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Mathematical modelling in nanotechnology

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The interaction of nano particles with conventional materials dramatically changes all the physical parameters, which usually characterize the bulk material. The nano particles constitute highly reactive isolated sites to the extent that it leads to a change in the electronic structure of the nano composite, and accordingly all the physical properties, such as thermal, mechanical and electrical properties become different from those of the bulk material. To successfully exploit nano composites as components and devices, this fundamental shift of physical properties must be properly understood and accurately modelled. While experimentation is crucial, a theoretical understanding is also necessary and with changed physical parameters, existing continuum theories may still be able to capture critical phenomena. This paper provides an introduction to some of the issues and the theoretical developments in nanotechnology involving the three topics of the enhanced thermal conductivity of nanofluids, electrorheological fulids and the mechanics of carbon nanotubes. It is presented with a view to identifying those areas where applied mathematical modelling might yield important insights.

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N. Thamwattana* and J. M. Hill*

Abstract

The interaction of nano particles with conventional materials dramatically changes all the physical parameters, which usually characterize the bulk material. The nano particles constitute highly reactive isolated sites to the extent that it leads to a change in the electronic structure of the nano composite, and accordingly all the physical properties, such as thermal, mechanical and electrical properties become different from those of the bulk material. To successfully exploit nano composites as components and devices, this fundamental shift of physical properties must be properly understood and accurately modelled. While experimentation is crucial, a theoretical understanding is also necessary and with changed physical parameters, existing continuum theories may still be able to capture critical phenomena. This paper provides an introduction to some of the issues and the theoretical developments in nanotechnology involving the three topics of the enhanced thermal conductivity of nanofluids, electrorheological fulids and the mechanics of carbon nanotubes. It is presented with a view to identifying those areas where applied mathematical modelling might yield important insights.

Introduction

The prefix nano means one billionth (i.e. 10^{-9}), so that a nanometer is one billionth of a meter. To emphasize how small a nanometer is, a human hair measures 50,000-100,000 nanometers across and the smallest objects which might be seen by the unaided human eye are approximately 10,000 nanometers (Ratner and Ratner, 2002). The word nanotechnology is used to describe technology performed on the nanoscale, typically less than a 1000 nm, and which has applications in the real world. The development

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of nanotechnology requires the collaboration of all of the sciences. At the nano level, the physical properties of materials, such as magnetic, electrical and elastic properties, are fundamentally different from those at the macro scale and it is important to appreciate at the outset that all such properties depend on scale as well as on the material. There are three important effects which distinguish nano-behaviour, and which do not occur in the macro environment; these are:

- interfacial or surface effects,
- the effects of scale,
- quantum effects due to a changed electronic structure.

All three effects are inter-dependent and consequences of the extremely small size. The first is the notion that nano particles are not inert in the host material, and that there is some interaction between the nano particle and the surrounding material, which is often modelled by a layer, which surrounds the nano particle but having different physical properties. The second notion is a statement that the associated mean-free path of the physical phenomena in question may well exceed the object dimensions, which essentially means that the physical process might "jump" the object. The third effect arises since the nano particles are so small that they impinge on the electronic structure of the host material, and change it in a manner which is not well understood, and which is not able to be accurately predicted. These three effects are not exclusive to one another, but are inter-related and rather serve to highlight important issues arising at the nano-scale. To successfully develop nanotechnology, the major challenges are to properly understand materials properties and, also to be able to correctly predict their behaviour under known conditions. While the sciences such as biology, chemistry and physics are important in terms of the determination of materials properties, mathematics provides the necessary modelling tool, which give the power of a reliable predictive capacity. In this paper, we review three particular areas; the enhanced thermal conductivity of nanofluids, the electrorheological effect of nano suspension liquids and the mechanics of carbon nanotubes, for which applied mathematical modelling might be effective.

Due to technological devices approaching the micro- and nano-scale, the requirement to cool such devices as quickly as possible has become an important issue. The use of traditional heat transfer fluids, such as water, oil and ethylene glycol has shown to be ineffective. Due to the greater thermal conductivity of solids than that of liquids, the suspending of solid particles in a liquid is expected to enhance the thermal conductivity of the system.

However, the suspension of particles of micrometer and larger sizes may cause the problems of abrasion, clustering and then settling and clogging the channels. This is a major problem particularly for micro- and nanotechnology. With this in mind, a new class of heat transfer fluids have been introduced, namely nanofluids. These fluids comprise a colloidal of solid nano particles in conventional heat transfer fluids. Generally, the sizes of the particle are below 100 nm and the volume fraction of nano particles used is in an extremely small range, 0.00026% to 10%. With their extremely small size and small volume fraction used, nanofluids form very stable colloidals, which are unlikely to cause settling and clogging problems. Further, experiments find a greater enhancement of thermal conductivity of nanofluids, for example, Eastman *et al.* (2001) show that only 0.3% volume fraction of 10 nm Cu particles in ethylene glycol can enhance the thermal conductivity up to 40%. Similar experimental results can be found elsewhere (see for example, Masuda *et al.* 1993, Lee *et al.* 1999, Wang *et al.* 1999, Choi *et al.* 2001, Patel *et al.* 2003 and Hong and Yang 2005). In this paper, we review some of the mathematical models which attempt to explain this phenomena.

This paper also focuses on electrorheological (ER) fluids, which are referred to a suspension of dielectric particles in non-conducting fluids. With an applied electric filed, the particles become polarized forming dipole chains and aggregating in columns, which leads to increases in viscosity and the shear stress of fluids. The ER effect is rapid, continuous with changes of electric field strength and completely reversible. ER fluids have been used in a number of applications. In the automotive industry ER fluids are used in many parts, such as electrically switched clutches, brakes, locks and shock absorbers. Recently, the use of ER fluids also extends to the area of hydraulic valve, robotic control and tension control system. For simplicity, we only consider here the situation where two bounded charge spherical particles embedded in a non-conducting medium under the external electric field. While there are a number of techniques, which are used to calculate the electrostatic force of attraction, we particularly employ the re-expansion method (Washizu, 1992). In this paper, we give an introduction to this method, and we present results compared to those obtained from other existing techniques.

Finally, this paper provides a general introduction to carbon nanotubes as well as focusing on the mathematical modelling for determining their mechanics. Because of their extreme properties, such as high strength, low weight, flexibility and thermally stable, both multi-walled and single-walled carbon nanotubes have many promising applications in nanomechanical systems. However, this is still a challenging area due to the lack of a theoretical understanding of their behaviour, and also their behaviour when they interact with the system environment. In this paper, we investigate the phenomenon

of nanoscale oscillators, or gigahertz oscillators (Zheng and Jiang, 2002). Based on Cummings and Zettl (2000) and Yu *et al.* (2000), Zheng and Jiang (2002) find that the sliding of the inner-shell inside the outer-shell of a multi-walled carbon nanotube can generate oscillatory frequencies in the gigahertz range. While there are difficulties for micromechanical oscillators to reach a frequency in the gigahertz range, it is possible for nanomechanical systems to achieve this. Here, we review some of the underlying mechanisms of the nanoscale oscillators and consider the mechanical model proposed by Zheng *et al.* (2002).

The following three sections deal with mathematical models for problems of the enhanced thermal conductivity of nanofluids, electrorheological fluids and the mechanics of carbon nanotubes respectively.

Thermal conductivity of nanofluids

As electronic devices become smaller and smaller, the amount of heat generated is proportionally higher and as a result the more effective heat transfer fluids are essentially needed. To serve this purpose, a new class of fluids called nanofluids is introduced. Nanofluids are engineered by suspending solid nanoparticles into conventional heat transfer fluids so as to enhance the thermal conductivity. Potential mechanisms of enhanced heat transport in nanofluids are proposed as follows.

- Brownian motion of the particles, by which particles move through the liquid and possibly collide, thereby enabling direct solid-solid transport of heat from one to another.

- Collision between base fluid molecules due to Brownian motion enables heat transport between molecules.

- High heat transport in the nano particles, since their thermal conductivity increases because most of their atoms are on the surface.

- Liquid layer at the particle surface, which has a higher thermal conductivity than the liquid itself.

- Nature of heat transport in nano particles. Macroscopic theories assume diffusive heat transport satisfying Fourier's law. For nano particles, heat is carried by phonons, i.e. by propagating lattice vibrations. Such phonons are created at random, propagate in random directions, are scattered by each other or by defects and thus justify the macroscopic description of heat transport. The phonon mean free path is

much shorter in the liquid than in the nano particles. Because the particles move constantly due to Brownian motion, locally they may be much closer and thus enhance coherent phonon heat flow among the particles.

- Effects of nano particles clustering. Keblinski *et al.* (2002) show the enhancement of thermal conductivity of nanofluids as packing fraction decreases and the effective volume of the cluster increases. A further increase of thermal conductivity can take place if particles do not need to be in contact, but just within a specific distance, allowing rapid heat flow between them.

In this section, we summarise some existing theoretical models, which have been used to study this phenomena.

The study of the thermal conductivity of suspensions of solid particles in fluids dates back more than one hundred years ago. Maxwell (1904) proposed the model for the determination of the effective thermal conductivity, k_{eff}, for random spherical particles suspended in fluid, namely

$$k_{eff} = k_f + \frac{3(k_p - k_f)\phi}{k_p + 2k_f - (k_p - k_f)\phi} k_f, \tag{1}$$

where k_f and k_p denote thermal conductivities of the base fluid and the particle respectively. Maxwell equation was derived from the electric permeability calculation for a compound medium on the basis of potential theory. This model is applicable to dilute suspensions for volume fraction $\phi < 1$ in a homogeneous host medium, where particles are considered to be isolated and have no interaction among them. The prediction of k_{eff} from Maxwell equation is accurate to order ϕ. Many authors, including Bruggeman (1935), extend this model to the second order. For a binary mixture of homogeneous spherical inclusions, the Bruggeman model gives

$$k_{eff} = \frac{(3\phi - 1)k_p + (2 - 3\phi)k_f + \{[(3\phi - 1)k_p + (2 - 3\phi)k_f]^2 + 8k_p k_f\}^{1/2}}{4}. \tag{2}$$

This model is based upon a mean field approach, and it takes into account the interaction among randomly distributed particles. Unlike Maxwell model, Bruggeman equation has no restriction on the volume concentration ϕ of the suspended particles. Furthermore, there are models that do not only take into account ϕ but also the particle shape. Hamilton and Crosser (1962) develop the Maxwell model to include the particle shape factor $n = 3/\psi$, where ψ is the sphericity, which is the ratio of surface area of a sphere, with

volume equal to that of the particle, to surface area of the particle. The Hamilton-Crosser model gives

$$\frac{k_{eff}}{k_f} = 1 + \frac{n(k_p - k_f)\phi}{k_p + (n-1)k_f - (k_p - k_f)\phi} \tag{3}$$

noting that the case $n = 3$ gives rise to Maxwell equation (1). Lee *et al.* (1999) show that Hamilton-Crosser model can be used to predict the thermal conductivity of nanofluids containing large agglomerated particles. The model also confirms that the thermal conductivity of non-spherical paricles is higher than that of spheres. However, the model predictions start to diverge from the experimental data at low volume fractions. This strongly suggests that the particle size is dominant in enhancing thermal conductivity of nanofluids.

Because of the observed nonlinear increases in the thermal conductivity of nanofluids, the proposed mechanisms have been used in collaboration with the existing theories, such as Maxwell's formula and the Hamilton-Crosser model to explain this enhancement (see Table 1). For further details on existing mathematical models of the enhanced thermal conductivity of nanofluids, we refer the reader to Tillman and Hill (2005). Although, a number of models have been proposed, due to the complexity at the nano level, this area still remains a challenging one, and most of the existing theory typically:

- incorporates only the particle shape and the volume concentration, whereas experiments confirm the importance of particle size,
- assume isotropic nano particles,
- assume Fourier's law for diffusive heat transport in both liquid and solid phases,
- do not take into account of the effects of particle clustering,
- do not take into account the particle mobility,
- do not take into account the effect of the liquid/solid interface,
- do not include temperature dependence.

Electrorheological fluids

Electrorheological (ER) fluids consist of suspensions of dielectric nano particles in a fluid of low dielectric constant. With an applied electric filed, the particles become polarized inducing an electrostatic force of attraction.

Table 1: Modifications of Maxwell's formula for predicting the enhancement of thermal conductivity in nanofluids

Modification	Authors	Year
Nanofluid as a binary mixture	Bruggeman	1935
Non-spherical particles	Hamilton & Crosser	1962
Nanoparticles with nanolayer	Yan *et al.*	1986
Maxwell model with nanolayer	Yu & Choi	2003
Ellipsoidal particles with nanolayer	Yu & Choi	2004
Nanoparticle-nanolayer-fluid theory, cluster size distribution	Wang *et al.*	2003
Correction due to Brownian motion	Xuan *et al.*	2003
Correction from both rotation and translational motions	Wang *et al.*	1999

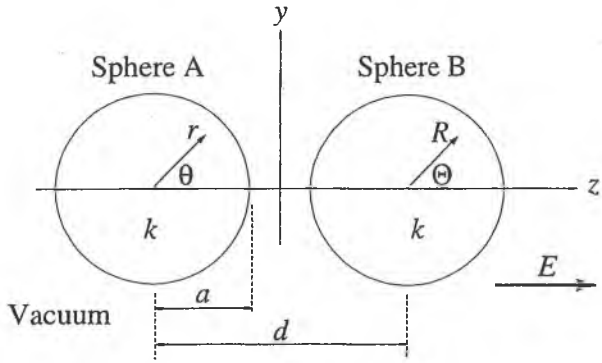

Figure 1: Geometry of the problem.

This then results in the particles forming dipole chains in the direction of the applied electric field. ER fluids are widely used in the automotive industry to make clutches, valves and dampers. In addition, they promise many more applications in the areas of artificial muscles and robotic control.

The problem of electric field induced forces between spherical particles is fundamental to electrorheological fluids. In particular, we consider the case where two spheres of bound charge are embedded in a vacuum and the external electric field is applied in the direction parallel to the line of centers of the two particles (see Figure 1). With an applied electric field, the spheres become polarized and interact with each other, which then generates further polarization. Wang *et al.* (1999) conduct an experiment to measure the field-induced interaction force between two spheres. In the experiment, two 6.3 mm diameter spheres of $SrTiO_3$ are placed at the interstices varying from 0.01 to 0.8 mm, and subject to electric fields of varying strength. Then, these authors compare the experimental result with some theoretical models; dipole model (Coulson, 1958), dipole model with local electric field correction (Davis, 1992a) and finite element method (Davis, 1992b), and state that these three methods are not valid for the case where the gap between two spheres is very small. In this paper, we summarize Cox *et al.* (2005), which attempt to address this issue. The solution technique adopted in Cox *et al.* (2005) is known as the method of multipole re-expansion around an axis of symmetry, which was originally proposed by Washizu (1992). This method allows the solution of Laplace's equation, which is solved at a number of origins, to be re-expanded around any other points lying on the axis of symmetry.

For an electrostatic problem without point sources of charges, the governing equation is Laplace's equation for the scalar electrostatic potential, $\nabla^2\phi = 0$. Since the specification of the problem, shown in Figure 1, is

symmetric around the z-axis, the solution to the Laplace's equation can be written as an expansion in Legendre polynomial and powers of r. Considering the problem, we have the potential in the vacuum outside of both particles

$$\phi_o = \sum_{n=0}^{\infty} \left[a_n \left(\frac{a}{r}\right)^{n+1} \mathrm{P}_n(\cos\theta) + A_n \left(\frac{a}{R}\right)^{n+1} \mathrm{P}_n(\cos\Theta) \right] - Ez, \qquad (4)$$

where P_n is the usual Legendre polynomial of order n. The former term of (4) represents a perturbation created by the polarization of each particle, while the latter term, $-Ez$, is the potential of the applied electric field. Inside the spheres A and B, the potential is respectively given by

$$\phi_i = \sum_{n=0}^{\infty} c_n \left(\frac{r}{a}\right)^{n} \mathrm{P}_n(\cos\theta), \quad \Phi_i = \sum_{n=0}^{\infty} C_n \left(\frac{R}{a}\right)^{n} \mathrm{P}_n(\cos\Theta). \qquad (5)$$

With the multipole re-expansion method (Washizu 1992), the solution of Laplace's equation, which is solved at a number of origins, can be re-expanded around any other points lying on the axis of symmetry. As given in Washizu (1992), the Legendre expansion of an axially symmetric potential in one spherical coordinate system can be re-expanded at another point on the symmetry axis in the form

$$\left(\frac{a}{R}\right)^{n+1} \mathrm{P}_n(\cos\Theta) = (-1)^n \left(\frac{a}{d}\right)^{n+1} \sum_{m=0}^{\infty} \frac{(m+n)!}{m!n!} \left(\frac{r}{d}\right)^{m} \mathrm{P}_m(\cos\theta), \qquad (6)$$

where this expansion is only convergent in the domain $r < d$. Therefore, from (4) and $z = r\cos\theta - d/2$ the potential in the vicinity $r < d$ of sphere A is given by

$$\phi_o = \sum_{n=0}^{\infty} \left[a_n \left(\frac{a}{r}\right)^{n+1} + b_n \left(\frac{r}{a}\right)^{n} \right] \mathrm{P}_n \cos(\theta) - Er\mathrm{P}_1(\cos\theta) + \frac{Ed}{2}\mathrm{P}_0(\cos\theta), \quad (7)$$

where b_n is given in terms of A_n as

$$b_n = -\left(\frac{a}{d}\right)^{n} \sum_{m=0}^{\infty} \left(-\frac{a}{d}\right)^{m+1} \frac{(m+n)!}{m!n!} A_m, \qquad (8)$$

or in terms of a_n,

$$b_n = -\left(\frac{a}{d}\right)^{n} \sum_{m=0}^{\infty} \left(\frac{a}{d}\right)^{m+1} \frac{(m+n)!}{m!n!} a_m. \qquad (9)$$

Once that a_n is determined, by using the expression above the solution for sphere B will be immediately obtained. With the above expressions and the appropriate boundary conditions of the continuity of the potential and the flux at the surface of the sphere, a_n and c_n are found to be given by

$$a_n = \frac{n(k-1)}{n(k+1)+1}\left(\frac{a}{d}\right)^n \sum_{m=0}^{\infty}\left(\frac{a}{d}\right)^{m+1}\frac{(m+n)!}{m!n!}a_m, \quad c_n = -a_n\frac{(2n+1)}{n(k-1)}, \tag{10}$$

where k is the dielectric constant of the particle. Following Washizu and Jones (1996), where the electrostatic force is calculated from Coulomb's law, Cox *et al.* (2005) obtained the explicit equation for the electrostatic force

$$F_e = \frac{4\pi\epsilon_0}{k-1}\sum_{n=1}^{\infty}[(n+1)(k+1)+1]a_n a_{n+1}, \tag{11}$$

where ϵ_0 denotes the permittivity of free-space.

The electrostatic force of attraction between two spheres is shown in Figure 2. From the figure, the result obtained from the re-expansion method is in a very good agreement with experimental results of Wang *et al.* (2003). This method is also shown to be more effective than other techniques employed in the Wang *et al.* (2003) paper. Currently, this method is used by the authors to investigate the cases where the particle geometries are more complicated and the interaction of particles in a chain.

Mechanics of carbon nanotubes

The discovery of carbon nanotubes in 1991 by Iijima creates an enormous impact on nanotechnology. This is due to that carbon nanotubes admit the unique and extreme properties that no man made materials have ever reached. The physical properties, particularly the electrical property, of carbon nanotubes strongly depend on the chirality or the helicity of the tubes. As shown in Figure 3, the chirality is determined by vector $\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2$, where n and m are integers ($n \geq m$), $\mathbf{a}_1$ and $\mathbf{a}_2$ are the base vectors. The vector $\mathbf{C}$ is generally referred to as (n, m). A carbon nanotube is called armchair if $n = m$, zigzag if $m = 0$ and chiral for other cases. The magnitude of the base vectors are $|\mathbf{a}_1| = |\mathbf{a}_2| = 0.246$. From Figure 3, one can find that the circumferential of the carbon nanotube is $|\mathbf{C}|$, which is defined by $|\mathbf{C}| = 0.246(n^2 + nm + m^2)^{1/2}$, and thus the diameter of a carbon nanotube is given by $|\mathbf{C}|/\pi$. As previously stated, the electrical property of a carbon nanotube is dependent on the chirality. If $n - m$ is divisible by 3 then the carbon nanotube is metallic, otherwise is semiconducting.

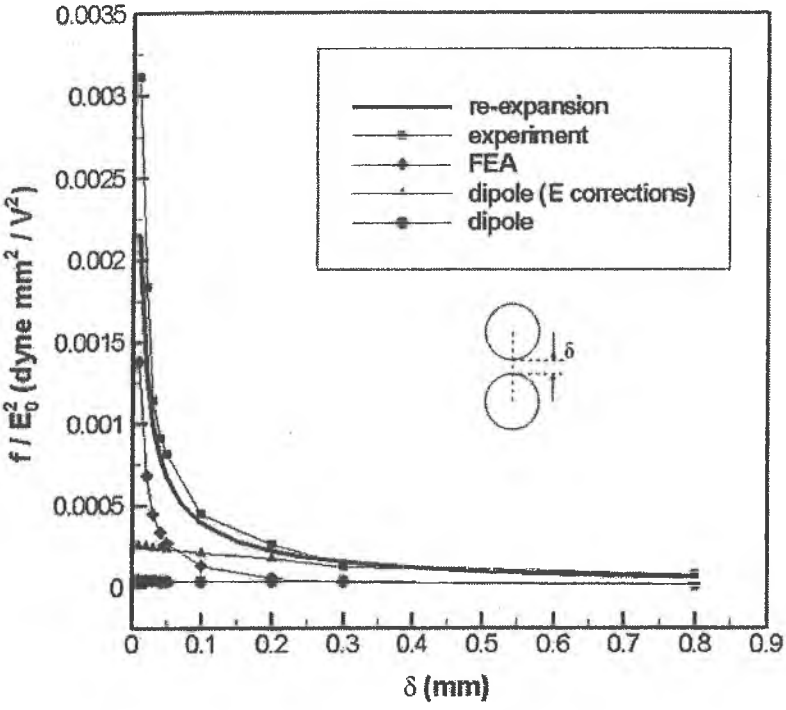

Figure 2: Comparison between the results originally reported by Wang *et al.* (2003), and Cox *et al.* (2005) result using re-expansion technique.

Much attention is drawn to carbon nanotubes due to their mechanical properties. The Young's modulus (elastic modulus) of a single-walled carbon nanotube lies close to 1 TPa, and the maximum tensile strength is close to 30 GPa. Because carbon nanotubes display superior mechanical properties such as ultra high elastic moduli, strength and low mass density, they have potential applications in composite materials and other mechanical systems. Further, the deformations are elastic and completely reversible even large deformation. The strong coupling between the electrical properties and mechanical deformation has many potential applications such as nanoscale sensors and nano-electro-mechanical systems (NEMS). Carbon nanotubes also display strong interplay between the mechanical deformation and electrical properties. Liu *et al.* (2004), for example, show that upon mechanical deformation, conducting carbon nanotubes may easily become semiconducting ones, but the semiconducting carbon nanotubes never become conducting. There are other fascinating properties of carbon nanotubes, such as magnetic and optical properties, we refer the reader to Ratner and Ratner (2002) and Dresselhaus *et al.* (1996), for example.

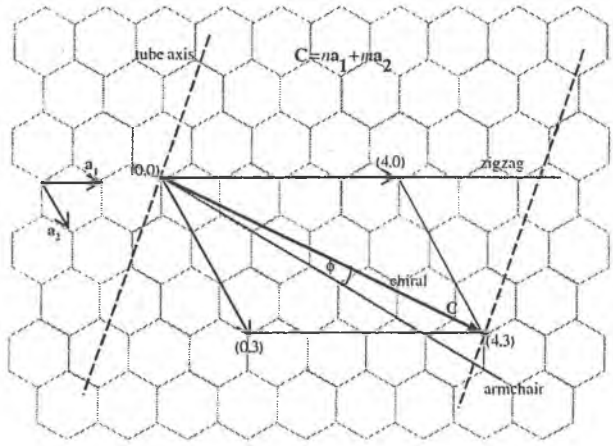

Figure 3: Chirality of carbon nanotbues.

Carbon nanotubes have promised many applications in nano-devices. One problem that has attracted much attention is the creation of nanoscale oscillators, or the so-called gigahertz oscillators. We note that while there are difficulties for micromechanical oscillators, or resonators, to reach frequencies in the gigahertz range, it is possible for nanomechanical systems to achieve this. Cumings and Zettl (2000) experiment on multi-walled carbon nanotube, where they remove the cap from one end of the outer shell and attach a moveable nanomanipulator to the core in a high-resolution transmission electron microscope (TEM). By pulling the core out and pushing it back into the outer shell, they report an ultra low frictional force against the intershell sliding. This is also confirmed by Yu *et al.* (2000). Cumings and Zettl (2000) also observe that the extruded core, after release, quickly and fully retracts inside the outer shell due to the restoring force resulted from the van der Waals interaction acting on the extruded core. These results led Zheng and Jiang (2002) and Zheng *et al.* (2002) to study the molecular gigahertz oscillators, where the sliding of the inner-shell inside the outer-shell of a multi-walled carbon nanotube can generate oscillatory frequencies up to several gigahertz. To estimate the oscillation frequency of a multi-walled carbon nanotube oscillator, Newton's second law is used, namely

$$M\frac{d^2\zeta}{dt^2} = F_{vdW}(\zeta) - F_r, \tag{12}$$

where M is the total mass of the inner core and ζ is defined as the distance between the centers of the inner core and the outer shell. The restoring force F_{vdW} is the van der Waals force resulting from the non-bonded interaction energy between the core and the outer shell and F_r denotes the intershell

sliding resistance force. Since experiments have shown that F_r is extremely small compared to the restoring force, Zheng and Jiang (2002) neglect F_r in the calculation. Further, Zheng *et al.* (2002) incorporate the sliding resistance force in the model of Zheng and Jiang (2002), where F_r is assumed to depend on the chirality of both shells in the intershell sliding.

Here, we focus only on the determination of F_{vdW}. Following Zheng *et al.* (2002), the van der Waals interaction energy between the core and the outer shell can be estimated using the Lennard-Jones pair potential of the interatomic interaction

$$\phi(d) = \frac{A}{a^6}\left(\frac{1}{2}\frac{d_0^6}{d^{12}} - \frac{1}{d^6}\right), \tag{13}$$

where the interatomic distance d is normalised by the carbon-carbon bond length $a = 0.142$ nm, the normalised van der Waals distance d_0 and the energy constant A are given by 2.7 and 24.3×10^{-79} Jm^6 respectively. For the core atom inside the outer shell, the van der Waals interaction energy between a single carbon atom of the core and all carbon atoms of the outer shell is of the form

$$\Phi = \sigma \int \phi(d)\ d\Sigma, \tag{14}$$

where the distance d here is the distance between an atom on the core and the surface element $d\Sigma$ on the outer shell. In a cylindrical coordinate system, where the z-axis is the common axis of the core and outer shell, an atom on the core is located by (r, θ, z), while $(r+s, \Theta, Z)$ for atom located at the outer shell, noting that s the intershell space. As such, the distance d is given by

$$d^2 = [r - (r+s)\cos\Theta]^2 + (r+s)^2\sin^2\Theta + Z^2. \tag{15}$$

In (14), the outer shell is assumed to have continuous distribution of carbon atoms of mean surface density $\sigma = 4\sqrt{3}/9a^2$. This approach has been previously used by Henrard *et al.* (1999). The integral (14) over the surface of the outer shell is given by

$$\Phi = \frac{4\sqrt{3}}{9a^2}\int_{-\pi}^{\pi}\left\{\int_{-\infty}^{\infty}\phi(d)\ dZ\right\}(r+s)d\Theta. \tag{16}$$

With d given by (15), Zheng *et al.* (2002) simplify the above integral to obtain

$$\Phi = \frac{\pi\sqrt{3}A}{96a^6}[21d_0^6E_{11}(s) - 64E_5(s)](r+s), \tag{17}$$

where E_m is the elliptic integral defined by

$$E_m(s) = (2r+s)^{-m}\int_0^{\pi/2}[1 - \kappa(s)\cos^2\omega]^{-m/2}d\omega, \tag{18}$$

and $\kappa(s)$ is given by

$$\kappa(s) = \frac{4r(r+s)}{(2r+s)^2}. \tag{19}$$

Zheng *et al.* (2002) are interested in the excess van der Waals interaction energy due to the extrusion of the core out of the outer shell. If ζ denotes the separation distance of the center of the core from the center of the outer shell due to extrusion, then the surface area of the portion of the core inside the outer shell is given by $\pi D[(L_c + L_o)/2 - \zeta]$, where L_c and L_o denote the length of the core and the outer shell respectively. The van der Waals interaction energy between the core and the outer shell is then given by

$$U(\zeta) = \frac{4\sqrt{3}\pi D}{9a^2}\left(\frac{L_c + L_o}{2} - \zeta\right)\Phi. \tag{20}$$

There is no effective extrusion if $\zeta \leq |L_o - L_c|/2$ and the van der Waals interaction energy is constant. As such, (20) is only valid for $\zeta > |L_o - L_c|/2$. Thus, the excess van der Waals interaction energy due to extrusion is given by $-(4\sqrt{3}\pi D/9a^2)\zeta\Phi$. As a result, the van der Waals restoring force resulting from the excess van der Waals interaction energy due to the extrusion is of the form

$$F_{vdW}(\zeta) = -\frac{dU(\zeta)}{d\zeta} = \frac{4\sqrt{3}\pi D}{9a^2}\Phi, \tag{21}$$

where $\zeta > |L_o - L_c|/2$. With (12) and (21), Zheng *et al.* (2002) are able to predict the oscillatory frequency of the double-walled carbon nanotube oscillator. The result for multi-walled carbon nanotube oscillator is also provided in Zheng *et al.* (2002), where similar approach is used.

Recently, Liu *et al.* (2005) also investigate the gigahertz oscillator. Instead of using multi-walled carbon nanotube, the high frequency is generated by a fullerene C_{60} oscillating inside a single-walled carbon nanotube. A fullerene C_{60}, commonly known as buckyball, comprises of sixty carbon atoms bonded in the shape of a soccer ball. We refer the reader to Dresselhaus *et al.* (1996) for details and properties of fullerenes. Mathematical modelling for this problem can be done following the approach used for multi-walled carbon nanotube oscillator.

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