Nanocars by Quantum Mechanics

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ABSTRACT: Nanocars including molecular motors are nanostructures that convert electromagnetic (EM) energy into mechanical motion. The EM energy may take various forms including light, thermal and Joule heat, and electron beams, e.g., nanocars move by simply heating the substrate, the form of heat being thermal kT energy. Here, k is Boltzmann's constant and T is absolute temperature. But the mechanism by which EM energy is converted into motion is not well understood. Molecular dynamics (MD) simulations of heat transfer in nanostructures is commonly used to derive temperatures causing observed motions But MD simulations of heat transfer in nanostructures are questionable because quantum mechanics (QM) restricts the thermal kT energy of the atom at the nanoscale. The QM restriction on MD may be understood from the heat capacity of the atom given by the Einstein-Hopf relation for the harmonic oscillator. At ambient temperature, the heat capacity of the atom resides at wavelengths in the far infrared (FIR) beyond 50 microns. Nanostructures by their size exclude all thermal radiation beyond about 1 micron, and therefore lack the heat capacity to support heat transfer. Hence, absorption of EM energy, say by a nanocar from a heated substrate cannot be conserved by an increase in temperature. Instead, conservation proceeds by the frequency up-conversion of absorbed FIR to the molecular EM confinement frequency of the nanocar that at near ultraviolet (UV) or higher levels charges the nanocar positive. In effect, nanostructures act as FIR to higher frequency up-conversion devices that are charged by the photoelectric effect, the charges producing electrostatic attraction and repulsive pair-wise forces between nanocars that cause the nanocar motions. Similar arguments allow QED radiation to explain the motions of molecular motors under Joule and electron beam heating.

KEYWORDS: Nanodragsters, nanocars, molecular motors, quantum mechanics

I. INTRODUCTION

Nanocars moving on a substrate evolved over the past decade from the positioning of atoms and molecules [1, 2] with a scanning tunneling microscope (STM). Today, thermal energy alone has been shown to both roll and slide a molecule along a surface, but the mechanism by which this occurs is not understood. In this regard, a brief background [3-9] is presented from which a QM mechanism is presented for review.

II. BACKGROUND

A. Molecular Nanocars

In 2005, Shirai, et al. [3] showed that C_{60} fullerenes could exhibit rolling translation and rotation on gold substrates. By pulling with the STM tip, the nanocar was manipulated to move to a desired position. Moving nanocars by pushing was not successful, even though pushing was an established procedure [1, 2] for positioning large organic molecules. Instead, pushing pivoted and moved the nanocars to the side.

Upon heating of the substrate, the nanocars remained stationary [3] up to temperatures of about 170 C. But at higher temperatures, the nanocars were observed to move in the plane of the substrate. Motion was not always translation in a direction perpendicular to the nanocar axels. At 200 C, the motion was observed to be a combination of translation and pivoting as though the nanocars were moving independent of each other. Above 225 C, the motion was too rapid and erratic to be imaged by the STM.

Nanocar wheel rolling instead of sliding was studied [3] with 3-wheeled vehicles. Heating to 225 C caused pivoting about a central point without translation confirming the wheels were rotating and not sliding.

B. Coaxial Nanotubes

In 2008, Barrerio, et al. [4] showed cargoes of chemicals could be transferred along a fixed coaxial wire of carbon nanotubes (CNTs). A short mobile CNT was moved on a CNT wire that spanned a distance of a few microns. The mobile CNT was claimed to be driven by thermal gradients produced by passing an electrical current through the CNT wire. A phonon current along the fixed CNT was thought to drag the mobile CNT.

The current flowing in the CNT wire was thought to produce high temperatures in the mobile CNT and cargo by Joule heating. In support of this claim, the data of Chen et al. [5] based on ramping bias voltages across the CNT wire was presented. The mobile CNT contained F_e wires and attached Al_2O_3 nanoparticles that were claimed to melt at 1540 and 2054 C, respectively. The α-C coating on the CNTs was also removed only to be recovered upon removing the voltage bias. On this basis, a cargo of a rectangular gold plate was found [4] to transform into a ball suggested the gold melted at temperatures of 1300 K.

Motion of the mobile CNT to either end of the fixed wire was found not to depend on the direction of the applied current. Electro-migration caused by electron collisions with impurities in the mobile CNT was therefore ruled out as the motion mechanism.

Instead, the thermal gradient along the fixed CNT wire was claimed [5] to be the mechanism of the mobile CNT motion. A net current of phononic excitations traveling from the hot spot to the ends of the fixed wire was thought to interact with and transfer momentum to move the mobile CNT.

To verify the claim that thermal gradients drive the mobile CNT, MD simulations [4] invariably showed the mobile CNT to move down the thermal gradient. The MD simulations show the mobile CNT to move at a velocity ~ 10^8 microns/s, but the experiments show far slower velocities from 1-10 microns/s.

C. Linear CNT Motor . . .

More recently, Somada, et al., [6] in 2009 studied a molecular linear motor comprising a mobile capsule-like CNT inside a fixed host CNT. The capsule was a short cylinder with hemispherical ends; whereas, the fixed CNT was a longer cylinder provided with ends called sides A and B comprising inwardly disposed capsules. Unlike nanocars and coaxial nanotubes, the capsule moves back and forth from heating by an electron beam.

The linear motion [6] of the capsule is far shorter than the few microns of CNT wire in [3]. The capsule is 0.95 nm in diameter and 3.2 nm long while the host is 1.6 nm diameter and 8.5 nm long giving a stroke of 3.3 nm for the cycle. The capsule motion under electron beam heating consists of stationary and rapid transient phases. At the ends of the host, the capsule is stationary from a few to tens of seconds before moving to the opposite end. The cycle is repetitive, although the stationary time varied.

The capsule is claimed to be stationary because of van der Waals (vdW) forces in the interactions with the capsule ends of host CNT. MD simulations Zambrano et al. [7] show capsule velocities from 100-400 m/s for thermal gradients from 1-3 K/nm. But the experiment showed the capsule actually traveled the 3.3 nm stroke on the order of seconds.

The CNT capsule mechanism [6] considers thermal equilibrium, vdW forces, and lattice fluctuations due to heating. But the host CNT is not symmetric, the side B having a longer length than side A, thereby allowing side B to lose more heat loss to the surroundings than side A, perhaps explaining why side A had longer stationary times than side B.

D. Langevin Dynamics

In 2009, Hedgeland et al. [8] studied the benzene molecule on a graphite surface. Pair-wise hard wall repulsion was assumed between benzene molecules. Long range repulsive forces were not considered. Friction and coupling to surface phonons were deduced from the MD based on the Langevin equation. The benzene-graphite motion was found to approximate continuous Brownian motion found in the experiment. But MD simulations long range electrostatics interactions were not performed.

E. Nanodragster

In 2009, Vives et al. [9] synthesized the nanodragster as an extension of early work on nanocars [3] to lower the temperature for thermal motion by replacing the C_{60} front wheels of the nanocar with smaller p-carborane wheels. Only the synthesis and initial imaging are reported.

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III. PROBLEM STATEMENT

To provide a QM explanation for the motion of nanocars including molecular motors on substrates based on QED induced EM radiation.

IV. THEORY

Nanocars in moving continually make and break contact with the substrate, the process inducing QED radiation that by the photoelectric effect charges the nanocars, thereby producing motion by electrostatic interactions. Generally, anytime a nanostructure detaches from a macroscopic structure, QED induces EM radiation that charges the nanostructure, e.g., in tribochemistry charges are produced as nanoparticles are rubbed off surfaces. See Prevenslik [10, 12]

Similarly, geckos are held to walls by electrostatic attraction because of submicron spatulae at the tip of their toe hairs. Since the spatulae have a higher index of refraction than the hairs, the spatulae are isolated nanostructures that convert kT energy acquired as the gecko steps on the wall to QED induced charge as its foot is lifted. See Prevenslik [11, 12]

With regard to nanocars, Fig. 1.depicts QED charging: 1(a) nanocars acquire kT energy by contact with heated surface, 1(b) emitting EM radiation upon breaking contact, and 1(c) recovering kT energy upon regaining contact with the heated surface.

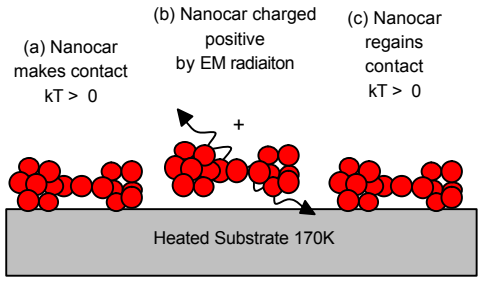

Fig. 1 Nanocar charging by EM radiation from kT energy acquired in contact with heated surface

Upon contact with the heated surface, the nanocar momentarily becomes a part of a macroscopic body that by QM is allowed to have kT energy. Upon moving, the nanocar is momentarily isolated having excess kT energy that is not allowed by QM.

Nanocars lack specific heat to conserve the excess kT energy which is in the FIR by an increase in temperature. Instead, QED induces the excess FIR

energy to be frequency up-converted to the EM confinement frequency of the nanocar that charges the nanocar positive by the photoelectric effect.

Nanocar thermal motion is therefore caused by electrostatic repulsion among neighboring nanocars. Alternatively, the charged nanocars can be moved by the electrical field of the STM tip.

A. QM Restrictions

QM confines the EM wavelength λ of photons in nanoparticles. For substrates [3] at 20 and 225 C, the Einstein-Hopf relation in Christy [13] for the harmonic oscillator at 300 and 500 K as a function of wavelength λ is shown in Fig. 2.

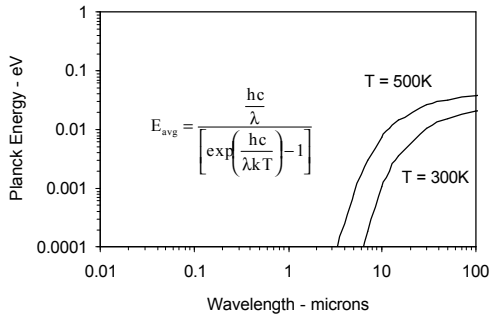

Fig. 2 Harmonic Oscillator at 300 and 500 K
In the inset, h is Planck's constant, and c the speed of light.

Fig. 2 shows atoms in nanocars have full kT energy in the FIR of 0.0258 and 0.043 eV for λ > 50 microns. Nanocar having wavelengths < 1 micron therefore exclude the available heat content of the atom and thereby lack the heat capacity to conserve absorb any EM energy by an increase in temperature.

B. EM Confinement Frequencies

QM precludes nanocars from conserving the absorbed thermal kT energy in the FIR by an increase in temperature. How FIR radiation is conserved by QED depends on the EM confinement.

1. Solid Nanoparticles In solid nanoparticles, Prevenslik [14] claimed the EM confinement is analogous to creating QED photons of wavelength λ by supplying EM energy to a QM box with walls separated by λ/2. For solid nanoparticles of diameter D and refractive index n_r, the absorbed FIR energy is up-converted by QED to the EM confinement frequency f of the nanoparticle creating QED photons having Planck energy E_P,

$$f = \frac{c}{\lambda}, \quad \lambda = 2n_r D, \text{ and } \quad E_P = hf \tag{1}$$

Only the fundamental frequency is considered.

2. Molecular Confinement Nanocars with fullerene C_{60} molecule wheels separated by alkynyl axles cannot be construed as a single solid continuum. But benzene molecules as well as short and capsule CNTs may be idealized as solid continuums.

Treating the nanocar as molecule rather than a continuum leads to the QM analogy of FIR absorption in the fundamental mode of the nanocar as a molecule. Morin et al. [15] found nanocars to absorb EM radiation in the near UV from 375-410 nm. Similarity with solid nanoparticles suggests FIR energy absorbed as the nanocar contacts the substrate is frequency up-converted by QED to the nanocar absorption wavelength. Taking λ = 400 nm as a typical fundamental wavelength,

$$\lambda = 400\,\text{nm} \quad \text{and} \quad E_P = 3.1\,\text{eV} \tag{2}$$

C. Vanishing Specific Heat

Both the Debye model of specific heat based on phonon vibrations of atoms in a lattice and Einstein's specific heat model of independent vibrations of the atoms as harmonic oscillators are only applicable to steady heat transfer in macroscopic structures. See Kittel [16]. At the nanoscale, non-thermal photons are created by the QED induced frequency up-conversion of absorbed FIR radiation. The energy U of a nanocar under molecular EM confinement with N_P photons having Planck energy E_P,

$$U = N_P E_P \tag{3}$$

where, only the fundamental mode of the nanocar need be considered. For the specific heat C given by ∂U/∂T,

$$C = 0 \tag{4}$$

V. ANALYSIS

A. EM Emission

Upon contacting the heated surface, the nanocars become part of a macroscopic structure that by QM is allowed to have kT energy. For nanocars comprised of N_A atoms and the surface at temperature T_H, the energy U absorbed,

$$U = 3kT_H N_A \tag{5}$$

Lacking specific heat, the nanocar conserves the absorbed kT energy in the FIR by the QED induced frequency up-conversion to the molecular EM confinement frequency of the nanocar. The number N_P of QED photons created,

$$N_P = \frac{U}{E_P} = \frac{3kT_H N_A}{E_P} \tag{6}$$

B. Electrostatic Charge

The charging of the nanocar by the photoelectric effect requires the QED photons to be first absorbed. Usually, the photons from an external source are first required to be absorbed by the nanocar, but there is efficiency η < 1 associated with the absorption.

However, QED photons are not externally supplied, but rather created within the nanocar molecules themselves, and therefore the absorption efficiency η is near unity. The charge q is,

$$q = \eta N_P \sim N_P \quad (7)$$

The threshold for nanocar motion is found [3] to occur at a substrate temperature of about 170 C. For the nanocar having N_A = 624 atoms and molecular EM confinement with Planck energy E_P 3.1 eV, The QED induced charge q in terms of the substrate temperature T_H is shown in Fig. 3.

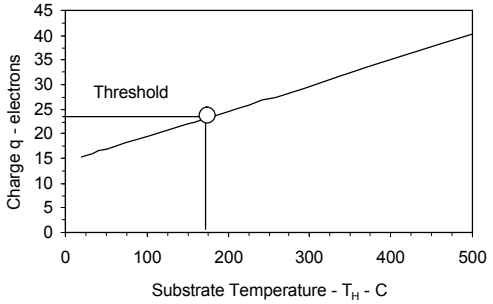

Fig. 3 QED Induced Charge and Thermal Threshold

VI. DISCUSSION

A. Nanocars and Nanodragsters

Nanocar motion from thermal heating of the substrate occurs by electrostatic repulsion from neighboring nanocars, the nanocar charges produced by QED induced charging. Observations [3] that nanocar motion begins as the substrate is heated to a threshold of 170 C is interpreted here by Fig. 3 that shows the QED induced charge q ~ 23 electrons is required to initiate motion. Substrate temperatures > 170 C increase the QED induced charge and corresponding nanocar motion.

Pivoting rather than translation about the center of 3-wheeled nanocars in Fig. 4(d) and (e) of [3] show the C_{60} wheels are rolling rather than sliding. The pivoting occurs because the charge center is not coincident with its geometric center. Pivoting occurs over a small rotation, and therefore continuous rotation is unlikely under thermal heating.

The electrical field of the STM tip relative to the substrate also acts to move the charged nanocars. Pulling nanocars with the STM tip suggests the positive charged nanocars are attracted to the negative charged STM tip.

Pushing causes direct contact between the tip and the nanocar that neutralizes the nanocar charge. Nanocar charges are not coincident with the geometric center, and therefore pushing is likely to cause pivoting and rotation before pulling reacquires QED induced positive charge and the nanocar is attracted once again to the negative charged STM tip. In contrast, large organic molecules are pushed [1, 2] with the STM tips because the near coincidence of charge and geometric centers allows rotation to go relatively unnoticed.

B. Coaxial Nanotubes

The motion of a short mobile CNT on a coaxial fixed CNT wire [4] is similar to the nanocar on a substrate [3] in that QED induced radiation charges the mobile CNT by the photoelectric effect. There is no need for a phonon current [4] to drag the mobile CNT in the direction of the thermal gradient.

QED induced radiation is produced because the mobile CNT and gold plate cargo lacking heat capacity cannot increase in temperature under Joule heating. The claim [4] that the gold plate under Joule heat melts at 1300 K to form spherical drops is not likely. Apparent melting can be explained by a Coulomb explosion at the nanoscale where intense EM fields produce atomic motion under Joule heating instead of high temperatures. Atomic motion breaks the bonds holding solids together thereby producing a plasma of charged particles. See Hashida et al. [17].

Moreover, the apparent melting [5] of F_e wires and Al_2O_3 nanoparticles under Joule heat used in support of the melting claim [4] may also be explained by the cold plasma in Coulomb explosions. The fact that the α-C coating [5] on the CNTs was removed under Joule heat and recovered upon subsequent removing the bias voltage suggests the plasma was cold and not hot. Hot plasmas tend to seal pores and on that basis can be distinguished from cold plasmas. QED induced radiation is consistent with cold plasmas.

Instead of high temperatures, QED photons are created that charge the mobile CNT positive with the free photoelectrons moving along the fixed CNT host to charge the closest end negative. The mobile CNT therefore moves toward the closest end under electrostatic attraction. Unlike electro-migration, the electrostatic charging of the mobile CNT does not depend on the direction of the electrical current

MD simulations [4] showing the mobile CNT to move down the thermal gradient lack meaning because there is no heat capacity [12] to support heat transfer at the nanoscale. The large disparity between the MD computed velocity of about 10^8 microns/s and the 1-10 microns/s found in the experiment support the argument that MD simulations of heat transfer are not applicable at the nanoscale.. Instead, MD simulations at constant temperature directed to mobile CNT motion under QED induced electrostatic attraction are recommended.

C. Linear CNT Motor

The linear CNT motor [6] comprises capsule-like CNTs inside a host CNT having ends A and B of inwardly disposed CNT capsules. Motion is claimed [6] to occur by a combination of thermal heating, vdW forces, and lattice distortions.

In contrast, QED induced electrostatic forces are more likely. Similarity is found with nanocars and coaxial nanotubes under thermal and Joule heating except that in the linear CNT motor heating is by an electron beam.

Consider the capsule in a neutral charge state held by vdW forces in the stationary position at end B of the host CNT as shown in Fig. 1(h) of [6]. QM precludes any temperature increase caused by electron beam heating. Instead, the capsule acquires a positive charge by QED induced photons created and absorbed within the capsule. Free photoelectrons move to end A along the host CNT. Over time, the electron beam heating produces an increasing electrostatic attraction of the capsule toward end A. Upon overcoming the vdW attractive force, the capsule moves rapidly < 0.5 s to the end A where its positive charge is neutralized. The cycle repeats.

Stationary times at A are longer (40-50 s) than at B (1-5 s) because of non-symmetry. With the capsule at A, the 'other longer tube at B' extracts heat from the electron beam that would not occur with the capsule at B. Hence, the time to charge the capsule at A is longer to overcome the same threshold vdW force.

MD simulations [7] showing the capsule traveling at velocities from 100-400 m/s while the experiment shows the 3.3 nm stroke is covered on the order of seconds supports the argument that MD simulations in nanoscale heat transfer are meaningless.

D. Langevin Dynamics

Langevin MD [7] simulations were found in agreement with experiment by assuming pair-wise hard wall repulsive interactions between benzene molecules on a graphite substrate. Long range repulsion was neglected based on helium-3 spin echo data. See Jardine et al. [18].

However, QED induced long range repulsive interactions may also be consistent with the spin echo results. The QED repulsion only acts over the time the molecules leave the substrate until the substrate is once again contacted. With the substrate charged negative, the positive charged benzene molecules are attracted to the substrate. Hence, the reacquisition time is very short and may not have been resolved in the spin echo [18] response. More study is required.

VII. CONCLUSIONS

- Preliminary QED theory and methodology for charge estimates in nanocars are presented for review. Further study and is required,

- QED methodology for charge estimates in short CNT cylinder and capsule motors are presented. Charge estimates to be presented in future updates.

- Langevin MD simulations for motions of benzene molecules son graphite should be modified by short duration long range QED induced repulsion.

- QM leaves interpretations of MD simulations of heat transfer in nanostructures without meaning.

- Nanostructures act as frequency up-conversion devices that induce QED radiations which charge the nanostructure, or are absorbed in the surroundings.

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