Validity of Molecular Dynamics Heat Transfer by Quantum Mechanics

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Abstract. MD is commonly used in computational physics to determine the atomic response of nanostructures. MD stands for molecular dynamics. With theoretical basis in statistical mechanics, MD relates the thermal energy of the atom to its momentum by the equipartition theorem. Momenta of atoms are derived by solving Newton's equations with inter-atomic forces derived by Lennard-Jones or L-J potentials. MD implicitly assumes the atom always has heat capacity as otherwise the momenta of the atoms cannot be related to their temperature. In bulk materials, the continuum is simulated by imposing PBC on an ensemble of atoms, the atoms always having heat capacity. PBC stands for periodic boundary conditions. MD simulations of the bulk are therefore valid because atoms in the bulk do indeed have heat capacity. Nanostructures differ. Unlike the continuum, the atom confined in discrete submicron structures is precluded by QM from having the heat capacity necessary to conserve absorbed EM energy by an increase in temperature. QM stands for quantum mechanics and EM for electromagnetic. Quantum corrections of MD solutions that would show the heat capacity of nanostructures vanishes are not performed. What this means is the MD simulations of discrete nanostructures published in the literature not only have no physical meaning, but are knowingly invalid by QM. In the alternative, conservation of absorbed EM energy is proposed to proceed by the creation of QED induced non-thermal EM radiation at the TIR frequency of the nanostructure. QED stands for quantum electrodynamics and TIR for total internal reflection. QED radiation creates excitons (holon and electron pairs) that upon recombination produce EM radiation that charges the nanostructure or is lost to the surroundings – a consequence only possible by QM as charge is not created in statistical mechanics. Valid and invalid MD simulations from the literature are illustrated with nanofluids and nanocars, respectively. Finally, valid and invalid MD solutions for the stiffening of NWs in tensile tests are presented to illustrate the unphysical findings if QM is ignored at the nanoscale. NW stands for nanowire.

Introduction

MD was initially developed [1, 2] 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 with inter-atomic forces derived from L-J potentials. In 1950, MD began [3] with MC simulations of bulk liquids with ensembles of atoms under PBC. MC stands for Monte Carlo. Indeed, PBC assure MD or MC solutions are consistent with the fundamental premise of statistical mechanics, i.e., the atoms always have temperature or equivalently heat capacity. But PBC are also consistent with QM. Indeed, PBC assure the EM confinement of atoms in the ensemble is long-wavelength consistent with the anharmonic region of QM where quantum corrections [2] are insignificant. Unequivocally, MD solutions of the bulk under PBC with atoms having heat capacity are valid by QM.

Today, MD simulations of the bulk are generally not performed, except to confirm the enhanced thermal conductivity of nanofluids by NPs, say copper NPs in liquid argon [4]. NP stands for nanoparticle. Generally, MD simulations are made of nanostructures that are unambiguously not periodic, e.g., discrete ordered atoms called nanocars [5]. In nanostructures, MD simulations that implicitly assume atoms have macroscopic heat capacity are thought to provide precise descriptions of atomistic behaviour, when in fact they are invalid by QM, let alone give unphysical results. 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 with regard to the true atomistic response of the nanostructure. Clearly, QM invalidates the MD of discrete nanostructures. To obtain valid QM solutions, MD programs require modifications consistent with QM, an illustrative example [6] of which is presented that contrasts valid with invalid MD solutions for the stiffening of NWs in tensile tests.

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 [7] is shown in Fig. 1.

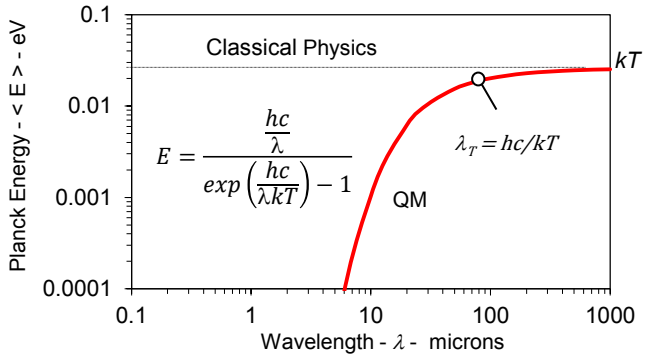

Fig. 1 Heat Capacity of the Atom at 300 K
E is Planck energy, h Planck's constant, c speed of light,
k Boltzmann's constant, T temperature, and λ wavelength

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, $\lambda_T \sim 48$ microns. By QM, atoms under EM confnement wavelengths $\lambda < 1$ micron have virtually no heat capacity to conserve EM energy by an increase in temperature.

TIR Confinement 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. Nanostructures have high surface to volume ratios. Provided the RI of the nanostructure is greater than the surroundings, absorbed EM energy is 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 is spontaneously converted to EM radiation. Hence, QED induces the creation of excitons in the surface of the nanostructure at the frequency of TIR confinement. But 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 [8] although the underlying physics is simple, i.e., EM radiation of wavelength λ is created by supplying EM energy to a QM box with sides separated by $\lambda/2$. Hence, QED up-converts absorbed EM energy to the TIR frequency given by the dimension d of the nanostructure. The Planck energy E of the QED radiation,

$$E = h\upsilon, \quad \upsilon = \frac{c/n}{\lambda}, \quad \lambda = 2d \tag{1}$$

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

QED induced radiation The consequence of QM that requires the heat capacity of the atom to vanish in nanostructures is the creation of QED induced radiation. Consider a NP resting on a surface as depicted in Fig. 2.

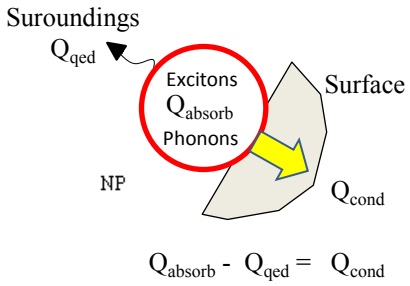

Fig. 2 QED Induced Radiation

Since absorbed Q_{absorb} energy cannot be conserved by an increase in NP temperature, conservation may proceed by conductive flow Q_{cond} into the surface by phonons or by the creation of excitons from QED radiation Q_{qed} inside the NP. However, phonons respond only after thermalization while QED conserves the Q_{absorb} energy spontaneously at the speed of light. Hence, absorbed heat Q_{absorb} is conserved by QED creating number N_{ex} of excitons inside the nanostructure instead of conduction by phonons. After recombination, the excitons produce EM radiation, but only a fraction η of which charges the NP, the remaining fraction (1- η) is lost to the surroundings

Discussion

QM validity is assessed for MD solutions selected from the literature, i.e., valid MD solutions in nanofluids [4] under PBC, and invalid MD solution for discrete nanocars [5] are shown in Fig. 3 (a) and (b), respectively. Both QM valid and invalid MD solutions are presented for a discrete nanowire [6] in a tensile test is shown in Fig. 3(c).

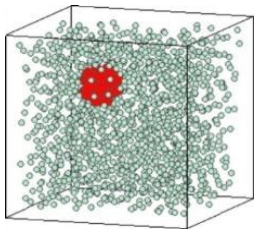

Fig. 3(a) - PBC – Nanofluid

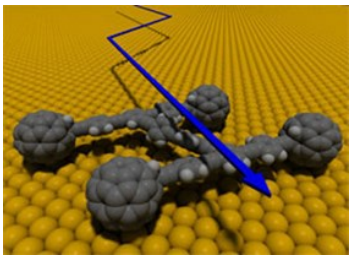

Fig. 3(b) - Discrete Nanocar

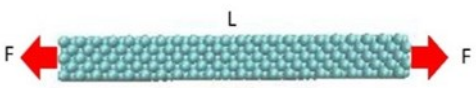

Fig. 3(c) =- Discrete Nanowire

Nanofluids Nanofluids comprising NPs in solvents are claimed to enhance the thermal performance of traditional heat transfer liquids. Standard MD simulations following procedures [1-2] were used [4] to verify the enhanced thermal conductivity of a nanofluid comprising 2 nm copper NPs in liquid argon using the 4 nm computation box shown in Fig. 3(a). Consistent with QM, PBC with atoms having heat capacity were assumed. 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 image neighbors that should be significant at 4 nm spacing were not included. Larger computation boxes that capture the long-range NP interactions are likely to reduce the increased Brownian movement and any thermal enhancement. Classical physics assumed in MD should not give higher thermal conductivity than that by standard mixing rules, but otherwise the MD solution [4] is valid and consistent with QM.

Nanocars Nanocars are nanostructures thought to convert heat into mechanical motion. Heat itself is not required as any form of EM energy may induce motion including light, Joule heat, and electron beams. In one experiment, large numbers of nanocars are laid down at random on a gold surface. Upon heating the surface, the cars are observed to move. But for clarity, only a single car is shown in Fig. 3(b). To understand the mechanism by which absorbed EM energy is converted into nanocar motion, MD simulations [5] were performed that showed the cars to distort, but not move. Indeed, the 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 summer 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 those in macroscopic cars. Fig. 1 shows the Planck energy of the atom in macroscopic cars under long wavelength EM confinement is the same as nanocars at wavelengths < 1 micron, and therefore the nanocar like your car would not be expected to move by statistical mechanics.

QM differs. Conservation proceeds by the QED induced creation of excitons by frequency up-conversion of absorbed heat to the TIR confinement frequency of the nanocar. Upon recombination, EM radiation at UV or higher levels is produced that charges all nanocars positive. Observed nanocar motion is therefore caused by mutual Coulomb repulsion

Nanowires Uniaxial tensile testing of silver NWs is thought to enhance Young's moduli above bulk properties. MD algorithms [6[modified consistent with the QM restriction that atoms in the NW are precluded from having the heat capacity to conserve the temperature of the grips that hold the NW in tensile tests. By QM, the NW cannot increase in temperature, but the grips impose their thermal kT energy on the NW. Lacking heat capacity, QED induces the NW to conserve the thermal kT energy of the grips by creating excitons that upon recombination produce EM radiation that charges the NW atoms positive and induces the triaxial stress state of Coulomb repulsion.

The MD simulation of the silver NW is modeled in the FCC configuration with 550 atoms having 8.18 Å sides and length L = 87.9 Å. The NW was stretched by imposing a step in displacement to cause the tensile forces F shown in Fig. 3(c). Valid MD solutions conserve thermal kT energy from the grips by QED induced charges producing Coulomb repulsion between NW atoms, while the invalid MD solution conserves thermal energy by increasing NW temperature. Valid MD solutions occur for the triaxial stress state of hydrostatic tension while invalid MD solutions occur in the uniaxial stress state as shown in Figs. 4 and 5, respectively.

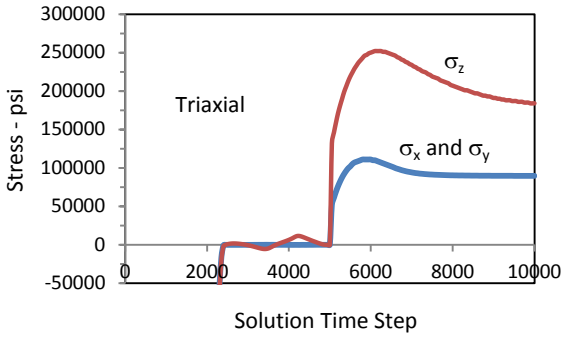

Fig. 4 Nanowire - Valid MD Solution

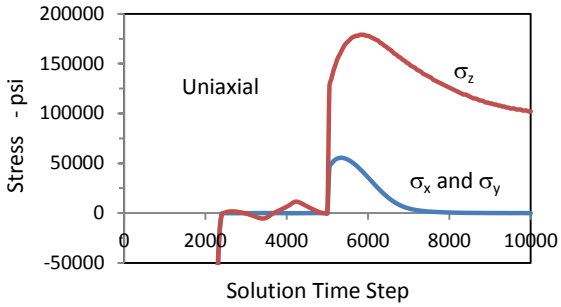

Fig. 5 Nanowire – Invalid MD Solution

Enhancement of Young's modulus Y above bulk Y_o depends on Poisson's ratio ν,

$$\frac{\mathbf{Y}}{\mathbf{Y_o}} = \frac{\mathbf{1}}{\mathbf{1} - \nu(\sigma_x + \sigma_y)/\sigma_z} \qquad (2)$$

where, $\nu < 0.5$. By QM, valid MD solutions show NWs stiffen as Young's moduli are enhanced $Y/Y_o > 1$ in the triaxial stress state $[(\sigma_x + \sigma_y) > 0]$. Invalid MD gives the unphysical solution that the NWs do not stiffen, i.e., the uniaxial stress state $[\sigma_x = \sigma_y = 0]$ giving $Y/Y_o = 1$.

Conclusions

By QM, MD based on statistical mechanics that assumes atoms have heat capacity is valid only for the bulk simulations under PBC.

QM invalidates MD of discrete nanostructures that assume atoms have heat capacity.

MD of discrete nanostructures is valid if modified by the QM restriction that the heat capacity of the atom vanishes.

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