Scaling laws for drop impingement on porous films and papers

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Scaling laws for drop impingement on porous films and papers

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This study investigates drop impingement on highly wetting porous films and papers. Experiments reveal previously unexplored impingement modes on porous surfaces designated as necking, spreading, and jetting. Dimensional analysis yields a nondimensional parameter, denoted the Washburn-Reynolds number, relating droplet kinetic energy and surface energy. The impingement modes correlate with Washburn-Reynolds number variations spanning four orders of magnitude and a corresponding energy conservation analysis for droplet spreading shows good agreement with the experimental results. The simple scaling laws presented will inform the investigation of dynamic interactions between porous surfaces and liquid drops.

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I. INTRODUCTION

Interesting phenomena can be observed when a liquid droplet impacts a liquid or solid surface. Crown formation of milk droplets upon impact with water represents a well-known example of this phenomena [1]. Recently, however, drop impingement on solid surfaces has gained significant attention. This is largely due to state of the art micro- and nanofabrication methods which have enabled novel functional surfaces. Among the functionalized surfaces, superhydrophobic surfaces have been a major thrust [2,3] in part due to their unique impingement properties. Conversely, drop impingement on highly wetting porous films or paper has been largely neglected. Though there have been investigations of the dynamics of droplets on porous media [4–8], most studies have explored thick surfaces where the droplet radius is negligible compared to the substrate thickness.

In this study we investigate droplet dynamics on highly wetting thin porous surfaces. First, we present a modified energy equation accounting for capillary effects that successfully captures droplet spreading upon impact on highly wetting porous surfaces. The modified energy equation reveals a dimensionless parameter denoted the capillary-Weber number, which expresses the relative influence of the matrix potential and the kinetic energy of the impinging drop. Additionally, dimensional analysis leads to a nondimensional parameter, which we will call the Washburn-Reynolds number (ReW), which strongly correlates with impingement modes on highly wetting porous surfaces. The Washburn-Reynolds number balances inertial effects of the impinging droplet and capillary transport in the porous film.

II. EXPERIMENTAL METHODS

Electrophoretic deposition (EPD) and breakdown anodization (BDA) were used to produce highly wetting micro- and nanoporous surfaces [9,10]. For EPD, TiO2 nanoparticles (20 nm, anatase, Sigma-Aldrich) and acetic acid were used to make 1 g/liter TiO2 suspensions. Electric potentials up to 120 V were supplied for 10–30 min during the anodization process to make thin films on the substrate. De-ionized (DI) water pH was adjusted to pH = 3 using nitric acid (70% ACS reagent, Sigma-Aldrich) for the electrolyte during BDA. The electrolyte was maintained at a specified temperature using a water reservoir surrounding the BDA cell. Titanium plates (Ultra Corrosion-Resistant Titanium Grade 2, 0.020 in. thick, McMaster) were used as anode and cathode for both EPD and BDA. BDA was conducted first to make microporous layers followed by EPD of TiO2 nanoparticles on the microporous layers to realize hierarchical structures. In BDA, the electric potential and the anodization time were varied to obtain different surface properties. In EPD, however, the same conditions were used on each surface to provide consistent nanoscale features. BDA results in microscale porous titania surfaces on titanium substrates [Fig. 1(a)]. Nanoscale porous layers were produced by EPD on the microporous surfaces with titanium dioxide nanoparticles [Fig. 1(b)].

The resulting surfaces display effective contact angles near 0° with high capillary pressures and spreading speeds. The porous surfaces showed near perfect wetting for several liquids including water, ethanol, ethylene glycol, and glycerol. The surfaces can be characterized with respect to capillary pressure, Pcap, and spreading speed constant, Ccap, through capillary rise measurements [12]. The capillary rise height, h, can be expressed as $h^2 = \frac{1}{2}C_{cap}^2$ (Washburn’s equation) [13], with $C_{cap} = \gamma r_c \cos \theta / \mu$, and $r_c$ is the effective capillary radius, $\gamma$ is the liquid surface tension, $\theta$ is the native contact angle of capillary surface, and $\mu$ is dynamic viscosity of the liquid. The value of $C_{cap}$ can be determined by the gradient of the time-dependent experimental capillary rise height. Capillary pressure can be obtained from the maximum rise height, $h_{max}$, and is expressed by $P_{cap} = \rho g h_{max} = 2\gamma r_c \cos \theta / \mu$.

When liquid droplets impact the surfaces, we observed four impingement modes (Fig. 2). We find that impingement modes are determined by the value of ReW = $U_o r_c \cos \theta / \mu$. Mode A1 consists of oscillating and spreading of the droplet. In Mode A2 the droplets show necking followed by fast spreading. Mode B consists of smooth spreading without oscillations or necking. Finally, Mode C is characterized by radial jetting and spreading. The Supplemental Material contains a high-speed video with examples of each impingement mode [14].
FIG. 1. Scanning electron microscope (SEM) images of as-prepared surfaces show microscale and nanoscale porous structures produced by breakdown anodization (BDA) (a) and electrophoretic deposition (EPD) (b), respectively [11]. The combined BDA/EPD process yields highly wetting micro- and nanoscale hierarchical porous structures.

III. THEORY

Energy conservation is employed to predict droplet spreading upon impact. The energy conservation approach has shown good agreement with experiments, and it has helped to find useful scaling parameters for droplet dynamics [16–18]. In this study we modify the energy equation with two additional terms accounting for viscous dissipation inside porous media and the matrix potential, which we denote as $\Phi_l$ and $E_{mp}$, respectively. The modified energy equation can be expressed as

$$\dot{E}_k + \dot{E}_g + \dot{E}_s + \dot{E}_{mp} + \Phi_l + \Phi_v + \Phi_c = 0,$$

where $E_k$ is the droplet kinetic energy, $E_g$ is the gravitational potential energy, $E_s$ is the surface energy of the droplet, $\Phi_l$ is line dissipation, and $\Phi_v$ is viscous dissipation inside the droplet.

For simplicity, we model water droplets impacting solid surfaces as cylinders with a time-dependent radius, $R(t)$, and height, $H(t)$ (Fig. 3) [16,17]. The model droplet has the same volume as the actual droplet. Assuming mass conservation (neglecting evaporation) and fluid incompressibility, the height and radius have the following relationship:

$$H(t) = \frac{V_0}{\pi R(t)^2},$$

where $V_0$ is the volume of the actual droplet with an initial diameter, $D_0$. The modeled droplet has the same impact velocity as the actual droplet and thus the same kinetic energy.

A. Kinetic energy

The kinetic energy of a droplet after impact can be calculated from the internal velocity field in the droplet. In the cylindrical model, we assume flow in the droplet is irrotational [19]. The vertical flow velocity, $v_z$, and the radial flow velocity, $v_r$, can be defined as

$$v_z = -\frac{2z}{R} \frac{dR}{dt} \quad \text{and} \quad v_r = \frac{r}{R} \frac{dR}{dt}.$$

These velocities are internal flow velocities at a specific instant such that $R$ and $dR/dt$ are spatially independent. The kinetic energy is

$$E_k = \frac{1}{2} \int \rho(v_z^2 + v_r^2) + g(z - H) \, dV,$$

where $\rho$ is the liquid density, $g$ is the acceleration due to gravity, and $V$ is the liquid volume.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$Re_w$</th>
<th>$t$ (ms)</th>
</tr>
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<tbody>
<tr>
<td>A1</td>
<td>0.01</td>
<td>4.5, 11.5, 19.3, 23.3, 32.3</td>
</tr>
<tr>
<td>A2</td>
<td>0.1</td>
<td>1.3, 8.0, 10.8, 12.8, 15.8</td>
</tr>
<tr>
<td>B</td>
<td>0.5</td>
<td>1.8, 3.5, 5.5, 9.0, 16.0</td>
</tr>
<tr>
<td>C</td>
<td>2.0</td>
<td>0.5, 0.8, 1.1, 1.5, 2.4</td>
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FIG. 2. Droplets show four different impingement modes depending on the Washburn-Reynolds number after impacting highly wetting porous surfaces. The Washburn-Reynolds number can be expressed as $Re_w = U_0 \rho r c \cos \theta / \mu$, where $U_0$ is the impact velocity, $\rho$ is the liquid density, $r$ is the effective capillary radius, $\theta$ is the surface contact angle, and $\mu$ is the liquid viscosity. Mode A1: compressing-oscillating, Mode A2: necking and spreading, Mode B: spreading, and Mode C: radial jetting and spreading (see Supplemental Material [14]). A high-speed camera (Photron) was used to record the behavior of liquid droplets on the surfaces. The scale bar in each image is 1 mm.

FIG. 3. (Color online) Schematic diagram of the cylindrical droplet impact model with time-dependent radius, $R(t)$, and height, $H(t)$. The model cylindrical droplet has the same volume and impact velocity as the actual droplet.
energy of the droplet can be obtained by integrating the internal velocities over the droplet volume, $V_0$, as follows:

$$E_k = \frac{1}{2} \rho \int_{V_0} (v_x^2 + v_y^2) dV$$

$$= \frac{\rho V_0}{2} \left(1 + \frac{4}{3} R^2 \frac{dR}{dt} \right)^2$$

$$= E_{k,o} \left(1 + \frac{16}{27} \frac{1}{R^6} \right) \left(\frac{dR^*}{dt^*}\right)^2,$$

(2)

with the initial droplet kinetic energy, $E_{k,o} = \frac{1}{2} \rho V_0^2$, the dimensionless drop radius, $R^* = R(t)/(D_o/2)$, and the dimensionless time, $t^* = t(U_0/D_o)$.

B. Gravitational energy

Utilizing the location of the time-dependent center of mass, $H(t)/2$, gravitational energy can be determined:

$$E_g = \rho g V_0 \frac{H(t)}{2} = \rho g V_0^2 \frac{2}{3} \frac{1}{R^2},$$

(3)

where the initial droplet gravitational energy is defined as $E_{g,o} = \frac{1}{2} \rho g V_0^2$.

C. Droplet surface energy

The surface energy of a droplet on a solid surface can be calculated by integrating the surface tension of the entire surface, $A$. In the cylindrical impact model, the surface tension of the liquid-solid interface can be obtained with Young’s equation, and the surface energy is found to be

$$E_s = \int_A \gamma dA = \gamma (A_{air} - A_{wet} \cos \theta_e),$$

where $A_{air}$ is the droplet surface area in contact with air, $A_{wet}$ is the wetted area (the projected area of the solid-liquid interface), and $\theta_e$ is the equilibrium contact angle on the surface. Since the surfaces used in this work exhibit complete wetting (i.e., contact angle near zero), the equation for a cylindrical droplet can be reduced as follows:

$$E_s = 2 \pi \gamma R H = 2 \gamma V_0 \frac{R}{3} = \frac{2 \pi \gamma D_o^2}{3} = \frac{E_{s,o}}{3} R^2,$$

(4)

with the initial droplet surface energy, $E_{s,o} = \pi \gamma D_o^2$.

D. Line dissipation

Dissipation occurs in the process of moving the contact line and the amount is proportional to the contact line speed, $v_R$, and an effective viscosity, $\mu_L$. According to the de Gennes approach [20], the line dissipation can be expressed by

$$\Phi_l = \frac{1}{2} \mu_L \int_s v_R^2 dS = \mu_L \pi R \left(\frac{dR}{dt}\right)^2$$

$$= \frac{1}{8} \mu_L \pi D_o U_o^2 \left(\frac{dR^*}{dt^*}\right)^2 = \frac{\Phi_{l,o}}{4} \left(\frac{dR^*}{dt^*}\right)^2,$$

(5)

where $s$ is the moving contact line, $v_R$ is the line velocity, $\Phi_{l,o} = \frac{1}{2} \mu L D_o U_o^2$, and $\mu_L$ can be obtained from

$$\mu_L = \frac{3 l^*}{\theta_e},$$

where $l^* = \ln(l_{max}/l_{min})$ with maximum length scale, $l_{max}$ (the droplet diameter), minimum length scale, $l_{min}$ (the microscopic length scale, $2r_c$ in this work), and $\theta_e$, the sliding contact angle, which is the contact angle at the interface of the droplet, the top surface of the porous layer, and air when the droplet is spreading, as shown in Fig. 4. In other words, the sliding contact angle is the advancing contact angle of the spreading droplet. Sliding contact angles were experimentally obtained from high-speed images at $2R/D_o = 2.5$ when the actual droplets were spreading after impact. For example, to obtain Fig. 6, sliding contact angles were determined to be 2.6°, 2.9°, 7.4°, 5.7°, and 19.6° for water, ethanol, ethylene glycol, a 60/40 (v/v) glycerol and water mixture, and a 90/10 (v/v) glycerol and water mixture, respectively.

E. Viscous dissipation inside a droplet

The total viscous dissipation in the boundary layer can be found by integrating the shear stress, $\tau$, multiplied by slip velocity, $v_s$, for the no-slip area, $A_s$. To calculate the shear stress generated in the boundary layer inside the droplet, the boundary layer thickness must be estimated. It is clear that the boundary layer thickness is time dependent from lubrication theory, and the time-dependent boundary layer thickness has shown close agreement with experimental results [21,22]. However, to simplify the analysis, we employ a time-independent boundary layer thickness assuming irrotational flow inside the droplet. In the literature [17–19,23], others have successfully formulated the kinetic energy and the viscous dissipation assuming irrotational flow and time-independent boundary layer thickness to predict the droplet behaviors. To calculate the shear stress, we assumed that the effective boundary layer thickness is $D_o/(2f_0)$, where $f_0$ is a correction factor, which was proposed by Bechtel et al. [18]. The
slip velocity, \( v_s \), was assumed to be the radial velocity, \( v_r \), and the no-slip area is equal to the projected area of the cylinder. Thus, we thus the following expression for viscous dissipation:

\[
\Phi_v = \int_{A_e} \tau_{vr} dA = \int_{A_e} f_s \mu \frac{v_r}{D_o} v_r dA \\
= \frac{\pi}{2} \frac{f_s \mu}{D_o} R^2 \left( \frac{dR}{dt} \right)^2 = \phi_{v, o} \frac{3}{64} f_b R^2 \left( \frac{dR^*}{dt^*} \right)^2, \quad (6)
\]

with

\[
\phi_{v, o} = \frac{2 U_o}{D_o} \quad \text{and} \quad f_b = \sqrt{\frac{\pi}{Oh}},
\]

where the Ohnesorge number is \( Oh = \mu / (\rho g D_o)^{1/2} \).

### F. Matrix potential

Matrix potential is the surface energy inside the capillary network that drives fluid transport [24]. The matrix potential is proportional to the wetted volume of the porous region and the capillary pressure [25]. Taking the droplet as the system of interest, work is done on the droplet so the matrix potential can be expressed as

\[
E_{mp} = -\int_{V_{wet}} \rho_{\text{cap}} dV = -\pi P_{\text{cap}} H_e R^2 = -E_{mp, o} f_c R^2, \quad (7)
\]

where \( V_{\text{wet}} \) is the volume of the wetted region, \( H_e \) is the height of the wetted region shown in Fig. 4, \( f_c \) is the ratio of the height of the wetted region to the pore diameter, \( 2r_e (f_c = H_e / 2r_e) \) (Fig. 4), and \( E_{mp, o} \) is the reference matrix potential,

\[
E_{mp, o} = 2r_e P_{\text{cap}} \pi \left( \frac{D_o}{2} \right)^2.
\]

Here, the thickness, \( H_e \), is the average height of the porous layer considering its void volume measured by a profilometer (measurement system: Tencor P-16 Surface Profilometer). The negative sign indicates that energy is put into the droplet.

### G. Viscous dissipation inside porous media

The shear stress, \( \tau_{vr} \), in the porous region can be approximated in the same manner used to estimate the viscous dissipation in the droplet (Eq. (6)) as follows:

\[
\tau_{vr} \approx f_c \mu \frac{v_r}{r_e},
\]

where \( v_r \) is the flow velocity in the porous region at a distance \( R \) from the center of the droplet (Fig. 4). If we assume that the contact line of the droplet coincides with the wetted boundary of the porous region, the total viscous dissipation inside the porous region can be expressed as

\[
\Phi_v = \int_{A_e} \tau_{vr} dA \approx \frac{\pi}{2} f_c \mu \frac{v_r}{r_e} R^2 \left( \frac{dR}{dt} \right)^2 = \phi_{v, o} \frac{3}{64} f_b R^2 \left( \frac{dR^*}{dt^*} \right)^2, \quad (8)
\]

where \( A_e \) is the non-slip area of the porous region and the characteristic viscous dissipation can be expressed as

\[
\phi_{v, o} = \frac{2 U_o}{D_o} \quad \text{and} \quad f_b = \sqrt{\frac{\pi}{Oh}},
\]

and the reference volume of the wetted porous region is \( V_{\text{wet, o}} = \pi H_e D_o^2 / 4 \).

### H. Energy conservation equation

When Eqs. (2)–(8) are substituted into Eq. (1), the final energy conservation equation can be obtained as a function of the time-dependent droplet radius,

\[
\frac{d}{dt} \left[ \left( \frac{1}{8} + \frac{16}{27} R^{*6/3} \right) \left( \frac{dR^*}{dt^*} \right)^2 + \frac{2}{3} \frac{1}{Fr} R^{*2} \right] + \frac{8}{15} \frac{1}{Wc} R^{*2} + \frac{3}{2} \frac{1}{Re} f_c R^* \left( \frac{dR^*}{dt^*} \right)^2 + \frac{3}{8} \frac{1}{Re} f_b R^2 \left( \frac{dR^*}{dt^*} \right)^2 = 0. \quad (9)
\]

Here, the initial drop diameter, \( D_o \), and impact velocity, \( U_o \), are used to formulate a dimensionless time, \( t^* = t / (D_o / U_o) \), and \( f_c = \mu_L / \mu \) is the dimensionless contact line viscosity. The first term is the kinetic energy of the droplet. The gravitational energy and the surface energy are a function of the Froude number, \( Fr = U_o^2 / g D_o \), and the Weber number, \( We = \rho D_o U_o^2 / \gamma \), respectively. The matrix potential is a function of the capillary-Weber number, \( Wc \), where

\[
Wc = \frac{\rho D_o U_o^2}{f_c \gamma \cos \theta} \quad \text{and} \quad E_{mp, o} = \frac{1}{2} \frac{\rho V_{wet, o}^2}{E_{mp, o}}, \quad (10)
\]

The capillary-Weber number is the ratio of the initial kinetic energy (\( E_{k, o} \)) of the droplet to the reference matrix potential (\( E_{mp, o} \)) corresponding to the initial wetted volume \( V_{wet, o} = \pi (D_o / 2)^2 H_e \) of the surface. In the case of either \( H_e = 0 \) (no porous region) or \( \theta = 90° \) (nonwetting), the capillary energy term is negligible. In the dissipation terms, we can see the dimensionless contact line viscosity, \( f_c = \mu_L / \mu \), the Reynolds number, \( Re = \rho D_o U_o / \mu \), and the capillary-Reynolds number, \( R_{re} = \rho r_e U_o / \mu \).

To solve Eq. (9) numerically, the initial conditions were specified in order to yield the same surface energy and kinetic energy as the real droplet [17]. Therefore, the radius and the impact velocity of the cylindrical model droplet
FIG. 5. (Color online) Schematic illustrations of droplet spreading on highly wetting porous surfaces. (a) At high capillary-Weber numbers (We > 10³), the kinetic energy determines droplet expansion, while the contact line and viscous effects dissipate mechanical energy. (b) At low capillary-Weber numbers (We < 10), the capillary energy (matrix potential energy) governs droplet spreading, and viscous dissipation is most prominent inside the porous region. These are slightly different from those of the real droplet used in the drop impingement experiment. First, we set the initial radius of the cylindrical model droplet as R(0) = Dc/2. The initial height of the cylindrical model droplet, H(0), can be calculated using mass conservation as H(0) = Vs/[πR(0)²], where Vs = (1/6)πDc³. The cylindrical model droplet has the same initial surface area as the real droplet, A_-model = A-real, where A-model and A-real are the surface areas of the cylindrical model droplet with radius R(0) and the real droplet with radius R-real, respectively. This information is used to calculate the initial radius of the cylindrical model droplet. The cylindrical model droplet has the same initial kinetic energy as the real droplet: \(\frac{1}{2} \rho V_s U_s^2 = \frac{1}{2} \rho V_{real} U_{real}^2\), where V-real and U-real are the volume and the impact velocity, respectively, of the real droplet used in the experiment. The initial droplet spreading speed, \(dR/dt|_{t=0}\), can be calculated using Eq. (2). As a result, the initial conditions for Eq. (9) are \(R^*(0) = 1\) and \(dR^*/dt|_{t=0} = 1.18\).

We find that each dissipation term in Eq. (9) has different significance depending on We, as shown schematically in Fig. 5. Contact line dissipation and viscous dissipation inside the droplet are important at high We [Fig. 5(a)]. However, for low We (We < 10), viscous dissipation inside the porous region is the main dissipation term in Eq. (1). As depicted in Fig. 5(b), line dissipation and viscous dissipation are negligible at low We because droplet expansion can be considered as a free surface flow driven by the capillary pressure in the porous region.

IV. RESULTS AND DISCUSSION

In Fig. 6 we compare the predicted droplet spreading obtained from Eq. (9) with the experimental results when We > 10³. The liquid and surface properties utilized are given in Table I. As suggested in Fig. 5, viscous dissipation inside the porous layer was not considered in the energy equation for high We. The surfaces showed varying \(P_{cap}\) and \(C_{cap}\) values depending on the liquid utilized. The predicted droplet spreading is in good agreement with the experimental data (Fig. 6). This suggests that the matrix potential is essential to appropriately predict droplet spreading. In spite of the geometrical simplifications, the energy equation captures the major energy transfer mechanisms during impingement.

We derived simplified energy conservation equations for four cases with different We, Fr, and We regimes to investigate the dependence of \(R^*(t)\) on each dimensionless parameter. To simplify the expressions, we ignored the constant values of each term and consider the line dissipation dominant because \(Re_{f-L}^{-1}\) is smaller than the other dissipation terms, as shown in Fig. 6. In addition, the initial conditions of \(R^*(0) = 0\) and/or \(dR^*/dt|_{t=0} = 1\) are used to derive the simplified energy conservation expressions as functions of dimensionless parameters. These initial conditions are different from those of the numerical solutions shown in Fig. 6. Table II provides a summary of the simplified energy equations and the dimensionless droplet radius change with different ranges of We, Fr, and We. From Table II, we see that the gravitational energy and the surface energy do not significantly affect droplet spreading. The kinetic energy influences expansion largely in the initial stage of impact, and the radius is asymptotic to a specific value dependent upon the Re. With respect to the matrix potential, the dimensionless droplet radius increases linearly with time, and the expansion rate is proportional to the ratio of Re to We. As the matrix potential is dominant in Table II, Eq. (9) can be simplified to \(dR^*/dt^* \propto Re/We\) for large \(t^*\) when the kinetic energy is dissipated (We << 1). This simplified equation means that the droplet expansion rate is determined by the ratio of Re to We.
Therefore, theoretically, \( R(t)^* \) does not achieve a constant value if the capillary pressure \( (P_{\text{cap}}) \) is nonzero. In Fig. 6, the curves for highly viscous liquids appear to converge to constant values but in actuality they slightly increase at a rate of \( \text{Re}_c/\text{We}_c \). In Fig. 6, the initial drastic increase of \( R^* \) is mainly attributed to the kinetic energy, and the linear increase of \( R^* \) after the initial stage of impact is due to the matrix potential. As a result, the assumption that line dissipation is dominant can be justified by comparing the simplified energy equations and the experimental data in Fig. 6. The kinetic energy and the matrix potential are the main driving forces for droplet spreading when \( \text{We}_c \gg 1 \) and \( \text{We}_c \ll 1 \), respectively. The initial droplet spreading results from the relationship between line dissipation and kinetic energy. After the kinetic energy is dissipated, the linear droplet spreading is due to the balance between line dissipation and matrix potential. Both spreading regimes are displayed in Fig. 6.

In the case of \( \text{We}_c < 10 \), viscous dissipation in the porous region is the dominant dissipation mechanism and the other dissipation terms are ignored, as shown in Fig. 5. To justify this assumption, note that \( \text{Re}_c \) is small relative to \( \text{Re} \) in the energy equation. When \( \text{Re}_c \) and \( \text{Re} \) are compared in the dissipation terms, however, we must carefully consider the no-slip area \( (A_c) \). In the viscous dissipation inside the droplet and the line dissipation, the contact surface between the droplet and the surface is assumed as the no-slip surface. This assumption is valid when \( \text{We}_c \) is sufficiently high (\( \text{We}_c > 10^3 \)). When \( \text{We}_c \) is small, however, the no-slip surface becomes a slip boundary because the flows inside the porous layer induce spreading via capillary pressure. Therefore, the viscous dissipation inside the droplet and the line dissipation are negligible when \( \text{We}_c \) is small (\( \text{We}_c < 10 \)). Furthermore, gravitational energy and droplet surface energy are much weaker than the matrix potential when \( \text{We}_c < 10 \) and \( R^* > 1 \). Therefore, the energy equation becomes a function of the viscous dissipation and matrix potential. In this case Eq. (9) for the dimensionless droplet radius becomes

\[
-\frac{d}{dt^*} \left( \frac{12}{\text{We}_c} R^2 \right) + \frac{1}{\text{Re}_c^2} \frac{3}{8} f_c R^2 \left( \frac{dR^*}{dt^*} \right)^2 = 0. \tag{11}
\]

From Eq. (11), the dimensionless droplet expansion rate is found to be

\[
\frac{dR^*}{dt^*} = \frac{64 \text{Re}_c}{f_c \text{We}_c} \frac{1}{R^*} \frac{C^*_{\text{cap}}}{R^*}. \tag{12}
\]

By integrating Eq. (12), the droplet radius can be expressed as

\[
R^2 = 128 \frac{\text{Re}_c}{f_c \text{We}_c} t^* = 128 C^*_{\text{cap}} t^*. \tag{13}
\]

As a result, \( R(t)^* \) only depends on \( t^* \) and \( C^*_{\text{cap}} \) and the initial condition of Eq. (13) is not needed.

Equation (13) effectively predicts the droplet radius change on wetting surfaces at low \( \text{We}_c \), as shown in Fig. 7. Here the independent axis is \( C^*_{\text{cap}} t^* \) and the dependent axis is \( R^2 \) in Fig. 7 to display the linearity of Eq. (13) and the corresponding experimental data. We used \( \text{We}_c \) less than 100 for the drop impingement experiments in Fig. 7, but the theoretical data obtained from Eq. (13) assume that \( \text{We}_c \) is less than 10. Our intent was to show that the experimental data become closer to the theoretical data when their \( \text{We}_c \) is close to 10. As shown in Fig. 7, the experimental data obtained with \( \text{We}_c \) higher than 10 show larger deviations from the theoretical data. However, the nearly linear experimental data, obtained when \( \text{We}_c \) is higher than 10, are recovered after initial impact because the kinetic energy is dissipated through the initial moments of droplet expansion. \( \text{We}_c \) only reflects the initial impact speed of the droplet. Therefore, after the droplet loses its kinetic energy the expansion more closely follows the theoretical prediction. This is why droplets with \( \text{We}_c \) higher than 10 show nonlinearity in the initial impact region. It reveals that the droplet expansion rate at low \( \text{We}_c \) is governed by the spreading speed constant, \( C_{\text{cap}} \). In highly viscous liquids, the initial kinetic energy is dissipated through droplet deformation resulting from viscous effects inside the droplet after impact; therefore the impingement modes of highly viscous liquids are confined to Mode A and mainly governed by the matrix potential.

We can see Modes A1 and B in Fig. 6 (high \( \text{We}_c \)), and Modes A1 and A2 in Fig. 7 (low \( \text{We}_c \)). In Figs. 6 and 7, we used the experimental data obtained from Modes A1 and B because the mass conservation is not valid in Modes A2 and C due to necking and jetting behavior, respectively. From the investigation of \( \text{We}_c \) and \( \text{Re}_w \), we can say that very low and

\[
\begin{array}{cccccccccc}
\text{Data} & \text{Surface} & \text{Fr} & \text{We} & \text{Re}_c & \text{Re}_w & \text{Re}_w & \text{Re}_c^* & \text{C}_{\text{cap}} & \text{Mode} \\
1 & A & 0.9 & 0.9 & 15 & 1.38 & 12.79 & 4.14 & 0.1 & A2 \\
2 & B & 0.7 & 1.2 & 7 & 0.63 & 8.22 & 1.47 & 0.2 & A2 \\
3 & H & 0.9 & 1.6 & 37 & 0.75 & 8.44 & 1.82 & 0.2 & A1 \\
4 & I & 1.3 & 2.0 & 81 & 0.57 & 5.92 & 3.32 & 0.1 & A1 \\
5 & J & 15.3 & 24.4 & 86 & 0.35 & 4.80 & 0.45 & 0.003 & A1 \\
6 & K & 0.1 & 0.2 & 43 & 0.01 & 0.14 & 0.01 & 0.002 & A1 \\
\end{array}
\]
TABLE I. Liquid and surface properties used in the drop impingement experiments and numerical simulations. The properties of the glycerol and water mixture were obtained from the literature [15]. Highly wetting porous titania (TiO₂) surfaces were produced by an electrochemical fabrication method [11]. The porous titania surfaces showed wide variations in capillary pressure and spreading speed. The thin layer chromatography (TLC) plates were obtained from Sigma-Aldrich. The gel-blotting paper is a chromatography paper (grade 230) obtained from Genesee Scientific. The coffee filter is a commercial product made by Melitta USA, Inc. The symbols correspond to the symbols in the plot of drop impingement modes (Fig. 8).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Surface</th>
<th>Liquid</th>
<th>Effective pore radius (r_e (\mu m))</th>
<th>Layer thickness (H_l (\mu m))</th>
<th>Droplet diameter (D_o (mm))</th>
<th>Surface tension (\gamma (mN/m))</th>
<th>Viscosity (\mu (cP))</th>
<th>Density (\rho (kg/m^3))</th>
<th>Capillary pressure (P_{cap} (Pa))</th>
<th>Spreading constant (C_{cap} (mm^2/s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Porous titania surface 1</td>
<td>Water</td>
<td>10.6</td>
<td>8.6</td>
<td>2.8</td>
<td>72.8</td>
<td>0.9</td>
<td>998</td>
<td>783</td>
<td>49</td>
</tr>
<tr>
<td>B</td>
<td>Porous titania surface 1</td>
<td>Water</td>
<td>10.6</td>
<td>8.6</td>
<td>2.2</td>
<td>72.8</td>
<td>0.9</td>
<td>998</td>
<td>783</td>
<td>49</td>
</tr>
<tr>
<td>C</td>
<td>Porous titania surface 1</td>
<td>Water</td>
<td>10.6</td>
<td>8.6</td>
<td>5</td>
<td>72.8</td>
<td>0.9</td>
<td>998</td>
<td>783</td>
<td>49</td>
</tr>
<tr>
<td>D</td>
<td>Porous titania surface 2</td>
<td>Water</td>
<td>13.4</td>
<td>9.2</td>
<td>2.8</td>
<td>72.8</td>
<td>0.9</td>
<td>998</td>
<td>1048</td>
<td>104.4</td>
</tr>
<tr>
<td>E</td>
<td>Porous titania surface 3</td>
<td>Water</td>
<td>13.1</td>
<td>9.2</td>
<td>2.8</td>
<td>72.8</td>
<td>0.9</td>
<td>998</td>
<td>930</td>
<td>88.6</td>
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<td>F</td>
<td>Porous titania surface 4</td>
<td>Water</td>
<td>13</td>
<td>9.2</td>
<td>2.8</td>
<td>72.8</td>
<td>0.9</td>
<td>998</td>
<td>773</td>
<td>72.2</td>
</tr>
<tr>
<td>G</td>
<td>Porous titania surface 5</td>
<td>Ethanol</td>
<td>8.85</td>
<td>9.5</td>
<td>2.2</td>
<td>72.8</td>
<td>0.9</td>
<td>979</td>
<td>1084</td>
<td>38.6</td>
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<tr>
<td>H</td>
<td>Porous titania surface 6</td>
<td>Ethylene glycol</td>
<td>28</td>
<td>10.5</td>
<td>2.8</td>
<td>47.3</td>
<td>16</td>
<td>1113</td>
<td>863</td>
<td>21.0</td>
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<tr>
<td>I</td>
<td>Porous titania surface 6</td>
<td>Glycerol 60%</td>
<td>25</td>
<td>10.5</td>
<td>3</td>
<td>67</td>
<td>9</td>
<td>1154</td>
<td>733</td>
<td>19.8</td>
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<tr>
<td>J</td>
<td>Porous titania surface 6</td>
<td>Glycerol 90% + water 10%</td>
<td>21</td>
<td>10.5</td>
<td>2.9</td>
<td>63.6</td>
<td>164</td>
<td>1232</td>
<td>665</td>
<td>0.85</td>
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<td>K</td>
<td>Porous titania surface 7</td>
<td>Glycerol</td>
<td>13.6</td>
<td>9.4</td>
<td>2.8</td>
<td>63</td>
<td>1258</td>
<td>1261</td>
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<td>L</td>
<td>Silica TLC</td>
<td>Water</td>
<td>4.2</td>
<td>250</td>
<td>2.8</td>
<td>72.8</td>
<td>0.9</td>
<td>998</td>
<td>959</td>
<td>9.5</td>
</tr>
<tr>
<td>M</td>
<td>Cellulose TLC</td>
<td>Water</td>
<td>5.8</td>
<td>100</td>
<td>2.8</td>
<td>72.8</td>
<td>0.9</td>
<td>998</td>
<td>1076</td>
<td>20.4</td>
</tr>
<tr>
<td>N</td>
<td>Aluminum TLC</td>
<td>Water</td>
<td>5.1</td>
<td>250</td>
<td>2.8</td>
<td>72.8</td>
<td>0.9</td>
<td>998</td>
<td>1546</td>
<td>22.4</td>
</tr>
<tr>
<td>O</td>
<td>Gel-blotting paper</td>
<td>Water</td>
<td>5.6</td>
<td>340</td>
<td>2.8</td>
<td>72.8</td>
<td>0.9</td>
<td>998</td>
<td>1395</td>
<td>24.0</td>
</tr>
<tr>
<td>P</td>
<td>Coffee filter</td>
<td>Water</td>
<td>7.9</td>
<td>120</td>
<td>2.8</td>
<td>72.8</td>
<td>0.9</td>
<td>998</td>
<td>1420</td>
<td>60.4</td>
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</tbody>
</table>

TABLE II. Simplified energy conservation equation and dimensionless droplet radius at different physical regimes. The line dissipation in Eq. (9) is considered dominant and the other dissipation terms are ignored to obtain simplified energy conservation equations as functions of common dimensionless parameters. The dimensionless droplet radius can be expressed as a function of the Reynolds number and another dimensionless parameter; therefore, we can characterize the droplet radius change with respect to the relative influence of the Reynolds number.

<table>
<thead>
<tr>
<th>Dominant effect</th>
<th>Dimensionless parameters</th>
<th>Simplified energy equation</th>
<th>Dimensionless droplet radius</th>
<th>Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic energy</td>
<td>(We \gg 1, Fr \gg 1, We_c \gg 1)</td>
<td>(\frac{d}{dt} \left( \frac{D_o}{\gamma} \right)^2 \approx -\frac{1}{16} Re \left( \frac{D_o}{\gamma} \right)^2)</td>
<td>(R^* = \sqrt{Re \tan \left( \frac{1}{2} \theta \right)})</td>
<td>Asymptotic to (Re^{1/2})</td>
</tr>
<tr>
<td>Gravitational potential energy</td>
<td>(We \gg 1, Fr \ll 1, We_c \gg 1)</td>
<td>(\frac{d}{dt} \left( \frac{1}{2} \frac{D_o}{\gamma} \right)^2 \approx -\frac{1}{16} Re \left( \frac{D_o}{\gamma} \right)^2)</td>
<td>(R^* = \left( \frac{Re}{Fr} \right)^{1/3})</td>
<td>Weak due to (\frac{1}{3}) power dependence</td>
</tr>
<tr>
<td>Surface energy</td>
<td>(We \ll 1, Fr \ll 1, We_c \gg 1)</td>
<td>(\frac{d}{dt} \left( \frac{1}{2} \frac{D_o}{\gamma} \right)^2 \approx -\frac{1}{16} Re \left( \frac{D_o}{\gamma} \right)^2)</td>
<td>(R^* = \frac{Re}{We_c} t^*)</td>
<td>Linearly proportional to (Re/We_c)</td>
</tr>
<tr>
<td>Matrix potential energy</td>
<td>(We \ll 1, Fr \ll 1, We_c \ll 1)</td>
<td>(\frac{d}{dt} \left( \frac{1}{2} \frac{D_o}{\gamma} \right)^2 \approx -\frac{1}{16} Re \left( \frac{D_o}{\gamma} \right)^2)</td>
<td>(R^* = \frac{Re}{We_c} t^*)</td>
<td>Linearly proportional to (Re/We_c)</td>
</tr>
</tbody>
</table>
number to obtain $R_w$. Using the liquids and surfaces in Table I, drop impingement experiments were conducted with varying impact velocities. It is worth noting that when the contact angle is small [$\cos \theta \sim 1$] the Washburn-Reynolds number $R_w$ is close to the capillary-Reynolds number $R_c$, the Reynolds number inside a single capillary tube with radius $r_c$ and flow speed $U_o$.

When the impingement modes were plotted with respect to $W_e$ or $R_w$, there were several orders of magnitude differences between mode transitions for different liquids. However, $R_w$ correlates with mode transitions for a wide range of liquid and surface properties, impact velocities, and for various highly wetting porous surfaces (Fig. 8). As shown in Fig. 8, increasing $R_w$ governs transitions between impingement modes. Interestingly, in Mode A ($R_w < 0.5$), observation of Mode A1 or Mode A2 appeared to vary with $\cos \theta/\Omega h^2$, where $\Omega$ is the Ohnesorge number expressed as $\Omega = \mu / (r_c \rho \gamma)^1/2$ and $\theta$ is the Young’s contact angle of the surface. This parameter has the same form of $C_{cap}/\nu$ for the Young’s contact angle is small, the surfaces generally show smooth spreading. Conversely, Mode A (low $R_w$) results in capillary driven flows. When the capillary radius is large and the contact angle is small, the surfaces generally show high spreading speed. This can result in oscillating motions (Mode A1) at low $C_{cap}$ and necking (Mode A2) at high $C_{cap}$. In Mode A, droplets spread largely due to the matrix potential since the initial droplet kinetic energy is negligible.

V. CONCLUSIONS

In this work, we propose an energy conservation equation to predict droplet spreading on highly wetting porous thin films. Notably, we find that the matrix potential must be included to accurately simulate droplet spreading. This effect can be evaluated with the capillary-Weber number, $W_e$, which is the ratio of the initial kinetic energy of the impinging droplet to the initial matrix potential. Furthermore, we discovered a dimensionless parameter, the Washburn-Reynolds number ($R_w$), which correlates with impingement modes on highly wetting porous surfaces. $R_w$ can be derived from dimensional analysis or the simplified energy equations at low and high $W_e$. At high $W_e$, the Weber number governs the droplet expansion rate but at low $W_e$, numbers, the dimensionless spreading constant, $C_{cap}^*$ governs droplet spreading. $R_w$ can be obtained from $W_e$ and $C_{cap}^*$. $R_w$ has the same form as the Reynolds number but possesses an effective length scale, $r_c \cos \theta$, which reflects the wetting properties of the surface. $R_w$ effectively correlates with impingement modes across a wide range of fluid and surface properties. $R_w$ provides useful insight into droplet dynamics and can be used to guide the design of highly wetting surfaces for applications ranging from spray cooling to paper microfluidics and inkjet printing.

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[26] The equation typically credited to Washburn is sometimes called the Lucas-Washburn or Bell-Cameron-Lucas-Washburn equation in honor of work by Lucas (1918) and Bell and Cameron (1906) that preceded Washburn’s original publication in 1921.