Thermocapillary-actuated contact-line motion of immiscible binary fluids over substrates with patterned wettability in narrow confinement

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(Received 7 February 2014; revised manuscript received 21 May 2014; published 20 August 2014)

We investigate thermocapillary-driven contact-line dynamics of two immiscible fluids in a narrow fluidic confinement comprising substrates with patterned wettability variations. Our study, based on phase field formalism, demonstrates that the velocity of the contact line is a strong function of the combined consequences of the applied thermal gradient and the substrate wetting characteristics. Finally, we evaluate different energy transfer rates and show that the dissipation due to fluid slip over the solid surface plays a dominating role in transferring energy into the contact-line motion. Our analysis, in effect, provides an elegant way of controlling the capillary filling rate in a narrow fluidic confinement by tailoring the applied temperature gradient and the substrate wettability in tandem.

DOI: 10.1103/PhysRevE.90.023011

PACS number(s): 47.55.nb

I. INTRODUCTION

Flows of binary fluid systems over solid surfaces are omnipresent in many natural phenomena and in many engineering processes such as inkjet printing, coating of solids with liquid films, polymers processing, enhanced oil recovery, textile manufacturing, and fabrication of photographic films and disk drives, to name a few [1-5]. The ubiquities of the contact-line motion, relevant to many applications of these types, have attracted several researchers to concentrate on the underlying dynamical interactions over interfacial scales [5-9]. Furthermore, in recent years, the growing demand of miniaturization has necessitated the transport of small volumes of fluids in different physical processes, particularly, in chip cooling systems, on-chip biomedical analysis, drug delivery, and space technology. Systematic interrogation of the transport processes through microfluidic systems, therefore, is essential to unveil the underlying flow physics, which leads to far ranging consequences as far as the effectiveness of those devices and systems is concerned. In these miniaturized platforms, progressively new research issues have emerged all over the globe, including nontrivialities on contact-line dynamics over miniaturized scales [4,10–14].

Contact-line dynamics of immiscible binary fluids over microfluidic substrates has most commonly been studied under pressure-driven flow conditions [11,13,15–20]. However, of late, there has been an ever-increasing interest to study the interfacial dynamics of two immiscible fluids in microfluidic substrates as the consequence of an imposed wettability gradient [21,22]. In many of the concerned applications, applied temperature or concentration gradient acts as a source for generating the necessary wettability gradient, thereby giving rise to a net interfacial force [23–28], and a consequent transport known as Marangoni flow [29,30].

Over recent years, researchers have made extensive studies on thermocapillary-driven microchannel flows, [31–37] as well as microfluidic transport over chemically patterned surfaces [24,38,39]. Considering these effects acting in tandem, researchers, in recent times, have studied the effect of applied

1539-3755/2014/90(2)/023011(12)

chemically patterned surfaces [24,40]. The underlying issues, however, may become significantly more nontrivial in case the flow system consists of two immiscible phases instead of a single phase, leading to possible nonintuitive interplay of interfacial forces over the relevant spatiotemporal scales. This may be attributed to the fact that the thermocapillary driving force, acting across the interface, varies continuously as the capillary progresses along the channel. This spatiotemporal variation leads to interesting flow features which are unique to thermocapillary actuation. More work concentrating the thermocapillary flow–driven contact-line motion of immiscible binary fluids needs to be done, including a systematic interrogation of different attributes that affect the interfacial dynamics of contact-line motion and its ultimate influence on the filling dynamics.

temperature gradient on the flow of single phase fluid over

Here, we attempt to investigate the contact-line dynamics of two immiscible fluids under simultaneous actions of a patterned wettability gradient and an externally applied temperature gradient, based on a free energy based order parameter (phase field) formalism. We demonstrate that the contact line experiences stick-slip (pinning-depinning) motion over the patched section of the channel, and its velocity can be delicately controlled by altering the interactions between the surface wettability gradients and the thermocapillary body force, as modulated by the applied temperature gradient and the rate of change of interfacial tension with temperature.

II. MATHEMATICAL FORMULATION

A. Outline

Here, we use the phase field method to capture the thermofluidic transport. Among the other different methods available in the domain of multiphase flow modeling, the phase field model is a very popular one and is widely used in the theoretical research community [13,15,22,32,41–45]. The widespread applicability of the phase field method is primarily attributed to a number of important features such as the existence of a thermodynamic basis, the implicit interface tracking capability, and riddance of stress singularity by introduction of slip at the fluid-solid interface. Below, we

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discuss the simulation setup and the mathematical framework for the present study.

B. Simulation setup

1. Problem geometry

Our primary goal of the present study is to model the thermocapillary flow of immiscible binary fluids A and B through a narrow fluidic channel as shown in Fig. 1, in the presence of a substrate having predesigned wettability variations. The length and height of the channel are L and 2H, respectively, while the origin of the coordinate system is attached to the left center of the channel. We consider that the width of the channel is sufficiently larger than its height, which, in essence, allows us to carry out two-dimensional flow analysis. It is to be mentioned here that without sacrificing the generality of the problem and considering the symmetrical nature of the problem, we have considered only the upper half of the channel for our numerical simulations, where the x axis and y axis are taken to span along the length and height of the channel, respectively. We consider that fluid A initially resides at the left portion of the channel and fluid B initially occupies the remaining portion of the channel. In the present study, we assume the walls of the channel to be decorated with two different kinds of chemical patches, placed periodically along the length of the channel. The chemical patches are prespecified with different wettabilities, expressed in terms of the static contact angle θ_s . The periodicity of the chemical patches starts from a distance L_1 from the left of the domain, and extends up to $L_2 = 2n P_w$, where n = (1, 2, ..., N) is the number of patches of a single kind and P_w is the width of each patch. The characteristics of the patches are defined by



FIG. 1. (Color online) Schematic depicting the solution domain along with the physical dimensions. The solution domain is the symmetric upper half of the channel and the origin is placed at the center of the left end of the channel. Fluids A and B initially reside in the left and right side of the channel, respectively. The channel walls are chemically patched so as to provide a designed wettability. The fluid temperatures at the inlet and outlet of the channel are maintained at T_H and T_C , respectively. Initial temperatures of both the fluids are T_r . An external temperature gradient [$\nabla T = (T_H - T_C)/L$] acts on the system, which, in conjunction with the substrate wettability, dictates the contact-line dynamics.

specifying the static contact angles as

$$\theta_{s} = \begin{cases} \theta_{A} \forall 2 (n-1) P_{w} \leq x' \leq (2n-1) P_{w} \\ \theta_{B} \forall (2n-1) P_{w} \leq x' \leq 2n P_{w} \end{cases}$$

where $x' = (x - L_1)$ and the subscripts A, B are used to describe the properties of fluids A and B, respectively. In addition to the patterned section of the channel, we also consider $\theta_s = \theta_A \forall 0 \le x \le L_1$, and $\theta_s = \theta_B \forall L_1 + L_2 \le x \le$ L. We specify a temperature gradient, $(T_H - T_C)/L$, across the channel by specifying temperatures at the inlet (T_H) and the outlet (T_C) of the channel, respectively. The transport in the capillary is actuated by thermocapillarity. As mentioned before, we use the phase field method to explore the interfacial dynamics of two immiscible fluids, which is discussed in the subsequent section.

2. Phase field model

In compliance with the phase field theory, we introduce a phase field variable ϕ , which is also known as the order parameter function, to characterize two immiscible fluids in a binary flow configuration. Here, we define the order parameter ϕ as $\phi = (n_1 - n_2)/(n_1 + n_2)$, where n_1 and n_2 are the number density of molecules of fluid A and fluid B, respectively. Therefore, in the present study, we use $\phi = 1$ to indicate fluid A, while $\phi = -1$ is used to identify fluid B (see Fig. 1). The interface separating two bulk phases has a nonzero but finite thickness, where the order parameter function varies smoothly between $\phi = -1$ and $\phi = 1$. However, $\phi = 0$ essentially represents a single isoline and indicates the nominal location of the interface of the binary fluid system. We use the following free energy functional to describe the thermodynamical behavior of the binary fluid system [7,12,18,22,41–43,46,47]:

$$F = \int_{\Omega} [\psi(\phi) + 0.5k |\nabla \phi|^2] d\Omega, \qquad (1)$$

where Ω is the fluid domain, *F* is the total energy, and *k* is the coefficient which determines the interfacial tension. The first term $\psi(\phi)$ in the above equation is the bulk free energy density and can be cast in the form of a double well potential as given by [41,42]

$$\psi(\phi) = \frac{\sigma}{\xi} (\phi^2 - 1)^2.$$
 (2)

Note that the two minima of the phase field variable ϕ correspond to the two stable phases i.e., fluid A and fluid B, respectively. In Eq. (2), σ is related to the interfacial tension by $\sigma = \frac{\sqrt{2k}}{3}$, and ξ is the diffuse interface thickness. The second term, $0.5k |\nabla \phi|^2$, on the other hand, takes care of the excess of the free energy owing to the presence of an interface in a binary fluid system.

The variational derivative of the free energy functional with respect to the order parameter ϕ gives rise to the chemical potential of the system and takes the following form:

$$G = \frac{\delta F}{\delta \phi} = \psi'(\phi) - k \nabla^2 \phi.$$
(3)

It is to be noted here that the phase field variable is advected in the flow domain owing to the presence of a velocity field, while the chemical potential gradient allows the order parameter to diffuse in the flow field as well. Below, we write the evolution equation of the phase field variable, which is also known as the much celebrated Cahn-Hilliard (CH) equation [42,43,48–50].

$$\partial_t \phi + \mathbf{u} \cdot \nabla \phi = \nabla \cdot (M \nabla G). \tag{4}$$

Note that **u** in the above equation is the velocity field, and the parameter M (M > 0) is a constant and termed as the mobility of the order parameter. The term $\partial_t \phi$ is the partial derivative of order parameter function with time t. The mobility M controls the diffusion across the interface and has a direct bearing on the stability and convergence of the solution. In the present study, we consider a constant mobility, the value of which is obtained from the Molecular Dynamics (MD) simulation results of Qian *et al.* [11].

The boundary conditions for Eq. (4) at the wall are given by [20]

$$\mathbf{n} \cdot \nabla G = 0,$$

$$\mathbf{n} \cdot \nabla \phi = -\tan\left(\frac{\pi}{2} - \theta_s\right) |\nabla \phi - (\mathbf{n} \cdot \nabla \phi) \mathbf{n}|,$$
(5)

where **n** is the outward pointing normal to the solid wall. The first boundary condition of Eq. (5) indicates no flux through the solid surface, while the second boundary condition locally adjusts the order parameter profile close to the boundary so as to maintain the value of contact angle θ_s imposed at the solid substrate and the order parameter to be constant along the tangent to the interface.

3. Interfacial hydrodynamics and its coupling with the phase field theory

In this subsection, we look at the relevant governing equations for interfacial hydrodynamics coupled with the phase field variable and recall the necessary interfacial jump conditions. The relevant transport equations for the incompressible fluid flow are governed by the Navier-Stokes system of equations. On the other hand, the temperature distribution in the flow field is of essential importance for the thermocapillary-driven flows, which in effect, demand for the solution of the energy balance equation. We do mention here that the present analysis does not consider the variation of density and viscosity of the phases with temperature. Also, different phase change phenomena such as evaporation and condensation are excluded in the present analysis. Below we write the required set of governing transport equations for the mass, momentum, and thermal energy, pertinent to the problem taken up in the present analysis [51,52].

Continuity (for incompressible flow):

$$\nabla \cdot \mathbf{u} = 0. \tag{6}$$

Momentum conservation:

$$\partial_t(\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) = -\nabla p + \nabla \cdot [\mu(\nabla \mathbf{u} + \nabla \mathbf{u}^T)] + F_e.$$
(7)

Energy conservation:

The temperature distribution in the flow field in the absence of phase change, dissipative work, and compression work done by pressure is governed by the equation as given below [25,37,43,53]:

$$\partial_t (\rho c_P T) + \nabla \cdot (\rho c_P \mathbf{u} T) = \nabla \cdot (k_T \nabla T). \tag{8}$$

The parameters ρ , μ , c_P , and k_T in the above set of equations are the fluid density, viscosity, specific heat capacity, and the thermal conductivity, respectively. We assume that the material properties ρ , μ , c_P , and k_T are constant in each phase.

It is important to mention here that term F_e in Eq. (7) takes care of the interfacial stress jump accounting the surface tension force owing to local curvature effect of the interface and the Marangoni stress that arises because of thermocapillary effect. The term F_e , which essentially indicates the volume distributed force acting over the interface, is given by [37,43]

$$F_e = \frac{3\sqrt{2}}{4} k^{1/2} \nabla \cdot [\sigma(T)(|\nabla \phi|^2 \mathbf{I} - \nabla \phi \otimes \nabla \phi)].$$
(9)

Note that the term $\sigma(T)$ in Eq. (9) is the interfacial tension, which for a thermocapillary flow essentially becomes a function of the temperature. However, in the present study we consider a linear relationship between the interfacial tension and the temperature for ease of analysis which is given by [25,54]

$$\frac{\partial \sigma}{\partial T} = \sigma_T = \frac{\sigma(T) - \sigma_r}{T - T_r} = \text{constant.}$$
(10a)

Using Eq. (10a), we can write interfacial tension as

$$\sigma(T) = \sigma_r + \frac{\partial \sigma}{\partial T}(T - T_r).$$
(10b)

It is to be mentioned here that the rate of change of interfacial tension with temperature is defined by the term $\frac{\partial \sigma}{\partial T}$ and the term σ_r indicates the interfacial tension at reference temperature T_r .

The above set of governing transport equations [Eqs. (4) and (6)-(8)] can be cast in nondimensional form as given below:

$$\partial_{\bar{t}}\bar{\phi} + \bar{\mathbf{u}}\cdot\bar{\nabla}\bar{\phi} = \frac{1}{\operatorname{Pe}}\bar{\nabla}\cdot(\bar{M}\bar{\nabla}\bar{G}),\tag{11}$$

$$\bar{\boldsymbol{\nabla}} \cdot \bar{\boldsymbol{u}} = 0, \tag{12}$$

$$\operatorname{Re} \bar{\rho}[\partial_{\bar{t}}(\bar{\mathbf{u}}) + \nabla \cdot (\bar{\mathbf{u}} \otimes \bar{\mathbf{u}})] = -\bar{\nabla} \bar{p} + \bar{\nabla} \cdot [\bar{\mu}(\bar{\nabla} \bar{\mathbf{u}} + \bar{\nabla} \bar{\mathbf{u}}^{T})] + \bar{F}_{e}, \quad (13)$$

$$\bar{\rho}\bar{c}_P[\partial_{\bar{t}}(\bar{T}) + \bar{\nabla}\cdot(\bar{\mathbf{u}}\bar{T})] = \frac{\bar{k}_T}{\mathrm{Ma}}\bar{\nabla}\cdot(\bar{\nabla}\bar{T}).$$
(14)

We consider the properties to be phase dependent and related to the order parameter as [7,41,43,55]

$$\bar{\rho} = 0.5(1 - \rho_r)\phi + 0.5(1 + \rho_r),$$

$$\bar{\mu} = 0.5(1 - \mu_r)\phi + 0.5(1 + \mu_r),$$

$$\bar{c}_P = 0.5(1 - c_{P_r})\phi + 0.5(1 + c_{P_r}),$$

$$\bar{k}_T = 0.5(1 - k_{T_r})\phi + 0.5(1 + k_{T_r}),$$

(15)

where $\rho_r = \rho_B/\rho_A$, $\mu_r = \mu_B/\mu_A$, $c_{Pr} = c_{PB}/c_{PA}$, and $k_{Tr} = k_{TB}/k_{TA}$ are the density, viscosity, specific heat, and thermal conductivity ratio of the two fluids, respectively.

Next, we enlist the important pertinent nondimensional parameters that influence the interfacial dynamics described by the above systems of equations. These parameters are given as follows: Péclet number, $Pe = \frac{u_c \xi^2}{M_c \sigma}$; Marangoni number, $Ma = \frac{\rho_A c_{PA} \xi u_c}{k_{TA}}$; capillary number, $Ca = \frac{u_c \mu_A}{\sigma_r}$; Reynolds number,

 $Re = \frac{\rho_A u_c \xi}{v_c}$. In addition to the above dimensionless parameters, ratios of different fluid properties such as the density ratio $\rho_r = \frac{\rho_B}{\rho_A}$, the viscosity ratio $\mu_r = \frac{\mu_B}{\mu_A}$, the specific heat capacity ratio, $c_{Pr} = \frac{c_{PB}}{c_{PA}}$, and the thermal conductivity ratio $k_{Tr} = \frac{k_{TB}}{k_{TA}}$ do also have an important role to play in the interfacial dynamics. We use the macroscopic properties of fluid A as the reference properties in the present study, while u_c is the velocity scale of the system under consideration. We calculate the characteristic velocity by balancing the thermocapillary force with the viscous drag acting over the interface, which gives $u_c \sim 10^{-5}$ m/s. In the present study, we consider the ratios of fluid properties as [13,43] $\rho_r = 1$, $\mu_r = 1$, $k_{Tr} = 1$, $c_{Pr} = 1$. Furthermore, the characteristic scales (velocity and the length scales) chosen in the present study along with the values of different fluid properties give the values of different dimensionless parameters Re, Ca, Pe, and Ma, which are of the O(0.01) or at most O(0.1).

It is important to mention here that since we neglect any phase change, the explicit coupling of the energy equation with phase field equation is absent and the variation of temperature in the flow field is implicitly linked with the evolution of phase field variable through the property relationship as given by Eq. (15). Since we consider the ratios of different fluid properties to be unity in the present study, the energy equation gets decoupled from the phase field variation. However, we do mention here that a change in the interfacial tension with the change in temperature, which we assumed in the present study to be varied following an equation of state as given by Eq. (10b), eventually leads to the local change in the topology of the interface. The local change in the interface curvature arising because of the variation of temperature gives rise to an additional term in the momentum balance equation, which is known as Marangoni force, as given by the first term of the right-hand side of Eq. (9).

We next discuss the boundary conditions for the governing transport equations mentioned above. It is important to mention here that the mathematical modeling of the problems related to contact-line dynamics comes across a fundamental difficulty of nonintegrable stress singularities [56,57]. In order to obviate the problem of stress singularity, attempts have been taken to employ the Navier-slip boundary condition in the macroscopic model to address the physics of the contact-line dynamics [58,59]. In this regard, the diffuse interface models have gained tremendous popularity owing to their inherent advantages associated to their mathematical framework, viz., the removal of stress singularity by introduction of slip at the fluid-solid interface [20,60-62]. We do mention in this context here that researchers have pointed out the inherent potential of the phase field method, to be precise the diffuse interface method, which introduces slip at the contact line thereby averting the adverse effect of the stress singularity problem [6,8,63,64]. However, in the present study, we use the Navier-slip boundary condition $(\bar{u}_{\parallel} = l_{s1,2}\partial_{\nu}\bar{u}_{\parallel})$ on the walls of the channel for the momentum equation, and the slip length specified on each stripe corresponds to those given in Ref. [13]. We consider one set of slip lengths given by $l_{s1} = 3.8$, $l_{s2} = 10$, where l_{s1} is used to specify slip length for the same type of fluid and patch combination and l_{s2} is used for an unmatched fluid-patch combination. We

assumed that both the fluids were initially at rest, so the initial velocity of the fluid over the entire domain $\mathbf{\bar{u}}(\bar{x}, \bar{y}, 0) = 0 \forall \bar{x}, \bar{y}$. Moreover, no penetration boundary condition $(\bar{v}_{\perp} = 0)$ is applied at the walls of the channel. We further consider the inlet (\bar{p}_{in}) and outlet gauge pressure (\bar{p}_{out}) to be zero for our simulations. The solution of the thermal energy equation necessitates the boundary condition for temperature at the system boundaries. We consider that both the walls of the channel are insulated $[-\mathbf{n} \cdot (-\bar{k}_T \mathbf{\bar{\nabla}} T) = 0]$, while we specify constant and uniform dimensionless temperatures \bar{T}_H and \bar{T}_C at the inlet and the outlet of the channel, respectively. For the sake of completeness, we schematically show, in Fig. 2, the computational domain including the governing transport equations and the appropriate boundary conditions in their nondimensional form.

C. Numerical implementation and model validation

In the present study, we have used the finite element multiphysics framework of COMSOL for solving the coupled phase field–Navier-Stokes-energy conservation system of equations as given by Eqs. (11)–(14). We have specified tolerance levels of 10^{-6} for all the numerical simulations. We have used the PARDISO solver and the generalized- α scheme for the time stepping method of COMSOL MULTIPHYSICS. In order to capture the flow physics of contact-line motion formed at the fluid-fluid-solid interface, we have used $\Delta x = \Delta y = 0.2\xi$ and used relatively finer mesh very close to the wall of the channel. It is to be mentioned here that although we use ξ as the length scale in the present study, the value of the effective Cahn number is 0.005 which gives a grid resolution sufficient to attain a sharp interface limit [8].

It is important to mention in this context here that before applying the temperature gradient to actuate bulk fluid motion, we initialize the phase field variable to form the interface of the two coexisting bulk phases ($\phi = \pm 1$). Initialization of the phase field variable, in essence, leads to an equilibrium interface profile following the solution of the equation:

$$G\left(\phi\right) = 0. \tag{16}$$

The equilibrium order parameter profile normal to the plane interface is given by [41]

$$\phi(z) = \tanh\left(\frac{z}{\sqrt{2\xi}}\right),\tag{17}$$

where z is the coordinate direction normal to the plane interface.

We further mention that from here onwards we will drop the bar signs from the variable symbols used to represent nondimensional quantities for the ease of presentation.

1. Model benchmarking and grid independence study

The modeling framework of the present study has extensively been benchmarked. We have primarily followed a dual benchmarking strategy delineated below.

Benchmark 1: Contact-line dynamics. We have benchmarked the phase field model for the moving contact-line problems using results reported in Wang *et al.* [13], whose model and numerical framework are in turn benchmarked



FIG. 2. (Color online) Schematic of the solution domain showing the governing transport equations and the appropriate boundary conditions. The channel wall is chemically patched, characterized by predefined contact angle θ_s . There is an externally applied temperature gradient, which actuates the fluid motion into the channel. The velocities \bar{v}_{\parallel} and \bar{v}_{\perp} are the components along the parallel and perpendicular to the surface.

against molecular dynamic simulations [11]. In Fig. 3(a) below, we show the variation of the contact-line velocity with distance along the channel. The results show extremely good agreement with those reported in Ref. [13].

Benchmark 2: Complete model including thermocapillarity. We have benchmarked our numerical model coupled with thermocapillarity with the experimental results reported in Ref. [40]. In Fig. 3(b), we show the variation of temperature difference along the length of the channel $[T(x) - T_c]$. One can see a good agreement between the simulation results obtained from the present study with the corresponding experimental observations reported in Ref. [40].

Grid independence study. We have also performed a grid independence study. In Figs. 3(c) and 3(d) we show the grid convergence results where we clearly depict the variation of the contact-line velocity as a function of distance along the channel for different grid resolutions and time step variations. The different parameters used in the grid independence study have clearly been mentioned in the figure caption. It is clearly evident that the variation of velocity with alteration in time step size is negligible. However, with change in grid size, we observe some variation in the contact-line velocity, which attenuates as the grid size is reduced below Δx , $\Delta y = 0.1\xi$, 0.2ξ . Accordingly, we have used grid size Δx , $\Delta y = 0.2\xi$ in all our subsequent studies.

III. RESULTS AND DISCUSSIONS

The thermocapillary flow-driven contact-line motion and the resulting capillary filling dynamics of immiscible binary fluids are likely to be influenced by a number of key parameters: (a) { T_H, T_r, T_C }, the inlet, reference, and outlet temperature of the fluid respectively; (b) $B = \frac{\partial \sigma/\partial T}{\sigma_r}$, the ratio

of the rate of change of interfacial stress with temperature to the interfacial stress at reference temperature; (c) P_w , the period of the surface patches; (d) the ratios of the different fluid properties, and (e) $r = \theta_A/\theta_B$, the contrast in the wettability over the patches. Since the interfacial stress at any reference temperature is always positive, a decreasing nature of the interfacial tension with increasing temperature makes the term B to be always negative. Accordingly, two different values of B (B = -0.02 and -0.04) have been considered in the present study to determine the contact-line motion in a thermocapillary flow environment. In the present study we have considered the values of the contact angles to be [13] $\theta_A=77.6^\circ$ and $\theta_B=102.4^\circ$ for most of the cases, which essentially leads to r = 0.7578. Moreover, in order to show the effect of wettability contrasts on the contact-line motion, we also consider four different values of r as [13] r =0.6453,0.48,0.40, and 0.3373. The domain dimensions used in the present study (see Fig. 1) are L = 100, $L_1 = 36$, and $L_2 =$ 24. The dimensionless half channel height has been taken to be H = 20 throughout the analysis. It is important to mention here that the typical values of dimensionless parameters considered in the present simulations are [43] Re = 0.01, Ca = 0.01, $Ma \approx 0.01$, and Pe = 0.02 unless otherwise mentioned.

A. Contact-line dynamics

Thermocapillary motion of the contact line of two immiscible fluids is an outcome of the alteration in the surface tension force acting over the fluid-fluid and fluid-fluid-solid interface owing to the temperature gradient applied along the channel. The surface tension gradient results in a force on the contact line, which eventually creates a tangential motion of the interface. Note that the alteration in the



FIG. 3. (Color online) *Model benchmarking:* (a) Contact-line velocity shown as a function of distance along the capillary. (b) Temperature distribution along the length of the channel. The simulations results using the present model are represented by the solid lines and the square markers are used to represent the results reported in Refs. [13] and [40], respectively. The results of the present numerical framework show fairly accurate match with the reported numerical and experimental results. *Grid independence study:* Contact-line velocity as a function of the location along the channel for (c) three different values of grid sizes and (d) three different time step values. For (c) and (d) the different parameters considered are patch width $P_w = 1.5$, $\{T_H, T_r, T_C\} = \{32, 16, 0\}$, Re = 0.01, Ca = 0.01, Ma = 0.01, Pe = 0.02, and B = -0.04.

surface tension force is a strong function of the temperature distribution in the flow field and is governed by Eq. (10b). Since the temperature distribution in the flow field dynamically changes with time, the net surface tension force acting over the interface, which is a strong function of the temperature distribution in the flow field, will also spontaneously change as the interface moves along the channel. Therefore, a unique feature of the present study is essentially the driving force of the flow actuating mechanism that changes continuously with time as the interface progresses along the channel.

Figure 4 shows the variation of contact-line velocities with surface wettabilities. In Fig. 4(a), we show the contact-line velocity along the length of the channel considering a constant contact angle. In order to do so, we consider two different values of the contact angle $\theta_s = 70.6^\circ$ and 77.6° , respectively. The different parameters considered in the present study have been mentioned in the beginning of the Results and Discussions section, which are in tune with those considered in Ref. [43].

One can see from Fig. 4(a) that the contact-line velocity increases gradually as the interface moves along the channel, and reaches a maximum. Further downstream of the channel,

as the driving force acting over the interface decreases progressively, it drops to zero. In Figs. 4(b) and 4(c), we show the contact-line velocity (v_{cl}) as a function of position along the channel for three different patch widths ($P_w = 0.75$, 1.5, and 3.0) and two different thermal actuation scenarios. The contact-line velocity (v_{cl}) shows a stick-slip behavior as the interface moves over the patches, which is inherent to typical wettability-gradient surfaces.

In order to study the influence of applied temperature gradient on the contact-line motion, we consider two different thermal actuation scenarios for each of the patch widths considered: (a) $\{T_H, T_r, T_C\} = \{32, 16, 0\}$ and (b) $\{T_H, T_r, T_C\} = \{20, 10, 4\}$. It is clear from Fig. 4 that the variation of the contact-line velocity obtained under different thermal actuations makes no qualitative difference. The magnitude of the contact-line velocity in case (b), however, appears to be less than that in (a). Relatively lower magnitude of the contact-line velocity in case (b), for all the patch widths considered, is essentially attributed to the lower magnitude of driving force acting over the interface because of the reduced thermocapillary body force owing to lower temperature gradient imposed along the channel. Interestingly, for the largest patch width $P_w = 3.0$ considered in the present study, the interface cannot



FIG. 4. (Color online) Contact-line velocity v_{cl} vs x: (a) for constant surface wettability $\theta_s = 70.6^\circ$, 77.6° and $\{T_H, T_r, T_C\} = \{32, 16, 0\}$. For three different patch widths $P_w = 0.75$, 1.5, and 3: (b) $\{T_H, T_r, T_C\} = \{32, 16, 0\}$ and (c) $\{T_H, T_r, T_C\} = \{20, 10, 4\}$. The other parameters are Re = 0.01, Ca = 0.01, Ma = 0.01, Pe = 0.02, and B = -0.04 in case (b) and -0.02 in case (c). For the constant wettability case, the contact-line velocity increases initially, reaches maximum, and finally becomes zero. The contact-line velocity shows oscillation as it moves over the chemically patterned surface, solely attributable to the (de)pinning mechanism of the contact line. The velocity of the contact line decreases gradually as the interface moves along the channel. For the smaller patch width $P_w = 0.75$ and 1.5, the interface traverses the patterned section completely. For the larger patch width $P_w = 3.0$, retreating of contact-line velocity following the reverse movement of the interface initiates as the interface comes over the unfavorable patch (B-like patch) before it crosses the entire patterned section of the channel.

traverse the entire patterned (patched) section; rather it gets pinned over an unfavorable patch (i.e., on a B-like patch) before it crosses the patterned surface, as can be seen from Fig. 4. The physical explanation of this kind of behavior of contact-line velocity essentially stems from the fact that the driving thermocapillary force acting over the interface continuously decreases as the interface progresses along the channel.

In Fig. 5, we show the variation of the magnitude of the temperature gradient acting across the contact line $(|\nabla T|_{cl})$ as it moves along the channel for different patch widths [Fig. 5(a)] and for different thermal actuation strengths [Fig. 5(b)]. The



FIG. 5. (Color online) Temperature gradient acting across the contact line as a function of x with variation of (a) patch width for $\{T_H, T_r, T_C\} = \{32, 16, 0\}$ and (b) thermal actuation strength for $P_w = 3.0$. It is important to note that as the interface progress, the temperature gradient acting across the contact line, which is the primary driving force, decreases monotonically. When the magnitude of the temperature gradient decreases below a threshold, the actuating force is not strong enough to drive the interface along and we observe interface pinning.

patch width considered for Fig. 5(b) is $P_w = 3.0$, while $\{T_H, T_r, T_C\} = \{32, 16, 0\}$ are considered for Fig. 5(a).

It is clear from Fig. 5 that as the interface progresses, the temperature gradient acting across the contact line decreases monotonically. When the temperature gradient falls below a threshold value (shown by dotted green circles), the Marangoni forces are no longer strong enough in dragging the interface along and we observe interface pinning. When the interface comes over the unfavorable patch further downstream from its commencement, a weak temperature gradient fails to weaken the oppositely acting interfacial surface tension originating from the wettability pattern, which, in essence, allows the interface to move back instead of having its forward movement. This phenomenon is consistently reflected in Figs. 4 and 6, where the contact-line velocity for the larger patch width becomes negative, following the movement of the interface in the reverse direction. For the larger patch widths, since the magnitudes of the maximum and the minimum contact-line velocity vary markedly, zones of variation of the temperature



FIG. 6. (Color online) Time sequence of the interface profiles for patch width $P_w = 1.5$ and 3.0 for (a) $\{T_H, T_r, T_C\} = \{32, 16, 0\}$ and (b) $\{T_H, T_r, T_C\} = \{20, 10, 4\}$. The crowding zone of the interface profiles as seen is essentially because of the pinning mechanism of the interface over unfavorable patches [B-like patches; shown by green color (light patch)]. With the progression of the interface along the channel, the net driving force acting over the interface decreases and the crowding zone of the interface profiles becomes relatively denser as indicated by I, II. A deep crowding zone of the interface profiles for $P_w = 3.0$ is due to the reverse motion of the interface following the retreating of the contact-line velocity. The reverse motion of the interface starts at the time when the interface comes over the unfavorable patch [B-like patches; shown by green color (light patch)] and the net driving force reduces substantially. For a relatively lower applied temperature gradient along the channel, the deep crowding zone appears earlier in the process owing to smaller magnitude of net driving force acting over the interface.

gradient are clear. Accordingly, we find distinct signatures of slip-stick behavior manifested as relatively flatter plateaus (shown by dotted red circles) in regions of contact-line slip and relatively steeper variation of the temperature gradient in regions of stick. Also, the retreating of contact-line velocity, as seen for the case of the largest patch width, $P_w = 3.0$, initiates earlier as the applied temperature gradient in the flow field decreases at a faster rate. With a decrease in the applied temperature gradient across the channel, the pinning states following the retreating motion of the contact line occur at a much earlier location (see Figs. 4 and 6). This is because the



FIG. 7. (Color online) Contact-line velocity v_{cl} vs x for (a) $\{T_H, T_r, T_C\} = \{32, 16, 0\}$ for patch width $P_w = 1.5$ for different values of contrast in wettability r = 0.7578, 0.6453, 0.48, 0.40, 0.3373. The other parameters are Re = 0.01, Ca = 0.01, Ma = 0.01, Pe = 0.02, and B = -0.04. The contact-line velocity shows oscillation as it moves over the chemically patterned surface. For the smallest contrast in wettability r = 0.3373, the amplitude of oscillations becomes higher and the amplitude of oscillations in contact-line velocity keeps on decreasing with increasing value of r. For all the values of r considered, the interface traverses the patterned section completely, albeit the retreating of the contact-line velocity follows the reverse movement of the interface initiates earlier as r decreases (see inset B).

temperature gradient decreases below the threshold value at a much earlier location. This is clearly evident from Fig. 5(b).

1. Effects of wettability contrasts of patches on the dynamics of the contact line

Figure 7 shows the variation of the contact-line velocity for different contrasts in wettabilities of the patches ($r = \theta_A/\theta_B$) placed at the walls of the channel, for a patch width of $P_w = 1.5$. The other parameters considered are Re = 0.01, Ca = 0.01, Ma = 0.01, Pe = 0.02, and B = -0.04. In tune

with the gradual decaying nature of the driving force acting across the contact line as the interface progresses along the channel, the contact-line velocity decreases gradually for all the values of r considered. The lower value of r indicates relatively stronger hydrophobicity (wetting strength of the B-type patch with respect to the displacing fluid, i.e., Fluid A) of the wall. Therefore, an acute pinning of the contact line for a relatively lower value of r (see inset A) and its ultimate consequence on the retreating of contact-line velocity at an earlier location (see inset B) is quite obvious, as clearly reflected in Fig. 7. Another important point to note is that the amplitude of oscillations of the contact-line velocity increases substantially with a decreasing value of r. This is essentially because of the increased wetting strength of B-type patches.

B. Capillary filing dynamics: The effects of temperature gradient

Figure 8 shows the variation of the capillary filling distance (x) with time (t) for different patch widths $P_w = 0.75, 1.5,$ and 3.0, respectively. Figures 8(a) and 8(b) depict two different thermocapillary actuation scenarios: (a) $\{T_H, T_r, T_C\} =$ $\{32, 16, 0\}, B = -0.04 \text{ and } (b) \{T_H, T_r, T_C\} = \{20, 10, 4\}, B =$ -0.02. Note that L_2 is the span of the chemically patched section, which is essentially our region of interest for the capillary filling time. The relative difference in the total filling times with different patches as seen from the above two figures is primarily attributable to the widths of the chemical patches considered. Quite notably, for the largest patch width $P_w = 3.0$ considered in the present study, the interface cannot traverse the patterned section completely; rather it starts retreating before it crosses the entire patterned length along the capillary. Having a closer look at Fig. 4 and the corresponding variation of capillary filling time depicted in Fig. 8, one can find that all the important features on the variation of contact-line velocity



FIG. 8. (Color online) (a) Time (t) vs capillary filling distance (x), for different patch widths: (a) $\{T_H, T_r, T_C\} = \{32, 16, 0\}$ and B = -0.04; (b) $\{T_H, T_r, T_C\} = \{20, 10, 4\}$ and B = -0.02. The other parameters are Re = 0.01, Ca = 0.01, Ma = 0.01, and Pe = 0.02. All the parameters and boundary conditions considered here correspond to those taken in Fig. 4. For a given applied temperature gradient and other different parameters, the filing time decreases with the decrease in patch width. For the larger patch width given by $P_w = 3.0$, the filing time shows oscillation following the phenomenon of the retreating of the contact line, and the displacing phase fluid cannot traverse the entire patterned section of the channel.

are aptly reflected in the variations in the filling times. As the patch width increases, the duration of pinning of the contact line over the unfavorable patches spans for a relatively longer period of time, leading to a larger filling time. On the other hand, the driving force acting over the interface continuously decreases as the meniscus progresses along the channel, owing to reduced magnitude of temperature gradient. Moreover, the net drag force acting over the interface gets enhanced by the wetting characteristics of the unfavorable patch. It is to be noted here that the magnitude of the drag force arising because of the wetting characteristics of the unfavorable patch will increase as we increase the patch width. Therefore, the reduced magnitude of temperature gradient together with the effect of higher drag over the interface at times when the interface comes in contact with the unfavorable patches results in a reverse motion of the contact line (see Fig. 4 for $P_w = 3.0$). The reverse motion of the contact line is essentially reflected on the capillary filling time, which we confirm by the appearance of oscillations in the variation of t vs x plots in Fig. 8. From the plot of capillary filling time for the patch widths $P_w = 0.75$ and 1.5, it is noteworthy that the contact line approaches a stationary profile after the contact line traverses the patterned section of the channel.

C. Energy budget of the moving contact line

We next analyze the total rate of energy dissipation as the interface progresses along the channel. We compute three different sources of energy transfer rates: the shear viscosity dissipation in the bulk $\dot{E}_{\rm viscous}$, the change of total kinetic energy $\dot{E}_{\rm kinetic}$, and energy transfer due to slip of fluid on the solid surface $\dot{E}_{\rm surface}$. The total energy dissipation \dot{E}_D can be written as

$$E_D = E_{\rm viscous} + E_{\rm surface} + E_{\rm kinetic}, \tag{18}$$

where

$$\dot{E}_{\text{viscous}} = \int_{\Omega} \mu(\phi) (\nabla \mathbf{u} + \nabla \mathbf{u}^T) : (\nabla \mathbf{u} + \nabla \mathbf{u}^T) d\Omega, \quad (19)$$

$$\dot{E}_{\text{kinetic}} = \int_{\Omega} 0.5 \frac{\partial \rho(\phi) \mathbf{u}^2}{\partial t} d\Omega, \qquad (20)$$

$$\dot{E}_{\text{surface}} = \int_{\Gamma} \frac{\mu}{l_s} \mathbf{u}^2 d\Gamma.$$
(21)

We would like to mention here that the order of the rate of dissipation due to the phase field diffusion near the sold surface (contact line) is negligible compared to the other dissipations [13] and, hence, we do not consider the same while calculating the total energy dissipation here. We next express these parameters in a nondimensional framework. In order to do so, we use the rate of change of surface energy $\sigma u_c \xi$, where ξ is the interface thickness (length scale of the present study) and u_c is the reference velocity, to make the above expressions dimensionless. The normalization, however, includes two dimensionless numbers, i.e., the Reynolds number (Re) and capillary number (Ca) as can be seen from the expressions given in Eqs. (23)–(25). We would like to mention in this context here that the typical values of Re and Ca that have been considered in the present analysis are mostly O(0.01), and accordingly, we consider Re = Ca = 0.01, while calculating different energy dissipation rates in the present section. In dimensionless terms,

$$\bar{E}_D = \bar{E}_{\text{viscous}} + \bar{E}_{\text{surface}} + \bar{E}_{\text{kinetic}}, \qquad (22)$$

where

$$\bar{E}_{\text{viscous}} = \int_{\bar{\Omega}} \operatorname{Ca} \bar{\mu}(\phi) (\nabla \bar{\mathbf{u}} + \nabla \bar{\mathbf{u}}^T) : (\nabla \bar{\mathbf{u}} + \nabla \bar{\mathbf{u}}^T) d\bar{\Omega}, \quad (23)$$

$$\bar{E}_{\text{kinetic}} = \int_{\bar{\Omega}} 0.5 \text{Re} \,\text{Ca} \,\frac{\partial \bar{\rho}(\phi) \bar{\mathbf{u}}^2}{\partial \bar{t}} d\bar{\Omega},\tag{24}$$

$$\bar{E}_{\text{surface}} = \int_{\bar{\Gamma}} \frac{\operatorname{Ca}\bar{\mu}(\phi)}{l_s} \bar{\mathbf{u}}^2 d\bar{\Gamma}.$$
 (25)



FIG. 9. (Color online) Evolution of different energy transfer rates as a function of time: (a) $\{T_H, T_r, T_C\} = \{32, 16, 0\}$ and (b) $\{T_H, T_r, T_C\} = \{20, 10, 4\}$. The different parameters are Re = 0.01, Ma = 0.01, Ca = 0.01, and Pe = 0.02. All the parameters and boundary conditions considered here correspond to those as taken in obtaining Fig. 4. Energy dissipation due to fluid slip at the wall is the highest among the three different rates of energy dissipations. All the energy dissipation rates are seen to decrease over the hydrophobic patches and become zero, while the contact line crosses the patterned section and moves towards the hydrophobic patch. The oscillation of the rate of the kinetic energy dissipation leads to a negative value in its variation.

Figures 9(a) and 9(b) show the variations of three different energy dissipation rates as a function of time, as the interface proceeds along the channel. The values of the relevant parameters have been mentioned in the figure caption. One can find that the surface energy dominates among the three different energy transfer terms. Note that all the energy transfer rates exhibit oscillatory trends as the contact line moves over the patched section of the channel. The underlying physics behind the appearance of undulations in the different energy transfer rates can be established from the existence of two different wavelengths of energy owing to different wetting strengths of the patterned substrate. The undulations in energy transfer rates give rise to oscillations in the contact-line velocity as one can find from Fig. 4. We can see from the above figures that, for the value of contact angle $\theta_s > 90^\circ$, which corresponds to a hydrophobic case (B-like patch in the present study), all the energy transfer rates decrease and finally become zero as the contact line crosses the patterned section of the channel. As such, the hydrophobic patches (i.e., B-like patch; $\theta_s = 102.4^\circ$) transfer markedly less energy into the motion of contact line in comparison to that of the hydrophilic patches (i.e., A-like patch; $\theta_s = 77.6^\circ$), which is in good agreement with the reported MD simulation results [22].

IV. CONCLUSIONS

In the present study, we have investigated the thermocapillary-driven contact-line dynamics of two immiscible fluids through a microfluidic channel having patterned substrate wettabilities. We have assumed that a constant temperature gradient applied along the channel sets the binary fluid system in motion. We have demonstrated that the applied temperature gradient plays a

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distinctive role towards modulating the interfacial dynamics of contact-line motion, which, in many aspects, is in sharp contrast with the corresponding implications in a pressuredriven flow paradigm. The main findings from our studies can be summarized as follows:

(i) The contact-line velocity exhibits a continual decreasing trend as the interface moves along the channel, for all the patch widths considered, as attributable to a continuously decaying thermocapillary force.

(ii) The appearance of oscillations in the variations of contact-line velocity is the direct consequence of the stickslip behavior of the contact line during the course of its motion. The velocity fluctuations keep on increasing with increases in the patch width. The velocity becomes the highest when the wetting strength of the chemical patch and the thermocapillary body force aid each other (i.e., in the A-like patch; $\theta_s = 77.6^\circ$), and becomes the lowest when both the forces oppose each other, essentially on the B-like patch for $\theta_s = 102.4^\circ$.

(iii) For the largest patch width $P_w = 3.0$, the contact-line motion gets pinned on the B-like patch before the interface traverses the entire patterned domain, resulting in meniscus retraction. Depending on the magnitude of applied temperature gradient, the location of the onset of the reverse movement of the contact line changes.

The inferences drawn from the present analysis implicate that the contact-line motion can be modulated as a combined consequence of the intrinsic surface wettability variations (as dictated by the chemical patches) and the imposed thermal gradients. By exploiting this interplay, it is plausible to turn the contact-line motion on and off at will, thereby improving the maneuverability of capillary filling in lab-on-a-chip based microfluidic devices.

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