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# Exploration into Particle Interaction Based On Molecular Dynamics Simulation of Fluid Viscosity in Nanochannels

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- *Research by V. Rudyak and A. Belkin, NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS. 2018, 9(3), P. 349-355*
- *Condensation and Commentary by Roderick Landreth, Union College*

## Condensation of the Research

### Purpose of Study

*to analytically determine the effect of the system on the viscosity of a contained fluid. Specifically, this study used SibMD molecular dynamics simulation software to find system constants determining the interaction of the system walls and the contained fluid. In completion, this is an exploration into factors that determine fluid viscosity and fluid structure in nano channels.*

### Background

With the increase in nano-scale structures in the fields of medicine, heat and power systems, filters and other common applications of fluid based transport processes, nanoscale systems are a powerful tool. Fluid Nanochannels in particular have a plethora of uses, and as technology develops on the nano-scale, more and more manufacturing techniques and applications are being discovered. Fluid micro and more recently nano-systems are being used to control the absorption of drugs, pumping in these channels, or energy conversion. Lab-on-a-Chip devices can use mesoporous materials to guide fluid through channels solely by capillary action, [1]. Material containing nanopores and junctions filter contaminants from fluids, just as their micro-scale equivalents filter cells in blood. Nanochannels can even aid in the study of fluids and their deformation, called rheology [2]. Here, capillary action compares the response of non-Newtonian fluids to theoretical MD modeling and classifies materials into Bingham plastics or Pseudoplastic, Dilated or Newtonian fluids. The increased use of nano-scale systems makes their understanding essential. In opposition to this, physical and chemical properties at the nano-scale differ significantly from a bulk system. In the production and use of nanochannels, studies today are recording unexpected responses pertaining to viscosity because of these properties [3].

The fabrication of these nanosystems is often done by use of photoresist, laser ablation, or more imaginative creation methods. Figure 1 shows a nanochannel manufactured using photolithography, layer by layer constructing the channel and hollowing it with electrochemical etching, making the metal at the center of the channel the anode in a reaction that causes an electrolyte to carry away the material to the cathode due to a charge difference.

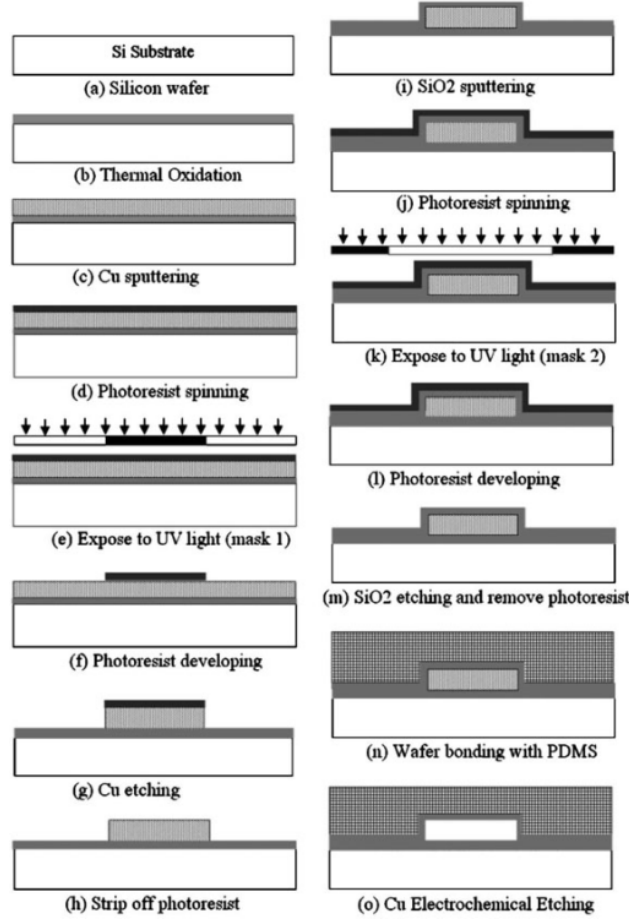


Figure 1: Fabrication of a nanochannel via photolithography, comprising layer deposition and etching with photoresist masks in a study reducing cost of manufacturing with electrochemical wet etching [4]

Nanofluids are commonly referred to as fluids that have nanoparticles proliferated throughout, differentiating nanofluid channels and fluid nanochannels, that use homogeneous fluids inside nano-scale channels. There are some issues with its uses, mostly continuity problems and differences from bulk systems. These include but are not limited to wall absorption and varying fluid densities & viscosities [5]. Fluid viscosity in a nano-system is important anywhere there is movement or fluid transport, for example even an accelerometer made solid-state in the nano scale oscillates through a fluid. Varying fluid densities can throw off accuracy in the example of an accelerometer, but in medical and filtering systems, light speeds are altered in different fluids and medicine distribution and mixing is dampened with increasing resistance of flow. Viscosity is the measure of deformation a fluid undergoes due to the application of shear stress, usually thought of as how easily it flows.

In this study, there's a large underlying assumption that the fluid is Newtonian, meaning that its deformation due to shear stress has a linear slope, and at zero applied force it does not deform. This is a good assumption for the fluids being modeled, being rarefied argon and benzene. Usually, viscosity is measured pertaining to the bulk fluid, which contains assumptions that do not include external forces acting on the fluid, such as the existence of a wall-fluid interface. When observed in bulk, properties like density, momentum transfer,

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or diffusion is the same in all directions, but when observing channels constructed from a countable number of molecules, their interaction with the system fluid cannot be ignored. These systems are complex despite a countable number of particles, because there are many interactions from each particle onto each other. This is a relationship more easily calculated by MD software.

In chemistry, tribology, nanosciences, and any field that carefully regarding the interaction of surfaces on a molecular level, often tools like specialized software analyse the system and find system relations. Molecular dynamics modeling software (in this case, SibMD) models Newtonian equations of force and motion from each particle on its surroundings. The SibMD software package used to solve nano-fluid transport problems does this by analytically integrating with newton equations of motion using the Schofield scheme, similar to Verlet method of numerical integration. The difference from the Verlet method, which is averaging two approaches of using the fundamental Euler equation, and the Beeman algorithm used in the Schofield method, is that the Beeman equation has a higher accuracy when approximating velocity. Both of these are fairly computationally simple in comparison to highly accurate techniques like the Runge-Kutta Four method. When a system involves thousands of particles, fewer computational resources are used with the Beeman algorithm making it the more feasible approach.

Some limitations that are applied to computational systems include a cutoff radius for interactive forces between particles to be registered, non-infinite potential energies, and the Lennard-Jones potential model is used to approximate the particle's interaction. There are more accurate potential functions, but due to its simplicity the computational model relies upon this, a function that was approximated to produce a bound state in a potential well. The particle is drawn towards the lowest energy level, and the between every particle the potential resembles figure 2.

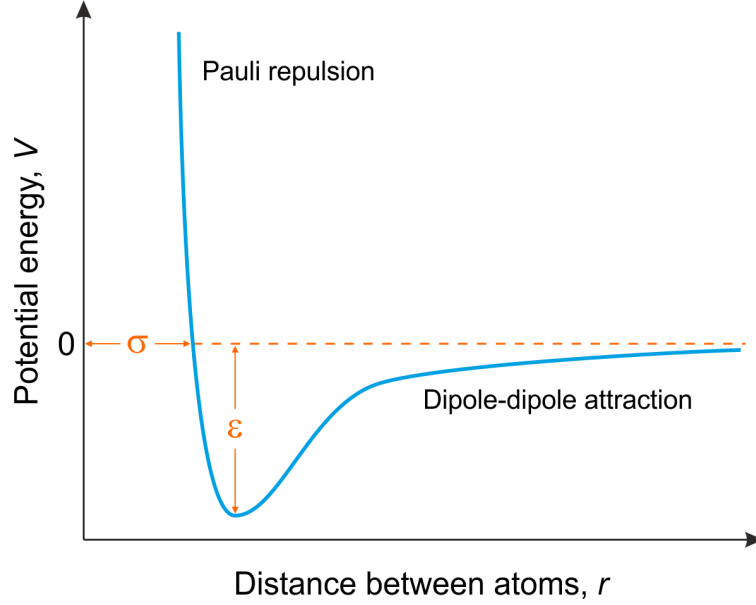


Figure 2: Lennard-Jones Potential well, exhibiting potential  $V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$ , where  $\sigma$  is the distance that the intermolecular forces become zero,  $r$  is the distance between the particles, and in the image,  $\epsilon$  is the depth of the well [6]

## Researcher's Approach

To be able to approach this problem computationally, a simplified system model of two square plates were used, each two molecules deep, the cross section similar to figure 3. At the center, the fluid properties were negligibly affected by the molecules at the edge of the plates, making the effects within the channel scaleable. Additionally, the molecules took the form of a face-centered cubic crystal system, similar to a silicon substrate used for the base creation of many fluid nanochannel systems. Relying on a simulation to provide very accurate data is often unsafe, so in addition to modeling the desired system, each fluid's viscosity was measured as a bulk material in the same software. This way, at the very least the viscosities can be comparatively analyzed with accuracy. Both tests were simulated with the same fluid temperature and pressure.

Pertaining to mechanical or thermal transport processes, Green Kubo relations predict transfer coefficients, of the form seen in equation 1. A form of Green Kubo formula expresses different components of viscosity, similar for those use by the bulk system, but expanded with the inclusion of several transport coefficients. These coefficients were found with fluctuation-dissipation relations. These pertain to a statistical mechanics theorem stating that energy dissipation processes are paired with a reverse process caused by thermodynamic fluctuations of particles.

$$\gamma = \int_0^\infty \langle \dot{A}(t) \dot{A}(0) \rangle dt \quad (1)$$

Non-equilibrium statistical mechanics models related the total viscosity, given by  $\epsilon$ , to a sum of the components of the interaction with the rest of the fluid,  $\epsilon_{ff}$ , and the fluid and

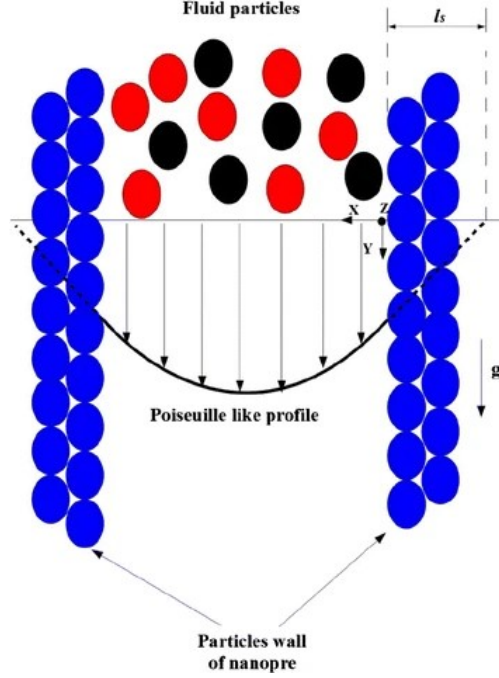


Figure 3: A similar study's model [7], though this study's aim was to model slippage along a wall with a binary fluid mixture, where each fluid differed in relative reactivity with the wall. It used a similar 2 molecule thick channel, the only difference being that a mixture of fluids flowed through it.

the wall,  $\epsilon_{fb}$ . Rudyak and Belkin related these coefficients to infinitesimal stress tensors, integrating to find a probabilistic average in terms of classical correlation functions. Like in quantum mechanical models of bound particles, equations 2 and 3 use the average over an equilibrium probability distribution denoted by angle brackets,  $\langle \rangle$ .

$$\frac{1}{5kT_f} \int_0^\tau \langle \hat{J}_f(0) : \hat{J}_f(t) \rangle dt \quad (2)$$

$$\frac{1}{5kT_f} \int_0^\tau \langle \hat{J}_b(0) : (\hat{J}_f(t) + \hat{J}_{fb}(t)) + \hat{J}_f(0) : \hat{J}_{fb}(0) \rangle dt + \frac{1}{5kT_b} \int_0^\tau \langle \hat{J}_b(0) : \hat{J}_{fb}(t) \rangle dt \quad (3)$$

In these equations, the  $\hat{J}$  signifies a flux, with the  $F_{ij}$  term in equation 4 referring to the interaction forces between molecules. Additionally,  $T$  is temperature,  $k$  is the Boltzmann constant,  $\tau$  is the time the viscosity plateaus,  $f$  refers to the molecules of fluid, and  $b$  the molecules of the wall molecules. Seeing these equations both shows the relationship between variables, and how complex and computationally expensive this would be, every  $\hat{J}$  being several sums through each affected particle.

$$\hat{J}_\alpha = \sum_{i=1}^{N_\alpha} \frac{\sigma_i \sigma_i}{m + \alpha} + \frac{1}{2} \sum_{i=1}^{N_\alpha} \sum_{\psi}^{f,b} \sum_{j=1}^{N_\psi} (r_i - r_j) F_{i,j}, \quad \hat{J}_{fb} = -\frac{1}{4} \sum_{i=1}^{N_f} \sum_{j=1}^{N_b} (r_i - r_j) F_{i,j} \quad (4)$$

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$\mathbf{r}_i$  and  $\mathbf{p}_i$  are respectively the radius and momentum of the  $i$ th particle with the phase  $\alpha$  and  $F_{ij}$

The program previously mentioned using analytical integration methods to evaluate these interactions gets more accurate with increased time resolution, since with so many particles inaccuracy can compound and lead to false conclusions. A large amount of resources went into the computation of particle interaction with extremely high resolution. These complex equations were analyzed every 1.09 femtoseconds and the result averaged over 5000 attempts to improve accuracy enormously.

Even with this simplified system and accuracy-corrected response, a source of error is also the constants in use in the analysis of the system, relating to the effective diameter of the molecule, the distance between molecule centers, and the depth of the potential well caused by the forces between molecules. The value of  $R_c$  is the maximum radius of interaction used, because the analytical method can't integrate infinitely and the limit of the interaction potential at  $\pm\infty$  is zero. This interaction potential related to  $r$  models the system similarly to a potential well with two dimensions, from wall to wall and from system entry point to exit point. The constants related to the interaction between particles follow a combination relation, as they were derived by the square of the bulk interaction coefficients.

## Accomplishments

Over the course of this project, Rudyak and Belkin produced components of viscosity related to kinetic and potential energy, and ran enough simulations to find correlations of how they vary with system parameters. Overall, the nanochannel contained a much higher potential than the bulk liquid, along with anisotropic changes in momentum transfer in the system with solid plane walls, consistent with the potential increasing sharply close to the walls. In the center of the channel the kinetic component of energy is almost isotropic as it is in the bulk fluid system model, but decays much faster due to the walls of the system slowing velocity with collisions.

The simulation's properties were individually varied to see how each affected the viscosity between the walls. As the system is modeled, the nanochannel fluid viscosity is a function of time. Within 3 picoseconds, the viscosity had peaked and then lowered into a plateau, as the main component of the viscosity is due to potential energy. The effective size of the molecules making up the walls has very little effect on the viscosity of the system  $\sigma_{bb}$ , though the depth of the potential well between particles  $\epsilon_{bb}$  did significantly change the values of viscosity relative to the bulk material. For example, argon in a channel of carbon consistently lowered the fluid viscosity below its bulk value, and aluminum walls increased the value well above. The change in distance between walls of the channel also altered the measured viscosity coefficients, though the effect on the viscosity differed with fluid. Figure 4 compares the relative viscosity coefficient measured with changing potential depths, and figure 5 measures changes in wall materials.

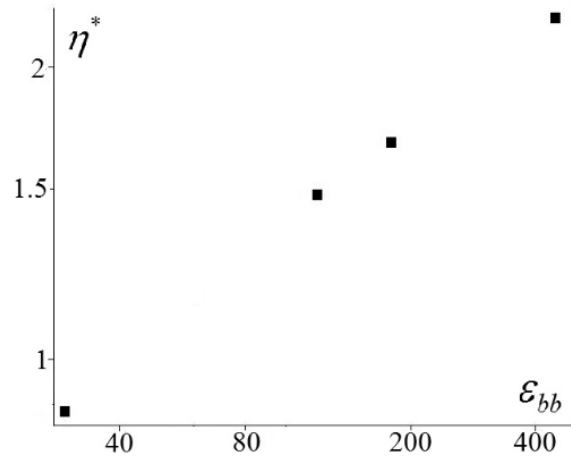


Figure 4:  $\eta^*$  is the ratio of measured channel viscosity to bulk viscosity of argon, in this case, and  $\epsilon$  is the depth of the potential well between wall molecules. In this system, the temperature is 160 K, and  $h = 27.2$  angstroms [8]

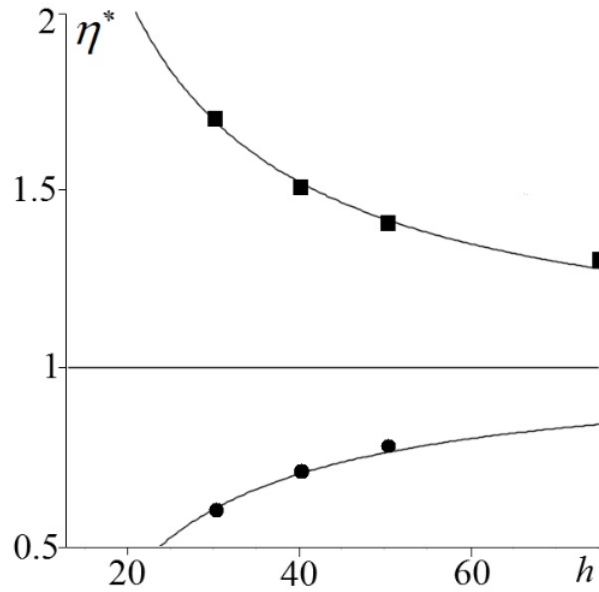


Figure 5: Here,  $\eta^*$  is the ratio of measured channel viscosity to bulk viscosity, and  $h$  is the distance between channel walls. There are two different wall being compared for their different responses, the bottom curve corresponding to  $C_6H_6$  fluid in a Carbon channel, and the top curve  $C_6H_6$  fluid in an Aluminum channel. The units of  $h$  are angstroms. [8]

As an example of simulation characteristics, the following constants were used while measuring the viscosity of argon in a silicon nanochannel. The distance between plates was  $27.2 \text{ \AA}$ , at a temperature of 160 K, with interaction coefficients  $\sigma = 3.405$ ,  $\epsilon/k = 119.8$ , and the term for reduced concentration of molecules  $n\sigma^3 = 0.4$ . This produced viscosity correlation functions that had a component based off potential energy that exceeded the

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bulk values, especially in the plane of the wall, though experienced a kinetic energy viscosity term that decayed faster. Both of these are because the wall adds potential energy, but the transfer of momentum between particles was in all axes significantly reduced because of interaction with the walls.

All in all, this study displayed that viscosity in nanochannels is a strong function of wall material, changing the momentum transfer within the channel drastically at this scale. The scientific community has noted significant reduction of resistance to flow of fluid inside microchannels, associated with the slip effect. Another component of this could be a reduction in viscosity. This study used two plane walls as a channel, but the more surface area available for the fluid to interact with, the more significantly viscosity is affected, so a circular tunnel or a porous material would have more significant deviation from bulk values.

## Commentary

The significance of this pertains to its applications, and further knowledge of the phenomenon causing many studies in nano-porous or Lab-on-a-Chip devices to exhibit significant differences in fluid flow than expected. Examples. While shedding light on a large cause of uncertainty in other experiments and providing a clear generalized summary of fluid relationships, this study could have supplied more information.

The article contains the information needed to do a similar project, but a few important details are left out or not considered. The published article could have included the actual dimensions of the system, instead saying it was large enough that the edge molecules do not effect the viscosity values produced. Without the actual system dimensions much of the repeatability is lost because if another lab were to try the same experiment, either the produced solutions are different because the walls are smaller than this study, or a very significant change in computation time would be caused if the walls were significantly larger than needed. Also, the procedure for making the solution more accurate is defined, but its justification is not. Calculations or previous MD testing would reveal whether that many tests are needed or if it will negligibly change the outcome. Proving system convergence would require a few more trials, but offer important results; if the test does not have to be repeated as many times then the computational expense would decrease, allowing for more relations to be tested and a broader category of data to be manipulated.

If further studied, knowledge of the interaction between solid bodied walls and a fluid can be put to use in many nano-scale systems. Alone, the fact that within systems different fluids of varying viscosities are potentially no longer required saves lots of resources and creates the option for new system configurations that are not possible today. The viscosity and material relationships in this study relate heavily to the use cases of Lab-on-a-Chip functions, relying on the fluid flow to complete tasks relating to separation or mixing. In 2019, MIT fabricated a microdevice able to diagnose sepsis, using very small amounts of sample to test for it, and the main time expense was the mixing of the liquids due to low Reynolds numbers. If both the flow rate and the mixing rate were controllable, this MIT Lab-on-a-chip is a great use case that can be greatly benefited [9]. This study, if continued, could provide ways to cause the same fluid to change flow rate within a system without a change of fluid or device, saving time and money. The also means different fluids would pass through the same system at different rates, potentially providing the means for detecting fluid types with a very small



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quantities, or filtering fluids based on their electrochemistry. The change in fluid viscosity paired inversely with the change in velocity in the nanochannels causes a change in Reynolds number. Changing the Reynolds Number within a fluid alters mixing rates as well, aiding the MIT lab-on-a-chip mentioned earlier. Initially filling nanochannels using capillary action is a way to measure fluid properties, and the article's findings could lead to a wider range of fluids this is effective for [1]. This is because after a certain viscosity and low enough surface tension, capillary action will not lead the fluid into the tube unless adhesion forces are altered.

After further studies, the manufacturing of devices that use fluid-wall interactions to change fluid transport time or mixing could be accomplished with much of the manufacturing technology that currently exists. Photolithography is a strong choice, relating back to figure 1 that shows the steps to create a nano or micro channel. Extra steps could be added to cover just the channel tops or bottoms with a different material that interacts with whatever the system fluid is. This would require new masks for the substrate, but otherwise no advancement in technology. A very powerful way to manufacture these nanochannels is self assembly. Current technology can self assemble 20 nm mesoporous titanosilicate channels of up to 500 nm long [1]. If this is developed further, the cost of manufacturing would dramatically decrease, though self assembly produces channel walls that have few material options because of the physical reactions needed to make the state with minimal energy the desired one. Laser ablation is also a method used to make zeolites, materials with pores on the nanoscale. As laser ablation is also used to create nanoparticles, and fluids flowing through nanoparticles as filters would exhibit similar characteristics to that of a fluid through a nanochannel, an interesting applications of this phenomenon for future research.

This is a very promising development that can offer significant benefits in both academic and industrial settings, though needs to be expounded upon with many different configurations for it to unleash its full potential.

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