Disorder-induced hysteresis and nonlocality of contact line motion in chemically heterogeneous microchannels

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(Dated: 16 December 2011)

We examine the motion of a liquid-air meniscus advancing into a microchannel with chemically heterogeneous walls. We consider the case where a constant flow rate is imposed, so that the mean velocity of the interface is kept constant, and study the effects of the disorder properties on the apparent contact angle for each microchannel surface. We focus here on a large diffusivity regime, where any possible advection effect is not taken into account. To this end, we make use of a phase field model that enables contact line motion by diffusive interfacial fluxes and takes into account the wetting properties of the walls. We show that in a regime of sufficiently low velocities, the contact angle suffers a hysteresis behavior which is enhanced by the disorder strength. We also show that the contact line dynamics at each surface of the microchannel may become largely coupled with each other when different wetting properties are applied at each wall, reflecting that the dynamics of the interface is dominated by nonlocal effects.

I. INTRODUCTION

Wetting phenomena are of paramount significance in numerous natural phenomena and technological applications. They are also central in many fields, from condensed matter physics and fluid mechanics to materials science, surface chemistry and biology. As a consequence, they have received considerable attention, both theoretically and experimentally for several decades (see Ref. 1 for a recent review).

Wetting phenomena typically involve a liquid-gas (usually air) interface advancing or receding on a solid substrate. The wetting characteristics of a solid substrate are usually quantified in terms of the contact angle at the three-phase conjunction, defined as the angle between the liquid-gas interface and the wetted area of the substrate. The intersection between the liquid-gas interface with the solid substrate is commonly referred to as contact line. When one of the two fluids moves against the other, the contact line has to move relative to the solid boundary. A problem of dynamic wetting that has attracted a lot of attention over the years is the history-dependence of the contact line, and in particular, the hysteresis behavior of the contact angle. Contact-angle hysteresis is usually characterized by a discontinuous jump between the measured contact angle of an advancing and a receding contact line in the zero velocity limit. It is now generally accepted that the origin of such hysteresis is mainly due to the presence of either chemical or topographical heterogeneities on the substrate²–⁴ and it is related to the presence of a wide range of possible metastable states that describe the equilibrium configuration of the contact line⁵. Several approaches for different wetting situations have been considered during the last years in order to understand such phenomenon. Examples include contact angle hysteresis in droplet motion induced by heterogeneous substrates⁶–⁸, or by shear flow⁹. However, a satisfactory description of the hysteresis in terms of the disorder properties of the substrate, e.g. density of the defects or disorder strength, is still lacking (see for example the discussion on hysteresis in the recent review by Bonn et al.¹¹). Likewise, another important issue in the physics of wetting phenomena is whether one can consider the dynamics of the contact line as a local process, i.e., a process that mainly depends on the local velocity close to the contact point, or, by contrast, a process dominated by non-local effects, i.e., long-range correlations along the liquid-gas interface that are a consequence of the global flow rate conditions applied at the system.

In the present study we address these questions by using as a model system for contact line motion a two-dimensional (2D) liquid-air meniscus advancing into a 2D Hele-Shaw-like microchannel with chemically disordered surfaces (our system is assumed translationally invariant in the transverse direction). The displacement of a fluid by another one in a microchannel is a subject of increasing interest in many engineering applications, especially within the framework of the rapidly growing fields of microfluidics and miniaturization of chemical devices¹⁰. A number of fundamental questions has also attracted significant attention over the last few years in particular in relation to the effects of the microchannel surfaces upon the contact line dynamics of a liquid-air meniscus advancing through the channel. These include, for example, how the wetting and/or roughness properties of the solid boundaries may induce complex phenomena like contact angle hysteresis⁴,⁷,¹¹,¹² or contact line pinning/depinning¹³–¹⁷. As we noted earlier, a satisfactory description of hysteresis in terms of the accessible control parameters of the system, such as strength of the disorder or distribution of defects, is still lacking. In fact, the same is true regarding pinning/depinning effects which however, are beyond the scope of this study. Clearly, achieving a systematic and rational description
of such complex wetting phenomena in terms of the disorder properties is crucial, both from a fundamental point of view and engineering applications.

Our microchannel consists of two parallel plates separated by a narrow distance which is much smaller than the dimensions of the channel plates, and is usually smaller than the capillary length $\ell_c$, denoting the relative importance between surface tension and gravity, which for most liquids is $\ell_c \sim 1 \text{ mm}^{18}$. In this case, (a) gravity does not play a significant role, and (b) channel surface heterogeneities and nonlocal effects arising from a competition between the relevant forces acting on the interface, e.g. surface tension and driving force, may play a crucial role in the contact angle dynamics. Regarding nonlocality, of particular interest is the study of possible correlations between the contact line dynamics at each surface plate, or more specifically, to understand under which conditions both contact lines can be considered independent from each other when they are perturbed by random heterogeneities, or otherwise they follow a coupled dynamics as a consequence of nonlocal effects.

We consider here a regime where diffusion processes dominate over advection processes. This means that any typical velocity is assumed to be sufficiently small so that the system is considered to be close to an equilibrium state. To model this situation, we make use of a diffuse interface model that enables contact line motion by diffusive transport of mass. The dynamics of the process is then described in terms of the model B (if we follow the Hohenberg and Halperin terminology$^{19}$), and the wetting properties are incorporated into the model via a surface energy term$^{20}$ that takes into account solid-fluid interactions. By imposing forced flow conditions, i.e., constant flow rate we focus on the effect of the disorder on the hysteresis of the contact angle and on the correlation between the dynamics of the contact lines of both walls. We show that the walls’ disorder produces an important effect on the measured apparent contact angle, inducing a hysteresis behavior between the advancing and receding motion which, in turn, is enhanced as the strength of the noise is increased. We also show that there exists a coupled dynamics between both contact lines which is particularly important when different wetting properties are applied at each surface channel. Although our study is restricted to a 2D system, it is a first step towards the understanding of the influence of chemical heterogeneities on the contact line dynamics in more complex, e.g. three-dimensional (3D) systems.

The structure of the paper is as follows. The problem formulation, physical set-up definition and the diffuse interface model we adopt are outlined in Sec. II. Our results on contact angle hysteresis and nonlocality are presented in Sec. IV. Finally, conclusions and perspectives are given in Sec. V.

![FIG. 1. (Color online) Sketch of the profile geometry for a 2D meniscus in a 2D chemically heterogeneous microchannel. The bottom panel shows how the contact angle is defined in our numerical results: the red solid line represents a quadratic fit to the interface points (solid circles), which allows to extrapolate the contact point (star). The contact angle is then defined as the angle between the line tangent to the interface at the contact point (dot-dashed line) with the wetted part of the substrate.](image-url)
the two phases in the potential double-well potential, the other in a finite region of width $\varepsilon$, the diffuse interface. (b) The effect of introducing a non-zero gradient of the chemical potential $\mu$ (via e.g. external forcing) is to destabilize one of the two phases in the potential double-well $V(\phi)$.

framework of the classical fluid mechanics approach. Another way to put it is that because of the diffuse character of the interface (effective) slip appears naturally through the introduction of the interface thickness and there is no need to impose it. On the other hand, working with diffuse-interface models may present also some difficulties arising from the fact that real systems have actually a much thinner and sharper interface. For this reason, one of the main requirements when computing phase-field models is to reach the so-called sharp interface limit (see for example the recent work in 28). From a numerical point of view, this means that the results do not depend on the thickness of the diffuse-interface, and therefore they are comparable to the results that one would obtain by using a classical fluid mechanics approach.

1. Equilibrium properties

In the phase-field approach, a locally conserved field, denoted as $\phi$, plays the role of an order-parameter by taking two equilibrium limiting values $+\phi_s$ and $-\phi_s$ that represent the liquid and air phases, respectively (see Fig. 2a). The interface position, $h(x,t)$, is then located at the points where the order parameter vanishes, i.e., $\phi[x, h(x,t)] = 0$. The equilibrium properties of the model are based on a Ginzburg-Landau formulation, where the total free energy of the system is given by

$$\mathcal{F}(\phi) = \int_\Omega d\phi f(\phi) = \int_\Omega d\phi \left[ V(\phi) + \frac{\varepsilon^2}{2} |\nabla \phi|^2 \right],$$

(1)

where $f(\phi)$ is the free energy density, $\Omega$ corresponds to the system domain, and the potential $V(\phi)$ is usually chosen as:

$$V(\phi) = -\frac{1}{2} \alpha \phi^2 + \frac{1}{4} \beta \phi^4,$$

(2)

with $\alpha$ and $\beta$ being positive constants in such a way that the equilibrium value for the phase field is given by $\phi_s = \sqrt{\alpha/\beta}$. The double-well form of the potential combined with the square gradient term of the free energy ensures the existence of a well-defined interface with a width $\zeta = \varepsilon/\sqrt{\alpha}$. In this formulation, the chemical potential is defined as $\mu = \delta \mathcal{F}/\delta \phi = V'(\phi) - \varepsilon^2 |\nabla \phi|^2$, so that one of the two phases can be destabilized in favor of the other, and hence forcing the interface to advance by imposing a non-zero chemical potential difference, $\Delta \mu \neq 0$, between the inlet of the system and the interface position (see Fig. 2b). In the case of a flat interface at equilibrium ($\Delta \mu = 0$), the profile of the order-parameter is given by

$$\phi(z) = -\phi_s \tanh \left( \frac{z - h}{\sqrt{2}\zeta} \right),$$

(3)

where $z$ is the direction perpendicular to the interface located at $z = h$. Also, the surface tension of the liquid-gas interface $\sigma_{lg}$ can be easily obtained as the excess free energy per unit surface area due to the inhomogeneity in $\phi$:

$$\sigma_{lg} = \frac{\varepsilon^2}{2} \int_0^\infty \left( \frac{d\phi}{dz} \right)^2 = \frac{2\sqrt{\alpha}}{3} \zeta \alpha \phi_s^2.$$

(4)

To take into account the wetting properties of the walls, the free-energy equation (1) is modified by adding an extra term associated with solid-fluid interactions:

$$\mathcal{F}(\phi) = \int_\Omega d\phi \left[ V(\phi) + \frac{\varepsilon^2}{2} |\nabla \phi|^2 + \int_s d\phi_s f_s(\phi_s) \right],$$

(5)

where $s$ denotes the solid surface. The function $f_s(\phi_s)$ in this additional term which enables us to introduce wetting effects into the model is related to the molecular interactions between fluid and solid, and it is usually expanded as a power series in $\phi_s$,

$$f_s = -a \phi_s,$$

(6)
where $a$ describes the preference of the wall for either the liquid phase ($a > 0$, hydrophilic conditions) or the air phase ($a < 0$, hydrophobic conditions). It is important to emphasize that the linear term in the expansion of $f_s$ turns out to be sufficient to describe partial wetting situations as the ones we are going to consider here. Note, however, that for situations closer to complete wetting (i.e., contact angles close to zero) higher order terms might need to be included in order to avoid effects induced by the formation of mesoscopic layers on the walls.

We non-dimensionalize our system by choosing the following dimensionless variables:

\begin{align}
\phi^* &= \phi/\phi_c, \quad r^* = r/L_x, \\
f^* &= f/(\phi_c^2 \alpha), \quad f_s^* = f_s/\sigma_g.
\end{align}

By minimizing the corresponding dimensionless free energy functional, Eq. (5), the equilibrium conditions are given by the relation $-\phi + \phi^3 = C_h^2 \nabla^2 \phi^*$, which gives the equilibrium profile for the phase field $\phi$, and corresponds to setting the chemical potential to zero, i.e., $\mu = \delta \mathcal{F}/\delta \phi = 0$, and the wetting boundary condition

\begin{equation}
\mathbf{n}_x \cdot \nabla \phi|_{s} = \frac{\gamma}{C_h} \frac{df}{d\phi_a} = -\frac{\gamma}{C_h} a,
\end{equation}

where the asterisks have been dropped and we have defined the Cahn number as $C_h = \zeta/L_x$, and $\gamma = 2\sqrt{2} \phi_c/3 \sigma_g$. Here, $\mathbf{n}_x$ is the unitary outward normal vector to the wall. Note that both the condition $\mu = 0$ and Eq. (8) describe the system at equilibrium when no flux is imposed at the inlet. For a constant value of $a$, the corresponding static equilibrium contact angle, $\theta_e$, can be obtained by making use of the Young-Dupré relation, $\cos \theta_e = (\sigma_{sg} - \sigma_{gl})/\sigma_g$, where $\sigma_{sg}$ and $\sigma_{gl}$ are the solid-gas and solid-liquid surface tensions, respectively, giving rise to the following relation

\begin{equation}
\cos \theta_e = \frac{1}{2} \left[(1 + A)^{3/2} - (1 - A)^{3/2}\right],
\end{equation}

where we have defined $A = \sqrt{2} \gamma a$. In this approach, the different surface tensions $\sigma_{sg}$ and $\sigma_{gl}$ can be obtained by integrating the free energy per unit area along the corresponding interfaces, solid-gas and solid-liquid.

2. Statistical properties of the chemical disorder

$A(z)$ will be taken as a stochastic variable and will play the role of a quenched disorder of different wetting properties. Of particular interest is the relation between the stochastic variable $A(z)$ and the resulting variable $\theta(z)$ representing the local equilibrium contact angle at each point $z$. To this end, we shall consider a Gaussian white noise for the variable $A$ with mean $A_m = \langle A \rangle$ and delta-correlated, $\langle A(z) A(z') \rangle = \sigma_A^2 \delta(z - z')$, where $\sigma_A$ is the disorder strength (standard deviation). By assuming small disorder strengths, $\sigma_A < 1$, Eq. (9) can be linearized around the mean value $A_m$, giving rise to

\begin{equation}
\cos(\theta) \simeq \cos(\theta_m) + \kappa (A - A_m),
\end{equation}

where the mean contact angle $\theta_m$ is given by Eq. (9) by replacing $A$ with $A_m$, and we have defined the constant $\kappa$ as:

\begin{equation}
\kappa = \frac{3}{4} \left[(1 + A_m)^{1/2} + (1 - A_m)^{1/2}\right].
\end{equation}

It can be readily seen that in the limit of small disorder strength, the new variable $\theta$ follows a Gaussian distribution with mean $\theta_m$ and standard deviation given by:

\begin{equation}
\sigma_\theta \simeq \frac{\kappa}{\sin \theta_m} \sigma_A.
\end{equation}

Figure 3 depicts the statistical properties of the variable $\theta$ calculated numerically from Eq. (9) given a sample of $N = 2 \cdot 10^6$ values of $A$ with mean $A_m = 0$ and $A_m = 0.4$, and for different disorder strengths ranging from $\sigma_A = 0$ up to $\sigma_A = 0.1$. These numerical results are compared to the analytical prediction given by Eq. (12) showing very good agreement. We observe that for the case of $A_m = 0.4$, the variable $\theta$ can be considered to be Gaussian for $\sigma_A \lesssim 0.1$.

3. Conserved dynamics

The dynamics of the phase field is assumed to follow a conserved equation based on a time-dependent Ginzburg-Landau Hamiltonian (model B in the Hohenberg and Halperin terminology), which in dimensional form is:

\begin{equation}
\frac{\partial \phi}{\partial t} = \nabla \cdot M \nabla \mu = \nabla \cdot M \nabla \left(-\alpha \phi + \beta \phi^3 - \varepsilon^2 \nabla^2 \phi\right),
\end{equation}

where $\mu$ is the chemical potential defined earlier, and $M(\phi)$ is a mobility parameter that in general depends on $\phi$. Here, we are using the so-called one-sided model, where the mobility is taken as $M = M_0$ in the liquid phase ($\phi > 0$) and $M = 0$ in the air phase ($\phi < 0$). To advance the interface we consider a driven system, where the mean velocity of the interface is fixed to a constant value. The relevant boundary condition at the inlet is obtained by fixing the gradient of the chemical potential at the left-hand side of the system:

\begin{equation}
\mathbf{n}_x \cdot \nabla \mu|_{z=0} = -v_m,
\end{equation}

where $\mathbf{n}_x$ is the unitary outward normal vector at the inlet of the microchannel. By imposing this boundary condition, the average velocity of the interface, $V = \frac{1}{L_x} \int x \, dx \, h(x, t)$ takes a positive value whenever $v_m > 0$ (the liquid advances in the channel) and a negative value whenever $v_m < 0$ (the liquid recedes).
We also take the initial position of the interface located at $m = 1$ in the liquid phase and $\zeta$ we use Eq. (7) in addition of what it is also known as model H in the Hohenberg and Halperin terminology\(^\text{19}\)—note that the model B we are using here can be obtained from model H in the limit of $Pe \rightarrow 0$ (see Appendix A for details).

### III. NUMERICAL SCHEME

The dimensionless phase-field model equation (15) is integrated numerically in a 2D domain of size $\ell_x \times \ell_z$ by imposing the wetting boundary conditions (8) at both walls, the driving condition (14) at the inlet of the microchannel, the initial condition (16), and the no-flux boundary condition at the walls. The size of the system in dimensionless variables is $\ell_x = 1$ and $\ell_z = 5$. We use an explicit fourth-order Runge-Kutta algorithm with adaptive timestep size, and a rectangular spatial discretization with grid $\Delta x = \Delta z = 0.05$. A smaller spatial grid $\Delta x = \Delta z = 0.025$ has also been used but it does not alter the numerical results. All numerical integrations presented in this study have been performed by setting the Cahn number to $C_h = 0.07$ and $A_m = 0.4$ (unless otherwise specified) as the mean value for the wetting properties of the walls, giving rise to the equilibrium contact angle $\theta_0 \simeq 54^\circ$. The value of the spatial noise $A$ at each point is numerically imposed as the following discretized white noise:

$$A = \frac{\sigma_A}{\sqrt{\ell_x \Delta z}} N(0, 1) + A_m, \quad (17)$$

where $N(0, 1)$ denotes a Gaussian variable of zero mean and variance one. Note that the factor $\sqrt{\ell_x}$ and $\sqrt{\Delta z}$ in the above equation originate from the variables non-dimensionalization and the spatial discretization, respectively.

The interface position, $h(x, t)$, is estimated by a linear interpolation of the zero of the phase field, $\phi(x, h(x, t); t) = 0$. This allows us to estimate the position of the contact point of the liquid-air meniscus at the wall surface by using a parabolic extrapolation of the nearest points of the meniscus. Once the location of the contact point is determined, the apparent contact angle, $\theta$, is defined as the angle formed by the wetted part of the wall with the tangent line to the meniscus at the contact point (see Fig. 1).

As we impose a constant flow rate condition, the accuracy of our numerical scheme was monitored by examining dynamically the following quantities,

$$\left\langle \frac{\partial \phi(x, z; t)}{\partial t} \right\rangle, \quad \left\langle |\phi(x, z)| \right\rangle, \quad \left(18\right)$$

where $\langle \cdot \rangle = 1/(\ell_x \ell_z) \int_{0}^{\ell_x} \int_{0}^{\ell_z} \cdot dx dz$. Note that the quantity on the left in (18) should be constant whereas the

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**FIG. 3.** (Color online) Statistical properties of the random contact angle $\theta$ given by Eq. (9) when $A$ is a random variable with Gaussian distribution of mean $A_m$ and standard deviation $\sigma_A$. Panels (a) and (b) show the probability density function of the variable $\theta$ calculated by using two different strengths $\sigma_A$ for $A_m = 0$ and $A_m = 0.4$, respectively. Squared and circle symbols correspond to the numerical data while the corresponding insets show the comparison between the numerically obtained standard deviation $\sigma_\theta$ with the analytical expression given by Eq. (12).
quantity on the right should fluctuate around a constant value. Both magnitudes turn out to be good indicators to estimate the order of the numerical error. Concerning the discontinuous mobility function \( m(\phi) \), let us remark that \( m \) is taken to be constant for \( \phi \in [1, 0.9] \), so that it is actually continuous along the interface area.

Finally, an important numerical issue that naturally arises in diffuse interface models is whether the sharp-interface limit can be numerically reached or not. As pointed out in Sec. II B, the achievement of the sharp-interface limit is a necessary condition for diffuse-interface numerical integrations, where the interface is usually much thicker than the actual one, and guarantees that the numerical results do not depend on the interface thickness. As it has been shown in the recent work by Yue et al.\(^{28} \), a numerical convergence criterion for such limit can be obtained in terms of the typical diffusion length of the process and the Cahn number \( C_h \). More precisely, these authors have shown that the sharp interface limit is numerically reached as long as the relation \( C_h < 4S \) holds, where \( S = \ell_D/L_x \), with \( \ell_D \) being the diffusion length. In our case we can write \( \ell_D \sim \sqrt{M_0/\phi_c} \), and in order to satisfy such numerical criterion, we have set the value \( S = 0.05 \), so that we have the numerical relation \( C_h = 0.07 < 4S = 0.2 \). We can therefore ensure that the numerical results presented in this study do not depend on the interface thickness. Figure 4 also shows the numerically obtained interface profile by choosing different values of the Cahn number ranging in \([0.03, 0.11]\), observing good convergence as \( C_h \to 0 \).

IV. RESULTS AND DISCUSSION

A typical evolution of the advancing meniscus over a chemically heterogeneous channel with \( \sigma_A = 0.1 \) and driving force \( v_m = 0.0025 \) is shown in Fig. 4. As the liquid phase advances, both the apparent contact angle at the top \( [\theta_t(t)] \) and bottom \( [\theta_b(t)] \) walls fluctuate with time. Our purpose in this section is to study both the dynamics and statistical properties of the apparent contact angles, and how their behavior depends upon the disorder strength \( \sigma_A \) and driving force \( v_m \).

A. Nonlocal effects in the contact line dynamics

As emphasized in the Introduction, an important question regarding wetting processes in microchannels is whether the dynamics of the interface is dominated by nonlocal effects arising from the flow rate conditions applied at the system. To investigate such effects on the apparent contact angle, we start by analyzing possible correlations between contact angles at both walls. To this end we consider a homogeneous top wall and a heterogeneous bottom wall with \( A_m = 0.4 \) and different disorder strengths, and we examine how the dynamics of the contact angle at the top wall is affected by the disordered

Figure 4 shows successive snapshots of the liquid-air meniscus invading a chemically heterogeneous microchannel with \( \sigma_A = 0.1 \), \( v_m = 0.0025 \), and \( A_m = 0.4 \) (\( \theta_c \approx 54^\circ \)). The bottom panel shows the interface profile computed by using different values of the Cahn number, ranging between \([0.03, 0.11]\).

Figure 5 displays the temporal dynamics of the apparent contact angle of the homogeneous top wall \( \theta_t(t) \) [(a)] and (b)] and the disordered bottom wall \( \theta_b(t) \) [(c)]. Solid and dashed lines correspond to different disorder strengths applied at the bottom wall, namely \( \sigma_A = 0.05 \) and 0.1, respectively. (a) and (b) correspond to a homogeneous wall with \( A_m = 0 \) (different from the bottom wall), and a homogeneous wall with \( A_m = 0.4 \) (equal to the bottom wall), respectively. The mean velocity is \( v_m = 0.005 \) in all cases.
bottom wall. More precisely, correlations between walls will be quantified by looking at the correlation factor:

\[ \rho_c = \frac{\langle \theta_t \theta_b \rangle - \langle \theta_t \rangle \langle \theta_b \rangle}{\sigma_t \sigma_b}, \]

(19)

where \( \langle \cdot \rangle \) denotes time average and \( \sigma_n^2 = \langle \theta_n^2 \rangle - \langle \theta_n \rangle^2 \) for \( n = t, b \).

We first consider the case of the top wall having the same mean value for \( A_m \) as the bottom wall, \( A_m = 0.4 \), and we choose two different disorder strengths for the bottom wall, namely \( \sigma_A = 0.05 \) and 0.1 [see Fig. 5(a)]. By using the above expression we obtain that \( \rho_c = 0.04 \) and 0.09 for \( \sigma_A = 0.05 \) and 0.1, respectively. We therefore conclude that in this situation both walls can be considered to be uncorrelated with each other, observing that the top contact angle is affected only by the usual fluctuations due to the lattice discretization. Note also that the mean contact angle value at the top wall \((\langle \theta_t \rangle \sim 60^\circ)\) does not depend on the disorder strength applied at the bottom wall. This is an important point that will be used in the next section to obtain averaged contact angles. We also note that similar results have been obtained for smaller systems \((C_h = 0.11)\) indicating that in these wetting conditions, both walls can indeed be considered as independent from each other.

Interestingly, when we repeat the same analysis in a setting having different mean wetting values between both walls, i.e., we choose \( A_m = 0 \) (neutral wetting) at the top wall and \( A_m = 0.4 \) at the bottom wall, we find \( \rho_c = -0.54 \) and \( -0.72 \) for \( \sigma_A = 0.05 \) and 0.1, respectively. This is a clear indication that both walls are now much more correlated with each other. Indeed, as it is shown in Fig. 5(b), the dynamics of the top contact angle is now coupled to the bottom one: fluctuations above the mean value occurring at the bottom contact angle are reflected as fluctuations below the mean value at the top contact angle, and vice versa. This effect is also evident from the negative sign of the correlator \( \rho_c \). Note also that the mean value at the top wall \((\langle \theta_t \rangle = 91.4^\circ)\) does not depend on the strength \( \sigma_A \), and is slightly higher than the expected neutral value of 90\(^\circ\). It is worth mentioning that this effect largely depends now on the gap between the walls, obtaining, for instance \( \langle \theta_t \rangle = 92.6^\circ \) for \( C_h = 0.11 \).

From a physical point of view, this nonlocal effect can be understood in terms of the mass conservation in the system. Consider first an ideal situation where both the top and bottom mean contact angle are around 90\(^\circ\) (neutral wetting), so that the interface position can be expressed as \( h(x,t) \sim V_t + h_0(\theta_t, \theta_b, x) \) with \( V \) being the mean interface velocity and \( h_0(\theta_t, \theta_b, x) \) the interface profile which depends upon both contact angles (note that \( h_0 = 0 \) for \( \theta_t = \theta_b = 90^\circ \)). If we consider that both contact angles are fluctuating in time with respect to their mean values, \( \theta_t = \langle \theta_t \rangle + \delta \theta_t(t) \) and \( \theta_b = \langle \theta_b \rangle + \delta \theta_b(t) \), the constant flow rate condition implies that \( \int_x dx \partial_t h(x,t) \) has to remain constant in time, and we therefore have the relation,

\[ \delta \theta_t = -\frac{I_b}{I_t} \delta \theta_b, \]

(20)

where the dot denotes time differentiation and \( I_n = \int_x dx \partial_t h_0(x,t) \) for \( n = t, b \). In more physical terms, the above expressions suggest that any fluctuation above (below) of the mean value at the bottom contact point will produce a change on the local curvature of the interface with the corresponding decrease (increase) of the chemical potential difference across the interface. This in turn will induce a local decrease (increase) of the local velocity which will need to be compensated with a fluctuation of opposite behavior at the top contact point. As a result, the top contact point is moved away from its equilibrium configuration, and a local diffusive process will occur trying to pull the contact point back to equilibrium. Our numerical results indicate that this is indeed the case when the top contact angle is fixed around the neutral value and the bottom contact angle is fluctuating around a different (smaller) mean value [cf. Fig. 5(b)]. In the other case, however, when both mean contact angles are equal and much smaller than the neutral one [cf. Fig. 5(a)], the dynamics at the top contact point is largely affected by the local pull force due to the wetting properties at the surface, with the eventual loss of the nonlocal character.

B. Disorder-induced contact angle hysteresis

We now proceed to study the dynamics of the apparent contact angle for both an advancing \((v_m > 0)\) and receding \((v_m < 0)\) motion of the contact line, with both walls being chemically disordered with the same mean value, \( A_m = 0.4 \). For this purpose, we shall perform a detailed statistical analysis of the time fluctuations of the contact angle by generating a sufficiently large number of different chemical disorder realisations.

In the advancing case, the position of the interface is monitored during a time interval \( T \), and at each time we calculate the apparent contact angle at both top and bottom walls, i.e., \( \theta_t(t) \) and \( \theta_b(t) \), respectively, and also the mean velocity of the interface, \( V = \int_x dx \partial_t h(x,t) \). We then switch the sign of \( v_m \) and repeat the process for the receding interface and during the same time interval as before. The resulting set of apparent contact angles and velocities are averaged over time for each case of motion, and also averaged over 20 different disorder realizations, obtaining \( \langle \theta_t \rangle \) and \( \langle \theta_b \rangle \) for the averaged top and bottom contact angles, respectively, and \( \langle V \rangle \) for the mean interface velocity. As shown in Sec. IV A, since we are considering both walls with the same mean value for the wetting properties \((A_m = 0.4)\), the top and bottom contact angles can be treated as independent variables, and therefore, we can also average them to get: \( \langle \theta \rangle = (\langle \theta_t \rangle + \langle \theta_b \rangle)/2 \). Finally, we look at the influence of
the disorder strength on the contact angle by taking different values of $\sigma \in [0, 0.1]$. It is worth to remark that the actual mean velocity $\langle V \rangle$ observed after disorder averaging it is slightly different than the imposed numerical value for the driving force $v_m$. To be more precise, due to the miscibility gap $\Delta \phi_c = 2\phi_c = 2$ (in the dimensionless equations) we observe that $2\langle V \rangle \sim v_m$ for all the values of the disorder strength.

Figure 6 shows the time evolution of the advancing bottom contact point $h_b(t)$. As a consequence of the forced flow boundary condition we observe a linear growth which can be described as $h_b(t) = \bar{h}_b(t) + \delta h_b(t)$, where $\delta h_b(t)$ represents the small fluctuations due to the chemical heterogeneities, and $\bar{h}_b(t)$ represents the mean growth of the contact point which can be approximated by a linear data fit [cf. Fig. 6(a)]. By plotting then the contact point fluctuations only, i.e., $\delta h_b(t) = h_b(t) - \bar{h}_b(t)$, we observe that the motion of the contact point is correlated with the corresponding contact angle: An increase of the local position in time (and hence increase of the local velocity) is reflected as a decrease on the contact angle level. It is important to emphasize that strictly speaking we do not observe here clear stick-slip motion (i.e., a situation where the contact point remains pinned for a finite period of time, and then suddenly depins and advances into another position). Note that any possible pinning-depinning motion induced by the weak hydrophilic heterogeneities we are dealing with is actually being smoothed out by the imposed constant flow rate. In this sense, we could observe stronger pinning effects had we considered, for example, a combination of hydrophilic and hydrophobic heterogeneities or topographical defects. We leave such an extension as a future work.

The results for $\langle \theta \rangle$ as a function of $\langle V \rangle$ for both advancing and receding motions and different disorder strengths are presented in Fig. 7(a). We first note that in the homogeneous case ($\sigma_A = 0$), the averaged contact angle approaches the same value, $\langle \theta \rangle \sim 58.5$, when both the limit of $\langle V \rangle \to 0^+$ and $\langle V \rangle \to 0^-$ are taken. Therefore, as expected, when the disorder in the system is switched off, these two limits are identical with each other and there is no hysteresis behavior. As we increase the disorder strength, however, these two limits no longer match as expected, when the disorder in the system is switched off, these two limits are identical with each other and there is no hysteresis behavior. As we increase the disorder strength, however, these two limits no longer match and we observe that the apparent contact angle suffers a hysteresis effect which is enhanced by the chemical disorder.

The linear behavior of the homogeneous case is split into two linear branches separated by a gap that depends on the disorder strength. This behavior is in qualitative agreement with the experimental results shown in Ref. 12. To quantify such behavior, we fit the numerical...
data of both the advancing (+) and receding (-) branch to a linear function, \((\theta_\pm) = m_\pm \langle V \rangle_\pm + \theta_\pm\), and the hysteresis gap is defined as:

\[
\Delta \theta = |\dot{\theta}_+ - \dot{\theta}_-|.
\]

Figure 7(b) depicts \(\Delta \theta\) as function of the disorder strength \(\sigma_A\), confirming that the hysteresis behavior is enhanced by increasing disorder strength. Note that larger fluctuations on the contact angle, i.e. larger disorder strength induce a larger error on the fitted parameters. Noteworthy is that our numerical results seem to point out a linear behavior between the hysteresis gap and the disorder strength, which is in agreement with previous studies on contact angle hysteresis\(^8\). In particular, by fitting the numerical data to a linear function at sufficiently large disorder strengths, we find the relation \(\Delta \theta = a\sigma_A + b\) with \(a = 12.2\) and \(b = 0.16\) [see dashed line in Fig. 7(b)].

Finally, it is worth mentioning that we have also performed simulations at higher velocities. We observed that for sufficiently high velocities, both in the advancing and receding case, the different values of the contact angles calculated for each disorder strength collapse onto the homogeneous curve. This indicates that at high velocities, the contact line cannot distinguish between weak or strong disorder, and as a consequence the averaged behavior corresponds to the homogeneous case. This is actually a very common situation observed whenever an interface is driven through a medium that is affected by a static (quenched) disorder (see for instance Ref. 36).

At sufficiently large values of the driving force, there is a clear scale separation between the motion of the advancing/receding front and the local fluctuations of the disorder. As a consequence, the quenched disorder behaves as an effectively temporal white noise with the eventual loss of any disorder-induced complex behaviour. However, as it was emphasized in Sec. II B, the results presented here are expected to be valid in a regime of low velocities, i.e. small Péclet numbers, where the diffusion mechanism is dominant over advection. Hence, strictly speaking for the higher velocity regimes and description of the motion in the region of larger Péclet numbers, an advective term should be introduced\(^27,34,35\).

V. CONCLUSION

We have examined numerically the effects of chemical heterogeneities on the forced motion of the contact lines of a liquid-gas meniscus invading a microchannel under forced flow (constant flow rate) conditions. We have made use of a diffuse-interface (phase-field) model that takes into account the wetting properties of the channel surfaces. We examined how the contact angle behaves as the disorder properties are altered and in particular the contact angle hysteresis due to the chemical heterogeneities.

We first focused on the possible correlations between apparent contact angles at both walls as a consequence of the nonlocal effects of the interface dynamics. By imposing a homogeneous top wall and a disordered bottom wall, we investigated how the dynamics of the top contact line is influenced by the bottom contact line fluctuations. Our results show that when the wetting properties at one of the walls are different from those applied at the other wall, both contact angles are coupled to each other: fluctuations above the mean at one wall produce fluctuations below the mean at the other wall, and vice versa. On the other hand, when both walls have the same mean wetting properties, this coupling effect is not observed. This analysis then suggests that nonlocal effects may be relevant on the dynamics of the contact line, so that any analytical and/or numerical approaches of contact line motion in microchannels and more general confined geometries, should take them into account.

On the other hand, a careful statistical study of the advancing and receding motion of the contact line has revealed that the apparent contact angle suffers a hysteresis behavior induced by the disorder of the walls. More precisely, we have shown that the value of the apparent contact angle in the limit of zero velocity depends on whether the contact line is advancing or receding, and it is characterized by a jump discontinuity, \(\Delta \theta\), that depends on the disorder strength of the chemical heterogeneities of the system. In particular, we have shown that such hysteresis behavior is enhanced with the disorder strength. It is important to emphasize that our results show how a purely diffusive process can generate a variation of the contact angle with the meniscus velocity including complex phenomena like hysteresis behaviour and/or nonlocal dynamics. This is also an indication that the above phenomena are generic and not linked to any hydrodynamics.

Of particular interest would be the extension of the present study to topographically heterogeneous substrates, which also have a significant effect on the wetting characteristics of the solid-liquid pair (e.g. Refs. 37–39). Furthermore, as also noted in the Introduction, the 2D system we considered can be viewed as a simplified version of a 3D system and serving as a first step towards characterizing contact line dynamics in microchannel chemically (or topographically) disordered in both the streamwise and spanwise direction. In this case, in addition to nonlocality and contact angle hysteresis we expect a number of phenomena and complexities which are likely to play a crucial role in the advancement of the liquid into the microchannel, such as kinetic roughening, pinning–depinning motion or avalanche dynamics of the contact line\(^14,16\). We hope to examine these and related problems in future studies.
Appendix A: Model B in the limit of small Peclet number

In this Appendix we point out under which conditions the phase field model we use in the present study, which is described in Sec. II B, can be obtained from other existing models that describe contact line dynamics.

We focus here on a regime where diffusion processes dominate over advection processes. It is important to emphasize, however, that in general both mechanisms can be important, and in order to take them into account, Eq. (13) describing the dynamics of the phase field has to be replaced by the following advection-diffusion equation:

$$\frac{\partial \phi}{\partial t} + v \cdot \nabla \phi = \nabla \cdot \left( \frac{M}{\eta} \nabla \mu \right), \quad (A1)$$

where $v$ represents the bulk velocity of the fluid. The above equation is then coupled to the Navier-Stokes equation for the velocity field:

$$\rho \frac{dv}{dt} = -\nabla p + \eta \nabla^2 v + \mu \nabla \phi, \quad (A2)$$

where $\rho$ and $\eta$ are the fluid density and viscosity, respectively, and $p$ represents the pressure. The model described by the above Eqs. (A1) and (A2) is usually referred to as model H (if we follow the Hohenberg and Halperin terminology\cite{19}) and, when solid-fluid interactions are also taken into account via a surface energy (see Eq. 5), it has been used to model several sort of wetting situations, such as droplet motion\cite{7,31,35}, or thin film dynamics\cite{40,41} (see also Refs. 25, 27, 28, and 30 for general aspects on this model).

By using now the dimensionless variables defined in Eq. (7) we can rewrite equation (A1) as:

$$\frac{\partial \phi}{\partial t} = C_{H}^2 \left( \nabla \cdot m \nabla \mu - P_{e} v \cdot \nabla \phi \right), \quad (A3)$$

where we have used the diffusion time scale $\zeta^2/M \sigma \alpha$ to non-dimensionalize time, and the Peclet number has been defined as:

$$P_{e} = \frac{V L_s}{M \sigma \alpha}, \quad (A4)$$

with the mean interface velocity $V$ being used as the characteristic velocity of the system. We can therefore see that in the limit of $P_{e} \to 0$, the above equation (A3) becomes completely decoupled from the Navier-Stokes equations (A2), obtaining a pure diffusive regime where the equation describing the contact line dynamics is given by Eq. (15) only.

ACKNOWLEDGMENTS

We are grateful to the anonymous referees for insightful comments and suggestions. We thank Julia M. Yeomans for fruitful discussions. We acknowledge the financial support of F.R.S.-FNRS (Belgian National Fund for Scientific Research), EU-FP7 ITN Multiflow and ERC Advanced Grant No. 247031.