

CAPILLARY MICROFLUIDICS FOR VISCOELASTIC FLUIDS

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Summary We discuss the effects of fluid viscoelasticity, inertia and capillarity during fast and slow absorption of droplets by fibrous porous conduits and micro-devices. The major attention is paid to applications of rheological viscoelastic effects to the development of new methods for handling and fraction separation of biopolymer solutions.

INTRODUCTION

In conventional microfluidic devices, fluids are pumped by applying either pressure drop or temperature or voltage differences. In biomedical technologies dealing with fluids of a complex rheology, the forced fluid transportation is sometimes hardly applicable. We present a new principle of controlled fluid transport at micro- and nanoscale. This approach is based on the phenomenon of spontaneous absorption of wetting fluids by porous materials. That is, capillarity drives the droplet self-propulsion without the need for any additional external mean. We study viscoelastic fluids and develop some theoretical and experimental approaches to tackle this problem. Aqueous solutions of polyacrylamide (PAM), polyethyleneoxide (PEO) and lambda-DNA are taken as model polymeric fluids.

WEISSENBERG EFFECT AND CAPILLARITY DRIVEN FLOW OF VISCOELASTIC FLUIDS THROUGH MICROCHANNELS.

First, we discuss the droplet absorption by capillaries (Fig.1). Absorption of droplets by capillaries of a few hundred microns in diameter is characterized by surprisingly high Reynolds numbers, which may exceed 100! At these conditions, the viscous forces seem to be negligible compared to the inertial, elastic, and capillary forces. Fluid elasticity caused by stretching of polymer molecules by velocity gradients is manifested by the appearance of a force, which is directed opposite to the direction of the meniscus motion. Essentially, the stretching of polymers in the channel gives rise to an extra stress additional to the pressure. This flow-induced stressing of viscoelastic fluids, known as the Weissenberg effect, causes a reduction of the capillary pressure at the meniscus. Effectively, the Weissenberg effect leads to a weakening of the driving force. A quantitative estimate of the Weissenberg effect can be done by considering the momentum balance for the moving liquid column. Neglecting Poiseuille friction and flow in the droplet, and assuming that the velocity and pressure at the capillary entrance are zeroth, one finds $0 = A[p + \rho U^2] - (\sigma_d - \sigma_w)L$, where ρ is fluid density, U is meniscus velocity, $(\sigma_d - \sigma_w)$ is the difference of surface energy densities of the dry and wet capillary, and p is the Weissenberg extra pressure. A is the cross sectional area of the capillary and L is its circumference. Calculation of the Weissenberg extra pressure within the Upper Convected Maxwell Model gives: $A p = 16 \lambda \eta U^2$, where λ is relaxation time and η is fluid viscosity. Collecting all terms, we obtain the relation between the initial velocity of droplet penetration and the parameters of the capillary and liquid as $U^2 = 2(\sigma_d - \sigma_w) / [1 + 16 \lambda \eta / \rho R^2]$, here R is the radius of capillary. Remarkably, the velocity U attains the maximum at the radius $R = 4 (\lambda \eta / \rho)^{1/2}$, which is independent of the wetting properties of liquids, but depends only on the rheological properties.

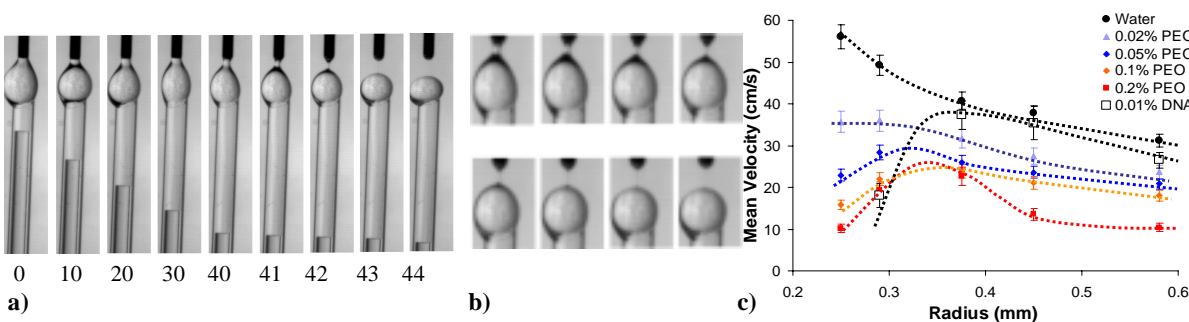


Figure 1. Penetration of 0.01% TE Buffer solution (8 pH) of lambda-DNA ($M=61 \times 10^6$ Da) into a glass capillary, ID=0.58 mm. Feeding needle on the top of a) and b) has ID= 0.51. The time under each picture is given in milliseconds. b) Dynaics of filament thinning. Enlarged pictures of a) taken between 41.25 and 43 ms, each picture is taken at 1/4000 frames per second. c) Mean velocity of meniscus as a function of radius of receiving capillary.

A systematic experimental analysis of the droplet absorption was done with a special optical electronic measuring system [1]. CMOS camera was used to film the meniscus propagation and the filament rupturing. A typical series of frames is presented in Figures 1a) and b). As seen, meniscus travels the path of about ten radii in a few milliseconds. During its motion, meniscus remains almost flat thus indicating that the velocity is approximately constant across the capillary. It is still a long way to go to reach the equilibrium shape. These findings contradict to a conventional believe that the meniscus shape equilibrates almost immediately. We pay a particular attention to the

analysis of flow patterns at the meniscus using special tracers. An asymptotic theory of flow with inertial and elastic forces as dominants supports the experimental observations.

The phenomenon of filament formation in polymer solutions and the mechanism of filament rupturing deserve a special consideration. The dynamics of filament thinning is recorded with a millisecond resolution. Real images and diffraction fringes are used to monitor the kinetics of filament thinning. Typical real images of bridge thinning and rupturing are shown in Figure 1b). The analysis of images shows that the filament changes its radius not only because of mechanical stretching, but also because of squeezing solvent out of the filament. We suggest a model to explain the kinetics of filament thinning and to relate the rheological parameters of the model to the experimental data.

While the hydrodynamic details of meniscus motion and associated flows are quite complicated and much different from what was expected, a qualitative description of the process can be captured by a simple one-dimensional model. In Figure 1c), we show the experimental data confirming the existence of a maximum velocity of absorption of viscoelastic droplets. Also, the one-dimensional approximation predicts that the meniscus travels about five capillary radii keeping the velocity constant. This is in agreement with experimental observations.

ABSORPTION OF VISCOELASTIC FLUIDS BY NANOFIBROUS SUBSTRATES.

Using the same experimental approaches, we study the process of droplet absorption by nanofibrous materials produced by spinning of carbon nanotubes and polymeric nanofibers. It is shown that the rate of absorption of viscous and viscoelastic fluids are significantly different. For nanoporous fibers made of SWNT (Fig 2a) we observe slow kinetics of absorption (Fig 2b). Namely, viscous fluids follow the Lucas-Washburn kinetics, but absorption of viscoelastic fluids is different. In the nanowebs produced by electrospinning, the rate of droplet absorption is extremely high. It takes a few milliseconds to absorb a millimeter sized droplet. It is remarkable, that while nanofibers are dissolvable in water, because of fast evaporation, there is no time to destroy the web. SEM micrographs of dried nanowebs reveal striking features of polymer/fiber interactions. Polymers in dilute solutions penetrate through the pores completely from one side of the sample to the other. No separation occurs in the regime of fast absorption. As a result, the sample after evaporation takes on a new morphology, namely, it becomes foamy. Polymers from solutions form lamellas with the thickness much less than the nanofiber diameter. These films span the pores, and the nanofibers serve as frames to hold the films (Fig. 2c). A theoretical analysis of slow and fast kinetics is based on the Maxwell model. We develop a model accounting for the flow in the droplet and in the porous substrate. As shown in experiments, flow through porous fibers and thin nanofibrous membranes is typically frontal. That is a droplet absorbing by nanoporous fibers sends fingers ahead of the visible contact lines. These fingers occupy the fiber cross-section completely. In this sense, the absorption is frontal. Same thing occurs for planar nanowebs. We have a ring of fluid that runs ahead of the visible contact line. Associated free boundary problems are featured by the presence of two fronts: the first is the contact line and the second is the front propagating ahead of the contact line. In the case of slow absorption by porous fibers, the problem is mathematically similar to the Stefan problem with a nonlinear undercooling kinetics that is solved analytically. The problem of droplet absorption by nanowebs reveals unusual features caused by an effective slip at the saturated web. We discuss in detail a role of high extension rates in the formation of foamy structures.

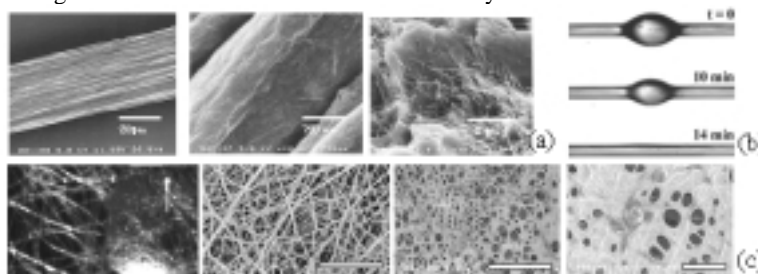


Fig. 2. SWNT fiber as nanofluidic conduit. a) Hierarchical pore structure of SWNT fiber; b) Dynamics of microdroplet spreading and absorption; c) change of nanoweb morphology after absorption of droplets of 0.05% of PAM. From left to right: microdroplet spreading over the nanoweb; dry nanoweb, bar corresponds to 15 microns; same after absorption; foamy structure, bar corresponds 6 microns.

We acknowledge the support of NIH through Grant R21 EB002889-01.

References

- [1] Bazilevsky, A.V., Kornev, K.G., Rozhkov, A.N., Neimark, A.V.: Spontaneous absorption of viscous and viscoelastic fluids by capillaries and porous substrates. *J. Colloid Interface Sciences*, **262**, 16-24, 2003.