Wetting angle hysteresis in microdrops

A.A.Borodin, S.V.Dukarov[*]

Scientific Center for Physics and Technology,
1 Novgorodskaya St., 61145 Kharkiv, Ukraine
* V.Karazin Kharkiv National University,
4 Svobody Sq., 61077 Kharkiv, Ukraine

The characteristic time of substrate plastic deformation due to surface tension forces of a liquid drop is estimated. The equilibrium conditions of a drop of varying volume on the convex ledge formed due to the deformation have been analyzed under account for partial relaxation of the elastic stresses. Contribution of those stresses to the wetting angle hysteresis (about 3°) has been estimated and the hysteresis value has been shown to increase for very small drops mainly due to reduction of the retreating angle caused by a strong substrate deformation. The hysteresis contribution to the decrease in the observable wetting angle of microdrops under evaporation attains significant values (about 10 to 16°).

Произведена оценка характерного времени пластической деформации подложки силами поверхностного натяжения жидкой капли. Выполнен анализ условий равновесия капли изменяющегося объема на образовавшемся в результате деформации выпуклом ранте, с учетом частично релаксировавших упругих напряжений. Приведена оценка их вклада в явление гистерезиса смачивания (~3°) и показано, что для капель очень малого размера величина гистерезиса увеличивается, в основном, за счет уменьшения угла оттекания, вызванного значительной деформацией подложки. Отмечено, что вклад гистерезиса в уменьшение наблюдаемого краевого угла смачивания испаряющихся микрокапель достигает существенных значений (10–16°).

Wetting angle hysteresis in microdrops

A.A.Borodin, S.V.Dukarov[*]

Scientific Center for Physics and Technology,
1 Novgorodskaya St., 61145 Kharkiv, Ukraine
* V.Karazin Kharkiv National University,
4 Svobody Sq., 61077 Kharkiv, Ukraine

The characteristic time of substrate plastic deformation due to surface tension forces of a liquid drop is estimated. The equilibrium conditions of a drop of varying volume on the convex ledge formed due to the deformation have been analyzed under account for partial relaxation of the elastic stresses. Contribution of those stresses to the wetting angle hysteresis (about 3°) has been estimated and the hysteresis value has been shown to increase for very small drops mainly due to reduction of the retreating angle caused by a strong substrate deformation. The hysteresis contribution to the decrease in the observable wetting angle of microdrops under evaporation attains significant values (about 10 to 16°).

Произведена оценка характерного времени пластической деформации подложки силами поверхностного натяжения жидкой капли. Выполнен анализ условий равновесия капли изменяющегося объема на образовавшемся в результате деформации выпуклом ранте, с учетом частично релаксировавших упругих напряжений. Приведена оценка их вклада в явление гистерезиса смачивания (~3°) и показано, что для капель очень малого размера величина гистерезиса увеличивается, в основном, за счет уменьшения угла оттекания, вызванного значительной деформацией подложки. Отмечено, что вклад гистерезиса в уменьшение наблюдаемого краевого угла смачивания испаряющихся микрокапель достигает существенных значений (~10−16°).

The specific surface energy of a small particle is known to depend on its size. The dimension dependence of the surface energy, σ_l, for a liquid phase can be revealed, for example, by measurement of wetting angle (related to σ_l by the Young equation as well as by considering the drop evaporation process that for small drops occurs at a rate proportional to $\exp(\sigma_l/r)$ [1, 2]. In this case, the experimental points of the evaporation curve show wave-like deviations from a smooth dependence. In works aimed at the direct wetting angle measurements, θ variations about 10 to 15° are also observed while the convolution and photometry methods used have an accuracy about 3 to 5° [2]. In both cases, it is just the wetting hysteresis that may be responsible for such deviations. The essence of this phenomenon consists in that the wetting perimeter becomes fixed, thus changing substantially the liquid drop behavior in some circumstances, e.g , during its evaporation. The purpose of this work is to consider reasons for this effect for microdroplets as well as to estimate the wetting hysteresis effect on the drop-substrate system parameters.

The wetting hysteresis was studied in several works [3, 4] It is just the microscale irregularity and the substrate non-uniformity that are believed to be main causes of that effect [4]. Numerous assumptions used in those works, however, are invalid to microdroplets, e.g., the microirregularity height of about 1 25 μm. In some systems, the wetting perimeter fixation is attained due to the mutual dissolution of liquid and solid phases [4]. Nevertheless,

the hysteresis can be observed also in systems where the mutual solubility is negligible, e.g , Au/C. Some authors [3] have noted that a substrate may undergo plastic deformation at high temperature due to the surface tension forces. In this case, a convex ledge is formed in the ternary contact zone. Comparison of different mass transfer mechanisms at short distances (about 10^{-8} m) allows to conclude on the decisive role of surface diffusion. In the ternary contact region, the surface tension of the liquid causes a local reduction of the chemical potential $\Delta\mu_P$ corresponding to the pressure applied, $\Delta\mu_P = -\sigma_l/\tau$ It is known also that the chemical potential of atoms at a curved surface includes an additive $\Delta\mu_K = \sigma_{lu}$ K (σ_{lu} is the specific surface energy of the substrate-liquid interface; K, the curvature).Thus, an energy-favorable equalizing of the substrate chemical potential may occur due to of its bending. Let the characteristic time of such a deformation be estimated. It follows from [5] that the deforming rate is

$$\frac{dU}{dt} = -\frac{D_S \omega^S n_0}{kT} \frac{\partial^2 \mu}{\partial S^2} \quad (1)$$

where D_S is the surface diffusion coefficient; n_0, the surface concentration of the substrate atoms; ω^S, their volume. The change of chemical potential μ at the surface S occurs mainly in the wetting perimeter region at distances of the order of the ternary contact zone width that can be assumed at a first approximation to be equal to that of the liquid transition layer, τ.

In the ideal case, the chemical potential equalizing $\Delta\mu = \Delta\mu_P + \Delta\mu_K = 0$ is attained at the curvature $K = (\sigma_l/\sigma_{lu}) \times (1/\tau)$. It is to note that the σ_{lu} value in the ternary contact region must differ from its macroscopic value and lie most likely between σ_{lu} and σ_u. Then the ledge height h at the curvature K will amount, e.g., 0.1 to 0.2 nm for a gold drop on carbon substrate. Taking $D_S \sim 10^{-15}$ m^2/s, $kT \sim 1.6 \cdot 10^{-20}$ J, $n_0 \sim 1.5 \cdot 10^{19}$ m^{-2}, $\omega^S \sim 1,7 \cdot 10^{-30}$ m^3, $\sigma_l = 1$ J/m^2, τ 10^{-9} m, we obtain the characteristic deformation time

$$t_c = h\frac{kT}{D_S n_0 \omega^{s^2} \sigma_l} \frac{\tau^3}{} \approx 10^{-1} \text{ c.}$$

Thus, under account for the experiment duration (usually 10^2 to 10^3 s), the ledge
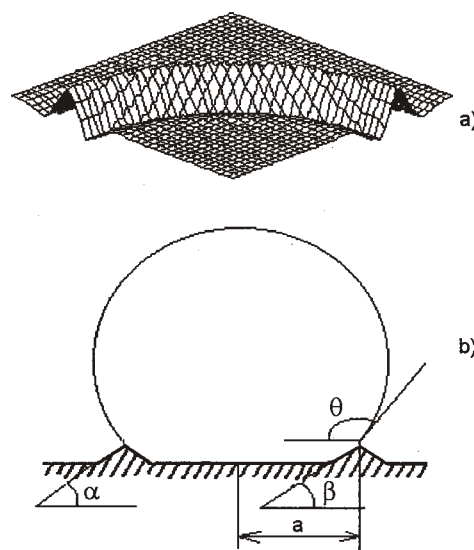

Fig. 1 Substrate post-deformation profile calculated from (1) (a) and adopted in this work to analyze the hysteresis (b).

can be concluded to be formed during the drop observation even if the wetting perimeter jumps occur often enough. That is, we can state that the drop itself gives rise to the substrate microscale irregularities. As an example, Fig. 1(a) presents a section of the substrate calculated as the solution of differential equation (1); the scale along vertical axis is enlarged for illustrative purpose. When considering the wetting hysteresis, the substrate profile will be assumed to be of a shape shown in Fig 1(b). The validity of that approximation is confirmed by comparison of Figs. 1(a) and 1(b).

The energy-favorable position is defined by the minimum of the free energy functional F·

$$F = \sigma_l S_l + (\sigma_S - \sigma_{S_l})S_{S_l} + W + PV + \mu N,$$

where S_l, S_{S_l} are the interfaces of corresponding phases at the approximation $a >> \tau$ adopted in this work, that is, when the transition layer thickness is much smaller than the wetting perimeter radius a; those amount to $S_l = 2\pi a^2/(1 + \cos\theta)$, $S_{S_l} = 2\pi a^2$; W, energy of the substrate elastic deformation. It is to note that in the wetting perimeter region, its normal component W_n is essentially completely relaxed under plastic deformation. The value W_n is defined in [6] as

$$W_n = \frac{3}{4}\frac{\sigma_l^2 a \sin^2\theta}{\pi E}(\ln 2 + \ln\frac{a}{\tau} - \frac{1}{2}).$$

Let us consider the change of the drop free energy δF when its volume change is δV for two cases. at a constant wetting angle θ and at a constant wetting perimeter a. It is just the more energy-favorable state that will be realized.

$$\delta F|_{\theta=const} =$$

$$= \left[\sigma_l\frac{\partial S_l}{\partial a} + (\sigma_S - \sigma_{S_l})\frac{\partial S_{S_l}}{\partial a} + \frac{\partial W}{\partial a}\right]\frac{\partial a}{\partial V}\delta V +$$

$$+ P\delta V + \mu\delta N;$$

$$\delta F|_{a=const} = \sigma_l\frac{\partial S_l}{\partial\cos\theta}\frac{\partial\cos\theta}{\partial V}\delta V + P\delta V + \mu\delta N$$

The partial derivatives of the interface areas at the substrate shown in Fig 1(a) can be determined as follows:

$$dS_l = -\frac{2\pi a^2}{(1 + \cos\theta)^2}d\cos\theta +$$

$$+ 2\pi a\left[\frac{2}{1 + \cos\theta} + \frac{\sin\gamma}{\sin(\theta - \gamma)}\right]da;$$

$$dS_{S_l} = 2\pi a\frac{\sin\theta}{\sin(\theta - \gamma)}da;$$

where $\gamma = \begin{cases} -\beta; & \delta V < 0 \\ \alpha; & \delta V > 0 \end{cases}$

For elastic energy, it can be written as:

$$dW = W_n\frac{2|da|}{\tau} = 2\pi a\sigma_l\omega|da|, \quad (2)$$

when $\omega = \frac{3}{4}\frac{\sigma_l\sin^2\theta}{\pi^2 E\tau}(ln2 + ln\frac{a}{\tau} - \frac{1}{2})$.

Other items involved in dW can be shown to be τ/a order infinitesimal, so those are neglected in this work. The derivatives $\partial a/\partial V$ and $\partial\cos\theta/\partial V$ can be found from the expression for the drop volume:

$$V = \pi\frac{a^3(1 - \cos\theta)^2(2 + \cos\theta)}{3\sin^3\theta}.$$

$$\frac{\partial a}{\partial V} = \frac{1}{\pi a^2}\frac{\sin^3\theta}{(1 - \cos\theta)^2(2 + \cos\theta)};$$

$$\frac{\partial\cos\theta}{\partial V} = -\frac{1}{\pi}a^3(1 - \cos\theta)^2\sin\theta.$$

The condition of the wetting perimeter fixation is $\delta F|_{\theta=const} > \delta F|_{a=const}$ or, under account for the above:

$$\cos\theta_0\frac{\sin\theta}{\sin(\theta + \beta)} + \frac{\sin\beta}{\sin(\theta + \beta)} + \omega < \cos\theta,$$

$$\delta V < 0; \quad (3)$$

$$\cos\theta_0\frac{\sin\theta}{\sin(\theta - \alpha)} - \frac{\sin\alpha}{\sin(\theta - \alpha)} \quad \omega < \cos\theta,$$

$$\delta V > 0. \quad (4)$$

Here θ_0 is the equilibrium wetting angle according to the Young equation, its dimensional dependence is to be taken into account for small drops [1, 2].

The critical angles corresponding to Eqs. (3) and (4) are referred to as the retreating angle θ_r and the attracting one θ_a, respectively If the elastic deformation energy is not accounted for, those angles take the obvious values $\theta_a = \theta_0 + \alpha$, $\theta_r = \theta_0 - \beta$. It is worth to note that the contribution of the relaxed energy of elastic deformation attains appreciable values, for example, for the Au/C system ($\sigma_l \sim 1$ J/m^2, $E \sim 4\cdot 10^{10}$ N/m^2, $r \sim 10$ nm), $\omega \sim 0.025$ and at $\theta \sim 120°$ the corresponding difference $\theta_a - \theta_r \sim 3°$

Thus, if the drop volume varies, for example, due to evaporation, its wetting perimeter remains unchanged while the condition (3) is valid, meanwhile, the wetting angle reduces smoothly down to the critical value θ_r. Then a breakdown of the wetting perimeter occurs and the drop takes the position corresponding to the Young value of θ. A new ledge is formed rather fast at the new position of the wetting perimeter and the process is repeated. It can be seen that at $a >> \tau$, both θ_a and θ_r depend only slightly on the drop radius. So, for the Au/C system, these angles are changed by 1° due to the increasing elastic energy contribution as the drop diameter grows from 20 to 1000 nm. The wetting hysteresis is illustrated by Fig 2 where the evaporation curve of an Au drop is shown calculated as the solution of equation for evaporating particle under account for varying wetting angle and the wetting perimeter jumps. The points denote the experimental data [7].

A significant value of Laplacian pressure in very small droplets (smaller than 10 nm) results in that the elastic deformation has the time to relax not only within the ternary contact region but also immediately under the drop. In this case, the substrate profile will be of somewhat other shape: together with the ledge along the drop pe-
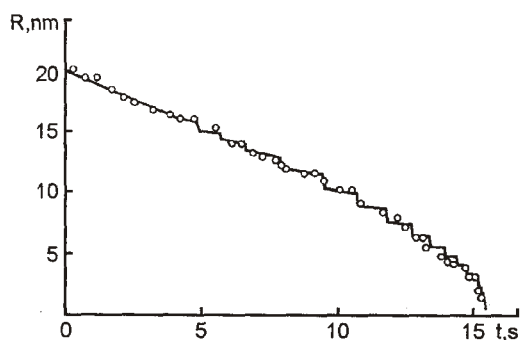
Fig. 2. Au drop evaporation curve under account for the wetting hysteresis. Points are experimental data [7].

Fig. 3. (a) Maximum θ deviation from the Young value; (b) $\theta - \theta_r$ difference for Au/C system as a function of the drop radius.

rimeter, a hollow may be formed under the drop, thus causing an increased hysteresis. Under these circumstances, the increase of $\theta_0 - \theta_r$ difference exceeds substantially that of the $\theta_a - \theta_0$ one. Taking into account the dimension-dependent diminution of the wetting angle, it can be concluded that, e.g , for the same Au/C system, the wetting angle for small (2 to 5 nm) drops may attain 65 to 70° at $\theta_0 = 138°$ This statement is evidenced by dimension dependences of $\theta - \theta_r$ and $\theta_0 - \theta_r$ (Fig 3) obtained by analyzing Fig 2. It is seen from Fig. 3(b) that the difference $\theta - \theta_r$ for small drops attains about 16° As a result, drops with a non-circular wetting perimeter (formed e.g by coalescence) may be stable on a substrate. This is due to that the drop may adhere partially to the ledges formed prior to coalescence.

It is to note that, as is seen from Eqs. (2) and (3), (4), the contribution of the elastic deformation energy is in proportion to the drop surface tension σ_l and the ledge height is also proportional to that quantity. Thus, the hysteresis can be concluded to be substantially smaller for drops with a low σ_l. In real circumstances, however, foreign adatoms are present inevitably on the substrate. For those atoms, once falling into
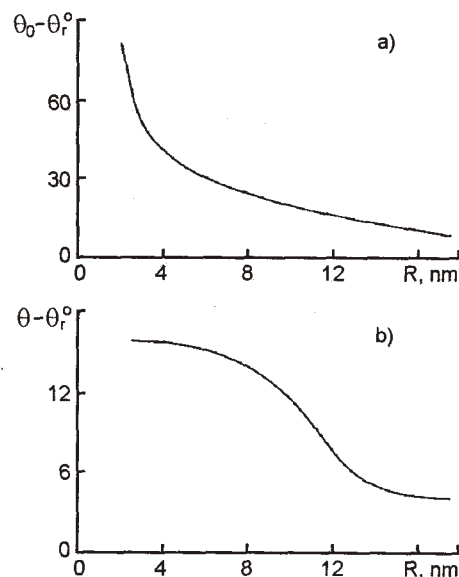
the ternary contact zone, it is energy favorable to remain therein. Thus, the wetting hysteresis is possible in such systems, too. When considering the behavior of such microsystems, account is to be made for possible deviations of the wetting angle from the Young value.

References

1 N T.Gladkikh, *Fiz. Tverd. Tela*, **31**, 13 (1989).
2. S.P.Chizhik, N.T.Gladkikh et al., *Metally*, No.4, 73 (1981).
3. V.A.Morokhin, B.A.Pastukhov, *Poverkhnost'*, No. 11, 151 (1983).
4. Yu.V.Naydich, R.P.Voytovich, *Adgezia Rasplavov i Paika Materialov*, **19**, 23 (1987).
5. Ya.E.Geguzin, Yu.S.Kaganovsky, Diffuzion Processes on a Crystal Surface, Moscow, Energoizdat, 1984 [in Russian].
6. A.I.Rusanov, *Kolloid. Zh.*, **37**, 678 (1985).
7 J.R.Sambles, *Proc. Roy. Soc.*, **324**, 339 (1971).