A Review of MD Simulations of Acoustic Absorption Mechanisms at the Nanoscale

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ABSTRACT

The use of nanoscopic fibres for acoustic absorption can potentially result in thinner liners than for conventional acoustic materials. Modelling acoustic mechanisms at the nanoscale requires molecular simulations as the flow behaviour at the nanoscale is in the transition regime (based on Knudsen number). Molecular Dynamics (MD) was identified as a suitable method for simulating the physical phenomena for acoustics. This paper presents a review of previous MD simulations of relevance to the physics of acoustic absorption mechanisms at the nanoscale that have included micro- and nano- scale flow properties and acoustic wave propagation. The paper also discusses additional simulations that can be performed to verify that MD models can be used to correctly simulate acoustic absorption at the nanoscale.

1. INTRODUCTION

Mechanisms of sound absorption are currently well understood for conventional porous acoustic materials having fibre diameters or pores on the microscale (down to 1 μm). The relative influences of the various mechanisms are, however, expected to change for materials with pores or fibres at the smaller nanoscale (down to 1 nm), while other mechanisms and non-linear effects may also have a significant influence. In order to investigate the absorption mechanisms for nanoscale materials, the flow and acoustic propagation within and around a nanotube acoustic absorber will need to be modelled using analytical or numerical approaches appropriate to the nanoscale. The current research aims to develop and implement an accurate and reliable simulation method to model the acoustic absorption mechanisms of carbon nanotubes (CNTs). Figure 1 exhibits a schematic of the modelling stage for vertically aligned (with the substrate) multiple nanotubes (CNT forest with millions of nanotubes per square centimetre grown on a silicon substrate), which in the simplistic way show the physical system of the interaction of sound waves within the tubes and also in between the tubes.

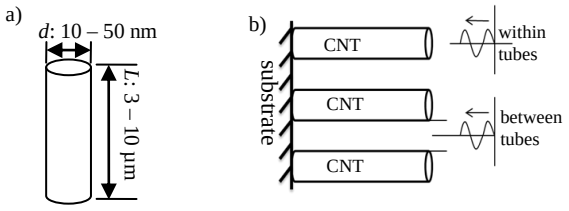

Figure 1. Schematics of the modelling to be undertaken showing (a) the dimension scale of the nanotube and (b) the arrangement of the multiple tubes for wave propagation (here just 3 tubes are shown for illustration).

Wave propagation in micro- and nanoscale flows are usually characterised by the confinement of the fluid environment (Czerwinska, 2009). The hierarchy of the mathematical models available to solve such types of fluid dynamics problem can be categorised into two groups as continuum and non-continuum methods according to the varying degrees of approximation (Hanford, 2008). Quantification of the validity of continuum models and deviation from this behaviour can be established by the Knudsen number, $Kn = \lambda/H$, which is a ratio of the molecular mean free path (λ) and characteristic length scale (H). For $Kn = 0$ to 0.001 the medium is considered to be in the continuum regime; for $Kn \geq 0.1$ the continuum approximation is considered to be invalid (Czerwinska, 2009; Hadjiconstantinou, 2002). For the nanoscale structures considered in this research, acoustic waves propagate in air (a polyatomic gaseous media), and the flow is through cylindrical channel nanotubes. The relevant length scales that determine the Knudsen number are the average molecular free path of air at standard temperature and pressure (STP), which is 65 nm (Karniadakis *et al.*, 2005), and the nanotube diameter, which is around 50 nm. Thus, the characteristic scale for carbon nanotubes is comparable to the molecular mean free path, which indicates a *transition flow* regime, because the value of Kn will be in the range of 0.1 to 10 ($Kn = 65/50 = 1.3$). The large value of the Knudsen number for air flow in nano fibres indicates that particle-based non-continuum approaches should be implemented for the investigation of the flow behaviour.

In non-continuum methods, the system is modelled at a microscopic level as particles, with the state of the gas described by the particle position and velocity in 3D space (Hanford, 2008; Czerwinska, 2009). In the last two decades, the most popular molecular simulation methods in acoustics and fluid dynamics for similar types of channel flow behaviour at the micro- and nanoscale are Molecular Dynamics (MD), the Lattice Boltzmann Method (LBM), and the Direct Simulation Monte Carlo method (DSMC). The LBM has been widely used due to its simplicity despite some deficiencies in the results, especially in the case of high Knudsen number *transition flow* regimes. On the other hand, DSMC has been used for the simulation of gaseous media more frequently than LBM because it overcomes errors related to compressibility issues, whereas MD has been applied for the simulation of solids (Mohan & Liang, 2008), liquids (Karniadakis *et al.*, 2005), gases (Barisik *et al.*, 2010) and gas mixtures (Kandemir & Sevilgen, 2008) with complex flow physics (Maruyama, 2002; Karniadakis *et al.*, 2005). Nevertheless, LBM is preferable over MD and DSMC, mainly because of LBM's simple collision rules and numerical efficiency. The drawback with MD and DSMC is their large

computation time. MD requires more computational time and cost than DSMC, but provides better accuracy. A review of the LBM and DSMC methods and their applications in micro channel and acoustic problems can be found in the authors' previous review article (Ayub *et al.*, 2011).

In the previous article (Ayub *et al.*, 2011), a comparison between the continuum and molecular approach, along with the limitations and disadvantages of molecular methods such as LBM and DSMC, was presented, as adopted from the literature It was demonstrated that the continuum models do not have the necessary features to simulate phenomena likely to be required to accurately model the acoustic absorption of nanoscale fibres, whereas the non-continuum particle-based simulation approach provides the required capabilities for solving this kind of flow problem. Based on the advantages and disadvantages of the methods along with the limitations that constrain the model to be selected for a particular problem, selection criteria can be set for a phenomenon to be simulated. In the case of nanotubes, the selected method must have the ability to simulate the following mechanisms:

1. Heat conduction to the absorber material from the air.
2. Thermal and viscous boundary layers and their interactions with the structure of the nanotubes.
3. Flexibility of nanotubes and coupling with acoustic waves.
4. Phenomena in gaseous media

Considering these criteria, DSMC was identified as having the most potential to simulate the acoustic flow propagation through fibres at the nanoscale (Ayub *et al.*, 2011). However, there are other factors that need to be considered for the nanoscale simulation of acoustic wave propagation through CNTs, such as coupled momentum and heat energy transfer, structural vibrations coupled with fluid pressure fluctuations (fluid/structure interactions), and the bi-directional nature of the heat transfer, which might also create a transient effect. Based on the previous application of these methods, the DSMC method is not applicable for particular structural vibrations since the method has limited application for rarefied gas flows with density variations (Bird, 1994). More importantly, use of DSMC gives time-independent averaged properties, which makes it difficult to directly estimate dynamic fluid properties such as viscosity, diffusion coefficients and kinetics (Jover *et al.*, 2012). Additionally, DSMC is still in the early stages of development for the simulation of bi-directional heat conduction and requires a major modification to include coupled momentum and heat energy transfer simultaneously. This creates a great challenge for DSMC simulation solvers to extend their features (Darbandi & Roohi, 2011). In contrast, MD has been efficiently implemented for the simulation of coupled fluid/solid interactions, structural vibrations, and bi-directional heat transfer. For instance, MD has been used to simulate flexural and tensile dynamic deformation behaviour including the vibrational frequencies of nickel (Ni) nanowire beams due to flexural bending (Mohan & Liang, 2008). In addition, MD was used successfully to simulate nanoscale effects by Kim (2009) and Banerjee (2008), in which coupled momentum and heat transfer were considered at the solid/fluid interface. MD has been used successfully in recent decades to simulate nanoscale flow because of its extensive applicability for complex flow physics and its accuracy. Hence, one may conclude that the MD method has the necessary features to simulate the physical phenomena simultaneously. A comparison of the simulation capabilities of the preferred methods, LBM, DSMC and MD, is shown in Table 1, which indicates that MD is the most suitable method for the simulation of acoustic wave propagation in CNTs.

This paper presents a review of previous MD simulations of relevance to molecular modelling of nanoscopic acoustic absorption mechanisms. The purpose of this review is to provide an overall assessment of MD simulation capability for various applications in nanoscale flow and acoustic problems and, in addition, to present a comparison of the previously simulated physics against the phenomena relevant to the current problem. Possible simulation difficulties/limitations in the audible frequency range will also be considered.

Table 1. Comparison among the preferred methods based on the simulation capability to capture the physical phenomena required for nanoscale acoustic flow modelling indicating MD as the most suitable method.

Approach	Structural Vibration	Bi-directional Heat Transfer	Compressible Media	Acoustics
LBM	X	X	X	√
DSMC	X	X	√	√
MD	√	√	√	√

2. MD SIMULATIONS OF NANO CHANNEL FLOW AND ACOUSTICS PROBLEMS

With recent developments in computational performance, MD has emerged as a popular simulation tool for nanoscale flow simulations. In the last decade, MD has been applied for the simulation of a variety of fluid flow phenomena on the nanoscale (Kandemir & Sevilgen 2008; Karniadakis *et al.*, 2005; Kim, 2009; Banerjee 2008).

This review is primarily focused on the capability of MD methods, based on their previous application to simulate the phenomena that are expected to accurately model nanoscale acoustic absorption in CNTs. A schematic of these likely physical phenomena is shown in Figure A in the Appendix, which includes:

1. Wave propagating media: polyatomic gas, compressibility of the media (changing density).
2. Acoustics: gas compression, vibrating piston in a simultaneous motion to generate wave front, hard wall.
3. Vibration: structural wall, pressure induced vibration, vibration induced pressure (fluid-structure interaction).
4. Heat Transfer: gas-solid-gas, gas-gas, solid-solid, thermo-acoustics: compressed gas heated and expanded gas cooled.
5. Coupling for multi-physics problem: bi-directional effects/coupling between the fluid and structure for fluid-structure interaction and heat transfer.

2.1 Wave propagating media at the nanoscale

In the case of acoustic wave propagation through a CNT, the propagating media will be air, which is a polyatomic, gaseous, and compressible medium. Compressibility of the medium will be an important factor for acoustic losses by heat conduction (Fahy, 2005; Ingard, 1994; 2009). This compression effect will be far greater for nanoscale wave propagation than for microscale flow due to the frequent collisions of molecules with the wall, together with collisions between the molecules. Compressibility will also be responsible for variations of the velocity and temperature profile of the flow. In the case of diatomic or polyatomic gas molecules, relaxation effects will dominate due to the transformation of transla-

tional energy into other forms of molecular energy involving rotation and vibration (Fahy, 2005). Thus, the absorption and dispersion of sound in a gas will have losses associated with the redistribution of the internal energy of the molecules known as relaxation losses (Hanford, 2008). Hence, it is essential for the selected method to be able to model the complex compressibility effect and relaxation process for diatomic or polyatomic molecules (Hanford, 2008). In this section, applications of MD simulations to investigate the flow properties of various compressible media, such as N_2, O_2, argon, methane, ethane, and air in nanochannels, is reviewed to demonstrate the capability of MD to simulate the physics.

A number of MD simulation studies have investigated fluid transport and diffusivity in nanochannels. Mutat *et al.* (2012) simulated methane (CH_4) gas flow through a single-walled carbon nanotube (SWCNT) by equilibrium (EMD) and non-equilibrium (NEMD) molecular dynamics to investigate molecular diffusion (self and transport diffusivity) of gas inside nanopores at various tube loadings. Ban & Huang (2012) studied gas permeation of CO_2/N_2 through a carbon nanotube membrane using MD to investigate the potential of flue gas separation. The purpose of the study was to develop and validate transport theory for gas separation and to gain a fundamental understanding of gas permeation through CNT membranes. Results showed that the simulations agreed with experimental measurements. Arora & Sandler (2006) conducted a similar study using EMD simulations to determine the separation performance of a nanotube membrane by simulating mass transport of pure N_2, O_2, and their mixture as air in a SWCNT at 100 K. Mao & Sinnott (2000) used MD simulations to study the movement of polyatomic molecules through nanotubes by modelling the diffusive and dynamic flow of methane, ethane and ethylene through SWCNTs at room temperature, while Tuzun *et al.* (1996) used MD to study helium and argon flow inside CNTs. Similarly, Liu *et al.* (2010), Sokhan *et al.* (2004) and Ackerman *et al.* (2003) used MD simulations effectively to study the self and transport diffusivity of N_2, Ar and Ne. In most of these cases, MD simulations captured the nanoscale transport properties successfully.

Other MD studies have mainly been concerned with flow properties such as the frictional stress, slip velocity, and slip length of typical compressible fluids flowing through the nanotubes. Kandemir & Kaya (2012) simulated lid-driven micro-cavity gas flow using hard-sphere molecules and a single-species gas. They investigated the major flow characteristics of lid-driven cavity flow (such as the formation of the primary vortex, pressure variations, and the velocity profile) under varying subsonic speeds and lid temperatures. Interesting behaviour of the compressibility in the micro-cavity was observed at low Mach numbers even though the regime is widely considered to be within the incompressible flow region. It was concluded in this work that compressibity and temperature variations in the flow could easily be included in MD with current computational capabilities; however, it was suggested that greater computational resources would be required to simulate higher Reynolds number (Re) flows. Mantzalis *et al.* (2011) used MD simulation to examine layering of CO_2 gas transported through a SWCNT subjected to variations of pressures and temperatures of 1-20 bar and 300-400 K, respectively, while Hu *et al.* (2007) simulated the air flow through an array of carbon nanotubes using MD. Longhurst & Quirke (2007) simulated temperature-driven pumping of decane through SWCNTs to investigate the possible applications of nanotubes for dynamic nanoscale reaction vessels. Although their simulation results were qualitatively accurate, they showed that the miniature vessels of nanotubes can develop very high pressures in the vessels due to the strong capillary forces, which also act to draw the molecules into nanopores. Chaudhri (2005) implemented MD methods to understand the fluid flow properties inside nanotubes by simulating argon gas flow inside SWCNTs. He studied the transport behaviour and structure of argon atoms for flow simulation cases similar to those of Tuzun *et al.* (1996), Dendzik *et al.* (2004), Lee & Sinnott (2004) and Mao and Sinnott (2000). Sokhan *et al.* (2002) studied steady-state Poiseuille flow in nanopores using NEMD by simulating the gravity-driven flow of methane through a long cylindrical pore of SWCNT at ambient conditions. Lee & Sinnott (2004) conducted NEMD simulations of gas flow of methane in several open-ended SWNCTs to study the transport behaviour of flow through nanotubes. They found that the molecular flow rate depends on the tube diameter but does not depend on the symmetric helical structure of the nanotubes, i.e. the methane gas transport does not get affected by the difference in helicities (armchair/zigzag) of CNTs. They observed non-equilibrium transport behaviour of methane flow caused by the minuscule dimensions of the systems indicating the unique mechanism for nanoscale flow. Liu *et al.* (2012) conducted an experimental investigation and MD simulations of the gas flow characteristics through nanopores with an emphasis on the friction and gas viscosity. They conducted the experiment with controlled flow rates in a flow tube with a pressure drop across nanopore membranes. Their MD simulations were of argon gas and an argon nanopore made of fixed atoms. MD results showed that the nanoscale flows have a much lower viscosity and friction coefficient than those in a microscale channel, due to less frequent intermolecular collisions between the gas molecules and more frequent collisions with the wall.

Barisik *et al.* (2010) used MD for the simulation of linear Couette flow of argon at Kn=10, which created a new benchmark for the simulation of high Knudsen number transition flows using MD. In their further work (Barisik & Beskos, 2011), they utilised MD for simulating shear-driven gas flows in nanochannels and revealed that the surface (solid) -gas (fluid) interactions had a significant effect on the velocity, density, shear stress and normal stress distributions at the interface. These kinds of behaviour were previously confirmed by other researchers (Kim, 2009; Banerjee, 2008) for nanoscale flow channels, which indicate the potential capability of the MD method, without requiring major modifications other than a slight improvement to the boundary wall model or potential energy model based on the requirements of the application under consideration.

2.2 Acoustics (pressure fluctuation and wave front)

A sound wave is a combination of compression and expansion of the propagating medium with rapid pressure fluctuations, which cause rapid changes in the velocity, density, and temperature of the medium. Due to these changes of temperature and velocity, thermal and velocity gradients will coincide with variations of pressure and density. As a consequence, in the case of nanoscale flow, boundary motion or body forces and momentum and heat transfer will occur simultaneously (Kim, 2009; Banerjee, 2008), and will have a substantial effect on the acoustic absorption mechanisms. Therefore, coupling of momentum and heat transfer during the simulation is essential for the selected method.

Nanoscale wave propagation involves acoustic flows with large disturbances due to frequent collisions with the wall (Bird, 1994), which will cause large variations in the temperature and density profile. In order to distinguish the large

flow disturbances, a large system size with large number of molecules must be simulated, which requires long simulation times (Bird, 1994). Therefore, it is necessary for the selected method to be suitable for large flow disturbances while yielding low statistical error. Due to the oscillatory motion of acoustic waves and the small characteristic length of the channel, there will be a possibility of transient and simultaneous heating and cooling of the gas across the channel. This effect is known as the thermo-acoustic effect (Swift, 2002), which the simulation method should be able to model.

Various MD studies of acoustic problems have been performed to simulate shock wave propagation in gaseous media. Yano (2012) applied large-scale MD simulations to clarify the presence of nonlinear and non-equilibrium processes in large amplitude and high frequency (~1 GHz) sound wave propagation in a gas (argon). It was observed that the wave front exhibited a stream-like profile instead of a wave-like profile, with the direct transport of mass, momentum, and energy, which moves with a larger speed than the sound speed of an ideal gas (Yano, 2012). This behaviour confirms the deviation from the classical behaviour of high-frequency linear standing-wave analysis. Deladerriere *et al.* (2008) used MD to measure the variation of the velocity of acoustic wave propagation in simplified nuclear glasses and pure silica, in order to understand the decrease in the Rayleigh velocity in materials subjected to elastic irradiation (Deladerriere *et al.*, 2008). Makeev *et al.* (2009) conducted a similar molecular simulation to study shock-wave propagation in a CNT reinforced composite material in an amorphous silicon carbide matrix. Their objective was to understand the effect of the presence of aligned nanotubes and their dynamic and structural changes on the shock wave structure and the composite materials. It was found that the presence of CNTs reduced the shock–wave velocity and modified the wave-front structure in impact velocities, which was considered to be due to changes in the degree of shock-induced heating and the resultant variation of viscosity in the shock-loaded target. Hofmann (2003) applied MD for shock-wave simulations in argon at critical density and a temperature of 306 K. He simulated steady and unsteady effects of shock-wave formation by using a piston set in impulsive motion (with velocities ranging from 300 to 900 m/s) to demonstrate the resulting density and temperature variations and directional temperatures across the shock waves. Valentini & Schwartzentruber (2009) studied the structure of normal shock waves in dilute argon by coupling the MD domain with a computational fluid dynamics (CFD) solver using a realistic Lennard-Jones (LJ) potential. The continuum solver was coupled with the atomistic region to correctly generate the inflow and outflow particle reservoirs, which allowed the simulation to achieve sufficient statistical accuracy to calculate the structure of the normal shock wave. A detailed comparison with DSMC and MD results showed near-perfect agreement for density and temperature profiles in the high temperature range of 300–8000 K. However, it was shown that the DSMC simulation with the variable-hard-sphere (VHS) collision model was not capable of reproducing the shock profiles, particularly the temperature profiles, over a broad temperature range. It was concluded that MD might be a valuable tool for more complex flows including highly non-equilibrium molecular processes for which experimental data is not unavailable. Valentini *et al.* (2013) studied the structure of normal shock waves in noble gas mixtures of Xe/He and Ar/He of various compositions. The MD results showed an overall good agreement with experimental data although two discrepancies were found: the prediction of the monotonic rise in the density profile for Xe/He shocks instead of an overshoot as observed in experiments, and the prediction of an overshoot in the temperature profile for Ar/He mixtures that was absent in the experiments. They showed that MD simulation is computationally feasible and capable of reproducing the experimental results for shock-wave structures at low densities. These implementations of MD again confirm its wide range of applicability for the complex physics of flow problems in acoustics.

2.3 Structural vibration (fluid/structure interactions) at the nanoscale

A CNT forest grown from a substrate material is shown in Figure 1b. The CNT walls are thin and are mounted such that they will vibrate like a cantilever beam. Acoustic pressure waves will induce structural vibrations in a tube as shown in Figure A(d) in the Appendix. Moreover, thermal molecular interactions at the interface between the gas molecules and nanotube atoms will create thermal vibrations of the solid atoms (Kim, 2009). These oscillations will create axial and rotational vibrations of the tube, which will also occur simultaneously with the oscillatory pressure wave. Hence the ability of the selected method to model fluid/structure interactions and structural vibrations is required.

Chen *et al.* (2011) simulated water flow passing a SWCNT using MD and continuum mechanics (CFD) to investigate the flow resistance and energy transfer between water molecules and CNTs induced by the nanoscale fluid/structure interactions. They observed a linear dependence between the drag force and flow velocity at a small Reynolds number up to 0.1, which could be predicted by Stokes law. However, at higher speeds (i.e. elevated Reynolds number), a significant deviation from linearity was identified from the MD simulations, indicating a reduction in the viscosity due to friction-induced local heating and flow-induced structural vibrations, resulting in a weaker drag force, which was not captured by CFD simulations. A significant increase of the CNT vibration was observed at higher flow speeds, induced by the excitation of low-frequency vibration modes, which had a substantial effect on energy transfer between the water molecules and the nanotube, indicating the importance of fluid/structure interactions for nanoscale flows. Li & Hong (2007) simulated gas transport of Ar molecules through silver (Ag) nanochannels using MD. They investigated the diffusion of gas under the combined effects of the vibration of the channel, gas/wall binding energy, and channel size. It was found that the vibration of the channel played an important role in gas transport through the nanochannels for strong fluid/structure binding energies. Insepov *et al.* (2006) used MD simulations to predict a new "nanopumping" concept using carbon nanotubes that would enable the pumping of gases or liquids through nanochannels. Fluid/surface interactions between the H_2 and He gas atoms and the SWCNT were explicitly incorporated in MD simulations to properly capture the "nanopumping" effect (i.e. activation of an axial gas flow inside the nanotubes at a macroscopic high velocity in the direction of a travelling surface wave). However, the characteristic frequency of the wave for activating the nanopumping effect was too high compared to the frequency required for the velocity to reach a hyperthermal value and the maximum effect was observed at approximately 38 THz (based on the chosen nanotube length of 10 nm). The effect was found to depend on the ratio of nanotube length and the wavelength of the surface wave.

2.4 Heat transfer (thermo-acoustic effect and heat conduction) at the nanoscale

Based on previous studies of nanoscale heat transfer (Kim, 2009; Banerjee, 2008), heat transfer plays a major role in nonlinearity and deviations from continuum behaviour in acoustic wave propagation. Although thermal interface resistance is the major factor contributing to the anomalous behaviour of nanoscale heat transfer, there will also be bi-directional heat transfer between the fluid and solid for CNTs in air: heat conduction through the solid wall and to the fluid outside the wall will occur, due to the fluctuating motion of the acoustic flow with the combination of compression and expansion. These various heat transfers will contribute significantly to the development of the thermal boundary layer, which is important for sound absorption at a boundary in a gas. Therefore, the selected method must be able to simulate bi-directional heat transfer, which should also be coupled with the variation in momentum.

Banerjee (2008) used MD to simulate hydrogen storage in CNTs and CNT growth and heat transfer in order to characterise nanoscale charge, mass, and thermal transport. He identified discontinuities in thermal transport and a novel growth mode for nanotubes that was successfully validated by experiment. Kim (2009) applied MD to simulate heat transfer in nanoscale liquid films. He simulated fluid/solid thermal interactions by accounting for thermal oscillations of the wall molecules and their influence on the fluid molecules, overcoming the limitations of previous simulations that considered the wall molecules as fixed molecules, and which were therefore unable to simulate the work done by moving wall molecules on the fluid. This method was found to successfully model heat conduction in nanochannels, allowing coupled momentum and energy transport to be simulated simultaneously (Kim *et al.*, 2008). Osman & Srivastava (2005) used MD to investigate transient heat-pulse propagation in SWCNTs of varying chirality and diameter. They studied temporal and spatial variations of the kinetic temperature in CNTs using MD simulations and observed the propagating wave packets induced by the heat pulse. It was found that heat pulses of picosecond duration generated several wave packets that propagated at the speed of sound corresponding to longitudinal acoustic (LA) phonons and twisted phonon modes (TW), second sound waves, and diffusive components. The simulations revealed that zigzag CNTs carry more heat energy than armchair nanotubes, which explains why zigzag CNTs show higher steady-state thermal conductivity than armchair CNTs, as reported in previous investigations. Thomas *et al.* (2010) applied MD simulations to examine the thermal conductivities (transition to fully diffusive phonon transport) of empty and water-filled SWCNTs with varying diameter and tube length. It was found that the required length to obtain fully diffusive thermal transport and the magnitude of the conductivity in empty CNTs decreased with tube diameter and that the conductivity was 20–35% higher than that in water-filled CNTs. The reduction of the thermal conductivity in water-filled CNTs was attributed to substantial low-frequency phonon scattering due to interactions with water molecules, indicating the influence of solid/liquid interactions on the thermal conductivity of nanotubes.

3. POTENTIAL CASES FOR MD SIMULATION OF ACOUSTIC ABSORPTION MECHANISMS

No MD simulations have been carried out previously for either compressible or incompressible nanoscale flow in which all physical phenomena relevant to acoustic absorption within CNTs in air were simultaneously considered. All of the cases were evaluated by comparing their simulated physics against the phenomena deemed relevant to acoustic absorption. This comparison is given in Table A in the Appendix. As indicated in the table, most previous MD simulations of nanoscale phenomena have been conducted to investigate flow properties. None have accounted for fluid/structure interactions, bi-directional heat transfer, or acoustic wave propagation in the audible frequency range or even in the ultrasonic frequency range. In order to verify that MD can simulate acoustic absorption mechanisms, for which a number of multi-physics criteria must be considered simultaneously, we have considered four different cases of previous molecular simulations, those conducted by Chen *et al.* (2011), Carlborg *et al.* (2008), Sokhan *et al.*, (2002), and Hadjiconstantinou & Garcia (2001). These validate the physics of structural vibration, bi-directional heat transfer, flow properties and compression effects, and acoustic effects, respectively. While each of these simulation cases does not replicate all of the physics that is relevant to the current problem, each case captures a subset of the relevant phenomena and together they can certainly demonstrate the ability of MD to account for all of the required physics at the nanoscale. The case presented by Chen *et al.* (2011) can be used to validate fluid/structure interactions between CNTs and water molecules, and structural vibrations of CNTs induced by energy transfer between the fluid and solid wall. The disadvantages of this case are the incompressible nature of the fluid flow and lack of consideration of flow inside the CNT. Flow inside the CNT might be important for acoustic wave propagation, in which gas flow occurs both inside and over the CNTs. Regarding the validation of acoustic effects, Hadjiconstantinou & Garcia (2001) simulated sound waves propagating in a dilute hard-sphere gas through a rectangular microchannel (not a CNT) using DSMC. These DSMC results can be compared with MD simulation results for an analogous physical arrangement. The MD simulation of transient heat-pulse propagation in a CNT conducted by Osman & Srivastava (2005) provides a suitable platform for simulating heat transfer in nanotubes, as the effects of phonon modes were taken into consideration. However, the ideal validation case would include the influence of solid/liquid thermal interactions. Nevertheless, Osman & Srivastava's (2005) study is an appropriate example for validating the simulation capability of MD for thermal energy transport in nanotubes. The simulation case of thermal boundary resistance conducted by Carlborg *et al.* (2008) can be considered to simulate the effect of fluid/structure interactions on heat transfer for capturing the bi-directional nature of heat flow. Their (Carlborg *et al.*, 2008) study used NEMD to simulate the heat pulse propagation in SWCNTs surrounded by argon matrices and demonstrated the contribution of the surrounding matrix and matrix phase (solid/liquid) on the energy transfer between the SWCNT and matrix. The simulation of methane gas flow in CNTs performed by Sokhan *et al.* (2002) is useful for validating the flow properties for a fluid through a CNT, as the properties were examined with variations of methane/CNTs interactions and the effect of solid surfaces on the fluid taken into consideration.

4. LIMITATIONS OF MD SIMULATIONS IN 2 Hz – 20 kHz FREQUENCY RANGE

MD has been applied to simulate solids, liquids, and dense gases because of its simplicity and accuracy, since it requires only the specification of a potential energy function to describe the interactions between the atoms (Valentini *et al.*, 2009). The use of potential energy functions to describe

complex systems makes MD ideal for the type of multi-physics simulation presented in this paper (Valentini *et al.*, 2009; 2013). However, the feasibility of a molecular simulation is limited by the required simulation time, which is determined by the mean collision time. For instance, in a simulation of a rarefied gas (density~ 10^{-4} kg/m^3), the mean collision time, τ, will be on the order of microseconds, as τ scales as the inverse of density. There is a wide separation of time scales between τ and the simulation time step of femtoseconds required to capture the interactions between colliding molecules, resulting in the need for substantial computational resources (Valentini *et al.*, 2009; 2013). Molecular simulations of acoustic wave propagation in gaseous media in the audible frequency range (0.02–20 kHz) are similarly limited, and must be able to simulate collision times of milliseconds (~10^{-3} s), thus requiring the simulation of time scales separated by 12 orders of magnitude. This is the reason why no MD studies to date have treated acoustic wave propagation in dilute gases in the acoustic frequency range. Previous molecular simulations using MD, DSMC, or LBM for acoustic wave propagation at the nanoscale were instead conducted with large amplitudes and high frequencies, in the GHz range (Hadjiconstantinou, 2001; 2002; 2003; Danforth & Long, 2004; Buick *et al.*, 2000; Yano, 2012; Makeev *et al.*, 2009). To achieve faster computations using MD simulations, atoms can be modelled as hard spheres, providing computationally inexpensive inter-atomic potential functions and creating strictly elastic collisions and allowing the system to be propagated with a variable time step corresponding to the occurrence of the next collision (Jover *et al.*, 2012; Hofmann, 2003). Salomons & Mareschal (1992) conducted pioneering MD simulations of a monatomic hard-sphere gas to obtain fluid properties across a shock wave (Valentini *et al.*, 2009). The description of molecules as hard spheres may provide a simplifying representation of intermolecular interactions that results in a less computationally expensive MD simulation, but long-range attractive interactions, coupling to continuous structural vibrations, and inelastic collisions cannot be readily captured (Valentini *et al.*, 2009). Furthermore, none of the widely available simulation packages, such as GROMCS, DL_POLY, LAMMPS and NAMD, are suitable for handling discontinuous potential functions natively (Jover *et al.* 2012). Several alternative approaches have been used to reduce the computational expense of MD simulations. For example, Valentini *et al.* (2009) used MD simulation to compute parameters and determine functional relations for collision models in DSMC, which could then produce accurate results more efficiently than MD. Performing a large-scale MD simulation at the millisecond scale can be achieved using supercomputers.

5. CONCLUSION

This paper presents a review of previous research on the application of molecular dynamics (MD) to study phenomena relevant to investigating nanoscale acoustic absorption mechanisms. A review of the use of MD simulations to study nanoscale flow and acoustics found that most of these simulations have been employed to explore nanoscale flow properties. Few simulations have considered fluid/structure interactions by accounting for vibrations. No MD simulations of acoustic wave propagation have been conducted in the audible frequency range. This review provides insight into the requirements of MD methods for successfully conducting molecular simulations to explore acoustic absorption mechanisms at the nanoscale. In particular, MD capabilities must be extended to the millisecond time scale to permit the study of acoustic wave propagation in the audible frequency range, which requires considerable computational resources. Development of an alternative simulation approach to MD may be required, although no potential method has been identified.

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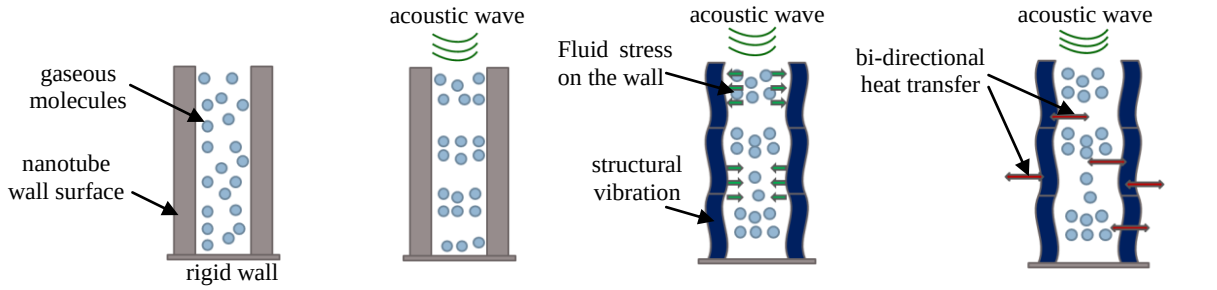
Appendix



(a) Wave propagating media (b) Acoustics (c) Structural vibration (d) Bi-directional heat transfer

Figure A. Schematics of physical phenomena required for acoustic flow modelling.

Table A: Comparison of potential validation cases for MD simulation of nanoscale flow indicates the suitability of those cases for each physical phenomenon.

Case	References	Structural Vibration	Bi-directional Heat Transfer	Compressible media	Acoustics	Approach	Material-Media
1.	Mantzalis *et al.* (2011)	X	X	√	X	MD	SWCNT-CO_2
2.	Ban & Huang (2012)	X	X	√	X	MD	SWCNT-CO_2/N_2
3.	Mutat *et al.* (2012)	X	X	√	X	DCV-GCMD & NEMD	SWCNT-CH_4
4.	Liu *et al.* (2010)	X	X	√	X	GCMC & MD	SWCNT bundle - Ar
5.	Jalili & Majidi (2007)	X	X	√	X	MD	SWCNT- Xe, Kr
6.	Li & Hong (2007)	√ (partially)	X	√	X	MD	2 nm nano-channel of Silver (Ag)- Ar
7.	Hu *et al.* (2007)	X	X	√	X	MD	SWCNT - Air
8.	Arora & Sandler (2006)	X	X	√	X	EMD	SWCNT – N_2/O_2/Air
9.	Insepov *et al.* (2006)	√	X	√	X	MD	SWCNT – H2/He
10.	Chaudhri (2005)	X	X	√	X	MD	SWCNT –Ar
11.	Tuzun *et al.* (1996)	X	X	√	X	MD	SWCNT – He/Ar
12.	Liu *et al.* (2012)	X	X	√	X	MD	Solid Ar – Gaseous Ar
13.	Dendzik *et al.* (2004)	X	X	√	X	MD	SWCNT – Ar
14.	Kos´mider *et al.* (2004)	X	X	√	X	MD	SWCNT – Ar
15.	Lee & Sinnott (2003)	X	X	√	X	MD	SWCNT – O_2
16.	Lee & Sinnott (2004)	X	X	√	X	MD	SWCNT-CH_4
17.	Mao & Sinnott (2000)	X	X	√	X	MD	SWCNT-CH_4/C_2H_6/C_2H_4
18.	Sokhan *et al.* (2004)	X	X	√	X	MD	SWCNT- N_2
19.	Ackerman *et al.* (2003)	X	X	√	X	DCV-GCMD & NEMD	SWCNT- Ar/Ne
20.	Sokhan *et al.* (2002)	X	X	√	X	NEMD	SWCNT - CH_4
21.	Chen *et al.* (2011)	√	X	√ (partially)	X	MD, CFD	Rigid\flexible SWCNT – SPCE/TIP3P Water
22.	Osman & Srivastava (2005)	X	√	X	X		SWCNT
23.	Thomas *et al.* (2010)	X	X	√	X	MD	SWCNT-Water
24.	Yano *et al.* (2012)	X	X	X	√ (partially)	MD	Rectangular box - Ar
25.	Hadjiconstantinou & Garcia (2001)	X	X	X	√	DSMC	Rectangular domain - Ar

Abbreviations:

- **DCV-GCMD**: Dual control volume-grand canonical MD
- **DSMC**: Direct Simulation Monte Carlo
- **DWCNT**: Double walled carbon nanotube
- **EMD**: Equilibrium Molecular Dynamics
- **GCMC**: Grand Canonical Monte Carlo
- **MD**: Molecular Dynamics
- **NEMD**: Non-Equilibrium Molecular Dynamics
- **SWCNT**: Single walled carbon nanotube