Molecular dynamics simulation of an argon cluster filled inside carbon nanotubes*

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The effects of the diameters of single-walled carbon nanotubes (SWCNTs) (7.83 Å to 27.40 Å) and temperature (20 K–45 K) on the equilibrium structure of an argon cluster are systematically studied by molecular dynamics simulation with consideration of the SWCNTs to be fixed. Since the diameters of SWCNTs with different chiralities increase when temperature is fixed at 20 K, the equilibrium structures of the argon cluster transform from monoatomic chains to helical and then to multishell coaxial cylinders. Chirality has almost no noticeable influence on these cylindrosymmetric structures. The effects of temperature and a non-equilibrium sudden heating process on the structures of argon clusters in SWCNTs are also studied by molecular dynamics simulation.

Keywords: carbon nanotubes, argon cluster, molecular dynamics simulation

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1. Introduction

Following the discovery of carbon nanotubes in 1991,[1] investigations of carbon nanotubes have come to the fore of material science and other sciences. Among these investigations, the filling of foreign materials into carbon nanotubes has received increasing attention in recent years due to their potential applications, which include nanometer-size test tube or nanomolds or templates,[2–4] recording media,[5–8] and nanosensors.[9] The applications can be related to the fact that the carbon nanotubes possess some excellent properties, such as uniform inner hollow cavity, good chemical stability, and large specific surface area. During the last decade, the structural and dynamical properties of small finite size systems, such as atomic and molecular clusters, have been extensively studied because their physical and chemical properties are significantly different from those of bulk materials.[10–13] The problem of cluster adsorption on different surfaces has been intensively studied, both experimentally[14] and theoretically,[15] due to the possible technological applications. The discovery of carbon nanotubes has opened up new possibilities for investigating the problem of gas adsorption. The geometry of the adsorbate system is highly dependent on the nanotube structure, and it can form one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) adsorbate phases. The interstitial channels between the bundles of carbon nanotube and the space within and outside single-walled nanotube are regions with the very attractive potential to adsorbate atoms and molecules. For example, rare gases, such as He,[16] Ne, and Xe,[17] show their quasi-one dimensionality when confined in narrow SWCNTs.[18] Interaction between the nanotube substrate and adsorbed argon atoms plays an important role in various applications, such as sensing, storing, purification, and isotope separation of gases.[14–17] Therefore the problem of argon cluster in nanotube and nanotube bundles has become a very important subject of experimental[19] and theoretical[20] studies. In 2004, Kośmider and Dendzik *et al.*[21] studied an argon cluster filled inside the SWCNTs. They considered only three nanotubes: two armchair nanotubes ((10, 10), (15, 15), and one zigzag nanotube (20, 0)). They found that in the case of armchair SWCNTs (10, 10) and (15, 15) (Figs. 1(a) and 1(b) in Ref. [21]), the innermost layer consists of a single atomic chain (not a spiral), while in the case of the zigzag SWCNT (20, 0), the innermost layer consists of the two spiral chains. So they concluded that the structure of the innermost layer depends on the chirality of the nanotube. It is obvious that there is not only the chirality difference between (20, 0) nanotube and the two nanotubes of (10, 10) and (15, 15) but also the diameter difference between them. Therefore, the above facts cannot logically determine whether these two kinds of differences are the real causes for the equilibrium structure of argon cluster filled in SWCNTs. Thus, we have tried to make the problem exactly clear. For this end, conducting a systematic molecular dynamics (MD) simulation study is necessary. Obviously, the effects of temperature

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on the equilibrium structure of argon cluster in SWCNTs and the non-equilibrium heating process are also very important and interesting problems, which also need systematic molecular dynamics study.

In this paper, we present the results of molecular dynamics simulation of argon clusters with atoms from 23 to 356 filled inside the armchair and zigzag SWCNTs with diameters from 7.83 Å to 27.40 Å. The atom numbers of argon clusters are proportional to the cross-sectional areas of SWCNTs. The length of each equilibration configuration of the argon clusters is about one fourth of the responding SWCNT, so that the end effect of SWCNTs can be neglected. The effects of the diameters of the single-walled carbon nanotubes (SWCNTs) and temperature on the equilibrium structure of filled argon cluster are investigated.

2. Computational methods

The diameters and properties of SWCNTs can be specified by the chirality (n, m), where n and m denote the components of the chirality vectors.[22] In this work, some armchair (n, n) and zigzag $(n, 0)$ SWCNTs are adopted. The bond length of the fixed carbon–carbon is 1.42 Å. The lengths of SWCNTs are 98.38 Å for armchair and 106.50 Å for zigzag.

In the simulation, argon atoms can move in the SWCNTs while the carbon nanotubes are fixed and rigid,[21,23] treating the wall as an external field. The reason for this treatment is that the energy of carbon–carbon covalent bond on SWCNTs is 711 kJ/mol, which is very much greater than the interaction energy of argon–carbon. This leads to great difficulty in changing the structure of SWCNT by filling argon atoms. The interactions of argon–argon and argon–carbon are modeled using the 12-6 Lennard Jones potential, which is given by

$$U_{\mathrm{LJ}}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right], \tag{1}$$

where r_{ij} is the interparticle distance, ε and σ are the energy and length scales, respectively. The parameters are as follows:

$$\varepsilon_{\mathrm{Ar-Ar}} = 1.67 \times 10^{-21}\ \mathrm{J}, \quad \sigma_{\mathrm{Ar-Ar}} = 0.340\ \mathrm{nm},$$
$$\varepsilon_{\mathrm{C-Ar}} = 8.75 \times 10^{-22}\ \mathrm{J}, \quad \sigma_{\mathrm{C-Ar}} = 0.3434\ \mathrm{nm}.$$

All of the quantities used in the simulation are dimensionless. The dimensionless quantities are as follows: $r^* = r/\sigma$ is for length, $T^* = k_{\mathrm{B}}T/\varepsilon$ for temperature, and $t^* = t\sqrt{(\varepsilon/m\sigma^2)}$ for time. The MD simulations are performed with a cutoff radius of 9.5 Å and a Verlet integration algorithm. Some canonical ensembles (NVTs) with velocity scaling temperature control method are used to obtain the designated temperatures. Each time step employed in the whole of our simulation is 1 fs. In Subsection 3.1, the initial argon clusters are placed in a regular cubic lattice at one end of a single-walled carbon nanotube in order to obtain each equilibrium configuration. The simulation time is 240 ps. In Subsection 3.2, the effect of temperature on the structure of argon cluster in SWCNTs is studied, and the total simulation time of each equilibrium structure is 700 ps. In Subsection 3.3, the dynamical relaxation process of argon cluster inside (35, 0) SWCNT at 40 K is studied, with the initial state of argon cluster being the equilibrium state at 20 K. When the temperature increases, the equilibration structure of argon clusters needs more time. The total simulation time is 700 ps.

3. Results and discussion

3.1. Structure of argon cluster filled inside (n,n) and $(n,0)$ SWCNTs at 20 K

Figure 1 shows the snapshots of equilibrium configurations of argon clusters inside (n,n) SWCNTs obtained at 20 K. The snapshots are viewed from the z direction (along the tube axis, i.e.,"the top view"). The types of the SWCNTs are (6, 6), (7, 7), (8, 8), (10, 10), (13, 13), (15, 15), (18, 18), and (20, 20), respectively. All the SWCNTs are 98.38 Å in length. The diameters of the SWCNTs are 8.14 Å, 9.49 Å, 10.85 Å, 13.56 Å, 17.63 Å, 20.34 Å, 24.41 Å, and 27.12 Å, respectively.

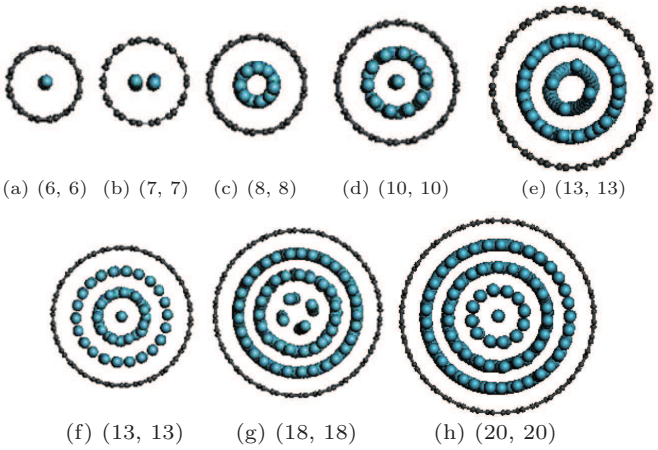


Fig. 1. (color online) Snapshots of equilibrium configurations of argon cluster filled in (n,n) SWCNTs at 20 K.

Figure 2 shows the snapshots of equilibrium configurations of argon clusters inside $(n,0)$ SWCNTs obtained at 20 K. The types of the SWCNTs are (10, 0), (13, 0), (14, 0), (17, 0), (20, 0), (22, 0), (26, 0), (31, 0), and (35, 0), respectively. All the SWCNTs are 106.50 Å in length. The diameters of the SWCNTs are 7.83 Å, 10.18 Å, 10.96 Å, 13.31 Å, 15.66 Å 17.22 Å, 20.36 Å, 24.27 Å, and 27.40 Å, respectively.

The scopes of the diameters of (n,n) and $(n,0)$ SWCNTs, and the numbers of the filled argon atoms are very close to each other. The length of each equilibrium configuration of argon clusters is about one fourth of the corresponding SWCNT.

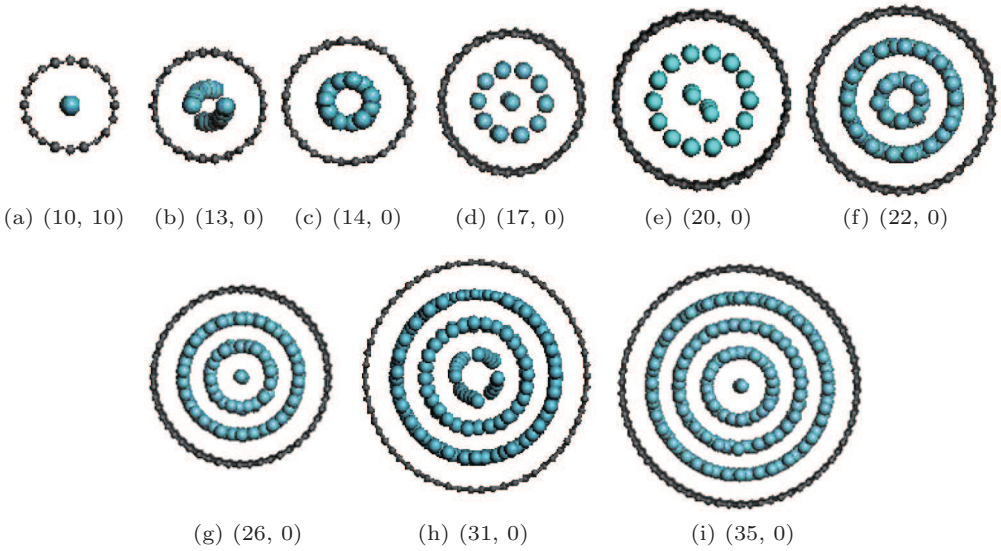


Fig. 2. (color online) Snapshots of equilibrium configurations of argon cluster filled in $(n,0)$ SWCNTs at 20 K.

From Fig. 1, we can see that the structure of the argon cluster inside the SWCNT seems to grow from a mono-atomic chain formed in the central axis of the thinner SWCNT. As the radius of SWCNT increases, it transforms through a double helical to a four-helical structure. Finally, it transforms into a cylindrical structure and its radius also increases. During this course, when the radius of cylindrical structure increases to some extent, another mono-atomic chain is again formed in the central axis, and so on. The above description for Fig. 1 can also hold for Fig. 2. Therefore, we obtain the conclusion that the structures of argon cluster inside (n,n) and $(n,0)$ SWCNTs depend on the diameter of nanotube and do not depend on the chirality. Thus, we correct the wrong conclusion presented by Kośmider *et al.*[21] Our conclusion is consistent with that drawn by Li *et al.* from their studies of the structural properties of gold nanoparticles, germanium nanowires within the fixed SWCNTs.[24–26]

The phenomenon of layered structure is ascribable to the following reason. Because the structure of the SWCNT is cylindrosymmetric plus a small detailed crystal lattice structure, the force field exerted on the argon atom by the SWCNT is a cylindrosymmetric force field plus a small fluctuation. Thus, the equilibrium configuration of the argon cluster must be cylindrosymmetric plus a small detailed structure. And so the total force field including the Ar–Ar interaction force exerted on argon atom is also cylindrosymmetric plus a small fluctuation. The cylindrosymmetric force part determines the radial structure of the argon cluster in SWCNT. Under low temperature, the argon atoms must be located at the minimum of the potential of the cylindrosymmetric force field.

3.2. Effect of temperature on the structure of argon cluster in SWCNTs

In order to discuss the effect of temperature on the structure of argon cluster in SWCNTs, two $(n,0)$ SWCNTs (22, 0) and (35, 0) are adopted. We increase temperature from 20 K to 45 K in steps of 5 K. When the temperature arrives at 40 K for (35, 0) SWCNT, all of the atoms aggregate in one layer, we will not need to discuss the structure of argon cluster at a higher temperature. Figure 3 shows the snapshots of equilibrium configurations of argon cluster in (22, 0) and (35, 0) SWCNTs at the above temperature.

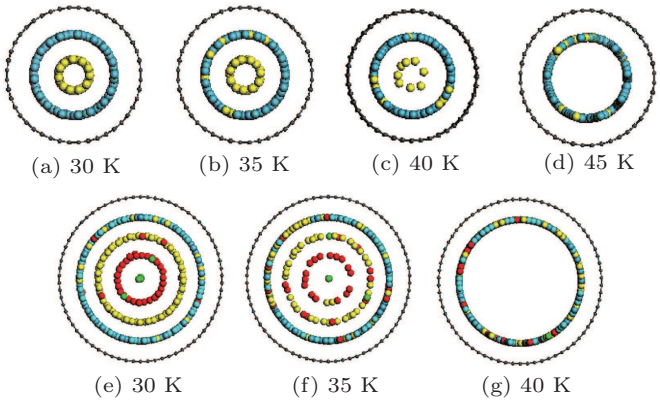
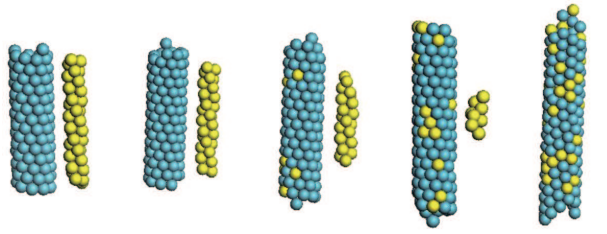


Fig. 3. (color online) Snapshots of equilibrium configurations of argon cluster filled in (22, 0) panels (a)–(d) SWCNT at 30, 35, 40, 45 K and (35, 0) panels (e)–(g) SWCNT at 30, 35, 40 K.

In order to investigate the structure of each layer in the argon cluster, we show the front views of argon cluster in (22, 0) SWCNT layer-by-layer in Fig. 4 and (35, 0) SWCNT in Fig. 5. We note that the first layer is the closest to the inner surface of SWCNT, and next to it is the second layer, etc. In order to differentiate atoms belonging to different layers, we adopt dif-

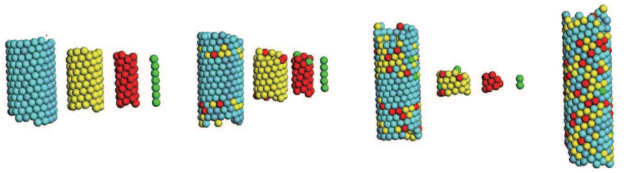
ferent colors. Blue, yellow, red, and green colors represent the first, second, third, and fourth layers, respectively.

As can be seen from Figs. 4 and 5, for each temperature between 20 K and 40 K (45 K), the atom number and the length of the layer of the argon clusters filled in the SWCNTs decrease gradually with the sequence number of layer for each radius of SWCNT. The difference in length between the innermost and outermost layers increases with temperature, especially when the temperature arrives at 45 K for (22, 0) SWCNT and 40 K for (35, 0) SWCNT, all atoms aggregate in the first layer. We can apply the above conclusions to other SWCNTs.



(a) 20 K (b) 30 K (c) 35 K (d) 40 K (e) 45 K

Fig. 4. (color online) Layer structures of the argon cluster filled in (22, 0) at different temperatures.



(a) 20 K (b) 30 K (c) 35 K (d) 40 K

Fig. 5. (color online) Layer structures of the argon cluster filled in (35, 0) at different temperatures.

We can also see from Figs. 4 and 5 that there is a diffusion phenomenon among different layers when the temperature goes over a critical value. The critical temperature of interlayer diffusion decreases as the increase of the diameter of SWCNTs: $\sim$ 35 K for (22, 0) and $\sim$ 30 K for (35, 0). Of course, our statement is somewhat rough. In fact, more strictly speaking, different couples of adjacent layers in a cluster have different critical temperatures of interlayer diffusion. The existence of these critical temperatures is attributed to the fact that there is a barrier in the cylindrosymmetric part of the total potential between any two adjacent layers.

Table 1 gives the average distances between the SWCNT inner surface and the first layer, and the average distances between adjacent layers of the argon clusters filled in the (35, 0) SWCNTs at 20 K. It can be found in Table 1 that the average distance increases gradually from the outside layer to the inside layer. The reason for this is as follows.

The number of atoms in a layer is proportional to the curvature radius of the layer. When the two adjacent layers are in the state of attraction, the mutual attractive force is approximately proportional to the product of the curvature radii of both layers. For three adjacent layers, we first assume that they are equidistant. It is obvious that the attractive force between the middle and outer layers is greater than that between the middle and inner layers. So the middle layer is expended toward the outer layer, it then arrives at an equilibrium state due to the balance between the repulsive force of the outer layer and the restoring force of itself. So, the distance between the middle and outer layers is less than that between the middle and inner layers.

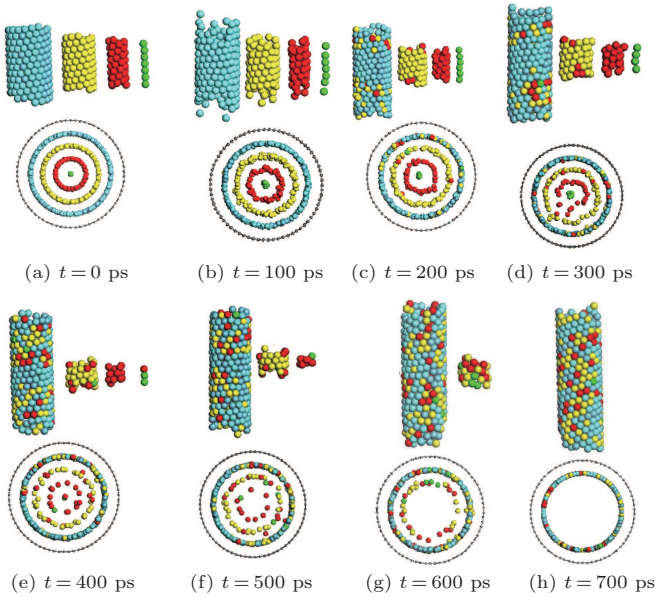
Table 1. Average distances between the SWCNT inner surface and the first layer and average distances between layers for the argon clusters filled in (35, 0) SWCNT. All distances are in units of Å.

From SWCNT to first layer	From second layer to first layer	From third layer to second layer	From fourth layer to third layer
3.275	3.280	3.30	3.845

3.3. Dynamical relaxation process of argon cluster in SWCNTs under sudden warming

For (35, 0) SWCNT, we make the temperature suddenly increase from 20 K to 40 K, we show the sequence of front and top view snapshots of atomic configurations for $T = 40$ K at different time steps in Figs. 6(a)–6(h).

From Fig. 6, we can see the dynamical process of the argon atoms in (35, 0) SWCNT under sudden warming. This shows that the argon atoms begin to diffuse among different layers at $t = 200$ ps and the diffusion has an outward tendency. This tendency is consistent with the trend of balance. At equilibrium (after $\sim$ 700 ps), all of the argon atoms aggregate in the first layer.



(a) $t = 0$ ps (b) $t = 100$ ps (c) $t = 200$ ps (d) $t = 300$ ps

(e) $t = 400$ ps (f) $t = 500$ ps (g) $t = 600$ ps (h) $t = 700$ ps

Fig. 6. (color online) Snapshots of atomic configurations for $T = 40$ K at different time steps.

4. Conclusion

The effects of the diameters of the SWCNTs (7.83 Å to 27.40 Å) and temperatures (20 K–45 K) on the structure of

argon cluster filled in SWCNTs are systematically studied by molecular dynamics simulation, based on the Lennard–Jones potential for argon–carbon and argon–argon interactions. As the diameters of SWCNTs with different chiralities increase at a fixed temperature, the structures of the argon cluster transform from a mono-atomic chain to helical, and then to multishell coaxial cylinders. The atom number and the length of the layer of the argon clusters decrease gradually with the sequence number of layer for each temperature and each diameter of SWCNT. The differences in atom number and length between any two adjacent layers increase with temperature, especially when the temperature reaches 45 K for (22, 0) SWCNT and 40 K for (35, 0) SWCNT, all of the atoms aggregate in the first layer. The chirality has almost no noticeable influence on any of these cylindrosymmetric structures. After the formation of an equilibrium structure, the interlayer diffusion can occur only when the temperature is higher than the critical temperature, which is determined by the barrier height in the cylindrosymmetric part of total potential between the two adjacent layers.

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