PHYSICAL REVIEW E 00, 006300 (2012) Analytical solutions of drying in porous media for gravity-stabilized fronts A. G. Yiotis and D. Salin Laboratoire FAST, Université Pierre & Marie Curie, Université d'Orsay Paris-Sud, CNRS, Orsay 91405, France E. S. Tajer and Y. C. Yortsos Mork Family Department of Chemical Engineering and Materials Science, University of Southern California, 6 Los Angeles, California 90089-1450, USA 7 (Received 17 June 2011; revised manuscript received 11 January 2012; published xxxxx) 8 We develop a mathematical model for the drying of porous media in the presence of gravity. The model incorporates effects of corner flow through macroscopic liquid films that form in the cavities of pore walls, mass 10 transfer by diffusion in the dry regions of the medium, external mass transfer over the surface, and the effect of 11 gravity. We consider two different cases: when gravity opposes liquid flow in the corner films and leads to a stable 12 percolation drying front, and when it acts in the opposite direction. In this part, we develop analytical results 13 when the problem can be cast as an equivalent continuum and described as a one-dimensional (1D) problem. 14 This is always the case when gravity acts against drying by opposing corner flow, or when it enhances drying 15 by increasing corner film flow but it is sufficiently small. We obtain results for all relevant variables, including 16 drying rates, extent of the macroscopic film region, and the demarkation of the two different regimes of constant 17 rate period and falling rate period, respectively. The effects of dimensionless variables, such as the bond number, 18 the capillary number, and the Sherwood number for external mass transfer are investigated. When gravity acts 19 to enhance drying, a 1D solution is still possible if an appropriately defined Rayleigh number is above a critical 20 threshold. We derive a linear stability analysis of a model problem under this condition that verifies front stability. 21 Further analysis of this problem, when the Rayleigh number is below critical, requires a pore-network simulator 22 which will be the focus of future work. 23

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I. INTRODUCTION

During the drying of a porous medium, initially fully 26 saturated by a volatile liquid, evaporation gives rise to a number 27 of liquid-gas interfaces. These are located in pore bodies, 28 29 that define the percolation front [Fig. 1(d)], but also reside in the cavities and corners along the pore walls in the form of 30 macroscopic liquid films, which develop as the bulk liquid-gas 31 menisci recede in the pore space [Figs. 1(b)-1(c)]. The 32 movement of these interfaces is controlled by the combined 33 action of capillary, gravity, and viscous forces. 34

As in all drainage processes, fluid transport through the liq-35 uid films is an important transport mechanism. Films provide 36 hydraulic connectivity between liquid-saturated regions that 37 may appear to be macroscopically disconnected [1,2]. Such 38 flows are induced by capillarity and driven by changes in the 39 curvature of the liquid-gas menisci [3,4]. These macroscopic 40 films should be clearly distinguished from thin films that 41 develop on flat surfaces of the pore walls as vapor molecules 42 are absorbed due to van der Waals forces. Liquid flow through 43 the latter thin films, as well as mass transfer by diffusion in 44 the film region, has been shown to be negligible compared to 45 corner flow in the cavities through macroscopic films [5]. 46

Recent drying studies have suggested that macroscopic 47 films provide hydraulic connectivity even at late times when 48 a significant amount of the liquid has evaporated [6-8]. If the 49 films reach the external surface S of the medium, wicking 50 action keeps the surface at least partially wet. As more films 51 get detached, the liquid content at the surface progressively 52 decreases. However, the surface remains saturated with the 53 evaporating species, even at small liquid content (liquid satu-54 ration), provided that the thickness of the external mass transfer 55

boundary layer is sufficiently larger than the characteristic pore size of the medium [9]. Under such conditions, the process is controlled by mass transfer through the boundary layer and characterized by a constant drying rate [the constant rate period (CRP) regime], which may last up to very late times [8,10].

At a certain length, liquid films cannot sustain capillary flow 61 over increasingly larger lengths and they become detached 62 [6,11–13]. Then, a completely dry region (absence of bulk 63 liquid and corner flow through macroscopic films) develops 64 between the evaporation front and the external surface. Drying 65 is now controlled by diffusion through this dry region and the 66 evaporation rate starts decreasing signaling the onset of the 67 falling rate period (FRP) [Fig. 1(d)]. 68

Previous studies have explored in detail various mathemati-69 cal models of drying, including those based on a pore-network 70 representation of the porous medium (developed by Fatt 71 [14]). These have progressed from simple percolation models 72 [15,16], to models that include corner film flow [17,18], and 73 more recently those incorporating the effect of an external 74 mass transfer boundary layer [10]. Absent has been the effect 75 of gravity, which in many applications can play an important 76 role. Indeed, in recent experiments [19-21] it was found 77 that incorporating gravity in drying is necessary to match 78 the experimental results. It is the objective of our work to 79 address the effect of gravity in the drying of porous media and 80 quantities such as film extent, film thickness, and drying rates. 81

In this paper we develop the mathematical formalism to incorporate the effect of gravity. This can be stabilizing or destabilizing, depending on the orientation of the porous medium [stabilizing when gravity opposes corner flow in the films (and thus drying) and destabilizing in the opposite case, set

assuming sufficiently strong buoyancy]. We provide analytical 87 solutions for relevant quantities when gravity opposes drying 88 and investigate the sensitivity to dimensionless variables, such 89 the bond number, the capillary number, and the Sherwood 90 as number. Attention is paid to drying curves and the conditions 91 that mark the transition between the constant (CRP) and the 92 falling rate (FRP) periods. When gravity enhances corner 93 film flow, an equivalent 1D continuum can still apply if 94 critical threshold for an equivalent Rayleigh number is а 95 exceeded. We derive such a condition and infer its validity 96 by a simplified stability analysis. For the more general case, 97 a detailed pore-network is needed. This is a subject for future 98 research [21]. 99

II. MODEL FORMULATION

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As in our previous studies [10,11,17], we postulate the 101 following [Fig. 1(d)]: An external mass transfer boundary layer 102 over the external surface S of the porous medium (sometimes 103 referred to as the product surface), where the evaporating 104 species is purged; an innermost region of pores, fully occupied 105 by liquid (liquid saturated region); and intermediate regions 106 containing pores partly occupied by liquid films (film region) 107 or not occupied at all (dry region), depending on the extent of 108 the process. The interface between the fully occupied and film 109 pores is typically a percolation front (which in the presence 110 gravity can be determined using invasion percolation in the of 111 presence of a stabilizing or a destabilizing gradient [22,23] 112 depending on the orientation). Gravity modifies both the 113 morphology of the percolation front, as well as the extent 114 of the film region by either enhancing or opposing corner flow 115 in the films. To understand its effects we consider that the 116 full problem can be cast as a 1D equivalent of drying from a 117 material bearing the geometrical characteristics of capillaries 118 with noncircular (i.e., rectangular) cross sections. This allows 119 for the modeling of corner flow in the form of films that develop 120 as the bulk liquid-gas meniscus recedes deeper in the pore 121 space [Figs. 1(a)–1(c)] [19]. 122

Within the film region the dominant mass transport mechanism is corner liquid flow through the films [5]. The films are then parametrized by the radius of curvature of the liquid-gas menisci r(x,t) along their length from the product surface S [11], taken at $\xi = 0$, to the percolation front, taken at an average position $\xi_p < 0$. Under capillary equilibrium, the excess pressure in the film is

$$P_l = -\gamma/r,\tag{1}$$

where γ is the interfacial tension and flow is unidirectional along direction *x* and described by a Poiseuille-type law [3,4]

$$Q_x = -\frac{C^* r^4}{\mu \beta} \left(\frac{\partial P_l}{\partial x} - \rho_l g_x \right).$$
(2)

Here μ is viscosity, g_x is the gravity component, ρ_l is density, 132 is the dimensionless flow resistance [3], C^*r^2 is the cross β 133 sectional area of the liquid film and C^* is a shape factor that 134 expresses the area available for fluid flow in the corners of the 135 capillaries. For the case of a square cross section $C^* = 4 - \pi$. 136 While valid for any gravity orientation [21], this paper will 137 be restricted only to the case when the x direction is aligned 138 with the gravity vector, namely $g_x = \pm g$. Taking into account 139

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Eq. (1), the above can be rewritten as

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$$Q_x = -\frac{C^* \gamma}{3\mu\beta} \frac{\partial r^3}{\partial x} + \frac{C^* r^4}{\mu\beta} \rho_l g_x.$$
 (3)

The mass balance for the evaporating species along the 141 capillary is 142

$$\frac{\partial V}{\partial t} = -\frac{\partial Q_x}{\partial x} - Q_{\rm ev},$$
 (4)

 $V = C^* r^2,$ $Q_{\rm ev} = -(2\pi r D_M/\rho_l)C_e/r_0[\partial\zeta/\partial n]$ 143 where is the evaporation rate in a cross section of the capillary, 144 r_0 is the average size of the capillary in the cross section, 145 D_M is the molecular diffusivity, C_e is the equilibrium 146 mass concentration, and $\zeta = C/C_e$ is the dimensionless 147 concentration. *n* is the normal to the interface and the brackets 148 denote an average over the dimensionless concentration 149 gradient at the interface. The above expression will not be 150 used further, however. In the following we will focus on two 151 distinct macroscopic regions: one in which the gas phase is 152 practically saturated by vapor and transport is through film 153 flow only, and another ahead of the film region, where the pore 154 space is completely dry and the transport is by diffusion in 155 the gas phase only. A macroscopic mass balance will connect 156 the two regions. 157

In dimensionless notation, this further reads

$$2\operatorname{Ca}_{f}\frac{C^{*}\rho_{l}}{\pi C_{e}}\frac{\partial\rho}{\partial\tau} = \frac{1}{\rho}\frac{\partial^{2}\rho^{3}}{\partial\xi^{2}} - \frac{3\operatorname{Bo}_{x}}{\rho}\frac{\partial\rho^{4}}{\partial\xi} - 2\operatorname{Ca}_{f}(1-\zeta) \quad (5)$$

where we introduced the dimensionless film thickness $\rho = \frac{159}{r/r_0}$ (not to be confused with the density notation), length $\xi = \frac{160}{x/r_0}$, and time $\tau = t D_M/r_0^2$, and we defined the dimensionless (161) capillary and bond numbers (162)

$$Ca_f = \frac{3\beta\pi\mu D_M C_e}{C^*\gamma\rho_l r_0}, \quad Bo = \frac{\rho_l g r_0^2}{\gamma}.$$
 (6)

In our notation, the *x* direction is always taken from the inside of the porous medium toward the external surface, therefore $Bo_x = -Bo$ corresponds to evaporation from the top (gravity-opposed drying), while $Bo_x = Bo$ corresponds to evaporation from the bottom (gravity-enhanced drying). 167

Proceeding with the conventional quasi-steady-state assumption and also considering that evaporation practically occurs only near the film tip (due to the saturated gas phase along the capillary) [11,17], the mass balance simplifies to

$$\frac{\partial q_x}{\partial \xi} = \frac{\partial^2 \rho^3}{\partial \xi^2} - 3 \operatorname{Bo}_x \frac{\partial \rho^4}{\partial \xi} = 0.$$
 (7)

The above formalism can also be generalized (e.g., to a pore 172 network). Its continuum equivalent reads 173

$$\nabla^{2} \left(\rho^{3} - 3 \operatorname{Bo}_{x} \int_{0}^{\xi} \rho^{4} d\xi \right)$$

= $-3 \operatorname{Bo}_{x} \left(\frac{\partial^{2}}{\partial u^{2}} \int_{0}^{\xi} \rho^{4} d\xi + \frac{\partial^{2}}{\partial \omega^{2}} \int_{0}^{\xi} \rho^{4} d\xi \right), \quad (8)$

where $u = y/r_0$ and $\omega = z/r_0$. When the right-hand side of 174 Eq. (8) is negligible, as in the specific case here of a 1D 175



FIG. 1. Schematics of drying from a capillary with a noncircular (i.e., square) cross section with the top side open to the ambient environment (a)–(c). The capillary is initially filled with a volatile liquid up to a certain height (a) (contact angle not shown here). As the liquid evaporates, the liquid-gas interface recedes in the capillary forming a meniscus, while liquid films develop at the corners of the capillary. Initially, the film tips reach up to the initial position of the liquid-gas interface (b). At later times, the film tips depin from their initial position and they recede deeper in the capillary following the movement of the bulk meniscus (c). Also shown in (d) later times of the more general drying problem from a porous medium bounded by an external mass boundary layer of thickness *d* over the product surface S. The pores can be classified in analogy with the single capillary problem as: (i) completely dry (dry region) where mass transfer is by diffusion only, (ii) pores invaded by the gas phase that contain liquid films at the pore walls (film region) where mass transfer is primarily through corner film flow, and (iii) pores that are fully saturated by the liquid phase (liquid saturated region). The evaporation front (film tips), ξ_i , is located at the interface between the dry and film regions. Lengths are in dimensionless notation.

176 continuum, we can write

$$\nabla^2 \left(\rho^3 - 3 \operatorname{Bo}_x \int_0^{\xi} \rho^4 d\xi \right) = 0, \tag{9}$$

¹⁷⁷ the 1D equivalent of which is Eq. (7). Checking the validity of ¹⁷⁸ this assumption in the pore-network simulations is a subject ¹⁷⁹ for future research [21].

In the dry region (where $\rho = 0$), the mass balance at steady state is the Laplace equation

$$\nabla^2 \zeta = 0. \tag{10}$$

For convenience and following earlier works, diffusion is also
assumed to apply within the external mass transfer boundary
layer [9,10] as well. However, these results also apply to a
convective boundary condition, as discussed further below.
Finally, continuity of mass fluxes at the film tips (evaporation
front in Fig. 1) reads at steady state

$$\frac{\partial \rho^3}{\partial n} = \operatorname{Ca}_f \frac{\partial \zeta}{\partial n},\tag{11}$$

188 where n denotes outer normal.

We proceed as in previous works [11,17] and develop a solution uniformly valid over both film and dry regions by defining the auxiliary variable

$$\Phi = \frac{\rho^3 - 3\mathrm{Bo}_x I + \mathrm{Ca}_f \zeta}{1 + \mathrm{Ca}_f},\tag{12}$$

192 where

$$I = \int_0^{\xi} \rho^4 d\xi. \tag{13}$$

This satisfies the Laplace equation over both the film and dry regions as required 193

$$\nabla^2 \Phi = 0 \tag{14}$$

and it is continuous with continuous fluxes at the yet-to-bedetermined evaporation front [Eq. (11)]. Equation (14) is then to be solved subject to the following boundary conditions.

(i) At the percolation front ($\xi = \xi_p \leq 0$), we have saturated 198 conditions, $\zeta = 1$, $\rho = 1$, hence 199

$$\Phi = \Phi_p \equiv 1 - \frac{3\text{Bo}_x I(\xi_p)}{1 + \text{Ca}_f}.$$
(15)

200

(ii) At the top of the mass boundary layer outside the porous 201 medium ($\xi = d$), we have $\zeta = 0$, $\rho = 0$, hence 202

$$\Phi_0 = 0. \tag{16}$$

The unknown position of the film tips is the place where $\rho = 0_{203}$ and $\zeta = 1$, hence $_{204}$

$$\Phi = \Phi_i \equiv \frac{\operatorname{Ca}_f}{1 + \operatorname{Ca}_f}.$$
(17)

Finally, at the product surface S ($\xi = 0$) mass flux continuity 205 applies 206

$$\left. \frac{\partial \Phi}{\partial \xi} \right|_{S^-} = \lambda \frac{\partial \Phi}{\partial \xi} \bigg|_{S^+},\tag{18}$$

where $\lambda > 1$ is the ratio of external to effective internal ²⁰⁷ diffusivities. At the same place Φ is discontinuous early in ²⁰⁸ the process. Namely, when the films reach the product surface, ²⁰⁹



FIG. 2. (Color online) Plot of the auxiliary variable Φ vs the dimensionless depth of the porous medium ξ in the 1D problem. The product surface is located at $\xi = 0$, the percolation front at $\xi_p < 0$ (not shown here) and the film tips at $\xi_i < 0$, where $\Phi(\xi_i) = \text{Ca}_f/(1 + \text{Ca}_f)$. The red line (∇) shows a solution for early times when $\xi_p > \xi_{\text{pc}}$, the film tips reach the product surface S, and Φ is discontinuous there. The blue line (\circ) shows a solution for later times when $\xi_p \leq \xi_{\text{pc}}$, the films have detached from S, and Φ is continuous there.

they have a finite thickness $\rho^* > 0$ on the porous medium side of the surface S-,hence $\Phi(S-) = \frac{\rho^* + Ca_f}{1+Ca_f}$, and zero thickness $(\rho = 0)$ just over the surface S+, $\Phi(S+) = \frac{Ca_f}{1+Ca_f}$. After the detachment of the films, however, Φ becomes continuous at $\xi = 0$.

The 1D solution of Eq. (14) is straightforward: Φ is linear in ξ subject to the above conditions. Schematics of such a solution are shown in Fig. 2 for the two different cases of the film condition at the product surface S. We proceed therefore by considering the two different cases, when gravity opposes or enhances drying, respectively.

III. GRAVITY-OPPOSED DRYING, $Bo_x = -Bo \leq 0$

²²² Consider, first, the case when gravity opposes drying ²²³ (Bo_x = -Bo and evaporation is from the top). The percolation ²²⁴ front is at $\xi_p \leq 0$ and the film tips at $\xi_i \leq 0$ (where $\xi_i \geq \xi_p$). ²²⁵ Here and in the material below, we assume that the percolation ²²⁶ front has not reached the bottom boundary of the medium, ²²⁷ located at $\xi = \xi_b$. This will be relaxed later.

At early stages the films are attached to S ($\rho^* > 0$ at $\xi = \xi_i = 0$). As drying proceeds, ρ^* decreases, and when ξ_p reaches a critical value ξ_{pc} (when $\rho^* = 0$), the films detach. From that point on, the position of the evaporation front recedes within the pore space, $\xi_i < 0$, while a growing dry region forms below the product surface, $\xi_i < \xi \leq 0$, where gas-phase diffusion is the controlling process.

A. Films terminate at product surface, $\xi_p > \xi_{pc}$

When the films end at the external surface S of the porous 236 medium, Φ is discontinuous there, 237

$$\Phi(S-) = \frac{\rho^{*3} + Ca_f}{1 + Ca_f}, \quad \Phi(S+) = \frac{Ca_f}{1 + Ca_f}.$$
 (19)

It is straightforward to show that the solution of Eq. (14) for $_{238}$ Φ is $_{239}$

$$\Phi(\xi) = \frac{\operatorname{Ca}_f}{1 + \operatorname{Ca}_f} \left(\frac{d - \xi}{d} \right) \quad \text{for} \quad 0 < \xi \leq d, \quad (20)$$

$$\Phi(\xi) = \Phi_p + \frac{\lambda \operatorname{Ca}_f}{1 + \operatorname{Ca}_f} \left(\frac{\xi_p - \xi}{\xi_p} \right)$$

$$= \Phi(S -) + \frac{\operatorname{Ca}_f}{1 + \operatorname{Ca}_f} \left(\frac{-\lambda \xi}{d} \right) \quad \text{for} \quad \xi_p \leq \xi < 0. \quad (21)$$

In this regime the mass flux is independent of time and constant 240

$$-\frac{\partial \Phi}{\partial \xi}\Big|_{S^+} = \frac{\operatorname{Ca}_f}{d(1 + \operatorname{Ca}_f)} \equiv \frac{\Phi_i}{d}.$$
 (22)

This defines the CRP regime, which lasts as long as the films the stay connected to the surface. The film thickness is obtained to the surface. The film thickness is obtained to the surface state the surface state s

$$\frac{d\rho^3}{d\xi} + 3\mathrm{Bo}\rho^4 = (1 + \mathrm{Ca}_f)\frac{\partial\Phi}{\partial\xi}\Big|_{\mathrm{S}^-} = -\frac{\lambda\mathrm{Ca}_f}{d}.$$
 (23)

This can be integrated once

(

$$\int_{\rho^*}^{\rho} \frac{3\rho^2 d\rho}{\left(\frac{\lambda C a_f}{d} + 3 B o \rho^4\right)} = -\xi.$$
 (24)

For compactness we will also use the hypergeometric function ${}_{245}$ ${}_{2}F_{1}(a,b;c;z)$ to represent the above integral [24] ${}_{246}$

$$\int_0^z \frac{3u^2}{a+3bu^4} du = \frac{z^3}{a} \bigg[{}_2F_1 \bigg(1, 3/4; 7/4; -3\frac{bz^4}{a} \bigg) \bigg].$$
(25)

The thickness of the film is thus

$$\rho^{3} \bigg[{}_{2}F_{1} \bigg(1, 3/4, 7/4, \frac{-3\text{Bod}}{\lambda \operatorname{Ca}_{f}} \rho^{4} \bigg) \bigg] - \rho^{*3} \bigg[{}_{2}F_{1} \bigg(1, 3/4, 7/4, \frac{-3\text{Bod}}{\lambda \operatorname{Ca}_{f}} \rho^{*4} \bigg) \bigg] = -\frac{\lambda \operatorname{Ca}_{f}}{d} \xi_{p},$$
(26)

while the dependence of ρ^* on the position of the percolation 248 front ξ_p can be obtained through 249

$${}_{2}F_{1}\left(1,3/4,7/4,\frac{-3\text{Bod}}{\lambda \text{ Ca}_{f}}\right)$$
$$-\rho^{*3}\left[{}_{2}F_{1}\left(1,3/4,7/4,\frac{-3\text{Bod}}{\lambda \text{ Ca}_{f}}\rho^{*4}\right)\right] = -\frac{\lambda \text{ Ca}_{f}}{d}\xi_{p}.$$
(27)

The end of the CRP is at the critical detachment position ξ_{pc} , 250 obtained by setting $\rho^* = 0$ in the above 251

$$-\frac{\lambda \, \text{Ca}_f}{d} \xi_{\text{pc}} = {}_2F_1 \left(1, 3/4, 7/4, \frac{-3\text{Bod}}{\lambda \, \text{Ca}_f} \right).$$
(28)

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Note that the external mass transfer variable occurs in the combination λ/d . It is not difficult to show that more generally it represents an equivalent mass transfer coefficient across the boundary layer. Indeed, if the flux condition at the surface was based instead on a convective mass transfer coefficient *h* (e.g., Flux = hC_{S+}), it can be readily shown that

$$\frac{\lambda}{d} = \text{Sh} \equiv \frac{hr_0}{D_{\text{eff}}}$$
 (29)

where we defined a Sherwood number Sh for the external mass transfer using the pore length r_0 and the effective internal diffusivity D_{eff} as the characteristic quantities. We remark that because we used the characteristic pore size above, the sodefined Sherwood number would usually take small values. From this point on we will use without loss the equivalence between Sh and d/λ .

It is also worth noting that the explicit effect of Bo can be removed from the above by rescaling all lengths by $-Bo_x = Bo > 0$: Then by defining $\hat{\xi} = Bo\xi$, Eq. (24) becomes independent of Bo

$$\int_{\rho^*}^{\rho} \frac{3\rho^2 d\rho}{(\tau+3\rho^4)} = -\hat{\xi},$$
(30)

²⁶⁹ where we introduced the single dimensionless parameter

$$\tau \equiv \frac{\text{ShCa}_f}{\text{Bo}}.$$
(31)

²⁷⁰ One can view τ as an equivalent Rayleigh number $Ra_{ev} = \frac{Ca_f}{Bo} = \frac{3\pi\beta}{C^*} \frac{C_e D_M \nu}{\rho_l g r_0^3}$ for evaporation in the presence of buoyancy ²⁷² (i.e., $\tau = Ra_{ev}Sh$) where $\nu = \mu/\rho_l$ is viscous diffusivity (as ²⁷³ also in the case of miscible fluids [25]). In this notation, the ²⁷⁴ equivalent of Eq. (27) is

$${}_{2}F_{1}\left(1,3/4,7/4,\frac{-3}{\tau}\right) - \rho^{*3}\left[{}_{2}F_{1}\left(1,3/4,7/4,\frac{-3}{\tau}\rho^{*4}\right)\right]$$

= $-\tau \hat{\xi}_{p}$ (32)

²⁷⁵ and that of the detachment time $\hat{\xi_{pc}}$ is

$$\hat{\xi}_{\rm pc} = -\frac{1}{\tau} \bigg[{}_2F_1 \bigg(1, 3/4, 7/4, \frac{-3}{\tau} \bigg) \bigg]. \tag{33}$$

Figure 3 shows profiles of the film thickness ρ^* just below the 276 product surface S- as a function of the rescaled position of the 277 percolation front $\hat{\xi_p}$ for different values of τ . The inset of the 278 same figure shows ρ^* vs the position of the percolation front 279 ξ_p for the corresponding values of Bo_x and a fixed value of the 280 capillary number Ca_f . As expected, the film thickness at the 281 product surface decreases as the percolation front recedes in 282 the pore space, higher values of Bo corresponding to shorter 283 films (due to stronger buoyancy) and earlier detachment times 284 (smaller values of the magnitude of ξ_p). 285

Figure 4 shows the critical rescaled position of the percolation front $\hat{\xi}_{pc}$ as a function of τ . The figures demonstrate that smaller capillary and Sherwood numbers lead to longer films. The critical percolation front location ξ_{pc} is a slowly increasing function of τ . An asymptotic analysis of the corresponding Eq. (33) shows that at sufficiently large times, namely large values of $-\hat{\xi}_{pc}$

$$-\hat{\xi}_{\rm pc} \sim J\tau^{-1/4},\tag{34}$$



FIG. 3. (Color online) Film thickness ρ^* at the surface vs the rescaled position of the percolation front $\hat{\xi_p}$ for various values of τ ; $\tau = 0.1$ (\Box), $\tau = 0.01$ (Δ), $\tau = 0.001$ (\bigcirc). Inset shows the film thickness at the surface ρ^* vs the position of the percolation front ξ_p for the corresponding values of Bo_x; Bo_x = -0.001 (\Box), Bo_x = -0.01 (\triangle), Bo_x = -0.1 (\bigcirc) when Ca_f = 0.001 and Sh = 0.1. The critical detachment time ξ_{pc} for each case is found when $\rho^* = 0$.

where the algebraic constant *J* can be expressed in terms ²⁹³ of the gamma function $J = 3^{-\frac{3}{4}}\Gamma(1/4)\Gamma(3/4) \simeq 1.462$. This ²⁹⁴ behavior is also demonstrated in Fig. 4. The magnitude of ²⁹⁵



FIG. 4. (Color online) Log-log plot of the rescaled critical detachment position $-\hat{\xi}_{pc}$ vs τ . The dashed line of slope $-\frac{1}{4}$ corresponds to the asymptotic prediction of Eq. (34).

the percolation front position is used as a proxy for time. Its 296 specific relation to time will be discussed in a later section. 297

B. Films terminate inside the porous medium, $\xi_p \leq \xi_{pc}$ 298

When the films have detached from S, the evaporation front 299 is at $\xi_i < 0$. Now the variable Φ is continuous at $\xi = 0$ (Fig. 2) 300 and we have 301

$$\Phi(\xi) = \Phi_i \left(\frac{d - \xi}{d - \lambda \xi_i} \right) = \Phi_p \left(\frac{d - \xi}{d - \lambda \xi_p} \right) \quad \text{for} \quad 0 \leqslant \xi \leqslant d,$$
(35)

$$\Phi(\xi) = \Phi_i \left(\frac{d - \lambda \xi}{d - \lambda \xi_i} \right) = \Phi_p \left(\frac{d - \lambda \xi}{d - \lambda \xi_p} \right) \quad \text{for} \quad \xi_p \leqslant \xi \leqslant 0.$$
(36)

The drying flux remains proportional to the gradient of Φ and 302 ³⁰³ from Eq. (35) we get

$$-\frac{\partial \Phi}{\partial \xi}\Big|_{+} = \frac{\Phi_i}{d - \lambda \xi_i}.$$
(37)

Now the drying rate decreases as ξ_i decreases. 304

As before, the film thickness ρ is the solution of 305

$$\frac{d\rho^3}{d\xi} + 3\mathrm{Bo}\rho^4 = (1 + \mathrm{Ca}_f)\frac{\partial\Phi}{\partial\xi}\Big|_{-} = -\frac{\mathrm{ShCa}_f}{1 - \mathrm{Sh}\xi_i} \quad (38)$$

306 OI

Q

0.4

0.2

0.0

-1000

-800

-600

ξ

-400

-200

$$\int_0^\rho \frac{3\rho^2 d\rho}{\operatorname{Sh}\frac{\operatorname{Ca}_i}{1-\operatorname{Sh}\xi_i} + 3\operatorname{Bo}\rho^4} = \xi_i - \xi \tag{39}$$

and in compact notation,

$$\rho^{3} \left[{}_{2}F_{1} \left(1,3/4,7/4, -3\rho^{4} \operatorname{Bo} \frac{1-\operatorname{Sh}\xi_{i}}{\operatorname{ShCa}_{f}} \right) \right]$$
$$= \frac{\operatorname{ShCa}_{f}}{1-\operatorname{Sh}\xi_{i}} (\xi_{i} - \xi).$$
(40)

By taking $\rho = 1$ at $\xi = \xi_p$, we obtain ξ_i as a function of ξ_p 308

$${}_{2}F_{1}\left(1,3/4,7/4,-3\mathrm{Bo}\frac{1-Sh\xi_{i}}{\mathrm{ShCa}_{f}}\right) = \frac{\mathrm{ShCa}_{f}}{1-\mathrm{Sh}\xi_{i}}(\xi_{i}-\xi_{p}).$$
(41)

With the percolation front location as a proxy for time, we 309 can determine all relevant variables, including the location of 310 the film tips ξ_i , as well as the film thickness profiles over $\xi_{i,311}$ However, in this regime the effect of Bo cannot be simply 312 rescaled out as before, except for the critical percolation time. 313 Indeed, by using the rescaled notation, the above become 314

$$\rho^{3} \left[{}_{2}F_{1} \left(1,3/4,7/4, -3\rho^{4} \frac{\mathrm{Bo} - \mathrm{Sh}\xi_{i}}{\mathrm{Bo}\tau} \right) \right]$$
$$= \frac{B\tau}{\mathrm{Bo} - \mathrm{Sh}\xi_{i}} (\hat{\xi}_{i} - \hat{\xi}), \qquad (42)$$

and

$${}_{2}F_{1}\left(1,3/4,7/4,-3\frac{\text{Bo}-\text{Sh}\hat{\xi}_{i}}{\text{Bo}\tau}\right) = \frac{\text{Bo}\tau}{\text{Bo}-\text{Sh}\hat{\xi}_{i}}(\hat{\xi}_{i}-\hat{\xi}_{p}).$$
(43)

The profile for ρ as a function of ξ is plotted in Fig. 5 for 316 various values of the dimensionless numbers Bo and Ca_f. 317 The familiar cubic dependence as the film tip is approached 318 is evident [11]. For larger values of Bo, the liquid films 319 become shorter as buoyancy forces increasingly dominate over 320 capillary forces and the films detach from the product surface 321 earlier [Fig. 5 (left)]. The effect of Ca_f is demonstrated in $_{322}$



1.0 1.0 0.8 0.8 0.6 0.6

0

0.4

0.2

0.0

-1000

-800

-600

ξ

-400

-200

0

307



FIG. 6. (Color online) The rescaled spatial extent of the film region $\hat{\xi}_i - \hat{\xi}_p$ as a function of the rescaled position of the percolation front $\hat{\xi}_p$ for different values of the parameter τ and Bo/Sh = 0.01; $\tau = 1$ (\Box), $\tau = 0.1$ (\bigcirc), $\tau = 0.01$ (\triangle). The dashed lines correspond to the asymptotic dependence of Eq. (44) at large values of $-\hat{\xi}_p$.

Fig. 5 (right), with smaller values of Ca_f leading to longer films as capillarity dominates over viscosity supporting liquid flow over longer distances in the porous medium. This results in later detachment times and a longer CRP that eventually leads to faster drying of the medium.

Figure 6 shows the rescaled extent of the film region $\hat{\xi}_i - \hat{\xi}_p$ 328 as a function of the rescaled percolation front position $\hat{\xi_p}$ for 329 various values of the dimensionless parameter τ . All curves 330 collapse to the same curve at early times, but increasingly 331 deviate later, when the two fronts appear to be separated by 332 only a slowly varying distance, which is the film region extent 333 and which is smaller as τ is larger. An asymptotic analysis of 334 Eq. (43) shows that at sufficiently large times, namely $-\xi_p \gg$ 335 1, we have 336

$$-\hat{\xi_p} \sim \frac{\operatorname{Ca}_f}{J^4} (\hat{\xi_i} - \hat{\xi_p})^4 = \frac{\tau \operatorname{Bo}}{\operatorname{Sh} J^4} (\hat{\xi_i} - \hat{\xi_p})^4,$$
 (44)

³³⁷ which is apparent in Fig. 6.

Before closing this section we note that the previous 338 analysis must be modified when the percolation front reaches 339 the lower boundary. Then the bulk liquid region, providing 340 liquid for the films, no longer exists and the remaining fluid 341 is contained only in the film region. The boundary condition 342 corresponding to the percolation front must now be replaced by 343 its counterpart $\Phi = (\rho_b^3 + 3\text{Bo}I_b + \text{Ca}_f)/(1 + \text{Ca}_f)$ at $\xi_p =$ 344 and the control parameter for evaporation is either the film ξb 345 thickness ρ^* at $\xi = 0$ or the thickness ρ_b at $\xi = \xi_b$. Again 346 we need to distinguish two cases, depending on whether 347 the films detach from the product surface prior to or after 348 the percolation front reaches the bottom of the medium. 349 In the first case, where $\xi_b \leq \xi_{pc}$, Eq. (42) is still valid provided 350

we set $\rho = \rho_b$ at $\xi = \xi_b$, hence

$$\rho_b^3 \bigg[{}_2F_1 \bigg(1, 3/4, 7/4, -3\rho_b^4 \frac{\operatorname{Bo} - \operatorname{Sh}\hat{\xi}_i}{\operatorname{Bo}\tau} \bigg) \bigg]$$
$$= \frac{\operatorname{Bo}\tau}{\operatorname{Bo} - \operatorname{Sh}\hat{\xi}_i} (\hat{\xi}_i - \hat{\xi}_b).$$
(45)

In the second case, where $\xi_b > \xi_{pc}$, it is Eq. (26) that is valid with $\rho = \rho_b$ at $\xi_p = \xi_b$ 353

$$\rho_b^3 \bigg[{}_2F_1 \bigg(1, 3/4, 7/4, -3\frac{\rho_b^4}{\tau} \bigg) \bigg] - \rho^{*3} \bigg[{}_2F_1 \bigg(1, 3/4, 7/4, -3\frac{\rho^{*4}}{\tau} \bigg) \bigg] = -\tau \hat{\xi}_b. \quad (46)$$

The corresponding expression for the flux, $\partial \Phi / \partial \xi$, remains ³⁵⁴ the same as do the evaporation rate expressions. ³⁵⁵

C. The drying curve 356

We proceed now by determining the drying curve. The $_{357}$ dimensional drying rate is obtained from its dimensionless $_{358}$ counterpart through the solution for variable Φ $_{359}$

$$\dot{\Im} = -\frac{D_M r_0^2 C_e (1 + \operatorname{Ca}_f) N_y N_z}{\operatorname{Ca}_f} \frac{d\Phi}{d\xi} \bigg|_{S+}, \qquad (47)$$

where N denotes size. Its constant value at the onset of the process during the CRP will be used to normalize all rates 361

$$\dot{\mathfrak{F}}_{\mathrm{CRP}} = D_M r_0^2 C_e N_y N_z \frac{1}{d}, \qquad (48)$$

hence

$$E = \frac{\dot{\Im}}{\dot{\Im}_{CRP}} = \frac{1}{1 - Sh\xi_i} = \frac{Bo}{Bo - Sh\hat{\xi}_i}.$$
 (49)

This provides a direct relationship between drying rates and the position of the film tips ξ_i , and through the relationship of the latter to the percolation front position ξ_p . To connect the variables to the process time, we will derive expressions for the overall liquid volumetric content, which we will denote as the liquid saturation, S_{res} . This is the combined sum of the bulk liquid in the pores below the percolation front and that contained in the liquid films. The bulk fluid contribution is $4(\xi_p - \xi_b)$ assuming $\xi_p \ge \xi_b$. The amount in the films S_f is obtained by integrating the cross sectional area of the film region $\xi_i - \xi_p$, which is proportional to ρ^2 , hence 363

$$S_f = -C^* \int_{\xi_i}^{\xi_p} \rho^2 d\xi.$$
 (50)

During the CRP we have

$$S_{f} = C^{*} \int_{\rho^{*}}^{1} \frac{3\rho^{4}d\rho}{\text{ShCa}_{f} + 3\text{Bo}\rho^{4}}$$

= $\frac{C^{*}}{\text{Bo}} \bigg[1 - {}_{2}F_{1} \bigg(1, 1/4, 5/4, -\frac{3}{\tau} \bigg) \bigg]$
 $- \rho^{*} \frac{C^{*}}{\text{Bo}} \bigg[1 - {}_{2}F_{1} \bigg(1, 1/4, 5/4, -\frac{3}{\tau} \rho^{*4} \bigg) \bigg], \quad (51)$

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³⁷⁵ while following detachment (during the FRP),

$$S_{f} = C^{*} \int_{0}^{1} \frac{3\rho^{4} d\rho}{\frac{ShCa_{f}}{1-Sh\xi_{i}} + 3Bo\rho^{4}}$$
$$= \frac{C^{*}}{Bo} \left[1 - {}_{2}F_{1} \left(1, 1/4, 5/4, -\frac{3}{\tau E} \right) \right], \qquad (52)$$

where we used Eq. (49). The overall liquid saturation, $S_{\rm res}$, is

$$S_{\rm res} = \frac{4(\xi_p - \xi_b) + S_f}{-4\xi_b}.$$
 (53)

The above equations relate implicitly the position of the percolation front ξ_p to the remaining liquid saturation. The relation to time results from the mass balance

$$\frac{dS_{\rm res}}{dt} = -E.$$
(54)

The above are valid before the percolation front reaches the bottom of the medium. After that condition is reached, the film thickness is obtained from Eqs. (45) and (46) and a similar procedure can be applied. For simplicity, details will be omitted.

The drying curve is a plot of the normalized evaporation flux *E* versus the liquid saturation S_{res} . By using the previous expressions we construct the plots shown in Fig. 7 that demonstrate the shape of the drying curve for different values of Bo and fixed values of Ca_f and Sh. The curves show a



FIG. 7. (Color online) Dimensionless drying rate *E* as a function of the liquid saturation S_{res} for different values of the bond number $[\text{Bo}_x = -0.1 \text{ (red-dashed line); } B_x = -0.01 \text{ (blue-dotted line);} Bo_x = -0.001 \text{ (green-dot-dashed line); } Bo_x = -0.0001 \text{ (orange$ $continuous line)] for Ca_f = 0.01, Sh = 0.1, and <math>\xi_b = -1000$. The smaller the effect of gravity, the longer the CRP. The curves correspond to a solution where the films detach from the product surface before the percolation front reaches the bottom of the medium, namely when $\xi_{\text{pc}} \ge \xi_b$. Note the difference in the curves at lower bond numbers as the bottom boundary is approached.

clear CRP, where E = 1, at early times (higher values of liquid 390 saturation $S_{\rm res}$) that lasts until the films detach from the product 391 surface S (when the percolation front reaches ξ_{pc}). The plot 392 shows that the CRP is shorter for higher values of the bond 393 number that corresponds to stronger buoyancy effects within 394 the films. After that time, the drying rate decreases rapidly as 395 a completely dry region of increasing extent develops between 396 the evaporation front ξ_i and the product surface. This regime 397 corresponds to the FRP. A last regime occurs at very low 398 residual saturations, when the percolation front reaches the 399 bottom of the medium, and the bulk liquid has evaporated. 400 This regime corresponds to the shrinking of the liquid films 401 and is particularly evident for higher values of Bo. It is also 402 interesting to note that the dimensionless drying rate E has 403 a value slightly greater than zero at the limit $S_{\rm res} \rightarrow 0$ that 404 corresponds to an evaporation front ξ_i located exactly at the 405 bottom of the medium ξ_b , namely $E_{\min} = \frac{1}{1 - \text{Sh}\xi_b}$. 406

Of importance is the critical saturation S_{res}^{c} when the CRP 407 regime ends, namely when the surface film thickness becomes 408 $\rho^* = 0$ for the first time. Its value depends on whether the films 409 detach from the surface before ($\xi_b \leq \xi_{pc}$) or after ($\xi_b > \xi_{pc}$) the 410 percolation front has reached the bottom boundary ξ_b . After 411 calculations, omitted for simplicity, we find 412

$$S_{\text{res},1}^{c} = 1 + \frac{1}{\tau \hat{\xi}_{b}} \bigg[{}_{2}F_{1} \bigg(1, 3/4, 7/4, -\frac{3}{\tau} \bigg) \bigg] \\ - \frac{C^{*}}{4\hat{\xi}_{b}} \bigg[1 - {}_{2}F_{1} \bigg(1, 1/4, 5/4, -\frac{3}{\tau} \bigg) \bigg], \quad (55)$$

in the first case, and

5

$$\Gamma_{\text{res},2}^{c} = -\frac{\text{Bo}S_{f}}{4\hat{\xi}_{b}} = -\frac{C^{*}\rho_{b}}{4\hat{\xi}_{b}} \bigg[1 - {}_{2}F_{1}\bigg(1, 1/4, 5/4, -\frac{3\rho_{b}^{4}}{\tau}\bigg) \bigg],$$
(56)

where ρ_b is given by

$$\rho_{b2}^{3}F_{1}\left(1,3/4,7/4,-\frac{3\rho_{b}^{4}}{\tau}\right) = -\tau\hat{\xi}_{b}$$
(57)

in the second. As expected, if the medium is infinitely long, the critical saturation is equal to 1. Figure 8 shows the critical saturation for various values of τ for this case. As expected the critical saturation parameter is a strong function of τ .

IV. GRAVITY-ENHANCED DRYING, $Bo_x = Bo > 0$ 419

A. 1D predictions

The previous analysis was developed under the condition 421 that gravity opposes liquid flow through the films where a 1D 422 effective continuum solution is valid. This may not necessarily 423 be the case when film flow is enhanced by gravity ($B_x > 0$). 424 Under this condition and for sufficiently strong buoyancy, both 425 the percolation and the evaporation front are likely to become 426 unstable, mass transfer through the porous medium will not 427 be sufficiently fast to balance gravity and establish a quasi-1D 428 regime, and the films will remain at the product surface for very 429

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FIG. 8. (Color online) Critical saturation S_{res}^c vs parameter τ when the films detach before the percolation front reaches the bottom of the medium ($\hat{\xi}_b < \hat{\xi}_{\text{pc}}$) for various values of $\hat{\xi}_b$; $\hat{\xi}_b = -20 \ (\Box)$, $\hat{\xi}_b = -10 \ (\Delta)$, $\hat{\xi}_b = -5 \ (\bigcirc)$. From the solution of Eq. (55).

long times leading to longer CRPs and a faster recovery of the
liquid. In the case, however, that gravity is not so strong, it is
possible that mass transfer can be sufficiently fast to convect
the gravity-draining liquid through the films and establish
a flow regime that can be approached with the previous
methods.

To determine if such a regime exists we consider the 1D analysis of the previous section for $Bo_x > 0$. In this case films will stay at the product surface S provided that a solution of the following equation, which is the counterpart of Eq. (24) for $Bo_x > 0$, exists:

$$\int_{\rho^*}^1 \frac{3\rho^2 d\rho}{\operatorname{ShCa}_f - 3\operatorname{Bo}\rho^4} = -\xi_p.$$
(58)

⁴⁴¹ Clearly, a necessary condition is that the integral does not⁴⁴² diverge, which is satisfied if

$$\operatorname{ShCa}_f > 3\operatorname{Bo} \Rightarrow \tau > 3.$$
 (59)

This condition is favored by stronger viscous forces (compared 443 gravity) and faster mass transfer in the dry region and over to 444 the product surface. Then, a solution to Eq. (24) exists and 445 can be computed as in the previous sections. The resulting 446 surface film thickness ρ^* at the surface as a function of the 447 percolation front position ξ_p is shown in Fig. 9 for the case 448 of gravity-enhanced drying ($Bo_x > 0$), and the cases of zero 449 gravity ($Bo_x = 0$) and gravity-opposed drying ($Bo_x < 0$). The 450 solution for $\rho^* = 0$ gives the critical position of the percolation 451 front ξ_{pc} . Larger values of Bo_x lead to later detachment times 452 and evidently longer CRPs. 453



FIG. 9. (Color online) Film thickness ρ^* as a function of the position of the percolation front ξ_p for the case of gravity-enhanced drying, $Bo_x = 0.0001 (\Box)$, when gravity is neglected, $Bo_x = 0 (\Delta)$, and when it opposes drying, $Bo_x = -0.0001 (\bigcirc)$. The CRP lasts longer when $Bo_x > 0$ as expected. $Ca_f = 0.01$, Sh = 0.1.

After the films detach, and always under the condition of 454 Eq. (59), their thickness is obtained through equation 455

$$\int_{0}^{\rho} \frac{3\rho^2 d\rho}{\left(\frac{\mathrm{ShCa}_f}{1-\mathrm{Sh\xi}_i} - 3\mathrm{Bo}\rho^4\right)} = \xi_i - \xi.$$
(60)

As the magnitude of ξ_i increases, however, the above integral 456 will diverge when the following condition is approached 457

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$$-\xi_{is} = \frac{\left(\frac{\tau}{3} - 1\right)}{\mathrm{Sh}} \text{ or } H = \frac{\pi\beta}{C^*} \frac{D_M C_e \nu}{\rho g r_0^2} - \frac{D}{\lambda}, \qquad (61)$$

where $H = (-\xi_{is})r_0$ and $D = dr_0$ are the dimensional position 458 and boundary layer thickness, respectively. This implies that 459 the evaporation front will become stationary at that location. 460 Inspection of Eq. (61) shows that this location consists of two 461 competing terms; one due to gravity involving τ , which does 462 not depend on surface tension, and another corresponding to 463 external mass transfer. Under the condition that diffusivity 464 within the medium and viscous forces are strong enough to 465 balance gravity, or that external mass transfer is not very 466 strong, films will detach and their tips will stabilize at a fixed 467 location. Such behavior is indeed demonstrated in Fig. 11. The 468 location of the evaporation front ξ_i reaches a stationary state 469 at sufficiently large values of time (position of the percolation 470 front ξ_p (inset of Fig. 11). It is interesting to note that the 471 film thickness profile in Fig. 10 is qualitatively different from 472 that of gravity-opposed drying. The film thickness becomes 473 almost constant and equal to unity away from the film tips, 474 and decreases rapidly to zero as that position ξ_i is approached. 475



FIG. 10. (Color online) Plot of the film thickness ρ vs $\hat{\xi}$ for the case of gravity-enhanced drying when Bo/Sh = 0.1, Ca_f = 1 and $\hat{\xi}_p = -8$. The film thickness remains practically constant and equal to unity along the entire length of the film region, except very close to the film tips $\hat{\xi}_i$, where it decreases sharply to zero.

This practically implies that the flow through the films is driven by gravity, rather that capillarity-induced pressure gradients, since the term $\frac{\partial r^3}{\partial x} \simeq 0$ in Eq. (3). The above analysis suggests that when the evaporation front

The above analysis suggests that when the evaporation front reaches the stationary state, the drying curve should exhibit a second period of constant drying rate (following the initial CRP and FRP) when the dimensionless drying rate becomes equal to $E = \frac{3}{\tau}$. This behavior is indeed demonstrated in Fig. 11.

B. Linear stability analysis of buoyant instability of an evaporation front

While the previous analysis showed that a stationary front 487 for the film tips is possible for a percolation front that 488 continuously recedes deeper in the pore space, it cannot 489 indicate whether it is in fact stable. To verify its stability we 490 consider a somewhat simpler approach in the absence of films, 491 shown in right side of Fig. 12. In this model, liquid (darker as 492 gray) drains downward due to gravity in a porous medium of 493 porosity ϕ and permeability k. At a finite location z = -H, it 494 evaporates and then diffuses through the medium (lighter gray 495 region) toward the outside of the medium where it is purged at 496 the mass boundary layer (white region). The concentration of 497 the liquid vapors is zero at z = D. We will find the stationary 498 states of this process and their stability. 499

Here we introduce the following dimensionless notation, where all lengths are normalized with H, concentration with c_e , pressure with $\rho g H$, fluid velocity with $k \rho g / \mu$, and



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FIG. 11. (Color online) Drying curve for the unstable case, $Bo_x > 0$, under the condition $\tau > 3$. The curve clearly exhibits two CRP regimes: an early one that lasts until the films detach from the product surface S–and a late one that occurs when the condition of Eq. (61) is satisfied. $Ca_f = 1.0$, $Bo_x = 0.01$, Sh = 0.1, and $\xi_b = -180$. Inset shows the corresponding position of the evaporation front ξ_i as a function of the position of the percolation front ξ_p . The stationary state solution for ξ_i corresponds to the solution of Eq. (61).

time with $\phi H \mu / k \rho g$. The evaporation front is considered at ⁵⁰³ location ⁵⁰⁴

$$\Upsilon \equiv z - f(y,t). \tag{62}$$

The relevant dimensionless Darcy's law, continuity and diffusion equations are respectively 506

$$\vec{u} = -\vec{\nabla}p + \vec{i},\tag{63}$$

$$\vec{\nabla} \cdot \vec{u} = 0$$
, and (64)

$$\nabla^2 \zeta = 0, \tag{65}$$

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where \vec{i} is the unit vector in the downward direction.

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At the interface the liquid pressure is assumed zero (equal 508 to the surrounding constant gas pressure and in the absence of capillary or surface tension effects) and the mass balance reads 511

$$u_n + \operatorname{Ra}_k \frac{\partial \zeta}{\partial n} = \phi v_n \equiv -\Upsilon_t / |\vec{\nabla}\Upsilon|, \qquad (66)$$

where $\operatorname{Ra}_{k} = \frac{C_{e}D_{M}v}{\rho_{I}gkH}$ is analogous to the above-defined number 512 for evaporation in porous medium and v_{n} is the normal 513 component of the interface velocity. At the product surface 514 z = 0, we have continuity of concentration and mass fluxes, 515 and at $z = d_{s}$, $\zeta = 0$. 516



FIG. 12. (Color online) (Left) Dispersion relation of the linear stability analysis for various values of Ra_k and $\lambda = 1$; $d_s = 1$. Ra_k = 0.8 (\bigcirc), Ra_k = 1 (\triangle), and Ra_k = 1.3 (\square). For Ra_k > 1 the condition of Eq. (73) is always fulfilled. (Right) Schematic of the process for the linear stability analysis of an evaporation front in the presence of gravity with Bo_x > 0. Liquid (darker gray region) drains downwards due to gravity and evaporates at position z = -H. It then diffuses through the porous medium and the mass boundary layer (lighter gray regions). The concentration of the liquid vapors is zero at z = D.

⁵¹⁷ The properties of the stationary state are easily derived;

$$f = -1; \quad p_0 = \left(1 - \frac{\lambda Ra_k}{\lambda + d_s}\right)(z+1);$$

$$\zeta_0 = 1 - \frac{\lambda(z+1)}{\lambda + d_s}; \quad -1 < z < 0;$$

$$\zeta_0 = \frac{d_s - z}{\lambda + d_s}; \quad 0 < z < d_s.$$
(67)

Importantly, this state requires that the liquid viscous flow rate
 is balanced by evaporation and diffusion into the surroundings.
 Expressed in terms of dimensional variables this condition
 reads

$$H = \frac{D_M C_e \nu}{k \rho g} - \frac{D}{\lambda}.$$
 (68)

Note the similarity of Eq. (68) to those of the stationary evaporation front, Eq. (61). Again, we note that the stationary front consists of two counterbalancing terms, one due to gravity and the other due to mass transfer. If gravity is sufficiently small, namely when

$$\mathrm{ShRa}_{\mathrm{k}}\frac{H}{r_0} > 1, \tag{69}$$

then a balance and a stationary state exists within the porous medium. The above condition is analogous to the condition $\tau > 3$, derived for the more general problem that accounts also for the liquid films.

For a linear stability analysis, we next take small (ϵ) perturbations at the front, of wave vector α and temporal growth rate σ

$$f(y,t) = -1 + \epsilon \exp(i\alpha y + \sigma t) \tag{70}$$

⁵³⁴ and corresponding perturbations on the pressure and ⁵³⁵ concentration. These are substituted and linearized in Eqs. (62) and (63) and the boundary conditions of Eq. (66). 536 After tedious calculations, we obtain the linears stability 537 dispersion relation for the rate of growth as a function of the 538 wave number 539

$$\sigma = \left(1 - \frac{\lambda Ra_k}{\lambda + d_s}\right) \alpha - \left(\frac{\lambda Ra_k}{\lambda + d_s}\right) \times \frac{\sinh \alpha d_s \sinh \alpha + \lambda \cosh \alpha d_s \cosh \alpha}{\sinh \alpha d_s \cosh \alpha + \lambda \cosh \alpha d_s \sinh \alpha} \alpha, \quad (71)$$

which is plotted in Fig. 12. As can be shown analytically, the 540 long-wave (small wave number) (LW) limit is stable, whereas 541 the short-wave (SW) limit could be either stable or unstable 542

$$\sigma_{\rm LW} = -\frac{\lambda^2 Ra_k}{(\lambda + d_s)^2}; \ \ \sigma_{\rm SW} = \left(1 - \frac{2\lambda Ra_k}{\lambda + d_s}\right)\alpha.$$
(72)

The condition for stability is therefore

$$2\mathrm{Ra}_{\mathrm{k}} > 1 + \frac{d_s}{\lambda}.\tag{73}$$

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Using Eq. (68) for *H*, the above reads

$$Ra_k > 0, \tag{74}$$

which is always satisfied. We conclude, therefore, that if the condition of Eq. (69) is satisfied, the evaporation front is stable. ⁵⁴⁶ By extension, we believe that the same applies to the general case described in the previous section under the condition $\tau > 3$. ⁵⁴⁹

V. CONCLUSION 550

We have presented a mathematical model for the drying 551 of porous media that accounts for capillarity-induced flow 552 through liquid films, the effect of gravity on the extent of 553 the film region, and mass transport through an external mass 554

boundary layer over the medium surface. By treating the 555 medium as a 1D continuum in the case when gravity opposes 556 drying, thus leading to a stable percolation front, we obtain 557 analytical expressions for all relevant variables, such as the 558 drying rates and the critical saturation that marks the transition 559 from the constant to the falling rate periods. Based on these 560 expressions, we study the effect of capillarity (expressed as 561 a film-based capillary number) and gravity (through the bond 562 number). In such cases, gravity opposes drying and leads to a 563 shorter CRP regime, shorter films, and reduction of the overall 564 drying rate. When gravity enhances film flow, the analytical 565 results are valid only when a suitably defined Rayleigh number 566 is sufficiently large to stabilize the front. This condition is 567 qualitatively similar to a condition obtained by considering 568 the linear stability analysis of a simpler 2D problem. We 569 find that in the latter case, there exists a solution where the 570

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evaporation front reaches a stationary state, thus leading to a second constant rate period regime that occurs after the films detach from the medium surface. The detailed analysis of the destabilizing case will be the subject of a pore-network study to be presented, along with supporting experimental results in future work. 576

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