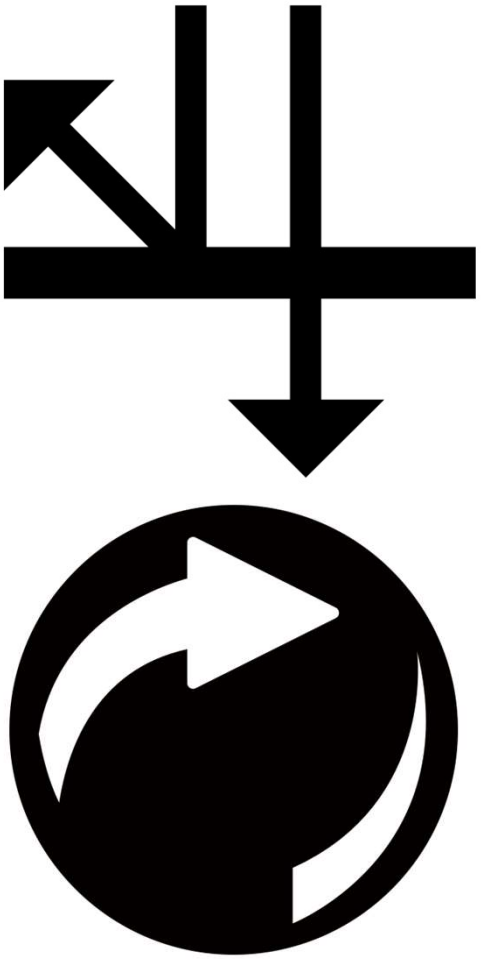
Engineering the Relationship between Fluid Structure and Transport under Nanoconfinement

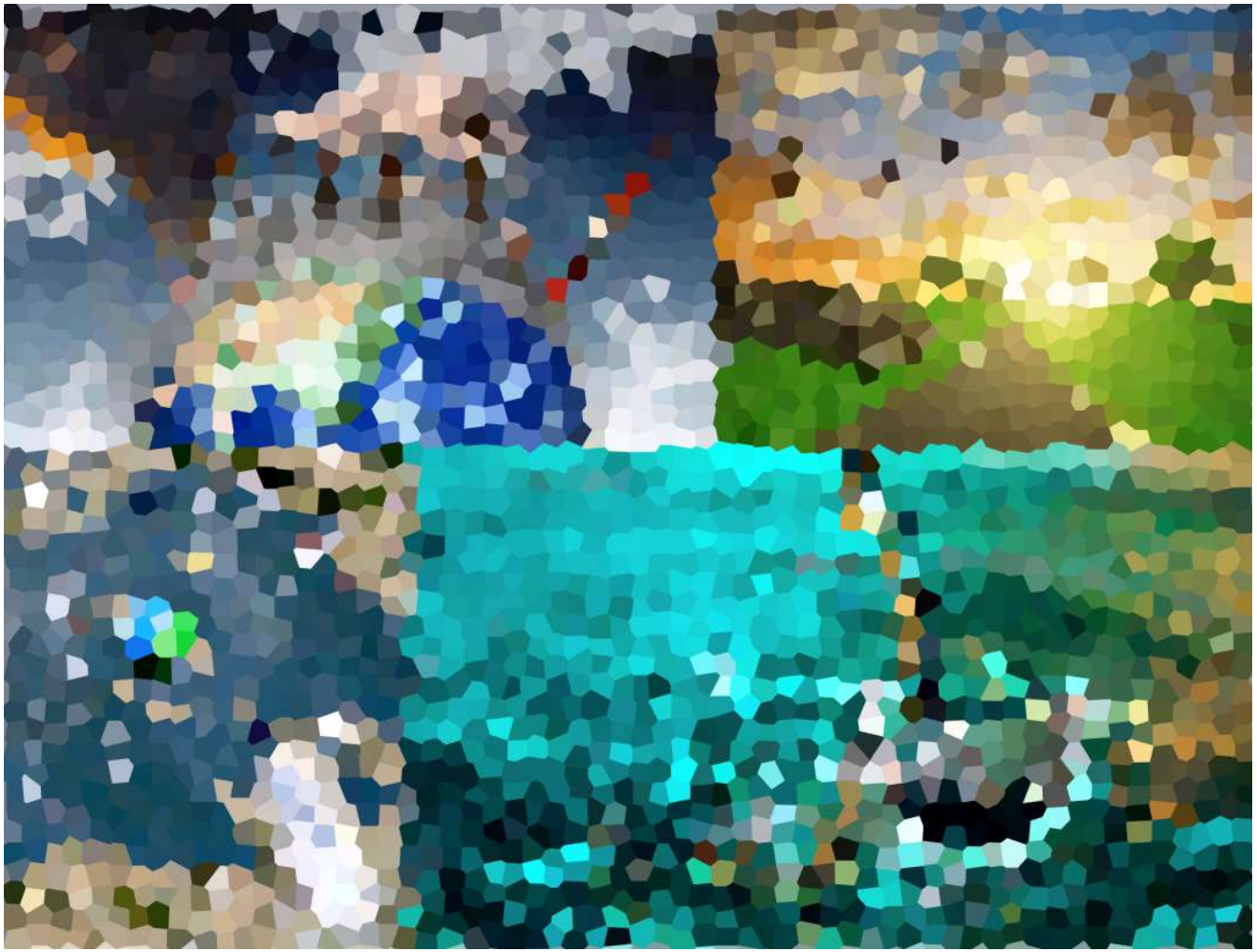
Gerald J. Wang

MIT Dept. of Mechanical Engineering

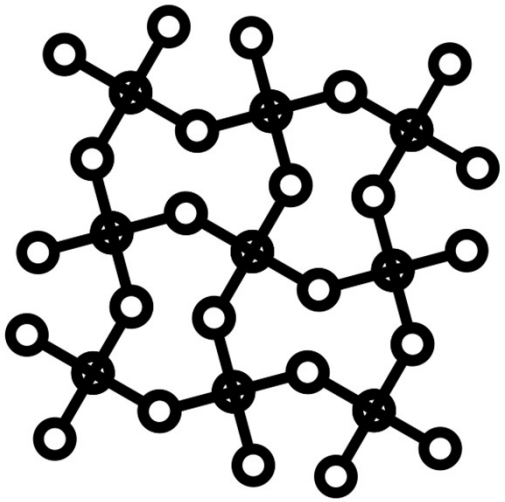
July 16, 2018



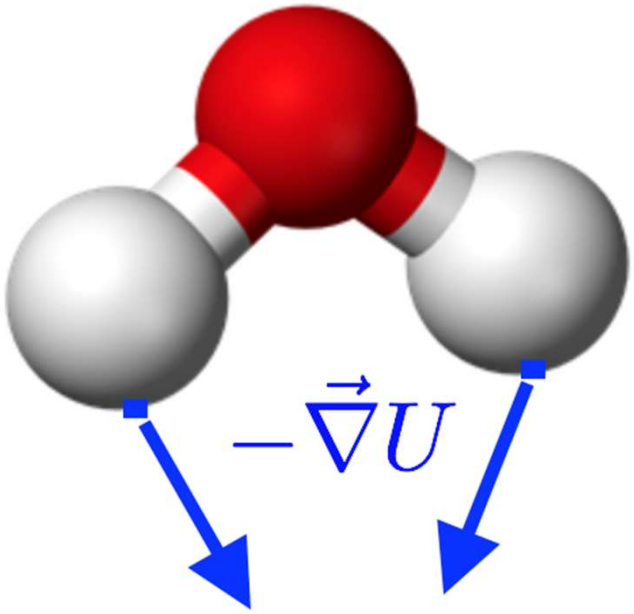
[Images courtesy of Energy Press, Institute for Leadership and Public Policy, WWF, U.S. Green Tech]

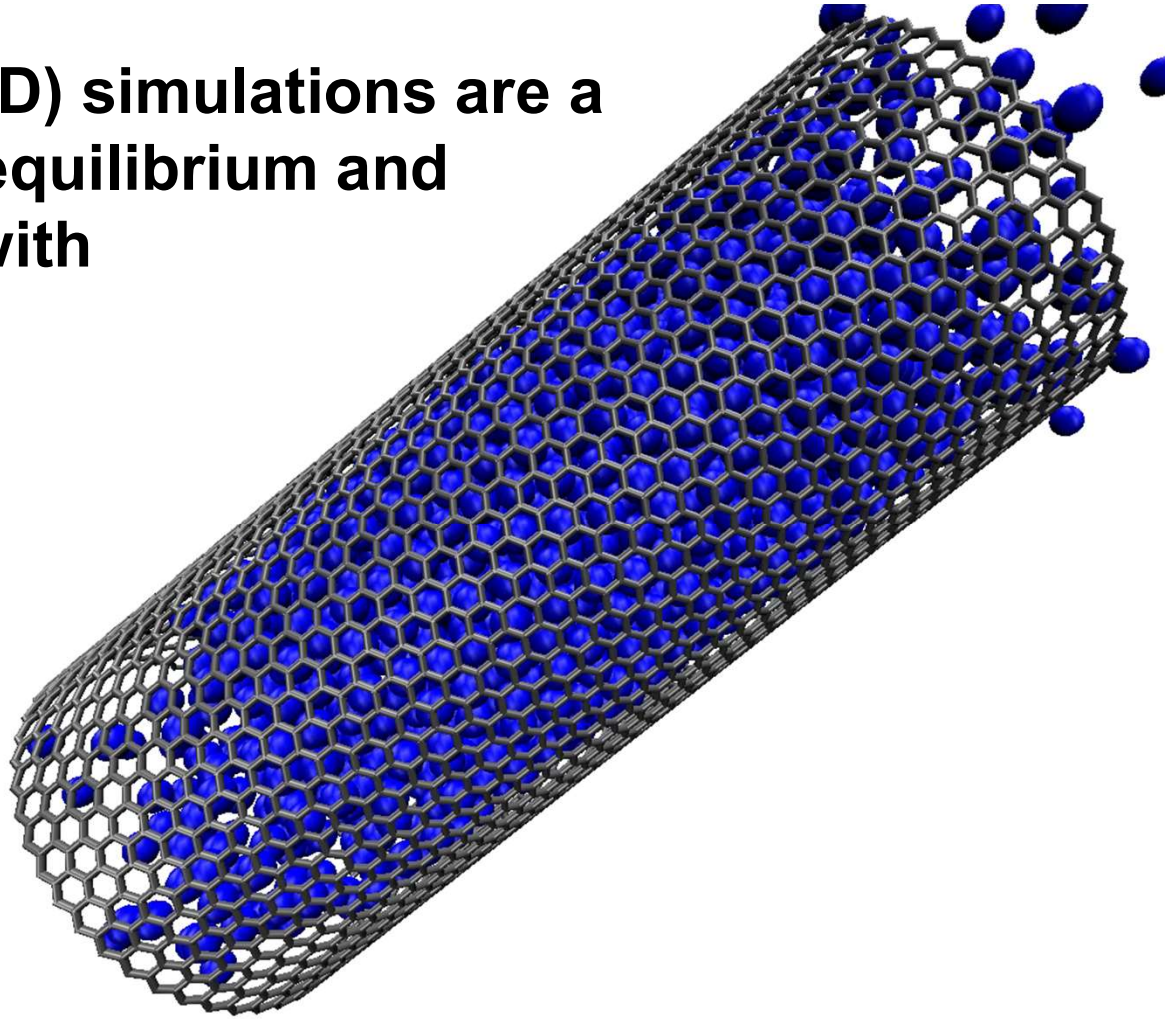


Thinking big by thinking small

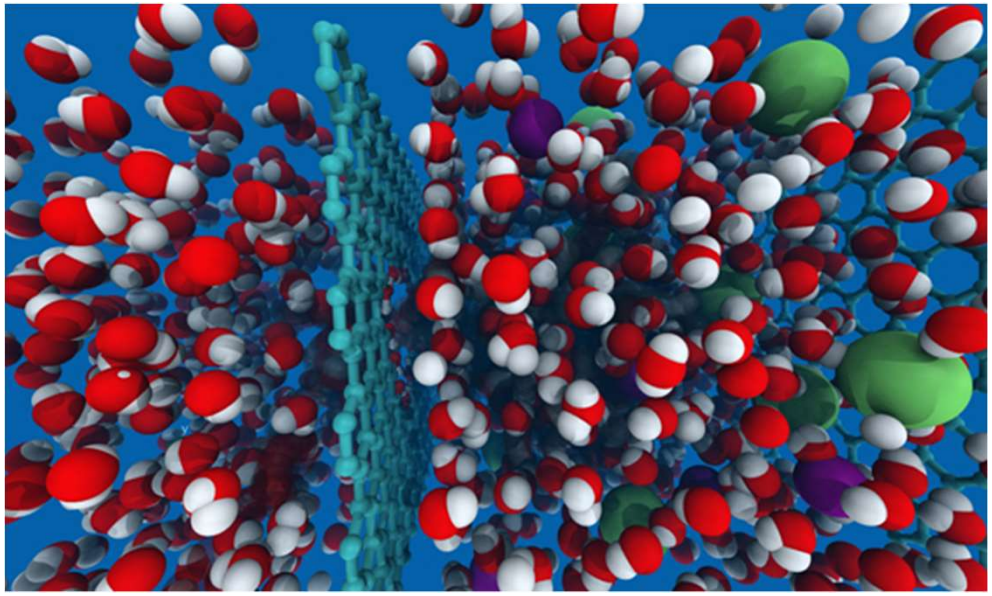


Molecular-dynamics (MD) simulations are a powerful tool to study equilibrium and transport phenomena with atomistic detail.





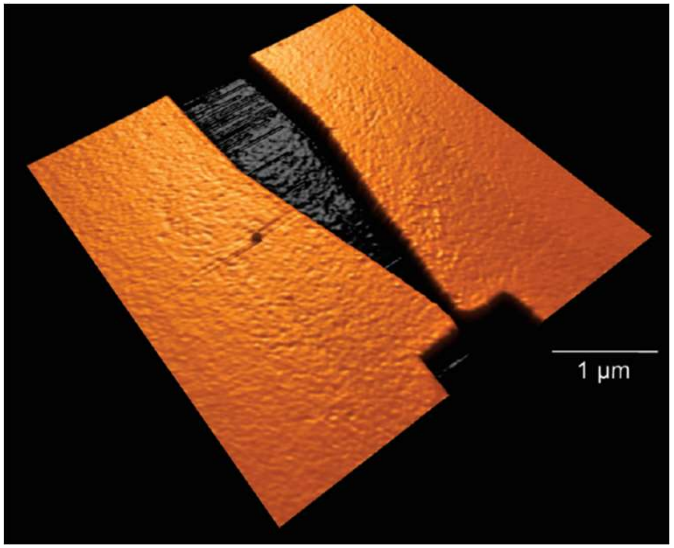
Fluids under nanoscale confinement exhibit remarkable properties, such as…

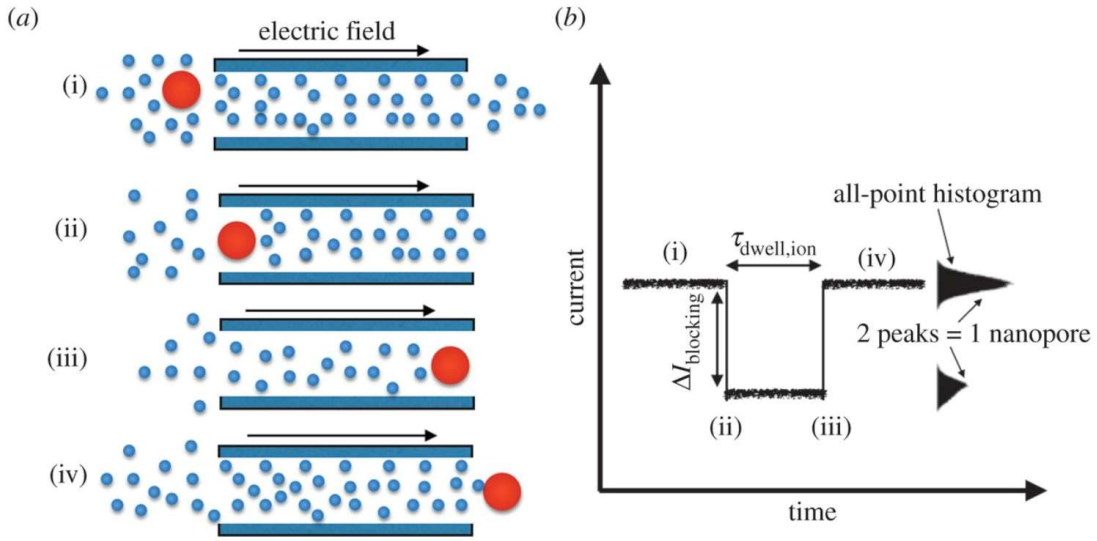


… fast and selective transport.

[Cohen-Tannugi and Grossman, *Nano Lett.* (2012)]

Fluids under nanoscale confinement exhibit remarkable properties, such as…





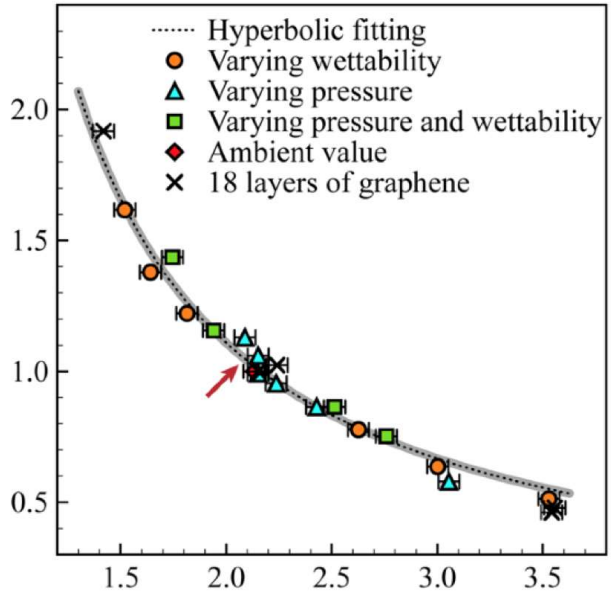
... sensitivity to transport of individual species.

[Kovarik and Jacobson, *Analytical Chem.* (2009)]

[Agrawal, Drahushuk, and Strano, *Phil. Trans. R. Soc. A* (2015)]

Fluids under nanoscale confinement exhibit remarkable properties, such as…

Relative Interfacial Thermal Resistance



Relative Water Density at Interface

… novel transport properties at solid interfaces.

[Alexeev et al., *Nano Lett.* (2015)]

Molecular mechanics and structure of the fluid-solid interface in simple fluids

Gerald J. Wang and Nicolas G. Hadjiconstantinou

Phys. Rev. Fluids **2**, 094201 (2017) – Published 5 September 2017

Just like a layered cake, fluid near a solid interface often arranges itself into clearly defined bands of density. The properties of this fluid layering are investigated, and a dimensionless group governing layer formation is introduced. A scaling relationship for high-density fluids is presented.

Always Gamble on an Empty Stomach: Hunger Is Associated with Advantageous Decision Making

Denise de Ridder*, Floor Kroese, Marieke Adriaanse, Catharine Evers

Department of Clinical and Health Psychology, Utrecht University, Utrecht, The Netherlands

Engineering the Relationship between Fluid Structure and Transport under Nanoconfinement

"How to Bake a (Nanoscale) Tiramisu"

Gerald J. Wang

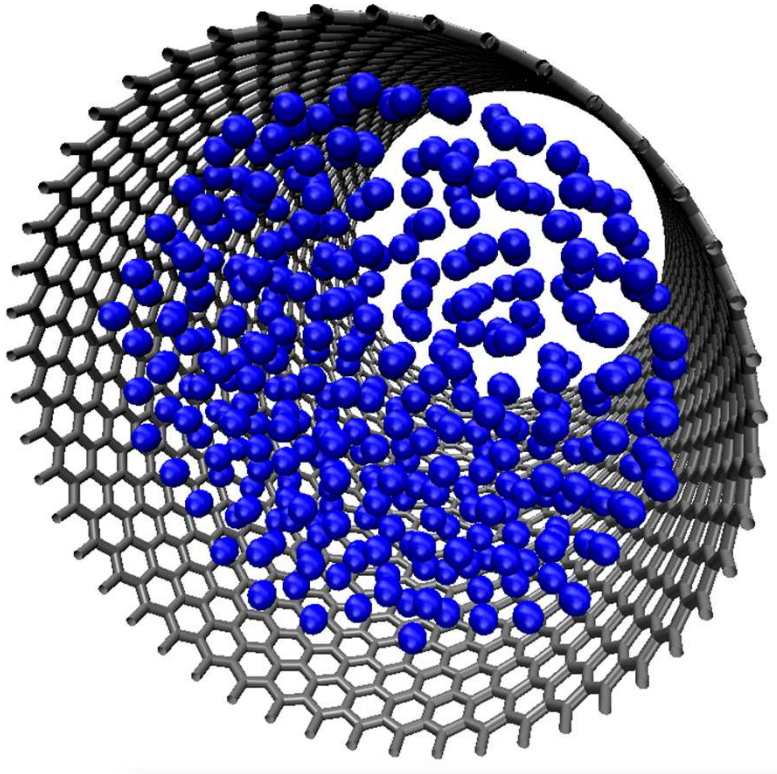
MIT Dept. of Mechanical Engineering

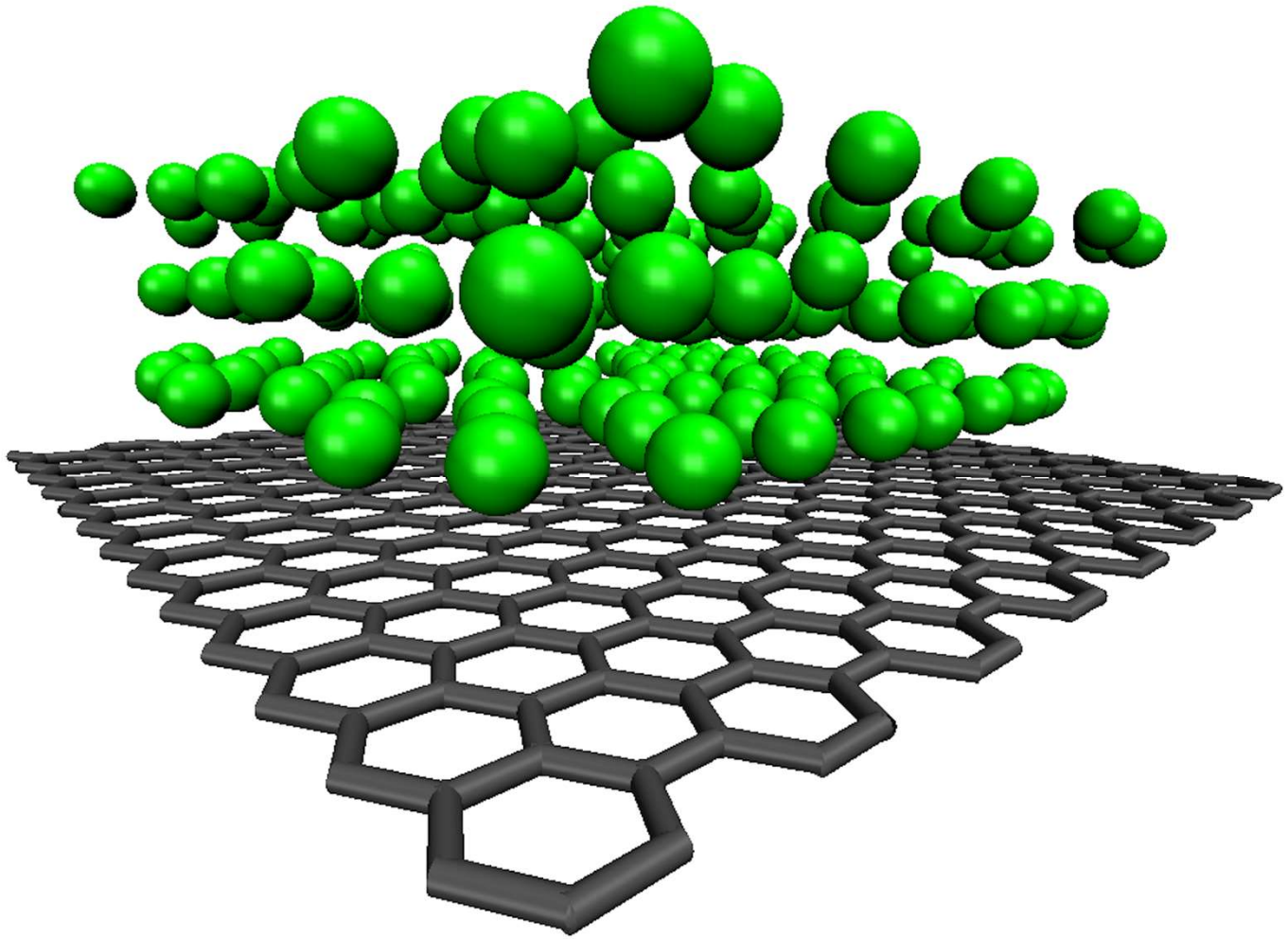
MITMECHE

July 16, 2018

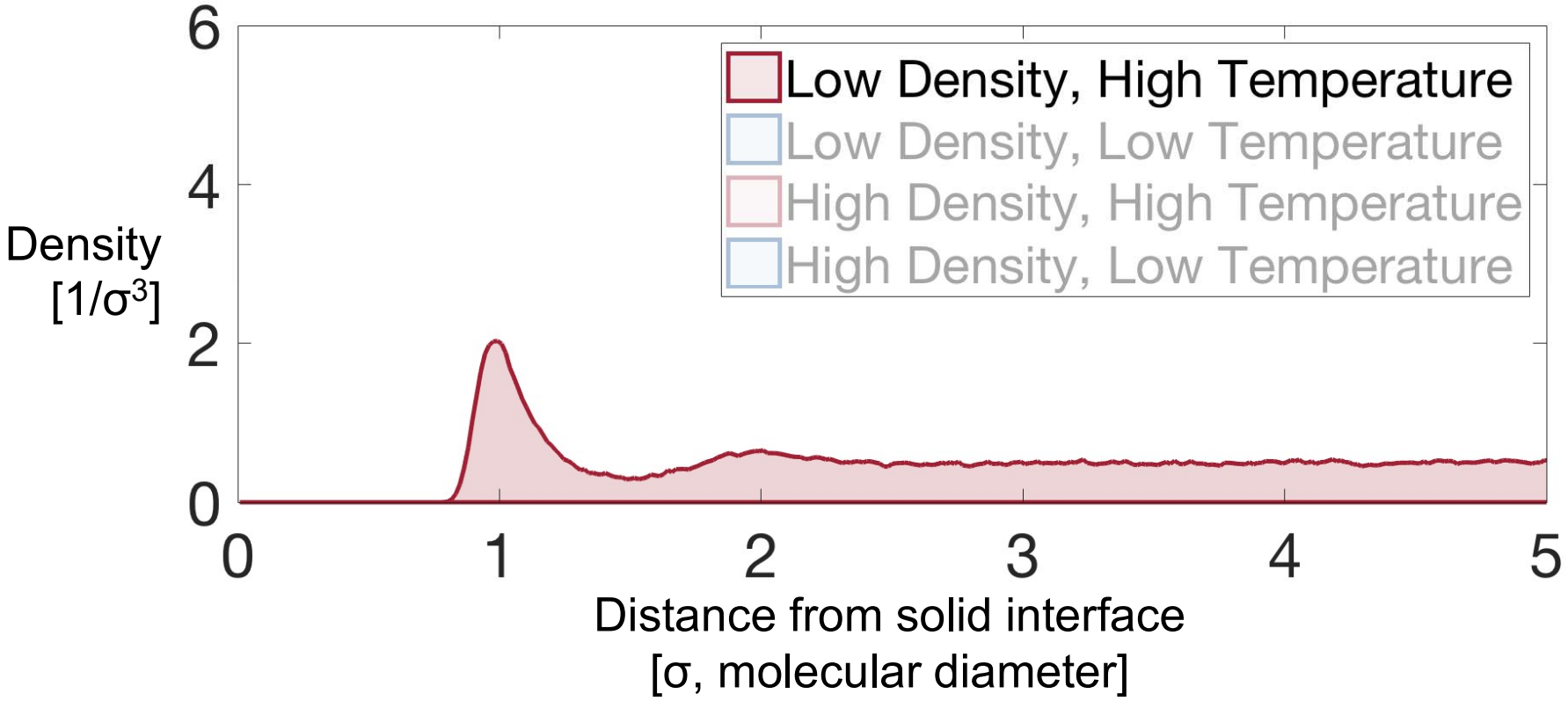
Structure → **Transport**

By serving as a template for local structure, solid surfaces function as cake pans for nearby fluid.



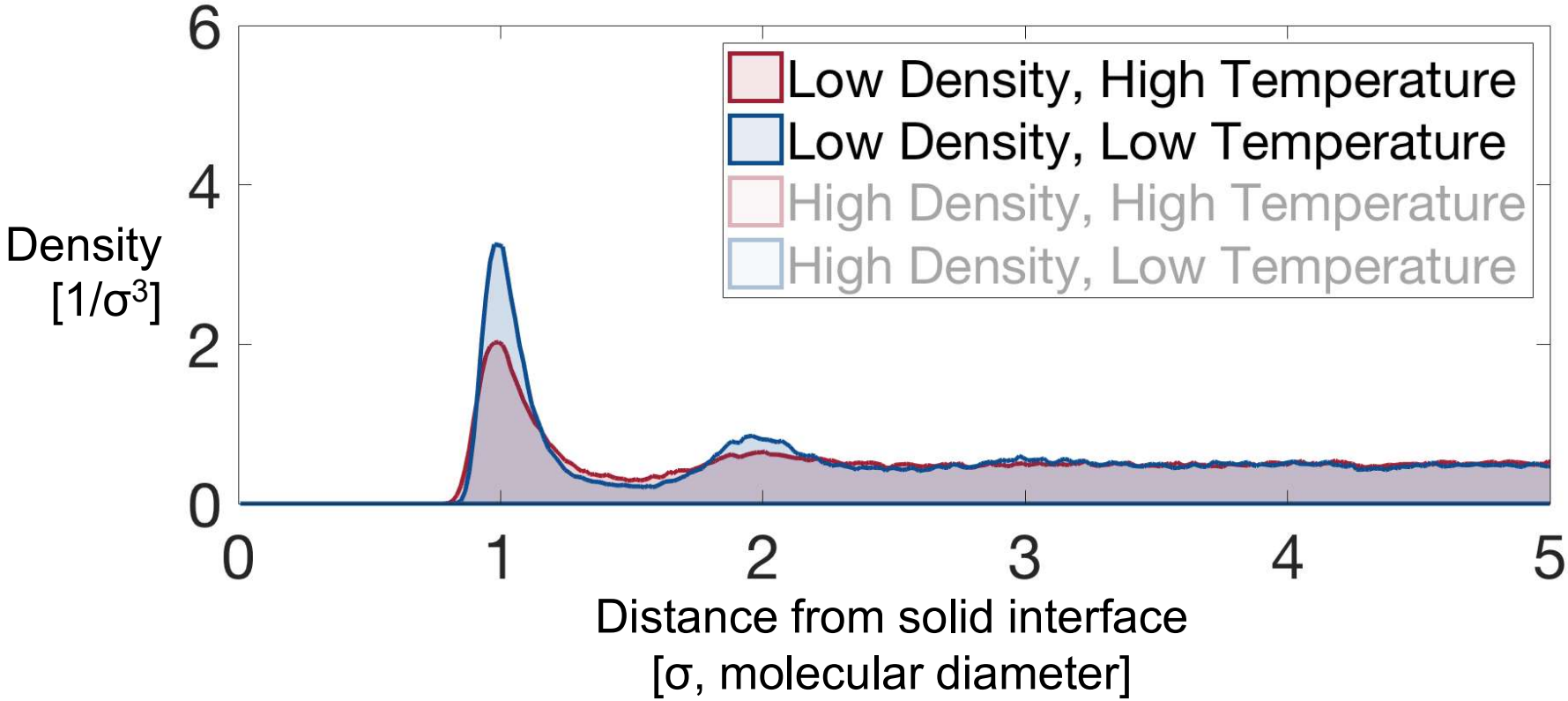


Ordering manifests as peaks on a spatial density profile.



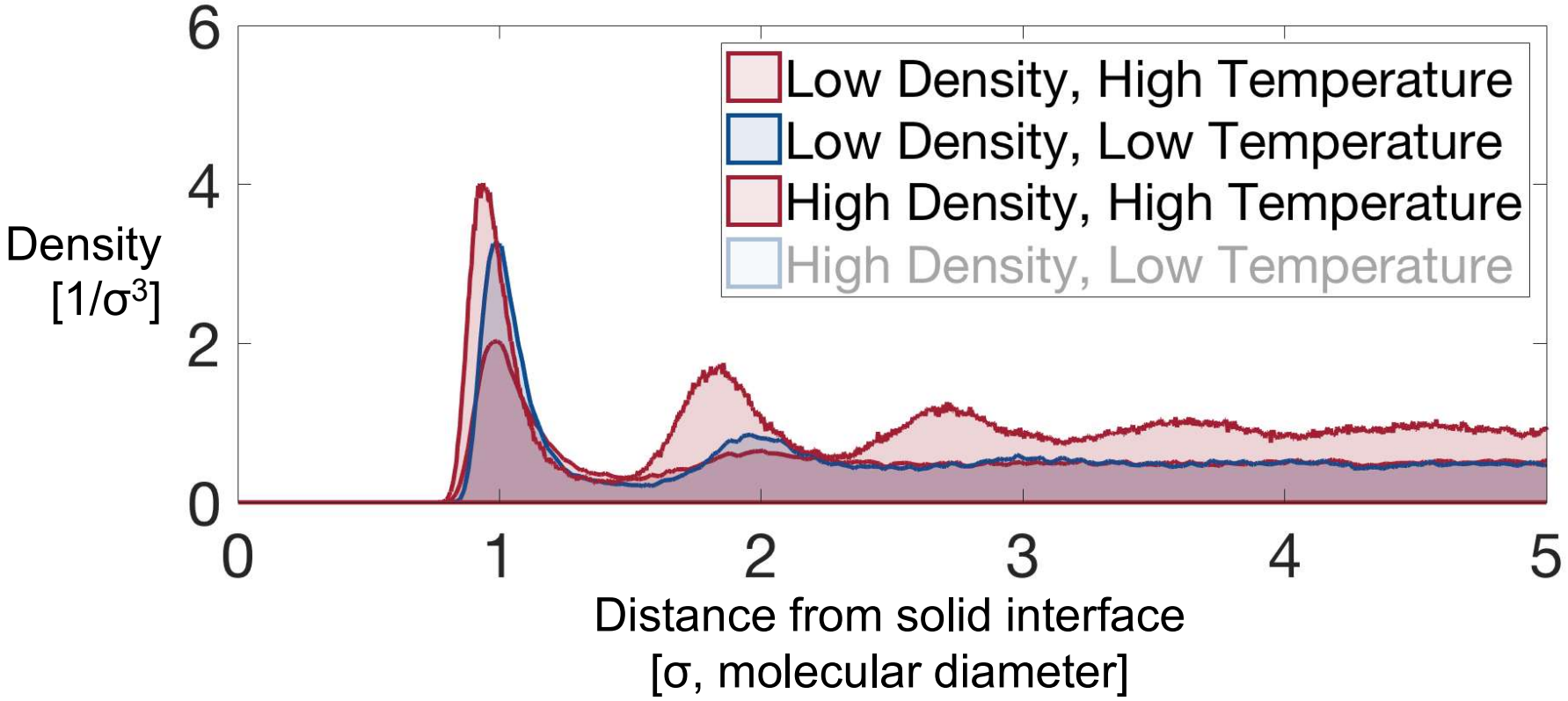
[Wang and Hadjiconstantinou, *Phys. Rev. Fluids* (2017)]

Ordering manifests as peaks on a spatial density profile.



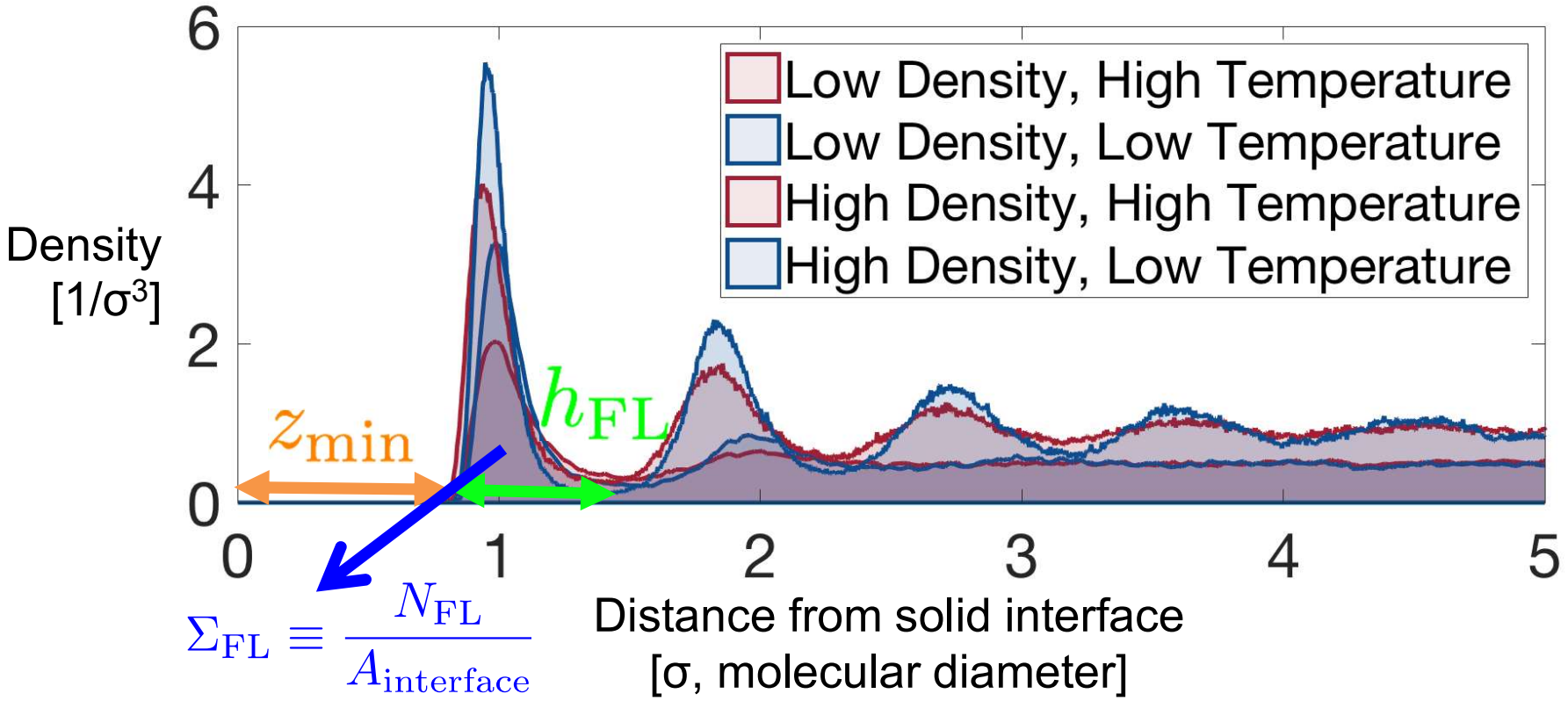
[Wang and Hadjiconstantinou, *Phys. Rev. Fluids* (2017)]

Ordering manifests as peaks on a spatial density profile.



[Wang and Hadjiconstantinou, *Phys. Rev. Fluids* (2017)]

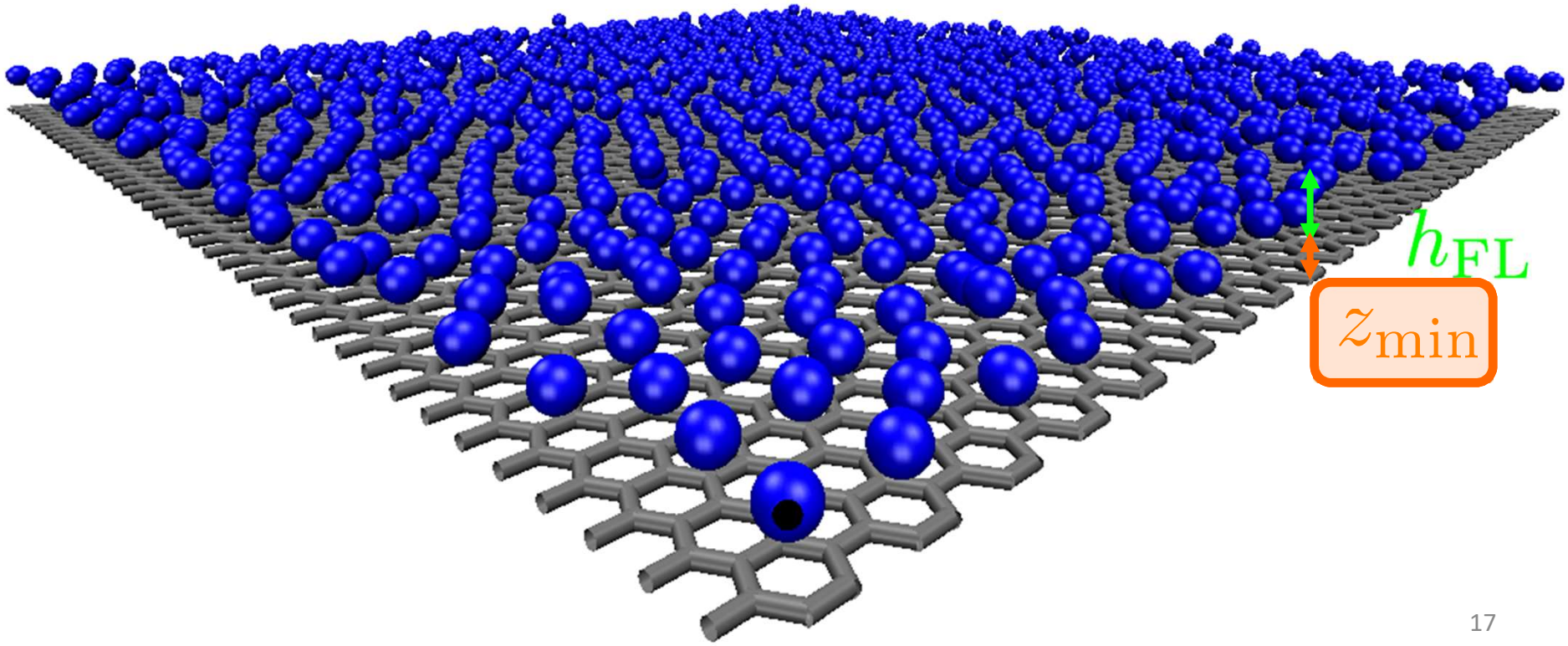
Ordering manifests as peaks on a spatial density profile.



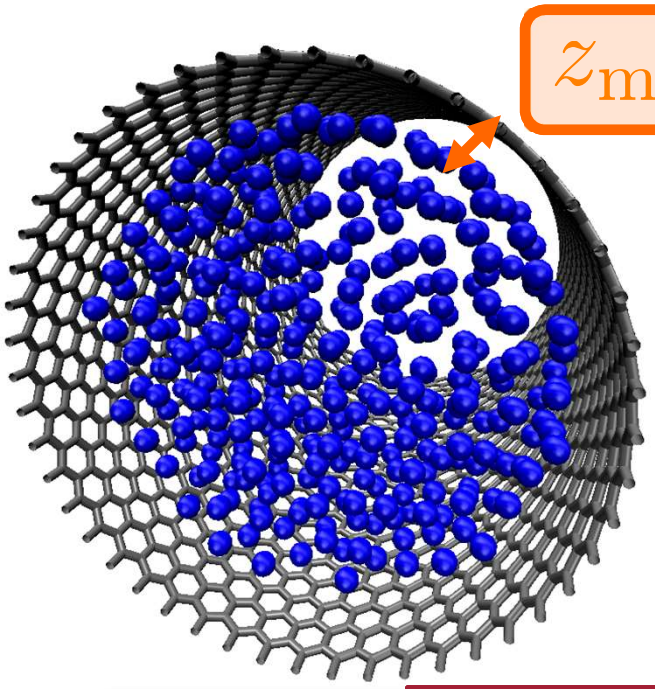
[Wang and Hadjiconstantinou, *Phys. Rev. Fluids* (2017)]

Molecular mechanics and statistical physics are the flour and butter of this work.

$$\Sigma_{\mathrm{FL}} \equiv \frac{N_{\mathrm{FL}}}{A_{\mathrm{interface}}}$$



Modeling fluid structure with mean-field theory...



Lennard-Jones potential…

$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Mean-field in cylindrical geometry…

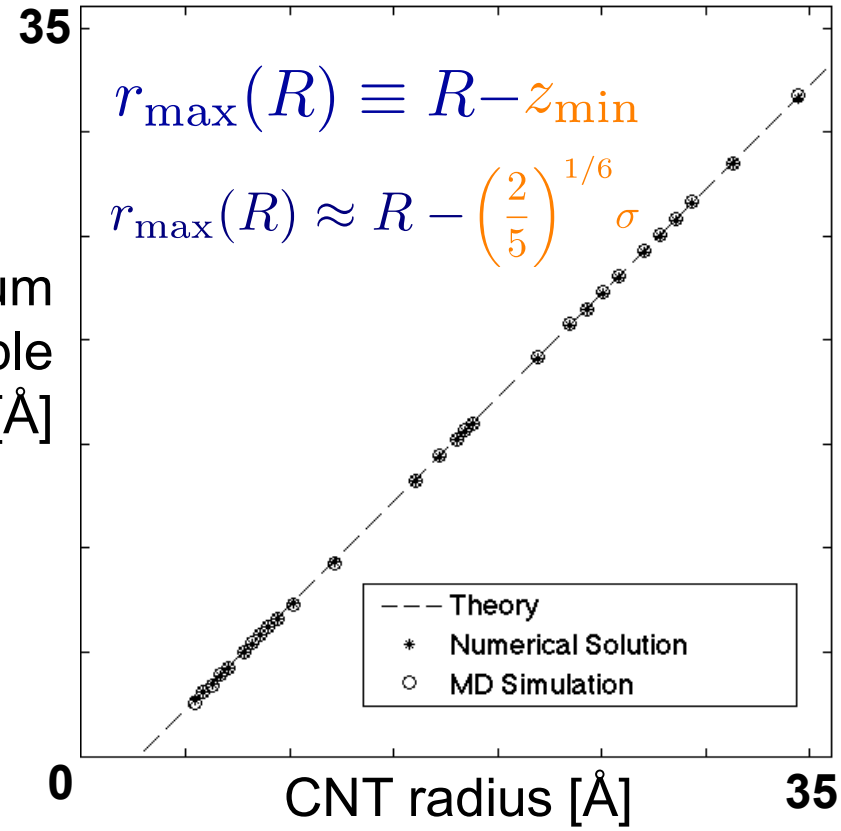
$$U(r) = n\pi^2\epsilon\sigma^2\left[\frac{63}{32}F_{-\frac{9}{2},-\frac{9}{2},1}\left(\frac{r^2}{R^2}\right)\left(\frac{R-r}{\sigma}\left(1+\frac{r}{R}\right)\right)^{-10} - 3F_{-\frac{3}{2},-\frac{3}{2},1}\left(\frac{r^2}{R^2}\right)\left(\frac{R-r}{\sigma}\left(1+\frac{r}{R}\right)\right)^{-4}\right]$$

$$U^*(r) \equiv \frac{1}{n\pi^2\epsilon\sigma^2}U(r) \qquad R^* \equiv \frac{R}{\sigma} \qquad \delta \equiv \frac{r}{R}$$

$$U^*(\delta) = \left[\frac{63}{32}F_{-\frac{9}{2};-\frac{9}{2};1}(\delta^2)\left(R^*(1-\delta^2)\right)^{-10} - 3F_{-\frac{3}{2};-\frac{3}{2};1}(\delta^2)\left(R^*(1-\delta^2)\right)^{-4}\right]$$

[Wang and Hadjiconstantinou, *Phys. of Fluids* (2015)]

Excellent agreement with MD simulation…

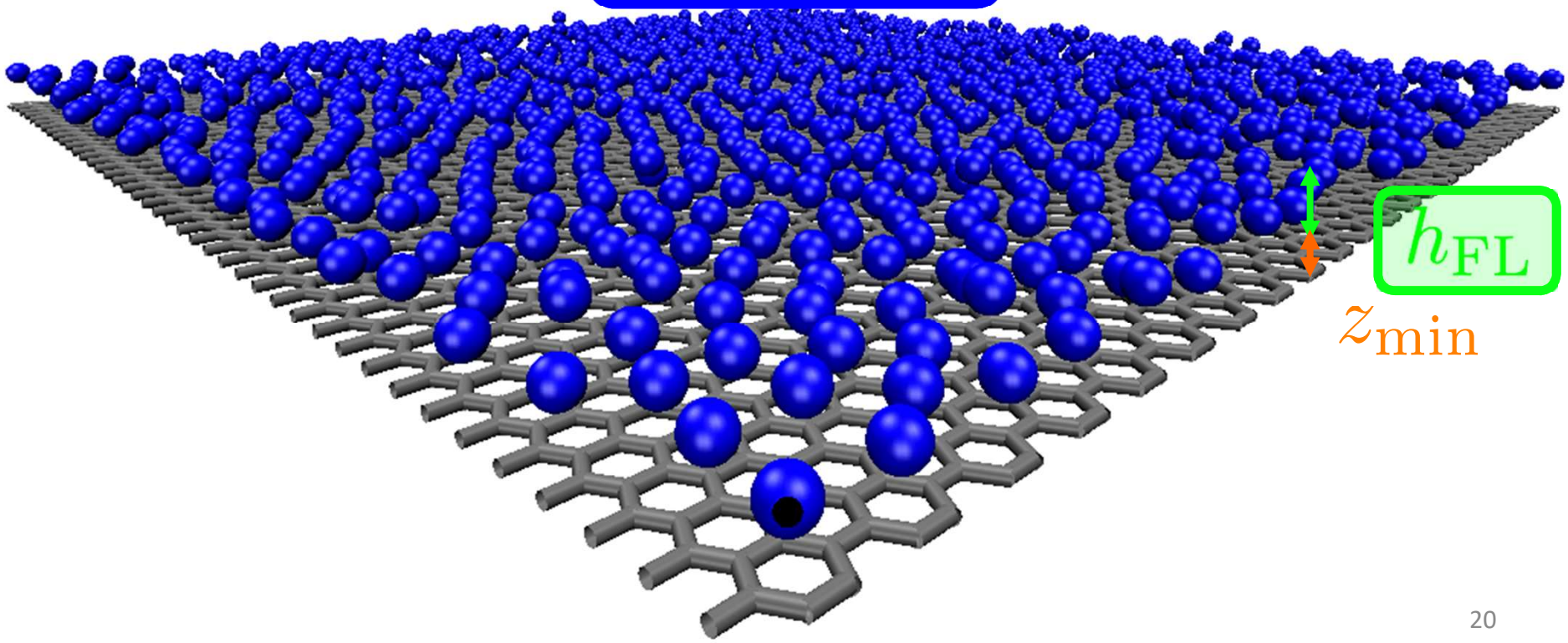


$$\left[\frac{63}{32}F_{-\frac{9}{2};-\frac{9}{2};1}(\delta^2)\left(R^*(1-\delta^2)\right)^{-10} - 3F_{-\frac{3}{2};-\frac{3}{2};1}(\delta^2)\left(R^*(1-\delta)^2\right)^{-4}\right] = 0$$

[Wang and Hadjiconstantinou, *Phys. of Fluids* (2015)]

Molecular mechanics and statistical physics are the flour and butter of this work.

$$\Sigma_{\mathrm{FL}} \equiv \frac{N_{\mathrm{FL}}}{A_{\mathrm{interface}}}$$



To bake a great cake, you have to start from scratch.

Starting from the steady Nernst-Planck equation…

$$\frac{d^2\rho}{dz^2} = -\frac{d}{dz}\left(\frac{\rho}{k_B T}\frac{d(U_\mathrm{w}+U_\mathrm{f})}{dz}\right) \qquad \frac{d\rho}{dz} = -\frac{\rho}{k_B T}\frac{d(U_\mathrm{w}+U_\mathrm{f})}{dz}$$

Re-cast the wall-fluid and fluid-fluid interactions; identify a small parameter…

$$\frac{U_\mathrm{w}}{k_B T} = \mathrm{Wa}\ \tilde{U}_\mathrm{w} \qquad \frac{U_\mathrm{f}}{k_B T} = \epsilon \mathrm{Wa}\ \tilde{U}_\mathrm{f} \qquad \epsilon = \frac{\rho_\mathrm{ave}\sigma_\mathrm{wf}\varepsilon_\mathrm{ff}}{n\varepsilon_\mathrm{wf}}$$

[Wang and Hadjiconstantinou, *Phys. Rev. Fluids* (2017)]

To bake a great cake, you have to start from scratch.

Fluid density is governed by…

$$\frac{d\rho}{dz} = -\mathrm{Wa}\ \rho\left(\frac{d\tilde{U}_{\mathrm{w}}}{dz} + \epsilon\frac{d\tilde{U}_{\mathrm{f}}}{dz}\right)$$

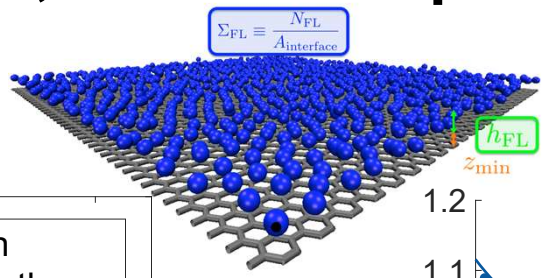
Consequently…

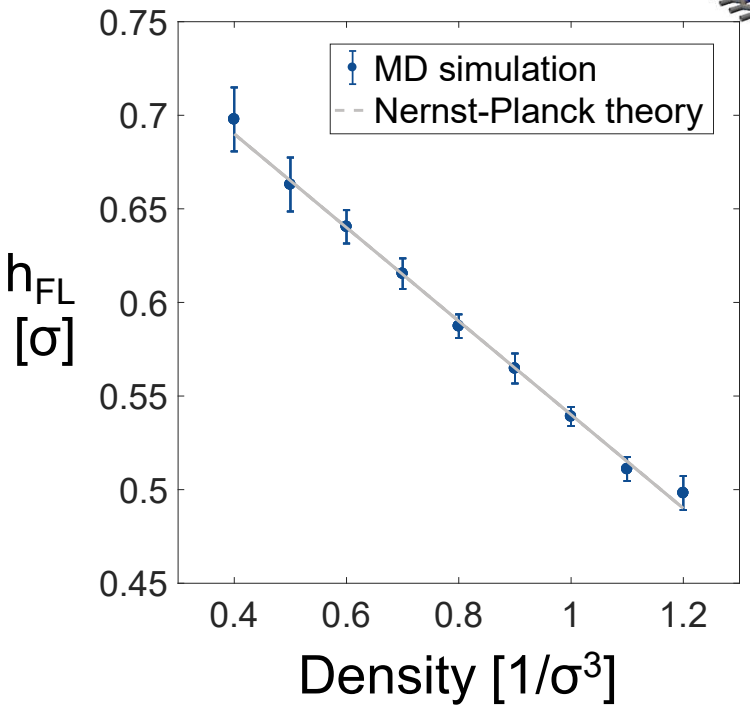
$$\Sigma_{\mathrm{FL}}(\rho_{\mathrm{ave}}, T) \approx a_1(T)\rho_{\mathrm{ave}} + a_2(T)\rho_{\mathrm{ave}}^2 + a_3(T)\rho_{\mathrm{ave}}^3$$

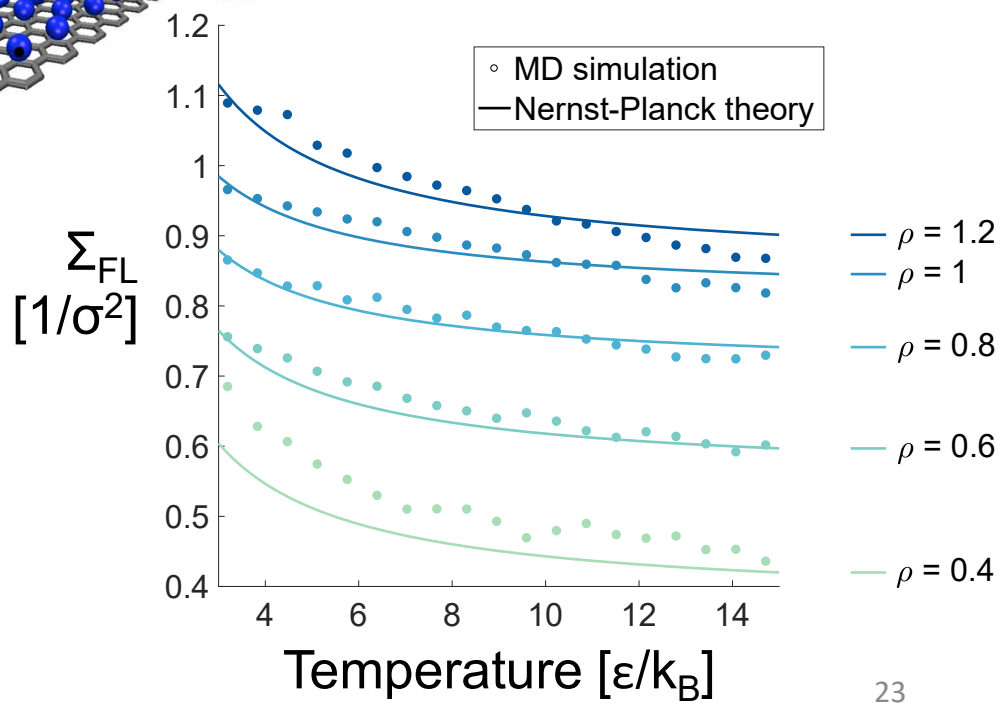
$$h_{\mathrm{FL}}(\rho_{\mathrm{ave}}) \approx h_0 - k\rho_{\mathrm{ave}}$$

[Wang and Hadjiconstantinou, *Phys. Rev. Fluids* (2017)]

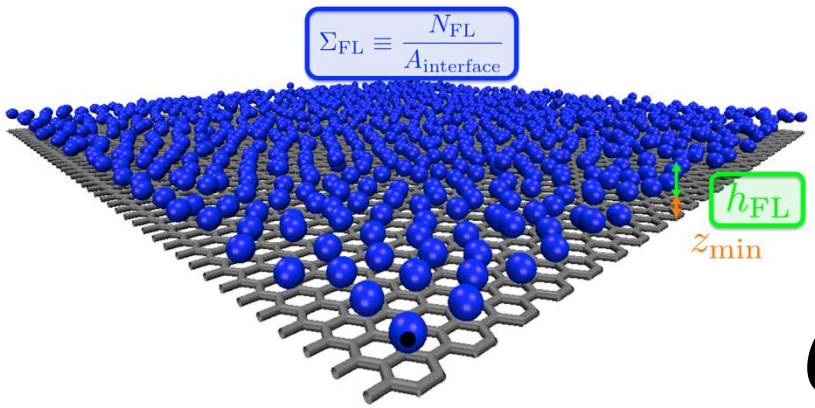
Cake structure depends on the density of the batter, the stickiness of the pan, and the temperature of the oven.







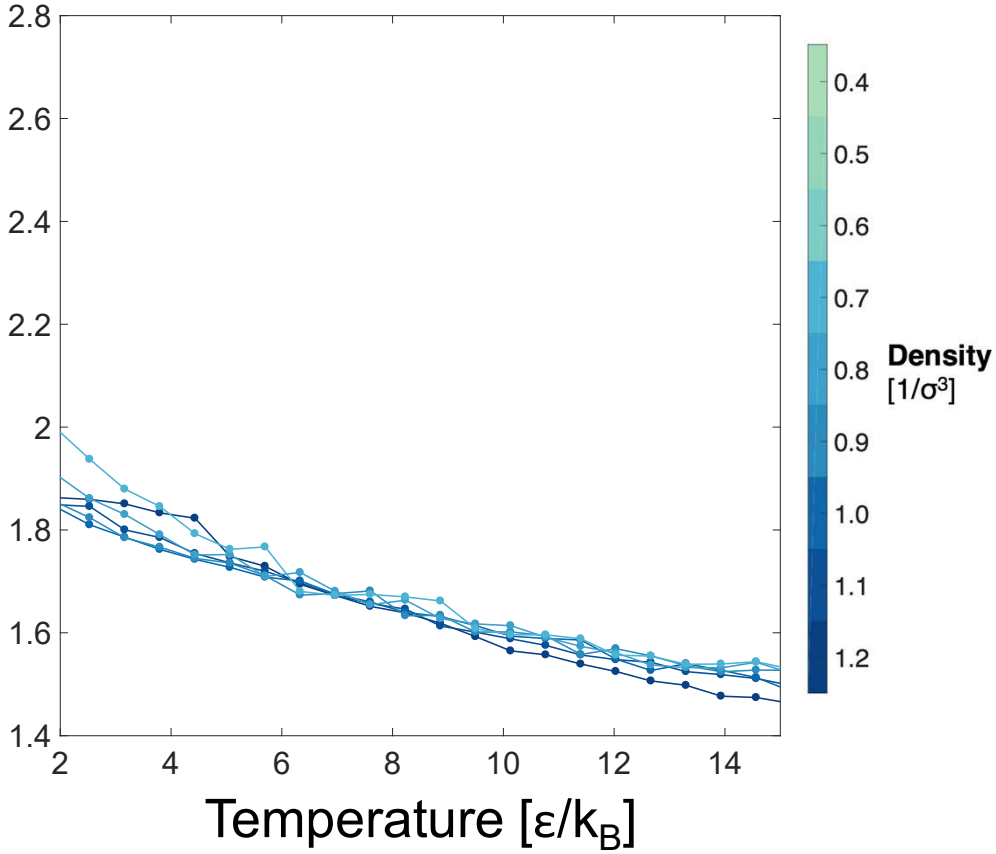
There is a universal recipe for fluid layering at an interface.



Density enhancement of the first layer:

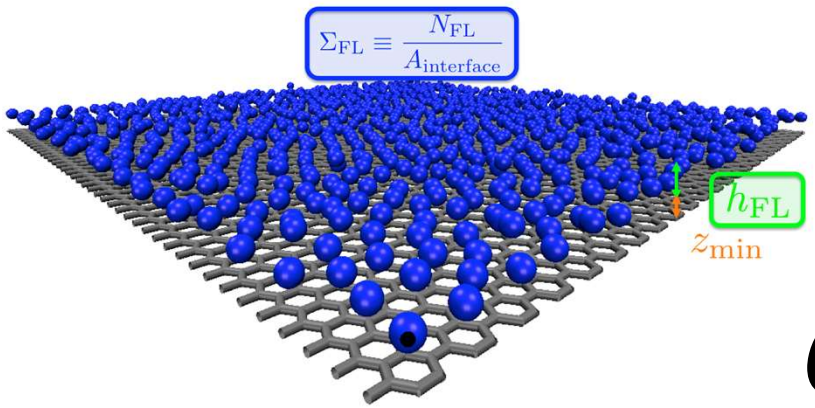
$$\mathcal{C} \equiv \frac{\rho_{\mathrm{FL}}}{\rho_{\mathrm{ave}}} = \frac{\Sigma_{\mathrm{FL}}/h_{\mathrm{FL}}}{\rho_{\mathrm{ave}}}$$

$\mathcal{C}$

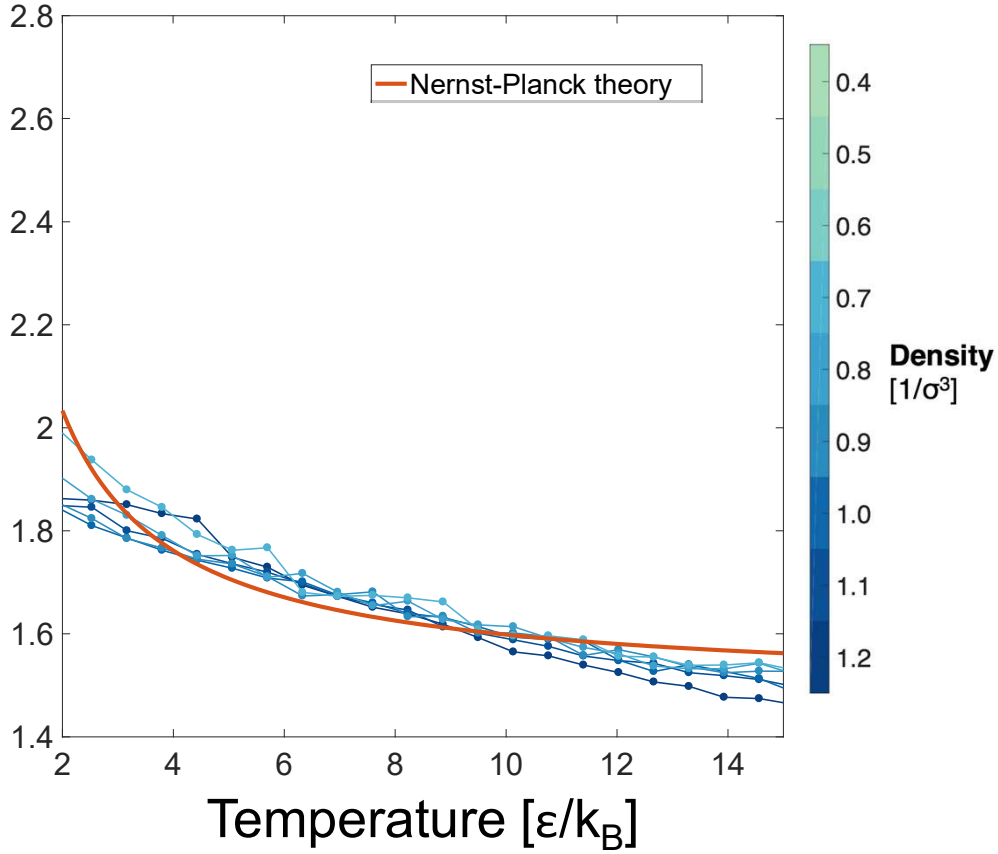


[Wang and Hadjiconstantinou, *Phys. Rev. Fluids* (2017)]

There is a universal recipe for fluid layering at an interface.



$\mathcal{C}$



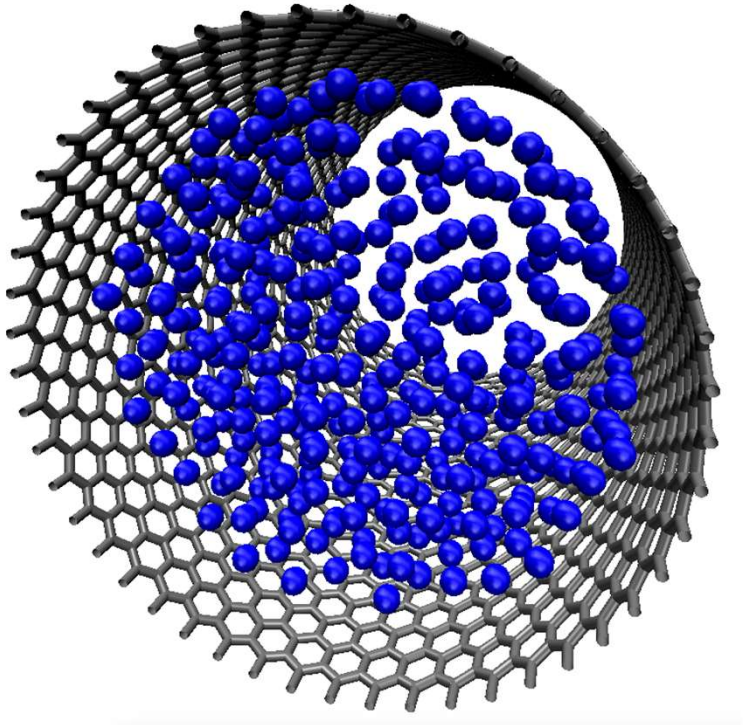
Density enhancement of the first layer:

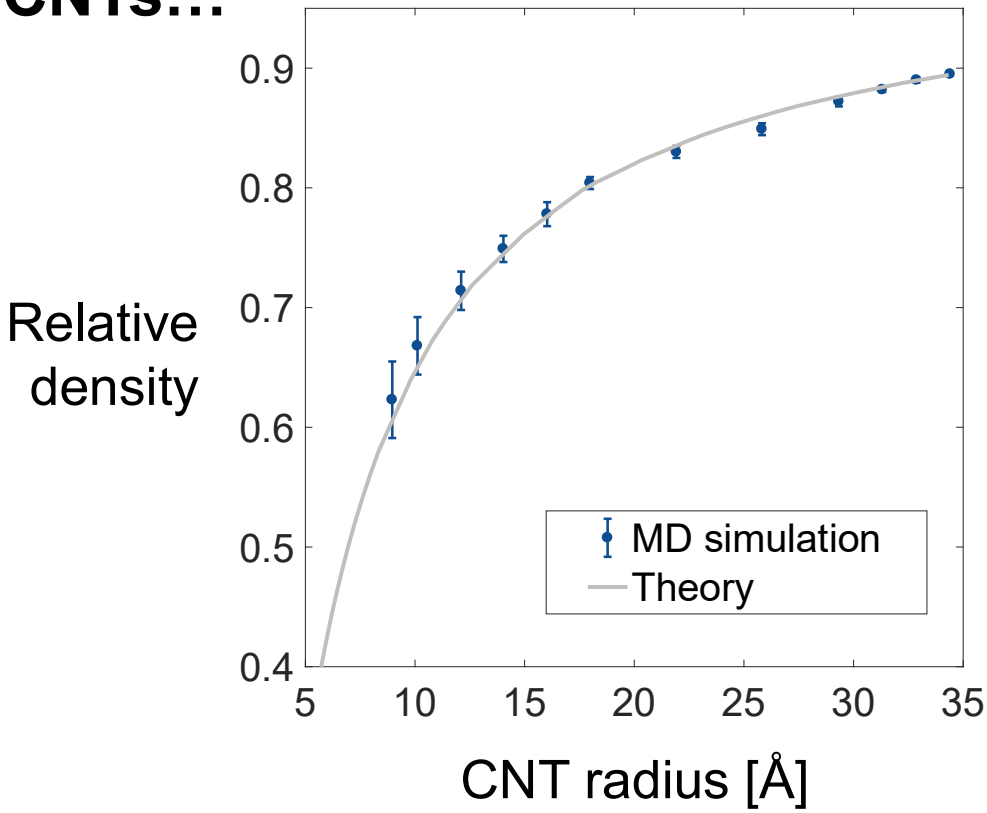
$$\mathcal{C} \equiv \frac{\rho_{\mathrm{FL}}}{\rho_{\mathrm{ave}}} = \frac{\Sigma_{\mathrm{FL}}/h_{\mathrm{FL}}}{\rho_{\mathrm{ave}}}$$

[Wang and Hadjiconstantinou, *Phys. Rev. Fluids* (2017)]

Structure → **Transport**

Using information about structure as a new ingredient for transport modeling: flow in CNTs…

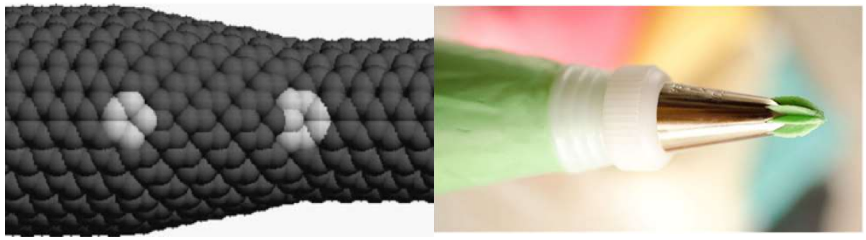




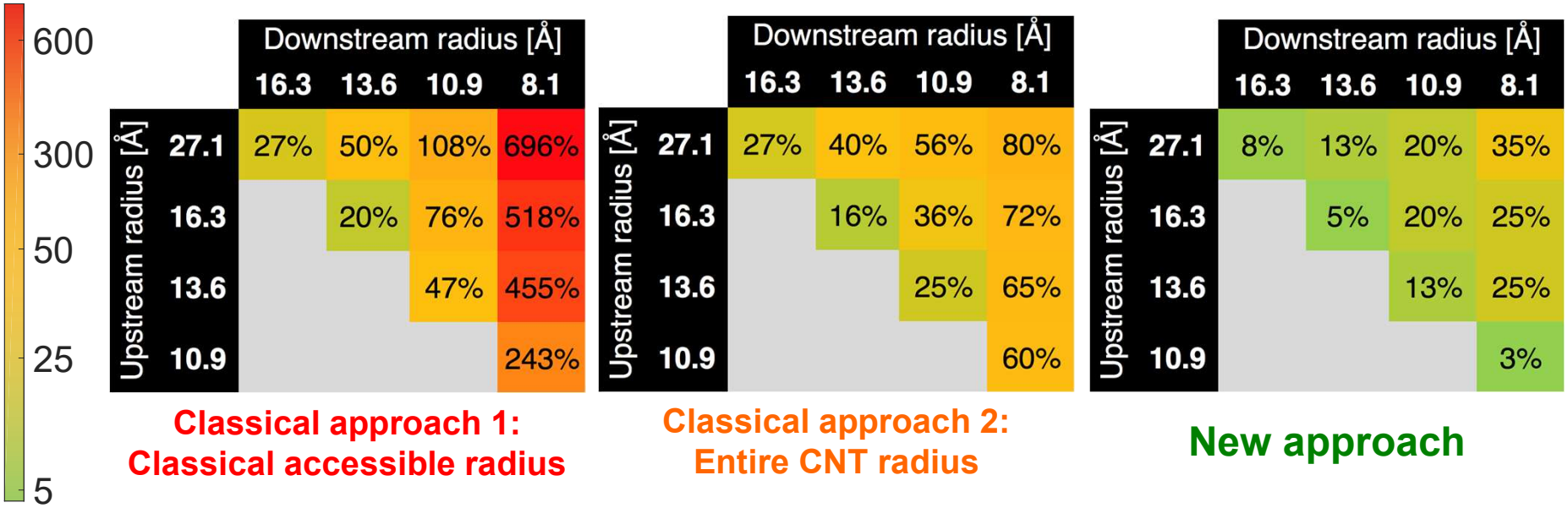
[Wang and Hadjiconstantinou, *Phys. of Fluids* (2015)]

Theory can yield significant improvements in modeling of nanofluidic devices.

Applied to a nanoscale frosting tip…



% error in flow rate



Classical approach 1: Classical accessible radius

Classical approach 2: Entire CNT radius

New approach

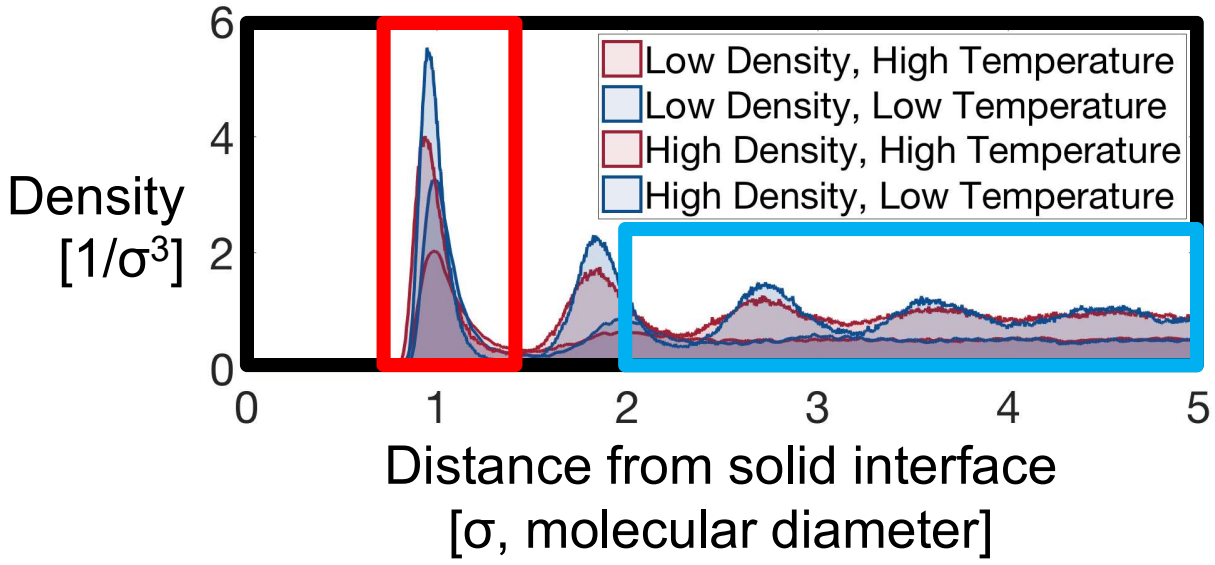
[Hanasaki and Nakatani, *Nanotech*. (2006)] [Wang and Hadjiconstantinou, *Phys. of Fluids* (2015)]

Using information about structure as a new ingredient for transport modeling: diffusion under confinement…

$$D_R = \frac{1}{N_R} \sum_{i=1}^{N_R} \frac{\langle r_i^2 \rangle}{6\Delta t}$$

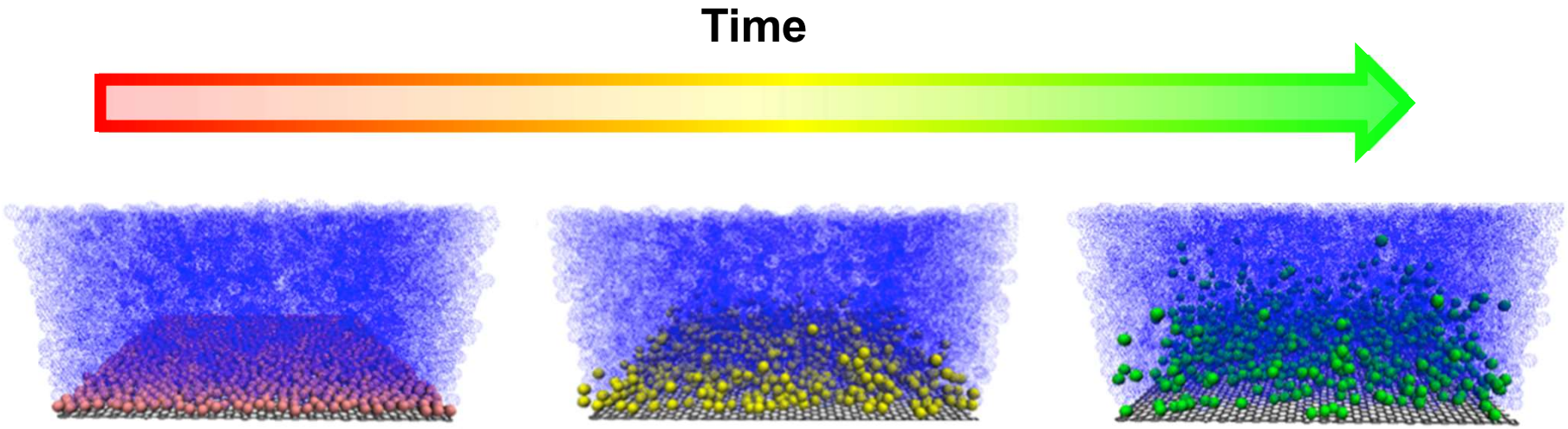
Track particles that are located in each region *R* where *R* can refer to…

- First layer (D_{FL})
- Bulk (D_{bulk})
- Entire system (D_{all})



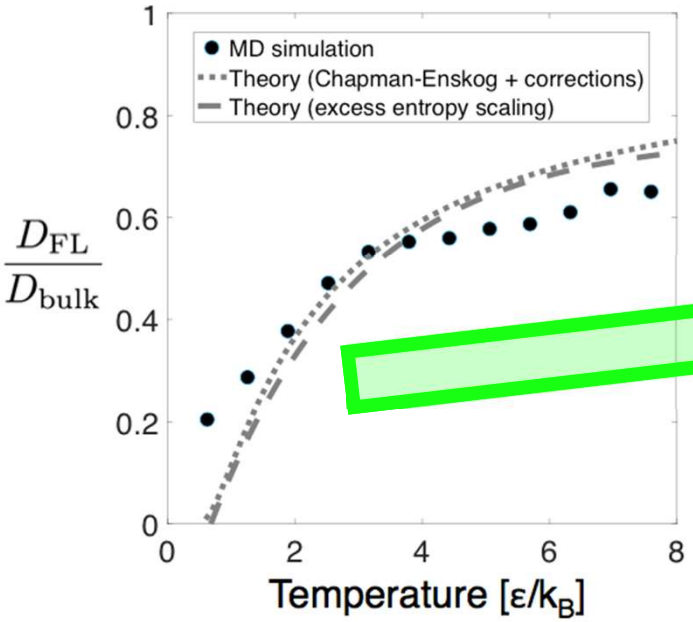
[Wang and Hadjiconstantinou, *Langmuir* (2018)]

Leverage knowledge of structure to improve models for transport: diffusion under confinement…

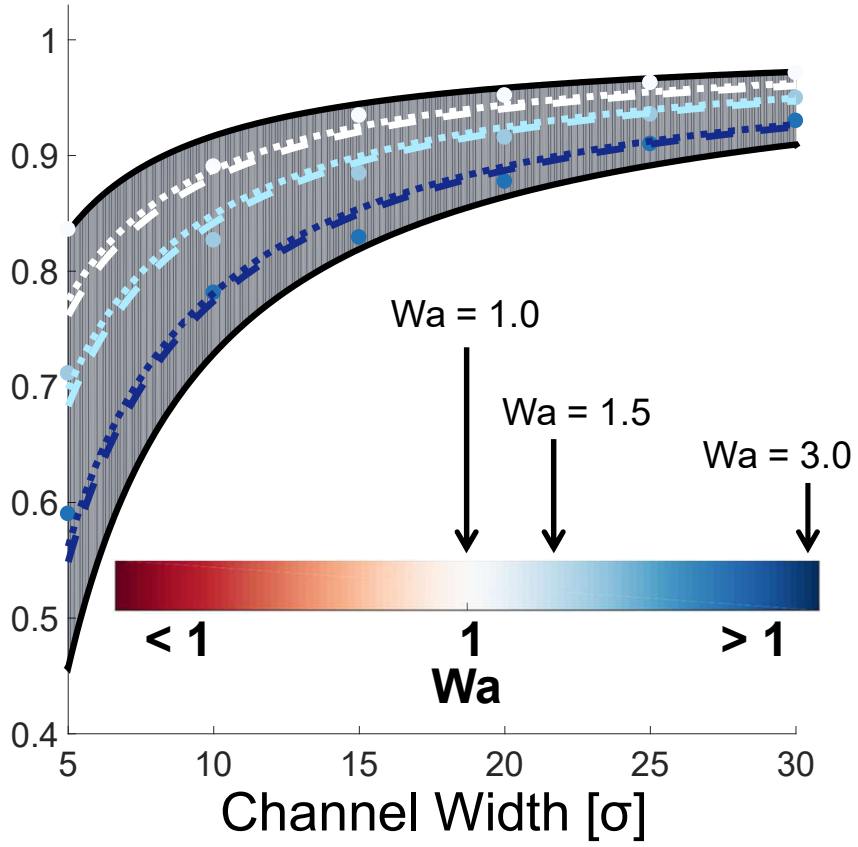


[Wang and Hadjiconstantinou, *Langmuir* (2018)]

Detailed modeling of first-layer diffusivity enables accurate prediction of the diffusivity ratio.



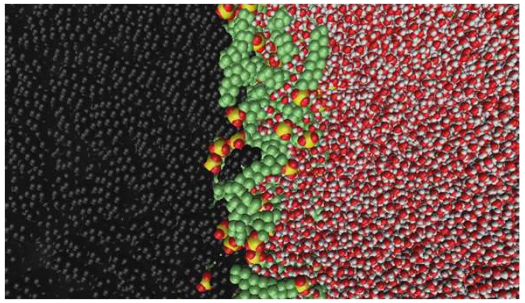
Diffusivity ratio



[Wang and Hadjiconstantinou, *Langmuir* (2018)]

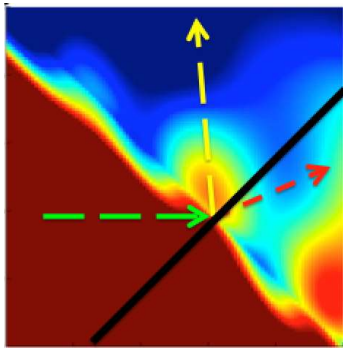
CSGF offers incredible academic freedom.

Area: Nanofluidics of surfactant solutions
Methods: MD, thermodynamics
Collaboration: U Brescia (Italy)



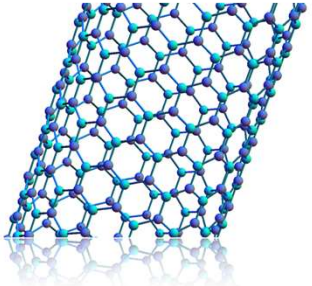
$\mathcal{O}(10^{-15})$

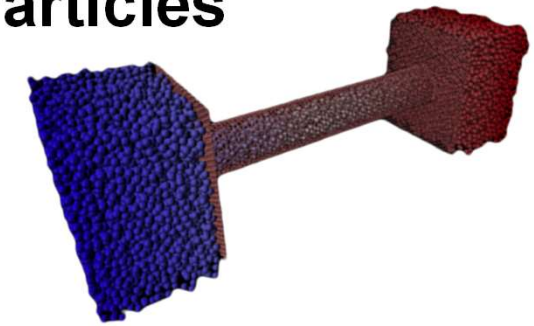
Timescale [sec]



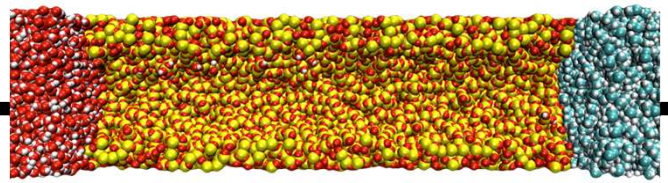
Area: Nanophotonics/ plasmonics
Methods: FDTD, electrodynamics
Collaboration: ANL

Discrete/Particles





Area: Nanofluidic structure and transport
Methods: MD, statistical physics, thermodynamics



$\mathcal{O}(10^{-6})$

Area: Nanoscale contact-line dynamics
Methods: MD, fluid dynamics
Collaboration: U Brescia (Italy)

Continuum/PDE

The benefits of the national lab practicum are tremendous… and sometimes unexpected!

- Try out a different potential career track.
- Apply for computational resources in the future.
- **Meet Hollywood celebrities**.

Walter White & Bogdan Wolynetz

Marius Stan

Argonne National Laboratory
Verified email at anl.gov - Homepage
computational materials sci…

Many thanks for funding and support from…

DOE CSGF

Argonne NATIONAL LABORATORY

Nicolas Hadjiconstantinou
MIT Mechanical Engineering

Petros Koumoutsakos
ETHZ Computational Science

Ju Li
MIT Nuclear Engineering

Daniel Blankschtein
MIT Chemical Engineering

Rohit Karnik
MIT Mechanical Engineering

Stephen Gray
ANL Center for Nanoscale Materials