

Applications of Radial Distribution Function (RDF $g(r)$) Tool in Statistical Analyses of Microcanonical Ensembles

Prof. Dr. Anant Babu Marahatta^{1,*}

¹Engineering Chemistry and Applied Science Research Unit, Department of Civil, Computer and Electronics Engineering, Kathford Int'l College of Engineering and Management (Affiliated to Tribhuvan University), Kathford Int'l Education & Research Foundation, Lalitpur, Nepal

*Corresponding author: abmarahatta@gmail.com/anant.marahatta@kathford.edu.np



Abstract – In the domains of quantum mechanics enriched mathematical formulations implementing theoretical/computational sciences and their efficient yet versatile parametrizations state-of-art iterative schemes, the large scale MD simulations of the microcanonical ensemble characterized with the constancy on number of particles N , volume V , and total energy E , and the comprehensive big data concept act as the mainstream paradigms. However, effective integrations of the MD produced massive datasets and the genuine assessments of its explicit trajectories by retrieving all the needy microscopic and macroscopic physicochemical properties are still considered as a challenging task. Towards resolving these bottlenecks to a large extent, the advanced computer aided molecular graphics and the specific programmatic schemes scripted mainly for executing the complex mathematical formulae stand as the frontline means. The radial distribution function (RDF $g(r)$) and its deterministic computational scheme is one of them which readily enables the users to describe probability density functions of each particle present in the simulating micro-canonical ensembles. In this study, the in-depth statistical analyses of the four different NVE ensembles set with the definite numbers of H_2O , H_3O^+ , SO_4^{2-} , HSO_4^- , SO_3^{2-} , and V^{n+} ($n = +2, +3, +4, +5$) are carried out by employing the RDF $g(r)$ scheme computationally, and the respective inter-particle interactions are quantitatively theorized. All the nanometer ranged radial distributions of every distinctive particles, their approximate pair distances, complex forming propensities, hydration abilities, dissolution phenomena, affinities towards acquiring free water molecules, etc. are found to be consistent with the pre-established experimental/theoretical datasets. The quantitative results conferred herewith are believed to be highly useful and directly applicable to understand the internal compositions of every particles in their own aqueous electrolyte systems of the batteries, humid weathers, acidic/alkaline solutions, marine ecosystems, soil and geological systems, micellar assemblies, medicinal solutions, biofluids, etc.

Keywords – MD Simulation, Radial Distance Analyses, Electrolytes, Laxatives, Humid Weather Scenario.

I. INTRODUCTION

In the emerging scientific domains, modernized educational paradigms, and creative yet innovative research and development sectors, the mathematical formulations and the quantum mechanics based users' friendly programmatic parametrizations have been playing very crucial roles since last few years as they act as the most indispensable computational means, and most probably the very effective state-of-art interpreting frontline tools [1–3]. The underlying facts behind this are; (a) rapid advancement of the computer technology compatible with the human generated programmatic codes designed for running complex mathematical derivatives, integrals, or the related non-linearities [1]; (b) massive uses of the quantum computing mainly for solving various complex mathematical formulations and for unlocking (proving) the multidimensional scientific ideas (hypothesis) that were previously thought as impossible [3]; (c) worldwide employments of the mathematical models and mathematical formulations based quantum mechanical packages for computing and retrieving highly resolved yet mostly precise datasets that are still considered as a bottleneck even in the viewpoints of sophisticated experimental facilities [4]; (d) prompt and

urgent calls of the mathematical algorithms for attempting complex iterative convergence procedures, complexity theories or chaos, competitive programming, recurrence relations, heavy computational calculations, big data processing statistics, etc. [5]; (e) extensive applications of the mathematics based quantum modeling and computational software in modern drug design and development techniques plus sometimes in decision making processes [3,5], etc. More particularly, the very fascinating yet prominent computational packages that are basically modeled based on the complex quantum mechanical formulations inclusive with many deterministic mathematical algorithms and principal modules of the Schrodinger platform exhibit recognizable potentialities with prominent deliveries. Accordingly, the contributions of the multidisciplinary quantum mechanical packages consistent with executing three dimensional rendering tools and structural visualization software in retrieving mathematical datasets from the human inaccessible/unreadable computational output files plus in converting them into the 3D molecular structures with magnificent visualizations are praiseworthy. For example, the quantum mechanics software packages namely Gaussian, GAMESS, Jaguar, Spartan, Amber, Molpro, QMCPACK, Vienna *Ab-Initio*, DFTB⁺, etc., and their graphical interfaces & rendering tools such as GaussView, Molden, Jmol, Visual Molecular Dynamics (VMD), Avogadro, Mercury, etc., are few of the well appreciable tools and techniques that are constantly in demand of the day to day research activities of the scientific domains, and of the advancement of diverse areas of chemistry and chemical education [6]. More particularly, the quantum mechanical features offered by them that are in fact dependent directly on their in-built mathematical parametrizations are indispensable means to inquire several unique research problems that lie beyond the imaginations of experiments such as status of the short-life spanned reaction intermediates and transition states, chemical reactions pathways, dynamical perspectives of the giant molecular assembly, ground state equilibrium electronic structures, vibrational frequencies, dipole moments to frequency dependent hyper-polarizabilities, similarity & conformational analyses, and many other QSAR & QSPR based physicochemical properties, etc. [3, 4, 6]. More importantly, the direct employment of these electronic structure packages in molecular dynamics (hereafter, MD) simulations, and the straightforward assessment of the mathematical tools featured in those potential graphical interfaces to handle thus derived massive datasets add substantial values to their rational applications. The radial distribution function (hereafter, (RDF($g(r)$))); a central tool to the statistical mechanics that describes probability density function genuinely is one of them [7].

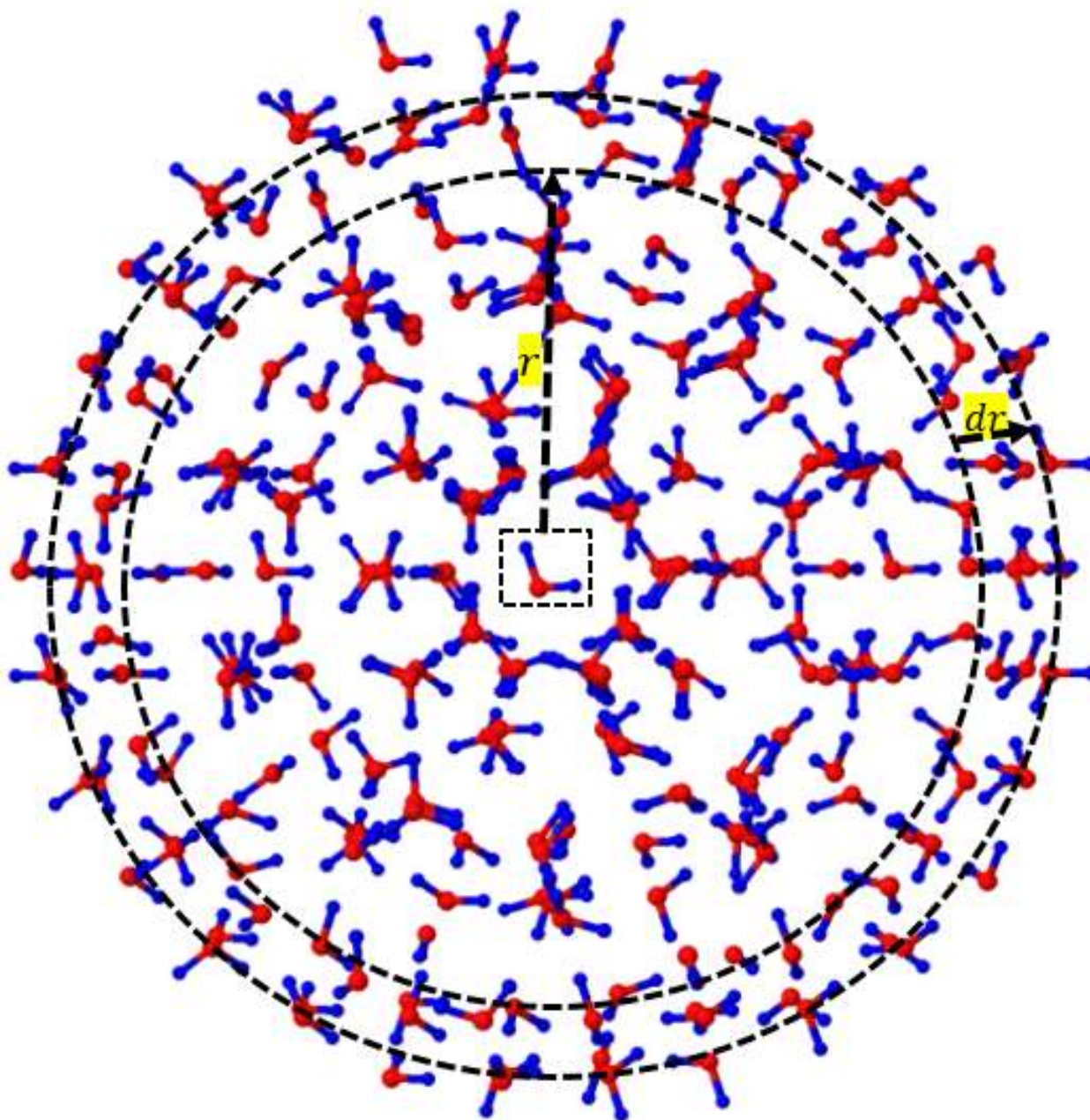


Figure 1. A part of molecular dynamics simulation assembly of the water molecules displaying the network of each explicit H_2O molecule. The hydrogen bonding between them is excluded for clarity. The central H_2O molecule (particle) is marked by the dotted square in reference to which probability of finding other H_2O molecules (or any particles) within the spherical region (thickness = dr) enclosed between a sphere of radius $(r + dr)$ and a sphere of radius r is measured. The efficient and easiest mean to formulate these mathematical variables, and then to determine the structural properties of the entire simulation cell is radial distribution function (RDF ($g(r)$)) as defined mathematically in eq. 1. The blue, and red spheroids represent H and O atoms respectively.

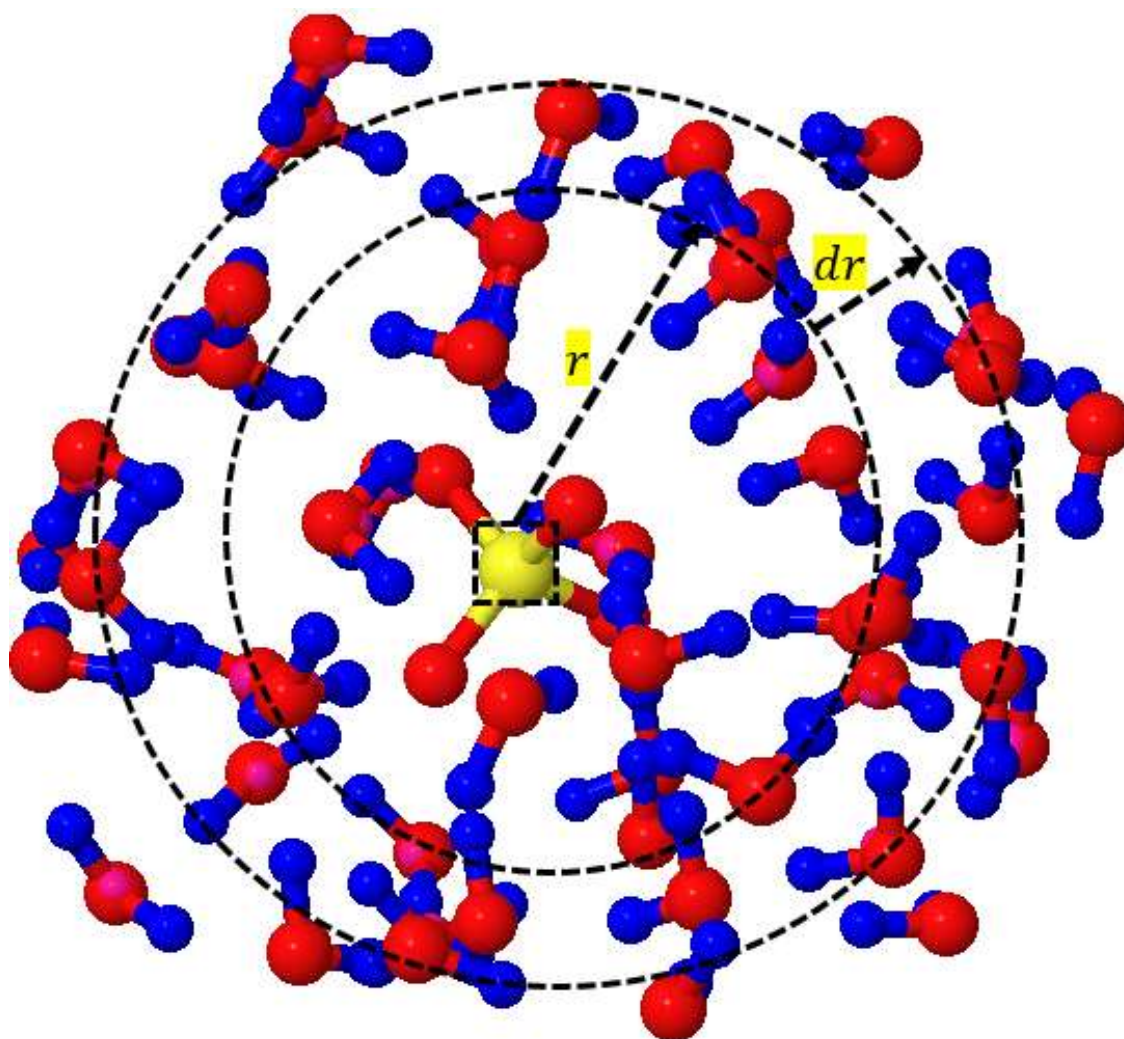


Figure 2. A part of molecular dynamics simulation assembly of the water molecules, and central divalent SO_4^{2-} ion. The intermolecular hydrogen bonding between them is excluded for clarity. The central SO_4^{2-} ion (particle) is marked by the dotted square in reference to which probability of finding any H_2O molecules (or any particles) within the spherical region (thickness = dr) enclosed between a sphere of radius $(r + dr)$ and a sphere of radius r is measured. The efficient and easiest mean to formulate these mathematical variables, and then to determine the structural properties of the entire simulation cell is radial distribution function (RDF ($g(r)$)) as defined mathematically in eq. 1. The blue, red, and yellow spheroids represent H, O, and S atoms respectively.

Actually, the MD derived trajectory datasets can only be converted into the faithful microscopic and macroscopic physicochemical properties if they are handled either with the advanced computer aided molecular visualization and manipulation softwares and many other rendering molecular graphical interfaces or with the users' scripted computer coding languages. The RDF is that type of the human scripted statistical tool that correlates a direct proportion of the radial variation of probability of finding any reference tagged particle (molecule, atom, ion, electron, etc.) mathematically as (eq. 1) (schematic diagrams are shown in Figure 1 and Figure 2);

$$g_{A-B}(r) = \frac{n_B}{4\pi r^2 dr} / \frac{N_B}{V} \quad (1)$$

Where;

r = Distance between a pair of the particles;

n_B = Average number of the pairs found at a distance between r & $(r + dr)$;

V = Total volume of the system;

N_B = Number of the pairs found in the whole system;

and is very much applicable to acquire the most essential quantitative interpretations required to elucidate many notable time-dependent physicochemical properties of the simulating micro-canonical assemblies, colloidal systems, particle dynamics including coordination number and number of neighbors, plasma physics, protein diffusions, liquid profiles, etc. [8–12]. Even though, the RDF features hosting C++ programming code based MacOS X, Unix, or Windows supported VMD software is freely available with needy source codes that can be linked directly to the MD derived gigantic trajectory datasets [13], the manually yet programmatically scripted coding languages written by incorporating all the mathematical formulations mentioned in eq. 1 are regarded as the most essential mean mainly to obtain the cost-compromise (low computational sources) and the practically relevant quantum mechanical solutions of the giant, moderate, and small sized simulation systems, and of their time-dependent trajectory series. Unlike the in-built VMD codes, the human scripted RDF scheme is relatively easily compiled and executed directly even under the low computer systems resources, and hence, can be assessed as per the needs of the users mainly to overview the scattering particles such as determination of how many atoms/ ions/molecules/fragments, etc. fall in the particular regions, identification of the average distribution of the particles around any specific tagged particle, elucidation of the time-averaged density of any constituent particles, statistical predictions of the local packing around any reference particles, determination of the distances between any pair of the atoms/ions/molecules/fragments, etc., and approximation of how many of such type pair distances lie into that particular sites. Additionally, the RDF formulated scripts can be extensively employed to investigate the microstructural properties of the battery materials such as battery composites, electrode materials, electrolyte compositions and its structural profiles, cations/anions arrangements/orderings, local distortions & distributions, polymeric membrane's proton conduction mechanisms, electrode– electrolyte interfacial structures (junction composition), etc. [7,8]. Beside this, the computationally executable RDF scripts is needful while revealing the insights into the hydration/complexation chemistry such as determinations of the multiple coordination shells and the specific coordination numbers, identifications of the solvation/hydration spheres and the structures around each simulating particle, investigations of the coordinating abilities of the transition metal ions M^{n+} with different type ligands, quantitative studies of the hydration moieties and stabilities of the aqua type metal complexes, predictions of the 3D metal-ligands spatial configurations, etc. All these potential applications of the RDF tool/scheme in the wide ranged scientific domains verify its features & computing abilities theoretically esteemed and practically bold, illuminative, quantitative, and mathematically descriptive. In this research report, the similar type programmatically designed RDF formulations and the associated scripting codes are executed mainly to investigate the (a) microstructures of huge water network (bulk water system), (b) internal structural compositions around any reference water molecule, (c) immediate hydration environments of the central divalent SO_3^{2-} & SO_4^{2-} ions, and the monovalent HSO_4^- ion, (d) solvation structures of the monohydrated proton (H_3O^+), and (e) hydration propensities of the bare transition metal ion M^{n+} (vanadium V^{n+} ; $n = +2, +3, +4, +5$ oxidation states are chosen as the representative ions). The quantitative results obtained from this study are believed to be quite useful not only to understand the internal complexities of the V^{n+} – electrolyte made battery systems (redox flow and solid states) and other M^{n+} (aq.) fluid based electronic technologies but also to visualize the immediate vicinities of the electrochemically active conducting ions, to acquire the aqueous environment of the water dissolved ionic radicals (both in the humid weather as secondary pollutants, and in the medicinal laxative solutions & nutrients enriched with SO_4^{2-}/HSO_4^- ionic species) and the most predominant effects of their dissimilar electronic charges to do so quantitatively, to predict the hydration number (n) owing to the stability of the metal ion aqua complexes $[M(H_2O)_n]^{n+}$, to envision the size of the water–ion clusters ($[SO_4(H_2O)_n]^{2-}/[HSO_4(H_2O)_n]^-$) and their direct impacts on the conductivity rates of the H_2SO_4 (aq.) supporting electrolytes based lead–acid battery systems, to illuminate the kosmotropic & chaotropic behaviors of such type radicals (environmental perspectives), to explain the microstructural arrangements of the real bulk water systems, to get the supportive yet significant information on the proton conduction phenomena of the SO_3^{2-} functionalized ion exchange membranes (such as Nafion), etc. This research paper is structured as: in section 2; computational methods, in section 3; results and discussions, in section 4; summary and conclusions.

II. COMPUTATIONAL DETAILS

The simulation cells (dimensions = $100 \times 100 \times 100 \text{ \AA}^3$) containing (a) neutral H_2O molecules, (b) divalent SO_3^{2-} & SO_4^{2-} ions, and monovalent HSO_4^- ion, (c) bare metal ions with variable oxidation states (in this case, vanadium V^{n+} ($n = +2, +3, +4, +5$), and (d) monohydrated proton (H_3O^+) were constructed as shown in Table 1. The four different specimen sets were

modeled by varying the oxidation states of the V^{n+} ion, but keeping the number of all other ions/ molecules constant. The magnificent images of each set was rendered through the VMD software, and are visualized explicitly. While fixing the number of SO_3^{2-} ions and H_2O molecules in each of the simulation sets, the standard value of the water content; $\lambda = 22$ ($\lambda = \frac{\text{Number of } H_2O}{\text{Number of } SO_3^{2-}}$) [14] of the SO_3^{2-} functionalized Nafion-117 membrane dipped into the liquid water system was seriously referred so that the particles' interactions with the SO_3^{2-} groups can be correlated directly for interpreting its ionic conduction mechanisms in the aqueous electrolyte systems/cells assembly.

Table 1. Number of particles present in each simulation cell

Simulation sets	No. of bare V^{n+} ions	No. of SO_3^{2-}	No. of H_3O^+	No. of SO_4^{2-}	No. of HSO_4^-	No. of H_2O
I	$V^{2+} = 16$	40	24	16	16	856
II	$V^{3+} = 16$	40	24	16	16	856
III	$V^{4+} = 16$	40	24	16	16	856
IV	$V^{5+} = 16$	40	24	16	16	856

The molecular dynamics simulator for each simulation set was designed accordingly, and run the respective iterative computations by implementing the required force-field databases and velocity Verlet dynamics algorithms. The standard MD time-step, length of the trajectory, sampling intervals, output geometry recurring steps, annealing criteria etc. were fixed within the reasonable computational scales. The AMOEBA force field [15(a)] was incorporated programmatically in order to address the non-bonding V^{n+} ions interactions and their polarization effects. Accordingly, the polarizable atomic multipole concepts, flexible three centered water model [15(b)], and the five-interacting-sites models with switching function [16] were embodied into the concerned MD simulator in order to deal with the interactions between the H_2O molecules themselves and with the H_3O^+ ions respectively. While the dynamics simulations of each particle residing in each simulation set were on the fly, no change in number of moles (N), volume (V), and energy (E) of the entire microcanonical systems were ensured; i.e. each simulating ensemble was subjected to attain NVE type by enforcing its total temperature T , total pressure P , total density D , and length of the simulation cell l constants; and each simulation cell was compressed for about 4 ns so as to maintain its equilibrium values of cell dimension ($l = 30\text{\AA}$), total internal kinetic temperature ($T = 300\text{ K}$), and the total cell density ($D = \sim 1.75\text{ g cm}^{-3}$) at standard scale.

The RDF $g(r)$ formulation required to handle the entire MD derived massive datasets of each simulation set and to retrieve the needful physicochemical properties from there was scripted by following the standard C++ programmatic steps outlined below:

- (a) The thickness of the shell dr (Figure 1 and Figure 2) of each concerned simulation cell was picked up programmatically.
- (b) All the values of r that represent the distance between a pair of the particles was looped as per the standard C++ coding format;
- (i) All the particles present in the spherical shell n_B (particles that lie in between the shell of radius r and $(r + dr)$) that surround the reference tagged particle were counted.
- (ii) Total number of the particles n_B were divided by the number of the pairs N_B found in the whole simulating system.
- (iii) Resulting number of the particles was divided by the volume of the spherical shell; $4\pi r^2 dr$ (the surface area $4\pi r^2$ was multiplied by the thickness of the shell dr).
- (iv) Thus obtained number value was divided by the particle number density $\left(\frac{N_B}{V}\right)$.

(v) Lastly, the whole script was checked just to ensure whether $g(r) = 1$ for the datasets without any structures or not.

This RDF script module was implemented computationally, and the RDF $g(r)$ value of each simulating particle was determined over the specific timescale of the MD run prior to plot RDF $g(r)$ as a function of the distance (r) (Å).

III. RESULTS AND DISCUSSIONS

The specific RDF $g(r)$ plots computed through the programmatic scripts over 900 ps of the MD run are shown in Figure 3 to Figure 8 where the inter-particle interactions terms are properly marked in the inset wherever necessary. The unique code letter (mostly the atomic symbol) for each central atom of each simulating particle was given to shorten the description parts associated with the particle distributions and microstructural configurations present around any tagged reference particle such as O_w , H_w , O_h , S_s , V^{n+} , $S_{SO_4^{2-}}$, H_{rad} , S_{rad} , etc. which respectively represent O and H centers of H_2O molecule, O center of H_3O^+ , S center of SO_3^{2-} , variable oxidation states of bare vanadium ($n = +2, +3, +4, +5$), S center of SO_4^{2-} , H and S centers of HSO_4^- radical. To make the writings concise yet comprehensive, each of these symbolic representations is explicitly mentioned in the caption of each Figure as well. The quantitative validations of all the RDF plots derived information are carried out by referring the pre-established experimental and theoretical datasets promptly so that the exact reasons that lie beyond the extensive nominations/applications of this mathematical tool in quantum mechanics based dynamics simulations can be acquired side by side. As shown in Figure 3(a) and Figure 3(b), the RDF plots describing the immediate environment around the reference (tagged) H_2O and H_3O^+ species stand as the most prominent means to elucidate how close these particles approach to each other while existing altogether in their own fluidly mixtures, electrolytic/conducting media, acidic aqueous solutions, atmospheric humid weather (H^+ as a secondary pollutant is released directly into the humid air), and so on. The same demonstrations eventually reveal the typical inter-molecular hydrogen bond (hereafter, H–bond) lengths and inter-nuclear bond distances between the H_2O molecules themselves of the bulk water system plus the networking patterns of the stable hydrated protons such as Zundel $[H_3O(H_2O)]^+$ and Eigen $[H_3O(H_2O)_3]^+$ states. For example, the intense peaks of $g_{(O_w-H_w)}(r)$ at $r_{max} \approx 1.8$ Å, $g_{(O_w-O_w)}(r)$ at $r_{max} \approx 2.8$ Å, and $g_{(H_w-H_w)}(r)$ at $r_{max} \approx 2.4$ Å ensure the experimentally/theoretically recorded typical H–bond distances between the H_2O molecules themselves of bulk water system, unique separation length between the central O atoms of the any two nearby H_2O molecules, and their distinctive inter-hydrogen gap in ultrapure bulk water systems [17]. Additionally, the second intense RDF peaks for them appeared at the respective radial distances $r_{max} \approx 4.1$ Å, $r_{max} \approx 3.1$ Å, and $r_{max} \approx 3.9$ Å envision the three dimensional structural configurations of the H_2O molecules arranged periodically. Similarly, the sharp RDF peaks of $g_{(H_h-O_w)}(r)$ at $r_{max} \approx 1.5$ Å, $g_{(O_h-O_w)}(r)$ at $r_{max} \approx 2.5$ Å, $g_{(O_h-O_h)}(r)$ at $r_{max} \approx 2.3$ Å, $g_{(O_h-H_w)}(r)$ at $r_{max} \approx 3.2$ Å, and so on confirm the *ab initio* derived departing distances between the mentioned central atoms of the Zundel and Eigen ions [17, 18]. These unique radial distances plus other quantitative magnitudes displayed in Figure 3(b) would be the most trustworthy evidence to guaranty that there is the formation of Zundel and Eigen states of proton while the monohydrated forms (H_3O^+ ; the most stable state) undergo rapid conduction (Grotthuss or vehicular type diffusion pathways) across the aqueous fluidly electrolytic media (battery systems). All these pre-established (experimental and theoretically (DFT level)) datasets compatible nanometer ranged quantitative structural descriptions retrieved from the respective RDF plots strengthen the value of the RDF tool significantly, and promote itself for the ample applications in statistical analyses.

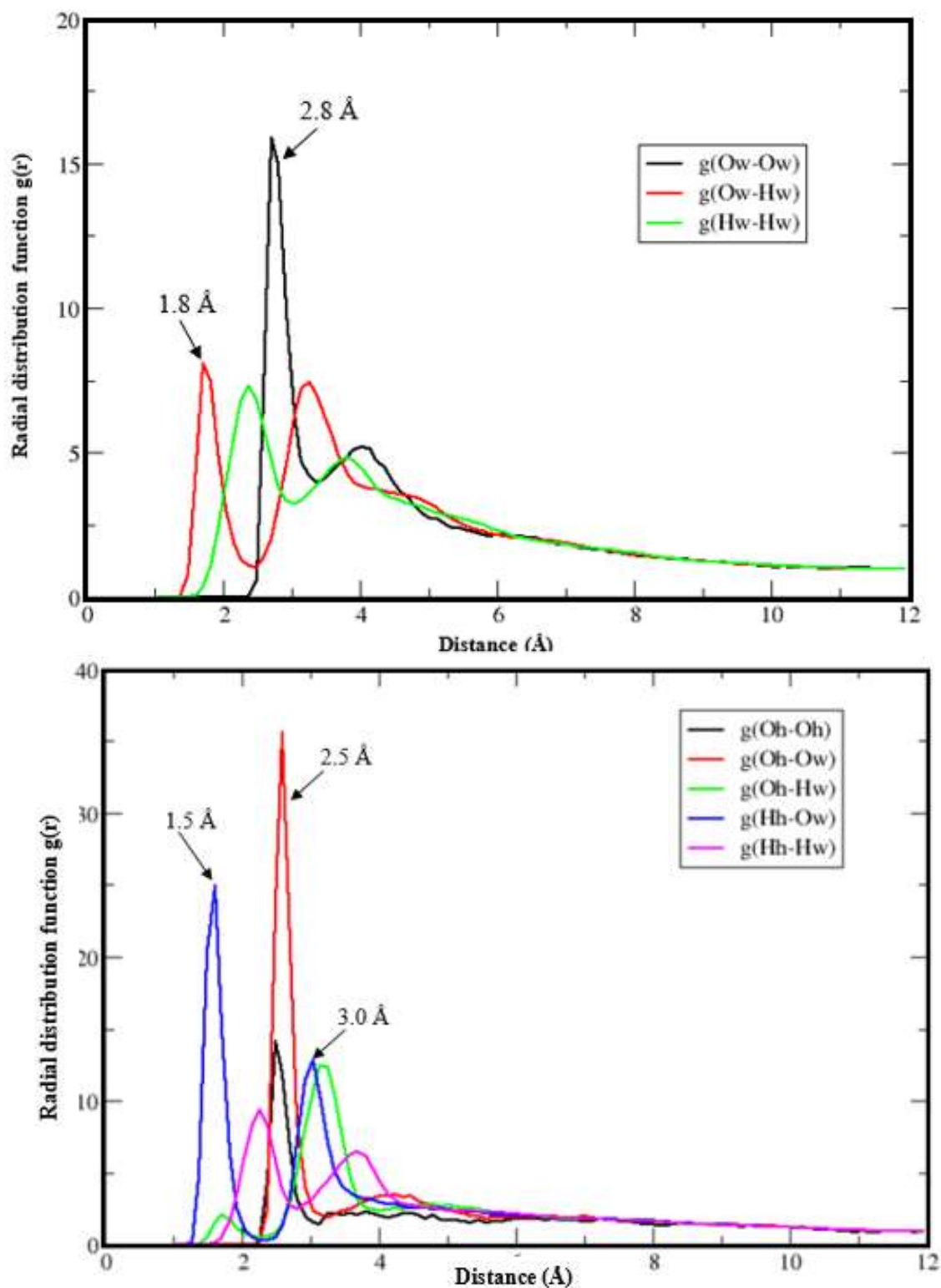


Figure 3. The RDF plots computed over 900 ps of the MD run showing microstructural patterns of (a) bulk water systems (O_w = O atom, and H_w = H atom of the H_2O); (b) aqueous acidic solutions (H_3O^+ = hydronium ion; O_h = O atom, and H_h = H atom of the H_3O^+).

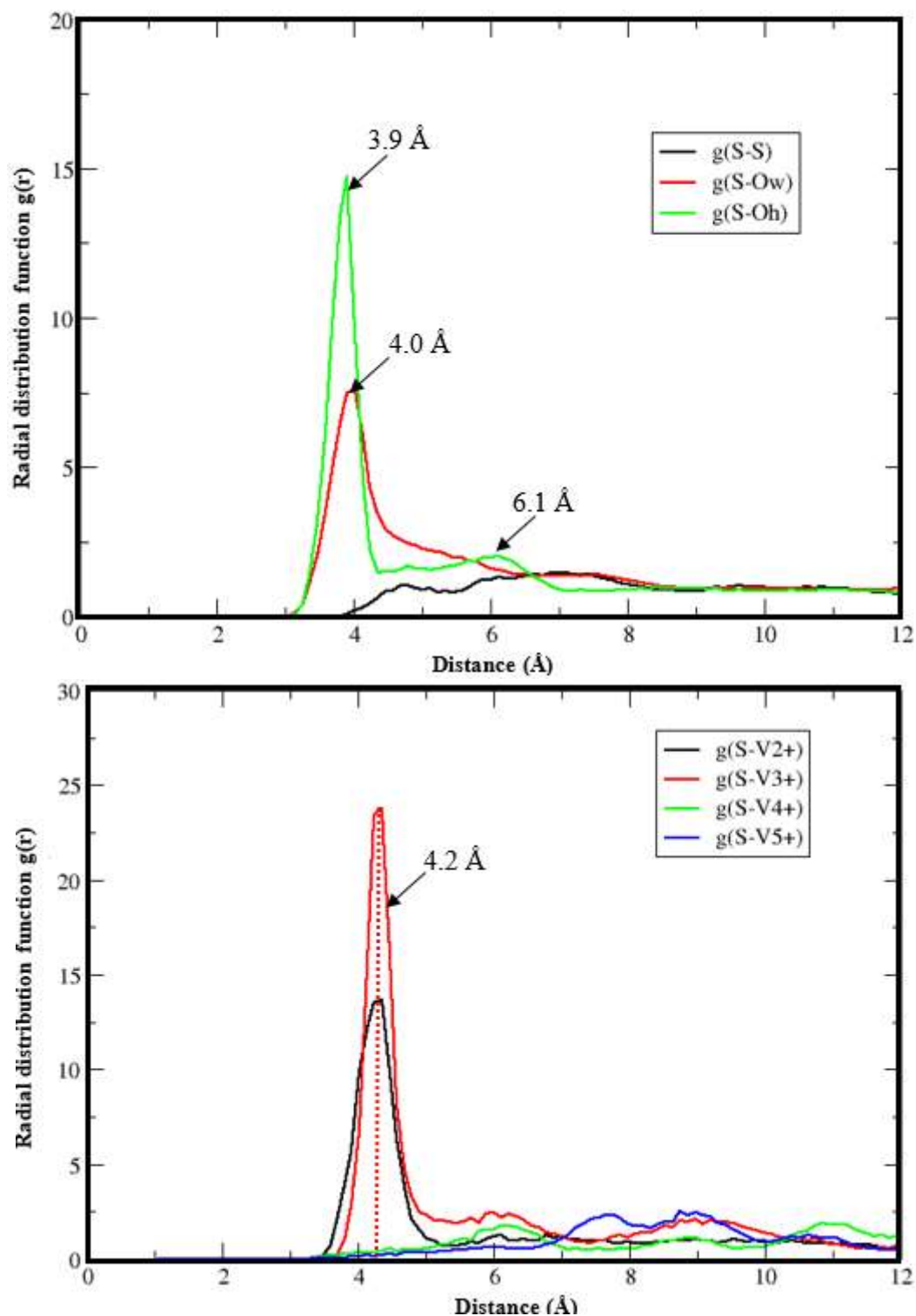


Figure 4. The RDF plots computed over 900 ps of the MD run showing microstructural patterns around any SO_3^{2-} ions (S = S atom of SO_3^{2-} ; O_h = O atom of H_3O^+ , O_w = O atom of H_2O , and V^{n+} = variable oxidation states of bare vanadium).

The statistical descriptions of the H_2O molecules, H_3O^+ ions, and variably charged bare state vanadium ions V^{n+} ($n = +2, +3, +4, +5$) present nearby to the divalent SO_3^{2-} ions can be carried out by the concerned RDF plots shown in Figure 4 (upper

figure). The green colored line for $g_{(S-O_h)(r)}$ shows relatively a narrower peak at $r_{max} = 3.9 \text{ \AA}$, and the sudden appearance of the first minimum at $r_{max} = 4.3 \text{ \AA}$ & the second broader peak at $r_{max} = 6.1 \text{ \AA}$; confirming the presence of dissimilar number density of H_3O^+ ions around the periphery of SO_3^{2-} before and after attaining the nodal state (zero or almost zero value). The red colored line for $g_{(S-O_w)(r)}$ displays a sharp yet relatively broad peak at $r_{max} \approx 4.0 \text{ \AA}$; explaining the most probable position of finding the maximum number density of H_2O around the vicinity of any reference SO_3^{2-} groups, and the comparatively non-zero value even after $4.2 \text{ \AA}$ radial distance elucidates the absence of a nodal region and quantifies the depleting number of H_2O molecules (inhomogeneous distribution) while the radial distances go on increasing. The black colored line showing the diffused type $g_{(S-S)(r)}$ peak for the SO_3^{2-} groups illuminate the existence of enough inter- SO_3^{2-} gaps; unlocking the possibility of residing sufficient number density of free H_2O molecules and the stable hydrated states of proton in between them. The appearance of this wide gap is because of the considerable electrostatic repulsions between the like charges of SO_3^{2-} groups. This RDF derived quantitative information is directly applicable to understand the protons conduction phenomena of the Nafion based polymeric membrane functionalized with the SO_3^{2-} groups because of which only it is extensively used in the modern battery technology comprising with the aqueous electrolyte systems as the major conducting media and the actually promoted carbon composites as the conducting electrodes [7, 19, 20]. Moreover, the micro-distributions of the variably charged V^{n+} ions present around the divalent SO_3^{2-} group are also illustrated diagrammatically in Figure 4 (lower figure) where the sharp RDF peaks for $g_{(S-V^{n+})(r)}$ appeared at $r_{max} = 4.2 \text{ \AA}$ region are clearly marked. These narrow yet intense peaks are explicitly assigned to approximate the number density of V^{2+} and V^{3+} ions gathered nearby to the SO_3^{2-} . The red colored line for $g_{(S-V^{3+})(r)}$ distribution is almost two times more intense than the black colored line sketched for $g_{(S-V^{2+})(r)}$; signifying the presence of more number density of V^{3+} than V^{2+} in the periphery of any reference SO_3^{2-} ions. This is because of the strongest electrostatic attractions created mainly by the +3 unit charge of the former vanadium species than that by the +2 charge unit of latter with the -2 charge unit of SO_3^{2-} group. It is well agreeable to the fundamental law of electrostatics as well: the strength at which two electrostatic charges repel or attract to each other depends directly on the magnitude of the charges bore by them, and the ability of the ions to exhibit significant polarization effects is governed mostly by their higher charges and smaller sizes. But, the RDF peaks for $g_{(S-V^{4+})(r)}$ and $g_{(S-V^{5+})(r)}$ radial distributions are relatively diffused type, *i.e.* no sharp peaks are observed in comparison to that with the $g_{(S-V^{3+})(r)}$ & $g_{(S-V^{2+})(r)}$, and the r_{max} for the diffused peaks seem quite longer than that for the latter species. In fact, the V^{4+} and V^{5+} ions are short representations of their exact oxovanadium ionic forms *viz.* VO^{2+} & VO_2^+ respectively. Therefore, the net electrostatic charge bore by the former and the latter species are +2 and +1 respectively. Despite the nominal charge variations in between them, the crucial roles are played by the O atoms attached to their central V. In either of the species, the negative poles are developed on the O atoms due to the substantial electronegativity differences ($\Delta\chi$) between the V ($\chi_V = 1.63$ in Pauling scale) and O ($\chi_O = 3.44$) which in principle make these ions to maintain a relatively longer gap with the SO_3^{2-} (electrostatic repulsions between the like charges). As a whole, the remarkable variation of the number density of V^{n+} ; $n = 2, 3$ and V^{n+} ; $n = 4, 5$ ions nearby to the SO_3^{2-} group, and their incomparable r_{max} values enlighten the higher propensity of the former set ions than the latter towards SO_3^{2-} . This quantitative information is highly useful to understand the internal distributions of the cations and anions in the periphery of SO_3^{2-} functionalized cation exchange membrane used preferentially in the redox flow battery composites (vanadium redox flow battery technology employs V^{n+} (aq.) as the most active electrolyte ions (cathodic side: V^{4+}/V^{5+} ; Anodic side: V^{2+}/V^{3+}), and the SO_3^{2-} functionalized Nafion as the most suitable cation exchange membrane). Besides these, the intensities of the V^{n+} ; $n = +2, +3, +4, +5$ ions towards attracting the free H_2O molecules (central O atom has two lone pair electrons) present nearby to them are quantitatively explained by the RDF plots displayed in Figure 5 where the quite narrower peaks appeared at $r_{max} \approx 3.0 \text{ \AA}$ are exclusively marked. These peaks in fact tell directly the number density of free H_2O molecules gathered around the vicinity of the dissimilarly charged bare V^{n+} ions; supporting the higher complex forming propensities of the bare transition metal ions (in this case, V^{n+}) even with the neutral type ligands (in this case, H_2O) [21]. This figure further deduces the hydration or the solvation intensities of the V^{n+} ions while dissolving their stable source compounds vanadyl sulfate ($VOSO_4$) salt into the aqueous solutions, and converting their redox species to each other through the redox flow type electrochemical cell. Since the V^{n+} ions in hydrated forms, *viz.* $[V(H_2O)_n]^{n+}$ attain bigger ionic size, the conduction mechanisms governed by them are of course relatively slower. However, no exemption of this complex forming (hydration) tendencies of the V^{n+} ions can be taken into account practically even though several ongoing practices are prevailed. The same is the reason why the vanadium redox flow battery technology is constantly suffering from the "water flooding" problem [7, 19, 20,

22] across the membrane separator. The same RDF plots display the nodal region or the completion site of the first hydration shell of the V^{n+} ions at $r_{max} < 4.0$ Å, and the initiation site of the second hydration shell at $r_{max} > 4.0$ Å along with pointing out the non-zero values of the number density of H_2O molecules in between them. This trend explains the ligand (in this case, H_2O) interchanging/ exchanging features of the transition metal ions in the course of stabilizing their hydrated complexes (the solvation layers remain dynamic rather fully static) [23].

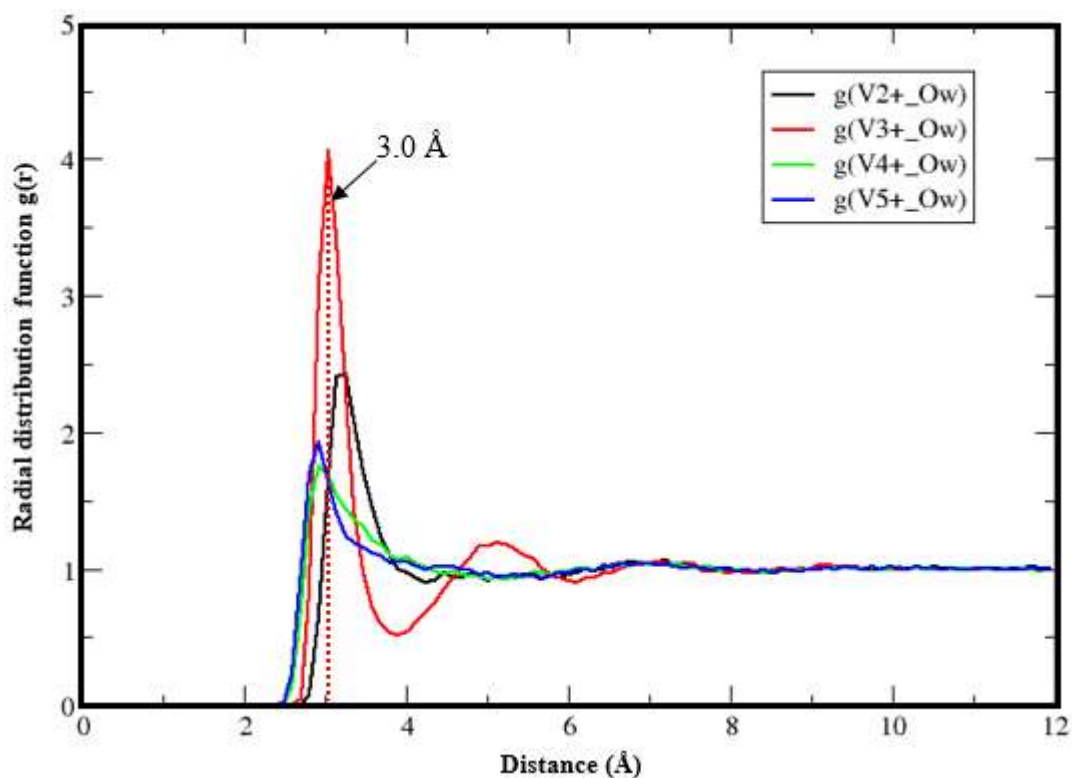


Figure 5. The RDF plots computed over 900 ps of the MD run showing the propensity of the vanadium ions with variable oxidation states towards free H_2O molecules; (O_w = O atom of H_2O , and V^{n+} ($n = +2, +3, +4, +5$) = variable oxidation states of bare vanadium).

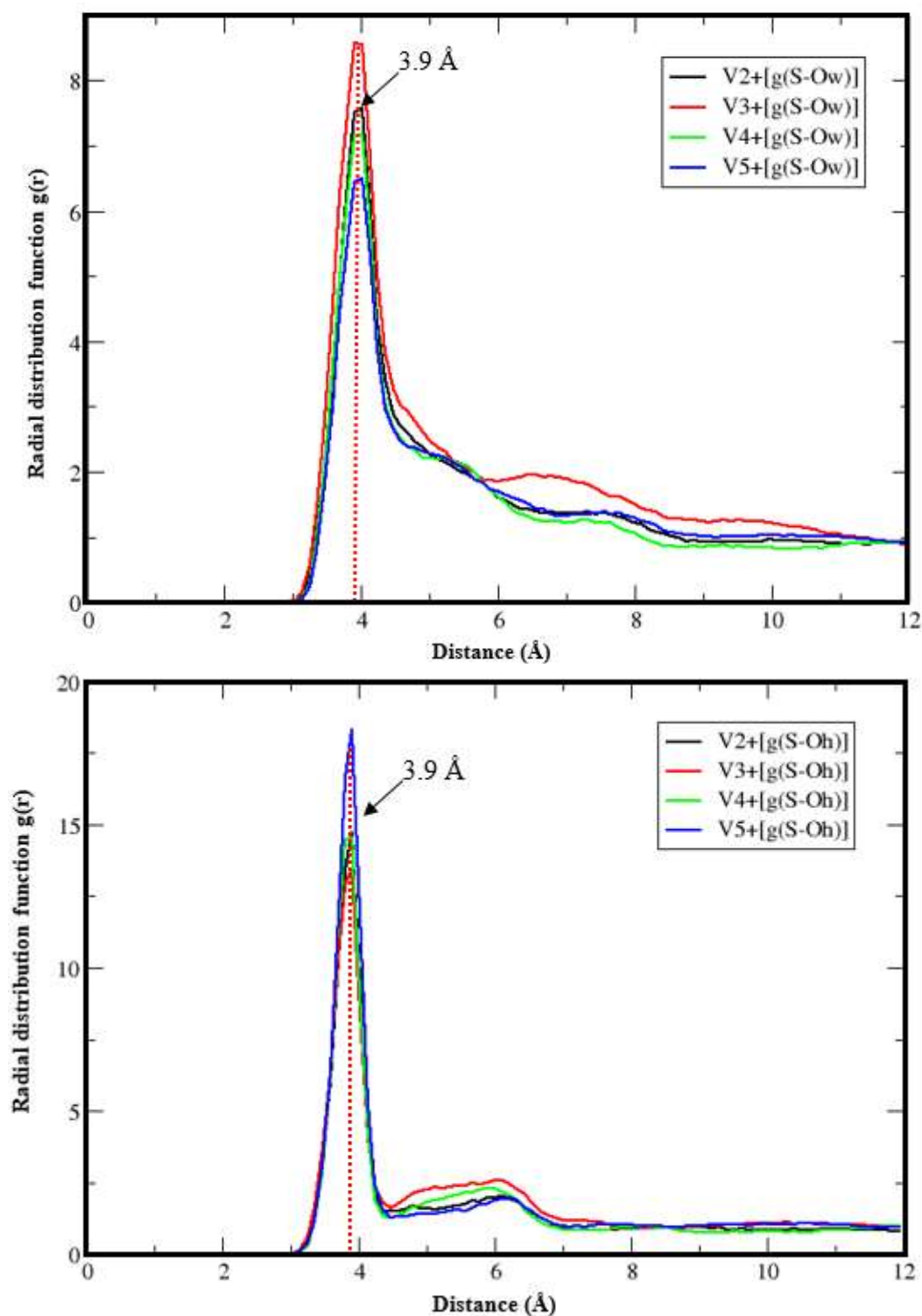


Figure 6. The RDF computed over 900 ps of the MD run showing the immediate environment of (a) water molecules, and (b) monohydrated proton (H_3O^+) around the divalent SO_3^{2-} ion while varying the oxidation states of vanadium V^{n+} consecutively.

The explanations related to the nanometer ranged structural arrangements of the H₂O molecules and H₃O⁺ ions in the

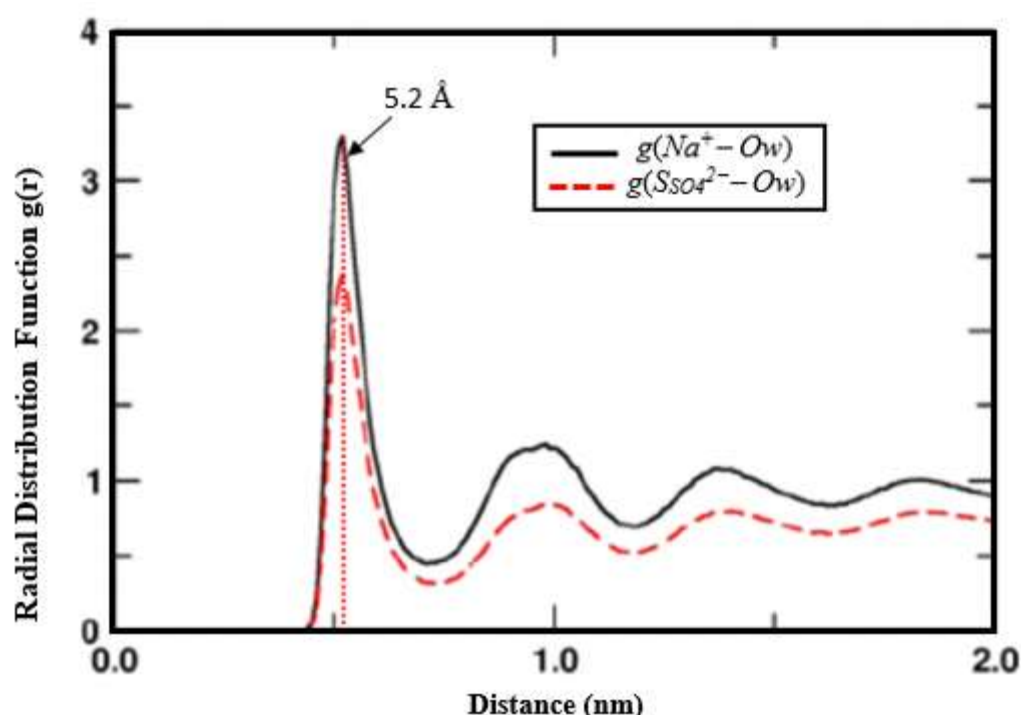


Figure 7. The RDF plots showing an immediate environment of water molecules around the monovalent Na⁺ (solid black line) and divalent SO₄²⁻ (dotted red line) ions (S = S atom of SO₄²⁻; O_w = O atom of H₂O). This figure is reproduced from ref [26] for the comparison purpose as the present MD simulation was unable to derive the concerned datasets produced over relatively longer timescale.

periphery of divalent SO₃²⁻ ions ($g_{(S-O_w)(r)}$ and $g_{(S-O_h)(r)}$) while varying the oxidations states of the vanadium can be retrieved from the corresponding RDF plots shown in Figure 6(a) and Figure 6(b) where the intensive yet narrower RDF peaks are explicitly labeled. In both cases, the concerned peaks are located at $r_{max} = 3.9\text{\AA}$ even while changing the oxidation states of the vanadium from +2 to +5 consecutively. It ensures us that the SO₃²⁻ radical has relatively the highest propensity of exhibiting dissolution/solvation phenomena while dissolving their water soluble compounds in aqueous media, and maintains the closest distance of $\cong 3.9\text{\AA}$ between its central S atom and the central O atoms of H₂O/H₃O⁺ in their solvated/hydrated clusters. It further stresses the fact that none of the ions remain fully non-solvated/non-hydrated while undergoing complete dissolutions into the preferential solvents or the aqueous media. These quantitative interpretations deliver the most essential information required to study the kinetics of oxygen exchange between the SO₃²⁻ ion and water [24], and the characterization of sulfurous acid (H₂SO₃), sulfite (SO₃²⁻), and bisulfite (HSO₃⁻) aerosol systems [25]. Accordingly, the RDF plots assigned to the $g_{(Na^+-O_w)(r)}$ and $g_{(SO_4^{2-}-O_w)(r)}$ radial distributions functions presented in Figure 7 show the intense peak at $r_{max} = 5.2\text{\AA}$; the longer distance than that appeared in the $g_{(S-O_w)(r)}$ and $g_{(S-O_h)(r)}$ plots (Figure 6). This magnitude in distance again underscores the utmost hydration/solvation propensities of the both monovalent Na⁺ and divalent SO₄²⁻ ionic species, and approximates the nearest distance of them with the O center of H₂O in their respective hydrated clusters that are more readily formed while dissolving the sodium and sulfate radicals based ionic salts in the aqueous media [26, 27]. This RDF predicted sulfate-water interactions phenomena are exclusively useful while enquiring the microstructural distributions of the active ions present in the H₂SO₄ supported electrolytic media and in the H₂SO₄ powered entire battery composites such as lead acid battery system technology where different forms of PbSO₄ are produced while discharging it. One can directly apply this radial distribution figures in order to deduce its electrolytic conduction mechanisms: "the hydrated ionic forms of the sulfate [SO₄(H₂O)_n]²⁻ are the most predominant species that undergo internal migration from their high concentration terminal point to the low concentration

terminal point of the battery" [28]. Similarly, the RDF produced sodium ion-water interactions phenomena and their $[\text{Na}^+(\text{H}_2\text{O})_n]$ bond lengths plus the sulfate-water interactions and their $[\text{SO}_4^{2-}(\text{H}_2\text{O})_n]$ distances give insights into the preferential yet deterministic concentrations of the laxative solutions (a sodium sulfate based medicine used to cleanse the bowels) used before conducting the colonoscopy type medical diagnosis [29].

Furthermore, the RDF plot of Figure 8(a) shows an inter-particle gap between the H atom of the HSO_4^- radical and the O atom of the H_2O exceptionally smaller. The concerned peak at $r_{\max} = 1.04\text{\AA}$ is marked in the same Figure. The physical meaning of this $r_{\max}$ lies in estimating the approximate inter atomic gap between $H_{\text{HSO}_4^-} - O_w$ centers while the HSO_4^- radical forms hydrated clusters with the peripheral H_2O molecules [30, 31]. It further means the closeness between the HSO_4^- & H_2O is as equal as that of the SO_4^{2-} & H_2O when they are in their respective hydrated forms; consistent with the DFT derived datasets ($H_{\text{HSO}_4^-} - O_w = 1.7\text{\AA}$ and $O_{\text{SO}_4^{2-}} - H_w = 1.9\text{\AA}$ [31, 27]). These specific descriptions given to their micro-hydrated clusters are quite useful in order to account for the internal ionic compositions of the variably concentrated aqueous H_2SO_4 solutions and of the aqueous electrolytes supported by it as this acid undergoes double ionization schemes due to its dibasic nature, and the proportion of $[\text{HSO}_4^-]$ and $[\text{SO}_4^{2-}]$ ions depend directly on the strength of H_2SO_4 solutions (if $[\text{H}_2\text{SO}_4] (aq.) = 1\text{M}$, the quantitative ratio of $[\text{HSO}_4^-] : [\text{SO}_4^{2-}] = 100\% : 1.3\%$ [27]; and if $[\text{H}_2\text{SO}_4] (aq.) < 1\text{M}$, $[\text{HSO}_4^-]$ goes on decreasing while $[\text{SO}_4^{2-}]$ goes on increasing, and so on). This means the two-step dissociation processes of the H_2SO_4 in aqueous solutions/fluids/electrolytic systems actually act as a potential source of the both $\text{HSO}_4^- (aq.)$ and $\text{SO}_4^{2-} (aq.)$ ions in them whose actual microstructural patterns can be visualized based on the RDF plots shown in Figure 7 and Figure 8(a). The exactly same type ions but $[\text{HSO}_4^-]$ as the most predominant one are also present in the aqueous H_2SO_4 based electrolyte solutions of the lead acid battery and vanadium redox flow battery systems. As shown in Figure 8(b), the close proximity of the variably charged vanadium ions V^{n+} ($n = +2, +3, +4, +5$) to the monobasic HSO_4^- radical is approximately not less than $3.8\text{\AA}$. The first $g_{(\text{V}^{n+}-\text{S}_{\text{rad}})(r)}$ peaks at $r_{\max} \cong 3.9\text{\AA}$ followed by the second peaks at $r_{\max} = 4.5\text{\AA}$ for each ionic state of vanadium genuinely justify the negligible chances of forming inter-nuclear complexes between them. It eventually means no excessive presence of HSO_4^- radicals in the H_2SO_4 supported/based electrolyte systems obstruct the conduction phenomena of the active electrolyte ions and their electrochemical redox reactions proceeding rates significantly if the obvious retardations caused by the inter-particle collisions occurred maximally during the conduction course and the impedance caused by the concerned polymeric membranes are excluded. Meanwhile, the non-zero probability of finding HSO_4^- radicals between the first and second RDF peaks highlight the utmost possibility of undergoing interlayer HSO_4^- ionic exchange readily.

As a whole, the entire quantitative results predicted by the RDF plots and their most relevant discussions plus the frequently referred experimental and theoretical evidences conferred throughout the above paragraphs significantly praise the extraordinary computing skills of the

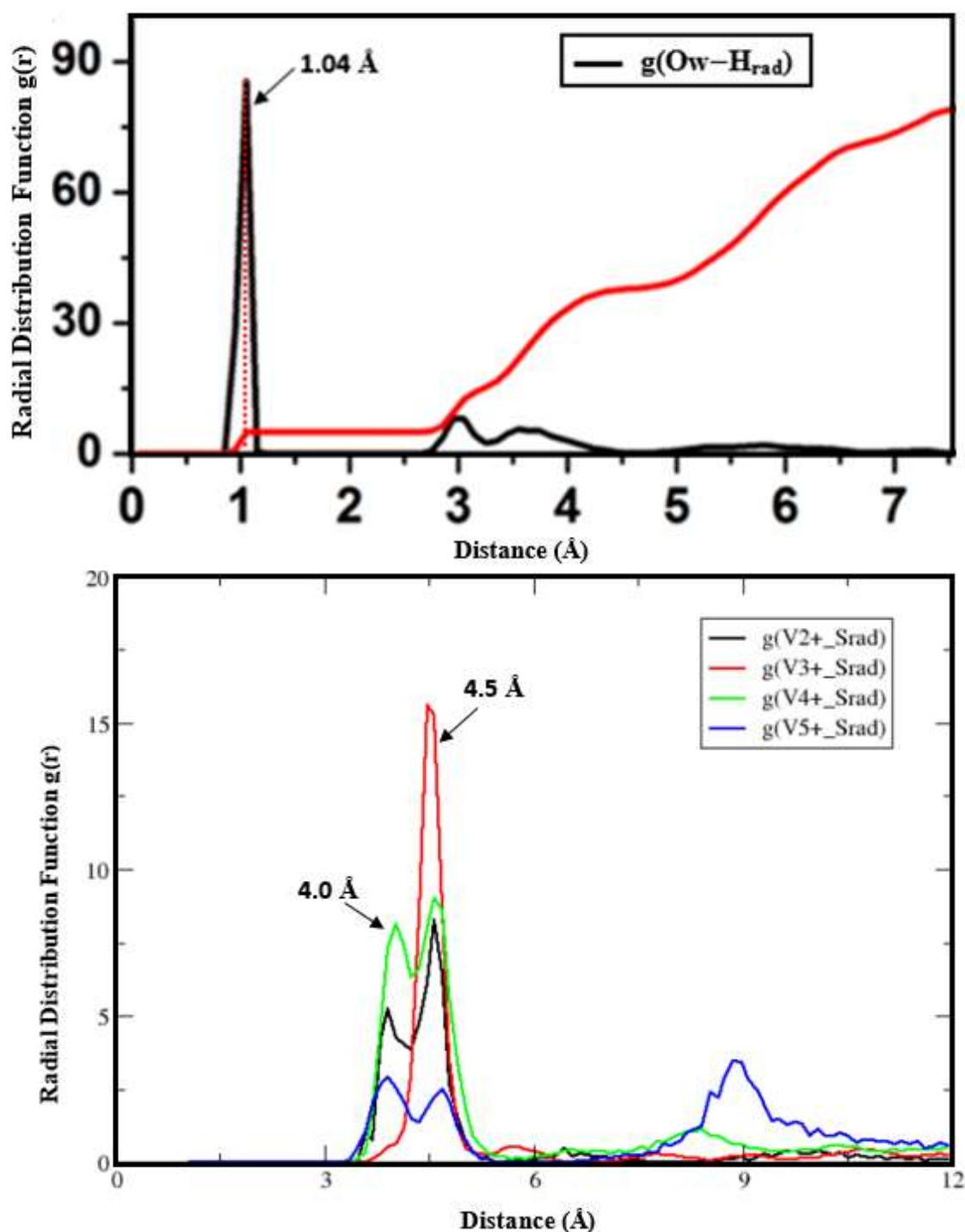


Figure 8. (a) The RDF plots showing the immediate environment of water molecules around the monovalent HSO_4^- ion ($\text{H}_{\text{rad}} = \text{H}$ atom of HSO_4^- radical, and $\text{O}_{\text{w}} = \text{O}$ atom of water molecule). This figure is reproduced from ref [30] for the comparison purpose due to the shortage of MD derived datasets produced over relatively longer timescale. The physical meaning of the red line is omitted here as it displays the RDF peaks derived through the *ab initio* based MD simulation [30]. (b) The RDF plots showing the interactions between the variably charged V^{n+} ions and the S atom of HSO_4^- radical (S_{rad}).

RDF determining mathematical tool. The formulations it undertakes, and the programmatic scripts it adopts for accessing the massive MD derived datasets readily even under the low computational resources make itself to stand as the standalone application. Most importantly, the explicit particles handling abilities and the solo molecules/ions picking programmatic module of this mathematical scheme add substantial values to its rational implementations. In principle, the same low-cost computing features of the RDF tool by incorporating all the needy functions lead itself to remain as the most prevalent yet preferential means of converting microscopic physicochemical properties of the wide ranged simulating systems to the realistic macroscopic properties, and of retrieving the exceptional yet needy characteristics from the human unreadable MD derived geometrical trajectories. These remarkable attributes eventually empower this mathematical tool to act most recognizably and appreciatively than others whom are also in frequent uses for assessing the specific type problems in computational/theoretical science domains.

IV. CONCLUSIONS

Since the worldwide employments of the mathematical models and the mathematical formulations based quantum mechanical schemes for computing large scale MD simulations trajectories are not new to the chemists, the precise evaluations of them and their explicit retrieving as the highly resolved yet mostly accurate human accessible datasets are still considered as a bottleneck. The similar impedances of safe handling of thus derived datasets are present even in the sophisticated experimental domains. The most potential means of resolving the same by acquiring the massive datasets in the human readable format, assessing them directly as per users' needs, and converting the big-data holding microscopic physicochemical properties to the macroscopic one are computationally scripted programmatic codes of the mathematical schemes. The radial distribution function RDF $g(r)$ is a similar type tool that incorporates the quantitative relations between the radial variations of probability of finding any particles (molecule, atom, ion, electron, etc.) around the reference one programmatically, and eases us to assess the massive datasets efficiently even under the low computational resources. In this study, the RDF $g(r)$ defining mathematical formulations were scripted programmatically, and executed the same for inquiring probability density functions of the four different microcanonical ensembles comprising with the specific number of free H₂O molecules, hydrated protons (H₃O⁺), monovalent bisulphate (HSO₄⁻) ion and the divalent sulphite (SO₃²⁻) & sulphate (SO₄²⁻) ions, and the variably charged bare vanadium ions V^{*n*+} (*n* = +2, +3, +4, and +5). This statistical tool was exclusively used mainly to determine the (a) nanometer ranged internal microstructures of the huge water network (bulk water systems), (b) immediate hydration environments of the aqueous divalent SO₃²⁻ & SO₄²⁻ ions, and the monovalent HSO₄⁻ & Na⁺ ions, (c) hydration structures of the monohydrated proton (H₃O⁺) and its most probable stable states, and (d) aqua complex forming propensities of the representative metal ion M^{*n*+} having consecutively varied oxidation states (in this case, vanadium V^{*n*+} ions).

The RDF derived radial distances of $g_{(O_w-H_w)(r)}$ at $r_{max} \approx 1.8\text{\AA}$, $g_{(O_w-O_w)(r)}$ at $r_{max} \approx 2.8\text{\AA}$, and $g_{(H_w-H_w)(r)}$ at $r_{max} \approx 2.4\text{\AA}$ mostly depicted the typical H-bond distance between the water molecules, unique separation length between their central O atoms, and their distinctive inter-hydrogen gap in ultrapure bulk water systems. The sharp RDF peaks of $g_{(H_h-O_w)(r)}$ at $r_{max} \approx 1.5\text{\AA}$, $g_{(O_h-O_w)(r)}$ at $r_{max} \approx 2.5\text{\AA}$, $g_{(O_h-O_h)(r)}$ at $r_{max} \approx 2.3\text{\AA}$, and $g_{(O_h-H_w)(r)}$ at $r_{max} \approx 3.2\text{\AA}$ confirmed the *ab initio* derived bond distances of the Zundel and Eigen states of the protons. The same datasets also ensured us their predominant formations in any aqueous acidic electrolyte systems while the monohydrated forms (H₃O⁺) conduct electricity dynamically with Grotthuss or vehicular type pathways. The RDF plots for $g_{(S-O_h)(r)}$ with a relatively narrower peak at $r_{max} = 3.9\text{\AA}$, and the sudden appearance of the first minimum at $r_{max} = 4.3\text{\AA}$ & the second broader peak at $r_{max} = 6.1\text{\AA}$ illuminated the existence of dissimilar number density of H₃O⁺ ions in the periphery of SO₃²⁻ before and after attaining the nodal state, and the similar plot for $g_{(S-O_w)(r)}$ with a sharp yet relatively broader peak at $r_{max} \approx 4.0\text{\AA}$ explained the most probable region of finding maximum number density of H₂O around the vicinity of any SO₃²⁻ groups. The appearance of the diffused type peak for $g_{(S-S)(r)}$ radial distribution of the SO₃²⁻ groups described the wider inter-SO₃²⁻ gaps which further unlocked the possibility of residing sufficient number density of free H₂O molecules and hydrated protonic states in between them. The micro distributions of the variably charged V^{*n*+} ions present nearby to any SO₃²⁻ group were also illustrated by the sharp RDF peaks assigned for the $g_{(S-V^{n+})(r)}$ at $r_{max} = 4.2\text{\AA}$. These narrower yet intense peaks explicitly approximated the number density of V^{*n*+} ions gathered nearby to the SO₃²⁻ group. Besides these, the RDF plot with sharp peaks for $g_{(V^{n+}-OH_2)(r)}$ at $r_{max} = 3.0\text{\AA}$ quantitatively supported the exceptional complex forming propensities of the bare transition metal ions (in this case, V^{*n*+}) even with the neutral type ligands. Accordingly, the radial distribution functions for $g_{(S-O_w)(r)}$ & $g_{(S-O_h)(r)}$ plotted by varying the oxidations states of V^{*n*+} ions predicted the nanometer ranged statistical configurations of the H₂O molecules and H₃O⁺ ions present nearby to the SO₃²⁻ group plus the higher propensity

of the latter species towards undergoing deterministic dissolutions. And, the RDF plots for the $g_{(Na^+-O_w)(r)}$ & $g_{(SO_4^{2-}-O_w)(r)}$ distributions assigned at $r_{max}=5.2\text{\AA}$ underscored the significant solvation abilities of the both monovalent Na^+ and divalent SO_4^{2-} ionic species. Thus speculated $[Na^+-(H_2O)_n]$ and $[SO_4^{2-}-(H_2O)_n]$ bond distances gave insights into the coordination geometry of these aqua complexes. Moreover, the RDF $g_{(SO_4^{2-}-H_2O)(r)}$ plot for the HSO_4^- and H_2O interactions predicted the radial distance r_{max} at $1.04\text{\AA}$ which readily approximated the inter atomic gap between the $H_{HSO_4^-} - O_w$ centers when they are coordinated to each other in their hydrated complexes of the form $[HSO_4(H_2O)_n]^-$. The closed proximity between the variably charged vanadium ions V^{n+} and the HSO_4^- radical $g_{(V^{n+}-SO_4)(r)}$ was also approximated as $r_{max} \cong 3.9\text{\AA}$ followed by the second strongest affinity at $r_{max} = 4.5\text{\AA}$. This information genuinely justified the superficial bonding complexes of them.

In conclusions, all the RDF produced quantitative results conferred throughout this article are believed to be highly useful and directly applicable to understand the solvation/hydration and dissolution phenomena of the monovalent (Na^+ , and HSO_4^-), divalent (V^{2+} , SO_4^{2-} , and SO_3^{2-}), and polyvalent (V^{3+} , V^{4+} , and V^{5+}) ionic species in their respective aqueous systems such as acid supported electrolytes of the specific electrochemical cells/batteries, humid weathers, acidic/ alkaline solutions, marine ecosystems, medicinal solutions, human body fluids, etc. More particularly, the RDF predicted radial distance/s for (a) Na^+ and SO_4^{2-} ionic hydrations are useful to inspect the practical concentrations of the laxative solutions pivotal to the colonoscopy medical tests, (b) HSO_4^- , SO_4^{2-} , and SO_3^{2-} solvation are applicable to study the kinetics of oxygen exchange between the SO_3^{2-} -ion and water, to characterize the H_2SO_3 , SO_3^{2-} , and HSO_4^- aerosol systems, and to illuminate their kosmotropic & chaotropic behaviors, (c) V^{n+} ionic interactions and the associated interpretations are useful to enquire the conduction rates of the active electrolyte ions and the "water flooding" problems of the redox flow battery systems, (d) SO_3^{2-} interparticle interactions are useful to get insights into the proton migration rates of the SO_3^{2-} functionalized Nafion based proton exchange membranes.

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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