

Mathematical and Computational Modeling to Study the Solvents Effect On Dynamics of O₂ Molecule

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ABSTRACT: In this work an attempt has been made to study the solvent effect on dynamics of a molecule. The proposed model consists of Langevin stochastic differential equation whose solution is obtained through Euler's method. A diatomic molecule O₂ has been taken and its dynamics has been studied in two different solvent. The proposed study is concluded through the comparison of simulation results obtained for the motion of a diatomic molecule O₂ in two different solvent. This model incorporates the important parameters like acceleration, intermolecular force, frictional force and random force.

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1. Introduction

Molecular dynamics (MD) simulation has been widely used to study the structural and dynamic properties of molecular systems. But, there exist at least two limitations': the approximation in the potential energy functions and the lengths of the simulations. To prolong the simulation time, stochastic dynamics (SD) based on the Langevin equation is a recommended approach in which only the relevant portion of the molecule is considered explicitly and the remainder of system such as solvent serves to provide an effective potential, a friction drag and a random force [1].

The focus of this study is on mathematical modeling based on the Langevin equation to study the solvent effect on dynamics of a diatomic molecule O₂. We have taken two different solvents, ethanol (polar) and benzene (non-polar solvent) to see the effects on dynamics or motion of a diatomic molecule O₂. We have determined and studied the important statistical parameters like variance in position, variance in velocity and covariance between position and velocity with respect to time for both solvent systems.

We have used forward Euler's method replacing continuous – time with discrete time step, finding values at times t_0, t_1, \dots . Usually $t_{n+1} - t_n$ is a fixed number Δt .

2. MATHEMATICAL MODEL

In the molecular dynamics study, the atoms in a molecule are treated as particles and move according to the Newton's equation of motion by relating intermolecular force to acceleration [4]. When we incorporate solvent effect then a particle or molecule moving in a fluid medium experiences two additional forces, frictional force due to the viscosity of the medium and random force or fluctuating force due to the collision of the molecule in the surrounding medium then the behaviour or dynamics of such molecule is given by Langevin equation [5].

$$m\ddot{x} = F(x) - \eta\dot{x} + \xi(t) \quad (1)$$

Here \ddot{x} and \dot{x} are the second and first derivative of x with respect to time respectively. The term on the left hand side is the product of mass of the molecule m and acceleration \ddot{x} . The first term on the right hand side is the inter molecular force, $F(x)$, due to the interaction between the atoms of a molecule. This is the same force used in Newton's equation of motion [3], and given as,

$$F(x) = -\frac{dV}{dx} = -\dot{V}(x)$$

Where, $V(x)$ = Intermolecular potential energy function

Here we have selected Harmonic potential energy function for simulation of model (1) i.e.

$$V(x) = \frac{k_s}{2} (x-b)^2$$

Where k_s and b are the force constants and ideal bond length of diatomic molecule O_2 respectively.

Then $F(x)$ can be written as

$$F(x) = -k_s (x-b)$$

The second term is a frictional force which describes the drag on the particle due to the solvent. The frictional force is proportional to the speed of the particle with the constant of proportionality being the friction coefficient.

$$F_{friction} = -\eta\dot{x}$$

where \dot{x} is the velocity of the particle and $\eta = 6\pi\eta R$ is the friction coefficient (η is the viscous force and R is the vander waals radius of imaginary spherical atom or molecule) [10]. The third force, $\xi(t)$, is the random or stochastic force due to thermal fluctuations of the solvent with the amplitude ϵ related to the temperature T and the frictional force η by the fluctuation dissipation theorem $\epsilon^2 = 2\eta mKT$ (where K is the Boltzmann's constant and T is the temperature) [1] and it can be defined as $\langle \xi(t)\xi(t') \rangle = \delta(t-t'), \xi(t) = \frac{dW_t}{dt}$, white noise or random force. Here W_t is a wiener process which follows Gaussian distribution since any suitably scaled sum of independent, random disturbances effect the position of a moving particle will result in a Gaussian distribution [6].

The Wiener process W_t is characterized by three facts [9]:

1. $W_0 = 0$.
2. W_t is almost surely continuous
3. W_t has independent increments with distribution $W_t - W_s \sim N(0, t-s)$ (for $0 \leq s \leq t$).

$N(\mu, \sigma^2)$ denotes the normal distribution with expected value μ and variance σ^2 . The condition that it has independent increments means that $0 \leq s_1 \leq t_1 \leq s_2 \leq t_2$ then $W_{t_1} - W_{s_1}$ and $W_{t_2} - W_{s_2}$ are independent random variables. The solvent is not explicitly represented but its effects on the explicit atoms come from the frictional and random forces. When the frictional and random forces are zero, the Langevin equations reduces to Newton's equation of motion [10].

Let

$$\frac{dx}{dt} = \frac{dX_t}{dt} = V_t$$

Then

$$m \frac{dV_t}{dt} = F(X_t) - \eta V_t + \epsilon \frac{dW_t}{dt}$$

Then equation (1) can be written in terms of X_t and V_t as follows

$$\begin{aligned} dX_t &= V_t dt \\ m dV_t &= F(X_t)dt - \eta V_t dt + \epsilon dW_t \end{aligned} \tag{2.1}$$

And equation (2.1) can be written in matrix notation as

$$d\begin{pmatrix} X_t \\ V_t \end{pmatrix} = P\begin{pmatrix} X_t \\ V_t \end{pmatrix}dt + \begin{pmatrix} 0 \\ 1/m \end{pmatrix}dW_t + k_s b \begin{pmatrix} 0 \\ 1/m \end{pmatrix}dt, \quad (2.2)$$

Where

$$P = \begin{pmatrix} 0 & 1 \\ -k_s/m & -\eta/m \end{pmatrix} \quad (2.3)$$

For numerical updates eq.(2.2) can be written as,

$$\begin{pmatrix} X_{n+1} \\ V_{n+1} \end{pmatrix} = s\begin{pmatrix} X_n \\ V_n \end{pmatrix}dt + \epsilon Q\Delta W_n + Qk_s b\Delta t, \quad (2.4)$$

here

$$s = \begin{pmatrix} s_{11} & s_{12} \\ s_{21} & s_{22} \end{pmatrix}, \quad Q = \begin{pmatrix} q_1 \\ q_2 \end{pmatrix}$$

and ΔW_n is sampled from a Gaussian distribution with mean zero and variance Δt , independently of ΔW_m for $n \neq m$.

Now, let the covariance matrix of equation (2.4) be [2].

$$\Sigma = \begin{pmatrix} \sigma_x^2 & \mu \\ \mu & \sigma_v^2 \end{pmatrix}$$

Where σ_x^2, σ_v^2 and μ are variance in position, variance in velocity and covariance between position and velocity respectively.

If $\begin{pmatrix} X_n \\ V_n \end{pmatrix}$ is Gaussian with mean zero and covariance matrix Σ , then the variance of constant term

$Qk_s b\Delta t$ will be zero and $s\begin{pmatrix} X_n \\ V_n \end{pmatrix}$ is Gaussian with mean zero and covariance matrix $S\Sigma S^T$. Thus the covariance matrix that results for eq. (2.4), Will be

$$\Sigma = S\Sigma S^T + \epsilon^2 qq^T \Delta t,$$

Or

$$S\Sigma S^T = \Sigma - \epsilon^2 qq^T \Delta t, \quad (2.5)$$

We can rewrite above eq. (2.5), in a suitable matrix form as follow

$$\begin{pmatrix} s_{11}^2 - 1 & 2s_{11}s_{12} & s_{12}^2 \\ s_{11}s_{21} & s_{11}s_{22} + s_{12}s_{21} - 1 & s_{12}s_{22} \\ s_{21}^2 & 2s_{21}s_{22} & s_{22}^2 - 1 \end{pmatrix} \begin{pmatrix} \sigma_x^2 \\ \mu \\ \sigma_v^2 \end{pmatrix} = -\epsilon^2 \Delta t \begin{pmatrix} q_1^2 \\ q_1 q_2 \\ q_2^2 \end{pmatrix} \quad (2.6)$$

3.FORWARD EULER METHOD:

By the Euler method, the position and velocity can be updated as follows:

$$X_{n+1} = X_n + V_n \Delta t, \quad (3.1)$$

$$mV_{n+1} = V_n - \eta V_n \Delta t - cX_n \Delta t + cl_0 \Delta t + \epsilon \Delta W_n$$

With the notation of (2.4),

$$s = I + \Delta t P = \begin{pmatrix} 1 & \Delta t \\ -k_s \Delta t / m & 1 - \eta / m \Delta t \end{pmatrix}, \quad Q = \begin{pmatrix} 0 \\ 1/m \end{pmatrix}$$

Which gives

$$s_{11} = 1, s_{12} = \Delta t, s_{21} = -\frac{k_s}{m} \Delta t, s_{22} = 1 - \frac{\eta}{m} \Delta t \quad \text{and} \quad q_1 = 0, q_2 = \frac{1}{m}$$

Now by substituting the above values in equation (2.6), and using Gauss Elimination method the following solution is obtained,

$$\sigma_x^2 = \frac{2\eta K T m (2m - \eta \Delta t + c \Delta t^2)}{(\eta - c \Delta t)(4mc - 2c \eta \Delta t + c^2 \Delta t^2)}$$

$$\sigma_v^2 = \frac{4\eta K T m c}{(\eta - c \Delta t)(4mc - 2c \eta \Delta t + c^2 \Delta t^2)},$$

$$\text{And} \quad \mu = \frac{-2\eta K T m \Delta t c}{(\eta - c \Delta t)(4mc - 2c \eta \Delta t + c^2 \Delta t^2)}$$

4. NUMERICAL RESULTS AND DISCUSSION:

We have taken a diatomic molecule O₂ in two different solvent ethanol and benzene respectively, and for this molecule we have taken the values for the parameters incorporated in above equations as follows [7, 3, 12]

$m = 1.38905 \times 10^{-23}$ pN.sec²/nm, $\eta = 3.4621 \times 10^{-9}$ pN.sec./nm. (Ethanol),

$\eta = 1.88 \times 10^{-9}$ pN.sec./nm. (Benzene), $KT = 4.1$ pN.nm (at room temperature), $k_s = 1140000$ pN./nm.

First, variance in position is calculated and plotted against time step Δt upto 10^{-14} sec. for both solvent ethanol and benzene after that in the same way variance in velocity and covariance are calculated and plotted against time step Δt upto 10^{-14} sec. for both solvent ethanol and benzene respectively as shown in Fig. 1, Fig. 2 and Fig.3 as follows.

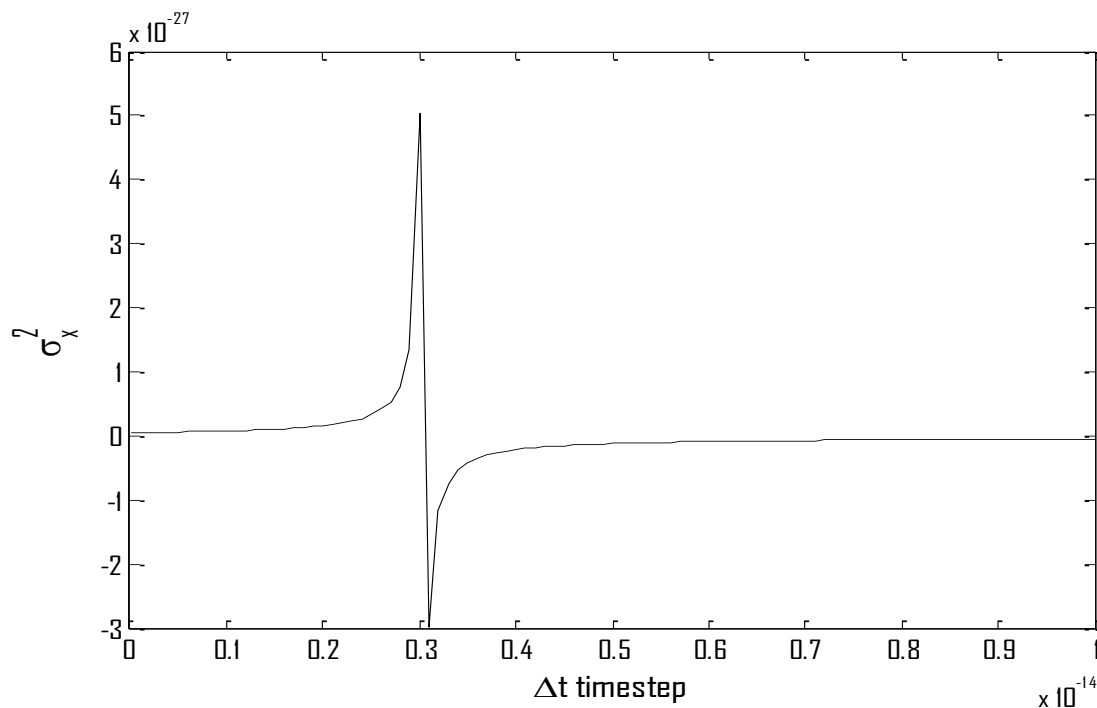


Fig. 1 Variance in position for ethanol vesrsus time step

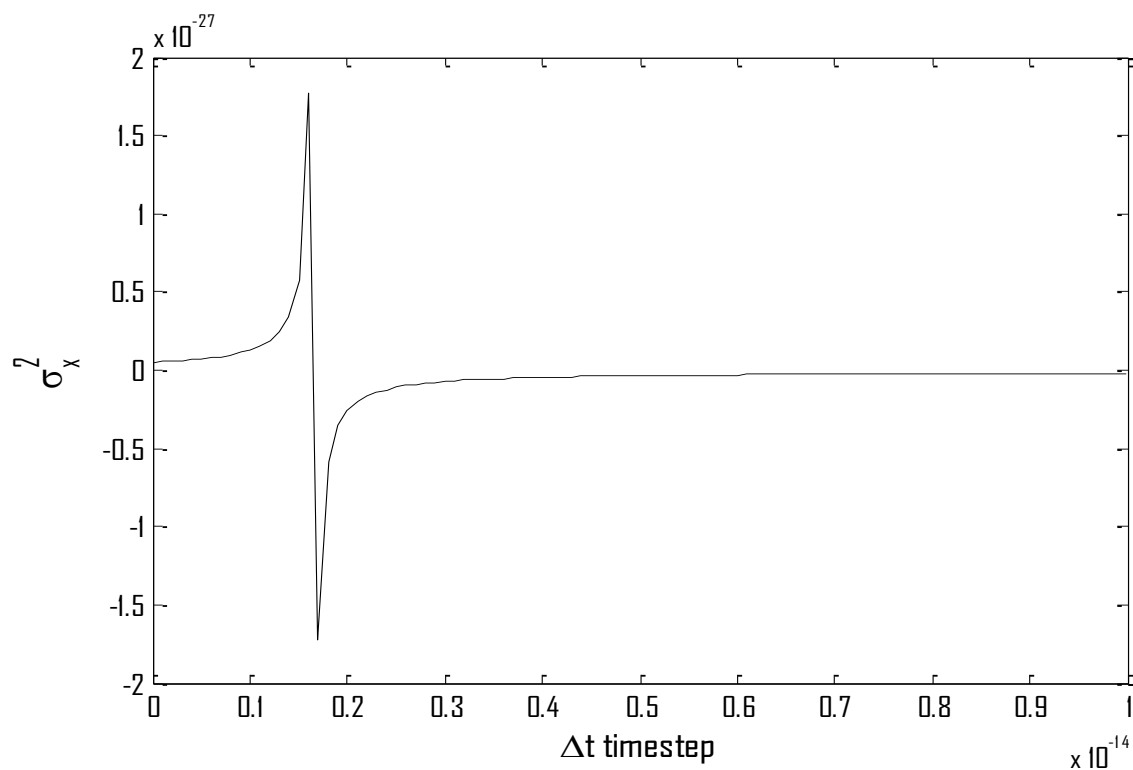


Fig.2 Variance in position for benzene versus time step

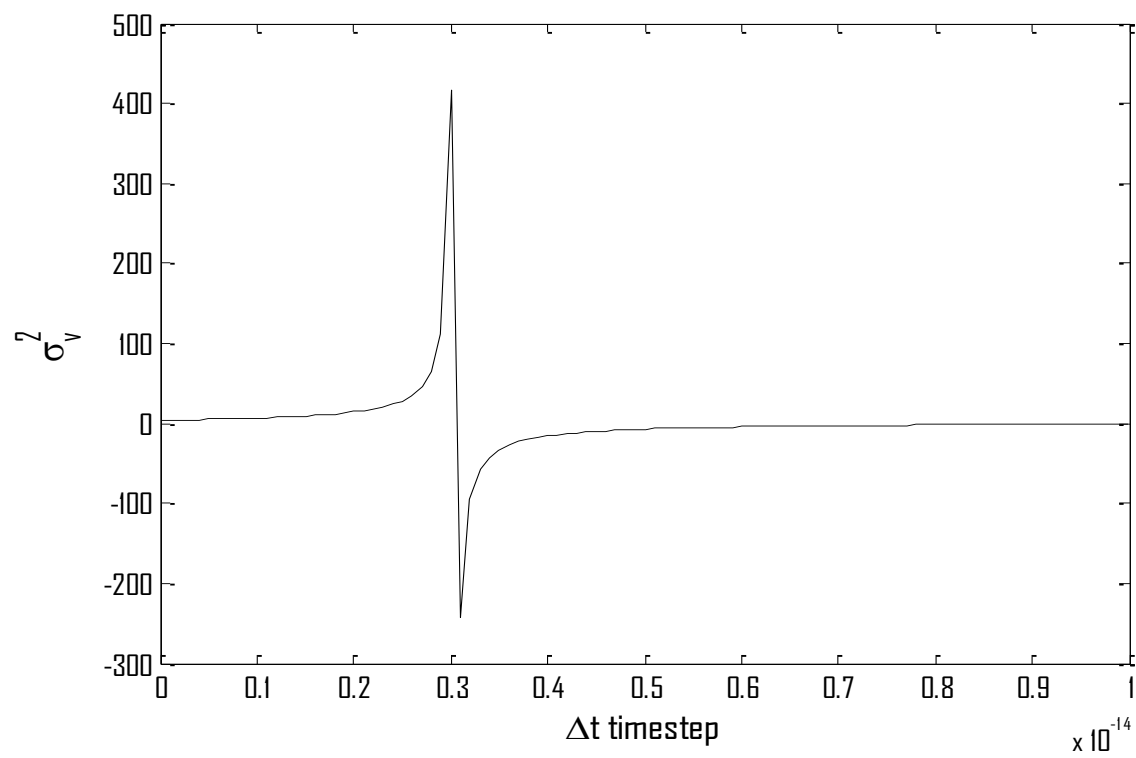


Fig. 3 Variance in velocity for ethanol versus time step

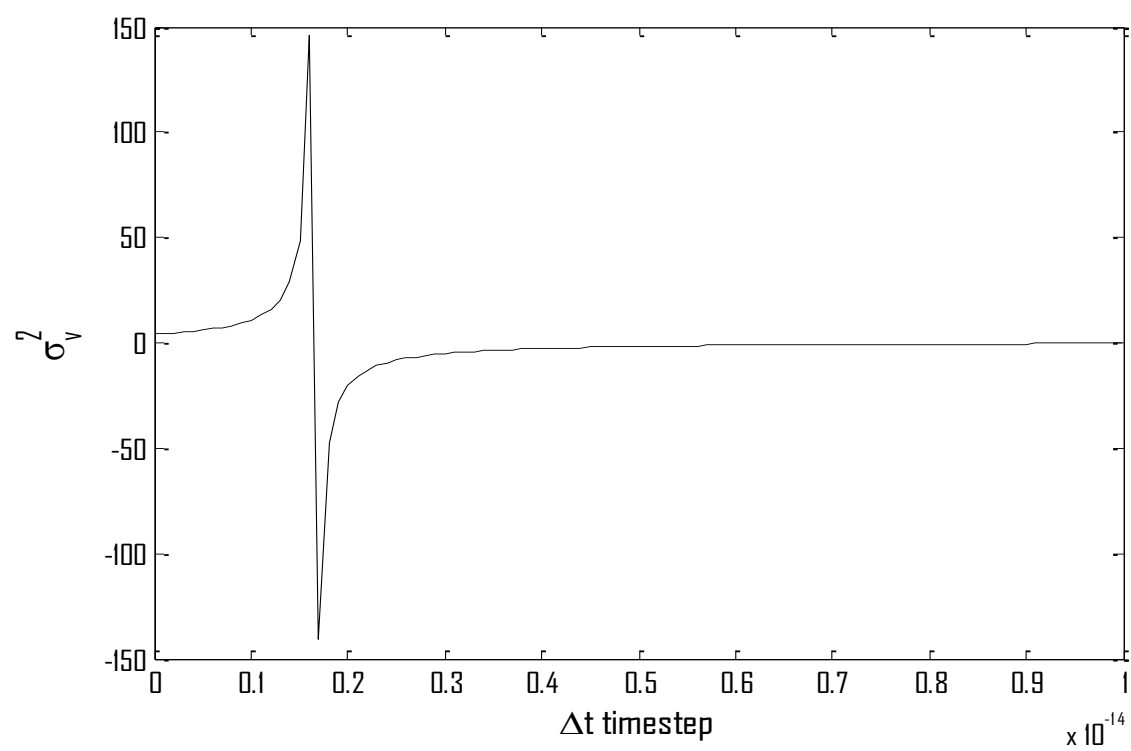


Fig. 4 Variance in velocity for benzene versus time step

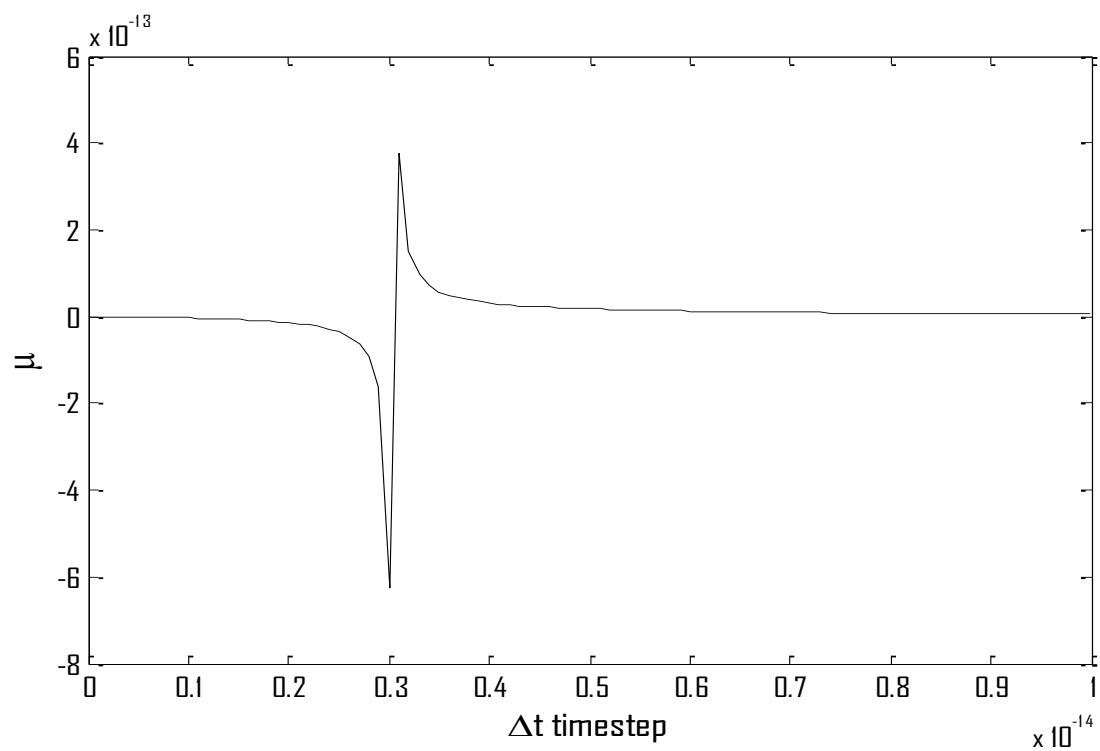


Fig.5 Covariance for ethanol versus time step

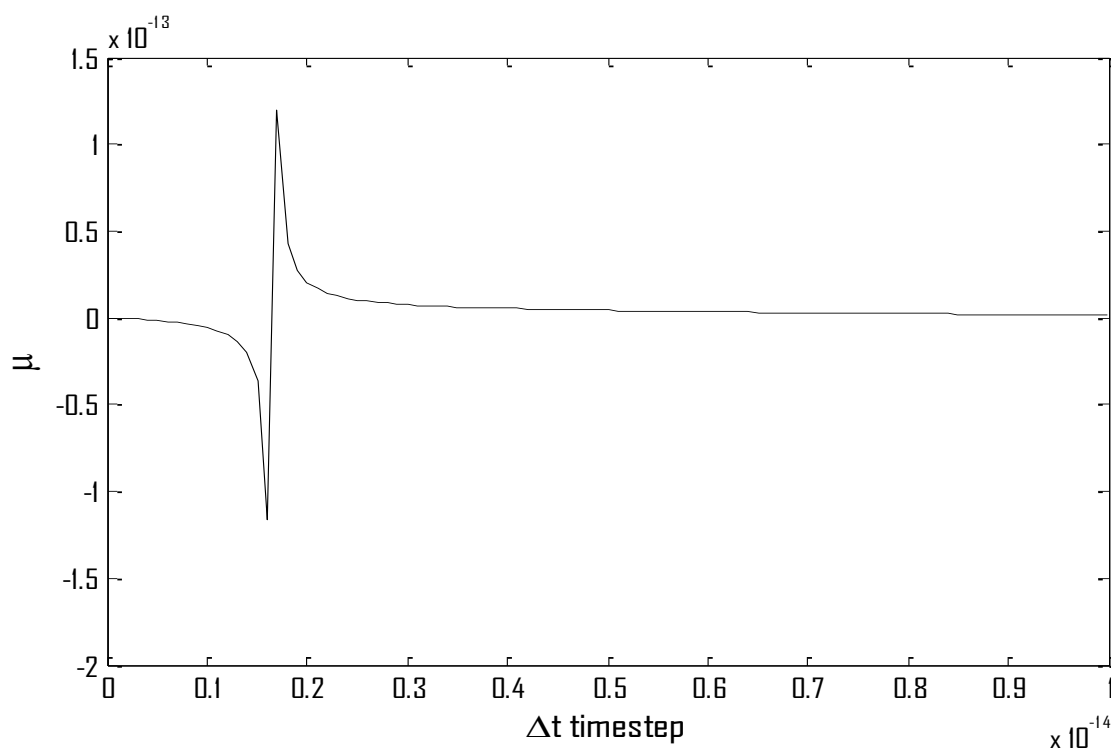


Fig.6 Covariance for benzene versus time step.

First of all variance in position (Fig.1 and Fig.2) for both the solvent (ethanol and benzene) is calculated. It is observed that variance in position for ethanol (Fig.1) increases steadily up to 3.6×10^{-15} sec. and after that it starts decreasing and increasing unexpectedly i.e. it starts showing the chaotic behavior after the time step 3.6×10^{-15} sec. Similarly, computed variance in position for benzene (Fig.2) shows that variance in position increases steadily up to 1.5×10^{-15} sec. and after that it starts decreasing and increasing unexpectedly i.e. it starts showing the chaotic behavior after the time step 1.5×10^{-15} sec. After that we have computed variance in velocity for both the solvent (Fig.3 and Fig.4) which shows that variance in velocity for ethanol (Fig.3) is stable upto 2.9×10^{-15} sec. and for benzene (Fig.4) it is stable up to 1.5×10^{-15} sec. and again after the same time steps it starts showing the chaotic behavior. Finally, the covariance (Fig.5 and Fig.6) between position and velocity is computed for both the solvent. It shows that both position and velocity vary together and then suddenly it shows the chaotic behavior again after the same time step 2.9×10^{-15} sec. and 1.5×10^{-15} sec. for ethanol and benzene solvent respectively. From these three observations of statistical parameter it can be concluded that the dynamics of the molecule O_2 becomes unstable after the same time step 2.9×10^{-15} sec. and 1.5×10^{-15} sec. for both ethanol and benzene respectively and then it starts showing the chaotic behavior i.e. it is not possible to go beyond 2.9×10^{-15} sec. and 1.5×10^{-15} sec. to study the dynamics of O_2 in ethanol and benzene solvent respectively. It is concluded that the solvent with higher viscosity (Ethanol) shows more stability in motion of a molecule in comparison to a solvent with lesser viscosity.

5. CONCLUSION:

The Langevin equation of motion is the starting point for the stochastic dynamics model. Molecular dynamics simulation provides atomic details of the structures and motions of the molecules which opens the way to simplify the description of interaction. We have applied Euler method for which the condition of stability is $k_s \Delta t^2 < \eta \Delta t$ or $\eta \Delta t < 2 + \frac{1}{2} k_s \Delta t^2$ [2]. Based on this condition we have attempted to see the effect of two different solvent to predict the maximum time steps to study molecular dynamics of the diatomic molecule O_2 and we have observed solvent with higher viscosity shows more stability in the motion of diatomic molecule O_2 . The present work of

mathematical modeling to study the solvent effect on dynamics of a molecule can be extended to complex molecules like protein, lipid etc. We can analyze important thermodynamic properties of the system by incorporating some more important parameters in the present model and then we can generate important information from the simulation. This work will contribute positively in studying the dynamics of a molecule and its important properties in a solvent.

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