

## THE WETTABILITY OF THE LIQUID-SOLID INTERFACE

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### ABSTRACT

*Presented paper is focused on setting up question of a solid/liquid interface adhesive force, especially in liquid movement dependence. Nowadays it is generally supposed, that the real liquid cleaves on the surface so, that the relative velocity of the liquid on the surface is zero. This condition doesn't obtain for the partial slip and slip (nonwetttable) materials. In this case isn't the adhesive force so large to the absolute cleaving of the liquid on the surface. It is shown in the paper that the adhesive force for the different types of surfaces (glass, Teflon, steel) has dramatically changed. The experiment is looking for the wall angle which starts the movement of the promptly defined drop in its gravity dependence. This angle characterizes the adhesive force similarly as the slip angle the surface tension. From the experiment is obvious, that the adhesive force for example the rustles steel material for example on the Teflon surface. For the adhesive force is except of the experiment derivate an expression, that puts together the irreversible stress vector and the liquid velocity vector on the runaround surface.*

### 1. INTRODUCTION

For the flow solution problems in the surface characteristics dependence is generally assumed that the fluid cleaves on the surface. It means that the relative velocity of the moving liquid equals zero. Therefore:

$$\mathbf{w} = \mathbf{c} - \mathbf{u} = \mathbf{0} \quad (1.1)$$

where  $\mathbf{c}$  – fluid velocity vector,  
 $\mathbf{u}$  – surface velocity vector of the moving body

This condition comes out the assumption of **totally no slipping (wetttable)** solid/liquid

interface. From the fluid flow point of view it means that close to the solid surface there are generating high velocity gradients. These are responsible for the main part of hydraulic losses.

The cleaving condition also arise the boundary layer creation, the flow separation and the turbulent fluctuation initiation as well.

The present technologies do product the new metallic and plastic materials, and different surface finishing, where the cleaving condition doesn't obtain.

Therefore it is necessary to develop the new methodic of the surface slipping towards the liquid, to formulate the new boundary condition determining the adhesive force the surface effects the liquid stationary or in motion.

### 2. COHESIVE AND ADHESIVE FORCES – SLIPPING AND FORCES IN THE LIQUID BOUNDARY LAYER

The positive intra-liquid molecular forces have quite a short range of influence, so the certain molecule should be effect by the others just from the very near region. The positive molecular forces (**cohesive forces**) region can be define by an around the molecule circumscription sphere of a very small radius  $r$ . The outside sphere placed molecules action forces to the certain molecule is insignificant.

When the certain molecule is situated anywhere inside the liquid, the molecule activity region is fulfilled by the liquid molecules and its effect to the certain molecule is symmetrically and the forces are canceled on average. Such molecule is in the free steady state (indifferent equilibrium).

But when the molecule occur a thin film that bounds with different media, there fall into the molecule activity region also the foreign materials

(other liquids or solids). The forces equilibrium is destroyed and the resultant of the forces applied to the certain molecule is non zero. If the liquid is bordering with a solid material the resultant of the liquid/solid forces calls an **adhesive** force. It causes the liquid adhesion to the solid surface. In case of bordering with the vapor - the molecules close to the border and on the border have part of their activity regions almost empty. The resultant of the forces in this film will direct into the liquid (the direction of the border normal).

The molecules that are on the liquid level effect on each other by forces, which are in tangential direction with respect to the liquid level. If the molecule is far from the place where liquid layer contacts another medium (wall), the tangential forces are canceled on average and the molecule should easily translate on the liquid level. On places where the liquid level touch the foreign material are the molecule activity region infiltrated by the foreign material molecules; the resultant of the forces is non zero.

### Internal pressure

The internal molecule (cohesive) pressure – take the level  $10^9$  Pa – is caused by the force from the liquid boundary level direction into the liquid (normal direction). Beside these pressure values are the outside pressures – for example  $10^7$  Pa – quite insignificant, that interpret the very low compressibility of liquid.

### Surface tension (stress) and wettability (no-slipping)

The molecular forces in the boundary layer provoke the same effect as there will be a *tensed elastic membrane* on the liquid level that wants to contract. In each liquid level (not just at the drops) there are tangential forces.

For the quantitative representation of the membrane tensility it is established a value, called *surface tension*.

$$\sigma = \frac{F}{l}. \quad (2.1)$$

The surface tension act all ways on the liquid surface. If we choose one arbitrary directed line segment of length  $l$ , there will be acting a total force  $F = \sigma l$ , which is perpendicular to the chosen line and tangential to the liquid surface. See Fig. 2.1.

**The surface tension depends on the liquid and contacting region characteristics and on the temperature (it will decrease with increasing temperature).**

The wettability ratio (factor) of the liquid-solid interface depends on the surface tension. It is characterized by the contact angle  $\Theta$ , see Fig. 2.1, though its use it is the surface energy of the liquid drop established. It holds that the low surface energy value shows the partial wettable materials (so called *hydrophobic*), on the other hand the high surface energy value shows the *hydrophilic* surfaces.

Set the surface energy of the solid material directly is very complicated, that's why are used the indirect methods. One of the easiest methods - the contact angle of the liquid drop on the solid surface is defined by the drop mechanical equilibrium between the three surface tensions  $\gamma$ : solid/vapor, solid/liquid, liquid/vapor (Fig. 2.1)

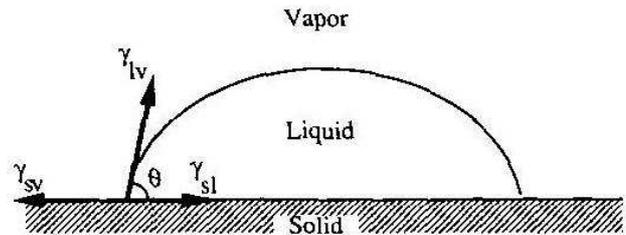


Figure 2.1 Surface tensions equilibrium

The solid body surface energy determined from the contact angle depends on the equation set by Thomas Young in 1805. This equation is generally known as a Young equation:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \quad (2.2)$$

where:  $sv$  (solid/vapor),  $sl$  (solid/liquid) and  $lv$  (liquid/vapor).

The mathematical models used in this work come out this equation. They are divided into one-, two-, three-liquid and regression model.

On such a principle were set the surface energies of five different surface types. Three of them were formed by a Teflon layer (black metallic paint TC 3072, normal black TC 1191, green TC 4111), next was formed by the synthetic dope (normally used for the airplane wings coating – white aero-plate), last of them was a glass.

### 3. EXPERIMENTAL RESULTS

1 – 2  $\mu\text{l}$  drops were applied on the surfaces by the micropipette Labopette. They were scanned by the CCD camera that was connected with the computer by the USB cable. The measuring system was invested with the special software (SEE software), where is implemented the testing liquids database. The measurement error of the contact angle were checked by the Student coefficient for the reliability level of 99,9%. The surface energy calculation was made by the Acid-Base method, which is part of the SEE software component. See the results in Tab. 1.

Specimen	Contact angle (°)			Surface energy mJ/m <sup>2</sup>
	1	2	3	
TC 3072	107.1 ± 4.4	90.9 ± 2.9	68.1 ± 4.9	24
TC 1191	94.1 ± 1.3	65.3 ± 5.6	44.8 ± 5.8	34
white plate	78.7 ± 3.2	49.5 ± 5.5	19.9 ± 2.9	43
glass	34.6 ± 4.6	30.7 ± 3.8	26.8 ± 5.6	50
TC 4111	109.2 ± 6.2	84.9 ± 5.1	64.2 ± 11.9	23

Table 1. 1- water, 2- ethyleneglycol, 3-  $\alpha$ -bromnaphthalene

From the given table is obvious, that the lowest surface energy show both Teflon kinds (TC 3072, TC 4111) by contraries the highest one has glass. Glass is markedly hydrophilic and shows the highest wettability towards the liquids.

The next experiment were focused on the above mentioned surface energy changes by the plasma effect. For the finishing were used the volumetric DB discharge in the pure nitrogen. The exposure time was 10 minutes (superabundant). See the results in Tab. 2.

Specimen	Contact angle (°)	
	before	after finishing
TC 3072	107.1 ± 4.4	68 ± 17
TC 1191	94.1 ± 1.3	43.9 ± 4.1
white plate	78.7 ± 3.2	36.0 ± 4.4
glass	34.6 ± 4.6	17.9 ± 6.6
TC 4111	109.2 ± 6.2	95.2 ± 7.6

Table 2.

The drop contact angles comparison before and after the plasma finishing process shows the **hydrophilic character of the plasma effect**.

It is necessary to do the experiments with water drops very quickly, because the water evaporates

fast in the temperature dependence – so it changes the volume and weight.

For no ideal surfaces that are not ideally smooth – should be the experimental result influenced by the existence of the air bubble in the microscopic caverns. Bubbles can dramatically change the experimental results and consequently the opinion to the surface wettability.

On the next figures 3.1 with the bubble and 3.2 without the bubble is clearly shown the experimental principle that was focused on the static adhesive force detection between liquid and solid in the bubble size dependence.



Figure 3.1

Figure 3.2

The evident influence of the air bubbles to the adhesive force value is clearly visible. Beside the above mentioned methods were done some other qualitative comparative experiments based on the inclined plane angle measurement while the drop running down. See Fig. 3.3, 3.4 and the liquid layer run down the inclined plane Fig. 3.5 – 3.8.

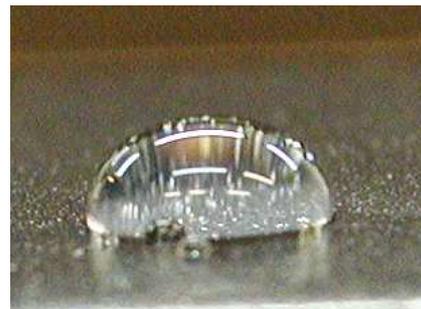


Figure 3.3



Figure 3.4

On the Figures there is visible the quantitative wettability difference between the white air-plate and Teflon plate TC 4111. Very low surface energy of the Teflon layer makes the water collection into the rope (in consequence of the liquid surface energy).

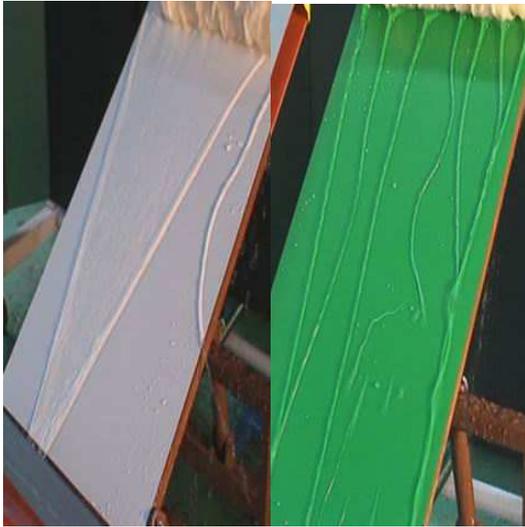


Figure 3.5

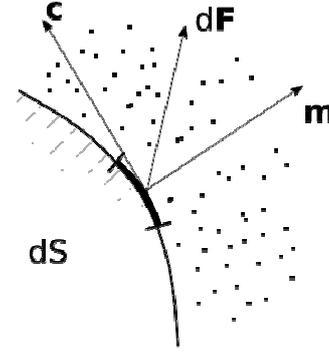
Figure 3.6



Figure 3.7 Figure 3.8

This effect is more visible on the liquid discharge from the tube to the inclined plate. Results are shown in figures 3.7 and 3.8. The surface energy characterized the node distance of the surface wave from the tube issue.

#### 4. BOUNDARY CONDITION OF THE LIQUID/SOLID INTERFACE



Let think of the surface  $dS$ , that is in contact with liquid. The adhesive force that affects the liquid is possible to write in the irreversible stress tensor  $\Pi_{ij}$  dependence:

$$dF_i = \Pi_{ij} m_j dS. \quad (4.1)$$

Because the liquid can slip on the partial wettable surface, its velocity is tangential and non zero on the surface  $S$ . It is assumed that the adhesive force counteracts the relative velocity vector and is proportional to the relative velocity. Then:

$$dF = -\mathbf{K} \mathbf{w} dS \text{ na } S. \quad \mathbf{K} = \mathbf{K}(\kappa_{ij}) \quad (4.2)$$

If we institute (4.2) to (4.1) we get the boundary condition for the partial wettable surface:

$$\begin{aligned} \sigma_i &= \Pi_{ij} m_j = -\kappa_{ij} (c_i - u_i) = -\kappa_{ij} w_j \\ \Pi_{ij} &= \int_0^t \psi(t - \tau) c_{ij}(\tau) d\tau \end{aligned} \quad (4.3)$$

where  $\mathbf{u}$  – body surface velocity,  $\mathbf{w}$  – relative velocity,  $\mathbf{m}$  – outside vector normal to the surface,  $c_{ij}$  – strain rate tensor,  $\psi$  – liquid memory

It is obvious (from 4.2) that the partial wettable surface stress vector corresponds with

the relative velocity vector on the surface. From this imply for the totally wettable surface it holds:  $k \rightarrow \infty$  and  $c_i = u_i$ .

Let's apply this boundary condition to the **laminar flow of the liquid between the concentric cylinders** of radius  $R_1$  - inside cylinder,  $R_2$  - outside cylinder. If want the liquid slipping on the partial wettable surface, there is a boundary condition:

$$\Pi_{ij}n_j = \kappa_{ij}(c_j - u_j), \quad m_j = -n_j, \quad (4.4)$$

or for the non rotating wall  $\Pi_{ij}n_j = \kappa c_i$ , (4.5)

where  $\kappa > 0$  is the adhesive force coefficient that is proportional to the velocity.  $\Pi_{ij}n_j$  is i-th stress vector coordinate on the solid/liquid interface.

For the above mentioned case we set the liquid with so called burned out memory that is defined by the generalized Dirac function  $\psi = \eta \delta(t)$ . It means  $\Pi_{ij} = 2\eta c_{ij}$ . In the polar coordinates:

$$\Pi_{r\varphi} = \eta \left( \frac{\partial c_\varphi}{\partial r} - \frac{1}{r} c_\varphi \right) = \kappa (c_\varphi - u), \quad u = \Omega R_1. \quad (4.6)$$

For the velocity  $c_\varphi$  it holds:

$$c_\varphi = \frac{A}{r} + B r, \quad (4.7)$$

where  $A, B$  are the integrating constants, that is necessary to set from the boundary conditions.

$$\begin{aligned} r = R_2 : \quad c_\varphi &= 0 \\ r = R_1 : \quad \Pi_{r\varphi} &= \kappa (c_\varphi - u) \end{aligned} \quad (4.8)$$

Surface speed  $c_\varphi$  and torque  $M_k$  is possible to write as:

$$c_\varphi = \frac{R_1^2 u}{2 \frac{\eta}{\kappa} R_2^2 + R_1 (R_2^2 - R_1^2)} \left( \frac{R_2^2}{r} - r \right) \quad (4.9)$$

$$M_k = - \frac{4\pi R_1^2 R_2^2 \eta u}{2 \frac{\eta}{\kappa} R_2^2 + R_1 (R_2^2 - R_1^2)}. \quad (4.10)$$

If the space  $H = R_2 - R_1$  between the discs will be thin, the dissipative function rate of the partial wettable surface  $D_N$  and wettable  $D_S$  surface is given as:

$$D_N = \frac{1}{1 + \frac{\eta}{H\kappa}} D_S. \quad (4.11)$$

Hence it is obvious that the dissipative function is easily influenced just when:

$$\frac{\eta}{H\kappa} \gg 1 \Rightarrow \kappa \ll \frac{\eta}{H}.$$

If  $H$  is ordered  $0,001m$ , then must be  $\kappa \ll 1 Pa \cdot s \cdot m^{-1}$ .

From the term (4.10) it is obvious, that the adhesive force coefficient  $\kappa$  can be evaluated by using the precise viscosimeter – by measuring the torque  $M_k$  for the known liquid viscosity.

## 5. CONCLUSION

It is visible from the paper, that the classical hydrodynamic theory doesn't render the flow around the particle wettable surface. Such a flow needs a new boundary condition that characterizes the adhesive forces effect on the liquid/solid interface. There is shown one the possible ways that is necessary to validate and complete by additional experiments. It is assumed that also the memory of the material will influence the results. New materials on the nanotechnology and titanium oxides bases are markedly nonwetable that affects the wall functions and will also need a turbulence models modification. Nonwetable materials will reduce the hydraulic losses that lead to necessary liquid transporting energy decreasing. The pump from the low wettable material achieved the 5% decrease of the hydraulic efficiency.

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