Heat Wave Driven by Nanoscale Mechanical Impact between C\textsubscript{60} and Graphene

Xianqiao Wang\textsuperscript{1} and James D. Lee\textsuperscript{2}

Abstract: This paper presents a novel physical phenomenon—heat wave propagation—at the atomic scale by investigating the collision of C\textsubscript{60} molecules with a graphene sample through molecular dynamics (MD) simulation. A correlation between mechanical wave and temperature variation has been captured at the early stage of collision to demonstrate that temperature variations behave in a wave motion, which contradicts the concept in classical continuum mechanics, whereas later temperature variations exhibit the properties of a diffusion equation. This intriguing result, called wave-diffusion duality, offers an insight into the thermomechanical coupling phenomenon of nanodevices. DOI: 10.1061/(ASCE)NM.2153-5477.0000044. © 2012 American Society of Civil Engineers.

CE Database subject headings: Nanotechnology; Wave propagation; Simulation; Diffusion; Temperature effects.

Author keywords: Molecular dynamics; Graphene; Buckyball; Collision; Heat wave; Wave-diffusion duality.

Introduction

A key issue in nanotechnology is understanding and controlling the thermomechanical coupling behaviors of nanostructures such as carbon nanotubes, buckyballs, and graphene. Since its discovery several years ago (Geim and Novoselov 2007), graphene has attracted enormous attention owing to its novel electrical, chemical, and mechanical properties. The high electron mobility of graphene gives rise to unique phenomena such as the quantum spin Hall effect and the enhanced Coulomb interaction; therefore, it is an excellent promising candidate for the next generation of logic devices (Novoselov et al. 2004; Novoselov et al. 2005; Zhang et al. 2005; Lin et al. 2008; Castro Neto et al. 2009). The superior mechanical properties of graphene make it ideally suitable for nanoelectromechanical (NEMS) applications such as in pressure sensing and in fabricating nanoresonators (Bunch et al. 2007; Bunch et al. 2008; Pei et al. 2010). In addition to its electronic properties, the thermal properties of graphene (Balandin et al. 2008; Ghosh et al. 2008; Hu et al. 2009) have fundamental and practical importance because of its superior thermal conductivity as a carbon nanotube (Kim et al. 1991). The superior thermal properties of graphene have also been studied by Zhang et al. (1993). To the best of the authors’ knowledge, however, very limited work exists in relation to the thermomechanical coupling phenomenon of collision between C\textsubscript{60} and graphene molecules.

In this paper, the authors present a molecular dynamics simulation study of the mechanical and thermal coupling behavior of the C\textsubscript{60} molecule when it collides with a graphene molecule at high kinetic energy. This paper is arranged as follows. The “Computational Model and Method” section introduces the computational model and methods used in the simulation. The “Results” section presents the results of the simulations. The “Conclusion” section discusses conclusions and directions for future studies.

Computational Model and Method

The nanocollision system, consisting of a graphene sample and a C\textsubscript{60} molecule, is performed by molecular dynamics simulation in which the interatomic carbon-carbon interactions are described by using the Tersoff potential (Tersoff 1989). The interatomic potential has the form

\[ E = \sum_i E_i = \frac{1}{2} \sum_{ij} V_{ij} \]  

\[ V_{ij} = f_c(r_{ij})[f_{d}(r_{ij}) + b_{ij}f_{s}(r_{ij})] \]  

where \( E \) is the total energy of the system, which is decomposed for convenience into a size energy \( E_i \) and a bond energy \( V_{ij} \). The
indexes \(i\) and \(j\) run over the atoms of the system; \(r_{ij}\) is the distance from atom to atom; and \(b_{ij}\) represents a measure of the bond order and is assumed to be a monotonically decreasing function of the coordination of atom \(i\) and \(j\). The function \(f_{R,K}\) represents a repulsive pair potential and \(f_{A}\) represents an attractive pair potential associated with bonding. The extra term \(f_{c}\) is merely a smooth cutoff function to limit the range of the potential because, for many applications, short-ranged functions permit a tremendous reduction in computational effort.

The functions \(f_{R}, f_{A},\) and \(f_{c}\) are simply

\[
f_{R}(r_{ij}) = A_{ij} \exp(-\lambda_{ij} r_{ij})
\]

\[
f_{A}(r_{ij}) = -B_{ij} \exp(-\mu_{ij} r_{ij})
\]

\[
f_{c}(r_{ij}) = \begin{cases} 1, & r_{ij} < R_{ij} \\ \frac{1}{2} \left( 1 + \frac{1}{2} \cos(\pi (r_{ij} - R_{ij})/(S_{ij} - R_{ij})) \right), & R_{ij} < r_{ij} < S_{ij} \\ 0, & r_{ij} > S_{ij} \end{cases}
\]

where

\[
b_{ij} = \chi_{ij}/(1 + \beta_{ij}^{2})^{1/2},
\]

\[
\xi_{ij} = \sum_{k \neq i,j} f_{c}(r_{ik}) \omega_{ik} g(\theta_{ik})
\]

\[
g(\theta_{ij}) = 1 + c_{ij}^{2}/d_{ij}^{2} - c_{ij}^{2}/[d_{ij}^{2} + (h_{ij} - \cos \theta_{ij})^{2}]
\]

\[
\omega_{ij} = 1, \quad \chi_{ij} = 1,
\]

\[
A_{ij} = (A_{ij})^{1/2}, \quad B_{ij} = (B_{ij})^{1/2};
\]

\[
\lambda_{ij} = (\lambda_{i} + \lambda_{j})/2, \quad \mu_{ij} = (\mu_{i} + \mu_{j})/2,
\]

\[
R_{ij} = (R_{ij})^{1/2}, \quad S_{ij} = (S_{ij})^{1/2}
\]

The variables \(i, j,\) and \(k\) label the atoms of the system; \(\theta_{ij}\) is the bond angle between bond \(ij\) and \(ik\). Single subscripts parameters such as \(A_{i}, B_{i}, S_{i}, R_{i}, \lambda_{i}, n_{i},\) and \(\mu_{i}\) are material constants, depending on the type of atom (i.e., C, Si, or Ge). The only assumption is that the atoms are point particles and chemically inert. The material constants involved in the Tersoff potential are constant with respect to temperature. Temperature varies with the dynamics of the system; however, the system uses an interatomic potential, which is temperature independent. The energy is modeled as a sum of pair-like interactions in which the coefficient of the attractive term in the pair-like potential depends on the local environment, giving a many-body potential. The Tersoff potential is also deemed as one of the most advanced and sophisticated three-body potential. It gives the correct cohesive energy and the equilibrium lattice constant of graphene. Researchers have also shown that the Tersoff potential is stable in long-time running, according to tests, and it gives fairly accurate results. The material constants of carbon are presented in detail, as follows:

\[
A = 1.3936 \times 10^{3} \text{eV} \quad B = 3.467 \times 10^{5} \text{eV};
\]

\[
\lambda = 3.4879 \times 10^{-11} \text{nm}; \quad \mu = 2.2119 \times 10^{-11} \text{nm};
\]

\[
\beta = 1.5724 \times 10^{-7}; \quad n = 7.2751 \times 10^{-1},
\]

\[
c = 3.8049 \times 10^{4}; \quad d = 4.384; \quad h = -5.7058 \times 10^{-1};
\]

\[
R = 1.8 \times 10^{-11} \text{nm}; \quad S = 2.1 \times 10^{-11} \text{nm}
\]

To investigate nanocollision-driven thermomechanical coupling behavior, the authors used a circle graphene sample having a radius \(R = 10.9 \text{nm}\) at \(z = 0\), combined with \(C_{60}\) molecule at \(z = 4.23 \text{nm}\) beyond the interaction range of the Tersoff potential (with nonperiodic condition in all directions), as Fig. 1 shows. The graphene sample is partitioned uniquely along the radial direction into 21 groups for temperature calculation and boundary setting. Along the radial direction, the groups of the graphene sample are numbered as Group 1, 2, \(\cdots\), 21 (from the center to the outside). In Fig. 1, atoms in Group 21, depicted in the outermost ring, are fixed as \(u_{i}(t) = 0\) to simulate the simple-supported boundary condition. The \(C_{60}\) group, numbered as Group 22, is located initially at a sufficient distance above the graphene sample and has negligible interaction with the graphene sample. It then impacts the graphene molecule with translational energy, \(E_{in}\), in the direction normal to the graphene molecule. The simulation is established by the code that the authors developed. The total runtime of the simulation is 7.8 ps, with the exception of the 100 ps relaxation time. The time step \(\Delta t = 1\) fs.

Before starting the simulation, a 100-ps relaxation is conducted to reach a quasi-static equilibration of the whole system. During that time, the temperature of the graphene approaches to 0 K. The purpose of relaxation is to rule out other noise effects and to make more pronounced the correlations between wave propagation and temperature variation. The \(C_{60}\) molecule is enacted as an impetus with an initial energy, \(E_{in} = 200\) eV.

Temperature at the nanoscale level is a dependent statistical variable that is derived from the velocity of a specified group of atoms. Temperature can be defined as a space-averaged variable of a group of atoms and

\[
T(t) = \frac{\sum_{i=1}^{N} m_{i} [v_{i}(t) - \bar{v}]^{2}}{3 k_{B} N}
\]

where \(N\) is the number of the group of atoms; \(m_{i}\) is the mass of atom \(i\); \(v_{i}\) is the velocity of atom \(i\); \(\bar{v}\) is the average velocity of the group of atoms; and \(k_{B}\) is the Boltzmann constant.

Fig. 1. Computational model of a nanocollision between the graphene sample and a \(C_{60}\) molecule
Results

Before discussing the main results, the authors would like to demonstrate the correctness and stability of their codes by virtue of the conservation of energy in the system. Fig. 2 shows the time evolution of energy variations from the initial values for the C60-graphene collision. The top line, bottom line, and middle line in Fig. 2 represent the potential energy variation (\(\Delta E_p\)), the kinetic energy variation (\(\Delta E_k\)), and the total energy variation of the whole system (\(\Delta E\)), respectively. Fig. 2 confirms that the total energy (\(E\)), which is the sum of the kinetic energy (\(E_k\)) and potential energy (\(E_p\)), is conserved because no dissipation exists in classical MD simulation.

The total energy of the \(n\)-atom system is

\[
E = E_k + E_p = \sum_{i=1}^{n} \frac{1}{2} m_i \dot{r}_i \cdot \dot{r}_i + E_p(r_1, r_2, \ldots, r_n)
\]

(8)

For atom \(i\), the governing equation is

\[
m_i \ddot{r}_i = F_i
\]

(9)

and the interatomic “constitutive relationship” is

\[
F_i = -\frac{\partial E_p}{\partial \dot{r}_i}
\]

(10)

where \(m_i\) is the mass of atom \(i\); \(\dot{r}_i\) is the current position of atom \(i\); \(F_i\) is the interatomic force acting on atom \(i\); and the superscript double dots is the second time derivation.

By using Eqs. (9) and (10), it can readily be demonstrated that

\[
\frac{dE}{dt} = \frac{d(E_k + E_p)}{dt} = \sum_{i=1}^{n} m_i \dot{r}_i \cdot \dot{r}_i + \sum_{i=1}^{n} \frac{dE_p}{d\dot{r}_i} \cdot \dot{r}_i
\]

\[
= \left\{ \sum_{i=1}^{n} m_i \dot{r}_i \right\} \cdot \dot{r}_i = \left\{ \sum_{i=1}^{n} m_i \dot{r}_i - \sum_{i=1}^{n} F_i \right\} \cdot \dot{r}_i = 0
\]

(11)

Therefore, numerical and theoretical perspectives confirm the conservation of energy. This result provides confidence for the MD simulation of carbon nanostructures on the basis of the Tersoff potential.

The purpose of the simulation is to capture the correlation between mechanical wave and temperature variation during the collision of a graphene molecule with a C60 molecule. To keep the graphene and C60 molecule intact during collision, the authors adopted an initial energy of 200 eV for C60 (Pan et al. 1998).

Fig. 3 presents the evolution of the displacement, \(u_z\), of the graphene sample under the deformed shape. The dark gray area in the center in Fig. 3 represents the minimum value of displacement \(u_z\) in the snapshot. The \(z\)-displacement of the atoms in the surrounding the dark inner circle remain close to 0. It is clearly obvious that a mechanical wave induced by collision with C60 molecules propagates in the graphene sample like a water ripple in a quiet pond. As time proceeds, the region with a negative displacement along the \(z\)-direction expands in the plane of the graphene.

Fig. 3. Displacement (\(u_z\)) sequence of snapshots of atomic arrangements; the dark gray area in the center represents the minimum value of displacement \(u_z\) in the snapshot
After collision, a fraction of the translational kinetic energy of the C_{60} is converted to the translational kinetic energy of graphene, notably in a mechanical wave mode. Fig. 4 shows the displacement $u_z$ response of different groups in the graphene during the process of collision. Because of the nonlocality and nonlinearity of the interatomic forces, the groups closest to the center of graphene have a greater magnitude of $z$-displacement than groups farther away from the center. The delay time of the mechanical motion also becomes more pronounced with the groups farther away from the center of graphene sample.

Fig. 5 exhibits the evolution of the temperature profile of the graphene molecule sample under the deformed shape. The black ring represents the maximum value of the temperature region in the snapshot. The dark gray area indicates that the temperature remains close to 0 K. The temperature variation clearly behaves in a mechanical wave motion. As time proceeds, the region with a maximum value of temperature moves outward along the radial direction, thereby clearly showing that temperature variation has a wave motion property. This can be understood by the fact that a fraction of the translational kinetic energy of the C_{60} has been converted to the internal vibration of the graphene molecule, especially in the heat wave mode. Fig. 6 depicts the temperature response of different groups in graphene during the process of collision. At the first peak stage, it is clear that the closer the group is to the center of graphene, the higher is the temperature of the group. After a long period, however, the temperature of each group approaches to nearly the same steady-state value of 50 K. Fig. 6 depicts the entire process provides insight into the wave-diffusion duality of temperature variation. This is because of the fact that, after the energy associated with the wave is converted into heat, it tends to spread out over the entire domain, rather than convert back. Comparing the results from Fig. 6 with the results from Fig. 4 shows that a correlation exists between the movements of the high temperature peak and the wave front. The results in this paper are intended to reflect qualitative behavior and should be seen as the proof of concept of the wave-diffusion duality of temperature variation.

![Fig. 4. Displacement ($u_z$) response of different groups in graphene during the process of collision](image-url)

![Fig. 5. Temperature sequence of snapshots of atomic arrangement; the black ring represents the maximum value of the temperature region in the snapshot](image-url)

![Fig. 6. Temperature response of different groups in the graphene sample during the process of collision](image-url)
Conclusions

This study unveils a novel physical phenomenon that temperature variation at the nanoscale level can behave as mechanical waves. The wave-diffusion duality of temperature variation offers a more fundamental insight into designing and fabricating nanodevices at various temperature or mechanical environments. Moreover, the results reported in this paper feature the potential for several nanotechnology applications assisted by thermal fluctuation. This includes the use of nanotubes as nanopipettes, fluid filtration devices, and targeted drug-delivery devices. However, experimentally controlling and detecting the dynamical process of heat wave remain challenges.

References