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# Temperature-dependent Thermodynamic Behaviors of Carbon Fullerene Molecules at Atmospheric Pressure

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**Abstract:** The study aims at investigating the linear and volumetric thermal expansion coefficients (CTEs) at temperature below the Debye temperature and phase transformation behaviors at atmospheric pressure of carbon fullerenes, i.e., $C_{60}$, $C_{70}$ and $C_{80}$, through a modified Nosé-Hoover (NH) thermostat method incorporated with molecular dynamics (MD) simulation. The calculated results are compared with those obtained from the standard NH and "massive" NHC (MNHC) thermostats and also with the literature experimental and theoretical data. Results show that at temperature below the Debye temperature, the CTEs of the fullerene molecules would significantly decrease with a decreasing temperature and tend to become negative at temperature below 5K. The present results are much more consistent with the literature experimental and theoretical data, in contrast to the other two thermostat algorithms. Besides, it is found that $C_{60}$ fullerene directly undergoes a solid-vapor phase transformation, instead of a solid-liquid phase transition, implying that the molecule will sublimate when heated rather than melt under atmospheric pressure. This phenomenon is coincident with that of graphite at pressures below 10MPa. The sublimation point of $C_{60}$ fullerene is about 4350±20K, comparable to that of graphite in the range of about 4000-4500K at pressures below 10 MPa.

**Keywords:** Thermal expansion coefficient, Phase transformation, Fullerene molecules, Molecular dynamics, Nosé-Hoover (NH) thermostat, Debye temperature

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## 1 Introduction

In recent year, carbon fullerenes have become popular in materials and electronic industries (Dresselhaus et al., 1996) due to their unique chemical and physical properties (Kroto et al., 1993). Among the many forms of carbon fullerenes, spherical fullerenes, also termed buckyballs, have been the hot topic of research for their technological applications in medicine, electronics, and nanotechnology, and thus, many of the researches have been devoted to the study of their unique chemical and physical properties (Prato, 1997). In literature, the temperature-dependent physical properties, such as thermal conductivity and elastic property (Soifer et al., 1999; Manghnani et al., 2001; Yagafarov et al., 2010), of carbon materials, including graphite, diamond and fullerene, have been extensively studied through various experimental and theoretical methods. As compared to experimental approaches, theoretical approaches such as molecular dynamics (MD) simulation tend to be more cost-effective and efficient, and thus are in widespread use in nanomechanics. For instance, Chen et al. (2007) and Cheng et al. (2009a b) estimated the elastic properties of carbon nanotubes (CNTs). Some other similar studies on the carbon materials can be found in the literature (Wei et al., 2002; Chakrabarty and Çağin, 2008; Jeng et al., 2009). In principle, standard MD simulation is performed in a micro-canonical ($N$, $V$, $E$) ensemble, where the number of atoms $N$, volume $V$ and total energy $E$ are conserved, rather than a canonical ($N$, $V$, $T$) ensemble, where the temperature $T$ instead of $E$ is conserved. Extensive studies on an extended MD method for canonical ensemble simulation have been made in literature, see, e.g., Langevin dynamic simulation (Ermak and Buckholz, 1980), Andersen's constant temperature MD simulation method (Andersen, 1980), the velocity-rescaling algorithm (Woodcock, 1971; Abraham et al., 1982), Berendsen et al.'s thermostat method (Berendsen et al., 1984), Nosé-Hoover (NH) thermostat method (Nosé, 1984; Hoover, 1985), Nosé-Hoover chain (NHC) thermostat method (Martyna et al., 1992) and "massive" NHC (MNHC) thermostat method (Tuckerman et al., 1993).

Of all the physical properties, thermodynamic properties, including thermal expansion coefficient (CTE), molten phase, sublimation point and melting point, have drawn increasing attention because they are directly related to their structural formation and transition and mechanical properties. By using the above methods, several investigators have reported the thermodynamic properties and phase transformation behaviors of carbon fullerenes. For instance, Yamaguchi and Maruyama (1998) studied the fullerene formation process by using the velocity-rescaling algorithm, and found that the fullerene-like structure was obtained when the control temperature was roughly in the range of 2500-3000K. By simulating the nucleation process of buckminsterfullerene ($C_{60}$) fullerene using the Langevin MD method, Chelikowsky (1991) found that the $C_{60}$ fullerene nucleates at temperature about 4000-5000K. Through the standard NH thermostat MD simulation, László (1998) also showed that the formation temperature of $C_{60}$ fullerene in various gases is about 4000K. By using the same approach, Kim and Tománek (1994) revealed that the melting point of $C_{60}$ fullerene is about 4000K, and the vapor phase occurs at a significantly high temperature of 10200K. Kwon et al. (2004) reported that the CTE of both $C_{60}$ and carbon nanotubes (CNTs) would become negative as the temperature is below 150K. By using the semi-empirical Assembly Module 1 (AM1) within the PC SPARTAN$^{TM}$ package (Wavefunction Inc., USA), Fang and Chang (2004) observed that the melting point of $C_{60}$ fullerene is only about 1400K. In the reported data of $C_{60}$ fullerene, there is a common feature in that there exists a fragment state in the high temperature phase transformation under atmospheric pressure, which is interpreted as undergoing a phase transition to a liquid state. Besides, a wide range variation in the calculated melting points for $C_{60}$ fullerene is observed, and roughly, they can be divided into two major sets: 1000-3000K and 4000-5000K. The reason of the large discrepancy in the predicted melting points of $C_{60}$ fullerene (i.e., from 1000-3000K to 4000-5000K) is still unkown. Moreover, it is also found that the phase transformation phenomena of the fullerenes are considerably distinct from those of graphite (Venkatesan et al., 1984; Steinbeck et al., 1985; Malvezzi et al., 1986; Senchenko, 1987; Bundy, 1989; Zazula, 1997; Asinovskii, et al. 2002; Savvatimskii, 2003; Savvatimskiy, 2005). For instance, for high purity graphite, similar to the present modeling assumption for fullerenes, a melting point of 4700±80K at pressures in the range of 50-220 MPa was reported (Senchenko, 1987). The experimentally well-established phase diagram of carbon, as based on the works of Steinbeck et al. (1985), Bundy (1989) and Zazula (1997), revealed that the phase transition points of graphite from a solid state to a liquid or vapor state range from 4000K to 4700K at different pressures. Specifically, at pressures below 10 MPa, graphite tends to sublimate rather than melt when heated up to about 4000-4500K, while at pressures ranging from 10-10000MPa, it becomes melted rather than vaporized when heated up to about 4500-4700K. Savvatimskii (2003) also indicated that the most reliable estimate of the melting point for graphite under pressures ranging from 10-300 MPa is in the 4800-4900K range after a systematic and comparative analysis that takes into account considerable amount of available information about the heating of graphite by an electrical current or a laser pulse. According to the published experimental and theoretical data, the crystalline hexagonal type of graphite would undergo a solid-to-vapor and a solid-to-liquid phase change, depending on the ambient pressure. In addition, the phase transition point for graphite is in the range of 4000-5000K at various pressure conditions, and a dependable estimate of the sublimation point of graphite, occurring at atmospheric pressure, is in the range of 4000-4500K. Basically, carbon fullerenes are intrinsically similar to graphite in structure, and have the same stable solid form of carbon, i.e., the crystalline hexagonal carbon, as graphite. It is reasonable to deduce that they would exist similar thermodynamic behaviors, which are, however, not seen in the previously reported data.

This study attempts to investigate the temperature-dependent linear and volumetric CTEs of several typical carbon fullerene molecules, namely $C_{60}$, $C_{70}$ and $C_{80}$, at temperature below the Debye temperature and atmospheric pressure condition through a modified Nosé-Hoover (NH) thermostat method incorporated with molecular dynamics (MD) simulation. The effects of the sampling methods on the calculated thermodynamic properties, in particular the CTE of carbon fullerene at temperature below the Debye temperature, are first explored. The major causes behind the large difference in the predicted thermodynamic behaviors of carbon fullerenes are also investigated. To achieve the goal, the limitations of the standard NH thermostat algorithm and its variants, including the NHC and MNHC, and also the advantages of the modified NH thermostat algorithm are addressed. The simulation results by the modified NH thermostat algorithm are compared with those calculated by the standard NH and MNHC thermostat method and also with the literature experimental and theoretical data. The alternative goal is to explore phase transformation behaviors (e.g., melting point, sublimation point) of $C_{60}$ fullerene molecule at atmospheric pressure, and in addition, to assess whether solid $C_{60}$ fullerene under the thermodynamic conditions will be converted into gaseous carbon atoms, just like graphite (Steinbeck et al., 1985; Bundy, 1989; Zazula, 1997), or liquid carbon, as well reported in the above literature.

## 2 Method

In the present MD simulation, three thermostat algorithms, namely the standard NH thermostat (Nosé, 1984; Hoover, 1985), the MNHC of length 4 on each degree of freedom, and the modified NH thermostat (Chen et al., 2011), are used to control the system temperature. The modified NH thermostat is developed for constant temperature simulation of solid system by incorporating the Debye theory to additionally account for the lattice vibrational energy and zero-point energy in the control of the system temperature. The displacements and velocities of the atoms in the carbon fullerenes at a different temperature can be then calculated from the constant temperature MD model. For the standard NH thermostat, the equation of motion is as follows:

$$\frac{d\vec{r}_i}{dt} = \frac{\vec{p}_i}{m_i} \quad (i = 1, 2, \cdots, N), \tag{1}$$

$$\frac{d\vec{p}_i}{dt} = -\frac{\partial U}{\partial \vec{r}_i} - \vec{p}_i \frac{p_\eta}{Q} \quad (i = 1, 2, \cdots, N), \tag{2}$$

$$\frac{d\eta}{dt} = \frac{p_\eta}{Q}, \tag{3}$$

and

$$\frac{dp_\eta}{dt} = 2\left[\sum_{i=1}^{N}\frac{\vec{p}_i^2}{2m_i} - \frac{3}{2}Nk_BT\right], \tag{4}$$

where $\vec{r}_i$, $\vec{p}_i$ and $m_i$ are the coordinates, momenta and mass of atom $i$, $N$ is the number of atoms of the system, U is the potential energy, $\eta$ and $p_\eta$ are two parameters relative to the additional degree of freedom and its virtual momenta of the external system, $k_B$ Boltzmann's constant, $T$ the externally set temperature and $Q$ the effective mass of the external system. From the equation of motion of standard NH thermostat, it can be found that the standard method is control system temperature with the ideal gas relation. However, when applied in a tightly bound system, such as solids, the algorithm may underestimate the system temperature, and so feedback excessive energy to the physical system. Based on solid state physics (Kittel, 1996), some serious problems can be explored in the excessive feedback energy, including causing large fluctuation in system energy at high temperature, thereby resulting in poor system stability, reduced solution accuracy and also early rupture of atomic bonds etc., and also yielding an inaccurate estimate of the thermal-mechanical behaviors and properties of solids. In literature, some premature atomic bond breaking phenomena (Lomba et al., 2000) were revealed when the analysis was carried out through quasi-steady state MD simulation with a standard NH thermostat. This may be the reason that transient instead of quasi-steady state analysis was performed in many previous works (Chelikowsky, 1991; Kim and Tománek, 1994; László, 1998) to predict the high-temperature material properties of carbon fullerenes. To retain the integrity of the fullerene molecule structure, a soft potential (Takada et al., 2004) can be alternatively applied, but unfortunately, it would unfavorably change the original properties of nanomaterials and even fail to fully resolve the problem. (Chen et al., 2011)

To make up this limitation of the standard NH thermostat, a modified NH thermostat method is proposed by the authors (Chen et al., 2011) by taking into account the effect of phonon by virtue of the vibrational energy of lattice and the zero-point energy. Accordingly, both the kinetic and potential energies of atoms are accounted for in the calculation of the system temperature. According to Debye theory (Kittel, 1996), the relationship between the vibrational energy of lattice and the zero-point energy and temperature can be derived as

$$U\left(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N\right) + \sum_{i=1}^{N}\frac{\vec{p}_i^2}{2m_i} = U_0 + 3Nk_BTD(x), \tag{5}$$

where $U_0$ is the zero-point energy, $D(x)$ the Debye function, $x$ a dimensionless temperature parameter, $x = \theta_D/T$, and $\theta_D$ the Debye temperature. Base on the energy-temperature relationship, the modified NH thermostat equations of motion can be written as

$$\frac{d\vec{r}_i}{dt} = \frac{\vec{p}_i}{m_i} \quad (i = 1, 2, \cdots, N), \tag{6}$$

$$\frac{d\vec{p}_i}{dt} = -\frac{\partial U}{\partial \vec{r}_i} - \vec{p}_i \frac{p_\eta}{Q} \quad (i = 1, 2, \cdots, N), \tag{7}$$

$$\frac{d\eta}{dt} = \frac{p_\eta}{Q}, \tag{8}$$

and

$$\frac{dp_\eta}{dt} = 2\left[U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) - U_0 + \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m_i} - 3Nk_B T D(x)\right]. \tag{9}$$

It has been proved by the authors (Chen et al., 2011) that the present Hamiltonian function can fully satisfy the total energy conservation condition and the momentum conservation condition as the sum of the external forces are equal to zero (Tuckerman et al., 2001). In addition, a theoretical proof that the calculated quantities by the modified MD method are exactly equivalent to the canonical ensemble results was also made in the work. Details of the derivation can be found in Chen et al. (2011).

## 3 Results

Canonical MD simulations using the standard NH, MNHC and modified NH thermostat algorithms are performed to investigate the temperature-dependent linear and volumetric CTEs and also the phase transformation behaviors of carbon fullerenes. In the MD simulation, the force field between two neighboring carbon atoms in $C_{60}$ fullerene is modeled with the Tersoff-Brenner potential (Erkoc, 1997), and a time step $\Delta t = 5\times10^{-16}$ second and a total of simulation time steps $2\times10^6$ are used. Basically, the number of equilibrating time steps is much larger than those used in Kim and Tománek (1994) and Fang and Chang (2004) to ensure the equilibrium of the molecular system. In addition, three types of sampling methods, namely the random (Haile, 1997), systematic (Haile, 1997) and average method (Kwon, et al., 2004), are applied to statistically extract the characteristic values from the MD simulation. After system equilibrium, samples are taken out of every $1\times10^3$, $5\times10^4$ and $1\times10^5$ time steps by using the above sampling methods, which are briefly termed “sampling steps” in the work. The effective mass Q for the standard and modified NH thermostat is all determined by (Tuckerman and Parrinello, 1994)

$$Q = 3Nk_BT_s\tau^2, \tag{10}$$

and that for the MNHC thermostat is given by (Tobias et al., 1993)

$$Q_i = \frac{m_i}{m_H}k_BT_s\tau^2, \tag{11}$$

where $\tau$ is a characteristic time scale chosen to be 0.5 psec, and $m_H$ the mass of a hydrogen atom.

### *3.1 Linear and volumetric CTEs of fullerenes*

Figure 1 shows the volume change ratio of $C_{60}$ fullerene versus temperature calculated by using the standard NH thermostat. The computed results by the three sampling methods are also shown in the figure. The results are also compared with those of the General Utility Lattice Program (GULP) (Gale and Rohl, 2003), as implemented in the Materials Studio$^{TM}$ package, where the force field between two carbon atoms is modeled with the Tersoff-Brenner (TB) potential and Berendsen thermostat is implemented for constant temperature simulation. Besides, the systematic sampling method is adopted to statistically collect the characteristic values from the MD simulation. It is found that the random and systematic sampling methods give a very comparable result regardless of the number of time steps for taking a sample. More importantly, only these two results can resemble those calculated by the GULP module. What surprises is that the simulation results by using the average sampling method would strongly depend on the number of time steps for taking a sample, where a larger number of sampling steps would lead to a smaller or even a negative volume change of the $C_{60}$ fullerene. For example, as shown in the figure, when a sample is taken out of every $5\times10^4$ time steps by using the average sampling method, a negative volume change or CTE is obtained in the temperature range of 0-250K. A similar result was predicted by Kwon et al. (2004). Figure 2 shows the calculated resulting geometries of the $C_{60}$ molecule structure at 300K by the average sampling method associated with the three different sampling steps, i.e., $1\times10^3$, $5\times10^4$ and $1\times10^5$. It is found that as the increase of the sampling steps, the $C_{60}$ molecule structure tends to undergo a gradual contracting process along two of the three major axes, thereby becoming a slender ellipsoid. As the number of sampling steps increases up to $1\times10^5$ (see, Fig. 2(c)), the $C_{60}$ structure would be fully compressed into a line. This unexpected phenomenon is a consequence of the technical limitation of the average sampling method. From the statistical point of view, the calculated properties should be independent of the sampling methods and also the number of time steps for taking a sample as long as the sample number is sufficiently large. Thus, it is believed that the Kwon et al's results are a special-case solution of the average sampling method.

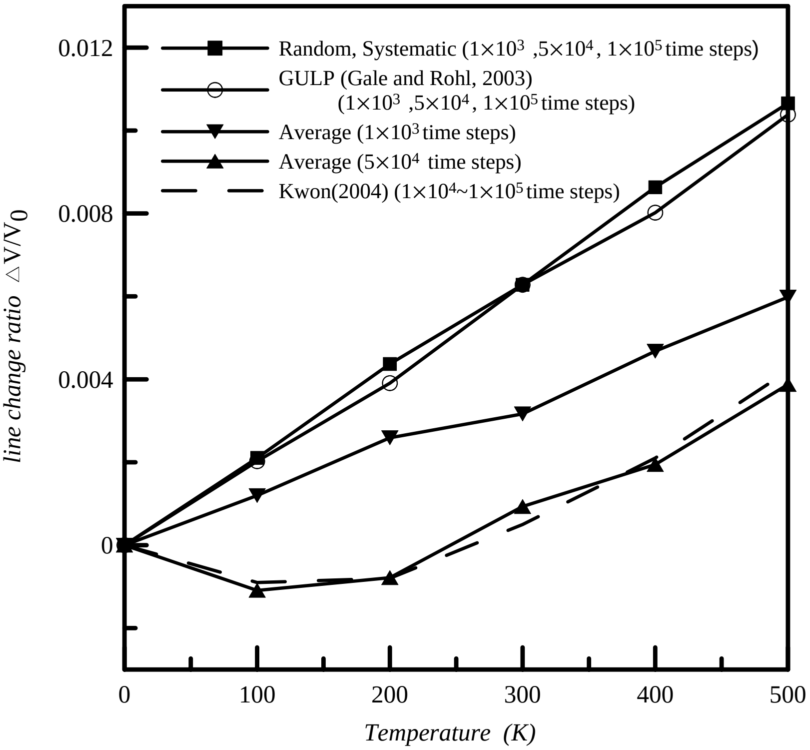
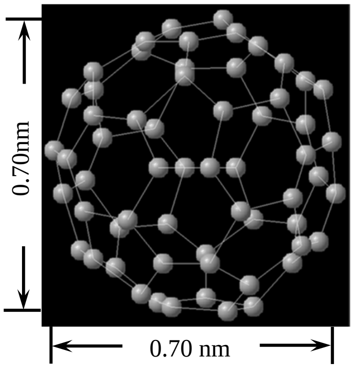
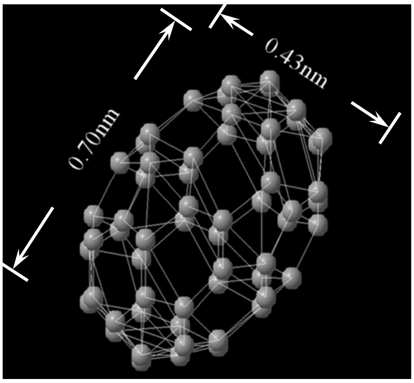


Figure 1: Influences of temperature on $C_{60}$ volume change by the standard NH thermostat using different sampling methods

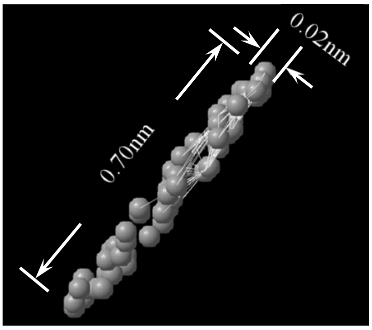
The line and volume change ratio in relation to temperature is presented in Fig. 3, associated with the three thermostat algorithms. Both the standard NH and MNHC thermostats show a linear dependence between the line change of the carbon fullerene and temperature throughout the temperature range while the modified NH thermostat demonstrates a nonlinear proportion at temperature below the Debye temperature. Moreover, the modified NH thermostat gives a smaller volume change than the other two methods. Further taking the first derivative of the line (volume) change ratio with respect to temperature yields the linear (volumetric) CTE $\alpha$ ($\beta$), and the results are shown in Fig. 4. In principle, for an isotropic material, the linear CTE should be equivalent to one-third of the volumetric CTE. Figure 4 shows that the calculated linear and volumetric CTEs of $C_{60}$ fullerene at



(a) $1\times10^{3}\Delta t$



(b) $5\times10^{4}\Delta t$



(c) $1\times10^{5}\Delta t$

Figure 2: The calculated resulting geometries of $C_{60}$ molecule structure at 300K by the average sampling method associated with three different sampling steps

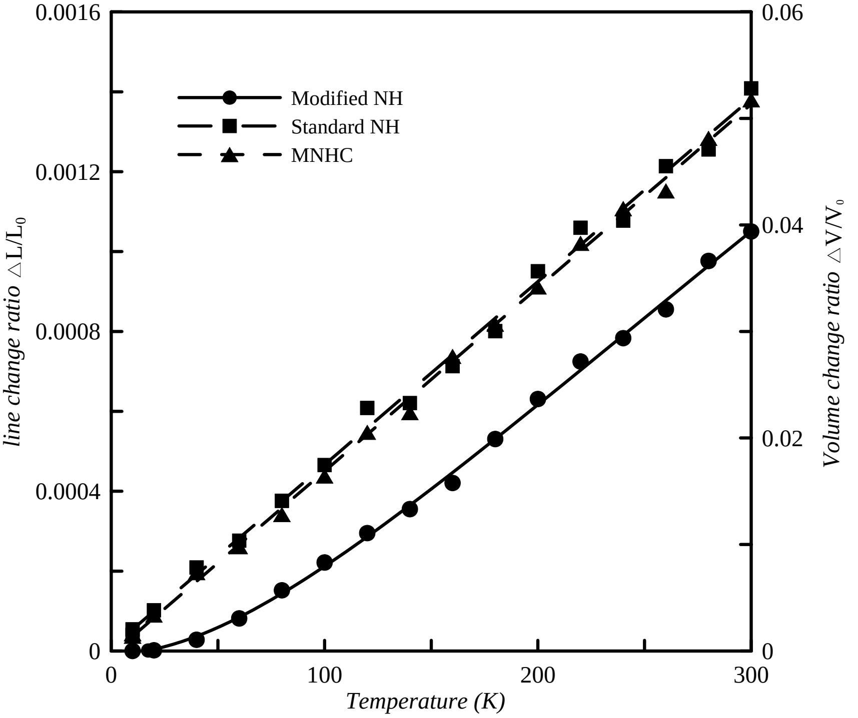


Figure 3: Effects of temperature on the line and volume change of $C_{60}$ fullerene by the standard NH, modified NH and MNHC thermostats.

low temperature by the modified NH thermostat decrease with a decreasing temperature, and tend to become a negative value as the temperature approaches to absolute zero, while those by the standard NH and MNHC thermostats are independent of the temperature. In literature, several studies have been conducted on this subject through experimental and theoretical approaches. For example, Gugenberger et al. (1992) and Aleksandrovskii et al. (2003) conducted measurement of the volumetric CTE of $C_{60}$ fullerene at very low temperature (<12K), and the results are also shown in Fig. 4. Their experimental results show that the CTE of the fullerene at low temperature would also decrease as the temperature drops, and most importantly, tends to become negative at temperature below 5K. The results are very consistent with those of the modified NH method, as shown in the figure. Moreover, at room temperature, Hamanaka et al. (2005) applied a high-resolution dilatometry to measure the linear CTE of $C_{60}$ fullerene, and found that the linear CTE is about $5.0\times10^{-6}$ $K^{-1}$. In addition, Zubov et al. (1997) theoretically explored the relation of the linear CTE of $C_{60}$ fullerene to pressure, and reported that

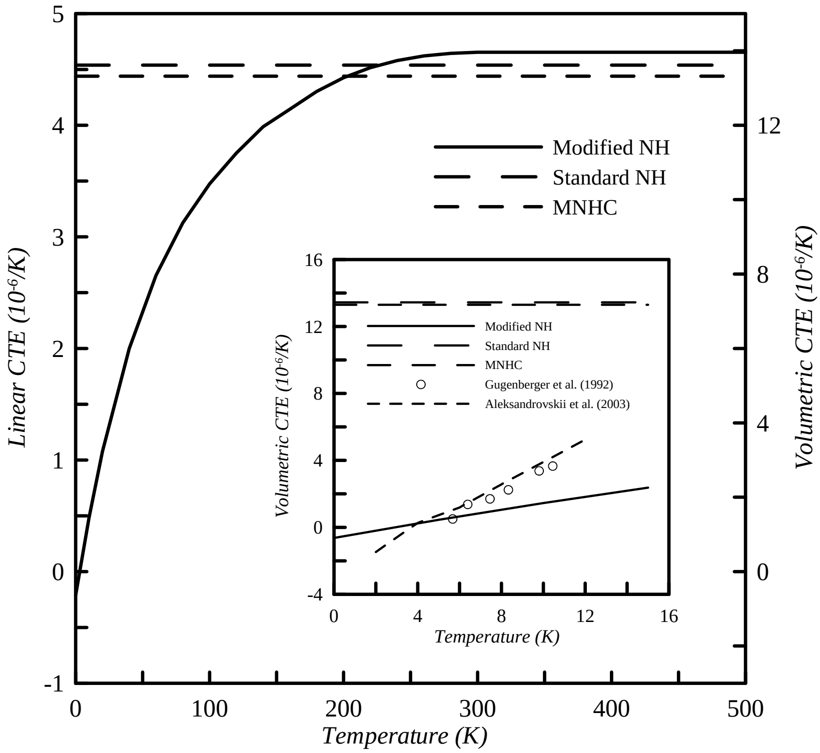


Figure 4: The relation of the linear and volumetric CTEs of $C_{60}$ fullerene to temperature by the standard NH, modified NH and MNHC thermostats at low temperature.

it will reach a converged value of $4.8\times10^{-6}K^{-1}$ at pressure equal to one atmosphere. By comparing them with the present estimates, it is found that only the modified NH thermostat method (i.e., $4.61\times10^{-6}K^{-1}$) can give a better agreement with the measurement data than the standard NH (i.e., $4.43\times10^{-6}K^{-1}$) and MNHC thermostat (i.e., $4.48\times10^{-6}K^{-1}$).

The temperature-dependent linear and volumetric CTEs of $C_{70}$ and $C_{80}$ fullerenes at low temperature are also explored by the modified NH thermostat algorithm, and the results are shown in Fig. 5, together with the results of $C_{60}$ fullerene. Likewise, negative CTEs occur at temperature approaching to absolute zero. Within the temperature range, the CTEs of $C_{60}$ (e.g., the linear CTE $4.65\times10^{-6}K^{-1}$ @300K) tends to be large than those of $C_{70}$ ($4.53\times10^{-6}K^{-1}$ @300K) and $C_{80}$ ($4.38\times10^{-6}K^{-1}$ @300K).

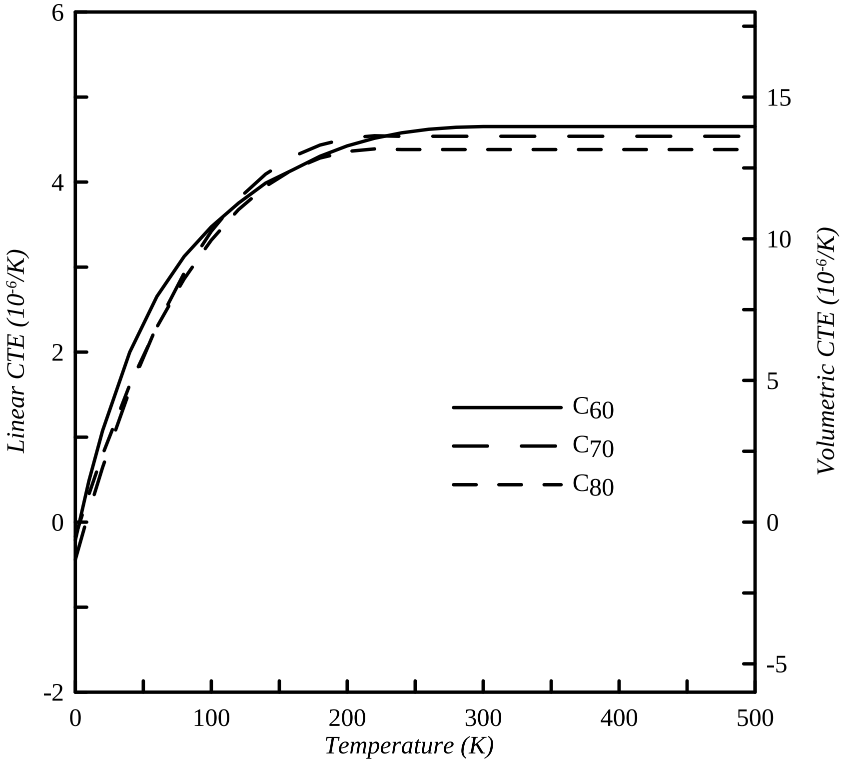


Figure 5: The temperature-dependent CTEs of $C_{60}$, $C_{70}$ and $C_{80}$ fullerenes by the modified NH thermostat.

### 3.2 Phase transformation behaviors of $C_{60}$ fullerene

The atomic structures of $C_{60}$ fullerene at different temperatures calculated using both the standard and the modified NH thermostats are shown in Fig. 6. Note that the results by the standard NH thermostat resemble those of the MNHC method, and thus are not shown here in. From the figures, no perceptible shape change can be observed in the $C_{60}$ atomic structure when $T \leq 300$K for the NH thermostat and $T \leq 2000$K for the modified NH thermostat. Furthermore, the standard NH thermostat demonstrates that the $C_{60}$ structure remains intact even though the structural deformation slightly increases with an increasing temperature as the temperature is up to 2000K (see, Fig. 6(a)). The $C_{60}$ structure is considered as the solid-phase fullerene. However, the calculation by the modified NH thermostat shows that not until the temperature reaches up to 4000K will the $C_{60}$ structure occur any significant structural deformation (see, e.g., Fig. 6(c)). Furthermore, as the temperature

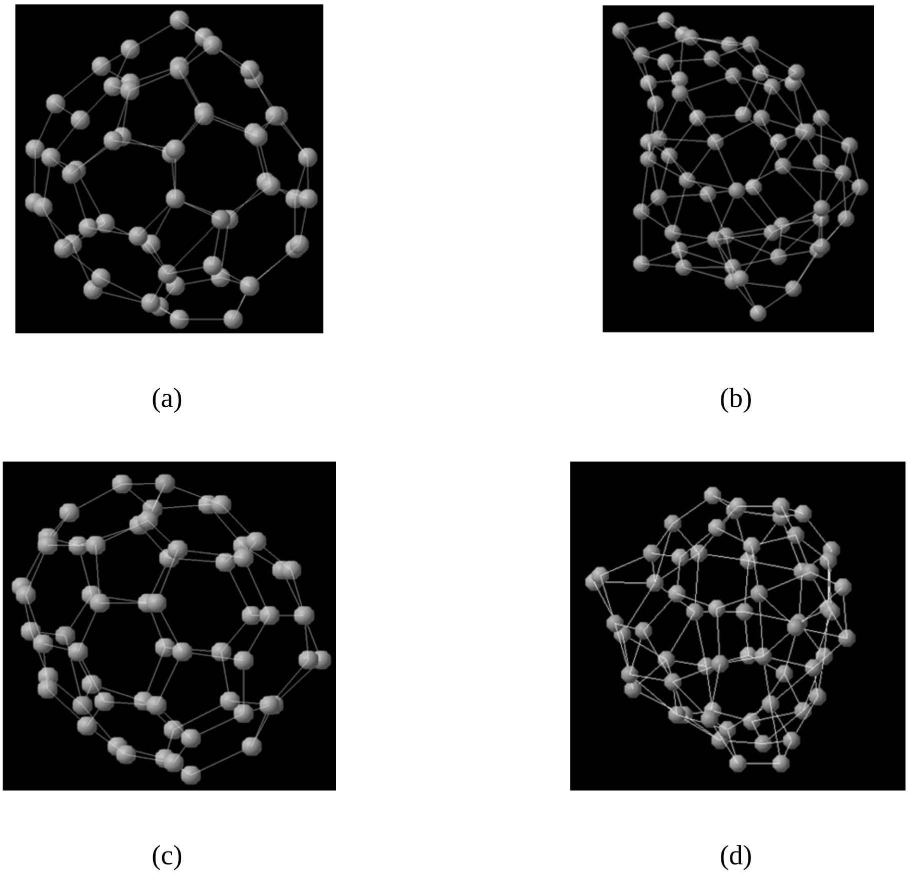
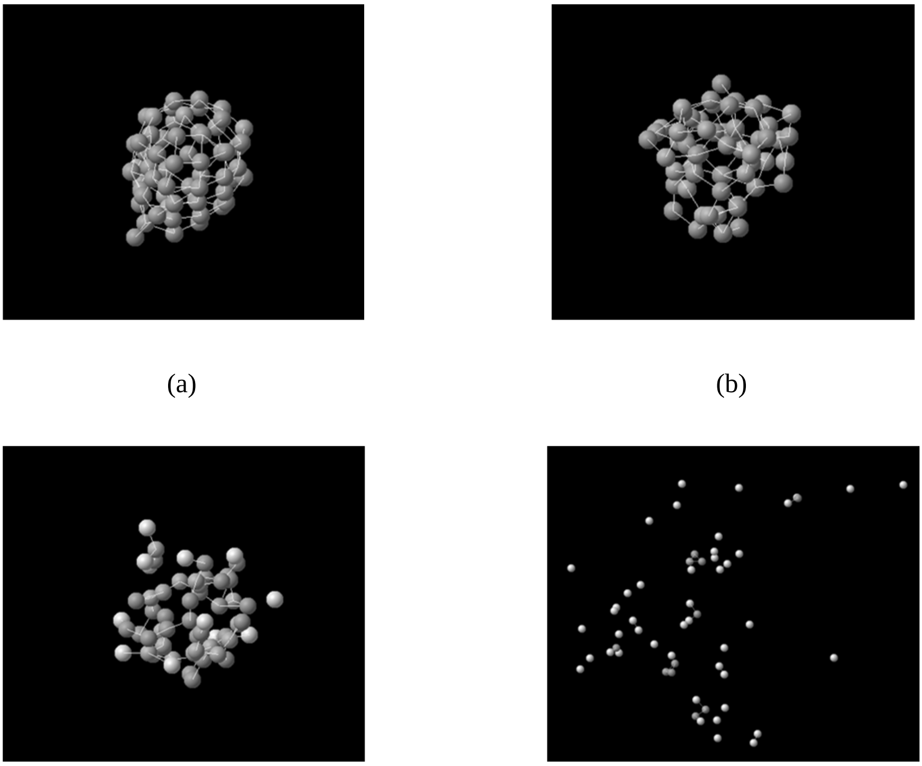


Figure 6: Calculated $C_{60}$ molecule structure at (a) T=2000K and (b) T=2800K (floppy phase) by the NH thermostat method, and at (c) T=4000K (solid phase) and (d) T=4300K (floppy phase) by the modified NH thermostat method.

increases beyond the aforementioned threshold temperatures, the bond length increases with an increasing temperature due to thermal expansion and the orientation of the bond angle. Accordingly, a much more significant structural deformation occurs and the geometry of the fullerene becomes non-axisymmetric or aspherical, as shown in Fig. 6(b) and (d), thereby developing a gradual onset of the floppy phase. In the stage, no bond fracture takes place in the $C_{60}$ structure even though there exists a significant structural deformation. Basically, the floppy phase of the fullerene structure remains a solid. The phase transition point of $C_{60}$ fullerene from solid to floppy by the standard NH thermostat (i.e., 2000K) is comparable to that



(a) (b)

(c) (d)

Figure 7: Snapshots of the vaporization process of $C_{60}$ fullerene at 4350±20K at the time of (a) 0.1 psec (b) 0.2 psec (c) 0.3 psec (d) 0.4 psec.

of Kim and Tománek (1994) (i.e., 2400K), but they all significantly deviate from that of the modified NH thermostat (i.e., 4000K). As the temperature approaches to 2900±50K for the standard NH thermostat and 4350±20K for the modified NH thermostat, a dramatic transition to a vapor phase is detected, where the fullerene structure will soon turn into a full rupture once a chemical bond starts to break.

The "snap-shots" of the $C_{60}$ structure evolution during vaporization process by the modified NH thermostat are shown in Fig. 7. In addition to a floppy phase, Kim and Tománek (1994) also reported several other phases, namely pretzel, linked chain and fragment phases, prior to attaining a gas phase. Transient simulation, instead of the commonly-used quasi-static simulation, may be why Kim and Tománek (1994) derived these exclusive phases. They increased the temperature of heat bath by a temperature increment ΔT = 400 K and 800 time steps for each temperature increment. Since it is a transient simulation, the calculated results are not a steady-state solution but a transient solution. For instance, their simulation results show that the linked chain phase takes place at 5000 K and the fragment phases at 5400 K, implying that the linked chain phase can only exist in a 400 fsec time. It is, thus, believed that the system has not yet reached equilibration. These exclusive phases are, however, not found in the present investigation using both the standard and modified NH thermostat. As inferred by Bundy (1963), the molecules of the liquid phase are probably graphite-like fragments due to that a very small fraction of bonds in the graphite lattice will be broken during melting. Thus, the linked chain and fragment phases are considered liquid, and the lack of these two phases may indicate that the carbon fullerene would sublimate rather than melt when heated under atmospheric pressure. The current result is coincident with the well-known nature of graphite, where it tends to change directly from solid graphite into gaseous carbon atoms, without going through a liquid state, at high temperature and atmospheric pressure or pressure less than 10 MPa (Steinbeck et al., 1985; Bundy, 1989; Zazula, 1997). The predicted phase transition point (i.e., 2900±50K) of $C_{60}$ fullerene by the standard NH thermostat under the atmospheric pressure condition is considerably smaller than the previous findings (Steinbeck et al. 1985; Bundy 1989; Zazula 1997) (i.e., 4000-4500K) for graphite and that of the modified NH thermostat (i.e., 4350±20K). On the other hand, the predicted sublimation point of $C_{60}$ fullerene by the modified NH thermostat (i.e., 4350±20K) stays within the reported temperature range, i.e., 4000-4500K, of the sublimation point of graphite (Steinbeck et al., 1985; Bundy, 1989; Zazula, 1997). From the above evidences, one may deduce that the $C_{60}$ structure presents a similar thermodynamic behavior as graphite at least at the atmospheric pressure condition. Chelikowsky (1991) reported a phase transition point (about 4000-5000K) for $C_{60}$ fullerene directly from “hot carbon plasma” to solid fullerene without invoking a preexisting nucleation subunit under atmospheric pressure. The present result is basically similar to the Chelikowsky’s result and the well-known phase transformation behaviors of graphite, where the fullerene would sublimate rather than melt at the threshold temperature and atmospheric pressure condition.

## 4 Conclusion

In the study, the modified NH thermostat is applied for constant temperature MD simulation of the temperature-dependent linear and volumetric CTEs at low temperature and phase transformation behaviors of carbon fullerenes at high temperature and atmospheric pressure condition. In contrast to the standard NH thermostat and MNHC, the modified one is much more effective and feasible for simulating solid system or dense matter at very low and high temperatures because of accounting for the contribution of phonons by virtue of the vibrational energy of lattice and the zero-point energy, derived based on the Debye theory. The advantages of the modified NH thermostat include the capability of reducing the high fluctuation of the instantaneous system temperature calculated by the standard NH thermostat method and avoiding an underestimate of the system temperature.

The average sampling method implies technical limitation in statistical extraction of the characteristic data from MD simulation because its calculated properties are strongly dependent on the number of sampling steps applied. As a result, the predicted negative volume changes or CTEs for $C_{60}$ fullerene in the wide temperature range 0-250K by the average sampling method with $5\times10^4$sampling steps and also by the Kwon et al.'s calculation are perhaps nothing but a special-case solution. Besides, at temperature below the Debye temperature, unlike the standard NH and MNHC thermostats that give a constant or temperature-independent estimate, the modified NH thermostat successfully predict the strong temperature dependence of the CTE of carbon fullerenes. In other words, only the modified algorithm can accurately reproduce the experimental data, where the CTE tends to decrease with a decreasing temperature. The calculation by the modified NH thermostat also gives a negative CTE estimate only at temperature less than 5K. Besides, the modified NH thermostat also provides a better agreement with the experimental data at room temperature than the other two thermostats.

Furthermore, the phase transformation behaviors of $C_{60}$ fullerene at high temperature and atmospheric pressure condition are successfully identified through both the standard and modified NH thermostats. It turns out that without considering the phonon effect, the standard NH thermostat is seemingly unable to yield an accurate prediction of the phase transformation behaviors or phase transition points of $C_{60}$ fullerene. At atmospheric pressure condition, only the solid, floppy and vapor phases but without the linked chain and fragment phases are observed in the structure evolution of $C_{60}$ fullerene as the temperature increases, revealing that the carbon fullerene would sublimate rather than melt when heated. The solid-vapor phase transition phenomenon is coincident with the well-known nature of graphite. Results also show that by the modified NH thermostat, the floppy phase of $C_{60}$ fullerene occurs at 4000K, and the associated sublimation point is 4350±20K, within the published range of about 4000-4500K for graphite at pressure below 10 MPa.

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