Molecular Dynamics of Heat Transfer and Quantum Mechanics

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Abstract

Molecular Dynamics (MD) is used in computational heat transfer to determine the thermal response of nanostructures. Finding basis in classical statistical mechanics, MD 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. Statistical mechanics always assumes the atom has thermal energy, or equivalently the capacity to absorb heat. Otherwise, the temperature of the atoms cannot be related to its thermal energy, the consequence of which is atoms in nanostructures have the same heat capacity as those at the macroscale. For bulk materials, MD heat transfer is performed for an ensemble of atoms in submicron computation boxes under periodic boundary conditions. Consistent with statistical mechanics, MD simulations of the bulk are valid because atoms having heat capacity in discrete submicron boxes under periodic boundary conditions are equivalent to those in the bulk that do indeed have heat capacity. Quantum mechanics (QM) differs. Unlike MD simulations of the bulk with atoms having heat capacity, QM precludes atoms in discrete nanostructures from having heat capacity. Nevertheless, the literature is replete with MD simulations of discrete nanostructures with atoms having heat capacity. Although consistent with statistical mechanics, MD of discrete nanostructures is invalid by QM. 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 at the nanoscale proceeds by the creation of non-thermal QED induced EM radiation that charges the discrete nanostructures by the photoelectric effect, or is emitted to the surroundings. QED stands for quantum electrodynamics and EM for electromagnetic. Examples of MD simulations are presented that by QM are valid or invalid and recommendations made for how invalid MD heat transfer of discrete nanostructures may be consistent with QM. For interacting nanostructures, MD heat transfer simulations consistent with QM are computationally intractable, and therefore finite element (FE) simulations are proposed using estimates of QED radiation from the nanostructures in programs such as ANSYS and COMSOL

Keywords: Molecular dynamics, nanostructures, heat transfer, statistical mechanics, quantum mechanics, quantum electrodynamics

I. Introduction

MD is commonly used to simulate heat transfer in discrete nanostructures, but MD was actually developed to determine the macroscopic transport properties of bulk liquids [1-3]. Finding theoretical basis in statistical mechanics, MD derives the momenta of an ensemble of atoms in submicron computational boxes based on the solution of Newton's equations. Historically, MD simulations were in fact preceded in the 1950's by Monte Carlo (MC) simulations, e.g., the virial coefficients were derived [4] with MC simulations of spherical particles in submicron 2D computational square boxes under periodic boundary conditions. Later, MC simulations [5] were based on atomic interactions given by Lennard-Jones potentials that allowed thermodynamic data for liquid argon to be compared with computer generated MC solutions. About this time, MD solutions of bulk liquids using hard spheres [6] were first proposed. In the 1960's, the MD simulation [7] of liquid argon was later followed by the seminal MD paper [8].

Since 1950, MD simulations [4-8] imposed periodic boundary conditions on the submicron computation boxes allowing the bulk properties of the liquid to be derived with a small number of atoms. Otherwise, the solution of Newton's equations for the large number of atoms in macroscopic volumes was intractable. However, in MD simulations of heat transfer, periodic boundaries assure the fundamental premise of statistical mechanics is satisfied, i.e., the atoms have macroscopic heat capacity. Not only is this consistent with statistical mechanics, but also with the fact that in the bulk liquid being simulated, all atoms do indeed have heat capacity. By statistical mechanics, MD solutions under periodic boundaries with all atoms having heat capacity are valid even though the computation boxes are submicron.

Today, MD simulations of heat transfer are not performed to derive bulk properties. Exceptions include MD to determine the thermal conductivity of nanofluids [9] comprising nanoparticles (NPs) in liquid argon. Indeed, the literature is replete with MD simulations of discrete nanostructures that are unambiguously not periodic [10-12]. Consistent with statistical mechanics, the atoms in the nanostructures are assumed to have macroscopic heat capacity, the MD simulations of which are thought to provide precise atomic descriptions of nanoscale heat transfer when in fact they are invalid because QM precludes atoms in discrete nanostructures from having heat capacity. In effect, MD simulations that assume atoms have heat capacity derive the thermal response of the nanostructure as if it were a scaled down macroscopic body, and therefore

are meaningless in the understanding of heat transfer at the nanoscale. Clearly, QM invalidates MD heat transfer of discrete nanostructures, but

What can be done to make discrete MD heat transfer consistent with QM?

II. Purpose

Clarify the QM validity of MD simulations of heat transfer under periodic boundary conditions and invalidity of MD for discrete nanostructures. Provide recommendations for performing MD heat transfer simulations in discrete nanostructures that are consistent with QM.

III. Theory

Classical heat transfer assumes atoms have heat capacity and conserve absorbed heat from EM sources (lasers, molecular collisions, electrical resistance, etc.) by an increase in temperature. Because of this, conduction, radiation, and convection have meaning in dissipating absorbed heat. QM differs in that the heat capacity of atoms in nanostructures (NPs, thin films, nanowires, etc.) vanishes, and therefore temperature changes do not occur. Hence, classical conduction, radiation, and convection that depend on temperature are meaningless. Heat transfer for an isolated NP is illustrated in Fig. 1.
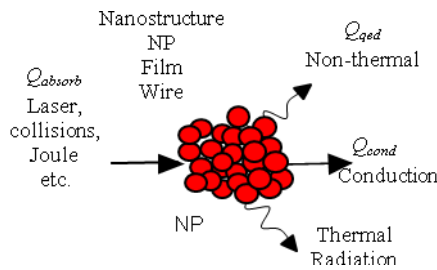

Figure 1 Heat transfer at the nanoscale showing a NP conserving heat from EM sources

Lacking changes in temperature, the NP conserves absorbed heat flow Q_{absorb} by the emission of QED induced radiation Q_{qed}. However, some conduction Q_{cond} may occur if the NP is in contact with a surface. Unlike thermal radiation by the Stefan-Boltzmann law important at high temperatures, QED induced emission is non-thermal EM radiation at the NP temperature. The heat flow balance is,

$$Q_{abs} - Q_{qed} = Q_{cond} \qquad (1)$$

QM Restrictions

Unlike statistical mechanics, QM restricts the heat capacity of atoms in nanostructures. The Einstein-Hopf relation [13] 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,

$$E = \frac{\frac{hc}{\lambda}}{\exp\left(\frac{hc}{\lambda kT}\right) - 1} \qquad (2)$$

where, h is Planck's constant, c the speed of light, k Boltzmann's constant and T absolute temperature. The QM relation for the Planck energy in relation to the classical oscillator by statistical mechanics is illustrated in Fig. 2.
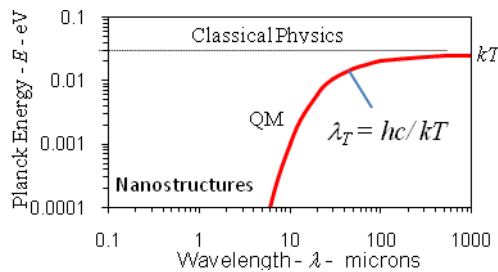

Figure 2 The Atom as a Harmonic Oscillator at 300 K.

By the equipartition theorem of statistical mechanics, the thermal energy of the classical oscillator is always kT allowing the atom to have the same heat capacity in nanostructures as at the macroscale. QM oscillators differ in that kT energy is only available for $\lambda > \lambda_T$ while kT energy is restricted for $\lambda < \lambda_T$. At ambient temperature, $\lambda_T \sim 50$ microns. Hence, Fig. 2 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 $\lambda_T < 1$ micron have virtually no heat capacity to conserve heat from any EM source by an increase in temperature.

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 observed 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 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 absorbed heat, QED induces the absorbed heat to undergo the spontaneous creation of photons *inside* the nanostructure. 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,

$$f = \frac{c/n}{\lambda}, \qquad \lambda = 2D, \qquad E = hf \qquad (3)$$

where, n is the refractive index and D the diameter of the NP. Unlike macrostructure QED emission at phonon frequencies, nanostructures have $\lambda < 1$ micron with QED emission occurring at frequencies f beyond the UV.

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. 3.
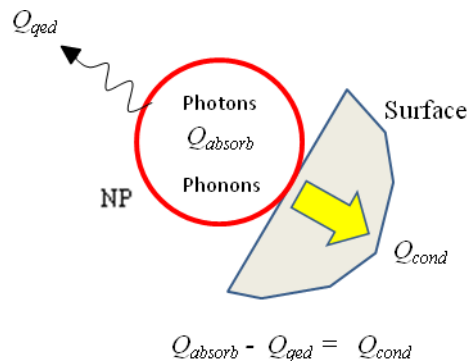

Figure 3 QED Induced Heat Transfer

Since absorbed heat Q_{absorb} cannot be conserved by an increase in NP temperature, conservation occurs by another path. One path is conductive flow Q_{cond} into the surface by phonons, and the other by emission of QED radiation Q_{qed} from QED photons. However, phonons respond to absorbed heat at acoustic velocities while QED photons move at the speed of light. Hence, absorbed heat Q_{absorb} is conserved promptly by QED emission before phonons respond, and therefore conductive heat transfer does not occur, i.e., $Q_{qed} \sim Q_{absorb}$. If the NP is isolated from the surface, the prompt QED emission occurs before the phonons in the NP respond.

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,

$$\frac{dN}{dt} = \frac{Q_{absorb}}{E} \qquad (4)$$

However, if the nanostructure sis 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_{absorb} that is conserved by Q_{qed} emission to the surroundings and conduction Q_{cond} into the substrate. Typically, the effective conductivity for thin-films is found [14] reduced from the bulk as the film thickness is reduced below 100 nm. However, the QED emission was excluded [15] from the heat balance, which if included, the conductivity does not decrease, but remains at bulk as the film thickness is decreased. If Q_{qed} is not included in the heat balance, Q_{cond} is thought [14] to be higher than actual, and therefore the thermal conductivity K is reduced from bulk to satisfy the heat balance. 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 UV and would not be normally observed. Because of this, the reduced thermal conductivity was explained [14] by scattering of phonons. However, prompt QED emission conserves absorbed Joule heat without conduction, making meaningless the notion of reduced conductivity by scattering of phonons when in fact conduction does not occur.

IV. Review of MD Simulations

The MD simulations [9-12] in the literature are reviewed in relation to the QM restriction that the atoms in discrete nanostructures do not have heat capacity, thereby invalidating any MD simulations claiming temperature changes, thermal conduction, and heat currents.

Nanofluids

Nanofluids comprising NPs in solvents are claimed to surpass the thermal performance of traditional heat transfer liquids. MD simulations following procedures using the Green-Kubo method [1-3] were used [9] 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. 4.
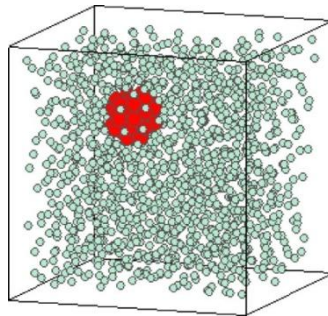

Figure 4 Nanofluid in Computation Box – Periodic Boundaries

Lennard Jones potentials were used to simulate the interactions between Cu atoms in the NP and between the Cu and Ar atoms. Results suggest enhanced thermal conductivity is caused by the increased movement of liquid argon atoms by Brownian motion in the presence of NPs. 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.

Nanocars

Nanocars including molecular motors are nanostructures [10] 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. 5
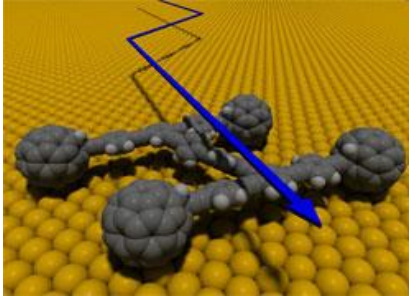
Figure 5 Discrete Nanostructure - Nanocar

The mechanism by which heat is converted into nanocar motion is not well understood. MD simulations [10] of heat transfer were performed to explain observed motions. However, MD heat transfer of nanocars is invalid because QM restricts 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 heat capacity as in our macroscopic cars. For classical physics by statistical mechanics, Fig. 2 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.

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

Carbon Nanotube (CNT) Actuator

MD simulations [11] have been used in attempts to explain how thermal gradients drive linear actuators consisting of the concentric CNTs shown in Fig. 6. 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.
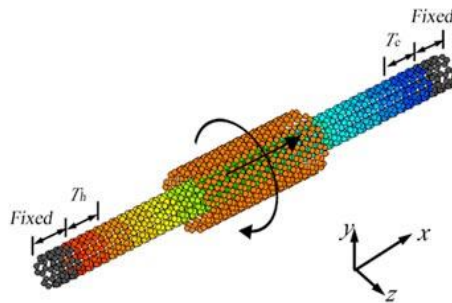

Figure 6 Discrete Nanostructure – Concentric CNTs

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 obviously 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 capacity as shown in Fig. 2. What this means is the mechanism of CNT linear actuators cannot be explained by MD based on classical statistical mechanics.

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.

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 [12] 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 - 1400K; blue 1400K - 2800K; green 2800K - 4200K; red above 4200K.
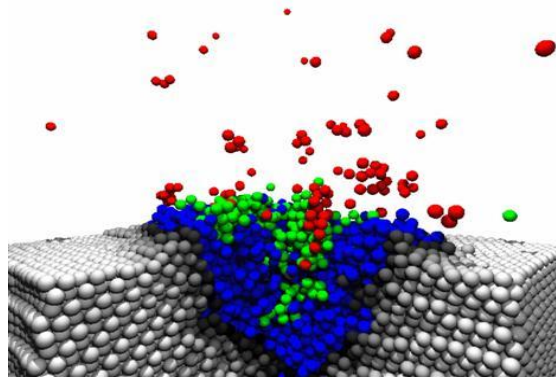

Figure 7 Discrete Nanostructure – Sputtering

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 from the saved history of thermostat heat and input into a FE simulation of melting over larger regions of the crystal.

V. Summary and Conclusions

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

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 charge or the emission of QED induced radiation. 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 reported 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.

The common belief that MD simulations provide a precise description of heat transfer in nanostructures not possible with classical physics using FE programs such as ANSYS or COMSOL is erroneous. MD and FE give equivalent results, but both are invalid by QM.

VI. Recommendations

Given the MD of discrete nanostructures is invalid by QM, the following procedure [16] is recommended to make the MD heat transfer simulation of nanostructures at least consistent with QM.

1. During the MD simulation, use the Nose-Hoover thermostat [1-3] to hold the temperature constant as required by QM. The QED radiation created in a nanostructure is its thermostatic heat.

2. At each time step, use the QED induced radiation to compute the thermal response of the surroundings and the charge in the nanostructures by the photoelectric effect.

3. Compute the thermal and dynamic response of the system of nanostructures.

Since the MD solution of heat transfer for even a few interacting nanostructures is computationally intractable, an alternative is to forego MD simulations altogether and instead make a FE simulation of the nanostructures and the

surroundings. Estimate the QED radiation for each nanostructure based on the heat absorbed from EM sources. Simple hand-calculations suffice. Input the QED radiation in a FE simulation to determine the macroscopic thermal and dynamic response consistent with QM. Include the charge created from QED radiation in generating electrostatic forces between nanostructures to determine their dynamic response.

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Thomas Prevenslik is a retired American living in Hong Kong and Berlin. He is a graduate of Carnegie Institute of Technology and the University of Pittsburgh. He spent most of his career as a Mechanical engineer in the nuclear power industry working on advanced reactors at Westinghouse. Later as a consultant, he worked for American and Japanese companies in computer simulations of structural dynamics and heat transfer in the diverse areas of optical telescopes, gas bearings, turbine engines, and molecular dynamics of chemical reactions. He became involved in nanoscale heat transfer because classical physics based on phonon theories by Einstein and Debye failed to provide rational explanations of observations. In contrast, he has promoted QED induced heat transfer based on the quantum mechanical requirement that the heat capacity of the atom vanishes at the nanoscale. Conservation of absorbed energy therefore cannot proceed by an increase in temperature, and instead QED creates photons *inside* the nanostructure that produce charge, or are emitted to the surroundings. QED heat transfer by photons avoids the numerous unphysical explanations of observations at the nanoscale based on phonons that suggests changing the mixing rules for nanofluids; reduced bulk thermal conductivity depending on film thickness; the fourth circuit element of memristors; molecular signaling by the lock and key mechanism in olfaction; and so forth. QED induced heat transfer by photons not only offers a rational approach inaccessible to nanoscale heat transfer by phonons, but in the far more diverse areas of nanostructure interaction with macroscopic systems.