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VALIDITY OF MOLECULAR DYNAMICS 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 in an ensemble are determined by solving Newton's equations with inter-atomic forces derived from Lennard-Jones potentials. MD therefore 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 in MD 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 valid because atoms in the bulk do indeed have heat capacity.

Nanostructures differ from the bulk. Unlike the continuum, the atom confined in discrete submicron geometries 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 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. The QED radiation creates excitons (holon and electron pairs) that upon recombination produce EM radiation that charges the nanostructure or is emitted to the surroundings – a consequence only possible by QM as charge is not created in statistical mechanics. Invalid discrete MD simulations are illustrated with nanofluids, nanocars, linear motors, and sputtering. Finally, a valid MD simulation by QM is presented for the stiffening of NWs in tensile tests. NW stands for nanowire.

.INTRODUCTION

MD is commonly used [1-3] to simulate the atomic response or discrete 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 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 QM as PBC assure the EM confinement of the atom is at long wavelengths where atoms do indeed have heat capacity. By statistical mechanics, MD solutions under PBC with all atoms having heat capacity are unequivocally valid

Today, MD simulations of the bulk under PBC are generally not performed. Exceptions include MD to derive the thermal conductivity of nanofluids, say copper NPs in liquid argon [9]. NP stands for nanoparticle. 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. To obtain valid MD solutions, standard MD programs are proposed modified to be consistent with QM 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.

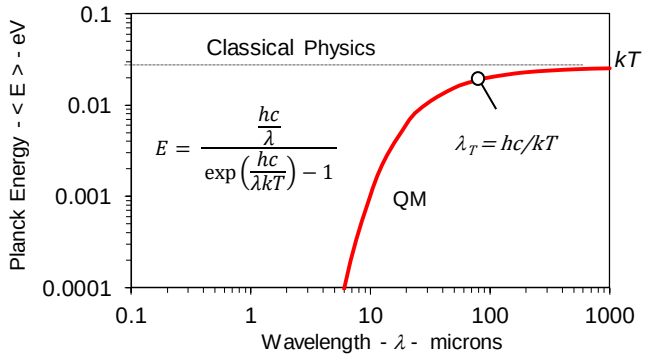

Fig. 1 Heat Capacity of the Atom at 300K
E is Planck energy, *h* Planck's constant, *c* speed of light
k Boltzmann's constant, *T* temperature, and λ wavelength

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, $\lambda_T \sim 40$ 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 and QED

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 λ 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,

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

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

Quantum Corrections

QCs of classical thermodynamics 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 [3]). 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*,

$$u = \frac{hc}{\lambda kT} \tag{1}$$

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 a nanostructure may be simply estimated as a nanoscale continuum 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 $\partial E/\partial T$ of the Einstein-Hopf energy *E* with respect to temperature *T*,

$$C_V = \frac{\partial E}{\partial T} = 3kN_A \frac{u^2 \exp^u}{[1-\exp^u]^2} \qquad (2)$$

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.

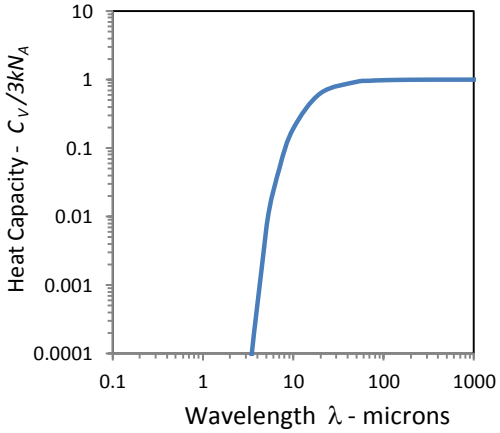

Fig. 2 QC of Heat Capacity at 300 K

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 $\lambda < \lambda_T \sim 40$ 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. .

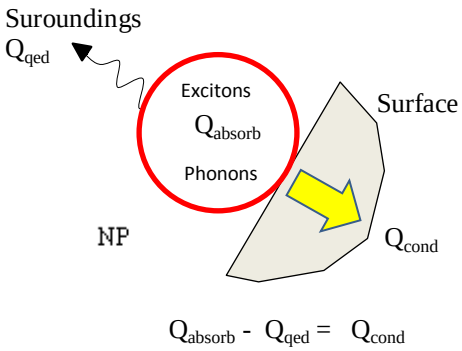

Fig. 3 QED Induced Radiation

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

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

$$\eta \frac{dN_{ex}}{dt} = \eta \frac{Q_{absorb}}{E} \qquad (3)$$

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_{cond} is still negated by TIR. QED radiation always conserves Q_{absorb} upon absorption elsewhere, but not by conductive heat Q_{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_{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 visually 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 copper NPs having a diameter of about 2 nm in a cubic computational box of 4 nm on a side for a total of 2048 atoms is depicted in Fig. 4.

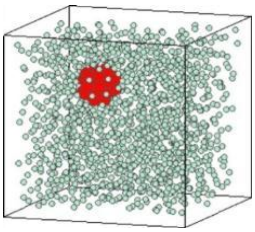

Fig. 4 PBC - Nanofluid

Lennard Jones potentials were used to simulate the interactions between copper and argon 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 any enhanced thermal conductivity. Classical physics assumed in MD should not give higher thermal 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 one 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.

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.

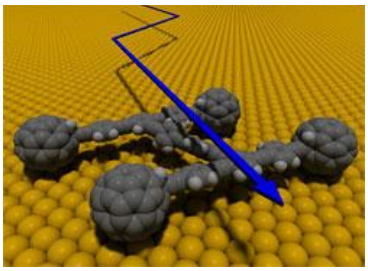

Fig. 5 Discrete Nanostructure - Nanocar

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 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 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 Coulomb repulsion between nanocars

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.

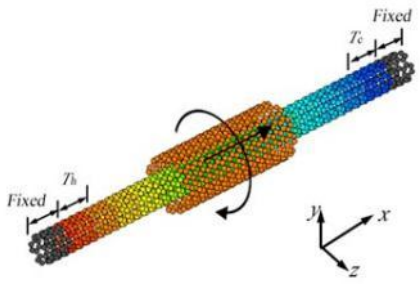

Fig. 6 Discrete Nanostructure – Concentric CNTs

The QM explanation of CNT motion is simple. QED creates more excitons at the hot end of the fixed CNT than at the cold end. EM radiation from recombination produces a charge gradient from, the hot to cold end. The outer CNT then moves by Coulomb repulsion to the cold end under the charge gradient. Classical MD simulations do not create excitons to produce the charge necessary to explain CNT motion.

Sputtering

KMC is a procedure for solving kinetic equations in non-equilibrium processes. KMC stands for kinetic Monte Carlo Unlike traditional MC, real time is included in the evolution of the system. The KMC simulation [12] of 5 keV argon atoms impacting a copper (111) crystal is shown in Fig. 7. The KMC simulation shows the emission of copper atoms from the crystal. The color temperature of the atoms: white - black > 300K, blue < 1400K; green < 4200K; red above 4200K.

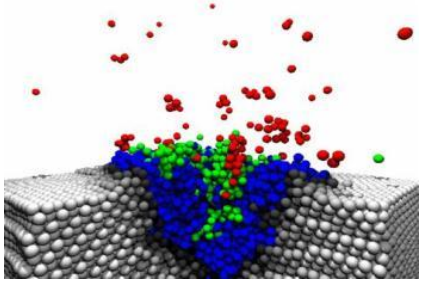

Fig. 7 Discrete Nanostructures - Sputtering

Since the copper crystal is submicron, the KMC simulation showing temperatures in excess of 300 K is invalid by QM. Melting of the copper occurs because the QED radiation loss to the surroundings is excluded in the simulation, but if included melting does not occur. By QM, sputtering of the copper atoms from the crystal has nothing to do with melting. Instead, sputtering is caused by the Coulomb explosion from the EM energy absorbed upon the penetration of argon atoms. Valid KMC solutions by QM require the atoms be maintained at ambient temperature, say by the Nose-Hoover thermostat [1-3]. Indeed, the QED radiation lost to the surroundings negates any temperature increase, let alone melting of the crystal.

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 in 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 produces EM radiation that charges the NW atoms positive. Coulomb repulsion between atoms induces a triaxial state of hydrostatic tension. Unlike bulk tensile specimens in a uniaxial stress state, NWs have enhanced mechanical properties because of the hydrostatic tension 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.

Fig. 8 Discrete Nanostructure – NW Stiffening

The QED induced hydrostatic pressure within the NW caused by repulsion of atoms from holon charges is given by the electrostatic potential U_{ES}. For the atom as a sphere of radius R_{atom} having unit electron charge e,

$$U_{ES} = \frac{3e^2}{20\pi\varepsilon_o R_{atom}} \tag{4}$$

where, ε_o is the permittivity of the vacuum.

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

$$U_{kT} = \frac{3}{2}kT_{grip} \tag{5}$$

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

$$\gamma = \frac{U_{kT}}{U_{ES}} = \frac{10\pi\varepsilon_o k R_{atom} T_{grip}}{e^2} \tag{6}$$

For T_{grip} = 300 K with the silver atom having R_{atom} = 1.45 Å, the fraction γ = 0.0065. During the MD solution, the Nose-Hoover thermostat maintained temperatures T < 0.01 K. The Young's moduli Y for various γ are shown in Fig. 9.

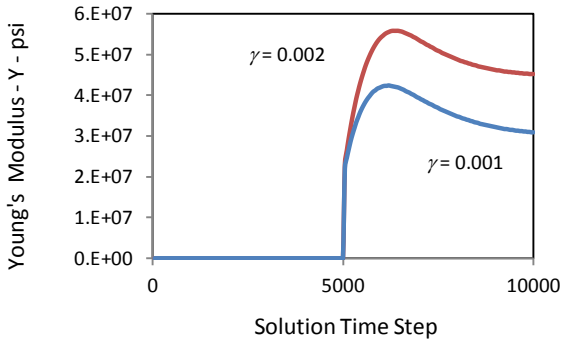

Fig. 9 Discrete Nanostructure – Young's Moduli of NWs

The QM solutions for γ = 0.001 and 0.002, give Young's moduli Y = 31 and 45x10^6 psi, respectively. The experimental Young's modulus of 26x10^6 psi is best approximated with the QM solution γ = 0.001. With the uniaxial Young's modulus Y_o ~ 17 x 10^6 psi, the stiffening enhancement is Y/Yo ~ 1.88. The QM solution for γ = 0.001 means only 1/6.5 or about 15 % of the kT_{grip} 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 safely 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 repulsive Coulomb forces are created from QED induced charge.

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