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Transport, phase transitions, and wetting in micro/nanochannels: A phase field/DDFT approach

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While the flow of a liquid in a macroscopic channel is usually described using hydrodynamics with no-slip boundary conditions at the walls of the channel, transport phenomena in microchannels involve physics at many different scales due to the interplay between the micrometric section of the channel and the micro- or nanometric roughness of the boundaries. Roughness can have many different effects such as increasing the friction between the liquid and the walls (leading to the macroscopic no-slip boundary condition) or on the contrary reduce it thanks to the Wenzel–Cassie–Baxter wetting transition induced by capillarity. Here we detail a phase-field/dynamic density functional theory model able to account for the wetting transitions, the resulting friction between the wall and the fluid, and compressible hydrodynamics at high viscosity contrast. © 2011 American Institute of Physics. [doi:10.1063/1.3557061]

I. INTRODUCTION

Modeling the dynamics of a system undergoing a phase transition is a notoriously difficult task. At the nanometric scale, molecular simulations can be performed to probe the phase equilibration, but the large scale dynamics of the phase transition remains inaccessible due to the smallness of the simulated system (few nanometers, few nanoseconds). At the macroscopic scale on the contrary, transport phenomena such as convection or heat transport can be investigated using continuum mechanics, but the phase transition produces moving phase boundaries that result in a complex free boundary problem. A complete description of the dynamics requires the coupling of a thermodynamic model for the phase transition with the large scale transport equations. Such a coupled dynamics is provided by phase-field (PF) models introduced in the 1980s and extended afterward to tackle this difficult problem.^{1–3} The main advantages of these models are their flexibility, their ability to account for complex phenomena in complex geometries (dendritic growth,^{1–3} viscous fingering,^{4,5} stress-induced instabilities in solids,⁶ Marangoni convection,⁷ droplet and vesicle dynamics,^{8–11} polymer blends,¹² etc.), and the simplicity of their numerical implementation. However, their use requires some care due to the diffuse nature of the phase boundaries they introduce. Although the phase boundaries are actually diffuse at the nanometric scale, they are sharp at the macroscopic level, and an overestimation of the interface thickness by several orders of magnitude can result in an overestimation of the interfacial tensions in the same proportion if appropriate treatments are not applied.^{4,13} However, we shall not consider macroscopic scales in this article, but rather focus on the application of PF models to their “natural” nano-

or micrometric scales, where many interesting phenomena become accessible with present-day technology. At these scales, continuum models can be used as well thanks to the formalism of density functional theory (DFT) that provides an exact framework to study inhomogeneous systems and phase coexistences at the molecular scale.¹⁴ The extension of this framework to dynamical situations has motivated very recently a large number of studies,^{15–18} that resulted in the formulation of dynamic density functional theory (DDFT). We shall combine PF approaches with DDFT (they are indeed very similar at this level of description) to investigate the long time dynamics of nano- or micrometric systems. This approach is intermediate between DDFT at short time scales and hydrodynamics at long time scales and thus bridges the scale between molecular simulations and more macroscopic approaches like lattice–Boltzmann for instance.^{19–27} We can thus investigate a large variety of phenomena in various different fields. An important field of applications in physics, biology, and chemistry is microfluidics where one or several fluids are driven in a microchannel network.²⁸ An important issue in this field is to control the friction between the liquid and the substrate of the channels:²⁹ reducing friction is an essential step to increase the efficiency of microfluidics devices. Producing superlubricant surfaces is thus an open challenge in this field, with different technological solutions. A possible solution inspired by nature (the famous “lotus leaf effect”) is to take advantage of the surface roughness to induce wetting transitions such as the “fakir effect,” where the liquid is suspended on the tips of the roughness.^{30,31} The cavities produced between the liquid and the surface are thus filled with gas (air or vapor or both) that plays the role of a lubricant.²⁹ But to measure the friction between the liquid and the wall, it is necessary to account for both the wetting transition (a local liquid–gas transition induced by the roughness) and the hydrodynamic flow. Other problems such as chemical reactions in microchannels,

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phase separations, condensation, or boiling are interesting as well and also involve a coupling between transport properties and phase transitions. PF/DDFT models are almost ideal to study these effects thanks to the separation of the time scales in these systems: while the relaxations at the molecular scales are very fast (picoseconds for liquids made of small molecules such as water), the time scale associated to the externally applied flow is much larger (milliseconds or even larger). As a consequence, we can assume a local thermodynamic equilibrium at the time scale of the external flow and use a continuum description of the fluid. It is then possible to investigate systems that are much larger than those considered in molecular simulations and to follow their dynamics during a much longer time. The model we discuss in detail here is quite generic. It couples a fluid exhibiting a first order phase transition to a hydrodynamic flow in the vicinity of a rough surface, and we will illustrate the ability of this model to predict non-trivial effects by showing results on the friction properties of a fluid in contact with a nanotextured surface. Preliminary results obtained with this approach were the subject of Refs. 9 and 26, our scope here is to give full details of the model and its implementation. We split the article in five sections: after the introduction part we describe the theoretical basis of the model in Sec. II, and present several results in Secs. III and IV: Sec. III is devoted to static results, i.e., wetting properties for planar and crenelated surfaces, wetting transitions, and capillary condensation, while in Sec. IV we discuss the dynamical properties like liquid/solid friction (slippage), capillary filling, the pinning–unpinning transitions on textured surfaces, and the contact angle hysteresis. Section V is our conclusion. For the sake of clarity, most of the technical parts concerning the numerical implementation or various theoretical analysis of the model will be found in Appendices and the supplementary information.³⁴

II. THE MODEL

A. The free-energy model

The local organization of a liquid or a gas close to a substrate is described by the DFT that provides in principle a generic and exact framework to investigate the wetting properties. This description is based on an exact expression for the grand-potential functional $\Omega[\rho]$, where $\rho(\mathbf{r})$ is the density profile of the molecules close to the substrate.¹⁴ Although the framework is exact, the formal expression for $\Omega[\rho]$ is implicit and cannot be used in practical situations (although it can be used to develop approximate expressions). Among the huge variety of approximate density functional theories, the simple square gradient expansion provides a robust tool to investigate the generic properties of an interface at small scale.^{13,35,36} This model is obtained by supplementing the bulk free energy of the fluid with a square gradient term in order to give the interface a finite thickness. This thickness is of the order of few Angstroms, and results from structural effects at the atomic scale. While the full formulation of the square gradient theory keeps track of the correlations inside the fluid, we shall use a simple mean-field-like model to investigate the generic properties of a fluid close to an interface.¹⁴ This

approach can, however, be refined for specific systems by using more realistic functionals. The simplified model we consider here is based on the van der Waals free energy density (for one particle species) to treat the bulk liquid–vapor coexistence,

$$f_{\text{bulk}}(\rho) = k_B T \rho \left\{ \log \left(\frac{\rho \Lambda^3}{1 - \rho b} \right) - 1 \right\} - a \rho^2, \quad (1)$$

where k_B is the Boltzmann constant. The two coefficients a and b are the van der Waals phenomenological coefficients: b is related to the exclusion volume, and thus to the short range forces, whereas a accounts for the attractive van der Waals forces treated in a mean-field way. In Eq. (1) ρ is the density of the homogeneous phase and Λ is the thermal de Broglie wavelength. To account for the presence of an interface, the homogeneous density can be replaced by the local density $\rho(\mathbf{r})$ in expression (1) but as discussed in Ref. 43 this local density approximation is not sufficient to account for a finite thickness of the interface. The simplest theory is to add a square gradient correction to the bulk free energy per unit volume (written in a dimensionless form),

$$f^*(\mathbf{r}) \equiv \frac{\sigma^3}{k_B T_c} f_{\text{bulk}}(\rho(\mathbf{r})) + \frac{w^2}{2} |\nabla \rho(\mathbf{r}) \sigma^3|^2. \quad (2)$$

In this form, we make use of the critical temperature $k_B T_c = 8a/27b$ and definition $b/\sigma^3 = 1$.¹³ Here, w is a length scale introduced by the square gradient term describing the interface thickness. Its value is in the order of a few Angstroms (like σ). If a substrate is present, an interaction potential has to be added to the free energy $F_{\text{wall}} = \int_V \rho(\mathbf{r}) V_{\text{wall}}(\mathbf{r}) d\mathbf{r}$. We shall use a Lennard-Jones potential to describe the interaction between an atom of the substrate and an atom of the fluid,

$$V_{\text{LJ}}(r) = 4\varepsilon \left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right), \quad (3)$$

where r is the distance between the two atoms and ε is the characteristic energy of the interaction. For simplicity, the σ used in the Lennard-Jones potential is the same quantity as the σ in the excluded volume term of the van der Waals equation. The effective wall potential V_{wall} can be described by the wall density ρ_{wall} and the pair distribution function $g_{\text{wall–fluid}}$ which leads to

$$V_{\text{wall}}(\mathbf{r}) = \int_V \rho_{\text{wall}}(\mathbf{r}') g_{\text{wall–fluid}}(\mathbf{r}', \mathbf{r}) V_{\text{LJ}}(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}'. \quad (4)$$

Inside the wall, the pair distribution function vanishes so that the integral stays finite. Thus we assume an effective wall potential at a finite value V_0 inside the wall and we shall not calculate the very complex pair distribution function, but rather use a simple ansatz,

$$V_{\text{wall}}(\mathbf{r}) = \inf \left\{ V_0, \int_V \rho_{\text{wall}}(\mathbf{r}') V_{\text{LJ}}(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' \right\}. \quad (5)$$

The full free energy functional is

$$F[\rho] = \int_V \left\{ f_{\text{bulk}}(\rho(\mathbf{r})) + \frac{W^2}{2} |\nabla \rho(\mathbf{r})|^2 + \rho(\mathbf{r}) V_{\text{wall}}(\mathbf{r}) \right\} d\mathbf{r}. \quad (6)$$

$W = w\sqrt{\sigma^3 k_B T_c}$ is the square gradient prefactor. The corresponding grand-potential writes

$$\Omega[\rho] = F[\rho] - \mu \int_V \rho(\mathbf{r}) d\mathbf{r}, \quad (7)$$

where μ is the chemical potential of the system. For a given substrate configuration, defined by $\rho_{\text{wall}}(\mathbf{r})$, the equilibrium density profile of the fluid is obtained by a minimization of the grand-potential functional (7) with respect to $\rho(\mathbf{r})$.

The main control parameters in this model are the temperature T , the interfacial thickness w , and the fluid–substrate interaction energy ε . The geometry of the substrate is defined by $\rho_{\text{wall}}(\mathbf{r})$ [a constant inside ($1/\sigma^3$) and 0 outside] and the average density of the fluid is controlled by μ .

B. The dynamical equations

The two fields that we shall consider to model the dynamics of the vapor–liquid mixture are the density field $\rho(\mathbf{r}, t)$ and the velocity field $\mathbf{v}(\mathbf{r}, t)$. The dynamics of the density field can take different expressions depending on the thermodynamic constraints that we apply on the system. If we work in isothermal condition with a fixed number of molecules (the usual case), the dynamics of the density field might take the form

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = \nabla \cdot \left\{ G^{\text{DDFT}} \rho \nabla \frac{\partial \Omega[\rho]}{\partial \rho} \right\}. \quad (8)$$

Indeed, with this prescription the number of molecules is conserved and we can recognize the convective flux $\rho \mathbf{v}$ in the left term. The right term is less usual and accounts for the coupling with the thermostat since we work at fixed temperature, an important point that we shall discuss now. At the molecular level, simulations such as molecular dynamics are usually performed with the help of a thermostat, that can itself be implemented in various ways³⁷ (effective friction, velocity rescaling, Langevin random forces, etc.). Interestingly, the precise method used to thermalize the system is not very important at equilibrium: the collective behavior of the molecules is weakly sensitive to the trajectory of a single one³⁸ (this is indeed why molecular dynamics actually works). We can thus expect the global behavior of a molecular ensemble to be weakly dependent on the thermalizing process, close to equilibrium. It has been shown quite recently from molecular considerations that the relaxation dynamics of an ensemble of particles in contact with a thermostat can be remarkably well described using Eq. (8). This equation is now the cornerstone of DDFT that was introduced few years ago by Marconi and Tarazona for Brownian particles¹⁶ (particles in contact with a Brownian thermostat), and that have been extended since to include hydrodynamics as well^{15,17,18} or to tackle the difficult problem of molecular fluids without thermostat.¹⁵ DDFT has also been used very recently to investigate nucleation problems³⁹ and is thus a very promising framework to overcome the limitations of molecular simulations which are usually restricted to small time scales. We use this approach here for two reasons: first, it is a convenient way to introduce a coupling between the fluid and the externally applied thermodynamic constraints that allows us

to switch from the canonical ensemble to the grand canonical ensemble when necessary (see below) and second it is the purpose of this article to investigate the dynamics of the fluid at nanometric scales, we thus need to account for the fast transients that occur at these scales. Indeed, it is important to mention that the thermalization process is very fast at molecular scale (few picoseconds) and the right term only plays a role in nonequilibrium situations. Very rapidly the system reaches a local equilibrium, where the density profile $\rho(\mathbf{r}, t)$ minimizes locally the functional $\Omega[\rho]$, and we recover in this case the macroscopic long time convection equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (9)$$

What dictates the relaxation time to local equilibrium is the prefactor G^{DDFT} that can be fixed in various ways. The usual prescription in PF models is to take $G^{\text{DDFT}} \rho \equiv G^{\text{CH}}$, where CH refers to Cahn and Hilliard, due to the similarity of the equations we obtain in this case with the CH theory, but contrarily the Cahn–Hilliard approach, G^{CH} refers here to a molecular time scale and not to a diffusion time between two different species. We used this ansatz here, for the sake of simplicity, and we choose G^{CH} to reproduce the self-diffusion constant of water molecules. We also checked that dividing this relaxation time by a factor of 10 does not affect the long time dynamics and has no effect on the steady states. G^{CH} can be used to define a time scale $\tau \equiv \sigma^2 / G^{\text{CH}}$. Also, a dimensionless time can be defined by $t = t_{\text{real}} / \tau$.

To probe phase equilibria, it is also interesting to consider a contact with a reservoir of matter and work in the grand-canonical ensemble where the chemical potential μ and temperature are fixed. A simple way to achieve this program is to substitute the matter conservation equation with

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = -G^{\text{AC}} \frac{\partial \Omega[\rho]}{\partial \rho}, \quad (10)$$

where we now consider an Allen–Cahn-like dynamics. With this prescription, we can investigate phase coexistences quite simply by tuning the chemical potential μ . Although the relaxation dynamics does not correspond to a real system, the equilibrium states satisfy the macroscopic transport equation (9) and the steady velocity field obtained in this case corresponds to the true hydrodynamic flow. Quantities, such as slip lengths, can thus be obtained with this method as well. The framework presented here is thus very generic and allows to model various physical situations.

The hydrodynamic transport is described by the momentum equation,

$$\frac{\partial \rho_m \mathbf{v}}{\partial t} + \nabla \cdot (\rho_m \mathbf{v} \mathbf{v}) = \nabla \cdot \Sigma - \rho \nabla \left(\frac{\delta \Omega[\rho]}{\delta \rho} \right) + \mathbf{f}_{\text{wall}} + \mathbf{f}_{\text{ext}}, \quad (11)$$

where ρ_m is the local mass density, $\Sigma = \eta(\nabla \mathbf{v} + (\nabla \mathbf{v})^t) + (\zeta - 2/3\eta)(\nabla \cdot \mathbf{v})E_3$ is the viscous stress tensor (with the first viscosity η , the second viscosity ζ , and the unit matrix E_3), and the extra contribution $-\rho \nabla(\delta \Omega[\rho]/\delta \rho)$ accounts for both the pressure tensor and the capillary force. The derivation of this expression is given in supplementary information³⁴ while the connection with the capillary force

are the subject of Appendix A. The external field $\mathbf{f}_{\text{ext}}$ can be a gravity field for instance. The continuous force field $\mathbf{f}_{\text{wall}}$ applied by the wall which moves with velocity $\mathbf{v}_{\text{wall}}$ (noncontinuous, zero for the upper half of the simulation box and $\mathbf{v}_{\text{wall}}$ at the bottom half) to the fluid is taken as a friction force,

$$\mathbf{f}_{\text{wall}}(\mathbf{r}) = -k\varepsilon\rho(\mathbf{r})(\mathbf{v}(\mathbf{r}) - \mathbf{v}_{\text{wall}}(\mathbf{r})) \times \int d\mathbf{r}' \left\{ \rho_{\text{wall}}(\mathbf{r}') \frac{1}{\sqrt{\pi}^3 \sigma^3} e^{-(\mathbf{r}' - \mathbf{r})^2 / \sigma^2} \right\}. \quad (12)$$

This force is proportional to the interaction energy ε between the solid and the fluid.^{29,40} This prescription enables us to reproduce correctly the evolution of the BC with the wetting properties. In particular, we obtain a continuous change from an intrinsic no-slip BC in a wetting situation ($\theta \sim 0^\circ$) to a partial slip BC with a slip length $b \sim 10$ nm (depending on the value of k) in a nonwetting situation ($\theta \sim 120^\circ$).

The numerical implementation is detailed in Appendix B. In all this article, we will use the molecular length scale σ as the unit length, $\tau = \sigma^2 / G^{\text{CH}}$ will define the molecular time and $k_B T_c$ the energy scale. We shall thus express all the numerical values with respect to these quantities. For details on the parameter choice, see Appendix C.

III. STATIC PROPERTIES: WETTING ANGLE AND CAPILLARY CONDENSATION

In this section, we shall establish a connection between the dimensionless fluid–substrate interaction energy ε and the wetting angle θ of the liquid phase. Furthermore, we will discuss capillary condensation and the effective wetting angles on structured substrates.

A. The planar interface

Two different methods can be used to measure the wetting angle θ : a direct measurement by computing the equilibrium shape of a drop placed on the substrate, and the measurement of the liquid–vapor, liquid–solid, and vapor–solid surface tensions. While both methods can be used and give the same results, the measurement of the surface tensions is much faster. The reason is visible in Fig. 1 where we show the shape of a droplet on the substrate in a partially nonwetting situation. A large scale system is required to obtain the entire drop shape, while the measurement of the surface tensions only involve very small boxes (the rectangles). In principle three runs are necessary to measure the surface tensions,

FIG. 1. Drop on a substrate. The contact angle can be measured directly from the shape or by a measurement of the three surface tensions γ_{LV} , γ_{SL} , and γ_{SV} on smaller volumes.

but since the liquid–vapor surface tension does only need to be determined once (for a given temperature T) and does not depend on the nature of the substrate.

1. The liquid/vapor interface

The surface tension of the planar liquid–vapor interface can be measured by minimization of the functional with respect to $\rho(\mathbf{r})$. We shall compare our findings using the numerical minimization scheme described in Appendix B with the analytical expression for γ_{LV} :¹³

$$\gamma_{LV} = W \int_{\rho_V}^{\rho_L} \sqrt{2 \{f_{\text{bulk}}(\rho) - \mu\rho + P\}} d\rho, \quad (13)$$

where P is the van der Waals pressure, ρ_V is the vapor density, and ρ_L the liquid one. This expression shows that the knowledge of $\rho(\mathbf{r})$ across the interface is not necessary to calculate the surface tension, we only need to perform a numerical integration with respect to ρ in the finite interval $[\rho_V, \rho_L]$. The value computed from this expression can be compared to the value determined by a direct minimization of the functional, using explicitly $\rho(\mathbf{r})$. The latter numerical scheme is only very weakly grid resolution dependent. The difference between the theoretical value and the simulation result is less than 0.2% for a grid spacing $h = 0.5w$ and temperature $T = 0.6k_B T_c$ (see supplementary information³⁴).

2. Liquid/solid and vapor/solid interfaces

The surface tension of a planar liquid–solid or vapor–solid interface of area A contained in a box of volume V (see Fig. 2) can be extracted from the definition of the grand-canonical potential Ω_V ,

$$\Omega_V = -PV + \gamma_{\text{planar}}A \iff \gamma_{\text{planar}} = \frac{\Omega_V + PV}{A}, \quad (14)$$

where P is the bulk pressure. Since the interface is diffuse, with a typical width w , the box size L_z in the normal direction (z axis) must satisfy $L_z \gg w$ to have two well separated bulk phases in the box. An equivalent but more explicit expression can be derived from Eq. (14) by extending L_z to infinity:

$$\gamma_{\text{planar}} = \int_{-\infty}^{\infty} \{P + \omega(\rho(z))\} dz, \quad (15)$$

where $\omega(\rho(z)) = f_{\text{bulk}}(\rho(z)) + (W^2/2)|\nabla\rho(z)|^2 + \rho(z)V_{\text{wall}}(z) - \mu\rho(z)$ is the local grand-canonical potential density. This expression shows that the surface tension can be computed from the equilibrium density-profile of the fluid $\rho(z)$ close to the wall [P is determined from ρ_{bulk} , the value of $\rho(z)$ far away from the wall]. Using this prescription, the solid–vapor and solid–liquid surface tensions γ_{SV} and γ_{SL} can be computed by a direct minimization of the functional in a small rectangular box, as explained in Appendix B, and the triple line contact angle θ can be calculated through Young's law,

$$\Gamma = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}, \quad (16)$$

that coincides with $\cos(\theta)$ when $|\Gamma| \leq 1$.

While the liquid–vapor interface is determined only by the parameter w in the square gradient term, the triple phase

FIG. 2. Intrinsic contact angle $\Gamma = \cos \theta$ as a function of ε .

contact angle is controlled by the parameters ε and σ . The wall potential V_0 , the lattice spacing h , and the Lennard-Jones parameter σ are chosen as: $V_0 = 2k_B T_c$, $h = 0.5w$, and $\sigma = 0.75w$. These prescriptions ensure a good numerical accuracy, a low dependence of Γ with respect to V_0 and a low computational cost, as discussed in the supplementary informations.³⁴ With this choice of parameters the interaction strength ε is the only remaining tune variable to determine Γ . Its dependence is shown in Fig. 2.

3. Capillary condensation

A first elementary property that the model must reproduce to account for liquid–vapor transitions in confined geometries is capillary condensation. To investigate this transition we consider a slit geometry where the two planar and parallel confining walls are separated by a distance D . Capillary condensation of the vapor phase into a liquid filling all the slit occurs when D becomes smaller than a critical distance D_{crit} that depends on the wetting angle θ of the confining surfaces. For a slit-geometry, the critical width is given by $D_{\text{crit}} = -(2\gamma_{LV} \cos \theta / \rho_L \Delta\mu)$ (Ref. 15) (see also the supplementary

FIG. 3. (a) Grand canonical potential Ω over $\Delta\mu \equiv \mu - \mu_{\text{sat}}$ for two values of the intrinsic contact angle: $\cos \theta = -0.5$, the nonwetting case, and $\cos \theta = 0.6$ the wetting situation. For each case, the horizontal branch corresponds to a vapor-phase and the falling branch to a liquid-phase inside the slit. The crossover of the two branches determines the capillary condensation point $\Delta\mu_c$. For an intermediate range of $\Delta\mu$, there are strong metastabilities observed. (b) $\Delta\mu_c$ over the thickness D of the slit. The positive values correspond to $\cos \theta = -0.5$ and the negative ones to $\cos \theta = 0.6$. For each case, the solid lines are the theoretical expression $\Delta\mu_c = -2\gamma_{LV} \cos \theta / \rho_L D$, while the points correspond to the simulations.

information³⁴), where $\mu_V(P_V) = \mu_L(P_L) = \mu = \mu_{\text{sat}} + \Delta\mu$ is defined as the offset from the chemical potential to the saturation $\mu_{\text{sat}} = (\partial F_{\text{bulk}} / (\rho) \partial \rho)_T|_{\rho=\rho_V}$.^{41,42} With nonconserved dynamics, the model can be used to study this transition. The left panel of Fig. 3 shows the grand canonical potential of a fluid in a slit. The green lines correspond to a wetting state ($\cos \theta = 0.6$) whereas the blue lines correspond to a nonwetting situation ($\cos \theta = -0.5$). The points are simulation results with either a vapor-phase as initial state or a liquid phase for various $\Delta\mu$. The branches on the right belong to a liquid equilibrium state while the branches on the left to a vapor one. In between these two regimes, one could probe metastable states. The crossover between the regime where the liquid phase is favored and the regime where the vapor-phase is favored is interpolated by the crossing point $(D, \Delta\mu_c)$ of the connecting lines. The right panel shows $\Delta\mu_c$ for several slit-widths D . For large D , there is a good agreement with the theoretical curves whereas for very small $D < 6\sigma$ the macroscopic theory assuming sharp interfaces become insufficient. However, it is remarkable that the macroscopic theory compares so well to the simulations for values of D as small as 8σ .

B. Crenelated surfaces

Textured surfaces have interesting properties since their artificial roughness can be used to control both wetting³¹ and hydrodynamic slippage.^{26,29,43–45} The first effect of roughness is to amplify the wettability as compared to an atomically smooth surface: since the contact area between the surface and the liquid is increased, the surface energies are amplified by a factor $r = A_{\text{micro}} / A_{\text{macro}}$, where A_{micro} is the actual area of the surface and A_{macro} is the area of the reference planar surface (often referred to as “macroscopic” or “effective” or “apparent”), see Fig. 4. However, this result is only valid when the fluid is in contact with the whole surface, i.e., when the fluid fills the crenels (Wenzel wetting state).⁴⁶ This is not always the case, in particular when the surface is nonwetting at the molecular scale, hybrid wetting configurations can be

FIG. 4. Crenelated surface, definition of the geometry and of the Wenzel and Cassie–Baxter wetting states.

FIG. 5. Wetting states obtained as a result of the model: only small subsystems need to be considered to get the macroscopic wetting angle: the wall is mirrored in the vertical direction for the sake of simplicity.

obtained like the Cassie–Baxter (or fakir) state where the liquid is expelled from the cavities, and floats on the tip of the crenels.³⁰

The wetting diagram relating the macroscopic (or effective) contact angle θ^{eff} to the microscopic (or intrinsic) contact angle θ of the reference smooth surface can easily be probed numerically by using the Young’s equation for θ^{eff} .^{30,32,33}

$$\cos \theta^{\text{eff}} = \frac{\gamma_{\text{SV}}^{\text{eff}} - \gamma_{\text{SL}}^{\text{eff}}}{\gamma_{\text{LV}}}, \quad (17)$$

where the effective surface tensions correspond to the wetting states that can be spontaneously formed during the simulation (see Fig. 5).

The corresponding effective surface tensions are obtained by an integration of the excess grand-canonical potential over all the system. Since the structure is translation invariant in the direction of the ridges, we can restrict the integration on a 2D section which is shown in Fig. 5. Please note that we do not consider a droplet geometry and thus no pinning effects are considered here. The integral is thus performed on the section and is divided by the periodicity L of the structure (the section of the reference surface):

$$2\gamma^{\text{eff}} = \frac{1}{L} \int_{\text{section}} \left(f(\rho_{\text{eq}}) + \frac{W^2}{2} |\nabla \rho_{\text{eq}}|^2 - \mu \rho_{\text{eq}} + P \right), \quad (18)$$

where ρ_{eq} is the equilibrium density profile in the subsystem, as shown in Fig. 5, and P is the bulk pressure. The factor 2 comes from the fact that two crenels are present in the box (the bottom and the top one). A simple macroscopic calculation using the intrinsic surface tensions multiplied by the contact area for each type of interface appearing in the contact region leads to the theoretical Cassie–Baxter–Wenzel wetting diagram presented in the inset of Fig. 6. The analytical expression for each branch is given and the solid lines correspond to the stable wetting states, while the dashes indicate possible metastable states. We plotted the three branches corresponding to the fakir (Cassie–Baxter) state, the Wenzel branch and finally the reverse-fakir branch that exists in the wetting region of the phase diagram. This theoretical diagram is compared in Fig. 6 with the PF model for three values of the aspect ratio d/L of the structure. Several interesting features can be

observed in this figure: First we observe all the branches of the theoretical diagram (inset of Fig. 6); next if we look at the lower left quadrant (the nonwetting region $\cos \theta < 0$), we can see that the theory agrees very well with the PF model for the fakir and the Wenzel states; but if we consider the upper right quadrant on the contrary discrepancies are clearly visible, the comparison between theory and the numerical model is only qualitative. The main reason why the wetting region differs from the nonwetting one is the presence of the liquid phase inside the cavities. In the nonwetting part of the diagram, the cavities are essentially filled with a gas phase that is only weakly affected by the confinement. When a liquid phase fills the cavities, two effects may occur: first the liquid is confined, and the surface energy inside the cavity can differ from the intrinsic one, and more important is the role of the corners that produce line contributions to the interfacial tensions. These corner energies can be estimated in the PF model by subtracting the ideal “macroscopic” contribution of the excess grand-canonical potential to its actual value. A definition of the ideal “macroscopic” contribution is somewhat difficult, since the local excess grand-canonical potential is affected by the confinement of the liquid between the crenels, but to isolate the corner contributions we can construct this “macroscopic” contribution by measuring the excess grand-canonical potential profile in the central region of each surface of the

FIG. 6. Measured wetting diagram for crenelated surfaces.

FIG. 7. Corner energies. (a) Excess grand-canonical potential, as measured at equilibrium. (b) Expected excess grand-canonical potential from macroscopic considerations (a) and (b) difference between the two: white means positive values, black corresponds to negative values. The gray background in all figures is the zero level. The dashed lines in (a) represent the grand canonical potential profiles that are propagated in the direction of the arrows to construct (b).

crenels in contact with the liquid, and we propagate this profile along the surface until it reaches the corners. An example of such reconstructed “macroscopic” grand-canonical potential profile is given in Fig. 7 where the corner energies are obtained by subtraction of the actual grand-canonical potential profile with the reconstructed “macroscopic” one. We can clearly see the contribution of the corners in the last picture (a) and (b): While the upper corners are “repelling” (positive corner energies) the inner corners are on the contrary “attractive” (negative corner energy). This effect is due to the attractive part of the interaction potential between the wall and the liquid: this potential is more attractive to molecules placed at an inner corner as compared to molecules next to a planar substrate. On the contrary at an outer corner the effective potential is less attractive in comparison with a flat substrate.

The corner energies can be included in the Cassie–Baxter–Wenzel macroscopic framework, at least for the Wenzel states: if ε_U and ε_D are the corner energies (per unit length) for the upper corner and the lower corner, respectively, one can easily obtain

$$\cos \theta^{\text{eff}} = \left(1 + 2\frac{d}{L}\right) \cos \theta - 2\frac{\varepsilon_U + \varepsilon_D}{L\gamma_{LV}} \quad (19)$$

for the Wenzel branch. These results are plotted in Fig. 6 for $d/L = 1/2$ and we can see that the agreement between the measured effective angle (the open circles) and the theory (solid line) is much better. Interestingly, these corner energies are not constant, but vary with the wettability of the substrate. We show in Fig. 8 the behavior of these line energies with the intrinsic wetting angle.

We can see in this figure that the contribution of corner energies $\varepsilon_U + \varepsilon_D$ is almost linear in $\cos \theta$ and the values are almost independent of the crenel height d , excepted maybe for the lowest value $d/L = 0.5$. While these effects are visible on the wetting diagram for nanometric structures, they should have a quite weak quantitative contribution for micronic systems (the corner contributions scale such as $1/L$, where L is the periodicity of the structure, and thus vanishes at large scale). One should not conclude that these effects are negligible. They play a key role in the metastability of the wetting

FIG. 8. Corner line energies as a function of the intrinsic wettability of the surface.

states, even at large scale, since the upper corners can pin the contact line, as we shall see in Sec. IV. This effect on the metastability is already visible on the wetting diagram plotted in Fig. 6: both the fakir, reverse fakir and Wenzel branches exhibit metastable states, and metastability is much stronger in the wetting part of the diagram, where the corner energies are important.

IV. DYNAMIC PROPERTIES: SLIP, FRICTION, AND CONTACT ANGLE HYSTERESIS

In this section, we will describe the dynamic properties of the model. We shall focus more particularly on the friction between the liquid and the wall and on the dynamics of the contact line.

A. Friction

The friction between a liquid and a surface can be described at the macroscopic level with the generic Navier boundary condition,

$$b \cdot \partial_z v_x(z)|_{z=z_s} = v_x(z)|_{z=z_s}, \quad (20)$$

where x is the direction of the flow, parallel to the surface of the wall (see Fig. 9), z is the direction normal to the surface, and v_x is the parallel component of the velocity field. This boundary condition involves two free parameters b and

FIG. 9. Navier's partial slip boundary condition.

FIG. 10. Large panel: Slip length b and position of substrate $z_s - z_{\text{wall}}$ as a function of the intrinsic angle θ in a slit geometry with a friction constant $k = 100 \tau \sigma$. Small panel: Velocity profile parallel to the slit with either flow-profiles. The linear and quadratic fit parameters are used to compute the slip length b and the position z_s where the slip boundary condition is applied. z_{wall} is indicated by larger tics ($z_{\text{wall}} = 3\frac{1}{3} \sigma$ and $22\frac{2}{3} \sigma$).

z_s that correspond, respectively, to the slip length (b) and the effective (or hydrodynamic) position of the wall (z_s).^{40,47}

One of the advantages of PF models is that no explicit boundary conditions at interfaces have to be defined since the interaction between the wall and the fluid results from the force field $\mathbf{f}_{\text{wall}}$. Effective (or macroscopic) boundary conditions can, however, be obtained as a result of the model. Indeed, the roughness of the walls (or the correlations between the wall and the liquid at the nanometric scales) is responsible for the production of a local flow in the vicinity of the walls. The slip-length as defined in Fig. 9 is obtained by fitting the flow field in the center of the microchannel for a Couette-flow and a Poiseuille-flow as it is described in Refs. 9 and 12. This method determines b and z_s without any assumption on the wall position.

1. Planar wall

Let us consider first a planar wall. Formula (12) defines the dissipation due to friction at the solid–fluid interface. Due to the construction of the model this term must be introduced to describe the dynamical interaction between the substrate and the fluid. This heuristic term gives correct decay of the slip length b as a function of the wetting angle^{29,40,48} (Fig. 10). The friction parameter k is chosen as $100 \tau \sigma$ in the intrinsic unit-system to give friction behaviors that are comparable to MD-simulation findings.⁴⁰ Higher values of k will give an intrinsic no-slip BC.

2. Crenelated wall

For a crenelated wall as considered in Fig. 4, the slip length can be determined as well by using the same prescription: a Couette- and a Poiseuille-flow are applied and extrapolated inside the walls to measure the effective slip length B and Z_s . We use capital letters for B and Z_s here to distinguish between the effective slip length of the textured wall and the intrinsic slip length b of the planar wall with the same

FIG. 11. Scaling law satisfied by $B_{||}$ as a function of b and L . The symbols correspond to the values obtained with the PF model for a crenelated surface, the dashed and dotted-dashed lines correspond to the simple approximation (21) for $\phi_s = 0.25$ and $\phi_s = 0.5$. It is remarkable that the obtained values of c are in quantitative agreement with Fig. 12 of Ref. 49, though the geometries are different (see text).

chemical nature. The main question for practical applications is to understand which length scale controls the slip length: the intrinsic slip length b or the periodicity of the structure L . Macroscopic calculations based on hydrodynamics have been done in Ref. 18 for a simplified geometry: the crenels in the Cassie–Baxter state are represented by an alternation of stripes of two types: stripes with infinite slip length represent the liquid–vapor interfaces sustained between the crenels while the stripes with a slip length b are representing the top of the crenels, where the liquid is in contact with the wall. The surface is planar for these calculations. It has been shown in particular that a flow parallel to the stripes can exhibit quite a large slip length $B_{||}$ which is proportional to the largest of the two length scales. If $\phi_s \equiv a/L$ denotes the fraction of the crenels in contact with the liquid in the Cassie–Baxter state, an approximate relation between $B_{||}$, b , and L can be written as

$$\frac{B_{||}}{L} \simeq \frac{1}{\phi_s} \frac{b}{L} + c, \quad (21)$$

where c is a constant close to 0.1 for $\phi_s = 0.5$ and between 0.1 and 0.3 for $\phi_s = 0.25$.¹⁸ We could check with our model (Fig. 11) that the slip length measured for the crenelated geometry in the Cassie–Baxter state agrees nicely with this expression. This nice behavior is somehow a crosscheck between the PF model that contains all the complexity of the dynamically moving interfaces, and the simplified geometry considered in Ref. 18. It is important to mention here that these results have been obtained at low capillary number (i.e., the liquid–vapor interface is not affected by the flow). A deformation of the interface by the flow at large capillary number may change the picture.

B. Flow in a channel and contact angle hysteresis

1. Washburn law

To test the dynamical behavior of the model the capillary force is used to pump the liquid phase into a pore with a

FIG. 12. Position l of the meniscus in the Washburn capillary over the time. The geometry is indicated schematically on the left of the figure, a reservoir contains the liquid that enters in the pore and climbs until it reaches the top (there is no gravity here). A snapshot of the actual system is shown on the left, it corresponds to the point indicated by the arrow. The simulation shows clearly the square-root relation showed by Washburn in 1921 (Refs. 50 and 51), and the theoretical line is calculated using the Washburn law with no adjustable parameter. l saturates when the meniscus reaches the top of the pore.

slit geometry.^{22,24} In 1921 Washburn gave a classical theory of the penetration of liquids into wetting pores.^{50,51} Considering a pore made from a perfectly wetting substrate, the transport velocity will be proportional to the pressure gradient and to $1/\eta$,

$$\mathbf{v} \propto \frac{1}{\eta} \frac{dp}{dx}. \quad (22)$$

The transport is driven by the Laplace pressure due to curvature c of the meniscus which is $-\gamma_{LV}c$. Assuming the position of the meniscus as l the pressure gradient $dp/dx \propto \gamma_{LV}c/l$ and noting $\mathbf{v} = dl/dt$ we get the well-known Washburn law for a slit geometry,

$$l^2 = \frac{D\gamma_{LV} \cos \theta}{3\eta} t, \quad (23)$$

where D is the distance between the confining planes in the slit geometry. To compute this capillary driven motion, we consider a system with a reservoir of liquid connected to the

pore, as depicted in Fig. 12. This figure shows the meniscus position in the simulation plotted over the time, compared with the theoretical curve. The agreement is quite good; all the parameters entering in the Washburn law have been measured separately and there is no adjustable parameter here. The pore thickness is $D = 9.66 \sigma$, $\gamma_{LV} = 0.342 k_B T_c / \sigma^2$, $\cos \theta = 0.6$, and $\eta = 1.78 \cdot 10^{-3} \sigma^3 / (k_B T_c \tau)$ for this simulation. The friction between the walls and the liquid is large enough to ensure a no-slip boundary condition. This is a strong test of the performance of the model since it couples the static properties of wetting to the dynamical penetration process.

2. Contact angle hysteresis

The synchronous solving of the density-evolution equation (8) and the transport equation (11) enables us also the study of stick–slip transitions of droplets on a rough wall. This paragraph demonstrates the ability of the model to investigate the contact angle hysteresis.

When a sticking drop is spread over an inclined surface with certain spatial heterogeneities several contact angles are observed as a function of the inclination³¹ or more generally as a function of the driving force. If the driving force F overcomes a certain threshold F_c the drop starts to move. At the point $F = F_c$ the maximal advancing contact angle θ_a at the front line of the drop and the minimal retarding contact angle θ_r at the rear of the drop define an interval around the equilibrium contact angle θ for which the drop sticks.

For simplicity we have considered a setup with regular heterogeneities as shown in Fig. 13. The force F is applied through a uniform acceleration field a similar to a gravity field oriented in the direction of F (see Fig. 13). Instead of measuring the contact angle directly, we used the more robust method of measuring the curvature radius of the drop around the centerline of the setup. Depending on the details of a direct measurement method both methods differ typically between 5° and 10° . Since the setup is at low capillary number ($Ca \leq 0.1$) we assume a circular shape of the drop in the channel center and fit the curvature radius to points on a iso-density contour as it is shown in Fig. 13. For further improvement of the estimation, we averaged the curvature radius R

FIG. 13. Drop in a slit geometry with crenelated walls and a horizontal driving force. The two images correspond to pinning situations: the left drop is pinned at the rear (the pinning point is indicated by a circle), and the right drop at the front. Pinning of an interface results in a deformation of its shape: pinning at the front increases the contact angle at the pinning point, whereas pinning at the rear decreases it. For contact angles between θ_r and θ_a the drop sticks at the pinning point.

FIG. 14. [(a) and (b)] Advancing radius R_a and retarding radius R_r of the drop pressed along a heterogeneous substrate as shown in Fig. 13 plotted over the position of the center of mass C for values of a ranging from $0.33\sigma/\tau^2$ to $1.33\sigma/\tau^2$. The center of mass is scaled by the period L . After overcoming the pinning point at the front line the interfaces relax rapidly to a larger curvature radius and vice versa for the retarding interface. The sticking drop marked in bottom panel belongs to the acceleration $a = 0.47\sigma/\tau^2$, where the drop is pinned at the rear line. The mark in the top left panel belongs to the acceleration $a = 0.33\sigma/\tau^2$. In this case, the drop is pinned at the front. This curve is shifted by one period to the right for better clarity. (c) Grand canonical potential Ω of the system as a function of the center of mass C . The gray highlighted regions show the jump/relaxation dynamics which can differ slightly with the applied acceleration while the slip-stick dynamics (white regions) are the same for different accelerations a .

over the best fit results of three different isodensity profiles. The contact angle is given by $\theta = \pi/2 + \arcsin(D/2R)$.

When the drop is moving, the rear and the front interfaces oscillate and we can follow the variation of their radii, R_a for the advancing front and R_r for the receding one. The left panel of Fig. 14 shows the curvature radius of the interfaces over the position of the drop center of mass C for various accelerations a . The x axis is scaled in the length unit of one crenel L , the periodicity of the system. Accelerations larger than $0.67\sigma/\tau^2$ are sufficient to move the drop over the heterogeneities, lower values correspond to a drop trapped by the crenels (sticking drops). The two configurations shown in Fig. 13 correspond indeed to the sticking case, and two pinning situations are possible in this case: a pinning of the rear line (left image) or a pinning of the front line (right one). The front line pinning corresponds to $a = 0.33\sigma/\tau^2$ while the rear line pinning has been obtained for $a = 0.47\sigma/\tau^2$. For these two cases the drop sticks to the crenels and its center of mass is thus fixed. After a transient the drop stops and the points corresponding to the steady configurations $a = 0.33\sigma/\tau^2$ and $a = 0.47\sigma/\tau^2$ are indicated by the two arrows on Fig. 14 (left). When $a \geq 0.67\sigma/\tau^2$ the drop moves and we can follow the variations of the front and rear radius as a function of the position of the center of mass in Fig. 14 (left). Interestingly, the variations of R_a and R_r are only weakly sensitive to the value of a in this regime, we can only note a difference in the relaxation dynamics after overcoming the pinning: The dynamics is slow as long as the meniscus is pinned, and the radius of curvature is thus only fixed by the position of the center of mass of the drop in this regime, while the

TABLE I. Average velocity v , advancing radius R_a , retarding radius R_r , and the corresponding contact angles θ_a, θ_r for different accelerations a in σ/τ^2 to extrapolate the contact angle hysteresis at $v \rightarrow 0$. v is the average velocity in σ/τ . The intrinsic equilibrium contact angle is $\cos \theta = -0.45$ and the effective contact angle is $\cos \theta_{\text{eff}} = -0.69$.

a	v	R_a	$\cos \theta_a$	R_r	$\cos \theta_r$	Ca
	$\rightarrow 0$	19.5	-0.87	33.6	-0.51	
0.67	1.05	19.4	-0.88	35.0	-0.49	0.02
0.80	1.75	19.3	-0.88	35.7	-0.48	0.03
1.00	2.48	19.3	-0.88	36.7	-0.46	0.05
1.33	3.57	19.1	-0.89	38.9	-0.45	0.07

dynamics is fast after unpinning, and we observe a dependence on a in this case. Unpinning occurs when the advancing (front) radius is minimal for a front line pinning, while it occurs when the receding (rear) radius is maximal for a rear line pinning. These extremal values of R_a and R_r can be converted in extremal values of the corresponding contact angles: unpinning occurs when the force is large enough to overcome a critical contact angle. We estimated these critical values by taking the maximal retarding contact angles θ_r with respect to the minimal advancing contact angles θ_a for the moving drops and extrapolate the values to the zero velocity limit. The results are printed in Table I. The receding contact angle $\cos \theta_r = -0.51$ we found is around the equilibrium contact angle $\cos \theta = -0.45$. Other groups^{23,25,27} report that θ_r is equal to θ but the deviation we observe here is a consequence of the microscopic structure we impose by the substrate (repelling corner energies). The advancing contact angle we found is $\cos \theta_a = -0.87$. This is also around the values, the other groups found.

Figure 14 (right) shows the grand canonical potential Ω of the system plotted over the center of mass of a drop with constant volume for several forces. If the drop is pinned the system stays in a steady state at a constant potential whereas the moving drops probe the full nonequilibrium profile of Ω . The figure presents a succession of peaks: the grand canonical potential barriers that the drop needs to overcome in order to move. The peaks look similar but are in fact not identical: two adjacent peaks correspond to a successive pinning of the front meniscus and a pinning of the rear meniscus (the difference is better seen if we look at the minima, the difference in the maxima is indeed small in the case we consider in Fig. 14). An interesting feature is the very weak dependence of the grand canonical potential landscape with respect to the force: for all forces which are sufficient to push the drop the potential is nearly the same. This shows that a model of a drop moving in fixed potential should be sufficient to describe the dynamics in this case.

Of course the pinning situation depends on the drop size. For certain drop sizes the pinning at the front and at the rear occurs together, while in other cases only one interface is pinned at the same time. Therefore the acceleration a_c which is needed to overcome the pinning varies but not the critical contact angle. We consider the influence of the drop size in Fig. 15. This figure shows the grand canonical potential Ω for drops with different volume but exposed to a constant acceleration to demonstrate the effect of synchronous pinning. To

FIG. 15. (a) Grand canonical potential Ω of drops with different sizes (shifted to be one upon the other) as a function of time t . The $\Delta\Omega$ barrier clearly varies strongly with the size of the drops. (b) Center of mass position C as a function of time. Due to the complex variations of $\Delta\Omega$ with the volume one observes moving drop and sticking drops alternating when the volume is increased. The volume ($\alpha = -5\%$, 0% , 8% , 14% , 17% , 21%) corresponding to the symbols in the main panel is indicated in the inset plot, which shows the mean velocity over the volume parameter $\alpha = (S - S_0)/S_0$.

show the sensitivity with respect to the drop size, we introduce the parameter $\alpha = (S - S_0)/S_0$ that indicates the variation of the drop volume S with respect to the reference drop (S_0) of Fig. 13: e.g., $\alpha = 10\%$ means that we increased the drop volume by 10% . First we can see that the peak of the potential which has to be overcome is quite sensitive to the drop size: the different curves in Fig. 15 (left) are superimposed to illustrate the $\Delta\Omega$ between the minimum and the maximum of the Ω -landscape. We selected the values of α that corresponds to a motion of the droplet in Fig. 15 (left), but changing the drop size for a given applied force can also result in the sticking of the drop, when rear and front pinning occurs at the same time. This effect is illustrated in Fig. 15 (right) where we can observe a succession of moving drops (pinning–unpinning motion of the drop) and trapped drops in a steady state.

V. CONCLUSION

We have presented in this article a PF/DDFT model to study the wetting properties and the dynamics of a fluid in a micro- or nanochannel. This model is able to reproduce the main phenomena that can occur in such situations: liquid/solid wetting transitions, slippage, capillary condensation, stick–slip motion on rough surfaces, advancing and receding contact angles, etc. The main advantage of this approach is the generic nature of the model: we only use a free energy model to describe the possibility of the transition, a potential interaction energy between the molecules of the fluid and the atoms of the boundaries, and a friction force between the fluid and the atoms of the wall. Based on these minimal ingredients at the nanometric scale, the model is able to predict the properties of the system in arbitrarily complex geometries: we are presently investigating the properties of surfaces with random roughness without modification of the model. This is particularly interesting in microfluidics where a continuity of length scales can exist ranging from nanometric effects to micrometric structures. One important feature is the pinning–unpinning transition of the contact lines that usually lead to strong metastabilities in these systems, which are naturally present in this approach. We, therefore, believe that this kind of model can be a good tool to probe the physics and the phase transitions induced by roughness. The model presented here was focused on the Cassie–Baxter–Wenzel wetting tran-

sition, but other transitions such as chemical transitions in microchannels can be investigated as well by adding extra phase fields (concentration fields) without much difficulty. As well as studying geometrical heterogeneities with this PF/DDFT model, it is straightforward to investigate chemical heterogeneities described by the external potential.

APPENDIX A: CONNECTION WITH THE LAPLACE LAW

We shall prove here that the term: $-\rho\nabla(\delta\Omega[\rho]/\delta\rho)$ contains both the volume contribution $-\nabla P$ and the surface capillary force $-c\chi_V\hat{n}$, where c is the local mean curvature of the interface (with the convention that it is positive for a sphere) and $\hat{n}$ is the normal vector pointing outside. To this end, we shall first identify the pressure tensor, and extract the capillary force from it.

1. The pressure tensor

This tensor can be identified by considering the identity

$$-\rho(\mathbf{r})\nabla\left(\frac{\delta\Omega[\rho]}{\delta\rho(\mathbf{r})}\right) \equiv -\rho(\mathbf{r})\nabla\left(\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}\right) \equiv -\nabla\cdot\mathbf{P}. \quad (\text{A1})$$

The first identity is straightforward since the grand potential functional derivative and the free energy functional derivative only differ by an additive constant: the chemical potential. The second identity is the definition of the pressure tensor $\mathbf{P}$. For the square gradient theory,

$$F[\rho] \equiv \int \left\{ f_{\text{bulk}}(\rho) + \frac{W^2}{2} |\nabla\rho|^2 \right\} dV, \quad (\text{A2})$$

thus

$$\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} = f'_{\text{bulk}}(\rho) - W^2\Delta\rho \quad (\text{A3})$$

and one can check that the pressure tensor⁵²

$$\begin{aligned} \mathbf{P}_{ij} = & \left(\rho \frac{df_{\text{bulk}}}{d\rho} - f_{\text{bulk}} - W^2\rho\Delta\rho - \frac{W^2}{2} |\nabla\rho|^2 \right) \delta_{ij} \\ & + W^2 \nabla_i \rho \nabla_j \rho \end{aligned} \quad (\text{A4})$$

satisfies the second identity.

The pressure tensor can be rewritten as

$$\mathbf{P}_{ij} = P_n \delta_{ij} + W^2 (\nabla_i \rho \nabla_j \rho - |\nabla\rho|^2 \delta_{ij}), \quad (\text{A5})$$

where $P_n = \rho df_{\text{bulk}}/d\rho - f_{\text{bulk}} - W^2\rho\Delta\rho + W^2/2 |\nabla\rho|^2$ is the normal pressure (i.e., in the direction of $\nabla\rho$). For a planar interface P_n is constant across the interface, but there is a jump when the interface is curved. Insertion of this last expression in the definition (A1) leads to

$$-\rho(\mathbf{r})\nabla\left(\frac{\delta\Omega[\rho]}{\delta\rho(\mathbf{r})}\right) = -\nabla P_n + W^2(\nabla\rho \cdot \nabla(\nabla\rho) - \Delta\rho \nabla\rho). \quad (\text{A6})$$

2. The capillary force

We shall now prove that $\mathbf{L} \equiv W^2(\nabla\rho \cdot \nabla(\nabla\rho) - \Delta\rho \nabla\rho)$ is the Laplace force. Since ρ varies in the normal direction

only (by definition), this force is normal by construction. Let us introduce the normal vector field,

$$\hat{\mathbf{n}} \equiv \frac{\nabla \rho}{|\nabla \rho|}, \quad (\text{A7})$$

the local curvature of the interface is defined as

$$c(\mathbf{r}) \equiv \nabla \cdot \hat{\mathbf{n}} = \frac{\Delta \rho}{|\nabla \rho|} - \frac{\nabla \rho \cdot (\nabla \rho \cdot \nabla)(\nabla \rho)}{|\nabla \rho|^3}, \quad (\text{A8})$$

which is positive for a spherical drop. This expression can be rewritten as

$$c(\mathbf{r}) = -\frac{\hat{\mathbf{n}}}{|\nabla \rho|^2} \cdot (\nabla \rho \cdot \nabla(\nabla \rho) - \Delta \rho \nabla \rho) = -\frac{\hat{\mathbf{n}} \cdot \mathbf{L}}{W^2 |\nabla \rho|^2}, \quad (\text{A9})$$

from which we deduce that $\mathbf{L}$ is

$$\mathbf{L} = -c(\mathbf{r}) W^2 |\nabla \rho|^2 \hat{\mathbf{n}}. \quad (\text{A10})$$

To identify the Laplace force, we need to recall that for a planar interface the surface tension can be written¹³

$$\gamma_{LV} = \int W^2 |\nabla \rho|^2 dz, \quad (\text{A11})$$

where z is the normal coordinate. Equation (A10) is thus a local expression for the Laplace force.

APPENDIX B: THE NUMERICAL IMPLEMENTATION

The grand potential variation can be computed easily for the square gradient theory using Eqs. (6) and (7)

$$\frac{\delta \Omega[\rho]}{\delta \rho} = f'_{\text{bulk}}(\rho(\mathbf{r})) + V_{\text{wall}}(\mathbf{r}) - W^2 \Delta \rho(\mathbf{r}) - \mu, \quad (\text{B1})$$

where $f'_{\text{bulk}}(\rho(\mathbf{r}))$, the derivative of the bulk free energy with respect to ρ , is known analytically. To simplify the algebra, let us define

$$\omega'_{\text{local}}(\mathbf{r}) \equiv f'_{\text{bulk}}(\rho(\mathbf{r})) + V_{\text{wall}}(\mathbf{r}) - \mu. \quad (\text{B2})$$

1. The density field

Using these two expressions, the transport equation for the density field reads

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = -G \omega'_{\text{local}}(\mathbf{r}) + G W^2 \Delta \rho(\mathbf{r}), \quad (\text{B3})$$

(with $G = G^{\text{AC}}$ or $-G^{\text{CH}} \Delta$) or equivalently

$$\frac{\partial \rho}{\partial t} - G W^2 \Delta \rho(\mathbf{r}) = -\nabla \cdot (\rho \mathbf{v}) - G \omega'_{\text{local}}(\mathbf{r}). \quad (\text{B4})$$

This form can be used to derive a semi-implicit scheme

$$\frac{\rho^{t+dt} - \rho^t}{dt} - G W^2 \Delta \rho^{t+dt}(\mathbf{r}) = -\nabla \cdot (\rho \mathbf{v})^t - G (\omega'_{\text{local}}(\mathbf{r}))^t, \quad (\text{B5})$$

where the notation t indicates the time at which the quantity is evaluated. We thus have

$$(1 - dt G W^2 \Delta) \rho^{t+dt} = \rho^t - dt [\nabla \cdot (\rho \mathbf{v})^t + G (\omega'_{\text{local}}(\mathbf{r}))^t]. \quad (\text{B6})$$

The right operator can be inverted easily in the Fourier space, to give

$$\rho_{\mathbf{k}}^{t+dt} = \frac{\rho_{\mathbf{k}}^t - dt [\nabla \cdot (\rho \mathbf{v})^t + G^{\text{AC}} (\omega'_{\text{local}}(\mathbf{r}))^t]_{\mathbf{k}}}{1 + \mathbf{k}^2 G^{\text{AC}} W^2 dt}, \quad (\text{B7})$$

where the quantity between the brackets is evaluated in the direct space, and Fourier transformed afterward. This scheme gives quite a robust numerical stability. For a conserved dynamics, G needs to be replaced by $-G^{\text{CH}} \Delta$, and the final expression becomes

$$\rho_{\mathbf{k}}^{t+dt} = \frac{\rho_{\mathbf{k}}^t - dt [(\nabla \cdot (\rho \mathbf{v}))_{\mathbf{k}}^t + G^{\text{CH}} \mathbf{k}^2 (\omega'_{\text{local}}(\mathbf{r}))_{\mathbf{k}}^t]}{1 + \mathbf{k}^4 G^{\text{CH}} W^2 dt} \quad (\text{B8})$$

in that case.

This scheme, however, does not ensure the positivity of $\rho(\mathbf{r})$ at time $t + dt$. This is particularly a problem when a vapor phase is present, which is the case in this study, but a simple ansatz can be used to prevent negative values in $\rho(\mathbf{r})$ at any time: the semi-implicit scheme written above provides an initial guess for $\rho^{t+dt}(\mathbf{r})$, that we shall call $\rho_{\text{implicit}}^{t+dt}(\mathbf{r})$, this value is next used to generate the actual value of $\rho^{t+dt}(\mathbf{r})$

$$\rho^{t+dt}(\mathbf{r}) = \rho^t(\mathbf{r}) \exp [\rho_{\text{implicit}}^{t+dt}(\mathbf{r}) / \rho^t(\mathbf{r}) - 1]. \quad (\text{B9})$$

When $\rho_{\text{implicit}}^{t+dt}(\mathbf{r}) / \rho^t(\mathbf{r})$ is close to 1, the usual case, one can easily check that this expression leads to $\rho^{t+dt}(\mathbf{r}) \simeq \rho_{\text{implicit}}^{t+dt}(\mathbf{r})$ to the leading order in $\Delta \rho(\mathbf{r}) / \rho^t(\mathbf{r})$ where $\Delta \rho(\mathbf{r}) \equiv \rho_{\text{implicit}}^{t+dt}(\mathbf{r}) - \rho^t(\mathbf{r})$.

2. The velocity field

The hydrodynamic equation is solved by splitting the velocity field into two components: the applied velocity field $\mathbf{v}_{\text{applied}}$ and $\mathbf{u}$ the remaining part. Periodic boundary conditions are applied at the edges of the simulation box for the density field $\rho(\mathbf{r})$ and the $\mathbf{u}(\mathbf{r})$ component of the velocity field. In the absence of external field

$$\frac{\partial \rho_m \mathbf{v}}{\partial t} + \nabla \cdot (\rho_m \mathbf{v} \mathbf{v}) = \nabla \cdot \Sigma - \rho \nabla \cdot \left(\frac{\delta \Omega[\rho]}{\delta \rho} \right) + \mathbf{f}_{\text{wall}}, \quad (\text{B10})$$

which we can rewrite as

$$\begin{aligned} \rho_m \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \frac{\partial \rho_m}{\partial t} + \mathbf{v} \nabla \cdot (\rho_m \mathbf{v}) + (\rho_m \mathbf{v} \nabla) (\mathbf{v}) \\ = \nabla \cdot \Sigma - \rho \nabla \cdot \left(\frac{\delta \Omega[\rho]}{\delta \rho} \right) + \mathbf{f}_{\text{wall}}, \end{aligned} \quad (\text{B11})$$

TABLE II. Model parameter in real units.

Parameter	Symbol	Value
Cahn-Hilliard constant	G^{CH}	$2.0 \times 10^{-9} \text{m}^2/\text{s}$
Allen-Cahn constant	G^{AC}	$2.0 \times 10^9 \text{s}^{-1}$
Particle diameter	σ	$1.0 \times 10^{-9} \text{m}$
Interfacial thickness	w	$1.33 \times 10^{-9} \text{m}$
Kinematic viscosity	ν	$1 \times 10^{-6} \text{m}^2/\text{s}$
Mass per particle	m	$3.0 \times 10^{-26} \text{kg}$
Critical temperature	T_c	500K
Boltzmann constant	k_B	$1.38065 \times 10^{-23} \text{J/K}$
Lennard-Jones prefactor	ε	$[1.72, 6.9] \times 10^{-21} \text{J}$

TABLE III. Scaling parameters of the lattice model.

Scaling-parameter	Symbol	Value
Length-scale	σ	1.0×10^{-9} m
Time-scale	$\tau = \sigma^2 / G^{\text{CH}}$	5.0×10^{-10} s
Energy-scale	$k_B T_c$	6.9035×10^{-21} J

making use of the transport equation for the density $\rho \equiv \rho_m / M$, where M is the molecular mass, we get for ρ_m

$$\frac{\partial \rho_m}{\partial t} + \nabla \cdot (\rho_m \mathbf{v}) = -MG \left(\frac{\delta \Omega[\rho]}{\delta \rho} \right), \quad (\text{B12})$$

and thus, the momentum equation can be written as

$$\rho_m \frac{\partial \mathbf{v}}{\partial t} + (\rho_m \mathbf{v} \cdot \nabla)(\mathbf{v}) = \mathbf{v} MG \left(\frac{\delta \Omega[\rho]}{\delta \rho} \right) + \nabla \cdot \Sigma - \rho \nabla \left(\frac{\delta \Omega[\rho]}{\delta \rho} \right) + \mathbf{f}_{\text{wall}}, \quad (\text{B13})$$

dividing both members by ρ_m , we get

$$\frac{\partial \mathbf{u}}{\partial t} \equiv \frac{\partial \mathbf{v}}{\partial t} = -\mathbf{v} \cdot (\nabla \mathbf{v}) + \mathbf{v} \frac{G}{\rho} \left(\frac{\delta \Omega[\rho]}{\delta \rho} \right) + \frac{1}{\rho_m} \left\{ \nabla \cdot \Sigma - \rho \nabla \left(\frac{\delta \Omega[\rho]}{\delta \rho} \right) + \mathbf{f}_{\text{wall}} \right\}. \quad (\text{B14})$$

When the local thermodynamic equilibrium is reached, $\delta \Omega[\rho] / \delta \rho(\mathbf{r})$ vanishes and the usual Navier–Stokes equation is recovered. This equation can be solved explicitly (semi-implicit methods have been tested, without noticeably improvement in the stability) in the Fourier space as

$$\mathbf{u}_{\mathbf{k}}^{t+dt} = \mathbf{u}_{\mathbf{k}}^t + dt \left(\frac{\partial \mathbf{u}}{\partial t} \right)_{\mathbf{k}}^t. \quad (\text{B15})$$

The full velocity field is thus obtained in the real space as $\mathbf{v} = \mathbf{u} + \mathbf{v}_{\text{applied}}$. Although the Fourier space is not strictly necessary for an explicit scheme, it is a convenient way to apply automatically the periodic boundary conditions on $\mathbf{u}$ at the boundary of the box. Furthermore it has been found that solving of the second derivatives is numerically more stable in the Fourier space. For computing the surface tension with Eq. (14) correctly, it is also needful to use the same scheme for the gradient term as in Eq. (8).

TABLE IV. Dimensionless parameters in the $(\sigma, \tau, k_B T_c)$ -unit system.

Parameter	Symbol	Value in $(\sigma, \tau, k_B T_c)$
Cahn–Hilliard constant	$G^{\text{CH}*}$	1
Allen–Cahn constant	$G^{\text{AC}*}$	1
Particle diameter	σ^*	1
Interfacial thickness	w^*	4/3
Kinematic viscosity	ν^*	500
Dynamic viscosity	η^*	6.67×10^{-3}
Mass per particle	m^*	1.7382×10^{-5}
Lennard-Jones prefactor	ε^*	[0.3, 1.00]
Friction parameter	k^*	100
Temperature	T^*	0.6
Liquid density	ρ_L^*	0.77
Liquid density	ρ_V^*	0.02

APPENDIX C: PARAMETERS

The parameters we used are listed in Tables II–IV. The kinematic and dynamical viscosity is roughly that of water at standard conditions. There are basically two time scales involved. First, the time scale of the PF diffusion and second the time scale of the hydrodynamic equations determined by the viscosity. We chose the smaller time scale, the diffusion one, to define the intrinsic unit system.

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