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Relaxation dynamics in small clusters: A modified Monte Carlo approach

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Abstract

Relaxation dynamics in two-dimensional atomic clusters consisting of mono-atomic particles interacting through Lennard-Jones (L-J) potential has been investigated using Monte Carlo simulation. A modification of the conventional Metropolis algorithm is proposed to introduce realistic thermal motion of the particles moving in the interacting L–J potential field. The proposed algorithm leads to a quick equilibration from the nonequilibrium cluster configuration in a certain temperature regime, where the relaxation time (τ), measured in terms of Monte Carlo Steps (MCS) per particle, vary inversely with the square root of system temperature ($\sqrt{T}$) and pressure (P); $\tau \propto (P\sqrt{T})^{-1}$. From this a realistic correlation between MCS and time has been predicted.

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Keywords: Monte Carlo simulation; Atomic clusters; Relaxation dynamics; L-J potential

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1. Introduction

The transformation of matter from nonequilibrium state to an equilibrium one depends strongly on the prevailing external and internal physical conditions. Among the external conditions, most important are pressure and temperature and internal condition refers to the interaction potential of the constituent atoms of the material. The high temperature state of any matter is a completely disordered chaotic state, the gaseous state. When such a system is allowed to cool down, keeping it in contact with a thermal bath maintained at lower temperature, it normally goes to a solid phase either directly or through an intermediate liquid phase depending on the external pressure. The structure of the final solid phase, whether it is an ordered crystalline or a disordered amorphous or glassy state, depends primarily on the cooling procedure. The study of the dynamics of relaxation of such systems towards equilibrium, received much importance in recent years [1–4]. Complex systems like glasses, peptides and proteins are found to exhibit different types of time evolution behaviours including

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exponential, multiexponential and asymptotic power-law relaxation [5–8]. Theoretical modeling of the physical phenomena include Adam-Gibbs (AG) model [9,10], time autocorrelation function analysis of master equation [5], molecular dynamics (MD) simulation [11,12], and Monte Carlo simulation [13]. These studies help in understanding some of the salient features of the relaxation dynamics in the glassy state at moderately low temperature, the so-called α-relaxation regime, leaving a many of the basic questions unanswered. In the low temperature α-relaxation regime, the most popular approach to study the phenomena involves analysis using a master equation [14] considering potential energy landscape (PEL) [5, 15–21]. These studies are helpful for qualitative understanding of the short-time and long-time relaxation processes. Molecular dynamics (MD) simulation [11], unlike master equation approach, deals with the problem in the microscopic level, but takes longer time to solve relevant equations of motions. A very recent MD simulation [12] in a super-cooled binary liquid proposes the α relaxation to be a sequence of rapid localized co-operative relaxation event in which small particle clusters participate. Monte Carlo simulation of similar systems at low temperature considering spin-glass (SG) model offer considerable difficulty due to the fact that the spin configurations tend to be trapped into any of the many local minima of the free energy function giving rise to slow dynamical process. This points to the necessity for the development of an efficient MC method. The multicanonical method [22], simulated tempering method [23] and exchange MC method (EMC) [13,24] take into account this particular issue. In spite of these sincere efforts, the predictions of the SG models are yet to be settled from the experimental point of view.

2. The model

Our present motivation is to investigate the relaxation dynamics using MC method. In contrast to the most popular SG model, in which the system is modeled by spins occupying specific lattice sites and interact with each other through a suitable Hamiltonian, we consider a more realistic model in which the constituent particles of the system are free to move and take any position in a two-dimensional space of constant area. The particles are assumed to be mono-atomic and interact through Lennard-Jonnes (L-J) potential. The initial configuration representing the disordered state at relatively high temperature is generated by placing the particles randomly in the two-dimensional space. The system temperature T is then suddenly reduced to a lower value keeping it in contact with a thermal bath and the dynamics to equilibrium is achieved through MC simulation. To introduce real thermal motion, we propose a modification of the conventional Metropolis

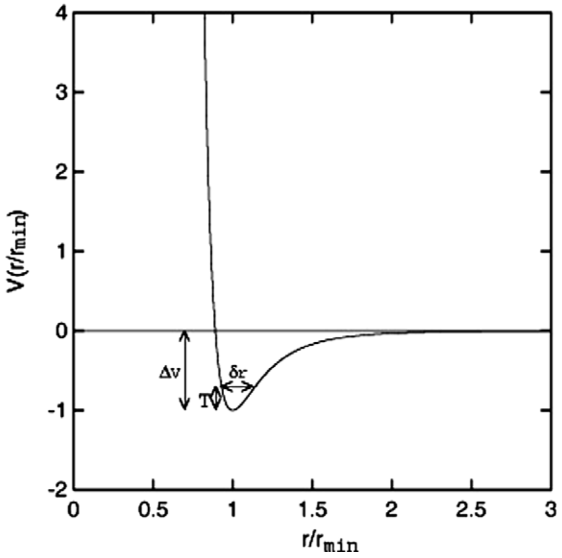

Fig. 1. The Lennard-Jones potential function V (normalised). $r_{\min}$ represents the distance at which the potential function becomes minimum. The allowed range of particle displacement at temperature T measured in units of the normalised potential is δr and Δv is the depth of the potential.

algorithm [25]. In the standard Metropolis algorithm, equilibrium system configurations are generated through a probabilistic calculation in which the change in potential energy of the constituent particles due to arbitrary displacement within a pre-assigned range δr from its previous occupied position is compared with the kinetic energy imparted through system temperature. We observe that the system dynamics depends very much on the choice of δr. In real physical systems however, particle motions depend on the system temperature T. To incorporate this temperature dependence to our simulation procedure, the allowed range of displacement δr is decided by the L–J potential function and the average kinetic energy possessed by the particles at temperature T (measured in units of the normalised interaction potential V). This is depicted in Fig. 1. The inter-atomic distances are measured in units of $r_{\min}$, the distance at which the potential function possesses the minimum value. With the introduction of such restricted Monte Carlo moves, we notice that the system attains the equilibrium configuration within $\sim 10^3$ Monte Carlo steps (MCS) per particle.

3. Results and discussion

We start with a disordered state generated by placing N point particles randomly in a two-dimensional space of equal length $L = 14$. In calculating any physical parameter, we generate at least three independent initial configurations and take average. The configuration generated with N particles corresponds to a particle concentration (density) $c = N/L^2$. To know the system configuration at any finite temperature T, the N particles are allowed to move through restricted Monte Carlo steps. After 50 moves per particle the root mean square deviation d of the particles from their previous positions are calculated. We found that d decreases sharply with the number of Monte Carlo steps S only when the system temperature remains within a certain range depending on particle concentration c. Below $c = 0.5$ small clusters having ordered structures are formed here and there and no long range order is found. For $c \geqslant 0.5$ the particles form a single cluster and if T lies within a certain range $T_1 < T < T_2$, d decreases sharply with S and fluctuates around a steady value d_{eq}. When T is outside the specified range as stated above, d fluctuates around a high value signifying the maintenance of the initial disordered state. Fig. 2 depicts the nature of variation of d with S for $c = 0.5$ at $T = 0.008$, 0.02, 0.12 and 0.18. We see that at $T = 0.008$ both d_{eq} and its fluctuations are large. The quantities show minimum value at $T = 0.02$ and starts increasing as T is increased. The d vs. S plot is fitted with an exponential function given by,

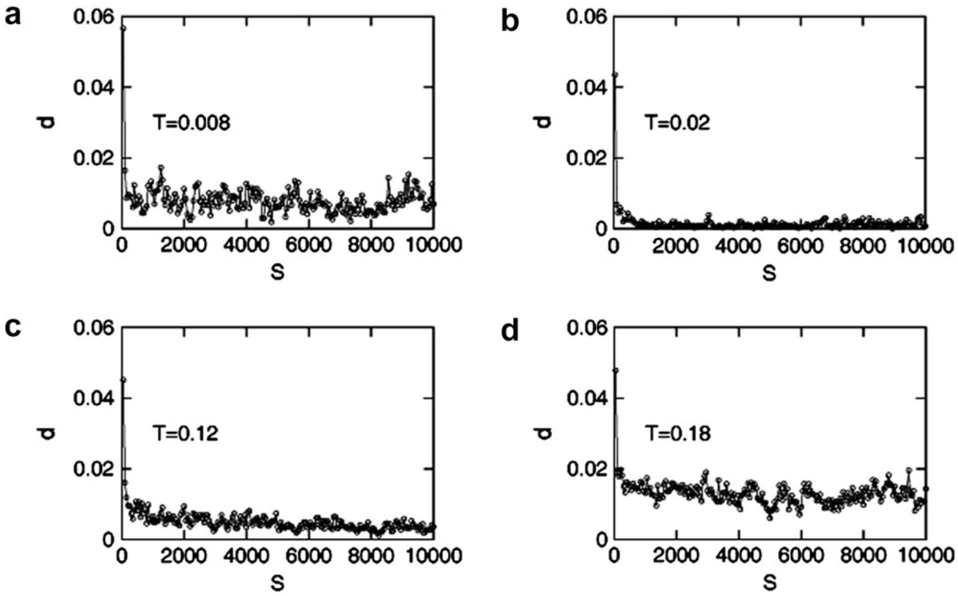

Fig. 2. Variation of root mean square displacement d_{rms} (in units of $r_{\min}$) with Monte Carlo steps S at $T = 0.008$, 0.02, 0.12 and 0.18.

$$d = d_0 + a\exp(-S/\tau) \tag{1}$$

The parameter τ gives the relaxation time in terms of Monte Carlo steps and d_0 gives the average value of the rms displacement d_{eq} at equilibrium configuration. In fact, there is no study relating Monte Carlo steps with real physical time. We assume a linear relationship between the two to study the relaxation behaviour of our system.

The variation of d_{eq} with T for $c = 0.5$ is presented in Fig. 3 which shows that d_{eq} decreases to a low value of $\sim 0.6 \times 10^{-3}$ unit (unit length corresponds to the value at which L-J potential has minimum value) at about $T_1 = 0.02$. It then starts increasing at a low rate up to $T_2 = 0.1$. The rate of increase is found to be higher and higher in the range from $T_2 = 0.1$ to $T_3 = 0.16$ and above T_3, respectively. From the slopes of this curve we identify the regions T_1T_2, T_2T_3 and above T_3 to be solid, liquid and gas, respectively. Below T_1 large values of d_{eq} and its fluctuations (Fig. 2(a)) indicate that no stable configuration is reached by the system of particles. In fact the state corresponding to this temperature regime is the glassy state for which the relaxation dynamics is very slow. T_1 may be identified with the glass transition temperature T_g. The nature of relaxation in this regime is quite interesting and will be treated later. For the present let us restrict our study above T_1. The equilibrium particle configurations reached at different temperatures above T_1 for $c = 0.5$ are depicted in Fig. 4. Fig. 4(a) shows the initial configuration in which some of the particles are found to occupy positions sufficiently close to each other. In fact, this represents an impractical situation and arises due to the fact that in generating this configuration we placed particles completely randomly without considering the hard-core repulsion imposed by the Lennard-Jones potential. However, the assumption of such an impractical initial configuration affects the results of the present study little since during simulation, within a few Monte Carlo steps ($\sim$5 MCS) the particles rearrange themselves to achieve a physically acceptable configuration. Our study shows that in the region $T_1 < T < T_2$, the system relaxes to a steady state with an ordered hexagonal solid like structure except a few defects. These defects arise as the system is quenched from a high temperature configuration. A typical particle configuration reached in this case is depicted in Fig. 4(b). This configuration remains almost unchanged with MCS except a little movement of the peripheral particles. In the range $T_2 < T < T_3$, d_{eq} as well as its fluctuations starts increasing. In this case, the system relaxes to a structure showing local orders with considerable number of defects and the configuration changes continuously indicating liquid like behaviour. Fig. 4(c) presents a snapshot of the particle configuration that is observed to change with MCS. For $T > T_3$, d_{eq} and its fluctuations increase further and no stable configuration is reached. The system shows gas like behaviour. Fig. 4(d) shows a snapshot of the particle configuration in this region. This config-

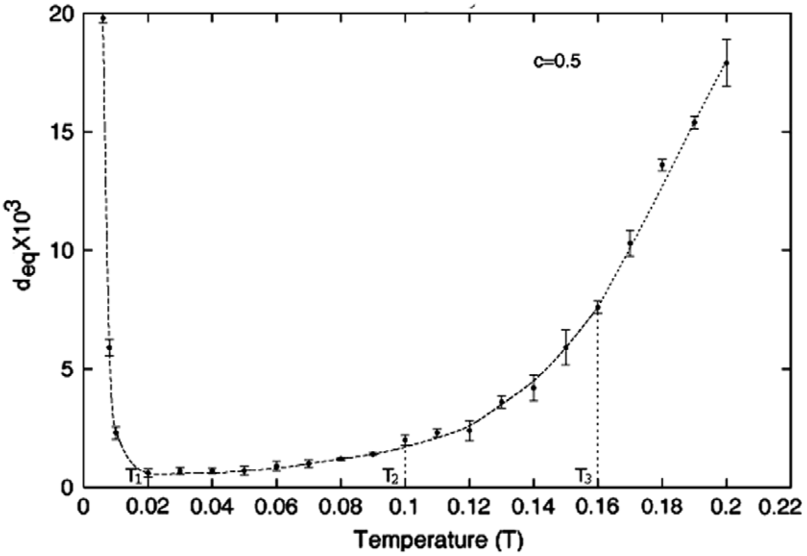

Fig. 3. Variation of d_{eq} (in units of r_{min}) with temperature (T) for $c = 0.5$. T_1T_2, T_2T_3 and above T_3 represent the solid, liquid and gaseous phases, respectively.

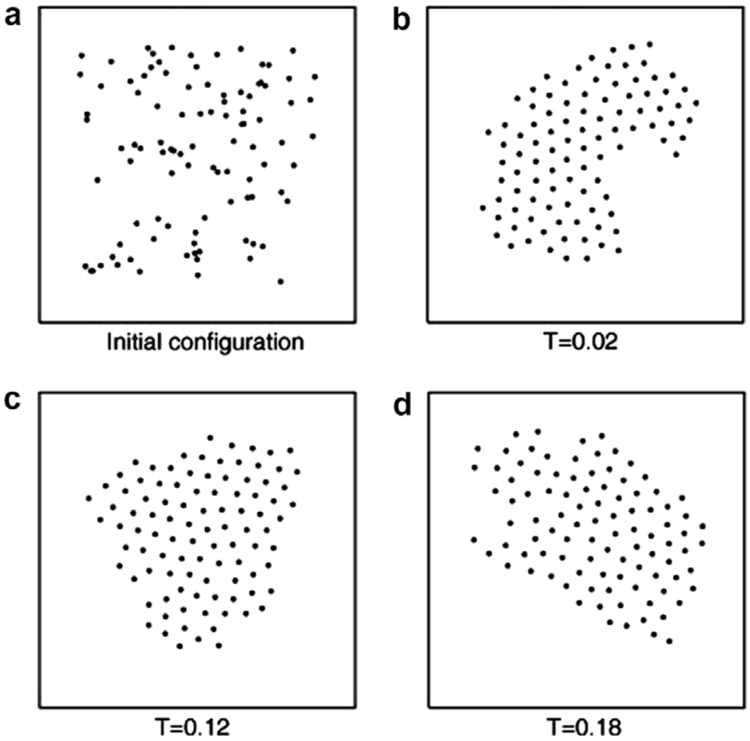

Fig. 4. The particle configurations at different temperatures (T). The initially generated random particle configuration corresponding to high temperature state is presented in (a) and those obtained after $S = 5000$ at $T = 0.02$, 0.12 and 0.18 are presented in (b), (c) and (d), respectively.

uration changes continuously with MCS. The behaviour of d_{eq} and observed change in particle configuration justifies the identification of the solid, liquid and gaseous states of the system. The equilibrium particle configurations in the solid phases obtained at $c = 0.7$ and 0.9 show that the equilibrium structures become more compact and rigid for higher values of c. According to Lindemann's criteria solid starts melting when d_{eq} is nearly 10% of the equilibrium spacing between the constituent atoms [26]. But the present simulation shows that melting occurs when d_{eq} is nearly 0.2% of the average lattice spacing. This may be caused by the lower dimensionality of the system considered.

Fig. 5 shows the variation of d_{eq} with temperature for two higher values of particle concentration, $c = 0.7$ and 0.9 along with that for $c = 0.5$. We observe that as c increases d_{eq} and its fluctuations decrease. In the region $T_1 = 0.02$ to $T_2 = 0.1$, the nature of variation of d_{eq} with T is almost same for all the three concentrations. Above T_2 the two curves for $c = 0.7$ and 0.9 show lower and lower rate of increase. In fact solid–liquid transition is expected to occur at higher and higher temperatures for these two concentrations respectively because they correspond to the situation at higher and higher pressures and the liquid phase for them will continue to higher and higher temperatures.

A qualitative analysis of the relaxation mechanism can be obtained considering the depth of the *L-J* potential well and the kinetic energy of the constituent particles. It is quite reasonable to expect that to achieve an ordered cluster configuration, the particles must possess a low kinetic energy compared to the depth of the potential well ($T < \Delta v$) as indicated in Fig. 1, so that any of them have a chance to get trapped by the potential minima while encountering another particle during their random thermal motion. The possibility of getting trapped will increase with the decrease of particle velocity. Again, the probability that a particle will encounter another one in a specified time interval increases with the increase of pressure. These two considerations led us to conjecture $\tau \sim (P\sqrt{T})^{-1}$, if T lies above some critical value viz. T_1, but not too large. For low temperature $T < T_1$, the particles will move slowly and take larger time to get trapped.

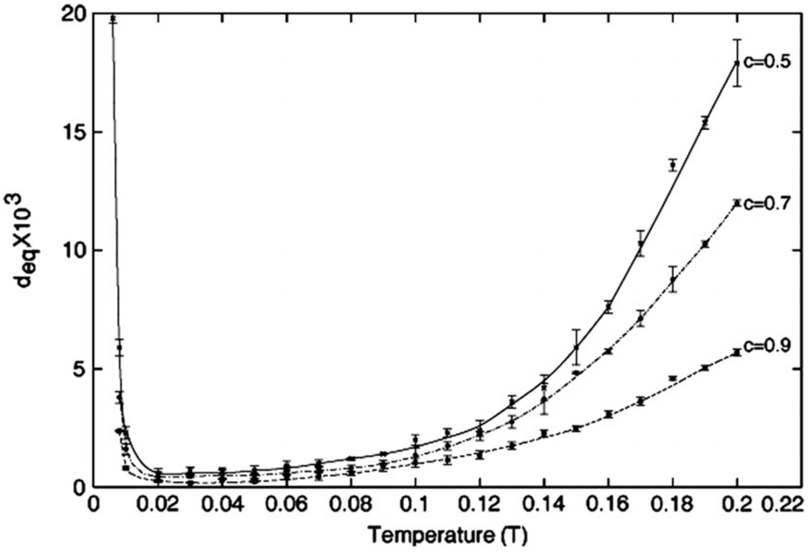

Fig. 5. Variation of d_{eq} (in units of $r_{\min}$) with temperature (T) for $c = 0.5$, 0.7 and 0.9.

Thus we expect that τ vs. T plot will show a minimum. Fig. 6 presents the variation of τ with T for $c = 0.5$, 0.7 and 0.9. For $c = 0.5$ the curve shows the existence of a reasonably sharp minimum, but as c is increased the minimum becomes flat and for $c = 0.9$ τ remains almost unchanged at its minimum value for higher T. The observation of such a minimum in τ vs. T plot is found to be consistent with the study involving master equation approach using potential energy landscape [27]. The τ vs. $T^{-1/2}$ plot for $T > 0.04$ fitted with straight-line graph yield three different lines as presented in Fig. 7. It is interesting to note that, the three curves meet near $T = 0.05$ indicating that at this temperature τ is minimum and independent of pressure, of course, if P lies above some critical value. The slopes m of these lines plotted against c show linear behaviour as depicted in Fig. 8 confirming that $\tau \sim (P\sqrt{T})^{-1}$, since $c \sim P^{-1}$.

One important consequence of the present simulation algorithm is that, it gives an estimate of MCS time in terms of actual time. We observe that for all of the three concentrations d_{eq} attains a minimum value at

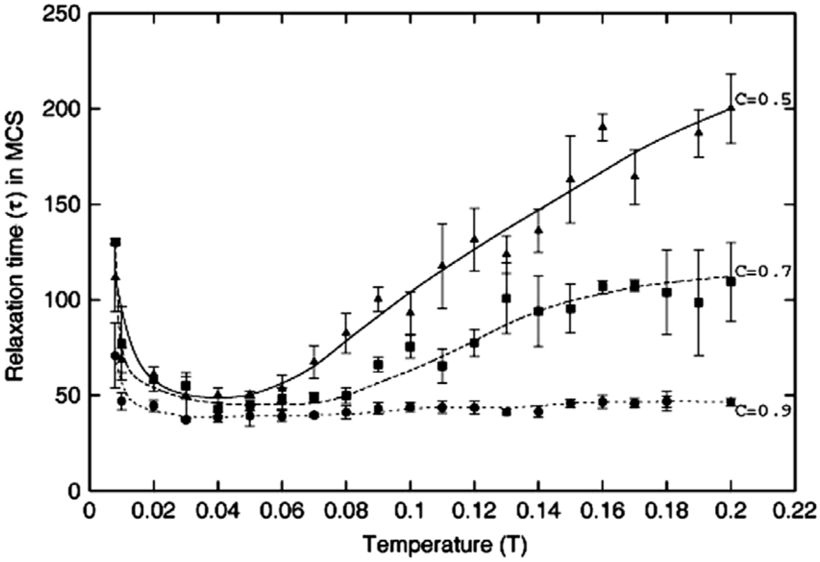

Fig. 6. Variation of relaxation time (τ) in MCS with temperature (T) for $c = 0.5$, 0.7 and 0.9.

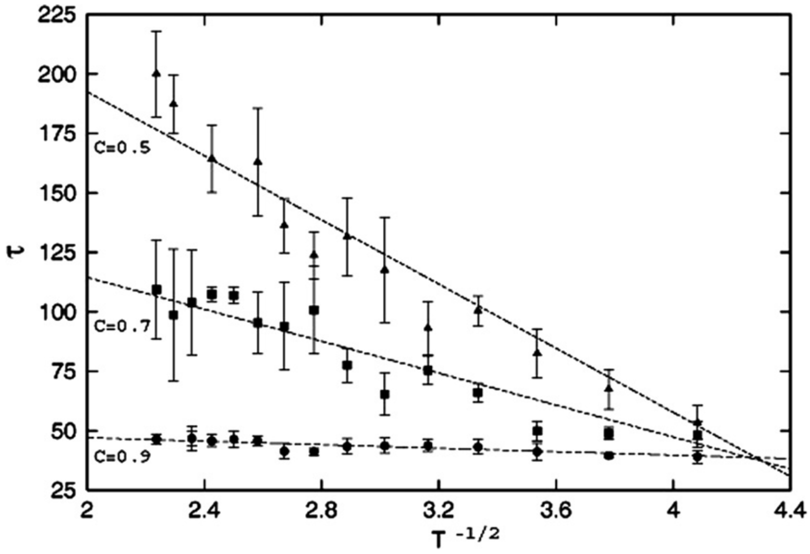

Fig. 7. Variation of relaxation time (τ) in MCS with $T^{-1/2}$ for $c = 0.5$, 0.7 and 0.9 for $T > 0.04$.

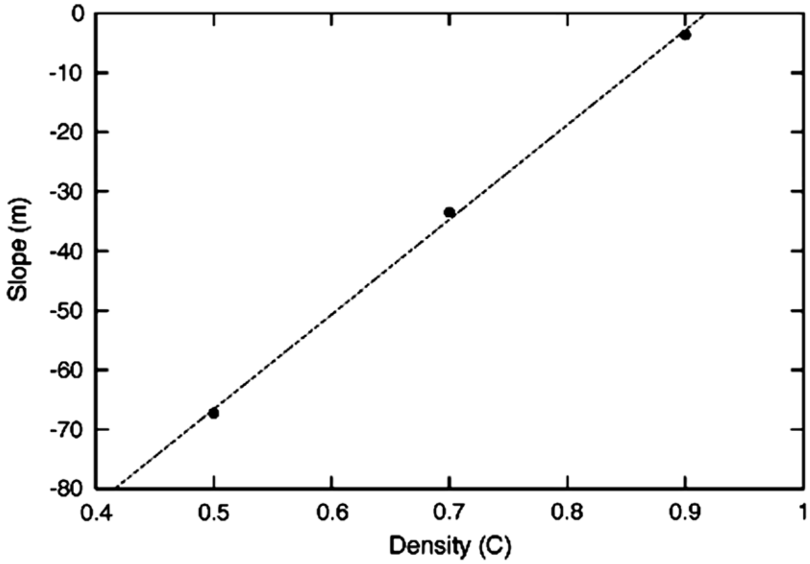

Fig. 8. Variation of slope (m) with particle concentration (c).

$T_1 = 0.02$. If the L-J potential is assumed to have a minimum of -1.0 eV at $r_{\min} = 1$ nm then T_1 corresponds to 0.02 eV. At this temperature, particles with mass ~10 amu will have an average velocity $\sim 0.4 \times 10^5$ cm/s and maximum allowable particle displacement will be $d_{\max} \cong 1.26$ nm. Thus the time step corresponding to 1 MCS will be ~0.002 ns and the relaxation time τ leading to ordered structure will be ~0.1 ns. This time will be larger for particles with larger mass, $\tau \sim \sqrt{\mathrm{m}}$.

4. Conclusion

To conclude, it is to be emphasized that we have presented a MC simulation procedure considering an improved algorithm taking into account the realistic thermal motion of the constituent particles. The important outcome of the proposed algorithm is that, it leads to quicker equilibration process predicting a realistic correlation between Monte Carlo time steps and actual time. Secondly, the study offers a logical understanding of the relaxation behaviour of a disordered gaseous system at a very high temperature when it is quenched to a lower temperature T keeping it in contact with a thermal bath maintained at constant T. It is observed that the system relaxes to a ordered stable configuration only when $T < \Delta v$ as expected. No stable configuration is achieved when $T \ll \Delta v$ or $T \gg \Delta v$. For $T \ll \Delta v$, the system is expected to show much slower relaxation phenomena as in glassy systems and this will be explored in future. In the temperature region T above T_1, the relaxation time τ, assumed to be proportional to MC steps, is found to be inversely proportional to P $\sqrt{T}$.

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