Phonon Scattering Dynamics of Thermophoretic Motion in Carbon Nanotube Oscillators

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ABSTRACT: Using phonon wave packet molecular dynamics simulations, we find that anomalous longitudinal acoustic (LA) mode phonon scattering in low to moderate energy ranges is responsible for initiating thermophoretic motion in carbon nanotube oscillators. The repeated scattering of a single mode LA phonon wave packet near the ends of the inner nanotube provides a net unbalanced force that, if large enough, initiates thermophoresis. By applying a coherent phonon pulse on the outer tube, which generalizes the single mode phonon wave packet, we are able to achieve thermophoresis in a carbon nanotube oscillator. We also find the nature of the unbalanced force on end-atoms to be qualitatively similar to that under an imposed thermal gradient. The thermodiffusion coefficient obtained for a range of thermal gradients and core lengths suggests that LA phonon scattering is the dominant mechanism for thermophoresis in longer cores, whereas for shorter cores, it is the highly diffusive mechanism that provides the effective force.

KEYWORDS: phonon scattering, carbon nanotube oscillator, thermophoresis, coherent LA phonon, nanoscale mechanical motion, vibrational energy transfer

Thermophoretic motion of nanoscale objects enclosed inside carbon nanotubes (CNT) is of considerable interest in realizing nanoscale mechanical devices. Several theoretical and experimental attempts have been made to explore the thermophoretically driven transport of gold nanoparticles,†‡ water molecules,§ CNTs¶∥ and fullerenes.¶ Thermophoretic motion of nanoscale objects enclosed inside carbon nanotubes (CNT) is of considerable interest in realizing nanoscale mechanical devices. Several theoretical and experimental attempts have been made to explore the thermophoretically driven transport of gold nanoparticles,†‡ water molecules,§ CNTs¶∥ and fullerenes.¶ Toward attaining a more precise controlled periodic oscillations have been realized by imposing thermal energy as tuned periodic pulses.¶ The essential driver for such motions is the net current of hot phonons that are generated by the imposed thermal gradient. While interacting, these hot phonons are scattered by the moving object and some of the vibrational energy is exchanged with translational energy of the moving body. However, there have been few attempts‡ to gain phonon level understanding of thermophoretic motion, and the exact underlying physical mechanism has remained elusive so far.

In this work, we first study single mode phonon wave packet scattering in coaxially sliding CNT oscillators in order to elucidate the role of individual phonons. We show that the scattering mechanism of longitudinal acoustic (LA) mode phonons is responsible for initiation of thermophoretic motion in CNT oscillators. We then impose a coherent LA phonon pulse on the outer tube and achieve LA phonon driven thermophoretic motion of the core. Finally, we show that LA phonon scattering is the dominant mechanism for thermophoretic motion in longer cores, whereas for shorter cores, it is the highly diffusive mechanism that provides the effective force.

Scattering of Single Mode Phonon Wave Packets. Phonon wave packet formalism provides a powerful computational framework for treating single phonon transport across interfaces.¶∥ In this approach, a phonon wave packet with polarization, s, and wavenumber, q0, at location, z0, is constructed from the linear combination of vibrational eigen modes of the lattice according to

\[ u_{q0} = \frac{A}{\sqrt{M}} \sum_q \exp \left[ -\frac{(q - q_0)^2}{2\sigma^2} \right] e_{\alpha q}(q) \exp[iq(z - z_0)] \]

(1)

where \( u_{q0} \) is the displacement from the ground state position of the \( k \)th base atom in the \( l \)th unit cell (located at \( z_l \)) along direction \( \alpha \). \( A \) is the amplitude of the wave packet, and \( M \) is the mass of the atom. \( e_{\alpha q}(q) \) is the phonon eigenvector corresponding to polarization, \( s \), and wavenumber, \( q \). \( \sigma \) is the broadening parameter in the Gaussian spread of the wave packet around \( q_0 \). The eigenvectors, \( e_{\alpha q}(q) \), and corresponding phonon frequencies \( \omega^s(q) \) are obtained by diagonalizing the dynamical matrix which is the Fourier transform of the force constant matrix. The phonon frequency vs wave vector plot gives the dispersion relation \( \omega^s(q) \).

Received: October 2, 2015
Revised: February 17, 2016
The oscillator consists of an open ended 50 nm long (5,5) CNT core within a one micron long (10,10) CNT outer tube. A wave packet of a specified wavenumber and specified polarization is generated in the outer tube far away from the inner core (500 unit cells to the left of the center, with $\sigma = 2\pi / 100a$, where $a$ is the lattice constant, giving a spread of 200 unit cells) and we study how the individual phonon travels through the outer CNT, interacts with the inner nanostructure, and generates a net driving force. Molecular dynamics simulations are conducted in microcanonical ensemble with a time step of 1 fs using LAMMPS.\(^{13}\) To ensure that anharmonic effects are completely avoided, the ground state ($\approx 0$ K) configuration is adopted in all wave packet simulations. As in previous works on phonon wave packet simulations of CNTs\(^{10,14,15}\) the polymer consistent force field (PCFF), parametrized based on ab initio calculations,\(^{16,17}\) is adopted to model the atomic interactions in ground state. For simulations at moderate to high temperatures, the empirical AIREBO\(^{18}\) potential has been adopted.

We first evaluate the energy transmission coefficient (the ratio of transmitted energy to the incident phonon wave packet energy). Figure 1 shows the transmission function of LA mode phonons for (10,10) CNT with (5,5) CNT-L50 as stationary core. The acoustic phonons with wavelengths very close to $\Gamma$-point are long enough to not interact with the inner nanostructure. Moving just right of the $\Gamma$-point, in the low energy range ($5–15$ meV), they are able to interact with the core and thereby cause significant scattering (down to $\approx 0.7$). When compared with LA mode transmission of CNTs having defects\(^{19}\) and functionalizations,\(^{14}\) the unique feature in the present transmission function is the broad dip in the low energy region. We understand that this dip is to be a signature for the presence of inner core. The high frequency part of the transmission function is similar to those in earlier CNT related studies\(^{10,14,15}\).

To understand the precise mechanism of interaction of LA phonon with the inner CNT, we analyzed the wave packet propagation by monitoring the temporal evolution of kinetic energy (KE) along the length of the oscillator (taken to be the KE of the first basis atom of each unit cell). In each of these three panel groups in Figure 2, the square plot corresponds to energy time history of the outer CNT, whereas the companion strip corresponds to the core. We choose phonons with three different energies (5.76, 9.18, and 12.3 meV) based on the transmission plot in Figure 1. These outline the profile of the first dip in transmission.

Irrespective of the transmission coefficient, a consistent scattering mechanism is observed over the range of energies corresponding to the first dip, of which three cases can be seen in Figure 2. At first, we observe the unscattered passage of LA mode phonon wave packet over the left end atoms of inner CNT. As the wave packet glides over the core, some part of the wave packet energy is transferred to the inner CNT. This part of wave packet continues to propagate in the core and is scattered by the right end of the core. The LA mode phonon wave packet creates the first scattering event only when it travels over the right end of the core. A substantial part of the packet is reflected back first through the inner CNT, part of which then is sent back along the outer CNT as it reaches the left end of the core. This creates a cycle of slowly decaying scattering events and represents anomalous reflection of LA phonon by the inner core.

The repeated collision of wave packet with the end atoms of the core will generate thermal forces on both the ends. The importance of unbalanced edge forces (which acts only on the edge atoms of the moving nanostructure) in initiating the
thermophoretic motion has been highlighted in a few earlier works. The dominant activity of edge atoms of gold nanoparticles inside a CNT due to imposed thermal gradient has been reported by Schoen et al. Asymmetry in the force profile along the length of cylindrical gold nanoparticle provides the initial driving force.

Figure 3a shows the KE absorbed by the core while the wave packet is propagating. Along with the three phonons with energies corresponding to Figure 2, another phonon with a higher energy (15.9 meV) is also plotted. We can see the time at which initial scattering occurring depends on the group velocity of the phonon. In all cases, the initial scattering provides the maximum KE to the core. Further, the pulsating edge atom activity can be seen as periodic spikes in the time evolution of KE of the core. After the initial pass of the wave packet over the core, it quickly attains the maximum KE and then slowly dissipates it back to the outer CNT. Irrespective of maximum KE attained, the lifetime of the quasibound state is almost same in all the four cases. The phonon of low transmission coefficient induces more KE to the core, in other words more the LA mode scattering the more KE the core can absorb.

The scattering of the wave packet at the two ends of the core generates the axial forces. For the phonon with the peak scattering (12.3 meV), the axial force experienced by the ends of the core (10 unit cells of core CNT on both sides considered as end atoms) is plotted with time in Figure 3b. These forces, it should be noted, are the effect of a single mode LA phonon and are not sufficient to overcome the local potential energy barrier. In contrast, the transverse forces are negligibly small, suggesting the absence of other modes such as TA, TW, RB in the scattering process. The unbalanced axial force, if large enough, would lead to directed motion of the core, as we show in the next section. Such large forces could arise due to the asymmetry in the average distribution of phonon collisions with the core when a finite thermal gradient is imposed on the outer CNT.

The present observation on LA phonon scattering mechanism—the way the phonon wave packet transfers energy into the inner core while gliding over it and the transferred energy scatters at the right side end of the core—clearly explains the initiation mechanism of thermophoretic motion of nanostructures (CNTs, C60, gold nanoparticles, water molecules) observed inside the CNTs. In all these works, we can see initially the core remains stationary for some time when the imposed thermal gradient slowly starts becoming effective. As the core receives phonons from the hot reservoir, it attains sufficient amount of energy to exceed the local potential energy barrier and to initiate motion.

Although earlier attempts to explain thermophoresis highlighted the importance of the unbalanced forces, our work for the first time connects it to phonon scattering and thus provides greater insight into the physical origin of effective thermophoretic motion. In single mode LA phonon scattering mechanism (see Figure 2b), the packet is repeatedly scattered by edge atoms of the inner CNT. However, the LA phonon scattering mechanism would depend on the inner nanostructure such as gold nanoparticle, water molecules or nanotube. In Schoen et al., the imposed low energy radial breathing mode facilitated the inner gold nanostructure to attain thermophoretic motion by releasing the contact from CNT casing. Nonetheless, the force causing the directed motion could be developed from the unbalanced edge forces.

**Thermophoresis by Coherent LA Phonon Pulse.** With the recent development of ultrafast laser techniques, exciting nonequilibrium heat transport phenomena have been achieved in nanoscale systems. In theoretical pursuit of such phenomena, several heat source models have attempted to mimic the ultrafast laser generated phonon excitation processes. These heating processes generate hot phonons of various polarizations and pump them toward the interface and are able to maintain a stable thermal gradient. Nevertheless, even by applying such local heating with subpicosecond duration it is difficult to generate a population of nonequilibrium phonons of one given polarization.

Coherent phonon pulse excitation of various polarizations and wave vectors has recently been achieved experimentally. The pump pulse duration should be shorter than the oscillation period of the phonon to be excited, which for nanotubes is in the order of tens of femto-seconds. Due to such short relaxation time, the electrons and holes generated by ultrafast pump excites a population of phonons coherently (via electron–phonon interactions) at the same time and with the same phase. In this work, we generate coherent phonon pulse by generalizing the single mode phonon wave packet (eq 1) in the form of a traveling wave whose amplitude is modulated by a Gaussian temporal window:

\[
\begin{align*}
\tilde{u}_{\alpha}^L(t) &= \frac{A}{\sqrt{M}} \sum_q \exp \left[ -\frac{(q - q_0)^2}{2\sigma^2} \right] \exp \left[ -\frac{(t - t_0)^2}{2\gamma^2} \right] \\
&\times \tilde{e}_{\alpha}^L(q) \exp \left[ i(q(z_l - z_0) - \omega(q)(t - t_0)) \right]
\end{align*}
\]

where \( \gamma \) is the broadening parameter to control the resolution of wave packet in temporal space. A similar approach to generating coherent phonon pulse was taken by Chen et al., but without the Gaussian spread in the wave vector space.

With \( t_0 = 100 \text{ fs} \) we set \( \gamma = 30 \text{ fs} \) such that Gaussian wave packet is all but absent outside the range of 10 to 190 fs.
pulse is imposed on the outer CNT of our micron-long oscillator at the same location as that of single mode LA phonon wave packet and with a wavelength corresponding to peak scattering, that is, at 12.3 meV (see Figure 1). The amplitude, $A$, of the packet is set such that the temperature at the pulse region initially (at $(t_0, z_0)$) is 2500 K, whereas the remaining system is maintained at 0.1 K.

The temporal evolution of local temperature on the one micron long (10,10) outer CNT is plotted in Figure 4 which represents the relaxation of the coherent LA phonon pulse. Propagation of different wave fronts with different group velocities, symmetrically away from the pulse region, can be seen. The slope of the first wavefront generated from the leading edge of the pulse region, equal to 15 km/s, is in accordance with the LA phonon group velocity (blue line in Figure 1). The initial location of the core is indicated by vertical dashed lines. Between 6−10 ps, the first LA wavefronts reach the left end of the core. These and later LA wave fronts interact with the core while gliding over it by supplying a share of their KE to it. However, the pattern of repeated scattering as shown in Figure 2 cannot be observed here. The reason is as follows. The LA wave front carries a much higher thermal energy (as the color scale indicates up to 10 K) in comparison with single mode LA wave packet (which is of few meV). Thus, in Figure 2, the core acts as a static interface causing a significant part of the packet to repeatedly reflect back and forth through both the inner and outer CNTs. However, as we show next, the coherent phonon pulse has enough energy to start displacing the core with its first scattering event itself, and consequently, there is no scope of repeated scattering in the moving core. In contrast, repeated reflections of the pulse from both ends of the outer tube (the first at the left end is seen at 20 ps and the first at the right end at 30 ps) will be shown to have significant effect on the core motion.

We now analyze different events in the core motion. Figure 5 shows that the first significant push on the core occurs around 12 ps. These forces are of the same order as earlier experimental\textsuperscript{29} and theoretical\textsuperscript{30} observations on sliding of inner CNTs through one unitcell length (2.45 Å). Unlike in the single mode LA phonon excitation (Figure 3b), the total force due to the coherent pulse builds up, and is able to overcome the local potential barrier at around 15 ps, after which the core starts moving. Figure 6a plots the net force (smoothed) on the inner core. Up until about 70 ps, the net force stays positive and is responsible for imparting sustained motion on the inner core.

Figure 4. Spatiotemporal isotherms of (10,10) outer CNT due to coherent LA phonon pulse. Pulse is imparted at 500 unitcells left of the core, initial position of the core is indicated by the vertical dashed lines. Temperature (K) is represented according to the color bar. The slope of the first wavefront propagating symmetrically both sides is closely matching with the group velocity of LA phonon.

Figure 5. Axial end forces on the core corresponding to the initiation of coherent LA phonon pulse driven motion.

Figure 6. Coherent LA phonon pulse driven thermophoretic motion of 50 nm long (5,5) CNT (a) center of mass axial force acting on the core, (b) kinetic energy absorbed by the core (red line, on left axis) and corresponding core velocity (orange line, on left axis), and (c) position of the core as a function of time. The initial displacement of the core is highlighted in the inset.
Between approximately 70 and 230 ps the net force starts fluctuating around zero due to repeated end reflections mentioned above, and following that, it strays more in the negative territory thereby slowing down the core. Figure 6b plots the steep rise in the velocity of the core (orange line, right axis) to about 15 m/s in the first 70 ps, after which it exhibits large fluctuations and begins to slow down starting at 230 ps to about 3 m/s at the end of the simulation time. The plot also shows the growth in KE of the inner core (red line) and suggests gradual heating of the core. Finally, Figure 6c plots the center of mass displacement of the core which clearly shows thermophoresis under the LA phonon pulse by traveling 7% of its length in the simulation time.

Is the LA Mode Special? Along with LA mode, we studied two other acoustic modes (TA and TW) and two optic modes (BR and FO) and found that the scattering mechanism showed by the LA mode (Figure 1 and Figure 2) only can initially generate a net axial force on core. The wave packets of BR and TW modes transfer almost no energy in to the inner core and show a consistent ideal transmission throughout the frequency range. TA and FO modes showed a significant scattering in the low energy region however the mechanism of scattering is distinct from that of LA mode. Unlike LA phonon, the mode characteristic of TA and FO phonons involve dominant transverse component of atomic displacements and hence no net axial force on the end atoms of the core. Interestingly, in a very recent observation, low frequency longitudinal phonon modes of CNT are found to cause an enhanced diffusion of encapsulated water molecules via an oscillating shear stress at the interface.

Thermophoresis under Sustained Thermal Gradient. We now try to identify conditions under which LA phonons no longer remain effective as drivers of thermophoresis. For this we take up a different set of MD simulations by imposing a sustained thermal gradient on a 100 nm long (10,10) outer CNT, fixed at both ends and initially equilibrated at 0.01 K. Twenty unit cells (≈ 5 nm) on both left and right sides are considered as thermostated regions. The left end is thermostated at $T_{L1}$ whereas the right end is maintained at 0.01 K. Imposing thermal gradient on a system with such a low temperature facilitates us to precisely observe the initial displacement of the core. In the absence of prior thermal effects, the axial forces on end-atoms of the core can be monitored. Five values of $T_{L1}$ are chosen: 500 K, 1100 K, 1500 K, 2000 K, and 2500 K corresponding to thermal gradients of 5 to 25 K/nm. Thermal gradients up to 25 K/nm have been imposed in earlier theoretical and experimental studies on CNTs.

Figure 7 shows the first 20 ps of thermophoretic motion of 50 nm long (s,s) CNT core under two different thermal gradients (11 K/nm and 25 K/nm). Unlike in single phonon wave packet and coherent phonon pulse simulations, here, due to the imposed thermal gradient, a flow of phonons of various frequencies and polarizations simultaneously originate from the hot reservoir and travel toward the core with their corresponding group velocities. The long wavelength LA phonons reach the core first due to their highest group velocity. Various polarizations of phonons in the propagating current of phonons interact with the core in their own characteristic manner.

The axial force pattern on end atoms of the core (Figure 7c) corresponding to the initial motion of the core (Figure 7a) is found similar to the LA mode scattering induced forces, more strikingly at the higher thermal gradient (Figure 7d). The initial rise in KE of core is shown in Figure 7b, due to the exchange of heat by a continuous flow of phonons, which further grows up to 350 eV before it saturates. Comparing this with the core’s KE in Figure 6b, we can conclude that coherent phonon pulse is a more efficient means of thermophoresis than conventional heating.

The vibrational spectra corresponding to the velocities of inner CNT (Figure 8) from the first 20 ps simulation clearly indicate that the core significantly interacts with long wavelength acoustic phonons, more strikingly at higher thermal gradients. The activity of phonons other than LA mode starts growing after the initial displacement of the core, which can be seen clearly at lower thermal gradients (Figure 8a).

Finally, core geometry is found to have a significant effect on whether LA phonon gets to play a dominant role in thermophoresis. We consider various cores inside the 100 nm long (10,10) outer CNT: a C60 ball, and (s,s) open-ended CNTs with length $L$ ranging from 5 to 60 nm. Figure 9a shows LA phonon transmission functions (up to 20 meV in the low energy region) for different core geometries. As the length of the core decreases, a significant reduction in amount of...
scattering is observed. Besides, the dip in transmission function corresponding to peak scattering shifts toward high frequency side, which indicates that the interaction of long wavelength (or high group velocity) phonons with shorter cores is not as severe as longer cores. Relatively slower phonons are found to interact with shorter cores. A complete absence of this dip for the case of C60 as core clarifies that shorter interacting nanostructures evades the LA phonon scattering and thus shorter cores cannot display unbalanced axial forces on end-atoms.

Figure 10 shows thermophoresis under the gradient of 11 K/nm with cores of various lengths. Under the influence of a temperature gradient VT, thermophoretic drift velocity of a moving body is simply \( u_T = -D_T \nabla T \), where \( D_T \) is the thermodiffusion coefficient or thermophoretic mobility. We plot \( D_T \) as a function of core length \( L \) in Figure 9b at different thermal gradients. Longer core drifts slower than shorter core. A striking effect of thermal gradient for \( L < 30 \text{ nm} \) can be seen. Note that, for the cores of \( L < 30 \text{ nm} \) and at higher thermal gradients, the length of outer CNT (100 nm) limits the drift velocity. However, for thermal gradients below 15 K/nm, the drift velocity becomes stable by the time the core reaches the end. Two distinct mechanisms of thermophoretic motion for \( L < 30 \text{ nm} \) and \( L > 30 \text{ nm} \) can be predicted from Figure 9b, which can be seen more clearly in Figure 10. For initiation of thermophoretic motion with \( L > 30 \text{ nm} \), LA phonon scattering is the dominant mechanism, whereas for \( L < 30 \text{ nm} \) a highly diffusive mechanism (hence the strong thermal gradient dependence) causes the effective force.

It is important to point out that the trends in Figure 9b are in qualitative agreement with length dependence of thermodiffusion of DNA in aqueous solutions \( (D_T \propto T^{(−0.25)}) \) as reported by Duhr and Braun,\(^*\) despite few orders of variation in the scales of \( L \) as well as \( D_T \). Ideal interface conditions in the present CNT system help provide such large (four orders higher than DNA\(^*\)) thermophoretic drift velocity. There have been several models (ranging from radiation pressure theory,\(^*\) interfacial tension gradient\(^*\) to hydrodynamic transport models\(^*\) and local thermodynamic equilibrium\(^*\)) to describe microscopic mechanism of thermophoresis in colloidal systems that have met with limited success. Our finding that thermophoretic motion in general is a manifestation of phonon scattering mechanism can help improve these models.

Conclusion. By showing that thermophoretic motion in coaxial CNTs is initiated by LA phonon scattering mechanism, this work builds a connection between phonon scattering dynamics and nanoscale mechanical motion. We have shown that the scattering mechanism of LA mode phonons, particularly in low to moderate energy ranges, generates a net axial force on the encapsulated nanotube. The length dependence of thermophoresis is elucidated by LA mode transmission functions. With the advent of experimental facilities to drive a particular phonon mode,\(^*\) it should be possible to displace the encapsulated nanostructure efficiently by driving the LA phonons of outer CNT. The knowledge of precise interaction mechanism of individual phonons with the inner nanostructure would lead to nanoscale motion control in nanomechanical and biotechnological applications.

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Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors are grateful to Vikas Varshney, Jonghoon Lee and Puneet Patra for insightful discussions. Some of the MD runs...
were performed on PARAM YUVA HPC for which we thank Centre for Development of Advanced Computing (CDAC), Pune.

**ABBREVIATIONS**

<table>
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<tr>
<th>LA</th>
<th>longitudinal acoustic</th>
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<tr>
<td>TA</td>
<td>transverse acoustic</td>
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<tr>
<td>TW</td>
<td>twisting acoustic</td>
</tr>
<tr>
<td>BR</td>
<td>radial breathing</td>
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<tr>
<td>FO</td>
<td>first order optic</td>
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