

Molecular Dynamic Simulation of Heat Capacities and Diffusion Coefficients as a Function of Temperature of Triatomic Molecules

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ABSTRACT

A molecular dynamic simulation has been performed using GROMACS in a LINUX platform, to study the heat capacity and diffusion coefficients of three tri-atomic molecular systems namely, water $\text{H}_2\text{O}(l)$, sulphur dioxide $\text{SO}_2(l)$ and nitrogen dioxide $\text{NO}_2(l)$ as a function of temperature. The simulated & experimental values of heat capacity for $\text{SO}_2(l)$ agreed well with a percentage error of the difference between the two being less than 0.05%. Heat capacity for $\text{NO}_2(l)$ when compared with the heat capacity of $\text{NO}_2(g)$, it is observed to be twice the value. This trend is observed in heat capacities of $\text{H}_2\text{O}(l)$ and $\text{SO}_2(l)$ as well. At low temperatures, the simulated graph showed similar variations to experimental and theoretical values obtained for the diffusion coefficient of $\text{H}_2\text{O}(l)$. Since, no literature data is found on heat capacity and diffusion coefficient of $\text{NO}_2(l)$ and diffusion coefficient of $\text{SO}_2(l)$, the present results could be considered as new findings.

1 INTRODUCTION

Heat capacity is a basic thermodynamic property, which could be used to characterize a liquid. It is directly linked with temperature derivatives of other basic thermodynamic functions and is therefore indispensable for calculation of differences in these functions between different temperatures. This invaluable information is widely used in Physics and Chemistry for establishing energy balances in thermodynamics for obtaining entropy and enthalpy values, and for calculating changes in reaction enthalpies with temperature. Since the knowledge of the heat capacities is also required for evaluating the effect of temperature on phase and reaction equilibria, variations in heat capacities serve as a sensitive indicator of phase transitions and are an important tool for understanding changes in the structure of liquid solutions.

In present work, a Molecular Dynamic (MD) simulation has been done in Linux platform using GROMACS (Groningen Machine for Chemical Simulations) to model triatomic liquid systems namely water (H_2O), sulphur dioxide (SO_2) and nitrogen dioxide (NO_2). The simulation is analyzed using the supplementary programs, RASMOL and GRACE [1]. The heat capacities and diffusion coefficients of these liquid systems are simulated as a function of temperature. For the simulation the number of molecules, pressure and temperature are fixed and therefore the set of systems obtained are canonical ensembles.

2 METHODOLOGY

2.1 Simulation box

In this study the size of the simulation box is chosen to be a size that contained 729 molecules of the required element. The simulation box is defined using the protein databank file (pdb), which is used to specify the coordinates of the entire molecular system. The pdb is created for the systems using a simple FORTRAN program 'mklts' (make lattice).

2.2 The molecular models used

Water is simulated using the extended single point charge model (SPC/E) given in GROMACS is adopted. The SPC/E is the simple point charge (SPC) model of water at 25°C with a few changes in parameters which improves effective pair potential, leading to better values for the diffusion coefficient and configurational energy which includes a self polarization energy correction [2]. It is a reparameterization of the single point charge (SPC) model for water [3]. New models for SO₂ and NO₂ were created. The basic data such as bond length, atomic mass and dipole moment is obtained [4]. The force constants of the molecules, although calculated, are not used as the rigid bond constraint is implemented. The charge distribution among its constituent atoms is calculated using the dipole moment of the molecule. The epsilon and sigma values for the Lennard-Jones (LJ) potentials needed to be adjusted to fit each model. The density of the system at equilibrium is taken as the comparing property. The epsilon and sigma values are adjusted until the volume of the output is close to the calculated volume for the 729 molecule system which gives the correct density. This was done using trial and error and the values which fitted best were taken. The epsilon and sigma for the S-O and N-O interactions is calculated using the Lorentz-Bertelot rules [5].

2.2 The simulation

The simulation is conducted in a specified period of time (say t) in which the coordinates of each molecule are recorded at small intervals of time (say Δt). Then a $t/\Delta t$ number of macroscopically identical but microscopically different systems are obtained. Each system is simulated for 2 ns at each temperature in four phases of 500 ps each. Using a function called g_energy [5], the total internal energy and volume of the system at the end of each simulation phase is obtained. The pressure is obtained from the log file of the run due to the property being constant. The obtained values of the total internal energy and the volume from each phase are averaged giving three values of total internal energy for the system, at each temperature. These three are averaged to calculate the final value for total internal energy and its standard deviation. Following this the enthalpy at each temperature is calculated and plotted against the temperature. The derivative of this curve is used to plot the heat capacity as a function of temperature. They are then compared with available literature values. The diffusion coefficients are also obtained for these simulations done at the same temperatures using GROMACS commands.

2.3 Calculations

Enthalpy of each system was calculated as a function of temperature by using, $H = U + PV$, where U is the average internal energy, V is the average volume and P is the externally set pressure of the system in L atm (simulation is NPT ensemble). The average internal energy: $U = 1/3(U_2 + U_3 + U_4)$ where U_2 , U_3 and U_4 are average internal energy of the system for second, third and fourth 500 ps blocks of the trajectory. Similarly, V the average volume was also calculated. Since the units of volume is in nm^3 and the pressure in atm units, a converting factor; 0.06023, was used to obtain the enthalpy in kJ/mol units. That is, $H = U + 0.06023PV$. Statistical errors were also calculated in standard manner. After calculating enthalpy of the system at different temperatures, the enthalpy values were fit into a 3rd order linear polynomial of temperature which gives, $H = a_0 + a_1T + a_2T^2 + a_3T^3$

With the above analytical function of enthalpy as a function of temperature, it was straight forward to evaluate heat capacity of the system as a function of temperature, by simply taking the derivative of H with respect to T , as $C_p = (dH/dT)_P$ which gives, $C_p = a_1 + 2a_2T + 3a_3T^2$

Diffusion coefficients of $\text{H}_2\text{O}(l)$, $\text{SO}_2(l)$ and $\text{NO}_2(l)$ were also evaluated using `g_msd` suit of GROMACS software package [5] as a function of temperature. These data also were fit to a fourth order polynomial of temperature, $D = d_0 + d_1T + d_2T^2 + d_3T^3 + d_4T^4$

3 RESULTS AND DISCUSSION

Table 1 depicts the coefficients of the functional form of the variation of enthalpy as a function of temperature and the heat capacity as a function of temperature for all three tri-atomic molecular systems considered in this research. Since the coefficients a_3 for $\text{SO}_2(l)$ and $\text{NO}_2(l)$ were too small they not included in the Table 1.

Table 1 Enthalpy as a third order polynomial function of temperature, $H = a_0 + a_1T + a_2T^2 + a_3T^3$ J mol⁻¹ K⁻¹, for molecular systems of $\text{H}_2\text{O}(l)$, $\text{SO}_2(l)$ and $\text{NO}_2(l)$

Molecular system	a_0	a_1	a_2	a_3
$\text{H}_2\text{O}(l)$	-58418	-8.112	2.819×10^{-1}	-3.300×10^{-4}
$\text{SO}_2(l)$	-34670	89.11	-1.308×10^{-2}	-
$\text{NO}_2(l)$	-32752	57.62	3.054×10^{-2}	-

3.1.1 Heat capacity of water

The heat capacity of $\text{H}_2\text{O}(l)$ obtained from the simulation results was compared with the experimental data [6] and are illustrated in Figure 1. The Figure1 shows that the calculated heat capacities are almost parallel to the experimental heat capacities indicating the same variation of the heat capacity at lower temperatures. The relatively large discrepancy of $15 \text{ J mol}^{-1} \text{ K}^{-1}$, may attribute to the calculation of electrostatic energy using spherical cut off method.

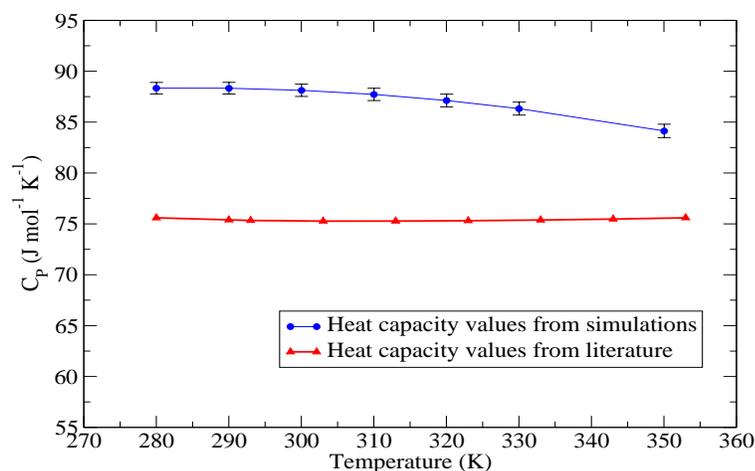


Figure 1 Heat capacity vs temperature of water

3.1.2 Heat Capacity of Sulphur dioxide

The Figure 2 shows both simulated and experimental heat capacities of $\text{SO}_2(l)$ as a function of temperature. The percentage error of the difference between the simulated and experimental values of heat capacity is less than 0.05%.

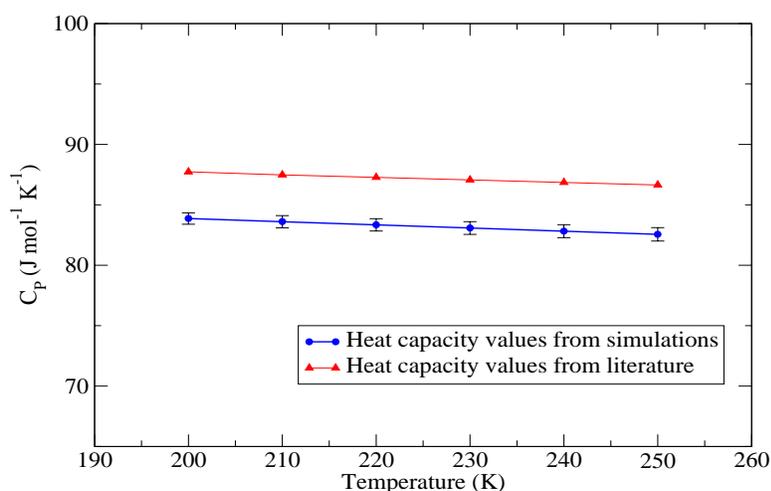


Figure 2 Heat capacity vs temperature of sulphur dioxide

The heat capacity against temperature plot for $\text{SO}_2(l)$ is found to be very close to a straight line with a negative gradient. The experimental literature values [7] obtained for the heat capacity of $\text{SO}_2(l)$ agrees well with the observed results apart from being slightly lower throughout by a constant value. The gradient of the experimental function obtained matched very well with the literature values. The small inaccuracies in the potential parameters (epsilon and sigma values of L-J potentials) could result in a slight deviation of the values.

3.1.3 Heat Capacity of Nitrogen Dioxide

Figure 3 shows the heat capacity as a function of temperature for $\text{NO}_2(l)$. An average rise in the heat capacity could be seen in $\text{NO}_2(l)$ unlike in $\text{SO}_2(l)$. The experimental research conducted on $\text{NO}_2(l)$ are very limited and experimental heat capacity values could not be found suggesting that the calculated heat capacity function is a novel result.

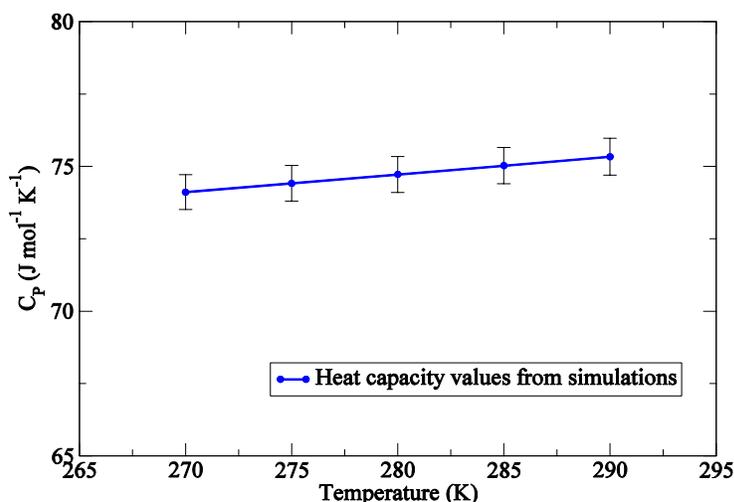


Figure 3 Heat capacity vs temperature of nitrogen dioxide

It can be seen that the gaseous phase heat capacity (C_p) values of $\text{H}_2\text{O}(g)$ and $\text{SO}_2(g)$ are approximately half of their average heat capacity values in the liquid phase, i.e. $\text{H}_2\text{O}(l)$ and $\text{SO}_2(l)$. This same trend is observed in NO_2 as well (Table 2). Using this trend as a viewpoint, it maybe argued that the values obtained for NO_2 in the simulation are fairly accurate.

Table 2 The comparison of heat capacities in liquid and gaseous phase for molecular systems of H_2O , SO_2 and NO_2

Tri-atomic molecular systems	C_p ($\text{J mol}^{-1} \text{K}^{-1}$) in gaseous phase	C_p ($\text{J mol}^{-1} \text{K}^{-1}$) in liquid phase
H_2O	34	87
SO_2	39	83
NO_2	36	74

According to Zabransky and Ruzicka, a substantial amount of important compounds still exist for which no experimental heat capacity data have been measured [8]. Authors state that there also exist many compounds for which the measured values of heat capacities are old, inaccurate or have been measured only at one temperature (mostly at room temperature, 298 K). The method used in this experiment can be utilized to study these compounds with ease.

3.2 Diffusion Coefficient as a function of temperature

Table 3 depicts the coefficients of the functional form of the diffusion coefficient as a function of temperature for all three tri-atomic molecular systems considered in this research.

Table 3 The diffusion coefficient as a fourth order polynomial function of temperature $D = d_0 + d_1T + d_2T^2 + d_3T^3 + d_4T^4$ J mol⁻¹ K⁻¹, for molecular systems of H₂O(*l*), SO₂(*l*) and NO₂(*l*)

Molecular systems	d_0	d_1	d_2	d_3	d_4
H ₂ O(<i>l</i>)	2820.6	-36.155	0.17335	-3.6862×10^{-4}	2.9378×10^{-7}
SO ₂ (<i>l</i>)	578.84	-10.24	0.067921	-1.9936×10^{-4}	2.1951×10^{-7}
NO ₂ (<i>l</i>)	323170	-4636	24.933	-0.05958	5.3376×10^{-5}

At low temperatures, the simulated graph (Figure 4) shows similar variations to experimental values [9] and theoretical values calculated using the Wilke and Chang equation [10] obtained for the diffusion coefficient of H₂O(*l*).

The theoretical values seem to deviate from the simulation values at higher temperatures. The diffusion coefficient values for SO₂(*l*) and NO₂(*l*) could not be compared with experimental values, as they were not available for the temperature ranges considered in the simulation. Experimental study of the self-diffusion of these molecules in the liquid phase has been limited, possibly due to the temperatures being in the super cooled region. Therefore, the obtained values from the simulation could be considered as novel results.

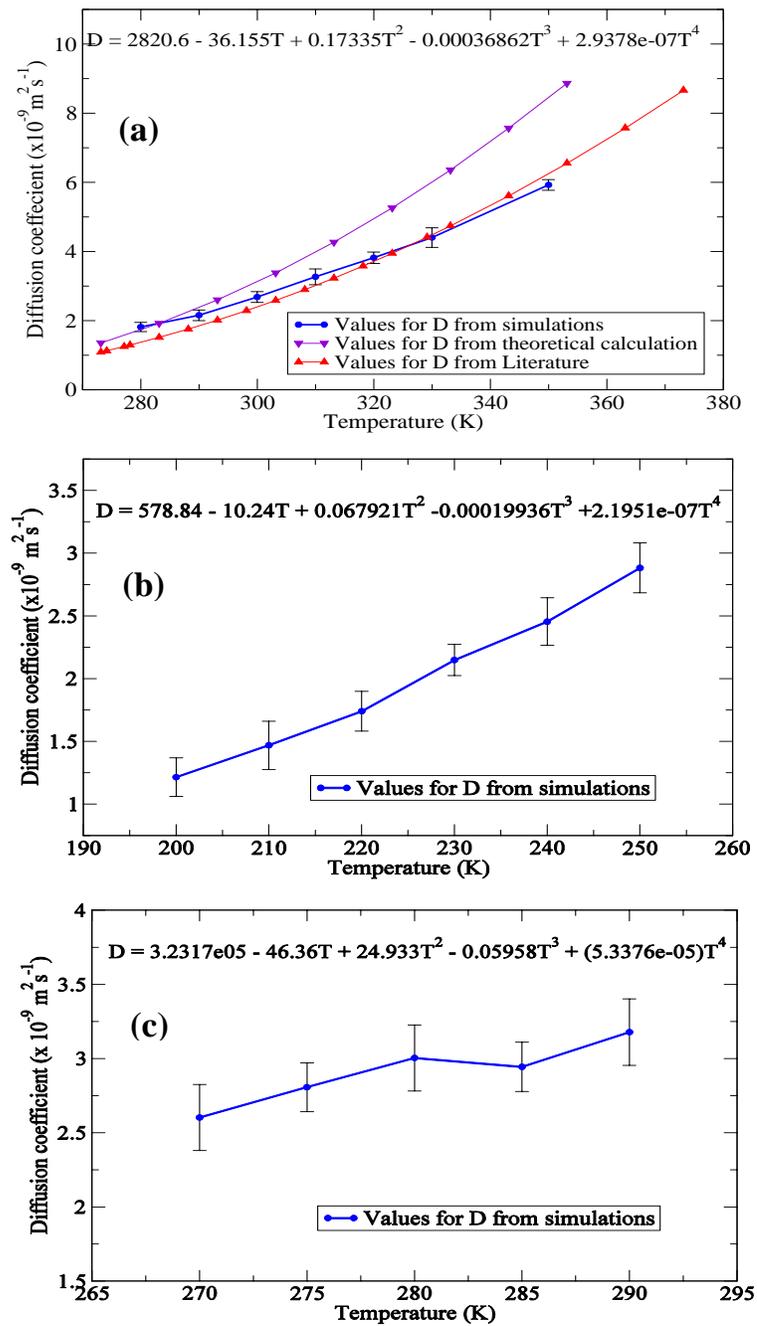


Figure 4 Diffusion coefficients (D) plotted against temperature for tri-atomic molecular systems of (a) $H_2O(l)$ (b) $SO_2(l)$ and (c) $NO_2(l)$

4 CONCLUSIONS

MD computer simulations using GROMACS have been utilized with a great degree of success to study the heat capacities and diffusion coefficients of tri-atomic molecular systems of $\text{H}_2\text{O}(l)$, $\text{SO}_2(l)$ and $\text{NO}_2(l)$ as a function of temperature. The heat capacities and diffusion coefficients of these molecules are plotted as functions of temperatures and compared with experimental values. The simulated and experimental values of heat capacity for $\text{SO}_2(l)$ agreed well with a percentage error of the difference between the two results being less than 0.05%. A comparison of average heat capacity values of these molecules in their gaseous phase is found to be approximately half of their corresponding average heat capacity values in the liquid phase. At low temperatures, the simulated graph showed similar variations to experimental values [9] and theoretical values [10] obtained for the diffusion coefficient of $\text{H}_2\text{O}(l)$. Since no literature data could be found on the heat capacity and diffusion coefficient of $\text{NO}_2(l)$ and the diffusion coefficient of $\text{SO}_2(l)$, the present results could be considered as new findings. This is an example, which shows how a MD simulation technique could be used to obtain results, which are hard to achieve in real time experiments.

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