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**DEPARTMENT OF CHEMICAL AND BIOMOLECULAR
ENGINEERING**

**“DETERMINATION OF DIFFUSION COEFFICIENT, DENSITY
AND VISCOSITY FROM METHANOL-WATER MIXTURE
USING METHANOL WATER MIXTURE”.**

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DECEMBER 5, 2019**

1. Introduction

Molecular Dynamics (MD) simulations are some of the most useful tools for the investigating molecular fluids behavior under various conditions and more complex biological systems. Due to breakthroughs in computing power like parallel computing, quantum computing and so on, a very large range of the simulation experiments can be reached. These gives us a way to connect macroscopic properties by to the microscopic properties and also validate theoretical models to better understand things at the atomistic level [1, 2].

These computations typically take much more computer time than classical thermodynamic models (i.e. from a few hours to several weeks of computing time, depending on system size). In industrial applications molecular simulation helps in estimating and developing properties of unknown chemicals, extreme conditions of temperature or pressure, and toxic compounds. The first part of this article provides a brief description of Molecular dynamic simulation and how it can be analyzed for approving experimental data. Later in the report, different properties of the system will be calculated with molecular dynamic simulation. The key underlying issues for accuracy are adequate configurational sampling and the quality of the description of the intermolecular energetics. The estimated properties are then compared with available experimental data and theoretical models.

2. Method

2.1- Why molecular dynamics method?

It is not possible to observe directly, phenomena that occur on the atomistic scale so we need a way to tell the story of the atoms as they move in space and time. In molecular simulations, molecules are allowed to interact for a fixed period of time, giving a view of the dynamic "evolution" of the system. In the most common versions, the trajectories of atoms and molecules are determined by numerically solving Newton's equation of motion for a system of interacting particles, where forces between the particles and their potential energies are often calculated using interatomic potentials or molecular mechanics force fields [3]. The equations solved are:

$$F_i = -m_i r_i \quad (1)$$

Where:

$$F_i = -\partial U / \partial r_i \quad (2)$$

$$r_i = d^2 r_i / dt^2 \quad (3)$$

Where F_i is force acting on particle i , r_i is Acceleration of particle i and m_i is mass of particle i . The force acting on each atom is obtained from a potential function U , such as that depicted below [4]:

$$U = \sum \frac{k_{ij}^b}{2} (r^{ij} - r_{eq}^{ij})^2 + \sum_{angle} \frac{k_{ij}^\theta}{2} (\theta^{ij} - \theta_{eq}^{ij})^2 + \sum_{dihedrals} k_{ij}^\phi [1 + \cos(n(\phi - \phi^{eq}))] + \sum_{i < j} [\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}] \quad (4)$$

Where the first three terms reflect intramolecular interactions between covalently bonded atoms and the last term describes the non-bonded interactions (van der Waals and electrostatic). The constants k^b , k^θ , and k^ϕ are force constants for the covalent bonds, bond angles, and dihedrals, respectively, r_{ij} are the distances between atoms i and j, A_{ij} and B_{ij} are the Lenard Jones parameters, and q is a partial charge [4]. An ensemble is typically used to estimate the properties of a real system. It is a very large number of systems, each constructed to be a replica on the macroscopic level. Ensemble averages of most average of dynamic property (A) can be gotten from:

$$\langle A \rangle = \sum_i A_i p_i \quad (5)$$

Where A_i is the value of A in quantum state i, p_i represents the probability of observing the i-th state, and the angled brackets denotes an ensemble average. The time averaged and the ensemble average are related by the Ergodic hypothesis which is as follows:

$$A_{t \rightarrow \infty} = \langle A \rangle \quad (6)$$

2.2- Relationship to physical properties

Transport effects on microscopic scale usually have the highest effects on the properties of most chemical and biological systems and this is one of the major reasons why we perform simulations. Transport properties like diffusion coefficient, shear viscosity, partial density and pressure can be estimated directly from an MD simulation as it is not possible to observe them directly [5,6]. To get the self- diffusion coefficient D_α^S of component α , you take the slope of the mean square displacement (MSD) at a long period of time using the Einstein equation. You can also calculate it by evaluating the integral of the velocity autocorrelation function using the Green-Kubo equations:

$$D_\alpha^S = \frac{1}{2dN_\alpha} \lim_{t \rightarrow \infty} \langle \sum_{i=1}^{N_\alpha} (r_i^\alpha(t) - r_i^\alpha(0))^2 \rangle \quad (7)$$

$$D_\alpha^S = \frac{1}{dN_\alpha} \int_0^\infty \langle \sum_{i=1}^{N_\alpha} v_i^\alpha(t) v_i^\alpha(0) \rangle dt \quad (8)$$

The shear viscosity and electrical conductivity can also be estimated using:

$$\eta = \frac{V}{Vk_B T} \int_0^\infty \langle \sigma_{XY}(t) \sigma_{XY}(0) \rangle dt \quad (9)$$

$$k_e = \frac{1}{3Vk_B T} \int_0^\infty \langle j_e(t) j_e(0) \rangle dt \quad (10)$$

Where η is shear viscosity, k_e is the electrical conductivity, σ_{XY} is the pressure tensor of the components. k_B is the Boltzman's constant and T is the temperature of the system.

2.3- LAMMPS Software

LAMMPS is a classical molecular dynamics code with a focus on materials modeling. It's an acronym for Large-scale Atomic/Molecular Massively Parallel Simulator. LAMMPS has potentials for solid-state materials (metals, semiconductors) and soft matter (biomolecules, polymers) and coarse-grained or mesoscopic systems. It can be used to model atoms or, more generically, as a parallel particle simulator at the atomic, meso, or continuum scale. LAMMPS development began in the mid 1990s under a cooperative research & development agreement (CRADA) between two DOE labs (Sandia and LLNL) and 3 companies (Cray, Bristol Myers Squibb, and Dupont).

LAMMPS integrates Newton's equations of motion for collections of atoms, molecules, or macroscopic particles that interact via short- or long-range forces with a variety of initial and/or boundary conditions. For computational efficiency LAMMPS uses neighbor lists to keep track of nearby particles. The lists are optimized for systems with particles that are repulsive at short distances, so that the local density of particles never becomes too large. On parallel machines, LAMMPS uses spatial-decomposition techniques to partition the simulation domain into small 3d sub-domains, one of which is assigned to each processor. LAMMPS molecular dynamics code contains several algorithms and force fields that have been developed over the years [8].

3. Result and Discussion

3.1-System definition

LAMMPS software is most efficient (in a parallel sense) for systems whose particles fill a 3d rectangular box with roughly uniform density. The system is defined by its size and shape, the number and types of molecules it contains, and the coordinates and velocities of all atoms. In this study MD simulation was carried out on a mixture of mixture of methanol and water to examine some physical and transport properties. This system consists of 600 molecules of water and 85 molecules of methanol. LAMMPS was used for the MD calculations. Simulation was performed using OPLS-UA [8] force field for 200 ps. Moltemplate was used to generate input files for the simulation which consisted of initial coordinates, bonds, angles, dihedrals and so on. The simulations were performed at four different temperatures 273, 283, 288, 293 k under atmospheric pressure using the microcanonical ensemble (NPE). Lenard-Jones parameters and partial charge for methanol molecule is seen in Table 1. Water molecules are modeled as TIP4P water model with their related parameters [11].

3.2- Diffusion coefficient of the methanol in the mixture

As the first step, diffusion coefficient of methanol molecules in a mixture of methanol-water has been studied by MD method. VMD was used to visualize the motion of the molecules and calculate the mean diffusion coefficients [10]. Diffusion coefficients of the mixture was also calculated. The calculated results of the diffusion coefficient were compared to the values gotten from the Wilke- Chang equation [14]. Results are shown in Table 1 and Fig 3:

$$D_{AB} = \frac{(117.3 \times 10^{-18})(\varphi M_B)^{1/2} T}{\mu V_A^{0.6}} \quad (11)$$

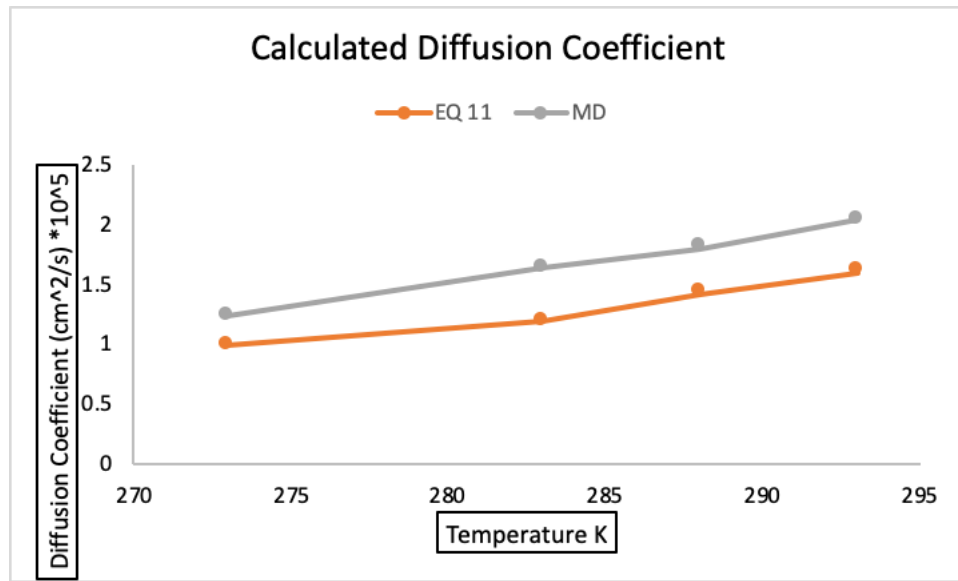


Figure 1. The effect of temperature on diffusion coefficient.

The available experimental data for diffusion coefficient of methanol in water are shown in Table 2 [14]. The averaged error between MD results and experimental value is about 12%, while this is about 10% between experimental value and Eq.11.

Temperature (K)	Diffusion coefficient by MD (cm ² /s)	Diffusion coefficient by Eq. 11 (cm ² /s)	Experimental value [11]
273	1.22 * 10 ⁻⁵	0.98 * 10 ⁻⁵	-
283	1.62 * 10 ⁻⁵	1.18* 10 ⁻⁵	-
288	1.81*10 ⁻⁵	1.42* 10 ⁻⁵	1.56 * 10 ⁻⁵
293	2.01*10 ⁻⁵	1.60* 10 ⁻⁵	1.80 *10 ⁻⁵

Table 1. Calculated Diffusion Coefficient of Methanol in Water by MD method

3.3- Density

The density of the mixture was also calculated at different temperatures and points in the box using the density profile tool developed in VMD by Toni Giorgino and they are shown in Table 2 and Fig. 2 [19]. The corresponding results can be seen in Table 2 and Fig. 2. The error between experimental [14] and calculated results is less than 1% which shows a good agreement.

Temperature (K)	Cal. Density (kg/m ³)	Exp. Density (kg/m ³) [11]	Error %
273	934.10	928.70	0.0057
283	927.27	922.10	0.0056
288	915.26	918.50	0.0037
293	916.54	915.60	0.0008

Table 2. Calculated and experimental density in different temperatures

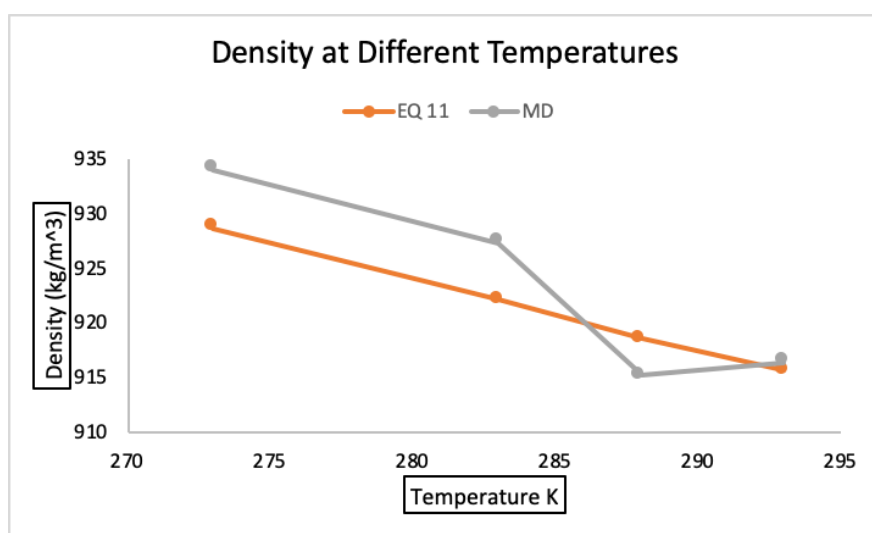


Figure 2. The effect of temperature on density for methanol-water mixture

3.4- Shear viscosity

Viscosities are calculated from the interactions of the molecules in microscopic scale. The calculated viscosities were then compared with experimental data. From Table 4 and Fig. 3, it is seen that viscosity decreases by increasing temperature, the same as experimental values.

Temperature	273 K	283 K	288 K	293 K
MD Calculated value	1.27	1.07	0.95	0.71
Experimental value [13]	1.06	0.9	0.85	0.74
Error %	17.8	14.3	8.6	4.23

Table 4. Average calculated and experimental viscosity of the methanol-water mixture

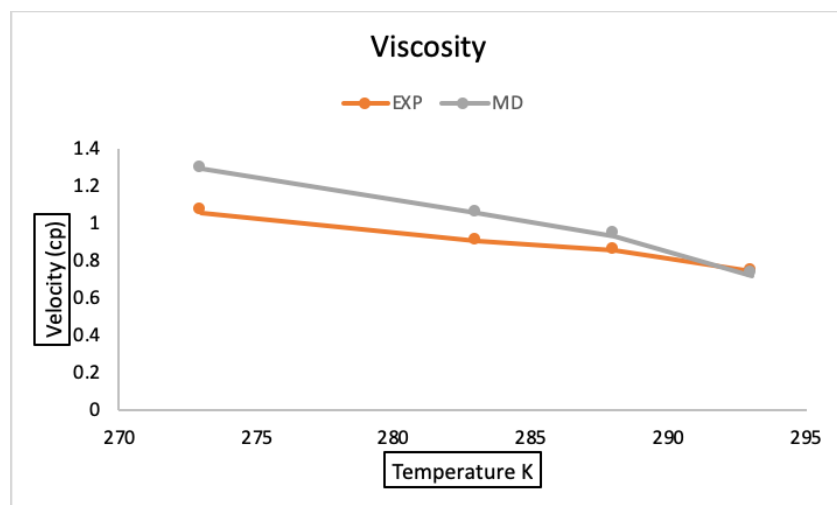


Figure 3. Viscosity of the methanol-water mixture at different temperatures

4. Conclusion

It has been shown using theoretical models and experimental data that MD simulations provide a very neat alternative to calculate density, shear viscosity, hydrogen bonding and diffusion coefficient for the mixture of methanol-water. LAMMPS software was used for this purpose. The simulation was performed up to 200 ps. The results show that the calculated diffusion coefficient is in good agreement with those obtained from the Wilke-Chang equation, both of which were approved by experimental data. The diffusion coefficient in all cases discussed increases linearly with temperature.

Density and Viscosity are also affected by temperature as it generally decreases with temperature with a decreasing deviation between MD and experimental data. MD is generally more reliable at higher temperatures. Overall, the results show the reliability of the MD method to calculate the physical properties of the systems. One can conclude that, this method may be used to determine the macroscopic properties of the systems, instead of practical methods in the laboratory.

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