Nanochannel Flow by Quantum Mechanics

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Abstract Water flow through nanochannels of carbon nanotubes is observed to be 2-5 orders of magnitude higher than predicted by assuming a no-slip condition at the channel wall consistent with the Hagen-Poiseuille equation of continuum mechanics. To explain this disparity, the fluid is generally thought to slip at the channel wall, but this is questionable because the calculated slip-lengths necessary to explain the flow enhancement exceed the typical slip on non-wetting surfaces by 2 to 3 orders of magnitude. Hence, fluid slip at the channel wall is an unlikely explanation for the observed flow enhancement in nanochannels. More likely flow enhancement is caused by the size effect of QM that causes the viscosity of the fluid to vanish in nanochannels that otherwise does not occur at the macroscale. QM stands for quantum mechanics. Vanishing fluid viscosity as the explanation of enhanced flow offers the advantage of allowing the Hagen-Poiseuille equation to remain valid at the nanoscale. In support of a vanishing viscosity in nanochannels, MD is performed for liquid argon to show the viscosity does indeed vanish in nanochannels. MD stands for molecular dynamics

Keywords: nanochannels, enhanced flow, quantum mechanics, molecular dynamics

1. Introduction

Water flow observed [1 - 3] through nanochannels in membranes of CNTs is found to be 2-5 orders-of-magnitude greater than those predicted by the no-slip Hagen-Poiseuille equation of continuum mechanics. CNT stands for carbon nanotube. To explain this surprising flow enhancement, slip at the wall of the nanotube is assumed because of the non-wetting nature of CNTs. For bulk water viscosity, the Hagen-Poiseuille relation [1] requires slip lengths of 50 microns to reproduce the measured flow in 7 nm CNT membranes. Since MD simulations [4] indicate that the water/graphene slip length is on the order of 50 nm, the required slip-length is 1000 times larger than that of non-wetting boundaries. Because of this, slip cannot be the mechanism for the significant flow enhancement in nanochannels. Another mechanism is at play.

In this regard, flow enhancement is more likely caused by the size effect of QM causing the viscosity of the fluid to vanish in nanochannels that otherwise does not occur at the macroscale. Vanishing viscosity as the explanation of enhanced flow allows the Hagen-Poiseuille equation to remain valid and support the observations of unbounded flow in nanochannels.

1.1 QM Restrictions and QED

Vanishing viscosity is the consequence of QM denying [5] the atom the heat capacity to conserve viscous heating by an increase in temperature. Fig. 1 compares classical physics with QM based on the Planck energy E of the atom given by the Einstein-Hopf relation [6] for the harmonic oscillator in terms of the kT energy. Here, k is Boltzmann's constant and T absolute temperature. Classical physics always allows the atom to have kT energy. QM differs in that kT energy depends on the wavelength λ of TIR confinement. By QM, kT energy is only available for atoms at the macroscale, i.e., for $\lambda > \lambda_T$ and otherwise is $<< kT$. Because of QM, the atom cannot conserve viscous heat in the nanochannel.

Instead, QED induces atoms in fluid molecules under the TIR confinement of the nanochannel to conserve frictional heat by the creation of EM radiation. QED stands for quantum electrodynamics, TIR for total internal reflection, and EM for electromagnetic. At the nanoscale, the TIR confinement creates EM radiation having sufficient Planck energy to ionize the fluid molecules, thereby charging the fluid atoms producing Coulomb repulsion that tends to avoid atomic contact and reduce fluid viscosity.

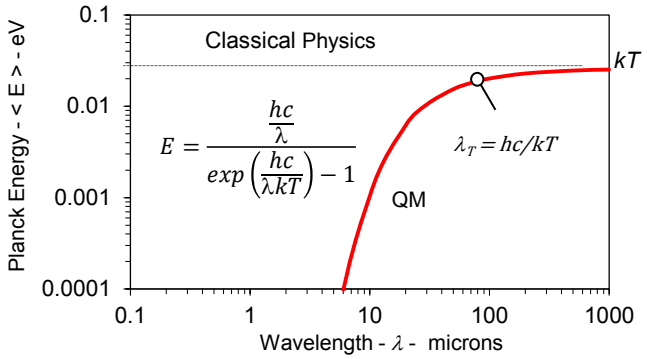

Figure 1 Heat capacity of the atom at 300K.
In the inset, *h* is Planck's constant, *c* is the speed of light, and λ is wavelength

To show the viscosity vanishes in nanochannels MD simulations would seem especially suited. However, MD computer programs, e.g., [7] finding basis in statistical mechanics allow the atom the heat capacity at the nanoscale forbidden by QM. What this means is the MD simulations [8, 9] of nanochannel flow that abound the literature are invalid [10] by QM. Because of this, standard MD computer programs require modification to simulate the QM effect of a vanishing heat capacity on the viscosity of the fluid.

2. Purpose

Perform MD simulations valid by QM to show the viscosity of liquid argon vanishes in nanochannels.

3. Theory

In nanochannels, the QM effect during fluid flow is illustrated in Fig. 2. The EM radiation from a laser heats the molecules under TIR confinement in the nanochannel while QED conserves the heat by creating EM radiation that ionizes the molecules.

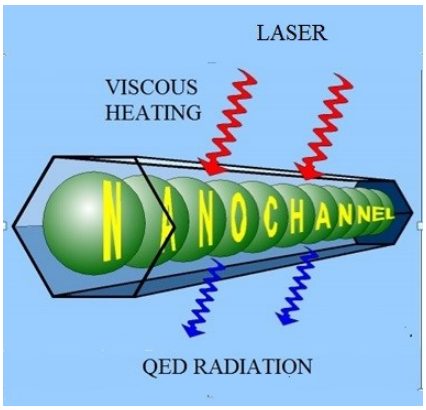

Figure 2 Nanochannel Ionization of Fluid Atoms by QED Radiation

However, lasers are not required. The fluid molecules flowing through the nanochannel produce viscous frictional heat that is induced by QED to create ionizing EM radiation at the TIR confinement wavelength λ of the nanochannel. Here, $\lambda = 2\,nd$, where n is the refractive index of the fluid and d the tube diameter or channel thickness. For $d < 100$ nm, the EM radiation has wavelengths λ in the UV and beyond, i.e., $\lambda < 300$ nm. In nanochannels, QED induced EM radiation has sufficient Planck energy to ionize most fluid molecules having ionization potentials of ~ 10 eV, I.e., wavelength $\lambda < 125$ nm that for $n = 1.5$ requires nanochannels having d < 45 nm. What this means is the viscosity in nanochannels vanishes as the fluid is highly charged with Coulomb repulsion producing a loosely bound frictionless state of flowing atoms.

3.1 Lennard-Jones Viscosity

The reduction in viscosity may be understood by considering the L-J potential between fluid-fluid and fluid-wall atoms. L-J stands for Lennard-Jones. Here, L-J parameter σ is the repulsive atom core and ε the attractive potential. Fig. 3 shows QED induced charge offsetting the ε attractive potential of the atom giving a zero net (atom + charge) attractive potential.

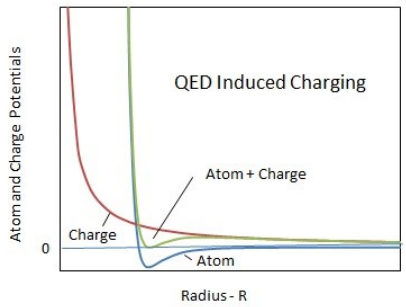

Figure 3 QED charging of Fluid Atoms producing Zero Net Attractive Potential

3.2 Valid MD Simulation and Model

MD simulations that are valid by QM require the viscous heat is not conserved by an increase in temperature and instead conserved by charging the atoms. MD solutions are therefore made near absolute zero temperature, say 0.001 K to avoid temperature changes. Usually, MD solutions of nanochannel flow are performed with Lees-Edwards [11] periodic boundary conditions. However, charging the atoms requires long range corrections that may be avoided by using a discrete MD model and considering all atoms without invoking a cut-off in force computations. On this basis, a discrete 2D model comprising 100 atoms in a BCC configuration of liquid argon under a constant shear stress was selected. The MD model in BCC is shown in Fig. 4.

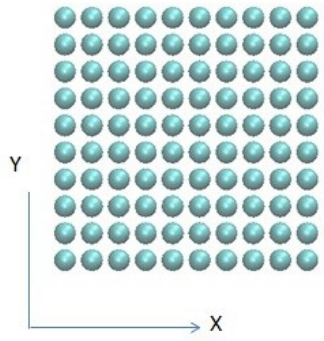

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Figure 4 Nanochannel 2D MD Model

3.3 MD Simulation and Results

The BCC configuration assumed liquid argon at a density of 1407 kg/m^3. The atomic spacing was 3.62 Å. The L-J potential for argon has σ = 3.45 Å and ε = 120 k. The MD computation box is 32.6 Å square. Time steps were < 2 fs.

The MD loading imposed a velocity gradient 3.06 x10^{10} / s normal to the flow direction having velocity of 100 m/s over the height of the MD box. . Unlike Lees-Edwards, the MD computation box became highly distorted after 150000 iterations. The distortion after 25000 iterations is shown in Fig. 5.

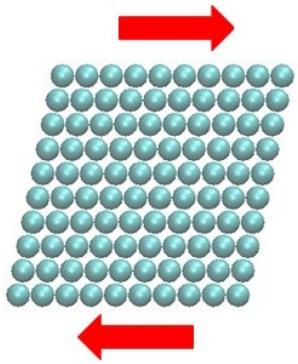


Figure 5 MD Solution – Distorted Computation Box

In the MD solution for liquid argon having ε = 120 k, the L-J viscosity converged to ~ 144 micro-Pa-s. Experimentally, the viscosity [12] of liquid argon at -130 C is 54 micro-Pa-s, but 175 micro-Pa-s has been [11] reported. Instead of performing MD for repulsive Coulomb forces between atoms including the attractive L-J potential ε = 120 k, the Coulomb repulsion was first simulated by neglecting Coulomb repulsion and simply reducing the attractive L-J potential by 100 X to ε = 1.2 k that gave viscosity of ~ 1 micro-Pa-s. The MD solutions of L-J viscosity for ε = 120 k and 1.2 k are shown in Fig. 6.

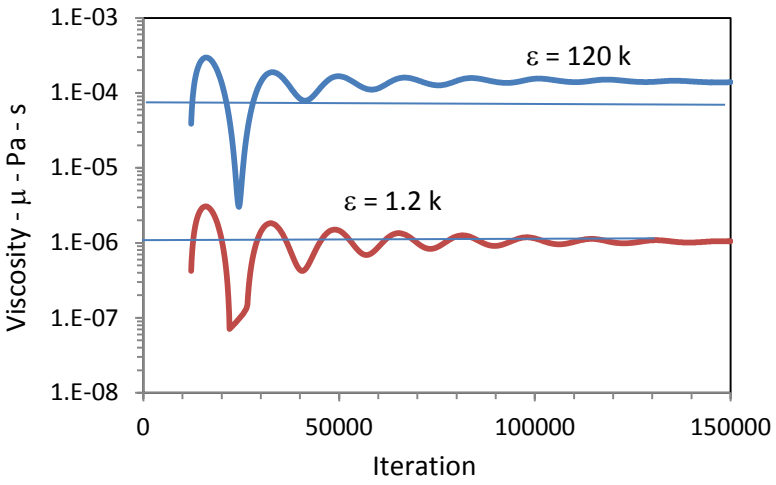


Figure 6 Argon Viscosity at ε = 120 k and 1.2 k

The 100 X reduction in L-J attractive potential produced a reduction of 144 X in viscosity. Because of this, MD solutions including Coulomb repulsion with the attractive potential is not necessary, but for completeness is presented to show frictionless flow is indeed present in nanochannels.

4. Extensions

Consistent with QM the viscosity of the fluid in nanochannels is shown to vanish by Coulomb repulsion offsetting the L-J attractive ε = 120 k potential.

4.1 Theory

The Coulomb repulsion occurs because QED induces the creation of charge from conserving viscous friction heat instead of increasing temperature. The electrostatic potential U_{ES}, for atoms separated by distance R having electron charge e is,

$$U_{ES} = \frac{e^2}{4\pi\varepsilon_o R} \tag{1}$$

where, ε_o is the permittivity of the vacuum. The L-J potential U_{LJ} between the atom pair is,

$$U_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right] \tag{2}$$

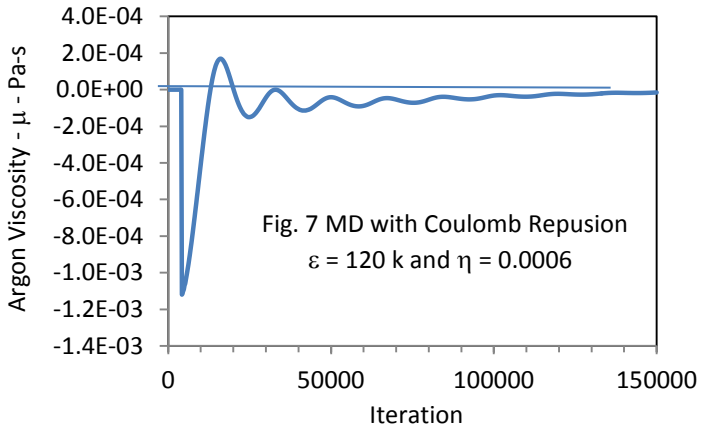
The L-J potential minimum occurs at $R = 2^{1/6}\sigma$ giving $U_{LJ} = -\varepsilon$. The fraction η_c of the available electrostatic energy U_{ES} to counter the attractive potential ε is,

$$\eta_c = \frac{U_{LJ}}{U_{ES}} = \frac{4\pi 2^{1/6}\sigma\varepsilon_o\varepsilon}{e^2} \tag{3}$$

Taking ε = 120 k for argon, the fraction η_c = 0.0027. The remainder (1-η_c) U_{ES} is radiated as EM radiation to the surroundings. However, Coulomb repulsion is collectively enhanced above that for a single atom pair, and therefore $\eta < \eta_c$.

4. MD Results

MD solutions were obtained for various η to determine the optimum at which the viscosity vanished. By trial and error, η = 0.0006 < η_c was found optimum as shown in Fig. 7.



The MD solution with Coulomb repulsion for Argon at ε = 120 k is observed to vanish. However, η = 0.0006 < η_c = 0.0027 means the collective effect of about 5 atom interactions is occurring. Flow enhancement above Hagen-Poiseuille at bulk viscosity is indeed frictionless and unbounded.

5. Discussion

5.1 Modified Hagen-Poiseuille Equation

The Hagen-Poiseuille equation modified [13] for slip gives the flow *Q* through a circular nanochannel of radius *r* under the pressure drop ΔP ,

$$Q = \frac{\pi r^3 (r + 4b)}{8\mu L} \Delta P \tag{4}$$

where, μ is the viscosity, *L* the channel length, and *b* the slip length.

The QED induced reduction in viscosity μ is observed to inversely enhance the flow *Q.* However, the flow *Q* is even further enhanced by slip *b*. Regardless, the QED induced reduction in viscosity is the dominant factor in flow enhancement.

5.2 Exit Losses

Unbounded flow in nanochannels [13] is consistent with QED induced vanishing viscosity. As long as the fluid is under TIR confinement by the channel walls, the flow is indeed frictionless. However, the fluid must eventually leave the nanochannel at which time there is no TIR confinement whereupon the atom regains it classical behavior and the flow velocity is diminished by viscous friction. Nevertheless, flow within the nanochannel is indeed frictionless and unbounded.

6. Conclusions

Surprisingly high flow in nanochannels is the consequence of QM that requires the heat capacity of the atom under TIR confinement to vanish and preclude the conservation of viscous heat by an increase in temperature. Instead, the viscous heat is conserved by QED inducing the creation of EM radiation that ionizes the fluid molecules to produce a state of Coulomb repulsion that overcomes the attractive potential of the atom thereby producing frictionless flow as the fluid viscosity vanishes.

Slip flow occurs in combination with QED induced vanishing viscosity to further enhance the flow. Absent QM, slip flow is relatively inconsequential because the viscosity remains at bulk.

For argon, the MD simulation consistent with QM by not conserving viscous heat with an increase in temperature under a constant velocity gradient gave a viscosity of 144 micro-Pa-s compared to an experimental value of 175 micro-Pa-s. By reducing the attractive L-J potential by a factor of 100, the viscosity was reduced to 1 micro-Pa-s. Flow is enhanced by a factor of 144.

MD solutions for argon having an attractive ε = 120 k L-J potential in combination with Coulomb repulsion between atoms need not be performed because taking ε = 1.2 k showed a 144 X reduction in viscosity. What this means is others [1-4, 8-9] may readily determine the reduction in viscosity in the MD simulation of their nanochannels by re-running at reduced attractive L-J potentials. However, the temperature should be held by the Nose-Hoover thermostat near absolute zero, say 0.001 K.

However, MD solutions for argon having a L-J attractive ε = 120 k potential in combination with QED induced Coulomb repulsion between atoms shows the viscosity vanishes for η = 0.0006. Since $\eta < \eta_c$ = 0.0027, the collective action of about 5 atoms is at play in a vanishing viscosity.

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