Flow of Fluids and Solids at the Nanoscale

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Abstract – The Hagen-Poiseuille equation of classical fluid flow that assumes a no-slip condition at the wall cannot explain the dramatic increase in flow found in nanochannels. Even if slip is assumed at the wall, the calculated slip-lengths are found exceed the typical slip on non-wetting surfaces by 2 to 3 orders of magnitude. Similarly, MD simulations of nanochannel flow cannot explain the flow enhancement. MD stands for molecular dynamics. In solids, classical kMC cannot explain how solid crystals in a nanotube under the influence of an electric current flow through a constriction that is smaller than the crystal itself. kMC stands for kinetic Monte Carlo. However, QM and not classical physics governs the nanoscale. QM stands for quantum mechanics. At the nanocale, fluid and solid atoms are placed under EM confinement that by QM requires their heat capacity to vanish. EM stands for electromagnetic. Unlike classical physics, QM precludes the conservation of viscous frictional heat by the fluid and solid atoms by the usual increase in temperature. MD and kMC based in classical physics therefore require modification for application at the nanoscale. Conservation of viscous heat at the nanoscale proceeds by QED inducing creation of EM radiation that ionizes the atoms to cause atomic separation under Coulomb charge repulsion. QED stands for quantum electrodynamics. MD simulations of liquid argon flow in a nanochannel using a discrete 2D model show the viscosity to vanish suggest the flow is upper bound by the frictionless Bernoulli equation, the simplified extension of which to the flow of a solid crystal through a nanotube suggests the solid, like the fluid moves as a loosely bound collection of charged atoms.

Keywords: MD, kMC, nanocale, flow, fluids, solids, classical physics, quantum mechanics, QED

1. Introduction

Water flow observed 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 classical physics Majunder, et al. (2005), Holt et al. (2006), Du, et al. (2011). 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, Majunder, et al. (2005) showed the Hagen-Poiseuille relation required slip lengths of 50 microns to reproduce the measured flow in 7 nm CNT membranes. Since MD simulations by Verweij et al. (2007) 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.

With regard to the flow of solids, experiments by Begtrup, et al. (2009) and Loffler et al. (2011) demonstrated the electrically induced motion of metal crystals through smooth uniform nanochannels of carbon nanotubes does not occur by melting. When current flows along the tube length, electromigration is thought to move in the crystals in the same direction as the electron flow. Recently, Coh et al. (2013) found that iron crystals under an electric current reform atom-by-atom to fit through a constriction in the nanochannel that is smaller than the crystal itself. Classical kMC simulations dependent on temperature inconsistent with QM were thought to explain crystal motion. But QM precludes temperature changes in nanotubes suggesting loss of atomic cohesion is caused by another mechanism.

In this regard, the flow of fluids and solids at the nanoscale is more likely the consequence of the size effect of QM causing the viscosity of the fluid or cohesion of the solid to vanish that otherwise does not occur at the macroscale. How QM causes viscosity and cohesion to vanish is an important purpose of this paper.

1. 1. Heat Capacity of the Atom

Vanishing viscosity of a fluid or cohesiveness of a solid at the nanoscale is the consequence of QM denying the atom the heat capacity to conserve viscous heat by an increase in temperature. Fig. 1 compares the Planck energy E of the atom by classical physics with QM for the atom as a harmonic oscillator given by Einstein and Hopf (1910).
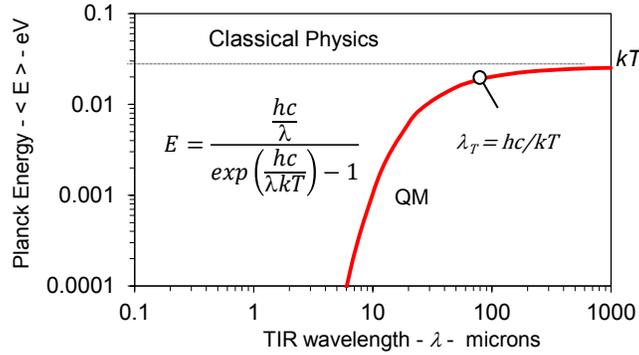

Fig. 1. Heat capacity of the atom at 300 K
In the inset, h is Planck's constant, c is the speed of light, and λ is wavelength,
k is Boltzmann's constant and T absolute temperature

Classical physics always allows the atom to have kT energy. QM differs in that heat capacity given by thermal kT energy of the atom depends on the TIR wavelength λ of EM confinement. TIR stands for total internal reflection. 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 fluid atoms in the nanochannel cannot conserve viscous heat by an increase in temperature. Similarly, the solid crystal atoms in the nanotube cannot increase in temperature to conserve Joule heat.

1.2. QED induced EM radiation

The QM requirement that the heat capacity of fluid atoms in nanochannels vanishes under TIR confinement precludes conservation of viscous heat by the usual increase in temperature. Instead, QED conserves viscous heat produced by the friction between fluid molecules in flow through the nanochannel by inducing the creation of EM radiation that charges the atoms in the molecules or is lost to the surroundings as shown by Prevenslik (2015). At the TIR confinement wavelength λ of the nanochannel, the Planck energy of QED radiation is sufficiently high to ionize the fluid molecules and charge the atoms to produce Coulomb repulsion between the atoms, the separation of which causing the viscosity to vanish. As shown for applications in Web-1, the TIR wavelength $\lambda = 2\,nd$, where n is the refractive index of the fluid and d the nanochannel diameter or height. 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 fluid viscosity in nanochannels vanishes as the fluid is highly charged with Coulomb repulsion producing a loosely bound frictionless state of flowing atoms.

2. Purpose

Perform MD simulations valid by QM to show the viscosity of liquid argon vanishes in nanochannels. Make simplified extensions of the findings to the flow of a crystal in a nanotube.

3. Analysis and Results

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

3. 1. Validity of MD

To show fluid viscosity vanishes in nanochannels, MD simulations would seem especially suited. However, MD computer programs, e.g., LAMPS (2010) finding basis in classical physics allow the atom to have the heat capacity at the nanoscale that is forbidden by QM. What this means is the MD simulations of nanochannel flow that abound the literature, e.g., Thomas and McGaughey (2008), Li (2009) are invalid by QM as shown by Prevenslik (2013). Because of this, the traditional MD computer algorithms given by Allen and Tildesley (1987) were modified to simulate the QM effect of vanishing heat capacity on fluid viscosity.

3. 2. Lennard-Jones Potentials

The reduction of viscosity in MD may be understood by considering the L-J potential between fluid atoms. L-J stands for Lennard-Jones. Here, the L-J parameter σ is the repulsive atom core and ε the attractive potential. Fig. 2 shows QED induced charge offsetting the ε attractive potential of the atom giving a zero net (atom + charge) attractive potential. In this way, the fluid viscosity vanishes as the atoms are no longer in frictional contact with each other.
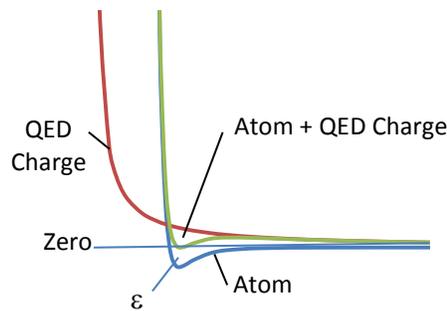
Fig. 2. QED charging of Fluid Atoms producing Zero ε Potential

3. 3. MD Simulation

MD simulations valid by QM require the viscous heat is not conserved by an increase in temperature and instead by charging the atoms. MD solutions are therefore made near absolute zero temperature, say 0.001 K to avoid temperature dependent atomic velocities. Usually, MD solutions of nanochannel flow are performed with Lees and Edwards (1972) 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 was selected as shown in Fig. 3.
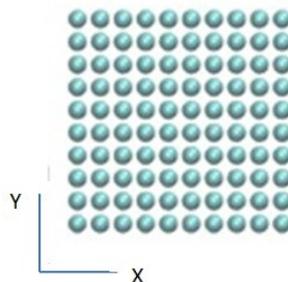
Fig. 3. Nanochannel 2D - MD Model

The BCC configuration assumed liquid argon at a density of 1407 kg/m^3. The atomic spacing was 3.62 Å in a 32.6 Å square MD computation box. The L-J potential for argon taken was σ = 3.45 Å and ε = 120·k. Time steps were < 2 fs. The MD loading was a velocity gradient of 3.06 x10^{10} s^{-1} normal to the flow direction having velocity of 100 m/s over the height of the MD box. Unlike Lees and Edwards (1972), the MD computation box becomes highly distorted after 150000 iterations. The distortion after 25000 iterations is shown in Fig. 4.
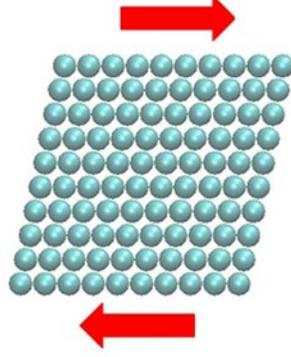

Fig. 4. MD Solutions – Distorted Computation Box

The Coulomb repulsion between all atoms is directly simulated by QED inducing 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 an atom pair,

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

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 $\varepsilon = 120$·k for argon, the fraction $\eta_c = 0.0027$. The remaining $(1-\eta_c)$ U_{ES} energy is radiated as EM radiation to the surroundings. However, Coulomb repulsion is collectively enhanced above that for a single atom pair, and therefore $\eta < \eta_c$. MD solutions were obtained for various η to determine the optimum at which the viscosity vanished. By trial and error, $\eta = 0.0006 < \eta_c$ was found optimum as shown in Fig. 6.
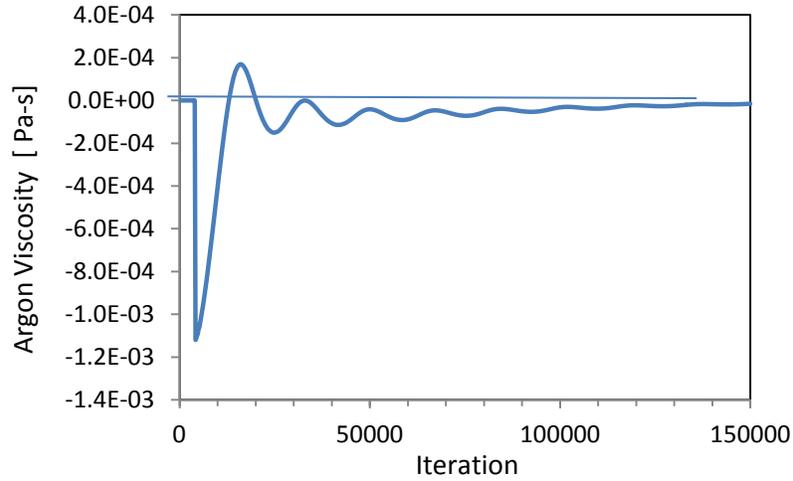
Fig. 6. MD with Coulomb Repulsion $\varepsilon = 120 \cdot k$ and $\eta = 0.0006$

The MD solution with Coulomb repulsion for Argon at $\varepsilon = 120 \cdot k$ 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 may be upper bound by the Bernoulli equation.

4. Discussion

4.1 Modified Hagen-Poiseuille Equation
The Hagen-Poiseuille equation modified by Sisan and Lichter (2011) 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.

4.2 Exit Losses
Unbounded flow in nanochannels Sisan and Lichter (2011) 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.

4.3 Bernoulli Equation
Vanishing viscosity suggests the flow in nanochannels should approach the frictionless flow given by the Bernoulli equation. The development of the Bernoulli equation from the QED energy equation in nanochannels is illustrated in Fig. 7.

Q_{QED}

$P_i\ T_i\ V_i$ →　→ $P_o\ T_o\ V_o$
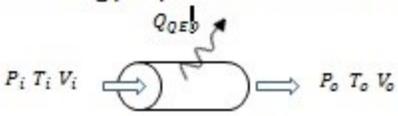
$$Q_{QED} = m\left(\frac{P_i - P_o}{\rho} + \frac{V_i^2 - V_o^2}{2} + C(T_i - T_o)\right)$$

$$V_i,\ C = 0 \rightarrow Q_{QED} = m\left(\frac{P_i - P_o}{\rho} - \frac{V_o^2}{2}\right)$$

Bernoulli Equation

$$Q_{QED} = 0 \rightarrow \quad V_o = \sqrt{2(P_i - P_o)/\rho}$$

$$m = A\sqrt{2\rho(P_i - P_o)}$$

Fig. 7. Bernoulli Equation in Nanochannels

Fig. 1 describes an incompressible fluid at the channel inlet in the $P_i\ T_i\ V_i$ state leaves the channel in the outlet $P_o\ T_o\ V_o$ state. P stands for pressure T for temperature, V velocity, m mass flow, and ρ density. Classically, viscous friction causes the fluid temperature to increase depending on the heat capacity C. QM differs as temperature changes do not occur because C vanishes. Instead, QED converts the viscous heat into EM radiation that ionizes the fluid molecules, or is lost to the surroundings. Since the inlet plenum velocity V_i is negligible, and since the ideal fluid is absent viscous heating, Q_{QED} radiation to the surroundings also vanishes, the consequence of which is the nanochannel flow is governed by the Bernoulli equation for frictionless flow.

In nanochannels, the application of the Bernoulli equation to flow measurements Majunder, et al. (2005), Holt et al. (2006), Du, et al. (2011) from experiments on various fluids reported in the literature in Table 1 of Sisan and Lichter (2011) is reproduced below in Table 1.

Table. 1. Nanochannel Flow compared to Bernoulli Equation

	liquid	μ (cp)	N	L (μm)	Q_M (cm³/s)	r_M (nm)	Q_{M0} (cm³/s)	$\mathcal{Q}$	b (μm)
Majumder (2005) et al.	water	1	10^9	34	9.62 / 16.9		1.79	5.37 / 9.44	- / -
	ethanol	1.1			12.4 / 5.89	$\langle r_v\rangle$=3.5 σ_w=1	6.07 / 5.06	2.04 / 1.16	- / -
	isopropanol	2	$3.4\cdot10^9$	126	1.47		3.10	0.47	24.11
	hexane	0.3			7.33		20.7	0.35	14.66
	decane	0.9			0.877		6.75	0.13	3.99
Majumder (2011) et al.	water	1	$2.4\cdot10^6$	81	$2\cdot10^{-8}$	$\langle r\rangle$=3.5 σ_w=1.0	$8.3\cdot10^{-9}$	2.40	-
Holt et al.	water	1	$2.5\cdot10^{11}$	2 / 3 / 2.8	7.47 / 2.23 / 1.97	$\langle r\rangle$=0.8 σ_v=0.15	4.68	1.60 / 0.48 / 0.42	- / 0.58 / 0.43
Du et al.	water	1	$2.4\cdot10^{10}$	$4\cdot10^3$	0.058	$\langle r\rangle$=5.0 σ_w=1.0	0.112	0.52	910
	hexane	0.31			0.154		0.362	0.43	630
	dodecane	1.34			0.082		0.084	0.97	30000

Q_M is the actual flow computed by Sisan and Lichter (2011) from published velocities. $Q_{M,0}$ is the flow given by the Bernoulli equation. Here, $\vartheta = Q_M / Q_{M,0}$ is the ratio of actual flow to the Bernoulli equation. As noted by Sisan and Lichter (2011) the $\vartheta > 1$ do not comply with known physics of fluid. What this means is $Q_M < Q_{M,0}$ or $\vartheta < 1$ or the frictionless Bernoulli flow is the physical upper bound for flow in nanochannels. However, water at CNT radii of 3.5 nm by Majunder et al. (2005), Holt et al.(2006) and radii of 0.8 nm by Du et al. (2011) shows $\vartheta > 1$ and is questionable. Nevertheless, the data for ethanol, isopropanol, decane, and hexane, show $\vartheta < 1$ or is reasonably close to 1 to support the argument that Bernoulli flow is indeed a valid estimate of to upper bound flow in nanochannels

4.4 Extensions to Solid Crystals in Nanotubes

With regard to the flow of solids, electrically induced motion of metal crystals through smooth uniform nanochannels of carbon nanotubes is generally thought caused by electromigration based on kMC simulations. Recently, Coh et al. (2013) using kMC found that iron crystals under an electric current reform atom-by-atom to fit through a constriction in the nanochannel that is smaller than the crystal itself. However, classical kMC simulations assume the atom has kT energy, but are invalid as QM requires kT to vanish as shown in Fig. 1. In this regard, Fig. 8 shows the analytical fit to the kMC solutions for $kT = 350$ K thought to simulate the experimental crystal velocity V. But as $kT \rightarrow 0$, V vanishes, i.e., the crystal does not move contrary to the experiment.
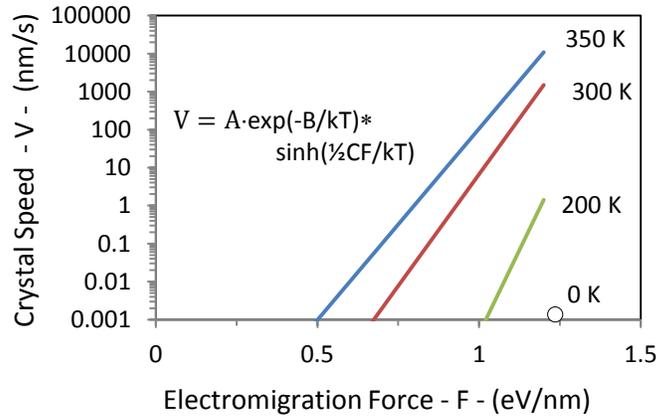

Fig. 8. Vanishing crystal velocity in kMC Simulations.
(A = 3.3 m/s, B = 1.2 eV, C = 1.4 nm)

Instead of temperature changes, QED conserves the Joule heat from the current passing through the nanotube by charging the atoms to produce a charge gradient in the nanotube. If the crystal is larger than the tube, the crystal also charges, but if the crystal is free to move within the nanotube charging is unlikely and crystal motion relies on its residual charge. For a voltage difference ΔV^* acting across nanotube length L, the force F across a crystal atom of dimension b having charge q = unit electron charge,

$$F = q\frac{\Delta V^*}{L}b \qquad (5)$$

Hence, the pressure P across the atom is, $P = F / b^2$. Similar to the Bernoulli equation as an upper bound to the fluid flow through the nanochannel, the velocity V of the solid crystal atom,

$$V = \sqrt{\frac{2P}{\rho}} = \sqrt{\frac{2q\Delta V^*}{bL\rho}} \qquad (6)$$

The Begtrup, et al.(2009) experiment gives V = 1.4 micron/s for L=2 micron long nanotube and ΔV^* = 0.2 Volts. For iron, b =0.22 nm and ρ = 7880 kg/m^3. Hence, V = 135 microns/s which is 2 orders of magnitude higher than found experimentally. Although the Bernoulli equation does upper bound the crystal atom velocity, the QED simulation although simple may not be sufficiently accurate.

5. Conclusion

The flow of fluids in nanochannels is reasonably upper bound by the frictionless Bernoulli equation. However, the flow of solids in nanotubes may require review to determine if higher flow velocities are occurring in the experiment to obtain closer agreement with the upper bound given by the Bernoulli equation.

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