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ORIGINAL CONTRIBUTION

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Individual Variables in Capillarity

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Abstract A novel type of surface variable, so-called individual quantities, has been introduced on the basis of dimensional analysis and the law of similarity. The parameters can be determined at least in one way. To make the parameters available, the algebraic uncertainty inherent in the individual representation (e.g. in Young's equation) can be eliminated. Thus, when this approach is applied, the surface tension of the solid surface can be determined easily.

Keywords Dimensional analysis · Law of similarity · Surface tension · Young's equation

Introduction

Capillary effects at interfaces, e.g., relating to the spatial extent of interfaces in heterogeneous systems, can be more or less interpreted to a certain degree in terms of traditional capillary theories [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. However, a common defect of these approaches is that they provide no general indication about how to determine the fundamental quantities, e.g. the surface tension of the solid surface. In special cases, these quantities can be estimated [17], but there is no exact way available to measure them. For arbitrary ad hoc conditions, therefore, their validity may be basically questionable.

Capillary effects do not constitute a distinct type of thermostatic interaction. The quantities related to the surface area can be interpreted on the basis of the theory of deformation. The four-variable Young equation describes the adjustment of the phases in the state of equilibrium. Although this formula contains both the surface tensions and the contact angle, the exact value of the surface tension of the solid phase cannot be derived from this single equation. As no further theoretical relationship exists, the indeterminacy cannot be lifted, even theoretically, within the domain of capillary variables [18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29]. The algebraic indeterminacy of the defining quantities casts doubt on the heuristic strength of the hypothetical interpretations.

A novel type of surface variable, so-called individual quantities, has been introduced, based on dimensional analysis and the law of similarity [30, 31, 32, 33, 34, 35]. A new, extended representation of capillary theory has thus been developed [36, 37]. This approach also provides a general method for determining the surface tension of solid surfaces.

The surface tension and the Curie equation

The physical quantities concerning the spatial elements of a heterogeneous system (e.g. volume domains, faces, edges, etc.) can be interpreted exclusively on the basis of deformation theory.

The canonical elastic potential of a system, E_{el}, contains the stress and deformation tensors, $\hat{p}$ and $\hat{\varepsilon}$, respectively. However, the characteristic function—considering the dynamic behaviour of the corpuscular structure—can also be expressed in an alternative form using non-canonical variables. The criterion for mechanical equilibrium can be expressed through the kinetic stress tensor, $\hat{P}$:

$$Div\,\hat{p} = Div\,\hat{P} + \vec{f} = \vec{0} \qquad (1)$$

The ponderomotive (acceleration) forces corresponding to the tensor $\hat{p}$ are compensated at each point of the system, but the conservative internal forces $\vec{f}$—unlike those of the surface—disappear only in the bulk phase. The potential $u(Q)$, corresponding to the internal force $\vec{f}(Q)$ at the point Q in the layer, can be described by a continuous and strictly monotonic function:

$$\vec{f} = -grad\,u$$

Various geometrical surfaces may be assigned to each interfacial layer. For instance, in the case of a solid surface (S) covered by a fluid layer (L) of finite thickness, we can take into account the interfaces between layer and bulk phases, simply or multiply connected phase boundaries, etc. These surfaces can be considered as Stefan-type equipotential dividing surfaces situated at various distances parallel to the enveloped surface. Thus, the surfaces, equivalently to the potential, can be characterized by the following function:

$$P_T(Q) - P_N(Q) = u(Q) - u\left(Q_{\varphi,\psi}\right) = S_{\varphi,\psi}(Q) \qquad (2)$$

$S_{\phi,\psi}(Q)$ is the so-called Stefan quantity and P_T and P_N are the length of tangential projection of the kinetic stress tensor $\hat{P}$ in the given surface. The interfacial layer $s_{\phi,\psi}$ of the phases $\{\phi,\psi\}$ can be divided into two neighboring regions by a Stefan surface passing through the inner point Q. The volume of these regions may be different, depending on the position of Q. However, as the thickness τ is very small, the surface areas of the Stefan surfaces are practically identical, and their change is defined by the tensor $\hat{\varepsilon}$ belonging to Q (Fig. 1).

Only a single intensive parameter can be derived from the deformations as well, which is related to the work due to expansion of the interfacial layer:

$$\gamma_{\varphi\psi}(Q) = \left(\int_{Q_\varphi}^{Q} \left|P_T(Q) - P_N(Q_\varphi)\right| d\tau + \int_{Q}^{Q_\psi} \left|P_T(Q) - P_N(Q_\psi)\right| d\tau \right)$$

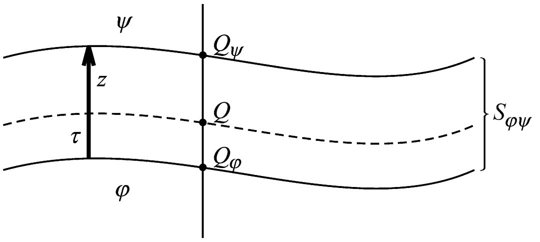

Fig. 1 Schematic representation of the phase boundary

The integral $\gamma_{\phi,\psi}(Q)$ is a scalar quantity that is everywhere positive, but its value depends on the position of Q (Q_ϕ,Q_ψ). Q_ϕ and Q_ψ are the corresponding points of the bulk boundaries.

A system of volume V, containing a number s of different interfacial layers (each with a surface area A_s and thickness τ) can be constructed by a continuous deformation starting from the corresponding reference states with a surface area A_s^0. If only interactions affecting the state of the {...,s,...} interfacial layers may occur, resulting in a change of the surface area $\Delta A_s(Q) = \left[A_s(Q) - A_s^0(Q)\right]$, then the change in elastic potential, i.e. the work of deformation, is

$$\Delta E_{el}(\{\dots, y_k, \dots\}; \{\dots, \bar{\varepsilon}_n V, \dots\}) = \\ = \iiint\limits_V \hat{p} : \hat{\varepsilon} dV = \sum_s \gamma_s(Q) \cdot [\Delta A_s(Q)] = extr.! \qquad (3)$$

where k is the number of interactions, and i represents the coordinates x,y,z. For conservation of the independent deformation quantities

$$\iiint\limits_V \varepsilon_{ii} dV = const.$$

Thus, if only internal changes take place, the volume is equal to that of the reference state, i.e. mean deformations necessarily vanish. $\gamma_{\phi\psi}(Q)$ can also be expressed with the potentials. The integral $\gamma_{\phi\psi}(Q) = \gamma(z)$ vanishes if $Q = Q^\sigma$ satisfies the following condition:

$$\frac{\partial}{\partial z}\gamma(z) = 2u(Q) - \left(u_0^\varphi + u_0^\psi\right) = 0.$$

Also

$$\left(\frac{\partial^2}{\partial z^2}\gamma(z)\right)_{Q^\sigma} = 2\left(\frac{\partial}{\partial z}u(Q^\sigma)\right) = 2\left|\vec{f}(Q^\sigma)\right| \geqslant 0,$$

since the internal forces within the layer never vanish. The function $\gamma_s(z)$ exhibits a minimum. The surface density of the elastic potential for a heterogeneous system with a single homogeneous surface can be expressed as

$$\frac{dE_{el}}{d\Delta A^{(z)}_{\varphi\psi}} = \frac{dE_{el}}{dA^{(z)}_{\varphi\psi}} = \gamma_{\varphi\psi}(z),$$

which is also a minimum, since homogeneity results in proportionality. Although $\gamma_s(Q)$ is an extremum only when $Q = Q^{\sigma}$, even so it is paradoxically compatible with the function E_{el}. Eq. 3 contains the product of $\gamma_{\phi\psi}(Q)$ and $\Delta A_s(Q)$, which is independent of the actual position of Q in each layer, owing to the additivity of the extensive parameters:

$$\gamma_{\varphi\psi}(Q).\Delta A_s(Q) = const.$$

(this is the *local invariance*). $\Delta A_s(Q)$ changes with Q as well (the conjugated quantities refer to the same surface), and it follows that all products corresponding to Q, e.g. that belonging to Q^{σ}, can be accommodated in the formula. The Stefan surface, which contains the extremum point, is by definition equal to the tension surface $s^{\sigma}_{\phi\psi}$ $s^{\sigma}{}_{\varphi\psi}$ of the interfacial layer, since it divides the so-called half-layer regions of the layer.

The surface tension $\gamma_{\phi\psi}$ of the layer $s_{\phi\psi}$ can be defined according to the extremum behaviour of the elastic potential,

$$\gamma_{\varphi\psi} = \lim_{Q \to Q^{\sigma}} \gamma_{\varphi\psi}(Q) = \min .! \tag{4}$$

Accomodating Eq. 4 into Eq. 3, the generalized Curie equation is obtained.

The surface tension is the sum of the exclusively positive partial quantities, the so called half-layer surface tensions. These tensions have a symmetrical algebraic structure. These physical quantities have a hybrid nature, containing parameters of both bulk and layer phases, and giving the excess energy of the half-layer compared to the bulk phase of identical volume.

Based on the definition in Eq. 4, the alternative measurement instructions for the experimental determination can be given. The unit function $c(Q) = 1$ can be integrated throughout the whole layer, while the Stefan quantity is monotonic and limited. For the half-layer s_{ϕ} $_{(\phi\psi)}$, according to the du Bois-Reymond mean value principle [38], the integral of the product of the two functions is

$$\int_{Q_{\varphi}}^{Q^{\sigma}} \left|u(Q) - u(Q_{\varphi})\right| d\tau \equiv S_{\varphi}(Q_{\varphi}) \int_{Q_{\varphi}}^{Q_{\xi}} d\tau + S_{\varphi}(Q^{\sigma}) \int_{Q_{\xi}}^{Q_{\sigma}} d\tau$$

$$= \left|u(Q^{\sigma}) - u(Q_{\varphi})\right| \cdot \overline{Q_{\xi}Q^{\sigma}},$$

since the Stefan quantity disappears along the surface (Q_{ξ} lies between Q_{ϕ} and Q^{σ}). The length $\overline{Q_{\xi}Q^{\sigma}} = \tau^{eff}_{\varphi(\varphi\psi)}$ is the effective thickness of the half layer $s_{\phi(\phi\psi)}$ (an analogous formula can be obtained for the other half layer, although the effective thickness may be different). Owing to the extremum, the potential $u(Q^{\sigma})$ is equal to the arithmetic mean of the bulk phase potentials (Stefan's Law [39]). The effective thickness of the whole layer, $\tau^{eff}_{\phi\psi}$ is the sum of the half layer thicknesses. After an identical transformation it can also be given as

$$\gamma_{\varphi\psi} = \frac{1}{2}\left|u(Q_{\psi}) - u(Q_{\varphi})\right| \cdot \tau^{eff}_{\varphi\psi}.$$

At the same time, the deviation of the bulk potentials can also be expressed by the layer-forces. If a curve L in the layer $s_{\phi\psi}$ runs parallel to the normal of the Stefan-surface, then the last equation can be written as

$$2\left(\frac{\gamma_{\varphi\psi}}{\tau^{eff}_{\varphi\psi}}\right) = \left|u^0_{\varphi} - u^0_{\psi}\right| = \left|(L)\int_{Q_{\varphi}}^{Q_{\psi}} \vec{f} d\vec{r}\right| = \left|(L)\int_{Q_{\varphi}}^{Q_{\psi}} f_N \, dr\right|, \tag{5}$$

where f_N is the normal projection of the force, and $\vec{r}$ is the position vector. Thus, the interfacial quantities $\gamma_{\phi\psi}$ and $\tau^{eff}_{\phi\psi}$ and their ratio are determined by the integral of the force, i.e. the potential distribution functions of the adjoining bulk phases, instead of the layer forces. As force is a vector, crystal lattices with different Miller indices have different projections, and hence different effective layer thicknesses and surface tensions. Paradoxically, a direct relationship exists between the bulk potentials and the layer quantities.

The extensive - intensive character of the capillary variables and their tensor order can be directly derived from Eq. 5. All of them are deduced quantities. Their values for a given pair of phases are defined by the relations for the independent fundamental variables, i.e. the values of the so called dimensional equations. Such state quantities may be the empirical surface tension formulae [40], electric polarizability, magnetic susceptibility, compressibility, the Sugden-parachor, critical data, etc. As traditional capillarity theory contains no dimensional equations, the numerical values of the variables cannot be determined. Consequently, the traditional methods of capillarity theory are incomplete, and have to be implemented by the fundamental quantities and the dimensional equations of the variables.

Equation 5 contains the absolute value of the bulk potential difference of the adjacent phases (ϕ;ψ). This is an *ab initio* positive function of the individual fundamental variables of the bulk potentials, $\{\ldots,_{\varphi}x_i,\ldots;\ldots,_{\psi}x_i,\ldots\}$. Thus, the alternative expressions for the surface quantities implicitly contain the variables of the bulk phase. The dimensional equations can be created with their identical transformation.

The collective capillary variables can be obtained from dimensional analysis. These variables depend symmetrically on the exclusively positive individual physical quantities of the adjoining phases.

The general dimensional equation and the individual phase parameters

In a consistent system of measurements between the $\{X\}$ numerical values of a physical quantity X and its unit $[X]$, in linear coordination the relationship $X=\{X\}[X]$ exists as well as their reciprocal relationship.

Based on the reciprocal relationship, in a system of measurements, a derived physical quantity S can be given as

$$\{X\}=f(\ldots,\{x_i\},\ldots),$$

and in a system S' that is consistent with S,

$$\{X'\}=f\left(\ldots,\left\{x_i^{'}\right\},\ldots\right)=f(\ldots,\lambda_i\{x_i\},\ldots)=\lambda\{X\}.$$

The positive values of λ or $\{....,\lambda_i,....\}$ depend on the units of the systems S and S', respectively. The relationship holds for values relating to a physical system, ω or Ω as well. Therefore,

$$q=\frac{f_\omega(\ldots,\lambda_i x_i,\ldots)}{f_\omega(\ldots,x_i,\ldots)}=\frac{f_\Omega(\ldots,\lambda_i x_i,\ldots)}{f_\Omega(\ldots,x_i,\ldots)}=\lambda.$$

The ratio $q=\lambda$ depends on the quantities $\{....,\lambda_i,....\}$, but is independent of the specific choice of chemical system. The systems S and S' may coincide. In this special case the numerical values $\{....,\lambda_i,....\}$ are equal to unity. If both the function f of this quantity and all the x_i may take only positive values, then

$$\begin{aligned}\left(\frac{\partial}{\partial\lambda_i}q\right)&=\frac{1}{f(\ldots,x_i,\ldots)}\cdot\frac{\partial f(\ldots,\lambda_i x_i,\ldots)}{\partial(\lambda_i x_i)}x_i\\&=\frac{\partial\ln f(\ldots,x_i,\ldots)}{\partial\ln(x_i)}=v_i\end{aligned}$$

must be satisfied, based on the logarithmic identity. The derivative v_i therefore depends only on the interactions represented by the physical quantities x_i. The total derivative of the function $X=f(\ldots,x_i,\ldots)$ is

$$\begin{aligned}d\ln X&=\sum_i\left(\frac{\partial\ln f}{\partial x_i}\right)_{\bar{x}_i}dx_i=\sum_i\left(\frac{\partial\ln f}{\partial\ln x_i}\right)_{\bar{x}_i}d\ln x_i\\&=\sum_i v_i d\ln x_i=d\ln\left(\prod_i x_i^{v_i}\right),\end{aligned}$$

and, owing to the positivity, the integral of X is

$$X=\prod_i x_i^{v_i}=\prod_i|x_i^{v_i}|,$$

if the integration constant is equal to 0.

This is the general dimensional equation (Wallot-formula). According to the last equation, the derived physical quantity, X, which is always positive, can be expressed as a power law function of the fundamental quantities of the independent partial interactions, x_i. The set of variables algebraically form an Abelian group [41, 42, 43]. The relationship is valid for both the numerical values and the units.

From the general Wallot formula, the special relationship

$$K_{\varphi\psi}=\left\{\prod_i\left|{}_\varphi x_i\right|^{v_i}\right\}\left\{\prod_i\left|{}_\psi x_i\right|^{v_i}\right\}=I_\varphi\cdot I_\psi \tag{6}$$

is also valid for those collective physical quantities of the interfacial layers (K), which are the symmetric functions of the relevant variables of the adjoining phases, $\{....,{}_\phi x_i,....\}$ and $\{....,{}_\psi x_i,....\}$, respectively. They can be separated and contracted into a single variable in each phase. Therefore, in the surface interaction the phases $\{\phi;\psi\}$ can each be characterized by a single individual variable expressing the total effect of the partial interactions [37, 38].

According to Eq. 6, all the collective surface variables are derived quantities. Based on the dimensional equation, a function Φ exists between the given quantity and the numerous independent scalar fundamental variables $\{....,x_i,....\}$. Thus, the material parameters depend only on their own bulk phase. Therefore, they represent the contribution of the singular phases to the "surface interaction". If

$$\{\ldots,i,\ldots\}\in\{\ldots,i_a,\ldots\}\cup\ldots\cup\{\ldots,i_z,\ldots\}$$

for the indices, i.e., the partial groups of parameters are identical to the symmetrical fundamental quantities $({}_aI_\varphi\times{}_aI_\psi)={}_aK_{\varphi\psi},\ldots$, then

$$K_{\varphi\psi}=\left({}_aI_\varphi\cdot{}_aI_\psi\right)\ldots\left({}_zI_\varphi\cdot{}_zI_\psi\right)=\left({}_aK_{\varphi\psi}\right)\ldots\left({}_zK_{\varphi\psi}\right) \tag{7}$$

i.e. Eq. 6 may be generalized for the variables of the partial groups as well.

The corresponding variables ($K_{\phi\psi}$ as well as I_ϕ and I_ψ) of the unified and the partial interactions separately span a hyperbolic paraboloid. Eq. 6 is identical to a Coulomb-type force function. From Eq. 6 and Eq. 7 it follows that it is unnecessary to identify the individual bulk quantities belonging to the collective surface quantities of the adjoining phases, if their combined value, the power product I_Φ can be determined for each phase, e.g. from experimental data (from surface tension of pairs of fluid phases, from adsorption isotherms, etc.).

The individual bulk phase properties determining the state of the phase boundary layers can be obtained from Eq. 5. The potential difference in Eq. 5 can be expressed from Eq. 6 and Eq. 7, and hence from the separate individual contributions of the phases $\{q_\phi;\,q_\psi\}$, as

$$\left|u_\varphi^0-u_\psi^0\right|=q_\varphi q_\psi.$$

At the same time, the potential difference governs the ratio of the surface tension to the effective layer thickness, i.e. the ratio $\left(\gamma_{\varphi\psi}\middle/\tau_{\varphi\psi}^{eff}\right)$ is equal to the product of the ratios of the individual phase contributions. If the individual contribution of the bulk phases are the following: for $\gamma_{\phi\psi}$ are χ_{ϕ} and χ_{ψ}, and for $\tau_{\varphi\psi}^{eff}$ are τ_{φ}^{eff} and τ_{ψ}^{eff}, then Eq. 5 can also be given by the symmetrical expression:

$$q_{\varphi}q_{\psi} \equiv \left(\sqrt{2}\frac{\chi_{\varphi}}{\tau_{\varphi}^{eff}}\right)\cdot\left(\sqrt{2}\frac{\chi_{\psi}}{\tau_{\psi}^{eff}}\right).$$

By exchanging the phase indices, the equation is self-transformed; i.e. the parameters characterize the bulk phases.

The expression

$$\left(\sqrt{2}\frac{\chi_{\phi}}{\tau_{\phi}^{eff}}\right) = q_{\phi}$$

defined for the single bulk phases $\Phi=\{\phi;\psi\}$ and having only eigen contributions of positive value, can be uniformly generalized for each of all the phases.

Among the parameters $\{\chi_{\phi},\tau_{\phi}{}^{\mathrm{eff}},q_{\phi}\}$ of the surface interaction, only two are independent, but the values of all three depend on the properties of the same bulk phase. The variables individually characterize the interacting phases (individual or material parameters). The variables $\gamma_{\varphi\psi}$, $\tau_{\varphi\psi}^{eff}$ $\gamma_{\varphi\psi}$, $\tau^{eff}{}_{\varphi\psi}$ and $|u_{\varphi}-\mathrm{u}_{\psi}|$ characterize the resultant layer, and thus depend on each adjoining phase. They are the collective state parameters. The latter are determined by variables that are positive in the whole range and, by algebraic relationship, identical for all the possible layers. Thus, the collective quantities can be given by formulae containing either the hybrid variables or only the bulk phase quantities.

The essential parameters determining the state of the interfacial layers are the cardinal physical quantities of the individual description. Their value depends exclusively on the state (and structure) of the bulk phase and, therefore, each phase can be characterized by a single value.

Discussion

The collective representation of the classical capillarity relations can also be expressed by individual variables corresponding to the individual contributions of the interacting phases, based on the dimensional theory. The collective and the individual representations describe the same state of the system, but with variables of different meaning and number.

The number of capillary quantities describing the state depends on the type of representation. Let us consider an equilibrium system with n phases. There is an interface belonging to each phase pair of this equilibrium system. In the representation based on the collective variables the quantities are the surface tensions. In a system containing s phases and s layers, the number of surface tensions can be given as

$$s = \binom{n}{2} = \frac{n!}{2!(n-2)!},$$

where $n \geq 2$. In the individual representation we need only n material tension parameters. This results in a smaller number of parameters if the number of phases is not less than four. The advantage of the individual representation is that all the quantities, unlike the collective ones, can be directly derived from measured data. If a phase of given properties participates in several equilibrium states, its parameter is perforce identical, and its value can therefore be determined by studying any of the corresponding systems.

The tension parameters determining the surface tension in an equilibrium ternary liquid system can be derived from the data of the three liquids as

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

The tension parameters of the vapour phase can be derived from the surface tension of the open surface and the tension parameter of the liquid phase:

$$\chi_V = \frac{\chi_V\chi_L}{\chi_L} = \frac{\gamma_{LV}}{\chi_L}.$$

Table 1 contains parameters calculated according to these equations. However, fluid parameters can also be derived in other ways.

The tension parameters of a solid phase can be calculated from Young's equation,

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

if the tension parameters of the fluid phases and the contact angle are known. The parameters can be determined at least in one way. Thus, the data of a phase in any state of matter is theoretically available. The layer thickness and the potential parameters can be deduced from the tension parameters. Owing to the availability of the parameters, the algebraic uncertainty experienced in the individual representation (e.g. in Young's equation) can be eliminated. Thus, when Eq. 6 is applied, the surface tension of the solid surface can be determined easily.

However, Eq. 6, unlike the reciprocal relationship, is valid only for a special set of the state properties, M:

$\{X;\ldots,x_i,\ldots\} \in M$

Table 1 Calculated χ_L and χ_V parameters

Liquid	γ_{LV} mN/m	$\gamma_{L,water}$ mN/m	$\gamma_{L,Hg}$ mN/m	χ_L $(mN/m)^{1/2}$	χ_V $(mN/m)^{1/2}$
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	7.0201	3.2620
Decane	23.90	51.20	–	7.1493	3.3429
Dodecane	25.44	–	–	7.3867	3.4440
Tetradecane	26.55	–	–	7.2889	3.6425
Hexadecane	27.76	–	–	7.5082	3.6972
Cyclohexane	24.70	51.00	378.0	7.1238	3.4672
Cis-decaline	31.65	51.80	–	7.2331	4.3757
Trans-decaline	29.50	51.40	–	7.1472	4.1274
Benzene	28.40	33.70	366.0	6.8976	4.1173
Toluene	29.30	35.70	357.0	6.7280	4.3543
o-Xylene	29.76	–	359.0	6.7657	4.3986
m-Xylene	28.47	–	357.0	6.7280	4.2315
p-Xylene	28.01	–	361.0	6.8034	4.1170
Dichloromethane	27.20	–	343.0	6.4642	4.2077
1,1-Dichloroethane	24.07	–	337.0	6.3511	3.7898
1,2-Dichloroethane	30.10	–	358.0	6.7469	4.4613
1,2-Dibromoethane	39.55	–	346.0	6.5207	6.0632
Chloroform	26.30	32.30	357.0	6.7280	3.9090
Carbon tetrachloride	28.80	45.00	359.0	6.7657	4.2567
1,1,2,2-Tetrabromo-methane	–	–	293.0	5.5219	9.0004
Chlorobenzene	33.20	38.10	352.0	6.6338	5.0046
Bromobenzene	37.00	39.30	350.0	6.5961	5.6093
Methyl iodide	30.34	–	304.0	5.7292	5.2956
Ethyl iodide	28.10	–	322.0	6.0684	4.6305
Nitrobenzene	43.70	25.50	350.0	6.5961	6.6251
Aniline	43.50	5.80	341.0	6.4265	6.7688
Methanol	22.50	–	384.0	7.2369	3.1090
Ethanol	22.30	–	383.0	7.2180	3.0894
Propanol	23.70	–	378.0	7.1426	3.3180
Butanol	24.50	–	378.0	7.1238	3.4391
Iso-butanol	23.40	–	343.0	6.4642	3.6199
Octanol	27.10	8.50	353.0	6.6526	4.0735
Ethyl-mercaptane	–	25.50	314.0	5.9176	3.9204
Acetic acid	27.50	–	329.0	6.2003	4.4352
Valeric acid	26.90	–	330.0	6.2192	4.3253
Methyl-acetate	25.70	–	388.0	7.3123	3.5146
Ethyl-acetate	24.80	–	384.0	7.2369	3.4268
Propyl-acetate	–	–	380.0	7.1615	3.3512
Butyl-acetate	–	–	375.0	7.0673	3.5657
Acetone	23.30	–	369.0	6.9542	3.3504
Dioxane	33.00	–	377.0	7.1049	4.6446
Water	72.40	–	380.0	7.1615	10.1096
Mercury	480.00	380.00	–	53.0612	9.0461

which are the symmetrical functions of the variables of the bulk phase satisfying the criteria of positivity.

The states of the surface layers in a heterogeneous system are, by definition, not independent of their own properties. The equations only state that these values can also be expressed by the individual fundamental quantities of the bulk phases. However, it is possible only if the structure is physically similar and if the physico-chemical properties of adjoining phases affect only the geometrical size of the layer. Therefore, the restrictions imposed by Eq. 6 are not optional but necessary conditions to be fulfilled.

The individual quantities can always be defined for the conservative character of the internal forces. Capillary theory can be expanded by introducing individual variables belonging to the collective quantities and by inclusion of Eq. 6. The exercise cannot be complete without taking into consideration the surface excess quantities.

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