

Motto: If we only knew what we are doing we would not call it: research.

Spontaneous spreading of liquids on substrates
with contrasting two types of substrates:
that of liquids and that of solids*

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A thermodynamic evaluation of spreading of liquid drops on substrates leads to a set of inequalities which have to be fulfilled for self-spreading to occur. The apparent necessity to determine the surface energy of solids is, however, illusory as a closer examination shows that the solid surfaces are so heterogeneous that no single value can be used to represent them.¹

The concept of contact angle has been around for several centuries and even the celebrated Young relationship quantifying that angle in terms of interfacial energies was first published in 1805 (Young Collected Works 1855). Ever since the appearance of contact angle concept it was the subject of innumerable discussions and much experimental work in multiplicity of systems ... used as a quick qualitative test to differentiate oleophobic from oleophilic types of surfaces with respect to the liquid used. One very bothersome side effect of all the experimental work was the seemingly unavoidable hysteresis of the contact angle. All the above discussions and work resulted in voluminous literature comprising many hundreds if not thousands of publications dealing with that

* Invited article

¹„contact angle is the angle formed by a thick liquid film, arrested in its spreading over a substrate in a three phase system: substrate/liquid/air. Monolayers may also form an angle but this would be invisible as is the monolayer itself whose behaviour is detected by secondary effects only.

topic. Of all those literature products I wish to give just two examples: “*Wetting, Spreading and Adhesion*” ed. J.F. Padday, publ. Academic Press (1978). It is an compilation of papers at a symposium held at Loughborough University, Leisterhire U.K. which was organized by the Colloid and surface Group of Chemical Industries U.K. and the second publication is “*Proceedings of the 2-nd International Congress on surface Activity*” vols. 1-5 , publ. Butterworth (1957). The Congress was held in London U.K. J.F. Padday book provides an excellent overview of the contact angle utilized in industry, while J.H. Schulman’s deals mostly with fundamentals and research results. Yet despite all the effort on the subject, there are still many puzzling and unanswered problems left. Most, if not all the published data deal with solid/liquid/air systems and hardly any with the liquid/liquid/air ones.

Spreading of liquids occurs as a result of a reduction in the total free energy of the system. The total free energy may comprise different forms of energy such as kinetic, gravitational and interfacial energy contributions. In order to get to the core of problems we simplify our considerations by disregarding extraneous particulars in a stepwise fashion. In the present case of self spreading liquids we limit our consideration to systems which do not react chemically or electrostatically between the liquid and the substrate. Then, we exclude systems whose kinetic energy preponderates. On reducing the volume of the liquid to drops we not only constrict the range of gravitational energy but reduce its magnitude in relation to the interfacial energy of the liquid. With solutions of aqueous tension close to 72 dynes/cm, erg/cm². A drop of a size such that 20-50 drops give 1 ml (1 g of liquid) the gravitational contribution to the system is 961/20 – 961/50, where 961 is the gravitational const. on earth, while the interfacial contribution is not affected at all. Under the above restrictions the self-spreading of drops will occur as a result o of reduction in the interfacial energy contribution alone. All spreading of liquids involves a substitution of the substrate/air (s a) interface by a film of liquid with two substrates: substrate/liquid s l and liquid/air l a. all three interfaces cover the same area A (area of wetting). Denoting the specific free energy, of a given interface, by appropriate suffix we have for spontaneous spreading the following inequality:

$$f_{sa} \cdot A > f_{sl} \cdot A + f_{la} \cdot A \dots (T_1)$$

and dividing by positive A the inequality remains the same i.e. $f_{sa} > f_{sl} + f_{la}$. (T₂)
or for a monolayer $f_{la} < f_{sa}$(T₃)

Harkins (1952) obtained an identified result from experimental data of monolayers spreading on liquid substrates. For a non-spreading situation an inequality opposite to (T₃) would obtain. We should note that the difference

$$\Pi = f_{sa} - f_{la}$$

is known as the surface pressure of the film or the driving force of its spreading.

We should observe that the driving force for thick film spreading is no longer a function of one term the surface tension of the liquid but now a function of the interfacial sl tension as well. From the equation given above it would appear that the determination of f_{sa} values would be highly desirable. However, before embarking on search and development of the required method it may be instructive to compare two types of substrates used: the liquid ones and the solid ones. The chief characteristic of all liquids is their fluidity which endows them as substrates with the case of cleaning by a simple procedure of scraping the top layer of the liquid off to a sufficient depth to remove the adsorbed impurities and the remnants of previously adhering phases. This allows their surfaces to be renovated to the original state by an inflow of fresh components from the underlying bulk phase. On the contrary the solids have rigidity which immobilizes the component atoms or molecules in a fixed grid extending throughout the given grain, the accumulation of which constitutes the given sample of solid. Any surface of that solid must of necessity cut across a number of grains with their different grids that is must be very heterogeneous and remain so unless a higher temp is used and sufficient time is allowed for rearrangement of the top semi-fluid to occur, but then the substrate is no longer that of the original solid. High vacuum may help to remove some or even most of the adsorbate but will be unable to renovate the surface as is the case of a liquid one. The heterogeneity of the solid substrate must be accepted as unavoidable and uncontrollable. Because of it whatever method is developed for determining f_{sa} will apply only to the particular patch, site, where the determination was made. It will not be a general characteristic of the surface used as a substrate. For that reason, I feel that hysteresis of contact angle and presum of surface energy f_{sa} is just a misnomer for heterogeneity of solid surfaces. For that reason alone, Young formula does not apply, because there is no uniform solid substrate, except for large cleavage faces of single crystals which are not generally used as substrates. Even then their cleaning has to be worked out.

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CURRICULUM VITAE



Jan Leja was born in Grodzisko, Poland in 1918. In 1939, his university studies of two years in Metallurgical Engineering at the Academy of Mining and Metallurgy in Kraków were discontinued due to World War II. From 1939 till 1942, Jan Leja was incarcerated in prisons and concentration camps in Siberia. Being fortunate to survive that ordeal, Jan Leja rejoined the Polish army in Russia and was sent to England for training. Once in England, his army training was in parachuting to be dropped back into Poland.

Fortunately Jan Leja was not dropped into Poland. Instead, he enrolled in Metallurgy at the Royal School of Mines toward the end of World War II, and was granted an A.R.S.M. and B.Sc. with first class honours in 1945. In 1947, he was also awarded a Diploma Ing. from the University of Kraków. His graduate research results from the Royal School of Mines were mis-used, and so in 1952 Jan Leja re-enrolled for postgraduate study at the University of Cambridge. He was granted a Ph.D. (Cantab.) in 1954 for his highly original work on "Molecular Interactions at Interfaces, as Applied to Flotation Phenomena". Jan Leja's graduate research work with his supervisor, Dr. Jack Schulmann, and colleagues at the Royal School of Mines contributed dramatically to our understanding of the functions of flotation frothers, particularly poly-oxyethylene and poly-oxypropylene type reagents. Prior to Jan Leja's work, little was known of the crucial molecular interactions of frother molecules with collector-coated mineral surfaces to affect bubble-mineral attachment. Interspersed between these periods of postgraduate study from 1949 to 1952, Jan Leja served as mill superintendent at the South West Africa Company Mine in Grootfontein, S.W. Africa.

Next, Jan Leja joined the Department of Mining and Metallurgy at the University of Alberta in 1957. He attained the rank of full professor in 1963. Jan Leja became Professor of Mineral Process Engineering at the University of British Columbia in 1965 and served admirably in that position until his retirement in 1983. Jan Leja has won several awards for his teaching and research in mineral process engineering. These include the Canadian Institute of Mining and Metallurgy ALCAN Award, an honorary degree of Doctor of Honorarius Causa from the Marie Curie-Skłodowska University in Lublin, Poland, and the University of British Columbia Walter Gage Teaching Award. Jan Leja has authored over 60 technical papers. He also holds four patents on mineral processing.