

COMPUTATIONAL AND STATISTICAL ASPECTS TO CLASSIFY THE SOLVENTS EFFECTS ON DYNAMICS OF O₂ MOLECULE

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ABSTRACT

In this study an effort has been made to classify the solvent effect on dynamics of a molecule by the means of statistical parameters. The proposed model comprises 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. The mathematical model includes the key constraints such as frictional force, intermolecular force, random force and acceleration.

KEYWORDS: Covariance matrix, Potential energy function, time step, Weiner process.

MSC: 65-C30, 37-A60, 00-A69

ABSTRACTO

En este estudio se ha hecho un esfuerzo por clasificar el efecto del disolvente sobre la dinámica de una molécula mediante parámetros estadísticos. El modelo propuesto consta de una ecuación diferencial estocástica de Langevin cuya solución se obtiene a través del método de Euler. Se ha tomado una molécula diatómica de O₂ y se ha estudiado su dinámica en dos disolventes diferentes. El estudio propuesto se concluye mediante la comparación de los resultados de simulación obtenidos para el movimiento de una molécula diatómica de O₂ en dos disolventes diferentes. El modelo matemático incluye las restricciones clave, como la fuerza de fricción, la fuerza intermolecular, la fuerza aleatoria y la aceleración.

PALABRAS CLAVE: Matriz de covarianza, función de energía potencial, paso de tiempo, proceso de Weiner.

1. INTRODUCTION

A good share of science depends on the flows of models that characterize our realism at different spatial and temporal scales. A model is a simplified and often theoretical depiction of an intricate natural structure. Models are used in science to assist, identify, hypothesize about, or simulate the behaviour of the natural structures they characterize. Moreover, models can be used to simulate aspects of the natural structure. A simulation is a rule-based review of the natural system's behaviour under applicable conditions using the model [11].

Molecular dynamics (MD) simulation extensively used to exploit the dynamic and structural properties of molecular systems. But, it has two drawbacks: the time spans of the simulations and the approximation in the potential energy. To extend the simulation time, Langevin equation based stochastic dynamics (SD) simulation is a widely acclaimed methodology in which merely the relatable part of the molecule is considered explicitly and the remnants of system like solvent supports to provide a friction drag, a random force and an effective potential [8].

The emphasis of this work is on mathematical modelling 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 resolute and calculated the important statistical constraints such as variance in velocity, variance in position, and covariance between velocity and position with respect to time for both solvent systems.

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

2. METHODOLOGY

In the theory of molecular dynamics, the motion of atoms (considered as particle) by linking acceleration to intermolecular force are governed by the Newton's equation of motion [6]. When the solvent effect on the motion of an atom or molecule flowing in a liquid medium incorporated then the motion of the molecule

is effected by two new forces, fluctuating force because of the collision of the molecule in the connecting medium and frictional force due to the viscidness of the medium then the motion of such molecule is given by Langevin equation [9]

$$m \frac{d^2 x}{dt^2} = F(x) - \eta \frac{dx}{dt} + \in \zeta(t) \quad \dots\dots\dots (1)$$

The expression on the leftward is the multiplication of mass of the molecule m and acceleration $\frac{d^2 x}{dt^2}$. The first expression on the rightward is the intra-molecular force, $F(x)$, because of the interface among the atoms of a molecule and define as [2].

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

Where, $V(x)$ = Intra-molecular potential energy function.

Here, Harmonic potential energy functions is chosen for the 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.

Now, $F(x)$ can be shown as,

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

The next expression denotes a frictional force on the molecule because of the viscidness of the solvent. This force with the constant of proportionality being the friction coefficient is directly proportional to the velocity of the particle

$$\text{Frictional Force} = -\eta \frac{dx}{dt}$$

Where, $\frac{dx}{dt}$ denote the swiftness of the particle and $\eta = 6\pi\gamma R$ is the friction coefficient (γ is viscous force and R is the vanderwaals radius of imaginary spherical atom or molecule) [7]. The third force, $\zeta(t)$, is the stochastic or random force, because of the thermal fluctuations of the solvent with the amplitude \in associated to the frictional force η and the temperature T given by $\in^2 = 2\eta mKT$ (where K is the Boltzmann's constant and T is the temperature) [8] and it can be defined as $\langle \zeta(t)\zeta(t') \rangle = \delta(t-t')$, $\zeta(t) = \frac{dW_t}{dt}$, random force or white noise. Here W_t is a wiener process which follows Normal distribution since any appropriately scaled sum of independent, random disturbances effect the position of a moving particle will outcome in a Normal distribution [3].

The Wiener process W_t is considered by three facts [3]:

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

The expression $N(\mu, \sigma^2)$ represents the normal distribution with mean valued μ and variance σ^2 . The fact that it has independent increments means $0 \leq s_1 \leq t_1 \leq s_2 \leq t_2$ then $W_{t_1} - W_{s_1}$ and $W_{t_2} - W_{s_2}$ are independent random variables. The solvent effect originates from the frictional and random forces on the explicit atoms. When the random and frictional forces are zero, the Langevin equation converted to Newton's equation of motion [7].

Let,

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

Then equation (1)

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

can be written and describe in terms of X_t and V_t as follows

$$\begin{aligned} dX_t &= V_t dt \\ m dV_t &= F(X_t) dt - \eta V_t dt + \epsilon dW_t \end{aligned} \quad \dots\dots\dots (2)$$

and equation (2) can be shown in matrix form as follows:

$$d \begin{pmatrix} X_t \\ V_t \end{pmatrix} = P \begin{pmatrix} X_t \\ V_t \end{pmatrix} dt + \epsilon \begin{pmatrix} 0 \\ 1/m \end{pmatrix} dW_t + k_s b \begin{pmatrix} 0 \\ 1/m \end{pmatrix} dt, \quad \dots\dots\dots (3)$$

where,

$$P = \begin{pmatrix} 0 & 1 \\ -k_s/m & -\eta/m \end{pmatrix} \quad \dots\dots\dots (4)$$

For numerical iterations eq. (3) can be shown as,

$$\begin{pmatrix} X_{n+1} \\ V_{n+1} \end{pmatrix} = s \begin{pmatrix} X_n \\ V_n \end{pmatrix} dt + \epsilon Q \Delta W_n + Q k_s b \Delta t, \quad \dots\dots\dots (5)$$

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 taken from the sample space of Normal distribution with zero mean and Δt variance, which is independent from ΔW_m for $n \neq m$.

Now, let the covariance matrix of equation (5) be [1].

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

Where μ , σ_x^2 and σ_v^2 are covariance between position and velocity, variance in position and variance in velocity respectively. If $\begin{pmatrix} X_n \\ V_n \end{pmatrix}$ follows Normal Distribution with mean zero and covariance matrix Σ , then

the variance of constant term $Q k_s b \Delta t$ will be zero and $s \begin{pmatrix} X_n \\ V_n \end{pmatrix}$ will follow Normal Distribution with zero mean

and covariance matrix $S \Sigma S^T$.

Hence the covariance matrix for eq. (5), is given by

$$\Sigma = S \Sigma S^T + \epsilon^2 q q^T \Delta t \text{ or } S \Sigma S^T = \Sigma - \epsilon^2 q q^T \Delta t \quad \dots\dots\dots (6)$$

We can rewrite above eq. (6) in an appropriate matrix system as follow:

$$\begin{pmatrix} s_{11}^2 - 1 & 2s_{11}s_{12} & s_{12}^2 \\ s_{11}s_{21} & s_{11}s_{22} + s_{12}s_{21} - 1 & s_{12}s_{22} \\ s_{21}^2 & 2s_{21}s_{22} & s_{22}^2 - 1 \end{pmatrix} \begin{pmatrix} \sigma_x^2 \\ \mu \\ \sigma_v^2 \end{pmatrix} = -\epsilon^2 \Delta t \begin{pmatrix} q_1^2 \\ q_1 q_2 \\ q_2^2 \end{pmatrix} \quad \dots\dots\dots (7)$$

The iterative expression for the position and velocity by the Euler method, can be written as follows:

$$X_{n+1} = X_n + V_n \Delta t, \quad \dots\dots\dots (8)$$

$$m V_{n+1} = V_n - \eta V_n \Delta t - k_s X_n \Delta t + k_s b \Delta t + \epsilon \Delta W_n$$

With the representation of (5),

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

This 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 (7), and using Gauss Elimination method the following solution is obtained,

$$\sigma_x^2 = \frac{2\eta KTm(2m - \eta \Delta t + k_s \Delta t^2)}{(\eta - k_s \Delta t)(4mk_s - 2k_s \eta \Delta t + k_s^2 \Delta t^2)}, \quad \sigma_v^2 = \frac{4\eta KTmk_s}{(\eta - k_s \Delta t)(4mk_s - 2k_s \eta \Delta t + k_s^2 \Delta t^2)}$$

$$\text{and} \quad \mu = \frac{-2\eta KTm \Delta t k_s}{(\eta - k_s \Delta t)(4mk_s - 2k_s \eta \Delta t + k_s^2 \Delta t^2)}$$

3. STATISTICAL ANALYSIS

A diatomic molecule O₂ was taken for the simulation in two different solvent ethanol and benzene respectively, with the values of the constraints included in above equations are as follows [5, 10, 4]

$m=1.38905 \times 10^{-23}$ 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 alongside time step Δt upto 10^{-14} seconds for both solvent ethanol and benzene after that in the same way variance in velocity and covariance are calculated and plotted alongside time step Δt upto 10^{-14} seconds for both solvent ethanol and benzene respectively as shown in Fig.1, Fig.2 and Fig.3, Fig.4 and Fig.5, Fig.6 as follows.

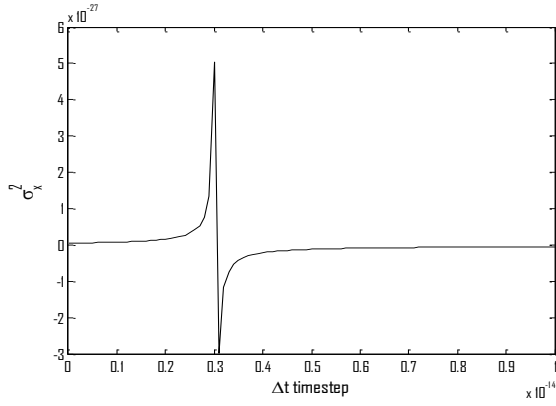


Figure 1: Variance in Position for ethanol versus time step

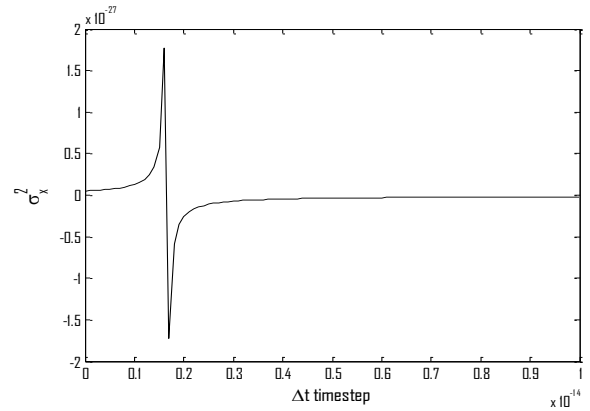


Figure 2: Variance in position for benzene versus time step

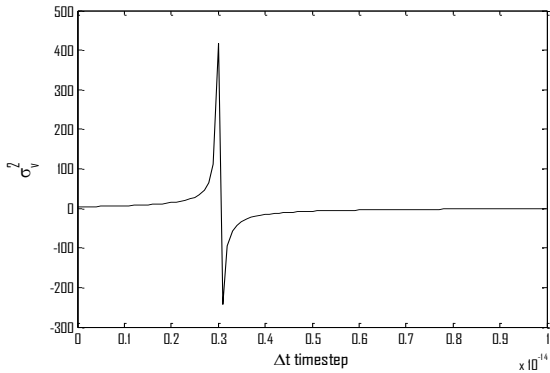


Figure 3: Variance in velocity for ethanol versus time step

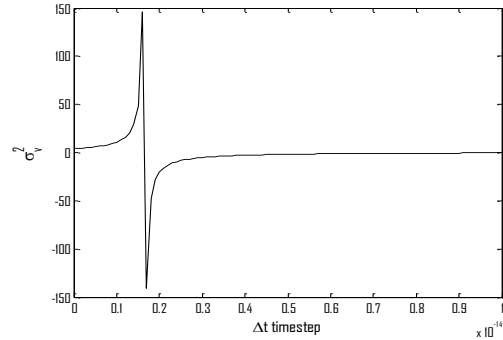


Figure 4: Variance in velocity for benzene versus time step

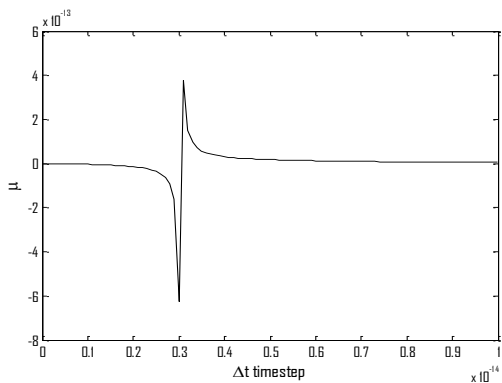


Figure 5: Covariance for ethanol versus time step

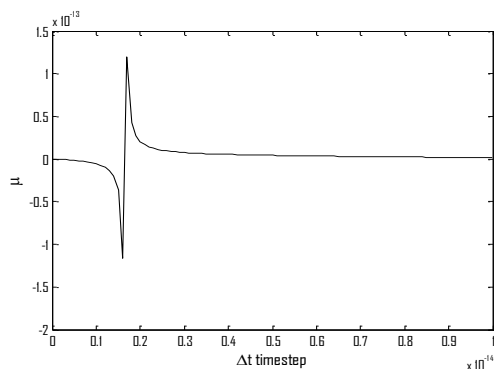


Figure 6: Covariance for benzene versus time step

4. RESULTS AND DISCUSSIONS

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 exhibiting the chaotic behaviour after the time step 3.6×10^{-15} sec. for very short duration of time and then it become stable. Similarly, computed variance in position for benzene (**Fig.2**) exhibits 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 exhibiting the chaotic behavior after the time step 1.5×10^{-15} sec. again for very short duration of time and then it become stable. After that variance in velocity was computed for both the solvent (**Fig.3** and **Fig.4**) which exhibits 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 exhibiting the chaotic behaviour for very short duration of time and then it become stable. 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 for very short duration of time and then it become stable. From these three interpretations of statistical parameter it can be established 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 exhibiting the chaotic behaviour for very short duration of time and then it become stable and almost constant. i.e. there is not much change in the motion of the molecule beyond 2.9×10^{-15} sec. and 1.5×10^{-15} sec. respectively. Therefore, it is not obligatory 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) gives longer time duration to exhibit the dynamics properties of a molecule in comparison to a solvent with lesser viscosity.

5. CONCLUSION

The Langevin equation of motion is the initial 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 $\eta \Delta t < 2 + \frac{1}{2} k_s \Delta t^2$ [1]. 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 gives longer time duration to exhibit the dynamics properties of a molecule. The present work of mathematical modelling to classify 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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