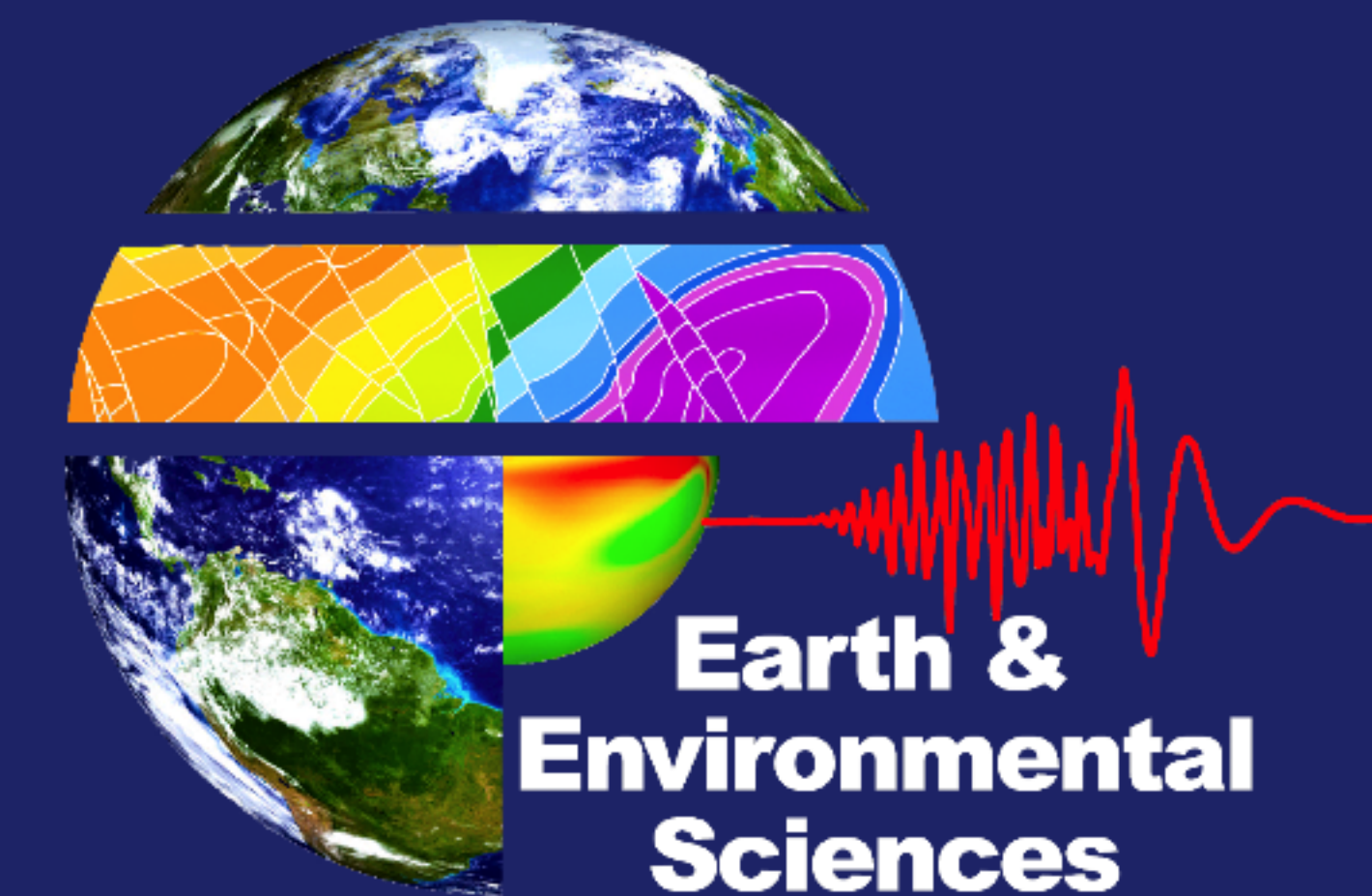


# Molecular Simulations of Kerogen Wettability

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## ABSTRACT

The economical hydrocarbon production from shale formations has brought a paradigm-shift in the energy landscape. The content and maturity of the organic matter in shale formation determine its hydrocarbon potential. Despite the significance of the organic pores in the storage and fluid flow, their surface chemistry is poorly-understood. Herein, we investigate the organic\kerogen pores. We have constructed a kerogen substrate where we placed a cylindrical droplet to avoid line tension. We measured the water/vapor and water/CO<sub>2</sub> contact angle. Intuitively, there is strong interdependence between the surface chemistry and wettability. However, the surface wettability is a multiscale concept. We directly measured the contact angle which is used to infer the wettability state of the surface. We also analyzing the intermolecular forces at the play aiming to find a microscopic measure of the wettability to replace the contact angle.

## Introduction

Understanding the fluid flow in shale nanopores is the key to devise developments strategies to improve the recovery factor. However, the wettability of the organic pores is still poorly-understood.<sup>1</sup> The complexity stems from the heterogeneity nature of the surface chemistry. Given the significant impact of wettability on the fluid flow in porous media<sup>2</sup>, we are proposing a workflow to study the wettability of organic pores.

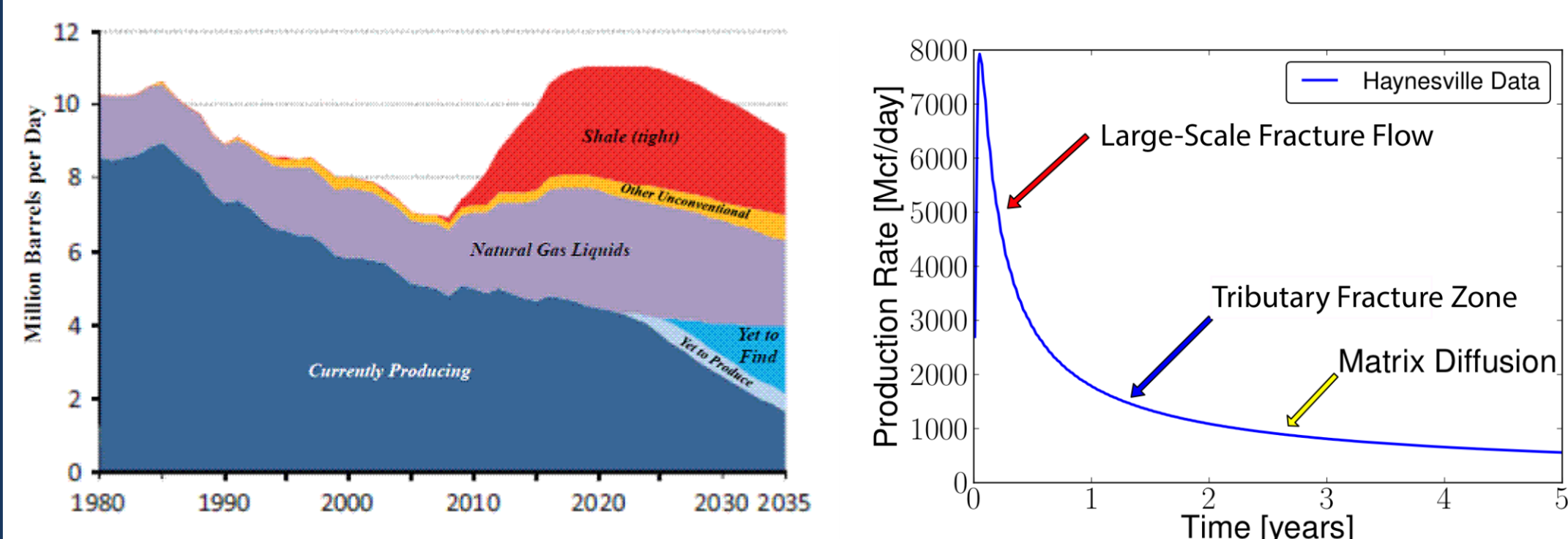


Fig. 1 a) US historical and projected oil production b) Typical production curve of shale well where the late production is controlled by the matrix processes .

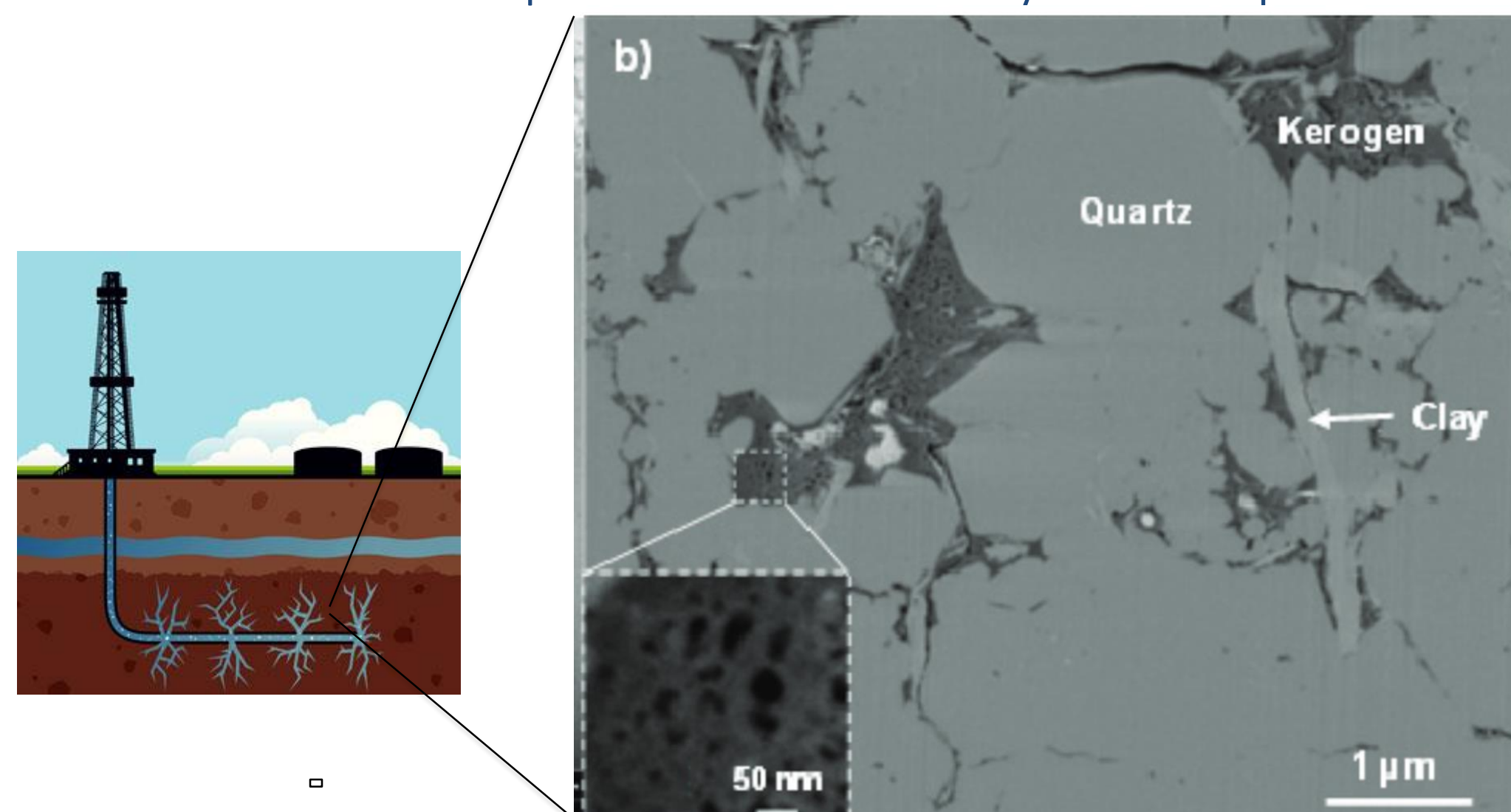


Fig. 2 Schematic of a horizontal well with multi-stage fractures along with a closer look of the rock fabric. The heterogeneity of the rock is evident with a significant presence of the organic matter.

## Methodology

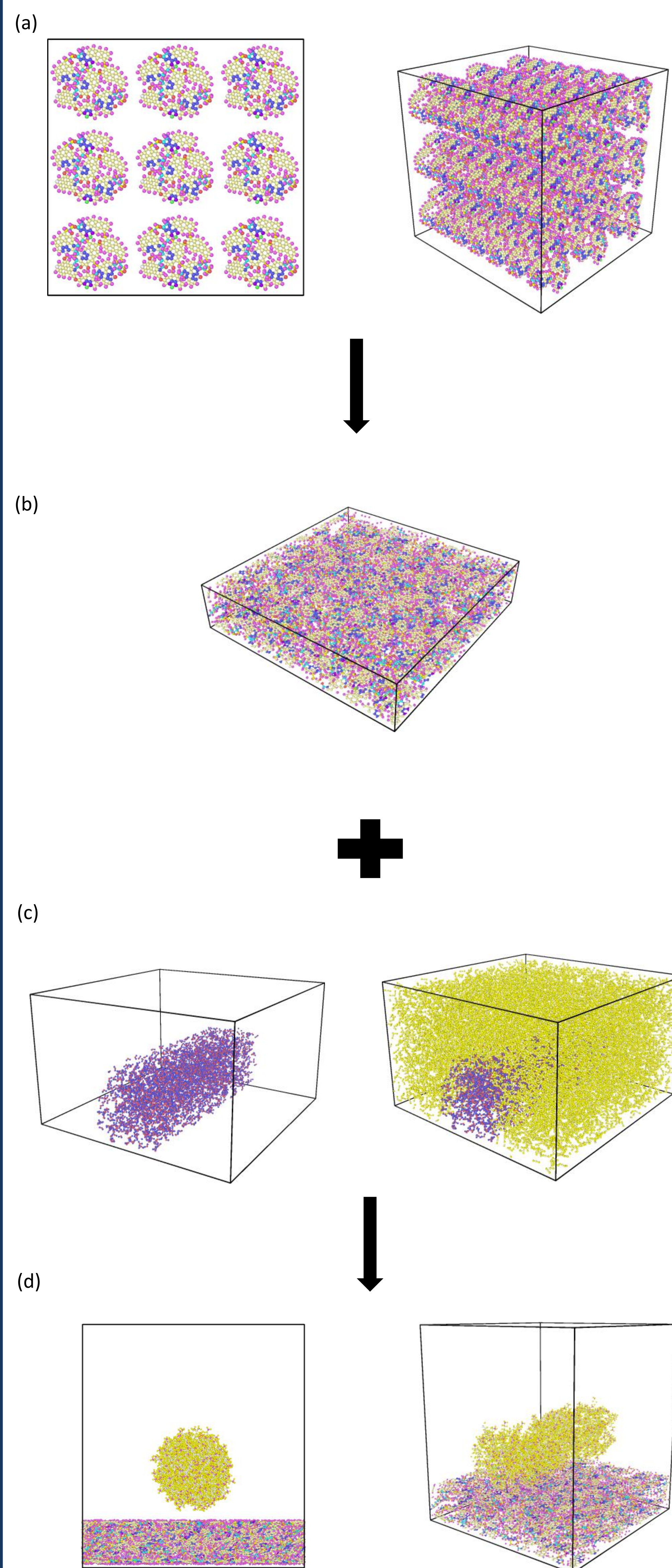


Fig. 3 Workflow to build the simulation system. a) 61 kerogen (over-mature) molecules are placed in a simulation box b) The simulation system is annealed from 1000 to 300 K over 100 ps where the cut-off of LJ interactions is 5 Å and the box volume is constantly deformed to achieve the desired density. After that, the system is equilibrated for 100 ps on NVT ensemble and 2 ns on the NPT ensemble. c) The cylindrical-droplets are equilibrated. d) Fluid and substrate are brought together and the production run lasts for 10 ns.

## Results

- The presence of carbon dioxide has shifted the wettability state of the substrate from water-wetting to almost completely CO<sub>2</sub>-wetting. We are currently conducting another set of simulations to measure the contact angle when one of the liquid phases is a hydrocarbon.
- We have analyzed the molecular interactions where we found that the wettability state of the kerogen is mostly driven by the VDW interactions.
- The current simulation is performed at 200 bar and 300 K. At these conditions, CO<sub>2</sub> is supercritical which might explain its superior wetting characteristics.

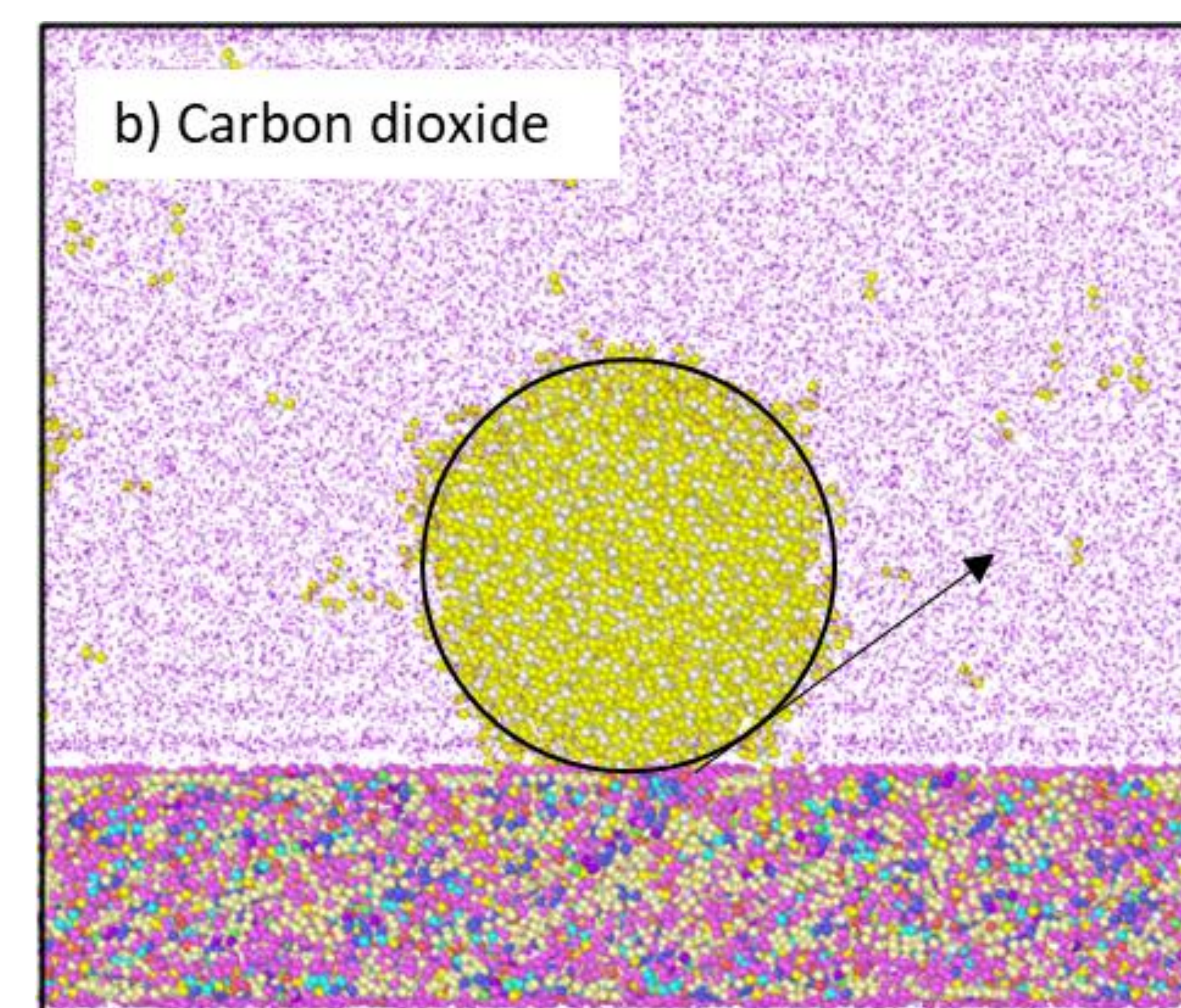
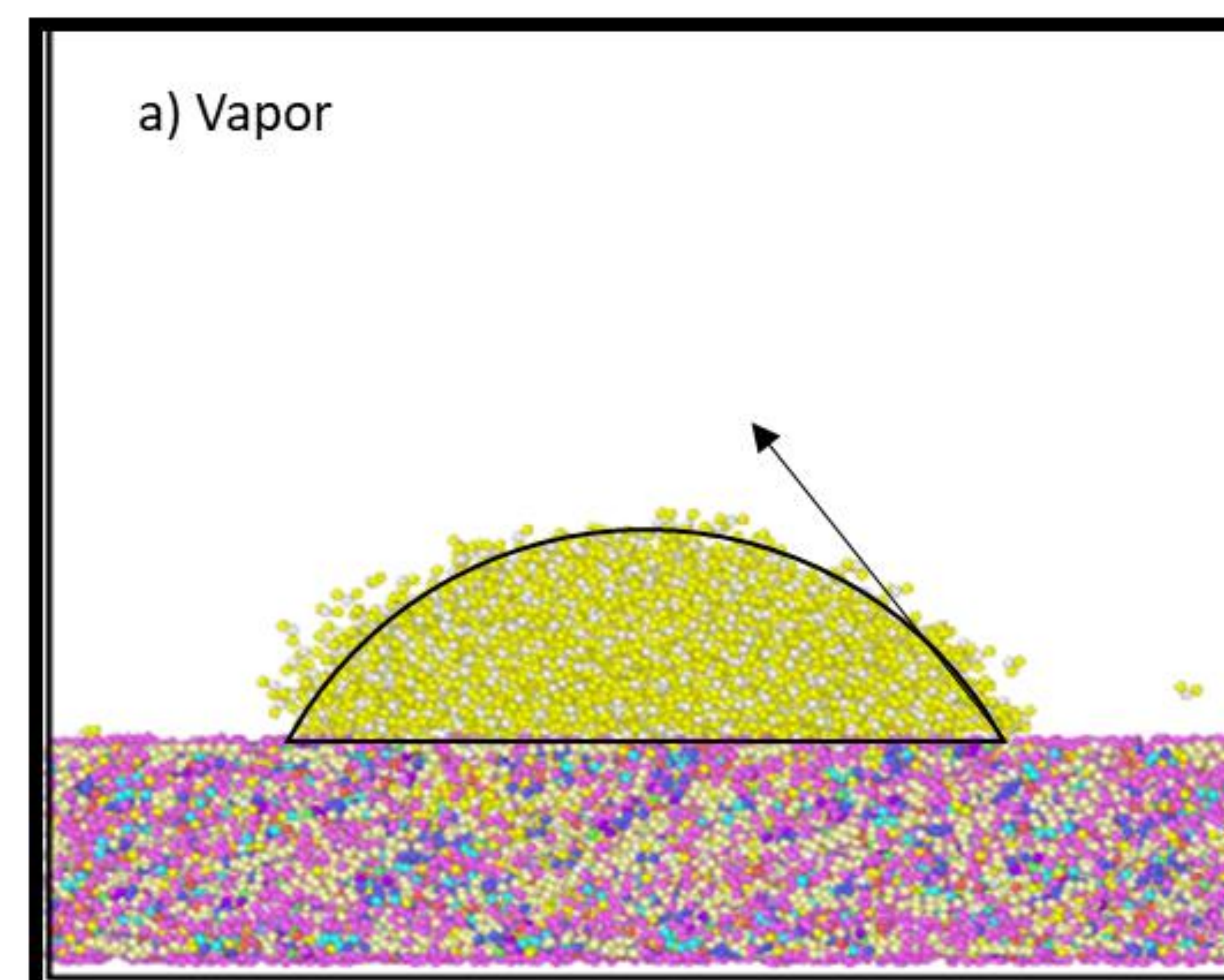


Fig. 4 Contact angle measurements at 300 K a) Water/vapor system b) Water/carbon dioxide system.

## Conclusions

- We are presenting a **workflow to study the wettability of the kerogen pores**. Although there is no definite chemical structure of the substrate, kerogen fragments is used to generate a substrate. According to the kerogen maturity, the structure of the kerogen fragments is tuned. Once the substrate is formed, a cylindrical droplet of the fluid is placed on the substrate. After equilibrium, the contact angle is measured.
- We observed a liquid-wetting nature for the kerogen surface. This wettability state is **shifted to CO<sub>2</sub>-wetting state in water/CO<sub>2</sub> systems**. This observation has significant implications in both hydrocarbon extraction and CO<sub>2</sub> sequestration.
- It is worth highlighting **the porosity and roughness nature of the kerogen substrate**. The common substrates used to study the wettability at the molecular scale are atomistically-smooth non-porous surface.
- Our ultimate goal is to devise **microscopic measures of the surface wettability**. Currently, the contact angle is the common measure, since it could be easily scaled to field applications. However, several concerns could be raised about the feasibility of molecular simulation to model a macroscopic analog of the fluid droplet.

## Future Work

The natural extension to the current work include these dimensions:

- Molecular forces**  
One of the powerful aspects of molecular simulation is the ability to decouple a complex phenomenon to the key driving forces. We are planning to leverage this tool by relating the observed contact angle with the intermolecular forces at play.
- Water salinity**  
The salinity of the water highly affects the wetting characteristics of the water. In addition, formation water is usually high-salinity brine.
- Surface roughness**  
We are planning to decouple the impact of the surface roughness and chemistry on the resulting contact angle.

## Reference

- Ho, T. A., Wang, Y., Ilgen, A., Criscenti, L. J., & Tenney, C. M. (2018). Supercritical CO<sub>2</sub>-induced atomistic lubrication for water flow in a rough hydrophilic nanochannel. *Nanoscale*, 10(42), 19957-19963.
- Zhao, J., Kang, Q., Yao, J., Viswanathan, H., Pawar, R., Zhang, L., & Sun, H. (2018). The Effect of Wettability Heterogeneity on Relative Permeability of Two-Phase Flow in Porous Media: A Lattice Boltzmann Study. *Water Resources Research*, 54(2), 1295-1311.