Validity ofHeat Transfer by Molecular Dynamics

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***Abstract*—Molecular Dynamics (MD) simulations of heat transfer based on classical statistical mechanics allow the atom to have thermal heat capacity through *kT* energy. Here *k* is Boltzmann's constant and *T* absolute temperature. MD simulations of the bulk using submicron computational boxes with periodic boundary conditions are therefore valid representations of the bulk where the atoms do indeed have thermal *kT* energy. However, MD is also performed today assuming atoms have thermal *kT* energy in discrete nanostructures which are not periodic. But lacking periodicity, MD solutions of discrete nanostructures are invalid by QM. Here QM stands for quantum mechanics. Unlike statistical mechanics, QM forbids atoms in discrete submicron nanostructures to have heat capacity, and therefore the nanostructure cannot conserve EM energy by an increase in temperature. Without temperature changes, thermal conduction is precluded at the nanoscale. Instead, conservation proceeds by the emission of non-thermal QED induced radiation to the surroundings. QED stands for quantum electrodynamics.**

Keyword-heat transfer, moilecular dynamics, statistical mechanics, quantum mechanics

I. INTRODUCTION

Molecular Dynamics (MD) is commonly used to determine bulk transport properties including thermal conductivity of macroscopic bulk liquids [1, 2]. MD gives the atomic response of atoms based on Newton's equations derived for ensembles of atoms in computational boxes. Even though the computation boxes are submicron that by QM requires the atoms to have zero *kT* energy, full *kT* energy is nevertheless assumed because in the bulk which is being simulated the atoms do indeed have *kT* energy. But this is only valid provided the MD solution is performed with periodic boundary conditions imposed on the computational box.

In this regard, MD simulations were in fact preceded by Monte Carlo (MC) simulations, e.g., the virial coefficients for the PVT equation of the liquid state were derived [3] with MC simulations of spherical particles in a submicron 2D computational square box with periodic boundaries.

However, MD simulations of heat transfer at the nanoscale are commonly performed today for discrete structures which are unambiguously not periodic [4-6, 8-9, 11-12]. Contrary to QM, MD simulations of discrete nanostructures erroneously assume the atoms to have kT energy.

Indeed, MD simulations of discrete nanostructures are displayed in the belief they provide precise explanations of heat conduction when in fact they are not valid because QM precludes the atoms in discrete nanostructures to have *kT* energy. By assuming $kT > 0$, the MD simulations in effect derive the heat transfer response of the nanostructure as if it were a macroscopic body.

MD simulations of heat transfer of absorbed EM energy in nanostructures are only valid provided periodic boundary conditions [7] are prescribed in the solution run. However, if the nanostructures are discrete, the thermal *kT* energy of the atoms should be set to zero.

II. PURPOSE

Clarify the QM validity of MD simulations of heat transfer under periodic boundary conditions and invalidity of MD for discrete nanostructures.

III. THEORY

Nanostructures (nanoparticles, thin films, nanowires, etc.) conserve absorbed Q_{ABSORB} energy from lasers, molecular collisions, and Joule heating by heat losses comprising Q_{TRANS} - transient heating of mass; Q_{COND} – conduction; Q_{THERM} - thermal radiation and convection; and Q_{QED} - QED induced emission of non-thermal radiation as illustrated in Fig. 1.

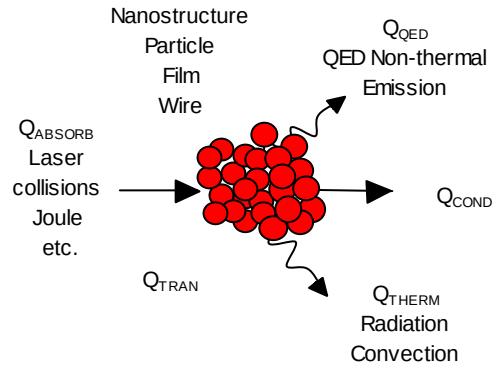

Figure 1. Heat transfer at the Nanoscale

Unlike thermal radiation given by the Stefan-Boltzmann law that is important only at high temperatures, QED emissions are non-thermal and occur at ambient temperature. The heat balance is,

$$Q_{ABSORB} = Q_{TRANS} + Q_{COND} + Q_{THERM} + Q_{QED} \qquad (1)$$

A. QM restrictions

QM restricts the kT energy levels of atoms in nanostructures. At 300 K, the Einstein-Hopf relation giving the average Planck energy for the harmonic oscillator in relation to kT and thermal wavelength is shown in Fig. 2.

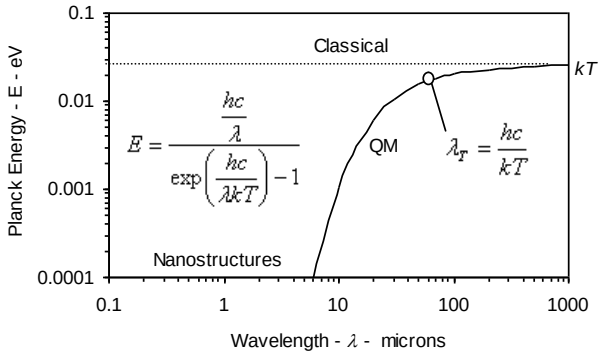

Figure 2. Harmonic Oscillator at $T \sim 300$ K

Classical oscillators have kT energy everywhere even at vanishing wavelengths, thereby allowing atoms to have heat capacity in nanostructures. QM oscillators differ in that classical kT energy is only allowed for $\lambda > \lambda_T$ and restricts kT for $\lambda < \lambda_T$. At ambient temperature, Fig. 2 shows the Planck energy is less than kT for $\lambda < 50$ microns with kT energy available only for $\lambda > 50$ microns. For nanostructures having $\lambda < 1$ micron, there is no heat capacity available by QM, and therefore EM energy is precluded from being conserved by an increase in temperature.

Since the nanostructures lack specific heat capacity, Q_{TRANS} may be neglected. Moreover, Q_{THERM} is neglected because high temperatures cannot occur. More importantly, there is no conductive heat flow Q_{COND} because QED emission promptly conserves absorbed Q_{ABSORB} energy far before the phonons respond. Hence,

$$Q_{QED} = Q_{ABSORB} \tag{2}$$

B. Feynman on Classical and QM Oscilltors

In the 1970's, Feynman [10] noted the differences between QM and classical thermal oscillators:

Classical physics by statistical mechanics allows the atom to have heat capacity at the nanoscale. QM also allows atoms to have heat capacity at the nanoscale, but only at high temperature, and.

Submicron wavelengths that fit into nanostructures have heat capacity only at temperatures > 6000 K. At 300 K, heat capacity is therefore "frozen out" at submicron wavelengths

Paraphrasing Feynman some 40 years later*:*

QM does not allow nanostructures at ambient temperature to conserve absorbed EM energy by an increase in temperature.

C. TIR Confinement

QED induced radiation is produced by NPs during the momentary TIR confinement of absorbed EM energy. TIR stands for total internal reflection. Although NPs have diameter $D << \lambda$, it is instructive to consider TIR for $D >> \lambda$. The equatorial TIR mode [15] traps absorbed EM energy at the NP surface, the number n of reflections around the QD depends on the wavelength λ of the incident radiation. As $\lambda \rightarrow D$, the ratio $\lambda/D \rightarrow 2$. The speed of light in the NP is the speed c in the vacuum reduced by its refractive index n_r giving the frequency f,

$$f = \frac{c / n_r}{\lambda} \qquad \lambda = 2D \tag{3}$$

NPs having $\lambda >> D$ have $\lambda/D = 2$ as for $D << \lambda$ because the speed of light c in a medium is independent of size. QED photon creation in the TIR mode is analogous with the QM analogy of creating photons of wavelength λ by supplying EM energy to a QM box with walls separated by $\lambda/2$. For the spherical NP as a QM box of diameter D, the Planck energy E induced by TIR confinement at wavelength λ is,

$$E = hf \qquad f = \frac{c}{\lambda} \qquad \lambda = 2n_r D \tag{4}$$

For NPs, thin films, and nanowires, the dimension D is the respective diameter, film thickness, and wire diameter.

D. QED Photon Energy and Rate

Classical heat transfer conserves absorbed EM energy by an increase in temperature, but in nanostructures is negated by QM. Instead, the Q_{ABSORB} energy is conserved by creating number N of QED photons *inside* the nanostructure having Planck energy

$$Q_{ABSORB} = NE \tag{5}$$

Similarly, power P absorbed by a nanostructure creates QED photons at a rate dN/dt,

$$P = \frac{dQ_{ABSORB}}{dt} = E\frac{dN}{dt} \tag{6}$$

IV. APPLICATIONS

A. Nanofluids

Nanofluids comprising NPs in solvents have been proposed to surpass the performance of currently available heat transfer liquids. MD simulations following [1, 2] procedures using the Green-Kubo method were used [7] to determine the thermal conductivity of a nanofluid of copper NPs in liquid argon. Periodic boundaries consistent with QM having kT energy of the atoms were assumed. For a 2% 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

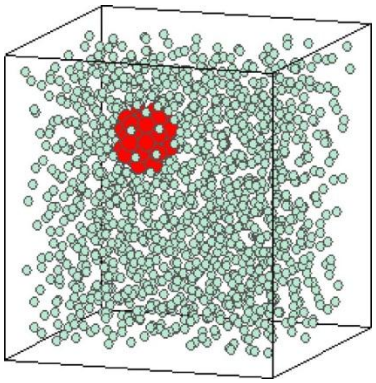

Figure 3. Nanofluid MD computational box

The interactions between Cu atoms in the NP and Ar atoms were modeled by standard Lennard Jones potential. Results suggest enhanced thermal conductivity is caused by the increased movement of liquid atoms in the presence of NPs. However, the long range interactions between the NP and its image neighbor that should be significant at 4 nm spacing were not included. Larger computational boxes that capture NP interactions with neighbors would also reduce the increased movement of liquid atoms and decrease any enhanced thermal conductivity found for the 4 nm computational boxes. Again, classical physics assumed in MD should not give higher conductivity than that given by standard mixing rules.

B. Nanocars

Nanocars including molecular motors are nanostructures [6] comprised of ordered atoms and molecules that convert 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. 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 the path of a single car is shown in Fig. 4.

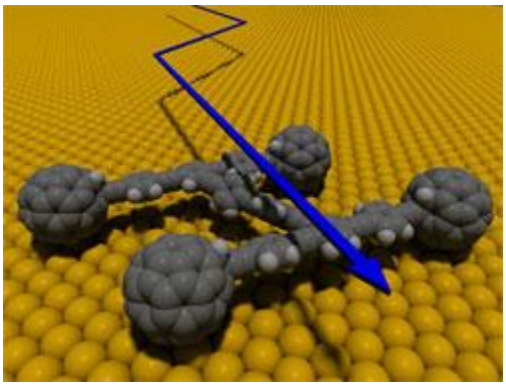

Figure 4. Nanocar on Gold Surfacce

The mechanism by which EM energy in the form of heat is converted into nanocar motion is not well understood. MD simulations of heat transfer are usually performed to explain observed motions But MD heat transfer of nanocars are invalid because QM restricts the heat capacity of atoms in the nanocars that by their size exclude all thermal radiation beyond about 1 micron. Hence, absorption of EM energy by the nanocar, say from a heated substrate cannot be conserved by an increase in temperature. It is not surprising therefore the MD solutions show the cars to distort, but not move.

But this MD result is expected in the 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 *kT* energy as if the nanocar were macroscopic.

QM differs. Instead, conservation of EM energy proceeds by the frequency up-conversion of absorbed FIR to the molecular TIR confinement frequency of the nanocar that at near UV or higher levels charges the nanocar positive by the photoelectric effect. Similarly, other nanocars are charged positive. Observed nanocar motion is then caused by electrostatic repulsions with other nanocars.

C. Carbon Nanotube

Since the discovery of CNTs, efforts toward the realization of CNT-nanostructures have been diminished by defects generated during the synthesis process. The effects of defects in CNT on thermal conductivity were studied [8] with MD simulations as shown in Fig. 5.

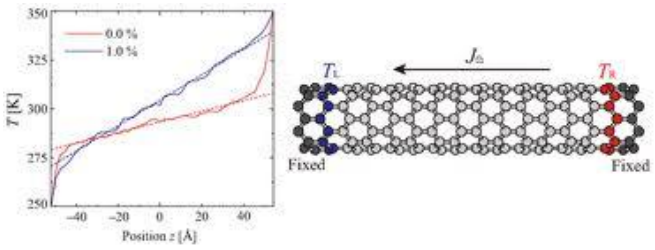

Figure 5. CNT Thermal Conductivity by Phonons

The MD simulation assumed different temperatures, T_L and T_R generate the thermal current J_{th} given in terms of conductivity K by,

$$J_{th} = -K \frac{\partial T}{\partial z} \tag{7}$$

From the equipartition theorem of statistical mechanics, the atom velocities v in terms of the mass m of carbon atoms,

$$v = \sqrt{\frac{3kT}{m}} \tag{8}$$

The MD simulations were characterized with parameter ρ corresponding to the concentration of vacancies. Fig. 5 shows the temperature profiles of the CNTs with ρ = 0.0 (red solid curve) and 1.0 % (blue solid curve). Note that the finite gradient behavior for ρ = 0.0 % means thermal transport in

CNTs is diffusive at room temperature This is in contrast with ballistic thermal transport in perfect CNTs with flat temperature profiles at low temperatures. In the vicinity of the left- and right-end layers of the CNT, the temperature profiles exhibit a strong nonlinear behavior, which is attributed to the scattering, but is more likely the effects of fixing the atoms at the support. .

Whether or not the scattering near the CNT ends is real may be inconsequential to the validity of MD simulation by QM. Indeed, the MD simulation may be meaningless because the *kT* energy of the atom vanishes at the nanoscale. Hence, the thermal current J_{th} vanishes, See Fig. 5. What this means is there is no conduction heat flow in the CNT nanostructure. Alternatively, the specification of temperatures at the ends of the CNT is unphysical.

D. CNT Actuator

MD simulations [9] have shown thermal gradient-induced actuation in double-walled CNTs to support the notion that heat flux can actuate the relative motion of the CNTs. Experiments have shown the thermal driving force is on the order of pico Newtons for a 1 K / nm temperature gradient. The driving force is found to be approximately proportional to the temperature gradient.

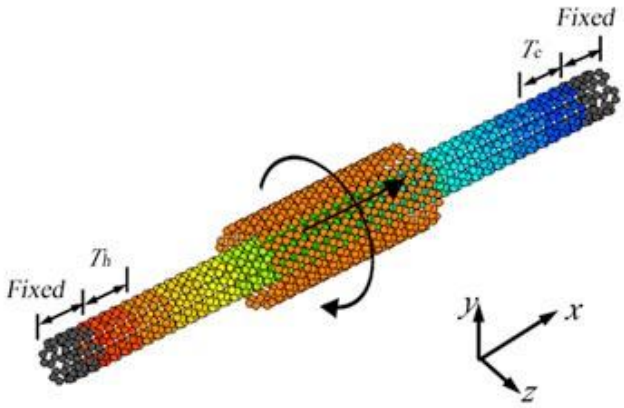

Figure 6. CNT Actuator

Actuation is claimed to be dependent on the chirality pairs of the double-walled CNTs and can be rotational, translational or helical when the system temperature is less than its critical temperature. But like the similarly heated single-walled CNT, the MD simulation allows the atoms to have *kT* energy contrary to QM. What this means is the nanoscale response is no different that it would be in the macroscopic world. Since heating a macroscopic equivalent will not obviously cause motion of any kind, the CNT nanostructure cannot similarly move. Instead, the observed actuator motion is likely caused by QED induced electrostatic forces as described for nanocars.

E. Surfacce Erosion

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. With this technique diffusion of ad-atoms on a surface is described .by jumping to any of the four next local energy minima on a (100) surface with a FIR frequencies. The evolution of the system is followed and then a new particle is deposited on the surface and the KMC process repeated.

A MD simulation [12] of 5 keV Argon atom impacting a Cu (111) crystal is shown in Fig. 7. Surface binding energy was lowered by 50% to enhance sputtering yield. The simulation results in emission of large clusters, which become detached from the target after typically 5 ps. The picture shows the development of the impact crater after 2ps. The color coding indicates temperature of the atoms: white - black 300K - 1400K; blue 1400K - 2800K; green 2800K - 4200K; red above 4200K.

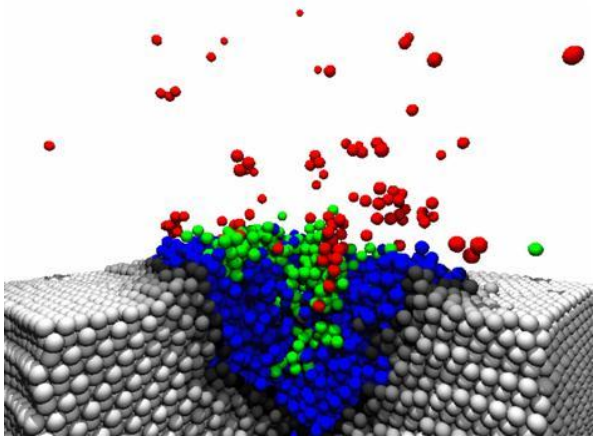

Figure 7. Film Growth and Erosion

The cluster sizes are not given, but by QED induced radiation are only valid for diameters D > 1 micron. Submicron NPs emit QED radiation that is lost to the surroundings or absorbed by the macroscopic surface to indirectly heat the sample.

F. Nanotrboloogy

In nanotribology, MD simulations allow the macroscopic properties of friction to be computed [13] based on atomic interactions. Fig. 8 shows the MD results at a later time after rubbing. The carrier substrate (in red) is partially coated with relatively soft and atomically lighter material (blue) that is rubbed with an opposite material that is significantly harder (red). The rubbing procedure is repeated several times. It is seen that in the course of the simulation, the blue substance is smeared out on the carrier and after a few cycles, no more significantly altered. Similarly, the grinding surface is visible (blue atoms settle on the lower surface).

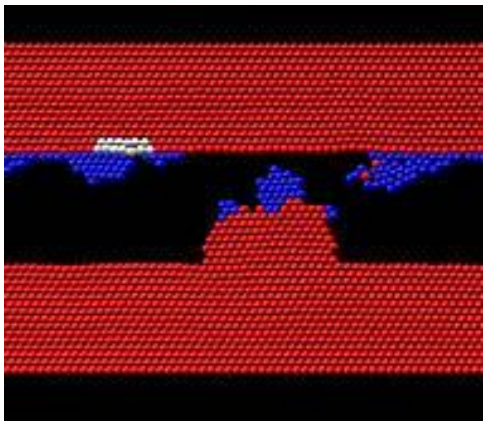

Figure 8. Nanotribology of Rubbing

Of interest is the temperature of the rubbed surfaces is maintained at 300K. However, rubbing friction typically is thought to increase temperature in similar MD solutions. Regardless, the MD simulation as a discrete nanostructure is invalid because $kT > 0$ is assumed by statistical mechanics.

V. DISCUSSION

QED induced radiation suggests is there is no conduction at the nanoscale. MD heat transfer of discrete nanostructures that assume the atom has *kT* thermal energy are meaningless at the nanoscale. MD simulations based on finite *kT* energy serve only as analysis of geometrically similar macroscopic structure having nothing to do with the nanoscale.

But heat transfer analysis of the nanoscale need not be performed. Indeed, the *a priori* assumption may be made that the nanostructure remains isothermal with the absorbed EM energy converted to QED radiation at frequencies equal to the fundamental TIR resonance of the nanostructure. Typically, the QED radiation is ionizing beyond the UV and acts to charge the nanostructure by the photoelectric effect.

In this arrangement, MD simulations may then be performed for the discrete nanostructures under isothermal conditions interacting with each other by electrostatic forces. Or the QED radiation from the nanostructure may be considered as EM energy to the macroscopic surroundings.

VI. SUMMARY AND CONC LUSIONS

QM requires zero specific heat capacity at the nanoscale be specified for both solids and liquids. But statistical mechanics allows finite specific heat at the nanoscale.

MD is based on statistical mechanics assumes atoms have *kT* energy which is valid provided transport properties of the bulk are derived where the atoms in submicron computation boxes do indeed have *kT* energy. However, MD simulations of heat transfer in discrete submicron nanostructures are not valid because QM requires the *kT* energy of the atoms to vanish.

Nanoscale heat transfer based on QM explains reduced conductivity in thin films by QED emission without modifying bulk conductivity.

QM forbids heat conduction at the nanoscale. Reductions in thermal conductivity by phonons are therefore meaningless. In fact, absorbed EM energy at the nanoscale is promptly conserved by QED emission of photons far before phonons respond.

Lacking specific heat at the nanoscale, absorbed EM energy is not conserved by an increase in temperature, but rather by the emission of non-thermal QED emission that may be measured by the 3 method.

MD and MC simulations of bulk thermal conductivity based on the full *kT* energy of atoms are *only* consistent with QM provided periodic boundary conditions are imposed on the computational boxes.

Zero specific heat is required for atoms in MD and MC simulations of discrete submicron nanostructures without periodic boundaries. In effect, zero specific heat means there is no conduction at the nanoscale.

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