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QUANTUM MECHANICAL STIFFENING OF NANOWIRES

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ABSTRACT

Over the past decade, the stiffening of NWs has been explained by classical physics, the mechanisms of which depend on their high surface to volume ratios. NW stands for nanowire. However, classical physics at the nanoscale usually gives unphysical results that may be avoided by QM. QM stands for quantum mechanics. In NWs, QM precludes the atoms from having the heat capacity to conserve the absorption of EM energy by an increase in temperature, say from the temperature acquired as the NW is gripped in tensile tests. Instead, conservation proceeds by the QED induced up-conversion of absorbed EM energy to the TIR frequency of the NW, the consequence of which is the creation of excitons (holon and electron pairs). EM stands for electromagnetic, QED for quantum electrodynamics, and TIR for total internal reflection. Upon exciton recombination, EM radiation is produced that charges the NW atoms or is lost to the surroundings. Standard MD algorithms are modified to be consistent with QM by allowing the QED induced charge to produce Coulomb repulsion between atoms instead of the usual increase in temperature. The MD simulations show QED induced Coulomb repulsion between atoms stiffens NWs in tensile tests by the formation of the triaxial stress state of hydrostatic tension that is not formed in the uniaxial stress state of tensile specimens at the macroscale.

INTRODUCTION

Observations of significant stiffening of NW's have been reported, although some findings suggest there is no stiffening. Because of this uncertainty, research on the mechanism for stiffening has been a subject of great interest. Numerous mechanisms [1] have been proposed including: high surface-to-volume ratios, surface stresses, bulk nonlinear elasticity, surface stiffness, surface tension, surface reconstruction, surface strain and stress, and skin depth energy pinning.

Generally, the stiffening of NW's is not based on direct measurements of material properties, but rather inferred from indirect measurements of increased resistance to buckling, enhanced resonant frequencies, and the like. In contrast, the traditional uniaxial tensile test of a NW gives mechanical properties directly, but is difficult to perform because of the nanoscopic size of the NW tensile specimen. Nevertheless, Young's modulus and yield stress of silver NW's in tensile tests was recently reported [2] that shows stiffening consistent with indirect measurements, the mechanism thought to be the high surface to volume ratio in combination with the annihilation of dislocations from fivefold twinning.

Stiffening mechanisms [3] proposed to date find basis in classical physics. Contrarily, stiffening is not observed at the macroscale, but rather only at the nanoscale. e.g., in < 100 nm diameter NW's. Hence, only QM having a size effect may explain stiffening in nanostructures.

In this paper, the QM restriction is invoked that the thermal *kT* energy (or heat capacity) of the atom vanishes at the nanoscale thereby precluding the conservation of EM energy by an increase in temperature, say from the thermal *kT* energy acquired from the grips in tensile tests of NW's. Instead, conservation proceeds by the creation of QED induced excitons. Upon recombination, EM radiation is produced that charges the atoms by Coulomb repulsion to stiffen the NW by the triaxial stress state of hydrostatic tension.

THEORY

QM Restrictions

Unlike classical physics, QM restricts the thermal *kT* energy of the atom or the heat capacity of nanostructures thereby precluding conservation of any form of EM energy by an increase in temperature. A comparison of the *kT* energy of the atom by classical physics and QM by the Einstein-Hopf relation [4] is shown in Fig. 1.

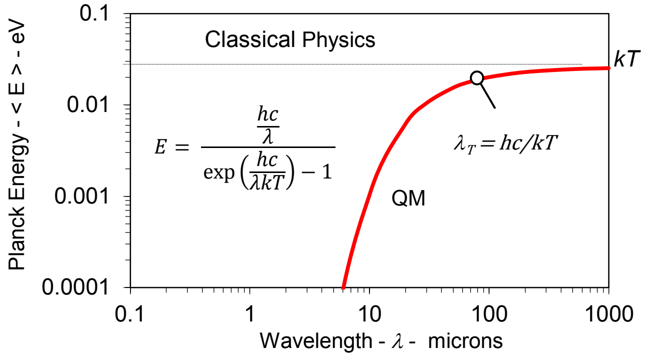

Fig. 1 Heat Capacity of the Atom at 300K
E is Planck energy, *h* Planck's constant, *c* speed of light,
k Boltzmann's constant, *T* temperature, and λ wavelength

Classical physics allows the atom to have the same kT energy in submicron 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, Fig. 1 shows the heat capacity of the atom is $< kT$ for $\lambda < 48$ 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.

EM 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. TIR has an important significance in nanostructures and need not be limited to light absorption.

Unlike macroscopic bodies, nanostructures have high surface to volume ratios, and therefore EM energy from any source (lasers, mechanical and Joule heat, electron beam irradiation, etc.) is absorbed almost entirely in their surface. Since the nanostructure surface coincides with the TIR wave function, QED induces the absorbed EM energy to undergo spontaneous conversion to surface QED radiation. However, TIR confinement is not permanent, sustaining itself only during EM energy absorption, i.e., absent absorption of EM energy, there is no TIR confinement and QED radiation is not created.

QED relies on complex mathematics as described by Feynman [5] although the underlying physics is simple, i.e., photons of wavelength λ are created by supplying EM energy to a submicron QM box with sides separated by $\lambda/2$. In nanostructures, QED up-converts absorbed EM energy to the frequency of TIR confinement. For NWs, the QED radiation energy E and frequency υ are:

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

where, n is the RI and d the diameter of the NW.

QM Induced Pressure

The QM pressure P_{QM} produced in the tensile specimen is a fraction η of the thermal kT energy acquired from the grips that produces the Coulomb repulsion between atoms, the remainder (1-η) lost to the surroundings. QM pressure is a cumulative effect from all atoms in the NW determined from the MD simulation. The QM pressure is,

$$P_{QM} = \eta \frac{NkT}{V} = \eta \frac{kT}{\Delta^3} \qquad (2)$$

where, N is the number of atoms in the volume V of the NW, i.e., $V/N = \Delta^3$ and Δ is the atomic spacing. In the NW, the thermal kT energy U_{kT} of the atom depends on the temperature $T_{\text{grip of}}$ the grips,

$$U_{kT} = \frac{3}{2} kT_{grip} \qquad (3)$$

For the silver NW with Δ = 0.409 nm with grips at T = 300 K and $\eta \sim 0.3$, $P_{QM} < 1.8 \times 10^7$ Pa ~ 2610 psi.

The QM pressure is caused by the Coulomb repulsion of atoms from the QED induced excitons that upon recombination produce EM radiation that charges the atoms or is lost to the surroundings. The electrostatic potential U_{ES}, for the atom as a sphere of radius R_{atom} having electron charge e,

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

where, ε_o is the permittivity of the vacuum.

Enhanced Young's Modulus and Yield Stress

In conventional tensile tests of macroscopic specimens, a positive strain stretching the specimen is produced, say in the longitudinal z direction. Since the tensile test is uniaxial, only the longitudinal stress σ_z exists and the σ_x and σ_y stresses in the orthogonal x and y directions vanish.

However, the stress state in tensile tests of nanoscale NWs is no longer uniaxial. QED induced Coulomb repulsion between atoms produces the triaxial stress state of hydrostatic tension where the orthogonal σ_x and σ_y stresses are positive and do not vanish. In effect, hydrostatic tension by the Poisson effect stiffens the NW by reducing the axial strain e_z for the same longitudinal σ_z stress as illustrated by,

$$e_z = \frac{1}{Y_o}\left[\sigma_z - \nu\left(\sigma_x + \sigma_y\right)\right] \qquad (5)$$

where, ν is Poisson's ratio and Y_o the bulk Young's modulus in the uniaxial stress state.

The Young's modulus Y in the triaxial stress state is,

$$Y = \frac{\sigma_z}{e_z} = \frac{Y_O}{1 - \nu(\sigma_x + \sigma_y)/\sigma_z} \tag{6}$$

The QED enhancement Y/Y_o depends on the triaxial stress state derived in the MD simulations. Assuming $\sigma_x + \sigma_y = 2\sigma'$, the QED enhancement Y/Y_o ratio for Poisson's ratio of silver $\nu = 0.37$ and the incompressible limit is shown in Fig. 2.

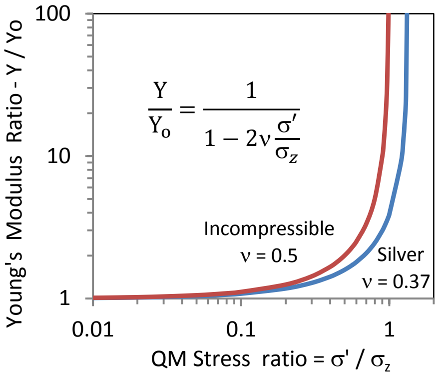

Fig. 2 QED Enhancement of Young's Modulus

The QED induced enhancement may be upper bound by $\sigma'/\sigma_z = 1$. For silver with Poisson's ration $\nu = 0.37$, the Young's modulus is enhanced $Y/Y_o < 3.8$. Regardless, the enhancement of yield strength is the same as that for Young's modulus.

SIMULATION

Standard MD computer programs based on statistical mechanics that implicitly assume the atoms have heat capacity could not be used to derive the Young's modulus of silver NW's. Instead, the Leapfrog algorithm [6] was modified consistent with the QM restriction that the heat capacity of the atom vanishes in NWs.

NW Model

The NW model geometry selected was a square cross-section having sides w and length L as illustrated by VMD graphics in Fig. 3. The silver wire 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.

Fig. 3 MD Model of NW under Longitudinal Loading

Lennard-Jones Potential

The L-J potential [7] was used to simulate the atomic potential U_{ij} of the NW atoms.

$$U_{ij} = 4\varepsilon\left[\left(\frac{\sigma}{R_{ij}}\right)^{12} - \left(\frac{\sigma}{R_{ij}}\right)^{6}\right] \tag{7}$$

where, R_{ij} the interatomic spacing between atoms i and j. For silver, $\sigma = 2.644$ Å and $\varepsilon = 0.345$ eV.

MD Pressure

The MD pressure P within the NW model [6] during equilibration and loading is,

$$P = P_{QM} + \left(NkT + \frac{1}{3}\sum_{\alpha}\sum_{\alpha>\beta} r\frac{dU}{dr}\right)/V \tag{8}$$

Equilibration

During equilibration, the NW was fixed at x = 0 and free at $x = L$. At the fixed end, only the z-coordinates of the atoms on were fixed; the x and y atom positions were free to move.

Consistent with the QM requirement that the atoms have vanishing heat capacity, the absolute temperature was held at $T < 0.01$ K by the Nose-Hoover thermostat. In effect, the MD simulation was performed at a temperature of absolute zero. During equilibration, the QM pressure P_{QM} is not used.

Loading and QM Pressure

The NW was displacement loaded by a step change δ in the z-direction at $z = L$. The force $F = AY_O\,\delta/L$ where the axial stress $\sigma_z = F/A$, and strain $\varepsilon_z = \delta/L$.

The QM pressure P_{QM} separating atoms i and j at positions R_i and R_j is defined by the Coulomb repulsive force F_{ij} modified by the fraction η given by the ration of the thermal U_{kT} to electrostatic U_{ES} energy,

$$F_{ij} = \eta\frac{e^2}{4\pi\varepsilon_o R_{ij}^2} \tag{9}$$

where,

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

Taking $T_{grip} = 300$ K and the silver atom having $R_{atom} = 1.45$Å, $e = 1.6\text{x}10^{-19}$ C, the full kT energy of the atom corresponds to the fraction $\eta = 0.0065$.

Time Step and Long Range Cut-Off

The MD solutions used time steps < 5 fs. Because of the long range Coulomb repulsion forces, the cut-off in summing the forces from all atoms was set at 50 Å that corresponds to over half of the NW specimen length.

Response

Uniaxial

In the uniaxial response, the QM pressure P_{QM} of Coulomb repulsion was excluded. Equilibration for 5,000 steps was followed by displacement loading to 10,000 steps. For $\delta = 0.5$ A, the displacement loading is shown in Fig. 4.

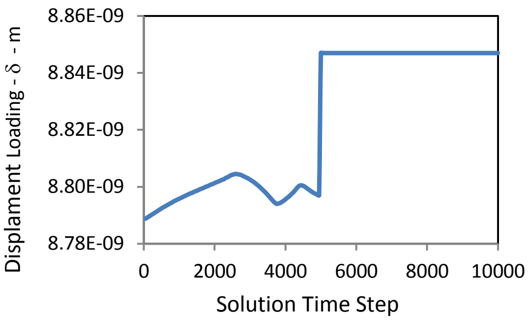

Fig. 4 Displacement Loading

After equilibration, the σ_x, σ_y, and σ_z stress is < 100 psi. Upon displacement δ loading, the stresses increased and at convergence, the σ_x and σ_y stresses vanished leaving only the σ_z stress. The σ_x and σ_y stresses were identical as shown for $\delta = 0.5$ Å in Fig. 5.

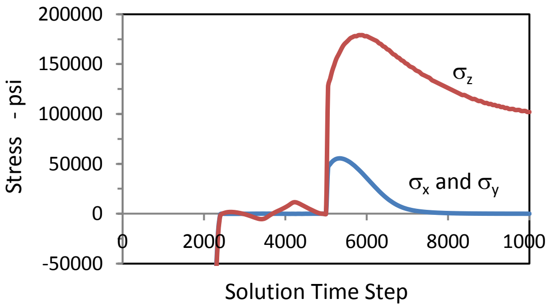

Fig. 5 Uniaxial Stress State - Stresses

Upon convergence at 10,000 steps, various displacement loadings δ were found to converge to Young's moduli $Y_o \sim 17 \mathrm{x} 10^6$ psi is shown in Fig. 6.

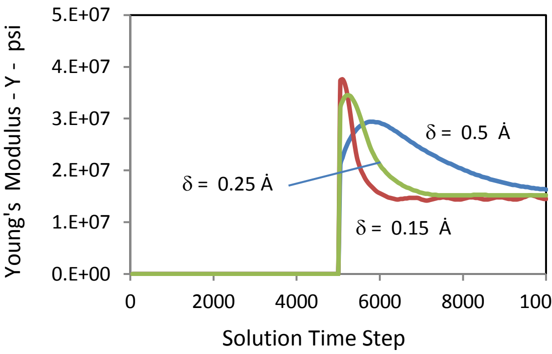

Fig. 6 Uniaxial Stress State - Young's Modulus

Triaxial

In the triaxial response, Coulomb repulsion between atoms produces the QM pressure P_{QM}. With full kT energy corresponding to $\eta = 0.0065$, the MD solution for $\eta = 0.001$ at a displacement $\delta = 0.5$ Å loading equilibration for 5,000 steps followed by loading for an additional 5,000 steps as shown in Fig. 7. Unlike uniaxial stress, the σ_x and σ_y stresses do not vanish. Applying an external hydrostatic tension P_{QM} pressure to the NW failed to enhance the Young's modulus as the σ_x and σ_y stresses vanished as for the uniaxial stress state.

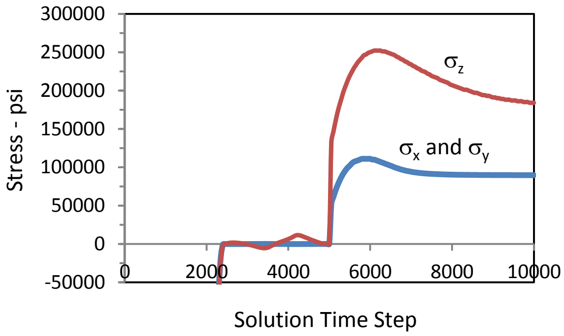

Fig. 7 Triaxial Stress State - Stresses

The Young's modulus Y and Poisson's ratio ν for displacement loadings $\delta = 0.5$ Å at fractions $\eta = 0.001$ and 0.002 are shown in Fig. 8 and 9.

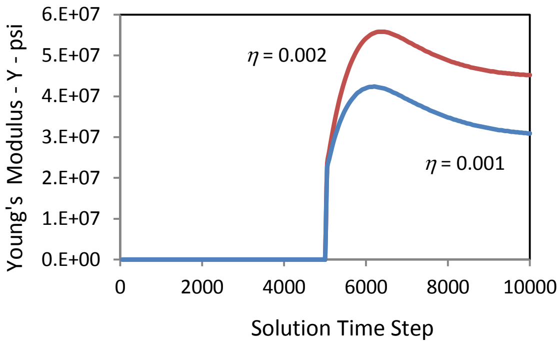

Fig. 8 Triaxial Stress State – Young's Modulus

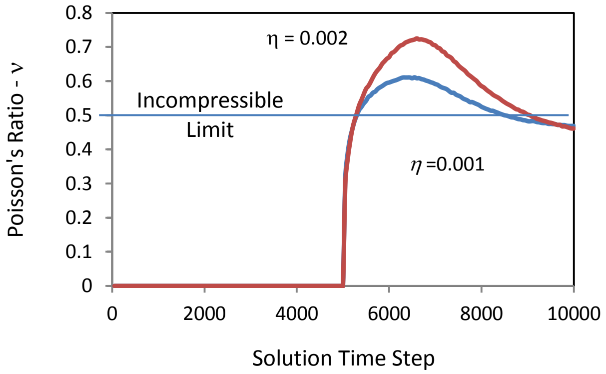

Fig. 9 Triaxial Stress State – Poisson's Ratio

DISCUSSION

MD Solution and Comparison to Data

Simulating the QM pressure with the fraction η of the kT energy by Coulomb repulsion produces the solutions for Young's modulus Y shown in Fig. 8. After convergence at 10,000 steps, the solutions for $\eta = 0.001$ and 0.002 give $Y = 31$ and $45\text{x}10^6$ psi, respectively. Fig. 9 shows the corresponding Poisson ratios approach $\nu = 0.47$ near the incompressible limit and not the Poisson's ratio $\nu = 0.37$ for silver. Indeed, the MD solutions confirm the incompressible stress state as the pressure $P = -(\sigma_x + \sigma_y + \sigma_z) / 3$ is always preserved.

Experimental data (Table I of [2]) on 34 nm diameter silver NW's show Young's moduli of $Y = 26\text{x}10^6$ psi. Therefore, the $\eta = 0.001$ QM solution giving $Y \sim 31\text{x}10^6$ psi best approximates the data. From Fig. 7, $\sigma_x = \sigma_y = 90{,}000$ psi and $\sigma_z = 180{,}000$ psi. From Fig. 2, the NW stiffening enhancement for $\nu = 0.47$ gives $Y/Yo = 1.88$ that is consistent with $Y_o = 17\text{x}10^6$ psi, i.e., the Young's modulus $Y \sim 32\text{x}10^6$ psi. The MD solution for $\eta = 0.001$ of silver NW's means only 1/6.5 or about 15 % of the full kT energy stiffens the NW, the remaining 85% lost to the surroundings as EM radiation.

EM Energy Sources and Stiffening

The MD simulation only considered the thermal kT energy of the grips as the heat source, but any EM energy absorbed by the NW also produces the stiffening effect. In this regard, the strain hardening (Fig. 2(a) of [2]) under a sequence of loading and unloading raised the ultimate tensile strength (UTS) to about 300,000 psi, or about 45x that of the yield of bulk silver at 6550 psi. The strain hardening is explained [2] by dislocation-induced shear, but the dislocations produce mechanical heat that like the thermal kT energy of the grips cannot be conserved by an increase in temperature. Instead, the UTS enhancement is more likely caused by the dislocation induced heating of the NW.

Other forms of absorbed EM energy also stiffen NWs, e.g., passing current through NW's is a source of Joule heat that again is induced by QED to produce hydrostatic tension from the Coulomb repulsion between atoms to enhance the Young's modulus. Indeed, electron beam irradiation is shown [8] to enhance the Young's modulus of tin oxide NW's by 40%.

Computation of Virial Stress

In the MD simulation of the NW, the σ_x, σ_y, and σ_z stresses are computed [9] from the virial theorem,

$$\sigma_{ij}^{V} = \frac{1}{V}\sum_{\alpha}\left[\frac{1}{2}\sum_{\beta=1}^{N}\left(R_i^{\alpha} - R_i^{\beta}\right)F_j^{\alpha\beta} - 3kT^{\alpha}\right] \qquad (10)$$

where, the positions of atoms α and β are R_i^{α} and R_i^{β}.

The controversy [9] whether the Cauchy stress is only the thermal excitation velocity and not the total velocity of the atoms is resolved by QM as thermal changes are precluded at the nanoscale, i.e., the atoms in the NW are not thermally excited by QM.

Shape of Fracture Surface

In the tensile tests of silver NW, the fracture surface is unusual. Unlike macroscopic tensile specimens, the NW specimen showed no diameter reduction or necking prior to failure as shown in Fig. 10.

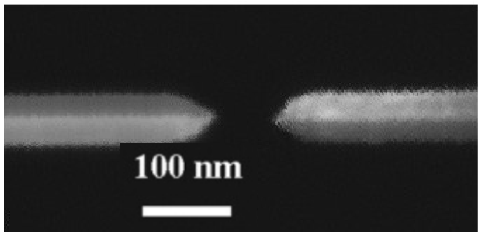

Fig. 10 Fracture Surface of Silver Nanowire

Dislocation-induced shear is thought [2] to explain the localized fracture surface. However, it is more likely the shape fracture surface is caused by the removal of silver atoms by Coulomb explosion from QED induced charge repulsion during strain hardening. Verification of Coulomb explosion in NW's by searching the SEM chamber for silver atoms or monitoring their emission during tensile testing is suggested. MD simulations of Coulomb explosions in NW's that are likely to show the ejection of silver atoms were not performed.

CONCLUSIONS

Classical physics assumes the atom always has heat capacity. QM differs by restricting the atom's heat capacity to vanishing small levels in nanostructures. Lacking heat capacity, absorbed Joule heat cannot be conserved by increases in temperature. Instead, conservation proceeds by the QED induced creation of excitons (holon and electron pairs) under the TIR confinement of the nanostructure, a process inaccessible to classical physics,

In tensile tests of silver NW's, the QED radiation is caused by the absorbed thermal kT energy from the temperature of the grips that hold the NW in combination with the heat associated with strain hardening. QED induces the creation of excitons that upon recombination produce EM radiation to charge the atoms thereby producing Coulomb repulsion between atoms to place the NW under hydrostatic tension. The Young's modulus of NW's is enhanced above that in the uniaxial tensile test because the QED induced hydrostatic tension by the Poisson effect produces a triaxial stress state that reduces the longitudinal strain for the same axial load.

MD solutions of an 8 Å square NW show the QED induced charge repulsion of silver atoms gives a Young's modulus of 31×10^6 psi comparable to the experimental value of 26×10^6 psi for the 34 nm NW. MD solutions by QM are computationally intensive and require computing power beyond the PC used in this paper, especially if the 34 nm diameter NW's are simulated.

The QED induced stiffening of NW's is not limited to tensile tests. Indeed, NWs may stiffen anytime EM energy is absorbed including Joule heat from passing current through the NW and electron beam irradiation.

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