JP Journal of Heat and Mass Transfer

Published Online: May 2016
http://dx.doi.org/10.17654/HM013020183
Volume 13, Number 2, 2016, Pages 183-192 **ISSN: 0973-5763**

ANALYTICAL SOLUTION OF THE PROBLEM OF SPEED DETECTION CAPILLARY ABSORPTION FOR A NANOTUBE

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Abstract

An analytical solution for the equation modeling the process of capillary absorption into nanotubes has been obtained. Initial-value classical and two-point problems have been researched and the relations allowing a determination of the height of rise and the velocity of movement of liquid in capillaries have been found. On the basis of the obtained laws, computing experiments have been conducted and a comparative analysis of the results has been presented.

Received: June 12, 2015; Revised: November 19, 2015; Accepted: November 28, 2015

Keywords and phrases: capillary, mathematical model, analytical solution, dimensional effects, computing results.

Communicated by Shuisheng He

1. Introduction

The first fundamental results in researching capillary absorption problems were obtained in the beginning of the last century [1, 2]. But despite a nearly century-long history of this research, it still remains current and practically significant [3-6]. First of all, such interest can be explained by the technological needs of modern manufacturers, and by successes in the development of new composite materials consisting of nanotubes. Therefore, the development of an experimental and theoretical basis for the research of capillary absorption is an important and perspective problem. Since this problem is nonlinear, numerical methods [7-9] have recently been used to solve it, with increasing frequency. At the same time, there are practically exact or approximate analytical estimations of liquid dynamics, or they are reduced to strongly simplified, sometimes linear relations [10, 11]. In this paper, we research one of the latest models for capillary absorption in nanotubes, which takes into account dimensional effects, and we present its general analytical solution and a number of computing experiments based on it.

2. Determination of Stream Function for Nanocapillaries

The volume of fluid flowing in the nanotube depends on the time, i.e., $V = V(t)$, so the Lagrangian for the liquid column can be written as

$$L = \frac{\rho V(t)\nu^2}{2} - U(h). \tag{1}$$

Substituting equation (1) the Lagrange equation:

$$\left(\frac{\partial}{\partial h} - \frac{d}{dt}\frac{\partial}{\partial \nu}\right)L = 0,$$

we obtain the equation of motion

$$\rho\left(V\frac{d\nu}{dt} + \nu\frac{dV}{dt}\right) = F. \tag{2}$$

The volume of liquid in the nanotube are equal: $V(t) = \pi R^2 h(t)$.

Therefore, equation (2) takes the form:

$$\pi R^2 \rho \left[h \frac{d^2 h}{dt^2} + \left(\frac{dh}{dt} \right)^2 \right] = F. \qquad (3)$$

In equation (3) is taken into account conservative and dissipative forces. The force with which the liquid is sucked into the nanotube, is

$$\pi R^2 \Delta p.$$

The force of viscous friction in this case, there:

$$-8\pi\eta h \frac{dh}{dt}.$$

Thus, we obtain the equation [12]:

$$h \frac{d^2 h}{dt^2} + \frac{8\nu}{R^2} h \frac{dh}{dt} + \left(\frac{dh}{dt} \right)^2 - \frac{\Delta p}{\rho} = 0, \quad \nu = \frac{\eta}{\rho}, \qquad (4)$$

where $h(t)$ - height of liquid rise in a capillary, R - capillary radius, ν - coefficient of kinetic viscosity, ρ - density, Δp - capillary pressure.

Let us present equation (4) in the following form:

$$h \frac{d^2 h}{dt^2} + \alpha h \frac{dh}{dt} + \left(\frac{dh}{dt} \right)^2 = \beta, \qquad (5)$$

where $\alpha = \frac{8\nu}{R^2}$, $\beta = \frac{\Delta p}{\rho}$.

Assuming that $h(t) \geq 0$, and substituting the required function, we obtain:

$$h(t) = \sqrt{u(t)}, \qquad (6)$$

as a result of simple transformations, we find:

$$h(t) = \left(\frac{2\beta t}{\alpha} + \frac{c_1}{e^{\alpha t}} + c_2 \right)^{1/2}, \qquad (7)$$

where $c_{1,2}$ - constants of integration.

We can integrate the following equation in a similar way:

$$h\frac{d^2h}{dt^2} + \left(\frac{dh}{dt}\right)^2 = \beta. \tag{8}$$

This equation is a special case of equation (4) and can also be found in scientific literature [12, 13] in descriptions of the capillary absorption process.

Since equation (8) does not contain R, in an obvious form, it does not allow for a full assessment of the dimensional effects. Therefore, to later consider both of the equations, let us present computing experiments for the case of equation (4) only.

Like for equation (4), substitution of required function (6) allows for a reduction in the question of solubility in equation (8) to the question of solubility in a linear differential equation, whose general integral, after inverse substitution, takes the form:

$$h(t) = \sqrt{\beta t^2 + c_3 t + c_4}, \tag{9}$$

where $c_{3,4}$ - constants of integration.

A peculiarity of obtained solutions (7) and (9) in determining the height of liquid phase rise in a capillary consists in that the straight line $t = 0$ is a tangent line for them that follows directly from equation (6). This circumstance testifies to the significant speed of liquid flowing into a capillary in the initial stage. On the other hand, there is the problem of determining the constants of integration c_i $(i = \overline{1,4})$ in the case of a classical initial-value problem.

Indeed, a statement of the Cauchy problem [14]:

$$h(t)|_{t=0} = h_0, \qquad h'(t)|_{t=0} = h_1, \qquad h_{0,1} - const., \tag{10}$$

both in the case of relations (7) and (9), assumes the presence of the additional condition $h_0 \neq 0$.

Let us demonstrate this by example, using relation (9). The reasoning for function (7) is similar.

Indeed, if $h_0 = 0$, then $c_4 \equiv 0$. By differentiating relation (9), we obtain:

$$h'(t) = \frac{1}{2}(\beta t^2 + c_3 t + c_4)^{-\frac{1}{2}} \cdot (2\beta t + c_3). \qquad (11)$$

It obviously follows from equation (11) that if $c_4 \equiv 0$ and $c_3 \neq 0$: $h'(t)|_{t\to 0} \to \infty$.

Thus, solutions such as (7) and (9), if $c_i \neq 0$, imply a presence of the condition $h_0 \neq 0$, i.e., a condition at which the height of liquid rise in a capillary, at the initial moment, is nonzero.

For equation (8) and, therefore, for equation (9), aside from the Cauchy problem, a two-point problem can also be set. Its difference from the initial-value problem (10) consists in that specification of the magnitude h_1, i.e., the speed of liquid flowing into a capillary at the initial moment, can be replaced with an equivalent condition, such as:

$$h(t)|_{t=T} = H, \quad T,\ H - const. \qquad (12)$$

Condition (12) turns out to be sufficiently effective when there are data on the height of liquid rise H at the moment $T \neq 0$. Both the intermediate values obtained experimentally and the maximum values for liquid rise in a capillary and for the time elapsed in this process can be used in the capacity of such parameters.

Thus, for problems (4) and (10) in case $h_1 \equiv 0$, we find:

$$c_1 = \frac{2\beta}{\alpha^2}, \quad c_2 = h_0^2 - c_1. \qquad (13)$$

In turn, for problems (8), (10) and (12), we obtain

$$c_3 = \frac{1}{T}[H^2 - h_0^2 - \beta T^2], \quad c_4 = h_0^2.$$

The approach realized here, with the limitations specified above, allows us not only to determine the height of liquid rise in a capillary, but also to estimate the speed of liquid flowing into a capillary at various stages by using only analytical relations. In doing this, the expression for the capillary absorption rate, in the case of equation (8), takes form (11), and in the case of equation (4) it takes the following form:

$$h'(t) = \frac{1}{2}\left(\frac{2\beta t}{\alpha} + \frac{c_1}{e^{\alpha t}} + c_2\right)^{-1/2} \cdot \left(\frac{2\beta}{\alpha} - \frac{\alpha c_1}{e^{\alpha t}}\right), \tag{14}$$

where the constants $c_{1,2}$ are determined by equation (13).

3. Computing Results

Let us present the results of the computing experiments conducted on the basis of relations (7) and equation (14). All calculations have been carried out for real values. Some of the data used are presented in the following table [15].

Table 1. Liquid parameter values at a temperature of 293,15K

Liquid	$\nu, \left[\frac{m}{s^2}\right]$	$\rho, \left[\frac{kg}{m^3}\right]$	$\sigma_3, \left[\frac{N}{m}\right]$
Oil (high-gravity)	$23{,}2*10^{-6}$	845	0,0285
Water	$1{,}003*10^{-6}$	998	0,0728
Ethanol	$1{,}200*10^{-6}$	789	0,0220
Nitrobenzene	$2{,}034*10^{-6}$	1203	0,0439

Capillary pressure has been calculated according to the formula [12]:

$$\Delta p = \frac{4\sigma_3}{R}\left[\sqrt{\frac{\sigma_1}{\sigma_3}} - \frac{1}{2}\right],$$

where σ_1 - the surface energy of the frame of the nanotube, which has been selected equal to $0{,}0453\,\mathrm{N/m}$, which corresponds to MWCNT capillaries with a radius of $R = 30 \pm 15\,\mathrm{nm}$ [16], σ_3 - the surface energy of the liquid phase.

The following figure presents the results of computing experiments conducted on the basis of the data from Table 1.

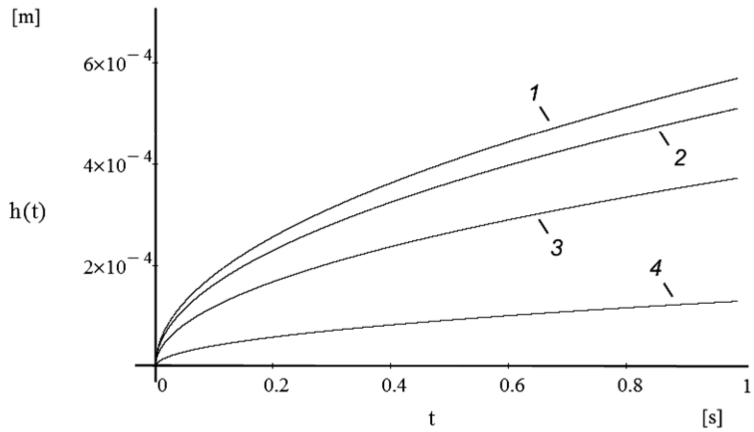

Figure 1. Capillary absorption plots: (1) ethanol, (2) water, (3) nitrobenzene, (4) oil.

All calculations have been realized in the MATCAD software package, for capillaries with a radius of $R = 15\text{nm}$, at $|h_0| = 10$ nanometer.

To determine the capillary absorption rate, computing experiments have been conducted on the basis of equation (14) with the same capillary radius values. One of the calculation plots is presented in Figure 2.

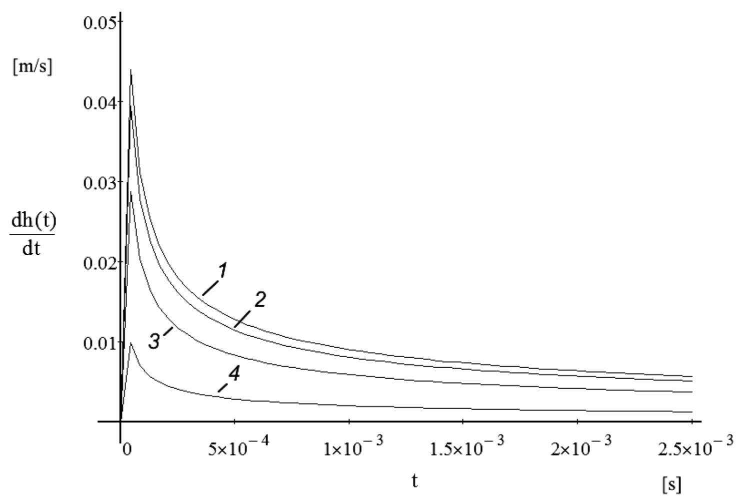

Figure 2. Plots for capillary absorption rate: (1) ethanol, (2) water, (3) nitrobenzene, (4) oil.

Computing experiments have demonstrated that dependencies similar to that presented in Figure 2 are also characteristic for other liquids. The initial stage, at which the maximum calculated values for capillary absorption speed can vary from 200 to 1050 m/s takes several milliseconds; after that, the capillary forces are compensated by viscous resistance.

4. Conclusion

The results of the research carried out allow us to assert that, with the capillary radius reduced to nanosizes, at the initial stages of liquid flowing into a capillary, one can observe not only an increase in absorption rate, but also a change of viscous flow into ballistic flow.

Besides, based on the obtained expressions for $h(t)$ it is possible to forecast the results of natural experiments. In particular, it can be expected that their realization can yield the following dependence:

$$h \sim t^{z}, \quad 1/2 \leq z < 1.$$

Let us note that such regularity is predetermined by the structure of equation (6). Besides, in the case of $c_{1,2} \equiv 0$ the parameter $z = 1/2$, corresponds to Washburn's equation.

The obtained results correspond to the results obtained in papers [8, 17] and testify to another (in comparison with typical absorption) mechanism of process for mass transfer in nanotubes [18-21].

Acknowledgement

The authors thank the anonymous referees for their valuable suggestions which let to the improvement of the manuscript.

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