ME 400 : Thesis

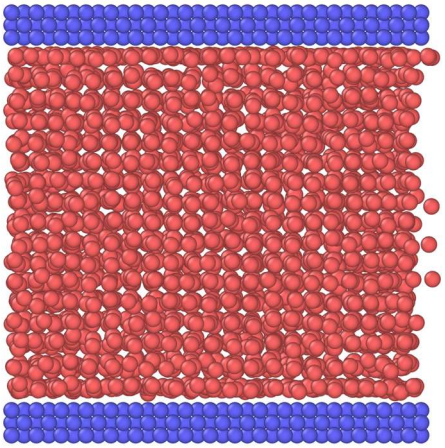
Effect of Surface Wettability On Specific Heat Capacity of Nano-confined Liquid

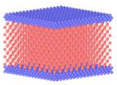
Thesis By

Priom Das (1610148) &
Zarif Ahmad Razin Bhuiyan (1610137)

Supervised By

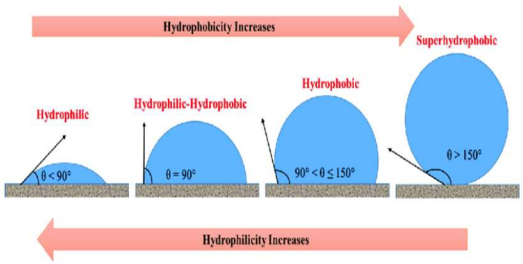
Dr. A. K. M. Monjur Morshed
Professor
Department of Mechanical Engineering
Bangladesh University of Engineering & Technology





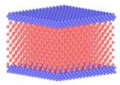
What is Surface Wettability and How it is defined ?

Wettability is defined as a liquid's ability to wet a surface and is determined through contact angle measurement.

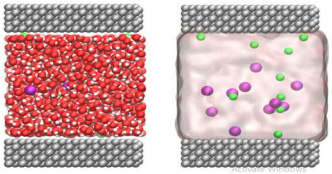


Contact angle (degree)	Surface Characterization
$\theta < 10°$	Superhydrophilic
$10° < \theta < 90°$	Hydrophilic
$\theta = 90°$	Hydrophilic-Hydrophobic
$90° < \theta \leq 150°$	Hydrophobic
$\theta > 150°$	Superhydrophobic

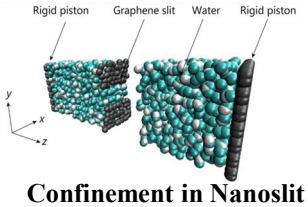
What is nanoconfined Liquid ?



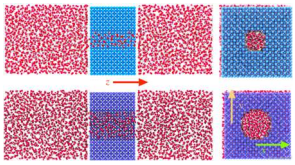
Nano-confined fluid (NCF) is defined as the fluid confined in a nanospace such as nanochannel, nanotube, nanopore and other complex nanospaces.



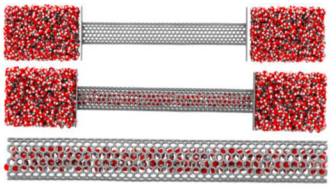
Electrolyte confinement in Graphite Nanochannel



Confinement in Nanoslit

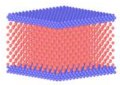


Confinement in Nanopore



Water confinement in Carbon Nanotube

Motivation for our work



❖ **Recent Research Trend**

- High capacitance Supercapacitor
- Biological Engineering (DNA sequencing)
- Ultrafast transportation of Confined water and ions

❖ **Experimental works are very scarce !!!!!!!!!!**

Structural properties	Behaviour of the relative directed motion
X-ray, neutron diffraction XPS, XAS, TEM, UED, *etc.*	AFM, SFA, SFB, QCM, *etc.* used to analyse flow resistance *via* getting *b* and friction coefficient Lack of effective methods *in situ* characterize flow resistance

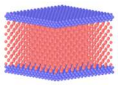
❖ **No proper theoretical description of mass and energy transport**

Nanoscale effects

- Size dependence
- Anisotropy
- Strong surface force (Wettability and roughness)
- Quantam effect
- Slip boundary condition

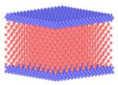
MD simulation is the answer to bridge the theoretical and computational gap !!!!

Thesis Outline



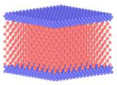
- Chapter 1 : Introduction
- Chapter 2 : Literature Review
- Chapter 3 : Simulation Methodology
- Chapter 4 : Modelling and Simulation procedures
- Chapter 5 : Results and Discussions
- Chapter 6: Conclusion
- Chapter 7 :Future Recommendation

Objectives

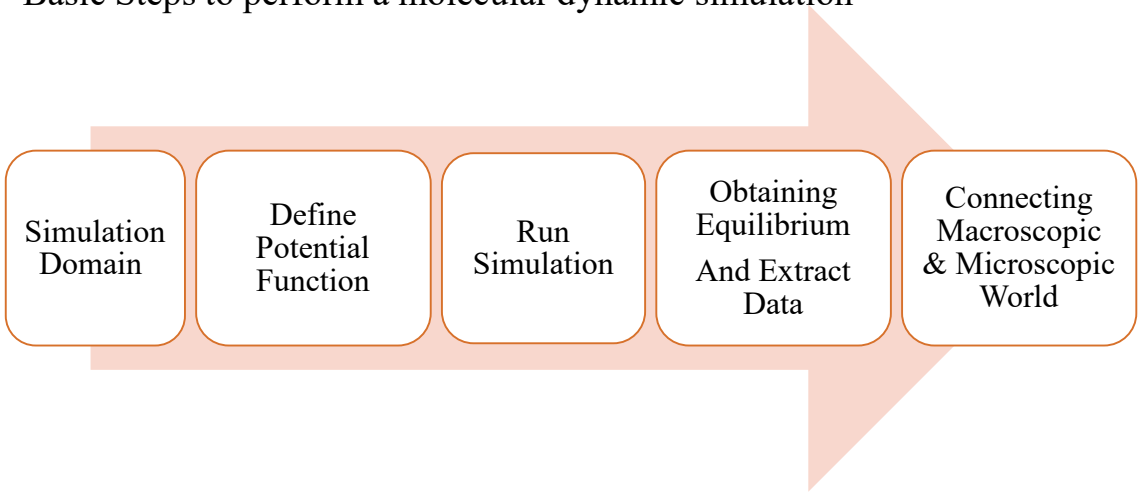


- ✓ To determine **heat capacity of liquid argon at fixed temperature for four different wettable surfaces.**
- ✓ To figure out how **maximum heat capacity**, critical gap thickness ,**range of gap thickness** changes with changing wettability .
- ✓ To describe possible reasons behind this **behavioral changes of of confined liquid** with surface wettability.

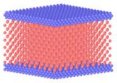
Simulation Methodology



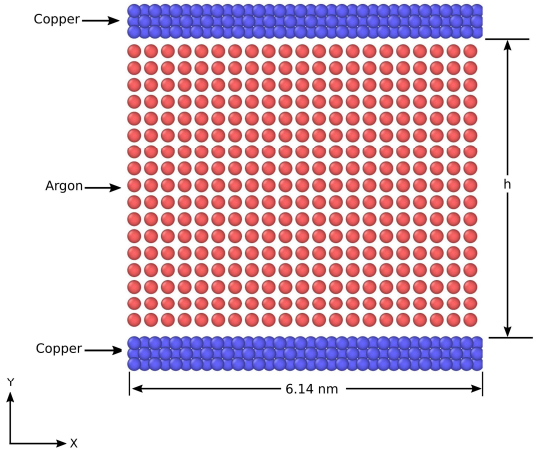
Basic Steps to perform a molecular dynamic simulation



Simulation Methodology



Simulation Domain



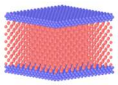
- ✓ Simulation box 6.14 $nm \times h \times 6.14\ nm$
- ✓ FCC Copper walls (lattice constant 0.585 nm)
- ✓ FCC Liquid Argon (lattice constant 0.3615 nm)
- ✓ h varies from 0.585 nm to 5.85 nm with step size 0.585 nm

Boundary Condition

- ✓ Periodic along x and z direction
- ✓ Fixed along y direction

Equilibrium Temperature is 100 K

Potential Function



Lennard Jones Potential function was used.

Interaction Strength

Length Scale

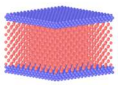
Cut off radius, $r_c = 2.5\sigma$

$$u(r_{ij}) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right], & \text{if } r_{ij} < r_c \\ 0, & \text{if } r_{ij} \geq 0 \end{cases}$$

Name of Pair	ε_{ij} (J)	σ_{ij} (nm)
Liquid-Liquid	1.67×10^{-21}	0.3405
Solid-Solid	6.59×10^{-20}	0.2340

Table: Lennard Jones Potential Parameter of Argon and Copper molecules.

Solid - Liquid Interface

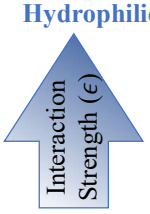


Wettability factor [3]

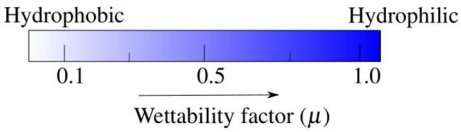
$$\varepsilon_{sl} = \sqrt{\varepsilon_s \varepsilon_l}$$

$$\sigma_{sl} = \frac{\sigma_s + \sigma_l}{2}$$

Lorentz – Bertholet mixing principle [1]



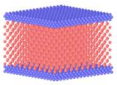
Wettability and Interaction Potential [2]



Effect of wettability factor (μ) on copper-argon interface.

[1]
[2]
[3]

Running a Simulation



Applying Nose Hover Thermostat for 10 ns → To equilibrate the system at 100 K

Velocity Verlet Algorithm for time Integration → Integrate the Equation of motion to update the atom position.

Time Step $= 5\ fs$

↓

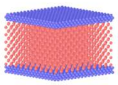
Check For Equilibrium

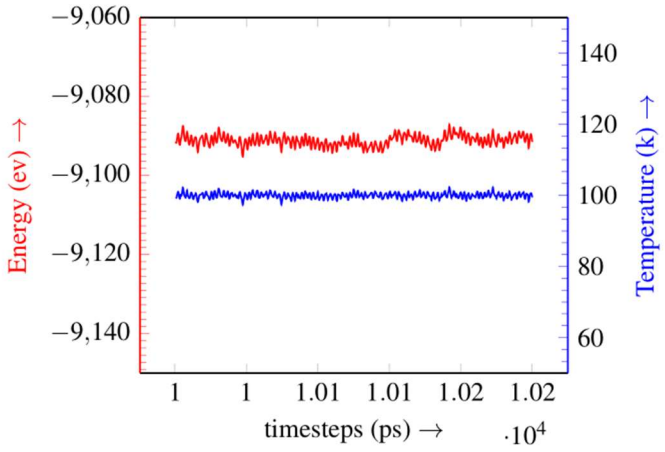
↓

Extract Data for 10 ns for post processing

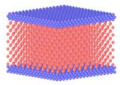
- ✓ Wettability factor $\mu = 0.1, 0.3, 0.5, 0.7$
- ✓ For each value wettability factor (μ), (h/a) varies for 1 to 10 with step size 1. Here, a is the lattice constant of argon.

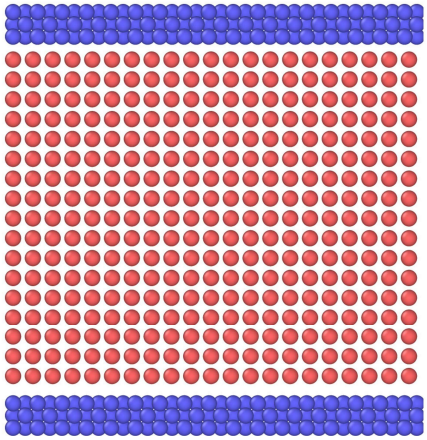
Ensuring Equilibrium and Liquid Phase of Argon



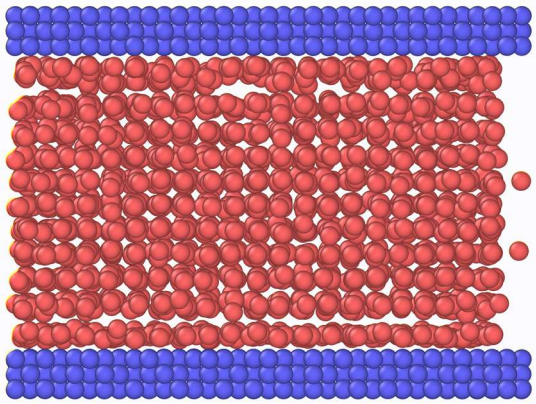


- ✓ Negligible variation of temperature and pressure over the time indicates the proper equilibrium of simulation domain
- ✓ Critical Temperature of argon 150.687 K and 4.86 MPa
- ✓ Saturation pressure at 100 K is 0.324 MPa
- ✓ In this study, confined argon was kept at 100 K and 10 MPa to ensure liquid phase.



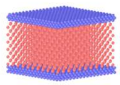


Initial State



Equilibrated State (time > 20 ns)

Connecting Microscopic & Macroscopic World



Specific Heat computed using fluctuation formula -

$$C_v = \frac{var(E)}{K_B T^2}$$

Here,
C_v = Specific heat of argon.
$var(E)$ = Variance of total energy of argon
K_B = Boltzmann Constant
T = Temperature of argon.

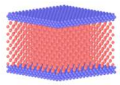
Under Ergodic Hypothesis $var\ (E)$ and T determined as following-

$$var(E) = \frac{1}{\tau}\int_0^\tau \left[E(t) - \langle E\rangle\right] dt = \langle E^2\rangle - \langle E\rangle^2$$

$$\langle ke\rangle = \frac{1}{\tau}\int_0^\tau \left[\frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}m_i v_i(t)^2\right] dt$$

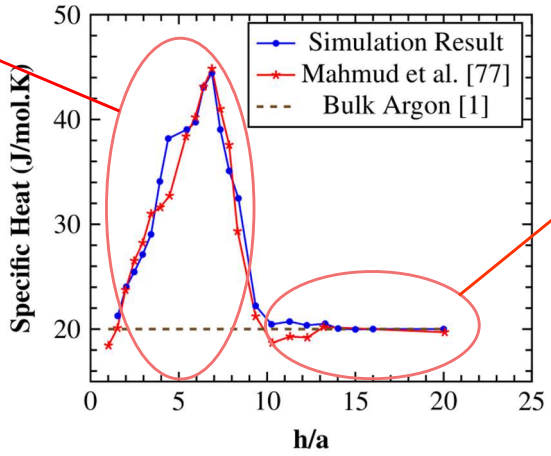
$$T = \frac{2}{N_{dof}K_B}\langle ke\rangle$$

Validation of Simulation Procedure



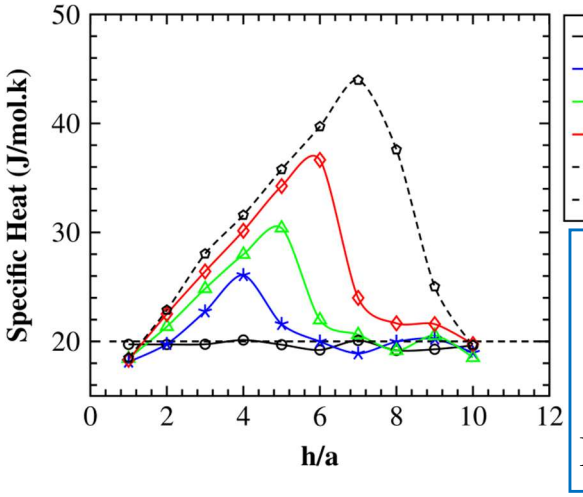
Specific Heat for Wettability Factor, $\mu = 1.0$

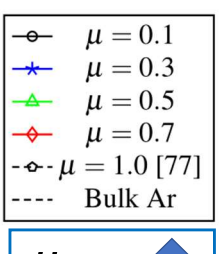
For h/a < 10
- Confinement Effect on C_v
- C_v match with Previous Study [Rifat at el.]

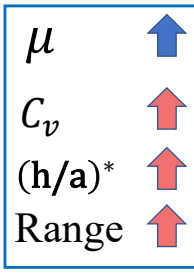


For h/a > 10
- No confinement Effect on C_v
- C_v match with bulk argon [NIST]

Result



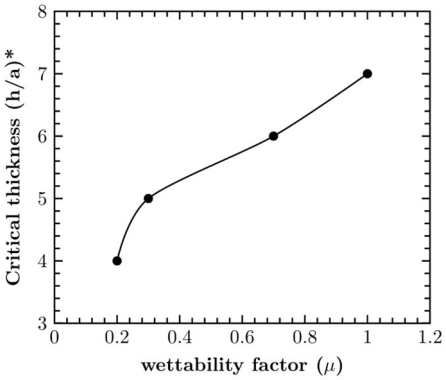


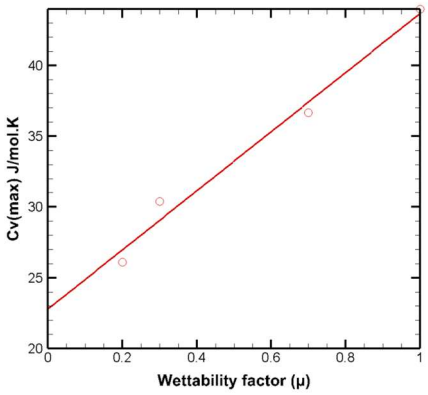


Three Key Findings

- ✓ Maximum heat capacity (Cv(max)=43.97J/mol.K) and critical gap thickness (h/a)* (gap thickness at which maximum heat capacity is obtained) decreases
- ✓ Range of gap thickness where the heat capacity of nanoconfined liquid surpasses that of bulk liquid diminishes
- ✓ Heat capacity of nanoconfined liquid tends to match its bulk equivalent.

Result



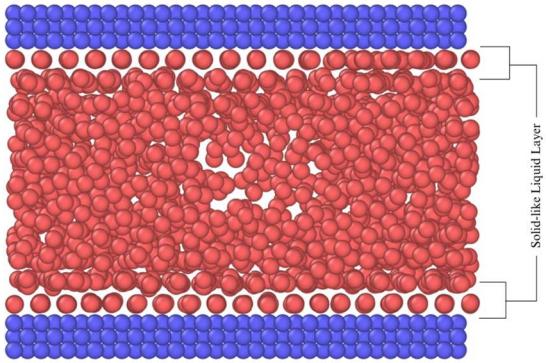


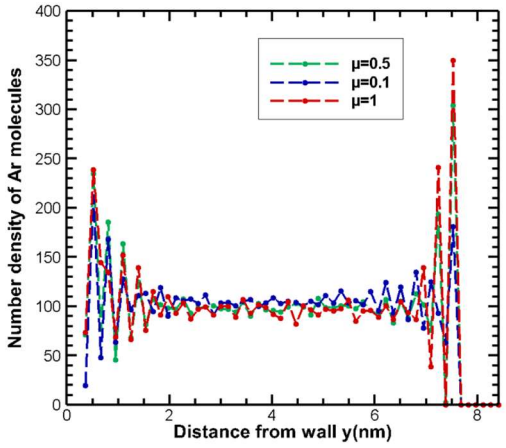
μ ↑ (h/a)* ↑

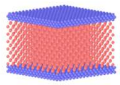
μ ↑ $C_{v,max}$ ↑

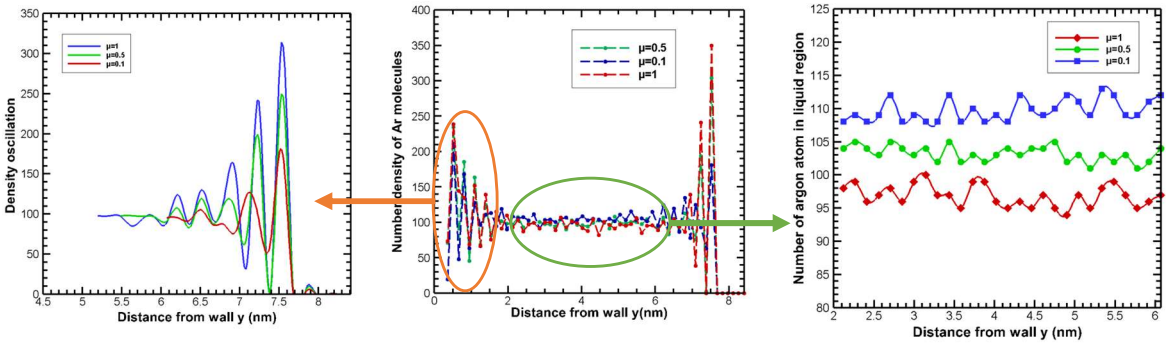
Discussion

Non uniform density distribution





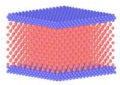


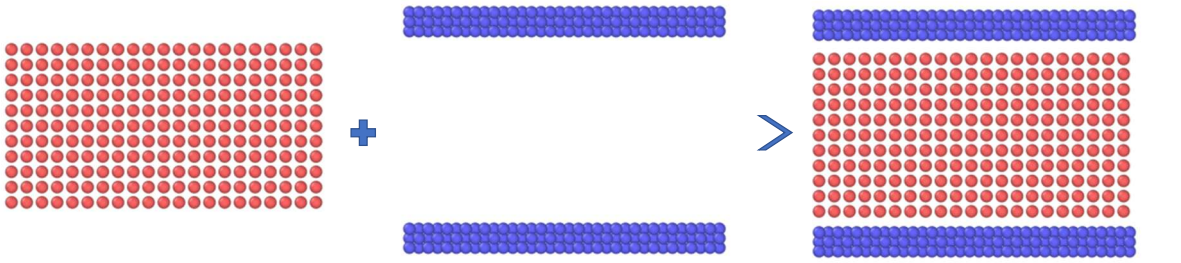


- Increasing the surface's wettability increases the degree of fluctuation of the number density profile near the wall.
- the density oscillation near the relaxes earlier with decreasing wettability.
- Number of heat carrying molecules reduces in the liquid region as the surface becomes more hydrophilic.

μ ↓ **Liquid argon** ↑

Change in Interface energy

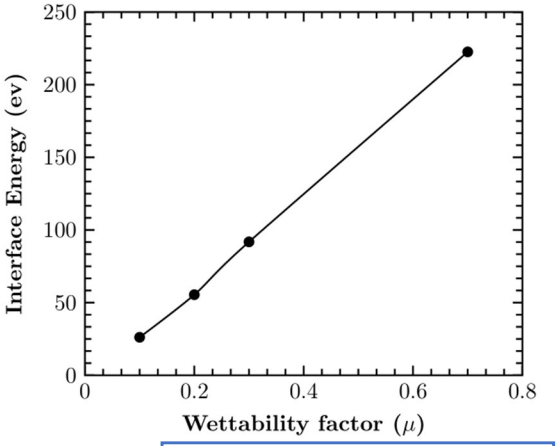




(b) Argon.(E=−70.77 eV) **(a)** Copper.(E=−8494.6 eV) **(c)** Confined argon between copper plates.(E=−8787.93 eV)

Interface energy = Energy of Argon atoms +Energy of Copper walls –Energy of confined Argon system

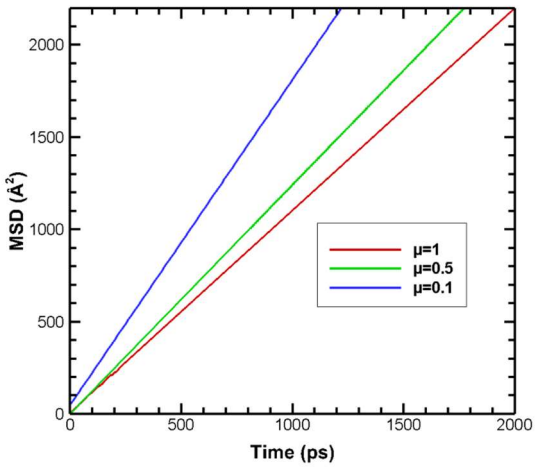
Change in Interface energy



μ ↑ IE ↑ Cv ↑

- Configuration with the highest interface energy has the highest heat capacity.
- Hydrophilic surfaces have more interface energy than hydrophobic ones.
- For μ = 0.1 lowest interface energy is generated so it also has the lowest value of heat capacity.

Mean Squared Displacement (MSD), Diffusion Co-efficient and Molecular Motion

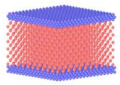


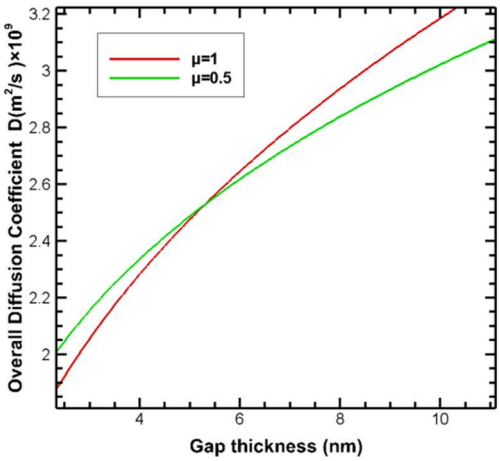
$$MSD(\tau) = <[\Delta r(\tau)]^2> = <[r(t+\tau) - r(t)]^2>$$

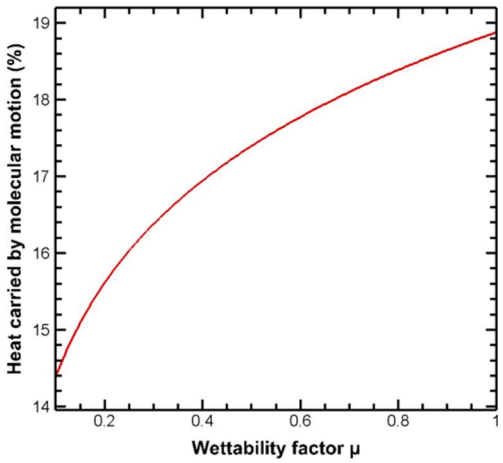
- MSD is less for hydrophilic surfaces due to the strong solid-liquid interaction
- h <= 5 nm Diffusion coefficient value is lesser for hydrophilic surface (μ=1).h >= 5nm value of self-diffusion coefficient is greater for hydrophilic surface.
- A higher self-diffusion coefficient value indicates higher molecular motion

μ ↑ MSD ↓

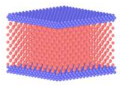
Mean Squared Displacement (MSD), Diffusion Co-efficient and Molecular Motion

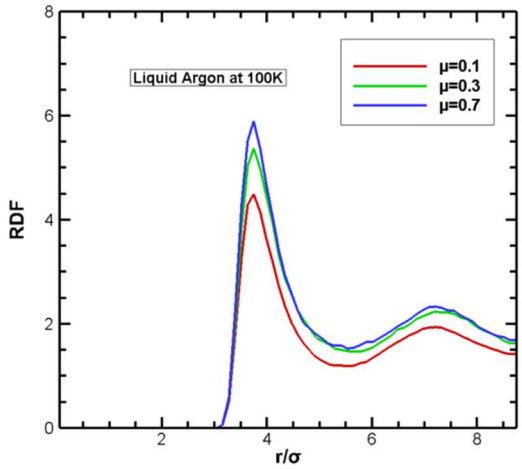






Radial distribution function (RDF)

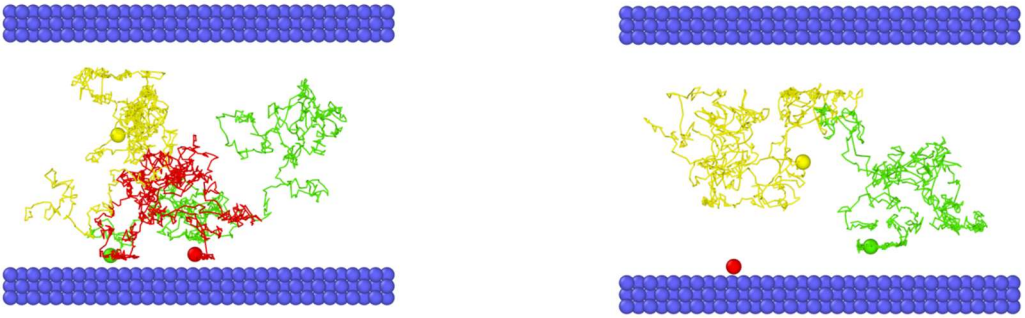




- As wettability increases, the initial peak value of RDF. A greater initial peak value indicates that the Ar molecules are better organized.
- Structured molecular distribution reduces heat Transmission for liquids resulting in an increase in heat capacity for hydrophilic surfaces

$\mu \uparrow \quad RDF \uparrow$

Guided Molecular Motion



(a) $\mu = 0.1$ (c) $\mu = 0.7$

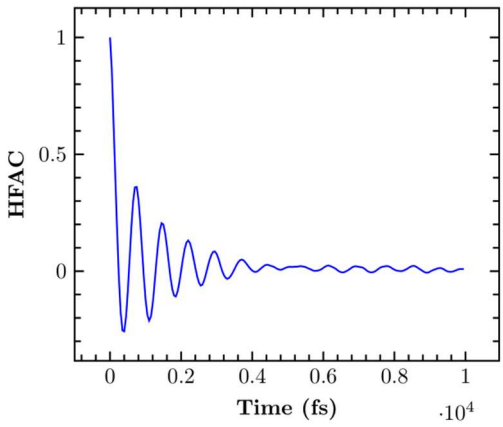
- The movement of argon atoms near the wall becomes more orderly and structured for more hydrophilic surface($\mu = 0.7$).
- The more organized molecular motion under hydrophilic confinement reduces heat transportation thus increasing liquid heat capacity

Overall thermal conductivity of the system

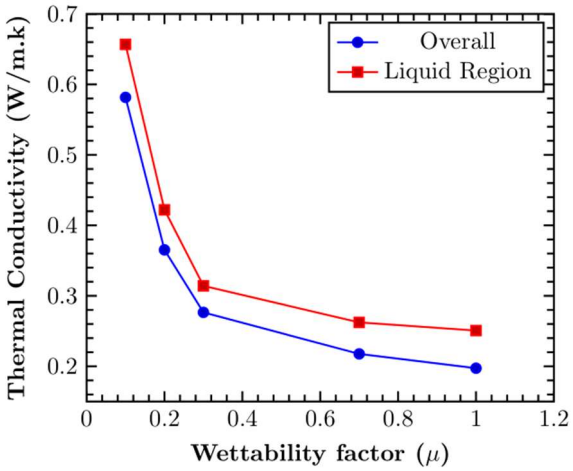
Green Kubbo Method

$$\mathbf{J} = \frac{1}{V}\left[\sum_i e_i \mathbf{v}_i + \frac{1}{2}\sum_i \sum_{i<j} (\mathbf{F}_{ij} \cdot (\mathbf{v}_i + \mathbf{v}_j))\mathbf{r}_{ij}\right]$$

$$\kappa = \frac{V}{3K_B T^2}\int_0^\infty < \mathbf{J}(0) \cdot \mathbf{J}(t) > dt$$



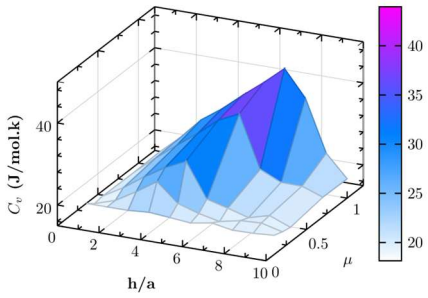
Overall thermal conductivity of the system



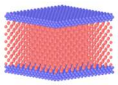
- Overall system thermal conductivity is lesser in magnitude than the thermal conductivity of argon atoms in the bulk region and it both decrease with increasing wettability.
- Reduced thermal conductivity yields increased thermal resistance, resulting in poor heat transfer
- Lower thermal conductivity implies higher heat retention capacity for a material

$\mu\uparrow \quad \kappa\downarrow \quad R_{th}\uparrow \quad C_v\uparrow$

Key Findings



- ✓ As wettability declines, the critical gap thickness (h/a)* (gap thickness at which maximal heat capacity is obtained) decreases.
- ✓ Maximum heat capacity, gap thickness, and surface wettability factor(solid-liquid inter-action strength (μ) all are correlated.
- ✓ The variation of heat capacity with changing wettability of the surface is ascribed to the simultaneous changes of both configurational and non-configurational contributions of the liquid under confinement.



"

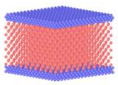
Nano-Technology is an idea that most people simply didn't believe

"

Ralph Merkle

THANK YOU

Future Recommendation



- ✓ In our work Argon is used as a working fluid. However, Argon is not a real fluid. It will be fascinating to watch how a real fluid, such as water, behaves when confined.
- ✓ To understand surface effect on confined liquid performance, different nanostructured surfaces and diverse patterns on the surface (microgroove, void, defect) can be modelled. Nanostructures should have a realistic shape and size so that they may be made and used in real-world circumstances.
- ✓ Surface materials such as Pt, Ag, and Al can be utilized to study the effect of surface material on the thermodynamic parameters of a nanoconfined liquid.
- ✓ Simultaneous temperature and wettability effects can be used to determine the temperature and wettability at which maximal heat capacity is achieved.