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Wenzel and Cassie-Baxter states of an electrolytic drop on charged surfaces

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In this paper, we provide a theory for the Wenzel and the Cassie-Baxter states of an electrolyte drop on charged surfaces. An electric double layer (EDL) develops when the electrolyte drop comes in contact with the charged surface. Therefore, the EDL free energy affects these states by triggering a hydrophilicity-inducing tendency. Consequently, an originally hydrophilic condition leads to a superhydrophilic Wenzel state, and an originally hydrophobic condition leads to a less hydrophobic Wenzel state. For the Cassie-Baxter state, this gives rise to the most remarkable situation of a hydrophilic (as compared to the original) Cassie-Baxter state.

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I. INTRODUCTION

Marble-like water drops on lotus leaves [1] or the water walking of the water striders without wetting their legs [2] or the repelling of water by the pigeon feathers [3] are examples where nature exhibits spectacular evidence of superhydrophobicity. All these natural phenomena are triggered due to intricate microscopic structures on the surfaces of such natural substances [4]. Mimicking such natural examples, researchers, over the past couple of decades, have attempted to engineer microtextured or nanostructured surfaces that can behave as superhydrophobic surfaces, [5–27] with a plethora of application potentials. The fundamental idea of varying the wettability by introducing surface heterogeneity, however, dates back several decades. Wenzel [28] demonstrated that geometric heterogeneity can make a drop attain what is known as the Wenzel state, in which the liquid drop is in complete contact with the surface (referred to as the wetted contact). On the other hand, Cassie and Baxter [29] demonstrated that on chemically heterogeneous substrates, in particular on substrates which are too rugged to allow complete conformation of the liquid to the solid substrate, the liquid drop attains the Cassie-Baxter or Fakir state. In this state, there are air (or vapor) pockets below the liquid, provided the energy penalty for the creation of the corresponding liquid-air (or liquid-vapor) interfaces is smaller than that associated with the event of liquid conforming to the solid. The extent of heterogeneity dictates which among these two states is the more favorable one, and depending on the operating conditions, one can induce a transition from one phase to another [13,16,24,25,27,30]. There have been a large number of studies on different fundamental aspects, application possibilities, and natural examples of these two distinct states and their mutual transition [1–3,31–48]; several of those investigations are nicely summarized in a few recent review articles [4,31–34].

The key reason for interest in studying the Wenzel and Cassie-Baxter states stems from the fact that they induce massive alteration of the wettability of the substrates. For example, when the drop is in the Wenzel state, an increase in roughness increases the hydrophilicity of a hydrophilic substrate and the hydrophobicity of a hydrophobic substrate [32]. On the other hand, a drop in the Cassie-Baxter state is always more hydrophobic than the original state (henceforth by the "original state" we shall refer to the state expressed by the equilibrium Young's angle θ_Y, corresponding to the given solid-liquid-vapor combination) [32]. Motivated by their importance, there have been studies that investigate the effect of the variation of different parameters, such as substrate geometry [16,20,26,30,49–54], evaporation [3,27,55–59], electrowetting [60–65], drop characteristics [49,50,54,66–70], etc., on the existence and the mutual transition of the Cassie-Baxter and the Wenzel states. However, quite remarkably, to the best of our knowledge there has been no study that investigates the Wenzel and Cassie-Baxter states for an electrolytic drop on a charged substrate. In other words, there is no investigation on the effect of the formation of an electric double layer (EDL), which develops spontaneously when the electrolytic drop comes in contact with a charged substrate, on the Wenzel and the Cassie-Baxter states. Microfabrication processes employed to design the pillar structures (used to trigger the formation of these states) often impart a charge on the substrates, just as there will be intrinsic surface charges on natural surfaces that demonstrate superhydrophobicity. Also the liquids in experimental or natural circumstances are bound to contain some dissolved ions. Under these circumstances, it is quite astonishing to realize that there are virtually no studies that discuss the effect of system-induced charges (or EDL) on the characteristics of these two states. This is even more surprising in light of the existence of a plethora of studies on charged superhydrophobic substrates [71–74].

In this paper, we study the formation of the Wenzel and Cassie-Baxter states by an electrolyte drop on a charged surface (or the effect of the EDL on the Wenzel and Cassie-Baxter states). There are important assumptions on the basis of which our theory has been developed. The most important assumption is the existence of a hierarchy of length scales. This means that we assume that the characteristic dimension of the drop is much larger than the surface roughness or surface features (this condition ensures that the average picture represented by the Wenzel and the Cassie-Baxter models remains valid [75–78]) and the surface roughness length scale is much larger than the characteristic EDL thickness (so that the ions forming the EDL effectively "see" the surface heterogeneity as a

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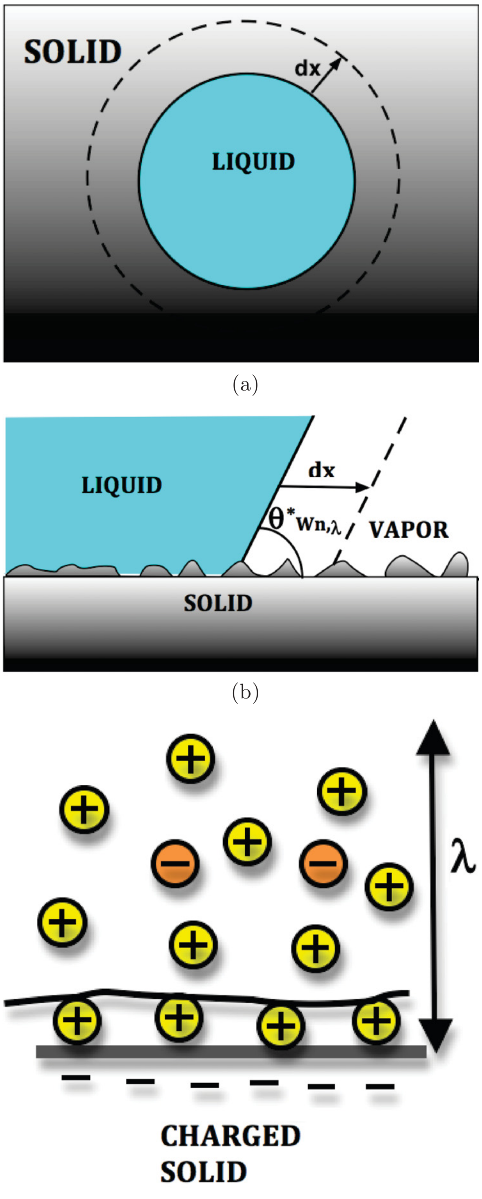
smooth flat surface). The second assumption, which will be evident from our theoretical model, is that we describe the EDL effects through the classical Poisson-Boltzmann model; therefore issues such as finite Stern layer consideration [79], finite ion size effect [80,81], effect of ion-ion interactions [82], etc., will be neglected. Third, we neglect the nontrivialities in the EDL formation and the resulting electrostatic potential at the perimeter of the drop, i.e., at the location of the three-phase contact line (TPCL). There are only a handful of studies on the EDL at the TPCL [83–88], and they too present a very sketchy approximate picture; therefore, in our analysis we shall neglect the contribution of the EDL at the TPCL.

The key idea of our problem is that the EDL effect contributes additional free energy for the Wenzel and Cassie-Baxter states. This triggers a hydrophilicity-inducing tendency to either of these states, with the effect showing a larger magnitude for larger ionic concentrations. We demonstrate that this is exactly analogous to the classical electrowetting scenario [89], where the electrowetting effects induce a more pronounced wetting behavior, although, in principle, the present effect is totally different from electrowetting. There are two key findings of our study. First, we find that due to the EDL effects, an originally hydrophilic state leads to a superhydrophilic Wenzel state, whereas an originally hydrophobic state leads to a hydrophilic Wenzel state. For an originally hydrophilic state, this behavior is qualitatively similar to the classical Wenzel picture (where hydrophilic becomes more hydrophilic [32], although the extent variation is much larger with the EDL effects), but for an originally hydrophobic state this behavior is the complete reverse of the classical Wenzel state (where hydrophobic becomes more hydrophobic [32]). Second, we observe that the EDL effects reduce the hydrophobic influence of the Cassie-Baxter state. This is in sharp contrast to the classical EDL-independent scenario, where the Cassie-Baxter state always leads to a more hydrophobic state as compared to the original state. In fact, for certain system conditions, at substantially large values of original contact angles θ_Y, we find that the consideration of EDL effects leads to a Cassie-Baxter state which is more hydrophilic than the original state. Therefore with EDL effects we hypothesize the most remarkable case of a hydrophilic (as compared to the original) Cassie-Baxter state. Therefore, in this paper we demonstrate the existence of *yet unknown* forms of the Wenzel and the Cassie-Baxter states (for electrolyte drops on charged surfaces) which exhibit characteristics substantially different from the classical Wenzel and Cassie-Baxter states.



(a)

(b)

(c)

FIG. 1. (Color online) Schematic for calculating the Wenzel state. The contact line moves on a rough surface from an initial position by a distance dx to reach the final position (depicted as a dashed line). In (a) we show the top view, whereas in (b) we show the front view. We magnify one location of the newly wetted area to show the EDL in (c). The length scale characterizing the EDL is the EDL thickness λ, which is substantially smaller than the surface heterogeneity (using the hierarchy of length scales assumption); therefore the EDL electrostatic potential distribution can be considered to be strictly one-dimensional.

II. THEORY

A. Effect of EDL on the Wenzel wetting state

We consider an electrolyte drop on a rough substrate (r is the substrate roughness, defined as the ratio between the real surface and the projected one, so that $r > 1$), i.e., the drop is in a Wenzel state [see Figs. 1(a) and 1(b)]. The substrate is charged: therefore there will be a formation of the EDL at the interface between the surface and the electrolytic drop. We intend to obtain the equilibrium condition that dictates the Wenzel state of the drop in the presence of the EDL interactions. For that purpose, we shall first calculate the change in free energy as the droplet is displaced by an infinitesimal distance dx [see Figs. 1(a) and 1(b)]. The movement of the contact line by dx is considered in a manner such that it leads to an increase in the solid-liquid surface area by an amount $rwdx$ (or an equivalent decrease in the solid-vapor surface area by an amount $rwdx$; here w is the width of the contact line). This causes an increase in the surface energy by $\gamma_{SL} r w dx$ (where γ_{SL} is the solid-liquid surface tension) and a decrease in the surface energy by $\gamma_{SV} r w dx$ (where γ_{SV} is the solid-vapor surface tension). Additionally, it leads to an increase in the liquid-vapor surface area by an amount $\cos\theta^*_{Wn,\lambda} w dx$ (where $\theta^*_{Wn,\lambda}$ is the modified contact angle of the drop in the Wenzel state with the EDL effects) and an increase in the surface energy by $\gamma_{LV}\cos\theta^*_{Wn,\lambda} w dx$ (where γ_{LV} is the liquid-vapor surface tension). The analysis up to this point is well documented in classical literature [32]. In this study we propose that the creation of the new solid-liquid surface area will imply an instantaneous formation of the EDL [at the solid-liquid interface in this newly wetted solid; see Figs. 1(a) and 1(b)], thereby leading to a net contribution of the EDL interaction energy, $W_{\text{EDL}} r w dx$ (here W_{EDL} is the per unit area free energy of the EDL), in the overall energy picture. We can hypothesize this instantaneous creation of the EDL in the wetted solid by noting that the time scale for the creation of the EDL $\tau_{\text{EDL}} \sim \lambda^2/D \sim 10$ ns to 1 μs (here $\lambda \sim 1$–10 nm is the EDL thickness and $D \sim 10^{-10}$ m^2/s is the diffusivity of the electrolyte ions). Please note that in W_{EDL} we do not account for the contribution of the EDL at the TPCL at the periphery of the drop. Considering the above physical picture, the net change in the free energy dE (per unit width w) can be expressed as

$$dE = r(\gamma_{SL} - \gamma_{SV} + W_{\text{EDL}})\,dx + \gamma_{LV}\cos\theta^*_{Wn,\lambda}dx. \quad (1)$$

For the equilibrium condition, we need $dE = 0$, so that from Eq. (1), we shall get

$$\cos\theta^*_{Wn,\lambda} = r\cos\theta_Y - r\frac{W_{\text{EDL}}}{\gamma_{LV}}, \quad (2)$$

where $\cos\theta_Y = \frac{\gamma_{SV}-\gamma_{SL}}{\gamma_{LV}}$ is the equilibrium Young's contact angle.

Therefore, Eq. (2) is the modified version of the equation of state for the Wenzel state, considering contributions of the EDL effect. It is easy to see that in the absence of the EDL effects (i.e., when $W_{\text{EDL}} = 0$), Eq. (2) yields the classical Wenzel equation [32], i.e.,

$$\cos\theta^*_{Wn,0} = r\cos\theta_Y, \quad (3)$$

where $\theta^*_{Wn,0}$ is the modified contact angle of the drop in the Wenzel state, without the EDL effects.

Also, we can find a close resemblance of Eq. (2) to the classical Young-Lippmann equation describing the electrowetting behavior (with $r = 1$) [89], with the contribution of the energy of the EDL interactions [in Eq. (2)] being replaced by the energy contributions originating from the applied voltage (for the electrowetting case). More details of this analogy will be discussed later.

Using Eq. (2), we can define an effective roughness r_{eff}, which will ensure that that we can rewrite Eq. (2) in the framework of the classical (EDL-independent) Wenzel picture [i.e., Eq. (3), with r being replaced by r_{eff}]. Physically, r_{eff} is the solid roughness that leads to the same contact angle (as that obtained with EDL effects) for a scenario that does not involve any EDL interactions. This r_{eff} can therefore be expressed as

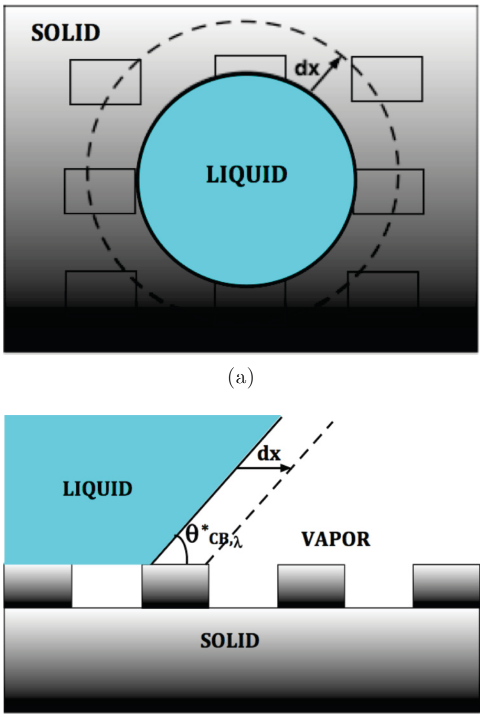
$$\frac{r_{\text{eff}}}{r} = \frac{|\cos\theta_Y - W_{\text{EDL}}/\gamma_{LV}|}{|\cos\theta_Y|}. \quad (4)$$

The extent to which this r_{eff} is modified in the presence of the EDL effects signifies the alteration of the surface roughness (in terms of the wettability of the drop) induced by the EDL effects.

B. Effect of EDL on the Cassie-Baxter wetting state

We next consider an electrolyte drop on a charged periodic array with entrapped air or vapor] (here ϕ_s is the fraction of the total surface area where there is solid-liquid contact), i.e., the liquid drop is in the Cassie-Baxter state (see Fig. 2). With the drop being electrolytic and the solid being charged, an EDL will form at the solid-liquid interface. Similar to the Wenzel problem, we first obtain the net free energy change by considering a movement of the contact line by dx in a manner such that there is an increase in the solid-liquid contact area. Following an exactly similar physical argument as in the previous case, we can express the change in free energy dE (per unit width of the contact line) in the Cassie-Baxter state as

$$\begin{aligned} dE = {} & \phi_s\gamma_{SL}dx + (1 - \phi_s + \cos\theta^*_{CB,\lambda})\,\gamma_{LV}dx \\ & - \phi_s\gamma_{SV}dx + \phi_s W_{\text{EDL}}dx, \end{aligned} \quad (5)$$



(a)

(b)

FIG. 2. (Color online) Schematic for calculating the Cassie-Baxter state. The contact line moves on pillars with entrapped air cavities from an initial position by a distance dx to reach the final position (depicted as a dashed line). In (a) we show the top view, whereas in (b) we show the front view. Similar to Fig. 1, an EDL will form on the wetted solid (not shown here), which will be strictly one-dimensional due to the hierarchy of length scales.

where $\theta^*_{CB,\lambda}$ is the modified contact angle in the Cassie-Baxter state with finite EDL effects. In Eq. (5), the first term on the right hand side denotes the increase in the surface energy due to the creation of an additional solid-liquid surface area, the second term represents the increase in the surface energy due to the creation of additional liquid-vapor surface area, the third term represents the decrease in the surface energy due to the destruction of an existing solid-vapor surface area, and the final term denotes the increase in free energy due to the formation of an EDL at the solid-liquid interface in the newly wetted solid. For the equilibrium condition, we need $dE = 0$, which yields

$$\cos\theta^*_{CB,\lambda} = \phi_s \cos\theta_Y - (1-\phi_s) - \phi_s \frac{W_{\mathrm{EDL}}}{\gamma_{LV}}. \tag{6}$$

Therefore, Eq. (6) is the modified version of the equation of state for the Cassie-Baxter state with finite contributions of the EDL effect. Please note that without the EDL effects (i.e., $W_{\mathrm{EDL}} = 0$), Eq. (6) leads to the classical Cassie-Baxter equation [32]:

$$\cos\theta^*_{CB,0} = -1 + \phi_s(1 + \cos\theta_Y), \tag{7}$$

where $\theta^*_{CB,0}$ is the modified contact angle of the drop in the Cassie-Baxter state, without the EDL effects.

Similar to the previous case, we can define an effective value of ϕ_s, which we will call $\phi_{s,\mathrm{eff}}$, such that we can use it to express the EDL effect in the classical Cassie-Baxter picture [i.e., Eq. (7), with ϕ_s being replaced by $\phi_{s,\mathrm{eff}}$]. Physically, $\phi_{s,\mathrm{eff}}$ is an effective fraction of the solid-liquid surface area that leads to the same contact angle (as that obtained with EDL effects) for a scenario that does not involve any EDL interactions. This $\phi_{s,\mathrm{eff}}$ can therefore be expressed as

$$\frac{\phi_{s,\mathrm{eff}}}{\phi_s} = \frac{|\cos\theta_Y - W_{\mathrm{EDL}}/\gamma_{LV} + 1|}{|\cos\theta_Y + 1|}. \tag{8}$$

The extent to which this $\phi_{s,\mathrm{eff}}$ is modified in the presence of the EDL effects signifies the alteration of the solid-liquid surface area (in terms of the wettability of the drop) induced by the EDL effects.

C. Estimation of the EDL free energy

From Eqs. (2) and (6), it is clear that one needs to obtain W_{EDL} (or the per unit area free energy associated with the formation of the EDL) in order to calculate the EDL-effect-modified Wenzel and the Cassie-Baxter states. Over the years there have been a plethora of investigations on the analytical quantification of the free energy associated with the formation of the EDL [90–92]. In this paper, we shall follow the calculations proposed by Manciu and Ruckenstein [92], who attributed three different components to the EDL free energy, i.e.,

$$W_{\mathrm{EDL}} = W_{\mathrm{EDL},el} + W_{\mathrm{EDL,ent}} + W_{\mathrm{EDL},ch}, \tag{9}$$

where $W_{\mathrm{EDL},el}$ is the electrostatic contribution, $W_{\mathrm{EDL,ent}}$ is the entropic contribution, and $W_{\mathrm{EDL},ch}$ is the chemical contribution to the EDL free energy (per unit area). All three components depend on the EDL electrostatic potential ψ, which on the basis of the assumption of the hierarchy of the length scale is strictly one-dimensional [i.e., $\psi = \psi(y)$] and describable by the Poisson-Boltzmann equation over a flat surface (discussed later). Under this condition, one can write [92]

$$W_{\mathrm{EDL},el} = \frac{1}{2}\epsilon_r\epsilon_0 \int_0^d \left(\frac{d\psi}{dy}\right)^2 dy \tag{10}$$

and

$$W_{\mathrm{EDL,ent}} = 2n_\infty k_B T \int_0^d \left[\frac{e\psi}{k_B T}\sinh\left(\frac{e\psi}{k_B T}\right) + 1 - \cosh\left(\frac{e\psi}{k_B T}\right)\right] dy. \tag{11}$$

In the above equations, n_∞ is the bulk ionic number density (i.e., the number density of the ions far away from the EDL), e is the electronic charge, $k_B T$ is the thermal energy, ϵ_0 is the permittivity of the free space, and ϵ_r is the relative permittivity of water. Also d is the distance from the substrate beyond which the effect of the EDL is negligible, i.e., either of the components $W_{\mathrm{EDL},el}$ or $W_{\mathrm{EDL,ent}}$ is zero [here we take $d = k\lambda$, where $\lambda = \sqrt{2\epsilon_r\epsilon_0 k_B T / n_\infty e^2}$ is the EDL thickness and $k \gg 1$ (we take $k = 10$)]. Last, Eq. (11) and the expression for the EDL thickness λ are valid for a symmetric $1:1$ electrolyte, although we can obtain expressions for multivalent asymmetric electrolytes.

The above two contributions to the free energy of the double layer, expressed in Eqs. (10) and (11), are both positive. However, it is well known that the overall free energy of the EDL must be negative, affirming the spontaneity in its formation [92]. Therefore, the third component of the free energy, $W_{\mathrm{EDL},ch}$, which represents the chemical free energy associated with the spontaneous formation of the EDL, must be negative and larger than the sum of the other two components. In their study, Manciu and Ruckenstein [92] demonstrated that the expression for $W_{\mathrm{EDL},ch}$ is strongly dictated by the physical condition in the presence of which the EDL is formed spontaneously. For example, depending on whether the EDL formation occurs under the conditions when the substrate ζ potential is constant (with charge density σ varying) or σ is constant (with ζ varying) or both ζ and σ are varying, the expression of $W_{\mathrm{EDL},ch}$ changes. In the present study, we consider the simplest possible condition where the EDL develops in the presence of constant wall ζ potential. Hence $W_{\mathrm{EDL},ch}$ can be expressed as [92]

$$W_{\mathrm{EDL},ch} = -\sigma\zeta = \left[\epsilon_0\epsilon_r\left(\frac{d\psi}{dy}\right)_{y=0}\right]\zeta, \tag{12}$$

where $\sigma = -\epsilon_0\epsilon_r(\frac{d\psi}{dy})_{y=0}$ is the substrate wall charge density.

It may be noted here that to evaluate the free energy components, we need the exact expression for the EDL potential ψ (which is one-dimensional in our analysis) and its first-order spatial derivative. For the solution of ψ, one needs to invoke the nonlinear Poisson-Boltzmann equation [93]:

$$\frac{d^2\psi}{dy^2} = \frac{2n_\infty e}{\epsilon_0\epsilon_r}\sinh\left(\frac{e\psi}{k_B T}\right). \tag{13}$$

The above equation can be solved analytically (under the condition $\psi = \zeta$ at $y = 0$ and $\psi = \frac{d\psi}{dy} = 0$ at $y \gg \lambda$) [93]

to obtain a closed form solution of ψ as

$$\psi(y)=\frac{4k_BT}{e}\tanh^{-1}\left[\tanh\left(\frac{e\zeta}{4k_BT}\right)\exp\left(-\frac{y}{\lambda}\right)\right]. \qquad (14)$$

Therefore

$$\frac{d\psi}{dy}=\frac{4k_BT}{e\lambda}\tanh\left(\frac{e\zeta}{4k_BT}\right)\frac{\exp\left(-\frac{y}{\lambda}\right)}{1-\tanh^2\left(\frac{e\psi}{4k_BT}\right)}. \qquad (15)$$

Once we have the explicit expressions for the different components of the EDL free energy, it is easy to observe that $W_{\mathrm{EDL}} \sim \epsilon_r\epsilon_0\zeta^2/\lambda$. Therefore the additional term in the equation of state of the Wenzel and Cassie-Baxter states, owing to the consideration of the EDL effects, will scale as $W_{\mathrm{EDL}}/\gamma_{LV} \sim \frac{\epsilon_r\epsilon_0\zeta^2}{\lambda\gamma_{LV}}$ [see Eqs. (2) and (6)]. Hence, the EDL contribution is exactly analogous to the electrowetting contribution (in that case one has applied an external voltage V across a drop sitting on a dielectric), with the ζ potential replacing the external potential V, the EDL thickness λ replacing the thickness of the dielectric, and the permittivity of the liquid replacing the permittivity of the dielectric. A similar analogy was proposed in one of our earlier investigations studying the contribution of the EDL in the dynamics of surface nanobubbles [88].

III. RESULTS AND DISCUSSION

A. Variation of the different components of the EDL free energy

In Fig. 3, we plot the three individual components of the EDL free energy (per unit area) and their resultant, which is the net EDL free energy. The magnitude of all components increases with the ionic concentration. This can be explained by the fact that the increase in ionic concentration lowers the EDL thickness, thereby enhancing the EDL potential gradient $d\psi/dy$. It can be clearly seen that both $W_{\mathrm{EDL},el}$ and $W_{\mathrm{EDL,ent}}$ are positive, but $W_{\mathrm{EDL},ch}$ is negative and larger than the sum of the other two components. Therefore, the net EDL free energy W_{EDL} is always negative, confirming the spontaneity in the formation of the EDL. Also, quite intuitively, an enhancement in the wall ζ potential enhances the overall EDL free energy, indicating that at a larger wall potential the propensity for the spontaneous formation of the EDL is enhanced.

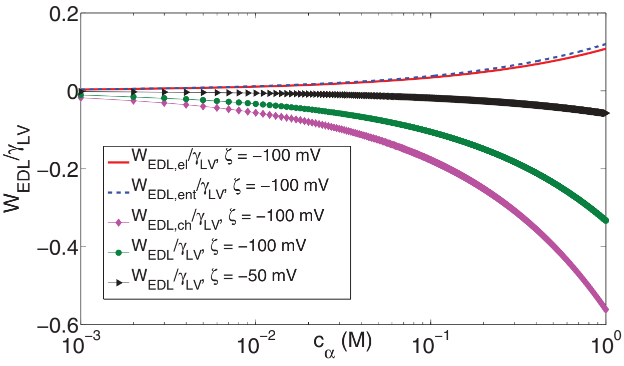
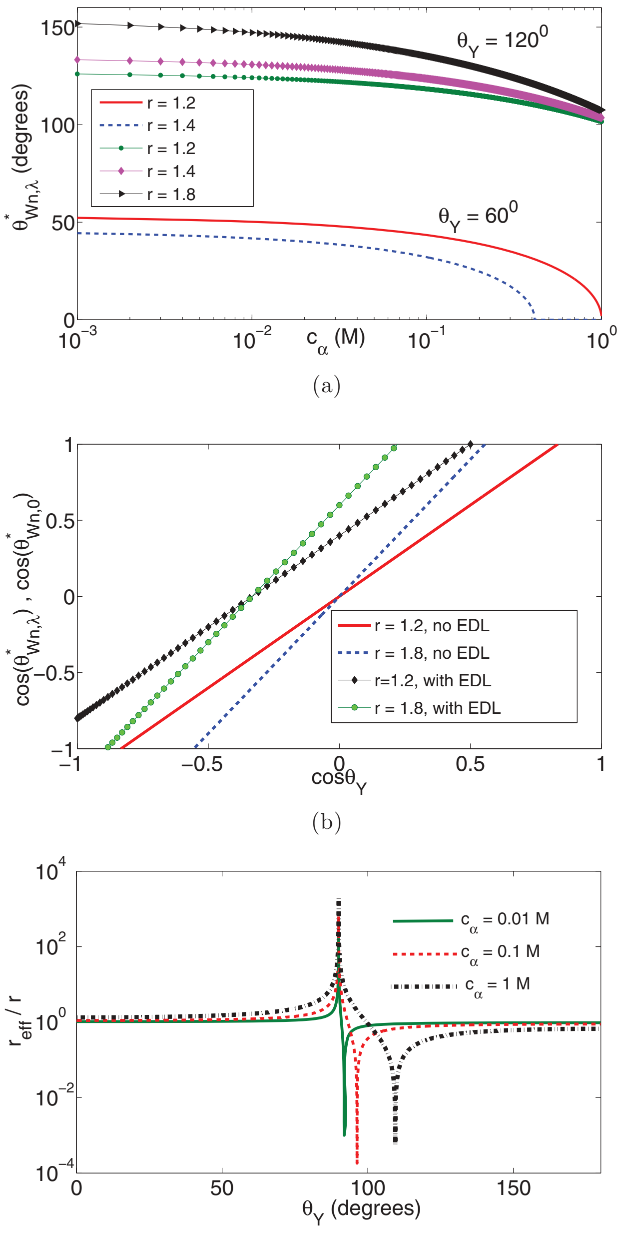


FIG. 3. (Color online) Variation of the different components of the per unit area EDL free energy W_{EDL}, nondimensionalized with γ_{LV}, with ionic concentration for different values of wall ζ potential. In the simulations, $\epsilon_0 = 8.8\times10^{-12}$ C/V m, $\epsilon_r = 79.8$, $k_B = 1.38\times10^{-23}$ J/K, $T = 298$ K, and $\gamma_{LV} = 0.072$ N/m.

B. Wenzel state in the presence of EDL effects

In Figs. 4(a) and 4(b) we demonstrate the variation of modified contact angle (on account of the consideration of the EDL effects) as a function of three parameters, namely, the roughness parameter r (here we take two arbitrary values



(a)

(b)

(c)

FIG. 4. (Color online) (a) Variation of $\theta^*_{Wn,\lambda}$ with ionic concentration for different values of r and θ_Y. (b) Variation of $\cos\theta^*_{Wn,\lambda}$ and $\cos\theta^*_{Wn,0}$ with $\cos\theta_Y$ for different values of r with ($c_\infty = 1M$) and without the EDL effects. (c) Variation of the dimensionless effective roughness [defined in eq.(4)] with θ_Y for different values of ionic concentration c_∞. Here we use $\zeta = -100$ mV. All other parameters are identical to that of Fig. 3.

of r that are greater than unity), bulk ionic concentration (or the EDL thickness), and the original (roughness-independent) equilibrium contact angle θ_Y. These two plots provide the central result of the paper regarding the EDL effect on the Wenzel state. We first study the variation of the actual EDL-induced contact angle as a function of the ionic concentration at selected values of the roughness parameter and original wettability of the substrate, dictated by θ_Y [see Fig. 4(a)]. An increase in ionic concentration, which induces a larger effect of the EDL free energy (see Fig. 3), increases the hydrophilicity of an originally hydrophilic substrate. This increase is substantially larger than the increase induced by the simple roughness effect for a classical EDL-independent Wenzel state. For example, when $r = 1.2$ and $\theta_Y = 60^\circ$, without the EDL effect $\theta = \theta_{Wn,0} \simeq 52.2^\circ$, whereas with the EDL effects $\theta = \theta_{Wn,\lambda} \simeq 2^\circ$ [for $c_\infty = 1M$; see Fig. 4(a)]. Therefore, we can infer that for an originally hydrophilic substrate, the consideration of the EDL effects induces a behavior that is analogous to the consideration of the Wenzel roughness effect (i.e., hydrophilic becomes more hydrophilic), but the extent of variation is substantially larger, with the potential of obtaining a superhydrophilic. Also, owing to this pronounced hydrophilicity-inducing tendency of the EDL effects, at larger values of r (where the EDL-independent lowering of the hydrophilic contact angle is substantially large), the window of ionic concentration values over which the EDL effects can be useful is narrowed because at larger ionic concentrations [i.e., for values of $c_\infty > c_\infty^c$, where c_∞^c is defined as $\theta^*_{Wn,\lambda}(c = c_\infty^c) = 0$] the liquid film will break.

The case of the originally hydrophobic substrate ($\theta_Y = 120^\circ$) is even more intriguing [see Fig. 4(a)]. The Wenzel roughness effect (without the EDL effects) makes a hydrophobic substrate more hydrophobic, i.e., triggering it towards superhydrophobicity. The larger the values of the roughness parameter r are, the stronger this behavior is. On the other hand, the consideration of the EDL effects attempts to lower this prominent hydrophobic behavior. This lowering, for substantially large ionic concentration, will totally nullify the roughness effect and will ensure a more hydrophilic substrate than predicted by θ_Y. Therefore, we see $\theta^*_{Wn,\lambda}(r = 1.2, c_\infty = 1M) = 101.6^\circ$ and $\theta^*_{Wn,\lambda}(r = 1.8, c_\infty = 1M) = 107.5^\circ$. Therefore, we can now define an EDL-effect-induced modified Wenzel state: the hydrophilic condition becomes (substantially) more hydrophilic (qualitatively identical to the classical Wenzel behavior), whereas the hydrophobic condition becomes less hydrophobic (qualitatively converse to the classical Wenzel behavior).

In Fig. 4(b), we provide the complete $\cos\theta^*_{Wn,\lambda}$ versus $\cos\theta_Y$ and $\cos\theta^*_{Wn,0}$ versus $\cos\theta_Y$ phase space for different values of the roughness factor r at a given value of c_∞. This phase space provides a broader data set, confirming our observations from Fig. 4(a). Also note that for larger values of r, all $\cos\theta^*_{Wn}$ versus $\cos\theta_Y$ curves (with or without the EDL effects) become steeper, indicating a more prominent influence of the roughness as well as the EDL effects. This phase space plot also provides a notion on the range of θ_Y over which the film can remain continuous. In accordance with the hydrophilicity-inducing tendency of the EDL effects, an originally hydrophilic drop breaks down very quickly (indicated by $\cos\theta^*_{Wn} \rightarrow 1$ for relatively small positive values of $\cos\theta_Y$), whereas an originally hydrophobic drop shows more stability (indicated by the fact that with the EDL effects larger negative values of $\cos\theta_Y$ can be spanned).

The hydrophilicity-inducing tendency of the EDL effects, as manifested by its influence on the Wenzel states [see Figs. 4(a) and 4(b)] as well as the Cassie-Baxter states (demonstrated later), can be physically argued by drawing an analogy to the electrowetting scenario. Both for this case and for electrowetting, the additional electrostatic surface energy works towards flattening the drop. However, there is one key intuitive difference between these two cases. For electrowetting, the additional energy is infused into the drop by application of an external electric field, whereas for the present case the electrostatic energy comes from the *in situ* created EDL resulting from the wetting of the substrate by the drop.

Based on the modifications induced by the EDL effects, we now attempt to define an effective roughness parameter r_{eff} [see Eq. (4)], which we plot in Fig. 4(c). As the EDL effect enhances and weakens the original Wenzel roughness effect for acute and obtuse contact angles (θ_Y), we find $\frac{r_{\mathrm{eff}}(\theta_Y < 90^\circ)}{r} > 1$ and $\frac{r_{\mathrm{eff}}(\theta_Y > 90^\circ)}{r} < 1$. We, however, observe two singularities for each of the plots (for a given c_∞). The first singularity occurs as $\theta_Y \rightarrow 90^\circ$, as can be explained from the expression of r_{eff}/r [see Eq. (4)]. $\theta_Y \rightarrow 90^\circ$ implies a physical limit where there is no effect of roughness for the EDL-independent case [we can easily infer that from the classical EDL-independent Wenzel expression; see Eq. (4)]. Therefore the EDL-induced alteration of the roughness shoots up as $\theta_Y \rightarrow 90^\circ$. This singularity makes $r_{\mathrm{eff}}/r \rightarrow \infty$, and as already stated, its location is identical for all concentration values (i.e., at $\theta_Y \rightarrow 90^\circ$). The second singularity makes $r_{\mathrm{eff}}/r \rightarrow 0$; therefore the EDL effect can be inferred to have made a rough substrate smooth. The location of the singularity with respect to θ_Y (we use θ_Y^{ss} for the corresponding θ_Y) varies for different concentration values [e.g., $\theta_Y^{ss}(c_\infty = 0.01M) = 92^\circ, \theta_Y^{ss}(c_\infty = 0.1M) = 96.3^\circ$, $\theta_Y^{ss}(c_\infty = 1M) = 109.4^\circ$]. This stems from the definition of r_{eff}/r, where we take the modulus of $(\cos\theta_Y - W_{\mathrm{EDL}}/\gamma_{LV})$ to define the effective roughness. This expression $(\cos\theta_Y - W_{\mathrm{EDL}}/\gamma_{LV})$ changes sign on either side of this singularity (which is effectively a pseudosingularity, as it appears due to a mathematical definition). In addition, this singularity ensures that on either side the variation of r_{eff}/r with θ_Y becomes nonmonotonic, i.e., for $\theta_Y < \theta_Y^{ss}$, r_{eff}/r decreases with θ_Y, whereas for $\theta_Y > \theta_Y^{ss}$, r_{eff}/r increases with θ_Y.

C. Cassie-Baxter state in the presence of EDL effects

From the equation of state of the classical EDL-independent Cassie-Baxter state [see Eq. (7)], we can easily see that $\theta^*_{CB,0} > \theta_Y$ for all values of ϕ_s and θ_Y, with $\theta^*_{CB,0}(\phi_s \rightarrow 0) \rightarrow 180^\circ$, $\theta^*_{CB,0}(\phi_s \rightarrow 1) \rightarrow \theta_Y$, and $\theta^*_{CB,0}(\theta_Y \rightarrow 180^\circ) \rightarrow 180^\circ$. Under these circumstances, consideration of the EDL effect and its hydrophilicity-inducing tendencies will imply significant modifications of the Cassie-Baxter state. These are described in Figs. 5(a) and 5(b), which form the central result of this paper regarding the Cassie-Baxter state. With finite EDL effects, there is a competition between the hydrophobic influence of the voids in the Cassie-Baxter state and the hydrophilicity-

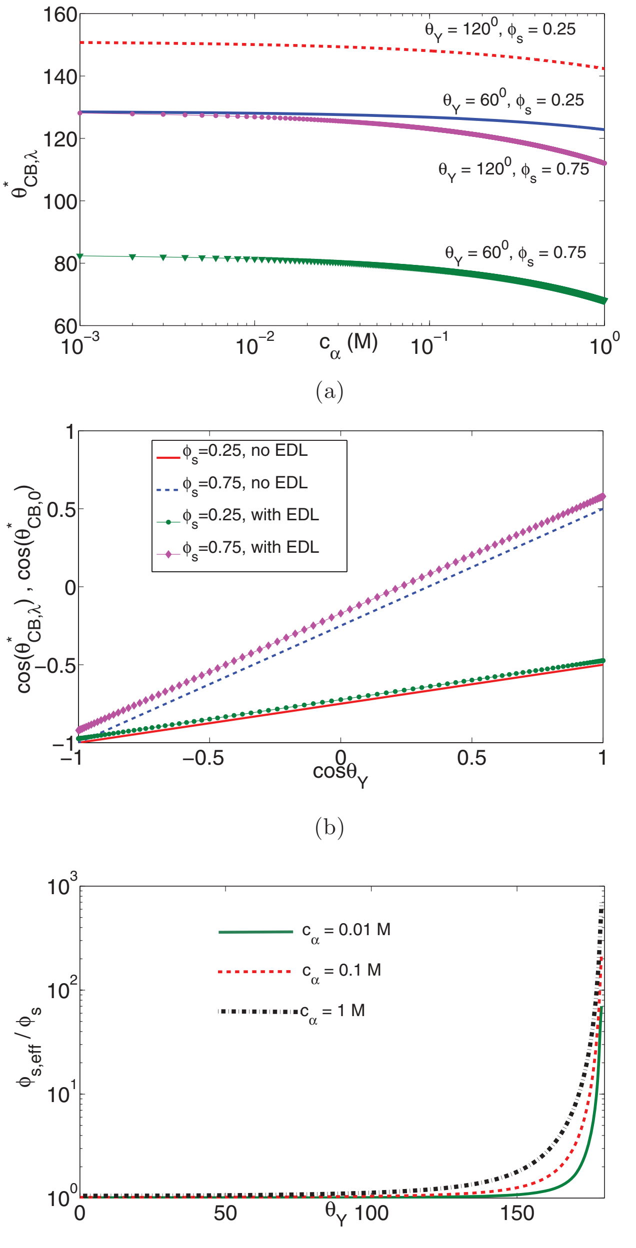


FIG. 5. (Color online) (a) Variation of $\theta^*_{CB,\lambda}$ with ionic concentration for different values of r and θ_Y. (b) Variation of $\cos\theta^*_{CB,\lambda}$ and $\cos\theta^*_{CB,0}$ with $\cos\theta_Y$ for different values of r with ($c_\infty = 1M$) and without the EDL effects. (c) Variation of the dimensionless effective solid fraction [defined in Eq. (8)] with θ_Y for different values of ionic concentration c_∞. Here we use $\zeta = -100$ mV. All other parameters are identical to those of Fig. 3.

inducing tendencies of the EDL effects, and depending upon the values of ϕ_s and θ_Y, one may witness $\theta^*_{CB,\lambda} < \theta_Y$ [e.g., $\theta^*_{CB,\lambda}(\theta_Y = 120^\circ, \phi_s = 0.75, c_\infty = 1M) = 112^\circ$; see Fig. 5(a)]. Therefore, quite remarkably, consideration of EDL effects may completely overhaul the classical Cassie-Baxter picture and introduce a yet unknown Cassie-Baxter state, where the final state is more hydrophilic than the original (dictated by θ_Y) state.

Figure 5(b) provides the $\cos\theta^*_{CB,\lambda}$ and $\cos\theta^*_{CB,0}$ versus $\cos\theta_Y$ phase space and confirms the observations of Fig. 5(a), in particular the remarkable situation where we have a Cassie-Baxter state that is more hydrophilic than the original one. It is also clear from Fig. 5(b) that the influence of the EDL effects in hydrophilization is most severe for larger (very hydrophobic) original contact angles. This can be understood by again referring to the original EDL-independent Cassie-Baxter state. As shown above, as $\theta_Y \to 180^\circ$, the difference between θ_Y and θ^* is minimized; therefore it is for such large obtuse angle values of θ_Y that the hydrophilization effect of the EDL gets most magnified.

To quantify the exact extent of the influence of the EDL, we plot the variation of $\phi_{s,\mathrm{eff}}/\phi_s$, defined in Eq. (8). As the EDL effect always reduces the extent of hydrophobicity (which, in turn, is triggered by the presence of voids or air gaps in the substrate), we always have $\phi_{s,\mathrm{eff}}/\phi_s \geqslant 1$. The most interesting situation is encountered for large obtuse angle values of θ_Y, i.e., when the relative EDL effects can be large enough to completely outweigh the effect of voids in the Cassie-Baxter state and make the system more hydrophilic as compared to the original system. For such systems, we find $\phi_{s,\mathrm{eff}} \gg \phi_s$, which will imply $\phi_{s,\mathrm{eff}} \gg 1$. This is completely nonintuitive in the sense that ϕ_s, representing the faction of solid, must be less than unity. However, such values of $\phi_{s,\mathrm{eff}} \gg 1$ imply that in order to explain the consequences of the EDL effects in the framework of the classical Cassie-Baxter picture one needs to have a solid with a surface area that is significantly higher than even the most ideal case of flat surface, i.e., $\phi_s = 1$. In fact, we can rewrite the classical Cassie-Baxter equation as $\cos\theta^* \simeq \phi_{s,\mathrm{eff}} \cos\theta_Y + \phi_{s,\mathrm{eff}}$ (with $\phi_{s,\mathrm{eff}} \gg 1$); i.e., we replicate a situation identical to the Wenzel state except for a constant.

IV. CONCLUSIONS

In this paper we have demonstrated the existence of EDL-effect-modified Cassie-Baxter and Wenzel states for an electrolytic drop on charged rough or patterned surfaces. We have shown that under optimal EDL characteristics, dictated by the ionic concentration and the substrate ζ potential, one can radically affect these two states. For an originally hydrophilic state, EDL effects lead to a superhydrophilic Wenzel state. This is an improvement on the classical EDL-independent Wenzel scenario where there is only a minor increase in the hydrophilicity of the originally hydrophilic state. Even more fascinatingly, for an originally hydrophobic state EDL effects lead to a hydrophilic Wenzel state. This is the complete opposite of the classical EDL-independent Wenzel state, where a hydrophobic substrate becomes more hydrophobic. For the Cassie-Baxter state, on the other hand, for suitable choices of the parameters characterizing the EDL, one can actually end up with a more hydrophilic (as compared to the original) Cassie-Baxter state. This is remarkable because the classical Cassie-Baxter state is always more hydrophobic than the original state. To conclude, we have discussed the classical problems of appearances of Wenzel and Cassie-Baxter states in light of EDL dynamics, and the results point towards the existence of *yet unknown* Wenzel and Cassie-Baxter states, which may bear great significance in understanding the behavior of liquid drops in natural and engineered textured surfaces.

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