VALIDITY OF MOLECULAR DYNAMICS BY QUANTUM MECHANICS

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INTRODUCTION

MD is commonly used [1-3] to simulate the atomic response or discrete solid nanostructures, although MD was initially developed to determine the macroscopic transport properties of bulk liquids. Finding theoretical basis in statistical mechanics, MD derives the momenta of an ensemble of atoms based on the solution of Newton’s equations.

Historically, MD simulations were in fact preceded in the 1950’s by MC simulations, e.g., the virial coefficients derived [4] with spherical particles in submicron 2D computational square boxes under periodic boundary conditions or PBC. MC stands for Monte Carlo. 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 followed by the Nicolas et al. [8] seminal MD paper.

Since 1950, MD simulations [4-8] imposed PBC on the submicron ensembles 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 is intractable. Moreover, in MD simulations, PBC assure the fundamental premise of statistical mechanics is satisfied, i.e., the atoms have 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 PBC with all atoms having heat capacity are valid even though the ensembles are submicron.

Today, MD simulations of the bulk are generally not performed. Exceptions include MD to derive the thermal conductivity of nanofluids comprising nanoparticles -NPs, say in liquid argon [9]. However, 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 behaviour when in fact they are invalid because QM precludes atoms in discrete nanostructures from having heat capacity.

In effect, MD simulations based on atoms having heat capacity derive the response of the nanostructure as if it were a scaled down macroscopic body, and therefore are meaningless in the understanding of atomic response at the nanoscale. Clearly, QM invalidates MD of discrete nanostructures. Instead, QED induced radiation is proposed to obtain the MD response at the nanoscale.

THEORY

QM Restrictions

Classical physics allows the atom to have thermal $kT$ energy or equivalently the heat capacity necessary to conserve absorbed EM energy (lasers, Joule heat, etc.) by an increase in temperature. A comparison of the thermal $kT$ energy of the atom by classical physics and QM by the Einstein-Hopf relation [13] is shown in Fig. 1.

![Fig. 1 Heat Capacity of the Atom at 300K](image)

$E$ is Planck energy, $h$ Planck's constant, $c$ speed of light

$k$ Boltzmann’s constant, $T$ temperature, and $\lambda$ wavelength

Classical physics allows the atom to have the same $kT$ energy in nanostructures as in macroscopic bodies. QM differs in that $kT$ energy is only available for $\lambda > \lambda_T$ and otherwise is $< kT$. At ambient temperature, $\lambda_T \sim 40$ microns. By QM, atoms under EM confinement wavelengths $\lambda < 1$ micron have virtually no heat capacity to conserve EM energy by an increase in temperature.

TIR Confine

In 1870, Tyndall showed light is trapped by TIR in the surface of a body if the RI of the body is greater than that of the surroundings. RI stands for refractive index. However, TIR need not be limited to light as any form of EM energy may be confined by TIR.

Discrete nanostructures have high surface to volume ratios. Provided the RI of the nanostructure is greater than the surroundings, absorbed EM energy is therefore almost entirely absorbed in its surface. But the surface fully participates with the shape of the TIR wave function, and therefore QED induces the absorbed EM energy to undergo spontaneous conversion to surface QED radiation. Hence, QED induces the creation of excitons at the frequency of the TIR confinement. However, TIR confinement is not permanent, sustaining itself only during the absorption of EM energy, i.e., absent absorbed EM energy, there is no TIR confinement and excitons from QED radiation are not produced.

QED relies on complex mathematics as described by Feynman [14] although the underlying physics is simple, i.e., photons of wavelength $\lambda$ are created by supplying EM energy to a QM box with sides separated by $\lambda/2$, i.e., QED up-converts the EM energy to the TIR resonant frequency given by the characteristic dimension $d$ of the circuit element. The Planck energy $E$ of the QED radiation,

$$E = h\nu, \quad \nu = \frac{c}{n\lambda}, \quad \lambda = 2d$$

where, $n$ is the RI of the circuit element. For film and spherical or cylindrical geometries, $d$ is the thickness or diameter.

Quantum Corrections

QC of classical thermodynamic provide recognized [1-3] procedures to assess the QM validity of MD after solutions are obtained. QC stands for quantum correction. Indeed, QC procedures are not new and have been known for some time. See e.g. (“Quantum Corrections” Sect. 2.9 of [1]). Of interest in QED induced radiation is the heat capacity of the atom in discrete nanostructures.

The QCs of molecules assume the atoms behave as a set of QM harmonic oscillators, the density of states given by the Fourier transform of the velocity autocorrelation function. The QC for the response of the thermodynamic variable is determined at each frequency of the density of states by the response of the QM oscillator, the total QC obtained by integrating over all frequencies.

For the water molecule, the QCs have been known [15] for 30 years, the generalized expressions for the constant volume heat capacity $C_v$ applicable to any QM system summarized in (Fig. 1 of [15]). The QC weighting function $W = Q - C$ is the difference between the quantum $Q$ and classical $C$ values of the thermodynamic variable. In terms of the parameter $u$,

$$u = \frac{hc}{\lambda kT}$$

All $W$ go to zero for $u < 1$ consistent with the low frequency anharmonic region of statistical mechanics where QCs are insignificant; whereas, $W$ for $u > 1$ correspond to the harmonic approximation where QCs are significant.

The QC for the heat capacity of nanostructures may be simply estimated as a nanoscale continuum at a single
frequency given (1) by its TIR confinement frequency. For TIR wavelengths less than 1 micron, Fig. 1 shows the heat capacity of nanostructures a priori vanishes. More precisely, the quantum $Q$ heat capacity for $C_V$ is given by the partial derivative $\frac{\partial E}{\partial T}$ of the Einstein-Hopf energy $E$ with respect to temperature $T$,

$$C_V = \frac{\partial E}{\partial T} = 3kN_A \frac{n^2 \exp^\mu}{[1 - \exp^\mu]^2}$$

(2)

where, $N_A$ is Avagadro’s number. The Einstein-Hopf relation does not include the ZPE in Planck’s derivation, but for $C_V$ is inconsequential because the partial derivative of the ZPE with respect to temperature vanishes. ZPE stands for zero point energy. The heat capacity $C_V$ at 300 K is shown in Fig. 2.

![Fig. 2 QC of Heat Capacity at 300 K](image)

Depending on TIR confinement, $C_V$ may vanish in nanostructures at ambient temperature, i.e., vanishing heat capacity need not require temperatures at absolute zero as in classical physics. Fig. 2 shows quantum heat capacity $C_V$ based on $\partial E/\partial T$ is less than classical at TIR confinement wavelengths $\lambda < 20$ microns. However, based on Planck energy $E$ alone, Fig. 1 shows the $kT$ energy of the atom is less than classical at $\lambda < \lambda_T \approx 40$ microns. Hence, $E$ is more restrictive than $\partial E/\partial T$ in defining the onset of reduced heat capacity. Under TIR confinement, the heat capacity vanishes for nanostructures having TIR wavelengths $< 1$ micron. One need not go further to conclude classical MD of discrete nanostructures having finite heat capacity is a priori invalid by QM.

**QED Induced Radiation**

QED induced radiation is the consequence of QM that requires the heat capacity of the atom to vanish in nanostructures. Consider a NP resting on a surface as depicted in Fig. 3. NP stands for nanoparticle.

![Fig. 3 QED Induced Radiation](image)

Since absorbed $Q_{\text{absorb}}$ energy cannot be conserved by an increase in NP temperature, conservation proceeds by other paths. One path is conductive flow $Q_{\text{cond}}$ into the surface by phonons, and the other by the creation of excitons from QED radiation $Q_{\text{qed}}$ inside the NP. However, phonons respond at acoustic velocities while QED conserves $Q_{\text{absorb}}$ energy at the speed of light. Hence, absorbed heat $Q_{\text{absorb}}$ is conserved promptly by creating excitons well before phonons respond, and therefore QED effectively negates thermal conduction by phonons in nanostructures, i.e., $Q_{\text{cond}} \sim 0$.

In QED induced radiation, absorbed heat $Q_{\text{absorb}}$ is conserved by $Q_{\text{qed}}$ creating number $N_{ex}$ of excitons inside the nanostructure, but only a fraction $\eta$ of which charge the NP, the remaining fraction $(1-\eta)$ upon recombination are lost as EM radiation to the surroundings. The QED excitons created at the rate $dN_{ex}/dt$ charge the nanostructure by,

$$\eta \frac{dN_{ex}}{dt} = \frac{Q_{\text{absorb}}}{E}$$

(3)

where, $E$ is the Planck energy of the QED radiation. However, for TIR confinement of the nanostructure, the RI of the nanostructure must be greater than that of the surroundings. Even if the nanostructure in contact with a surface, conductive heat $Q_{\text{cond}}$ is still negated by TIR. QED radiation always conserves $Q_{\text{absorb}}$ upon absorption elsewhere, but not by conductive heat $Q_{\text{cond}}$ by phonons.

Typically, the effective conductivity for thin-films is found [16] reduced from the bulk for submicron film thicknesses, but the film heat balances [17] excluded QED radiation loss. However, if included, the conductivity is not reduced, but instead remains at bulk. Excluding $Q_{\text{qed}}$ 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. Regardless, explaining reduced thermal conductivity of thin films by scattering of phonons is unnecessarily complex compared to the simplicity of QED induced radiation that the conductivity simply remains at bulk.
DISCUSSION

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 [9] to determine the thermal conductivity of a nanofluid consisting of copper NPs in liquid argon. Consistent with QM, PBC 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.

![Fig. 4 PBC - Nanofluid](image)

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 L-J interactions between the NP and its image neighbors that should be significant at 4 nm spacing were not included. Larger computational boxes that capture the long-range 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 are nanostructures comprised of ordered atoms and molecules that convert heat into mechanical motion. The heat may take various forms of EM energy including light, Joule heat, and electron beams. In the experiment, a large number of nanocars are laid down at random on a gold surface. Upon heating the surface, the cars are observed to move. For clarity, only a single car is shown in Fig. 5.

![Fig. 5 Discrete Nanostructure - Nanocar](image)

The mechanism by which absorbed EM energy is converted into nanocar motion is not well understood. MD simulations [10] were performed to explain observed motions. However, MD of nanocars is invalid because QM requires the heat capacity of atoms to vanish. Hence, absorption of heat by the nanocar from the substrate cannot be conserved by an increase in temperature. It is not surprising therefore, MD simulations show the cars to distort, but not move.

Linear Motors

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.

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 capacity as shown in Fig. 1 for the QM oscillator.
Stiffening of Nanowires

Uniaxial tensile testing of silver NWs showed [18] enhanced Young’s moduli and yield stress above bulk properties. Classical MD was modified [19] consistent with the QM restriction that atoms in the NW are precluded from having the heat capacity to conserve thermal energy by an increase in temperature. By QM, the isolated NW cannot increase temperature, but the macroscopic grips that stretch the NW require the NW to acquire their temperature, i.e., a NP resting on a macroscopic surface becomes a part of that surface and acquires its \( kT \) energy. Lacking heat capacity, QED induces the NW to conserve the \( kT \) energy of the grips by creating excitons that upon recombination produce EM radiation by charging induces Coulomb repulsion between atoms placing the NW in a state of hydrostatic tension. Unlike bulk tensile specimens in a uniaxial stress state, NWs have enhanced mechanical properties because of the triaxial stress state induced by QED.

The MD simulation of the silver NW was modeled in the FCC configuration with an atomic spacing of 4.09 Å comprising 550 atoms having sides \( w = 8.18 \) Å and length \( L = 87.9 \) Å. The NW was stretched by force \( F \) induced by fixing one end and imposing a step in displacement at the other end as shown in Fig. 8.

\[ U_{ES} = \frac{3e^2}{20\pi\varepsilon_0 R_{atom}} \]  

where, \( \varepsilon_0 \) is the permittivity of the vacuum.

In the NW, the thermal energy \( U_{kT} \) of the atom depends on the grip temperature \( T_{grip} \),

\[ U_{kT} = \frac{3}{2} kT_{grip} \]  

The QED induced pressure tending to separate the atoms is simulated by defining the fraction \( \gamma \) of the electrostatic \( U_{ES} \) energy corresponding to the thermal \( U_{kT} \) energy of the atom.

\[ \gamma = \frac{U_{kT}}{U_{ES}} = \frac{10\pi\varepsilon_0 k R_{atom} T_{grip}}{e^2} \]
For $T_{grw} = 300$ K with the silver atom having $R_{atom} = 1.45$ Å, the fraction $\gamma = 0.0065$. During the MD solution, the Nose-Hoover thermostat maintained temperatures $T < 0.01$ K. The Young’s moduli $Y$ for various $\gamma$ are shown in Fig. 9.

![Young's Modulus - Y - psi](image)

**Fig. 9 Discrete Nanostructure – Young’s Moduli of NWs**

For $\gamma = 0.001$ and 0.002, the Young’s modulus $Y = 31$ and $45 \times 10^6$ psi; respectively. The experimental Young’s modulus of $26 \times 10^6$ psi is best approximated with the QM solution $\gamma = 0.001$. With the uniaxial Young’s modulus $Y_o \sim 17 \times 10^6$ psi, the stiffening enhancement is $Y/Y_o \sim 1.88$. The QM solution for $\gamma = 0.001$ means only 1/6.5 or about 15% of the $kT_{grw}$ energy stiffens the NW, the remaining 85% lost to the surroundings as QED radiation.

**CONCLUSIONS**

MD simulations based on statistical mechanics that assume atoms have heat capacity are valid only for the properties of the bulk under PBC. Unlike statistical mechanics, QM precludes atoms in discrete nanostructures from having heat capacity, the consequence of which is that sources of EM energy (lasers, molecular collisions, etc.) absorbed in nanostructures are conserved by the creation of QED induced excitons that upon recombination produce EM radiation that charges the nanostructure or is emitted to the surroundings.

Classical MD simulations of discrete nanostructures are a priori invalid by QM. Arguments that MD is consistent with statistical mechanics may be dismissed as QM governs atomic behaviour at the nanoscale.

Discrete MD simulations based on statistical mechanics that assume atoms have heat capacity do not produce charge and erroneously conserve heat by an increase in temperature.

Classical MD of discrete nanostructures is invalid by QM, but consistency with QM may be found by modifying the MD programs to conserve absorbed EM energy by creating excitons that charge the nanostructure instead of increasing its temperature as in statistical mechanics.

In the MD of NWs in tensile tests, more study is required to confirm the procedures in simulating the QM requirement that temperatures do not increase, but rather that repulsive Coulomb forces are created from QED induced charge.

**REFERENCES**