Vibrating Nanotube–based Nano Powder Production System

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ABSTRACT

A nanotube being placed in a vapor atmosphere will provoke condensation of vapor on the tip of nanotube giving rise to a nano droplet formation. Under a resonant mechanical excitation condition the nano droplet may become unstable and lose touch with the tip of the nanotube. This is how nano droplets may be created. Theoretical and experimental research to verify this idea is being conducted. It was shown that the stability of a nano droplet at the end of a carbon nanotube depends on mechanical properties of the carbon nanotube, droplet size, thermal noise, amplitude and frequency of external excitation.

***Keywords*:** carbon nanotube, nanodroplet, ultrasound

1 BASIC IDEA

Ultra-fine particles with a narrow size distribution have enormous application potential in many areas. However, very few of the current nano powder production technologies are capable of providing nano-sized particles with a relatively narrow size distribution. In most cases, this is due to inadequate control over the nucleation, growth and subsequent agglomeration stages of the particle formation process. In this paper, we present a nano powder production method that is expected to provide a good control over the aforementioned three stages of particle formation.

Basic idea of this method is as follows: a nanotube being placed in a vapor atmosphere will provoke condensation of vapor on the tip of the nanotube giving rise to a nano droplet formation. Without intervention, this nano droplet is stabilized at the tip by surface tension and van der Waals forces (Fig.1). Under a resonant mechanical excitation condition the nano droplet may become unstable and lose touch with the tip of the nanotube. This is how nano droplets may be created.

2 BACKGROUND

Since its discovery in 1991 [1] carbon nanotubes attracted research activities in science and engineering devoted to their promising applications [2,3]. Because of their structural perfection, carbon nanotubes possess particularly outstanding physical properties. They are remarkably stiff and strong, conduct electricity, and are projected to conduct heat even better than diamond.

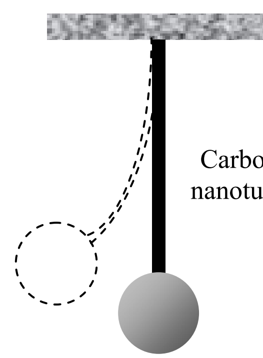

Fig. 1. Schematic of carbon nanotube loaded with a fluid nanodroplet.

Although carbon nanotubes have diameters only several times larger than the length of a bond between carbon atoms, continuum models have been found to describe their mechanical behavior very well. The application of continuum-elasticity methods shows remarkable correspondence with molecular dynamics simulations [4,5]. From continuum mechanics point of view for small deformations, nanotubes may be treated as elastic beams. The equation of motion of such a beam is (see, [6,7]):

$$\rho A \frac{\partial^2 u}{\partial t^2} + EI \frac{\partial^4 u}{\partial x^4} = f(x) \tag{1}$$

where u is the beam displacement due to its bend, ρ is the density of the material in the nanotube wall, A the cross-sectional area of nanotube, E Young's modulus, I the moment of inertia of nanotube cross-section, and $f(x)$ a distributed applied load.

Normally, in elasticity theory, Young's modulus E represents a material property applicable for any type of deformation. It should be noted here that a single value of Young's modulus cannot be uniquely used to describe bending, tension and compression of the beam. The reason is that tension, compression and bending are mainly governed by different bonds between carbon molecules. Hence, E in Eq.(1) denotes the Young's modulus for bending. Moreover, it is expected that tension/compression phenomena will play a minor role in the proposed phenomenon.

The natural frequency of an elastic beam clamped at one end and free at the other is:

$$\omega_n = \frac{\beta_n^2}{l^2}\sqrt{\frac{EI}{\rho A}} \tag{2}$$

where l is the length of the beam, β_n is the root of an equation that is dictated by boundary conditions. Taking into account that

$$A = \pi\left(R_{out}^2 - R_{in}^2\right), \quad I = \frac{\pi}{4}\left(R_{out}^4 - R_{in}^4\right) \tag{3}$$

one obtains for the natural frequency

$$\omega_n = \frac{\beta_n^2}{2l^2}\sqrt{\frac{E\left(R_{out}^2 + R_{in}^2\right)}{\rho}} \tag{4}$$

where R_{out} and R_{in} are outer and inner radii of a carbon nanotube, respectively.

The first experimental measurements of Young's modulus in multiwalled carbon nanotubes were made by Treacy et al. [8]. They took large bundles of carbon nanotubes, and attached them to the edge of a hole in nickel rings for transmission electron microscopy observations. The carbon nanotubes are so small and light that thermal motion of molecules may have substantial impact on their state leading to their intrinsic thermal vibrations. Assuming equipartition of the thermal energy among vibrating modes (Eq. (4)), it was shown that the standard deviation, Δ, of the nanotube tip due to thermally induced vibrations is related to the Young's modulus and temperature through the following equation

$$\Delta^2 = \frac{16 l^3 kT}{\pi E\left(R_{out}^4 - R_{in}^4\right)}\sum_n \beta_n^{-4} \tag{5}$$

where T is the temperature, k is the Boltzmann constant. This mean square vibration amplitude has been measured for different temperatures and the mean value of Young's modulus was found to be of 1.8 TPa with an uncertainty of ± 1.4 TPa.

In [9] an electromechanical excitation was used as a method to initiate the resonance frequencies of multiwalled carbon nanotubes. For tubes of small diameter (less than about 12 nm), they found frequencies consistent with the Young's modulus being in the range of 1 TPa. However, for larger diameters, the bending stiffness was found to decrease.

3 THEORETICAL JUSTIFICATION

To provide theoretical justification for the proposed idea we, *at first*, will estimate if the frequency range we need to work with is appropriate for use and can be achieved in the laboratory experiments. In our estimations we consider two representative examples: multiwalled carbon nanotube and single-walled carbon nanotube.

For the multiwalled carbon nanotube we take Young's modulus of E = 2 TPa and R_{out} = 5 nm, R_{in} = 2 nm. The density of multiwalled carbon nanotube is estimated as ρ = 2,150 kg/m^3 [8]. For the single-walled carbon nanotube, we take an estimated Young's modulus of E = 1 Tpa, R_{out} = 0.75 nm, and R_{in} = 0.41 nm. The thickness of nanotube wall is equal to the interlayer distance in graphite ΔR = 0.34 nm, because each individual single-walled carbon nanotube involves only a single layer of rolled graphene sheet [10]. The density of carbon nanotube is taken to be equal to that of graphite ρ = 2,500 kg/m^3 [11].

One can then use Eq. (4) to calculate resonance frequencies of nanotubes of different lengths. We consider here only the fundamental mode for which β_0 = 1.875 [7]. The results are plotted in Figure 2. It is clear from this figure that the fundamental mode is strongly dependent on the nanotube length. For nanotubes with a length between 1 μm and 1 mm the resonance frequency changes from megahertz to hertz ranges. The resonance frequency of single-walled nanotubes seams to be lower than that of multiwalled ones. In order to work with a frequency of about 20 kHz (the most commonly used frequency in laboratory experiments with ultrasound) one should use multiwalled nanotubes of about 50 μm long or single-walled carbon nanotubes of about 16 μm long. Recent advances in nanotube synthesis [12] have made possible the growth of nanotubes of such lengths.

Being very small, carbon nanotubes will be subject to thermal noise. So, as a s*econd* step, we would like to estimate the contribution from the vibrations of thermal origin. One can use Eq. (5) to calculate the deflection of the tip. We consider here the superposition of all vibrational modes. The results for room temperature, T = 300 K, are plotted in Figure 3. It is clear from this figure that the intensity of thermal vibrations is strongly dependent on the nanotube length. For nanotubes of length between 1 μm and 1 mm the amplitude of thermal noise vibrations changes from nanometer to millimeter ranges.

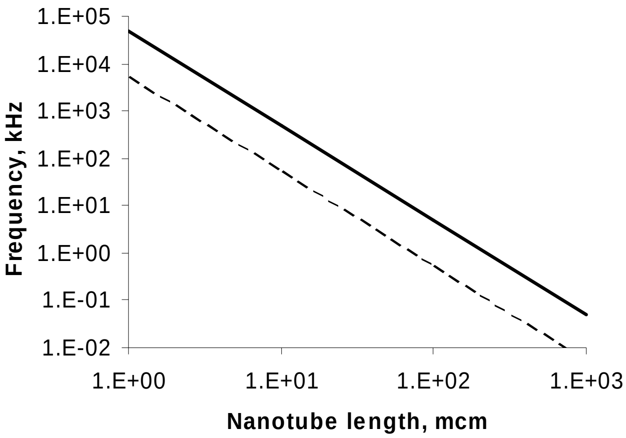

Fig. 2. Resonant frequencies of carbon nanotubes clamped at one end and free at the other. Solid line: multiwalled carbon nanotube (R_{out} = 5 nm, R_{in} = 2 nm, E = 2 TPa, ρ = 2,150 kg/m^3). Dashed line: single-walled carbon nanotube (R_{out} = 0.75 nm, R_{in} = 0.41 nm, E = 1 TPa, ρ = 2,500 kg/m^3).

Thermal vibrations seem to be more pronounced for single-walled nanotubes than for multiwalled ones. At a frequency of about 20 kHz, which corresponds to the multiwalled nanotube of about 50 µm in length and single-walled carbon nanotube of about 16 µm in length, one should expect the amplitudes of thermal vibrations of about 0.4 µm and 5 µm, respectively. This is an indication that one should perform a detailed investigation of the influence of thermal noise on the acoustically induced nanotube oscillations.

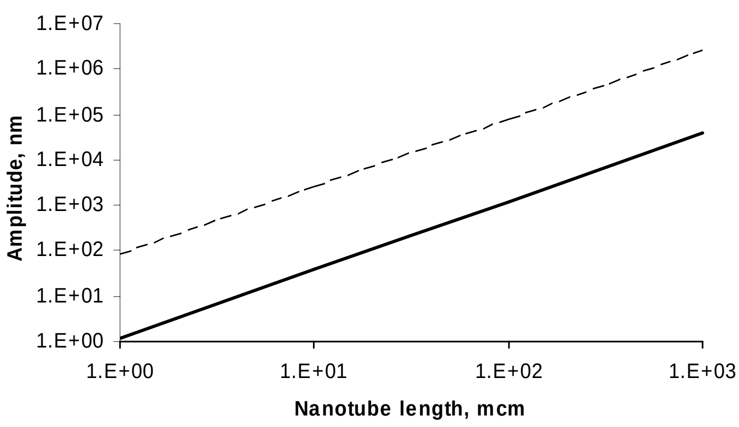

Fig. 3. Thermal vibration amplitudes of carbon nanotubes clamped at one end and free at the other. Solid line: multiwalled carbon nanotube (R_{out} = 5 nm, R_{in} = 2 nm, E = 2 TPa, ρ = 2150 kg/m^3). Dashed line: single-walled carbon nanotube (R_{out} = 0.75 nm, R_{in} = 0.41 nm, E = 1 TPa, ρ = 2,500 kg/m^3).

Although the amplitude of thermal oscillations is substantial, the question arises if those oscillations will play important role in the stability of a nano droplet attached to the tip of nanotube. In other words, will these oscillations have enough intensity to rip nano droplets off the tip? Hence, as the *third* step, we need to estimate the forces that a nano droplet at the tip experiences due to thermal vibrations of the nanotube.

The force that tends to keep the nano droplet at the tip is surface tension force which is estimated as

$$F_\sigma = 2\pi R_{out}\sigma \tag{6}$$

where σ is the surface tension coefficient of the fluid. When the tip of a nanotube performs oscillations with an amplitude Δ and frequency ω_0, it moves with a periodic acceleration of which the amplitude is about $\omega_0^2\Delta$ (here the frequency of the fundamental mode is used for the estimation purposes).

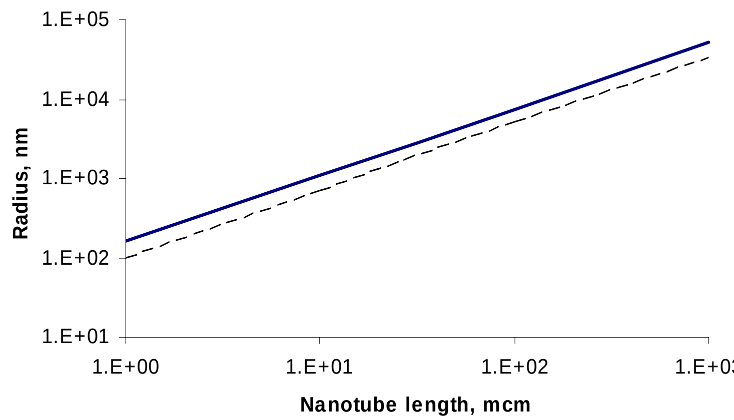

Fig. 4. Critical radii of liquid the droplets attached at the free end of carbon nanotubes. Solid line: multiwalled carbon nanotube (R_{out} = 5 nm, R_{in} = 2 nm, E = 2 TPa, ρ = 2150 kg/m^3). Dashed line: single-walled carbon nanotube (R_{out} = 0.75 nm, R_{in} = 0.41 nm, E = 1 TPa, ρ = 2,500 kg/m^3).

Naturally, the fluid droplet attached to the tip experiences the inertia force of

$$F_i = \frac{4}{3}\pi R_d^3 \rho_d (2\pi f_0)^2 \Delta \tag{7}$$

and the gravity force of

$$F_g = \frac{4}{3}\pi R_d^3 \rho_d g \tag{8}$$

Here R_d and ρ_d is the droplet radius and density of the fluid, g is the gravitational acceleration.

Assuming, for estimation purposes, that all these forces act along the vertical line, we come to the stability condition:

$$F_\sigma > F_i + F_g \tag{9}$$

The Eq. (9) leads to the equation for a critical droplet radius

$$R_d = \left[\frac{3R_{out}\sigma}{2\rho_d\left(4\pi^2 f_0^2 \Delta + g\right)} \right]^{1/3} \tag{10}$$

which means that the droplets of radii larger than R_d will be ripped off from the tip of nanotube.

Having in mind that the resonance frequency f_0 and amplitude of thermal vibrations Δ both depend on the nanotube length, one can estimate the critical droplet radius as a function of the nanotube length. The results are shown in Figure 4. Here for estimation purposes the density and surface tension coefficient of water are used. For nanotubes of length between 1 μm and 1 mm the critical radius changes from hundred nanometers to centimeter ranges. Although thermal vibrations may have strong impact on the amplitude of vibrations of the nanotube, as shown above, they do not have enough intensity to destroy the stability of a nano droplet attached to a nanotube tip. Namely, at a frequency of 20 kHz which corresponds to a multiwalled nanotube of about 50 μm in length and single-walled carbon nanotube of about 16 μm in length, thermal vibrations may rip off the droplets from the tip only if they are relatively large: about 4 μm for the case of a multiwalled nanotube, and 1μm for single-walled nanotube.

That is why we suggest using the acoustically induced nanotube oscillations to create nano droplets. Of course, the resonance properties of a nanotube is expected to be affected by the nano droplet attached to its end, heat exchange between the nanotube and the nano droplet, and the kinetics of condensation, etc. These issues will be addressed in the future research.

4 NANO POWDER PRODUCTION SYSTEM

Herein proposed is a vibrating nano-tube or nano-rod based nano powder production system that promises to deliver a better control over the nano particle size distribution. This system involves a planar array of carbon nanotubes that are suspended from a vibrating plate to form a particle formation zone. A stream of metal vapor carried by a carrier gas is directed to flow into this zone in which the vapor condenses onto the surface of nanotubes. The thermally controlled nanotube surface serves as a preferred site to promote well-controlled heterogeneous nucleation. The growth of nuclei is controllably limited by the size of the nanotube and the vibration frequency and amplitude of the nanotube. The droplets grown to a controllably specified size are continuously shaken off the nanotubes. This step of shaking-off also acts to prevent the condensed particles from aggregating or coalescing among themselves on the nanotube surfaces. The shaken-off droplets are directed to flow through a cooling or passivating zone to further prevent agglomeration. The technological goal is to develop a method of using carbon nanotubes to produce nano particles of controllable sizes and high monodispersity.

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REFERENCES

[1] Iijima S., (1991), Helical microtubules of graphitic carbon, *Nature* **354** (6348): 56-58.

[2] Goddard W. A., III *et al*., Eds. (2003), *Handbook of Nanoscience, Engineering, and Technology*, CRC Press.

[3] Goldstein A. N., (1997), *Handbook of Nanophase Materials*, Marcel Dekker Inc., NY.

[4] Yakobson B.I., Smalley R.E., (1997), Fullerene nanotubes: $C_{1,000,000}$ and beyond, *American Scientist* **85**: 324-337.

[5] Yakobson B.I., Brabec C.J., Bernholc J., (1996), Structural mechanics of carbon nanotubes: From continuum elasticity to atomic fracture, *Journal of Computer-Aided Materials Design* **3**: 173-182.

[6] Timoshenko S., Gere J., (1988), *Theory of Elastic Stability*. McGraw-Hill. New York.

[7] Meirovich L., (1986), *Elements of Vibration Analysis*. McGraw-Hill. New York.

[8] Treacy M.M.J., Ebbesen T.W., Gibson J.M., (1996), Exceptionally high Young's modulus observed for individual carbon nanotubes, *Nature* **381**: 678-680.

[9] Poncharal P., Wang Z.L., Ugarte D., Heer de W.A., (1999), Electrostatic deflections and electromechanical resonances of carbon nanotubes, *Science* **283**: 1513-1516.

[10] Yu M.F., Files B.S., Arepalli S., Ruoff R.S., (2000), Tensile loading of ropes of single-wall carbon nanotubes and their mechanical properties, *Phys. Rev. Lett.* **84**: 5552-5555.

[11] Weast R.C., Selby S.M., Hodgman C.D. (eds), (1965), *Handbook of Chemistry and Physics.* The Chemical Rubber Co. Cleveland.

[12] Journet C. et al., (1997), *Nature* **388**: 756.