JIChE06
The Sixth Jordan International Chemical Engineering Conference
12 – 14 March 2012, Amman, Jordan

SELF DIFFUSION COEFFICIENT OF LENNARD-JONES FLUID USING TEMPERATURE DEPENDENT INTERACTION PARAMETERS AT DIFFERENT PRESSURES

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ABSTRACT

Estimation of diffusion coefficient is of great importance in industrial processes. It finds its application in rating of existing units, designing of new equipment and units and also in research and development. The main proposition of this work is that introducing temperature dependent interaction parameters instead of the current practice of using temperature independent interaction parameters may lead to improvement in the prediction of self-diffusivity. Self-diffusivities of atomic argon were evaluated by means of the mean square displacement or the Einstein method using equilibrium molecular dynamics (MD) at a pressure of 13 bar and a temperature range from 90 K up to 135 K in the isobaric, isothermal *NPT* ensemble. The simulation was carried out using both temperature dependent and temperature independent interaction parameters. Temperature dependent interaction parameters simulations, in general, produce more accurate self-diffusivities than the values computed by temperature independent interaction parameters simulations. Comparing the two approaches, the relative percentage error is reduced by about 67% and the RMSD is reduced by about 64% by using the temperature dependent parameters approach, This is consistent with our previous work in the Gibbs ensemble for the generation of coexistence vapor-liquid equilibrium curves. Finite size effects were studied for systems of (500, 1000 and 2000) atoms, the results indicate slight improvement in the computed self-diffusivities, however the improvement is marginal when compared to the computational time which was doubled as the number of atoms doubled. The effect of time step size was also investigated on time step sizes of (2, 4, 6 and 8) fs; results indicate that time step size of 2 fs was sufficient to produce more accurate self-diffusion coefficient values. The effect of pressure was studied at pressures of 58.6 bar, 104.04 bar and 136.8 bar, the results shows that up to a pressure of 58.6 bar the proposed approach gives better estimation for the self-diffusivity of argon. For a pressure range between 58.6 bar and 104.4 there is no significant difference between both methods, while for a pressure greater than that the common approach of using temperature independent interaction parameters gives more accurate values than the proposed approche.

Keywords: *Self-diffusion, molecular dynamics, , temperature dependent, Lennard-Jones, etc*

INTRODUCTION

Diffusion or molecular diffusion is the process in which molecules of one substance are transported from one part of the system to another part by means of their kinetic energy acquired from the interactions with their neighbors. It is characterized by the diffusion coefficient, which is a measure of the diffusive mobility of a molecule relative to other molecules. Self-diffusivity is a special case that describes the motion of molecules of the same material in the absence of any gradients that could cause mass transfer (Bird *et al*, 2002). Estimation and prediction of diffusivities of substances is of great importance in industrial processes, it finds its application in rating of existing units, designing and developing new units and equipments and also in research (Wei-Zhong *et al*, 2008).

Several models are available for describing intermolecular forces. The Lennard-Jones pair potential is an effective model for describing intermolecular forces of simple fluids and is widely used in computer experiments (Wei-Zhong *et al*, 2008) (Meier *et al*, 2001). The main proposition of the present work is that introducing temperature dependent interaction parameters to Lennard-Jones model (well depth ε and collision diameter σ) instead of the current practice of using temperature independent interaction parameters, may lead to improvement in the prediction of self-diffusivity. Thus, the aim of this study is to estimate self-diffusivity of argon described by Lennard-Jones model using molecular dynamics simulation with temperature dependent interaction parameters using the isotheral – isobaric ensemble (NPT) and the Einstein's relationship. The temperature dependence of these parameters is obtained from literature (Al-Matar, *et al*, 2008) (Sulieman, 2007). Subsequently, a comparison between the generated self-diffusivities values of the two approaches and the available data in literature will be carried out.

There was a work done in generating phase diagram of a Lennard-Jones fluid using temperature dependent interaction parameters (Al-Matar, *et al*, 2008) (Sulieman, 2007). Also there are recent researches on fitting temperature dependent parameters to certain properties of heavy gases (Zarkova and Pirgov, 1995) (Zarkova *et al*, 1999). However, no research has been reported regarding the usage of temperature dependent parameters of Lennard-Jones model in determining diffusion coefficient via molecular dynamics.

THEORY

Lennard-Jones Pair Potential

Lennard-Jones pair potential is used to describe the intermolecular force between argon atoms *i* and *j* separated be a distance r_{ij}. Any two molecules attract each other at long separation distance, and repel each other when they come closer (Hirschfelder *et al*, 1964) (Reed and Gubbins, 1973):

$$u(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{1}$$

In computer simulations using Lennard-Jones model, the potential must be truncated at some point named the cutoff radius, R_{cut}, usually set to $R_{\mathrm{cut}} = 2.5\sigma$, where at separation distance greater than the cutoff radius, the forces exerted between the two molecules are zero. The purpose of this is to reduce the computational effort, since the forces exerted at larger distances are very small and can be neglected (Rapaport, 2004) (Frenkel and Smit, 2002) (Heyes, 1998):

$$u(r_{ij}) = \begin{cases} u(r_{ij}) \neq 0 & r_{ij} \leq R_{cut} \\ 0 & r_{ij} > R_{cut} \end{cases} \tag{2}$$

Theory of Molecular Dynamics

Molecular dynamics is a method in which atoms or molecules are allowed to interact for a period of time by approximations of known physics, giving a view of the motion of particles. It is much like doing real experiments, first one need to prepare a system with certain number of particles (sample), the classical equations of motion are solved numerically for the molecules of the system using a suitable potential model until it reaches equilibrium then performing the actual measurements to evaluate system properties. However, to be able to measure an observable quantity of the system, it must be first expressed as a function of position and momenta of the particle in the system. Molecular dynamics, in its usual form applies numerical integration for Newton's equation of motion (Rapaport, 2004) (Frenkel and Smit, 2002) (Heyes, 1998) (Sadus, 2002):

$$\boldsymbol{F_i} = m\frac{d^2r}{dt^2} \tag{3}$$

$$\boldsymbol{F}_i = -\boldsymbol{\nabla_i}u(r) \tag{4}$$

Where ***F*** is the net force vector on the *i-th* molecule, *m* is the mass and ***r*** is the position vector of the *i-th* particle. The force on each molecule is obtained from the interaction potential as in Eq. (4) that is in this research the Lennard-Jones pair potential.

Positions and velocities of the particles are computed by integrating the equations of motion using finite difference algorithm at equal time intervals. One of the most used algorithms are the ones developed by Verlet that is the velocity Verlet leapfrog algorithm, which makes use of the half-time-step velocities to calculate positions and velocities of particles (Frenkel and Smit, 2002) (Heyes, 1998) (Sadus, 2002):

$$\boldsymbol{r_i}(t + \Delta t) = \boldsymbol{r}_i(\boldsymbol{t}) + \boldsymbol{v_i}(t + \Delta t/2)\Delta t \tag{5}$$

$$\boldsymbol{v_i}(t + \Delta t/2) = \boldsymbol{v_i}(t - \Delta t/2) + \frac{d^2\boldsymbol{r_i}(t)}{dt^2}\Delta t + O(\Delta t^3) \tag{6}$$

$$\frac{d^2\boldsymbol{r_i}(t)}{dt^2} = \frac{1}{m_i}\boldsymbol{F_i} = -\frac{1}{m_i}\sum \boldsymbol{\nabla}.u(r) \tag{7}$$

There are a few methods to control temperature, the simplest, involves velocity scaling or coupling with heat-bath, other more complicated approaches are the Andersen and Nosé-Hoover thermostats (Frenkel and Smit, 2002) (Sadus, 2002). In this research a special form of Nosé-Hoover thermostats developed be Berendsen is used, in which the friction coefficient *λ* rather than its time derivative varies according to the following equation rather than its derivative (Heyes, 1998):

$$\lambda = \left(\sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{2m_i} - \frac{gkT}{2}\right)/Q \tag{8}$$

Where Q = *gkTτ*^{2}, *g* is the degrees of freedom in the system (*g* = *3N – 4*) for a thermostated monatomic system with zero momenta and *τ* is thermostat relaxation time typically about 0.5 (Heyes, 1998).

In some cases, it is more useful to perform molecular dynamics simulation under constant pressure, the isobaric molecular dynamics is a generalization of the microcanonical ensemble NVE that allows the cell volume to fluctuate around a mean value to give the desired pressure that is set at the beginning of the simulation. Andersen's algorithm is used in this study, the equations of motion for Andersen's constant pressure are (Heyes, 1998) (Sadus, 2002):

$$\frac{d\boldsymbol{p}_i}{dt} = \boldsymbol{F}_i - \frac{\boldsymbol{p_i}}{3}\frac{d\ln V}{dt} \tag{9}$$

$$\frac{d^2V}{dt^2} = \frac{VL(P_A - P_D)}{Q_P} \tag{10}$$

Where *V* is the volume of the system, *L* is the side length of the simulation box, P_A is the actual pressure of the system, P_D is the desired pressure and Q_P is a constant as in Nosé-Hoover thermostat used to optimize equilibration of the system without severely affecting the dynamical relaxation mechanism of the system. For simple liquids a reasonable choice would be Q_P = $(N/\rho)^{1/3}/20$ [13]. The actual pressure is obtained from (Sadus, 2002):

$$P_A = \frac{2}{3V}\sum_{i=1}^{N}\frac{\boldsymbol{p_i}\cdot\boldsymbol{p_i}}{2m_i} - \frac{1}{3V}\sum_{J>i}^{N}\boldsymbol{r}_{ij}\frac{\partial u(\boldsymbol{r}_{ij})}{\partial \boldsymbol{r}_{ij}} \tag{11}$$

Self-diffusivity can be determined by two different but equivalent methods. One is based on velocities of the particles known as Green-Kubo method, the other is based on the positions of the particles and known as Einstein method (Wei-Zhong *et al*, 2008) (Meier *et al*, 2001) (Frenkel and Smit, 2002) (Rapaport, 2004).

The Green-Kubo relationship involves the integration of the velocity auto-correlation function (VACF), which is an equilibrium property that measures the correlation between velocity of a particle at different times method (Wei-Zhong *et al*, 2008) (Meier *et al*, 2001) (Frenkel and Smit, 2002) (Rapaport, 2004) (Heyes, 1998) (Song, *et al*, 2003):

$$D = \frac{1}{3N}\int_0^\infty \langle \sum_{i=1}^{N}\boldsymbol{v_i}(t).\boldsymbol{v}_i(0)\rangle dt \tag{12}$$

Where *t* is simulation time, $\boldsymbol{u}_i$ is the velocity vector of the *i*-th atom at time *t*, *N* is the total number of simulation particles and the term $1/N\langle\sum_{i=1}^{N}\boldsymbol{v}_i(t).\boldsymbol{v}_i(0)\rangle$ is the velocity auto-correlation function. However, Einstein's method, which is used in this study; relates the mean square distance travelled by a certain particle over a certain time interval. At the limit of observation time goes to infinity, self-diffusivity in terms of MSD is (Wei-Zhong *et al*, 2008) (Meier *et al*, 2001) (Frenkel and Smit, 2002) (Rapaport, 2004) (Heyes, 1998) Song, *et al*, 2003):

$$D = \lim_{t\to\infty}\frac{1}{6Nt}\langle\sum_{i=1}^{N}[\boldsymbol{r_i}(t) - \boldsymbol{r_i}(0)]^2\rangle \tag{13}$$

Where $\boldsymbol{r}_i$ is true displacement vector of the *i*-th atom at time *t* and the term $\langle\sum_{i=1}^{N}[\boldsymbol{r_i}(t) - \boldsymbol{r_i}(0)]^2\rangle$ is the MSD.

SIMULATION DETAILS

In this work, the NPT ensemble was used in a molecular dynamics simulation to compute self-diffusivity of argon at 13.07 bar and temperature range from 90 K up to 135 K at temperature intervals of 5 K using Einstein relationship. The effect of step size was studied at step sizes of 2×10^{-15} s, 4×10^{-15} s, 6×10^{-15} s and 8×10^{-15} s to determine the most suitable step size for the simulations. The effect of simulation duration time was studied at 1.5×10^{6} steps, 3×10^{6} steps and 5×10^{6} steps. Systems of (500, 1000 and 2000) atoms were studied to determine the finite size effects on the computed self-diffusivities of argon. Accelrys Materials Studio version 4.0 package was used to carry out the simulation. The simulation cell was generated in a simple cubic box at 90 K then relaxed for 100,000 time steps using the NVT ensemble for time considerations, then production runs were performed using NPT ensemble. Periodic boundary condition was applied during both the relaxation run and production runs. Initial velocities were generated from Boltzmann's distribution and the integration method used was velocity Verlet leapfrog algorithm. Sampling of the production runs was performed at 1000 time steps intervals and analyzed to obtain MSD as a function of time that were further analyzed in Microsoft EXCEL to obtain the slope of the line, self-diffusivities were then calculated from Einstein relationship. Temperature and pressure were controlled using Berendsen and Andersen methods respectively. The Lennard-Jones interaction parameters used for temperature independent simulations are: $\varepsilon/k = 119.8\ K$ and $\sigma = 3.405\ \mathring{A}$ (Brown, and Clarke, 1984). For the temperature dependent interaction parameters they were calculated from the following equations (Al-Matar, *et al*, 2008) (Sulieman, 2007):

$$\varepsilon/k = 117.7 + \frac{778.0}{T} \tag{14}$$

$$\sigma = 3.672 - \frac{22.3}{T} \tag{15}$$

Where ε/k is measured in Kelvin, σ is measured in $\mathring{A}$ and T is the absolute temperature in Kelvin. Simulation details are listed in Table 1.

Table 1: Details of the simulation carried out using NPT ensemble

Property	Number of atoms		
	500	1000	2000
Cell dimensions ($\mathring{A}$)	28.90×28.90×28.90	36.40×36.40×36.40	45.90×45.90×45.90
Cutoff radius ($\mathring{A}$)	2.5σ		
Step size (*fs*)	2		
Number steps in production runs	1.5×10^6		
Number of relaxation steps	1×10^5		
Thermostat decay constant τ (*ps*)	0.1443		
Isobaric cell mass parameter (*amu*)	20		

RESULTS AND DISCUSSION

Effect of simulation step size

The effect of step size was studied on a system of 500 atoms and number of steps of 1.5×10^6 steps using temperature independent interaction parameters to determine the most suitable time step size. Figure 1 shows self-diffusivity as a function of *1/T* for four step sizes along with experimental data of (Naghizadeh and Rice, 1962), it is clear that there is no big difference between the simulated self-diffusivity calculated using different simulation time steps. However, a step size of 2×10^{-15} s gave the lowest average relative percentage error with shortest average computer time as it is clear in Table 2.

Effect of simulation duration time steps

The effect of simulation duration time was studied on a system of 500 atoms and simulation time step size of 2×10^{-15} s using temperature independent interaction parameters to determine the most suitable simulation run time. Figure 2 shows self-diffusivity as a function of *1/T* for three different simulation steps along with experimental data of (Naghizadeh and Rice, 1962), it is clear that there is no significant difference between the results of different number of simulation time steps. However, simulations using 1.5×10^6 steps gave the lowest average relative percentage error with shortest average computer time, as it is clear in Table 3

Table 2: Average relative percentage errors and average computer run times for the studied simulation time steps

Simulation Time Step Size *S*	Average Relative Percentage Error *%*	Average Computer Run Time *min*
2×10^{-15}	19.5	97
4×10^{-15}	21.3	123
6×10^{-15}	20.5	144
8×10^{-15}	22.6	162

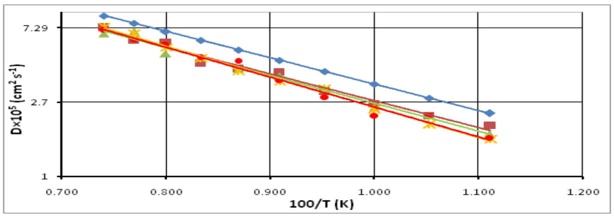


Figure 1: Self-diffusion coefficient of argon at different simulation time step sizes compared with experimental results for a system of 500 atoms and simulation run time of 1.5×10^6 simulation steps. (♦) Experimental data from (Naghizadeh and Rice, 1962), (■) 2×10^{-15} s. (▲) 4×10^{-15} s. (✳) 6×10^{-15} s. (●) 8×10^{-15} s

Table 3: Average relative percentage errors and average computer run times for the studied number of simulation steps

Number of simulation Time Steps	Average Relative Percentage Error *%*	Average Computer Run Time *Min*
1.5×10^6	19.5	97
3.0×10^6	21.5	214
5.0×10^6	22.7	360

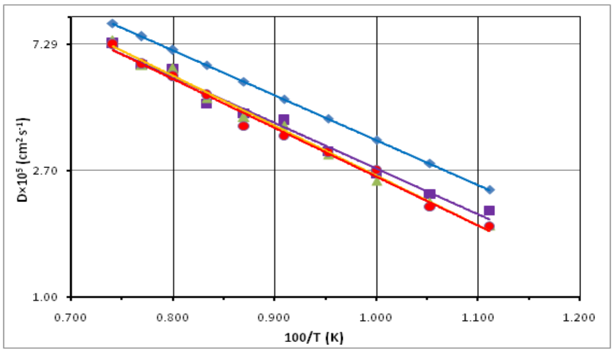


Figure 2: Self-diffusion coefficient of argon at different simulation duration times compared with experimental results for a system of 500 atoms and time step size of 2×10^{-15} s. (♦) Experimental data from (Naghizadeh and Rice, 1962), (■) 1.5×10^6 steps. (▲) 3×10^6 steps. (●) 5×10^6 steps

Effect of finite ensemble size

The effect of finite ensemble size was studied on a systems of (500, 1000 and 2000) atoms, simulation steps of 1.5×10^6 and simulation time step size of 2×10^{-15} s using temperature independent interaction parameters. Figure 3 shows the computed self-diffusivity of the three ensemble sizes as a function of *1/T*. It is clear that as the system ensemble size increased the computed values of self-diffusivity gets closer to the experimental values. This is due to the fact that larger systems are more closer to the real systems and the effect of the boundaries is less than that of smaller systems because more atoms are present in the bulk rather than near the surfaces of the system. However, the gain in accuracy is marginal compared to the computation time, as it is clear in Table 4, the table shows that as number of atoms doubles the computation time also doubles

Table 4: Average relative percentage errors and average computer run times for systems of (500, 1000 and 2000) atoms

Number of Atoms	Average Relative Percentage Error %	Average Computer Run Time *Min*
500	19.5	97
1000	19.3	186
2000	18.8	377

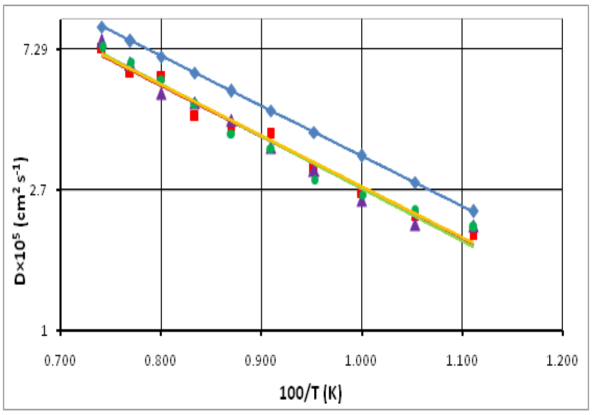
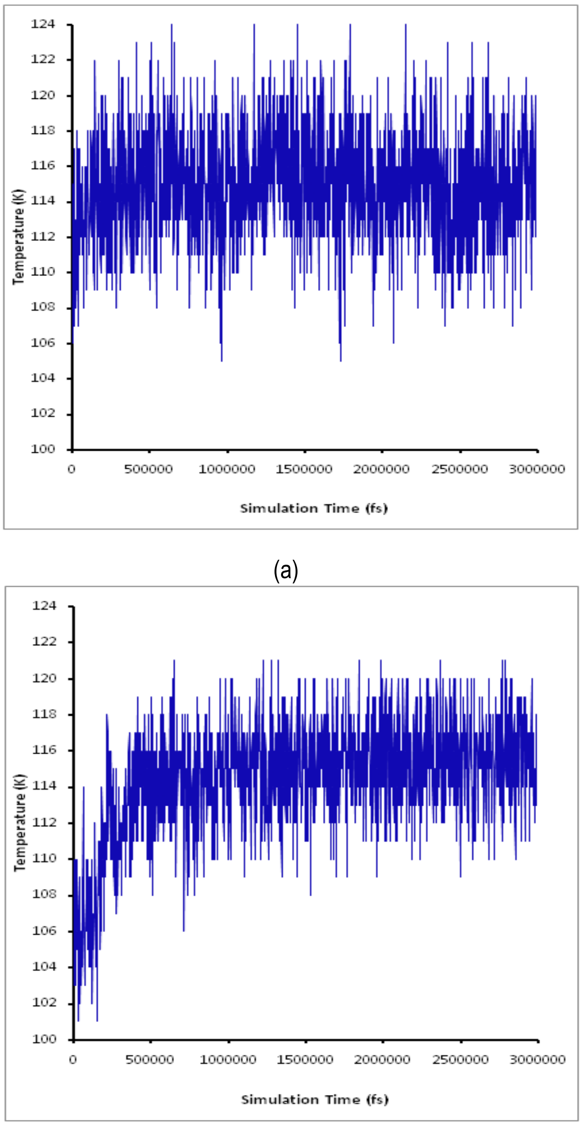


Figure 3: Self-diffusion coefficient of argon at different number of atoms compared with experimental results for time step size of 2×10^{-15} s and simulation time of 1.5×10^6 steps. (♦) Experimental data from (Naghizadeh and Rice, 1962), (■) 500 atoms. (▲) 1000 atoms. (●) 2000 atoms

Qualitative behavior of the simulation

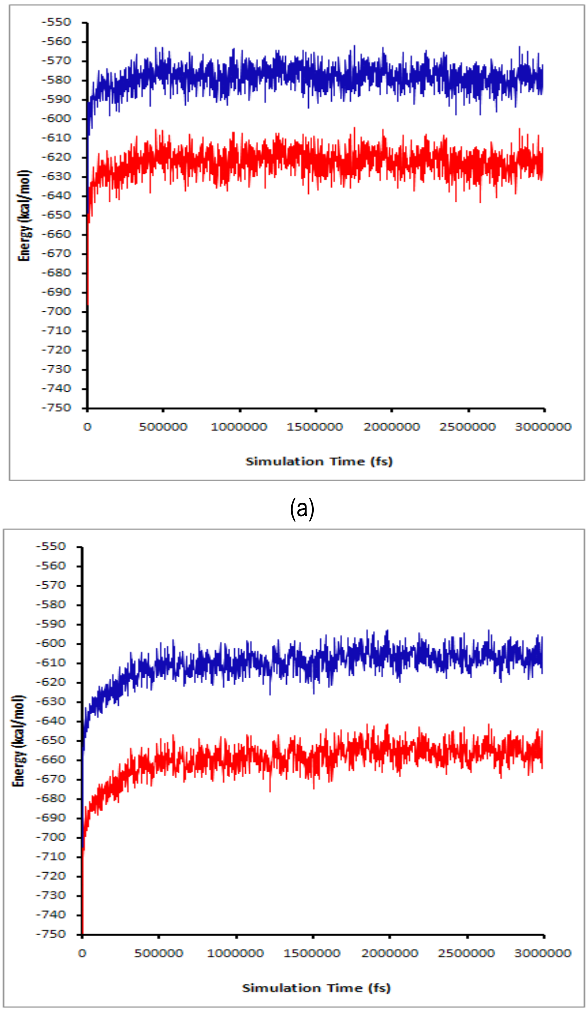
Figure 4 to Figure 7 shows the temperature fluctuations, energy fluctuations, velocity auto-correlation function VACF and the radial distribution function RDF at a temperature of 115 K. The temperature and energy fluctuations figures shows that the proposed approach produced less fluctuations and smother curves. The energy fluctuations figure shows that argon atoms simulated by using temperature dependent interaction parameters have more energy than the use of temperature independent interaction parameters method; this means that the atoms became more mobile. The velocity auto-correlation function figure indicates that the area of VACF curve under the *x*-axis produced by using the proposed approach is slightly less than the area of the curve produced by using the common approach of using temperature independent interaction parameters. Since the self-diffusivity decreases as the area under the *x*-axis increases; this implies that higher self-diffusivities are computed by the proposed approach (Tanaka *et* al,1983),. From the radial distribution function curve it can be seen that the atomic density produced by using temperature dependent interaction parameters at shorter atoms separation distances are less than the atomic density produced using the temperature independent interaction parameters. This means more atoms exist at longer distances when using the proposed approach than that of the common approach. This is an indication of higher kinetic energy and mobility as shown by energy fluctuation figure. Figure 8 shows the mean square displacement MSD as a function of the simulated argon atoms collisions time at 115 K. It is clear that the use of temperature dependent interaction parameters approach produced higher MSD and the slope of the line is more than that produced by using temperature independent interaction parameters. This also indicates that the atoms have more kinetic energy and mobility with the proposed approach.



(a)

(b)

Figure 4: Temperature fluctuations during simulation time for a system of 500 atoms with a simulation time step size of 2×10^{-15} s and run duration of 1.5×10^6 simulation steps at temperature of 115 K. (a) Temperature independent interaction parameters, (b) Temperature dependent interaction parameters



(a)

(b)

Figure 5: Energy fluctuations during simulation time for a system of 500 atoms with a simulation time step size of 2×10^{-15} s and run duration of 1.5×10^{6} simulation steps at temperature of 115 K. (a) Temperature independent interaction parameters, (b) Temperature dependent interaction parameters, (———) non bond energy, (———) potential energy

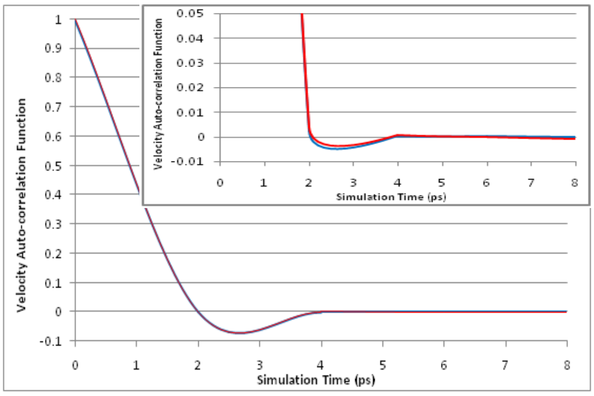


Figure 6: Velocity auto-correlation function for a system of 500 atoms with a simulation time step size of 2×10^{-15} s and run duration of 1.5×10^{6} simulation steps at temperature of 115 K. (———) Temperature independent interaction parameters, (———) Temperature dependent interaction parameters

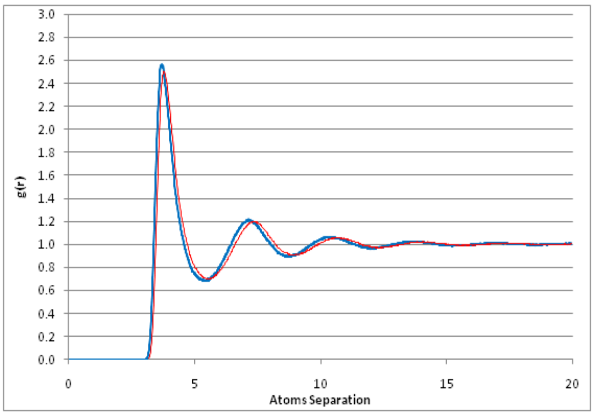


Figure 7: Radial distribution function *g(r)* as a function of atoms separation in Å for a system of 500 atoms with a simulation time step size of 2×10^{-15} s and duration time of 1.5×10^{6} simulation steps at temperature of 115 K. (———) Temperature independent interaction parameters, (———) Temperature dependent interaction parameter

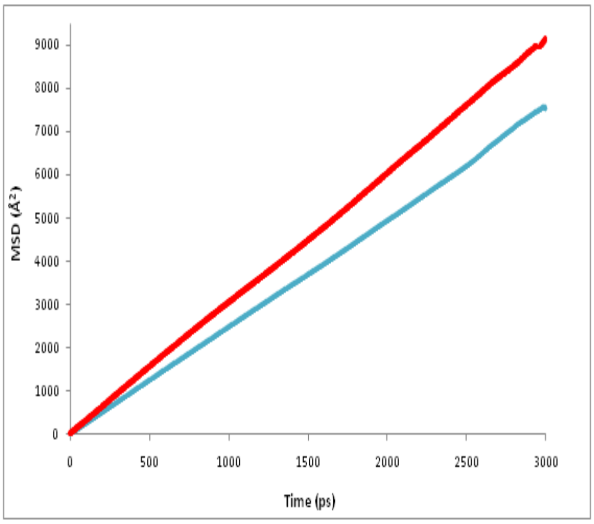


Figure 8: MSD as a function of argon atoms collision time using temperature dependent and temperature independent interaction parameters for a system of 500 atoms with a simulation time step size of 2×10^{-15} s and duration time of 1.5×10^{6} simulation steps at temperature of 115 K. (———) Temperature independent interaction parameters, (———) Temperature dependent interaction parameter

Effect of temperature dependent interaction parameters on simulated self-diffusivity of argon

The effect of temperature dependent interaction parameters on the computed self-diffusivities of argon at 13.07 bar is shown in Figure 9 and Table 5. The proposed approach resulted in a significant improvement for the computed self-diffusivities of argon. The average relative percentage error in the computed self-diffusivities with the current practice of using temperature independent interaction parameters was 19.5%, while the proposed approach of using temperature dependent interaction parameters resulted in average relative percentage error of 6.4%. This is an improvement of 67.0%. However, in both cases the computed self-diffusivities are still lower than the experimental results. Another criterion was used to verify the obtained results is by comparing the root mean square deviation RMSD (Press *et* al, 1992). the proposed approach of using temperature dependent interaction parameters has RMSD of 0.39, while the conventional method of using temperature independent interaction parameters has RMSD of 1.07, the overall improvement in terms of RMSD is 63.6%.

The higher self-diffusivities computed by the proposed approach can be explained depending Figure 4 to Figure 8; these plots indicates that the introduction of temperature dependent interaction parameters resulted in shifting the atoms to higher energy level and the atoms appears to have more kinetic energy and therefore more diffusive or mobile. The RDF figure shows higher atom densities at longer atoms separation distances, when using the proposed approach. This will result in harder collisions and larger velocities after collisions. This can be explained that by using temperature dependent interaction parameters with LJ model reduces the well depth and widens the region around it which results in reducing the effect of attractive forces, while the use of the temperature independent interaction parameters over estimates the effect of attractive forces.

Wie-Zhong *et al.* (2008) reported results for a system of 500 argon atoms and simulation time step size of 2×10^{-15} s shows a relative percent error of about 10% for both self-diffusivity calculated from Einstein relation (MSD) and Green-Kubo relation (VACF), while the method of using temperature dependent interaction parameters proposed in the present work gives an average relative percentage error of 6.4%.

Rahman (1964) reported self-diffusivity of argon of 2.43×10^{-5} cm^2 s^{-1} for a system of 864 atoms at 94.4 K and a value of 5.67×10^{-5} cm^2 s^{-1} at 130 K, the proposed approach in this study resulted in values of 2.62×10^{-5} cm^2 s^{-1} at 95 K and 7.98×10^{-5} cm^2 s^{-1} at 130 K (see Table 5). Comparing the results of Rahman and the proposed approach with experimental values of Naghizadeh and Rice, it is clear that the use of temperature dependent interaction parameters result in more accurate self-diffusivities at higher temperatures.

Song *et al.* (2003) reported a result 2.48×10^{-5} cm^2 s^{-1} for a system of 1728 argon atoms at 94.4 K using the NVT ensemble and 2.47×10^{-5} cm^2 s^{-1} using the NPT ensemble, their results are still quite far from the experimental value of about 2.83×10^{-5} cm^2 s^{-1} (obtained using interpolation of experimental results (Naghizadeh and Rice, 1962). It should be noted that the result of the presented proposed approach was 2.62×10^{-5} cm^2 sec^{-1} at 95 K is still closer to the reported experimental value.

Effect of pressure on simulated self-diffusivity of argon

Figures10 with Table 6 shows the combined effect of pressure and temperature dependent interaction parameters, the effect of pressure was studied at three pressures (58.6 bar, 104.4 bar and 136.8 bar) and compared with experimental values of (Naghizadeh and Rice, 1962). The results indicates that as the pressure increases; the estimated self-diffusivities using common approach are getting closer to the experimental values, while the proposed approach resulted less accurate values. Also it is clear that as the pressure increases the proposed approach over estimated the self-diffusivity values; while the temperature independent approach still gives lower self-diffusivities than the experimental values except at very high pressure (136.8 bar) where both approaches over estimated the self-diffusivity values.

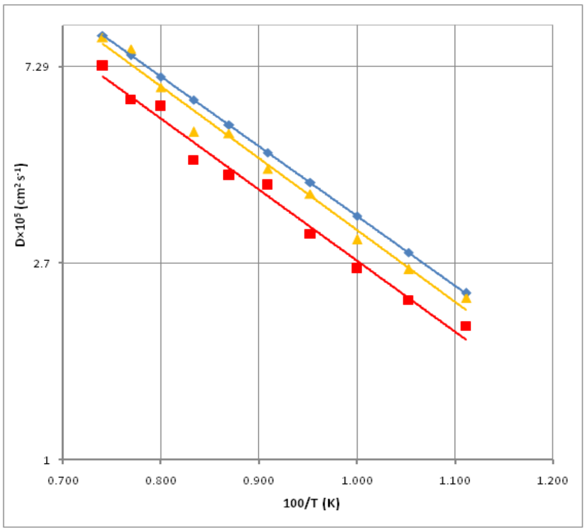


Figure 9: Self-diffusion coefficient of argon using temperature dependent and temperature independent interaction parameters for a system of 500 atoms with a simulation time step size of 2×10^{-15} s and run duration of 1.5×10^{6} simulation time steps at pressure of 13.07 bar (♦) Experimental data from (Naghizadeh and Rice, 1962), (■) Temperature independent interaction parameters. (▲) Temperature dependent interaction parameters

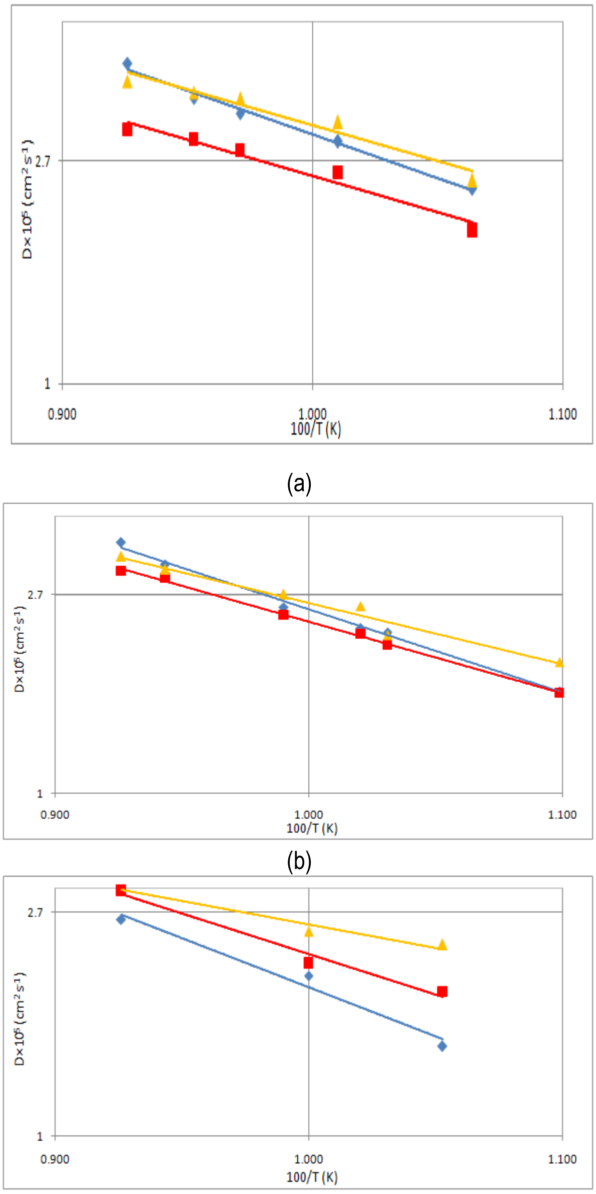
Table 5: Self-diffusivity of argon using temperature independent and temperature dependent interaction parameters for a system of 500 atoms and simulation time step size of 2×10^{-15} s and run duration of 1.5×10^{6} simulation time steps at pressure of 13.07 bar

Temperature K	D_{exp}×10^5 *cm^2 s^{-1}*	Temperature Independent Interaction Parameters		Temperature Dependent Interaction Parameters	
		D×10^5 *cm^2 s^{-1}*	Relative Error %	D×10^5 *cm^2 s^{-1}*	Relative Error %
90	2.32	1.97	15.3	2.27	2.4
95	2.85	2.24	21.6	2.62	8.2
100	3.43	2.63	23.3	3.05	11.2
105	4.06	3.13	23.0	3.84	5.4
110	4.73	4.02	15.1	4.35	8.0
115	5.43	4.21	22.5	5.20	4.2
120	6.17	4.55	26.3	5.24	15.1
125	6.94	5.98	13.9	6.58	5.2
130	7.74	6.18	20.1	7.98	3.2
135	8.55	7.33	14.3	8.47	1.0
Average Relative Error %			19.5		6.4
RMSD			1.07		0.39

D_{exp}: experimental results of (Naghizadeh and Rice, 1962).

By looking at Table 6; it could be concluded that the method of temperature dependent interaction parameters gives better predictions for the estimated values of self-diffusivities than the common approach. At pressure ranging from 60 bar up to 105 bar it seems that both approaches have the same accuracy, while at pressures higher than that the method of temperature independent interaction parameters gives better predictions but with over estimation of the self-diffusivity values.

One explanation for this behavior, is that at higher pressures the atoms are more compacted and much closer to each other, therefore other intermolecular forces starts to play a significant effect between the argon atoms that are not accounted for by Lennard-Jones pair potential. Another explanation also that Lennard-Jones potential parameters (well depth and collision parameters) may also be functions of pressure and temperature, this assumption of course needs further investigation and deeper study.



(a)

(b)

(c)

Figure 10: Self-diffusion coefficient of argon using temperature dependent and temperature independent interaction parameters for a system of 500 atoms with a simulation time step size of 2×10^{-15} s and run duration of 1.5×10^{6} simulation time steps (♦) Experimental data from (Naghizadeh and Rice, 1962), (■) Temperature independent interaction parameters. (▲) Temperature dependent interaction parameters. (*a*) at pressure of 58.6 bar, (*b*) at pressure of 104.4 bar, (*c*) at pressure of 136.8 bar

Table 6: Self-diffusivity of argon using temperature independent and temperature dependent interaction parameters for a system of 500 atoms and simulation time step size of 2×10^{-15} s and run duration of 1.5×10^{6} simulation time steps at pressure of 58.6 bar, 104.4 bar and 136.8 bar

Pressure *Bar*	Temperature *K*	$D_{exp}\times10^5$ $cm^2\ s^{-1}$	Temperature Independent Interaction Parameters		Temperature Dependent Interaction Parameters	
			$D\times10^5$ $cm^2\ s^{-1}$	Relative Error %	$D\times10^5$ $cm^2\ s^{-1}$	Relative Error %
58.6	94	2.38	1.98	16.9	2.47	3.8
	99	2.94	2.56	12.9	3.20	8.9
	103	3.34	2.82	15.6	3.56	6.7
	105	3.57	2.96	17.1	3.66	2.5
	108	4.16	3.09	25.8	3.83	7.9
	Average Relative Error %			17.7		5.9
	RMSD			0.46		0.16
104.4	91	1.67	1.65	1.3	1.93	15.5
	97	2.24	2.10	6.2	2.20	1.5
	98	2.28	2.21	2.9	2.55	11.7
	101	2.54	2.43	4.2	2.70	6.2
	106	3.15	2.93	6.9	3.06	2.8
	108	3.50	3.03	13,4	3.27	6.7
	Average Relative Error %			5.8		7.4
	RMSD			0.17		0.15
136.8	95	1.49	1.90	8.1	2.33	33.0
	100	2.04	2.15	0.7	2.47	15.9
	108	2.61	2.96	5.3	3.02	7.4
	Average Relative Error %			4.7		18.8
	RMSD			0.17		0.33

D_{exp}: experimental results of (Naghizadeh and Rice, 1962).

NOMENCLATURE

amu	Atomic mass unit
Ar	Argon
D	Diffusion coefficient
D_{exp}	Experimental value of diffusion coefficient
F	Force vector
fs	Femto second
g	Degrees of freedom
J	Mass flux vector
k	Botzmann's constant
L	Side length of simulation box
LJ	Lennard-Jones pair potential
m	Mass
MD	Molecular dynamics
MPa	Mega Pascal
MSD	Mean square displacement
N	Number of particles
NVE	Microcanonical ensemble
NPT	Isothermal-isobaric ensemble
NVT	Canonical ensemble
P	Pressure
p	Momenta
P_A	Actual pressure of the system

P_D	Desired pressure
Ps	Pico second
Q	Constant in Nosé -Hoover thermostat
Q_p	Constant used in Andersen algorithm to control pressure
R	Particles separation
R	Position vector
R_{cut}	Cutoff radius
RDF	Radial distribution function
RMSD	Root mean square deviation
T	Time
T	Temperature
T_A	Actual temperature of the system
T_D	Desired temperature
U(r)	Potential energy
V	Velocity
V	Volume
VACF	Velocity auto-correlation function

Greek Letters

Δ	Small change
$\boldsymbol{\nabla}$	Gradient vector
ε	Well depth
λ	Thermostat factor of Nosé -Hoover
ρ	Density
σ	Collision diameter
τ	Thermostat relaxation time factor

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