# CHAPTER 5 Simulating Thermomechanical Phenomena of Nanoscale Systems

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# 5.1 Introduction

The manner in which we use and control heat is of great importance both technologically, and within our daily lives. Roughly 90% of the energy that we use today has been involved in the generation to and conversion from heat (*e.g.*, coal or gas power plants, combustion engines for transportation, and nuclear energy, to name only a few). The efficiency of these processes is limited by the control we have over the storage and transport of heat within materials. Most practical thermal-energy systems that are involved in transport, storage, and/or conversion operate far from their limits.

Since thermal transport is a materials phenomenon, it is useful to compare our understanding of it with other transport properties such as the conduction of electrons. Since the discovery of electricity, research on charge transport in materials has pushed the extremes of electrical conductivity, which now spans over 20 orders of magnitude. In 1947 the transistor was invented, which permitted external tuning of electrical conductivity in the solid state—and forming the foundation for information processing and beginning the digital age. The societal impact of research in electrical conduction has been and will continue

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to be enormous. In contrast, heat transport in condensed matter has received much less attention. For example, the thermal conductivity of current solid materials spans only 5 orders of magnitude at room temperature and its external tunability is limited. With the exception of the Carnot limit to heat engines, we really do not know what limits, if any, exist regarding the fundamental processes of thermal energy transport and conversion, and storage. There are currently no thermally superconducting materials, nor are any existing materials perfect thermal insulators.

An equivalent paradigm shift in thermal transport would be the use of frequency-dependent thermal properties; that is, exploiting properties of materials that depend on the thermal energy being concentrated at specific frequencies. Such opportunities may exist in new thermal phenomena that occur in nanoscale materials. The aim of this chapter is to provide an overview of the methods for simulating thermal phenomena at the nanoscale. After giving a brief overview of some of the experimental progress that is driving this field we survey the current computational methods highlighting their strengths, and the major challenges that still face the simulation of heat. This is followed by two detailed case studies in which selected methods have been used to study nanoscale thermomechanical behaviour, showing how these tools can be used, and what insight they can give. The examples given are in the study of dissipation in CNT resonators, and frequency-dependent heat transport across weak nanoscale interfaces. The chapter finishes with a discussion of the major challenges still facing simulation of heat, and the outlook to new applications of thermal properties.

# 5.2 Examples of Recent Experimental Progress

There have been recently a number of exciting advances in our ability to control heat flow that have primarily been achieved with the use of nanoscale systems. Accompanying the advances in engineering thermal properties have been breakthroughs in or ability to measure thermal transport and to characterize thermal behaviour at this small scale. Together, these experimental developments show that we can extend the current boundaries of thermal conductance, and they call on scientists to develop more accurate and predictive methods for computing thermal conductance and for simulating thermomechanical phenomena in nanoscale systems. A brief survey of the experimental advances in nanoscale thermal properties that is motivating the need for new computational approaches is given here.

## 5.2.1 Increasing Thermal Conductivity

As long ago as 1941<sup>1</sup> it was recognised that the mean free path of longitudinal acoustic phonons diverges as their frequency approaches zero.<sup>i</sup> In the absence of internal scattering mechanisms this would mean that a material's thermal

<sup>&</sup>lt;sup>i</sup>An infinitely long-wavelength mode is a quasistatic compression that must have an infinite mean free path in order to satisfy Newton's laws.

conductivity would *increase* with the size of the material. In bulk materials there are a plethora of defects, interfaces and other scattering mechanisms that limit the mean free path, and make the thermal conductivity size invariant in practice. Single-walled carbon nanotubes and graphene sheets are composed of a single layer of atoms and are not bulk materials (one cannot distinguish between a surface and an internal atom in a CNT). With no interfacial scattering the only mechanisms for restricting the mean free path of long-wavelength modes are anharmonic phonon interactions and isotopic effects. The result of this is that single-walled CNTs can exhibit very large thermal conductivity along their length, and that the tubes must be very long (up to 10 µm) before  $\kappa$  stops increasing with tube length.<sup>2-5</sup> CNTs hold much hope for engineering new materials with very efficient thermal conduction for uses in thermal management; however, much of the heat transported along a CNT is conveyed by flexural and torsional modes. These important heat-carrying modes only move unimpeded when the CNT is free standing; the modes are quickly scattered if the CNT is in contact with a substrate (or another CNT) reducing the thermal conduction by as much as two orders of magnitude.<sup>6,7</sup> Nevertheless, applications have been proposed for using CNTs as heat guides. A very recent and innovative application has been to use CNTs as a heat guide to set up rapidly propagating thermal reaction waves in a reacting medium.<sup>8</sup> Bundles of CNTs are coated with an exothermically reactive mixture, and when the reaction is initiated rapid heat conduction along the tube speeds up the propagation speed of the reaction front. Most interestingly the passage of the reaction front has been found to be accompanied by a large electrical thermopower pulse in the tubes that is proportional to the speed of reaction propagation.

The use of CNTs in other (nonreactive) thermal management applications has also been demonstrated. Vertically aligned "forests" of CNTs have been proposed for efficient thermal management of computer chips, where removal of heat can be the limiting factor in device performance, and where the power densities that must be removed can be extremely high.<sup>9</sup> Vertically aligned forest structures utilize the full thermal transport potential of the CNTs, limited only by contact resistance at the CNT ends. Other researchers have used embedded networks of CNTs to engineer highly anisotropic thermal conductivity in composite materials and to tailor the cooling properties of oils with the addition of a suspension of CNTs.<sup>10</sup> In these cases the heat is carried across a sparse network of CNTs. In order to travel long distances the heat must be passed between CNTs at the nexus points where they overlap within the network, and this process has its own resistance, which is found to be large. Transport in these networks—both electrical and thermal—exhibits a percolation transition in which if the network is too sparse there are insufficient nodal connections linking the tubes and they will not create a contiguous pathway through the material. Remarkably, the percolation transition for conduction of electricity occurs at a lower network density than it does for the conduction of heat. This is surprising as the networks are composed of CNTs with a distribution of different diameters and chiralities with roughly only one third of them being metallic; this implies that there is also a wide distribution of thermal contact resistance, with many junctions being electrically conductive but highly resistive to heat.

### 5.2.2 Reducing Thermal Conductivity

In crystalline solids a fundamental lower limit of thermal conductivity can be conceived by imagining that the mean free path of a phonon cannot be any shorter than the intrinsic lattice spacing (similar conceptual limits can be derived for amorphous solids). These limits are somewhat artificial, however, being only a limit in which one model of heat flow no longer makes sense. Thus, while these limits can provide useful guidelines when designing thermal systems, there are no rigid reasons why thermal resistance cannot surpass these limits in some cases. This has in fact been observed experimentally for roughened Si nanowires<sup>11</sup> that have been shown to transport heat below the perceived lower limit of conductance.

Beyond the fundamental question on limits of thermal transport it is often desirable to increase the thermal resistance of a given material without greatly altering other properties. An important technological example of this are thermoelectric materials, for which it is desirable to minimize lattice thermal conduction without altering the electrical properties of the material. In this case, one can take advantage of the fact that the mean free paths of charge carriers (holes and electrons) are much smaller than the mean free path of lattice vibrations (phonon wave packets), and thus one can nanostructure the material on a length scale that will confound traveling-wave phonons, but that is invisible to charge carriers. Experimentally, this was first approached by growing multilayered materials with controlled layer thicknesses. This is a topdown approach that allows one to finely control the structure at the angstrom level in one direction. Another top-down approach is to create a nanoscale grain structure in the material by deformation or powder processing. This approach has been successful for further improving the thermopower of established thermoelectric semiconductor materials.<sup>12</sup> Examples of other more exotic approaches to suppressing thermal conduction include roughened nanowires, nanoporous materials, and metamaterials that possess a phonon bandgap. Recently, films containing nanoscale tubular pores running through the film thickness have been found to suppress thermal conductivity by several orders of magnitude.<sup>13,14</sup>

## 5.2.3 Characterisation

In addition to advances in the ability to fabricate structures at the nanoscale there has been significant progress in the ways that one can measure thermal properties. Length-dependent thermal conductance has been measured on single CNT, and Si nanowires, lying across a set of heating stages.<sup>4,15–17</sup> Using this approach Chang *et al.* demonstrated thermal rectification along carbon

and boron nitride nanotubes that have been asymmetrically decorated with platinum carbide.

An alternative noncontact method of measuring heat transport properties in nanoscale structures is by time-domain thermoreflectance. This is a pumpprobe technique in which a short (pico or nanosecond) laser pulse locally heats the sample (raising the temperature by only a few degrees). The heating changes the optical reflectance of the sample, and a probe laser beam is used to measure this change in reflectance as the heat dissipates. Cahill and coworkers<sup>18,19</sup> have found that by making the region of material that is heated smaller than the mean free path of some of the phonons these phonons leave the hot region ballistically, allowing one to measure the contribution of different phonon frequencies to thermal transport.

## 5.2.4 Nanoscale Phenomena

In addition to the greater range of thermal conductance that can be achieved with nanoscale materials, the nanometer-sized systems provide new thermal phenomena that are unique to this length scale. Making one or two dimensions of a system small (while leaving the others macro-or mesoscopically large) results in objects that are in effect two-, or one-dimensional. These objects still live in a three-dimensional space (mathematically they are said to have a codimension greater than one). Low-dimensionality systems possess new low-frequency phonon mode shapes in which the object deforms into the unconstrained dimension. Films and surfaces gain surface Lamb waves, beams possess flexural and torsional modes, and tubes and fullerenes have radial breathing modes and cyclops modes.<sup>20</sup>

The symmetries of these low-dimensional modes can give rise to subtle thermal effects. Interatomic potentials are asymmetric, near equilibrium close to harmonic, as we move further from equilibrium the potential softens as the bond is stretched and stiffens when compressed. The most important anharmonic term in the representation of an atomic bond is the cubic term,  $d^{3}E_{ij}/dR_{ij}^{3}$ . Yet the symmetry of a nanostructured material combined with the symmetry of the vibrational mode can result in modes that are symmetrical, and where the fourth-order anharmonic term dominates. To see this, consider a nanotube. Imagine sitting on the surface of a zigzag nanotube watching the motion of atoms as the tube undergoes a torsional oscillation. We see that for each torsional cycle an atomic bond stretches twice; the mode is symmetrical and the cubic term in the bond potential  $d^3 E_{ij}/dR_{ij}^3$  results in a quartic term  $d^4E_{tor}/da_{tor}^4$  dominating the anharmonicity of the modes. Following the motion of the radial breathing mode (RBM), on the other hand, we see that it is asymmetric, and the cubic term  $d^3 E_{\rm RMB}/da^4_{\rm RBM}$  dominates. Thus, through the increased freedom of a codimension greater than one, it is possible to obtain vibrational modes with a mixture of differing symmetry of anharmonicity, although the structure is constructed with only asymmetric bonding potentials. Another simple example of this is a tensioned one-dimensional chain of atoms connected by harmonic potentials. The "string-like" modes of the chain are very strongly anharmonic because as the string oscillates the chain length is increased, increasing the overall tension in the chain. This effect can result in a negative coefficient of thermal expansion along the chain length, and is observed in carbon nanotubes that contract along their axis when they get hotter.<sup>21,22</sup>

Reducing the dimensionality of an object can cause other significant changes in properties. Diffusion in systems with two or fewer dimensions is space filling—that is given an infinite amount of time a random walker will visit every lattice site—this is not the case for three-dimensional spaces. A mathematical connection between diffusion and heat conduction results that heat flow in lowdimensional objects does not obey Fourier's law. For the case of one-dimensional systems the thermal conductivity of the system is found to scale with the length of the system,  $\kappa \sim L^{\alpha}$ , with  $\alpha$  being reported between 0.3,<sup>23</sup> and 1/3.<sup>24</sup> This has important implications for modeling thermal transport in low dimensions: in simulation one often extrapolates the scaling of their results with system size in order to estimate macroscale properties or to check convergence. This result implies that there is *no* length scale convergence in one-dimensional systems.

#### 5.2.5 Quantum Phenomena

The examples given thus far are purely classical arising only due to restricted dimensionality; however, advances in characterisation and fabrication at the nanoscale have allowed researchers to measure several purely quantum effects of atom motion. Roukes and coworkers, by cooling down a free-standing SiN membrane supported by four phonon waveguides, were able to freeze out all but the lowest-frequency vibrational modes in the waveguides and were able to measure ballistic conduction through just the four lowest-frequency modes (one longitudinal, two flexural, and one torsional) in each waveguide.<sup>25</sup> They found the quantum of thermal conductance,  $g_o$ , to match the Landauer equation  $g_o = \pi^2 k_B^2 T/(3h)$ , approaching the quantum limit of measurement.

A different quantum measurement effect that is close to the grasp of current experimental methods is the direct observation of zero-point motion and the Heisenberg uncertainty in a mesoscopically large mechanical system. Gigahertz nanoscale resonators can be frozen to their ground state at milikelvin temperatures, but one must also be able to sensitively detect the displacements associated with this motion which are on the subangstrom scale. Beyond establishing that quantum-mechanical effects are observable in mechanical systems containing many billions of atoms, interesting applications for quantum computing are found if the system is coupled to a quantum-mechanical two-level system.<sup>26</sup>

## 5.2.6 Far-from-Equilibrium Behaviour

Traditionally, the way that we have controlled and transport heat in solids has been close to equilibrium—a usage that is reflected in the established theories of

heat flow such as the Boltzmann transport theory (BTT) in which heat carriers transport thermal energy between regions that are in local thermal equilibrium. In recent years, however, there have been examples of nanoscale devices (or phenomena) that take advantage of thermal behaviour far away from equilibrium, that is, where thermal occupation of vibrational modes does not correspond to the Bose–Einstein distribution (the local temperature is not well defined) but is instead athermally distributed amongst the system's vibrational modes. Operating away from equilibrium allows one to take advantage of the mechanical properties of a system at a particular set of frequencies and thus enables the exploitation of a wider range of thermal behaviour than can be achieved at equilibrium.

An athermal phonon population (APP) can arise in suspended carbon nanotube (CNT) resonators through either frequency-specific Joule heating of optical phonons (at K and  $\Gamma$ ),<sup>27–30</sup> or by direct driving<sup>31,32</sup> (or cooling<sup>33</sup>) of low-frequency flexural modes. In the former case this causes the electrical conduction to saturate at high voltage, and in the latter the resulting APP can dramatically reduce the resonator's quality factor.<sup>34,35</sup> APPs can also arise when heat is conducted across CNT interfaces.<sup>10,36</sup> Taking advantage of the APP leads to strategies for engineering interfacial thermal conductivity,<sup>37,38</sup> and may be important in the recently discovered thermal power waves in CNTs.<sup>8</sup> Biological systems can also display nonequilibrium thermal-energy distributions. Enzymatic reactions can result in a large heating of localised modes in the protein. This heat must be dissipated efficiently without denaturing the enzyme, and is transferred through a restricted set of localised vibrational modes without heating the enzyme as a whole<sup>ii</sup>.<sup>39,40</sup> A similar "energy funneling" phenomenon is observed in virus capsids<sup>41</sup> in which laser heating of high-frequency modes is funneled into a handful of low-frequency mechanical modes—an effect that can may be exploited for selectively destroying harmful viruses.<sup>42</sup> In the second of the case studies given later in this chapter we discuss APPs that arise from frequency-selective transmission of heat in two weakly interacting objects, and we show how this can be exploited for applications in chemical sensing.

# 5.3 Survey of Simulation Methods

There are two approaches to computing thermal properties of nanoscale systems. If the theory behind the property of interest is well understood one may compute the property directly, perhaps using simulation or first-principles calculations to obtain the values of input parameters. An example of this approach is the use of density-functional theory (DFT) to compute a material's phonon density of states and then using that information to compute the specific heat as a function of temperature. This approach works well for calculating intrinsic properties of a system that are not dependent on size or geometry. An alternative approach that is valuable for system-specific

<sup>&</sup>lt;sup>ii</sup>A similar concept is important for barrierless termolecular reactions.

properties is to use atomistic simulation to model the behaviour directly. This approach can be thought of as performing an experiment within the computer *(in silico)* instead of in the laboratory. An advantage of direct simulation is that as one has the full atomistic trajectory of the system in time it is often possible to dissect the data to determine features that are contributing strongly to the phenomenon under study, and to gain insight into how one can alter the system to change it. Both approaches—direct calculation, and computer experiment—are important and complementary as will become evident in the rest of this chapter.

One of the most important thermal properties for engineering applications is the thermal conductivity of a material,  $\kappa$ , which is defined by the phenomenological Fourier's law that relates the steady-state<sup>iii</sup> thermal flux,  $J_Q$ , to the local temperature gradient:

$$\boldsymbol{J}_{\mathrm{Q}} = -\boldsymbol{\kappa} \cdot \nabla T. \tag{5.1}$$

Here, we review several well-established methods for predicting the lattice contribution to  $\kappa$  at the nanoscale. Calculation of  $\kappa$  provides good examples of both direct computation approaches and *in silico* experiment, and in this context we discuss the general advantages and challenges of these two approaches (beyond just computing  $\kappa$ ). At the end of this section we go beyond the mean thermal conductance to examine far-from-equilibrium thermal behaviour, and the methods can be used as the basis of studying other thermomechanical phenomena in nanoscale systems, as will be shown in the case studies that follow this section.

#### 5.3.1 Direct Computation of $\kappa$

In crystalline solids, heat is carried by moving scattering lattice vibrations, and one can therefore write the thermal flux using the Boltzmann transport equation (BTE):<sup>iv</sup>

$$J_{\rm Q} = \sum_{\rm branches} \int_{0}^{\infty} \omega \hbar \beta \nu(\omega) \lambda(\omega) \rho_{\nu}(\omega) \frac{\partial N(\omega, T)}{\partial T} \nabla T.$$
(5.2)

Here, the sum is performed over all phonon branches and polarisations, and  $v(\omega)$ ,  $\lambda(\omega)$ , and  $\rho_v(\omega)$  are, respectively, the group velocity, mean free path, and volumetric density of states for phonons with frequency  $\omega$ .  $\beta$  is a

<sup>&</sup>lt;sup>iii</sup>We restrict discussion to the steady-state properties. Inclusion of time dependence to Fourier's law ignores the fact that heat travels with a finite velocity and thus for describing transient thermal solutions one must use the relativistic heat conduction equation, or the Cattaneo equation, which is beyond the scope of this chapter.

<sup>&</sup>lt;sup>iv</sup> Note that the BTE is a very general equation for describing the motion of particles in a fluid that is away from equilibrium. Only in 2010 has the general form of the equation been rigorously proven for systems close to equilibrium. For simplicity, we jump straight to the form appropriate for the motion of a phonon gas, and further simplify by assuming isotropy so that  $\kappa$  becomes a scalar quantity rather than a tensor.

dimensionless geometric factor and  $N(\omega, T)$  is the number of phonons occupying a mode with frequency  $\omega$  at temperature *T*. Strictly, one must solve for *N* ( $\omega, T$ ) self-consistently; however, close to equilibrium this can be approximated by the Bose–Einstein distribution.

The BTE is very general and may be extended to include the ballistic contributions to transport that can occur in very small systems. Computing  $\kappa$ becomes a matter of computing  $\beta$ , v,  $\lambda$ , and  $\rho_v$ , and the accuracy of one's prediction relies on how accurately each of these terms are computed. The terms v and  $\rho_v$  can be computed from first-principles methods. The physics of scattering in the system is encapsulated in the mean free path term and includes: 3- and 4-phonon anharmonic scattering processes; electron-phonon interactions; and scattering from surfaces, interfaces, and impurities. The detail with which one includes these factors will determine the ultimate accuracy of the prediction.

One important advantage of directly calculating  $\kappa$  from the BTE is that the quantum mechanical nature of heat is treated correctly—both in terms of the selection rules for phonon creation and annihilation, and the occupation of the vibrational spectrum. The difficulty is in quantifying all the detailed geometry-specific phonon transition rates.

In a system with a high degree of disorder, propagating phonon states are not well defined and the phonon gas model of transport is no longer appropriate. Allen and Feldman<sup>43</sup> and others have developed a model description relevant to such a system. They classify the quanta of vibrational energy (*vibrons*) in an amorphous system into: *propagons*, that reside in low-frequency plane-wave-like modes; *diffusons*, that reside in nonlocalised but nonpropagating (stationary) modes; and *locons*, that occupy high-frequency localised modes that are above the mobility edge. The majority of heat conducted through these systems is mediated by phonon transitions between diffusion modes.

#### 5.3.2 Computing $\kappa$ by Direct Simulation

A material's intrinsic resistance to conducting heat is due to phonon scattering that stems from anharmonicity in the interatomic interactions. As enumerating and computing all the scattering processes is difficult, a potentially more appealing approach is simply to accurately compute the anharmonicity of the atomic interactions and then use this within molecular dynamics (MD) simulations to measure the thermal conductivity *in silico*. The simulation will numerically account for all of the phonon-scattering processes without having to identify them *a priori*.

The most intuitively straightforward method for computing  $\kappa$  in this manner is to impose a thermal gradient in a system and simulate it using MD. One can straightforwardly set up a molecular dynamics simulation in which two (distant) slabs of atoms within a solid are thermostatted to different temperatures. By measuring the work done by the thermostats at each side of this thermocouple one finds the heat current that is transported down the thermal gradient in the intervening material between the slabs. However, while this approach most resembles a real experiment, it is fraught with several challenges, some that are common to all MD simulations, and some (such as the size of the simulation cell and the use of thermostats) that can be overcome with more carefully designed simulations.

In the computational setup described above, the temperature in the intervening material does not vary smoothly between the two thermostatted regions but experiences a discontinuous step at the boundary with the thermostatted regions—making the temperature gradient hard to control computationally. More significant, (especially in terms of computational affordability) is that the computational cell must be large enough to accommodate the mean free path of the heat-carrying phonons; and these can be several hundreds of nanometers. While this is large from the point of view of computational tractability, it is often still very small compared to the temperature difference, resulting in a large  $\Delta T$ , which can throw into question the validity of the linear response approximation.

An alternative approach is to switch the roles of cause and effect, so that rather than impose a temperature gradient one imposes a fixed thermal flux by adding (non-net-translational) kinetic energy at a constant rate to the atoms in one region, and removing heat at the same rate in the cold slab. This procedure was first developed by Müller-Plathe<sup>44</sup> and is often referred to as reverse nonequilibrium molecular dynamics (RNEMD). The approach is applicable to many transport phenomena and is also used for computing the viscosity of fluids.<sup>45</sup> The approach still suffers from requiring a very large computational cell but the system converges to the steady state more rapidly than the direct nonequilibrium MD approach described above.

It is possible to move away from the nonequilibrium approaches altogether, and instead to simulate a system at equilibrium in the microcanonical ensemble (NVE) and make use of the fluctuation-dissipation theorem that relates the linear response properties of a system out of equilibrium to the dissipation of thermal fluctuations within the system at equilibrium. The Green–Kubo method<sup>46</sup> relates the thermal conductance  $\kappa$ , to the autocorrelation function of the fluctuations in the heat flux  $J_{\rm O}$ , at equilibrium:

$$\kappa = \frac{1}{T^2 k_{\rm B} V} \int_{0}^{\infty} \mathrm{d}t C(t), \qquad (5.3)$$

with  $k_{\rm B}$  the Boltzmann constant, V the volume of the cell and the correlation function C(t) defined by:

$$C(t) = \int \mathrm{d}\tau J_{\mathrm{Q}}(\tau) J_{\mathrm{Q}}(\tau+t) = \langle J_{\mathrm{Q}}(\tau); J_{\mathrm{Q}}(\tau+t) \rangle, \qquad (5.4)$$

$$J_{\rm Q}(t) = \frac{\mathrm{d}R}{\mathrm{d}t},\tag{5.5}$$

$$R = \sum_{i} r_i h_i. \tag{5.6}$$

Here, the term R can be considered the centre of energy, as the sum of the positions of all atoms weighted by the sum of their potential and kinetic energies.<sup>v</sup> One advantage of the Green–Kubo method (in addition to its computational simplicity) is that as the heat-flux correlation function decays much more rapidly than the heat-carrying phonon's mean lifetime, the system size that must be simulated can be many times smaller than is required for none-quilibrium MD methods.<sup>47</sup>

For all of their intuitive appeal, using MD simulation to *in silico* measure  $\kappa$  suffers from several important and fundamental challenges, the most important of which is that the simulations are *classical*—that is, the trajectories of the atoms are integrated according to Newtonian mechanics without any quantum-mechanical phenomena included. This is usually justified by stating that for most elements at room temperature the atoms are sufficiently heavy that their de Broglie wavelength is negligible and the atoms can be treated classically. A notable exception is hydrogen, whose small mass does make quantum-mechanical effects significant and makes simulation of water particularly troublesome.<sup>77</sup> While this reasoning is true it overlooks two other quantum effects, first, that the permitted energy of vibrational modes is quantised with occupation  $E_n = \omega \hbar (n + \frac{1}{2})$ , and that the quanta of energy (that we refer to as phonons, not the modes that they occupy) are bosons and so fill the available states according to the Bose–Einstein distribution.

This has *two* consequences: First, not all modes have a uniform amount of energy—low-frequency modes will hold more energy than higher-frequency modes according to relation  $\langle E_i(T) \rangle = \omega_i \hbar / exp(\omega_i \hbar \beta) - 1$ , where,  $\beta = 1/k_B T$ , is the reciprocal temperature. At temperatures below the Debye temperature,  $T_D$ , the high-frequency modes with be unoccupied and will possess only their zero-point energy. This stands in direct contrast to a classical system in which all the modes may have a continuum of energy, and where on average *all* the modes will have the same energy regardless of the temperature. For this reason molecular dynamics simulations are usually performed at temperatures above  $T_D$ , where at least the participation of all vibrational modes is a reasonable assumption (although the filling of the modes is still incorrect). Alternatively, simulations may be performed at low temperatures if the phenomena of interest only involves low-frequency modes, and if it can be shown that the activity of high-frequency modes does not influence the behaviour of these low-frequency modes.

The second consequence of the quantum harmonic oscillator is that when heat is transferred from one mode to other modes (*i.e.* when phonons are

<sup>&</sup>lt;sup>v</sup>The potential energy of an atom can be poorly defined for many-body potentials; however, it is usual to approximate the local bonding energy to be shared between participating atoms in a pairwise fashion.

created and annihilated) the participating phonons must follow strict selection criteria such that the sum of the frequencies of the participating modes before and after the transition event are equal. No such restrictions are present in classical systems. The importance of this for MD simulations is that one cannot assume that the processes observed are directly transferable to real quantum-mechanical systems. Goddard and coworkers have shown that in the case of diamond at temperatures above  $T_{\rm D}$ , the quantum correction to the classical Green–Kubo calculated  $\kappa$  is small.<sup>47</sup>

Besides the fundamental quantum-mechanical deficiencies of MD simulations there are also some practical considerations. Thermodynamic properties are an ensemble average over all the possible states of the system. While in principle MD simulations are ergodic and will correctly sample phase space the time it takes to do so is very long, much longer than the duration that can be feasibly achieved in a single simulation. In a single MD simulation the systems trajectory only samples a narrow region of phase space, if we are to properly average over phase space we must run many simulations starting with very different initial conditions in order to attain a representative sampling on the ensemble.

#### 5.3.3 Gaining Insight from Simulations

Despite the many limitations and deep-rooted challenges for simulating thermal phenomena with MD methods, it is still a widely used tool that can be powerful for gaining physical insight if it is used judiciously. The main reason for this is that one knows the positions and velocities of every atom in the system during a MD simulation (knowledge that is out of reach from a real experiment). Armed with this raw data it is often possible to tease out subtle mechanisms of heat transport, scattering, and dissipation. This can be particularly useful when designing structures that suppress or enhance the mobility of phonons within a particular band of frequencies. Extending the analogy of the computer experiment these methods are like the characterisation tools of the real experimenter: they do not interfere with the physics used to simulate the system, but are used to interpret the results of simulation. The last part of this review of computational methods focuses on these numerical "characterisation" methods for distilling insight from raw MD simulation data.

Considerable insight can be gained simply by watching an animation of atomic motion in an MD simulation. One gains a mental picture of what the atoms are doing and one can quickly spot anomalous behaviour. As a method this is not very rigorous, it is a challenge to be sure that the animation is representative of the statistical ensemble, and it is difficult to disseminate movies in the traditional publishing format. However, the human brain is very good at spotting visual patterns (sometimes too good, finding patterns that are not there): watching a movie of simulated atom motion can quickly help one to identify bugs, or spot whether seemingly interesting results are merely artifacts of the system setup. It can also help identify interesting and physically meaningful behaviour on which more sophisticated and rigorous numerical characterisation methods can be trained.

A more rigorous method of "watching" the atoms was employed with great success by Phillpot, *et al.*<sup>48</sup> These researchers launched phonon wave packets at high-angle grain boundaries in Si and taking snapshots of the average kinetic energy of the atoms within slices of the computational cell, they followed the envelope of vibration as it collided with the interface, and were able to identify the mixture of scattered and transmitted wave packets. The method was used to determined which vibrational frequencies are transmitted most efficiently across the grain boundaries.

Much information can be learned from the vibrational spectrum of a nanoscale object, which as was mentioned above, can differ greatly from bulk systems. One consolation of the classical limitations of MD is that we can compute the vibrational spectrum (more or less) for free from any *equilibrium* MD simulation that we perform by Fourier transforming the autocorrelation function of the total kinetic energy. This can be done for any temperature, and while the spectrum must be weighted by the Bose–Einstein distribution to obtain the correct intensities the MD will capture the shift in mode frequencies due to filling of anharmonic modes.

The zero-temperature phonon spectrum for a nanoscale system can also be computed directly by diagonalising the Hessian matrix or the dynamical matrix (depending on whether the system is molecular or extended). Both of these methods have the advantage that in addition to the frequencies of the modes, one also obtains their eigenvectors. For very large systems with many millions of atoms, finding *all* the eigenvectors becomes computationally expensive; however, one can search sequentially for the lowest-frequency modes by recasting the matrix diagonalisation as an energy-minimisation problem, a method developed by Sankey *et al.*<sup>49</sup> for computing atomistically the vibrational modes of virus capsids.

Knowing the eigenvectors for the vibrational modes permits one to search through them, classifying the modes based on their symmetry or their spatial character, and to identify which modes are dominating the thermal phenomenon under study. For example, if one has a complex system of weakly interacting molecular units, such as a double-walled CNT, it permits one to identify modes that are confined to each individual CNT and those modes that are shared between the tubes. Obviously the shared modes will be most important for transmitting heat between the inner and outer walls of the CNT.

There are other ways of classifying modes based on their spatial extent. Allen and Feldman *et al.*<sup>50</sup> have classified the modes of amorphous Si, into propagating, diffusive, and localised modes. The lowest-frequency modes extend across the full extent of the system and can be thought of as propagating wavelike deformation modes. The wavelengths are much longer than the scale of the structural heterogeneity and the mode feels the average mechanical properties of the material—the limit being the infinite-wavelength mode corresponding to a homogeneous eigenstrain. At intermediate frequencies the modes become weakly localised, in that the wavelength of the modes becomes comparable to their mean free path. Above this so called Ioffe–Regal limit<sup>51</sup> the modes are diffusive, and the majority of heat is transported by energy exchange through these modes. The highest-frequency modes are short and localised around structural anomalies. These transport little heat and are said to be above the mobility edge.

Various approaches for measuring the degree to which a mode is localised have been developed by different researchers. Galli *et al.*<sup>14,52</sup> have computed the "participation ratio", p of the eigenmodes in a number of nanoscale systems with one or two reduced dimensions. The participation ratio of mode *i* is a measure of the fraction of atoms in the system that are participating in the displacement of this mode and is defined as:

$$p_i = \frac{1}{N} \left( \sum_{j=1}^{N} \left( \boldsymbol{\varepsilon}_{ij} \cdot \boldsymbol{\varepsilon}_{ij} \right)^2 \right)^{-1}, \tag{5.7}$$

where *N* is the total number of atoms, and  $\boldsymbol{\varepsilon}_{ij}$  is the displacement vector of the *j*th atom due to mode *i* with  $\sum_{j=1}^{N} \boldsymbol{\varepsilon}_{ij} \cdot \boldsymbol{\varepsilon}_{ij} = 1$ . Fully delocalised modes have *p* ranging between 1 and 0.5 with localised modes having smaller *p* with the limit that a mode localised to a single atom has n = 1/N. Yu and Leitner<sup>40,53</sup> have

that a mode localised to a single atom has p = 1/N. Yu and Leitner<sup>40,53</sup> have sorted the vibrational modes of a large protein molecule by their exponential localisation length,  $\xi$  by best fitting exp  $(|\mathbf{r} - \mathbf{r}_0|/\xi)$  to the decay of the mode's amplitude away from the mode's centre  $(\mathbf{r}_0)$ . Using this approach, an inverse correlated was found between localisation length and mode frequency.

Armed with the knowledge of some or all of the vibrational modes of a system one can project these modes onto the atomic displacements and velocities at any time during an MD simulation to obtain the instantaneous amplitude, a(t), and velocities,  $\dot{a}(t)$ , of the modes.

$$a_i(t) = \sum_{j=1}^{N} \boldsymbol{\varepsilon}_{ij} \cdot (\boldsymbol{r}_j(t) - \boldsymbol{r}_j^{\mathrm{o}}), \qquad (5.8)$$

$$\dot{a}_i(t) = \sum_{j=1}^N \boldsymbol{\varepsilon}_{ij} \cdot \boldsymbol{v}_j(t).$$
(5.9)

From computing the velocity of individual modes in this way during an equilibrium MD simulation one can calculate the mode's lifetime,  $\tau_i$ , by integrating the normalised autocorrelation function of the mode velocity.<sup>6,54</sup> Integrating gives the time it takes for the velocity autocorrelation function to decay, which is the *average* time after which the oscillation has lost coherence with itself. Galli and coworkers have shown the power of this approach by multiplying the computed lifetimes by the phonon group velocity,  $v_g$  (the gradient of the phonon dispersion) to calculate the phonon mean free paths,  $\lambda = v_g \tau$ . The mean free path appears in the BTE (eqn (5.2)), and thus computing this from simulation permits one to attribute each mode's contribution to the total heat transport.

Mode projection also yields insightful information from nonequilibrium MD simulations where knowledge of the modes not only allows one to analyse the results of a simulation but also excite a simulation away from equilibrium in a carefully chosen way. Adding an instantaneous velocity and/or displacement to the system along a mode's eigenvector excites a single vibrational mode. After excitation, by simulating in the microcanonical ensemble one can follow the system as it relaxes back to equilibrium. This scheme has been widely used for uncovering the detailed mechanisms of energy transfer in a diverse array of systems, including: phonon scattering at grain boundaries,<sup>48,55</sup> energy relaxation within protein molecules<sup>41,56</sup> and damping in CNT resonators.<sup>34,35</sup> More detailed examples of the use of the phonon projection are given in the two case studies later in this chapter. Here, we give a pedagogical discussion of frequency-dependent energy transfer. The aim is to show the types of information that can be gleaned from MD simulations using mode projection, and some of the areas in which care must be taken.

As a test system, let us consider the case of two identical carbon (10, 0)carbon nanotubes. The tubes are lying adjacent and parallel to each other, and they are weakly bound together by the van der Waals interactions between them. The tubes are (10, 0) tubes with a 4.2-nm periodic repeat distance, and they are in a vacuum. Full details of the simulation setup can be found in ref 36. After optimising the structure of an *isolated* single tube, its eigenmodes are computed using the frozen phonon method. Note that this only gives stationary solutions, not traveling modes—it is equivalent to diagonalising the dynamical matrix at  $\Gamma$  for the whole computational cell. The second identical tube is now introduced and the system is again optimised—the two tubes are attracted to each other and flatten very slightly where they "touch" to maximize this attraction. The normal modes of the isolated CNT are not the normal modes of this new composite system; nevertheless, it is instructive to interpret the transfer of energy in terms of the modes of the isolated CNT. We now excite just one mode in one CNT by displacing it. In this example, we choose the radial breathing mode RBM of the left-hand CNT that we call tube A.<sup>vi</sup> The system of the excited and relaxed tube is simulated in the microcanonical ensemble. Mode projection is used to compute the amplitude and velocity of each mode measured relative to the ground state of the relaxed double-tube structure at every timestep ( $r_i^0$  in eqn (5.8) is the atomic positions in the optimised double-tube system). Before the projection is performed care must be taken to unwrap any atoms that have crossed the periodic boundaries, and if the tube has randomly rotated it must be mapped back into the orientation in which the Hessian matrix was computed. The set of mode energies at a time t are represented as a smoothed spectrum by summing a set of Lorentzian functions centred at the

<sup>&</sup>lt;sup>vi</sup> Besides the mode that has been externally excited, the tubes are at absolute zero. This is an unusual and hypothetical situation that is seemingly problematic for classical dynamics. However, as all modes have *zero* energy using classical mechanics it is justified any time t = 0. Moreover, as we are only following the first stages of the relaxation of this energy before all become classically occupied, the use of MD remains justified for the short timescale simulated here. The simulations were repeated at finite temperatures and the same behaviour was observed.

mode frequencies and weighted by the mode energies. This approach to obtaining the vibrational spectrum is considerably more computationally expensive than the velocity correlation method, and less straightforward to implement; however, it gives us the excited spectrum at every time step, rather than averaged over some simulation time. Plotting the instantaneous spectrum against time gives the surface plots shown in Figure 5.1.

Examining the plots in Figure 5.1 reveals a surprising amount of information. First, we can follow the first cascade of energy as the excitation of the RBM in the "hot" CNT relaxes towards equilibrium. Four distinct energy-transfer events are distinguishable: (a) First, energy is transferred resonantly from the RBM in the hot tube to the RBM in cold tube. The transfer is frequency-selective and the frequency of the heat is preserved after being exchanged between tubes; (b) Next, the energy in the cold tube's RBM is scattered anharmonically into a mode with exactly half the frequency of the RBM. It can be shown by examining the eigenmodes that this frequency halving transition arises because the RBM is *asymmetrically* anharmonic whereas the half-frequency mode is not;<sup>36</sup> (c) The half-frequency mode in the cold tube transfers the excitation resonantly back to the equivalent mode in the hot tube, where (d) some of the energy is anharmonically scattered back into the initially excited RBM.

In addition to following the cascade of energy transitions, the projection data reveals much information about the nature of the participating modes. While the projection scheme computes the exact instantaneous kinetic energy of each



Figure 5.1 Plots showing the relaxation of the excited RBM in one of a pair of parallel carbon nanotubes. Four distinct energy transfer events are distinguishable: (a) hot tube resonantly exchanges energy from RBM into RBM in cold tube, (b) energy is scattered anharmonically within cold tube from RBM into a modes with half the frequency, (c) resonant exchange of energy from cold tube to hot between half frequency modes, and (d) anharmonic scattering within hot tube from half frequency mode to RBM.

mode, the potential energy is only estimated using the harmonic approximation. This inaccuracy can be used to our advantage. Comparing the over-(and/or under) estimation of the potential energy with the kinetic energy of a mode provides important information regarding the degree of anharmonicity in the mode, whether the anharmonic terms stiffen or soften the mode, and whether anharmonicity is asymmetric (as is the case for the radial breathing mode of a CNT). This information can be compared with and corroborated by computing the frequency shift of the mode relative to the frozen-phonon limit (computed from the power spectrum of the mode's velocity autocorrelation function). Comparing the amplitudes of a mode's potential and kinetic energy can also be used to identify nonresonant oscillations. The row of small peaks below 1 THz in the spectra of both the hot and cold tubes are an example of this. It is found that this oscillation has very little kinetic energy and is mostly comprised of a quasistatic elastic deformation of the low-frequency flattening modes of the tube. The excitation is artificial, and is not caused by these modes oscillating but by a much slower oscillation between the two tubes as a whole. The tubes "chatter" together under the influence of the van der Waals interaction. As the tubes come close together they flatten slightly (like a bouncing tennis ball) and it is the deformation of this flattening that gives rise to the serrated row of peaks.

Thus far, we have discussed the use of mode projection as a characterisation tool for interpreting the results of MD simulation; however, as mode projection gives information about the instantaneous state of the system there is no reason why this information cannot be fed back into the simulation and used to direct it. For example, knowing the eigenmodes of a system and using projection to determine their occupancy allows one to envision using external driving forces to regulate the energy in specially selected modes. This could be used for: continually driving a system away from equilibrium (as is done experimentally in driven nanomechanical resonators); enforcing a Bose-Einstein occupation of the classical modes; or even in schemes for efficiently searching phase space for rare events. While such procedures are not yet widely used they are being actively developed. Praprotnik et al. have shown that molecular dynamics can be performed efficiently in phonon space just as easily as in Cartesian space,<sup>57</sup> while Parinello et al.58 have developed a Lengevin thermostatting algorithm that uses history-dependent (that is, correlated) noise to drive particular frequency modes without the need for mode projection. The continued development of these types of algorithms means that MD-for all of its classical shortcomings—will continue to be an important and powerful tool for studying nanoscale thermal behaviour both at equilibrium, and far from it.

# 5.4 Example: Heat Flow in a Nanoscale Material; Intrinsic Dissipation in CNT Resonators

Carbon nanotubes possess a number of properties that make them attractive for use as resonating members in many nanoscale devices. The use of CNT resonators has already been demonstrated as a radio tuner,<sup>59</sup> an entire radio

receiver,<sup>60</sup> and a radio transmitter.<sup>61</sup> In addition, CNT resonators have been used to measure minuscule masses,<sup>31</sup> even down to the mass of a single Au atom,<sup>32</sup> and to approach the quantum limits of vibration.<sup>62</sup> In addition to these demonstrated applications the potential uses for CNT resonators are much broader, being applicable to any nanoscale device that requires controlled vibration, such as gyroscopes, mechanical processing of signals, and simple mechanical time keeping. The reason why CNTs are so suitable are multifold: CNTs' extraordinarily high stiffness combined with their low density enables them to attain very high natural frequencies, and frequency sensitivity. That CNTs are quasi-one-dimensional or string-like provides well-defined strategies for tuning their frequency—for example one may alter their length or put them under tension. Finally, CNTs can be both driven, and sensed, electronically by a number of different methods, making it possible to integrate CNTs into more complex nanoelectromechanical systems (NEMS) in which the resonator is only one part of the device.

To date, the biggest impediment to the use of CNTs as resonators is their very poor quality factor, Q, which when measured at ambient temperatures (and under conditions of constant driving) falls in the range of 8-300. (Q is defined to be  $2\pi$  times the inverse fraction of oscillator energy lost per cycle, and may be thought of as roughly the number of oscillations it takes for the energy to be reduced by 99.8%.) This result has been resistant to improvement, having been observed both under vacuum and at ambient pressure; in both cantilevered and doubly clamped geometries with many different clamping methods; and through many different measurement techniques.<sup>31,63–66</sup> Only recently by cooling to milikelvin temperatures have Os in excess of 10<sup>5</sup> been attained.<sup>62</sup> The universally poor ambient temperature results suggest that an intrinsic damping mechanism may be dominant. Macro- or mesoscopic theories of intrinsic damping from sources such as switching of defect states, thermoelastic damping, and phonon drag relate dissipative behaviour to the thermal energy in the system, that is, the background temperature  $T_{\rm bg}$ . 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. Roukes et al.<sup>67,68</sup> and others<sup>69</sup> have suggested that the intrinsic thermoelastic damping mechanism is capable of producing very low O factors in CNTs due to their very small surface-to-volume ratio-although other researchers disagree on the importance of this mechanism.<sup>70</sup> Previous computational work by Jiang et al., of an open-ended, cantilevered CNT found Q = 1500 at 293 K, with the unexpected temperature dependence:  $Q \sim T^{-0.36}$ , although the authors did not explicitly identify an intrinsic damping mechanism.

The question of whether a poor quality factor is intrinsic is one into which *in silico* experiments can lend considerable insight. In the computer, one can simulate a carefully chosen idealised test system in which all extrinsic sources of dissipation have been removed. Simulating such a system it is possible to see: First, if intrinsic damping alone can account for the poor Q factors; and second, to identify the mechanisms of intrinsic damping with the goal of finding ways to mitigate them. We recently performed such a study that leads to the

discovery of a new and surprising dissipation mechanism—one that can yield Mpemba-like behaviour in the cooling of an excited mode. The work is described here in order to serve as one example of how computational methods can be used to gain insight into nanoscale thermal phenomena.

The messy system of a doubly clamped suspended CNT resonator was represented in the idealised test system as a short section of a periodically repeated (along its axis) single-walled CNT, isolated in a vacuum and free from defects and mass impurities. This setup removes dissipation sources from defect migration, clamping friction, and gas damping. The effect of periodic boundary conditions is to add a clamping of sorts by restricting the number and wavelength of the CNT's flexural modes. The frequencies of flexural modes in the unclamped tube are higher than the modes of the same wavelength in the doubly clamped counterpart as there is no centre-of-mass motion. Instead of simulating the resonator under conditions of constant driving—as is the case for the experimentally measured Q—the resonator was simulated in the microcanonical ensemble as an initially excited flexural mode was allowed to the ring-down.

A typical simulation proceeded as follows: (1) The structure of a (10,0) CNT (simulated using the AIREBO potential for carbon–carbon interactions<sup>71</sup>) was relaxed, and the periodic repeat distance optimised.<sup>vii</sup> (2) the stiffness matrix for the system was computed and then diagonalised to yield the tube's eigenmodes, and their frequencies. (3) The tube was heated to a desired background temperature,  $T_{\rm bg}$ , and allowed to equilibrate. (4) An instantaneous velocity was added to the system along *one* particular eigendirection (usually that of the second flexural mode) such that the total *average* temperature of the system is raised by the amount  $T_{\rm ex}$ . (5) Ring-down was simulated (NVE) during which the vibrational energy distribution in all of the modes of the CNT is tracked using the mode-projection algorithm described above. The excitations of the flexural mode were large; however, despite the energetic excitations it was found that the mode remained reasonably harmonic, containing at most a 5% anharmonic contribution to the potential energy.

This study relies extensively on *in silico* experiments to investigate dissipation mechanisms. It is therefore imperative to ensure that the computational methods used are meaningful. It should be noted that the simulations were performed using classical molecular dynamics at temperatures well *below* the Debye temperature for the CNT. This is justified *a posteriori* by the finding that it is low-frequency modes that are participating in the dissipation mechanism. Simulating at low temperatures allows observation of the dissipation with little obfuscating thermal noise, and therefore is preferable if it can be physically justified. Leaving aside the issue of mode occupancy, a more fundamental problem is the use of classical mechanics to simulate the

<sup>&</sup>lt;sup>vii</sup> The length of the tube was typically 8.4 nm, which it should be noted has an aspect ratio considerably lower than a typical NEMS resonator, and additionally possesses no residual axial tension. The short tube length was chosen to reduce the computational cost of the mode-projection scheme.

dissipation of an energy that is quantised. Yet, as a more suitable method that includes quantised dynamics is lacking, classical dynamics is used with the understanding that the physical interpretation of the results is limited. Similarly, interatomic forces were computed using empirical potentials that were formulated to capture the energetics of carbon and hydrogen bonding across a range of bonding coordinations. There is no reason to expect this to correctly represent the anharmonic character of the carbon-carbon bond in a CNT. Thus, it is necessary to verify the robustness of the reported simulation results to changes in interatomic potential. The results of the simulations *are* found to be sensitive to changes in the interatomic potential: however, the overall qualitative behaviour is not. This may be in part because the dissipative behaviour is due to the shapes of the low-frequency modes, which are largely dictated by the tubular geometry rather than the details of the potential. As the qualitative trends do not depend on how the simulations are performed one is justified to draw general and meaningful conclusions.

The ring-down curves for the second flexural mode of a 8.4-nm long (10,0) CNT, with a background temperature of  $T_{bg} = 5$  K, and with increasing levels of initial excitation is shown in Figure 5.2(a). It can be seen that the attenuation of the oscillation follows a sigmoidal path, with larger initial excitations being completely damped in a shorter time than softer excitations. Figure 5.2(b) shows the ring-down profile for a 150 K excitation in tubes with increasing thermal background. As the background temperature rises the region of fastest attenuation is moved to earlier times.

To interpret the attenuation profiles in Figures 5.2(a) and (b) it is instructive to consider the attenuation of a simple damped harmonic oscillator with temperature-dependent dissipation. The equation of motion for such an oscillator is given by

$$\ddot{u} = -\omega^2 u - B(T_{\rm bg})\dot{u},\tag{5.10}$$

where  $u, \omega, B$ , are respectively the oscillator's displacement, (undamped) frequency, and mass-weighted drag coefficient, with the overdot indicating the derivative with respect to time. If the period of oscillation is short in comparison to the attenuation time ( $\omega \gg B/2$ ), then we may ignore the oscillatory behaviour, noting instead that the rate at which energy is lost to drag is proportional to twice the kinetic energy, and thus the total energy in the oscillator decays according to

$$\dot{E}(t) = -B(T_{bg})E(t).$$
 (5.11)

As a first approximation, the drag term is assumed to take the form of a firstorder Taylor expansion:  $B(T_{bg}) = B_o + B' \Delta T_{bg}$ , with B' positive. The increase in background temperature is simply the energy lost from the oscillator divided by C, the specific heat of the background, so that  $\Delta T_{bg} = (E_o - E(t))/C$ . Solving eqn (5.11) gives the attenuation profile,



**Figure 5.2** Plots (a) & (b) show the MD simulated ring-down profiles for the second flexural modes in 8.4 nm long (10,0) CNTs. In all cases the data is the average of 10 separate simulations with differing initial conditions; the data is plotted with a broad line thickness chosen such that it encloses the deviation of the averaged data. Plot (a) shows tubes with initial  $T_{bg} = 5 \text{ K}$  and  $T_{ex} = 50, 100, 150, 200, \text{ and } 300 \text{ K}$ . Plot (b) show the attenuation profile in tubes with initial  $T_{ex} = 150 \text{ K}$ , and  $T_{bg} = 5, 10, 50, 100, 150, 200, 400$ , and 400 K. Plots (c) & (d) show trends in simulation profile of a closed, damped harmonic oscillator (eqn (5.12)) when independently increasing  $T_{ex}$ , and  $T_{bg}$ , respectively.

$$E(t) = E_{\rm o} \frac{B_{\rm f}}{B_{\rm f} - B_{\rm i}(1 - e^{B_{\rm f}t})},$$
(5.12)

(plotted in Figures 5.2(c) and (d)) where  $B_i = B_0$  is the initial damping coefficient, and  $B_f = B_o + B'E_o/C$  is the damping coefficient when the system is fully relaxed. This simple model displays many of the features of the molecular dynamics simulations in Figures 5.2(a) and (b), including an inflection in the attenuation profile (if the damping coefficient more than doubles as the system relaxes), as well as the trends that arise from independently increasing  $T_{ex}$  or  $T_{bg}$ . Using a simplified "toy" model such as this is often very instructive for interpreting simulation results. In this case the model that might have initially seemed as surprising sigmoidal attenuation of the resonator's ringing is entirely consistent with the computational setup. However, the model is also *overly* simple and there are features in the simulation results that the model cannot capture; still, by using the model as a starting point one can also learn where to look for new and interesting behaviour.

#### 5.4.1 Mpemba-Like Behaviour

A consequence of simulating in the microcanonical ensemble is that the CNT is a closed system; energy dissipated from the excited flexural mode accumulates in the rest of the vibrational modes of the tube, raising  $T_{\rm bg}$ . Increasing  $T_{\rm ex}$ independently from  $T_{\rm bg}$  changes the average temperature of the system and thus one would expect a different attenuation profile. More remarkable is the cooling of the excited mode in systems in which the same total energy,  $T_{\rm t} = T_{\rm bg} + T_{\rm ex}$ , but differing *initial* partitioning of this energy between the flexural mode and the background (shown in Figure 5.3(a). Starting a simulation further from equilibrium (that is with larger initial  $T_{\rm ex}/T_{\rm bg}$ ) causes the system to reach equilibrium in a shorter time! We refer to this astounding, and counterintuitive behaviour, as "Mpemba-like" in analogy with the Mpemba effect<sup>72</sup> in which it is observed that when hot water and cold water are put into a freezer the hot water freezes first.<sup>viii</sup>

While the dissipation mechanisms active during the cooling of water are very different from the damping within a CNT we will see that in both cases the system is able to reach equilibrium faster because both systems contain a hidden variable, and in both cases the cooling results in changes in the hidden variable that do not follow a unique pathway.

Figure 5.3(b) shows the ring-down time for increasing initial  $T_{\rm ex}$  in systems for which  $T_{\rm ex} + T_{\rm bg} = 300$  K. Two measures of the ring-down time are plotted: the time taken for excitation to be damped to a fixed lower threshold; and the interval over which the excitation is diminished by a set fraction—both measures decrease the further one starts from equilibrium. As with the Mpemba effect, relaxing faster to equilibrium the further one starts from it can only occur if the cooling pathway is not unique, but instead depends on the system's initial conditions—as illustrated by the inset plot in Figure 5.3(a).

From the ring-down profile of the simulated CNT resonator one can compute the Q factor at any time t as  $Q(t) = -\omega E(t)/E(t)$ , where  $\omega$  is the

viii The Mpemba effect was and still is somewhat controversial. There are a number of differing explanations for the phenomenon that range from the practical to the fundamental. An example of the former is the hot water in the ice cube tray melts a layer of surface ice on the freezer shelf thus making better thermal contact. Just one example of a fundamental explanation of the Mpemba effect is that the cooling of the water is mediated by convection currents that have inertia and momentum. Once established in a hot liquid-with a large driving force they are maintained as the liquid cools. Cooling then depends on the average temperature T (which has no memory) and the convective flow C (which is dependent on the liquid's thermal history). The convective flow C provides the history-dependent hidden variable. The Mpemba effect is also controversial because of the manner in which it became popularised-through the observations of a Tanzanian school by George Mpemba (although the effect had been commented on much earlier by other natural philosophers, including Aristotle and Francis Bacon<sup>73</sup>)—and how it seems to directly challenge intuitive scientific understanding. In fact the Mpemba effect makes no challenge to established science or the scientific method, it only holds a mirror to the way that we do science in practice and the barriers that we have for updating our personal intuitive scientific understanding when we are presented with more evidence. A good discussion of the Mpemba effect, and its history is given by Jeng.<sup>73</sup>

frequency of the excited mode.<sup>ix</sup> Figure 5.3(c) shows the change in the Q factor accompanying the attenuation of a CNT. The Q drops from close to 1900 by more than 95% to 37 and then is seen to recover towards 1000 after 20 ps. The origin of this huge suppression of the Q and its subsequent recovery can be understood by using the projection algorithm to track how the energy populates the background modes once it has been dissipated from the flexural mode. The evolution of the background population is shown in Figure 5.3(d). It can clearly be seen that the energy goes first into low-frequency modes-close to the frequency of the flexural mode—before dispersing across the full vibrational spectrum of the CNT. This nonuniform filling of the background modes is due to a small set of key "gateway modes" that act as strongly nonlinear channels for dissipation. These gateway modes and the role that they play is examined in more detail later in this section. However, without knowing how the gateway modes work it can be seen that the nonequilibrium distribution of energy in the background modes that they give rise to provides a hidden variable that is the necessary ingredient in for Mpemba-like behaviour.

The very simple model in eqn (5.12) does not exhibit the Mpemba-like behaviour that is observed in CNT's simulations. Reducing the initial  $T_{\rm ex}/T_{\rm bg}$  ratio in the model has the effect of starting the attenuation from further along the same universal ring-down pathway, and thus increasing the initial distance from equilibrium always results in longer cooling time. Additionally, in this model the *Q*-factor decreases monotonically in time and does not show the recovery that is seen in Figure 5.3(c).

Armed with the insight from the nonuniform filling of the thermal background gained from the mode projection (Figure 5.3(d)) one can construct a slightly more sophisticated model of the CNT damping process. Rather than assuming that the energy is dissipated into a single reservoir of background modes we can subdivide the background into two. One subreservoir, called the low-frequency background, is the set of modes that interact strongly (and nonlinearly) with the excited flexural mode. The remainder of the modes that interact less strongly make up the other thermal bath that is referred to as the high-frequency background. The strongly interacting group is referred to as the low-frequency background because in Figure 5.3(d) it can be seen that the modes that receive dissipated energy first have in general lower frequencies—although it is important to note that the frequency of the mode is of no importance for this model. The relaxation of this three-body model is now governed by three heat dissipation rates: The power dissipated from the excited mode into the low-frequency background,  $p_{ex \rightarrow l}$ , power dissipated from the flexural mode into the high-frequency background,  $p_{ex \rightarrow h}$ , and the rate of heat transfer between the low- and high-frequency backgrounds  $p_{l \rightarrow h}$ . To correctly couple the three thermal reservoirs in a manner that reaches the correct thermodynamic equilibrium a phenomenological form of the dissipation eqn (5.11) is modified such that

<sup>&</sup>lt;sup>ix</sup> In practice, this is done by fitting a smoothing spline to the data in order to minimize the fluctuations in  $\dot{E}(t)$ .



$$p_{\alpha \to \beta}(t) = -B_{\alpha\beta}(T_{\beta}) \left( \frac{T_{\alpha}}{C_{\alpha}} - \frac{T_{\beta}}{C_{\beta}} \right) C_{\text{tot}},$$
(5.13)

where  $C_{\alpha}$  and  $C_{\text{tot}}$  are specific heat of the individual reservoir  $\alpha$ , and the total specific heat of all the reservoirs combined. The quantity  $T_{\alpha}C_{\text{tot}}/C_{\alpha}$  then represents the temperature (that is the locally time averaged kinetic energy) of a mode within reservoir  $\alpha$ . Note that this is different from  $T_{\alpha}$  that was defined to represent the heat in the sets of modes in terms of its contribution to the temperature of the system as a whole.

This model in eqn (5.13) is solved numerically using as an initial condition that the temperature of the two background sets are the same. It is found that the extra degree of freedom in the system afforded by the two background reservoirs is sufficient to reproduce all of the features of the simulated CNT ring-down data—including the observation of Mpemba-like behaviour, and the recovery in Q. Figure 5.4(a) shows a relaxation profile of the model fit to the CNT attenuation profile from Figure 5.3(c), for which the 3 linear dissipative terms, one nonlinear dissipative term, and the number of modes in the low-frequency background were used as fitting parameters. Figure 5.4(b) uses the same model parameters as in (a) with differing  $T_{ex}/T_{bg}$  ratios showing Mpemba-like behaviour.

The model plotted in Figures 5.4(a) and (b) is intended to be illustrative rather than predictive. It shows that there are two key ingredients that are needed in order to observe the Mpemba-like behaviour seen in the CNTs: nonlinear dissipation (caused by heating), and an internal degree of freedom (caused by heterogeneous heating of the background modes). For the fit in Figure 5.4(a) six fitting parameters were used, which is a lot, and one must not read too much meaning into them. There is, however, one parameter from which some insight can be gained: the number of modes in the low-frequency background. The tail in the ring-down profile occurs when the excited flexural mode comes into local

Figure 5.3 Plot (a) shows MD simulated total ring-down profiles (computed as for Fig. 5.2(a) and (b)) for the simulations in which the total energy  $T_{\rm bg} + T_{\rm ex} = 300 \,\mathrm{K}$  but with different initial partitioning ratios,  $T_{\rm ex}/T_{\rm bg}$ . As with the Mpemba effect the mode cools faster if it starts hotter! The inset plot shows the cooling curves 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 no universal cooling trajectory. Total ring-down times plotted in (b), measured as the time taken to decay to an excitation of 1.5 eV/atom (i.), and time to lose 88% of initial energy (ii.). Plot (c) shows ring-down (solid line) overlaid with the *Q*-factor (circles) for initial  $T_{bg} = 5 \text{ K}$ ,  $T_{ex} = 150 \text{ K}$ . The surface plot (b) shows how the dissipated energy from this simulation is distributed over the spectrum of the CNT's background vibrational modes. The region of rapid damping is marked by (ii.). 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.



Figure 5.4 Attenuation profile predicted by the coupled dissipation model (eqn (5.13)). Plot (a) show the model (thin line) with parameters crudely fit to simulation data (thick line) for a CNT with initial  $T_{bg} = 100$  K, and  $T_{ex} = 200$  K. Plot (b) shows the model prediction (with the same fitting parameters) for the simulation data plotted in Figure 5.3(a). It is clear that the fit is far from perfect, however the major features remain. Most importantly, the model reproduces the Mpemba-like behaviour.

equilibrium with the low-frequency background, and the initial height of this tail in turn depends on the number of modes in this low frequency set—that is, the number of modes that interact strongly with the excited flexural mode. To obtain a good fit to the CNT simulation results this number must be between about 3 and 10 that agrees well with the finding from the mode projection that there are a small number of gateway modes that trigger rapid dissipation.

The Mpemba effect in the freezing of water is counterintuitive because one assumes that as hot water has cooled down it passes thought the same state as water that is initially cool. This is not the case. The rate of dissipation of heat from the cooling water depends not on the average temperature of the water but on a number of history-dependent hidden variables such as the temperature gradient and convective circulation. While the detailed origins of the Mpemba effect in water are not fully agreed upon it is clear that the effect is possible because of internal degrees of freedom within the system that are not described by the average temperature of the system. In this work it is demonstrated that an abstraction of the same phenomena is possible in other systems such as CNT resonators. It has been shown that: (1) the dissipation results in the formation a history-dependent athermal filling of vibrational modes that is not described by the average temperature, and (2) the dissipative state of the system is extremely sensitive to this athermal phonon population.

#### 5.4.2 Gateway Modes

Having established the importance of gateway modes for Mpemba-like cooling it is worth examining the role that the gateway modes play. Again this can be done by taking advantage of the experiments being performed *in silico*.

Using the mode projection it is possible to identify which of the low-frequency modes were receiving the dissipated energy and within this subset of low-frequency modes it is found that there are two "gateway modes" that act as strongly nonlinear channels for dissipation. For the 8.4 nm (10,0) CNT these gateway 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 remainder of the energy in the background are shown in Figure 5.5(a). Once the gateway modes accumulate a little bit of energy they open efficient channels for rapid dissipation from the excited flexural mode. In the simulation it is possible to externally add a small excitation to a gateway mode. Exciting either of the gateway modes by as little as 1.5 K triggers the immediate onset of strong dissipation and suppression of the *Q* factor. Similarly, exciting the other low-frequency recipient modes had no effect.

That the gateway modes are the first and third flexural modes of the periodic CNT arouses suspicion that the observed gateway behaviour in the MD simulations is simply an artifact of the limited system size. It is necessary then to conduct two tests of the size dependence. The most trivial test is to repeat the study for CNTs with increasing periodic repeat distance to establish that gateway-mode dissipation is unique to neither (10,0) nor 4.2 nm periodically repeated tubes. A second, and more insightful, test of the size dependence on the gateway modes is to simulate a longer CNT in which the excited flexural mode still exists, but which is incommensurate with the wavelength of the two gateway modes.

Ring-down of the equivalent 1.5 THz flexural modes of 8.4 nm tubes was simulated in tubes 1.5, 2 and 3 times as long.<sup>x</sup> The attenuation of these modes is plotted in Figure 5.5(c). 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 the system finds a different but less-effective gateway mode (a flexural mode with wavelength 6.3 nm) to dissipate the 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

<sup>&</sup>lt;sup>x</sup> That is, modes with the same frequency as the third, fourth and sixth flexural modes of these tubes, respectively.



**Figure 5.5** Plot (a) shows the energy in the excited flexural mode, the high and low frequency gateway modes, and the remainder of the background modes, during ring-down. Graphic (b) shows a schematic representation of the dissipation pathway and the role of the gateway modes in the CNT. The energy in the excited mode, the gateway modes, and the remaining background is represented by the filling of three receptacles, with the thickness of the arrows indicating the rate of energy transfer between receptacles. Plot (c) shows the ring-down of the 1.5 THz flexural mode in tubes with 8.4, 12.5, 16.7, and 25.1 nm periodic repeat distances.

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-nm and 16.7-nm tubes but the gateway modes of the 8.4-nm tube become active first. This hints that there could be many modes that can perform the gateway role; however, those that are most effective at it do so first, eliminating the need for other modes to act as dissipation gateways. Importantly, these 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.

It is now possible to pull together the understanding of the Mpemba-like behaviour with the insight into the gateway modes into a cartoon model of the dissipation process in the CNT, shown schematically in Figure 5.5(b). Computer "experiments" were performed of the intrinsic dissipation in CNTs. For reasons of computational expedience, dissipation was observed during ringdown rather than under the experimentally measured conditions of constant driving, however this approach revealed the formation of an athermal population of background phonons and a concomitant change in quality factor.

The consequence of these observations for a real NEMS device could be of great practical importance. A real CNT resonator under vacuum can only lose heat through its clamped ends. It is therefore very likely that under conditions of constant driving the occupancy of phonon modes will be far from the equilibrium distribution, and that this will in some way impact the qualify factor of the tube. The implication is two-fold: (1) In order to properly understand the *O* factor of driven systems one must consider the whole phonon population, (2) by understanding the full phonon population distribution we can gain strategies for externally changing it and thus can engineer the dissipative properties of the system. Moreover, if it is found that an athermal phonon affects the dissipative properties of other systems besides CNTs these issues will also be relevant in other NEMS devices. If this is the case then the gateway mechanism provides one with several avenues for improving O 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<sup>33</sup> or quantum back action<sup>74</sup>). The phenomenon of triggering rapid damping externally by *adding* more energy could find important applications such as in the ability to minimize unwanted vibrations in CNTs. It could be used for actively blocking heat flow along CNTs and providing a way to mechanically filter thermal transport.

# 5.5 Example: Heat Flow Between Nanoscale Materials; Exploiting Frequency-Selective Thermal Transport for Chemical Sensing

At the beginning of this chapter it was discussed that exploiting far-fromequilibrium conditions in nanoscale systems can permit us to take advantage of heat that is athermally distributed across frequency—that is, using the properties of a select frequency band. In the survey of the computational "characterisation tools" the example was given of frequency-selective thermal transport between weakly coupled objects. In this case study, it is shown how this concept could be applied in a new approach to chemical sensing that could be both highly sensitive *and* label-free. Simulation in combination with numerical characterisation tools are used to provide a proof-of-concept, and then to develop guidelines to help experimental researched in the development of the method in practice.

Current strategies for sensing hazardous airborne chemicals, such as pollutants or chemical-warfare agents, must compromise between focused sensitivity and breadth of vigilance. Mechanically based chemical methods provide one avenue to ultrasensitive detection. These methods detect binding of analyte to a resonator by the accompanying change in surface stress or resonant frequency. The sensitivity of this method increases inversely to the lengths scale of the resonator, with nanoscale resonators able to detect an analyte in parts per trillion. The specificity of the method, however, is provided by the functionalised coating—and thus the flexibility of the approach to a rapidly evolving watch-list of chemical threats depends on how rapidly one can develop newly targeted chemical functonalisation. In contrast, spectroscopic methods for chemical sensing are "label-free", that is, they require no preconditioning in order to identify a given analyte. Unfortunately, they can only achieve satisfactory sensitivity by concentrating and segregating the analyte with a chromatography step.

As a route to chemical sensing that provides both sensitivity and label-free selectivity it has been proposed to exploit frequency-selecting thermal transport that can occur across weak nanoscale interfaces to probe analyte molecules in a way that is both mechanical and spectroscopic in nature. The method, referred to as nanomechanical spectroscopy (NRS),<sup>75</sup> uses an array of tuned nano-mechanical resonators that become excited in the presence of a hot analyte with a particular vibrational frequency. (The graphics (a) and (b) in Figure 5.6 illustrate the NRS concept and its comparison to optical spectroscopy.) Taken together, the array of resonators can be likened to a stringed musical instrument; the vibrational spectrum of each analyte strikes a unique chord that can be used to identify it. Sensing the analyte is then reduced to resolving the relative excitations of the nanoresonator array. This task of "listening" to the strings is itself nontrivial; it requires being able to measure an excitation in a single vibrational mode of an ultrahigh-frequency resonators, with nanosecond resolution.



Figure 5.6 A schematic comparison of NRS with traditional optical spectroscopy. Panel (a) depicts in very general terms an optical spectroscopy method, in which the vibrational modes of an analyte are interrogated with a laser. Electron-phonon coupling transduces the illuminating radiation and the measured spectrum that results is used to identify the analyte. Panel (b) depicts the proposed NRS method in which a heated analyte interacts directly with a series of nanomechanical probe resonators. If a probe is in resonance with a vibrational mode in the analyte, then vibrational energy is exchanged; thus, the analyte excites a unique chord in the array of probes that can be used to identify it.

In order to demonstrate the NRS principle we turn again to an idealised test system that can be easily simulated with MD and that can be analysed unambiguously. The simplest possible analyte is used, namely an H<sub>2</sub> dimer. This has only one vibrational mode-the bond stretch-and the frequency of this mode is tuned by making the H atoms artificially heavy. For the probe resonator a (10,0) single-walled (and periodically repeated) CNT is used. This allows us to efficiently bring all of the characterisation apparatus described above to bear on this problem. To start, the dimer is positioned randomly at the CNT surface and given a large ( $\sim 1100 \text{ K}$ ) excitation of its bond stretch (as shown in Figure 5.7). The CNT is initially at absolute zero. (Classical simulation of this system setup is justified by the same arguments used for the case of two parallel CNTs above). The system is simulated in the microcanonical ensemble. The analyte (dimer) and probe (CNT) are weakly coupled *via* the van der Waals forces, and this mediates the transfer of energy from the dimer to the tube. The weak binding also permits a slow bouncing oscillation of the dimer on the tube surface, causing the dimer to migrate randomly along the tube. Figure 5.8 shows the evolution of the spectrum of vibrations excited in a CNT that is in contact with a dimer tuned to oscillate at 10 THz.

It can clearly be seen from Figure 5.8 that for a 10-THz analyte most of the vibrational energy that is transferred to the CNT occupies modes with frequencies closest to 10 THz, *i.e.* modes in resonance with the dimer. This demonstrates that information about the vibrational frequency of the analyte is communicated to the probe, and remains localised in frequency for an experimentally measurable duration. The dissipation of energy in the excited mode in the tube is small, as the tube was initially at 0 K. Simulations in which the tube has an initial background temperature show the same qualitative behaviour although with increased dissipation from the resonantly excited



**Figure 5.7** Typical simulation setup. Panels (a) and (b) show respectively the initial and final configurations of the system. In panel (b) the internal displacements within the CNT have been artificially amplified to show that it is a flexural mode in the tube that has been primarily activated.



**Figure 5.8** Mean excitation of CNT due to interaction with a single dimer vibrating at 10 THz. The plots are the average of 29 simulations. Plot (a) shows the full excitation spectrum in the CNT. A clear resonant peak is visible at 10 THz. Plot (b) shows the partitioning of the thermal energy between the stretch mode of the analyte, and the resonant modes and background models in the CNT. The inset plot shows the first nanosecond of resonant signal for the first 15 individual simulations (thin lines) with the mean plotted in bold. It can be seen that the trajectories are stochastic, with energy repeatedly exchanging back and forth between the dimer and CNT.

mode. An interesting feature in Figure 5.8(a) is the small excitation of modes with twice the frequency of the dimer. This arises from the strong anharmonicity in the van der Waals interaction rectifying (frequency doubling) the force that the dimer exerts on the tube.

Figure 5.8(b) shows the partitioning of the total thermal energy in the system between the dimer's stretch mode, and the resonant and off-resonant modes in the CNT. It can be seen that in the 10 ns simulated less than half of the energy in the dimer's stretch has transferred to the CNT, and very little energy is transmitted into the dimer's rotational and translational modes (due to the atomic mass of the dimer being relatively large). The set of resonant modes in the CNT was chosen to be those within 0.4 THz of the dimer frequency-a window just wide enough to enclose the full resonant ridge along 10 THz in Figure 5.8(a). The plotted "resonant signal" is the summed energy of the modes in this window-effectively a narrow-bandpass filtering of the full vibrational spectrum. The inset plot shows individual heating trajectories of the resonant modes over the first nanosecond for 15 of the simulations. It can be seen that there is a wide distribution in the trajectories but also that each individual trajectory follows a rapidly fluctuating stochastic pathway in which heat is both added and removed randomly, with only a gradual accumulation of energy.

Averaging a portion of the spectrum in Figure 5.8(a) at early times between 90–100 ps gives a measure of the response of the CNT resonance probe to a 10-THz analyte vibration that can be compared to the response due to analytes of different frequencies. By repeating the simulations with dimers of different frequencies one obtains a map of the response of the probe to analytes spanning

its entire frequency range, the first 20 THz of which is shown in Figure 5.9. The fact that the CNT response surface is excited primarily along the diagonal in this plot shows that the excitation of the probe remains resonant—that is, sharply localised at the dimer frequency—for all analyte frequencies. This result represents a critical proof of concept important for a functional NRS: it ensures that there is a one-to-one mapping between the frequency of the measured probe signal and the vibration in the analyte that caused it. There are no strong off-resonant signals that could cause a false positive. Moreover, the presence of the analyte does not strongly alter the frequency of the modes of the CNT— which would blur the frequency specificity of the probe. Unlike mass-sensing approaches that rely on the analyte binding causing a frequency shift in the resonator, here the analyte is only very weakly bound to the probe through the van der Waals interaction, which vitiates the effects of mass loading.

Having established that the principle of the NRS method works one can examine the simulations more closely to glean information that will help optimize the NRS device performance. First, the simulations give a picture of the analyte moving randomly on the surface of the CNT rapidly exchanging energy back and forth with the CNT. We can use this picture as the basis for a simple mathematical model of stochastic energy transfer. This model predicts that one can maximize the rate of energy transfer and narrow the resonant frequency band if one can engineer the strength of interaction between the dimer and CNT and the frequency of their bouncing. Secondly, in Figure 5.8(b) it can be seen that both the resonant and off-resonant modes of the CNT become excited. An obvious question is: are the background modes of the CNT excited only due to dissipation from the resonant modes or are they also excited directly by the analyte (and if so is there anything that we can do to prevent it?). Here, we can take advantage of the noise due to the constant random shuttling of energy. It is found that the noise in the analyte and the noise in the background modes have very different frequency components. Moreover, it is found that the noise in the resonant mode is closely anticorrelated to both the analyte and background, but there is no correlation between the analyte's noise and the background modes. In other words, the resonant channel for energy transfer is extremely efficient and almost all the energy transferred into the CNT is mediated by resonant exchange—there is little improvement to be made here. Finally it can be seen from the plot in Figure 5.9 that the resonant signal measured in the CNT is stronger for lower frequencies. The CNT is effectively self-filtering for the low-frequency signal. This property can be used advantageously and can help set some guidelines for the realisation of a working NRS device. The most sensitive sampling frequency of each probe resonator is its lowest-frequency mode; thus one should design the spectroscope so that one can monitor the occupation of this mode in each of the probes in the array. This one guideline vastly simplifies the process of selecting nanoscale objects to act as probe resonators, by choosing families of objects with controllable geometries that change the fundamental frequency. Several examples of this are fullerenes where the radius of the fullerene determines the frequency of its breathing and flattening modes or the fundamental mode of a suspended or



**Figure 5.9** Scan of the excitation response of a CNT nanomechanical resonance probe to molecular vibrations with frequencies over the entire frequency range of the CNT. Only the first 20 THz of the scan are plotted as the response of the probe at higher frequencies was negligible. The response spectrum of the probe for each analyte frequency is an average of the excited spectrum between 90 to 100 ps of the simulation.



**Figure 5.10** Mode frequency for families of nanoscale objects. The data plotted at high frequencies show the frequency of the lowest frequency mode and the breathing mode for fullerenes as a function of their diameter. The dashed line shows the frequency of the radial breathing mode for CNTs as a function of their diameter (with data plotted using Eklund and Dresselhaus fitting formula  $\omega$  [cm<sup>-1</sup>] = 244/d<sup>2</sup> [nm]<sup>76</sup>). The shaded region plotted at lower frequencies shows the frequencies of the lowest frequency flexural mode of a single walled CNTs as a function of length for a range of stable chiralities and diameters. The mode frequencies for both the fullerenes and CNTs were calculated using the REBO potential.

cantilevered nanowire or nanotube, determined by length and radius. By way of example, the lowest-frequency modes for fullerenes and the flexural modes of CNTs are plotted as a function of their tuning dimension in Figure 5.10. It can be seen that together these modes span nearly 3 decades in frequency space and thus, if used as nanomechanical resonance probes for NRS, could potentially permit detection of a wide range of molecular vibrations.

In this case study we have shown that lots of subtle information can be learned from MD simulations of even the simplest systems. However, we must beware not to push the interpretation too far. We have shown that the resonant effect is significant, but in the simulation the transfer of energy is *continuous* not by discrete jumps as is the case for a quantum system. In this sense we have made progress to the extent possible for a *classical* MD approach, but there is much that can be learned if we could correctly simulate quantised energy transfer. There is much work still to be done in this field, and much to be understood by doing so.

# 5.6 Conclusions and Outlook

In this chapter we have explored different approaches to simulating thermal behavior in nanoscale systems, and the relationship between simulation and direct computation. The chapter started with a survey of experimentally demonstrated thermal properties that can be found in nanoscale systems. Making use of nanoscale structured systems has the potential to radically alter the way that we both use, and think about heat. The fundamentals of thermodynamics were solved during the industrial revolution in the era of the steam engine but heat remains as technologically important now as it was then. Moving to the nanoscale allows us to control heat in unprecedented ways, permitting engineering of phonon band structure, and manipulation of structure at the length scale of the phonon mean free path. Achieving the full potential of heat at the nanoscale requires not only devising novel ways of exploiting heat but also advancing our fundamental understanding of thermal energy in nanoscale systems, and developing the computational tools required to study it. As we hope this chapter has demonstrated, this is an exciting field, in which there is much work to be done.

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