Transport properties of methane, ethane, propane, and n-butane in water

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Transport properties of Methane, Ethane, Propane, and n-Butane in Water

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In this work, we have estimated self diffusion coefficients along with the binary diffusion coefficients of mixtures of alkane (methane, ethane, propane and n-butane) in SPC/E water(H_2O). Molecular dynamics study of a binary mixture of alkane gas and SPC/E water, with alkane as solute and water as solvent, have been carried out at different temperatures ranging from 283.15 K to 333.15 K. We have taken a dilute solution of 3 alkane (methane, ethane, propane and n-butane) molecules and 971 water molecules in a system. The role of interaction in the structure of the constituents of the system as a function of temperature is studied with the help of the radial distribution function (RDF) and the coordination numbers. The self-diffusion coefficient of the constituents of the mixture was calculated by using mean square displacement (MSD) and the binary diffusion coefficients of alkane in water have been calculated by using Darken's relation. The results are then compared with the available experimental values. The values of self-diffusion coefficients of water from the present work come in good agreement with the experimental values within 9% error. The binary diffusion coefficients of ethane, methane, propane and n-butane lie in between the previous experimental values performed by D. L. Wise and G. Houghton, and P. A. Witherspoon and D. N. Saraf. The estimated values lie within 30% error to each of the previously reported experimental values. The dependence of the diffusion coefficients on temperature is approximated by Arrhenius-type exponential relationship.

Keywords: Alkane, Diffusion Coefficient, Molecular dynamics, Coordination numbers, Arrhenius behavior

I. INTRODUCTION

Molecular Dynamics (MD) simulations provide a powerful technique for predicting and understanding the structure, function, dynamics, and interactions of atoms and molecules starting from a simple to complex systems in Physics, Chemistry, Biology and Materials Sciences. These techniques are valued because they provide a movie of what atoms do in real life, assuming a given potential energy function. This serves as a complement to conventional experiments, enabling us to learn something new, something that cannot be found out in other ways[1–6]. MD simulations also can be used to make quantitative predictions of thermodynamic and transport properties, with applications in fields including protein folding, drug discovery, chemical engineering, and nanoengineering[7]. The two main families of computer simulation technique are molecular dynamics (MD) and Monte Carlo (MC); additionally, there is a whole range of hybrid techniques which combine features from both. The obvious advantage of MD over MC is that it gives a route to dynamical properties of the system: transport coefficients, time-dependent responses to perturbations, rheological properties and spectra[1,2]. Alkanes are saturated hydrocarbons that consist

only of the elements carbon (C) and hydrogen (H), where each of these atoms are linked together exclusively by single bonds. The smaller members of the alkane family are gases, while the larger are liquid and solid compounds. First four members (lighter alkanes) of alkane series are methane, ethane, propane, and butane with molecular formula CH_4, C_2H_6, C_3H_8, and C_4H_{10} respectively. Some of the common uses of them are are heating, electricity generation, cooking, production of polymers, serves as intermediate in the synthesis of drugs, pesticides and other chemicals. They are also used as propellants in aerosol sprays and have a number of industrial applications beyond fuels, including uses in cosmetics and plastics[8–12]. Furthermore, the first four memebers of alkanes are also neutral analogs of amino acid side chain. Amino acid side chain analogs represent a natural test case for biomolecular interaction[13,14].

As different species of a mixture move under the influence of concentration inhomogeneity, molecular diffusion occurs. The kinetics of many micro structural changes that occur during preparation, processing and heat treatment of materials include diffusion. The typical examples are nucleation of new phases, diffusive phase transformation, precipitation

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and dissolution of a second phase, homogenization of alloys, recrystallization and thermal oxidation[15]. It plays a vital role in variety of biospheric and atmospheric sciences. Diffusion is basic for transport of matter and for ionic conduction in disordered materials[16,17].

Alkanes are hydrophobic molecules, and as such its solubility in water is rather low, and alaknes molecules tend to aggregate when solvated in water. This behavior is more clearly exhibited by longer n-alkane chains, which may be considered as polymers of methane. The diffusion, solubility or hydrophobicity of hydrocarbons (alkanes) in water is a basic consideration in many processes like processing of natural gases and petroleum, understanding the tertiary structure of proteins, as well as the important role it plays as a driving force in a number of processes occurring within living cells[18–20]. The diffusion coefficients of short n-alkane molecules in water for wide ranges of temperatures and pressures have been repeatedly measured experimentally and from numerical simulations during the last 3-4 decades. The experimental values of binary diffusion coefficients of alkane-water mixture have been obtained by D. L. Wise and G. Houghton in 1966,[21] by using the rate of collapse of small bubbles in gas free water. Also, P. A. Witherspoon and D. N. Saraf in 1965,[22] have been obtained by using the capillary cell method. The binary diffusion coefficients of the two experimental works, obtained by D. L. Wise and G. Houghton[21] are deviated at most 76 % than that as obtained by P. A. Witherspoon and D. N. Saraf[22]. Most recently, V. K. Michalis *et al.*[23] calculated the diffusion coefficients of light n-alkanes in water over a wide range of temperature and pressure by numerical simulation method. The calculated diffusion coefficients agree well to some of the earlier experimental results but these results are forcefield parameter dependent. The authors in[23] have used TraPPE[24] force field for the representation of n-alkane. The TraPPE is a united atom model in which methyl (CH_3) and methylene (CH_2) groups of alkanes are represented as two point particles (pseudo-atoms along the alkane chain connected with bonds of fixed length) and positively charged hydrogen atoms are merged with an electronegative carbon atom in each group. All groups have zero charge and hence Coulomb interactions are excluded. The number of dihedral (or torsion) interaction constants is less and therefore the parametrization becomes simpler. The total energy also becomes lower. This model seems less realistic though it takes the least computational cost. On the other hand, OPLS-AA[25] is an all-atom model for alkane that includes Coulomb interaction and the changes in the distribution of the electron density (due to the po-

lar covalent bonds inside molecules) create non-zero atomic charges. Due to explicit hydrogen atoms, OPLS-AA uses a more complex form of dihedral interaction and there is more steric clashes between hydrogen atoms on neighboring molecules. There is both Coulomb and Lennard-Jones interactions. The Coulomb interaction and the more complicated torsion should give the difference in the physical properties though it needs the more computational cost. All-atom model is more realistic than that of united atom model, so it is better to use OPLS-AA to reproduce and predict transport properties of alkanes[26,27]. Such discrepancies in previous experimental works and forcefield parameter dependent of diffusion coefficients calculated by numerical simulation motivated us to carry out a computational work by different forcefield to study the diffusion phenomena of alkane in water. Our results obtained from simulation also can be used as a crude reference for any further studies of diffusion in complex fluid mixtures and improve our understanding of hydrocarbons and other more complex biological macromolecules in water.

The outline of the paper is as follows: In Sec. II, we discuss the theory of diffusion and method of calculation of diffusion coefficient. Computational details of the our work are stated in Sec. III. Results of the our work are presented in Secs. IV. Our conclusions are collected in Sec. V.

II. DIFFUSION COEFFICIENT

Diffusion is the process by which matter is transported from one part of the system with higher concentration to the another part of the system with the lower concentration as a result of random molecular motion. The driving force of diffusion is thermal motion of the molecules. The higher concentration of a species in a system at a particular site corresponds to its higher value of chemical potential. The net transport of the mass takes place from the region of higher chemical potential to the region of lower chemical potential. At the end of such net transport, the system attains a situation where there exists same value of chemical potential in the system. In this situation, free energy of the system is minimum and hence its entropy becomes maximum; system is at dynamic equilibrium[28]. The response property of a system to a concetration gradient is measured by diffusion coefficient[1]. The diffusion in a homogeneous system where no chemical concentration gradient exists is known as self-diffusion and the corresponding diffusion coefficient is called self-diffusion coefficient[29]. The mathematical expression

to calculate self-diffusion coefficient from molecular positions is famously known as Einstein relation[1,2]. For 3-D system,

$$D = \lim_{t \to \infty} \frac{\langle [\mathbf{r}_\alpha(t + t_0) - \mathbf{r}_\alpha(t_0)]^2 \rangle}{6\,t} \qquad (1)$$

where α denotes the type of component (solute or solvent) and t_0 is any time origin. The angled brackets $\langle \ldots \rangle$ indicate the ensemble average. The ensemble average is taken over all atoms of the component α in the simulation and all time origins[30]. The method using Einstein relation for calculating diffusion coefficients is known as mean square displacement (MSD) method.

In this work, we calculate the self diffusion coefficients of both the components i.e. alkane (methane, ethane, propane, n-butane) and water (H_2O) which can be used to estimate the binary diffusion coefficient using Darken's relation[31]

$$D_{AB} = N_B\,D_A + N_A\,D_B \qquad (2)$$

where D_A, D_B are the self diffusion coefficients of species A and B respectively and N_A, N_B are the corresponding mole fractions.

III. COMPUTATIONAL DETAILS

A. Molecular Models

The SPC/E (simple point charge/extended) potential model[32] is used in all the simulation for water as a solvent. The OPLSS-AA (Optimized Potentials for Liquid Simulations-All Atom) potential model[25] is used for alkanes (methane, ethane, propane, n-butane) as solute. The system under study consists of 3 alkane (methane, ethane, propane, n-butane) molecules and 971 water molecules separately. In classical force fields like OPLS-AA, the potential functions are derived empirically to describe the atomic interactions. The atoms are treated as spherically symmetric particles and are considered to be connected through covalent bonds to form molecules. Each and every atom experiences a force resulting from its pairwise additive interactions with the rest of the system. The total potential energy U_{tot} includes contributions from both bonded and non-bonded interactions[33]. The bonded interactions are bond stretching (2-body), bond angle (3-body) and dihedral angle (4-body) interactions. A special type of dihedral interaction (called improper dihedrals) is used to force atoms to remain in a plane or to prevent transition to a configuration of opposite

chirality (a mirror image). The non-bonded interactions are represented by the Lennard-Jones potential and Coulomb potential. Therefore, the total potential energy function of a system can be written as as[33]:

$$U_{tot} = U_{bonded} + U_{non-bonded}$$
$$U_{tot} = U_{bond} + U_{angle} + U_{dihedral} + U_{LJ} + U_{Coul} \quad (3)$$

The bond stretching between two covalently bonded atoms i and j is represented by harmonic potential[33]

$$U_{bond}(r_{ij}) = \frac{1}{2}k_{ij}^b(r_{ij} - b_{ij})^2 \qquad (4)$$

where k_{ij}^b is the force constant and b_{ij} is the equilibrium bond length between two atoms i and j. The bond angle vibration between a triplet of atoms $i - j - k$ is also represented by a harmonic potential on the angle Θ_{ijk}[33]

$$U_{angle}(\Theta_{ijk}) = \frac{1}{2}k_{ijk}^\Theta(\Theta_{ijk} - \Theta_{ijk}^0)^2 \qquad (5)$$

where k_{ijk}^Θ is the force constant and Θ_{ijk}^0 is the equilibrium bond angle.

The proper dihedral angle is defined by the angle between the ijk and jkl planes. In this study, we have used the following dihedral potential (Ryckaert-Bellmans potential)[33] for alkanes:

$$U_{RB} = c_0 + c_1(1 + \cos\phi) + c_2(1 - \cos2\phi) + c_3(1 + \cos3\phi) \qquad (6)$$

where ϕ is the dihedral angle and c_0, c_1, c_2, c_3 are constants. The bonded parameters for water and alkanes are given in the table (I).

TABLE I. Force-field (bonded) parameters for SPC/E water and OPLS-AA Alkanes. The units of equilibrium bond length (b) and equilibrium bond angle (Θ^0) are nanometer (nm) and degrees (^{o}) respectively. Similarly, the units of k^b, k^Θ and c_i (c_0, c_1, c_2, c_3) are $kJmol^{-1}nm^{-2}$, $kJmol^{-1}rad^{-2}$ and $kJmol^{-1}$ respectively.

SPC/E	k_{OH}^b	345000.0	b_{OH}	0.1000
H_2O	k_{HOH}^Θ	383.0	Θ_{HOH}^0	109.47
	k_{CH}^b	284512.0	b_{CH}	0.1090
	k_{CC}^b	224262.4	b_{CC}	0.1529
OPLS-AA	k_{HCH}^Θ	276.144	Θ_{HCH}^0	109.47
Alkanes	k_{HCC}^Θ	313.800	Θ_{HCC}^0	109.47
	k_{CCC}^Θ	488.273	Θ_{CCC}^0	109.47
Dihedral (Torsional) Potential (Alkanes)				
H-C-C-H	c_0	0.62760	c_1	1.88280
	c_2	0.00000	c_3	−2.51040
H-C-C-C	c_0	0.62760	c_1	1.88280
	c_2	0.00000	c_3	−2.51040
C-C-C-C	c_0	2.92880	c_1	−1.46440
	c_2	0.20920	C_3	−1.67360

The non-bonded interatomic interaction is the sum of Lennard- Jones interaction (U_{LJ}) and Coulomb

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interaction (U_{Coul}), that can be written as:

$$U_{\alpha\beta}(r_{ij}) = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{6}\right] + \frac{q_{i\alpha}\,q_{j\beta}}{4\pi\epsilon_0\,r_{ij}}$$

$$(7)$$

where r_{ij} is the Cartesian distance between the two atoms i and j; α and β indicate the type of the atoms. The non-bonded parameters for alkanes and water is given in the table (II)

TABLE II. Force-field (non-bonded) parameters for SPC/E water and OPLS-AA Alkanes.

	Atoms	σ (nm)	ϵ (kJ/mol)	charge (q)
SPC/E	OW	0.316557	0.650194	-0.8476 e
Water	HW	0.00000	0.00000	+0.4238 e
OPLS-AA	C(CH$_4$)	0.35000	0.276144	-0.240 e
Alkanes	C(CH$_3$)	0.35000	0.276144	-0.180 e
	C(CH$_2$)	0.35000	0.276144	-0.120 e
	H	0.25000	0.125520	+0.060 e

Here OW and HW represent the oxygen and hydrogen atoms of the water molecules respectively and C(CH$_4$), C(CH$_3$) and C(CH$_2$) are the methane, methyl and methylene carbon atoms of the alkane molecules respectively. The parameters for the non-bonded Lennard-Jones interaction between two different atoms for OPLS-AA force field are written as[33]:

$$\sigma_{\alpha\beta} = (\sigma_{\alpha\alpha} \times \sigma_{\beta\beta})^{\frac{1}{2}} \qquad (8)$$

$$\epsilon_{\alpha\beta} = (\epsilon_{\alpha\alpha} \times \epsilon_{\beta\beta})^{\frac{1}{2}} \qquad (9)$$

B. Simulation procedure

MD simulation was carried out in a cubic box with periodic boundary conditions[2] using **GROMACS 4.6.5**[34,35]. The distance to the edge of the box from the solute (alkane) is an important parameter for defining the size of the box. Since we are using periodic boundary conditions, we must satisfy the minimum image convention. That is alknane (solute) should never see its periodic image, otherwise the forces calculated will be spurious. The size of the box defined here is sufficient for just about any cutoff scheme commonly used in simulations. After solvation, addition of 971 water molecules and 3 alkanes molecules in simulation box, energy minimization is carried out with a cut off restriction of 1.0 nm to avoid unphysical van der Waals contact caused by the atoms that are too close[33]. Energy minimization brings the system to equilibrium configuration, removes all the kinetic energy from the system, reduces

thermal noise in structure and brings the system to one of the local minimum. Steepest descent algorithm has been used for energy minimization and the algorithm stops when the maximum of absolute value of force components is smaller than the specified value[33]. The energy (potential) of the system after energy minimization is shown in figure (1).
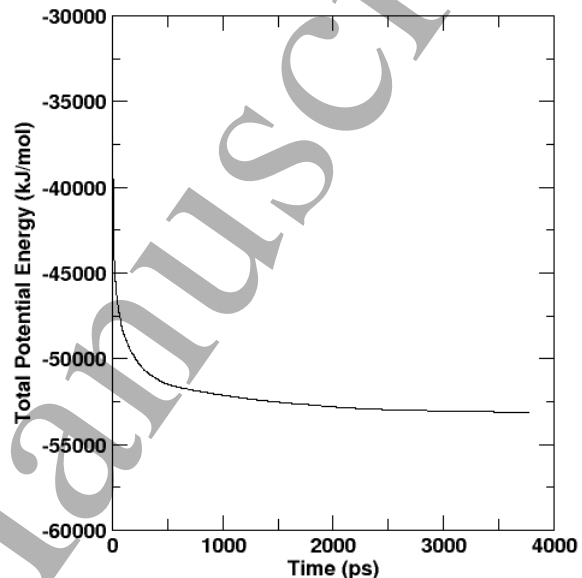

FIG. 1. Plot of potential energy as a function of time after energy minimization for methane-water system.

After energy minimization, isobaric-isothermal (NPT) equilibration was carried out at different temperatures, from 283.15 K to 333.15 K and a pressure of 10^5 Nm^{-2} by using *velocity-rescaling* thermostat[36] and Berendsen barostat[37] at a coupling time $\tau_t = 0.01$ ps and $\tau_p = 0.8$ ps respectively. We used MD integrator[38] with time step size 2 fs for 10^9 steps, which makes equilibration run of 200 ns. The velocity is generated initially according to a Maxwell distribution function at a specified temperature[33]. All the bonds are converted to constraints using SHAKE algorithm[39]. During equilibration short range coulomb interaction and Lennard Jones interaction each with a cut off parameter of 1.0 nm were considered with periodic boundary conditions[2]. The long range Coulomb interaction is handled via the PME (Particle Mesh Ewald) algorithm[40,41] with fourier spacing 0.12. We monitored the temperature, pressure, density, and energy of each studied system to bring it in thermodynamic equilibrium because dynamic property like diffusion coefficient varies with such parameters. The density and simulated temperatures at different coupling temperatures for propane in water are shown

in table (III).

TABLE III. Values of simulated temperature (T_{sim}) and density at various coupling temperatures (T_{co}) of propane-water system.

S.N	(T_{co}) K	(T_{sim}) K	$\rho_{sys}(kg/m^3)$	$\rho_w(kg/m^3)$[29,42]
1	283.15	283.144±0.005	993.834±0.043	998.19
2	293.15	293.152 ±0.010	989.386±0.042	997.30
3	297.95	297.949±0.005	986.872± 0.033	- -
4	303.05	303.050±0.006	984.104±0.029	- -
5	303.15	303.152±0.003	984.051± 0.031	995.61
6	308.25	308.242±0.001	981.093± 0.053	- -
7	313.15	313.153 ±0.007	978.44 ± 0.059	994.20
8	315.75	315.753±0.003	976.435± 0.050	- -
9	323.15	323.142 ±0.003	971.565 ±0.031	992.17
10	333.15	333.152 ±0.006	964.396 ± 0.048	987.99

Table (III) shows that our simulated value of system density is in maximum deviation of around 1% with that of water density. After equilibration run we perform the production run to calculate the equilibrium properties of the system such as diffusion coefficient by fixing the number of particles, volume and temperature i.e. NVT ensemble. We use *velocity-rescale* thermostat for this case. We don't couple the system to a fixed pressure and use the structure obtained after equilibration run by which we fix the volume of the system. The production run was carried out for 100 ns with the time step of 2 fs.

IV. RESULTS AND DISCUSSION

In this section, we discuss the structural and dynamical properties of the constituents of the systems.

A. Radial Distribution Function

Radial distribution functions (RDF) were obtained from the simulations, in order to analyse the local structure around the solute and solvent molecule. Radial distribution function (RDF) gives the idea of distribution of neighboring molecules with respect to the reference molecule considered in the calculations. In periodic systems, RDF shows sharp peaks and troughs up to infinity where the separations and heights are the characteristics of the lattice structure. In liquids however, RDF oscillates up to certain orders and then attains constant value as unity[43]. We have calculated RDF $g(r)$ of oxygen atoms of water molecules $g_{OW-OW}(r)$, oxygen of water and methyl (CH$_3$) and methylene (CH$_2$)

carbons of alkanes (methane, ethane, propane, butane) $g_{C-OW}(r)$.

Figure 2(a) represents the RDF of oxygen atoms of water molecules at different temperatures. For the structure of the water molecule, the centre of mass is practically the same as the oxygen centre, which is also the van de Waals sphere centre. This makes the results for the oxygen atom representative of the whole water molecule. The figure explores three different peaks which implies that the molecules are correlated up to third solvation shell. The value of σ for OW-OW is 0.3165 nm, and the van der Waals radius $(2^{1/6}\sigma)$ is 0.3553 nm[33]. The figure 2(a) shows that excluded region remains fairly independent (0.276 ± 0.002 nm) of changing temperature. It also calculates that the excluded region is smaller than the van der Waals radius which indicates the contributions from other potentials in addition to the van der Waals potential[29] (see Fig.2b). The first peak position remains at the same position within the error of ± 0.002 nm as a function of temperature. The magnitudes of all the peaks in RDFs decrease on rising temperature. Furthermore, the width of the peaks increases on increasing temperature. Both variations are the consequences of excess volume created in the system and the decrease in co-ordination number with increase in temperature. These results show that the movement of the particles enhances and the solvent becomes less structured as temperature is increased. The figures 2 (a) and that of 2 (b)[29] show that Lennard-Jones plus Coulomb potential covers almost entire potential except many body effects. The second peak and third peak positions of the $g_{OW-OW}(r)$ are 0.450 ± 0.002 nm and 0.680 ± 0.002 nm respectively. These results are in good agreement with the available references[44,45]. From the simulations, we found that the RDFs between oxygen atoms of water molecules in different alkane-water system are identical in all respects. It showed that the presence of the solute molecule in an infinite dilution has a negligible effect on the global structure of the solvent.

The RDF between carbon of alkane and the oxygen of water describes solute-solvent interaction. Figure (3) shows the RDF between the methyl (CH$_3$) and methylene (CH$_2$) carbons of the alkanes and the oxygen atom of water, calculated from the simulations at 293.15 K. In figure (3), it can be seen that height of the both CH$_3$ − OW and CH$_2$ − OW peak clearly decrease with increase in the length of the carbon atoms of the alkane. The methyl carbon groups can always approach the water molecule at closer distances (first peak position ∼ 0.38 nm), and the corresponding peaks are systematically more intense than the CH$_2$ − OW for distances under ∼ 0.47 nm. Moreover, the magnitude as well as the excluded re-
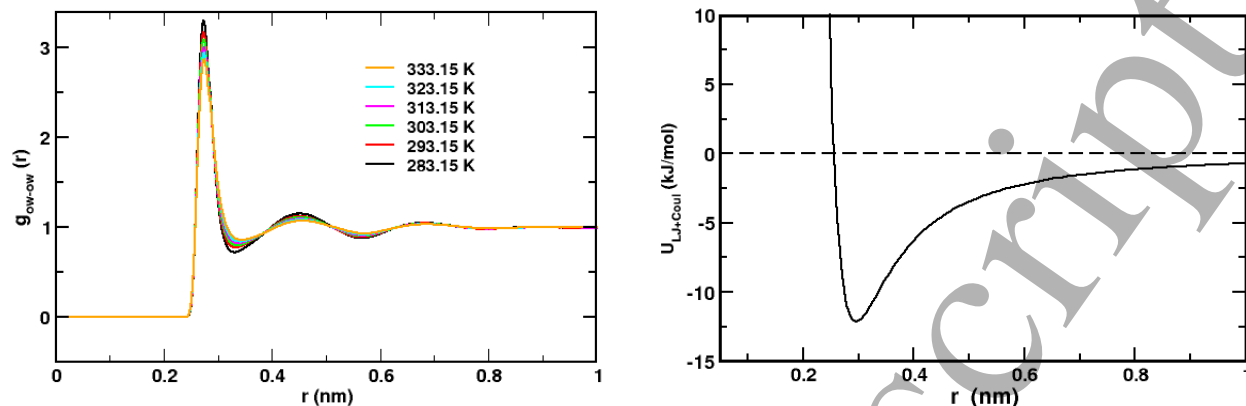
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FIG. 2. (a) RDF of oxygen atoms of water molecules at different temperatures (left) (b) Lennard-Jones plus Coulomb ($U_{LJ+Coul}$) potential as a function of distance for two different isolated water molecules[29] (right)
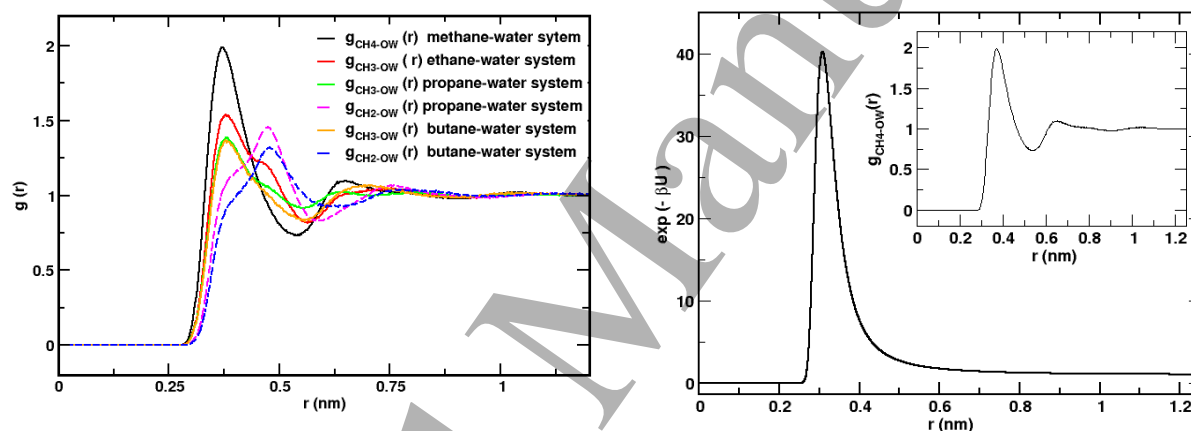

FIG. 3. Radial distribution functions between CH_3 (solid lines) and CH_2 (dotted lines) and oxygen atom of water molecule at 293.15 K.

FIG. 4. Plot of exponential of negative of interaction potential between carbon atom of methane and water molecule at 293.15 K. Inset: g(r) of carbon atom of methane and water molecule at 293.15 K.

gions for g_{CH3-OW} and g_{CH2-OW} are different. This is because methyl and methylene carbon do not possess the same partial charge. Furthermore, when oxygen of water (OW) approaches to methyl carbon, it (or the water molecule) also experiences the interactions due to three hydrogens attached to methyl carbon and when oxygen of water (OW) approaches to methylene carbon, it (or the water molecule) experiences the interactions due two hydrogens attached to methylene carbon. This means when OW approaches to these carbons of alkane, it does not exactly experience the same nature of interaction field around methyl and methylene carbon.

Fig.(4) represents the plot of exponential of negative of Lennard-Jones and Coulomb potential between carbon atom of methane and water molecule as the function of interatomic separation and the corresponding radial distributaion function at 293.15 K. The maximum of $\exp(-\beta U)$ (0.31 nm) and the first peak position (FPP) of the coreesponding radial distribution function (0.37 nm) are diffrent. This shows that Lennard-Jones plus Coulomb potential doesn't cover almost entire potential.

Furthermore, to obtain the number of interaction sites or co-ordination number (N_c) of each type in a coordination shell around the reference site, we have integrated the radial distribution functions (RDFs) as[43]:

$$N_c = \int_0^{r_{min}} 4\pi \ \rho \ g(r) r^2 dr \qquad (10)$$

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Where r_{min} is the radius of the coordination shell (location of the RDF minima) and ρ is the number density. We have estimated the number of sites of a given groups or molecules around another groups or molecules, as a function of the distance from its centre.

In figure (2), for $g_{OW-OW}(r)$, the peak maxima (r_{max}) of the first shell are obtained at 0.276 nm and the minima (r_{min}) at 0.334 nm for all the alkane-water system. The first shell coordination number was found to be 5.3 ± 0.1 for water molecules. These values or the coordination numbers are in good agreement with the available reference values[44,45]. The first shell co-ordination number of water molecules around methyl carbon is $n_H \sim 23$, in agreement with the MAS NMR data[46]. The first cell co-ordination number of water for methylene carbon is greater than that of methyl carbon. Furthermore, to test the solubility of alkanes in water, we have calculated free energy of solvation of methane, ethane, propane and n-butane in water at 300 K. The estimated free energy of solvation for methane, ethane, propane and n-butane in water are 9.08 ± 0.12, 9.02 ± 0.19, 9.61 ± 0.21, and 10.99 ± 0.18 in units of kJmol^{-1} respectively. The values of free energy of solvation follows the same trend as reported by H. S. Ashbaugh et al.[47]. The combination of these effects; RDF analysis, co-ordination numbers of methyl and methylene carbons of alkanes and free energy of solvation of alkanes in water, suggests that the methyl groups of alkane molecules have a preferential tendency to be dissolved in the vicinity of water molecules and that this tendency decreases with chain length. The details of the structural properties with the co-ordination numbers of water molecules around the methyl and methylene carbons of alkane-water system is provided in table IV.

TABLE IV. Strucural paramerters from MD simulaion of alkane-water system at 293.15 K. The positions of the first maxima (r_{max}), first minima (r_{min}), and co-ordination numbers (N_c) in the first shell of the radial distribution functions are presented.

system	groups	r_{max}(nm)	r_{min}(nm)	N_c
CH4-H2O	CH4-water	0.371	0.542	23.11
C2H6-H2O	CH3-water	0.378	0.565	25.49
C3H8-H2O	CH3-water	0.381	0.555	23.18
C3H8-H2O	CH2-water	0.474	0.588	28.52
C4H10-H2O	CH3-water	0.378	0.558	22.22
C4H10-H2O	CH2-water	0.478	0.606	30.14

B. Diffusion Coefficients

The self-diffusion coefficient of alkane (methane, ethane, propane, butane) and water are calculated by using Einstein's relation (MSD method).
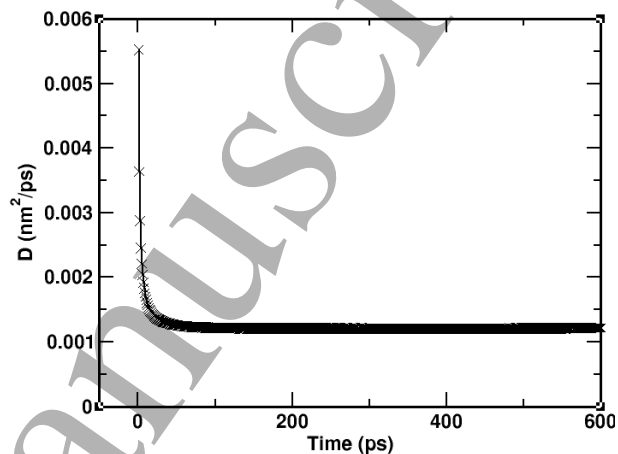

FIG. 5. Plot of Diffusion coefficient (D) $= \langle r^2(t) \rangle / 6\ t$ vs time of ethane at 283.15 K.

The figure (5) shows the variation of diffusion coefficient (D) $= \langle r^2(t) \rangle / 6 * t$ with time for ethane at temperature T $=283.15$ K. In figure (5), at first the diffusion coefficient is high due to ballistic motion and later as time passes it remains constant after 2 ns. This constant portion of the graph gives the diffusion coefficient[29].
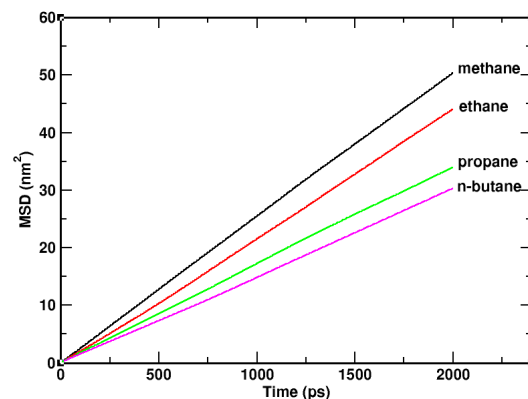

FIG. 6. Plot of mean square displacement (MSD) vs time of alkanes (methane, ethane, propane, n-butane) in water at temperature 333.15 K.
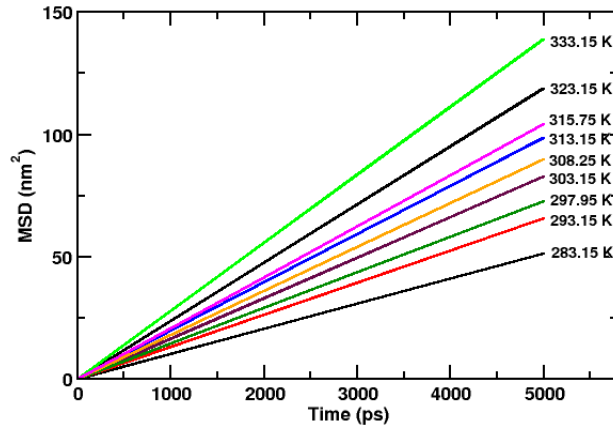
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FIG. 7. Plot of MSD vs time of water at different temperatures.

Figure (6) and figure (7) show the MSD plot of propane and water at different temperatures respectively. The value of self-diffusion coefficients of the desired species is calculated using equation (1). In our case, we have a simulation time of 100 ns and the best statistics for alkane (methane, ethane, propane and n-butane) molecule is found within 2 ns which can also be justifiable from figure (5) and is very small in comparison to simulation time; this is due to lesser number of alkane molecules. For water molecule best statistics is found within 5 ns due to larger number of water molecules. The binary diffusion coefficient of the alkane-water system is estimated using Darkens relation (Eq.2). Our system consists of 3 alkane molecules (methane, ethane, propane and n-butane each) and 971 water molecules, a separate sytem, so the mole fraction for alkane is 0.003 and that of water is water is 0.997. The binary diffusion coefficient is very close to that of self-diffusion coefficient of solute in the mixture due to low solute concentrations studied in this work.

TABLE V. Self-diffusion coefficients of water at different temperatures and the reference experimental values

Temperature (K)	Diffusion Coefficients ($\times 10^{-9}$ m^{2}s^{-1})	
	Simulated Value	Experimental Value[48]
283.15	1.71 ± 0.009	1.54
293.15	2.18 ± 0.006	2.02
297.95	2.43 ± 0.036	–
303.05	2.70 ± 0.008	–
303.15	2.73 ± 0.005	2.59
308.25	3.01 ± 0.040	–
313.15	3.30 ± 0.080	3.24
315.75	3.46 ± 0.092	–
323.15	3.95 ± 0.085	3.96
333.15	4.64 ± 0.120	4.77

TABLE VI. The simulated value of binary diffusion coefficient of alkanes (methane, ethane, propane, n-butane) and also the references for them as a function of temperature are listed.

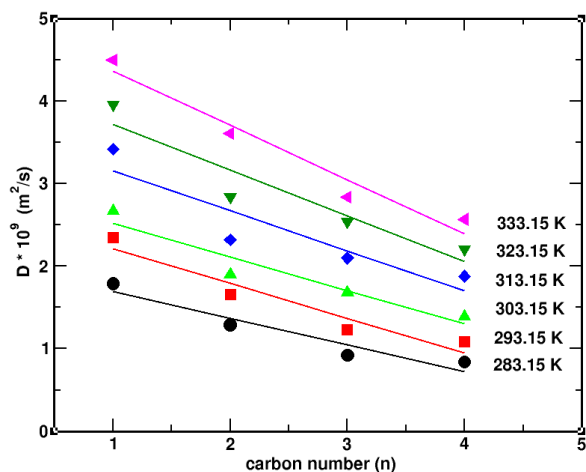|		Diffusion Coefficient ($\times 10^{-9}$ m^{2}s^{-1})		
System	Temp.(K)	Simulation	Expt. (1)[21]	Expt.(2)[22], Expt.(3)[49]
CH4-H2O	283.15	1.79 ± 0.10	1.9	—
	293.15	2.08 ± 0.08	2.4	1.49 ± 0.04 (3)
	297.95	2.35 ± 0.08	—	1.88 ± 0.01 (2)
	303.05	2.56 ± 0.12	—	—
	303.15	2.60 ± 0.06	3.0	—
	308.25	2.80 ± 0.11	—	2.12 ± 0.03 (2)
	313.15	3.34 ± 0.10	4.2	2.38 ± 0.07 (3)
	315.75	3.50 ± 0.08	—	2.41 ± 0.02 (2)
	323.15	3.96 ± 0.12	4.7	—
	333.15	4.36 ± 0.09	6.7	3.55 ± 0.15 (3)
C2H6-H2O	283.15	1.29 ± 0.10	1.6	—
	293.15	1.54 ± 0.11	2.3	1.20 ± 0.06 (3)
	297.95	1.66 ± 0.08	—	1.52 ± 0.03(2)
	303.05	1.89 ± 0.06	—	1.59 ± 0.025 (2)
	303.15	1.90 ± 0.06	2.8	—
	308.25	2.18 ± 0.08	—	1.72 ± 0.02 (2)
	313.15	2.32 ± 0.08	3.3	1.94 ± 0.04 (3)
	315.75	2.45 ± 0.10	—	1.95 ± 0.03 (2)
	323.15	2.84 ± 0.10	4.1	—
	333.15	3.61 ± 0.14	4.9	2.94 ± 0.12 (3)
C3H8-H2O	283.15	0.93 ± 0.08	1.3	—
	293.15	1.23 ± 0.03	1.8	0.97 ± 0.02 (3)
	297.95	1.41 ± 0.08	—	1.21 ± 0.04 (2)
	303.05	1.60 ± 0.08	—	1.27 ± 0.02 (2)
	303.15	1.65 ± 0.07	2.4	—
	308.25	2.81 ± 0.08	—	1.39 ± 0.01 (2)
	313.15	1.97 ± 0.10	2.7	1.77 ± 0.04 (3)
	315.75	2.10 ± 0.06	—	1.59 ± 0.02 (2)
	323.15	2.53 ± 0.10	3.5	—
	333.15	2.85 ± 0.09	4.4	2.71 ± 0.05 (3)
C4H10-H2O	283.15	0.84 ± 0.08	0.83	—
	293.15	1.09 ± 0.09	1.4	0.89 ± 0.04 (3)
	297.95	1.26 ± 0.08	—	0.96 ± 0.04 (2)
	303.05	1.39 ± 0.08	—	1.03 ± 0.04 (2)
	303.15	1.41 ± 0.07	1.9	—
	308.25	1.70 ± 0.10	—	1.12 ± 0.03 (2)
	313.15	1.90 ± 0.08	2.5	1.59 ± 0.04 (3)
	315.75	2.00 ± 0.08	—	1.28 ± 0.01 (2)
	323.15	2.25 ± 0.06	3.3	—
	333.15	2.58 ± 0.10	4.3	2.51 ± 0.05 (3)

FIG. 8. The variation of simulated values of binary diffusion coefficinets of alkanes in water with the numbers of carbon atoms in the alkane chain at different temperatures

Figure (8) shows the variation of binary diffusion coefficients of the molecule with increasing the numbers of carbon atoms of the alkane chain. The diffusion coefficents of the molecules decreases with increasing the number of carbons present in the alkane molecules. Thus, the diffusion coefficients of methane is highest and that of n-butane is lowest among the studied system.
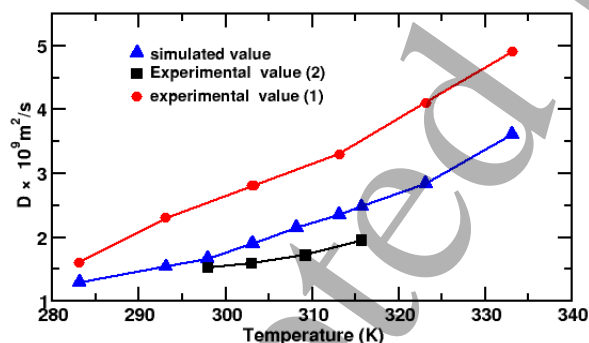

FIG. 9. Simulated and experimental values of binary diffusion coefficients of ethane-water system at different temperatures

The values of self diffusion coefficients of water (H_2O) and binary diffusion coefficients of alkane (methane, ethane, propane, n-butane) in water along with the references at different temperatures are presented in table (V) and table (VI) respectively . The comparison of the values from the tables and also from other references explores that self-diffusion coefficients of water from the present work, in general, come in very good agreement with the previ-

ous studies[29,42,48,50]. The experimental and simulated values of self-diffusion coefficients of water in all system are in good agreement with maximum deviation of 11% at 283.15 K[48]. The simulated values of alkane, on the other hands, show different attitude towards the references[21–23,49]. They lie very well in between the experiment performed by (1) D. L. Wise and G. Houghton[21] and (2) P. A. Witherspoon and D. N. Saraf[22]. Figure (9) is the comparision of simulated values with the experimental values[21,22] of binary diffusion coefficients of ethane-water system at different temperatures. They lie very well in between the experimental values[21,22] within the error of 33%. The deviations of the simulated values with the experimental values follows the same trends in all alkane-water system. There are very large differences in the values of the binary diffusion coefficients reported by them[21,22]. The diffusion coefficient for both the solute (alkane) and solvent (water) molecules increases with the enhanced temperature, which is due to the increase in the velocity of the molecules, as per relation of the thermal energy with temperature. Moreover, as the density of the system decreases with increasing temperature, the space available for the alkane molecules to execute random-walk motion increases[50]. Finally, based on these facts, the mean squared displacement increases and this change is incorporated by Einsteins relation to yield an increased self-diffusion coefficient.

C. Temperature dependence

Diffusion coefficients of a system generally depends strongly on temperature, being low at low temperatures and are found to be increased with increase in temperature. Temperature variations in diffusivity is explained by the Arrhenius formula[15].

$$D = D_0 \exp\left(-E_a/R\,T\right) \tag{11}$$

which can be expressed as

$$lnD = lnD_0 - E_a/R\,T \tag{12}$$

where, D_0 denotes the pre-exponential factor, also called frequency factor, E_a is the activation energy for diffusion, T is the absolute temperature, $R = N_A\,k_B$ is molar gas constant whose value is is 8.31 J mol^{-1}K^{-1}. Both E_a and D_0 are called the activation parameters of diffusion. The simulated binary diffusivities of table (VI) have been fitted to Arrhenius-type expression equation (12) by least squares method, the pre-exponential constant D_0 and the activation energy E_a are reported in table (VII).

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TABLE VII. Table for Activation energies and pre-exponential factors for diffusion of various studied system .

system	E_a (kJ mol^{-1})	$D_0 \times 10^7 m^2/s$
CH4-H2O	15.13	7.00
C2H6-H2O	16.18	11.86
C3H8-H2O	17.81	18.67
C4H10-H2O	18.38	22.63
H2O	15.59	13.12

FIG. 11. Arrhenius diagram of the simulated and experimental value of water.

Figure(10) shows the temperature dependence of diffusion coefficient of alkane in water. As the simulation data fit to the equation (11), the temperature dependence of diffusion coefficient follows Arrhenius behavior. From figure (10), it is seen that the diffusion coefficients increase with increase in temperatures. This could be due to the fact that at higher temperature the difference in the density of the system (i.e. alkane and water) and water increases with increase in temperature (see table (III)). Figure (11) shows the temperature dependence of diffusion coefficient of water in the system containing water and alkane. Figure (11) explicitly shows the temperature dependence of diffusion coefficient of water also follows Arrhenius behavior.
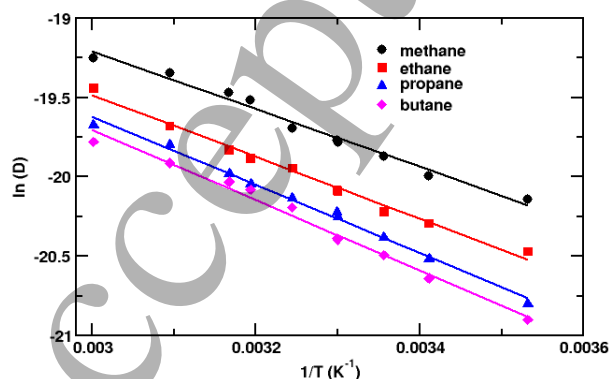
V. CONCLUSIONS

In this work, we have computed self diffusion coefficients along with binary diffusion coefficients of the system containing 971 water (H_2O) molecules and 3 alkane (methane, ethane, propane, n-butane) molecules over a wide range of temperatures from 283.15 K - 333.15 K, using molecular dynamics simulation technique. The Extended Simple Point Charge (SPC/E) model of water and Optimized Potential for Liquid Simulations- All Atom (OPLS-AA) of alkane were used. Here alkane molecule acts as a solute and water (H_2O) as a solvent. Prior to the production run for the calculation of structure and transport properties, we monitored the temperature, energy, density of the studied system during equilibration to know the equilibrium state of the system.

Structural properties has been studied using radial distribution function (RDF) and co-ordination number of the interaction cites has been calcualted integrating RDF to the first co-ordination shell. The obtain RDFs show that the system becomes less structured at high temperatures. The equilibrium structural properties of both the components (alkane and water) were studied calculating corresponding radial distribution function (RDF) namely $g_{OW-OW}(r)$ RDF of oxygen atoms of water molecules, $g_{CH_3-OW}(r)$ RDF of carbon atom of methyl group of alkane and oxygen atom of H_2O , $g_{CH_2-OW}(r)$ RDF of carbon atom of methylene group of alkane and oxygen atom of H_2O.

The main aim of our work was to study diffusion phenomenon of the mixture of water and alkane and study its temperature dependence. The self-diffusion coefficients of water and alkane (methane, ethane, propane and n-butane) was estimated using Einstein's method separately. The diffusion

FIG. 10. Arrhenius diagram of the simulated values of binary diffusion coefficients of alkane in water.

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coefficients of water are deviated within 11% of the available experimental data. The binary diffusion coefficient of the system was calculated using Darken's relation. The values of binary diffusion coefficients of alkane in water do not agree well with the previous experiments. values . It lies in between these two experimental values of D. L. Wise and G. Houghton and P. A. Witherspoon and D. N. Saraf and the deviation is increasing with increase in temperature. The Arrhenius diagram (plot of natural logarithm of diffusion coefficient vs inverse of temperature) was plotted for self-diffusion coefficients of water and binary diffusion of the alkane-water system separately and it showed temperature dependence of diffusion coefficient of

both are of Arrhenius type.

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