

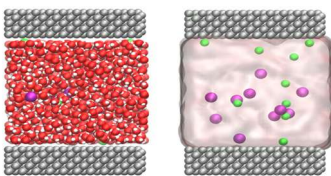
Thermal Properties of Liquid Entrapped between Hybrid Wettability Surface

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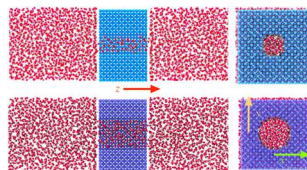


Thermal Properties of **Liquid Entrapped** between Hybrid Wettability Surface[†]

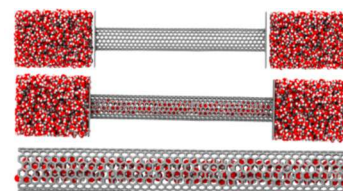
Entrapped Liquid: Fluid entrapped in a nano-space such as nanochannel, nano-tube, nano-pore and other complex nano-spaces. This also known as **nano-confined liquid (NCL)**.



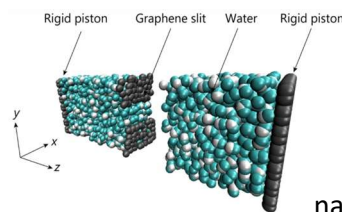
nano-channel



nano-pore



nano-tube



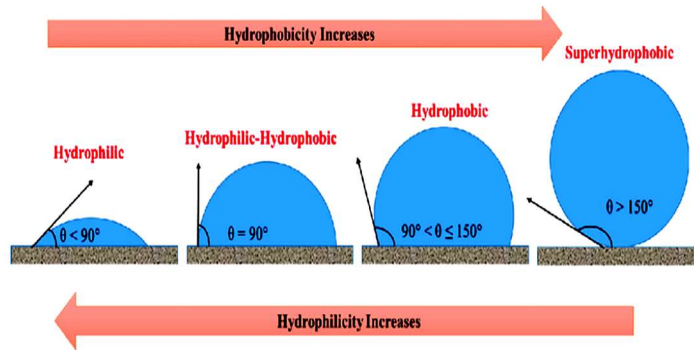
nano-slit

[†] Das et al., Computational Materials Science 244 (2024): 113232.



Thermal Properties of Liquid Entrapped between Hybrid Wettability Surface

Wettability: Wettability defined as liquid ability to wet a surface which is determined by contact angle measurement.



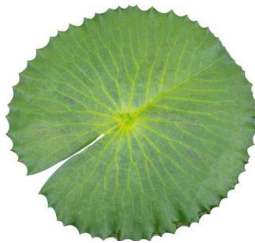
Hydrophilic – water attracting

Hydrophobic – water repelling

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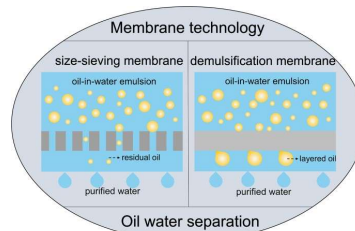
Thermal Properties of Liquid Entrapped between Hybrid Wettability Surface

Hybrid Wettability refers to a surface or material property where **different regions** exhibit **varying wettability characteristics**, such as being hydrophilic (water-attracting) and hydrophobic (water-repelling) simultaneously.

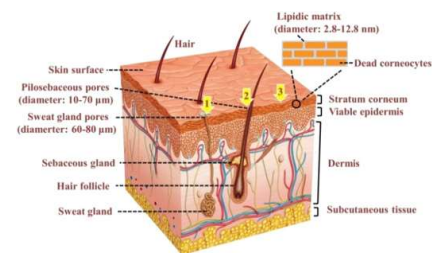


Lotus Leaves

Nano-scale variation of wettability, self-cleaning



Nano-engineered hybrid wettability membrane enhance Oil-water separation

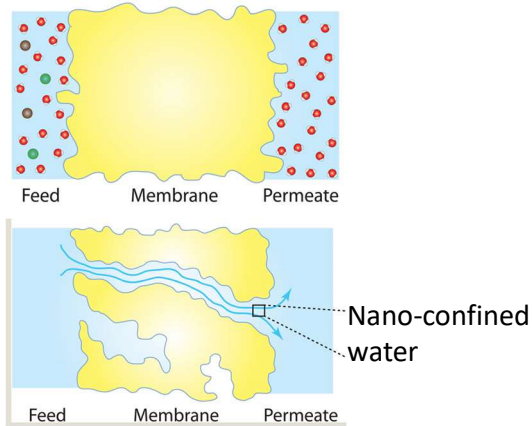


Human Skin

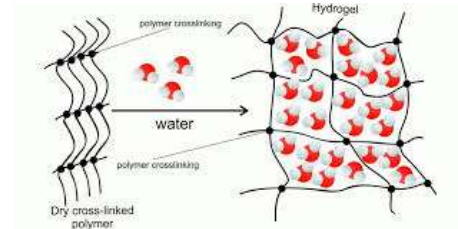
hydrophilic sweat glands surrounded by hydrophobic lipid layers

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Motivation



Membrane: May reconcile pore flow and solution friction model (Heiranian et al.)



Hydrogel: viscosity of confined water in hydrogel may be related to the mechanical behavior of hydrogel (Lei et al.)



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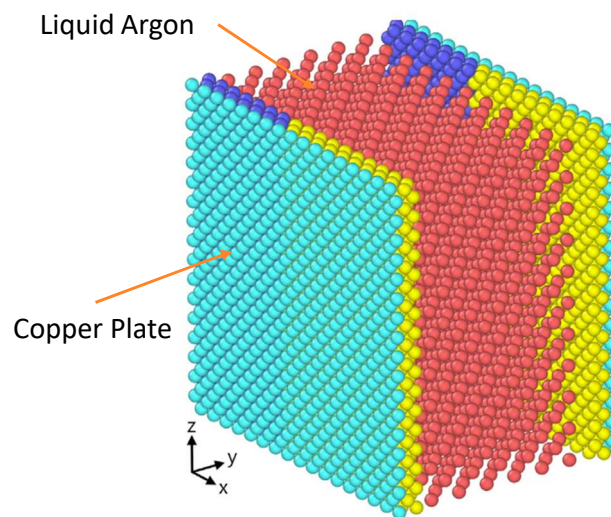
A simple model consist of liquid Argon entrapped between Copper plates

Why Argon?

- Easy to model (Only atomic interaction, No bond or molecules)
- Computationally inexpensive
- But powerful to gain insight.

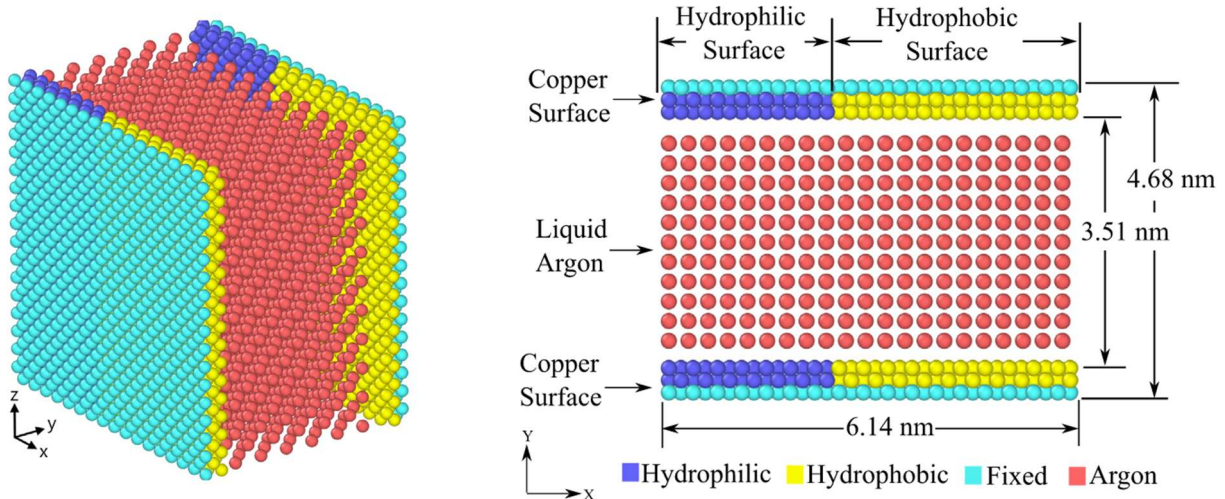
Why Copper?

- Modelling wettability is straightforward.
- Atomic interaction can be modelled using LJ pair potential.



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A simple model consist of liquid Argon entrapped between Copper plates



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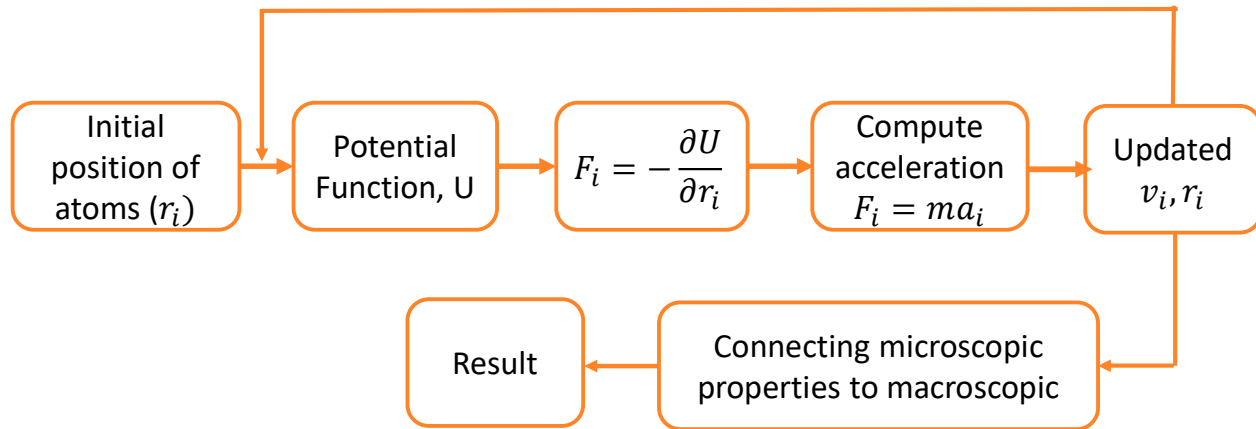
Objectives

- ✓ To determine specific heat, thermal conductivity and diffusion co-efficient of the entrapped argon.
- ✓ To investigate the effect of the percentage of hydrophilic portion on these properties.
- ✓ To determine the effect of different hybrid wettability surface on these properties.
- ✓ To analyze and explain the findings.



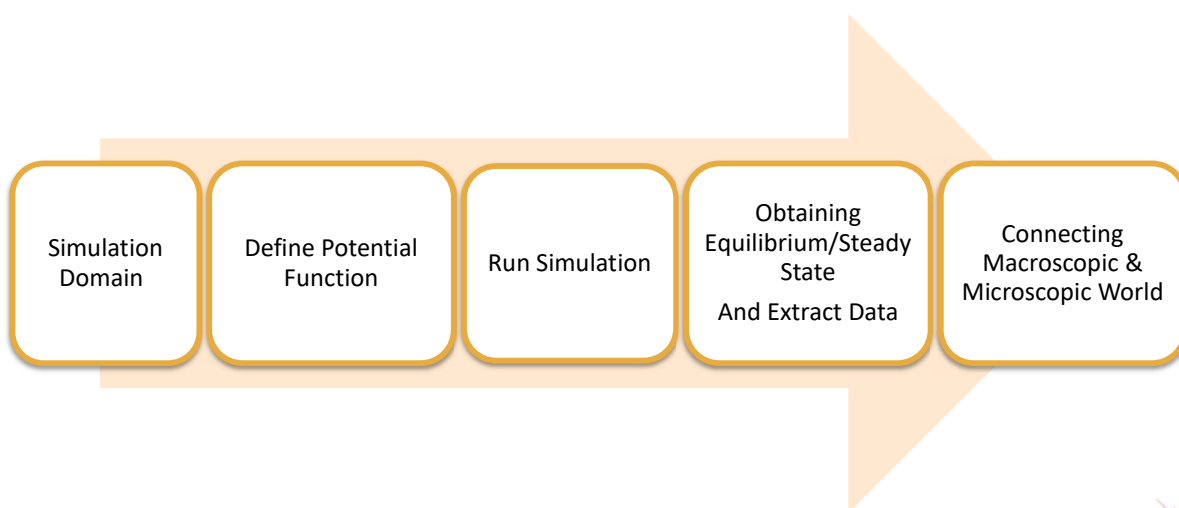
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Introduction to Molecular Dynamics



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Basic Steps to perform Molecular Dynamic Simulation



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Potential Function

Interaction Strength Length Scale Cut off radius, $r_c = 2.5\sigma$

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

Table 1

Values of parameters that governs Lennard-Jones (LJ) potential function [33,39,40].

Name of pair	ϵ_{ij} (J)	σ_{ij} (nm)
Ar-Ar	1.67×10^{-21}	0.3405
Cu-Cu	6.59×10^{-20}	0.2340



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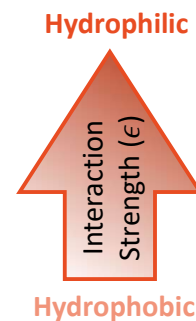
Potential at Solid-Liquid Interface

Wettability factor [3]

$$\epsilon_{Ar-Cu} = \sqrt{\epsilon_{Ar-Ar} \epsilon_{Cu-Cu}}$$

$$\sigma_{Ar-Cu} = \frac{\sigma_{Ar-Ar} + \sigma_{Cu-Cu}}{2}$$

Lorentz – Bertholet mixing principle [1]



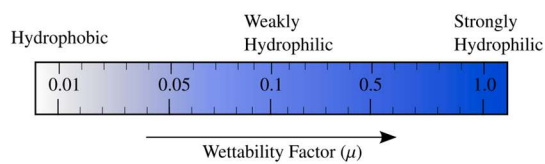
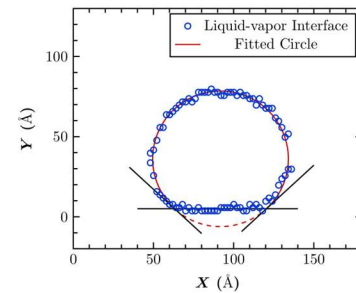
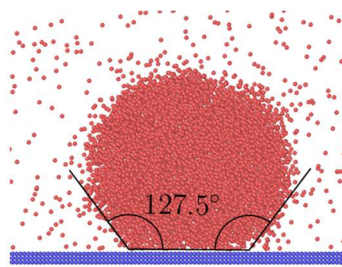
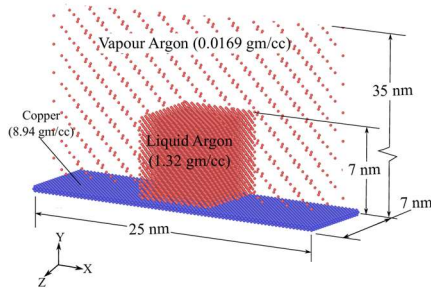
Wettability and Interaction Potential [2]

- [1] M. Allen, D. Tildesley, D. Tildesley, Computer simulation of liquids, in: Oxford Science Publications, Oxford University Press, 2017
- [2] D.T. Semiromi, A. Azimian, Molecular dynamics simulation of nonodroplets with the modified Lennard-Jones potential function, Heat Mass Transf. 47 (2011) 579–588.
- [3] Z. Liang, H.L. Tsai, Effect of molecular film thickness on thermal conduction across solid-film interfaces, Phys. Rev. E, Stat. Nonlinear Soft Matter Phys. 83 (2011), <https://doi.org/10.1103/PhysRevE.83.061603>.



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Inverse relation between wettability factor (μ) and contact angle (θ)

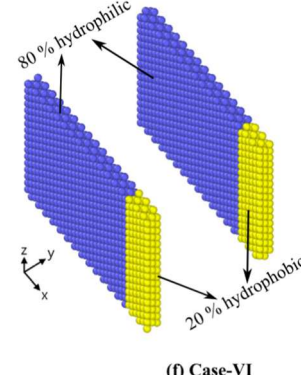
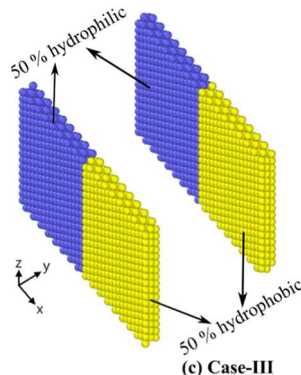
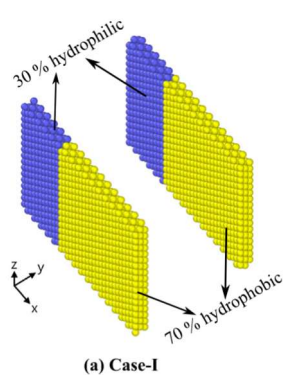


Hydrophobic μ Hydrophilic

- Relation between contact angle (θ) and wettability factor (μ) is determined by separate MD simulations
- Three Regions are defined based on wettability factor
 - Hydrophobic ($\mu = 0.01 - 0.05$)
 - Weakly Hydrophilic ($\mu = 0.05 - 0.5$)
 - Strongly Hydrophilic ($\mu = 0.5 - 1.0$)

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Modelling of hybrid wettability surface by changing percentage of hydrophilic area

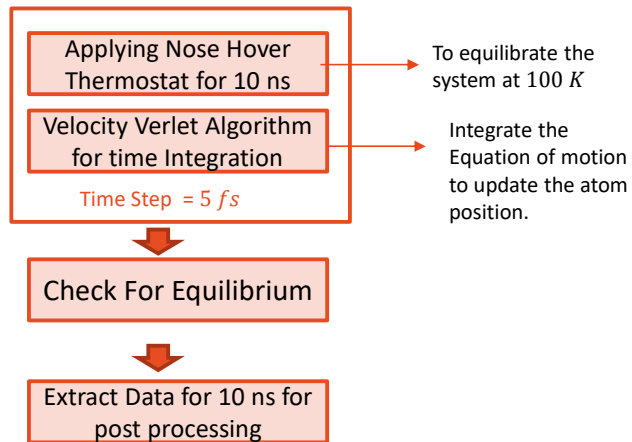


Type of surface	Wettability factor for	
	hydrophobic Surface (μ_o)	hydrophilic surface (μ_i)
Hybrid-I	0.02	0.5
Hybrid-II	0.02	1.0
Hybrid-III	0.05	0.5
Hybrid-IV	0.05	0.5

- 4 types of surface for 4 different pair of wettability factor.
- For each type of surface, percentage of hydrophilic portion increases from 30% to 80% with step of 10%. Total 6 cases.

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Simulation methodology to determine specific heat capacity



Specific Heat computed using **fluctuation formula** -

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

Here,

C_v = Specific heat of argon.

$\text{var}(E)$ = Variance of total energy of argon

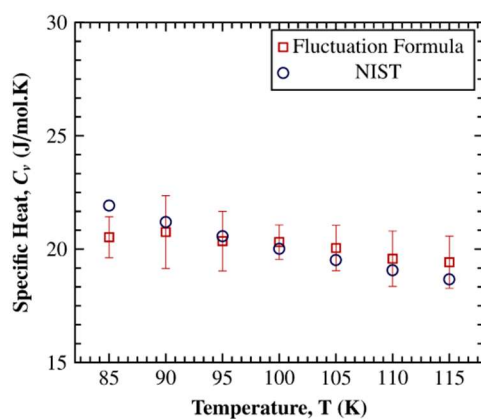
K_B = Boltzmann Constant

T = Temperature of argon.



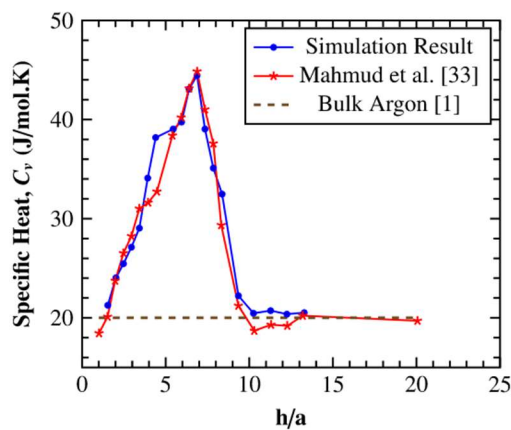
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Close matching with previous data validate the simulation methodology



(a)

Specific heat of unconfined argon at 100K from NIST close to computed data.



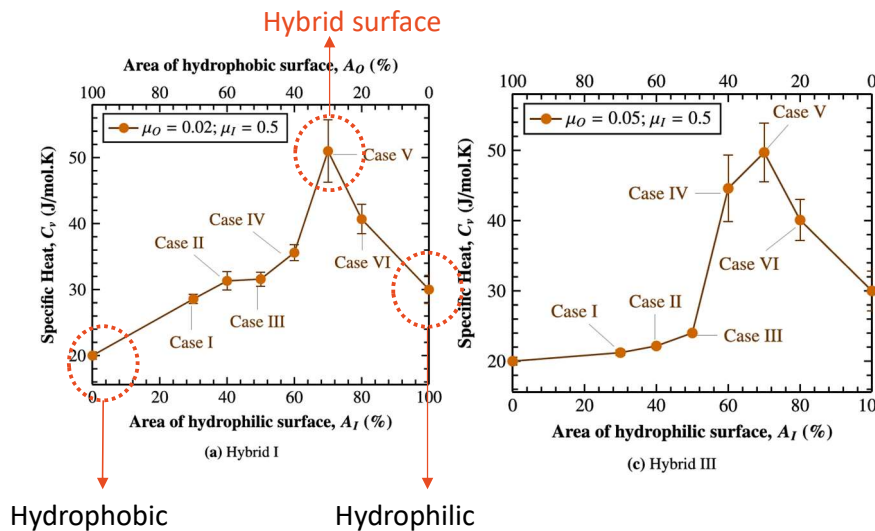
(b)

Specific heat of confined argon at 100K matches previous study



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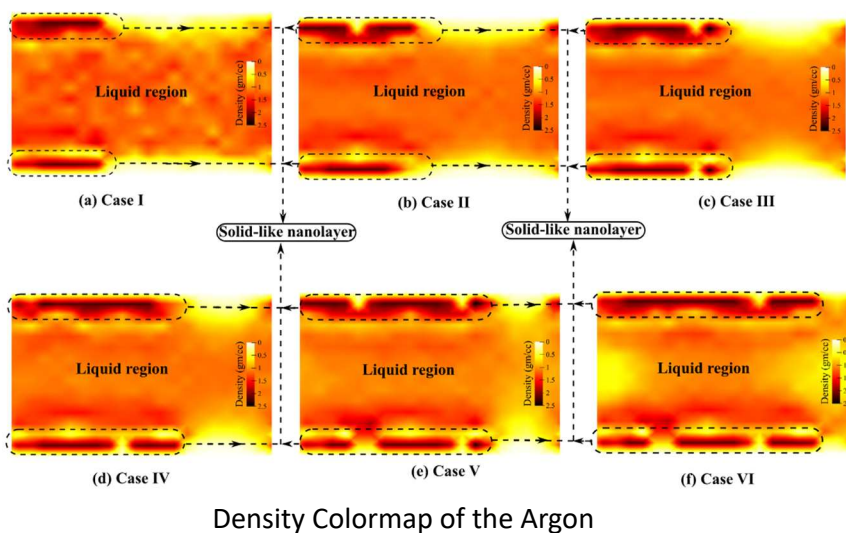
Specific heat surpasses the both purely hydrophobic and hydrophilic cases



- Specific heat capacity **increase** with increasing hydrophilic portion up to a **maximum** value.
- Then **specific heat decreases** with increasing value of hydrophilic area.
- Maximum value of **specific heat surpasses** both **pure hydrophobic** or **hydrophilic** surface.
- Same trend observe for all 4 types of hybrid surface.

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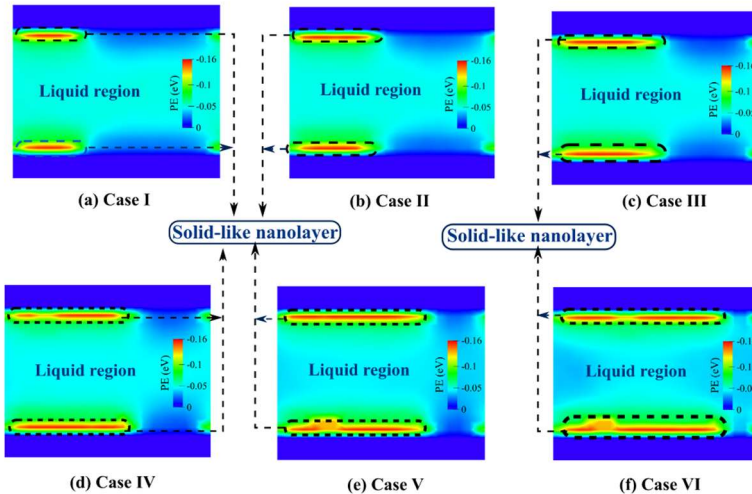
Two distinct regions: solid-like layer and Liquid region



- Two distinct region
 - High density** region near the hydrophilic wall – **solid-like layer**
 - Low density** region at middle – **liquid-region**
- Solid-like** region **grows** with the increasing area of hydrophilic portion.

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Solid-like layer strongly attracted by the hydrophilic area of the copper plate



- Strong surface attraction force near hydrophilic wall create a potential well.
- Nearby layers of hydrophilic wall (**solid-like layer**) has characteristics **similar to solid**.



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A hypothesis to explain the anomalous trend of specific heat

“Specific heat of liquid region decrease with the increasing hydrophilic area, in contrast, specific heat of solid-like layer increase. This two opposite trend culminates the maximum specific heat capacity”

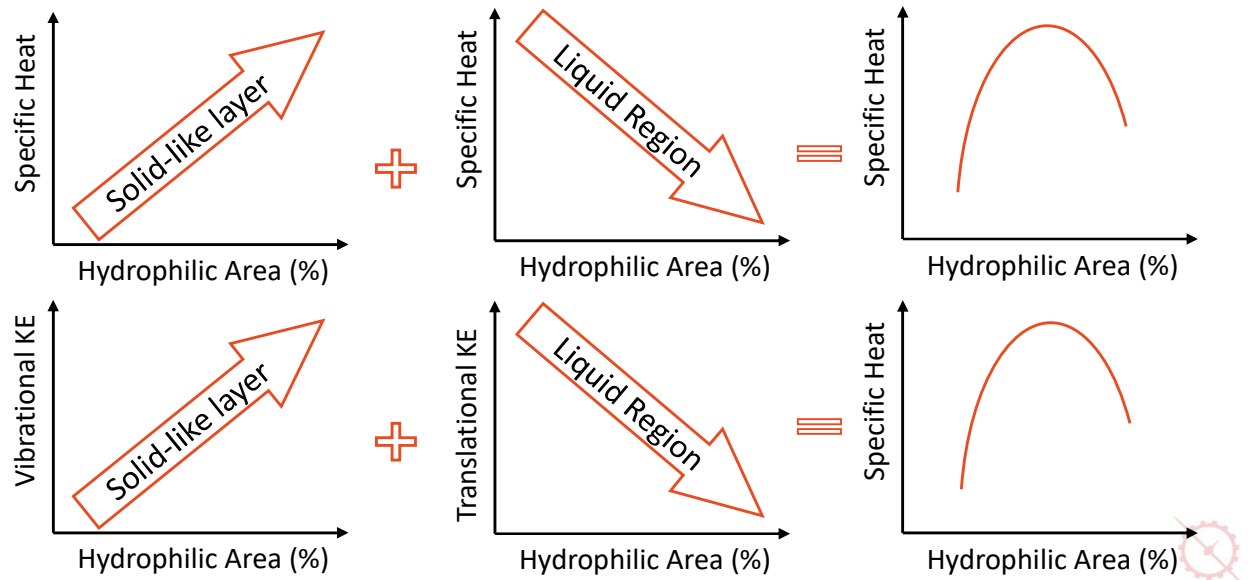
- Increasing specific heat means, argon molecules has stored more energy if temperature increase. Argon molecules require higher number energy storage mode.
- In solid-like layer, as behave like a solid, vibration energy modes are dominated.
- In liquid region, translation energy modes are dominated.

“In solid-like layer vibration kinetic energy increases, in liquid-region translational kinetic energy decreases as hydrophilic area increases.”



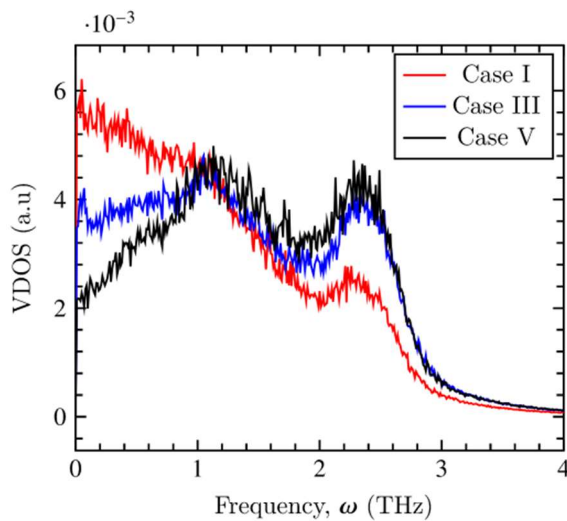
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Hypothesis: Specific heat of solid-like layer and liquid region show opposite trend



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Higher peak of VDOS support the hypothesis



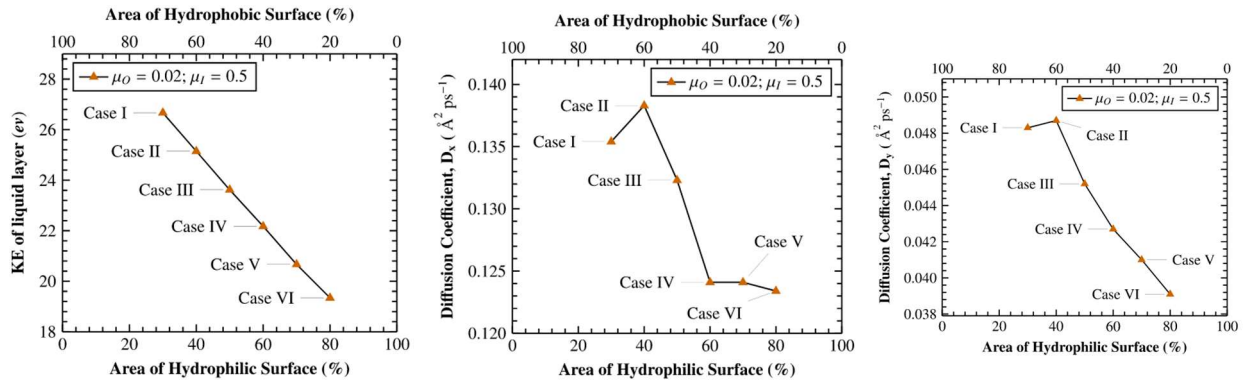
Vibrational Density of State (VDOS) of **solid-like layer**:

- Higher peaks indicate that a **greater number of molecules involves** in this frequency. Ultimately leads to **higher heat capacity**.
- **Peaks at zero frequency** indicate the **collective motion** of the molecules.
- Peaks at zero frequency decreases as surface more wettable which signifies the **solid-like behavior**.

↑ ↑ ↑
Hydrophilic Peak of VDOS Vibrational Energy

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Decreasing kinetic energy corroborate the hypothesis



Diffusion co-efficient and Kinetic energy of liquid region:

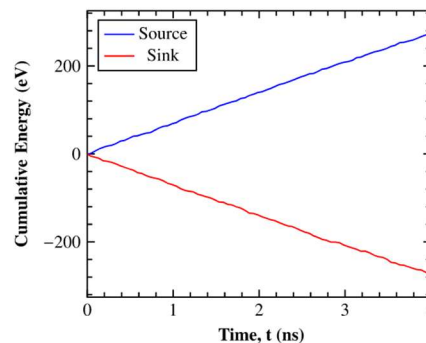
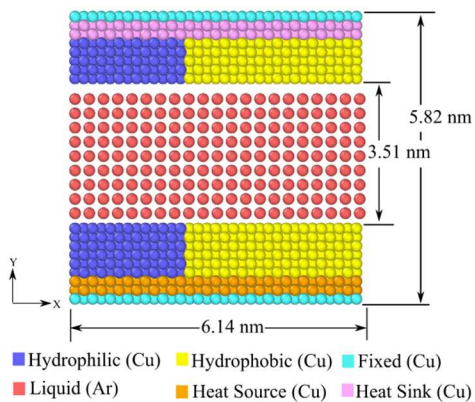
- Decreasing diffusion co-efficient indicate the **restricted molecular mobility**.
- This indicate the lower energy storage ability of the liquid region.



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Interfacial Thermal Resistance

Simulation Methodology

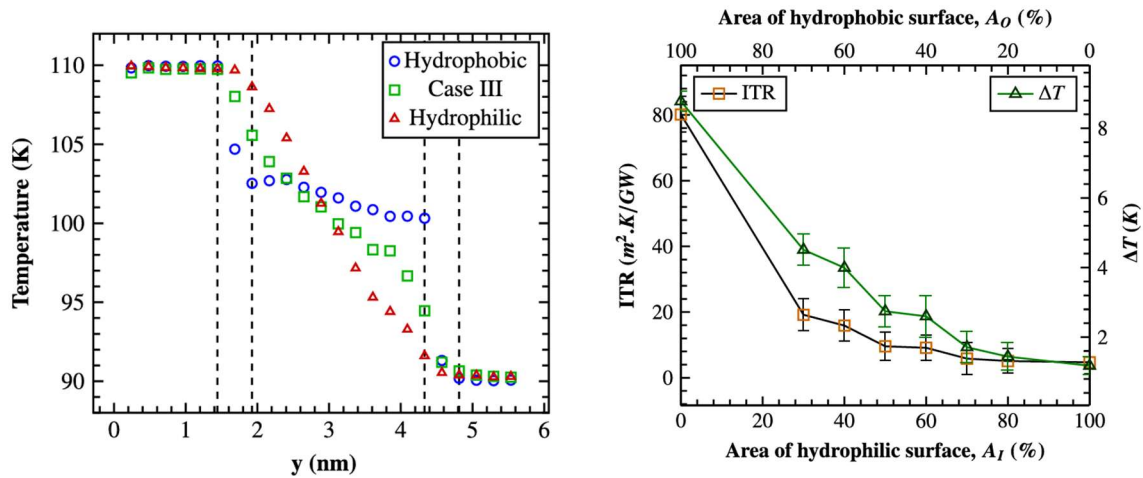


- NEMD simulation to determine Interfacial thermal resistance.
- Constant temperature difference (20°C) maintain between source and sink.
- Heat current obtain from cumulative energy transfer from source to sink
- Symmetric cumulative energy indicate **steady state** condition of the system



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Interfacial Thermal Resistance



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Conclusion

- Liquid argon exhibit higher capacity entrapped between hybrid wettability surface compared to pure hydrophobic or hydrophilic surfaces.
- Specific heat capacity of liquid argon depends on the percentage of hydrophilic portion of the hybrid wettability surface.
- Structural and dynamic changes occurs in the confined liquid. Two distinct region (solid-like and liquid region) is observed. Opposite behavior of these two region leads to anomalous behavior.
- ITR also a consistent decline with increasing hydrophilicity of surface

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