

## Electronic Supplementary Information

### Mimicking Wettability Alterations using Temperature Gradient for Water Nanodroplets

Chirodeep Bakli<sup>1</sup>, Sree Hari P D<sup>2</sup> and Suman Chakraborty<sup>3,\*</sup>

<sup>1</sup>Department of Mechanical Engineering, Indian Institute of Technology Ropar, Rupanagar  
140001, INDIA.

<sup>2</sup>School of Engineering, The University of Edinburgh, Edinburgh EH9 3FB, UK.

<sup>3</sup>Department of Mechanical Engineering, Indian Institute of Technology Kharagpur,  
Kharagpur 721302, INDIA.

#### Simulation Details

The molecular dynamics simulations performed here use water as the fluid and the substrate wettability is varied to mimic different chemical structure. The water molecules are modeled using Simple Point Charge/Extended (SPC/E) model<sup>1</sup>, which has 3 sites: one Oxygen (charge: -0.8472e) and two Hydrogen (charge: +0.4236e) sites. The intermolecular interactions between pairs of molecules are based on a combination of Lennard-Jones (LJ) potential shifted up at cut-off distance<sup>2</sup> and Coulomb potentials:

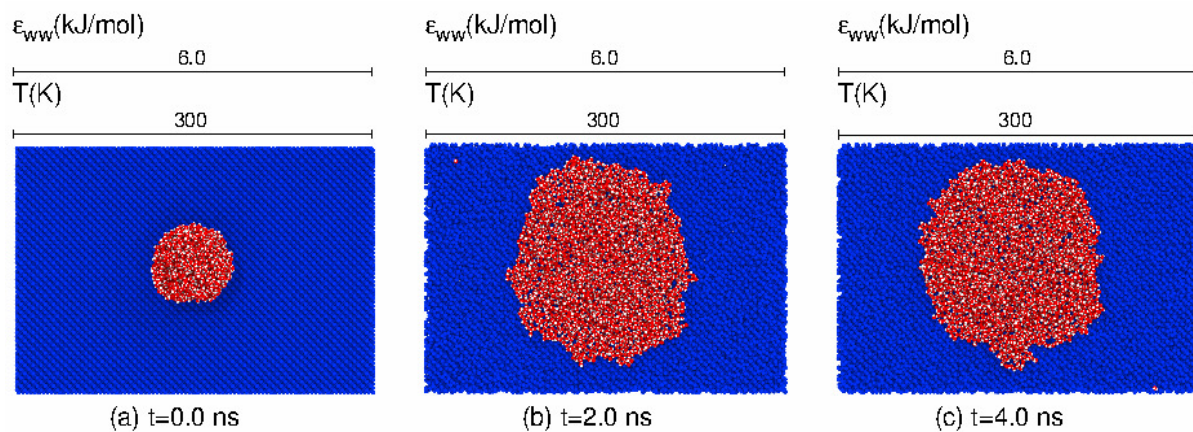
$$u_{ij}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 - \left( \frac{\sigma_{ij}}{r_c} \right)^{12} + \left( \frac{\sigma_{ij}}{r_c} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r}$$

where  $\epsilon_{ij}$  and  $\sigma_{ij}$  are the LJ energy and length parameters between sites  $i$  and  $j$  respectively,  $r$  is the distance between the sites,  $q_i$  is the charge at site  $i$  and  $\epsilon_0$  is the permittivity of vacuum. A cut-off distance of  $r_c = 9.8 \text{ \AA}$  is used for LJ interactions. The spring constant for vibrations of wall atoms is selected such that their vibration will not exceed a threshold value<sup>3</sup>. The long range electrostatic interactions are evaluated using particle-particle particle-mesh (PPPM) algorithm. The interaction parameters for hetero-nuclear interaction are determined using the Lorentz-Berthelot mixing rules. The LJ potential parameters used in the study are given in TABLE 1.

TABLE 1: Lennard-Jones potential parameters used in the study.

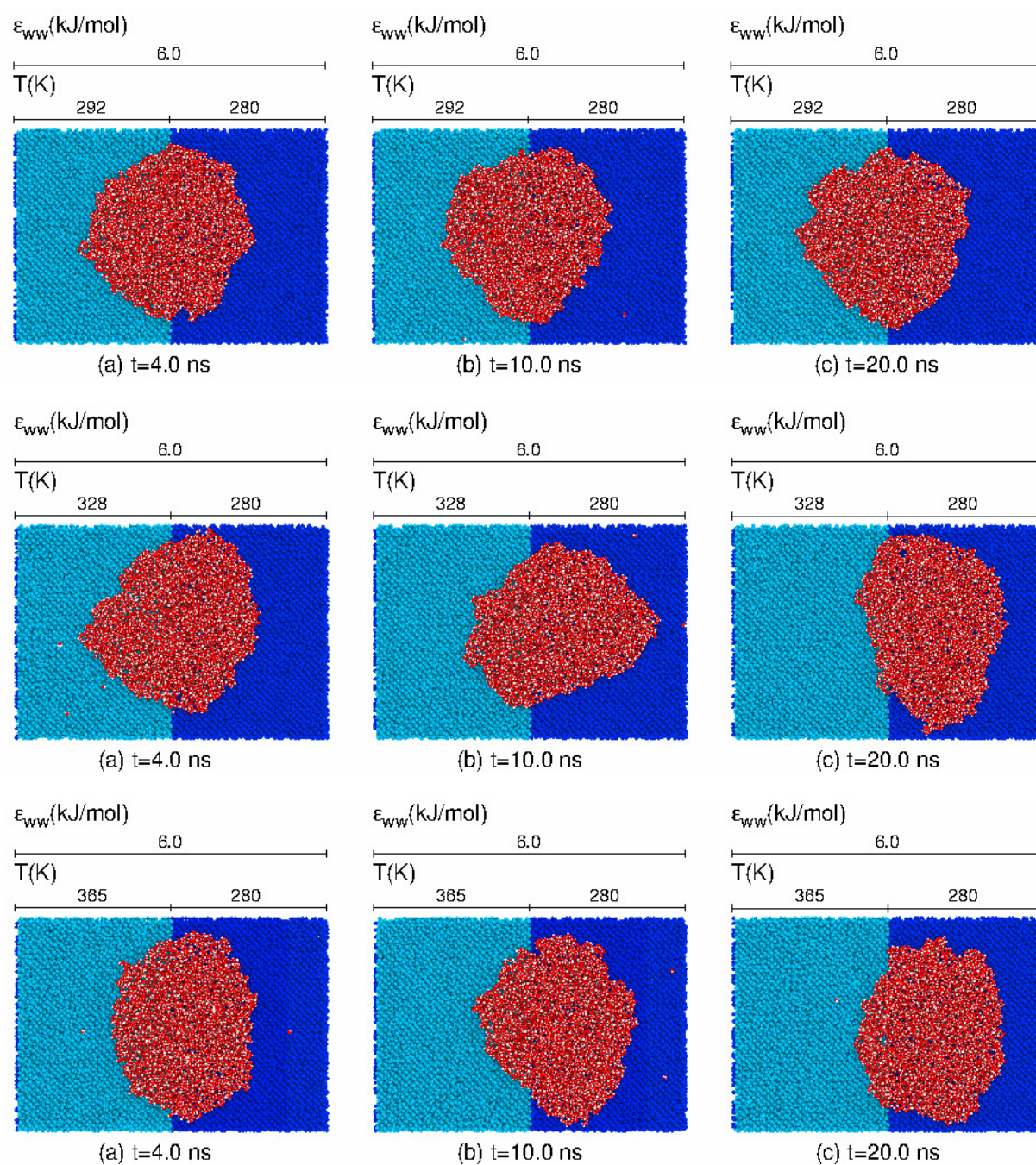
Site	$\epsilon(kJ / mol)$	$\sigma (\text{\AA})$
H	0	0
O	0.650	3.16
Substrate ( $\epsilon_{ww}$ )	0.6-6.0	3.82

Initially, a water cube containing 2500 molecules is equilibrated in a large simulation box and a spherical nanodroplet is obtained. This droplet is then placed over a substrate surface of 21120 atoms arranged in FCC lattice structure with lattice constant 5.43 Å (Fig. S1). The substrate is 24 nm in length, 16.5 nm in span and the thickness is chosen such that the next layer of atoms comes outside the cut-off distance of water-substrate LJ interaction. The attraction between water molecules and the substrate surface will pull down the droplet, initiating the equilibration of droplet over the surface. On a very high hydrophilic surface, complete spreading of the droplet can be observed. The LJ parameters chosen for the wall atoms ensured a contact angle less than 5° for the completely wetting surface. We were able to measure a contact angle of about 8° for  $\epsilon_{ww} = 5.3$  from independent sessile droplet measurements obtaining static contact angle and for greater values of  $\epsilon_{ww}$ , the surface is considered to be completely wetting. On the other hand, the static contact angle simulations for a non-wetting surface with  $\epsilon_{ww} = 0.9$  gives a contact angle of 113°. As the droplet spreads on the surface, its centre-of-mass moves down and attains a steady value over time. The simulation box is periodic in all directions. The length of the box in all directions is kept very large compared to the size of the droplet in order to avoid interactions between periodic images. A Berendsen thermostat with a damping parameter of 200 fs, is applied on the wall to keep its temperature at 300 K during equilibration. The temperature of the water droplet is not controlled by any means. The system is equilibrated for 4 ns in a micro-canonical ensemble with a time step size of 2 fs. In this paper, we discuss the creeping motion of a water nanodroplet over the substrate surface induced by variation in surface temperature. The production run is carried out for 20 ns.

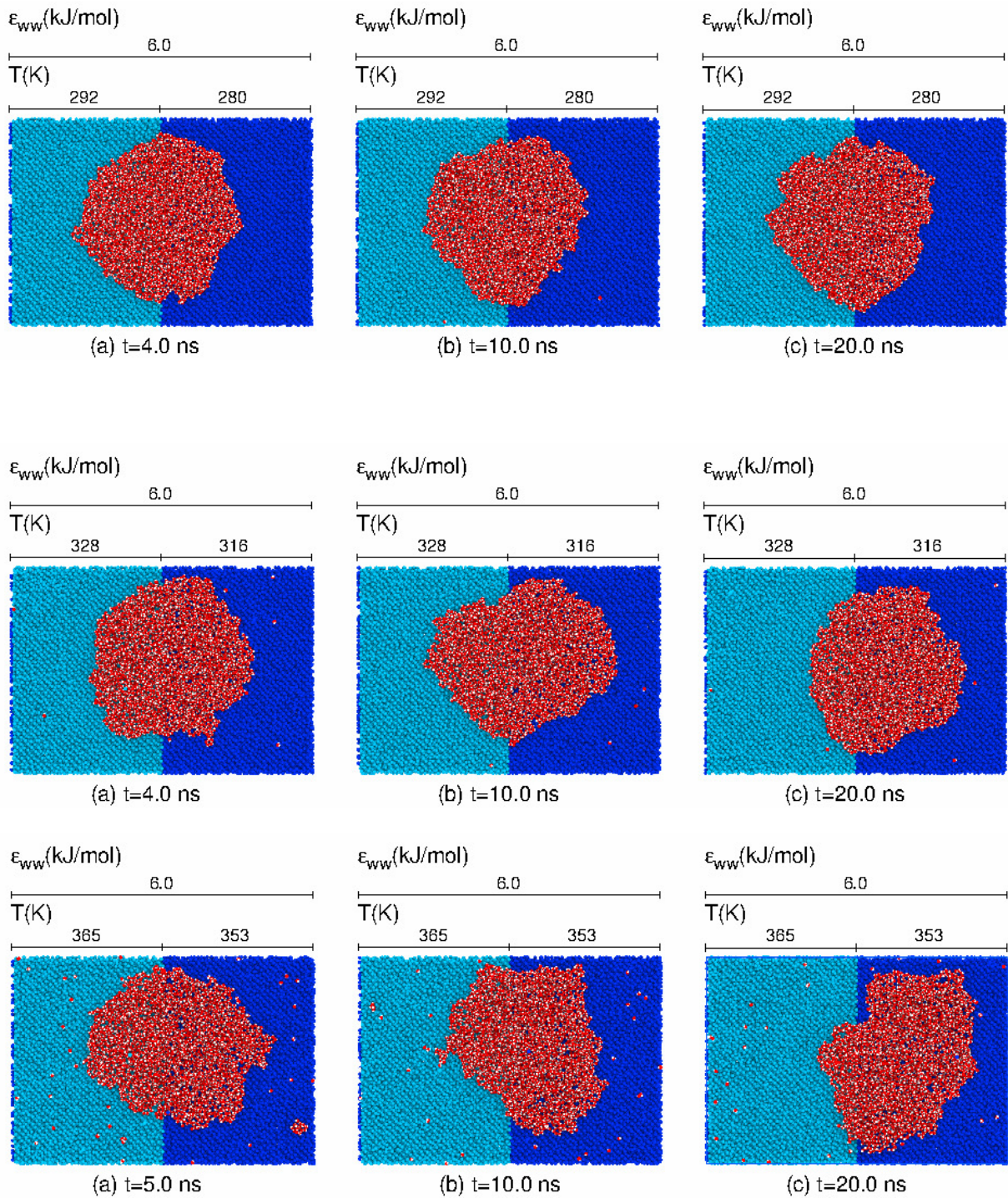


**Fig. S1:** Evolution of a water film from a droplet on a hydrophilic surface at uniform temperature. A water droplet is initially placed over a hydrophilic substrate, which is kept at 300 K. The droplet equilibrates over time and attains a steady value for its centre-of-mass.

## Simulation Results



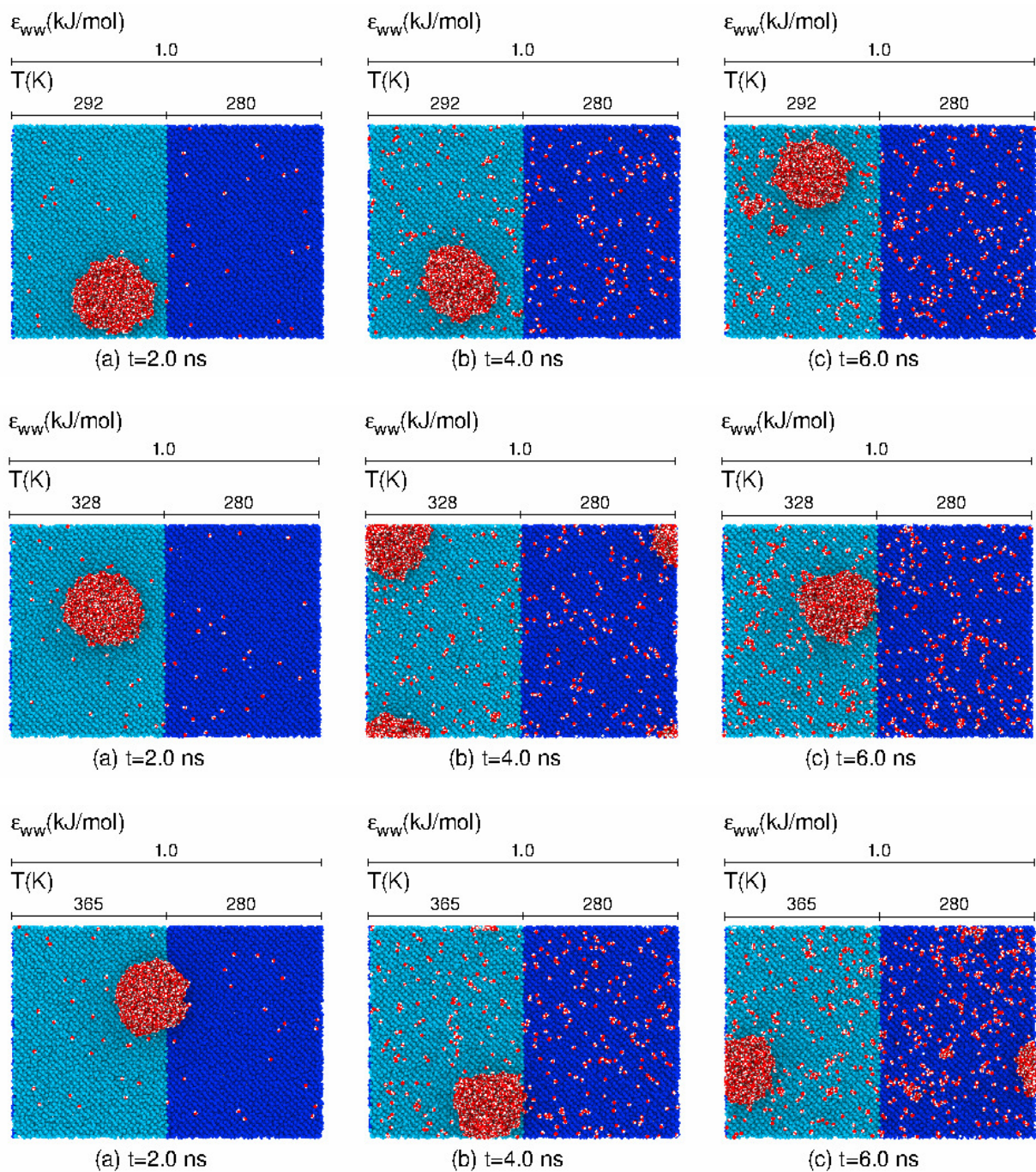
**Fig. S2:** Film evolution on a hydrophilic surface with different values of temperature jump across the centerline. The droplet/film is observed to move toward cooler regions in all the cases with rapid motion observed for higher temperature gradient.



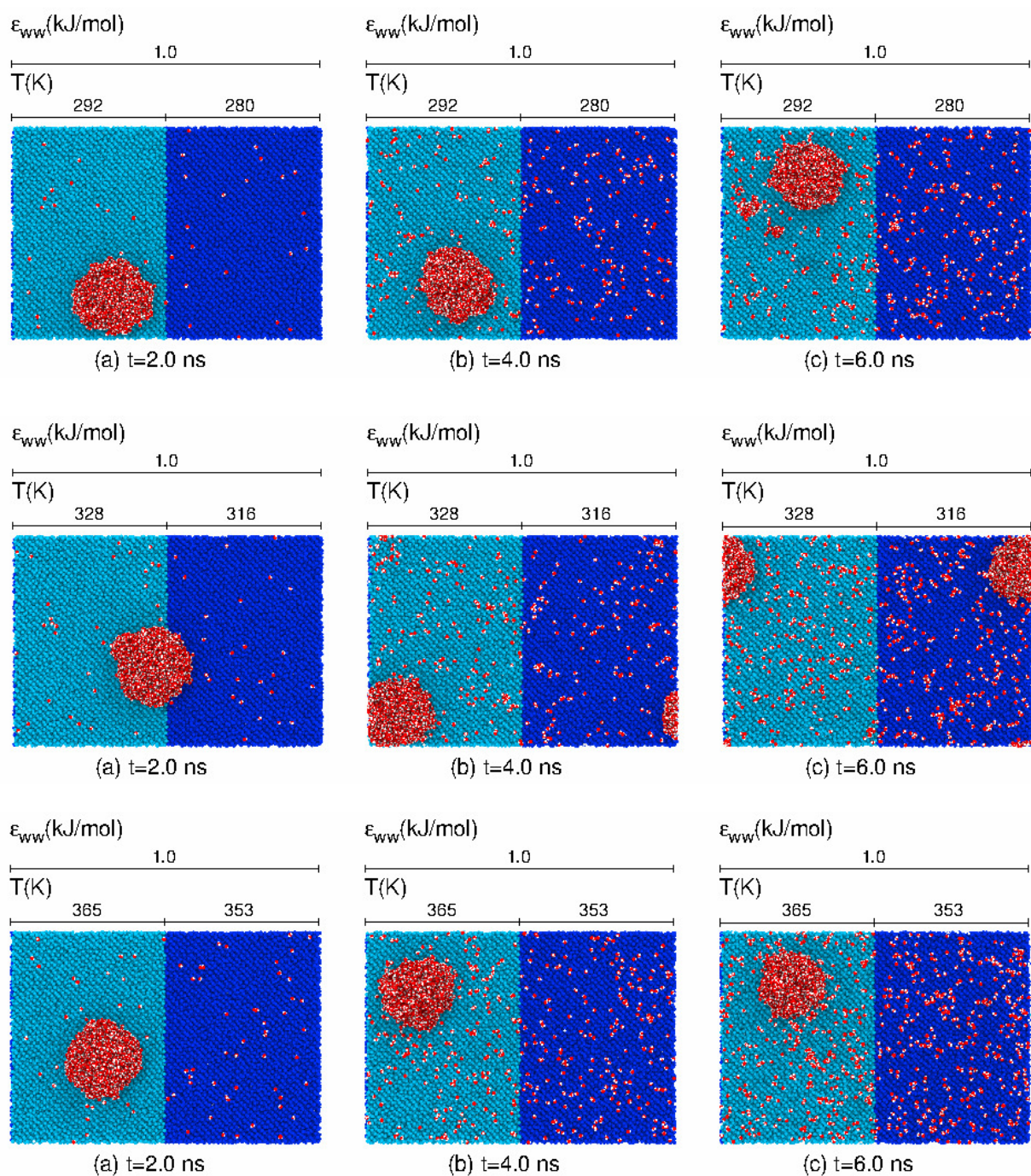
**Fig. S3:** Film evolution on a hydrophilic surface with same value of temperature jump (12 K) across the centerline but different mean temperature. The droplet/film is observed to move toward cooler regions in all the cases with rapid motion observed for higher mean substrate temperature.

With a temperature jump at the center of a completely wettable surface, it is clearly seen that the movement of the liquid is towards the colder side. This corroborates with the Marangoni

flow of water from zones of higher surface energy to lower surface energy. However, we observe another interesting trend from comparing Fig. S2 and Fig. S3 which leads us to the fact that on any surface, irrespective of the wettability, droplet or film locomotion is affected by mechanisms other than the Marangoni effect. This observation is in line with the competing forces prediction for Marangoni flow on hydrophobic surfaces. Fig. S2 depicts evolution of film for different values of temperature gradient with the lower temperature kept fixed at  $280\text{ K}$ . With increase in temperature gradient, the motion of the droplet toward colder side is expedited which is evidently due to larger surface tension gradient at the liquid-vapor interface that is created by larger temperature gradient at the solid surface. On the other hand, Fig. S3 depicts enhanced motion of the film toward colder regions for higher mean temperature irrespective of the same temperature gradient. Fig. S3 depicts three different cases of temperature jump where the value is set to be  $12\text{ K}$  in each of the cases but the temperature on both the halves of the surface is increased from  $280\text{ K}/292\text{ K}$ ,  $316\text{ K}/328\text{ K}$  and  $353\text{ K}/365\text{ K}$ . If Marangoni forces, as classically described, were the only major forces operating on the droplet, then each of these cases would have registered a same rate of droplet motion. However, the degree of film translocation is much higher for greater mean surface temperature. The rate of film locomotion for different values of mean surface temperature and temperature gradient can be seen in fig. 3 of the main paper. Fig. 3 (a) shows the evolution of the position of the center of mass of the molecular aggregate after being placed at the centerline for the cases shown in Fig.S2. Fig. 3 (b) demonstrates the same for the cases shown in Fig.S3. The associated phenomenon with higher average substrate temperature is the appearance of more vapor molecules over the film. Thus the process of vapor diffusion across the interface augments the Marangoni forces and leads to rapid motion of the film or droplet.



**Fig. S4:** Droplet evolution on a hydrophobic surface with different values of temperature jump across the centerline. The droplet is observed to move toward warmer regions in all cases.



**Fig. S5:** Droplet evolution on a hydrophobic surface with same value of temperature jump (12 K) across the centerline but different mean temperatures. The droplet is observed to move toward warmer regions in all the cases with rapid motion observed for higher mean substrate temperature.



The motion of the droplet on a hydrophobic surface with temperature jump is observed to be from colder to warmer side. The fluctuations in the velocities are larger but it is seen that the translocation toward the warmer side is faster for higher mean substrate temperature. However, there is no noticeable rise in velocity of the droplet with increase in temperature gradient. The rate of motion of droplets with variable temperature (fig. S5) and variable gradient (fig. S4) is graphically summarized in fig. 4 of the main paper.

## References

- 1 H. J. C. Berendsen, J. R. Grigera and T. P. Straatsma, *J. Phys. Chem.*, 1987, **91**, 6269–6271.
- 2 J. E. Jones, *Proc. R. Soc. A Math. Phys. Eng. Sci.*, 1924, **106**, 463–477.
- 3 P. A. Thompson and M. O. Robbins, *Phys. Rev. Lett.*, 1989, **63**, 766–769.