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Evaluation of dynamic microscopic advanced angle for droplet on flat surface

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Abstract The paper presents a short description of the model of the phenomenon of droplet spreading in presence of a liquid film, as well as the experimental facility, calculations methodology and results of experimental research concerning determination of the boundary angle at which droplet begins to slide on the horizontal or inclined surface of the plate. Values of boundary angle have been applied to estimate the microscopic dynamic advanced angle of the droplet on the flat surface in presence of a liquid film.

Keywords: Wetting process, Wetting angle, Droplet, Liquid microfilm

Nomenclature

A	–	constant
A_d	–	dispersion coefficient
B	–	constant in Eq.(17)
b	–	latent heat of vaporization, J/kg
C	–	constant
Ca	–	Capillary number
d	–	diameter, m
g	–	gravitational acceleration, m/s^2
p	–	pressure, N/m^2
r	–	radius of control volume, m
R	–	radius of droplet's base, m

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t	–	temperature, °C
T	–	absolute temperature, K
u	–	characteristic velocity, m/s
V	–	volume, m^3
We	–	Weber number

Greek symbols

α	–	actual slope angle interfacial surface liquid – gas of control volume of liquid, deg
β	–	spreading factor
γ	–	slope angle of plate's surface, deg
δ	–	thickness of microfilm, m
ε	–	parameter
ζ	–	parameter (characterizing the effect of changes in liquid pressure on the local phase-change temperature at the interface – description in the text)
θ	–	dynamic microscopic advanced angle, deg
λ	–	thermal conductivity, W/(m K)
μ	–	coefficient of static friction
ν	–	kinematic viscosity, m^2/s
ρ	–	density, kg/m^3
σ	–	surface tension, N/m
φ	–	humidity, %

Subscripts

d	–	dispersion,
g	–	gas
Ham	–	Hamaker
l	–	liquid
n	–	saturation
w	–	wall
0	–	initial

Superscripts

$+$	–	nondimensional

1 Introduction

Streams of droplets find practical applications in coating of surfaces of solid bodies with thin films of liquid [19,20]. In some technical applications, most of all in nanotechnology, the presence of a thin liquid microfilm on the surface affects significantly the wetting process by droplets [2,14,21]. The process of droplet's spreading depends on the fact if the surface had been before wetted by liquid [14]. Prior presence of droplets or streams of liquid on the surface causes that molecules of liquid can remain on it. Thus, the succeeding droplets impinge and spread on the surface that is wetted [23]. On the other hand, the surface of a solid body is surrounded with the gas phase of pure vapor or a mixture of gases. As a result of chemical affinity of gas molecules to solid body molecules, increase of gas molecules concentration occurs by the surface [14]. Gas molecules are attracted to the surface as a result of intermolecular forces or as a result of formed intermolecular bonds. Adsorption of gas molecules changes the surface tension of the solid body-gas interface [14,16]. Dynamic wetting angle changes as well [3,5,12,21]. Author [21] proposed also the model of the phenomenon of wetting by droplets in presence of liquid microfilm. The model relates to the equilibrium of forces in radial direction. In the paper [23], the results of initial model's verification with application of water droplets are given. Paper [22] presents initial experimental research that allows estimation of the microscopic dynamic wetting angle in relation to macroscopic measurement of inclination angle of the surface with deposited water droplet. However, big spread of measured values of inclination angle of the surface suggests the necessity of further modification of the experimental stand.

The aim of the present paper is to estimate the microscopic dynamic advanced angle of a droplet spreading on the flat surface. The angle is to be estimated from final equation derived from the model of phenomenon of droplet's spreading on the surface of a solid body covered by a liquid microfilm, proposed by author [21]. For calculations, it is required to determine experimentally the boundary angle at which droplet starts to slide from the flat, inclined surface of the plate. The angle will be measured on the experimental stand modified by author.

2 Model

Detailed description of the model of droplet spreading in presence of liquid microfilm is given in paper [21]. The present paper gives only a shortened description of the proposed model. Droplet, after its contact with the surface, starts to spread and then it stops. In the moment of standstill, a quasi-equilibrium state forms between the region of absorbed liquid film coating the surface and the microscopic region of spreading droplet. Just for the above state, equation of radial equilibrium for control volume of droplet has been written, with the following simplifying assumptions:

- surface is horizontal, smooth, heterogenic and free from microimpurities,

- surface is coated with a thin liquid microfilm on which the liquid spreads,
- there is a lack of thermal interactions among surface, droplet and environment; the liquid's spreading process is isothermal,
- liquid is homogeneous,
- as a result of intermolecular forces in interfacial liquid-gas region in the liquid microfilm and in the microscopic region, additional pressure is arising which is called the disjoining pressure [15],
- it is assumed that Van der Waals forces affect dominantly the value of intermolecular relations [6,7,13,14,16,18].

The element of liquid's volume in microscopic region (Fig. 1) is affected by forces directed radially and caused by: liquid microfilm, liquid from the basic droplet's volume, neighboring layers of liquid in the microscopic region, gas and by component of base reaction force.

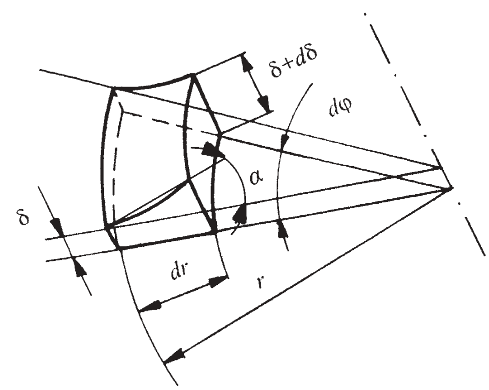

Figure 1. Control volume of liquid.

Equation of radial equilibrium for the considered liquid control volume is given by relation [21]:

$$p_l \frac{d\delta}{dr} + \delta \frac{dp_l}{dr} - p_g \tan \alpha - \mu \rho_l g \delta = 0 . \quad (1)$$

If only the Van der Waals forces are significant, Eq. (1) can be written as follows:

$$\frac{2 A_d}{\delta^3} \frac{d\delta}{dr} - \mu \rho_l g \delta = 0 . \quad (2)$$

If droplet is treated as a rigid body, it can be assumed that the coefficient of static slide friction equals the tangent of angle of inclination of the surface on which the rigid body rests, to the horizontal plane

$$\mu = \tan \gamma \ . \tag{3}$$

Equation of radial equilibrium (2), after incorporation of Eq. (3) reads as follows:

$$\frac{2\,A_d}{\delta^3}\frac{d\delta}{dr} = \rho_l\, g\, \delta \tan \gamma \ . \tag{4}$$

For the borderline between the absorbed liquid microfilm region and the contact region, the following condition is valid:

$$r = R, \quad \delta = \delta_0 \tag{5}$$

and

$$\frac{d\delta}{dr} = \tan \alpha = \tan \theta \ . \tag{6}$$

It is assumed that inclination angle between the interfacial liquid-gas surface and hypothetical surface of the solid body (to the surface of liquid microfilm) is dynamic microscopic advanced angle (Fig. 2). Tangent of microscopic advanced angle of droplet can be obtained from the transformed equation of radial equilibrium (4):

$$\tan\theta = \frac{\rho_l\, g\, \delta_0^4}{2\,A_d} \tan\gamma \ . \tag{7}$$

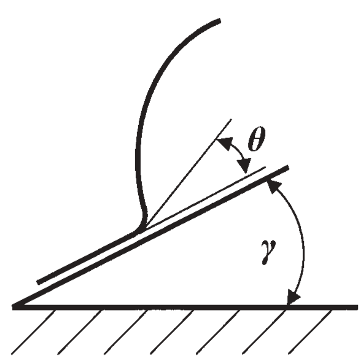

Figure 2. Characteristic angles (scheme).

Determination of microscopic advanced angle requires determination of the thickness of liquid microfilm in the moment when droplet stops its movement and determination of macroscopic inclination angle of the surface on which the droplet rests. It is also necessary to know the dispersion constant for the system droplet-material the surface was made of.

Thickness of adsorbed film can be estimated from the model given by Ajaev [1]:

$$\delta = \delta^{+}\mathrm{Ca}^{1/3} R_0 \; . \tag{8}$$

The model is valid for uniformly heated surface. In order to apply the model for a nonheated surface, it is assumed that the surface is minimally heated and temperature difference equals only $(T_w - T_n) = 0.01$ K.

Dimensionless thickness of absorbed film is determined by relation

$$\delta^{+} = \left(\frac{\zeta^{+}\varepsilon^{+}}{T_0^{+}}\right)^{1/3} \; . \tag{9}$$

In Eq. (9), there are three dimensionless parameters. The first one characterizes the effect of changes in liquid pressure on the local phase-change temperature at the interface:

$$\zeta^{+} = \frac{\sigma_0}{b\rho R_0 Ca^{1/3}} \; . \tag{10}$$

The second one is the disjoining pressure parameter:

$$\varepsilon^{+} = \frac{|A_{Ham}|}{\sigma_0 R_0^2 Ca} \; , \tag{11}$$

and the third one represents the non-dimensional temperature:

$$T_0^{+} = \frac{T_0 - T_n}{\mathrm{Ca}^{2/3} T_n} \; . \tag{12}$$

Capillary number in Eqs. (8) and (10–12) is defined as

$$\mathrm{Ca} = \frac{\nu \rho u}{\sigma_0} \; . \tag{13}$$

The characteristic velocity in (13) is given by equation:

$$u = \frac{\lambda T_n}{\rho b R_0} \; . \tag{14}$$

The surface tension σ_0 is determined at the equilibrium saturation temperature T_n, and characteristic liquid's parameters b, λ, ν, ρ are determined at given temperature of liquid.
The radius of spreading droplet can be calculated from relation

$$R_0 = \beta d_0/2 \; . \tag{15}$$

The diameter of spherical droplet is the function of its volume

$$d_0 = \left(\frac{6V_0}{\pi}\right)^{1/3} \; . \tag{16}$$

The spreading factor β can be evaluated from the semi-empirical equation given in [21]:

$$\beta = B\left(\frac{\mathrm{We}}{6} + 2\right)^{0.5} \; . \tag{17}$$

For water droplet the constant B equals to 0.87 [21]. If water droplet is slowly deposited on the surface, then the Weber number is near zero ($\mathrm{We} \cong 0$), and the spreading factor equals to $\beta \cong 1.23$.

3 Experimental stand and methodology

Modified experimental stand consists of a stable, leveled base with bevel protractor (Fig. 3). A plexiglass plate is fastened to the mobile arm of the protractor. It is possible to place tested plates on the plexiglass plate. Position of the arm of protractor can be controlled by means of an electric engine. The engine revolves uniformly and, by means of mechanical transmission, it causes the rising movement of the protractor. The mobile arm of the protractor can be stopped at any position by switching off the engine. Droplets are deposited by means of a micropipette fastened on the stand. After the droplet is deposited, the mobile, rotational extension arm of the stand makes it possible to remove the micropipette from above the tested surface.

The paper presents research made for a glass plate, where water droplets with given volumes are dropped by means of a pipette. Parameters characterizing roughness of the plate, that is the arithmetic average of the roughness profile, equal respectively: $R_a = 0,023\,\mu$m and $R_z = 0,180\,\mu$m. Roughness is decisive for local inclination of the surface, and thus, it can affect also the values of investigated angle [8,9,11,17]. According to Marmur [8,9], on rough surface of the plate, a droplet with given volume can be characterized by a number of equilibrium states, corresponding to local minimums on the run of free energy, respectively. Each of the above states is related by its own value of wetting angle. The values of wetting angle differ slightly.

The day before measurements, the tested surface was washed with distilled water. Before each measurement, the plate was leveled. Water droplets with a given volume in the range from 5×10^{-9} to 50×10^{-9} m^3 were placed on the surface by means of a pipette.

Figure 3. View of working stand.

Droplets' volumes were changed every 5×10^{-9} m^3. Next, inclination angle of the plate was changed very slowly by means of the electric engine until the moment when droplet's movement on the surface began. The inclination angle was read by means of the protractor. At the same time, ambient temperature and air humidity were measured. On the basis of the inclination angle of the surface, according to Eq. (3), it was possible to determine the coefficient of static friction, and estimate the microscopic dynamic advanced angle by means of Eq. (7).

4 Results

Research was carried out in two cycles. In the first cycle of research on a given day, measurements of inclination angle of the surface were made only for one droplet's volume. Mean values of inclination angle were calculated on the basis of *ca.* 10 measurements of the parameter, after elimination of gross errors. Ambient temperature changed minimally during the measurements. Difference between the highest and the lowest ambient temperature values equaled about 1.5 K. Average value of ambient temperature equal to 22.3 °C was assumed for further considerations. Relative air humidity changed in the range 20–40%. Changes of relative air humidity, however, were quite high and they could affect the wettability of the surface [21].

Because of the above fact, it was decided to carry out the research for the inclination angle of the surface at variable droplet volume and at approximately invariable temperature and humidity, for the second cycle of research for the given day. During the research, the mean air temperature equaled 21.15 ± 0.15 °C, and mean humidity equaled 52.5 ± 2%.

Results of research on boundary inclination angle at which droplet begins to slide from the surface of the glass plate are presented in Fig. 4, which shows the average inclination angle of the plate in relation to volume of water droplets for both cycles of research (runs I and II).

It was stated that, in the investigated range of droplets' volume changes, increase of droplet's volume was in favor of the decrease of the value of inclination angle of the plate at which the sliding movement of the droplet began. A similar relation among these parameters was obtained during the initial research [22]. Carried out experiments showed that air humidity could meaningfully affect the inclination angle of the plate, and thus the coefficient of static friction.

Experimentally determined inclination angle of the plate was applied to estimate the values of dynamic microscopic advanced angle of water droplet on the flat surface. Dynamic microscopic advanced angle of droplet was calculated from Eq. (7). Evaluation of this angle required knowledge of thickness of the liquid film in the moment when spreading water droplet stopped its movement.

In order to determine the values of liquid microfilm thickness, Ajaev's model [1] was initially assumed. The model is discussed in Section 2 of the paper. It was assumed in the present investigations that saturation temperature of water was only slightly lower than the temperature of the plate, $(T_w - T_n) = 0.01$K. In turn, temperatures of water and of plate were equal to ambient temperature. Physical parameters of water for respective temperatures are given in Tab. 1 [10].

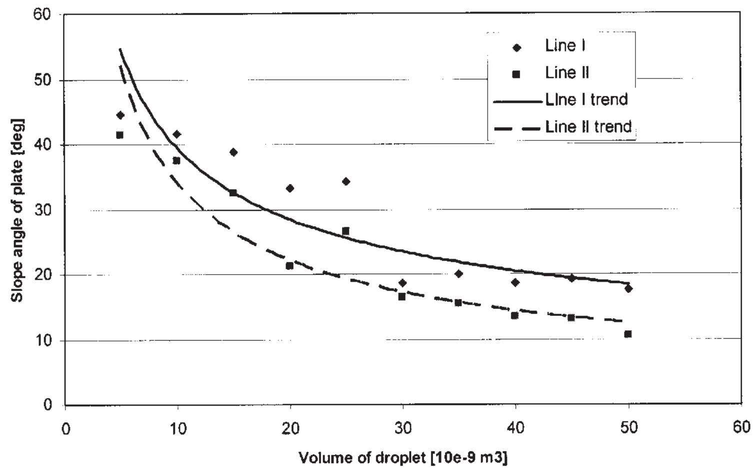

Figure 4. Inclination angle of the plate in relation to droplet volume.

Table 1. Physical parameters of water and characteristic coefficients for Eqs. (19)–(25).

Parameter	Symbol	Unit		
Saturation temperature	t_n	°C	22.30	21.15
Density	ρ	kg/m^3	997.5	997.9
Latent heat of vaporization	b	kJ/kg	2448.5	2451.1
Thermal conductivity	λ	W/(mK)	0.603	0.601
Kinematic viscosity	ν	m^2/s	0.960×10^{-6}	0.983×10^{-6}
Surface tension	σ	N/m	0.07235	0.07252
Coefficient	C_1	m^2/s	7.2944×10^{-8}	7.2313×10^{-8}
Coefficient	C_2	m	9.6546×10^{-10}	9.8342×10^{-10}
Coefficient	C_3	$m^{2/3}$	2.9972×10^{-8}	2.9815×10^{-8}
Coefficient	C_4	m	8.3894×10^{-10}	8.2168×10^{-10}
Coefficient	C_5	$m^{3/2}$	34.6492	34.3598
Coefficient	C_6	$m^{7/9}$	8.9864×10^{-7}	8.9337×10^{-7}
Coefficient	C_7	$m^{1/3}$	8.8817×10^{-10}	8.8841×10^{-10}

After transformation of Eqs. (15)–(17), the radius of droplet spread on the plate in the function of its volume can be determined:

$$R_0 = \beta \left(\frac{3V_0}{4\pi} \right)^{1/3} . \tag{18}$$

Next, all parameters necessary to determine the liquid film thickness can be related only to the above radius by substitution of values of physical parameters of water given in Tab. 1. in Eqs. (8)–(14). Then, respectively:

- characteristic velocity (14),

$$u = C_1 R_0^{-1}, \tag{19}$$

- Capillary number (13),

$$\mathrm{Ca} = C_2 R_0^{-1}, \tag{20}$$

- parameter characterising the effect of changes in liquid pressure on the local phase-change temperature at the interface (10),

$$\zeta^{+} = C_3 \left(R_0 \right)^{-2/3}, \tag{21}$$

- nondimensional parameter (11),

$$\varepsilon^{+} = C_4 R_0^{-1}, \tag{22}$$

- nondimensional temperature (12),

$$T_0^{+} = C_5 R_0^{2/3}, \tag{23}$$

- nondimensional thickness of water film (9),

$$\delta^{+} = C_6 \left(R_0 \right)^{-7/9}, \tag{24}$$

  and thickness of adsorbed film (8),

$$\delta = C_7 \left(R_0 \right)^{-1/3}, \tag{25}$$

  are only functions of radius R_0, related to droplet's volume V_0.

Values of characteristic coefficients C in Eqs. (19)–(25) are given in Tab. 1. It results from calculations, that in the investigated range of temperatures, values of coefficient C_7 are nearly equal. So, it is assumed for further calculations that the coefficient equals $C_7 = 8.88 \times 10^{-10}$ m$^{1/3}$.

Dispersion coefficient for water droplets spreading on the surface of a glass plate is given by Wayner *et al.* [15], with application of Hamaker constant given by Gregory [4] ($A_{Ham} = 5.86 \times 10^{-20}$J). Dispersion coefficient equals $A_d = 3.11 \times 10^{-21}$J.

Figure 5 presents the change of water microfilm thickness with droplet's volume. It can be stated that thickness of the liquid microfilm decreases with increase of droplet's volume. Thickness of the liquid microfilm is related to the kind of intermolecular forces present in the liquid microfilm. In the investigated model, Van der Waals intermolecular forces are significant. According to Wayner Jr, [16] and Stephan [13], the range of their influence is from 0.2 to 10 nm. Thus, the liquid microfilm thicknesses calculated from Eq. (25) are included within the above range. It should be noted that the applied model of Ajaev [1] allows only to approximately estimate the microfilm thickness on the surface because the model is valid mainly for the heated plate.

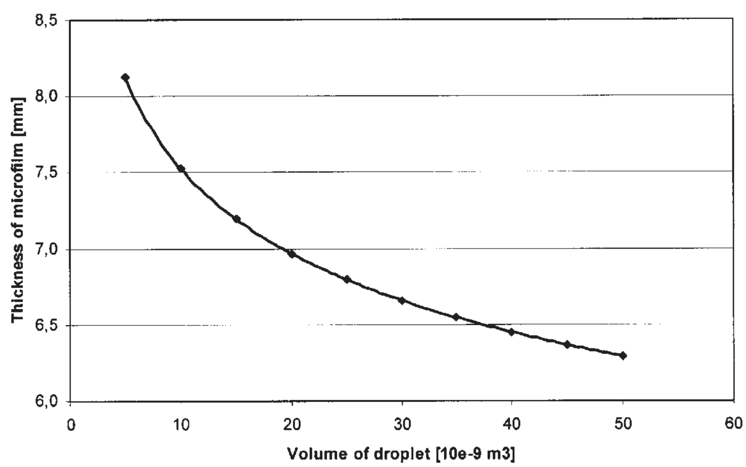

Figure 5. Thickness of the liquid microfilm in relation to droplet's volume.

In paper [23], author calculated the value of acceleration of gravity for the site of carried out measurements, that is, for Szczecin (Poland). The gravity equals to $g = 9.8137$ m/s^2. Figure 6 presents tangent values calcu-

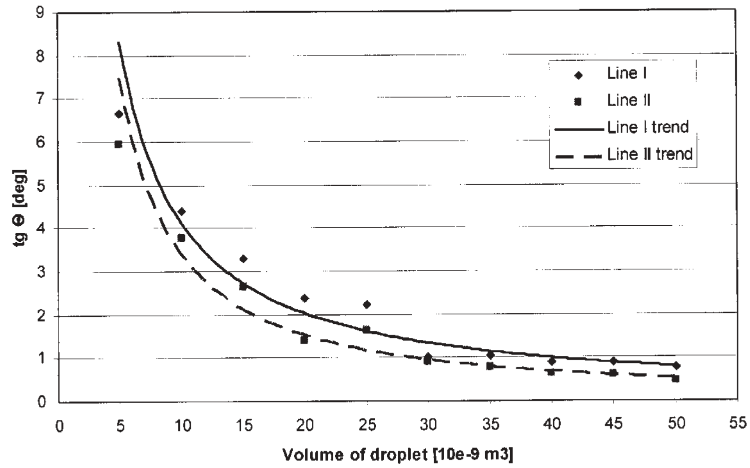

Figure 6. Tangent of dynamic microscopic advanced angle in relation to inclination angle of the plate ($R_a = 0.023\,\mu$m).

lated from Eq. (7) for dynamic microscopic advanced angle of water droplet in the function of boundary inclination angle of the plate in the standstill moment of the spreading droplet. Tangents of small angles equal approximately their values. The run of trend I relates to the first cycle of research, where relative humidity of the surrounding air changes in the range of 20–40%. On the other hand, run II shows changes of microscopic dynamic advanced wetting angle when relative humidity of the surrounding air is nearly constant and equals $52.5 \pm 2\%$. On the basis of Fig. 6, it can be assumed that higher relative air humidity in the surrounding of droplet causes that microscopic dynamic advanced wetting angle decreases.

5 Conclusions

According to the carried out research, the value of dynamic microscopic advanced angle can only be estimated in relation to volume of the water droplet. Droplets with higher volumes are characterized with smaller values of microscopic dynamic advanced wetting angle. The carried out research shows that humidity change of the surrounding air causes changes of values of microscopic dynamic advanced wetting angle. When humidity of the air surrounding the droplet is higher, the analysed angle is smaller. In order to precisely determine values of dynamic microscopic advanced angle, it is recommended to carry out further experimental research to determine thickness of liquid microfilm and boundary inclination angle of the plate at the same time.

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References

[1] Ajaev V.: *Spreading of thin volatile liquid droplets on uniformly heated surfaces. J. Fluid Mech.* **528**(2005), 279–296.

[2] Blake T.D., Clarke A., De Coninck J., De Ruijter M. Voue M.: *Droplet spreading a microscopic approach*. Colloids and Surfaces. A.: Physicochemical and Engineering Aspects **149**(1999), 123–130.

[3] Duszan E.B.: *On the spreading of liquids on solid surfaces: static and dynamic contact lines*, Annu. Rev. Fluid Mech. **11**(1979), 371–400.

[4] Gregory J.: *The Calculation of Hamaker constants*. Adv. Colloid Interface Sci. **2**(1969), 396–417.

[5] Haley P., Miksis M.J.: *The effect of the contact line on droplet spreading*. J. Fluid Mech. **223**(1991), 57–81.

[6] Israelachvilli J.N.: *Intermolecular and Surface Forces*. Academic Press, London 1991.

[7] Majumdar A., Mezic I.: *Instability of ultra-thin water films and the mechanism of droplet formation on hydrophilic surfaces*. Trans. ASME J. Heat Transfer **121**(1999), 3, 965–970.

[8] Marmur A.: *Equilibrium contact angles theory and measurement*. Colloids and Surface A. Physiochemical and Engineering Aspects **116**(1996), 55–61.

[9] Marmur A.: *Contact-angle hysteresis on heterogeneous smooth surface theoretical comparison of the captive bubble and drop methods*. Colloids and Surface A. Physiochemical and Engineering Aspects **136**(1999), 209–215.

[10] Rivkin S.L., Aleksandrov A.A.: *Thermophysical Properties of Water and Steam*. Energia. Moscow 1980 (in Russian).

[11] Rybnik R., Trela M.: *Influence of substrate materials and surface roughness on the contact angle of sessile drops*. In: Tagungsmaterialen VII Internationales Symposium Wärmeaustausch und Erneuerbare Energiequellen, Szczecin-Świnoujście 7-9.09.1999, 315–324.

[12] Sciffer S.: *A phenomenological model of dynamic contact angle*, Chem. Eng. Sci. **55**(2000), 5933–5936.

[13] Stephan K.: *Influence of dispersion forces on phase equilibria between thin liquid films and their vapour*. Int. J. Heat Mass Transfer, **45**(2002), 4715–4725.

[14] Van Carey P.: *Liquid-Vapor Phase-Change Phenomena*. Hemisphere Publishing Corporation, Taylor&Francis, Bristol 1992.

[15] Wayner P.C. Jr., Kao Y.K., LaCroix L.V.: *The interline heat-transfer coefficient of an evaporating wetting film*. Int. J. Heat Mass Transfer, **19**(1976), 487–492.

[16] Wayner P.C. Jr.: *Intermolecular forces in phase-change heat transfer: 1998 Kern Award review*. AIChE J. **45**(1999), 10, 2055–2068.

[17] Wolansky G., Marmur A.: *Apparent contact angles on rough surface the Wenzel equation revisited*. Colloids and Surface A. Physiochemical and Engineering Aspects **156**(1999), 381–388.

[18] Yeh E.K., Newman J., Radke C.J.: *Equilibrium configuration of liquid droplets on solid surfaces under the influence of thin-film forces, Part II. Shape calculations*. Colloids and Surfaces. A.: Physicochemical and Engineering Aspects **156**(1999), 525–546.

[19] Zapałowicz Z.: *Conditions for appearance of droplet structure and a liquid film on a horizontal heated wall surface for selected liquids*. Arch. Thermodynamics **21**(2000), 1-2, 73–85.

[20] Zapałowicz Z.: *Macroscopic model of droplet spreading over a horizontal surface*. Arch. Thermodynamics **24**(2003), 3, 55–68.

[21] Zapałowicz Z.: *Effect of a droplet stream and air on the surface of a solid body*. Technical University of Szczecin Publishers, Szczecin 2007 (in Polish).

[22] Zapałowicz Z.: *Evaluation of dynamic microscopic advanced angle for droplet on flat surface*. In: Proc.. of the 6th International Conference on Transport Phenomena in Multiphase Systems, HEAT 2011. June 28 – July 2, 2011, Ryn, Poland (M.E. Poniewski, S. Alabrudziński, Eds.), ISBN 978-83-62081-53-0, 415–418, 2011.

[23] Zapałowicz Z.: *Initial verification of the model of droplet's spreading on the solid body surface in presence of liquid microfilm*. The Scientific Proceedings of Riga Technical University, Ser. 12, Heat and Power and Thermal Physics, Riga, RTU (accepted for publication).