Properties of liquids in an asymmetric confinement

By

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Acknwoledgments:

Edwin Tendong and
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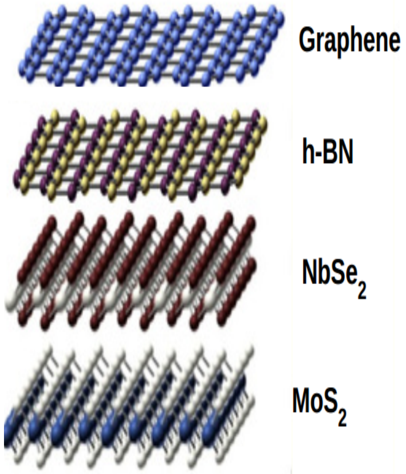
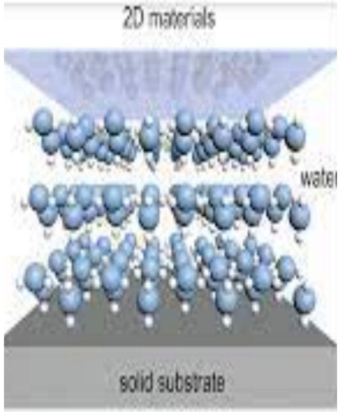
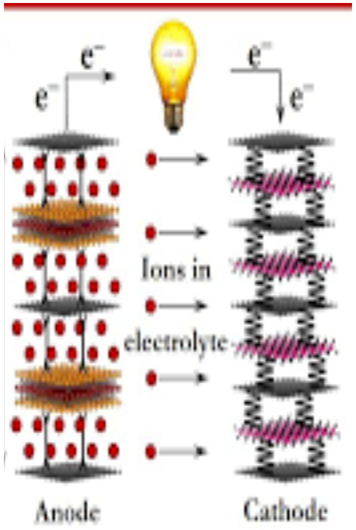
Introduction

Fluid nano-films can be trapped between layers of 2D van der Waals heterostructures





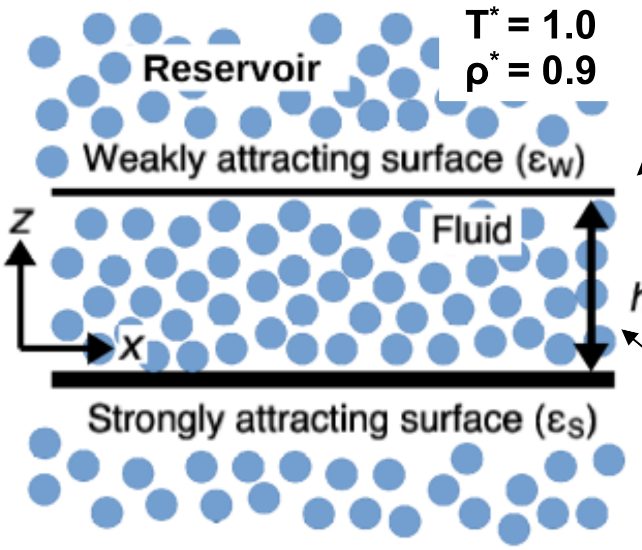


Properties of fluids at nano confined interfaces can be exploited for numerous applications such a as (a)water desalination (b) energy storage

Fig. adapted from Accounts of chemical research 48.1 (2015): 119-127.and *Nano Convergence 1.1 (2014): 1-8 and Nature Energy 2.7 (2017): 1-6.* respectively.

Structure, phase behavior and viscoelastic response of fluid in asymmetric nanoconfinement

1.1 : Model and Simulation details:



Schematic of simulation cell.

$$V_\alpha(z) = 4\varepsilon_\alpha\left[\frac{2}{15}\left(\frac{\sigma}{z}\right)^9 - \left(\frac{\sigma}{z}\right)^3\right]$$

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

Fluid-fluid interactions

$$\xi = \frac{\varepsilon_{\mathbf{s}}}{\varepsilon_{\mathbf{w}}}$$

asymmetry

Simulation scheme

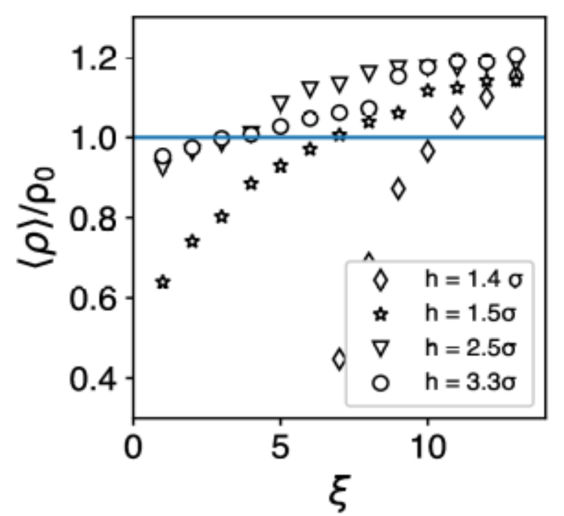
Determine chemical potential of bulk phase point

Carry out **GCMC Simulations** (Constant chemical potential) for **different values of symmetry. Calculate structural quantities**

For **5 random configurations** from each GCMC simulation. perform **NVE simulations Calculate viscoelastic properties averaged over the 5 trajectories**

Structure and phase behavior

(a)



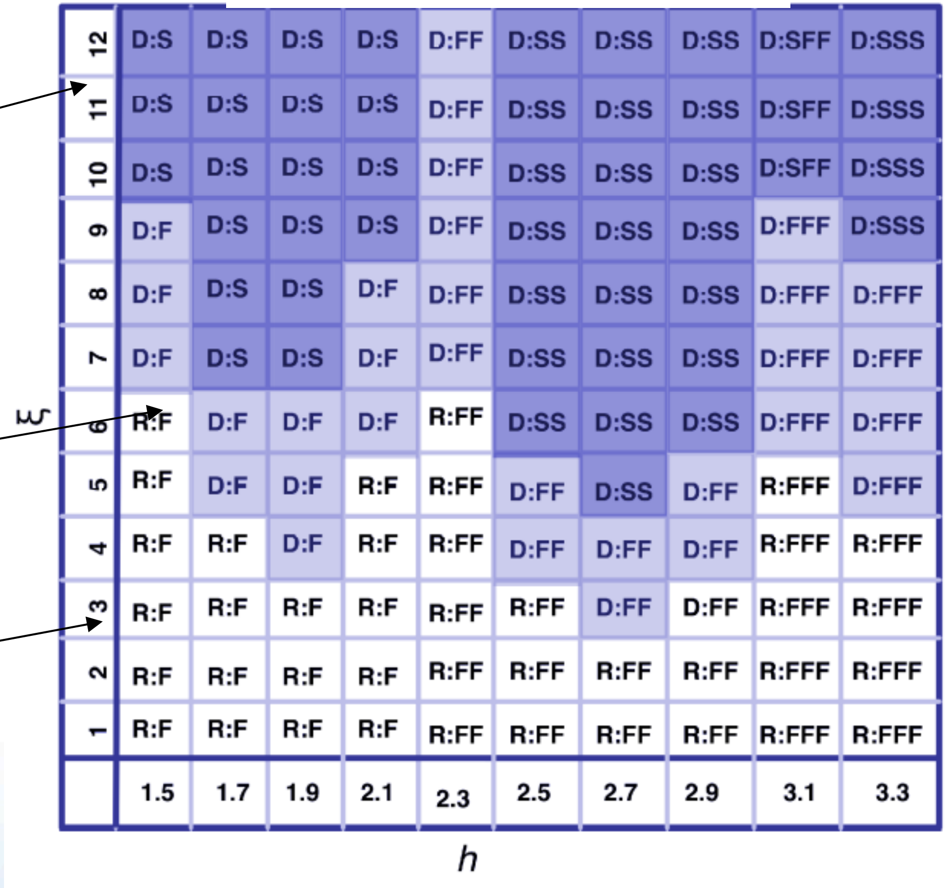
$$\Psi_6 = \left\langle \left| \frac{1}{N_j} \sum_{k}^{N_j} e^{i6\theta_{jk}} \right| \right\rangle$$

(b)

D and S

D and **F**

R and **F**



12	D:S	D:S	D:S	D:S	D:FF	D:SS	D:SS	D:SS	D:SFF	D:SSS
11	D:S	D:S	D:S	D:S	D:FF	D:SS	D:SS	D:SS	D:SFF	D:SSS
10	D:S	D:S	D:S	D:S	D:FF	D:SS	D:SS	D:SS	D:SFF	D:SSS
9	D:F	D:S	D:S	D:S	D:FF	D:SS	D:SS	D:SS	D:FFF	D:SSS
8	D:F	D:S	D:S	D:F	D:FF	D:SS	D:SS	D:SS	D:FFF	D:FFF
7	D:F	D:S	D:S	D:F	D:FF	D:SS	D:SS	D:SS	D:FFF	D:FFF
6	R:F	D:F	D:F	D:F	R:FF	D:SS	D:SS	D:SS	D:FFF	D:FFF
5	R:F	D:F	D:F	R:F	R:FF	D:FF	D:SS	D:FF	R:FFF	D:FFF
4	R:F	R:F	D:F	R:F	R:FF	D:FF	D:FF	D:FF	R:FFF	R:FFF
3	R:F	R:F	R:F	R:F	R:FF	R:FF	D:FF	D:FF	R:FFF	R:FFF
2	R:F	R:F	R:F	R:F	R:FF	R:FF	R:FF	R:FF	R:FFF	R:FFF
1	R:F	R:F	R:F	R:F	R:FF	R:FF	R:FF	R:FF	R:FFF	R:FFF
	1.5	1.7	1.9	2.1	2.3	2.5	2.7	2.9	3.1	3.3

ξ

h

Phase Diagram

Different structural phases of asymmetrically confined LJ-fluid in **h - ξ** plane. Symbols **R** and **D** stand for phases **rarer** or **denser** than the bulk phase respectively, while **F** and **S** denote bond-orientationally **disordered** or **ordered** fluid layers respectively.

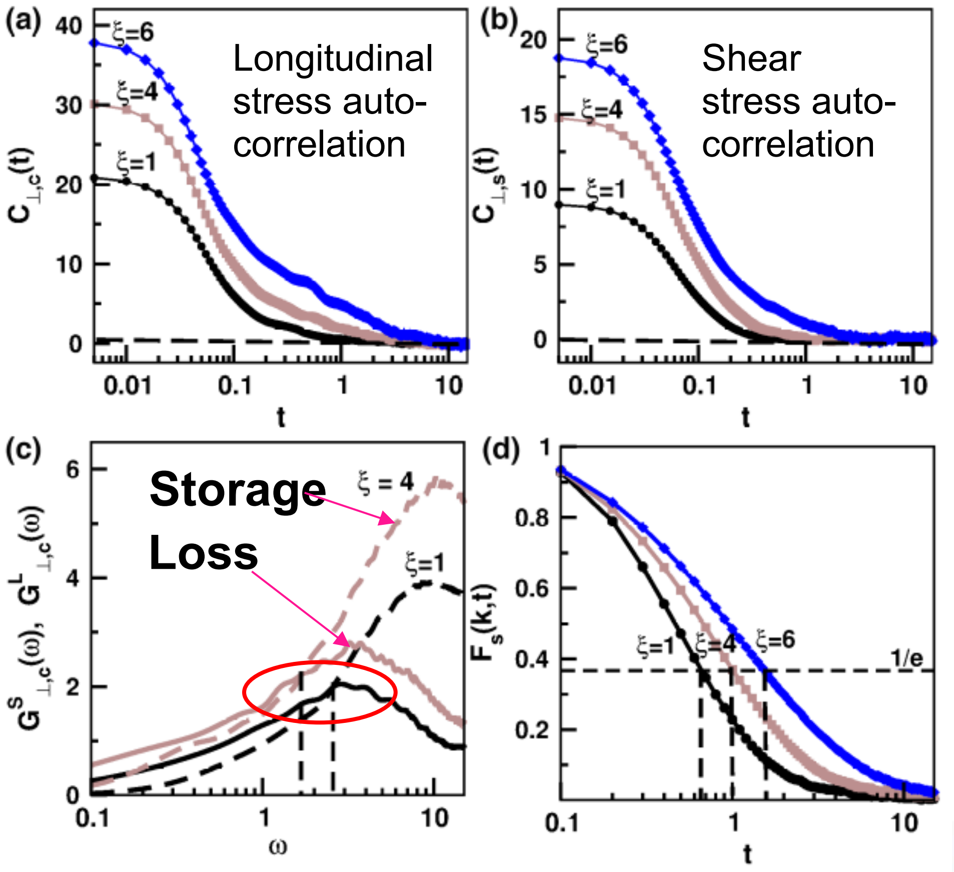
Viscoelastic response

- We do MD simulations in NVE ensemble using the configurations from the GCMC simulations
- The frequency dependent viscosity is calculated using the **generalized Green-Kubo relation**

$$\boxed{\eta_{\alpha\beta}(\omega) = \frac{V}{k_B T}\int_0^\infty C_{\alpha\beta}(t)e^{-i\omega t}dt \quad = \quad \eta'_{\alpha\beta}(\omega) - i\eta''_{\alpha\beta}(\omega)} \qquad (\alpha, \beta = x, y, z)$$

One obtains the **Loss** and and **Storage** Moduli respectively as:

$$G^L_{\alpha\beta}(\omega) = \omega\eta'_{\alpha\beta}(\omega) \qquad\qquad G^S_{\alpha\beta}(\omega) = -\omega\eta''_{\alpha\beta}(\omega)$$



The viscoelastic relaxation time is the inverse frequency at which the Loss modulus is equal to the storage modulus

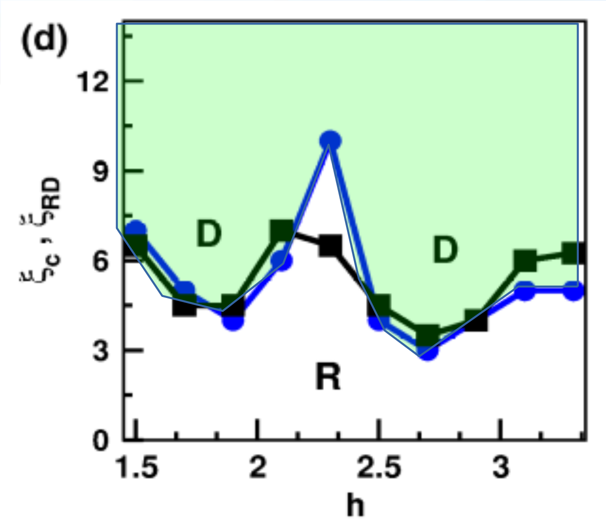
$$G^S_{\perp,c}(\omega_o) = G^L_{\perp,c}(\omega_o)$$

$$\tau_{\perp,c} = \frac{1}{\omega_o}$$

1.3 contd. : Viscoelastic response

Comparing the structural relaxation time τ_R and the viscoelastic relaxation time $\tau_{\perp,c}$

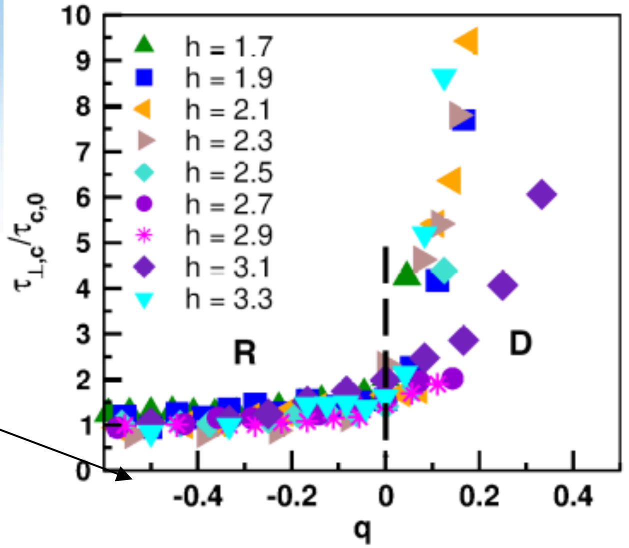
(1)



The profile traced by ξ_c closely matches that of ξ_{RD}

(2)

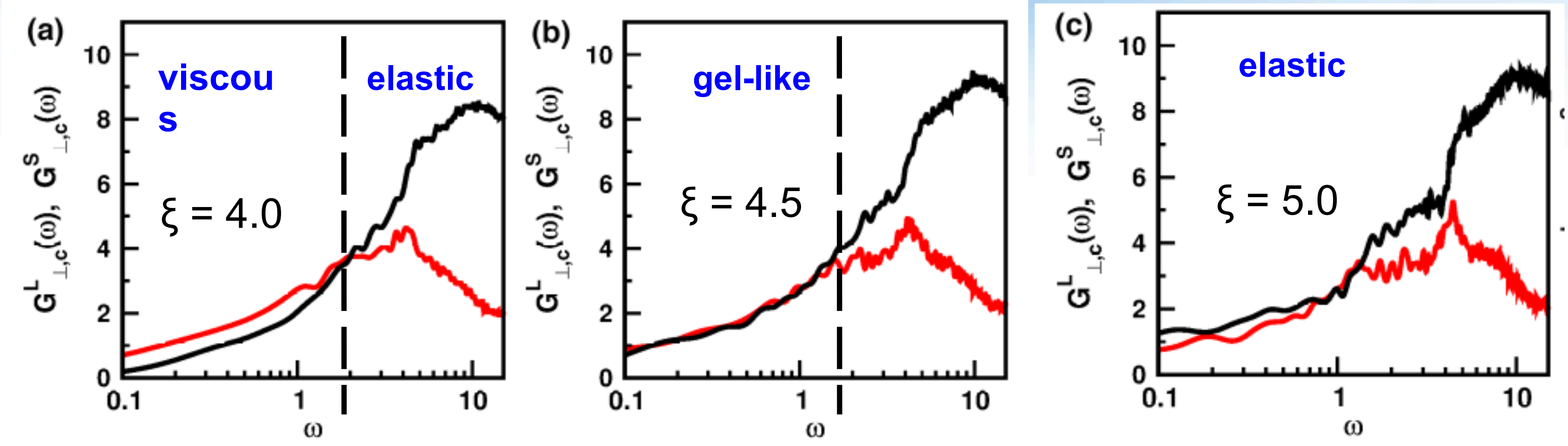
$$q = \frac{(\xi - \xi_c)}{\xi_c}$$



Viscoelastic relaxation time as a function of the scaled asymmetry, for different slit widths

1.3 contd. : Viscoelastic response

Response close to Fluid-Solid transition



Summary

1) We find a **R** → **D** crossover and **F** → **S** transition with increasing asymmetry ξ
2) Two regime trend in viscoelastic relaxation, universal for different slit heights, driven by contributions from the strongly and weakly adsorbed fluid layers.
3) The **F** → **S** transition shows an intermediate coexistence region with gel-like response.

TWAS-SN Bose Postgraduate Fellowship

Thank You