NANO LETTERS

2009
Vol. 9, No. 11
3699-3703

Anomalous Dissipation in Single-Walled Carbon Nanotube Resonators

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Received May 29, 2009; Revised Manuscript Received September 10, 2009

ABSTRACT

We observe a new anomalous and transient process of intrinsic dissipation in simulations of the ring-down of flexural modes in single-walled carbon nanotube (CNT) resonators. The effect is pronounced, causing the quality factor of the mode to be reduced by more that 95% for tens of picoseconds. The anomalous dissipation depends on the CNT temperature and the energy in the mode, and remarkably increasing the excitation energy in the resonator causes it to decay to zero faster. By tracking the cascade of energy as it dissipates we identify "gateway" modes that provide important channels for dissipation. The processes we observe show that an athermal phonon population accompanying dissipation can strongly influence the quality factor in nanoelectromechanical devices.

Among their numerous potential applications, carbon nanotubes (CNTs) hold great promise as nanoscale ultrahigh frequency resonators for uses such as low-power wireless communication[1−3] or mass and chemical sensing.[4−6] The potential of CNTs as resonators in nanoelectromechanical systems (NEMS) is due not just to the CNT's quasi-one-dimensional structure and its remarkable stiffness but because, as resonators, there are numerous methods by which the CNTs can be both driven and sensed electronically.[2,4,7−11] One important limiting factor to the widespread use of CNTs in NEMS is their disappointing quality factors, Q at ambient temperatures (with Q^{-1} the fraction of energy lost by the resonator every cycle). While much progress has been made in developing CNT resonators over the past few years, with reported resonant frequencies now reaching 1.3[7] and 3.1 GHz,[9] it is only recently that major progress has been made in minimizing sources of dissipation.[11] A major challenge is that it can be difficult to recognize which is the primary source of dissipation with potential sources coming from gas damping, clamping losses, defect scattering, as well as intrinsic phonon−phonon dissipation mechanisms such as thermoelastic losses.

Experimentally measured Qs for the flexural mode of suspended CNTs at ambient temperatures have ranged from as low as eight[9] to several hundred.[6,10] The dissipative behavior at ambient temperatures is robust, having been measured for a variety of clamping configurations and measurement methods,[4,6,7,10] in both single- and multiwalled tubes.[9] Air damping has been predicted theoretically to contribute to the Q factor[12] although Q factors measured under vacuum[4,9,10] show little improvement over those measured in ambient air.[7,9] Very recently Q factors in excess of 10^5 have been reported in highly defect free CNTs cooled to millikelvin temperatures at which the driven mode (and modes nearby in frequency) is not thermally activated. The only common factor to these experimental works is that the Q factor was measured during continuous driving. That there has been little success at improving CNT resonator quality factor at ambient temperatures suggests that intrinsic dissipation mechanisms may be playing a significant role, and thus computational approaches are ideally suited to provide key insights.

Macro- or mesoscopic theories of intrinsic damping from sources such as switching of defect states, thermoelastic damping, and phonon drag relate dissipative behavior to the thermal energy in the system, that is, the background temperature T_{bg}. These theories have been successfully used to describe dissipation in some nanoscale systems, particularly those where phonons are diffusive and phonon lifetimes are shorter than the period of the resonator.[14,15] Jiang and co-workers[16] have simulated the ring-down of open-ended, cantilevered, single- and double- walled CNTs and found relatively large quality factors (in excess of 1000) with an

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10.1021/nl901706y CCC: $40.75
Published on Web 10/28/2009

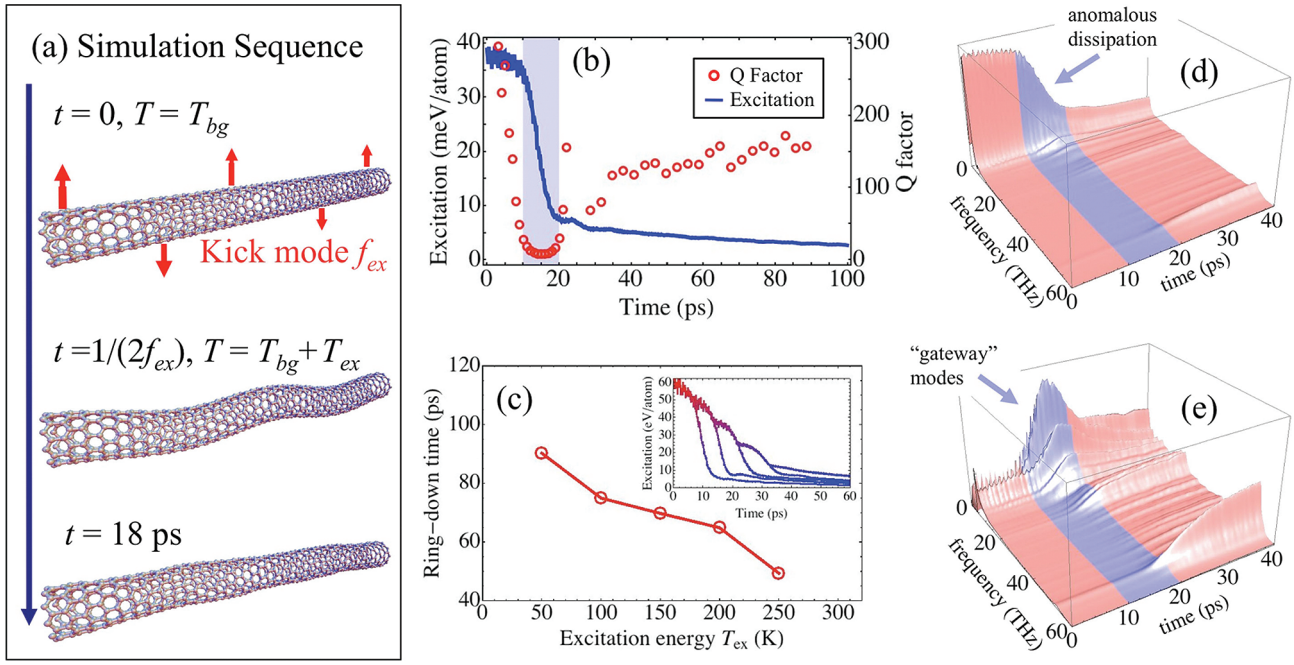

Figure 1. Graphic illustrating the simulation procedure (a), and the observed anomalous dissipation during ring-down. Plot (b) shows the ring-down of the energy (blue) in the second flexural mode excited to $T_{ex} = 150$ K in a 8.4 nm (10,0) CNT initially at $T_{bg} = 5$ K. At this excitation, the fraction of anharmonicity, that is, the fraction by which the true potential energy differs from the harmonic approximation, is 6.7%. The evolution of the Q factor for this tube is plotted in red circles on the same axes with the region of anomalous dissipation shaded in pale blue. The plotted data is the average of 10 simulations with the thickness of the plotting line chosen to encompass the standard error in the set of simulations. Plot (c) shows the total ring-down time for the simulations in which the total energy $T_{bg} + T_{ex} = 500$ K but with different initial partitioning ratios, T_{ex}/T_{bg}, between excited and the background modes. As with the Mpemba effect (see text),[18] the mode cools faster if it starts hotter. The cooling curves for each of the 5 data points is shown in the inset plot. The cooling curves have been shifted in time so that the more weakly excited simulations commence on the cooling path for more strongly excited simulations. It can be clearly seen that there is not a unique cooling trajectory. Plot (d) shows the relaxation of $T_{ex} = 150$ K of vibrational energy (with a frequency of 1.5 THz) over all the modes of the CNTs (which have initial thermal energies of $T_{bg} = 5$ K) during the first 40 ps of ring-down. The region of anomalous damping is marked by the blue stripe. Plot (e) shows the evolution of energy in just the background modes of the tube, that is, the same spectrum of energy as (d) but with the contribution from the excited mode omitted. It can clearly be seen that the dissipated energy does not reach the high frequency background modes until the end of the period of anomalous dissipation.

unexpected temperature dependence of Q. Other theoretical predictions vary greatly on the importance that they attribute to thermoelastic losses within CNTs.[14,15]

Here we describe the observation of a new behavior: anomalous and transient intrinsic dissipation that causes a sudden reduction of quality factor during ring-down of CNTs. In contrast to existing models of intrinsic dissipation this anomalous dissipative state is not described by the average resonator temperature. Crucially, our observations are made during ring-down, and in our simulations we are able to follow the cascade of energy as it dissipates, identifying "gateway" modes that provide important channels for dissipation. The processes we observe give important insights of dissipation that may be relevant to many different continuously driven resonators at the nanoscale.

Ring-down of flexural modes in single-walled CNTs was simulated with classical molecular dynamics using force fields that include anharmonic interactions between the atoms. In order to probe only intrinsic friction mechanisms, we consider pristine continuous tubes with no physical clamping. A clamping of sort is imposed by periodic boundary conditions, however the flexural modes differ from a doubly clamped beam, having no center of mass motion and consequently a higher frequency. (It should be noted that the aspect ratio of the simulated tubes are considerably lower than in typical NEMS resonators, and there exists no residual axial tension.) A typical simulation (shown schematically in graphic Figure 1a) proceeded as follows: the tube, initially at equilibrium, was heated (in a vacuum) to some desired temperature, T_{bg}. A flexural mode in the tube was excited by the addition of an instantaneous velocity to the atoms along the mode's eigenvector. This excitation adds vibrational energy to the system equivalent to raising its temperature by T_{ex} (although the additional energy is concentrated in a single mode). The ring-down of this excited mode is simulated in the microcanonical ensemble during which the distribution of thermal energy in all the vibrational modes of the system was tracked by projecting atomic displacements and velocities. The modal energy tracking scheme is described elsewhere[17] and will therefore not be detailed here. The tubes simulated were all (10,0) zigzag tubes with periodic lengths varying from 4 to 25 nm, and the mode excited was typically the second flexural mode. The second flexural mode was chosen so that there were lower frequency modes that could participate in the dissipation. The excitation of the modes was generally strong, larger

than in continuous driving experiments; however, the fraction of anharmonicity, that is, the fraction by which the true potential energy differs from the harmonic approximation, is typically less that 10%. While the temperatures of all the simulations used in this study were well below the Debye temperature for a CNT, simulating at low temperatures allows us to observe the dissipation with little obfuscating thermal noise. The findings that it is the low frequency modes that participate in dissipation, and that the dissipation mechanism remains unchanged at high temperatures justify the initial use of classical dynamics a posteriori.

Figure 1b shows the ring-down and corresponding Q factor for the flexural mode of 8.4 nm (10,0) CNTs (initially with $T_{bg} = 5$ K) averaged over a number of simulations. The excitation can be seen to be abruptly dissipated during the region shaded in pale blue. The quality factor drops precipitously from an initial value of ~300 to a value of ~8, a reduction of more than 95%. After roughly 10 ps of strong dissipation and with ~20% of the initial energy remaining, the Q factor recovers to a value of ~150. We refer to this period of reduced resonator quality as "anomalous dissipation".

There are two striking features of this anomalous dissipation. First, the anomalous behavior does not begin as soon at the flexural mode is excited; rather, there is some delay time before the anomalous behavior "turns on". Second, the anomalous behavior has a finite duration and "turns off" well before the flexural mode has equilbriated. After the anomalous regime ceases, temperature dependent exponential decay continues (see inset log-plots in the supporting material). The waiting time before the onset of anomalous dissipation is strongly dependent on the thermal background, whereas the duration and intensity of the anomalous dissipation depend on the energy of the initial excitation (see Supporting Information). So strong is this latter dependence that it causes modes with more energy to reach equilibrium in a shorter time.

Figure 1c shows the total ring-down time for five sets of simulations in which the total vibrational energy in the systems is the same ($T_{bg} + T_{ex} = 500$ K) but the initial partitioning of this energy between the excited and background modes is different. A consequence of simulating the ring-down of a CNT resonator in the microcanonical ensemble is that the energy lost from the excited flexural mode goes into the thermal bath of other modes in the CNT, raising the background temperature, T_{bg}, and keeping the total energy ($T_{ex} + T_{bg}$) constant. Thus in Figure 1c, the simulations with the largest excitation must visit the initial (T_{ex}, T_{bg}) state of the other simulations as they ring down. While with larger excitation we expect more anharmonic coupling and thus a larger rate of dissipation, when T_{ex} has cooled the anharmonic interaction will be reduced and we would expect less dissipation. Yet the total time taken to ring-down is shorter for larger initial T_{ex}. This seemingly counterintuitive result is analogous to the Mpemba effect in which ice cubes freeze in a shorter time if the water is hot when it is first put into the freezer.[18] (A good discussion of the Mpemba effect that focuses on its counterintuitive nature is given by Jeng.[19]) Just as with the Mpemba effect it implies that the dissipative behavior of the system is dependent on some internal state that is not uniquely described by the temperature. This point is clearly demonstrated by comparing the ring-down curves in the inset plot in Figure 1c. These are analogous to the cooling curves of freezing water. The curves have been shifted in time so that the more weakly excited simulations commence on the cooling path for more strongly excited simulations. Rather than follow the cooling path for the more strongly excited system the trajectories immediately diverge, with the initially cooler system decaying more slowly. That there is no unique trajectory for energy dissipation indicates that the background temperature alone does not describe the anomalous dissipation.

It should be stressed that it is not the sigmoidal shape of the decay in Figure 1b−e that indicates anomalous dissipation; in fact, a sigmoidal attenuation profile might be expected if the damping increases with the background temperature. Simulating in the microcanonical ensemble means that T_{bg} rises as the excited mode rings down and thus increases the dissipation. A simple analytic model for linear damping that includes this temperature dependence can exhibit a sigmoidal attenuation profile (see Supporting Information) but cannot describe the anomalous dissipation. It is the details of this dissipation profile that make it anomalous: the nonunique decay path and the recovery of the quality factor.

The origin of the anomalous dissipation can be understood by examining how the dissipated energy is distributed into the background modes of the tube. Figure 1d shows the relaxation of the excited energy distribution toward thermal equilibrium over the whole vibrational spectrum of the tube. To more clearly observe the distribution of energy in the background modes the same data is replotted in Figure 1e with the contribution from the excited flexural mode removed (i.e., just the modes contributing to T_{bg}). A low frequency peak can clearly be seen during the anomalous dissipation, indicating that it is a subset of modes nearby in frequency that are the first to receive the dissipated energy, and they quickly dissipate it to other modes across the full vibrational spectrum of the tube.

On further examination, it is found that there are two particular modes within the recipient set that receive more energy than the others. For the 8.4 nm (10,0) CNT these "favored" modes are a third flexural mode that is coplanar with the excited mode, and the fundamental bending mode, out of plane with the excitation. The energy in both of these modes, and the accumulated energy in the background are shown in Figure 2a. The excitation of these two favored modes is qualitatively different. The higher frequency mode is excited first, and only remains excited during the anomalous regime. In contrast, the lower frequency mode continues to ring after anomalous dissipation has ceased.

The importance of these two modes goes beyond providing a strong channel for dissipation; these modes play a fundamental role in initiating the anomalous dissipation, and we hence call them "gateway" modes.

The participation of the gateway in turning on anomalous dissipation was confirmed by ring-down simulations in which

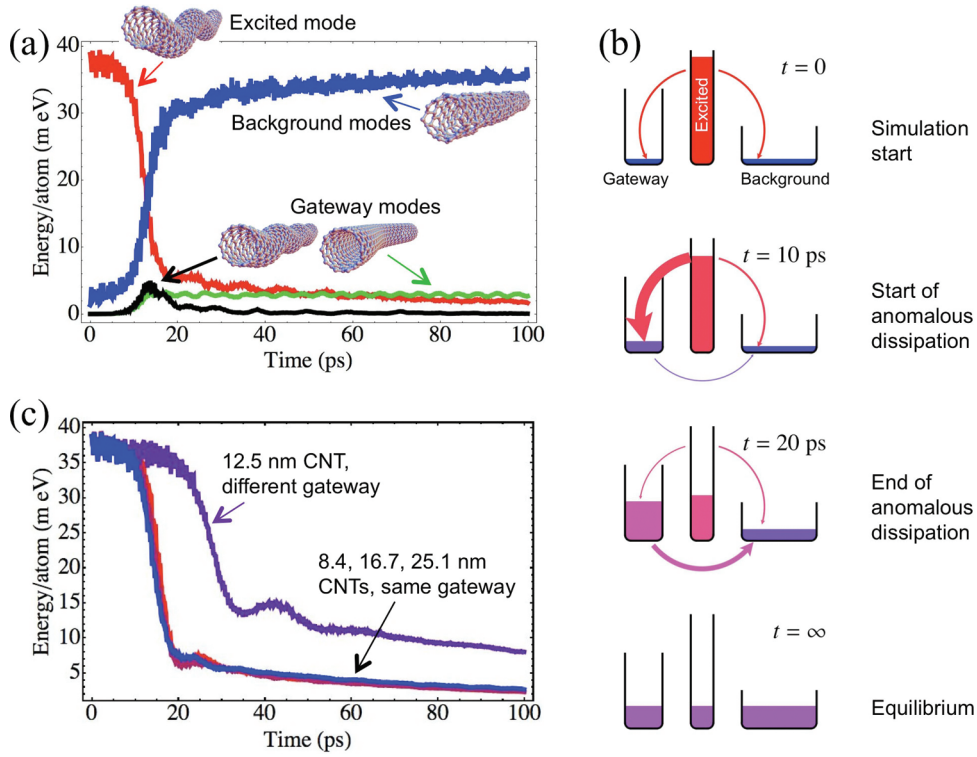

Figure 2. The gateway modes mechanism. Plot (a) shows the energy in the excited flexural mode (red), the high and low frequency gateway modes (black and green, respectively), and the remainder of the background modes (blue), during ring-down of a 8.4 nm (10,0) CNT. Graphic (b) shows a schematic representation of the dissipation pathway and the role of the gateway modes during anomalous dissipation. The energy in the excited mode, the recipient modes, and the remaining background modes is represented by the filling of the three receptacles, with the thickness of the arrows indicating the rate of energy transfer between these collections of modes. Plot (c) shows the ring-down of the 1.5 THz flexural mode of tubes with 8.4, 12.5, 16.7, and 25.1 nm periodic repeat distances.

an additional mode was given a small external excitation. Exciting either of the gateway modes by as little as 1.5 K would trigger the immediate onset of strong dissipation. Similarly exciting the other low frequency recipient modes was found to change the duration before the onset of anomalous damping (because the total energy in the system is different) but did not immediately trigger its onset. This phenomenon of triggering rapid damping externally by adding more energy could find important applications in other NEMS devices. For example, if an oscillator that exhibits this behavior were used as a radio transmitter, the rapid damping phenomenon would allow for rapid switching off of the transmitted signal.

While it is demonstrated that the gateway modes activate anomalous dissipation, the mechanism by which they instrument this is not clear. It is not known whether these two modes act as physical channels for the energy into other low frequency modes, or if they merely permit these modes to couple directly to the excited mode. It is also not known if both gateway modes act in the same way. The excited and gateway modes are coupled anharmonically; however, we speculate that anomalous dissipation involves the interaction of multiple vibrational modes. Using constrained dynamics, the effect of other modes was frozen out by restricting the system to move only along the plane in phase space defined by the eignevectors of the excited flexural mode and one of the gateway modes, thus reducing the dynamics to a particle moving in a two-dimensional well. Even with the addition of Lengevin noise to simulate the influence of the background modes no significant exchange of energy between the excited and gateway mode was observed. Constrained dynamics were also performed for trios of modes, that is, including one additional mode with the excited and gateway modes. This was simulated for all trios of low frequency modes (below 4 THz), and these also showed no significant exchange of energy unlike the full blown MD simulation, indicating that the coupling involves the interaction of multiple modes. An alternative origin of the anomalous dissipation could come from the nonlinearity inherent in doubly clamped beam resonators. The fixed ends of the beam require that lateral deflections of the beam are accompanied by an axial elongation that stiffens the beam and nonlinearly couples deflections in normal directions. Recent theoretical work[20] has predicted that due to this beam elongation a driven doubly clamped CNT resonators should exhibit a transition to nonplanar skipping-rope like motion at large driving forces.

In addition to activating anomalous dissipation, the gateway modes may explain why the anomalous dissipation turns off before the system reaches equilibrium. We speculate that the excited mode comes to near local thermal equilibrium with the gateway modes and the other recipient modes nearby in frequency with recipient modes acting as a phonon bottleneck. A similar process in which a phonon bottleneck creates a long-lived athermal phonon population has recently been observed experimentally in the dissipation of optical

phonons in CNT field effect transistors.[21] The entire sequence of dissipation through the background modes of the simulated CNT resonators is shown schematically in Figure 2b.

The robustness of the observed anomalous dissipation and the gateway mechanism was tested in three further computational "experiments". Simulations were repeated with modified interatomic potentials (described in the Supporting Information) changing the anharmonic interactions between atoms. While this altered the time and duration of anomalous dissipation the overall qualitative behavior remained unchanged. This may be in part because the dissipative behavior is due to the shapes of the low frequency modes. These are largely dictated by the tubular geometry rather than the details of the interatomic potential. Two investigations of the size dependence on the anomalous behavior were conducted. In the first (described in the Supporting Information), simulations of other tubes were performed to establish that that anomalous dissipation is not unique to either 4.2 nm bending or (10,0) tubes. In a second test of size dependence, ring-down was simulated of equivalent 1.5 THz flexural modes of 8.4 nm tubes in tubes 1.5, 2, and 3 times as long; that is, modes with the same frequency so the third, fourth, and sixth flexural modes of these tubes, respectively. The attenuation of these modes is plotted in Figure 2c. Both of the gateway modes in the 8.4 nm tube are incommensurate with the 12.5 nm tube and they do not exist. In this intermediate-sized tube, a different mode (a flexural mode with wavelength 6.3 nm) acts as a gateway for dissipated energy. The longer 16.7 nm tube possesses all the vibrational modes of the 8.4 nm tube in addition to a further 2400 modes. However, despite the additional modes the gateway modes of the 8.4 nm tube are the preferred path for dissipation. The longest 25.1 nm tube possesses all of the modes of the 12.5 and 16.7 nm tubes but the gateway modes of the 8.4 nm tube become active first. Importantly, these simulations show that the action of gateway modes is not an artifact of the computational cell size but does depend on which gateway modes are permitted by the periodic boundaries of the computational cell.

We have reported here the observation of an anomalous mechanism for intrinsic dissipation during ring-down of flexural vibrations in CNT resonators. The implications of this observed behavior for continuously driven NEMS devices could be significant (particularly those where intrinsic dissipation dominates), and as experimentally measuring ring-down is difficult, it provides a means of practically testing our observations. During ring-down we observe the CNT to self-organize from being weakly dissipative into a highly dissipative state. Under a continuous driving force it is likely that the tube becomes trapped in this anomalous regime. If this is the case then the gateway mechanism provides one with several avenues for improving Q factor. Resonator lengths could be selected carefully so as to exclude important gateway modes, or tubes could be decorated with other nanoparticles in order to shift the frequency of gateway modes. Alternatively, gateway modes could be identified and externally cooled (such as by laser cooling[22] or quantum back action[23]). The gateway mechanism could also be exploited to minimize unwanted vibrations in CNTs. It could be used for actively blocking heat flow in CNTs and providing a way to mechanically filter thermal transport. Finally, it is important to emphasize that, like the Mpemba effect, the anomalous dissipation is not defined by the average temperature of the system but rather by how the thermal energy is distributed over frequency. In nanoscale systems, where the avenues for heat loss can be limited, dissipation processes can often induce just such an athermal phonon population. Thus, in computing Q factors for these resonators it is necessary to move beyond a ground-state model of dissipation.

Acknowledgment. This project received funding from the Defense Threat Reduction Agency-Joint Science and Technology Office for Chemical and Biological Defense (Grant HDTRA1-09-1-0006), and under the auspices of the National Science Foundation by University of California Berkeley under Grant 0425914304. G.L. acknowledges partial support from the Politecnico of Torino.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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NL901706Y