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Apply surface wettability gradient to non-wetting capillary: A simulation study on spontaneous droplet flow

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The present work simulates a concept about how to drive droplet flowing through non-wetting (hydrophobic) capillaries without any external force by using many-body dissipative particle dynamics. By decorating the capillary segments with wettability gradients, a droplet with proper radius can be absorbed by the non-wetting capillaries and then constantly flow through the capillary. The simulation results show the droplet can keep flowing through the whole capillaries under certain wettability gradients and the flow velocity also depends on the degree of the wettability gradients. The average wettability of the whole capillary is also essential for the continuous flowing, higher non-wetting capillaries can still keep the flowing with low wettability gradients due to less surface adhesion. A strategy on how to achieve longer flow pathway is also presented. It is also find that unbalanced uptake of droplet via lateral heterogeneous surfaces cannot stir the inside flow of the droplet. The simulation results could inspire the new design of microfluidics in which the transportation of droplet is an important aspect. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5047450

I. INTRODUCTION

Microfluidic systems have been proven to be useful platforms for many applications in physics, chemistry, biotechnology or even logical devices.1 By studying concerned processes in such small systems, researchers can easily and precisely control the evolution of physical processes, chemical reactions and at the meanwhile reduce the consumption of resources. Thus, microfluidic systems have gained increasing popularity for its usefulness and economy. The manipulation of droplets is one of the most important aspects in microfluidics since many processes happen within a droplet, or need the transportation of droplets.2–4 How to drive droplets moving continuously in the tubes is, therefore, becoming a key technology in the development of microfluidics. Some ways are employed to produce driving forces, such as electrostatic, thermal or optical sources. However, to use these sources of power, supporting devices like pumps, valves and connectors must be included. These supporting devices will add extra difficulties to the design of systems, or even introduce cross-contamination. Thus, to develop microfluidics without pumps and related supporting devices has become essential for the design of new types of microfluidics.

Recent studies have shown that surface-engineering-induced wettability gradient could be used as a driving force to propel a small droplet moving on surfaces.4–12 Wettability is the intrinsic property of the surfaces and could be very stable and long-term after the production of surfaces. Thus, these surfaces could be promising materials in the design of pumpless microfluidic systems. Three main ways are frequently used to produce wettability gradients on surfaces: surface-shape-induced,5...
surface-texture-induced,6–8 and chemistry-induced wettability gradients,4,9,10 or a combination of them.11,12 The common ground of the three ways is that they all force the droplets to form an unstable liquid/air interface with disordered shape, and thus break the equilibrium state of the droplet, unbalanced forces or directional net force then appear. Ultimately the droplets are forced to move to a more stable state, leading to the spontaneous and directional movement of the droplet. More mathematical and graphical explanations can be found in previous literatures.5,6,12

However, most previous studies focus on driving droplet movement on open or flat surfaces.4–12 The study of droplet flow in confined surfaces like capillaries should be more practical in some microfluidic systems since most droplet transportation happens in the tubes.1,2 It is common sense that droplet can penetrate into hydrophilic capillaries spontaneously whilst it is harder to start the droplet penetration into a non-wetting capillary. In the present work, we study droplet flowing in hydrophobic capillaries instead of hydrophilic ones to fill this research gap. Many-body dissipative particle dynamics (MDPD), as a particle-based numerical tool at mesoscale, is employed to simulate the interaction between droplet and capillaries with different wettability.

II. NUMERICAL METHOD

A. Many-body dissipative particle dynamics (MDPD)

Dissipative particle dynamics (DPD) is a particle-based and coarse-graining numerical method developed to address problems at mesoscales.13,14 The motion of particles in DPD system accords to Newton’s second law and the interaction between any two particles are governed by three types of forces: conservative, dissipative, and random forces. After the creation of this original DPD, many new features have been developed and new variants have been added into DPD family, such as energy-conserving DPD (eDPD),15 smoothed DPD (sDPD),16 transport DPD (tDPD),17 charged DPD (cDPD)18 and DPD with short-range repulsive and long-range attractive forces.19 Some reviews give very good summary of the development and applications of DPD.20,21

In the present work, a many-body version of DPD, MDPD,22 is actually employed. MDPD introduces a van der Waals loop in the equation of state and thus enables itself to simulate the state of vapor-liquid coexistence. The three forces in MDPD can be described as below:

\[ F^C_{ij} = A_{ij} \omega^C(r_{ij}) e_{ij} + B_{ij}(\bar{\rho}_i + \bar{\rho}_j) \omega_d(r_{ij}) e_{ij} \]  

\[ F^D_{ij} = -\gamma \omega^D(r_{ij}) (e_{ij} \cdot v_{ij}) e_{ij} \]  

\[ F^R_{ij} = \sigma \omega^R(r_{ij}) \xi_{ij} e_{ij}. \]  

In which \( \omega^C(r_{ij}) = 1 - r_{ij}/r_c \), \( \omega_d(r_{ij}) = 1 - r_{ij}/r_d \), \( \omega^D(r_{ij}) = \sqrt{1 - r_{ij}/r_c} \) and \( \omega^R(r_{ij}) = \sqrt{\omega^D(r_{ij})} \) are weight functions. \( r_{ij} \) is the distance between two interacting particles, \( r_c \) is the cutoff radius of the interaction, \( r_d \) is the local density cutoff radius. \( \bar{\rho}_i \) and \( \bar{\rho}_j \) are the local density of two interacting particles and can be calculated by Eq. (4) and (5):

\[ \bar{\rho}_i = \sum_{i \neq j} \omega \rho(r_{ij}) \]  

\[ \omega \rho(r_{ij}) = \frac{15}{2\pi r_d^3} (1 - \frac{r_{ij}}{r_d})^2. \]

And \( \sigma \) is the noise amplitude and \( \gamma \) is the friction coefficient, they are coupled by \( \sigma^2 = 2\gamma \) to keep the system temperature.

B. Boundary condition and wettability

Since the repulsive part in conservative force is quite soft to prevent fluid particles unphysically penetrating into solid walls, some boundary conditions have been proposed to address this issue.23,24 A recently proposed boundary condition24 is employed in this simulation. This boundary
TABLE I. The main parameters in the MDPD simulation.

| Name of parameter                  | Symbol of parameter | Value (in MDPD unit) |
|------------------------------------|---------------------|----------------------|
| Attractive coefficient             | $A$                 | -80                  |
| Repulsive coefficient              | $B$                 | 25                   |
| Cutoff radius in $\omega^A(r_{ij})$| $r_c$               | 1.0                  |
| Cutoff radius in $\omega^B(r_{ij})$| $r_d$               | 0.75                 |
| Random coefficient                 | $\sigma$            | 1.0                  |
| Empirical velocity-Verlet coefficient| $\lambda$         | 0.65                 |
| Time step                          | $\Delta T$         | 0.01                 |
| Temperature of the system          | $k_B T$             | 1.0                  |

condition is easy to implement and takes the distribution of solid particles, the minimal distance between the fluid and solid particles, and the velocity of the fluid particle into consideration. Previous applications of this boundary condition have proven that it can effectively avoid the fluid particles penetrating into walls and meanwhile keep the wettability property well.

The capillaries in the simulations are modelled by cutting a big enough and pre-equilibrated raw material with particle number density 12. The droplet is cut from pre-equilibrated raw material with particle number density 9, and it is equilibrated again to reach a more stable state. By adopting parameters listed in Table I and varying attractive coefficient $A_{ij}$ between solid particles and fluid particles, different wettability of a given material can be produced and the relationship between $A_{ij}$ and water contact angle is plotted in Fig. 1.

In the present simulation, the gravity effect is neglected since the concerned length scale is very small, e.g., at meso/microscale. Thus, the capillary-effect-dominated interaction between solid walls and droplet can be focused on. The capillary is divided into 3 segments evenly and different wettability is assigned to the segments, then a heterogeneous capillary with three intrinsic contact angles $\theta_1$, $\theta_2$ and $\theta_3$ for each segment is obtained. $\theta_3 > \theta_2 > \theta_1 > 90^\circ$ is satisfied to form the wettability gradient along the capillarity. A very gentle initial approaching velocity is given to the droplet to start the contact with the first segment of the capillary. An initial state of the droplet and capillary is shown in Fig. 2.

![FIG. 1. The relation between the solid-fluid attractive coefficient $A_{ij}$ and the contact angle, the initial radius of the testing droplet is 9. Two typical droplet states on substrates with different wettability are also shown.](image-url)
FIG. 2. The initial state of the droplet and capillary. $\theta_{S1}$, $\theta_{S2}$ and $\theta_{S3}$ denote the intrinsic contact angles of the three segments, the red arrow indicates the decreasing direction of the contact angles.

III. RESULTS AND DISCUSSION

A. Spontaneous absorption of the droplet by non-wetting capillaries

How the droplet could be absorbed by the non-wetting capillaries should be first explained. As common physical phenomena widely happening in nature, a hydrophilic capillary can absorb liquid from a reservoir and on the other hand, a hydrophobic capillary will drain the liquid out of itself, the relation between the wettability of the capillaries and the flow direction of liquid can be described by Eq. (6):

$$h = \frac{2\gamma \cos \theta_s}{\rho g R_t}.$$  \hspace{1cm} (6)

Where $\gamma$ is the liquid-air surface tension, $\theta_s$ is the contact angle on the contacting capillary, $\rho$ is the liquid density, $g$ is gravity and $R_t$ is the radius of the capillary. When $\theta_s < 90^\circ$, the capillary is hydrophilic and $h$ will be positive, meaning absorption of liquid; When $\theta_s > 90^\circ$, the capillary is non-wetting or hydrophobic, $h$ will be negative, thus the liquid will be forced out of the capillary.
However, when replacing the liquid with a droplet, things would be different. Marmur \textsuperscript{26} found the droplet would introduce curvature into the liquid-air interface and thus an extra term should be added into Eq. (6), as shown by Eq. (7):

\[ h = \frac{2\gamma \cos \theta_s}{\rho g R_t} + \frac{2\gamma}{\rho g R_d}. \]  

(7)

In which \( R_d \) is the initial radius of the droplet. Since the new term \( \frac{2\gamma}{\rho g R_d} \) is always positive, it is possible when the first term in the right hand side of Eq. (7) is negative and \( R_d \) is small enough, \( h \) would be positive again. Recent experiments and simulations show that the spontaneous uptake of droplet into non-wetting can really happen when meet some requirements.\textsuperscript{25,27–30} In this simulation, we use capillaries with radius \( R_t = 8 \). According to Eq. (7), the spontaneous uptake would happen when \( h > 0 \) or \( R_d < -R_t/\cos \theta_s \) by rephrasing terms in the right hand side. Because the most hydrophobic entry segment of the capillaries is \( \theta_s = 140^\circ \), thus \( R_d \) should be always smaller than 10.44 to ensure the spontaneous uptake in all simulations. Finally, we choose a droplet with initial radius \( R_d = 9 \).

### B. Droplet flowing through hydrophobic capillaries

The length of the segments \( L \) should be selected carefully to enable the spontaneous flow. \( L \) must ensure the droplets contact with at least two segments simultaneously. In this simulation, \( L = 13 \) is used. The other lengths are also tested and the results shows that if the capillary is too long, for example \( L = 15 \), the droplet cannot contact two segments at the same moment, thus the flow cannot continue.

Fig. 3 shows a time-dependent evaluation process of droplet flowing through the capillary with \( \theta_{S1} = 140^\circ \), \( \theta_{S2} = 120^\circ \) and \( \theta_{S3} = 100^\circ \). When the droplet totally enters the capillary (after Fig. 3c), to keep the flowing, the droplet must contact at least two different segments at the same time. That’s to say, the droplet front and back must be on different segments to form two convex surfaces with different radii. That is because the liquid-air surface tension \( \gamma \) is unique for a given liquid, but the Laplace pressure, \( P = \frac{2\gamma}{R} \), could be different due to different radius \( R \) of the droplet curvature, for example, the back radius \( R_{\text{back}} \) and the front radius \( R_{\text{front}} \) of the same droplet. Then an unbalanced net force directing to the higher wetting area will be generated due to \( P_{\text{back}} > P_{\text{front}} \) and drive the droplet flowing along the heterogeneous capillary.

Fig. 4 shows how curvatures (1/R) and displacement of the droplet mass centre vary with time. The whole curvature curves can be divided into two parts, a dynamic part and an equilibrium part. Fig. 3 demonstrates snapshots of the dynamical part. The dynamic part can be further divided into three stages according to where the droplet front is. As shown in Fig. 3, from a to c, the droplet front is on the first segment, this stage is marked as S1 in Fig. 4; from c to e is S2; and from e to h is S3. S1 has been analyzed in detail in our previous study,\textsuperscript{25} Fig. 3b and 3c correspond to \( T_2 \) and \( T_3 \) in Ref. 25, respectively. From the three stages we can see that the front curvature decreases gradiently which is in coincidence with the fact that the contact angles decreases gradiently along the three segments. It is interesting to notice that, in S2, the back curvature witnesses a counter-intuitive second wave and the peak value is even higher than the first peak in S1. This second wave always exists even when we

![FIG. 3. A time-dependent evaluation process of droplet flowing through the capillary, the length of the capillary is 39 with single segment length \( L = 13 \), as marked on the right.](image-url)
FIG. 4. The time-dependent evaluation of the droplet front curvature and the displacement of the droplet mass center.

change the wettability gradient. We assume the discordant varying of advancing and receding contact lines may contribute to this to some extent. In the equilibrium part after Fig. 3h, through there still exists a curvature difference between the back and front of the droplet, the unbalanced force is too small to drive the flow.

C. Effect of wettability gaps

In this section, we further compare the effect of different wettability gaps on the flowing of a droplet through the capillaries. We first keep the wettability gaps constant but vary the wettability of the first segments, or the entry segments. When the gaps are set at 20°, 10° and 5°, the entry wettability is set at 140°, 130°, 110°, 100° and 90°, we can observe that the droplet enters faster through the higher wetting entry segment, but then slows down when it goes further into the capillaries, as shown in Fig. 5a to c. We can understand this as the droplet front forms a convex surface with larger radius or even flat surface when $\theta_{S1} = 90^\circ$ on the entry segment with higher wetting property, as the droplet back is still outside of the capillaries, the radius of the back keeps the same, the curvature difference will be larger than capillaries with lower wetting entry segments, thus bigger net force will be generated to drive the droplet advancing faster. However, when the droplet totally enters the capillary, under the same wettability gaps, the higher wetting segments will produce more surface adhesion and then slow down the further flowing of the droplet. Fig. 5a also shows that less time is required for droplet flowing through hydrophobic capillaries than through hydrophilic capillaries. Also, by comparing Fig. 5a and 5b we can find larger wettability gap is essential to constantly driving the droplet flowing, but it is not the only requirement. As can be seen in Fig. 5c, though the wettability gap is quite small, only 5° to be exact, the droplet can still flow through the whole capillary with contact angles $\theta_{S1} = 140^\circ$, $\theta_{S2} = 135^\circ$ and $\theta_{S3} = 130^\circ$. That’s to say, if the average wettability of the whole capillary is highly hydrophobic, the droplet could still be driven by low wettability gradients due to low surface adhesion. For the capillaries with same entry segments but different wettability gradients in Fig. 5d, the simulation results show larger wettability gradients can cause faster droplet flowing and the flowing speed of droplet decreases with the decrease of wettability gradients.

D. Achieve a longer flow pathway

We also simulate how droplet flows in capillaries with wettability gradient 2.5° and find the droplet only flows from segment with contact angle 140° to the segment with contact angle 135°. For capillaries with wettability gradient 5°, the droplet can flow from segment with contact angle 140° to segment with 100°. For capillaries with wettability gradients 10° and 20°, the droplet can flow
from segment with contact angle 140° to segments below 90°. A question is thus deserved to ask: how to achieve the longest flow pathway via wettability gradient? For example, if we want a droplet to flow from a segment with contact angle 140° to a segment with contact angle 90°, how to arrange the segments to make the droplet flow longer? Based on the current simulation data we know: with gradient 2.5°, the droplet can only flow through 3 segments; with gradient 5°, it can flow through 9 segments; with gradient 10° and 20°, the droplet can flow through 6 and 3 segments, respectively. Here, we can combine the wettability gradients to optimize the capillary. Firstly, let the droplet flow
from a segment with contact angle 140° to a segment with 135°, with a wettability gradient 2.5°, 3 segments thus involved; then to a segment with contact angle 100°, with wettability gradients 5°, 7 segments involved; then to a segment with contact angle 90°, with wettability gradient 10°, 1 segments therefor involved. Finally, an optimized flow pathway with 11 segments can be obtained. Fig. 6 shows the time-dependent evaluation of the displacement of the droplet mass center for this optimized capillary. However, this predicted longest path is just based on our limited simulation data. Even longer flow pathway could be achieved when further adjust the wettability gradients.

E. Heterogeneous wettability gradient cannot stir the droplet

In this section, we show a failed simulation about a concept on stirring the droplet by lateral heterogeneous wettability gradient. To stir droplet inside the capillaries is always a challenge in the microfluidics field since it is a critical process for effective chemical and biological reactions. Since the droplet can be driven to flow by wettability gradient, we further consider how to stir the droplet also by the wettability gradient. To clearly demonstrate the concept, 2D simulations are performed. The main parameters and boundary condition in the 2D MDPD simulations can be found in our
previous study. Fig. 7 shows the configurations of the three capillaries, the main difference is that for each segment, the right parts have different wettability from the left parts (except Fig. 7a as a control simulation). At the very beginning, we expect the heterogeneous wettability gradients could stir the droplet due to the unbalanced lateral wetting property. If so, the streamlines inside the droplet would be directionally changed when the droplet proceeds through the border of two segments and this change will be indicated by the flow streamlines of the fluid particles. The lateral displacements of 9 randomly selected fluid particles for each simulation are recorded. However, though the droplet flows in an unbalanced way due to the lateral heterogeneity of wettability of each segments (as shown in the time-dependent snapshots in Fig. 7), the displacement profiles from the three simulations (see the left panels of Fig. 7) are very random and show no evidence that the streamlines of the particles moves in any regular way, for example, changing the flow direction regularly when moving through the interface between two segments. In other word, the surfaces do not affect the flow streamline of the particles inside the drople. This simulation result could be explained by the moving fashion of droplets on surfaces. McCarthy and coworkers mentioned a “tank tread” droplet moving fashion: the main part of the droplet is kept stationary while only molecules in the front and rear part around the moving contact line move, or wet and dewet the surface. In our simulation, the particles in the bulk area of the droplet do keep their own moving style (random moving) and not be affected by the heterogeneous surfaces.

IV. CONCLUSIONS

In the present work, we numerically study the droplet spontaneously flowing through non-wetting capillaries with surface wettability gradient. Simulation results show that droplet could be absorbed by a non-wetting capillary with proper radius. Wettability gradient of the capillary can cause unbalanced force to a droplet and therefore the droplet can be driven to flow. Large wettability gradient is required for the continuous flowing through the capillary. Without large wettability gradient, the droplet can still keep flowing if the average wettability of the whole capillary is hydrophobic enough since less surface adhesion reduces the friction between solid/liquid interface. To elongate the flow pathway, a mixed wettability gradients strategy is proposed. The simulation results also show that the heterogeneous lateral wettability of the capillaries cannot stir the inside of the droplet as expected. The simulation of the concept could provide useful information for the practical design of functional capillary in microfluidics.

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