



Excess population of the dipole moment controls the total moment in bulk tetrahydrofuran

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Abstract

The total moment in a bulk solvent determines the value of the static dielectric constant of the solvent. It is determined from the aggregates of the dipole moment of each of the solvent molecule. As the molecules are free to rotate and translate, it is difficult to predict the total moment from the individual dipole moment. This work investigates the behavior of the individual dipole moment and its relation to the total moment in bulk tetrahydrofuran (THF) solvent. Molecular dynamics simulation with carefully parametrized partial charges and Van der Waals parameters was used to reproduce the experimental bulk static dielectric constant and the density of THF. The effect of the individual dipole moment of the THF molecules was analyzed and compared to the total moment of the bulk THF. From the simulation, it was found that THF molecules dipole moment values were directed in the same and in the opposite direction of the total moment vector. The excess dipole moment population of the THF molecules was determined to be the main factor that controls the behavior of the total moment. Temperature has not to affect the total population of the THF molecules, and to the total moment in bulk THF solvent.

Keywords: Dipole moment, total moment, molecular dynamics simulation, bulk solvent, THF

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1. Introduction

The static dielectric constant of a bulk solvent determines the relative polarity of the solvent. The relative polarity of a solvent plays important roles in various fields of chemistry. In statistical mechanics, the static dielectric constant is directly proportional to the total moment of the bulk solvent, M , where M is (a vector) defined as the addition of all individual dipole moment, μ , (vector) of the molecules of the bulk solvent (Fig. 1) [1]. The value of static dielectric constant is related to the thermal fluctuations of M [2].

As the molecules of the bulk solvent are free to move, the direction of μ can vary. The value of M is affected by the angle and the direction of each individual μ . If the angle is almost perpendicular to M , the contribution of μ to the value of M is small, whereas if the angle is parallel to M , the contribution of μ to M is large. On the other hand, if the direction of μ is in the same direction as M , then μ will contribute to increase the value of M , and vice versa. Thus, the individual μ affects the total moment M .

Despite the obvious cause-and-effect between μ and M , the relation between μ to M is not well understood. The effect of the angle and the direction of each μ to the M

has not been studied previously. The effect on the temperature to the M and μ angle and direction is also a grey area. In addition, many studies involving the M fluctuation uses the Stockmeyer fluid or water [3,4]. As far as the author knows, there has been no study of the fluctuation of M related to the individual μ performed using real solvent. This work aims to look at the behavior of the dipole moment μ and the way that it affects the total moment M in the tetrahydrofuran (THF) solvent.

2. Materials and methods

2.1. Materials

The simulation was performed using the AMBER16 molecular dynamics package together with the AMBERTools software [5-8]. The software Avogadro was used to generate the THF structure [9]. The software Packmol was used to create the bulk THF system [10]. The R.E.D. Tools [11, 12] with RESP [13] and GAMESS [14] were used to generate the initial partial charges, whereas all other parameters were obtained from the General AMBER Force Field (GAFF) [15,16]. The analysis was performed using the *cpptraj* package from the AMBERTools and custom-made C++ programs.

To ensure that the results are valid for real bulk THF, the partial charges and the Van der Waals parameters used in the simulation are modified such that the simulation reproduces the static dielectric constant and bulk density of pure THF. This is performed by scaling the charges and modifying the Van der Waals well-depth until the static dielectric constant and the bulk density matches the experimental values. The values of static dielectric and bulk density for the modified partial charges and Van der Waals used for the production calculation are shown in Table 1.

2.2. Methods

In general, the methods are as follows. R.E.D. Tools was used to generate initial partial charges for determine the values of static dielectric constant and density of the THF system. The partial charges, and if necessary, the Van der Waals parameters were then manually modified and used in subsequent simulations. This process was repeated until a set of partial charges and Van der Waals parameters that reproduce the experimental static dielectric constant and density of THF was obtained. The trajectory from the simulation that reproduces the experimental static dielectric constant and density of THF was analyzed in detail. The directions and angles of all of the individual μ were determined, averaged, contrasted and compared against M at every time step of the simulation. The related equation to evaluate the static dielectric constant from non-polarizable classical molecular dynamics simulation is [17-19]:

$$\epsilon_s = \frac{4\pi}{3k_B T \epsilon_0 V} (\langle M^2 \rangle - \langle M \rangle^2) + 1 \quad (\text{Eq.1})$$

Here, ϵ_s is the static dielectric constant, k_B is the Boltzmann constant, T is the temperature, ϵ_0 is the static dielectric constant of vacuum, and V is the volume of the bulk solvent. M is the previously mentioned total moment and is defined as $M = \sum \mu_i$.

All simulation contained a system of 500 THF molecules in a cubic box with a dimension of approximately $32\text{\AA} \times 32\text{\AA} \times 32\text{\AA}$. For the simulations, a 0.5fs time step was used. Each simulation was run for 100ns. All simulations were performed at 298K and 1bar pressure, using the Langevin dynamics algorithm. The temperature control was performed using the fictitious collision every 1ps. The pressure control was performed using the Berendsen thermostat. The data was collected every 1ps.

3. Results and discussion

3.1. The arrangement of the dipole moment

From the simulation, at any instantaneous moment, there are μ that point in the same direction as M , and μ that point in the opposite direction of M . While most of the time, the number of μ that point in the same direction as M is in excess, there are a few instances where the number of μ that point in the opposite direction of M is in excess (see Table 2). In theory, because of thermal fluctuation, it is more likely for the molecules to be in random order [2]. An

arrangement where all of the molecules μ point in the same direction can be highly energetic. Thus, an arrangement where all the μ point in the same direction does not occur. In this case, the result from the simulation is in good agreement with theory.

3.2 The effect of the angle and the dipole moment direction on the total moment

Using the dot product of each individual μ and the total moment M , the angle between the two variables were calculated. It is possible for M to increase because of the collective angles of all the μ that point in the same direction as M , or because of the collective angles of all μ that point in the opposite direction as M . There are many angles that can be evaluated in the system. However, the easiest one is the average angle.

To see whether there is any effect of the angle on the values of M , the average angle of all μ that are in the same direction as M as well as the average angle of all μ that are in the opposite direction as M were plotted (Fig. 2). As can be seen from the plot, the average angles change too rapidly across time. This contrasts with the M that takes longer to change its values and trend of the values (increasing or decreasing). This different behavior in the average angle and total moment M makes it impossible to see any relation between the two properties.

The effect of the direction of μ to M was analyzed by plotting the number of excess μ (that point in the same or the opposite direction as M) at each time step (Fig. 3). As can be seen from the plot, the number of excess μ shows trends that are similar to M . The direction of the plot of M can be predicted by only looking at the plot of the excess μ . The result suggests that the excess μ can be used to predict the value of M (although some scaling might be needed to exactly match the value of M at each time step).

3.3. The effect of the frequency of data collection

As the μ of each molecule fluctuates, the frequency at which the position of each μ is recorded can affect the results. For example, if the frequency of the position recording is faster than the period for the μ to change its position, the result from Section 3.2 might not be observed. To look at the effect of the data collection frequency, the simulation was repeated with the data collected every 2ps and every 0.01ps. The plot of the average angle and M (Fig. 4) and the excess μ and M (Fig. 5) were generated.

From Fig. 4, it is obvious that it is impossible to relate the average angle with the total moment M . The average angle changes quickly compare to the total moment. It can be concluded that the average angle cannot be related to the values of M .

In contrast, Fig. 5 shows that the excess μ population still mimics the total moment quite accurately at lower data collection frequency. However, as the frequency

is lowered to $1/100^{\text{th}}$ of a picosecond, the similarity diminishes. This suggests that there is a limit at which the data collection frequency can be performed. It is estimated that from this result, the ideal data frequency collection to capture the excess μ population ability to mimic the M is about 1ps or 1THz.

3.4 The effect of temperature

One of the uncertainties in the Eq. 1 is the effect of the temperature on the physical system. In Eq. 1, there are two physical quantities that can vary, the total moment M and the bulk volume V . Since temperature is written as independent in the Eq. 1., the actual physical effect of temperature is not well understood. To investigate this, the simulation is repeated, this time varying the temperature to 308K, 318K and 328K. The same analysis was then performed on the μ and M .

Fig. 6 shows the plots of excess μ population and M at temperature of 298K, 308K, 318K and 328K. From the plots, the excess μ population still mimics the total moment

at all temperatures. In addition, Table 3 shows the average excess population for a simulation of 100ns data at these different temperatures. The result shows that the average excess μ population at these temperatures is similar and that the temperature has no effect on the average number of excess μ data.

Going back to the widely used equation to determine the static dielectric constant from non-polarizable classical molecular dynamics equation (Eq. 1), the temperature effect of the static dielectric constant can be attributed to the fluctuation of the bulk volume of the molecule and has no relation whatsoever to the fluctuation of the total moment.

The result suggests that the total moment of a particular chemical species is an inherent property of the chemical species. Given any molecule, the total moment of the bulk molecule will always be similar. The change in the static dielectric constant and the result from thermal fluctuation is because of the change in the volume only.

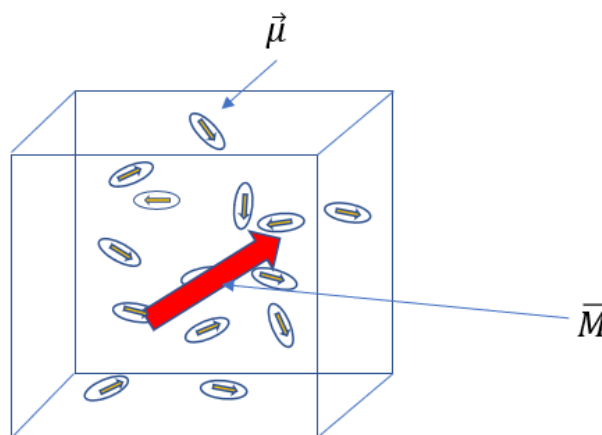


Fig. 1: The relation between dipole moment, μ , and total moment, M

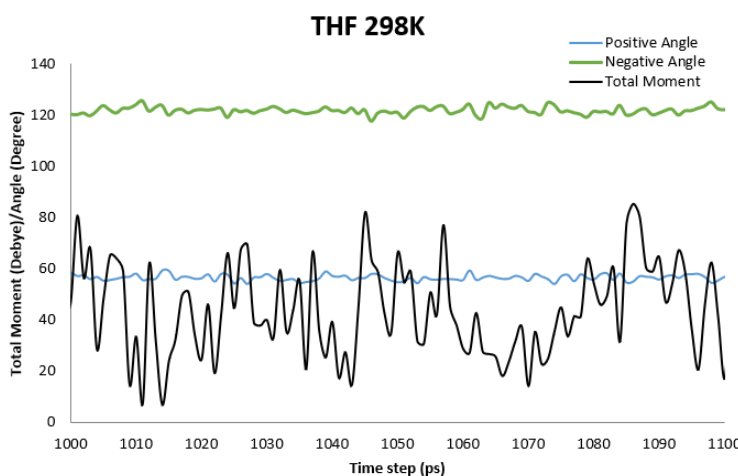


Fig. 2: The plot of average angle against the total moment, M at 298K

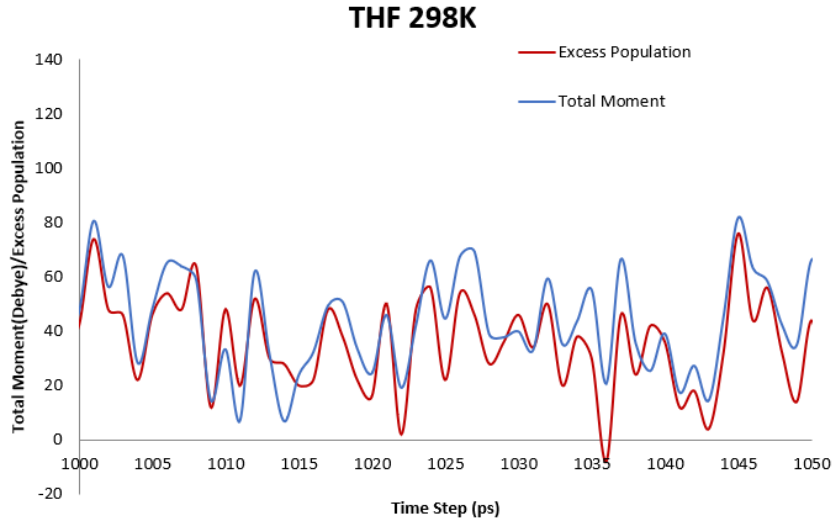


Fig. 3: Plot of the excess population and M at 298K

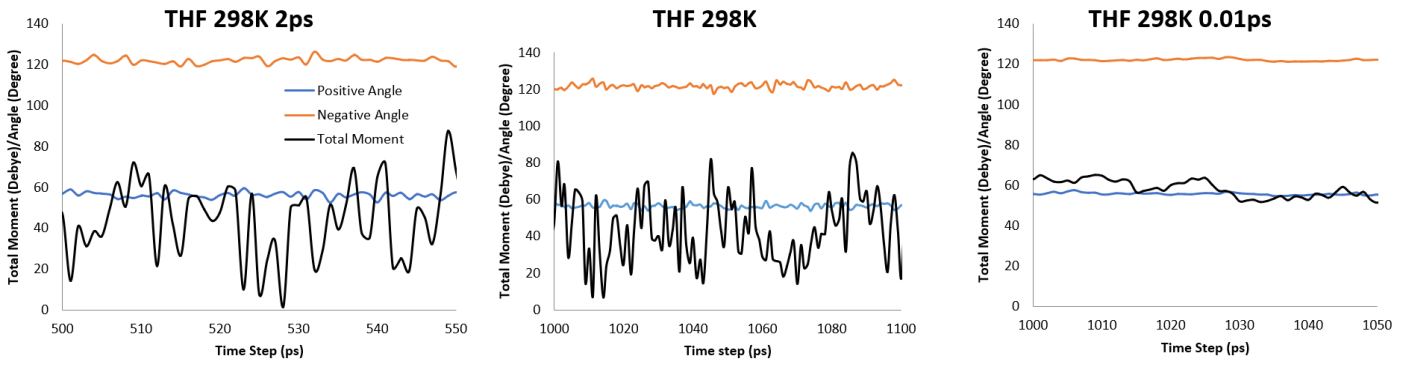


Fig. 4: The plot of average angle and M at various data collection frequency

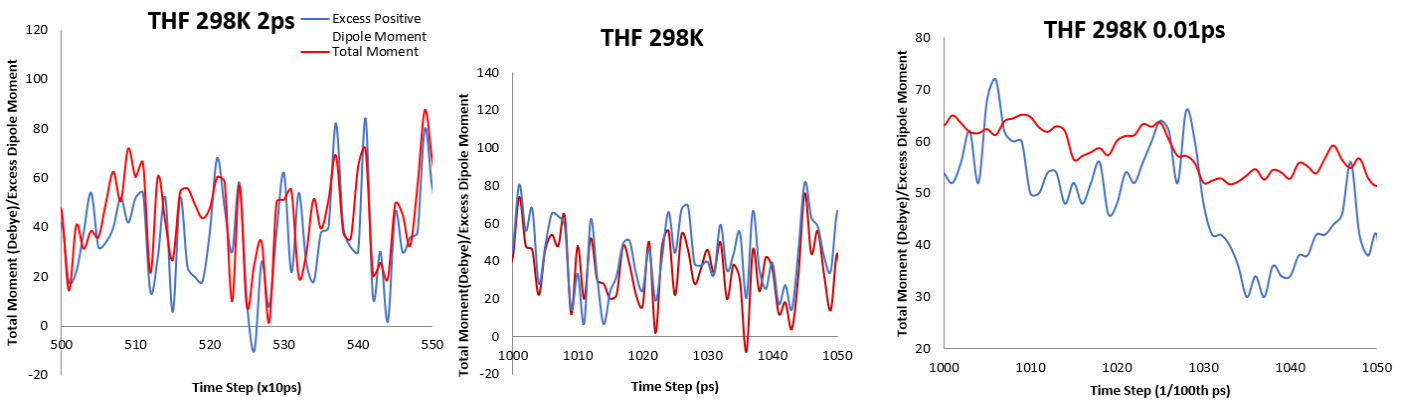


Fig. 5: The plot of excess population and M at various data collection frequency

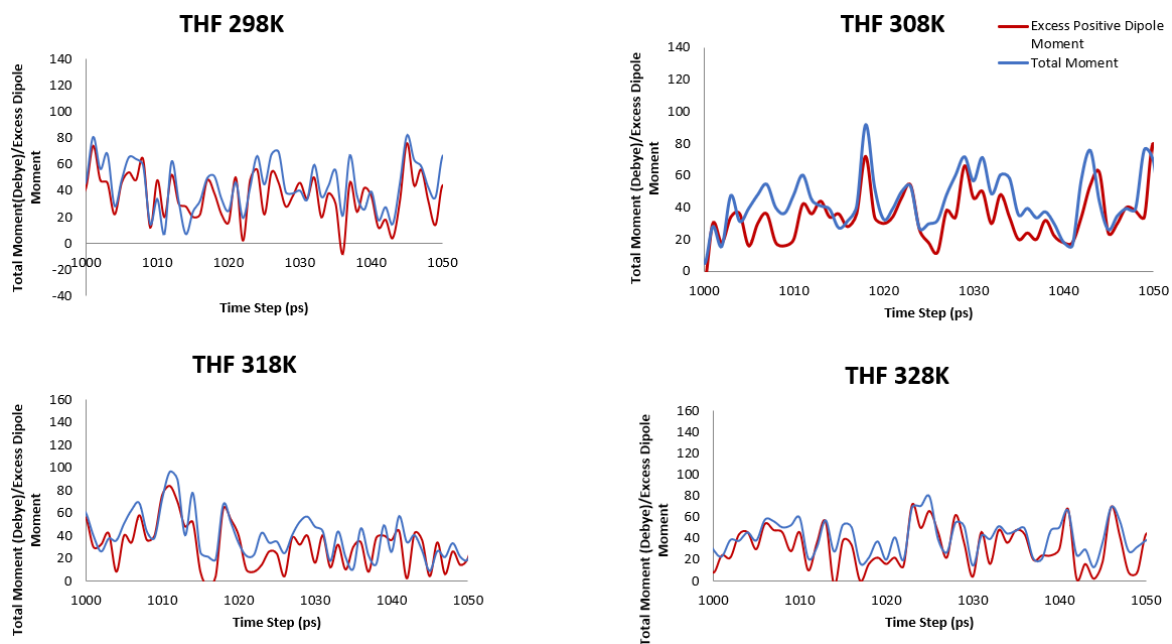


Fig. 6: The effect of temperature variation on the excess dipole moment and M

Table 1: The static dielectric constant and bulk density from the partial charges and Van der Waals parameters used in the simulation

TEMPERATURE (K)	SIMULATION		EXPERIMENTAL	
	STATIC DIELECTRIC CONSTANT	BULK DENSITY (g/ml)	STATIC DIELECTRIC CONSTANT ²⁰	BULK DENSITY ²¹
298	7.849	0.8858	7.881	0.8846
308	7.428	0.8732	7.652	0.8734
318	7.071	0.8604	7.422	0.8625
328	6.763	0.8474	7.320	N/A

Table 2: Partial values for Excess Population and Total Moment. At step 20, there are more individual dipole moment that points in the opposite direction of the total moment in the bulk solvent

TIME STEP	NUMBER OF POSITIVE DIPOLE MOMENT	NUMBER OF NEGATIVE DIPOLE MOMENT	EXCESS POPULATION	TOTAL MOMENT (DEBYE)
14	260	240	20	45.3082
15	267	233	34	73.4926
16	261	239	22	38.2194
17	266	234	32	27.9973
18	265	235	30	8.35537
19	276	224	52	27.682
20	269	231	38	17.959
21	262	238	24	41.4178
22	254	246	8	53.8804
23	238	262	-24	109.577

Table 3: The average excess dipole moment, μ and average total moment, M at various temperatures

TEMPERATURE (K)	AVERAGE EXCESS DIPOLE MOMENT POPULATION	AVERAGE TOTAL MOMENT (DEBYE)
298	37.717	45.777
308	37.648	45.600
318	36.728	44.844
328	36.736	45.246

4. Conclusions

From the results, the excess population of the individual dipole moment predicts the total moment in the bulk solvent well. On the other hand, the angle of the individual dipole moment appears to have no control of the total moment in the bulk solvent. It can thus be concluded that at the molecular level, the static dielectric constant value for a bulk solvent depends on the total excess individual dipole moment of the constituent molecules that point to the same direction as the total moment in the bulk solvent.

Temperature variation study can also be important to determine the excess population of the individual dipole moment at various temperatures especially at temperatures near the freezing point of the bulk solvent. In this work, it was shown that, as the temperature of the bulk solvent is varied, the total moment and the excess dipole moment does not vary with temperature. It can be concluded that the temperature variation of the static dielectric constant is related to the change in the volume of the bulk molecules. The results show in this study is for one bulk solvent that has a relatively low static dielectric constant. The study should be extended to other bulk solvent before the conclusion can be generalized to all solvents.

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