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Invalidity of Molecular Dynamics in Heat Transfer

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Molecular Dynamics (MD) simulations based on classical statistical mechanics always allow the atom to have thermal heat capacity. Quantum mechanics (QM) differs in that the heat capacity of atoms in submicron nanostructures vanishes. Nevertheless, MD simulations of heat transfer in discrete nanostructures are routlinely performed and abound in the literature. Not only are discrete MD sumultions invalid by QM, but give unphysical results, e.g., thermal conducitvity in nanofluids is found to exceed standard mixing rules while in solid metal films depends on thickness. QM negates the heat capacity of atoms in discrete nanostructures, thereby precluding the usual conservation of absorbed electromagnetic (EM) energy by an increase in temperature. Instead, conservation proceeds by QED inducing the absorbed EM energy to create non-thermal EM radiation *inside* the nanostructure that by the photoelectric effect chargea the nanostructure, or is emitted to the surroundings. QED stands for quantum electrodynamics. Unphysical results occur because QED induced radiation is not included in the nanoscale heat balance, but if included physical results for discrete nanostructures are found. Examples of unphysical MD simulatons are presented.

Keywords: molecular dynamics, quantum mechanics, statistical mechanics.

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1. INTRODUCTION

MD is used in computational heat transfer to determine the thermal response of nanostructures. With theoretical basis in statistical mechanics, MD [1-3] relates the thermal energy of the atom to its momentum by the equipartition theorem. Momenta of atoms in an ensemble are determined by solving Newton's equations with inter-atomic forces derived from Lennard-Jones potentials. Unlike the size effect of QM, statistical mechanics always assumes the atom has heat capacity, as otherwise the momenta of the atoms cannot be related to their temperature. Statistical mechanics assumes the atom has the same heat capacity at the nanoscale as at the macroscale.

In heat transfer simulations of bulk materials, MD is performed for an ensemble of atoms in submicron computation boxes under periodic boundary conditions (PBC). See e.g. nanofluids [4]. PBC allow bulk simulations in submicron computation boxes with only a small number of atoms, as otherwise MD simulations of the bulk are intractable. Because of this, MD of atoms having heat capacity in computation boxes under PBC is physical because equivalence is found to atoms in the bulk that do indeed have heat capacity

MD of discrete nanostructures differs. Unlike MD simulations of the bulk with atoms having heat capacity, QM precludes atoms from having heat capacity. Nevertheless, the large number of MD simulations of discrete nanostructures having heat capacity abound in the literature. See e.g. [5,6]. Although consistent with statistical mechanics, MD of discrete nanostructures [7] is not only invalid by QM, but also give unphysical results, e.g., standard mixing rules [8] are violated for nanofluids; thermal conductivity of thin films [9] depends on thickness, molecular motors are thought [10] to translate by thermal gradients, and so forth.

Indeed, the difference between QM and statistical mechanics is of fundamental significance in the MD of nanoscale heat transfer. By QM, atoms in discrete nanostructures lacking heat capacity cannot conserve heat by an increase in temperature, and therefore the classical modes of heat transfer – convection, radiation, and conduction that depend on temperature have no meaning. Instead, conservation proceeds by the creation of non-thermal QED induced EM radiation that charges the discrete nanostructures by the photoelectric effect, or emitted to the surroundings.

2. PURPOSE

The purpose of this paper is to describe how QM requires the heat capacity of the atom in nanostructures to vanish thereby precluding the conservation of absorbed EM energy by an increase in temperature. Conservation then proceeds by the QED induced creation of photons *inside* the nanostructure and creates charge by the photoelectric effect or is emitted as QED radiation to the surroundings. MD simulations of discrete nanostructures that assume the atom has heat capacity by statistical mechanics and do not create QED radiation are therefore invalid and unphysical, examples of which are presented.

3. THEORY

3.1 QM Restrictions

Unlike statistical mechanics, QM restricts the heat capacity of atoms in nanostructures. The Einstein-Hopf relation [11] for the harmonic oscillator giving the dispersion of Planck energy E with the EM confinement wavelength λ is the measure of the capacity of the atom to absorb heat. QM in relation to the classical oscillator by statistical mechanics is shown in Fig. 1.

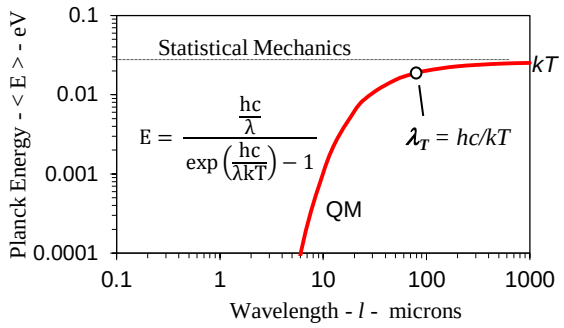

Fig. 1 Heat Capacity of the Atom at 300K

By the equipartition theorem of statistical mechanics, the classical oscillator allows the atom to have the same heat capacity in nanostructures as the macroscale. QM oscillators differ in that kT energy is only available for $\lambda > \lambda_T$ while heat capacity is restricted for $\lambda < \lambda_T$. At ambient temperature, $\lambda_T \sim 50$ microns. Fig. 1 shows the heat capacity of the atom is less than kT for $\lambda < 50$ microns with full kT energy available only for $\lambda > 50$ microns. By QM, atoms in nanostructures having $\lambda < 1$ micron have virtually no heat capacity to conserve heat from any EM source by an increase in temperature.

3.2 TIR Confinement

Lack of heat capacity by QM precludes heat from EM sources to be conserved in nanostructures by an increase in temperature. However, the absorbed heat must still be conserved, and therefore conservation proceeds during TIR confinement by creating QED induced radiation *inside* the nanostructure. TIR stands for total internal reflection. TIR has a long history beginning with Tyndall in 1870 who discovered if the refractive index of a body is greater than that of the surroundings, absorbed light is trapped at its surface. In nanostructures, TIR has an important significance [12] and need not be limited to light absorption. Unlike macrostructures, nanostructures have high surface to volume ratios, and therefore heat from any EM source (lasers, molecular collisions, electrical resistance, etc.) is absorbed almost totally in the NP surface. Since the nanostructure surface corresponds to the TIR wave function of the NP, QED induces the absorbed EM energy to undergo the spontaneous creation of photons *inside* the NP. However, TIR confinement is not permanent, but rather sustains itself only during heat absorption, i.e., absent heat absorption, there is no TIR confinement and QED radiation is not created.

Taking the spherical NP as the idealized shape of the most common nanostructure, the TIR confinement of heat creates QED photons at frequency f having Planck energy E,

$$f = \frac{c/n}{\lambda}, \qquad \lambda = 2d, \qquad E = hf \tag{1}$$

where, n is the refractive index and d the diameter of the NP.

3.3 QED Induced Heat Transfer

QED induced heat transfer is the consequence of the QM requirement that the heat capacity of the atom vanishes in nanostructures. Consider the NP resting on a surface as depicted in Fig. 2.

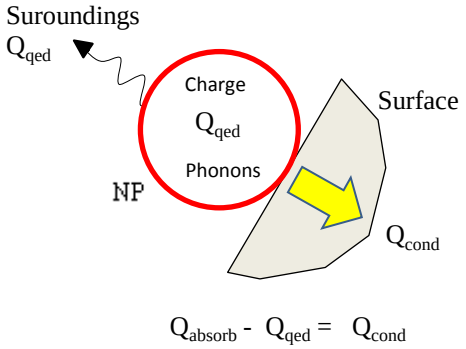

Figure 2 QED Induced Heat Transfer

Since absorbed heat Q_{absorb} cannot be conserved by an increase in NP temperature, conservation occurs by other paths. One path is conductive flow Q_{cond} into the surface by phonons, and the other by creation of QED radiation Q_{qed} inside the NP that in turn is conserved by the creation of charge by Einstein's photoelectric effect or by emission to the surroundings. However, phonons respond to absorbed heat at acoustic velocities while QED radiation moves at the speed of light. Hence, absorbed heat Q_{absorb} is promptly conserved by QED radiation well before phonons respond, and therefore conductive heat transfer does not occur, i.e., $Q_{cond} \sim 0$. If the NP is isolated from the surface, the prompt QED emission occurs before the phonons in the NP respond. See response to comment in [12].

In QED induced heat transfer, absorbed heat Q_{absorb} is conserved almost totally by creating number N of QED photons *inside* the nanostructure that produce electrical charge by the photoelectric effect. The QED photons are created at the rate dN/dt,

$$\frac{dN}{dt} = \frac{Q_{abs}}{E} \tag{2}$$

However, if the nanostructure is in contact with a surface, conductive heat Q_{cond} must be considered. In nanoscale thin-films attached to macroscopic substrates, electrical current through the film produces Joule heat Q_{abs} that is conserved by both Q_{qed} emission to the surroundings and conduction Q_{cond} into the substrate. Typically, the effective conductivity for thin-films is found [9] reduced from the bulk for film thickness less than 100 nm. However, QED radiation was noted [13] not to be included from the heat balance, but if included, the conductivity does not decrease, and instead remains at bulk as the film thickness is decreased. Excluding Q_{qed} from the heat balance is understandable because the QED emission from thin films having thickness $d < 100$ nm occurs at Planck energy $E > 6.2$ eV, which is beyond the ultraviolet (UV) and would not be normally observed. Because of this, the reduced thermal conductivity was explained [9] by

scattering of phonons. However, prompt QED radiation conserves absorbed Joule heat without conduction, making meaningless the notion of reduced conductivity by scattering of phonons when in fact conduction does not occur.

4. APPLICATIONS

4.1 Nanofluids

Nanofluids comprising NPs in solvents are claimed to surpass the thermal performance of traditional heat transfer liquids. MD simulations following procedures [1-3] were used [4] to determine the thermal conductivity of a nanofluid consisting of copper NPs in liquid argon. Consistent with QM, periodic boundaries with atoms having heat capacity were assumed. For a Cu nanofluid, the NP diameter is about 2 nm in a cubic computational box of 4 nm on a side having a total of 2048 atoms as depicted in Fig. 3.

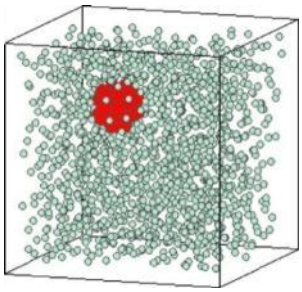

Figure 3 PBC - Nanofluid

Lennard Jones potentials were used to simulate the interactions between Cu atoms in the NP and between the Cu and Ar atoms. Results suggest NPs enhance thermal conductivity by the increased Brownian motion of liquid argon atoms. However, the long-range interactions between the NP and its image neighbors that should be significant at 4 nm spacing were not included. Larger computational boxes that capture NP interactions with neighbors would reduce the increased Brownian movement of liquid atoms and decrease any enhanced thermal conductivity found for the shorter computational boxes. Classical physics assumed in MD should not give higher conductivity than that given by standard mixing rules, but otherwise the MD solution is valid and consistent with QM.

4.2 Nanocars

Nanocars including molecular motors are nanostructures [5] comprised of ordered atoms and molecules that convert heat into mechanical motion. The heat may take various EM forms including light, Joule heat, and electron beams, e.g., nanocars are observed to move by simply heating the substrate. In a typical experiment, a large number of nanocars are laid down at random on a gold surface. Upon heating the gold surface, the cars are observed to move. For clarity, only a single car is shown in Fig. 4.

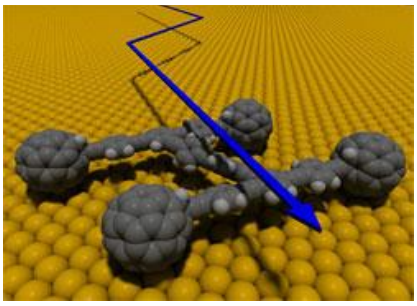

Figure 4 Discrete Nanostructure - Nanocar

The mechanism by which heat is converted into nanocar motion is not well understood. MD simulations [5] of heat transfer were performed to explain observed motions. However, MD heat transfer of nanocars is invalid because QM requires the heat capacity of atoms. Hence, absorption of heat by the nanocar from the substrate cannot be conserved by an increase in temperature. It is not surprising therefore, the MD simulations show the cars to distort, but not move.

However, this MD result is expected in our macroscopic world. If you park your car with the brakes off in a flat parking lot on a hot day, you would not expect it to move and collide with other cars. Macroscopic results are found in MD simulations because atoms in nanocars are assumed to have the same heat capacity as in our macroscopic car. For classical physics by statistical mechanics, Fig. 1 shows the Planck energy of the atom in a macroscopic car under EM confinement at long wavelengths is the same as that in nanocars at short wavelengths, and therefore neither car would be expected to move upon heating the supporting surface.

QM differs. Conservation proceeds by the QED induced frequency up-conversion of absorbed heat to the TIR confinement frequency of the nanocar that at ultraviolet or higher levels charges the nanocar positive by the photoelectric effect. Similarly, other nanocars charge positive. Observed nanocar motion is therefore caused by electrostatic repulsion between nanocars

4.3 Linear Motors

MD simulations [10] have been used in attempts to explain how thermal gradients drive linear actuators consisting of the concentric CNTs shown in Fig. 5. By heating the ends of the fixed CNT, the outer CNT is found to move toward the cold end of the fixed CNT. The thermal driving force is found proportional to the temperature gradient.

However, MD simulations did not show any motion of the outer CNT. By adding a thermophoretic spring, motion was observed in the MD response, but then only a thermophoretic analysis having nothing to do with MD is required. The MD simulation showing the outer CNT did not move under the temperature gradient across the fixed CNT is consistent with our macroscopic world, e.g., heating a macroscopic equivalent of the CNT nanostructures, say concentric pipes would not cause motion of the outer pipe. Similar to nanocars, the problem is atoms in the MD simulation of the CNTs and those in macroscopic pipes have the same heat ca-

pacity as shown in Fig. 1. What this means is the mechanism of CNT linear actuators cannot be explained by MD based on statistical mechanics.

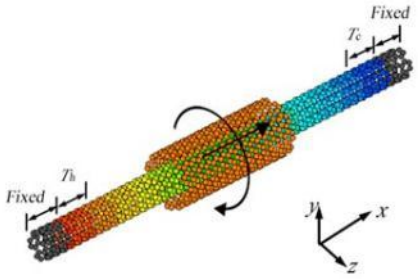

Figure 5 Discrete Nanostructure – Concentric CNTs

The QM explanation of CNT motion is simple. More QED radiation is produced at the hot end of the fixed CNT than at the cold end. By the photoelectric effect, the hot end is therefore charged positive more than the cold end. The outer CNT then moves by repulsion to the cold end under the charge gradient. MD simulations cannot explain the CNT motion because charge is necessary and classical physics does not produce charge.

4.4 Sputtering

The Kinetic Monte Carlo technique (KMC) is a procedure for solving kinetic equations in non-equilibrium processes. Unlike traditional MC, real time is included in the evolution of the system. The KMC simulation [6] of 5 keV argon atoms impacting a Cu (111) crystal is shown in Fig. 7. The KMC simulation shows the emission of large clusters of Cu atoms from the crystal. The color coding temperature of the atoms: white - black > 300K, blue < 1400K; green < 4200K; red above 4200K.

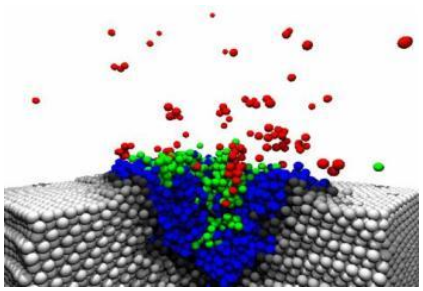

Fig. 6 Discrete Nanostructures - Sputtering

The extent of the KMC model is observed to be submicron, and therefore the temperatures found that exceed melting of copper are proof the KMC simulation is invalid by QM. However, the KMC solution may be made at least consistent with QM by holding the temperature constant with the Nose-Hoover thermostat [1-3] during the solution run. The QED emission may then be estimated [7] from the saved history of thermostat heat and input to a finite flement simulation of melting over larger regions of the crystal.

5. CONCLUSIONS

MD simulations of heat transfer based on statistical mechanics that assume atoms have heat capacity are valid only for PBC.

Unlike statistical mechanics, QM precludes atoms in discrete nanostructures from heat capacity, the consequence of which is that heat from EM sources (lasers, molecular collisions, Joule heat, etc.) absorbed in nanostructures is conserved by the creation of QED radiation that charges the nanostructure by the photoelectric effect, or is emitted to the surroundings. Classical heat transfer by radiation, convection, and conduction that depend on the temperature of the nanostructure are no longer valid. Similarly, Fourier's heat conduction equation is not valid for discrete nanostructures.

MD simulations of discrete nanostructures in the literature are invalid by QM. Arguments that MD is consistent with statistical mechanics may be dismissed as QM governs heat transfer at the nanoscale.

In discrete MD simulations, absorbed heat is conserved by the creation of QED photons that produce charge by the photoelectric effect. Conversely, discrete MD simulations based on classical physics having heat capacity do not produce charge and erroneously conserve absorbed heat by an increase in temperature.

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