Use of the String Method to Find Minimal Energy Paths and Energy Barriers of Droplets on Superhydrophobic Surfaces

Kellen Petersen [C, S]
Courant Institute of Mathematical Sciences, New York University, New York, NY, U.S.A.
kellen@cims.nyu.edu

Interest in superhydrophobic surfaces has increased due to a number of interesting advances in science and engineering. Here we use a diffuse interface model for droplets on topographically and chemically patterned surfaces in the regime where gravity is negligible. We then apply the constrained string method to examine the transition of droplets between different metastable/stable states. The string method finds the minimal energy paths (MEPs) which correspond to the most probable transition pathways between the metastable/stable states in the configuration space. In the case of a hydrophobic surface with posts of variable height and separation, we determine the MEP corresponding to the transition between the Cassie-Baxter and Wenzel states. Additionally, we realize critical droplet morphologies along the MEP associated with saddle points of the free-energy potential and the energy barrier of the free energy. We analyze and compare the MEPs and free-energy barriers for a variety of surface geometries, droplets sizes, and static contact angles ranging from partial wetting to complete wetting. We also introduce an unbiased double well potential in the diffuse interface model by introducing a chemical potential that is fixed for a given simulation. We find that the energy barrier shifts toward the Wenzel state along the MEP as the height of the pillars increases in the topographically patterned case while a shorter energy barrier exists and is more centered along the MEP for pillars of shorter height. More importantly, we demonstrate the string method as a useful tool in the study of droplets on superhydrophobic surfaces by presenting a numerical study that finds MEPs in configuration space, critical droplet morphologies and free-energy barriers which in turn give us a greater understanding of the free-energy landscape.