

Phase Transformation Behavior of C₆₀ Fullerene under Atmospheric Pressure

Wen-Hwa Chen^{1,2}, Chun-Hung Wu¹ and Hsien-Chie Cheng^{3,4}

Abstract: The phase transformation behaviors of C₆₀ fullerene under atmospheric pressure are reported using a proposed thermostat molecular dynamics method designed for a solid system. We find that C₆₀ fullerene directly undergoes a solid-vapor phase transformation, instead of a solid-liquid phase transition, at a specific threshold temperature. It reveals that C₆₀ fullerene will sublime when heated rather than melt under atmospheric pressure. This phenomenon is coincident with that of graphite at pressures below 10MPa. The sublimation point of C₆₀ fullerene, rather than the melting, is about $4350\pm 20\text{K}$, locating in the published range of about 4000-4500K for graphite at pressures below 10 MPa.

Keywords: Phase transformation, C₆₀ fullerene, Molecular dynamics, Nosé-Hoover (NH) thermostat

1 Introduction

In recent year, the fullerene molecules have been used in, such as, optical and electronic industries (Dresselhaus et al. 1996), due to their unique electronic and structural properties (Kroto et al. 1993). Among those structural properties, the thermal properties at high temperature, including molten phases and melting points, have drawn considerable attention in research because these properties are related to their formation. In literature, extensive experimental and theoretical methods have been applied for characterizing the thermal properties and phase transformation behaviors of carbon materials, including graphite, diamond and fullerene. As compared to experimental approaches, theoretical approaches such as molecular dynamics (MD) simulation tend to be more cost-effective and efficient, and thus

¹ Department of Power Mechanical Engineering, National Tsing Hua University Hsinchu, Taiwan 30013, ROC

² National Applied Research Laboratories, Taipei, Taiwan, 10622, R.O.C.

³ Department of Aerospace and Systems Engineering, Feng Chia University, Taichung, Taiwan 40724, ROC

⁴ National Center for High-Performance Computing, Hsinchu, Taiwan, 30076, R.O.C.

are in widespread use in nanomechanics. 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 and under which many experiments are performed, 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) and Nosé-Hoover (NH) thermostat method (Nosé 1984; Hoover 1985). By using these methods, several investigators have reported the phase transformation behaviors of C_{60} fullerene. For example, 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. Chelikowsky (1991) deduced that the melting point of C_{60} fullerene is about 4000–5000K by simulating the nucleation process of C_{60} fullerene using the Langevin MD method. Through the NH thermostat MD simulation, László(1998) reported that the formation temperature of C_{60} fullerene in various gases is about 4000K. By way of the same method, Kim and Tománek (1994) showed that the melting point of C_{60} fullerene is about 4000K, and the vapor phase occurs until at 10200K. By using the semi-empirical AM1 module within the PC SPARTAN software (Wavefunction Inc., USA), Fang and Chang (2004) observed that the melting point of C_{60} fullerene is only about 1400K.

In these reported data, a similar feature is observed, in which there exists a fullerene-like fragment state for C_{60} fullerene in the high temperature phase transformation under atmospheric pressure, interpreted as a phase transition to a liquid state. Besides, a wide range variation in the calculated melting points for C_{60} fullerene is observed, where they can be roughly divided into two sets: 1000-3000K and 4000-5000K. The phase transformation phenomena of C_{60} fullerene 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 C_{60} fullerene, a melting point of 4700 ± 80 K at pressures in the range of 50-220 MPa was reported (Senchenko 1987). The experimentally well-established phase diagram of carbon, as based on (Steinbeck et al. 1985; Bundy 1989; Zazula 1997), also revealed that the phase transformation points of transferring graphite from the solid to the liquid or to the vapor range from 4000K to 4700K at different pressures.

Specifically, graphite tends to sublime rather than melt at pressures below 10 MPa when heated up to about 4000-4500K, and melt rather than vaporize under pressure ranging from 10-10000MPa 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. The remarkable difference in the predicted melting points of C₆₀ fullerene (i.e., from 1000-3000K to 4000-5000K) and their difference from graphite can be probably attributed to the limited capability of the conventional thermostat methods and the different choice of the number of equilibrating time steps in the MD simulation.

2 Method

From the structural viewpoint, C₆₀ fullerene has the same stable solid form of carbon, i.e., the crystalline hexagonal carbon, as graphite; thus, it is reasonable to deduce that both should exist in the same range of thermodynamics condition. Unfortunately, it is not seen in the reported data of C₆₀ fullerene. In the study, we aim at exploring the phase transformation behaviors of C₆₀ fullerene under the atmospheric pressure condition through a proposed thermostat MD simulation. The alternative goal is to examine whether solid C₆₀ fullerene will be turned 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, under the atmospheric pressure condition. The proposed thermostat MD method based on the modification of the NH thermostat method is developed particularly for simulating a solid system at constant temperature. The method considers the effect of phonon by virtue of the vibrational energy of lattice and the zero-point energy. Consequently, both the kinetic and potential energies of atoms are taken into account 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

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) + \sum_{i=1}^N \frac{\vec{p}_i^2}{2m_i} = U_0 + 3Nk_B T D(x), \quad (1)$$

where U_0 is the zero-point energy, $D(x)$ the Debye function, x a dimensionless temperature parameter, $x = \theta_D/T$, and θ_D the Debye temperature. A theoretical proof that the calculated quantities by this proposed MD method are exactly equivalent to the canonical ensemble results is made by proving that the calculated partition function is equal to that in canonical ensemble. Furthermore, the force field between two carbon atoms of C_{60} fullerene is modeled with the Tersoff-Brenner potential (Erkoc 1997). For each MD simulation of a specific temperature (or a temperature increment), a time step $\Delta t = 5 \times 10^{-16}$ second and 2×10^6 equilibrating time steps 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) for ascertaining the equilibrium of the molecular system.

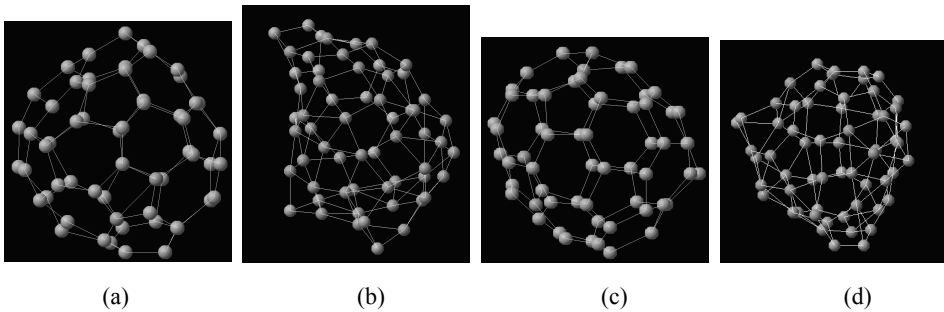


Figure 1: C_{60} structure obtained at (a) $T=2000K$ and (b) $T=2800K$ (floppy phase) using the NH thermostat method, and (c) $T=4000K$ (solid phase) and (d) $T=4300K$ (floppy phase) using the proposed thermostat method.

3 Results

The predicted atomic structures of C_{60} fullerene at different temperatures using both the NH thermostat and the proposed thermostat MD simulations are shown in Fig. 1. It is found that no perceptible shape change in the C_{60} atomic structure is observed when $T \leq 300K$ for the NH thermostat MD simulation and $2000K$ for the proposed thermostat MD simulation. As $T \leq 2400K$ for (Kim and Tománek 1994), $2000K$ for the NH thermostat method (see, e.g., Fig. 1(a)) and $4000K$ for the proposed model (see, e.g., Fig. 1(c)), the C_{60} structure remains intact even though

the structural deformation slightly increases with an increasing temperature. The C₆₀ structure is termed the solid-phase fullerene. As the temperature increases beyond the aforementioned threshold temperatures, the bond length is enlarged with temperature increase due to thermal expansion and the bond angle is spread out. A gradual onset of the floppy phase occurs, as shown in Fig. 1(b) and 1(d), respectively, where a much more significant structural deformation is observed, and the geometry of the fullerene becomes non-axisymmetric or aspherical. In this stage, no bond fracture occurs in the C₆₀ structure, and thus the floppy phase of fullerene structure remains a solid. The phase transition point of C₆₀ fullerene from the solid to the floppy state given in (Kim and Tománek 1994) (i.e., 2400K) is quite comparable to that of the NH thermostat MD method (i.e., 2000K) but significantly less than that of the proposed model (i.e., 4000K). As $T \approx 2900 \pm 50\text{K}$ for the NH thermostat method and $4350 \pm 20\text{K}$ for the proposed model, a dramatic transition to a vapor phase is detected, where the fullerene structure turns into a full rupture once one chemical bond begins to break. This reveals that the fullerene structure presents a very brittle fracture behavior at high temperature and low pressure condition.

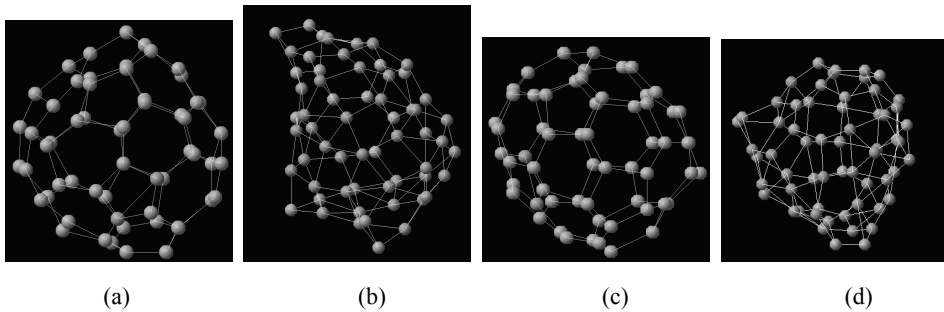


Figure 2: Vaporization process of C₆₀ fullerene at $4350 \pm 20\text{K}$ at the time (a) 0.1psec (b) 0.2psec (c) 0.3psec (d) 0.4psec

The “snap-shots” of the C₆₀ structure during vaporization process, obtained from the proposed model, are shown in Fig. 2. In addition to a floppy phase, Kim and Tománek (1994) reported additional pretzel, linked chain and fragment phases prior to attaining a gas phase. These unique phases are, however, not found in the present investigation using both the NH thermostat method and the proposed model. 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 sublime 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 from solid graphite into gaseous carbon atoms, rather than liquid carbon, under atmospheric pressure or pressure less than 10 MPa (Steinbeck et al. 1985; Bundy 1989; Zazula 1997) at high temperature. The phase transition point of C_{60} fullerene obtained from the NH thermostat method under the atmospheric pressure condition (i.e., $2900\pm 50K$) 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 proposed model (i.e., $4350\pm 20K$). On the other hand, the predicted sublimation point of C_{60} fullerene using the proposed model (i.e., $4350\pm 20K$) stays in the range of 4000-4500K for graphite (Steinbeck et al. 1985; Bundy 1989; Zazula 1997). From these facts, one can deduce that the C_{60} structure exists in the same wide range of thermodynamics conditions as graphite, at least under the atmospheric pressure condition. Even though Chelikowsky (1991) reported a similar phase transition point (about 4000–5000K) for C_{60} fullerene based on the simulation of the nucleation process, the phase change from solid graphite to liquid carbon under the atmospheric pressure condition basically contradicts to the present results and the phase transformation behaviors of graphite.

4 Conclusion

In summary, the phase transformation behaviors of C_{60} fullerene under the high temperature and atmospheric pressure condition are identified through both the NH thermostat MD method and the present thermostat MD method that takes into account the contribution of phonon by virtue of the vibrational energy of lattice and the zero-point energy. We find that without considering the phonon effect, the NH thermostat method seems to be unable to give an accurate estimation of the phase transformation point of C_{60} fullerene. Under atmospheric pressure at high temperature, only the solid, floppy and vapor phases but without the linked chain and fragment phases are observed in C_{60} fullerene, revealing that the carbon fullerene would sublime rather than melt when heated. The solid-vapor phase transition phenomenon is coincident with that of graphite. Results also show that the floppy phase of C_{60} fullerene occurs at 4000K, and the associated sublimation point is $4350\pm 20K$, within the published range of about 4000-4500K for graphite (Steinbeck et al. 1985; Bundy 1989; Zazula 1997) at pressures below 10 MPa. Besides, it turns out that the fullerene structure presents a very brittle fracture behavior at high temperature and low pressure condition.

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