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Activated drying in hydrophobic nanopores and the line tension of water

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We study the slow dynamics of water evaporation out of hydrophobic cavities by using model porous silica materials grafted with octylsilanes. The cylindrical pores are monodisperse, with a radius in the range of 1–2 nm. Liquid water penetrates in the nanopores at high pressure and empties the pores when the pressure is lowered. The drying pressure exhibits a logarithmic growth as a function of the driving rate over more than three decades, showing the thermally activated nucleation of vapor bubbles. We find that the slow dynamics and the critical volume of the vapor nucleus are quantitatively described by the classical theory of capillarity without adjustable parameter. However, classical capillarity utterly overestimates the critical bubble energy. We discuss the possible influence of surface heterogeneities, long-range interactions, and high-curvature effects, and we show that a classical theory can describe vapor nucleation provided that a negative line tension is taken into account. The drying pressure then provides a determination of this line tension with much higher precision than currently available methods. We find consistent values of the order of -30 pN in a variety of hydrophobic materials.

drying transition | hydrophobicity | kinetics | nanobubbles | mesoporous silica

A remarkable property of water is its ability to form nanosize bubbles, or cavities, on hydrophobic bodies (1). Since their first direct observations through atomic force microscopy about a decade ago (2, 3), surface nanobubbles on hydrophobic surfaces have raised considerable interest, and they are believed to play a major role in surface-driven phenomena, such as boundary slip-page of water flows, heat transfer at walls, vaporization and boiling, surface cleaning, etc. (4, 5). In a different context, the evaporation of water in the vicinity of hydrophobic bodies has been studied as a core mechanism for the hydrophobic interaction mediated by water (6–8), which plays a central role in biological matter. The formation of cavities able to bridge hydrophobic units provides a driving force for protein folding and supermolecular aggregation (9). Simulation examples of such drying-induced phenomena include the collapse of a polymer chain, multidomain proteins, and hydrophobic particles (9–13).

Despite their direct observation, the easy formation and the high stability of nanobubbles on hydrophobic bodies still raise fundamental questions (5, 14, 15). Because of significant theoretical work, it is now established that, at the scale of the nanometer, macroscopic concepts apply: hydrophobicity is described by interfacial energies, and the drying transition in hydrophobic confinement is a first-order transition triggered by the nucleation of a critical vapor bubble (1). The energy barrier limiting the kinetics of this transition is a strong signature of nanobubbles properties. Evaporation kinetics has also been pointed out as the most direct measure of the importance of hydrophobic collapse in protein folding (9). However, rate effects in the drying transition have not received much attention. A few numerical studies have addressed the rate of evaporation of liquid water confined between hydrophobic plates (16–19). The nucleation barrier has

been measured with different methods, and it has been shown to increase strongly with the slit separation. The classical theory of capillarity has been shown to overestimate the numerical findings (17, 18). The classical capillarity is a key framework to understand nucleation phenomena, but it is based on macroscopic considerations and does not include specific features, like fluctuations or line energies that can affect interfaces at nanometric scales. There is, however, no consensus about the leading effect at these scales. Fluctuations are invoked in ref. 18 to explain the observed nucleation barrier reduction, whereas line tension is shown to account for the observed deviations in ref. 19. Experimental studies are scarce, because the rate or time variable is generally ignored in studies of adsorption and desorption of confined liquids.

Here, we use highly ordered nanoporous silicas to study the dynamics of water evaporation in hydrophobic confinement. Molecule-templated silicas (MTSs) have quasi-1D mesopores shaped in the form of cylinders of monodisperse radius adjustable from 1 to 5 nm. These model materials have been used as nanoscale laboratory to study the phase diagram of confined liquids (20, 21). In previous works (22, 23), we used silane-grafted MCM-41 (Mobil Crystalline Material 41) to study water confined by hydrophobic walls. Liquid water penetrates into the nanopores at high pressure, reaching 500 bars for nanometer-sized pores. The intrusion pressure of water in the cylindrical pores scales as the inverse of their radius down to radii of 1.3 nm, according to the Laplace law of capillarity (Eq. 1):

$$P_{\text{int}} = -\frac{2\gamma_{\text{lv}}\cos\theta}{R_p} = 2\frac{\gamma_{\text{sl}} - \gamma_{\text{sv}}}{R_p}, \quad [1]$$

with γ_{sl} , γ_{sv} , and γ_{lv} being the solid/liquid, solid/vapor and liquid/vapor surface tensions, respectively. This intrusion law shows the model character of hydrophobized MTS to provide a geometrically and energetically well-defined confinement. The drying transition is obtained by lowering the pressure. Liquid water becomes metastable and finally, empties the nanopores at a pressure P_{ext} lower than the intrusion pressure (24). The drying pressure P_{ext} is not described by the Young–Laplace law (1) and increases with temperature (23). Those features are in good qualitative agreement with a drying triggered by the nucleation of a critical vapor bubble on the pore walls.

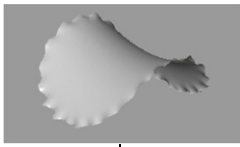
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Finally, the effect of long-range interactions can be estimated from the value of the disjoining pressure $A_{slv}/6\pi D^3$, where A_{slv} is the wall-vapor-liquid Hamaker constant, and D is the distance of a meniscus portion to the wall. In the heart of the pore, with a typical Hamaker constant of 10^{-20} J, the disjoining pressure is of the order of 5 bars, which is not relevant. It is more important close to the contact line. This effect is, indeed, described by the thermodynamic concept of line tension introduced by Gibbs more than a century ago to account for the excess energy caused by long-range interactions close to a three-phases contact line (36, 37). With an expected magnitude of the order $\tau \sim \gamma_{lv}a$ (a being the molecular size, and $\tau \sim 20$ pN for water), line tension plays a significant role only for liquid objects of nanometric size in the three dimensions of space. In contrast to surface tension, it can be negative and thus, reduce the energy of a sessile nanobubble. Experimental determinations of line tension are, however, notoriously difficult, and values reported for water on different substrates vary greatly in amplitude (from 10^{-11} to 10^{-6} N) and sign and tend to depend on the method used (37, 38). The most direct methods, based on the size dependence of the contact angle of sessile drops/bubbles (39), are limited by the difficulty of exact contact angle measurements at the required scale (1–100 nm) (40) and the bias induced by surface heterogeneities (41). In a previous work, Lefevre et al. (22) attributed the low energy barrier for the drying of silanized MCM-41 to a negative line

Fig. 7. The reference extrusion pressure P_{ext}^o as a function of temperature in the three materials. The dashed line is the best fit obtained by fitting the line tension in Eq. 6. The pore radii, contact angles, water surface tension, and expressions of K_1 , K_2 , and K_3 are listed in [SI Text, section I](#). In each material, we allow a small linear variation $\tau(T) = \tau_o(1 + \alpha(T - T_o))$. The thermal coefficient α is of the order -10^{-3} K^{-1} (Table 1). For comparison, the thermal coefficient of water surface tension in the same range is $-2.4 \cdot 10^{-3} \text{ K}^{-1}$.

quoted in Table 1 are calculated using the microscopic quantities $b = 1 \text{ \AA}$, $\nu = 10^{12} \text{ s}^{-1}$, and $L = 10 \text{ }\mu\text{m}$. Changing the ratio $b/\nu L$ by a factor 10 or 0.1 changes τ by less than $\pm 0.6 \text{ pN}$ (that is, 1 to 2.5%). The line tension found has consistent values for the three materials ranging from -23 pN in MCM-41 to -35 pN in SBA-15. To account fully for the temperature variation of P_{ext}^0 , we have allowed a small thermal variation $\tau(T) = \tau_0[1 + \alpha(T - T_0)]$ (Fig. 7 and Table 1). The absolute value $|\alpha|$ of the thermal coefficient is less than 10^{-3} K^{-1} , to be compared with the thermal coefficient of water surface tension in the same range, $-2.4 \times 10^{-3} \text{ K}^{-1}$.

The values that we find here are of the same amplitude but opposite sign to the line tension of water measured on hydrophilic surfaces, such as quartz (43) and silica (39). On strongly hydrophobic surfaces, measurements have focused on the shape of nanobubbles. State-of-the-art investigations have not evidenced a variation of the contact angle with the bubble size (40, 44, 45), corresponding to an upper amplitude of about 100 pN for the line tension of water. Therefore, we compare our results with the systematic study by Weijs et al. (42) performed for Lennard-Jones fluids, although the water/silane/silica system investigated here is chemically different. The (negative) line tension is characterized by the ratio of the tension length $l = -\tau/\gamma_{\text{lv}}$ to the molecular size a . The ratios found here (with $a = 2.7 \text{ \AA}$) are from 1.2 to 1.9, which is in good agreement with thermodynamic expectations and in qualitative agreement with the work by Weijs et al. (42) ($l/a = 0.82$ at contact angle 117°).

Finally, we find a difference of about -20% (respectively, $+20\%$) for the line tension in MCM-41 (respectively, SBA-15) with respect to HMS. This difference could be because of the topography of the pore walls (SBA-15 is known to have a rougher surface than MCM-41) or a systematic trend with the solid surface curvature, such as described in ref. 46.

Conclusion

In summary, we have shown here that the drying of water brought into metastable equilibrium inside hydrophobic cavities is a dynamical process with slow logarithmic dynamics. This finding illustrates the importance of carrying out dynamical rate-dependent study of adsorption and desorption phenomena. Such studies are a sensitive probe of the specific mechanisms that control the formation and dynamics of nanobubbles on hydrophobic surfaces. Here, we find that the mechanism that allows one to interpret quantitatively the rate dependence of the extrusion pressure is the thermally activated appearance of a critical vapor nucleus that can be well-described by the macroscopic theory of capillarity, if a negative line tension of water is taken into account. Our approach provides an accurate independent estimate of this line tension, which is consistent with what can be

Table 1. Nucleation volume and line tension in the various materials

	MCM-41	SBA-15	HMS
R_p^*	1.34 ± 0.1	2.16 ± 0.25	1.54 ± 0.1
$\theta_{50^\circ\text{C}}^\dagger$	114.8°	119.1°	115°
$\delta\theta(^\circ/\text{K})^\ddagger$	0.036	0.077	0.059
V_c^\S	10.2 ± 1.5	51 ± 17	17.8 ± 2.7
$P_{\text{ext}}^0(50^\circ\text{C})^\S$	178	60.2^*	109.4
$\tau_{50^\circ\text{C}}^\P$	-23.3	-35.5	-30.1
$\alpha(^\circ\text{C}^{-1})$	-1.0×10^{-3}	-0.8×10^{-3}	-0.7×10^{-3}

*Pore size (nm).

† Intruding contact angle at 50°C ; $\theta(T) = \theta_{50^\circ\text{C}} + \delta\theta(T - 50)$.

‡ Nucleation volume (nm^3).

§ Reference extrusion pressure at 50°C (bar; $t_0 = 1 \text{ s}$).

¶ Line tension at 50°C (10^{-12} N); $\tau(T)/\tau_{50^\circ\text{C}} = 1 + \alpha(T - 50)$.

Table 2. Other characteristics of the materials

	MCM-41	SBA-15	HMS
$R_{\text{BJH}} - R_{\text{BDB}}$ (nm)	$1.25 - 1.43$	$1.91 - 2.40$	$1.44 - 1.64$
R_p (nm)	1.34 ± 0.1	2.15 ± 0.25	1.54 ± 0.1
$P_{\text{int}}(50^\circ\text{C}; \text{bar})$	432.1	291.1	325.5
$\theta_{50^\circ\text{C}}$	114.8°	119.1°	115°
$\delta\theta(^\circ/\text{K})$	0.036	0.077	0.059
$K_1(\theta_{50^\circ\text{C}}) - K_2(\theta_{50^\circ\text{C}})$	$4.27 - 3.24$	$4.28 - 2.614$	$4.27 - 3.21$
$K_3(\theta_{50^\circ\text{C}})$	12.366	12.422	12.37

inferred from simulation data or atomic force measurements of droplet shapes. The existence of a negative line tension is an important ingredient for understanding the very high stability of nanobubbles on hydrophobic surfaces and the vaporization of water from repellent cavities, and it has wide implications for heterogeneous cavitation, hydrophobic interactions in biological matter, and more generally, properties of very small liquid objects. Additional work is under progress to study the compressibility of the water/silane hydrophobic interface in the mesopores (47).

Materials and Methods

The MCM-41 was synthesized from the structuring agent octadecyltrimethylammonium bromide ($\text{C}_{18}\text{NMe}_3\text{Br}$) as described in ref. 27. MCM-41 is a model material presenting independent cylindrical pores that are hexagonally ordered and have a smooth internal surface. SBA-15 was synthesized from the triblock copolymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ as a structuring agent under acidic medium at 60°C for 24 h (29). SBA-15 also has a hexagonal arrangement of cylindrical pores, but depending on the synthesis temperature, these mesopores can be connected by a secondary network of smaller micropores. We chose a temperature of 60°C , which prevents the micropores from growing and creating interconnections (29). The HMS was prepared with C_{16}NH_2 as the structuring agent, with a ratio $\text{EtOH}/\text{H}_2\text{O} = 0.19$ at an ambient temperature for 24 h (31). The HMS has a smooth internal surface but is less ordered than MCM-41, and the pore network can be randomly connected in few locations. The three mesoporous silicas are silanized by grafting chlorodimethyloctylsilane as described in ref. 48. Before and after silanization, the MTS was characterized by nitrogen adsorption at 77 K (49). The pore size determination was done using two methods: the Barret-Joyner-Halenda method (50), which is classically used but has been shown to underestimate the pore size of hydrophilic silica (49), and the Broekhoff-de Boer method. The pore size of the hydrophobic materials is taken as the average of the two results $R_p = (R_{\text{BDB}} + R_{\text{BJH}})/2$, and the uncertainty is taken as their difference $\Delta R_p = (R_{\text{BDB}} - R_{\text{BJH}})/2$. The values are gathered in Table 2.

The experimental device, cell preparation, and obtention of the P-V isotherms of water in the hydrophobic materials are detailed in ref. 25. The intrusion (respectively, drying) pressure is defined as the average pressure value on the corresponding plateau. The intrusion pressure depends weakly on the intrusion rate, and we use quasistatic values obtained at a rate of 0.1 s^{-1} . It also depends very weakly on temperature, because $P_{\text{int}} = P_{\text{int}}(T_0) + \Delta P_{\text{int},T}(T - T_0)$. The Young contact angle derived from Eq. 1 also changes with temperature, because $\theta = \theta(T_0) + \delta\theta(T - T_0)$. Values for the three materials are summarized in Table 2.

In the data analysis, we use the following expressions to interpolate the functions K_1 , K_2 , and K_3 with $90^\circ \leq \theta \leq 135^\circ$:

$$K_1(\theta) = 4.1661 + 0.11242 \times \sin(0.11819 \times \theta + 0.16478),$$

$$K_2(\theta) = 20.32 - 0.14879 \times \theta, \text{ and}$$

$$K_3(\theta) = 3.355 + 0.14136 \times \theta - 0.00054762 \times \theta^2.$$

The theoretical calculation of the shape and energy of a vapor bubble in a cylinder in the presence of a line tension is performed with a finite element method and a relaxation algorithm.

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