041, 2008.

[13] Y. B. Wu and N. R. Aluru, "Graphitic carbon-water nonbonded interaction parameters," *J. Phys. Chem. B*, vol. 117, pp. 8802–8813, 2013.

[14] R. W. Hockney and J. W. Eastwood, *Computer Simulation Using Particles*. Taylor and Francis, Inc., 1988.

[15] S. A. Nose, "A unified formulation of the constant temperature molecular dynamics methods," *J. Chem. Phys.*, vol. 81, pp. 511–519, 1984.

[16] W. G. Hoover, "Canonical dynamics-equilibrium phase-space distributions," *Phys. Rev. A*, vol. 31, p. 16951697, 1985.

Narayana R. Aluru Narayana R. Aluru received the B.E. degree (with honors and distinction) from the Birla Institute of Technology and Science, Pilani, India, in 1989, the M.S. degree from Rensselaer Polytechnic Institute, Troy, NY, in 1991, and the Ph.D. degree from Stanford University, Stanford, CA, in 1995. He was a Postdoctoral Associate at the Massachusetts Institute of Technology (MIT), Cambridge, from 1995 to 1997. In 1998, he joined the University of Illinois at Urbana-Champaign (UIUC) as an Assistant Professor. He is currently a Professor in the Department of Mechanical Science and Engineering at UIUC. He is also affiliated with the Beckman Institute for Advanced Science and Technology, the Department of Electrical and Computer Engineering, and the Bioengineering Department at UIUC.

Dr. Aluru received an NSF CAREER Award in 1999, the NCSA faculty fellowship in 1999 and 2006, the 2001 CMES Distinguished Young Author Award, the Xerox Award for Faculty Research in 2002, the ASME Gustus L. Larson Memorial Award in 2006, the USACM Gallagher Young Investigator Award in 2007, and was named a Willett Faculty Scholar by the College of Engineering at UIUC for the period $2002 - 2009$. He is a Subject Editor of the JOURNAL OF MICROELECTROMECHANICAL SYSTEMS, served as an Associate Editor of the IEEE TRANSACTIONS ON CIRCUITS AND SYSTEMS II for $2004 - 2005$, and currently serves on the Editorial Board of a number of other journals.

Vishal Nandigana Vishal V. R. Nandigana obtained his B.E from college of Engineering, Guindy, Anna University, India, in 2008. He obtained his M.S from University of Illinois at Urbana Champaign, Urbana, IL, in 2010. He later obtained his PhD from University of Illinois at Urbana Champaign, Urbana, IL, in 2016. In 2016, he worked for Intel corporation in Portland, Oregon as a Sr. Imaging scientist. Currently, he is working as an Assistant Professor in Mechanical Engineering department in Indian Institute of Technology, Madras.

Mohammad Heiranian Mohammad Heiranian obtained his B.E in Mechanical engineering from the University of Manitoba, Canada, in 2012. Later, he obtained his M.S in theoretical and applied mechanics from the University of Illinois at Urbana-Champaign, Urbana, IL,, in 2016. He is currently working on his PhD at the University of Illinois at Urbana-Champaign, Urbana, IL.

His research interests include nanotechnology, nanofluidics, computational biophysics and computational nanoscience.