Capillary Rise of Liquids in Nanopores

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(Dated: 01/23/2006)

We present measurements on the spontaneous imbibition (capillary rise) of water, a linear hydrocarbon (n-C$_{16}$H$_{34}$) and a liquid crystal (8OCB) into the pore space of monolithic, nanoporous Vycor glass (mean pore radius 5 nm). Measurements on the mass uptake of the porous hosts as a function of time, $m(t)$, are in good agreement with the Lucas-Washburn $\sqrt{t}$-prediction typical of imbibition of liquids into porous hosts. The relative capillary rise velocities scale as expected from the bulk fluid parameters.

I. INTRODUCTION

Spontaneous imbibition, the capillary rise of a wetting liquid in a tube or more generally spoken a porous host, plays a crucial role in such different areas as oil recovery, printing, cooking and fluid transport in living organisms [1]. It is governed by a balance of capillary action versus viscous drag and gravity forces. Therefore, the details of the imbibition process, e.g. the morphology and speed of the advancing imbibition front depend sensitively on fluid parameters (viscosities $\eta$ of displacing and displaced fluid and interfacial or surface tensions $\sigma$) and on the structure of the porous host.

Here, we shall present experiments on spontaneous imbibition of liquids into nanoporous, monolithic silica glass. We will demonstrate that such experiments allow one to explore flow properties of liquids in restricted geometry. A topic which is of importance for lubrication, transport of liquids through biomembranes and folding of proteins - not to mention the growing, technological and scientific interest concerning the physics of liquids in nanodevices, e.g. carbon nanotubes [2, 3, 4, 5, 6, 7, 8].

As porous host we have chosen “thirsty” Vycor glass, a nanoporous silica glass which is permeated by a 3D network of interconnected, randomly oriented pores [9]. In order to play with the complexity of the imbibing fluids we have chosen three different liquids: water, a chain-like, linear hydrocarbon (n-C$_{16}$H$_{34}$) and a rod-like liquid crystal (4-Cyano-4'-n-octyloxybiphenyl, 8OCB).

II. EXPERIMENTAL

A cuboid (0.4 x 0.43 x 2.65 cm$^3$) was cut from a Vycor rod (Corning, code 7930) with a diamond saw. Prior to using the Vycor sample and after each imbibition experiment we subjected the host to a cleaning procedure with hydrogen peroxide and sulphuric acid followed by rinsing in Millipore water and drying at 70 °C in vacuum. The cleaned glass was colorless. In agreement with former results on the pore structure of samples from this Vycor batch [10], the mean volume porosity, $\Phi$ and mean pore diameter, $r_m$ was determined to $\Phi=30\%$ and $r_m = 5$ nm, resp.

Water cleaned by a Millipore filtering setup was used for the water imbibition experiment. N-hexadecane (99.5% purity) was purchased from Aldrich and the 8OCB sample (99% purity) from Synthon Chemicals (Germany). The capillary rise experiments were performed at room temperature, $T=22\,^\circ\text{C}$ for water and the n-alkane, whereas we have chosen a temperature of $85\,^\circ\text{C}$ for the imbibition experiment on 8OCB. In the bulk state, the liquid crystal is at that temperature in the isotropic phase.

The mass uptake of the porous hosts as a function of time, $m(t)$, was recorded gravimetrically with an electronic balance after gently immersing the monoliths into glass vessels containing the bulk liquids. Right upon contact of the bottom facet of the glass matrix with the surface of the bulk liquid, we observed for all samples a jump in $m(t)$. It can be attributed to the formation of a macroscopic liquid meniscus at the bottom perimeter of the matrix, which happened typically within a couple of seconds after contact of surface and matrix. Since we are interested in the immersion of the liquid into the inner pore space, we will present data sets after subtracting this mass jump in the following. In principle, one has also to worry about buoyancy forces acting on the porous host and inertia effects in the very beginning of the imbibition process [11, 12]. However, both contributions are negligible in our experiments, a statement supported by the data presented below.

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III. RESULTS

The mass uptake of the porous host by the imbibition of water, n-C$_{16}$H$_{32}$ and 8OCB are plotted in Fig. 1 as a function of time. For the three investigated liquids we find distinct, monotonic increasing mass uptake curves and the mass uptake rate, $dm(t)/dt$ is monotonically decreasing with time. Due to the fast imbibition process in the case of water, we find additionally to the monotonic increase a saturation of the mass uptake at $t=27100s$ and $m_s=m(27100s)=0.136g$. At that time the advancing water front reaches the top of the porous monolith. The value $m_s$ compares well with the overall mass uptake expected for a complete filling of the free pore space of the cuboid, 0.136g.

The time behavior shown in Fig. 1 for the immersion of
the three liquids into the porous monolith is well known from capillary rise experiments in tubes and can be derived by simple phenomenological arguments: Provided the liquid wets or partially wets the tube walls (contact angle, \( \Theta < 90^\circ \)), the liquid is sucked into a tube of radius \( r \) by the capillary pressure, \( p_{\text{cap}} \), given by the Laplace equation:

\[
p_{\text{cap}} = 2\sigma \cos \Theta / r
\]

The tube geometry calls for a Hagen-Poiseille type flow pattern, where the viscous drag implies that the volume flow rate

\[
d\mathbf{V}(t) / dt \sim 1/\eta \ l(t)
\]

and thus the corresponding mass flow rate is given by

\[
dm(t) / dt \sim \rho p_{\text{cap}} / \eta \ l(t)
\]

, where \( \rho \) is the mass density of the liquid. The variable \( l(t) \) refers to the height of the liquid column that has already been filled up with liquid at time \( t \). A length which is at any time proportional to \( m(t) \) in a capillary rise experiment. Thus one arrives at a quite simple relation for \( m(t) \) and its time derivative:

\[
m(t) dm(t) / dt \sim \rho^2 p_{\text{cap}} / \eta \sim \rho^2 \sigma / \eta \cos \Theta \quad (1)
\]

In a capillary rise experiment one has also to consider gravity forces, however, for the tiny tubes or pores investigated here, the gravity pressure is negligible compared to \( p_{\text{cap}} \). Relation 1 is solved by

\[
m(t) \sim \rho \sqrt{\sigma / \eta \cos \Theta \sqrt{t}} \quad (2)
\]

Thus the mass uptake in a capillary rise experiment should show a \( \sqrt{t} \) behavior and it is sensitive to the fluid parameters (\( \sigma, \eta, \rho \)) and the fluid wall interaction (via the contact angle \( \Theta \)). Relation 2 is known as Lucas-Washburn law \cite{13, 14} and the square of the second prefactor of relation 2 as imbibition speed, \( v_i \). Porous media, as employed in our experiments, can be considered as complex networks of simple tubes. Therefore, neglecting details of the structure of our porous host, such as the connectivity of the pores, their tortuosity and the pore size distribution, we should also expect a \( \sqrt{t} \)-behavior for \( m(t) \). In agreement with this conclusion, the data points of our experiments, plotted versus \( \sqrt{t} \), can be nicely fitted with straight lines – see lower panel of Fig. 1.

Since we used for all three experiments the same matrix with the same pore microstructure and the same macroscopic extensions we can eliminate the unknown proportionality factors of relation 1 by a calculation of relative imbibition speeds, \( v_i \). The resulting quantities should scale according to the ratio of the bulk fluid parameters, provided the continuous-type, macroscopic flow description as well as the macroscopic fluid parameters are valid for the capillary rise phenomenon studied. In order to check this, we calculated values of the bulk imbibition speeds, \( v_{i,bulk} \) by using literature parameters for \( \eta \) and \( \sigma \) and contact angles on planar silica. We normalized those imbibition speeds to the value of water:

\[
v_{i,ir} = v_{i,bulk} / v_{i,bulk}(\text{water})
\]

From the ratio of the square of the slopes of \( m(t) \) in Fig. 1 (lower panel) divided by \( \rho \), we extracted the imbibition speeds, \( v_{i,conf} \), in nanoporous silica and, again, normalized them by the one of water. As one can see in Tab. 1 we get a reasonable good agreement of \( v_{i,ir} \) and \( v_{i,conf} \) for the liquids investigated. Given the uncertainties in the literature values of the bulk fluid parameters, which we estimated to be 5-10%, the small deviations between \( v_{i,ir} \) and \( v_{i,conf} \) are well within the expected error margins of \( v_{i,ir} \).

It should also be noted that the decreasing mass uptake rate implicates that one probes also a continuous range of flow velocities in the pores during a given imbibition experiment, and thus a continuous range of shear rates. Assuming a no-slip boundary condition, one can estimate, e.g. for the water experiment, a decrease of the shear rate from \( 10^4 \) 1/s in the very beginning to 1/s at the very end of the experiment. Thus, the constant slopes of the Lucas-Washburn-law in Fig. 1 as a function of time implicate also the absence of any detectable shear-thinning or shear-thickening effects for the liquids studied.

IV. SUMMARY

We have demonstrated that simple capillary rise experiments in nanoporous hosts allow one, in principle, to study the relative magnitude of fluid parameters of liquids confined in nanopores. In the case of water, n-hexadecane and 8OCB we observe capillary rise velocities that scale as expected from the bulk fluid parameters. Thus, we find no hints of a breakdown of the continuous-like description of the hydrodynamic flow of these liquids in nanoporous silica. This result achieved in a capillary flow geometry, and thus in a flow experiment with Hagen-Poiseuille type flow geometry, is maybe not too surprising, if one recalls the observations reported for microscopic thin films between mica surfaces in the surface force apparatus setup (Couette flow geometry) \cite{20, 21, 22}. There, deviations from the bulk fluidity have been reported for film thicknesses on the order of a
TABLE I: Bulk fluid parameters and imbibition speeds of the three liquids investigated. The notation is described in the text.
(The bulk fluid parameters for water were taken from ref. [15], the ones of n-C$_{16}$H$_{34}$ from ref. [16] and the parameter of 8OCB from ref. [17, 18, 19].)

| Substance      | T (°C) | η (mPas) | σ (mN/m) | ρ (g/cm$^3$) | $\sigma/\eta$ (m/s) | Θ (°) | $v_{\text{bulk}}$ (m/s) | $v_{\text{ir}}$ | $v_{\text{ir}}^{\text{conf}}$ |
|----------------|--------|----------|----------|--------------|---------------------|-------|------------------------|----------------|--------------------------|
| water          | 23     | 0.95     | 72.25    | 1.00         | 72.75               | 0     | 72.75                  | 1.000          | 1.000                     |
| n-C$_{16}$H$_{34}$ | 22     | 3.1      | 27.15    | 0.77         | 8.77                | 5     | 8.77                   | 0.121          | 0.128                     |
| 8OCB           | 35     | 0.6      | 27.00    | 0.98         | 2.81                | 5     | 2.80                   | 0.039          | 0.036                     |

couple of monolayers and below, only.

It is understood, that we can miss deviations in the absolute transport properties of the spatial confined liquids by the type of experiment and analysis presented. Our findings allow, however, only two alternative conclusions: Either the macroscopic description of the nanofluidity in Vycor is valid for all three liquids, or it is invalid, but deviates in the same direction and probably for a similar reason for all three substances. In fact, we assume that the second alternative is the correct one. Experiments on the absolute fluid transport properties of Vycor glass have been reported in the literature [23, 24], that indicate the existence of one or two strongly adsorbed immobile or less mobile layers of molecules at the silica pore walls. A finding which is reminiscent of the two distinct regimes that one finds in sorption isotherms of simple molecules, e.g. argon, in Vycor, i.e. an initial layer growth and a subsequent formation of pore condensate in the center of the pores [25]. Presumably the microscopic boundary layer exists also for water, n-C$_{16}$H$_{34}$ and 8OCB in Vycor and decreases or increases the absolute flow rates through the pores depending on its mobility and the resulting slippage at the pore wall [2 3 1 5].

Last but not least, we would like to mention, that the imbibition front in Vycor is a fine example of an advancing interface in a random environment [1]. Therefore, imbibition experiments on the capillary rise of liquids in this porous host are also interesting in order to study kinetic roughening of such interfaces in nanostructured environments.

Acknowledgments

This work has been supported within the DFG priority program 1164 (Grant No. Hu 850/2).

[1] M. Alava, M. Dubé, and M. Rost, *Advances in Physics* **53**, 83 (2004).
[2] M. Urbakh, J. Klafter, D. Gourdon, and J. Israelachvili, *Nature* **430**, 525 (2004).
[3] J.M. Drake and J. Klafter, *Physics Today* **43**, 46 (1990).
[4] S. Granick, Y. X. Zhu, and H. Lee, *Nature Materials* **2**, 221 (2003).
[5] L.D. Gelb and A.C. Hopkins, *Nanoletters* **2**, 1281 (2002).
[6] M. Majumder, N. Chopra, R. Andrews, and B.J. Hinds, *Nature* **438**, 44 (2005).
[7] C.M. Megaridis, A.G. Yazicioglu, J.A. Libera, and Y. Gogotsi, *Physics of Fluids* **14**, L5 (2002).
[8] S. Supple and N. Quirke, *Phys. Rev. Lett.* **90**, 214501 (2003).
[9] P. Levitz, G. Ehret, S.K. Sinha, and J. M. Drake, *J. Chem. Phys.* **95**, 6151 (1991).
[10] D. Wallacher and K. Knorr, *Phys. Rev. B* **63**, 104202 (2001).
[11] C.H. Bosanquet, *Philos. Mag.* **45**, 525 (1923).
[12] D. Quéré, *Europhys. Lett.* **39**, 533 (1997); P.G. de Gennes, F. Brochard-Wyand, and D. Quéré *Capillarity and Wetting Phenomena*, Springer NY (2004).
[13] R. Lucas, *Kolloid Z.* **23**, 15 (1918).
[14] E.W. Washburn, *Phys. Rev.* **17**, 273 (1921).
[15] R.C. Weast and M.J. Astle, eds., *Handbook of Chemistry and Physics*, CRC Press, Florida (1981).
[16] D. Small, *The Physical Chemistry of Lipids*, Plenum Press, NY (1986).
[17] J. Jadzyn and G. Czechowski, *J. Phys.: Cond. Matter* **13**, L261 (2001).
[18] D. Langevin, *J. Physique* **37**, 901 (1976).
[19] A. Zywockinski, S.A. Wieczorek, and J. Stecki, *Phys. Rev. A* **36**, 1901 (1987).
[20] U. Raviv, P. Laurat, and J. Klein, *Nature* **413**, 51 (2001).
[21] J. Israelachvili, P.M. McGuigan, and A.M. Homola, *Science* **240**, 189 (1988).
[22] M. Rusth and S. Granick, *Langmuir* **16**, 8368 (2000).
[23] P. Debye and R.L. Cleland, *J. Appl. Phys.* **30**, 843 (1959).
[24] B. Abeles, L.F. Chen, J.W. Johnson, and J.M. Drake, *Isr. J. Chem.* **31**, 99 (1990).
[25] P. Huber and K. Knorr, *Phys. Rev. B* **60**, 12657 (1999).