Conceptual modeling of temperature effects on capillary pressure in dead-end pores

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Abstract. The effect of temperature on the liquid–gas interface and consequently on the capillary pressure in unsaturated dead-end pores is conceptually modeled in this paper. Trapping of non-wetting fluid (e.g., air) in the dead-end pores impacts the capillary pressure–saturation relationship and affects the continuous flow of wetting fluids. In the dead-end pore, which is assumed to be a simple vertical cylindrical capillary tube with one end closed and the other end open to the liquid body, the dependence of solid–liquid and solid–air interfacial tensions on temperature and its subsequent effects on the contact angles are deduced. A non-linear ordinary differential equation, using the Young–Laplace equation, in terms of a contact-angle-sensitive temperature function is derived and numerically solved using the fourth order Runge–Kutta method. This temperature function is used to obtain the capillary pressure–temperature relationship for a solid–liquid–air capillary system. Two example problems, first a glass–water–air capillary system and second a polytetrafluoroethylene–n-hexadecane–air capillary system, are solved here. A linear decrease in capillary pressure with temperature is observed, suggesting that entrapped air affects capillary pressure in dead-end pores. A similar linear decrease in capillary pressure, consistent with experimental observations, is observed for open-end pores.

Keywords. Dead-end pores; Young–Laplace equation; capillary pressure; temperature; numerical modeling.

1. Introduction

Void space in unsaturated soil consists of two phases of fluid – *wetting* and *non-wetting*. Two-phase flow in unsaturated soil is governed by *capillary pressure vs. saturation relationship* (CPSR) [1] and is generally obtained through some standard empirical relationships [2, 3] fitted to experimental data for a particular soil. Capillary pressure is defined as the pressure difference across the interface of the two immiscible fluids – *wetting* and *non-wetting* fluids, and is determined by the surface tension and curvature of the interface [4]. In a wet situation, the residual non-wetting fluid remains trapped in the crevices of pores or in dead-end pores due to the presence of wetting fluid and provides an interface between wetting and non-wetting fluids. During air sparging, which is a groundwater re-mediation technique to displace water with the injection of air, there are chances that the air bubble remains in dead-end pores [5]. Dead-end pores are also known as stagnant pockets [6]. Their geometry, i.e. closed end (one end is closed and other is connected to the *active* pores), makes the fluids in these zones stagnant as the name suggests. Thus any change in these zones affects capillary pressure or CPSR for a given degree of saturation and affects the flow characteristics in the soil. Trapping of non-wetting

fluid is one of the reasons for the hysteresis effect of CPSR and vice versa [7]. Appropriate drainage of irrigated lands is one of the most important factors in improving the yield from agricultural fields as well as preventing water logging and salinity [8, 9]. During the subsurface drainage of excess liquid from irrigated lands, the liquid starts to come from all corners of soil to the main pore channels and subsequently moves to the ditches or perforated pipes. However, due to suction or capillary pressure, the liquids from the stagnant zones contribute less to the flow and may also resist the drainage flow. Thus dead-end pores can play a role during the drainage phenomena through soil pores.

The increase in surface and subsurface infrastructures to accommodate the needs of ever-rising human population, along with global warming, has led to the rising of subsurface temperature [10, 11]. Temperatures in and around big cities are becoming high to higher and this is known as *urban heat island effect* [12–16]. This has a further impact on the groundwater hydrology [17] and has already affected all the terrestrial water storage (sum of groundwater, soil moisture, surface water, snow and ice) [18]. Subsurface temperature can affect the physics of fluid inside the soil in terms of capillary pressure. In this paper, we attempt to gain a conceptual insight into the temperature effects on capillary pressure inside the dead-end pores that to the best of our knowledge hitherto has been very rarely studied.

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Dead-end pores are generally studied in reference to diffusion within mobile and immobile or dead-end pores [19–23] and in reference to oil recovery through different techniques [24–29]. Therefore this paper tries to understand the much overlooked dead-end pores of soil and their influence on the flow characteristics in terms of capillary pressure (as also mentioned by Fatt [30]). Temperature effects on capillary pressure in general were studied by many researchers [31–35] and are found to be elusive still today. This paper considers the dead-end pore as a capillary tube with one end closed and another end in touch with an infinite source of wetting fluid. This assumption is justified as one end of dead-end pores is usually connected to the main flow channel or *active* pores. Air is taken as non-wetting fluid in this study. The Young–Laplace equation is invoked and differentiated with respect to temperature with some assumptions for our problem domain. A differential equation of a *temperature function* is obtained and consequently, capillary pressure is deduced from this function. Through example problems, we present the effects of properties of air, liquid, and solid as well as the physical dimension of the dead-end pore on capillary pressure-*vs.*-temperature relation. In a subsequent section, the capillary pressure-*vs.*-temperature relation is derived in the same way for an open-end capillary tube for comparison purposes.

2. Mathematical modeling

In this paper, capillary pressure (P_c) is introduced as an explicit function of two distinct variables – temperature-dependent variables (say, $G(T)$) and temperature-independent variables (say, M) i.e. $P_c(T) = P_c(G(T), M)$. The capillary pressure *vs.* temperature is assumed to be a non-hysteric one for a particular liquid saturation, as suggested and verified by researchers [33, 34, 36]. Therefore, a single relationship will be sufficient for both heating and cooling curves, i.e. both curves are actually the same – no hysteresis – no two values of P_c at single T . Then the total derivative of $P_c(G, M)$ with respect to temperature T will be

$$\frac{dP_c}{dT} = \frac{\partial P_c}{\partial G} \frac{dG}{dT} + \frac{\partial P_c}{\partial M} \frac{dM}{dT} = \frac{\partial P_c}{\partial G} \frac{dG}{dT} + 0 = \frac{\partial P_c}{\partial G} \frac{dG}{dT}. \quad (1)$$

Similarly, from here onwards, it is assumed that every other physical property is either a function of temperature (like $G(T)$) or not (like M). Under static equilibrium scenario in a cylindrical capillary tube with a spherical meniscus (assumed) (figure 1), the Young–Laplace equation is [37]

$$P_c = \frac{2\sigma}{r} \cos \theta, \quad (2)$$

where σ is the surface tension of the liquid (N/m), θ the contact angle between the air–liquid interface and the solid surface (deg) and r the radius of the capillary tube (m). The Young’s equation at static equilibrium is [38]

Figure 1. A schematic of liquid rise in a capillary tube.

$$\gamma_{sa} - \gamma_{sl} = \sigma \cos \theta, \quad (3)$$

where γ_{sl} is the interfacial tension between solid and liquid surfaces (N/m), and γ_{sa} is the interfacial tension between solid and air surfaces (N/m).

Assuming that the whole system is in static equilibrium in capillary tube, the capillary pressure at the interface or meniscus is $P_c = P_{\text{air}} - P_{\text{liquid}}$, where P_{air} is the pressure of air in the closed section of the tube (N/m² or Pa) and P_{liquid} is the pressure in liquid immediately under the meniscus (Pa) [37, 39]. Air in the closed section is assumed to be an *ideal* gas (where there are no intermolecular forces and interactions among gas molecules) and thus follows the ideal gas law [40]:

$$P_{\text{liquid}} = \frac{nRT}{V_{\text{air}}} - P_c, \quad (4)$$

where R is universal gas constant (N-m/K-mol), n number of moles of gas (or air) (mol), T temperature (K) and V_{air} volume of air (m³).

The liquid pressure in the capillary tube is assumed to conform to the law of hydrostatics [39]. Since the pressure in the liquid is connected to an active or main channel, the pressure in the liquid in capillary gets reduced towards meniscus level above the channel and thus the liquid pressure at the bottom of the meniscus is

$$P_{\text{liquid}} = P_{\text{ref}} - \rho gh, \quad (5)$$

where P_{ref} is the pressure at the bottom of the tube (taken as atmospheric pressure like water table, P_{atm} for simplicity and assumed to be temperature-independent) (Pa), ρ the density of liquid (kg/m³), g the acceleration due to gravity (9.81 m/s²) and h the height of liquid rise in the tube (m) (see figure 1).

Comparing Eqs. (4) and (5), we have

$$P_{\text{atm}} + P'_{\text{liquid}} = \frac{nRT}{V_{\text{air}}} - P_c, \quad (6)$$

where $P'_{\text{liquid}} = \rho g(-h)$.

As air cannot escape in the case of closed-end pore, the mass of air will be a constant, and therefore, the number of moles of air (n) is treated as a temperature-independent variable. Differentiating Eq. (6) with respect to temperature T and with the help of Eqs. (2) and (3), we get

$$\frac{dP'_{\text{liquid}}}{dT} = \frac{nR}{V_{\text{air}}} - \frac{nRT}{V_{\text{air}}^2} \frac{dV_{\text{air}}}{dT} - \frac{2}{r} \left(\frac{d\gamma_{\text{sa}}}{dT} - \frac{d\gamma_{\text{sl}}}{dT} \right). \quad (7)$$

Volume of the air section above the air–liquid interface in the capillary tube can be rearranged to get a contact-angle-sensitive temperature function $f_{\theta}(T)$ as follows:

$$V_{\text{air}} = \pi r^2 H_{\text{air}} + \frac{\pi r^3}{\cos^3 \theta} \left(\frac{1}{3} \sin^3 \theta - \sin \theta + \frac{2}{3} \right), \quad (8a)$$

$$\frac{V_{\text{air}}}{\pi r^3} - \frac{H_{\text{air}}}{r} = \frac{1}{\cos^3 \theta} \left(\frac{1}{3} \sin^3 \theta - \sin \theta + \frac{2}{3} \right) = f_{\theta}(T), \quad (8b)$$

where H_{air} is the height of the air section in the capillary tube (m) (see figure 1).

According to studies done by other researchers [38, 41–43], the liquid–air interface or meniscus can adjust itself for small pressure changes to nullify the imbalance without any vertical movement. Hence the meniscus gets stuck or pinned at the *hardly* smooth natural surface of the solid. This pinning phenomenon or formally *contact line pinning* (CLP) causes the contact angle hysteresis (a difference between the maximum and minimum θ) [44]. Contact angle hysteresis, therefore, suggests that there is no unique value for contact angle even at static equilibrium [45]. The authors in this research opine that this phenomenon may or is rather probable to happen for temperature variation within a certain range of temperatures (say ΔT). Within this range, meniscus behaves as elastic and liquid sticks to the solid surface before meniscus starts moving (after surpassing some *energy barrier* [see [46, 47], for more details]). As an example, it takes $T \sim 10^3$ K for water–air meniscus even to overcome one nanometer of defect on quartz glass substrate if pinned [48–50]. Thus, CLP implies that H_{air} is independent of temperature within this small interval of temperature, in which the translation motion of the meniscus along the solid surface is absent, i.e. $dH_{\text{air}}/dT = 0$.

Applying the assumption of $dH_{\text{air}}/dT = 0$, substituting Eq. (8b) in Eq. (7) and after some simplifications, we have

$$\begin{aligned} nRT \frac{df_{\theta}(T)}{dT} &= nR \left(f_{\theta}(T) + \frac{H_{\text{air}}}{r} \right) \\ &\quad - \pi r^3 \left(f_{\theta}(T) + \frac{H_{\text{air}}}{r} \right)^2 \frac{dP'_{\text{liquid}}}{dT} \\ &\quad - 2\pi r^2 \left(f_{\theta}(T) + \frac{H_{\text{air}}}{r} \right)^2 \left(\frac{d\gamma_{\text{sa}}}{dT} - \frac{d\gamma_{\text{sl}}}{dT} \right). \end{aligned} \quad (9)$$

Grant [34] argued that interfacial tension is a linear function of temperature, and the difference of their temperature derivatives ($d\gamma_{\text{sa}}/dT - d\gamma_{\text{sl}}/dT$) in Eq. (9) becomes a constant (let us say this constant is C_{γ}).

Meniscus height H_m is deduced as (see figure 1)

$$H_m = H_{\text{liquid}} - h = r(\sec \theta - \tan \theta), \quad (10)$$

where H_{liquid} is the height of the liquid section. Equation (8b) can be rewritten with help of Eq. (10) in terms of H_m as

$$H_m^3 + (3r^2)H_m + (-6r^3 f_{\theta}) = 0. \quad (11)$$

On solving Eq. (11), we have three roots for H_m , among which one is a *real* root and other two are *conjugate complex* roots. The real root of Eq. (11) is

$$\begin{aligned} H_m(f_{\theta}) &= - \frac{r^2}{\left(3f_{\theta}r^3 + \sqrt{r^6 + 9f_{\theta}^2 r^6} \right)^{1/3}} \\ &\quad + \left(3f_{\theta}r^3 + \sqrt{r^6 + 9f_{\theta}^2 r^6} \right)^{1/3}. \end{aligned} \quad (12)$$

From Eq. (6) $P'_{\text{liquid}} = -\rho gh = -\rho g(H_{\text{liquid}} - H_m(f_{\theta}))$ (see figure 1). The derivative of P'_{liquid} with respect to T is

$$\frac{dP'_{\text{liquid}}}{dT} = \rho g \frac{dH_m}{df_{\theta}} \frac{df_{\theta}}{dT}, \quad (13)$$

since H_{liquid} is constant due to CLP condition. Substituting Eq. (13) in (9) and performing some arithmetic operations and simplifications, a differential equation of f_{θ} with respect to T is obtained:

$$\begin{aligned} T \frac{df_{\theta}}{dT} + \rho(T) \left[(A_1 f_{\theta}^2 + A_2 f_{\theta} + A_3) \frac{dH_m}{df_{\theta}} \right] \frac{df_{\theta}}{dT} \\ + (B_1 f_{\theta}^2 + B_2 f_{\theta} + B_3) = 0, \end{aligned} \quad (14)$$

where the intermediary temperature-independent terms are

$$\begin{aligned} A_1 &= \frac{g\pi r^3}{nR}, A_2 = \frac{2g\pi r^2 H_{\text{air}}}{nR}, \\ A_3 &= \frac{g\pi r H_{\text{air}}^2}{nR}, B_1 = \frac{2\pi r^2 C_{\gamma}}{nR}, \\ B_2 &= \frac{4\pi r H_{\text{air}} C_{\gamma}}{nR} - 1, B_3 = \frac{2\pi H_{\text{air}}^2 C_{\gamma}}{nR} - \frac{H_{\text{air}}}{r} \text{ with} \\ \frac{dH_m}{df_{\theta}} &= \frac{r^3 [r^2 + (3f_{\theta}r^3 + D)^{2/3}]}{D(3f_{\theta}r^3 + D)^{1/3}} \text{ where } D = \sqrt{r^6 + 9f_{\theta}^2 r^6}. \end{aligned}$$

Equation (14) is a non-linear first-order ordinary differential equation. Equation (14) can be solved using an analytical or numerical method. In this paper, we solve Eq. (14) using the fourth-order Runge–Kutta (RK4) numerical method (see [51] to know more about RK4).

At a particular temperature (say T_p), liquid rises through capillary effect through the open-end section of the one-end-closed capillary tube. The calculation of the number of moles of gas before and after the capillary rise is as follows. Before the liquid starts to enter into the tube, only air molecules fill up the tube. Initially let the number of moles of air be n_i . After a certain time, the liquid meniscus will reach some height and stop, and the whole system reaches static equilibrium. Again, let the number of moles of air in the portion between the water meniscus and top closed end of the capillary tube be n_f . It is assumed that there is no loss of air molecules or no air is dissolved in the liquid from the moment of touch of the capillary tube on the water surface in the infinite reservoir to the time to reach Jurin height. Then the number of moles of air is $n_i = n_f = n$. Accordingly, the number of moles of air is

$$n = \frac{(P_{\text{air}})_i (V_{\text{air}})_i}{RT_p}, \quad (15)$$

where $(P_{\text{air}})_i = P_{\text{ref}} = P_{\text{atm}}$, $(V_{\text{air}})_i = V_T = \pi r^2 H_T =$ total volume of the capillary tube and H_T is the total height of the capillary tube (m).

Capillary pressure can be evaluated from Eq. (6) as a function of temperature, i.e. as temperature function $f_\theta(T)$, which can be obtained from Eq. (14) as

$$P_c = \frac{nRT}{V_{\text{air}}} - P_{\text{atm}} + \rho g h, \\ P_c(T) = \frac{nRT}{V_{\text{air}}(f_\theta(T))} - P_{\text{atm}} + g\rho(T)(H_{\text{liquid}} - H_m(f_\theta(T))). \quad (16)$$

In Eq. (14) as well as in Eq. (16), the density of liquid ($\rho(T)$) can be given as direct input through available empirical relationship of density of liquid vs. temperature from different sources [52, 53].

3. Results

The concepts developed in Section 2 to determine the capillary pressure for solid–liquid–gas system in a closed-end capillary tube that mimics the dead-end pores in soils are used to solve two example problems as shown below.

3.1 Example 1 (solid: glass and liquid: water)

A glass–water–air (G–W–A) combination is considered as the solid–liquid–gas system in this example for the capillary action. One end of the cylindrical glass tube is open and the other end is closed. Let the temperature of air in the empty closed-end cylindrical capillary glass tube be initially 298.15 K (figure 1). The Standard Temperature and Pressure (STP) used in this research have the temperature value at 298.15 K and pressure at 101325 Pa. The empty glass tube is placed

inverted with the closed end at the top and the open end just touching the water surface in the reservoir (figure 1). After a certain time, water rises to the Jurin height, $h = (2\sigma \cos \theta_{\text{eq}})/(r\rho g)$ under static equilibrium [39] (θ_{eq} is the contact angle at the static equilibrium, i.e., static contact angle or otherwise known as *equilibrium* contact angle [54]). The assumption here is that the Jurin height or capillary rise will be the same for the closed-end capillary tube. This assumption is kept valid by keeping the Bond number (Bo) [55] to be much less than 1, i.e. assuring that the surface forces will be dominant. Therefore, the condition for the radius of the tube is $r \ll \sqrt{(\sigma/\rho g)}$. The radius of the tube is assumed based on the soil pore size, i.e. approximately 50 μm [56, see table 2] satisfying the afore-mentioned condition of Bo . The total height of the capillary tube, which is 0.50 m, is based on the assumption that the total height has to be more than the maximum possible Jurin height (i.e. the capillary height when $\theta_{\text{eq}} = 0^\circ$). Table 1 gives the necessary values of the parameters of the system. From experimental results of Liechti *et al* [57], and studies from Dean [52] and Mohr *et al* [58], the parameters for this example analysis are adopted.

First, the function $f_\theta(T)$ is calculated for the desired temperatures from the given reference temperature (i.e. 298.15 K). To solve Eq. (14), the values of the intermediary terms A_1, A_2, A_3, B_1, B_2 and B_3 are needed. For the computation of these six intermediary terms, three parameters, i.e. H_{air}, n and C_γ , are evaluated from the basic parameters given in table 1. The steps to calculate these three parameters are as follows: (a) H_{air} can be calculated as $H_{\text{air}} = H_T - (H_m + h)$ (H_m can be obtained from Eq. (10) with θ_{eq}), (b) n can be obtained from Eq. (15) taking T_p as initial temperature, 298.15 K and (c) the solid interfacial surface energies are evaluated from the following equations (found from Girifalco and Good [59] using Eq. (3)) using empirical laws of contact angle, surface tension of liquid and liquid density variations with temperatures.

Interfacial energy between glass and air can be calculated as

$$\gamma_{\text{ga}}(T) = \sigma(T) \left(\frac{(1 + \cos \theta(T))^2}{4(\Phi(T))^2} \right), \quad (17)$$

and interfacial energy between glass and water can be as

$$\gamma_{\text{gw}}(T) = \sigma(T) \left(\frac{(1 + \cos \theta(T))^2}{4(\Phi(T))^2} - \cos \theta(T) \right), \quad (18)$$

where $\Phi(T) = 4(\mathcal{V}_g \mathcal{V}_w(T))^{1/3} (\mathcal{V}_g^{1/3} + (\mathcal{V}_w(T))^{1/3})^{-2}$ and $\mathcal{V}_g, \mathcal{V}_w$ are molar volumes of glass and water, respectively. Molar volumes: $\mathcal{V}_g = \mathcal{M}_g/\rho_g = (60.45 \times 10^{-3} \text{ kg/mol})/(2.52 \times 10^3 \text{ kg/m}^3) = 23.99 \times 10^{-6} \text{ m}^3/\text{mol}$ [61] and $\mathcal{V}_w = \mathcal{M}_w/\rho(T) = (18 \times 10^{-3} \text{ kg/mol})/\rho(T)$, where $\mathcal{M}_g$ and $\mathcal{M}_w$ represent the molar masses of glass and water, respectively (kg/mol) and ρ_g and $\rho(T)$ are densities of glass

Table 1. Parameters used for calculation in glass–water–air system.

Parameter	Description	Value	Reference
σ	Surface tension of water at 298.15 K	71.99×10^{-3} N/m	Dean [52]
ρ	Density of water at STP	996.66 kg/m ³	Dean [52]
g	Acceleration due to gravitation	9.81 m/s ²	Mohr <i>et al</i> [58]
θ_{eq}	Equilibrium contact angle of water on glass	50°	Liechti <i>et al</i> [57]
r	Radius of the tube	50×10^{-6} m	Assumed
R	Universal gas constant	8.314 N-m/K-mol	Mohr <i>et al</i> [58]
H_T	Total glass tube height	0.50 m	Assumed

and water, respectively (kg/m³). Thermal sensitivity of glass is neglected and throughout the paper, the thermal sensitivities of solids in general are neglected because of low thermal coefficient values compared with the liquid counterpart. Data of temperature variations of density, contact angle and surface tension of water are obtained from Dean [52], Neumann [62] and Vargaftik *et al* [63], respectively. Using Eqs. (17) and (18), figure 2 is drawn for different temperatures using available data of the literatures. Linear fit to the data gives the slope values as needed to evaluate C_γ as -8.414×10^{-6} N/m-K.

Using the information of slopes from figure 2 as well as using other input parameters from table 1, the temperature-independent intermediary terms in Eq. (14) are obtained. Using all the above values and $f_\theta(T_s = 298.15 \text{ K}) = (V_{air}/(\pi r^3) - H_{air}/r) = 0.190021$ (from Eq. (8b)) as initial value in the RK4 method, the function $f_\theta(T)$ is calculated for different constant temperatures. Those values of T and $f_\theta(T)$ along with the density values of water at those temperatures from Dean [52] are substituted in Eq. (16) to calculate the capillary pressure, P_c (figure 3). Even though the results are shown as a continuous line, the values of P_c at different temperatures are distinct. The subsurface temperature range fluctuates typically, as an example, around 5–10 K throughout the year as measured by Popiel *et al* [60] at Poznan city in Poland. Therefore we have assumed $\Delta T = 10 \text{ K}$ (298.15–308.15 K) to test our theory and comparison purposes only. Temperatures can further be increased or decreased as your chosen preference with a known initial value. Here the assumption is that temperature range is always within *certain* ΔT to maintain CLP, as mentioned earlier during derivation. It has been checked for further values and it is found that it follows the same trend. For brevity, these results are not included in this paper.

3.2 Example 2 (solid: polytetrafluoroethylene or PTFE and liquid: n-hexadecane)

In the second example, a polytetrafluoroethylene–n-hexadecane–air (P–N–A) combination is considered as the gas–liquid–solid system. The physical parameters as well as the ambient conditions and the size of the capillary are the

Figure 2. Interfacial tension of glass–air and of glass–water vs. temperature plots (γ_{ga} vs. T and γ_{gw} vs. T). **Figure 3.** Capillary pressure vs. temperature plot for G–W–A system.

same as in Example 1 (figure 1). The relevant basic parameters for this study are given in table 2.

Let the temperature of air throughout in the empty closed-end cylindrical PTFE tube be initially at 298.15 K (figure 1). Values of surface tension and equilibrium contact angle of n-hexadecane on PTFE at STP are taken from Neumann *et al* [64]. Density values of n-hexadecane are taken from the website of Dortmund Data Bank [65]. Values of H_{air} and n are obtained in the same way as suggested in Example 1 using the values of basic

Table 2. Parameters used for calculation in PTFE–n-hexadecane–air system.

Parameter	Description	Value	Reference
σ	Surface tension of n-hexadecane at 298.15 K	27.09×10^{-3} N/m	Vargaftik <i>et al</i> [63]
ρ	Density of n-hexadecane at STP	771.44 kg/m ³	Dean [52]
g	Acceleration due to gravitation	9.81 m/s ²	Mohr <i>et al</i> [58]
θ_{eq}	Equilibrium contact angle of n-hexadecane on PTFE	46°	Neumann [62]
r	Radius of the tube	50×10^{-6} m	Assumed
R	Universal gas constant	8.314 N-m/K-mol	Mohr <i>et al</i> [58]
H_T	Total PTFE tube height	0.20 m	Assumed

parameters from table 2. As far as calculation of interfacial tensions $\gamma_{\text{PTFE-air}}$ and $\gamma_{\text{PTFE-n-hexadecane}}$ are concerned, they are directly extracted from the experimental results of Neumann *et al* [64] (reproduced in figure 4). These values can also be obtained from Eqs. (17) and (18) as before. The $\gamma_{\text{PTFE-air}}$ vs. T and $\gamma_{\text{PTFE-n-hexadecane}}$ vs. T graphs are plotted (figure 4) and the difference in slopes ($C_\gamma = -5.643 \times 10^{-5}$ N/m-K) is obtained from linear fit to those data. Using all these values, the intermediary terms of Eq. (14) are calculated; putting the initial value of $f_\theta(T_s = 298.15 \text{ K})$ as 0.213005 in the RK4 method, Eq. (14) is solved for different temperatures. As before, the capillary pressure is calculated and plotted against those temperatures (figure 5) using $f_\theta(T)$ values in Eq. (14) through $H_m(T)$, $V_{\text{air}}(T)$ and density vs. temperature data ($\rho(T)$) (Dortmund Data Bank [65]).

4. Discussion

Results show a linear decrease in capillary pressure as temperature rises. This is consistent with experimental results [33, 66], though here is the case for dead-end pores. Grant [34] suggested this phenomenon to be a universal one, i.e. capillary pressure follows a decreasing linear relationship with temperature for almost every system. In our case, two examples consist of two very different

systems and yet follow the same trend. However, the volume of gas in the tube decreases with the raising of the liquid. The gas law suggests that the pressure of the gas in the capillary should increase during the capillary rise of liquid while other state variables remain constant. Therefore, while temperature changes, the gas and liquid pressures both respond differently. Densities of liquid and gas, i.e. the packing of molecules and intermolecular forces between molecules, are different in liquid and in gas or ideal gas (where there are no intermolecular forces and interactions) and they behave differently as temperature changes. To understand these pressures and to get a better view of what is going on, air and liquid pressure for G–W–A and P–N–A systems are shown disparately in figures 6 and 7. These pressures are just across the air–liquid interface (just below and above the interface).

Figures 6 and 7 show that pressure in liquid for both cases increases with temperature whereas air pressure reduces with temperature. However, air pressure in P–N–A system changes more with temperature than that of G–W–A system and hence it eventually affects the capillary pressure more. It is interesting to know whether there is an intrinsic reason for this or it is something extrinsic or a combination of these two.

For these examples, the radius (r) and the total height (H_T) of the capillary tube are assumed. However, the importance of these parameters on capillary pressure is not ascertained and therefore the exercises are done to evaluate

Figure 4. Interfacial tension of PTFE–air and of PTFE–n-hexadecane vs. temperature plots ($\gamma_{\text{PTFE-air}}$ vs. T and $\gamma_{\text{PTFE-n-hexadecane}}$ vs. T) reproduced from figure 1 of Neumann *et al* [64]. **Figure 5.** Capillary pressure vs. temperature plot for P–N–A system.

Figure 6. Variations (%) of capillary pressure and pressures in air and water vs. temperatures are plotted for G-W-A system. P stands for pressure. P_{initial} means the pressure at reference temperature 298.15 K.

Figure 7. Variations (%) of capillary pressure and pressures in air and n-hexadecane vs. temperatures are plotted for P-N-A system. P_{initial} is the pressure at reference temperature 298.15 K.

capillary pressures for different values of H_T and r (figures 8–11 and 12–15, respectively).

The analyses substantiate that both the physical dimensional factors are important while calculating the capillary pressure from the fact that the magnitudes of capillary pressure drastically change with the change in radius and total height of the tube. Since the top end of the capillary tube is closed, and as per the assumption that gas solubility in liquid is null, the numbers of gas molecules before the capillary rise and after attaining the Jurin height remain the same.

Figures 8–15 reveal one important thing about the entrapment of air and its effects of temperature variation on capillary pressure. As the height of the tube increases, for cases involving the same Jurin height and the same parameters, the volume for the entrapped air is more. Therefore, the magnitude of air pressure is less for higher tubes as compared with the shorter tubes. Similarly, the capillary pressure is high for shorter tubes as the entrapped space for air is low. For very long vertical tubes, the

Figure 8. Capillary pressure vs. temperature plots. Plots for G-W-A system with (a) $H_T = 0.40$ m and (b) 0.60 m.

Figure 9. Capillary pressure vs. temperature plots. Plots for P-N-A system with (a) $H_T = 0.175$ m and (b) 0.225 m.

Figure 10. Variation (%) of capillary pressure vs. temperature for G-W-A system with $H_T = 0.40$, 0.50 and 0.60 m. P_{initial} means the pressure at reference temperature 298.15 K.

entrapped air gets more space, which decreases the gaseous pressure, and they behave more like open-end tubes. Figures 10–15 show that with increasing r and H_T , capillary pressure becomes sensitive to temperature more and more for both example cases.

Figure 11. Variation (%) of capillary pressure vs. temperature for P–N–A system with $H_T = 0.175, 0.20$ and 0.225 m. P_{initial} means the pressure at reference temperature 298.15 K.

Figure 14. Variation (%) of capillary pressure vs. temperature for G–W–A system with $r = 40, 50$ and $60 \mu\text{m}$. P_{initial} is the pressure at reference temperature 298.15 K.

Figure 12. Capillary pressure vs. temperature plots. Plots for G–W–A system with (a) $r = 40 \mu\text{m}$ and (b) $60 \mu\text{m}$.

Figure 13. Capillary pressure vs. temperature plots. Plots for P–N–A system with (a) $r = 40 \mu\text{m}$ and (b) $60 \mu\text{m}$.

4.1 Open-end capillary tube

The thermal effects of capillary pressures in open-end tubes are briefly investigated after seeing the effects of vertical length on capillary pressure in closed-end tubes. With the same explanation provided for the temperature effects on

Figure 15. Variation (%) of capillary pressure vs. temperature for P–N–A system with $r = 40, 50$ and $60 \mu\text{m}$. P_{initial} is the pressure at reference temperature 298.15 K.

capillary pressure for closed-end tubes, the concept is extended to describe the effects of temperature on capillary pressure in open-end capillary tubes. However, the mathematical expressions (or equations) are modified to take into account the difference in gas pressure at the open end of the capillary. The gas or air pressure can be evaluated as in Maggi and Alonso-Marroquin [67] from the following expression:

$$P_{\text{air}}(T) = P_{\text{atm}} - \rho_{\text{air}}(T)gH_T, \quad (19)$$

where P_{atm} is the pressure at the phreatic surface of the water table outside the tube (which is atmospheric pressure) and P_{air} is the pressure in air just at the top of the tube (assumed to be the same as that inside in the tube). Since the open end provides room for escape of gas molecules, the density of air, as well as the volume of air, differs significantly from that of closed-end tubes. Substituting $P_{\text{air}}(T)$ in lieu of $(nRT)/(V_{\text{air}}(f_{\theta}(T)))$ in Eq. (16) and using Eq. (19), one gets

$$P_c(T) = -g\rho_{\text{air}}(T)H_T + g\rho(T)(H_{\text{liquid}} - H_m(f_\theta(T))). \quad (20)$$

The same calculations and solution procedures as performed for the closed-end tube are repeated to find $f_\theta(T)$ from Eq. (14). We used the same data sets of Examples 1 and 2 that were used for closed-end capillary tubes, here, for open-end pore problems. After solving for $f_\theta(T)$ in Eq. (14), it is substituted in Eq. (12) to consequently evaluate $H_m(f_\theta(T))$. Using a fitting relationship of temperature and density of the liquid (as used before) and of air ($\rho_{\text{air}}(T)$) [68], the capillary pressures are computed for different temperatures (figure 16).

In the case of open-end pores, the magnitude of capillary pressure is lower than that of closed-end pores. This is due to the escape of gas molecules through the open end during the capillary rising of liquid. For both the closed-end as well as the open-end capillary pores, the capillary pressure reduces linearly due to increasing temperature and thus proves the claim of Grant [34] as mentioned before about the universality of the trend of linear drop of temperature vs. capillary pressure relationship. However, one of the reasons may be that the increase in temperature excites the gas particles and this excitation raises the velocity of air molecules and thus the momentum of gas particles. Consequently, it forces the solids and liquids and expands the gas volume more compared with the liquid volume. Therefore, the difference between gas pressure and liquid pressure gets reduced as temperature rises and thereby causes a reduction in capillary pressure. Another observation is that capillary pressure is more sensitive to temperature in open-end than that of dead-end pore system, and figure 17 reveals this fact as the percentage drop of P_c at 298.15 K from $-0.015\%/K$ (dead-end) to $-0.551\%/K$ (open-end) for G–W–A whereas it is $-0.030\%/K$ (dead-end) to $-1.263\%/K$ (open-end) for P–N–A. It can be hypothesized following figures 8–15 that the capillary pressures in very long closed-end capillary tubes may behave almost the same way as in open-end tubes. Entrapment length of air or H_{air} (see figure 1) has an important role in capillary pressure

Figure 16. Capillary pressure vs. temperature plot for (a) G–W–A system (open-end) and (b) P–N–A system (open-end).

magnitude. Equilibrium contact angle also has an effect on $P_c(T)$. Slope values of P_c vs. T , while changing θ_{eq} in dead-end cases, can vary from -1.04 Pa/K (with $\theta_{\text{eq}} = 40^\circ$) to -0.824 Pa/K (with $\theta_{\text{eq}} = 60^\circ$) for G–W–A, and from -3.102 Pa/K (with $\theta_{\text{eq}} = 36^\circ$) to -2.855 Pa/K (with $\theta_{\text{eq}} = 56^\circ$) for P–N–A. Soil pore size (radius) can range from ~ 0.05 μm ('cryptopore') to 2500 μm ('macropore') [56]. The dimension of the capillary tube along with θ_{eq} can give an idea of an approximate range of slope values for the dead-end case. With pore radius changing from 1 (with $\theta_{\text{eq}} = 10^\circ$) to 1000 μm (with $\theta_{\text{eq}} = 80^\circ$) with $H_T = 150$ m while keeping other terms constant in the case of G–W–A, slope changes from ~ -57.9 to -4 Pa/K and similarly in the case of P–N–A but only with $H_T = 7.5$ m, slope changes from ~ -162.4 to -1.2 Pa/K. Therefore 10 K change in temperature can drop the capillary pressure from 12 – 40 to 579 – 1624 Pa. Nevertheless, for both cases, the linear drop of capillary pressure with temperature is observed, even though the two are very different systems. This validates the equation derived in this paper qualitatively if not quantitatively [33] as only a single capillary tube is considered and dealt with. Grant [34] mentioned that relative drop in capillary pressure at 298 K is typically around $-1\%/K$, and the early results show the relative drop at 298.15 K to be around $-0.551\%/K$ and $-1.263\%/K$ for G–W–A and P–N–A, respectively.

As P_c is found to vary linearly with T , Eq. (16) can be replaced with a simple linear relation: $P_c = a_0 + a_1 T$, where a_0 (Pa) and a_1 (Pa/K) are fitting parameters. Following figures 3 and 5, a_0 and a_1 can be obtained: (1) for G–W–A system, $a_0 = 63877.437$ Pa (standard error or SE: 0.515), $a_1 = -0.939$ Pa/K (SE: 0.002); (2) for P–N–A system, $a_0 = 101909.086$ Pa (SE: 0.466), $a_1 = -2.989$ Pa/K (SE: 0.002). This simple relation may hold for most systems but does miss out some intricate physics underneath. Empirical relationships of physical parameters and temperature are nowadays easily available or can be obtained through standard experiments. Equation (16) gives much

Figure 17. Comparison plots of capillary pressures in dead-end and open-end capillary systems. Variation (%) of capillary pressure vs. temperature plots for both (a) G–W–A and (b) P–N–A systems. P_{initial} means pressure at reference temperature 298.15 K.

broader picture than that of a one-parameter or two-parameter model. Here, two generic cases are solved as the data of these materials are available. With regard to heterogeneous soils, depending upon soil chemistry and thermal experiments upon soil, the temperature dependence of physical properties like ρ_{liquid} vs. T , σ_{liquid} vs. T (as in [52]), $\theta_{\text{liquid-on-soil}}$ vs. T (as in [69]), etc. can be obtained and then utilized as input parameters in similar example problems described earlier. Dead-end pores can be identified by some conventional methods (electric logging formation factor, mercury injection capillary pressure and miscible displacement, etc.) as mentioned by Jackson and Klute [21] or as mentioned by Fatt *et al* [70] and most recently by Phirani *et al* [71] and these methods can provide an effective size as well as the volumetric fraction of dead-end pores. The method proposed here can be modified or extended to deal with the more generic cases like the liquid flux. Thermal gradient of capillary pressure contributes to the liquid flux in unsaturated soil as $-K \frac{\partial \psi}{\partial T} \nabla T$ [72], where K is the unsaturated hydraulic conductivity (m/s) and $\psi = P_c/(\rho g)$ (m). The term $\frac{\partial \psi}{\partial T}$ can be decomposed into three parts as

$$\frac{\partial \psi}{\partial T} = \underbrace{\omega_D \frac{\partial \psi}{\partial T} \Big|_{\text{dead-end}} + \omega_O \frac{\partial \psi}{\partial T} \Big|_{\text{open-end}}}_{\text{unsaturated}} + \underbrace{\omega_S \times 0}_{\text{saturated}}$$

with $\omega_D + \omega_O + \omega_S = 1$ and $\omega \in [0, 1]$.

Here three weighting factors (ω) indicate volumetric fraction of dead-end pore (ω_D) (saturated or unsaturated), of open-end unsaturated pores (ω_O) and of open-end saturated pore (ω_S) relative to total void in an averaging volume of soil. When the entire soil is saturated, the temperature derivative term becomes zero and does not contribute to actual liquid flux. However, we limit the present study as described here and suggest the generic cases as future scope along with sophisticated experimentations.

5. Conclusions

The dead-end pores are assumed to be capillary tubes with one end closed and the effect of temperature on liquid–gas meniscus is analysed. The shape of the meniscus in the capillary tube is considered to be spherical. As the translation displacement of the meniscus is neglected, the effect of temperature on capillary pressure is worked out by first identifying the change in meniscus curvatures due to incremental variation in temperature and thereby the changes in the interfacial tensions that consequently cause the change in capillary pressures. This whole concept is represented using a differential equation in this paper, in which the dependent variable is a new term called temperature function. The differential changes in meniscus

height (H_m) were evaluated. Thus the capillary pressure is calculated from meniscus height values and density values at different temperatures relative to a chosen reference temperature. For both the G–W–A and P–N–A systems, the results show a linear drop of capillary pressure with temperature. An important observation in dead-end pores or closed-end tubes is that of the significance of entrapped air in terms of r and H_{air} as well as the value of θ_{eq} in computations of capillary pressure at different constant temperatures. The effect of temperature on liquid–gas meniscus in the open-end capillary tube also showed a linear drop of capillary pressure with temperature. However, the magnitudes of capillary pressures are much lower compared with the dead-end pore cases. Closed-end capillary tube with very large air column at the top behaves approximately like the open-end tube with respect to capillary pressure vs. temperature relationship. The results presented here are consistent with the experimental data qualitatively. In addition, the paper, for the first time, provides a conceptual insight into the significance of dead-end pores on the capillary pressure vs. temperature relationship or on CPSR at a particular liquid saturation or on the thermal component of liquid flux. Further research could focus on robust pore-scale modeling through novel experiments and instrumentation on dead-end pores as well as on soil as a whole.

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List of symbols

a	fitting parameter
Bo	Bond number ($= \rho g r^2 / \sigma$)
C_γ	$(d\gamma_{\text{sa}}/dT - d\gamma_{\text{sl}}/dT)$ (N/m-K)
ΔT	range of temperatures (K)
f_θ	contact-angle-sensitive temperature function
G	temperature-dependent variables
γ	interfacial tension (N/m)
g	acceleration due to gravitation (m/s^2)
h	Jurin height (m)
H	height (m)
K	unsaturated hydraulic conductivity (m/s)
M	temperature-independent variables
$\mathcal{M}$	molar mass (kg/mol)
n	number of moles of gas (mol)
ω	weighting factor (m^3/m^3)
P	pressure (Pa)
P'	hydrostatic pressure ($= -\rho g h$) (Pa)

r	radius of the capillary tube (m)
ρ	liquid density (kg/m ³)
R	universal gas constant (N-m/K-mol)
σ	surface tension of liquid (N/m)
ψ	capillary potential or head (m)
T	temperature (K)
θ	contact angle (deg)
V	volume (m ³)
$\mathcal{V}$	molar volume (m ³ /mol)

Subscripts

atm	atmospheric
c	capillary
D	dead-end
eq	equilibrium
f	final
g	glass
i	initial
m	meniscus
O	open-end
p	particular
ref	reference
s	standard
S	saturated
sa	solid–air
sl	solid–liquid
T	total
w	water

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