Micro-capillary condensation/evaporation by critical relative humidity

Habib Jalili[1,2], Tariq Ouahbi[1], Said Taibi[1], Joanna Eid[1,2], Ichrak Hamrouni[1]

1 Université Le Havre Normandie, Normandie Univ, LOMC, UMR 6294 CNRS, 76600 Le Havre, France.

[2] AI Environnement, FACEA Group, R&D Department, Noisy le Grand, France

Abstract. The problem of surface moisture and condensation inside microstructures is complex and depends on the physicochemical characteristics of both the atmosphere and the surfaces. The relative humidity within a pore is a function of the temperature, mixing ratio, pore geometry, and presence and nature of soluble salts and can be considerably pores types as well as on atmospheric relative humidity. However, although the phenomenon of capillary condensation or evaporation is a complicated process, it would be useful to introduce a critical relative humidity and temperature in micropores structures. To examine the mechanisms of condensation and evaporation of water in micropore structures, we report the critical relative humidity in the capillary pores, cylindrical and square types and as well as dependency of the critical relative humidity on temperature and various contact angles.

Keywords: Capillary condensation and evaporation, Critical relative humidity, Kelvin equation, Contact angle, Complete Kelvin equation

I. INTRODUCTION

Fluids confined within micropores or nanopores have garnered considerable interest among scientists and engineers owing to their diverse applications in various fields such as in building materials (Yuan et al., 2024), unsaturated porous media (Mchirgui, 2012) and cloud physics (Casans et al., 2023). These encompass unconventional oil and gas extraction, fuel cell technologies, heterogeneous catalyst development, adsorption processes, drying methodologies, water purification techniques, and climate engineering endeavours (Falk et al., 2015; Salahshoor et al., 2018). Due to the robust interactions between fluids and pore walls, fluid density distribution within nanopores is uneven, resulting in significantly different fluid behavior from bulk conditions. Experimental and modelling studies have demonstrated that fluids confined in capillary pores may undergo capillary condensation or evaporation at vapor-phase pressures different from the saturation pressure observed in bulk phases (Corma et al., 1995; Scherer, 1990). However, it is useful to distinguish between the formation of droplets in the free atmosphere and the condensation onto a surface, or inside internal pores. In practice, the mechanism of capillary condensation is intricate and somewhat obscure, although the fundamental equation that controls the condensation in micropores also governs the formation of drops in the atmosphere, a topic familiar to meteorologists. In the atmosphere, water vapor becomes saturated at relative humidity of 100%,

when the air temperature reaches the dew point. The saturation vapor pressure can be calculated by Magnus and Tetens formula or Clausius–Clapeyron relation. But the saturation pressure which also called vapor tension in capillary pores is calculated by the Kelvin formula (Lawrence, 2005). In another word, the properties of fluids confined in nanopores cannot be simply predicted by the conventional equation of state modeling. So, to predict the phase behaviour of the phase component in a capillary pore, with a assumption of that he vapor phase (or humid air) behaves as an ideal gas and the liquid phase is incompressible and pure water, one can derive the Kelvin equation (Elliot, 2001; Shardt and Elliott, 2018). Figure 1 shows a schematic illustration of capillary and surface condensation in equilibrium condition.

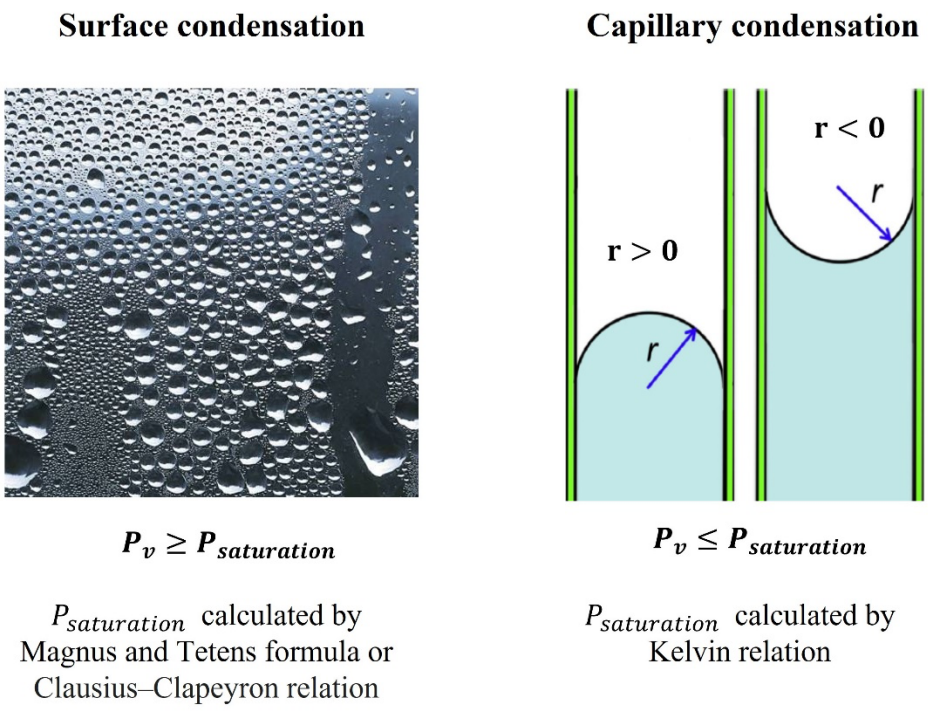

FIGURE 1. Surface condensation and capillary condensation dependency on water vapor saturated pressure $(P_{saturation})$ calculated by different equations.

In recent years, capillary condensation attracts the researcher's interest in various domain to understand this phenomenon, Yang et al. (Yang et al., 2016) combined atomic force spectroscopy with the well-established theory of capillary condensation to provide a novel means of determining the thickness of the aqueous interfacial layer on NaCl (001) over a wide range of relative humidity. And, experimentally they measured the surface conductance as a function of humidity as an indicator of salt dissolution into this interfacial layer. In another research, Tanaka et al. (Tanaka et al., 1998) applied time-correlation function analysis of IR spectroscopy to investigate the alterations in the reorientation state of acetonitrile molecules during capillary condensation. They analyzed the phenomena before and after capillary condensation onto the mesoporous silica media. Hu et al. (Hu and Yu, 2024) investigated the isothermal sorption of water vapor in nanopores under four

humidity conditions. A new approach based on Young's Laplace equation was developed for determining the equilibrium water sorption in nanoporous media, demonstrating a relative error ranging from 0.24% to 10.42% between the experimental and calculated outcomes. In this study, we analyse the simplified Kelvin equation and its relation to the geometrical function of the capillary, which include the radius or diameter of the capillary for square and cylindrical form. The novelty of this study is to introduce the graphical method for microcapillary condensation /evaporation using the critical relative humidity versus geometrical function. By defining the critical relative humidity, capillary condensation/evaporation could be parametrized in microchannels.

II. Complete Kelvin equation

W. THOMSON, later Lord Kelvin, (1870) (Thomson, 1871), developed an equation which implied that the vapor pressure of a material in thermodynamic equilibrium over a curved surface differs from that over a plane surface. Its equation is based on the macroscopic thermodynamics for the vapor and liquid phase equilibrium with assuming that the humid air behaves as ideal gas, and the pure water as a liquid phase is incompressible. His derivation was based on the consideration of the equilibrium between a liquid (phase 2), contained in a capillary channel, and its vapor (phase 1). Gibbs derived independently the Kelvin equation based on chemical potentials (Elliot, 2001; Skinner and Sambls, n.d.).

$$\mu^v(T, P^v) = \mu^L(T, P^L), \tag{1}$$

$$P^v - P^L = P_{cap} = \frac{4\,\sigma\,\cos\,(\theta)}{d} \tag{2}$$

Where, μ^v and μ^L are pure component vapor- and liquid-phase chemical potentials, respectively. Under the assumption of ideal gas behavior for the vapor phase and the incompressibility of the liquid phase, which can exist below the bulk saturation pressure (P_{sat}), chemical potentials of the vapor and liquid phases can be defined as follows (Pruppacher and Klett, 2010):

$$\mu^v(T, P^v) = \mu^v(T, P_{sat}) + \Re T\, ln\left(\frac{P^v}{P_{sat}}\right), \tag{3}$$

$$\mu^L(T, P^L) = \mu^L(T, P_{sat}) + V_m(P^L - P_{sat}), \tag{4}$$

In which $V_m$is the bulk liquid molar volume, $\Re$ is the universal gas constant. However, by combining the Equations of (1) and (4), equation below were reached,

$$\Re T\, Ln\,(\tfrac{P^v}{P_{sat}}) = V_m(P^L - P_{sat}), \tag{5}$$

Substituting Eq. (2) into Eq. (5) yields the complete Kelvin equation, for capillary channel,

$$\ln\left(\frac{P^v}{P_{sat}}\right) = \frac{4\sigma V_m\, Cos(\theta)}{d\,\Re\,T} + \frac{V_m}{\Re\,T}\,(P^v - P_{sat}) \tag{6}$$

In the complete form of Kelvin equation, Eq. (6), the capillary pressure is often considered to be much larger than the difference between the vapor-phase pressure and bulk saturation pressure (Elliot, 2001), i.e.,

$$\frac{4\sigma\, Cos(\theta)}{d} \gg P^v - P_0 \tag{7}$$

Then, Eq. (6) transformed to the simplified Kelvin equation, or simply recognized as "Kelvin formula" (Dexter and Richard, 2009),

$$\ln\left(\frac{P^v}{P_{sat}}\right) = \frac{4\sigma V_m\, Cos(\theta)}{d\,\Re\, T} \tag{8}$$

Where, P^v , P_{sat} and d depict the water vapor pressure, saturated pressure, and the diameter of the capillary channel, respectively. And σ, θ, $\Re$, V_m and T represent the surface tension of the water, contact angle, universal gas constant, water molar volume and temperature, respectively. Vargaftic et al. (Vargaftik et al., 1983) has demonstrated a table for the surface tension of water from 0.01 to 374°C and an interpolating equation which represents the values in the table to well within their estimated uncertainties. These experimental values are well represented by the Eq. (9),

$$\sigma = B\left[\frac{T_C - T}{T_C}\right]^{\mu}\left[1 + b\left(\frac{T_C - T}{T_C}\right)\right] \tag{9}$$

Where, B, b, T_C and μ are constant with the values of $235 * 10^{-3}\ [N.m^{-1}]$, -0.625 , $647.15\ [K]$ and 1.256 , respectively. Figure 2 demonstrates the where the surface tension and contact angle applied in capillary channel during the equilibrium condition.

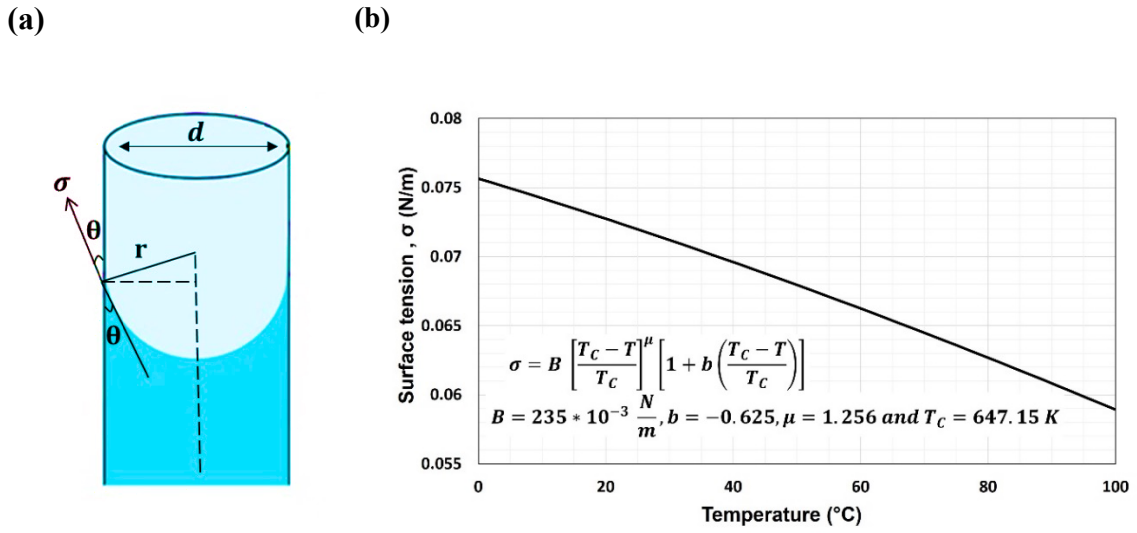

FIGURE 2. (a) illustrates the equilibrium condition associated parameters, contact angle (θ), pore diameter (d), meniscus radius (r). (b) Surface tension as plotted by formula parameterized by Vargaftic et al. (Vargaftik et al., 1983)**.**

III. Capillary condensation and critical point

By considering the Kelvin formula in Eq. (8) and another well-known relation introduced by the Edlefsen and Anderson, 1943 (Edlefsen and Anderson, 1943),

$$\varphi = \frac{P_v}{P_{sat}} \tag{10}$$

The Eq. (8) can be expressed as relative humidity (φ),

$$\varphi\,(d)^{*} = 100 * exp\,(\ \frac{4\sigma V_m\ Cos(\Theta)}{d\ \Re\ T}\ ) \tag{11}$$

This provides us the dependency of the relative humidity and meniscus curve. And capillary condensation occurs in cylindrical channel, as condensed water makes smaller and smaller the radius of curvature of a cylindrical meniscus, determining a condition of unstable equilibrium and accelerating the condensation. When a capillary is full of water, a spherical meniscus forms at the beginning of the capillary and the evaporation starts in a reversible way. Figure 3 illustrates the schematic of capillary condensation and evaporation in micro capillary channel. The diameter or radius of pore is the critical point in this phenomenon, Critical relative humidity is $\varphi = \varphi\,(d)^{*}$ which is in equilibrium with the radius of curvature of the pore. The parameter of d is the diameter of the pore when the condensation begins. For lower relative humidity it cannot fill because of the reversible condensation-evaporation.

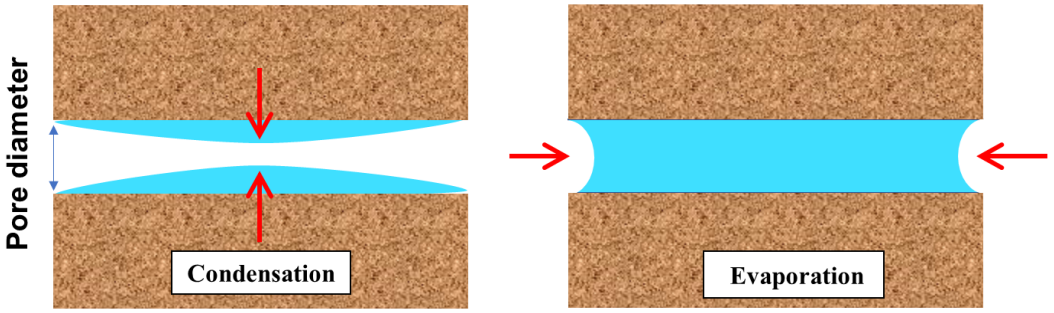

FIGURE 3. A schematic demonstration of capillary condensation and evaporation. Initiated as a cylindrical meniscus thickens, condensation occurs until the capillary is filled. When evaporation occurs, the meniscus retreats deeply inside the capillary channel.

IV. Discussion on critical relative humidity

In this section, critical humidity is going to discuss on the cylindrical and square channels with radius of r for "cylindrical "and length of L for "square ". By evaluating the capillary pressure in both square and cylindrical, we found the similar valued and critical points for both types of channels, as can be seen in Figure 4, the relation of capillary pressure for both channels. The term of $(\frac{2}{\sqrt{\pi}})$ is equal to 1.128, allowing for the consideration of both the capillary pressure of cylindrical and square channels with an approximation of similarity between them ($P_{cap,\text{cylindrical}} \cong P_{cap,square}$) (Slider, 1983).

In porous bodies, or in general, over a hydrophilic surface, the water molecules in contact with the material are adsorbed and strongly bound with the internal surface due to the presence of dipoles or image forces; the binding is so strong that this water is considered to be in the solid state.

Beyond this solid layer, other water molecules are in the liquid phase and free. The problem of surface moisture and condensation is complex and depends on the physicochemical characteristics of both the atmosphere and the surface. The relative humidity within a pore is a function of the

temperature, mixing ratio, pore geometry, and presence and nature of soluble salts and can be considerably different from pore to pore as well as from atmospheric relative humidity (Monteith and Unsworth, 2013).

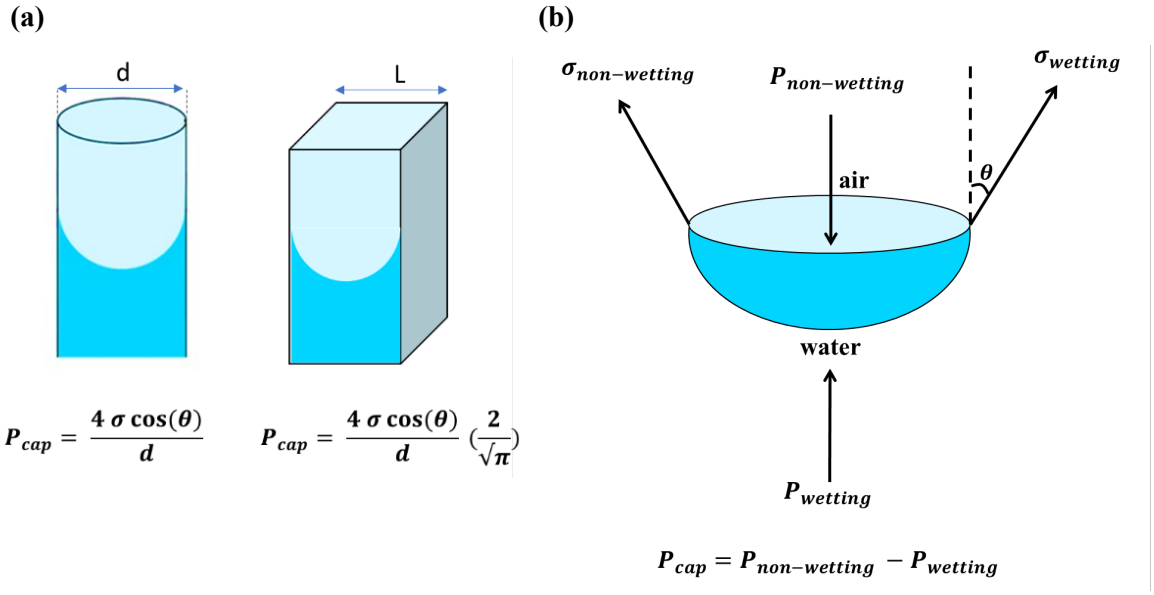

FIGURE 4. (a) The relation between the square channel and cylindrical channel with same cross section areas ($\pi \frac{d^2}{4} = L^2$). (b) General illustration of capillary pressure for air as non-wetting phase and water as wetting phase.

In the capillary condensation, the smaller pore, the lower relative humidity required for equilibrium with the water meniscus. For each capillary pore, condensation begins at a low critical relative humidity $\varphi\,(d)^*$ determined by the effective radius of curvature of the pore r_p or here we defined as diameter of pore to be able to plot the square and cylindrical channel in one plot. This is the geometric radius of the curvature of the pore minus the thickness of the mono- or bimolecular layer of water molecules adsorbed and strongly bound. Both condensation and evaporation are reversible and strictly follow any increase or decrease of the ambient relative humidity level, always being in equilibrium ("Chapter 1 Microclimate, air and temperature," 1998; "Chapter 6 Atmospheric water and stone weathering," 1998). The critical relative humidity plotted based on the Kelvin equation for both cylindrical and square microchannel with approximation of "$P_{cap,\text{cylindrical}} \cong P_{cap,square}$", as shown in Figure 5.

According to Figure 5, increasing the temperature or by fluctuation of temperature is not really significant in micro capillary condensation in a comparison of contact angle. In contrast to the contact angle, temperate in critical relative humidity definition does not influence critical point in capillary condensation. At its opposite point, the contact angle ($\boldsymbol{\theta}$) which demonstrates the angle between a liquid surface and a solid surface where they meet. More specifically, it represents the angle formed at the intersection between the surface tangent on the liquid-vapor interface and the tangent on the solid-liquid interface., as shown previously in Figure 2. It quantifies the wettability of a solid surface (Rabbani et al., 2018; Shi et al., 2018). By increasing the contact angle or in other

words having a non-wettable surface, critical relative humidity is also increasing. The maximum contact angle when it becomes °90 we have the straight line of 100% in critical relative humidity which shows the capillary condensation only can be reached in this relative humidity. Nevertheless, this critical relative shows the importance of critical relative humidity that in case of wettable surface, °0, capillary condensation can be reached even in lower relative humidity.

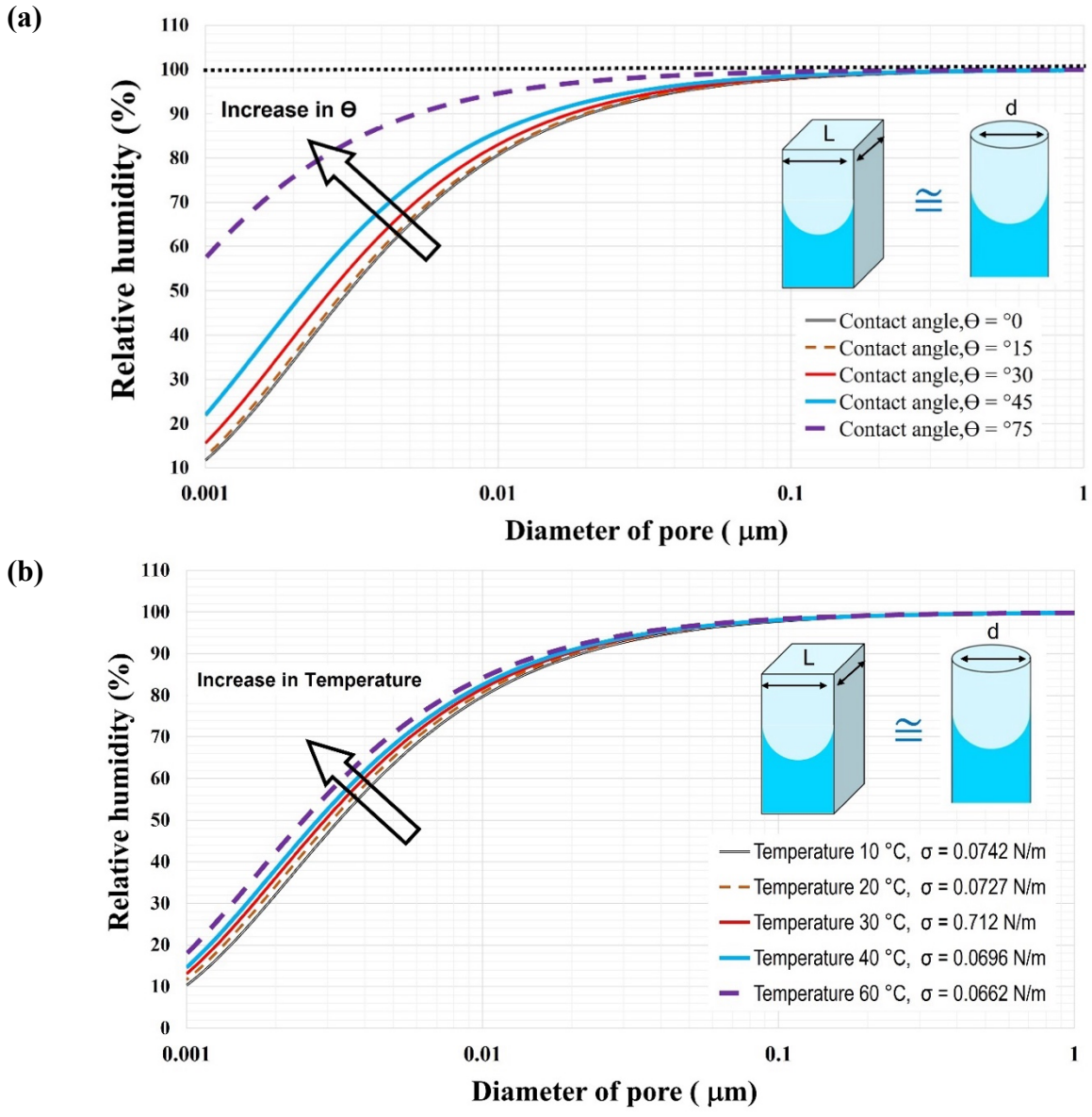

FIGURE 5. Critical relative humidity ($\varphi\ (d)^*$) relation in capillary condensation/evaporation at various (a) contact angle (Θ) in T = 293.15 K, (b) Temperature which also has changed the surface tension for a complete wettable surface with a contact angle of °0, $\Theta = °0$.

V. Conclusion

Capillary condensation and evaporation are an extremely important phenomenon that can be addressed by microphysics of clouds relating to cultural heritage conservation. The mechanisms for droplet formation or homogenous nucleation are the starting point for discussing this phenomenon. In reality, this phenomenon is complex and rather unfamiliar due to the various parameters influence the microdroplet formation. In this study, simplified kelvin equation used for defining the critical relative humidity in capillary pores whatever in cylindrical or square. The critical relative plotted as a function of the diameter of channel, from 0.001 $\boldsymbol{\mu m}$ to 1 $\boldsymbol{\mu m}$. Temperature fluctuation and contact angle which is physical properties of the surface channel in microcapillary has been investigated. To conclude, we described a graphical method based on the critical relative humidity for capillary condensation/evaporation within the various pore structures. This paper highlighted the critical relative humidity dependency on pores diameter, contact angle and temperature. We found that temperature in the nano-channel (0.001 $\boldsymbol{\mu m}$) has not aa significant impact on critical point in capillary condensation of water. And, as pore size increasing or in a higher diameter, the critical point reaches to bulk critical point. In addition, we realized the contact angle significantly influences this critical point of relative humidity which is the surface parameter of a channels. Future efforts would be on parametrize the capillary condensation as a vapor phase is not ideal gas, one of the important simplifications of Kelvin formulation and considering the complete form of Kelvin equation or different models on critical relative humidity.

REFERENCES

Casans, A., Rejano, F., Maldonado-Valderrama, J., Casquero-Vera, J.A., Ruiz-Peñuela, S., Van Drooge, B.L., Lyamani, H., Cazorla, A., Andrews, E., Lin, J.J., Mirza-Montoro, F., Pérez-Ramírez, D., Olmo, F.J., Alados-Arboledas, L., Cariñanos, P., Titos, G., 2023. Cloud condensation nuclei activation properties of Mediterranean pollen types considering organic chemical composition and surface tension effects. Atmospheric Environment 310, 119961. https://doi.org/10.1016/j.atmosenv.2023.119961

Chapter 1 Microclimate, air and temperature, 1998. , in: Developments in Atmospheric Science. Elsevier, pp. 3–41. https://doi.org/10.1016/S0167-5117(98)80004-9

Chapter 6 Atmospheric water and stone weathering, 1998. , in: Developments in Atmospheric Science. Elsevier, pp. 161–193. https://doi.org/10.1016/S0167-5117(98)80009-8

Corma, A., Fornes, V., Rey, F., Cervilla, A., Llopis, E., Ribera, A., 1995. Catalytic Air Oxidation of Thiols Mediated at a Mo(VI)O2 Complex Center Intercalated in a Zn(II)-Al(III) Layered Double Hydroxide Host. Journal of Catalysis 152, 237–242. https://doi.org/10.1006/jcat.1995.1078

Dexter, A.R., Richard, G., 2009. Water Potentials Produced by Oven-Drying of Soil Samples. Soil Sci. Soc. Am. J. 73, 1646–1651. https://doi.org/10.2136/sssaj2008.0294N

Edlefsen, N.E., Anderson, A.B.C., 1943. Thermodynamics of soil moisture. Hilg 15, 31–298. https://doi.org/10.3733/hilg.v15n02p031

Elliot, J.A.W., 2001. On the Complete Kelvin Equation. Chemical Engineering Education 35, 274–278.

Falk, K., Coasne, B., Pellenq, R., Ulm, F.-J., Bocquet, L., 2015. Subcontinuum mass transport of condensed hydrocarbons in nanoporous media. Nat Commun 6, 6949. https://doi.org/10.1038/ncomms7949

Hu, Y., Yu, Q., 2024. Experimental and theoretical studies on water adsorption and capillary condensation in nanopores of calcium carbonate. Geoenergy Science and Engineering 236, 212740. https://doi.org/10.1016/j.geoen.2024.212740

Lawrence, M.G., 2005. The Relationship between Relative Humidity and the Dewpoint Temperature in Moist Air: A Simple Conversion and Applications. Bull. Amer. Meteor. Soc. 86, 225–234. https://doi.org/10.1175/BAMS-86-2-225

Mchirgui, W., 2012. Modélisation des transferts hydriques dans les milieux poreux partiellement saturés par homogénéisation périodique : Application aux matériaux cimentaires (phdthesis). Université de La Rochelle.

Monteith, J.L., Unsworth, M.H., 2013. Principles of environmental physics: plants, animals, and the atmosphere, 4th ed. ed. Elsevier/Academic Press, Amsterdam ; Boston.

Pruppacher, H.R., Klett, J.D., 2010. Microphysics of Clouds and Precipitation, Atmospheric and Oceanographic Sciences Library. Springer Netherlands, Dordrecht. https://doi.org/10.1007/978-0-306-48100-0

Rabbani, H.S., Zhao, B., Juanes, R., Shokri, N., 2018. Pore geometry control of apparent wetting in porous media. Sci Rep 8, 15729. https://doi.org/10.1038/s41598-018-34146-8

Salahshoor, S., Fahes, M., Teodoriu, C., 2018. A review on the effect of confinement on phase behavior in tight formations. Journal of Natural Gas Science and Engineering 51, 89–103. https://doi.org/10.1016/j.jngse.2017.12.011

Scherer, G.W., 1990. Theory of Drying. Journal of the American Ceramic Society 73, 3–14. https://doi.org/10.1111/j.1151-2916.1990.tb05082.x

Shardt, N., Elliott, J.A.W., 2018. Isobaric Vapor–Liquid Phase Diagrams for Multicomponent Systems with Nanoscale Radii of Curvature. J. Phys. Chem. B 122, 2434–2447. https://doi.org/10.1021/acs.jpcb.8b00167

Shi, Z., Zhang, Y., Liu, M., Hanaor, D.A.H., Gan, Y., 2018. Dynamic contact angle hysteresis in liquid bridges. Colloids and Surfaces A: Physicochemical and Engineering Aspects 555, 365–371. https://doi.org/10.1016/j.colsurfa.2018.07.004

Skinner, L.M., Sambls, J.R., n.d. THE KELVIN EQUATION--A REVIEW.

Slider, H.C., 1983. Worldwide practical petroleum reservoir engineering methods. Second edition.

Tanaka, H., Iiyama, T., Uekawa, N., Suzuki, T., Matsumoto, A., Grün, M., Unger, K.K., Kaneko, K., 1998. Molecular mechanism of capillary condensation of acetonitrile vapor on MCM-41 with the aid of a time-correlation function analysis of IR spectroscopy. Chemical Physics Letters 293, 541–546. https://doi.org/10.1016/S0009-2614(98)00819-7

Thomson, W., 1871. LX. *On the equilibrium of vapour at a curved surface of liquid*. The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science 42, 448–452. https://doi.org/10.1080/14786447108640606

Vargaftik, N.B., Volkov, B.N., Voljak, L.D., 1983. International Tables of the Surface Tension of Water. Journal of Physical and Chemical Reference Data 12, 817–820. https://doi.org/10.1063/1.555688

Yang, L., He, J., Shen, Y., Li, X., Sun, J., Czajkowsky, D.M., Shao, Z., 2016. Nanoscopic characterization of the water vapor-salt interfacial layer reveals a unique biphasic adsorption process. Sci Rep 6, 31688. https://doi.org/10.1038/srep31688

Yuan, L., Takada, S., Fukui, K., 2024. Study on mold and condensation risks after vacancy of residential space with walls in contact with the ground. Journal of Building Engineering 89, 109300. https://doi.org/10.1016/j.jobe.2024.109300