Influence of various factors on the spreading kinetics

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Abstract. It was found that at the stage of fast spreading (τ ≤ 0.02ε) at constant driving force within the wetting perimeter, the following exerts the main impact on the spreading kinetics: inertial forces that prevent spreading and change their sign when the speed slows, viscous resistance forces, the influence of which increases in proportion to the growth of the thickness of the boundary layer and vertical forces, which begin to appear when the spreading velocity slows down.

1. Introduction
A large number of works is devoted to wetting and spreading problems [1–20]. It is known that the driving force of wetting and spreading is the reduction of free energy of the system mainly by reducing the free surface energy in the process of replacing two solid and liquid surfaces with a common interfacial boundary.

The Young’s equations are usually used in wetting and spreading analysis. In [5–9] it was shown that the Young’s equation obtained within the framework of the molecular theory of capillarity can be correctly used only under equilibrium conditions on a non-deformable surface in the absence of wetting [3]. Under irreversible wetting and spreading conditions, when θ < 90° the adhesion energy $W_{ad} > W_{coh}$ is the work of cohesion, the Young’s equation does not work since $\cos \theta$ cannot be greater than 1. The equation also does not take into account the vertical component of the total vector resulting in deformation of the substrate. Hence, the kinetic regularities of the stage of fast drop spreading over the solid surface are considered, and the influence of various factors (inertial forces, viscosity and vertical forces) on the spreading process is studied.

2. Methods and materials
Features of the mechanism and kinetics of the spreading process are discussed in [1–20, etc.]. Two main cases should be considered: 1) Absence of wetting and spreading or reversible (limited [1]) wetting and spreading, when the liquid drop can be easily removed from the surface (wetting angle $\theta > 90°$). In reversible processes, liquid adhesion to the solid phase results from intermolecular interaction (e.g. Van der Waals forces). 2) Wetting and spreading of liquid with different intensity on solid and liquid surface or irreversible spreading at $\theta < 90°$. In irreversible spreading, adhesion results
from the formation of chemical bonds. The interaction energy at irreversible adhesion is two orders of magnitude greater and makes $\sim 10^7$ kJ/mol. The drop can be partially removed from the surface only during its cohesive fracture in the area of the interfacial boundary. Whereas, a thin layer of liquid phase remains on the surface. In this case, as a result of chemisorption of liquid clusters by the solid phase atoms, the elementary wetting act ends with the formation of a common interfacial boundary. An important conclusion follows from this definition. In systems far from chemical equilibrium, mass transfer processes will occur across a common interfacial boundary (dissolution and diffusion of liquid atoms into the solid phase). In the first case, the absence of wetting and, accordingly, dissolution enables efficient selection of materials for storage and transport of reactive substances and food media, and the lower the adhesion, the lower the resistance to liquid flow through channels and capillaries. In the second case, wetting enables dissolution and saturation of the surface of the solid phase with liquid atoms. Mass transfer processes in the area of interfacial boundary significantly change rheological and physicochemical properties of contacting solid and liquid phases and their compounds.

The driving force of wetting and spreading is the reduction of free energy of the system mainly by reducing the free surface energy in the process of replacing two solid and liquid surfaces with a common interfacial boundary. Figure 1 shows the balance of forces at the edge of the lying drop.

The Young’s equations are commonly used in wetting and spreading analysis:

$$\cos \theta = \frac{(\sigma_{lv} - \sigma_{sw})}{\sigma_{lv}}$$

and

$$\cos \theta = 2\frac{W_s}{\sigma_{lv}} - 1.$$  

In [5-9] it was shown that the Young’s equation obtained within the framework of the molecular theory of capillarity can be correctly used only under equilibrium conditions on a non-deformable surface in the absence of wetting [3]: $\theta > 90^\circ$ and $W_s < W_k$.

Under irreversible wetting and spreading conditions, when $\theta < 90^\circ$ and the adhesion energy $W_k > W_s$ is the work of cohesion, the Young’s equation does not work since $\cos \theta$ cannot be greater than 1. Spontaneous spreading corresponds to a positive value of the spreading coefficient $S = \sigma_{lv} - (\sigma_{sw} + \sigma_{ws}) > 0$. In this case, $\sigma_{sv} - \sigma_{sw} > \sigma_{ws}$ and in the Young’s equation, the value $\cos \theta > 1$. The equation does not take into account the vertical component of the total vector leading to deformation of the substrate, the peculiarities of the solid phase and liquid structure in the area of the interfacial boundary. A new record of Young’s equation is proposed:

$$\cos \theta = N^d \left(\frac{\sigma_{lv} - \sigma_{sw}}{\sigma_{lv}}\right) \sigma_{lv}^d,$$

where $N^d \leq 1$, $\sigma^d$ – dynamic tension at interfacial boundaries, $N^d$ – function that includes an unknown scalar equation that takes into account the peculiarities of non-equilibrium spreading. At $N^d = 1$ we get the known Young’s equation [5].
drop begins to bend the film and at the final stage of spreading wraps into it under the vertical force. Figure 1a shows that three surface tensions in no form can the drops come into equilibrium, since $\sigma_{nw}$ and $\sigma_{nw}$ lie in one plane and are directed against each other, and the third one $\sigma_{nw}$ is located at an angle. Therefore, there is an uncompensated force applied to the outline of the drop and directed vertically upward. The convex surface of the drop creates Laplacian capillary pressure that presses it to the flat surface. On flat surface this pressure is zero ($R \to \infty$), and at convex it is equal to $P = 2\sigma_{nw} / R_{nw}$. In order for capillary pressure to be balanced over the entire drop-limiting surface, it is necessary to form a well beneath it so that all three forces along the contour are compensated, i.e. $2\sigma_{nw} / R_{nw} = 2\sigma_{nw} / R_{nw}$. Thus, strictly speaking, the Young’s equation applies to the non-equilibrium case.

The well is found in the absence of wetting, as well as in experiments on the interaction of mutually insoluble metals (Fe+Pb, Mo+Sn, etc.) and low-soluble metals, as well as in iron wetting of oxide materials and borosilicate melts of tungsten and rhenium [4, 12–16]. It was found that the surface of the solid phase is deformed at high temperatures and over more than 2...10 hours under the influence of unbalanced surface forces. A rib-shaped cuff (Fig. 1 c) is thus formed, the height of which increases with time and can reach 10 μm at high temperatures with a width of up to 5 μm [15]. Vertical forces $F_i = \sigma_{nw} \sin \theta$ increase as the value $\theta$ approaches $90^\circ$. A stretched state region occurs along the wetting perimeter. The transport of the substance (viscous flow mechanisms, surface diffusion, evaporation – condensation) will be carried into this area, leading to the formation of a cuff. A well also occurs during dissolution of solid phase atoms in melt [16]. Thus, the measured value $\theta$ depends not only on the nature of the interfacial interaction (ratio of $\sigma_{nw}$, $\sigma_{nw}$ and $\sigma_{nw}$), but also on the intensity of dissolution processes. In this case, when a well is formed (Fig. 1c), the measured value $\theta$ is less than the true edge angle $\theta = \theta + \varphi$.

Figure 1b shows a profile of the equilibrium state of the system according to the second Neumann-Gibbs capillary equation

$$\sum \sigma_i \hat{i}_j = 0 \quad (\sigma_i - \text{interfacial tensions}, \hat{i}_j - \text{unit vectors tangent to the phase boundaries}),$$

which in the projection on the vertical and horizontal axes gives:

$$\sigma_{nw} \cos \psi = \sigma_{nw} \cos \theta + \sigma_{nw} \cos \varphi \quad \text{and} \quad \sigma_{nw} \sin \theta = \sigma_{nw} \sin \psi + \sigma_{nw} \sin \varphi.$$  

If you put the value of the angle $\psi = 0$ [4, 13–14] due to its small value or difficulty to determine, it is possible to measure $\sigma_{nw}$ and $\sigma_{nw}$ in one experiment by measuring the value $\sigma_{nw}$ separately using equations:

$$\sigma_{nw} = \sigma_{nw} \cos \theta + \sigma_{nw} \cos \varphi.$$  

The use of equations at $\psi = 0$ requires special analysis. In [13] at the equilibrium of the Pb drop on the Fe surface at 920 °C a reasonable value $\sigma_{rr}$ for Fe that equals 1645 mJ/m2 was determined. On the other hand, from the experimental data given in [14] we see that the values $\sigma_{nw}$ and $\sigma_{nw}$ in the melt drop Cd+ system (Cd-Sn) decrease with time within 8 hours in argon and 2 hours in glycerol, which contradicts the physics of the process. Obviously, after achieving the chemical equilibrium, the system’s tendency to achieve mechanical equilibrium, resulting in surface warping, cannot lead to the decrease in $\sigma_{nw}$ and $\sigma_{nw}$ [7–9].

In general, the force leading to non-equilibrium spreading looks as follows:

$$F_i = F_i^d(\sigma_{nw} - \sigma_{nw}) - 1/1 N^i \sigma_{nw} \cos \theta \pm$$

$$F_i(\tau) - F_i(\tau) - P_1(\tau) + P_2(\tau),$$

where $F_i^d(\sigma_{nw} - \sigma_{nw})$ – true driving force determined by the decrease in free surface energy during the spreading process when replacing solid and liquid surfaces with a common interfacial boundary. At $\sigma_{nw}(\tau) = -\sigma_{nw}$, $F_i^s = \sigma_{nw} + \sigma_{nw}$, $W^s = \sigma_{nw} + \sigma_{nw} + \sigma_{nw} 1/1 N^i \sigma_{nw}^s \cos \theta$ – the contribution of this spreading retardant component is determined by $\sigma_{nw}$ that varies from the initial $\sigma_{nw}$ to equilibrium $\sigma_{nw}$ and an increase in $\cos \theta$ as the decrease $\theta$, $F_i(\tau)$ – inertial force preventing spreading with a maximum value at the start of spreading, acts until the start of the second spreading stage. As the
speed of movement slows down, the inertia force changes its sign, facilitating the movement of the liquid.

\[ F_i(\tau) \] — viscous resistance force, which increases in proportion to the growth of the thickness of the boundary layer \( \delta = \sqrt{\nu \tau} \). The process of dissolution on the perimeter of wetting will also increase the strength of the flow resistance while increasing the viscosity of the boundary layer fluid.

\[ P_d(\tau) = 2\sigma_{\infty} / R_{\infty}(\tau) \] — Laplacian capillary pressure, which presses a drop having a convex surface with a radius of curvature \( R_{\infty} \).

\[ P_d(\tau) \] prevents leakage and its contribution decreases over time.

\[ P_v(\tau) \] — vertical force deforming the surface of the solid phase, the action of which begins to manifest itself as the contribution of inertia forces \( F_i(\tau) \) decreases.

\[ P_g \] — gravity field will contribute to spreading.

According to experimental data, it is common to distinguish between: 1) a fast spreading stage (up to 0.02 seconds) and 2) a slow spreading stage from 0.03 sec to 10 minutes or more. The slow spreading stage is typical for systems with strong chemical interaction resulting in the formation of chemical compounds in the surface layer of the solid phase. This stage is determined by the kinetics of diffusion processes and the liquid spreading over a layer of chemical compounds (intermetallides), as well as in the case of oxide films and organic contaminants on the surface. In the vast majority of cases, upon contact of clean surfaces, the first stage is completed within \( \tau < 0.02 \) seconds. At further 10 minutes or more, the values of the edge angle do not change [8, 17–20].

Kinetic patterns of fast spreading stage and the role of viscous resistance forces. Let us consider the fast spreading stage that is typical for all systems and independent of the chemical activity of the interacting phases. At this stage, the drop flows over the surfaces, occupying its main area. The spreading rate, like that of any process, is determined by the ratio of a driving force to resistance forces, mostly inertial and viscous forces. Based on the analysis of numerous experimental studies [3–9, 15–20] it was found that in the first stage of fast spreading \( (t_1 = 0...5 \cdot 10^{-3} \text{ sec}) \) the radius of the drop \( r \) increases from time \( \tau \) according to the linear law \( r = K_1 \tau \), in the second stage \( t_2 = 5 \cdot 10^{-3} \) to \( 1.4 \cdot 10^{-2} \) sec there is a parabolic dependence of spreading \( r^2 = K_2 \tau \). The spreading rate decreases on average from 1.8 to 0.4...0.6 m/s (Fig. 2–3). The linear dependence \( r^2 \) on \( \tau \) at this stage confirms the constancy of radial consumption and, hence, the constancy of driving forces. Since fresh layers of liquid flow onto a clean solid surface \( F_{av}^d \) is constant. The driving force at the periphery of the drop has a maximum value \( F_{av}^d = \sigma_{\infty} - \sigma_{av}(\tau) = \text{const} \) and is determined mainly by dynamic values of the interfacial tension \( \sigma_{av}(\tau) \). At this stage, \( \sigma_{av}(\tau) \) has the minimum value and can make \( \sigma_{av}(\tau) > 0 \) [5-9].

If drop movement is significantly slowed down and equilibrium values of concentration are reached on its periphery during mass transfer, the driving force of spreading is significantly reduced [5–8]: \( F_{av}^d = \sigma_{\infty} - \sigma_{av} << F_{av}^d \). As the thickness of the flowing liquid layer decreases, its thickness \( h \) becomes commensurate with the thickness \( \delta \) of the boundary layer, which at the surface has a maximum viscosity gradient. The velocity of the drop slows down as the driving force becomes insufficient to overcome the viscous resistance and friction at the solid surface, and the third stage \( (t_3 = 1.4 \cdot 10^{-2} \text{ sec up to } (2...9) \cdot 1.4 \cdot 10^{-2} \) sec) occurs at which \( r^2 = K_3 \tau \). The spreading rate and driving force decrease by \( 1...2 \) orders, and \( n \) increases to \( 3...4 \). At the end of this period, in the process of mutual dissolution, the diffusion zone reaches a triple point on the periphery of the drop. Interfacial tensions \( \sigma_{av} \) and \( \sigma_{\infty} \) reach equilibrium values and the fourth stage of slow spreading \( t_4 = (2...9) \cdot 10^{-2} \text{ sec to } 1...30 \text{ sec and more } 1...10 \) min; \( r^2 = K_3 \tau, n = 8 \). Thus, where a variable viscosity boundary layer is formed at the surface of the solid phase, the liquid droplet cannot flow into the liquid phase film of minimum
thickness in the 3...4 molecular layers (6...12Å) and generally $\theta_{min} \geq 3...4^\circ$. To confirm this, the works [5–8] carried out estimates to determine the thickness of the boundary layer.

On the role of inertial forces in non-equilibrium spreading. At the initial point of contact, the spreading rate $V = 0$, and then under the action $F_{vis}$ having the maximum value at this stage, the drop begins to flow rapidly. High Reynolds number values $\sim 4500$ at initial spreading rates and drop oscillations after flowing onto the substrate indicate that the spreading occurs in inertial resistance mode. This is further confirmed by the fact that the effect of temperature decreases as the spreading rate increases. Besides, the calculation of speed constants – K coefficients in equations $r^n = K\tau$ at the initial stage according to Ya.I. Frenkel’s equation for viscous flow, gives velocity values different by more than an order from experimental [16–20].

**Figure 2.** Spreading of Zn, Pb, Sn and Pb alloys with Sn on iron surface [17]. The dependence of the drop base radius $r$ on time $\tau$ (a) and velocity $V$ on $\Delta\sigma(\sigma)$. Same as Figure 2a, experimental points are connected by lines (b)

**Figure 3.** Changes in the drop base radius $r$, contact angle and spreading rate $V = K\Delta\sigma$: a – lead on iron at 350 °C; b – tin on iron at 235 °C; c – zinc on iron at 450 °C. Points – experimental values connected by lines, and dashed lines – calculated values [18]

Experimental data [17–18] given in Fig. 2 and 3 confirm the change of inertial forces action sign. With careful consideration of the experimental points, relatively large deviations from the middle curves can be seen. If you connect the experimental points with lines (Fig. 2b and 3), the wave movement of the drop front due to the periodic change of the sign of inertial forces becomes obvious. When the motion of the drop is slowed by viscous forces, inertial forces begin to act in the opposite direction resulting in vibration of the drop.

### 3. Results

Thus, the kinetics of drop spreading is determined by a variety of factors. The analysis of the driving forces shows that when there is a constant driving force on the peripheries of the drop, the growing force of the viscous resistance acts on it. The increase in the thickness of the boundary layer by law $\delta = \sqrt{\tau}$ decreases the spreading rate and stops the movement. Where it is possible to dissolve the solid phase in the liquid, there will be an increase in the viscosity of the boundary layer. When a drop of
equilibrium concentrations is reached in the process of mass transfer, the driving force of spreading is significantly reduced. At high flow rates at the first and second stages, in addition to viscous resistance forces, inertial forces play a determining role, which change their sign over time.

The critical values of edge wetting angles are considered in [5, 8]. The edge angles $\theta$ cannot be equal 0.09 and 180°. The value $\theta$ cannot be zero, since the angle at the edge of the equilibrium liquid phase film of minimum thickness in 3...4 molecular layers (6...12Å) is not zero and minimum values $\theta_{\text{min}} \geq 3^\circ...4^\circ$. The values $\theta$ on the solid and liquid surfaces are always less than 180°, since equality $\theta = 180^\circ$ implies a vapor layer separating the drop from the surface. The drop or soft particle of spherical shape approaching the surface of the solid body falls under the influence of far-acting attraction forces and then short-acting Brownian repulsion forces, which will lead to tensions in it. Calculations of molecular forces acting at a distance of 0.1 μm show that these tensions cause local deformation relative to the soft bodies prior to their contact, i.e. prior to the moment of action of the Brownian repulsion forces. Thus, the soft particle loses its original spherical shape and the point Hookian contact is excluded. The value $\theta$ also cannot be 90°. At $\theta > 90^\circ$ there is no wetting, dispersion forces are in effect and the drop can be separated from the surface. At $\theta < 90^\circ$, chemical bonding occurs in the contact zone, accompanied by irreversible drop spreading.

4. Conclusion
1. The driving forces of the separation are analyzed and kinetic regularities of the stage of fast separation of the drop on the solid surface are considered.

2. It was found that the deceleration of the spreading rate at constant driving force is caused by the increase in the thickness of the viscous boundary layer according to the law $\delta = \sqrt{\nu \tau}$, which decreases the spreading rate and stops the movement. At high flow rates at the first and second stages, in addition to viscous resistance forces, inertial forces play a determining role, which change their sign over time. The analysis of effect of vertical forces on the spreading kinetics was performed and critical values of edge angles were determined.

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