

Study of Droplet Motion on Temperature-responsive Surface

(温度応答性表面における液滴運動の研究)

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A novel absorber with its surface treated with temperature-responsive material (PNIPAM) is proposed and its mechanism is studied in this paper. The temperature-responsive surface enables the formation of a thin liquid film on the absorber surface, which has the potential to increase the absorbing efficient. This research focus on the mechanism of the droplet movement, as well as the wetting transition of the temperature-responsive surface. The CFD exhibits the droplet impact motion on the surface by established physical models and a good result was observed. To investigate the phases change process and wetting characteristics of temperature-responsive polymer, molecular dynamics simulations (MD) was performed to predict the structure of this polymer and the phase change process. Finally, nano wetting behavior play an important role in ensuring reliability and feasibility of the new approach, but investigation of that remains a key challenge.

Key words: Droplet motion, Temperature-responsive surface, wetting transition, CFD, MD.

1 Introduction

The importance of environmental energy system motivates the search for new technologies. Currently, even though absorption refrigeration system is practical in many occasions, it still suffers from several disadvantages[1]. The main reason for the large volume and low performance of conventional absorption refrigeration system is due to the existence of free surface for both the generator and absorber shown in Fig. 1..

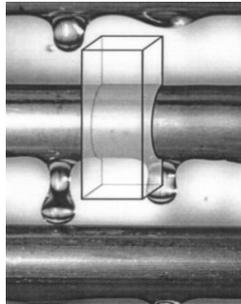


Fig. 1 Unwetted surface on the absorber tube

In this paper, a temperature-responsive absorber surface is proposed which helps the formation of evenly distributed thin solution film, which is expected to largely enhance the absorption performance.

2 New Approach

2.1 Temperature-responsive polymer

PNIPAM is a temperature-responsive polymer, it will go through phase transition under different temperatures. A LCST (Lower critical solution temperature) exists that if the temperature falls below the LCST, PNIPAM becomes hydrophilic. On the other hand, if its temperature rises above the LCST, PNIPAM will become hydrophobic shown in Fig. 2. By

forming a PNIPAM layer on the absorber surface, the heat transfer surface can be used with higher efficiency.

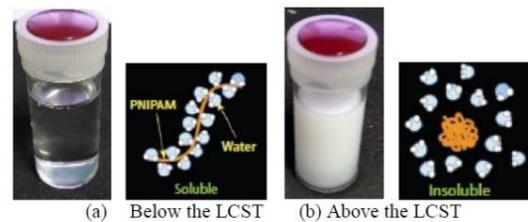


Fig. 2 Performance of PNIPAM (a) below the LCST and (b) above the LCST.

2.2 Temperature-responsive surface

As shown in Fig. 3, pillars with square cross sections was fabricated on the surface and was characterized by the width of the pillar $a=25 \mu\text{m}$ and the gap length $b=15 \mu\text{m}$ between pillar next to each other. Height of the pillar was set to $h=30 \mu\text{m}$. Then, PNIPAM brush layer was grafted on the textured silicon substrates[2] to obtain the temperature-responsive surface with various wettability from superhydrophilicity to superhydrophobicity at different temperature 20°C and 40°C , respectively.

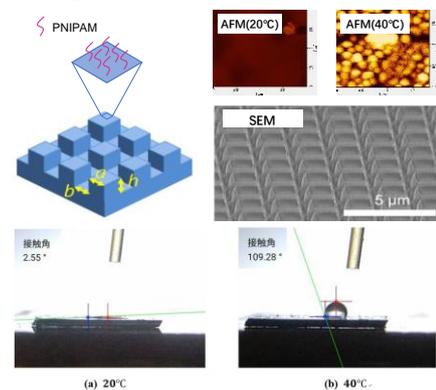
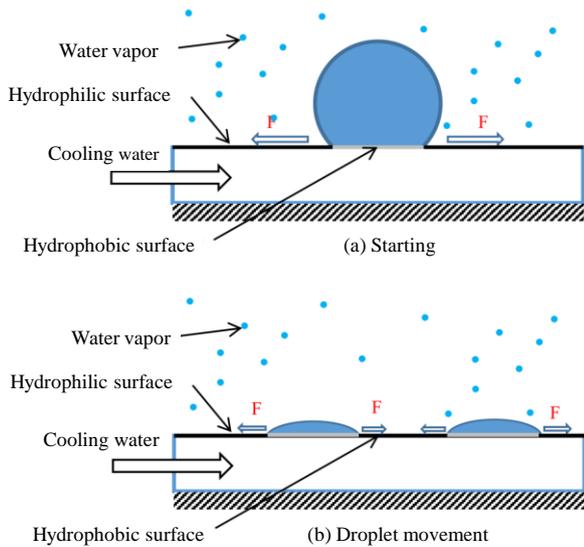


Fig. 3 Microtextured temperature-responsive surfaces with responsive wettability under different temperatures Mechanism

2.3 Mechanism

Fig. 4 shows a schematic of the droplet behavior on PNIPAM-coated heat transfer surface. From the starting as shown in Fig. 4(a), when the water vapor is absorbed by the solution, heat releases from the droplet which creates a local high-temperature region. Making the heat transfer surface hydrophobic. Meanwhile, as the surrounding heat transfer surface is still hydrophilic, the droplet will be stretched by the surface tension. As a result, the solution droplet automatically moves toward wetted surface to the dry surface. Moreover, assuming that the movement continues during the absorption period as shown in Fig. 4(b), a evenly distributed thin liquid film will be formed that



covers the entire heat transfer surface.

Fig. 4 Schematic of droplet on a temperature-responsive surface

3 Theoretical Analysis

3.1 Wetting transition

The basic understanding of the phase change process of PNIPAM polymer is shown in Fig. 5

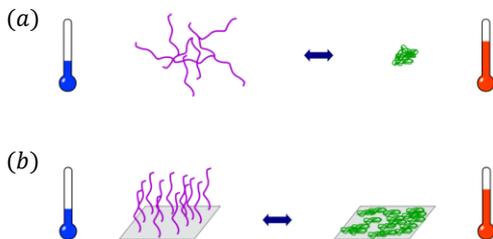


Fig.5 Schematic of phase change process of PNIPAM polymer(a) in solution or(b) on solid substrate.

In aqueous solution, the PNIPAM homopolymer chain undergoes a coil to globule transition when across the LCST shown in Fig. 5 (a). Such that it transfer from soluble to insoluble state due to losing the ability to hydrate the water molecules around it.

For the rough substrates with PNIPAM modification

At low temperatures, the extended conformation of PNIPAM chains and intermolecular hydrogen bonding with water molecules results in high surface free energy, therefore a small water contact angle. The surface is hydrophilic and water enters the microstructures beneath the water drop. In this situation, surface roughness plays the dominant role and intensifies the hydrophilicity, and it can be explained by Wenzel's state[3] shown in Fig. 6 (a). In contrary, at higher temperatures, the collapsed conformation of PNIPAM chains caused by intramolecular hydrogen bonding between C=O and N-H groups in PNIPAM chains leads to low surface free energy and large contact angle of water droplet shown in Fig. 6 (b). The brush layer is hydrophobic and the rough surface traps air. The microstructures also contribute to the increase in the air/ water interface and thus further enhance the hydrophobicity at high temperature.

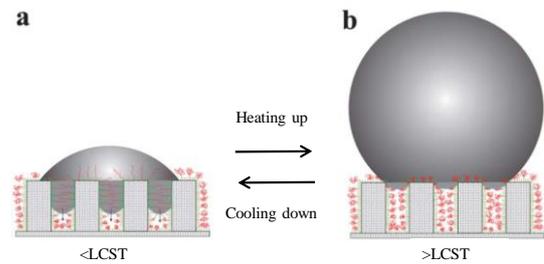


Fig. 6 Schematic of the mechanism of droplet on rough PNIPAM modified substrate (a) extended state of polymer chain, (b) collapsed state of polymer chain

3.2 Droplet multiscale dynamical wetting

In this study, this research is a droplet impinging and spreading dynamical wetting phenomena coupling of macroscopic and molecular scales shown in Fig. 7

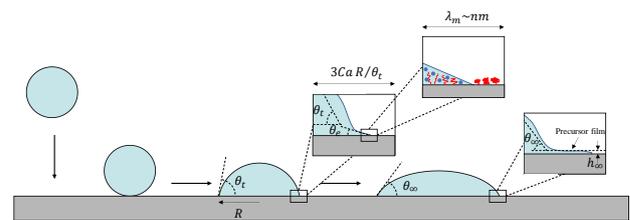


Fig. 7 Schematic of a droplet spreading on a flat PNIPAM-modified surface

4 Macroscopic Scale: Droplet Motion

4.1 Physical model

In our research, we investigate the small-size droplet which radius of droplet is around 1mm such that surface tension plays the essential role of the droplet motion according to the capillary length of LiBr/Water solution droplet[4]. In this case, the solution flow rate is usually maintained such that droplet flow exists between the coolant tubes. And a square region at the

top center of the tube plays the role of the feeder or distributor as a plate surface as shown in Fig. 8.

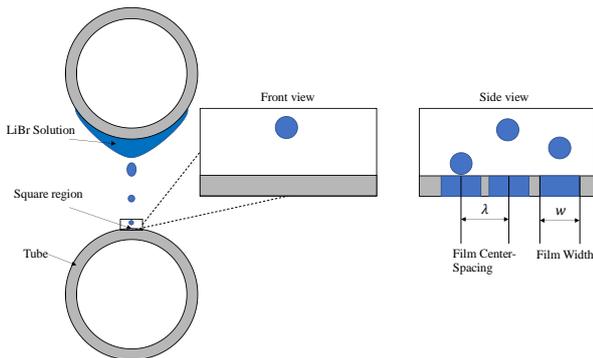


Fig. 8 Schematic of small droplets fall between tubes

And we assuming the mixing of water vapor and LiBr solution complete before the droplet impinging the surface and there should be an interface layer which play the role of absorbing water vapor and its temperature should be always approach to saturation temperature. Such that, we simplified the mass transfer due to the concentration of LiBr solution and focused on the heat transfer process. Generally, the heat transfer can be described in two processes as demonstrated in Fig. 9. Firstly, a solution droplet which interface layer absorbs water vapor as a heat source releases the heat to the surface when it reach the surface, then, at the same time, the sub-cooling water as a cooling source continuously takes the heat away from the surface by flowing under the tubes.

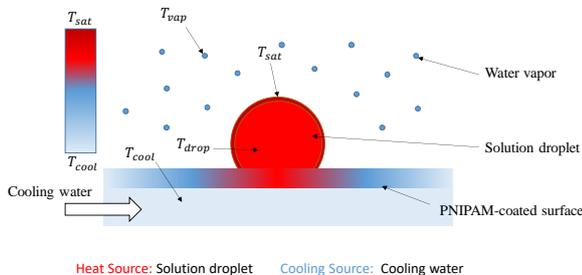


Fig. 9 Schematic of heat and mass transfer process

4.2 Simulation results and discussion

A commercially available CFD package (Fluent) was used to implement and develop the model. The flow was assumed to be incompressible, Newtonian and laminar throughout the solution domain due to the low Reynolds numbers (<500): even though impact events can lead to locally high velocities, they do not generate turbulence in a manner that requires special modeling.

Fig. 10 shows the droplet behavior as it falls down the various surfaces. In order to eliminate the effect of early contact when the droplet impacting perpendicularly to a wall will always entrap a small air bubble under its center and hence we can focus on the surface properties, the initial condition is set as spherical droplet and its bottom is just contact with the flat surface. Such that

depending on a series of settings of surface parameters: (a) hydrophobic surface, (b) temperature-responsive surface without relaxation time and (c) temperature-responsive surface with relaxation time, the later-time dynamics of the impact exhibit different behavior, ranging from spreading and recoiling in these cases. It is to be noted that the snapshots presented in Fig. 10 are not equal time differences. Instead, time steps at which the droplet display features of have been carefully selected and presented.

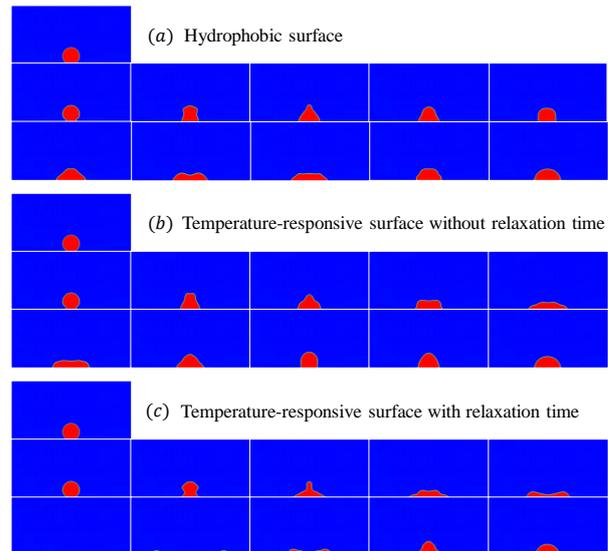


Fig. 10 Snapshots of droplet impact behavior on various surfaces:(a) hydrophobic surface, (b) temperature-responsive surface without relaxation time and (c) temperature-responsive surface with relaxation time

In all cases, no splashing is observed, the droplet simply spreads over the surface until it reaches a maximum radius, then, the droplet's retraction belong to recoiling motion, not rebound and jet are observed. The dynamics are controlled by subtle balances between inertia, viscosity and capillary forces. An important outcome of a drop impact on a solid substrate is the maximum spreading radius. This parameter cannot be used to calculate the wetting ratio directly, but in order to form a thin solution film on the surface, larger maximum spreading radius contribute to better performance. So the temperature-responsive properties help enhance the performance of heat transfer of the surface.

5 Molecular Scale: Polymer

5.1 The conformation of the PNIPAM chain

Fig. 11 shows the copolymerization of PNIPAM monomers to form a polymer chain and our construction of this polymer chain in MD simulation[5,6].

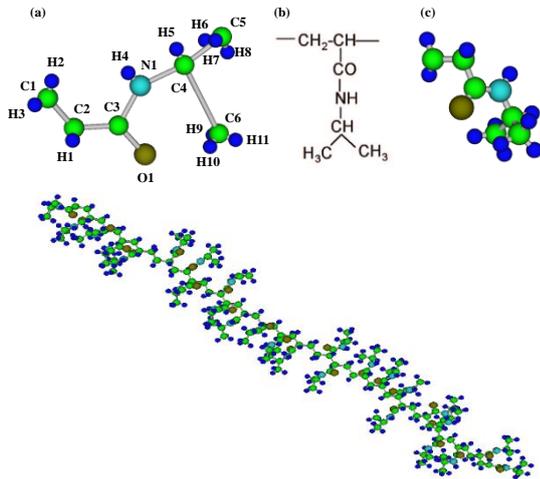


Fig. 11 Conformation of the PNIPAM monomer and initial construction of the 26-units polymer chain.

5.2 Phase transition

Fig. 12 shows the conformations of the PNIPAM polymer chain at the end of the 40 ns simulations from initial preparation, which reach equilibrium state at 293K, 305K and 318 K, corresponding to the temperature lower than LCST, equal to LCST, and higher than LCST, respectively.

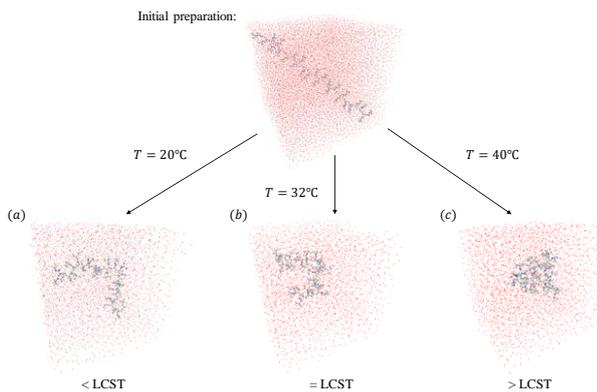


Fig. 12 Phase transition of a PNIPAM chain in aqueous solution.

It is obvious that the final structure of the copolymer is globular at 40°C after the hydrophilic–hydrophobic transition, which is much more compact than the corresponding coil conformation at 20°C. When across the LCST at 32°C, the polymer exhibits a U-shaped conformation between the coil and globule state.

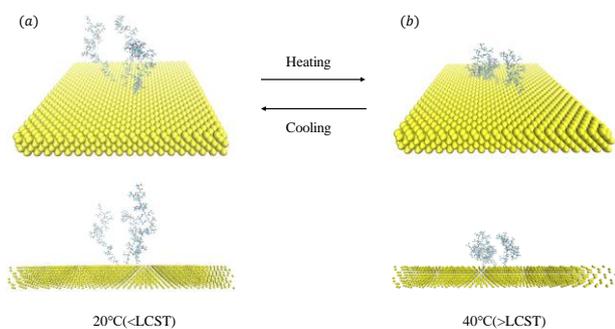


Fig. 13 Phase transition of three hydrated PNIPAM grafted chains on silicon substrate

Fig. 13 shows the phase transition of three grafted chains on silicon substrate via heating and cooling. Upon cooling down in temperature, the PNIPAM chains are highly swollen below the LCST. Whereas, upon heating up in temperature, PNIPAM chains are collapsed into tight clusters.

5.3 Nano wetting

We attempt to investigate the nano wetting behavior of our PNIPAM-modified surfaces by placing a nano droplet onto the top of the polymer brushes layer shown in Fig. 14.

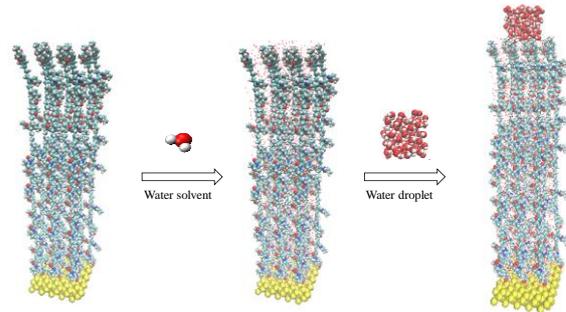


Fig. 14 Initial preparation of nano droplet on hydrated PNIPAM-grafted brushes on silica substrate

6 Conclusions

6.1 Conclusions

In this study, investigation of droplet motion on temperature-responsive is conducted theoretically, numerically in various perspectives. We discussed experimental and the theoretical progress revealing the physical mechanisms behind these dynamical wetting transitions. By using CFD simulation, we demonstrated the droplet impact on the temperature-responsive surface has potential to enhance heat transfer considerably. By using full-atomistic MD simulation, we investigated the mechanism of the LCST behavior hydrated PNIPAM polymer both in aqueous solution and onto silicon substrate. In the end, an attempt was made to investigate the nano droplet wetting behavior.

Reference

- [1] Z. F. Li and K. Sumathy: *Renew. Sustain. energy Rev.*, vol. 4, no. 3, pp. 267–293, 2000.
- [2] M. Kato, M. Kamigaito, M. Sawamoto, and T. Higashimura: *Macromolecules*, vol. 28, no. 5, pp. 1721–1723, 1995.
- [3] X. Liu et al.: *Soft Matter*, vol. 7, no. 2, pp. 515–523, 2011.
- [4] S. Jeong and S. Garimella: *Int. J. Heat Mass Transf.*, vol. 45, no. 7, pp. 1445–1458, 2002.
- [5] T. Kondo: *Polym. Sci.*, vol. 35, p. 717, 1997.
- [6] S. G. Lee et al.: *J. Phys. Chem. C*, vol. 116, no. 30, pp. 15974–15985, 2012.