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ORIGINAL CONTRIBUTION

Obtaining surface tension from contact angle data by the individual representation approach

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Abstract Young equation is the fundamental equation of wetting theory in which the connection among the surface tensions, $\gamma_{\varphi\psi}$ and the contact angle, θ_L, are given. The surface tension of solid surfaces, however, cannot be obtained directly from the Young equation. In this paper, the application of the individual representation theory is demonstrated for the determination of surface tensions of solids (or any phase pair) using experimentally obtained contact angle data. According to this approach, the state of the interfacial layers depends upon, by definition, the properties of the bulk phases in every heterogeneous system, and thus, it complements the traditional capillary theory.

Keywords Contact angle · Substantial parameters · Surface tension · Critical surface tension

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Introduction

The most important goal of the investigations of wetting from both theoretical and practical point of view is to reveal the relevant physical quantities and relationships that determine the adhesion of solid and fluid phases [1–4].

The surface tension of solids cannot be derived directly from the Young equation (Eq. 1) [5], which describes—in equilibrium—the connection among the contact angle, θ_L (or rather $\cos\theta_L$ (Rehbinder number)) and surface tensions (γ_{SV}: solid-vapour, γ_{SL}: solid-liqiud, γ_{LV}: liquid-vapour) [5]:

$$\cos\theta_L = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{1}$$

Although several semiempirical relationships such as Good-Girifalco, Fowkes, etc. equations were suggested in the literature ("traditional approach" [6–9]), the possibility to determine surface tension is still not ensured. In spite of the intense research during the last five decades, attempts to invent a procedure to obtain the surface tension values of solid surface from experimental data remained basically unsuccessful [10–16].

The relationships of capillary theory contain quantities, which are compatible with the algebraic-analytical formalism of canonical thermostatics. The availability of the surface tension in the present work is based on the individual representation approach [17–20] in which the surface tension is expressed in terms of multiplicative substantial parameters which are determined by only one phase. The method differs significantly from the traditional treatment in which the surface tension is expressed in terms of additive components of surface tension: "collective parameters" which are determined by the two adjacent phases. The background of the traditional approach is that the potential (U) of a bulk phase is expressed by summing up the different types of potentials (e.g., dispersive and nondispersive contributions, etc.). For k types of potential at a point (Q) in the interfacial layer:

$$U(Q) = \sum_k u_k(Q) \tag{2}$$

Therefore, the "resultant" surface tension of the layer $\left(\gamma_{\varphi\psi}\right)$ can be composed of k number of independent components, and that number is identical with the number of affecting force types. Hence, the surface tension can be given by different and "collective" surface tension components:

$$\gamma_{\varphi\psi} = \sum_k {}_k\gamma_{\varphi\psi} \tag{3}$$

The conservative character of the inner forces makes possible the introduction of substantial parameters in the bulk phase. However, the multiplicative individual variables are, by definition, different from the aforementioned additive-type components of surface tension. In the individual representation, the collective layer quantities are replaced for the individual fundamental quantities that only depend on the single bulk phase properties and are defined by the electric polarizability, magnetic susceptibility, compressibility, Sugden's parachor, critical variables, evaporation heat, temperature, etc. While the traditional additive quantities are derived on the basis of the types of physical–chemical interactions existing between the studied phases, the substantial parameters include all possible interactions (i.e., not only dispersion components). This approach in the present paper offers a relatively simple solution for the determination of solid surface tension values using the exact deformational theoretical definition of surface tension and, in general, also gives the conditions of the determination of surface tensions for any phase pairs. Thus, a model can be developed, which ensures the complete availability of the quantities. By the application of the dimensional analysis and the theory of similitude [21–26] for the individual characterization of the phases in the capillary interactions, this theory is formulated through the definition of a new type of fundamental variables: the substantial parameters (see e.g., the works of Pászli et al. [17–20] summarized in Appendix I). Because the basics of the individual representation theory have already been reported [20], this paper only gives the general idea of this theory instead of a detailed discussion.

The individual contribution of phases φ and ψ to the surface tension, $\gamma_{\varphi\psi}$, can be taken into consideration by the corresponding tension (substantial) parameters, χ_φ and χ_ψ (Eq. 4).

$$\gamma_{\phi\psi} = \chi_\phi \chi_\psi \tag{4}$$

The theoretical background of Eq. 4 can be outlined as follows: a relationship (Eq. 5) can be concluded from the additivity of bulk potentials, on the bases of deformation theory of surface tension [20].

$$\gamma_{\varphi\psi} = \frac{1}{2}\left|U_{0\varphi} - U_{0\psi}\right| \cdot \tau_{\mathrm{eff}} \tag{5}$$

where $U_{0\varphi}$ and $U_{0\psi}$ are the potentials in the bulk phases, and τ_{eff} is the effective thickness of the interfacial layer. Applying the dimensional analysis it can be derived that the difference of bulk potential energies $\left(\left|U_{0\varphi} - U_{0\psi}\right|\right)$ only depends on the corresponding bulk phase (individual) parameters (q_φ and q_ψ) as follows [20] (Eq. 6, also see Appendix I):

$$\left|U_{0\varphi} - U_{0\psi}\right| = q_\varphi \cdot q_\psi \tag{6}$$

If it stands, the surface tension of the phase pair $\{\varphi;\psi\}$ can also be expressed by bulk phase quantities exhibiting individual characteristics instead of layer quantities of "collective" characteristics (Eq. 4). The capillarity state of any system is characterized unambiguously if every substantial parameter is known. The substantial parameters—defined by only a single phase—are cardinal physical quantities of the individual representation of the capillarity: the mathematical model system consists of the substantial parameters and the relevant relations among these substantial parameters. These parameters can be established generally to any—vapour, liquid, or solid—phase, but the value for the different phases of the same chemical entity (e.g., liquid water and ice) will be different.

Previously, papers were reported about the stagnation phenomenon at solid/fluid interfaces [17], state equation of the boundary layer [18], the extended capillary theory [19], and the individual parameters in capillarity [20] in terms of the individual representation concerning adsorption phenomena on solid surfaces. The main purpose of the present work is to show how one can apply the individual representation approach for the determination of surface tension of solids that will be demonstrated for real surfaces by using a set of contact angle data obtained from the literature.

Applications of the individual parametric representation

Determination of the substantial parameters

If a phase of fixed state participates simultaneously in several various equilibria, it forms interfacial layers of different surface tensions in connection with different phases. Its parameter, however, obviously does not depend on the type of equilibrium. If the mutual solubility can be neglected, the

Table 1 Surface tensions and substantial parameters of selected test liquids at ambient temperature (see the full table in the work of Pászli [20])

Liquid	γ_{LV} mN/m	$\gamma_{L,\text{ water}}$	$\gamma_{L,\text{ Hg}}$	χ_L (mN/m)$^{1/2}$	χ_V
Hexane	19.50	51.20	380.0	7.1615	2.7228
Heptane	20.30	50.70	377.0	7.1049	2.8571
Octane	21.70	50.90	375.0	7.0673	3.0704
Nonane	22.90	–	372.5	7.0218	3.2660
Decane	23.90	51.20	–	7.1493	3.3429
Dodecane	25.44	–	–	7.3867	3.4440
Tetradecane	26.55	–	–	7.2889	3.5129
Hexadecane	27.76	–	–	7.5082	3.6573
Glycerol	32.27	–	384.0	7.2364	4.5988
Water	72.40	–	380.0	7.1615	10.1235
Mercury	480.0	380.0	–	53.0612	9.0461

state of a fluid bulk phase is independent of that of the adjacent phases, and therefore the ratio of interfacial tensions calculated for the pairs of fluid phases containing the common (L) liquid phase e.g. $\{\varphi_L;\varphi_{L'}\}$ and $\{\varphi_L;\varphi_{L''}\}$ are also independent of the "common" liquid (also see Appendix II, Eq. A11). Therefore, the substantial tension parameters of liquids can be calculated from the surface tensions of three liquid phases being in equilibrium pair-wise with each other (Eq. 7) and from the formulae obtained by cyclic permutation of the subscripts (also see Appendix II).

$$\chi_1 = \sqrt{\chi_1^2} = \sqrt{\frac{\chi_1\chi_2}{\chi_2\chi_3}\chi_1\chi_3} = \sqrt{\frac{\gamma_{12}}{\gamma_{23}}\gamma_{13}} \tag{7}$$

In the case of gaseous phases, the tension parameter can be determined if the surface tension and the tension parameter of the liquid phase are known (Eq. 8).

$$\chi_V = (\chi_V\chi_L/\chi_L) = (\gamma_{LV}/\chi_L) \tag{8}$$

Table 1 shows some tension (substantial) parameters for different liquids calculated from measured quantities (measured values are taken from the works of Pászli et al. [17–20, 27]).

On the basis of the Young equation (Eq. 1), substantial parameter of any solid phase can be derived as follows. In the individual representation, the following relationship stands (based on Eq. 4)

$$\frac{|(1/\chi_L) - (1/\chi_V)|}{(1/\chi_S)} = |\cos\theta_L|. \tag{9}$$

It can be proved theoretically that the three-phase equilibrium can be realized in an ordinary or a reversal state which is dependent on the relative greatness of the substantial parameters of the individual phases. Hence, the difference of reciprocal values of the substantial parameters can be negative or positive resulting two algebraic equations. Equation 9 with the absolute values combines both of the possible relationships. The description of ordinary and reversal states will be the topic of our forthcoming publication. The absolute value unifies algebraically both of the two cases. Beside the measurable contact angle, Eq. 9 contains only quantities of the bulk phases and defines the relations of the parameters. Consequently, if the parameters of the fluid phases and experimentally established Rehbinder's number are known, the parameter of the solid phase can be expressed from the measured quantities as written below:

$$\chi_S = \left|\frac{\gamma_{LV}}{\chi_V - \chi_L}\cos\theta_L\right|. \tag{10}$$

The difficulties of determining the surface tension of a solid surface originates from the fact that the Young's equation contains four variables (only two of them can be measured) making the equation indefinite for surface tensions. However, Eq. 10 provides a defined algebraic method for the χ_S quantities due to the fact that the number of independent variables and that of independent equations are identical. Thus, the surface tension of solid surfaces can be determined directly by Eq. 4, if all the tension parameters of the pertinent fluid phases and the contact angle are available.[1]

In Table 2, some calculated tension parameters are presented based on the measurements of Kwok [28, 29] and on the data in Table 1. As can be seen, the error of calculated χ_S quantities of a single solid surface is significant though, the standard deviation of the average χ_S value does not exceed 15% in the most cases (see standard deviations in Table 2). The uncertainty can be diminished by applying more test liquids for the determination. It should be noted that the parameters of solids can be determined more accurately by the U-type manometer method (see Appendix II). It should be noted that for (chemically) modified surfaces the tension parameter corresponds to the modifying layer and not to the substrate which is in line with the principle of independent surface action [30, 31].

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[1] Theoretically, the data are independent of the chemical–material characteristics of wetting fluid phase.

Table 2 Some examples for the calculation of substantial parameters based on the measurements of Kwok [29, 30] and the data presented in Table 1

Solid phase	Fluid phase	θ_L (deg)	χ_s (mN/m)$^{1/2}$	$\overline{\chi}_s$ (mN/m)$^{1/2}$	Standard deviation of χ_s (mN/m)$^{1/2}$	γ_{SV} (mN/m)
FC-722 coated mica	Water	118.69	–	2.24	0.46	–
	Glycerol	111.73	1.9839			9.12
	cis-Decaline	79.56	1.7692			7.74
	Hexadecane	75.94	2.7938			10.33
	trans-Decaline	73.38	2.4166			9.97
Teflon	Dodecane	47.8	4.3340	4.21 (4.69 including 1-octanol)	0.18 (0.96 including 1-octanol)	14.93
	Tetradecane	52.6	4.0062			14.59
	1-Octanol	54.4	6.1162			24.91
	Hexadecane	53.9	4.2916			15.87
Perfluorocapric acid	Hexane	52.9	2.6498	2.18	0.36	7.21
	Heptane	58.4	2.5090			7.17
	Octane	61.9	2.5570			7.85
	Nonane	65.4	2.5366			8.27
	Decane	67.2	2.4330			8.13
	Dodecane	71.7	2.0260			6.98
	Tetradecane	73.9	1.8289			6.66
	Hexadecane	76.7	1.6753			6.19
	Ethanol	70.0	1.8470			5.71
	Propanol	71.8	1.9351			6.42
	Butanol	72.7	1.9760			6.80
	Octanol	78.8	2.0405			8.31
FC-725	Dodecane	71.02	2.0988	2.09	0.01	7.22
	Hexadecane	73.41	2.0795			7.69
Perfluorocaprylic acid	Octane	60.0	2.7145	2.37	0.29	8.33
	Decane	65.8	2.5736			8.60
	Dodecane	68.0	2.4170			8.32
	Tetradecane	71.0	2.1475			7.82
	Hexadecane	74.0	2.0074			7.42
Perfluorovaleric acid	Decane	70.5	2.0958	2.43	0.26	7.00
	Dodecane	67.5	2.4692			8.50
	Tetradecane	65.5	2.7352			9.96
	Hexadecane	70.5	2.4313			8.99
Perfluorocaproic acid	Octane	59.0	2.7959	2.54	0.25	8.58
	Decane	64.5	2.7029			9.03
	Tetradecane	68.8	2.3850			8.69
	Hexadecane	71.8	2.2747			8.41
Perfluorobutyric acid	Decane	61.0	3.0439	2.80	0.23	10.17
	Dodecane	64.5	2.7777			9.57
	Tetradecane	67.0	2.5769			9.39

Determination of surface tension of solids

The surface tensions of selected solid surfaces have also been calculated based on the individual representation theory and the results are included in Table 2. It can be seen that the surface tension values fall in the range of 8.1–15.2 mN/m that corresponds to hydrophobic surfaces. It is worth comparing these values with the experimentally determined critical surface tensions of the pertinent surfaces (Hare et al. [32]) (see Table 3). The relationship between the critical surface tension, γ_c, and the surface tension of the solid can be derived on the basis of the individual representation theory considering a series of aqueous solutions of nonvolatile surfactants:

$$\gamma_c = \gamma_{SV} \frac{\chi_V}{\chi_S + \chi_V}. \tag{11}$$

As can be seen from Eq. 11, the critical surface tension should be smaller than the surface tension of the solid–

Table 3 Comparison of critical surface tension values [32] and solid/vapor surface tensions obtained by the individual representation approach (see Table 2) for selected fatty acids

Fatty acid monolayer	Shorthand designation (no. of carbon atoms: no. of unsaturated bonds)	Surface tension from the individual representation approach (on mica, also see Table 2) (mN/m)	γ_c (on Pt foil) (mN/m)
Perfluorobutyric acid	4:0	9.39–10.17	9.2
Perfluorovaleric acid	5:0	7.00–9.96	9.0
Perfluorocaproic acid	6:0	8.41–9.03	8.6
Perfluorocaprylic acid	8:0	7.42–8.60	7.9
Perfluorocapric acid	10:0	5.71–8.31	6.1

vapor interface. It can be concluded from the data of Table 3 that the maximum values of surface tensions determined from the individual representation approach decrease with increasing number of carbon atoms in the fluorocarbon chain and are somewhat higher than the corresponding critical surface tensions.

Further important consequences

Based on the individual representation, some further important relationships can be deduced. If the Δ_{LV} symbol is introduced as follows (Eq. 12):

$$|(1/\chi_{\mathrm{V}})-(1/\chi_{\mathrm{L}})|=\Delta_{\mathrm{LV}}; \tag{12}$$

The connection between the Rehbinder's number and χ_{s} is linear according to the "parametric" Young equation (Eq. 9):

$$\cos\theta_{\mathrm{L}}=\chi_{\mathrm{s}}\,\Delta_{\mathrm{LV}} \tag{13}$$

Consequently, for the same fluid phase pair, the relation of the parameter of the solid phases and the Rehbinder's number is linear, as it is illustrated in Fig. 1, where some of these linear functions are presented for the aforementioned experimentally obtained contact angle data [28, 29]. It is interesting to note that in Fig. 1, the linear function, theoretically, has to intercept the (0;0) point. However, this point cannot be justified by measurements because vacuum has the lowest parameter value around 1.7 $(\mathrm{mN/m})^{1/2}$ [20].

Also, the experimentally obtained Fig. 2 confirms the linear relationship between Δ_{LV} and ($\cos\theta_{\mathrm{L}}$) values of different fluid phase pairs for the same solid surfaces. The slope of the straight lines provides χ_{S}. By substituting Eq. 4 into Eq. 12 and then performing identical transformations it can be concluded that the parameter of an "unknown" fluid (L or V) on the surface of the same solid can be determined as the positive roots of the following relation (Eq. 14):

$$\chi_{\mathrm{L}}=\frac{\mp\gamma_{\mathrm{LV}}|\cos\theta_{\mathrm{L}}|+\sqrt{\gamma_{\mathrm{LV}}^{2}\cos^{2}\theta_{\mathrm{L}}+4m^{2}\gamma_{\mathrm{LV}}}}{2m} \tag{14}$$

(where i=L or V) if the slope (m=χ_{S}), surface tension of the fluid phase pairs (γ_{LV}) and the corresponding contact angles are available. Hence, the tension parameters of fluid phases can be calculated for an appropriate reference surface if the surface tension of the phase pairs, γ_{LV} and the contact angles, θ_{L} measured on the reference solid surface are available. Otherwise, we should know the surface tension values obtained adjacent to (for instance) mercury surface for the determination of fluid tension parameters. (Such a precise method is reported in the works of Dunken et al. [33–35] and also shown in Appendix II [36]).

As a consequence of Eq. 13, the ratio of the Rehbinder numbers of two liquids (Eq. 15), $\{L';L''\}$ corresponding to the same solid surface is

$$\frac{\cos\theta_{\mathrm{L'}}}{\cos\theta_{L''}}=\frac{\Delta'_{\mathrm{LV}}}{\Delta''_{\mathrm{LV}}} \tag{15}$$

that is defined absolutely unambiguously by the quality of the fluid phases. Consequently, the value of that ratio, corresponding to the series of different solid surfaces, is identical for each surface. Analogously, the ratio of Rehbinder's numbers obtained for two different solids with the same liquid–fluid phase pair will give identical value using any liquid–fluid phase air on the pertinent solids. Moreover, the individual representation—*mutatis mutandis*—is applicable for amorphous solids and crystals as well as for solutions. For the latter ones, the relations are more complex than those derived for pure liquids (see the works of Pászli et al. [17–20, 27, 37, 38]).

Hence, the revised "traditional" capillary theory [39] and the parametric representation actually complement each other.

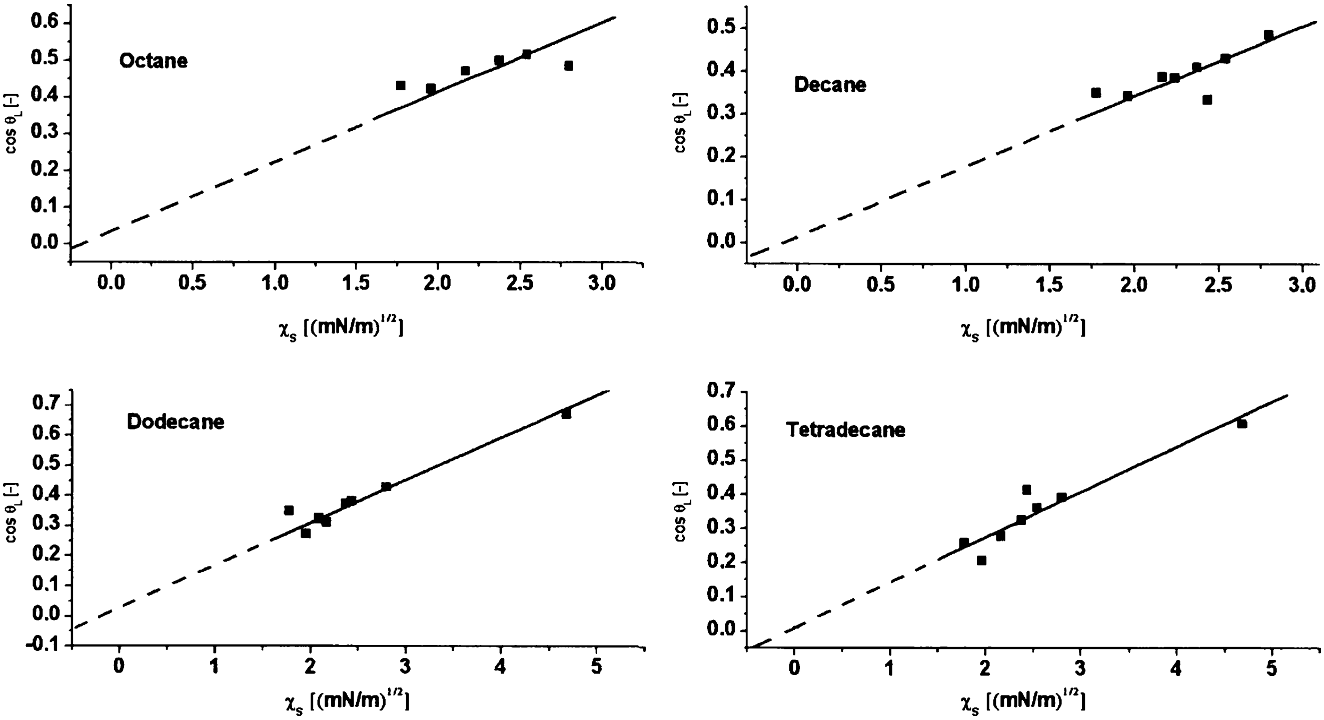

Fig. 1 Selected examples for the linear relationship between the tension parameter of the solid phases and the Rehbinder's number for the same fluid phase pairs (data are obtained from the work of Kwok [28, 29]). Liquids are indicated on the graphs

Conclusion

On the basis of the deformation theory of surface tension with the use of the dimensional analysis, the new type of variables of the capillarity can be established in which the variables characterize the phases individually (substantial parameters).

Those different theorems that are based on dividing the surface free energy into components, in general, do not take into account the restrictions of the theory of similitude, and

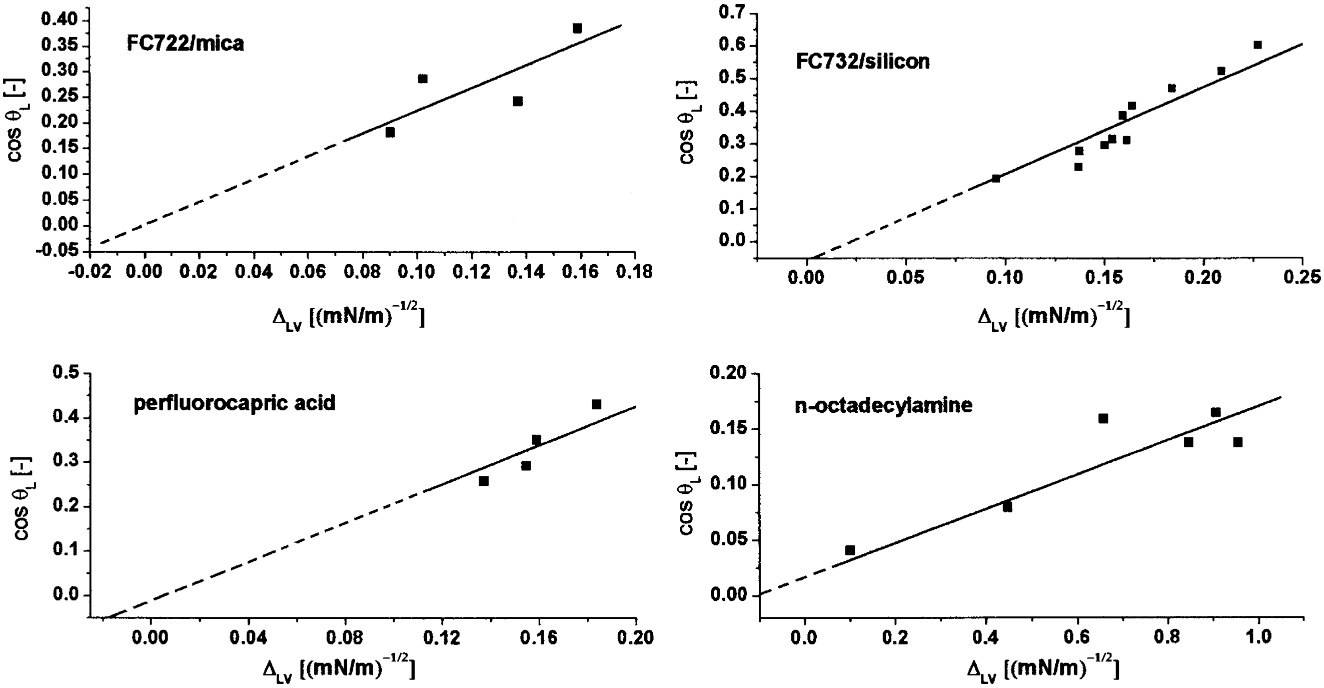

Fig. 2 Selected illustrations for the linear function between Δ_{LV} and ($\cos\theta_L$) values of different fluid phases measured on the same solid phase (data are obtained from the work of Kwok [28, 29]). Solids are indicated on the graphs

therefore the principle of "Ockham's razor"[2] is not fulfilled. However, this principle is obviously fulfilled in the individual representation.

With the use of the substantial parameters which characterize the surface tension entirely, the resultant complete capillary theory can be built up in line with the Gödel's theorem [40, 41].[3] The advantage of this representation (and method) is that its basic quantities—unlike the collective variables—are only traditional experimental data: surface tensions of liquids and contact angles. Thus, the application of novel measurement methods is unnecessary. Every relation of the individual representation is based on substantiated knowledge of other disciplines; thus, this theory does not include any ad hoc assumption, and its statements are, therefore, conclusive.

With the application of this representation, the general method for the determination of the surface tension of solids can be established on the basis of contact angle measurements.

The main results of this paper are the following:

1. Theoretical background of the calculation of surface tensions from experimental contact angle data has been surveyed based on the individual representation.
2. It has been proved—using some well-known model surfaces from the literature—that the individual representation theory provides an efficient and useful alternative approach to calculate surface tensions of solid surfaces from experimentally determined contact angles.
3. It has been shown that the individual representation theory proposes a linear relationship between $\cos\theta_{\mathrm{L}}$ as a function of χ_{S} or Δ_{LV}. The linear relationship between the aforementioned quantities has been proved by using experimentally determined data.

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Appendix I

Background of the individual representation of capillary theory

The set of variables of the traditional capillary theory are formed by nonscalar physical quantities those can be described as functions of their scalar components. The general dimension equation stands, by definition, for scalar variables (see e.g., [11–13]). Therefore, it stands automatically for the variables of capillarity (characterized by the same tensorial order, i.e., they are also scalar) that are material constants and primarily correspond to the local, individual features of the bulk of phase ϕ. The variables of capillarity are for instance, the collective-type surface tensions, $\gamma_{\varphi\psi}$ of phases, $\phi\in\{\varphi,\psi\}$, and in general, the fundamental variables, $\{\ldots,_{\varphi}x_i,\ldots\}$ those correspond to thermal, mechanical etc. interactions, and they define the intermolecular potential, u_ϕ.

The (positive and scalar) surface tensions of different phase pairs are—in a paradox manner—the function of fundamental variables that determine potentials of bulk phases.

Based on the general dimensional equation, Bakker's surface tension (see e.g., [7, 8, 14]) is the following:

$$\gamma_{\varphi\psi}\left(\ldots{}_{\varphi}x_i;{}_{\psi}x_i,\ldots\right)=\left|\left({}_{\varphi}x_1\right)\left({}_{\psi}x_1\right)\right|^{v_1}\ldots\left|\left({}_{\varphi}x_n\right)\left({}_{\psi}x_n\right)\right|^{v_n} \tag{A1}$$

where v_i is an universal constant of the *i*th interaction-type. The individual quantities, ${}_{\varphi}x_i$ characterizing the interactions separately, are the phase-wise separated and unified contributions that are the substantial parameters (see Eq. A2) and, thus, they define the resultant interaction.

$$\chi_\phi\left(\ldots,{}_{\phi}x_i,\ldots\right):=\prod_i\left|{}_{\phi}x_i\right|^{v_i} \tag{A2}$$

Analogous expressions (Eqs. A3 and A4) exist for bulk phase (individual) parameters, q_ϕ (see Eq. 6) and the effective thickness of the interfacial layer, τ_ϕ^{eff} (see Eq. 5), in which N_i and W_i are also universal constants of the *i*th

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[2] Ockham's razor: also spelled Occam's razor, also called low of economy, or low of parsimony. It is a principle stated by William of Ockham (1285–1347/49), that *Pluralitas non est ponenda sine necessitate*; "Plurality should not be posited without necessity." The principle gives precedence to simplicity; of two competing theories, the simplest explanation of an entity is to be preferred. The principle is also expressed "Entities are not to be multiplied beyond necessity." (source: Ockham's razor (2006). In *Encyclopaedia Britannica*. Retrieved June 12, 2006, from Encyclopaedia Britannica Premium Service: http://www.britannica.com/eb/article-9056716).

[3] Gödel's theorem proves that there exist meaningful mathematical statements that are neither provable nor disprovable, now or ever. Neither provable nor disprovable, that is, not simply because human thought or knowledge is insufficiently advanced but because the very nature of logic renders them incapable of resolution, no matter how long the human race survives or how wise it becomes.

interaction-type corresponding to the given equation, i.e. q_ϕ or τ_ϕ^{eff}:

$$q_\phi(\ldots,{}_\phi x_i,\ldots) := \prod_i |{}_\phi x_i|^{N_i} \tag{A3}$$

$$\tau_\phi^{\mathrm{eff}}(\ldots,{}_\phi x_i,\ldots) := \prod_i |{}_\phi x_i|^{W_i} \tag{A4}$$

Substantial parameters also characterize the whole phase, ϕ in the capillary interaction because due to Eq. A1, the surface tension value of adjacent phases is given by the mutually unambiguous projection (Eq. A5):

$$\gamma_{\phi\psi} = \chi_\phi \chi_\psi. \tag{A5}$$

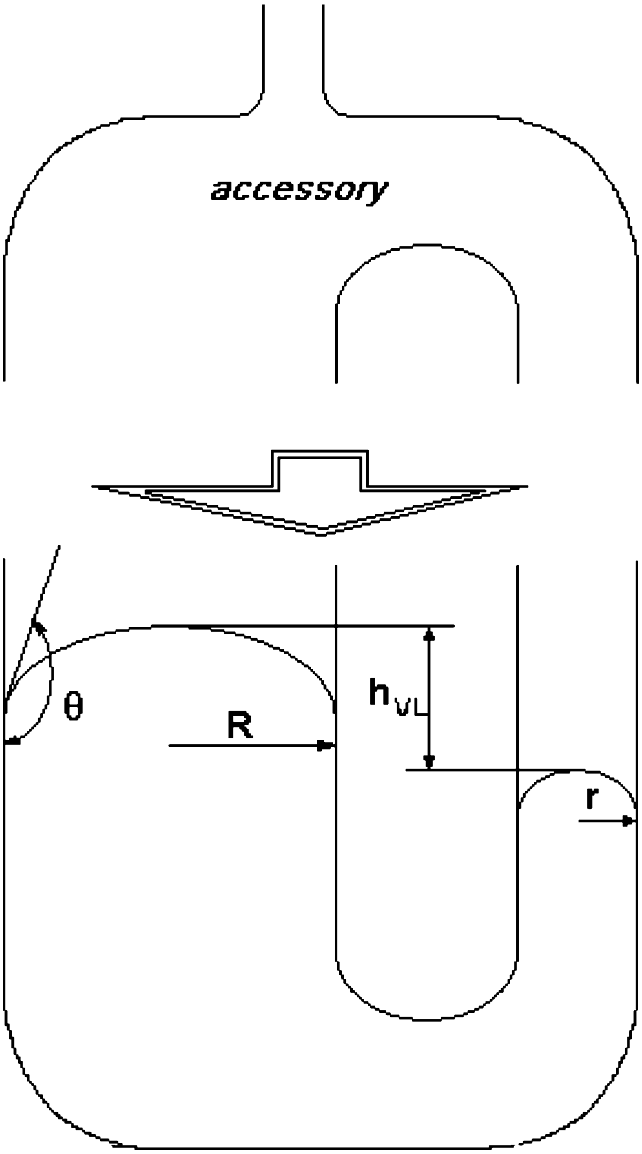

Fig. 3 Scheme of the U-type manometer filled with Hg

The $\gamma_{\varphi\psi}$ and its multiplicative components (χ_φ and χ_ψ) form a saddle surface, moreover, χ_ϕ is the univalent function of the potential, u_ϕ, i.e., $\chi_\phi = \chi_\phi(u_\phi)$.

In general, fundamental quantities can be approximated with satisfactory accuracy by the following functions (Eq. A6):

$${}_v x_y = \frac{y_{\mathrm{crit}}}{n_y}(1 - y_{\mathrm{red}})^{n_y} \tag{A6}$$

that contains the reduced quantities $\frac{y}{y_{\mathrm{crit}}} = y_{\mathrm{red}}$ where $y=\{T; p\}$ is the actual canonical quantity and $y_{\mathrm{crit}}=\{T_{\mathrm{crit}}; p_{\mathrm{crit}}\}$ is the critical quantity, is the power, that is a positive, whole or fraction number. In Eq. A6, n_{y} is the so-called critical exponent. The validity of Eq. A6 can be theoretically justified. The "individual" interaction quantities in critical state (identically with the surface tension of the liquid/vapor interface) disappear.

Appendix II

Determination of the surface tension of liquids by a U-type glass manometer

The U-type glass manometer method has already been published elsewhere [36]. It is mentioned in this study only because of the limited availability of that source.

1) For the determination of surface tension of liquid (L)/vapor (V) interface, γ_{VL}, the U-pipe (see Fig. 3) is filled with the studied liquid up to ca. 1/3 part then the equipment is placed on an optical desk without any accessory to read carefully the difference between the liquid levels, h_{VL} existing in the vertical tubes due to their different radii. One of the tubes is macrosized with inner radius of R, the other one is a capillary with inner radius of r. Reaching the equilibrium, h_{VL} is recorded.

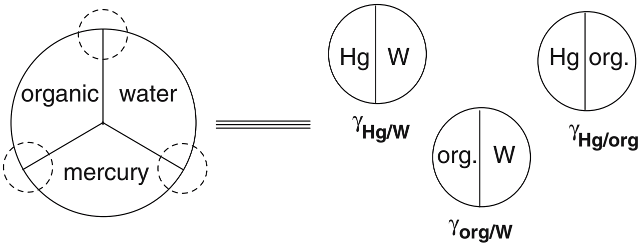

Fig. 4 Any mutually insoluble organic/aqueous/mercury system can be considered as three two-phase systems

2) For the determination of two-liquid surface tension of mercury and test liquid (γ_{HgL}), the same U-pipe is filled with mercury up to ca. 1/3 part and an accessory (see Fig. 3) is connected to the equipment. Next, such amount of test liquid is filled on the mercury to form a meniscus in the accessory tube. Then, reaching equilibrium h_{HgL} is read carefully.
3) Step 1 and step 2 have to be repeated with a calibration liquid of known surface tension (γ^{cal}).
4) Calculation: considering equilibrium between the phases, $\gamma_{\alpha\beta}$, surface/interfacial tension can be calculated from the measured heights as follows:

$$\gamma_{\alpha\beta}=\frac{1}{2}\left\{\frac{1}{[(1/R)\pm(1/r)]\cos\theta}\left(\rho_{\mathrm{inf}}-\rho_{\mathrm{sup}}\right)g\right\}h_{\mathrm{VL}} \tag{A7}$$

Note that for one-liquid case, ρ_{inf} is the density of the liquid and $\rho_{\mathrm{sup}}=0$. For two-liquid case, ρ_{inf} is the density of mercury and ρ_{sup} is the density of the liquid layered on mercury. If $\theta<90°$ then positive sign, if $\theta>90°$ then negative sign is taken in the bracket. If θ is approximately identical for the studied and the calibration liquids, the following relation may approximate the surface tension:

$$\gamma_{\alpha\beta}=\gamma^{\mathrm{cal}}\frac{\rho_{\mathrm{inf}}-\rho_{\mathrm{sup}}}{\rho_{\mathrm{inf}}^{\mathrm{cal}}-\rho_{\mathrm{sup}}^{\mathrm{cal}}}\frac{h_{\mathrm{HgL}}}{h_{\mathrm{cal}}} \tag{A8}$$

From these data the substantial parameters of the liquid and the vapor phase can be calculated by the following equations (at ambient temperature, see Table 1.). For the liquid phase [21]:

$$\chi_{\mathrm{L}}=\frac{\gamma_{\mathrm{HgL}}}{53.0612(\mathrm{mN/m})^{1/2}}. \tag{A9}$$

For the vapor phase:

$$\chi_{\mathrm{V}}=\frac{\gamma_{\mathrm{LV}}}{\chi_{\mathrm{L}}} \tag{A10}$$

Substantial parameters of other liquids are available, as follows:

In case of an organic/aqueous/mercury system where the phases are mutually insoluble in each other (see Fig. 4).

For two liquids Eq. A11 stands:

$$\frac{\gamma_{\mathrm{LL}^{I}}}{\gamma_{\mathrm{LL}^{II}}}=\frac{\chi_{\mathrm{L}^{I}}}{\chi_{\mathrm{LL}^{II}}}=f\left(\mathrm{L}^{I},\mathrm{L}^{II}\right) \tag{A11}$$

Any substantial parameter can be obtained from Eq. 7 based on known surface tensions of the organic and the aqueous phases, and that of mercury. The substantial parameter of a vapor phase can be calculated from Eq. 8.

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