The Optimum Maximum Allowed Displacement in Monte Carlo Simulation of Lennard-Jones Potential Point Particles

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Abstract

In this paper, periodic systems of N point particles with Lennard-Jones potential are simulated in three dimensional space using Monte Carlo technique. The maximum allowed displacement used in Monte Carlo simulation of any N-particle system controls the convergence of the calculated potential energy to its physical situation. The optimum maximum allowed displacement associated with 50% acceptance rate is found. Since Lennard-Jones potential is a short range one, it is considered to be zero beyond some cut-off radius. The optimum dimensionless cut-off radius in the Lennard-Jones case is 2.5, which is used in simulations. An explicit mathematical formula for the optimum maximum allowed displacement as a function of both temperature and density is obtained. This formula is predicted by fitting the Monte Carlo results using the fitting tools in Matlab.

Keywords: *N-particle system, Lennard-Jones Potential, Monte Carlo Simulation, Maximum Allowed Displacement.*

Introduction

The Lennard-Jones (LJ) potential is one of the most important mathematical models that describes the energy of interaction between two particles, usually, neutral atoms or non-polar molecules (Born and Oppenheimer, 1927). This potential is used to study the nature and stability of small clusters of interacting particles in crystal growth and random geometry of liquids (Hoare and Pal 1971).

It also appears in molecular dynamics to simulate many particle systems ranging from solids, liquids and gases. In addition, this potential appears in the study of the motion of stars and galaxies in the universe among other applications (Subirana and Chavela 2004).

The common used form of the LJ potential between neighboring particles is given by (Mie, 1903)

$$U_{LJ}(r) = 4\varepsilon[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}] \tag{1.1}$$

where ε is the strength of the attraction between particles, σ is the intermolecular separation at which the potential energy vanishes, and r is the distance between the centers of the two particles. The first term of Equation (1.1) describes the repulsive potential between particles, which arises from Pauli's Exclusion Principle (Condon and Shortly, 1951). The second term describes the attractive potential, and depends on van der Waal's forces (Evans, 2009; Yip and La Rubia 2009).

The minimum value of the LJ potential occurs at the distance $r_0 = 2^{\frac{1}{6}}\sigma$. If the distance between any two particles is greater than r_0 , attraction happens between them; otherwise, a repulsion happens. By reducing the units, Equation (1.1) becomes

$$U_{LJ}^{*}(r^{*}) = 4[\left(\frac{1}{r^{*}}\right)^{12} - \left(\frac{1}{r^{*}}\right)^{6}] \tag{1.2}$$

where $U_{LJ}^{*} = \frac{U_{LJ}}{\varepsilon}, r^{*} = \frac{r}{\sigma}$.

One of the advantages of the LJ potential is that it falls off quickly, and only those particles within a near environment have much effect. As a result, it is possible to limit (or cut off) the maximum range of the interaction. The common choice of the reduced cut off distance (r_{cut}^{*}) of LJ potential energy is in the range between 2 and 3 (Landau and Binder 2009). A typical value for this distance is 2.5 (Hurst 2008). Hence, Equation (1.2) can be written as

$$U_{LJ}^{*}(r^{*}) = \begin{cases} 4\left[\left(\frac{1}{r^{*}}\right)^{12} - \left(\frac{1}{r^{*}}\right)^{6}\right], & if\ r^{*} \le r_{cut}^{*} \\ 0, & if\ \ r^{*} > r_{cut}^{*} \end{cases} \tag{1.3}$$

In the present work, a system of *N* point particles is studied, and it is assumed that the pairwise force between any two of them is unaffected by the positions of the other particles. This kind of approximation is, therefore, suitable for gases and liquids. The intermolecular forces are also assumed to be independent of the velocities. Hence, the total potential energy $U_{LJ}^{*}(r^{*})$ for the system of interest is given by

$$U^{*}(r^{*}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} U_{LJ}^{*}\left(r_{ij}^{*}\right) \tag{1.4}$$

where r_{ij}^{*} is the reduced distance between the particles i and j.

In order to study such complex systems, a suitable computational techniques are needed. One of the most important simulation techniques that is usually used is the Monte Carlo (MC) method (Allen and Tildesley, 1987; Frinkel and Smit, 2002; Jana, 2011; Landau and Binder, 2009; Rosenbluth et al., 1953; Sadus and Richard, 2002). The idea of MC simulation is sampling microscopic states that are statistically significant for long-time averages of physical quantities (Frinkel and Smit, 2002; Newman and Barkema, 1999). These states will be picked up with a biased probability (Frinkel and Smit, 2002). This needs averaging the desired observable quantity over all the states of the system, and weighing each state by the Boltzmann probability (Ferguson et al., 1999). Markov process is the best procedure that is used for selecting states according to this probability (Frinkel and Smit, 2002; Gallager, 2013; Greenberg, 2008).

The probability of the transition from state n to state m depends only on the difference in the total energy, $U_m^{*} - U_n^{*}$. A simple and efficient method for calculating the transition probability is the Metropolis algorithm (Hermann and Binder, 2010; Rosenbluth et al., 1953). In this algorithm, the transition probability from the state n to state m is given by

$$W(n \to m) = \begin{cases} e^{-\frac{U_m^{*} - U_n^{*}}{T^{*}}}, & if\ U_m^{*} > U_n^{*} \\ 1, & if\ U_m^{*} \le U_n^{*} \end{cases} \tag{1.5}$$

where T^{*} is the reduced temperature of this system and it is given by $T^{*} = \frac{TK_B}{\varepsilon}$ (T is the real temperature, and K_B is the Boltzmann constant).

Changing the state of the system can be done by randomly moving one particle. This move must be controlled by a maximum displacement allowed for this particle, $dmax$. Finding the optimum choice, $O{-}dmax$, of the maximum allowed displacement is the main goal of this paper. The

advantage of using $O{-}dmax$ in the simulation of such complex systems will give fast convergence to the equilibrium state.

The Optimum Maximum Allowed Displacement

The optimum behavior of the convergence in MC simulation and efficient sampling procedure that leads to fast equilibration can be achieved by using $O{-}dmax$.

The $O{-}dmax$ leads to high statistical accuracy and saves lot of time needed to obtain the desired averages in the simulation convergence without affecting the equilibrium values (Ferguson, 1999). Two main conditions the displacement vector has to satisfy: First, it must be randomly chosen, which can be achieved by a random numbers generator in the computer, second, its magnitude has to be carefully chosen. The magnitude of the move may become out of the whole simulation box, or it may be very small. This depends on $O{-}dmax$.

The position of a particle i in every metropolis MC step is defined by (Rosenbluth et al., 1953)

$$\overrightarrow{r_i^{*(N)}} = \overrightarrow{r_i^{*(0)}} + dmax.(\vec{1} - 2\vec{\gamma}), \tag{2.1}$$

where $\overrightarrow{r_i^{*(N)}}$ and $\overrightarrow{r_i^{*(0)}}$ are the new and the old locations of the particle i , respectively, $\vec{1}$ is the vector [1,1,1], and γ is randomly chosen from the box [0,1]×[0,1]×[0,1]. Using Equation (1.5), the probability of this move will be given by [19]

$$w\left(\overrightarrow{r_i^{*(0)}} \to \overrightarrow{r_i^{*(N)}}\right) = \min[1, \frac{P\left(\overrightarrow{r_i^{*(N)}}\middle| R_i\right)}{P\left(\overrightarrow{r_i^{*(0)}}\middle| R_i\right)}] \tag{2.2}$$

Here, $P\left(\overrightarrow{r_i^*}\middle| R_i\right) = constant.e^{-\frac{U_m^* - U_n^*}{T^*}}$ is the conditional probability that finds the particle at the position $\overrightarrow{r_i^*}$ when the location of all other $N{-}1$ particles, defined by the set $R_i = \{\overrightarrow{r_1^*}, \ldots..\overrightarrow{r_{i-1}^*}, \overrightarrow{r_{i+1}^*}, \ldots \ldots \overrightarrow{r_N^*}\}$, are fixed.

The acceptance ratio of the simulation, F, which is the ratio between the accepted moves to the total number of moves, depends on $dmax$. As mentioned before, if, on one hand, the magnitude of $dmax$ is chosen to be big, a lot of particles movements are not be going to be accepted. On the other hand, if the magnitude of $dmax$ is chosen to be small, the neighboring configurations will be highly correlated since all the states in the Markov chain are the same, and any essential change of the configuration will need many particles displacements (Rosenbluth et al., 1953). Both cases

are not effective in the computational technique, since they lead to increasing the computational work (Frinkel and Smit, 2002; Richet, 2001). In their research, many authors mentioned the effect of $dmax$ on simulations they have done (Coutinho and Canuto, 2003; Coutinho et al., 2004; Flach and Wilke, 2010; Goldman, 1983; Montani, 1992; Mountain and Thirumalai, 1994; Nauchitel and Pertsin, 1980; Okeeffe and Orkoulas, 2009; Panagiotopoulos et al., 1986; Tiana et al., 2007; Vorholz et al., 2002). Experience indicates that $dmax$ associated with acceptance rate 50% is often desirable for MC simulation. However, there is no theoretical basis or systematic verification for the optimality of $dmax$ associated with this traditional acceptance rate (Sados and Richard, 2002). In addition, this suggested optimal $dmax$ is affected by the properties of the system under consideration.

In this paper, N-point identical particle systems in a constant volume V, at constant temperature T,($NVT-$canonical ensemble), are systematically studied. This research is a reproducing of the results obtained in (Al-Shraydeh, 2015).

In our system, particles move under the action of LJ potential; the simulation is performed in order to get a mathematical formula of the $O-dmax$ that is associated with 50% acceptance rate as a function of temperature and density. Each state space is defined by all outcomes. Given the present state n, a particle is picked up and randomly moved according to Equation (2.1) to get the new state m. The energy of each state is calculated and then the Metropolis algorithm acceptance criteria are used to get the accepted states. Also, since our simulations are applied to infinite systems, a suitable periodic boundary condition is considered in this work. The detailed discussion about periodic boundary conditions can be found in (Allen and Tildesely, 1987; Chandler, 1987; Newman and Barkema, 1999).

Results and Discussion

The MC technique is used to simulate a system of 128 particles in three dimensions. The number of particles and the number of MC sweeps are chosen to be sufficient to get the desired results. Also, the values of the temperature and the density have been carefully chosen to cover the physical conditions of the system. In addition, the value 2.5 of the dimensionless cut-off radius r_{cut}^{*} is traditionally used in the simulation of systems with Lennard-Jones potential. This value is checked to be the best cut-off radius in the sense of accuracy and convergence speed. The simulation of the

system is done at a given temperature, density, and $dmax$ in order to obtain the acceptance rate F. Fig. 1 shows $dmax$ as a function of F at $T^* = 4.2$ and $\rho^* = 1.5$ as an example, where $\rho^* = \frac{N\sigma^3}{V}$. The simulation results data show that the relation between F and $dmax$ is exponential. By fitting the results shown in Fig.1, the best mathematical formula that represents the relation with minimum error is

$$F = ae^{b(dmax)} \tag{3.1}$$

which is equivalent to

$$dmax = \frac{1}{b}\ln(\frac{F}{a}) \tag{3.2}$$

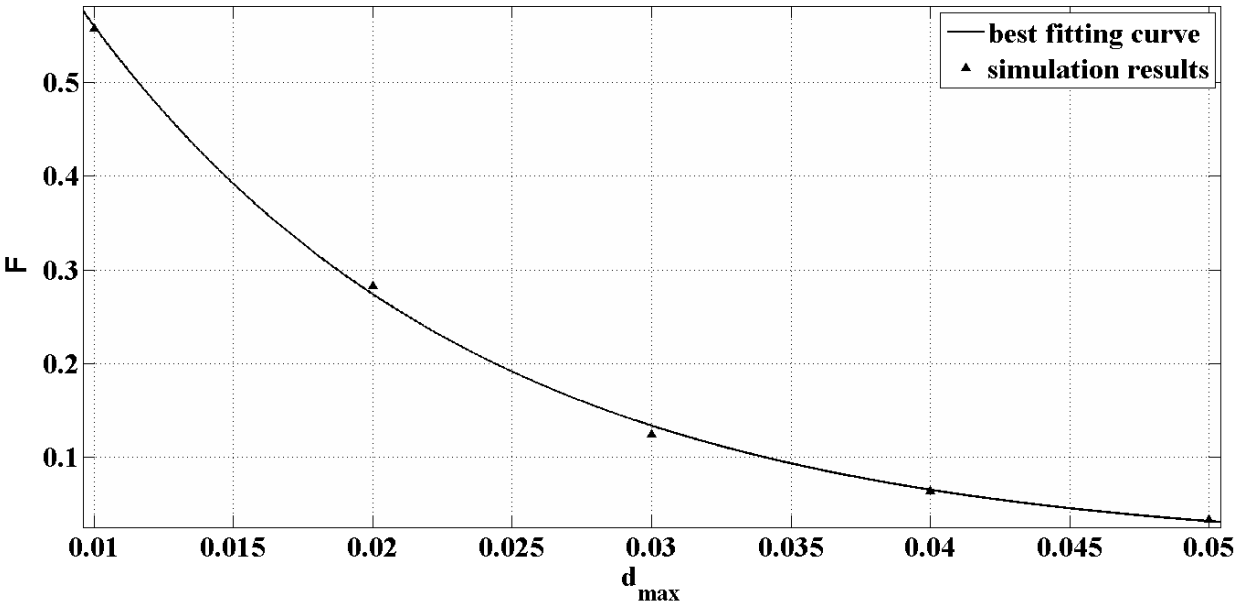

Figure 1. Maximum allowed displacement versus acceptance rate at $T^* = 4.2$ and $\rho^* = 1.5$

where a and b are constants. Substituting F=0.5 in Equation (3.2) will give the value of $O{-}dmax$. In the case of $T^* = 4.2$ and $\rho^* = 1.5$, the values of a and b are 1.145 and -71.51, respectively, and the determination coefficient obtained from the fitting curve in Fig.1 is $R{-}square$=0.999. The procedure was repeated for $T^* = 4.2$ at different values of ρ^*: (0.3125, 0.375, 0.4375, 0.50, 0.625, 0.75, 1.0, 1.25, 1.75, and 2.0). Samples of the simulation results for F as a function of $dmax$ are shown in Fig.2, and the values of a, b, $O{-}dmax$ and the determination coefficient $R{-}square$ are shown in Table.1. It is clearly seen that there is a dependency between $a, b, O - dmax$, and ρ^* at

fixed temperature; the values of a increase by increasing ρ^*, while the values of b and $O-dmax$ decreases.

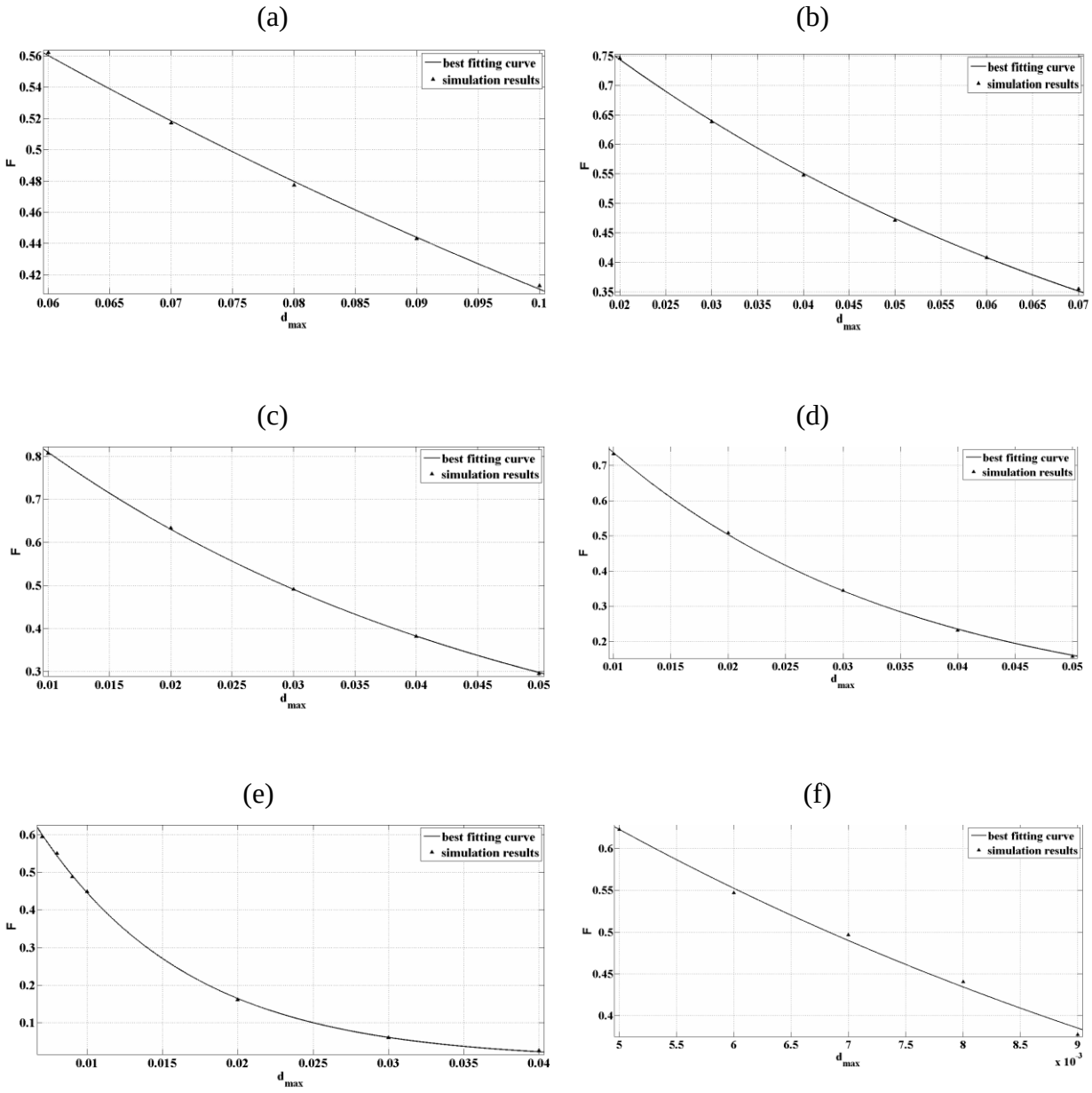

Figure 2. The best fitting curves of the maximum allowed displacement versus acceptance rate at $T^* = 4.2,\ for\ \rho^* = (a)0.3125, (b)0.5, (c)0.75, (d)1.0, (e)1.75, (f)2.0$

The relation between ρ^* and $O-dmax$ for fixed temperature is shown in Fig. 3 and is supposed to be of the form

$$O - dmax = Ke^{L\rho^*} \tag{3.3}$$

where K and L are constants (in the case of $T^* = 4.2$, K=0.1451,and L=−2.114).

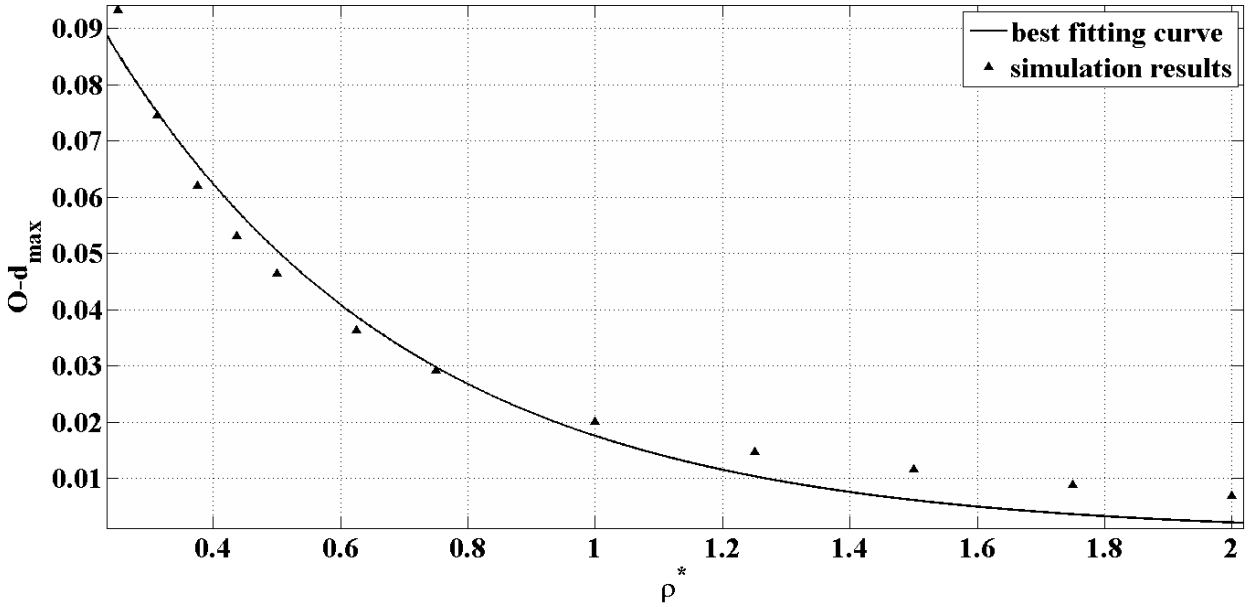

Figure 3. Density versus optimum maximum allowed displacement at $T^* = 4.2$

The above procedure is repeated for different values of T^*:(1.0,1.5,2.0,2.5,2.9,3.4,3.8,5.0 and 6.0). At each value of T^* , the simulation is done for the all values of ρ^* used in the case of $T^* = 4.2$. Results show that $O{-}dmax$ follows Equation (3.3). The data obtained from the simulation as well as the data obtained from (3.2) are plotted and shown in Fig.4.

From the data presented in Fig.4, it is clearly notable that the values of K and L depend on temperature. Therefore, equation (3.3) can be written as

$$O - dmax(T^*, \rho^*) = K(T^*)e^{L(T^*)\rho^*} \tag{3.4}$$

Table.1: The values of a, b, $O-dmax$, and $R-square$ for $T^* = 4.2$ at different values of ρ^*

$\rho*$	a	b	$O-dmax$	$R-square$
0.3125	0.8919	-7.753	0.0746	0.9988
0.375	0.9557	-10.43	0.0621	0.9992
0.4375	0.9612	-12.29	0.0531	0.9993
0.50	1.004	-15.00	0.0464	0.9996
0.625	1.027	-19.81	0.0363	0,9999
0.75	1.039	-25.00	0.0292	0,9998
1.00	1.078	-38.12	0.0201	0.9997
1.25	1.122	-54.70	0.0147	0.9998
1.50	1.145	-71.51	0.0115	0.9991
1.75	1.207	-99.76	0.0088	0.9996
2.00	1.135	-120.00	0.0068	0.9951

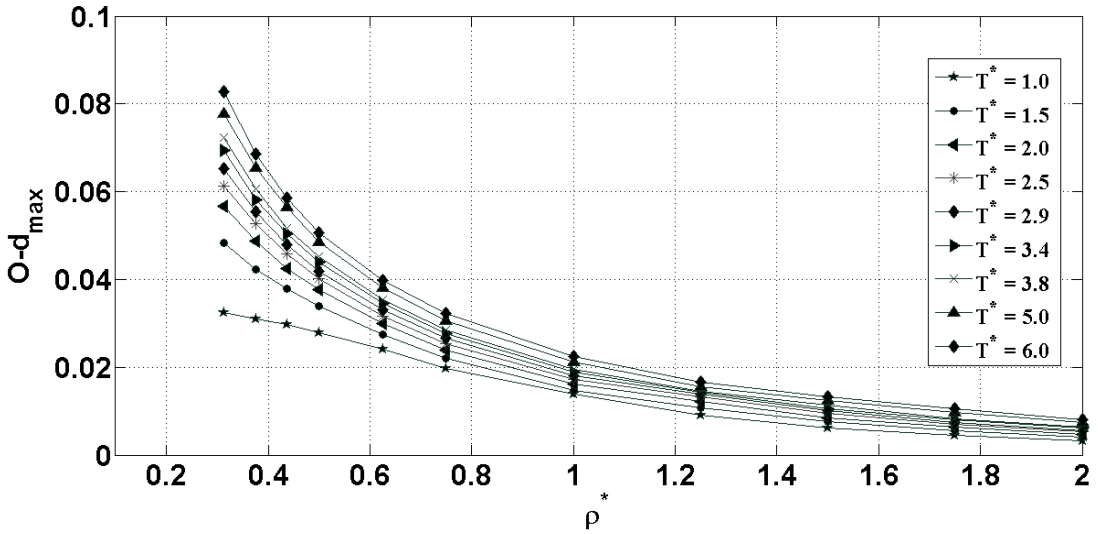

Figure 4. Density versus optimum maximum allowed displacement at different values of temperature

To obtain mathematical formulas for K and L as functions of T^*, their values, shown in Table 2, are fitted using Matlab. Fig.5 shows the best fitting curves for K and L. Their mathematical formulas are given by

$$K(T^*) = -0.1417(T^*)^{-0.4681} + 0.1937 \quad (3.5)$$

with $R{-}square$=0.9975, and

$$L(T^*) = -0.4829(T^*)^{-2.58} - 1.804 \quad (3.6)$$

with $R{-}square$=0.9898.

Table 2. The values of the constants K and L, and the value of $R{-}square$ at different values of T^*.

T^*	K	L	$R{-}square$
1	0.05166	-1.32	0.9923
1.5	0.07838	-1.639	0.9969
2	0.09252	-1.723	0.9920
2.5	0.1004	-1.741	0.9897
2.9	0.1067	-1.763	0.9869
3.4	0.114	-1.795	0.9849
3.8	0.1185	-1.805	0.9829
5	0.1252	-1769	0.9810
6	0.1341	-1.798	0.9771

In addition to the determination coefficient, the residual plot and the ANOVA test have been done, as an example, for $T^* = 2.9$. The results show the high accuracy of the approximation using Equation (3.4) in comparison with the simulation results. Fig.5 shows the residuals. The ANOVA test using SPSS gives P value equals to 0.000, F value equals to 879, R-Square=.99, and the correlation coefficient equals 0.99. This shows that there is no remarkable differences between the simulation results and those of Equation (3.4).

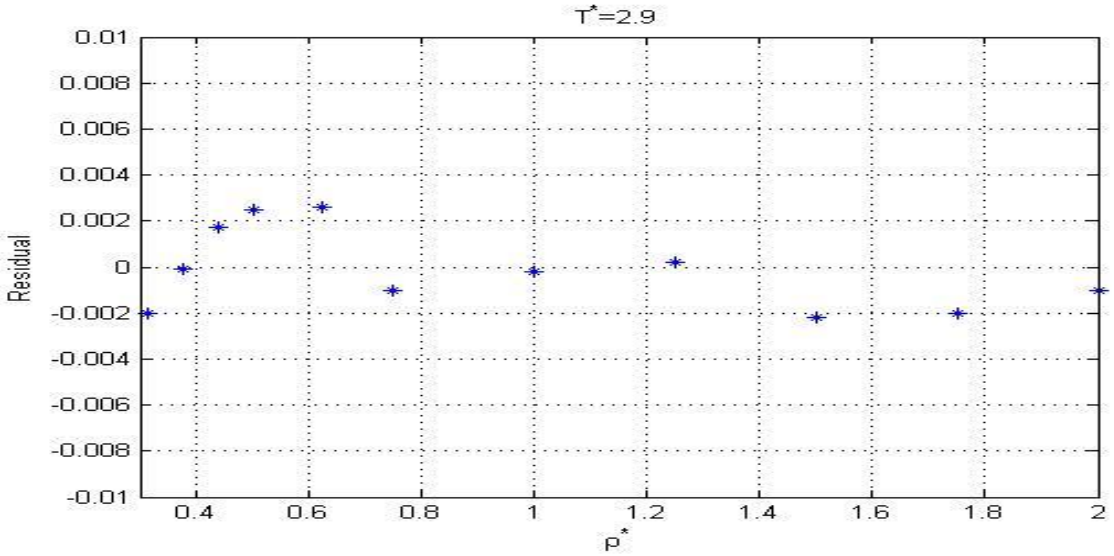

Figure 4. Differences between the simulation results of *O-dmax* and the calculated results by equation (3.4)

Conclusions

A system of 128-point particles with Lennard-Jones potential in an *NVT*-ensemble is simulated using Metropolis Monte Carlo method with a suitable periodic boundary conditions. The cut-off radius used in this study is 2.5. The maximum allowed displacement $dmax$ associated with 50% acceptance rate is found. This gives the best convergence of simulation to the equilibrium state of the system. The mathematical representation of the relation between $O{-}dmax$ and both temperature and density is found and formulated by Equation (3.4).

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الحد الأقصى الأمثل للنزوح المسموح به في محاكاة مونت كارلو لجزيئات لينار جونز النقطية

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الملخص

في هذه الورقة البحثيه ، تم محاكاة الأنظمة الدورية لجسيمات نقطية عددها N مع طاقة لينارد جونز في الفضاء الثلاثي الأبعاد باستخدام تقنية مونتي كارلو. الحد الأقصى للنزوح المسموح به المستخدم في محاكاة مونت كارلو لأي نظام جزيئي عدده N يسيطر على تقارب الطاقة الكامنة المحسوبة مع وضعها المادي. تم العثور على الحد الأقصى الأمثل للنزوح المرتبط بمعدل قبول 50٪. ونظرًا لأن الإمكانيات هي قصيرة المدى، فإنها تعد صفرًا إلى ما بعد نصف قطر القطع. يبلغ نصف قطر القطع الأمثل بلا أبعاد في حالة لينارد جونز 2.5، والذي يستخدم في عمليات المحاكاة. وتم الحصول على صيغة رياضية صريحة للحد الأقصى الأمثل المسموح به كدالة لكل من درجة الحرارة والكثافة. وتم توقع هذه الصيغة من خلال ملاءمة نتائج مونت كارلو باستخدام أدوات التركيب في Matlab.

الكلمات الدالة: *نظام جسيمات نقطية عددها N ، طاقة لينارد جونز ، محاكاة مونت كارلو ، الحد الأقصى المسموح به للنزوح.*