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Tubes and containers at the nano and microscales: Statics and dynamics

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Abstract. We review how coaxial carbon nanotubes (CNTs) and vesicular nanotubes exhibit nonlinear oscillations and how theoretical models match with experimental observations. In particular, we discuss how coaxial CNTs may be modelled by mechanical analogues with interactions mediated by nonlinear spring forces with weakening elastic constants in addition to a weak van der Waals-like interaction. The model's predictions are in remarkable agreement with quantum mechanical calculations for the system. Predicted oscillatory frequencies are also in agreement with those reported in the literature. We then discuss our theoretical work on nanotubes in a biological system: Nanotubes that are drawn out from micrometre-scale vesicles and which exhibit very interesting dynamics. Our theoretical model reproduces all aspects of the force–extension curves reported in the experimental literature and completely explains the dynamics of vesicular nanotubulation and force fluctuations. The serrations seen in the force–extension curves are explained to be a consequence of stick–slip dynamics.

Keywords. Coaxial carbon nanotubes; vesicles; nanotubulation; nonlinear oscillations; stick–slip phenomena.

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1. Introduction

Systems at the micro and nanoscales often show interesting dynamics and unexpected dynamics. Explaining experimentally observed mechanical behaviour can be non-trivial, especially as dynamical behaviour at such small scales may be interpreted incorrectly as just artifacts of thermal fluctuations. Very often, observations of such systems are constrained by experimental limitations due to the very small scales of the systems. Thus, while in some instances, theoretical models have proved adequate to explain experimental observations, in other cases, these have yet to be verified in the absence of systematic experiments that could have validated the theoretical predictions.

The problem is compounded by the fact that various physical effects, acting at various spatial scales, could give rise to experimentally measurable effects, and unless these are all taken into account, obtaining a satisfactory theoretical model would be an elusive task.

In this work, we will briefly review the observations made of nanotubes and vesicles, and the theoretical work explaining their nonlinear oscillations.

In section 2 we describe a nonlinear spring model for coaxial double-walled carbon nanotubes (DWCNTs) that very nicely duplicates the interaction energy of the system as obtained by quantum-mechanical density functional theory (DFT) calculations. Earlier theoretical work in the literature on modelling oscillations in DWCNTs include that of Cox *et al.* [1] who looked at oscillations in nanotube bundles, and others who have considered frictional and van der Waals forces in analytical treatments and molecular dynamics simulations [2, 3]. However, no work in the published literature we know of, other than that of Mishra and Ashok [4], compares the results obtained by a phenomenological model to that obtained from actual quantum mechanical calculations, and moreover finds them in good agreement.

Section 3 discusses the dynamics of a phospholipid-walled vesicle pulled mechanically at constant velocity, causing a nanotube to form. The dynamics of the system is interesting as force–extension curves reported in experiments show serrations and various other interesting dependencies of the curves on surface tension, vesicle radius, pulling velocity, etc.

Theoretical work on the other hand has predominantly focussed on the shape of the system, and by and large have excluded the time evolution of the vesicle–nanotube system, with the serrations being implicitly ignored as being a consequence of thermal and noise effects in the experimental set-up. In Refs [5, 6], for example, no serrations are obtained in the force–extension curve, and dynamics of the process are not addressed (the changes in the vesicle–tubule system with respect to time are not considered). They restrict themselves to investigating the shape evolution under near stationary conditions. Their models yield a serration-free curve that would correspond to a nano-tubulation process where all internal relaxations have been completed and that too only for the case where the vesicle is maintained at constant surface tension. Such a smooth curve is unrealistic when compared to what is seen experimentally. The only work that addresses and explains all the features reported in the experimental literature is the theoretical model proposed by Ashok and Ananthakrishna [7], which explains the dynamics of the system. All the features of experimental force–extension curves (for example, such as those in Cuvelier *et al.* [8, 9] or Roopa *et al.* [10, 11]) are reproduced using the model [7]. The smooth, un-serrated curve in Refs [5, 6] is also obtained in the regime where pull velocity v_a is sufficiently small that relaxation oscillations have died down and no serrations are seen (plot shown as inset in figure 5).

2. Single and multi-walled carbon nanotubes (SWCNTs and MWCNTs)

Carbon nanotubes (CNTs) are of potential practical importance due to their large elastic modulii and their mechanical strength which make them ideal candidates for parts for nanoscale machinery. The use of DWCNTs and MWCNTs, respectively, as nanogears, nanorotors, molecular motors and ratchets have for long been an attractive proposition since they were first observed experimentally. One early use that was hypothesized was in constructing a space elevator, although the problem of synthesizing them in sufficient lengths for that purpose remains a hindrance.

An SWCNT consists of a rolled sheet of graphene. Depending on how the rolling is done, and at what angle, the relative arrangements of the carbon atoms on the lattice will vary, and also determine the diameter of the tube. The SWCNT can be one of the three types, that are termed as armchair, chiral or zigzag. The reader is referred to the extensive literature in this field for more details – see, for example [12].

DWCNTs (and MWCNTs) consist, as their names suggest, of two (or more) concentric SWCNTs that are stabilized by mutual interactions between their walls, including van der Waals forces. The mutual sliding between the walls of these structures varies depending on whether they are commensurate or not. In the absence of defects, these MWCNTs (see Ref. [13]) show very low friction between the CNT walls.

The work of Cummings and Zetl [13] indicated that DWCNTs oscillate in the frequency range of 0.1–1 GHz. This has naturally led to investigations into their possible use as oscillating elements in electromechanical devices. Rivera *et al.* for example, have performed molecular dynamics simulations on DWCNTs, allowing the inner tube to be pulled out and then retracted and concluded that the oscillations of the nanotubes are damped, and the system can be thought of as a nanoscale mechanical shock-absorber [2, 3].

Other work that have focussed on the mechanical oscillations of CNTs include a model by Cox and collaborators [1] who investigate the oscillations of a single-CNT placed in the midst of a concentric ring of other CNTs, using a 6–12 Lennard–Jones potential function to model the van der Waals interaction. They obtain an oscillatory frequency of the CNT approximately in the range of 50–80 GHz.

2.1 *DWCNT interaction modelled as nonlinear springs*

Density functional theory (DFT) calculations for DWCNTs have yielded interaction energies for the system, as a function of inter-wall separation as well as longitudinal displacement of the inner CNT along the axis of the DWCNT [4]. In addition, interaction energies for the system have been calculated for armchair–armchair configurations of DWCNTs showing the feasibility of their use as nanobearings, ratchet wheels and nanogears.

A simple mechanical model was proposed by Mishra and Ashok [4] for the DWCNT as a nanospring, which yielded results in surprisingly close agreement with that obtained from quantum mechanical DFT calculations. The tubes of the DWCNT were modelled as a pair of concentric cylinders of total length L, with wall-separation r, each with a number of molecular units (of length L_m) placed one atop the other, the inner tube moving outward along the central axis by a distance x.

These can be considered as pairs of concentric rings of atoms, the inner ring having M atoms and the outer ring N atoms, interacting by means of N identical springs. This was a non-Hookean system, assuming spring softening (or hardening) to occur as the inner tube moved outwards.

The other interactions between the tubes included a short-range $1/r^6$ van der Waals interaction; a harmonic, stabilizing potential acting radially between the parts of the CNTs that were concentric and monotonically reduced as the inner tube moved out was also present. The interaction energies of the coaxial CNTs are

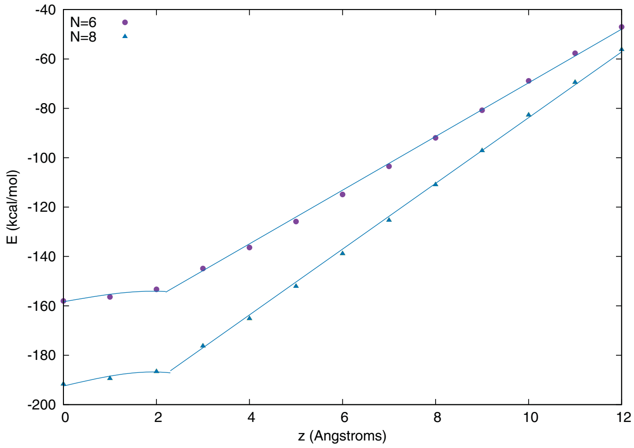

Figure 1. Plots of interaction energy ΔE vs. axial distance z for $N = 6$ and $N = 8$ for 12 Å long DWCNTs. Data points are obtained from DFT calculations, while solid curves are obtained from the nonlinear spring model.

given by

$$E_{\mathrm{In}} = E_0 + \frac{Nkx^2}{2} - \frac{Nkx^3}{3L} + \frac{Nkr^3}{L}\tan^{-1}\left(\frac{x}{r}\right) - Nkr^2\left(\sec(\tan^{-1}(x/r)) - 1\right) + \frac{c}{r^6} + \frac{(pNkr^2)}{2}\frac{L-x}{L}, \quad (1)$$

$$E_{\mathrm{Out}} = E_0' - \frac{Nkx^3}{3L} + \frac{c}{r^6} + \frac{(pNkr^2)}{2}\frac{L-x}{L}, \quad (2)$$

where E_{In} corresponds to the interaction energy of the system when the inner tube has moved only a short length along the axis (comparable to the length of a molecular unit L_m) and E_{Out} is the interaction energy of the system when the displacement of the inner nanotube is significantly larger than L_m. The magnitude of the radial harmonic interaction is adjusted by p, the tuning parameter. p itself depends on N through $p \sim N^{-0.32}$. The contribution to the above interaction energy from the effective restoring force F_{spring} on the inner CNT due to the nonlinear springs alone comes from

$$F_{\mathrm{spring}} = -Nkx\left(1 - \frac{x}{L}\right) + \frac{Nkxr}{(r^2 + x^2)^{1/2}}\left(1 - \frac{x}{L}\right). \quad (3)$$

The fixed points of the system $(x^*, \dot{x}^*)$ are located at the origin and at $(L, 0)$. The non-trivial fixed point is a saddle, indicating that pulling the inner tube beyond $x = L$ will make the co-axial system unstable, as expected. The interaction energies of the DWCNT system as obtained from DFT calculations are very nicely reproduced by this simple, mechanical and non-linear spring model, as seen in figure 1. This model gives a value of the spring constant that is approximately 0.34 N/m (for DWCNT of length 6 Å) to 0.41 N/m (for DWCNT of length 12 Å). The natural oscillation frequency then becomes, in the Hookean approximation, about 78–109 GHz (for 6 Å DWCNTs considered) to 60–85 GHz (for DWCNTs of length 12 Å), which fall in the 50–80 GHz range reported elsewhere. Further details can be found in Ref. [4].

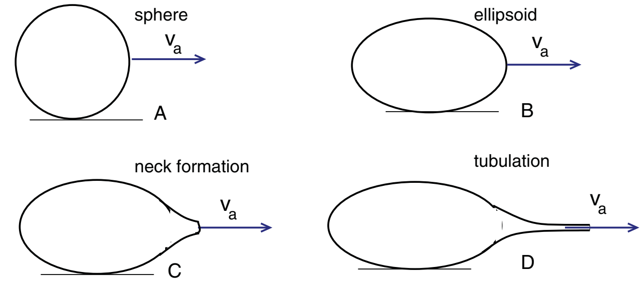

Figure 2. Schematic diagram showing the various stages of vesicle deformation when pulled at constant pulling velocity v_a as envisaged in a three-stage model. An ideal spherical vesicle (**A**) gets deformed to an ellipsoid (**B**). With time, the ellipsoid gets deformed forming a neck (**C**), and eventually nanotubulation occurs (**D**).

3. Dynamics of vesicular nanotubulation

Vesicles are micrometre size containers or bags with phospholipid walls present in biological systems, and are responsible for the inter- and intra-cellular transport of chemicals. Vesicles can be unilamellar or more frequently, multilamellar. When the vesicular fluid membrane is mechanically pulled at constant velocity, the membrane deforms allowing a nanotube to be pulled out, which process is termed vesicular nanotubulation. The process is schematically shown in figure 2. The dynamics of this deceptively simple process is far from obvious and until recently, theoretical descriptions of the phenomenon were incomplete. The experimental procedure typically followed is as follows: a vesicle is either adhered to a substrate (for example, a glass slide) or is connected to a lipid reservoir through a micropipette, and then pulled at constant velocity (for example, by an atomic force microscope (AFM) tip or using optical tweezers, or by some other methods) [8–11, 14–16]. This causes a nanotubule to be extracted from the vesicular body, while the force (f) required to pull out the nanotube to a distance (x) is observed. While the force–extension curve depends on the conditions of the experiment, some features are seen universally, such as the irregular force drops. Most of the theoretical studies [5, 6, 14, 15, 17–19] in the literature on tether extraction from vesicles have focussed

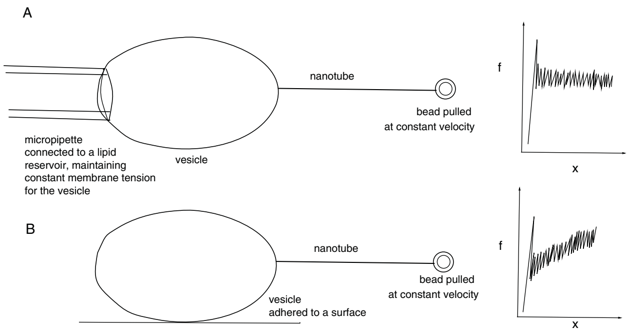

Figure 3. Schematic representations of typical experimental set-ups reported in the literature, with free-hand sketches showing the nature of the corresponding force–extension curves. (**A**) Shows the vesicle maintained at constant membrane tension, unlike (**B**). The vesicle is much larger than the 'tether' drawn out by the adhering bead pulling at it at constant velocity; vesicular dimensions are in micrometres while the tether has a cross-section three orders of magnitude smaller, in nanometres, and hence appears almost like a line in comparison with the vesicle body.

on the geometrical shape of the vesicle–nanotubule system that depends on the experimental conditions. These are essentially under near-stationary conditions, and the evolution with time of the vesicle–nanotube system, is not investigated; nor are the experimental parameters such as the pull velocities or vesicle radius, which are so important, taken into account in treatments of the force–extension curve. The irregular force drops or serrations in the f–x curve have been completely ignored by most of the above-cited references. This is surprising as these are characteristic of relaxation oscillations and an indication of the phenomena driving the dynamical behaviour of the system. The work of Ashok and Ananthakrishna [7] was the first one to address these features as well as explain all the features seen in experimental f–x curves, and this shall be briefly discussed.

3.1 *Experimental features of the force–extension curve*

Characteristic features seen in f–x curves include, first, a linear elastic part. There is then a force drop, followed by a plateau that might be horizontal, or have a gentle, positive slope, accompanied throughout by serrations. Increasing the pull velocity increases the elastic threshold. Increasing the vesicle radius also reduces the force values. These features were present in various experiments reported in the literature [8–11] and none of these had been addressed in theoretical models preceding Ref. [7]. Figure 3 shows a schematic diagram illustrating typical set-ups in a vesicle-pulling experiment. Figure 3A shows the vesicle connected to a lipid reservoir by means of a micropipette that keeps the membrane tension constant, and pulled at mechanically at constant velocity by a bead adhered to it, extracting a long, thin 'tether'. The corresponding force–extension curve after the initial rise and fall shows a plateau. Figure 3B shows the vesicle (without any reservoir that could maintain constant membrane tension) adhered to a surface and gain pulled at by a bead at constant velocity, causing tether formation. The corresponding force–extension curve shows a gentle rise. The vesicle's dimensions are typically in micrometres and the 'tether' pulled out has a cross-section in nanometres. For full details of such experiments and actual experimental curves, the reader is referred to, for example, Refs [9, 10].

3.2 *Stick–slip dynamics and vesicular nanotubulation*

That the serrations are dynamical in nature and are not thermal fluctuations can be clearly seen from an inspection of the f–x curve in Refs [8, 9]. The slip in the graph corresponds to be of the order of around 10 $k_B T$, clearly indicating that this is much larger than what could be attributed to thermal effects [7]. The model proposed in Ref. [7] considers the system as a three-stage phenomenon as the vesicle is pulled out into a nanotube: Stage 1 corresponds to the deformation of the spherical vesicle to an ellipsoid. An important feature of the model is that the volume of the vesicle is conserved even after deformation. The changing geometry of the system is accounted for through the change in curvature energy. Similarly, the increase in the surface area is considered using the surface tension of the vesicle.

Stage 2 deals with the formation of the neck, and here, elasticity theory for shells is applied to estimate the force required to deform an elastic shell. Local curvature plays a very important role, as each phospholipid molecule has to be pulled across. Finally, stage 3 corresponds to tubulation, where the change in curvature energy of the vesicle, as it further deforms from an ellipsoid to a tube, is calculated, while considering the effective spring constant for the system to be changing as the tube elongates. These three stages are illustrated in the schematic diagram shown in figure 2. Frictional and dissipative forces have also to be considered, and a rate-dependent force law included to account for the viscoelastic response of the vesicular material as it is pulled. The reader is referred to Ref. [7] for the very many details involved. Figure 4 illustrates the geometry of the vesicle–nanotube system used in the model. The pulling of the vesicle by a bead of mass m adhering to it is a non-equilibrium process and the general equation describing the bead as it is pulled is

$$m\ddot{x} = f - F_r, \tag{4}$$

where f is the applied force and F_r is the response of the vesicle. Let $R(t)$ denote the mean radius of the main vesicular body as a function of time as it is

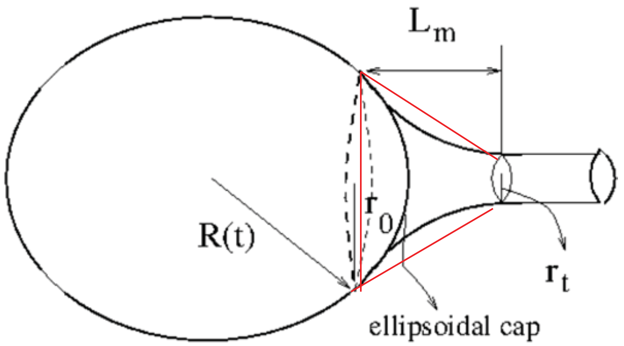

Figure 4. Schematic diagram showing the vesicle–nanotube system. The solid lines in red show the approximation of the neck as a conical geometry.

pulled out by a distance $x(t)$, R_0 being the initial radius. F_r comprises of contributions from various terms, namely, the force $F_{\rm ell}$ required to deform the spherical vesicle into an ellipsoid, the point elastic force F_n that is required to pull out the vesicular shell by a distance L (up to a maximum of $L_m = \sqrt{2/3}r_0$, considering plastic flow for spheroidal shells), $F_{\rm tube}$ which accounts for the force required for a change in curvature energies as the vesicle geometry is deformed during nanotube formation and a force F_{nc} required to be overcome by a lipid molecule to be pulled past the curvature at the base of the neck at the start of nanotubulation. It turns out that: $F_{nc} \approx \alpha\pi\kappa\sqrt{4/15}/L_m$, $\alpha \geq 1$ being a numerical factor.

$$F_n = \frac{L^{1/2}E'h^{5/2}}{R(t)}, \tag{5}$$

where $E' = (6/5)(1-\nu^2)^{-3/4}E$, E being the Young's modulus, ν is the Poisson's ratio and h the thickness of the shell. The neck geometry is modelled as a cone of constant slope for simplicity, and the nanotube as a cylinder of constant cross-section. Assuming that the volume of the vesicle is conserved, we find from geometrical considerations that:

$$\begin{aligned} F_{\rm ell} =& 16\pi\kappa(R(t)-R_0-x) \\ &\times\left\{\frac{\partial R}{\partial x}\left(\frac{R(t)}{(R_0+x)(2R(t)-R_0-x)^2}-\frac{1}{R_0^2}\right)\right. \\ &\left.+\frac{1}{R_0^2}-\frac{R(t)^2}{((R_0+x)^2(2R(t)-R_0-x)^2)}\right\} \\ &+4k_\sigma\pi\Delta A+k_\sigma\frac{x(t)r_0}{R(t)}, \end{aligned} \tag{6}$$

where r_0 is the radius of the base of the cone, k_σ is the surface tension and ΔA is the change in area per unit length with respect to the sphere. One finds that

$$F_{\rm tube} = \pi\kappa\left(\frac{1}{r_t}-\frac{4}{R_0}\frac{(1-R(t)/R_0)r_t^2}{R(t)^2}\right), \tag{7}$$

where r_t is the radial cross-section of the nanotube.

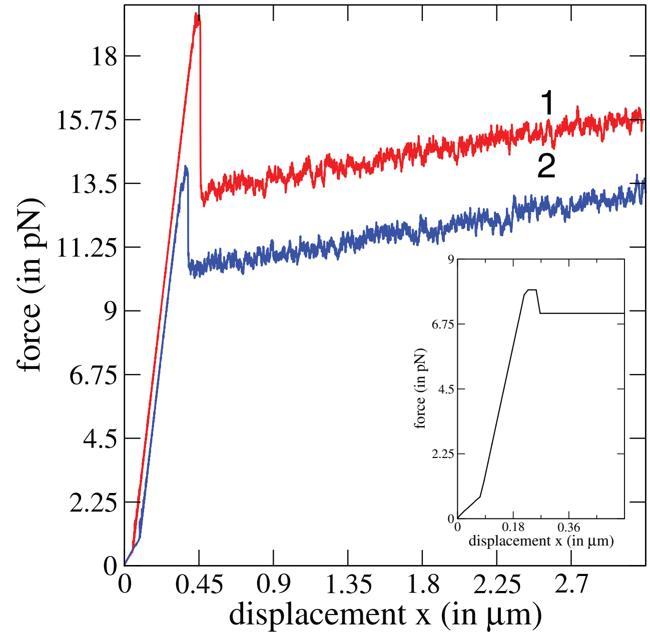

Figure 5. Representation of force–extension curves for non-constant surface tension. Curve 1 is for lower vesicle radius than curve 2. The inset shows a force–extension curve at constant surface tension (hence the horizontal plateau) for a pull velocity v_a that is less than v_m for which the force $F_{\rm fr}(v_a)$ increases with v_a. In this regime, sufficient time is there for all internal relaxations to be completed and no serrations are seen in the f–x curve.

The rate of pulling out the nanotube from the vesicle influences the extent of internal flows as well as relaxation for the viscoelastic vesicular material. This rate-dependent vesicular response can be described by a frictional force law $F_{\rm fr}(\dot{x})$. For modelling this, a functional form is required which supports a stick–slip process in the neck and a velocity-weakening law there. We choose:

$$F_{\rm fr}[\dot{x}] = \frac{F_0\dot{x}/v_m}{(1+(\dot{x}/v_m)^2)}. \tag{8}$$

Here, v_m is the value beyond which $F_{\rm fr}$ decreases with velocity $\dot{x}$. There are also contributions from the elastic stretching of the tubule and the vesicle and a viscous resistance $-\beta\dot{x}$ at the neck and along the tube. These forces can together be written as:

$$F_{e,f} = -\beta\dot{x} - \epsilon'[k'x + F_{fr}(\dot{x})], \tag{9}$$

where $\epsilon' = 0$ for $x < L_m$ and $\epsilon' = 1$ for $x > L_m$, and k' is the effective spring constant of the tubule. k' can be either weakening (for a flat serrated f–x curve) or constant in time (for a rising curve with non-zero, positive slope). Thus we have:

$$\begin{aligned} F_r &= F_n + F_{nc} - F_{e,f} + F_{\rm ell} + F_{\rm tube} \\ \dot{f} &= k_{\rm eff}(v_a - \dot{x}). \end{aligned} \tag{10}$$

k_{eff} denotes the effective spring constant of the vesicle. For $v_a \geq v_m$, these equations are unstable. The results of these calculations have been shown in figure 5, which are in excellent agreement with experimental observations. Further details may be found in [7, 20].

4. Conclusions

The dynamics of systems at the nanoscale, such as have been discussed in this work, can be very complex. Nonetheless, an intelligent choice of approximations while modelling the system under consideration can give very good results and explain the physical processes responsible for experimental observations. The approximation of the interaction of DWCNTs by nonlinear springs yields useful, predictable results [4]. One is able to predict the frequency of small oscillations as well, obtaining results in conformity with the literature. The model of the vesicular system shows the importance of considering local geometry in capturing the dynamics of the system as a whole. The serrations seen in the force–extension curves are shown to result from stick–slip dynamics caused due to frictional forces as the lipid monolayers of the vesicular membrane are drawn out [7].

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