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Wetting of Surfaces and Interfaces: 
a Conceptual Equilibrium Thermodynamic Approach

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Abstract

Owing to the focus on molecular engineering of intelligent materials, growing interest has been focused on the specific interactions occurring at molecular distances from a surface. Advanced experimental techniques have been developed including instruments able to measure directly interactions at nanometer distances and to identify special structural features with comparable perpendicular and lateral resolution. With this new information at hand, the theories of molecular interactions have been re-evaluated and developed further to encompass specific interactions such as Lewis and Brønsted acidity and basicity. However, the new theories are based on critical approximations, making the upscaling to macroscopic condensed systems uncertain. Therefore, the aim of this study was to evaluate some recent models by introducing macroscopic work functions (cohesion, adhesion, spreading and immersion) of wetting of solid surfaces within the proper conceptual thermodynamic (macroscopic) framework. The properties of binary and ternary systems are discussed with the focus on four non-ideal inorganic (SiO₂ and TiO₂) model substrates. The results obtained after applying the recent and more traditional models for dispersive and specific (polar) interactions are compared with those utilizing simplifying assumptions. The sources of uncertainties are sought, e.g. from the contribution of surface pressure determined from contact angle and adsorption isotherms. Finally, the influence of chemical and structural heterogeneities and also external stimuli on wetting is briefly discussed.

1.1

Introduction

Owing to the focus on molecular engineering of intelligent materials, growing interest has been focused on the specific interactions occurring at molecular distances from a surface. Advanced experimental techniques have been developed including instruments able to measure directly interactions at nanometer dis-
tances and identify special structural features with the same perpendicular and lateral resolution. Consequently, the theories developed for the dispersive interaction of hydrocarbons has been re-evaluated and developed further to encompass specific interactions such as both Lewis and Brønsted acidity and basicity. However, the new theories are based on molecular properties for which the upscaling to macroscopic condensed systems includes a number of critical approximations.

This chapter takes the opposite, conceptual approach. The basic thermodynamic functions are chosen as the basic framework by introducing macroscopic work functions (cohesion, adhesion, spreading and immersion) of wetting of solid surfaces. The properties and wetting processes characterizing binary and ternary systems are discussed with reference to recent molecular models and more traditional models for dispersive and specific (polar) interactions including surface pressure and adsorption approaches. The Lewis and Brønsted acid–base interaction is carefully separated, since they diverge both in strength and distance. This fact is frequently disregarded. Care is taken to use systematic and clear indexing.

A number of new simplifying experimental procedures to utilize the models developed are suggested. Again, the different frameworks that the models represent are kept apart and later compared mutually with key properties. In order to facilitate the comparison of the data presented, the analysis is focused on four non-ideal solid samples of silica and titania at equilibrium. Finally, the influence of chemical and structural heterogeneities and also external stimuli on wetting is placed within the same thermodynamic conceptual framework.

### 1.2 Thermodynamic Reference Parameters

The state of a system is defined by its internal energy \( U \) or \( E \), which equals the sum of heat \( Q \) and work \( W \). For a spontaneous reaction to occur \( U \) is expected to be negative. Using the conventions for heat and work we may write the differential equation

\[
dU = dQ + dW
\]

(1)

It should be noted that \( U \) is a state function and is thus dependent solely on the initial and final state \( dU \approx \Delta U \), whereas the work \( dW \) is dependent on the path between these two states. IUPAC recommends that both are positive when there is an increase in energy of the system. For reversible processes the heat exchange is customarily exchanged for the entropic work \( dQ = TdS \). The change of work is defined as the product of two conjugative properties, the change being given by the extensive property multiplied by its intensive conjugated pair (Table 1.1) [1]. All the work functions are exchangeable and must be considered when defining the internal energy.
Selecting the most typical set of parameters for a system containing two homogeneous phases (α and β) separated by one flat interface, we obtain for the differentials of the internal energy \( U \) of each phase \[
\begin{align*}
\mathrm{d}U &= T\mathrm{d}S - P\mathrm{d}V + \gamma\mathrm{d}A + \mu\mathrm{d}n
\end{align*}
\]
As shown, the change is directed only to the extensive properties, while the intensive variable are kept constant (\( \mathrm{d}W = -P\mathrm{d}V + \gamma\mathrm{d}A + \mu\mathrm{d}n \)). The differentials of the intensive state variables have been omitted as stated specifically by the Gibbs-Duhem relationship:
\[
\begin{align*}
\mathrm{Sd}T &= \mathrm{Vd}P + \mathrm{Ad}\gamma + \mathrm{nd}\mu = 0
\end{align*}
\] (3a)

The Helmholtz energy \( (F \text{ or } A) \), the enthalpy \( (H) \) and the Gibbs free energy \( (G) \) are all related to the internal energy:
\[
\begin{align*}
\mathrm{d}F &= \mathrm{d}(U - TS) = -S\mathrm{d}T - P\mathrm{d}V + \gamma\mathrm{d}A + \mu\mathrm{d}n \quad (3\text{b}) \\
\mathrm{d}H &= \mathrm{d}(U + PV) = T\mathrm{d}S + V\mathrm{d}P + \gamma\mathrm{d}A + \mu\mathrm{d}n \quad (3\text{c}) \\
\mathrm{d}G &= \mathrm{d}(H - TS) = -S\mathrm{d}T + V\mathrm{d}P + \gamma\mathrm{d}A + \mu\mathrm{d}n \quad (3\text{d})
\end{align*}
\]
Each of them considers different dependences on the working state variables, \( T, P, V \) and \( S \). An extended evaluation of these relationships is presented elsewhere [1].

If more than one component (liquid mixture) or if more than one surface (crystal facets) is accounted for, a summation over these variables must be considered separately. Since non-relaxed solid surfaces are included in the considerations, it is advisable to distinguish specifically the relaxed surface tension of the liquid components denoted \( \gamma \text{/mN m}^{-1} \) (force) from the (strained) surface energies of the solids denoted \( \sigma \text{/mJ m}^{-2} \) (energy). Assuming that a pure liquid (L) is placed in contact with a smooth and homogeneous solid surface (S), maintaining the temperature and pressure and composition constant, we may, in the absence of other work functions, derive the Young equation [2] in the following way (Fig. 1.1):

<table>
<thead>
<tr>
<th>Process</th>
<th>Extensive variable</th>
<th>Intensive variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>Entropy</td>
<td>Temperature</td>
</tr>
<tr>
<td>( P-V )</td>
<td>Volume</td>
<td>Pressure</td>
</tr>
<tr>
<td>Chemical</td>
<td>Amount</td>
<td>Chemical potential</td>
</tr>
<tr>
<td>Surface</td>
<td>Surface area</td>
<td>Surface tension (energy)</td>
</tr>
<tr>
<td>Electric</td>
<td>Amount of charge</td>
<td>Electric potential</td>
</tr>
<tr>
<td>Magnetic</td>
<td>Magnetization</td>
<td>Magnetic field strength</td>
</tr>
</tbody>
</table>
where the subscript $i$ represents $V$ = vapor, $L$ = liquid and $S$ = solid. At equilibrium:

$$\frac{dG}{dA} \approx \Delta G/A = 0 = \sigma_{SV} - \gamma_{LV}(\cos \theta_{SL}) - \sigma_{SL}$$

Hence under these circumstances (but only then) the work function equals the Gibbs free energy per unit area with an opposite sign.

The change in free surface energy may also be expressed by the Dupré equation [3] for the work of adhesion:

$$\frac{dG}{dA} \approx \Delta G/A = \Delta G^a = -W_a = \sigma_{SL} - \gamma_{LV} - \sigma_{SV}$$

The contact angle can be determined graphically, geometrically by assuming that the drop is represented by a hemisphere and by deriving it from the expression for the Laplace pressure [4]. Note that the pinning of the three-phase contact line (tpcl) may be represented by the frictional surface tension vector directed perpendicular to the surface.

Combining the Young and Dupré equations, the work done at the interface may be defined as four key wetting (work) functions (omitting the differential sign):

**Cohesion:** $W_C = C_{LL} = 2\gamma_{LV}$  \quad or \quad $C_{SS} = 2\sigma_{SV}$  

**Adhesion:** $W_A = W_{SL} = \sigma_{SV} + \gamma_{LV} - \sigma_{SL} = \gamma_{LV}(\cos \theta_{SL} + 1)$  

**Spreading:** $W_S = S_{SL} = \sigma_{SV} - \gamma_{LV} - \sigma_{SL} = W_{SL} - C_{LL} = \gamma_{LV}(\cos \theta_{SL} - 1)$  

**Immersion:** $W_I = I_{SL} = \sigma_{SV} - \sigma_{SL} = \gamma_{LV} \cos \theta_{SL}$
However, as shown, the work functions are defined for the separation of the interconnected phases (work done by the system), while the Gibbs free energy for adhesion is usually defined as uniting the surfaces. Hence for a spontaneous process they have opposite signs!

If the processes occurring at the sharp solid–liquid interface (S) alone are considered, then the Gibbs dividing plane may be applied, being characterized by a zero volume and a zero surface excess of the liquid. For a single surface, when the two homogeneous phases have been subtracted \((V^S = 0)\) \((\alpha \text{ and } \beta)\), we find [5]

\[
\begin{align*}
\delta F^S &= \delta (U^S - TS^S) = -S^s \delta T + \gamma \delta A + \mu \delta n^S \\
\delta H^S &= \delta (U^S - \gamma A) = T \delta S^S - A \delta \gamma + \mu \delta n^S \\
\delta G^S &= \delta (H^S - TS^S) = -S^s \delta T - A \delta \gamma + \mu \delta n^S
\end{align*}
\]

Fig. 1.2 The interrelationships between the first- and second-order partial derivatives according to the working state variables \(V, T, P\) and \(S\) and the free energies \(F\) and \(G\) on the one hand and \(U\) and \(H\) on the other for processes at the Gibbs surface.
Note that if the IUPAC recommendation for the surface enthalpy is followed, then neither the Gibbs free energy nor the enthalpy can be used to derive the Young equation. If the PV work is excluded ($V^s=0$), then it would appear to be more appropriate to equate the internal energy and the enthalpy in order to maintain the symmetry of the equations. However, if both the absolute value and the difference in the surface pressure is taken to be opposite to that of the surface tension (energy), then $PdV$ terms and the $VdP$ of the bulk systems correspond to the $πdA$ and the $Adτ$ terms of the surface system, respectively [6].

It should be particularly pointed out that a conceptual analysis of the hierarchy of thermodynamic parameters (the Thermodynamic Family Tree [1]) both for bulk systems and for interfaces [6] reveals that the traditional “work” state parameters ($T–S$ and $P–V$) are only sensitive to dramatic changes, providing information on the order of the phase transitions (Fig. 1.2). On the other hand, the next class of partial derivative parameters (heat capacities $C_p$, $C_V$ and compressibilities $K_T$, $K_S$) and their cross-derivatives (their ratio $γ$, cubic expansion coefficient $α$ and pressure coefficient $β$) are sensitive to higher order interactions, such as hydrogen bonding or Lewis acidity and basicity. In particular, they provide information on the extension of the interaction such as the cooperativity of molecular association (cf. lambda transitions). This has not been fully understood by those relating particular molecular properties to the macroscopic thermodynamic network (Fig. 1.2).

1.3 Wetting in Idealized Binary Systems

Viewed from the point of view of thermodynamics, the models for dispersive (hydrocarbon) interactions are usually based on the van der Waals gas law. The van Laar model for hydrocarbon liquids considers the components to be mixed in the ideal gaseous state and the non-ideality is averaged geometrically. These considerations form a base for the modeling of the dispersive interaction parameters.

1.3.1 Models for Dispersive Solid–Liquid Interactions

Traditionally, medium to long chain length ($C_6–C_{16}$) saturated hydrocarbon liquids have been utilized as standards for the fully dispersive (London) interactions with solids. Thus, the standard method of Zisman [7] relies on a range of contact angles measured for such hydrocarbons on a solid. When plotted as $\cosθL$ against the surface tension of the liquids, the extrapolation to $\cosθ_{SL}=1$ for experimental points falling on a straight line gives the critical surface tension (not surface energy), which is considered to correspond to the surface energy of the solid ($σ_{SV} ≈ γ_{crit} ≈ limγ_{LV}$). In Fig. 1.3, $\cosθ_{SL}$ is plotted as a function of the surface tension of seven probe liquids on silica [8].
It is seen that octane represents the critical liquid ($\gamma_{\text{crit}}$) for the hydrophobic silica, but its surface tension is too small for the determination of the surface tension of hydrophilic silica. Hexadecane may be considered to represent the critical liquid for the hydrophilic silica. On the other hand, water seems to have a too high surface tension in order to comply with the trend of the other probe liquids on hydrophobic silica. It thus appears that there exist a frame within the surface tensions and the surface energies are sufficiently close in order to provide physically relevant information. Outside this range the results extracted may be seriously distorted.

Instead of using the total surface tension, Fowkes subtracted a dispersive part and evaluated the excess as the surface pressure of a vapor film [9]. Later, Zettle-moyer, for example, identified this fraction as a polar ($\gamma_{\text{LV}} - \gamma_{\text{LV}}^d$) component [10]. The polar interaction should be understood as a specific (molecularly arresting) interaction without any specific nature (e.g. dipolar) in mind. This procedure enabled experimentalists also to use a broader range of probe liquids. Two straightforward alternatives for averaging the work of adhesion have been proposed based on the dispersive component of the surface tension/energy [9, 10]:

\[
\begin{align*}
W_{\text{SL}} &= 2(\sigma_{SV/\text{LV}}^d)^{1/2} \quad \text{geometric average} \quad (8\ a) \\
W_{\text{SL}} &= \sigma_{SV}^d + \gamma_{\text{LV}}^d \quad \text{arithmetic average} \quad (8\ b)
\end{align*}
\]
Combining these models with the previous definition of the work of adhesion gives the following expressions for the interfacial tension assuming that $\gamma_{LV} \approx \gamma_{LV}^{d}$ and $\sigma_{SV} \approx \sigma_{SV}^{d}$:

$$\sigma_{SL} = \sigma_{SV} + \gamma_{LV} - 2(\sigma_{SV}^{d} \gamma_{LV}^{d})^{1/2} \approx (\sqrt{\sigma_{SV}^{d}} - \sqrt{\gamma_{LV}^{d}})^2$$  \hspace{1cm} (9a)

$$\sigma_{SL} = \sigma_{SV} + \gamma_{LV} - (\sigma_{SV}^{d} + \gamma_{LV}^{d}) \approx 0$$  \hspace{1cm} (9b)

Owing to the square of the term in parentheses, the geometrically averaged interaction is always attractive, but for the critical surface tension ($\sigma_{SL}^{d} \approx \gamma_{LV}^{d} \approx \gamma_{crit}$) the interfacial surface tension vanishes. For the arithmetic mean the interfacial tension is irrespectively zero. This is inherent to the definition.

In the Scatchard-Hildebrand and the Regular Solution models the solution interaction is documented as the solubility parameter ($\phi$). For the relationship with the surface tension ($\gamma \approx k_{S}V^{1/3}\phi$) Hildebrand [11] suggested $k_{S} = 0.0376$ and $\gamma = 2.326$, and Beerbower [12] arrived at $k_{S} = 0.0714$ and $\gamma = 2.000$. The interfacial energy in the last case thus be related to the solubility parameters as

$$\sigma_{SL} \approx (k_{S}\phi_{S} - k_{L}\phi_{L})^{2}$$  \hspace{1cm} (10)

where $k_{L} = \sqrt{k_{S}} = 0.2763$.

Girifalco and Good [13] offered a geometric mean procedure involving the total surface tensions/energies corrected by a ratio ($\Phi$). For London-van der Waals interactions it is represented by the ratio of arithmetic averaging to geometric averaging of the work of adhesion. For non-specific interactions this ratio is close to unity even when the substances are appreciably different, thus claiming equal validity for the geometric and arithmetic averaging procedures. Wu presented a harmonic mean model for the dispersive and polar interactions equaling the ratio when the ionization potentials are replaced by the surface tension/energy components [14]. Neumann and Sell suggested an equation of state model with an exponential dependence on the surface tension/energy components [15]. These methods have found only limited use and are not dealt with here.

Fowkes related the Hamaker constant to the GG ratio. For a solid–liquid contact he arrived at the following relationship [9]:

$$A_{SL} = \sqrt{A_{SV}^{2} - 2\Phi\sqrt{A_{SV}A_{LV}} + A_{LV}^{2}}$$  \hspace{1cm} (11a)

Only when $\Phi$ is not too far from unity (or when the ionization potentials are not too different), the equation reduces to

$$A_{SL} = (\sqrt{A_{SV} - \sqrt{A_{LV}}})^{2}$$  \hspace{1cm} (11b)

in symmetry with geometric averaging of the dispersive interfacial energy (Eq. 9a). The van der Waals gas law constants have also been related to the molecu-
lar Hamaker constant and the surface tension for liquids and surface energies for solids [16–18]:

\[
A_{LL} = k_A \gamma_{LV} d_0^2
\]

(12 a)

\[
A_{SS} = k_A \sigma_{SV} d_0^2
\]

(12 b)

where \(k_A \approx 75.40\) for van der Waals liquids, 100.5 for pure hydrocarbons and 10.47 for semi-polar liquids. The equilibrium distance between the molecules in the condensed medium \((d_0)\) has been reported to be \(0.22 \pm 0.05\) nm [16] and \(0.13 < d_0 < 1.7 \pm 0.01\) nm [17, 18]. It is therefore obvious that the specific (polar) interactions should be considered as an excess from the ideal gaseous state.

Owing to the direct relationship between the surface tension/energy and the work of cohesion \(C\) on the one hand and the Hamaker constant \(A\) on the other for fully or nearly dispersive substances, we can relate the work of cohesion and the Hamaker constant to the contact angle:

\[
C_{SS} = 0.25 C_{LL} (\cos \Theta_{SL} + 1)^2
\]

(13 a)

\[
A_{SS} = 0.25 A_{LL} (\cos \Theta_{SL} + 1)^2
\]

(13 b)

Conversely, the latter equation offers the possibility of estimating \(\cos \Theta_L\) from tabulated data.

Fowkes [9] developed a method for evaluating the work of adhesion from geometric averaging \((G)\) of the dispersive components of the surface tension or surface energy. Combining the Young-Dupré and Fowkes geometric average models for the work of adhesion gives the Young-Dupré-Fowkes (YDF) equation \((\gamma_{LV} = \gamma_{OV} \approx \gamma_{SV}^d)\):

\[
W_{SO}(G) = \gamma_{OV} (\cos \Theta_{SO} + 1) = 2(\sigma_{SV}^d \gamma_{OV}^d)^{1/2}
\]

(14 a)

\[
\sigma_{SV}^d(G) \approx 0.25 (\gamma_{OV}^d) (\cos \Theta_{SO} + 1)^2
\]

(14 b)

Rewritten in terms of \(\cos \Theta_{SO}\), we obtain

\[
\cos \Theta_{SL} = -1 + 2(\sigma_{SV}^d)^{1/2} (\gamma_{LV}^d)^{1/2} / \gamma_{LV} \approx -1 + 2(\sigma_{SV}^d) / (\gamma_{LV}^d)^{1/2}
\]

(14 c)

If \(\cos \Theta_{SL}\) is plotted against \(1/(\gamma_{OV}^d)^{1/2}\) for fully dispersive liquids or \((\gamma_{LV}^d)^{1/2} / \gamma_{LV}\) for polar liquids, a straight line should be obtained with slope \(2(\sigma_{SV}^d)^{1/2}\). For geometric averaging the line should moreover cross the ordinate at \(-1\). The latter requirement is a crucial intrinsic standard to ensure that polar interactions do not seriously distort the slope providing the dispersive component of the solid.

In Fig. 1.4 it is shown that the expectation is fulfilled only for the silanized hydrophobic silica sample [8]. The more polar the surfaces are the smaller is the slope. For hydrophilic titania both octane and hexadecane have too small
surface tensions for the determination of but \( \alpha \)-bromonaphthalene has a matching surface tension. As compared with Fig. 1.3 the requirement of matching surface tensions with surface energies become again evident. For some time the deviation from \(-1\) was used as a measure for the polarity of the solid surface or as an indication of the presence of a vapour film on the surface [9]. Thus water (and EG) seems to be unsuitable for the characterisation of hydrophobic silica.

Combining the Young-Dupré and the arithmetic average (\( A \)) equations for a fully dispersive system, we obtain the Young-Dupré-Zettlemoyer (YDZ) equation (\( \gamma_{LV} = \gamma_{OV} \approx \gamma_{OV}^d \)) [10]:

\[
W_{SO}(A) = \gamma_{OV}(\cos \Theta_{SO} + 1) = (\sigma_{SV}^d + \gamma_{OV}^d) \\
\sigma_{SV}(A) \approx \gamma_{OV} \cos \Theta_{SO}
\]

(15 a)

(15 b)

Obviously, the dispersive surface energy \( [\sigma_{SV}^d(A)] \) equals the work of immersion when \( \Theta_{SO} \to 0 \), since \( \sigma_{SL}^d \approx 0 \). The arithmetic and geometric surface energies and the GG ratio for our model substrates (cf. Fig. 1.4) determined with the probe liquids are collected in Table 1.2 [8].

The influence of non-matching liquids on the determination of surface energies is obvious. With octane and in most cases hexadecane the surface energy is independent of the properties of the solids, equalling the surface tension of the

---

**Fig. 1.4** YDF-plot of \( \cos \Theta_{SL} \) of the probe liquids (see Fig. 1.3) plotted against the reduced surface tension of hydrophobic silica (spheres) and hydrophilic titania (squares). The frames encompass the probe liquids having matching surface tensions with the surface energies of the solids [8, 42].
(completely wetting) liquid. Only ABN and DIM provide a surface energy which reflects the expectations. On the other hand all probe liquids give a comparable (low) surface energy of the hydrophobic silica. Zettlemoyer [10] compared the arithmetic mean with the geometric mean for a more polar metallic mercury surface and found that the former method was much more sensitive to show salient polarities of unsaturated and halogenated hydrocarbons unavailable with the geometric averaging (Table 1.3).

Obviously, if one component is (nearly) zero, the geometric average vanishes whereas the arithmetic remains significant. This insensitivity of the geometric mean to respond to specific interactions has also been widely noted using the Regular Solution model [19].

### Table 1.2 Arithmetic (A) and geometric (G) averaging of the dispersive surface energy $\sigma_{SV}$ and the ratio $\Phi$ for four solid model surfaces with octane, hexadecane, $\alpha$-bromonaphthalene and diiodomethane [8].

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_{SV}$ (A) (mJ m$^{-2}$)</th>
<th>$\sigma_{SV}$ (G) (mJ m$^{-2}$)</th>
<th>$\Phi$ ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Octane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$–hydrophobic</td>
<td>22.2</td>
<td>22.2</td>
<td>1.00</td>
</tr>
<tr>
<td>SiO$_2$–hydrophilic</td>
<td>22.2</td>
<td>22.2</td>
<td>1.00</td>
</tr>
<tr>
<td>TiO$_2$–hydrophobic</td>
<td>22.2</td>
<td>22.2</td>
<td>1.00</td>
</tr>
<tr>
<td>TiO$_2$–hydrophilic</td>
<td>22.2</td>
<td>22.2</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>Hexadecane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$–hydrophobic</td>
<td>23.1</td>
<td>23.3</td>
<td>0.99</td>
</tr>
<tr>
<td>SiO$_2$–hydrophilic</td>
<td>28.1</td>
<td>28.1</td>
<td>1.00</td>
</tr>
<tr>
<td>TiO$_2$–hydrophobic</td>
<td>28.4</td>
<td>28.4</td>
<td>1.00</td>
</tr>
<tr>
<td>TiO$_2$–hydrophilic</td>
<td>28.4</td>
<td>28.4</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>$\alpha$-Bromonaphthalene</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$–hydrophobic</td>
<td>21.6</td>
<td>24.6</td>
<td>0.88</td>
</tr>
<tr>
<td>SiO$_2$–hydrophilic</td>
<td>39.4</td>
<td>39.6</td>
<td>0.99</td>
</tr>
<tr>
<td>TiO$_2$–hydrophobic</td>
<td>37.8</td>
<td>38.0</td>
<td>0.99</td>
</tr>
<tr>
<td>TiO$_2$–hydrophilic</td>
<td>44.3</td>
<td>44.3</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>Diiodomethane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$–hydrophobic</td>
<td>15.6</td>
<td>21.7</td>
<td>0.72</td>
</tr>
<tr>
<td>SiO$_2$–hydrophilic</td>
<td>40.2</td>
<td>40.7</td>
<td>0.99</td>
</tr>
<tr>
<td>TiO$_2$–hydrophobic</td>
<td>39.6</td>
<td>40.2</td>
<td>0.99</td>
</tr>
<tr>
<td>TiO$_2$–hydrophilic</td>
<td>45.2</td>
<td>45.3</td>
<td>1.00</td>
</tr>
</tbody>
</table>
The work of immersion offers a sensitive mean to determine the dispersive component of the surface tension/energy. If we relate the Gibbs free surface energy from the Gibbs-Helmholtz equation with the surface tension/energy, we may write

$$
\Delta G_s^i = \Delta H_s^i + T[\partial(\Delta G_s^i)/\partial T]_p = \Delta H_s^i + T[\partial(\sigma_s)/\partial T]_{p,n}
$$

where $i = V, L$. Since $\Delta G_1 = \Delta G_{SL}/A = -I_{SL} = \sigma_{SL} - \sigma_{SV}$, the equation takes the form

$$
\Delta H_i^i = \Delta G_i^i - T(d\Delta G_i^i/dT)
$$

$$
\Delta H_i^i = \sigma_{SL} - T[\partial(\sigma_{SL})/\partial T]_{p,n} - \sigma_{SV} + T[\partial(\sigma_{SV})/\partial T]_{p,n}
$$

where $\Delta H_i^i = \Delta H_{SL}/A = (H_s^i - H_S^i)/A$. Substituting Young’s equation, we obtain

$$
\Delta H_i^i = -\gamma_{LV} \cos \Theta_{SL} + T[\partial(\gamma_{LV} \cos \Theta_{SL})/\partial T]_{p,n}
$$

$$
\Delta H_i^i = -\gamma_{LV} \cos \Theta_{SL} + T \cos \Theta_{SL}[\partial(\gamma_{LV})/\partial T]_{p,n} + T\gamma_{LV}[\partial(\cos \Theta_{SL})/\partial T]_{p,n}
$$

$$
\Delta H_i^i + I_{SL} = T \cos \Theta_{SL}[\partial(\gamma_{LV})/\partial T]_{p,n} + T\gamma_{LV}[\partial(\cos \Theta_{SL})/\partial T]_{p,n}
$$

It is therefore possible to relate the enthalpy of immersion to the temperature dependence of the surface tension of the test liquid and the change of its contact angle with the solid. In Fig. 1.5, the immersion enthalpy is calculated using Eq. (18 b) and compared with those determined using calorimetry [20].

However, as discussed in the Introduction, the relationships introduced correspond to the two phases in equilibrium with the interface, which is different from the process occurring solely at the interface. For hydrocarbons on hydrophobic surfaces (implied for all equations), the temperature dependence of the surface tension is usually small [21] {\(-\Delta S_{LV}\beta = [\partial(\gamma_{LV})/\partial T]_{p,n} \approx -0.1 \text{ mJ m}^{-2} \text{ K}^{-1}\)}, which simplifies the calculation.

We may use the geometric averaging of the interfacial energy to express the Gibbs free energy of immersion:
The expression is again dramatically simplified if the arithmetic mean is applied for $\gamma_{LV}$:

$$\Delta G^s = \Delta G_{SL}/A = -I_{SL} = \sigma_{SL} - \sigma_{SV} = \gamma_{LV} - 2(\sigma^d_{SV}/\gamma^d_{LV})^{1/2}$$ (19a)

$$\Delta H^s_I = \gamma_{LV} - 2(\sigma^d_{SV}/\gamma^d_{LV})^{1/2} - T\{[\partial(\gamma_{LV})/\partial T]_{P,n} - 2\sqrt{\sigma^d_{SV}}[(\partial\sqrt{\gamma^d_{LV}})/\partial T]_{P,n}\}$$

$$- 2\sqrt{\gamma^d_{LV}}[(\partial\sqrt{\sigma^d_{SV}})/\partial T]_{P,n}$$ (19b)

The expression is again dramatically simplified if the arithmetic mean is applied for $\gamma_{LV}$:

$$\Delta G^s = \Delta G_{SL}/A = -I_{SL} = \sigma_{SL} - \sigma_{SV} = \gamma_{LV} - (\sigma^d_{SV} + \gamma^d_{LV})$$ (20a)

$$(\Delta G^s)^d \approx -\sigma^d_{SV}$$ (20b)

$$\Delta H^s_I = -\sigma^d_{SV} + T[(\partial(\sigma^d_{SV})/T]_{P,n}]$$ (20c)

For a dispersive probe liquid (O) on low-energy surfaces, we find at room temperature that [10]

$$(\Delta H^s_I)^d \approx -\sigma^d_{SV} + 298(-0.07) \approx -\sigma^d_{SV} + 21$$ (21)

Note that Eq. (21) states that the temperature dependence (entropy contribution) is constant when considering the dispersive surface energy of the solid.

Van Oss et al. [17, 18] introduced an extended scale for the non-specific interaction by choosing halogenated hydrocarbons as probe (oil, O) liquids. The most popular of them, diiodomethane (DIM; $\gamma^w_{OV} \approx \gamma_{OV}=51 \text{ mN m}^{-1}$) and $\alpha$-bromonaphthalene (ABN; $\gamma^w_{OV} \approx \gamma_{OV}=44 \text{ mN m}^{-1}$) have a cohesive energy ($C_{OO} = 2\gamma^w_{OV}$ mN m$^{-1}$) which is about double that of dispersive probe hydrocarbon liquids ($18<\gamma^w_{OV}<26 \text{ mN m}^{-1}$) [22]. This reduces the contribution of the specific interaction to only a fraction of its “polar” value and distorts the scaling published previously in the literature. The designation Lifshitz-van der Waals (LW) component emphasizes the fact that the contribution is considered to include the semi-polar (Debye and Keesom) interactions of the slightly acidic halocarbons. As discussed, these are largely erased in geometric averaging, but remain observable using arithmetic averaging [10].
However, as discussed in relation to Figs. 1.3 and 1.4 the high surface tension of ABN and DIM are superior for high energy surfaces, while O and HD are applicable to low energy surfaces. In the past most model studies were made on polymers with a rather low surface energy. In conclusion, we may define two different alternative scales for the surface tension/energy:

\[
\gamma_{LV} = \gamma_{LV}^d + \gamma_{LV}^p \quad \text{and} \quad \sigma_{SV} = \sigma_{SV}^d + \sigma_{SV}^p
\]  
(22a)

\[
\gamma_{LV} = \gamma_{LV}^{1W} + \gamma_{LV}^{A\delta} \quad \text{and} \quad \sigma_{SV} = \sigma_{SV}^{1W} + \sigma_{SV}^{A\delta}
\]  
(22b)

It should be pointed out that maintaining the traditional designation “polar” for non-dispersive interactions does not mean that they are solely dipolar in origin, but non-specific in a more general chemical sense.

1.3.2 Contribution from the Surface Pressure of (Gaseous) Molecules and Spreading of Liquid Films

The ideal solid surface model assumes a smooth homogeneous surface structure, resembling that of a liquid. The model is suitable for the definition of the wetting of (mainly) hydrophobic surfaces. In reality, the surface of semipolar or polar surfaces is always covered by an adsorbed, condensed layer of vapor which reduces the surface energy considerably [9, 10, 23–25]. As shown in Fig. 1.6 the contribution of the surface pressure is quite dramatic on polar surfaces, but small on hydrophobic surfaces. We therefore consider the influence of an adsorbed vapor layer in equilibrium with its own liquid (drop). The surface pressures are defined as

\[
\pi_{L(L)} = \gamma_{LV} - \gamma_{L(L)} \approx \gamma_{L}^p - \gamma_{L(L)} \approx 0
\]  
(23a)

\[
\pi_{S(L)} = \sigma_{SV} - \sigma_{S(L)} \neq \sigma_{S}^p - \sigma_{S(L)}
\]  
(23b)

The contribution of an adsorbed vapor layer to the surface tension of the liquids may be considerable, but has been found to be negligible for our model systems [8]. In the previous equations the vapor (V) denotes the adventitious adsorption of ever-existing vapor from the environment. Hence in practice the work of adhesion represents the displacement of V by L. This vapor dramatically lowers the surface energies. The Dupré equation takes the form {note the designation \(W_{S(L)L} = W_{S(L)|L}\), i.e. preadsorbed (L)}:

\[
W_{S(L)L} = \sigma_{S(L)} + \gamma_{L(L)} - \sigma_{SL} \approx \sigma_{SV} - \pi_{S(L)} + \gamma_{LV} - \sigma_{SL}
\]  
(24a)

\[
W_{S(L)L} = W_{SL} - \pi_{S(L)} \implies \pi_{S(L)} = W_{SL} - W_{S(L)L}
\]  
(24b)
We now consider the Young equation for these two limiting states:

\[
\sigma_{S(L)} - \sigma_{SL} = \gamma_{LV} \cos \theta_{S(L)L} = \sigma_{SV} - \pi_{S(L)} - \sigma_{SL} \tag{25a}
\]

\[
\sigma_{SV} - \sigma_{SL} = \gamma_{LV} \cos \theta_{SL} \tag{25b}
\]

\[
\pi_{S(L)} = \gamma_{LV} [\cos \theta_{SL} - \cos \theta_{S(L)L}] \tag{25c}
\]

since \( \gamma_{LV} \approx \gamma_{L(L)} \). Obviously, the surface pressure of polar liquid vapors on the solid surface can be determined from the change in contact angle on adsorption of the liquid vapor replacing the air. As shown in Fig. 1.6, this contribution can be substantial for polar surfaces [8].

A more consistent value for the surface pressure may be determined from the adsorption isotherm of liquid vapors on evacuated (powder) samples. For the surface pressure of the monomolecular film we may write [10]

\[
\pi_{S(L)}^0 = \sigma_S^0 - \sigma_{S(L)} = RT \int_{\gamma_L=0}^{\gamma_L=\gamma_L^{(mon)}} \Gamma_L \ln(P_L/P_L^*) \tag{26a}
\]

\[
\pi_{S(L)} = (RT/M_LA_w) = \int_{\gamma_L=0}^{\gamma_L=\gamma_L^{(mon)}} w_L \ln(P_L/P_L^*) \tag{26b}
\]
where \( \pi_0^{S(L)} \) and \( \sigma_0^{S} \) (\( 0=\) reference state vapor free surface in vacuum), \( \Gamma_{L} = \) surface excess (\( \approx w_L/M_I A_w \)), \( \Pi_{L}^{*} = \) (partial) pressure (\( \bullet = \) at standard pressure = 1 bar), \( A_w = \) specific surface area of the sample, \( w_L = \) weight ratio of adsorbate to substrate and \( M_L = \) molar mass of adsorbent. Note that for monolayer coverage \( P_{mon} \) corresponds to \( \Gamma_{L,mon} \). It should be noted that this equation is restricted to the monolayer adsorption and it should be revised for multilayer and infinitely thick films equaling the work of spreading. For an infinitely thick (duplex) film, we find [10]

\[
S_{SL}^{0} = \sigma_0^{S} - \gamma_{L(L)} - \sigma_{SL} = RT \int_{\Gamma_{L}=0}^{\infty} \Gamma_{L} d\ln(P_L/P_L^{*})
\]  

(27)

These two states are illustrated in Fig. 1.7.

The liquid close to the tpcl can therefore microscopically be divided into three distinct regions: the bulk liquid, the unstable transition region and the vapor film. The thickness of the liquid collar has been related to the work of spreading [26]:

\[
h = (3\gamma_{LV} d_0^2/2S_{SL})^{1/2} = (3A_{LL}/2k_A S_{SL})^{1/2}
\]  

(28)

where \( d_0 \) again denotes the mean distance between the molecules, \( 0.18<d_0<0.26 \) nm, in the substance. The development of a contact line tension \( \tau (\approx 10^{-11} \text{ J m}^{-2}) \) contributes to the macroscopic \( \sigma_{SL} - \sigma_{SV} \) surface energy balance only for very small droplets, i.e. the line tension is of the order \( \tau/\sigma_{SL} (\approx 10^{-11} \text{ J m}^{-1}/10^{-2} \text{ J m}^{-2} \approx 1 \text{ nm}) \). However, line tensions up to \( 10^{-5} \text{ J m}^{-1} \) have been reported [27], corresponding to experimentally verified liquid collars in the millimeter range [29]. The contribution of the line tension can be introduced as a corrected contact angle over the Young contact angle:

\[
\cos \Theta_{SL}^{*} = \cos \Theta_{SL} - (\tau / \gamma_{LV}) = \cos \Theta_{SL} - (\tau / r_c \gamma_{LV})
\]  

(29)

where \( \gamma_{LV} \) is the surface tension of the liquid and \( \kappa \) is the curvature of the contact line [27] or the local radius of curvature \( r_c \) of the contact line [28]. A linear dependence is thus expected of \( \cos \Theta_{SL}^{*} \) upon the local curvature of the contact line. In kinetic considerations, a hydrodynamic model is usually applied for the unstable phase condensed liquid halo whereas a molecular kinetic model is applied on the gaseous vapor film [30].

The difference between these two integrals is represented by the shaded area (van der Waals loops) [10]. Subtraction gives the work of spreading on a vapor-covered surface:

\[
S_{S(L)l} = S_{SL}^{0} - \pi_{S(L)}^{0} = \sigma_{S(L)} - \gamma_{L(L)} - \sigma_{SL} = RT \int_{\Gamma_{L(mon)}}^{\infty} \Gamma_{L} d\ln(P_L/P_L^{*})
\]  

(30)
The amount adsorbed can also be evaluated from a simple experiment. The sample plate is hooked on to a balance and placed in an almost closed sample cell above, but not in contact with the liquid. Then the change in weight is monitored as a function of time. The surface of the sample plate is known \( A = A_w \cdot w^* \), specific surface area times the weight), as is the molecular surface area of water \( \sqrt{\frac{3}{\pi}} = \frac{3V_L}{\pi r_L N_A} = \frac{A}{N_m^0} \). The number of molecules at the saturated surface is \( N_m^0 = n_m^0 \cdot A = A/N_m^0 \). Multiplying by \( RT \), we may therefore calculate the surface pressure of the liquid vapor, \( \pi_{S(L)} = \sigma_{SV} - \sigma_{S(L)} \), from gravimetric data. Alternatively, the amount adsorbed on a flat surface can be determined utilizing, e.g., ellipsometry [29].

Introducing the work of cohesion, \( C_{L(L)L} = 2\gamma_{L(L)} \approx C_{LL} \), we find for the work of spreading of the bulk liquid:

\[
\begin{align}
S_{S(L)L} &= W_{S(L)L} - C_{L(L)L} = \sigma_S - \gamma_{L(L)} - \sigma_{SL} \tag{31a} \\
S_{S(L)L} &= \sigma_{SV} - \pi_{S(L)} - \gamma_{LV} - \sigma_{SL} \tag{31b} \\
S_{S(L)L} &= S_{SL} - \pi_{S(L)} \tag{31c}
\end{align}
\]

These equations apply since the original reference state \( (\sigma_S^0) \) is subtracted from the equation. Following the formalism introduced, the work of adhesion of the wetting liquid in equilibrium with its own vapor \( W_{S(L)L} \) may thus be subdivided into the work of adhesion \( W_{SL} \) in the absence of an adsorbed film and the surface pressure of the vapor film on the solid \( \pi_{S(L)} \):

\[
\begin{align}
W_{S(L)L} &= \gamma_{L(L)} \left[ \cos \theta_{S(L)L} + 1 \right] = \gamma_{LV} (\cos \theta_{SL} + 1) - \pi_{S(L)} \tag{32a} \\
S_{S(L)L} &= \gamma_{L(L)} \left[ \cos \theta_{S(L)L} - 1 \right] = \gamma_{AV} (\cos \theta_{SL} - 1) - \pi_{S(L)} \tag{32b}
\end{align}
\]
At the critical point of complete wetting \((\cos \Theta_{SL}=1)\), the work of adhesion equals the difference between the work of cohesion of the liquid and the surface pressure of the film \(W_{S(L)L}=C_{LL}-\pi_{S(L)}\). Then, the negative surface pressure equals the work of spreading: \(S_{SL}=\pi_{S(L)}\).

Table 1.4 collects the work of immersion, adhesion and spreading when the reference state was a vapor-free surface in vacuum. The contribution from the surface pressure of adsorbed vapor films is, depending on the system, considerable (unequal probe liquids) or predominant (most polar surfaces). It is therefore not surprising that wetting vapors and liquids are used to lower the surface energy when machining, drilling or grinding polar solids. Note that \(W_{SL}^0 \approx \gamma_{SL}^0 + \gamma_{LV}^0\) and \(S_{SL}^0 \approx \gamma_{SL}^0 - \gamma_{LV}^0\) (cf. Eq. 6 b–d).

Since the work of spreading from the monomolecular film to a condensed surface is zero \(S_{SL}^0=0\), Eq. (30); \(\Theta_{SL}=0\), obviously the surface pressure equals \(S_{SL}^0 = -\pi_{S(L)}\).

The surface pressure of the probe liquids used as examples in Fig. 1.6 were determined from the contact angle difference in air and under saturated vapor. The results of these calculations are collected in Table 1.5.

For TiO\(_2\) (anatase) the following saturation surface pressures/work of adhesion have been found [25]: 46/86 \((n\)-heptane\), 108/154 \((n\)-propyl alcohol\) and 196/340 \(H_2O\). Although the surface pressure of the monomolecular film (Eq. 26) is only a fraction of this saturation value (Eq. 27), the values reported in Table 1.4 are almost negligible. ABN and DIM produce, however, a significant surface pressure on hydrophilic TiO\(_2\). As shown, the vapor surface pressure of the polar liquids is considerably greater on all sample surfaces. The surface pressure on hydrophilic TiO\(_2\) is greatest, whereas the other varies in an irrational way from positive to negative values. The latter are again due to \(\Theta_{S(L)L}<\Theta_{SL}\). The influence of adventitious vapors competing for the adsorption sites is obvious, i.e. \(\pi_{S(L)L} \ll \pi_{S(L)}^0\).

Combining the Young and Dupré equations with Fowkes’ geometric averaging gives the Young-Dupré-Fowkes (YDF) equation including the contribution from the surface pressure:

\[
W_{S(L)L} = \gamma_{L(L)}[\cos \Theta_{S(L)L} + 1] = 2(\sigma_{SV}^{dL})^{1/2} - \pi_{S(L)}
\]

\[
\cos \Theta_{S(L)L} = -1 + [2(\sigma_{SV}^{dL})^{1/2} - (\pi_{S(L)})]/\gamma_{L(L)}
\]

Hence the deviation of the slope of the line through the experimental points plotted as a function of \(1/\gamma_{L(L)}\) (Fig. 1.8) may be interpreted in part as a contribution from the surface film pressure. As an intrinsic consistency test the line should pass through \(-1\) at \(1/\gamma_{L(L)}=0\).

In the absence of a surface pressure the equation equals the YDF equation (14 c).

Note that the contact angle measured in air and in saturated probe liquid vapor differ considerably in particular for hydrophilic surfaces. This observation
Table 1.4 Work of immersion, adhesion and spreading (mJ/m$^2$) for silica and titania-liquid vapor pairs determined from vacuum [24].

<table>
<thead>
<tr>
<th>Solid</th>
<th>Vapor</th>
<th>$\gamma_{SL}^0$</th>
<th>$W_{SL}^0$</th>
<th>$S_{SL}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>Water</td>
<td>316</td>
<td>388</td>
<td>244</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>n-Propanol</td>
<td>134</td>
<td>158</td>
<td>110</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Benzene</td>
<td>81</td>
<td>110</td>
<td>52</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>n-Heptane</td>
<td>59</td>
<td>79</td>
<td>38</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Water</td>
<td>300</td>
<td>370</td>
<td>228</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>n-Propanol</td>
<td>114</td>
<td>138</td>
<td>90</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Benzene</td>
<td>85</td>
<td>114</td>
<td>56</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>n-Heptane</td>
<td>58</td>
<td>78</td>
<td>38</td>
</tr>
</tbody>
</table>

Table 1.5 Surface pressure of octane, hexadecane, $\alpha$-bromonaphthalene, diiodomethane, ethylene glycol and formamide and water on different solid substrates calculated from the measured contact angle in air and in saturated vapor (Eq. 25 c) [8, 42].

<table>
<thead>
<tr>
<th></th>
<th>Octane</th>
<th>Ethylene glycol</th>
<th>Formamide</th>
<th>Water</th>
<th>Diodomethane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\pi_{S(L)}$</td>
<td>$\pi_{S(L)}$</td>
<td>$\pi_{S(L)}$</td>
<td>$\pi_{S(L)}$</td>
<td>$\pi_{S(L)}$</td>
</tr>
<tr>
<td>SiO$_2$–hydrophobic</td>
<td>0.0</td>
<td>SiO$_2$–hydrophobic</td>
<td>3.3</td>
<td>SiO$_2$–hydrophobic</td>
<td>–3.2</td>
</tr>
<tr>
<td>SiO$_2$–hydrophilic</td>
<td>0.0</td>
<td>SiO$_2$–hydrophilic</td>
<td>5.7</td>
<td>SiO$_2$–hydrophilic</td>
<td>0.0</td>
</tr>
<tr>
<td>TiO$_2$–hydrophobic</td>
<td>0.0</td>
<td>TiO$_2$–hydrophobic</td>
<td>–4.6</td>
<td>TiO$_2$–hydrophobic</td>
<td>0.3</td>
</tr>
<tr>
<td>TiO$_2$–hydrophilic</td>
<td>0.0</td>
<td>TiO$_2$–hydrophilic</td>
<td>7.1</td>
<td>TiO$_2$–hydrophilic</td>
<td>3.3</td>
</tr>
<tr>
<td>SiO$_2$–hydrophobic</td>
<td>0.2</td>
<td>SiO$_2$–hydrophobic</td>
<td>–6.8</td>
<td>SiO$_2$–hydrophobic</td>
<td>0.0</td>
</tr>
<tr>
<td>SiO$_2$–hydrophilic</td>
<td>1.7</td>
<td>SiO$_2$–hydrophilic</td>
<td>7.0</td>
<td>SiO$_2$–hydrophilic</td>
<td>3.3</td>
</tr>
<tr>
<td>TiO$_2$–hydrophobic</td>
<td>0.0</td>
<td>TiO$_2$–hydrophobic</td>
<td>3.1</td>
<td>TiO$_2$–hydrophilic</td>
<td>6.3</td>
</tr>
<tr>
<td>TiO$_2$–hydrophilic</td>
<td>0.0</td>
<td>TiO$_2$–hydrophilic</td>
<td>12.7</td>
<td>TiO$_2$–hydrophilic</td>
<td>19.1</td>
</tr>
<tr>
<td>$\alpha$-Bromonaphthalene</td>
<td>–0.7</td>
<td>SiO$_2$–hydrophobic</td>
<td>8.9</td>
<td>SiO$_2$–hydrophilic</td>
<td>6.3</td>
</tr>
<tr>
<td>SiO$_2$–hydrophobic</td>
<td>–1.1</td>
<td>SiO$_2$–hydrophilic</td>
<td>6.3</td>
<td>SiO$_2$–hydrophilic</td>
<td>0.0</td>
</tr>
<tr>
<td>TiO$_2$–hydrophobic</td>
<td>1.5</td>
<td>TiO$_2$–hydrophobic</td>
<td>19.1</td>
<td>TiO$_2$–hydrophilic</td>
<td>0.3</td>
</tr>
<tr>
<td>TiO$_2$–hydrophilic</td>
<td>6.4</td>
<td>TiO$_2$–hydrophilic</td>
<td>31.7</td>
<td>TiO$_2$–hydrophilic</td>
<td>6.3</td>
</tr>
</tbody>
</table>

1.3 Wetting in Idealized Binary Systems
was discussed previously (Fig. 1.6). However, the plot for hydrophobic silica breaks into two parts at ABN, the low energy liquids extrapolating to octane at \(\cos \Theta_{\text{SL}} = 1\) and the high-energy liquids, including water to the expected intercept \(-1\) at \(1/\gamma_{\text{LV}} = 0\). The surface pressure obviously does not explain the deviation of hydrophilic silica from this point, but should rather be devoted to specific interactions.

Recalling the Young-Dupré-Zettlemoyer (YDZ) equation, we may express the work of adhesion in terms of the arithmetic averaging:

\[
W_{\text{S(L)}L} = \gamma_{\text{L(L)}} [\cos \Theta_{\text{S(L)}L} + 1] = (\sigma_{\text{SV}}^d + \gamma_{\text{LV}}^d) - \pi_{\text{S(L)}}
\]  

(34a)

\[
\cos \Theta_{\text{S(L)}L} = -1 + [\sigma_{\text{SV}}^d + \gamma_{\text{LV}}^d - \pi_{\text{S(L)}}] / \gamma_{\text{LV}}
\]  

(34b)

As an intrinsic consistency test the line should pass through \(-1\) at \(1/\gamma_{\text{LV}} = 0\), which is obeyed by ABN, DIM, EG, FA and W. For hydrocarbons \(\gamma_{\text{LV}} \approx \gamma_{\text{LV}}^d\) we have

\[
\cos \Theta_{\text{S(L)}L} \approx (\sigma_{\text{SV}}^d - \pi_{\text{S(L)}}) / \gamma_{\text{LV}}
\]  

(34c)

for which the line should pass through zero at \(1/\gamma_{\text{LV}} = 0\). This expectation is fulfilled for the O-HD-ABN branch of hydrophobic silica in Fig. 1.8. ABN is thus represented in both liquid series. Obviously Eq. (34c) may be used to evaluate...
the applicability of the arithmetic averaging for a range of probe liquids. When \( \gamma_{\text{LV}} \neq \gamma_{\text{LV}}^d \) the YDZ Eq. (15 b) does not apply. We cannot deduce from Fig. 1.8 the preference between Eqs. (33 b) and (34 c). Table 1.6 reports on the difference between arithmetic and geometric averaging of \( \sigma_S^d \) using heptane (\( \gamma_{\text{H}} \approx \gamma_{\text{H}}^d \)) as probe liquid.

For polar solids, the arithmetic and geometric averaging provide divergent values for the dispersive component of the solids. One reason is obviously the fairly large surface pressure. However, the ratio between the geometric and arithmetic components, equaling the Girifalco–Good ratio (\( \Phi \)), remains fairly constant in the range 0.6–0.8, being substantially above unity assumed for dispersive interaction.

### 1.3.3 Models for Specific Polar (Lewis) Interactions

Starting from the truly dispersive (London) interactions of hydrocarbons, there is a broad range of molecular interactions of Lewis nature. However, as discussed, the Debye and Keesom interactions diverge from the traditional van der Waals range to the Coulomb range when molecularly arrested or “frozen” upon adsorption on the surface sites [31].

In the classical treatment of surface interactions, the total contribution is subdivided into a dispersive part and a polar part. The latter should be understood as specific (molecularly arresting) interactions without any particular (e.g. dipolar) interaction in mind [10]:

\[
\gamma_{\text{LV}} = \gamma_{\text{LV}}^d + \gamma_{\text{LV}}^p
\]

\[
\sigma_{SV} = \sigma_{SV}^d + \sigma_{SV}^p
\]
Introducing arithmetic and geometric averaging of the dispersive component for the solid, we may now calculate the specific (polar) interaction as $\gamma_{LV} \neq \gamma_{OV}$ 

\[\sigma_{SV}^p(A,O) = \sigma_{SV} - \gamma_{OV} \cos \Theta_{SO}\]  

(36a)

\[\sigma_{SV}^p(G,O) = \sigma_{SV} - 0.25(\gamma_{OV})(\cos \Theta_{SO} + 1)^2\]  

(36b)

However, since the surface energy of the solid ($\sigma_{SV}$) is unknown, we cannot utilize these simple equations. Instead, we may calculate the specific (polar) work of adhesion by using the dispersive surface energy of the solid determined with the reference oils to calculate the polar work of adhesion ($W_{SL}^p$) in the following way:

\[W_{SL}(I) = \gamma_{LV}(\cos \Theta_{SL} + 1) = W_{SL}^d + W_{SL}^p\]  

(37a)

\[W_{SL}^p(A) = W_{SL} - [\sigma_{SV}^d(A,O) + \gamma_{LV}]\]  

(37b)

\[W_{SL}^p(G) = W_{SL} - 2[\sigma_{SV}^d(G,O)\gamma_{LV}^{1/2}]\]  

(37c)

Note that the separate determination of $\sigma_{SV}^d(O)$ using a fully dispersive liquid (oil, O) is specifically indicated.

Assuming that also the polar contributions are additive, the arithmetic averaging available to resolve the polar component of the surface energy of the solid may be represented as

\[\sigma_{SV}(A)^p = W_{SL}^p(A) - \gamma_{LV}\]  

(38a)

\[\sigma_{SV}(A)^p = \gamma_{LV} \cos \Theta_{SL} - \sigma_{SV}^d(A,O) = \gamma_{LV} \cos \Theta_{SL} - \gamma_{OV} \cos \Theta_{SO}\]  

(38b)

Although it has been considered unacceptable to apply geometric averaging to any interaction of a specific nature, we also consider this option (Eq. 37c):

\[\sigma_{SV}(G, I)^p = [W_{SL}^p(G)]^2/4\gamma_{LV}^p\]  

(39)

If the dispersive surface tension of the probe liquid (L) and oil are almost equal ($\gamma_{LV}^d \approx \gamma_{OV}^d \approx \gamma_{OV}$), we may also assume that the reference oil fully represents the dispersive interaction and write considering Eq. (38b):

\[W_{SL}^p(II) = W_{SL} - W_{SL}^d = \gamma_{LV}(\cos \Theta_{SL} + 1) - \gamma_{OV}(\cos \Theta_{SO} + 1)\]  

(40a)

\[\sigma_{SV}^p(G, II) = [\sigma_{SV}^p(A) + \gamma_{LV}^p]^2/4\gamma_{LV}^p\]  

(40b)

The specific (polar & AB) surface energy components (Eq. 38b) of hydrophobic silica is plotted as a function of the surface tension of the probe oils ($\gamma_{OV}$) in Fig. 1.9 (for details, see Ref. [42]).
As shown, the specific component is quite consistent for all probe oils ranging from 0 to 5 mJ/m$^2$. A slightly larger scatter is found for DIM.

Most new methods rely on a geometric (product) averaging of the directional specific interactions. When applying arithmetic averaging, maintaining the previous symmetry, all terms cancel out, making it unavailable for this purpose. One may collectively express the Lewis interaction models representing monodentate acid–base bimolecular pairing with each (monodentate) site possessing both an electrostatic and a covalent binding character:

$$Y = D_1D_2 = X^A_1X^B_2 + Z^A_1Z^B_2$$  \hspace{1cm} (41)

where $Y$ is a generalized property or a state variable (typically G, F or H), $D$ is the dispersive interaction, the A and B interaction between the molecular pairs 1 and 2. Such models are, for example, those of Drago and Gutmann (see Table 1.7).

As shown, none of these models considers in particular the non-specific interactions which in later developments of the models are subtracted from the generalized property $Y$. Consequently, most of the scales refer to poorly solvating solutions (or gas mixtures) of acidic and basic molecules. The latter are based on enthalpy alone, which was shown to be a tentative property and does not
include the entropic contribution to the Gibbs free energy. As discussed in a previous section, none of the properties are related to the second derivatives sensitive to salient interactions such as the Lewis interactions.

In a recent paper, Peterson made a conceptual analysis of these types of models and made a matrix transformation producing the following constants [39]:

\[ X^+ = \frac{1}{\sqrt{2}}(X_1^A + X_2^B) \quad \text{and} \quad X^- = \frac{1}{\sqrt{2}}(X_1^A - X_2^B) \quad (42 \text{a, b}) \]

\[ Z^+ = \frac{1}{\sqrt{2}}(Z_1^A + Z_2^B) \quad \text{and} \quad Z^- = \frac{1}{\sqrt{2}}(Z_1^A - Z_2^B) \quad (42 \text{c, d}) \]

He concluded that the positive diagonal \( X^+ \) and \( Z^+ \) matrix terms represent the concept of “like strengths attract their like”. The negative \( X^- \) and \( Z^- \) terms represent the situation when “opposite sites attract each other”; the larger the difference, the greater is the attraction. He suggested that all types of interactions could contribute to the wetting phenomena. The analysis is interesting since it makes it possible to evaluate the terms separately. However, depending on the instrumental method utilized, the empirical constants obtained from fitting to experimental data refer to enthalpic or free energy surface components.

1.3.4 Partial Acid and Base Components

The method of van Oss et al. (vOCG) [17, 18] is related to the geometric derivation procedure of the Lifshitz-van der Waals (LW) contribution [\( \sigma_{SV}(G) = \sigma_{SV}^{LW}(G) \)]. As for the division into dispersive and polar components, the LW forces are particularly considered and subtracted from the total surface tension/energy to give the specific acid–base (AB) component [\( \sigma_{SV}(G) = \sigma_{SV}^{AB}(G) \)]. However, in the vOCG model, each probe molecule and surface are assigned both acidic and basic sites (bidentacy), which interact with their counterparts independently. Also, the intrinsic interaction between these sites is allowed for. Hence for bidentate (one acidic and one basic site) probe liquids we find

<table>
<thead>
<tr>
<th>Property (Y)</th>
<th>D term</th>
<th>X term</th>
<th>Z term</th>
<th>Additional term</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log K^{AB} )</td>
<td>N/A</td>
<td>S(strength)</td>
<td>( \sigma ) (soft)</td>
<td>N/A</td>
</tr>
<tr>
<td>( \log K^{AB} )</td>
<td>N/A</td>
<td>S(strength)</td>
<td>( \sigma ) (soft)</td>
<td>s(teric)</td>
</tr>
<tr>
<td>( \Delta H^{AB} )</td>
<td>N/A</td>
<td>E(lectrostatic)</td>
<td>C(ovalent)</td>
<td>d(esolvolation)</td>
</tr>
<tr>
<td>( -\Delta H^{AB} )</td>
<td>N/A</td>
<td>e(lectrostatic)</td>
<td>c(ovalent)</td>
<td>D(ispersive)</td>
</tr>
<tr>
<td>( -\Delta G^{AB} )</td>
<td>N/A</td>
<td>A(cidic)</td>
<td>B(asic)</td>
<td>N/A</td>
</tr>
</tbody>
</table>

a) The models refer to the models of Gutmann et al. [33, 34], Maria and Gal [35], Handcock and Marciano [36], Drago and Wayland [32], Kroeger and Drago [37] and Della Volpe and Siboni [38].
where vOCG denote $\gamma_{LV}^A$/$\sigma_{SV}^A$ the acid (electron acceptor) component and $\gamma_{LV}^B$/$\sigma_{SV}^B$ the base (electron donor) component of the surface tension/energy. For comparability with the literature values, the values in Table 1.8 were assumed to be representative. The AB work of cohesion is as usually twice this value, $C_{LL}^{AB} = 2\gamma_{LV}^{AB}$ and $C_{SS}^{AB} = 2\sigma_{SV}^{AB}$. For monodentate (one acid or one base site), the AB term vanishes for the respective component.

Similarly, the work of adhesion is taken as the sum of the LW and AB contributions, the latter being defined as $17, 18$

$$W_{SL}^{AB} = W_{SL} - W_{SL}^{LW} = 2[(\sigma_{SV}^{AB}/\gamma_{LV}^{AB})^{1/2} + (\sigma_{SV}^{LW}/\gamma_{LV}^{LW})^{1/2}]$$  \hfill (44 a)

$$W_{SL}^{LW} = \sigma_{SV}^{LW} + \gamma_{LV}^{LW} - \sigma_{SL}^{LW}$$  \hfill (44 b)

Again, if one of the AB pairs is monodentate, the term involving this surface tension/energy vanishes. Combining the AB work of adhesion we obtain the AB component of the interfacial energy:

$$\sigma_{SL}^{AB} = \sigma_{SV}^{AB} + \gamma_{LV}^{AB} - 2[(\sigma_{SV}^{AB}/\gamma_{LV}^{AB})^{1/2} + (\sigma_{SV}^{LW}/\gamma_{LV}^{LW})^{1/2}]$$  \hfill (45 a)

$$\sigma_{SL}^{AB} = 2[(\sigma_{SV}^{AB}/\gamma_{LV}^{AB})^{1/2} + (\gamma_{LV}^{LW}/\gamma_{LV}^{LW})^{1/2}] - 2[(\sigma_{SV}^{AB}/\gamma_{LV}^{AB})^{1/2} + (\sigma_{SV}^{LW}/\gamma_{LV}^{LW})^{1/2}]$$  \hfill (45 b)

$$\sigma_{SL}^{AB} = 2[(\sqrt{\sigma_{SV}^{AB}} - \sqrt{\gamma_{LV}^{AB}})(\sqrt{\sigma_{SV}^{AB}} - \sqrt{\gamma_{LV}^{AB}})]$$  \hfill (45 c)

The last equation indicates that the AB interaction is repulsive if $\gamma_{LV}^{AB} > \sigma_{SV}^{AB}$ and $\gamma_{LV}^{AB} < \sigma_{SV}^{AB}$ or if the reverse is true. In practice, the bimolecular bidentate interaction has the symmetry of a three-phase (non-specific) liquid contact (see below).

If the LW component of the solid has been determined with the LW probe oils (O) according to one of the methods indicated above, we may write according to the vOCG model for the work of adhesion for two bidentate AB probe liquids K and L $17, 18$

$$W_{SK}^{AB} = W_{SK} - 2[\gamma_{LV}^{LW} G(O)_{SL}^{LW}]^{1/2} = C\sqrt{\sigma_{SV}^{AB}(K)} + D\sqrt{\sigma_{SV}^{AB}(K)}$$  \hfill (46 a)

<table>
<thead>
<tr>
<th>Probe liquid</th>
<th>$\gamma_{LV}$</th>
<th>$\gamma_{LV}^{LW}$</th>
<th>$\gamma_{LV}^{AB}$</th>
<th>$\gamma_{SV}^{AB}$</th>
<th>$\gamma_{SV}^{LW}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
<td>21.8</td>
<td>51.0</td>
<td>25.5</td>
<td>25.5</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>48.0</td>
<td>29.0</td>
<td>19.0</td>
<td>1.92</td>
<td>47.0</td>
</tr>
<tr>
<td>Formamide</td>
<td>58.0</td>
<td>39.0</td>
<td>19.0</td>
<td>2.28</td>
<td>39.6</td>
</tr>
</tbody>
</table>
\[ W_{SL}^{AB} = W_{SL} - 2[\sigma_{SV}^{LV} (G, O)^{LV}]^{1/2} = E\sqrt{\sigma_{SV}^{G}}(L) + F\sqrt{\sigma_{SV}^{L}}(L) \]  

where \( W_{SK} = \gamma_{KV}(\cos \Theta_{SK} + 1) \), \( W_{SL} = \gamma_{LV}(\cos \Theta_{SL} + 1) \), \( C = 2\sqrt{\gamma_{KV}} \), \( D = 2\sqrt{\gamma_{KV}} \), \( E = 2\sqrt{\gamma_{LV}} \) and \( F = 2\sqrt{\gamma_{LV}} \). Since \( \sigma_{SV}^{G}(K) = \sigma_{SV}^{G}(L) \) and \( \sigma_{SV}^{L}(K) = \sigma_{SV}^{L}(L) \), the acid and base components of the solid may then be obtained according to [17, 18]

\[ \sqrt{\sigma_{SV}^{G}} = (W_{SK}^{AB}F - W_{SL}^{AB}D)/(CF - DE) \]  

\[ \sqrt{\sigma_{SV}^{L}} = (W_{SL}^{AB}C - W_{SK}^{AB}E)/(CF - DE) \]  

The \( \sigma_{SV}^{G} \) values calculated from Eqs. (45) and (47) are included in Fig. 1.9. The \( \sigma_{SV}^{G} \) and \( \sigma_{SV}^{L} \) components are presented in Fig. 1.10.

The problem with this method is that it may produce negative values for \( \sqrt{\sigma_{SV}^{G}} \) and \( \sqrt{\sigma_{SV}^{L}} \), which are squared artificially to positive numbers. In order to control this problem, the intrinsic self-consistency check of recalculating \( W_{SK}^{AB} \) and \( W_{SL}^{AB} \) from the evaluated \( \sigma_{SV}^{G} \) and \( \sigma_{SV}^{L} \) using Eqs. (12 a) and (12 b), respectively, must be applied! If either of the acid–base adhesions does not agree with those calculated from the equations

\[ W_{SK}^{AB} = (\cos \Theta_{SK} + 1) - 2[\sigma_{SV}(G, O)^{LV}]^{1/2} \]  

\[ W_{SL}^{AB} = (\cos \Theta_{SL} + 1) - 2[\sigma_{SV}(G, O)^{LV}]^{1/2} \]

they must be disregarded as intrinsically inconsistent.

Apart from the problems related to the use of halogenated hydrocarbons as LW references, the polar liquids utilized are of a predominantly basic character. It therefore seems rational to consider one or all of the liquid(s) as almost pure monodentate base(s). This is in accord with vOCG [17, 18], who state: “If either the acidic or basic property is negligible and the other property is appreciable, the substance is termed monopolar”. The “degree of monodentacy” of the probe liquids is given in Table 1.9.

As shown, water has the largest AB component, but a zero base dominance. Glycerol has the second largest AB contribution, the largest absolute base com-

### Table 1.9 Degree of basicity of the non-aqueous probe liquids suggested by vOCG [42].

<table>
<thead>
<tr>
<th>Probe liquid</th>
<th>( \gamma_{LV} )</th>
<th>( \gamma_{LV}^{AB} )</th>
<th>( \gamma_{AB}^{LV} )</th>
<th>( \gamma_{SV}^{G} )</th>
<th>( \gamma_{LV}^{L} )</th>
<th>( \gamma_{LV}^{G} ) (%) \text{ a)}</th>
<th>( \Delta\gamma_{LV}^{G} ) / ( \gamma_{LV}^{G} ) (%) \text{ a)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
<td>21.8</td>
<td>51</td>
<td>25.5</td>
<td>25.5</td>
<td>70.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Glycerol</td>
<td>64</td>
<td>34</td>
<td>30</td>
<td>3.92</td>
<td>57.4</td>
<td>46.9</td>
<td>93.2</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>48</td>
<td>29</td>
<td>19</td>
<td>1.92</td>
<td>47.0</td>
<td>39.6</td>
<td>95.9</td>
</tr>
<tr>
<td>Formamide</td>
<td>58</td>
<td>39</td>
<td>19</td>
<td>2.28</td>
<td>39.6</td>
<td>32.8</td>
<td>94.2</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>44</td>
<td>36</td>
<td>8</td>
<td>0.50</td>
<td>32</td>
<td>18.2</td>
<td>98.4</td>
</tr>
</tbody>
</table>

\( \gamma_{LV}^{AB} \) (%) = \( (\gamma_{LV}^{AB}) / \gamma_{LV} \) \times 100 and \( \Delta\gamma_{LV}^{G} / \gamma_{LV}^{G} \) (%) = \( (\gamma_{LV}^{G} - \gamma_{LV}^{G}) / \gamma_{LV}^{G} \) \times 100.
Fig. 1.10 The acid (left) and base (right) surface energy components of hydrophobic silica calculated with the models defined in Fig. 1.9 plotted as a function of the surface tension of the probe liquids (for details see text and [42]).
ponent, but the second smallest base dominance. Ethylene glycol seems to have the overall most favorable properties. With reference to the Girifalco–Good quotient it is expected that the arithmetic/total work of adhesion should not be too different from the geometric work of adhesion \( \Phi \approx 1 \). The partial contributions should then add up to the total values. However, the base components exceed the AB-component and even equal the total surface tension (EG). Although mathematically consistent, the geometric averaging seems to produce rather unphysical values. Instead of becoming involved in the complicated vO CG averaging discussed above, a monodentacy is considered instead. Thus, since \( \gamma_{KV}^{A} \approx 0 \) we may write the AB work of adhesion as [42]

\[
W_{AB}^{SK} = W_{SK} - W_{LW}^{SK} \approx W_{SK}^{A(B)} = 2[\sigma_{SV}^{A}(K)\gamma_{KV}^{S}]^{1/2}
\]

\[
\sigma_{SV}^{A}(K) = \left[\frac{W_{SK}^{A(B)}}{4}\right]^{1/2}
\]

The superscript A is used in order to distinguish the \( \sigma_{SV}^{A} \) component from the \( \sigma_{SV}^{B} \) component. The problem is, however, that no probe liquid has been reported with as pure acidity as the nearly pure basic solutions suggested for the vO CG model. Therefore, we choose another way of calculating the \( \sigma_{SV}^{B}(L) \) component. The acid–base contribution to the adhesion can be calculated by accepting that the LW probe (O) oil can fully represent the non-specific interaction (cf. Eq. 40 a). A matching of the LW component of the AB liquid (L) is then advisable \( \gamma_{LV}^{A} \approx \gamma_{LV} \approx \gamma_{OV} \). In Eq. (38 b) it was assumed that \( \gamma_{LV}^{A} \approx \gamma_{LV} - \gamma_{LV}^{LW} \). In this case we may write [42]

\[
W_{SL}^{AB(I)} = W_{SL} - W_{SO}^{LW} = \gamma_{LV}^{A} \cos \Theta_{SL} + 1 - \gamma_{OV}^{A} \cos \Theta_{SO} + 1
\]

\[
W_{SL}^{AB(II)} = \gamma_{LV}^{A} \cos \Theta_{SL} - \gamma_{OV}^{A} \cos \Theta_{SO} + \gamma_{LV}^{A}
\]

\[
W_{SL}^{AB} = 2[\sigma_{SV}^{A}(K)\gamma_{LV}^{S}]^{1/2} + (\sigma_{SV}^{B}(L)\gamma_{LV}^{S})^{1/2}
\]

Rewritten in terms of the basic solid component, we find [42]

\[
\sigma_{SV}^{B}(L) = \left\{ W_{SL}^{AB} - 2[\sigma_{SV}^{A}(K)\gamma_{LV}^{S}]^{1/2} \right\} / 4\gamma_{LV}^{S}
\]

Depending on the way in which the work of adhesion is calculated (Eq. 50 a and b) for introduction into Eq. (50 d) the indexing is \( \sigma_{SV}^{A}(I) \) or \( \sigma_{SV}^{B}(II) \). These A and B components are compared with the corresponding parameters in Fig. 1.10. As shown the values produced are rather consistent for each probe liquid, but with an enhanced spread for DIM, being dependent on the model used. Yet another way is to derive a computational \( \cos \Theta_{SL}^{AB} \):

\[
W_{SL}^{AB} = \gamma_{LV}^{A} \cos \Theta_{SL}^{AB} + 1
\]

\[
W_{SL}^{AB} = \gamma_{LV}^{A} \cos \Theta_{SL} + 1 - \gamma_{OV}^{A} \cos \Theta_{SO} + 1
\]
However, \( \sigma_{SV}(\text{III}) \) (Eq. 51d) equals \( \sigma_{SV}(\text{II}) \) (Eq. 50d). It should be noted that if a faction of the surface were assigned both to the dispersive and the polar (AB) surface, Eq. (51c) would equal the well known Cassie equation for chemical heterogeneous surfaces discussed below!

In the calculations the AB contribution of water has artificially been divided into two equal contributions (25.5 mN m\(^{-1}\), Table 1.4). The reference to water is rational since all acid–base scales have been related to some particular property of water. However, in order to better reflect the true balance between the acid–base character for water, a strongly weighted acid contribution has been suggested on experimental and theoretical grounds by a number of authors \cite{40, 41}. The most extreme balance suggested by Della Volpe and Siboni \cite{38} is given in Table 1.10.

As the most extreme case, we may again use the strongly weighted acid contribution suggested for water by Della Volpe and Siboni \cite{38} and compare its predominant acidity with the predominant basicity of the other \( \nu \text{OCG} \) probe liquids (Table 1.11).

Although the A/B balance is slightly changed also for ethylene glycol and formamide, their nearly pure basicity remains. The strongly dominant acidity of
water suggests that water may be taken as an acidic probe. The base component
is then obtained simply as (cf. Eq. 49 b) [42]

\[ W_{SL}^{AB} \approx W_{SL}^{B(A)} = 2[\sigma_{SV}^{B}(W)]^{1/2} \] (52 a)

\[ \sigma_{SV}^{B}(W) = [W_{SW}^{B(A)}]^{2}/4\gamma_{WV}^{a} \] (52 b)

The use of water is specifically denoted. We may then proceed to calculate the
total and AB component of the surface energy [42]:

\[ \sigma_{SV} = \sigma_{SV}^{LW} + \sigma_{SV}^{AB} = \sigma_{SV}^{LW} + 2[\sigma_{SV}^{A}(K)\sigma_{SV}^{B}(W)]^{1/2} \] (53)

The \( \sigma_{SV}^{L} \) and \( \sigma_{SV}^{B} \) components are compared with the corresponding parameters in Fig. 1.10, and the \( \sigma_{SV}^{AB} \) component is reproduced in Fig. 1.9 (for details, see [42]). The surface energy components calculated with each model introduced for the model surfaces introduced in Fig. 1.3 are plotted as a function of the surface tension of the probe liquids in Fig. 1.11. It is particularly rewarding to note that the mono-bi and mono-mono dentate models closely agree with the bi-bi dentate vOCG model, when corrected for the DVS acid-base balance.

The geometric averaging principle can be maintained for total surface energies and surface tensions by applying the GG ratio \( \Phi \). The work of adhesion is then

\[ W_{SL} = 2[(\Phi_{SV}\sigma_{SV})(\Phi_{LV}\gamma_{LV})]^{1/2} = 2\Phi_{SL}(\sigma_{SV}\gamma_{LV})^{1/2} \] (54)

i.e. \( \Phi_{SL} = (\Phi_{SV}\Phi_{LV})^{1/2} \). However, since the numerical value of the GG ratio is mostly unknown, it does not provide any advantages over the vOCG model. We can instead use the arithmetic equivalent for the separation of the acid (a) and base (b) components from the total specific (polar) part of the surface tension and surface energy (cf. Eq. 4) [42]:

\[ \gamma_{LV}^{p} = \gamma_{LV} - \gamma_{LV}^{d} = \gamma_{LV}^{a} + \gamma_{LV}^{b} \] (54 a)

\[ \sigma_{SV}^{p} = \sigma_{SV} - \sigma_{SV}^{d} = \sigma_{SV}^{a} + \sigma_{SV}^{b} \] (54 b)

Considering Eqs. (6 a) and (6 b), we may now define the work of acid–base interaction:

\[ W_{SL}^{p} = W_{SL} - W_{SL}^{LW} = \gamma_{LV}(\cos \Theta_{SL} + 1) - [\sigma_{SV}^{d}(A, O) + \gamma_{LV}^{d}] \] (55 a)

\[ W_{SL}^{p} = (\sigma_{SV}^{a} + \gamma_{LV}^{b}) + (\sigma_{SV}^{b} + \gamma_{LV}^{a}) \] (55 b)

\[ W_{SL}^{p} = \sigma_{SV}^{p} + \gamma_{LV}^{p} - \sigma_{SL}^{p} = (\sigma_{SV}^{a} + \gamma_{LV}^{b}) + (\gamma_{LV}^{a} + \gamma_{LV}^{b}) - \sigma_{SL}^{p} \] (55 c)

Combining the last two equations, it is obvious that the arithmetic averaging being symmetric with the vOCG model predicts that the interfacial tension
(\(\sigma_{SV}^b\)) is always zero at equilibrium. Thus, the arithmetic averaging does not lend itself for calculations of interfacial energies. With reference to the Hard–Soft Acid–Base (HSAB) principle, we define that if one of the sites of the acid–base pair is absent the other cannot interact and the entire parentheses vanish. This principle for monodentacy is also applied in the vOCG model. Combining Eqs. (21a) and (21b) and rearranging we find an exceedingly simple expression for the surface energy:

\[
\sigma_{SV} = (\sigma_{SV}^b + \sigma_{SV}^d(A, O)) = \gamma_{LV} \cos \Theta_{SL} = I_{SL}
\]

This expression equals the work of immersion which agrees with Eq. (15b) for fully dispersive liquids. Note that \(\sigma_{SV}^b \approx \sigma_{SV}\). For dispersive systems, the equation may be tested for consistency by extrapolating \(\gamma_{LV} \cos \Theta_{SL}\) to \(\Theta_{SL} = 0\):

\[
\lim(\gamma_{LV} \cos \Theta_{SL}) = \gamma_{LV}^d \approx \gamma_{crit}^d \approx \sigma_{SV}^d
\]

Obviously a Zisman like plot is recovered. Replotted as the work of immersion against the surface tension of the liquids Neumann et al. have identified the surface energy of the solid as the maximum crossing point of the lines defined by \(\Theta_{SL} = 0(\gamma_{LV} < \sigma_{SV})\) and \(\sigma_{SV} \approx \text{constant}(\gamma_{LV} > \sigma_{SV})\) [13].

As shown the break point may, indeed, be identified for the hydrophobic surfaces. For the hydrophilic surfaces the break point is less clear.
When considering enthalpic relationships, the state of the surface film must also be kept in mind. For polar liquids adsorbing on polar surface sites on an otherwise hydrophobic surface, it has been found that the enthalpy of immersion may rise with the degree of vapor coverage (cf. Fig. 1.7) [10]. This means that the film has a greater affinity for the vapor molecules than the bare surface. The enthalpy of (mono-molecular) adsorption ($\Delta H_{\text{ads}}^g$) may be related to the enthalpy of adhesion ($\Delta H_A^*$) of multilayer adhesion (or spreading):

$$\Delta H_{\text{ads}}^g = \Delta H_{\text{ads}}^g / A = (\Delta H_{\text{i(L)}}^g - \Delta H_{\text{i(V)}}^g)$$

(58a)

$$\Delta H_A^* = \Delta H_{\text{ads}}^g + \Delta H_{\text{liq}}^g$$

(58b)

where the molar enthalpy of liquefaction is $\Delta H_{\text{m,liq}}^g$ ($\Delta H_{\text{liq}}^g = \Gamma_1 \Delta H_{\text{m,liq}}^g$). The first part ($\Delta H_{\text{ads}}^g$) relates to the adsorbed (gaseous) film while ($\Delta H_A^*$) accounts also for the condensation of the multiplex film. All the terms are negative. The enthalpy of immersion for the vapor covered and the precoated sample is:

$$\Delta H_{\text{i(V)}}^g = \Delta H_{\text{SL}}^g / A = (H_{\text{SL}} - H_{\text{SV}}) / A$$

(59a)

$$\Delta H_{\text{i(L)}}^g = \Delta H_{\text{SL}}^g / A = (H_{\text{SL}} - H_{\text{SL(L)}}) / A$$

(59b)

The difference between immersion enthalpy of vapor and liquid covered sample is:

$$\Delta H_{\text{ads}}^g = (\Delta H_{\text{i(V)}}^g - \Delta H_{\text{i(L)}}^g) = \left(\Delta H_{\text{SL}}^g - \Delta H_{\text{SV}}^g\right) / A$$

(60a)

The enthalpy of adsorption is typically determined utilizing the Clausius–Clapeyron relation for the isosteric heat of adsorption ($Q_0$):

$$\Delta H_{\text{ads}}^0 = \int_{\Gamma_{\text{L},0}}^{\Gamma_1} Q_0 \ln \Gamma_1$$

(61)

Hence the change in the immersion enthalpy may be expressed as

$$\Delta H_{\text{i(V)}}^g - \Delta H_{\text{i(L)}}^g \approx \Gamma_1 (\Delta H_{\text{m,ads}} - \Delta H_{\text{m,liq}})$$

(62)

In this way it expresses the energy change of the adsorbate in moving from the bulk liquid to the solid surface if the solid is negligibly perturbed and lateral interactions are similar in the adsorbed film to those in the bulk liquid.

Fowkes and Mostafa [43] suggested relating the work of adhesion to the (exothermic) enthalpy per mole of acid–base adduct formation at the interface ($-\Delta H_{\text{ab}}^b$) with a function $f$ supposed to convert the enthalpic quantity [$\Gamma_{\text{ab}}^b(-\Delta H_{\text{ab}}^b)$] to the Gibbs free energy for AB interaction:

$$W_{\text{SL}}^{\text{AB}} = W_{\text{SL}} - W_{\text{SL}}^{\text{W}} = -\Delta G_{\text{f}}^{\text{AB}} = f[\Gamma_{\text{ab}}^b(-\Delta H_{\text{ab}}^b)]$$

(63)
where $I_{ab}^{ab} = N_{N}^{A} / N_{A}$ is the number of moles of accessible acid or base functional groups per unit area of the solid surface determined by colorimetric titration or adsorption isotherms of the Lewis sites. Assuming that the temperature dependence does not influence the division into LW and AB contributions, we recall Eqs. (19) and (20):

$$\Delta G_{i}^{S} = \Delta G_{SL}^{S}/A = \Delta H_{i}^{S} + T[(d\Delta G_{i}^{S})/dT]_{p,n} = \Delta G_{i}^{LW} + \Delta G_{i}^{AB} \quad (64)$$

Then, introducing the Fowkes model:

$$\Delta H_{i}^{AB} = \Delta H_{SL}^{AB}/A = I_{ab}^{ab} \Delta H_{i}^{ab} = (1/f)\Delta G_{i}^{AB} \quad (65 \text{ a})$$

$$\Delta H_{i}^{AB} = \Delta G_{i}^{AB} - T[(d\Delta G_{i}^{AB})/dT]_{p,n} \quad (65 \text{ b})$$

we may derive the condition for the equality of $\Delta G_{i}^{AB}$ as [44]

$$1/f = 1 - [d(\Delta \ln G_{i}^{AB})]/d \ln T]_{p,n} \quad (66)$$

Alternatively, we assume that the arithmetic averaging of the surface energy components applies ($\sigma_{SL}^{AB} = 0$). Then, as shown in Eq. (65 a) we may write:

$$\Delta G_{i}^{AB} = -W_{SL}^{AB} = -\sigma_{SV}^{AB} = \Delta H_{i}^{AB} - T(d(\sigma_{SV}^{AB})/dT)_{p,n} \quad (67)$$

We may thus rewrite the $f$-factor in the form:

$$f = -\sigma_{SV}^{AB}/\Delta H_{i}^{AB} = 1 - \{T[d(\sigma_{SV}^{AB})/dT]_{p,n}/\Delta H_{i}^{AB}\} \quad (68 \text{ a})$$

$$f = 1 + T(\Delta \sigma_{SV}^{AB})/(\Delta H_{i}^{AB}) \quad (68 \text{ b})$$

---

**Fig. 1.12** The Fowkes $f$ factor as a function of temperature for bromoform–poly(methyl methacrylate) (circles), dimethyl sulfoxide (DMSO)–poly(vinyl chloride) (squares), DMSO–[polyethylene/poly(acrylic acid), 5%] (triangles) and DMSO–[polyethylene/poly(acrylic acid), 20%] (diamonds) (from [44], with permission)
Fig. 1.12 shows that the $f$ factor is substantially less than unity in most cases and increases with temperature. Obviously, for these systems the prediction of a straightforward relationship does not exist between the enthalpy and free energy for the acid–base interaction.

It should be noted that the Drago model [32, 33] refers to the enthalpy of formation of one-to-one molecular adducts in the gas phase and in poorly coordinating solvents. In the latter case, the enthalpy of the non-specific interactions must be subtracted to obtain $\Delta H_{\text{sl}}^{\text{AB}}$, which, according to Eq. (21), can be approximated as

$$\Delta H_{\text{sl}}^{\text{AB}} = \Delta H_{\text{i}} - \Delta H_{\text{i}}^{\text{LW}} \approx \Delta H_{\text{i}} + \sigma_{\text{sv}}^d - 21 \quad (69)$$

Alternatively, we may recall the enthalpy of immersion (Eq. 17):

$$\Delta H_{\text{i}}^{\text{AB}} = \sigma_{\text{SL}}^{\text{AB}} - T[\partial(\sigma_{\text{SL}}^{\text{AB}})/\partial T]_{\text{p,n}} - \sigma_{\text{SV}}^{\text{AB}} + T[\partial(\sigma_{\text{SV}}^{\text{AB}})/\partial T]_{\text{p,n}} \quad (70\text{a})$$

$$\Delta H_{\text{i}}^{\text{AB}} = \sigma_{\text{SL}}^{\text{AB}} - \sigma_{\text{SV}}^{\text{AB}} - T[\partial(\sigma_{\text{SV}}^{\text{AB}} - \sigma_{\text{SV}}^{\text{AB}})/\partial T]_{\text{p,n}} \quad (70\text{b})$$

$$\Delta H_{\text{i}}^{\text{AB}} = -\gamma_{\text{LV}}^{\text{AB}} \cos \theta_{\text{L}}^{\text{AB}} + T[\partial(\gamma_{\text{LV}}^{\text{AB}} \cos \theta_{\text{L}}^{\text{AB}})/\partial T]_{\text{p,n}} \quad (70\text{c})$$

$$\Delta H_{\text{i}}^{\text{AB}} = -\gamma_{\text{LV}}^{\text{AB}} \cos \theta_{\text{L}}^{\text{AB}} + T(\partial(\cos \theta_{\text{L}}^{\text{AB}})/\partial T)_{\text{p,n}} + T \cos \theta_{\text{L}}^{\text{AB}} [\partial(\gamma_{\text{LV}}^{\text{AB}})/\partial T]_{\text{p,n}} \quad (70\text{d})$$

where $\cos \theta_{\text{L}}^{\text{AB}}$ may be derived in the way described above. This approach seems, however, to be an unacceptably tedious approach. Douillard and Médout-Marére extended the vOCG division of the components to the enthalpic contribution [45]:

$$H_{\text{sl}}^o = H_{\text{sv}}^o + H_{\text{lv}}^o - 2(H_{\text{sv}}^{\text{LW}} H_{\text{lv}}^{\text{LW}})^{1/2} - 2((H_{\text{sv}}^o H_{\text{lv}}^o)^{1/2} + (H_{\text{sv}}^o H_{\text{lv}}^o)^{1/2}) \quad (71)$$

where the components of the heat of immersion are

$$\Delta H_{\text{i}}^o = (H_{\text{sl}}^o - H_{\text{sv}}^o)/A = \Delta H_{\text{i}}^{\text{LW}} + \Delta H_{\text{i}}^{\text{AB}} \quad (72\text{a})$$

$$\Delta H_{\text{i}}^{\text{LW}} = H_{\text{lv}}^{\text{LW}} - 2(H_{\text{sv}}^{\text{LW}} H_{\text{lv}}^{\text{LW}})^{1/2} \quad (72\text{b})$$

$$\Delta H_{\text{i}}^{\text{AB}} = H_{\text{lv}}^{\text{AB}} - 2((H_{\text{sv}}^o H_{\text{lv}}^o)^{1/2} + (H_{\text{sv}}^o H_{\text{lv}}^o)^{1/2}) \quad (72\text{c})$$

If the immersion is first done in non-specific liquids, then $\Delta H_{\text{i}}^{\text{LW}}$ can be subtracted from the total heat of immersion for acidic and basic probes to give the acid–base components. Alternatively, the acidic or basic probes are titrated to the solid dispersed in the non-specific liquid displacing the LW molecules from the AB sites. Douillard and Médout-Marére suggested using the Fowkes $f$ function to convert the enthalpies further to surface energy components of the vOCG model discussed previously. As shown above, the latter suggestion is bound to fail.
The conversion into arithmetic averaging maintaining the symmetry of the vOCG model is not possible, since the subtraction of the terms involving the acid–base components cancels the interfacial terms altogether. However, since the extensive experimental material analyzed by Drago is enthalpic in origin, we may rewrite his $E$ and $C$ constants as partial enthalpies:

$$
\Delta H^\text{AB}_I = \Delta H_I - \Delta H^\text{LV}_I = (H^{\text{EA}}_I H^{\text{EB}}_I) + (H^\text{CA}_I H^\text{CB}_I) \tag{73}
$$

In this way, all the accumulated data are made available for monodentate acid–base reactions immediately. Thus, the immersion is first done in pure LW liquids to give the $H^{\text{AB}}_I$ contribution.

Alternatively, we may, in line with the Douillard and Médout-Marère (DMM) geometric model, apply the much simpler arithmetic averaging model:

$$
H^\text{SL}_I = H^\text{SV}_I + H^\text{LV}_I - (H^\text{SV}_I + H^\text{LV}_I) - [(H^\text{A}_I + H^\text{B}_I) + (H^\text{A}_I + H^\text{B}_I)] \tag{74}
$$

The components of the heat of immersion are by symmetry

$$
\Delta H^\text{SL}_I = (H^\text{SL}_I - H^\text{SV}_I)/A = \Delta H^\text{LV}_I + \Delta H^\text{AB}_I \tag{75a}
$$

$$
\Delta H^\text{LV}_I = H^\text{LV}_I - (H^\text{SV}_I + H^\text{LV}_I) \tag{75b}
$$

$$
\Delta H^\text{AB}_I = H^\text{AB}_I - [(H^\text{A}_I + H^\text{B}_I) + (H^\text{A}_I + H^\text{B}_I)] \tag{75c}
$$

In all these cases, the state molecular gaseous film should be kept apart from the condensed liquid film including the enthalpy of condensation and the behavior of the bulk liquid (see Fig. 1.7).

As discussed in the Introduction, rather than aiming for the free energies ($F$ and $G$) as done in the discussion above, one should relate the enthalpy to heat capacity instead. For the free energies, all interactions are balanced against each other and thence only a break point is recorded for free energies at first-order phase transitions. For enthalpy this produces a sudden jump to a new level, which is sharper the more extensive the phase transition is. However, the salient interactions are sensitively reflected only for the second order derivative properties, such as heat capacities, expansivities and compressibilities [1, 6].

Consider the distribution of a probe between acidic (or neutral) solution (state A) and basic surface sites (state B):

$$
A \leftrightarrow B \Rightarrow K = \frac{x_B}{x_A} = \frac{x_B}{1 - x_B} \tag{76}
$$

where the system is considered ideal, i.e. the activity coefficients have been set equal to unity. The heat capacity of such a system will first contain contributions from the probe in each state and may be written as [46]

$$
C^\text{intra}_P = x_A C^A_P + x_B C^B_P \tag{77}
$$
The latter is termed “intra” in order to distinguish it from another possible contribution, which can arise from shifts in the equilibrium populations of each site with temperature. If there is an enthalpy difference between states A and B ($\Delta H^{AB}$), then the equilibrium shift is obtained through

$$d\ln K/dT = [d\ln K/dx_B]dx_B/dT = \Delta H^{AB}/RT^2$$  \hspace{1cm} (78)

After derivation and rearranging, we may write

$$dx_B/dT = x_A x_B \Delta H^{AB}/RT^2$$  \hspace{1cm} (79)

Now, the heat adsorbed for this equilibrium shift will contribute and “inter-state” heat capacity, defined as [46]

$$C_p^{\text{inter}} = dH/dT = (dH/dx_B)(dx_B/dT) = \Delta H^{AB}(dx_B/dT)$$  \hspace{1cm} (80)

Insertion of $(dx_B/dT)$ gives

$$C_p^{\text{inter}} = x_A x_B (\Delta H^{AB})^2/RT^2$$  \hspace{1cm} (81)

Hence the total heat capacity has been related to both Gibbs free energy ($\ln K$) and the enthalpy change of the acid–base site binding ($\Delta H^{AB}$) [46]:

$$C_p = C_p^{\text{intra}} + C_p^{\text{inter}} = x_A C_p^A + x_B C_p^B + x_A x_B (\Delta H^{AB})^2/RT^2$$  \hspace{1cm} (82)

Corresponding relationships can also be written for the other second derivatives from the Gibbs free energy, i.e. the expansivity and the isothermal compressibility [46]:

$$E = E^{\text{intra}} + E^{\text{inter}} = x_A E^A + x_B E^B + x_A x_B (\Delta H^{AB} \Delta V^{AB})/RT^2$$  \hspace{1cm} (83)

$$K_T = K_T^{\text{intra}} + K_T^{\text{inter}} = x_A K_T^A + x_B K_T^B + x_A x_B (\Delta V^{AB})^2/RT^2$$  \hspace{1cm} (84)

where the cubic expansion coefficient $a = E/V$ and the isothermal compressibility coefficient $\kappa_T = K_T/V$ [1].

The interstate contribution will be maximum at $x_A = x_B = 1/2$ (i.e. $K = 1, \Delta C^{AB} = 0$) and its maximum will depend on $(\Delta H^{AB})^2$, $(\Delta H^{AB} \Delta V^{AB})$ or $(\Delta V^{AB})^2$. When squared the inter-state contribution is always positive, regardless of the sign of the enthalpy change. It must be acknowledged that in this system, $x_A$ and $x_B$ cannot be varied at will, except by changing the temperature or pressure. The limiting cases where the inter-state contribution is small, i.e. $x_A \rightarrow 0$ or $x_B \rightarrow 0$, originate from either very large or very small equilibrium constants. It is now understood that very weak (van der Waals) interactions will yield rather small contributions to $C_p^{\text{inter}}$. On the other hand, such interactions are sensitively reflected in $K_T^{\text{inter}}$. Intermediate Lewis acid–base interactions such
as hydrogen bonding with energies several times RT are expected to produce
greater effects on $C_p^{\text{inter}}$. The expansivity ($E^{\text{inter}}$) is expected to be sensitive to
both types of interaction. The real potential of ($C_p^{\text{inter}}, E^{\text{inter}}, K_T^{\text{inter}}$) measure-
ments may thus be fully appreciated as a selective emphasis on contributions
which correspond to a particular range of interaction energies.

1.4 Wetting in Idealized Ternary Systems

In order to rationalize the concepts, we describe the processes of wetting using
half-spheres having unit target area directed towards the dividing plane. The
work of cohesion and adhesion are illustrated in Fig. 1.13.

![Fig. 1.13 The work of cohesion ($X = 1$) represents the separation of the same phase and the work adhesion ($X = 2$) two phases (half droplets) in contact, thus bringing them in contact with (their) vapor.](image)

We consider specifically the three phases discussed previously, i.e. the liquids
(K and L) and the solid (S) (Fig. 1.14). We may now easily derive the work of
spreading for each pair of phases, disregarding the third phase (vapor, V) at the
three-phase contact-line (tpcl). For non-condensed (vapor) phases the surface
tension is negligible. In the indexing the most condensed phase is written first:

\[
\begin{align*}
W_{KL} &= \gamma_{KV} + \gamma_{LV} - \gamma_{KL} \\
S_{KL} &= \gamma_{LV} - \gamma_{KV} - \gamma_{KL} \\
S_{KL} &= W_{KL} - C_{KK} \\
W_{SK} &= \sigma_{SV} + \gamma_{KV} - \sigma_{SK} \\
S_{SK} &= \sigma_{SV} - \gamma_{KV} - \sigma_{SK} \\
S_{SK} &= W_{SK} - C_{KK} \\
W_{SL} &= \sigma_{SV} + \gamma_{LV} - \sigma_{SL} \\
S_{SL} &= \sigma_{SV} - \gamma_{LV} - \sigma_{SL} \\
S_{SL} &= W_{SL} - C_{LL}
\end{align*}
\]

(85 a) (85 b) (85 c)

In all cases the upper phase is like a reversed process considered to spread on
the lower one, until the work of adhesion and work of cohesion are equal. We
shall make use of these binary systems when considering the phase equilibrium
in three-component systems.

We may expand the optional work of adhesion in terms of the surface ten-
sions of two liquids ($K = 1$ and $L = 2$) previously discussed in contact with a sol-
id ($S = 3$), assuming that they are fully immiscible with each other (more con-
densed phase first):
When three phases are brought into contact, the situation is rendered much more complex. In addition to the binary contact area we have to consider a three-phase contact point (tpcp) (Fig. 1.15). Assuming that the outer curved lines remain excluded from the considerations, the following options for the processes appear reasonable (no particular indexing order):

If only one third (phase 1) is separated, we find for the work of adhesion (process I)

\[
W_{123}^{(I)} = 2\gamma_1 + \gamma_2 + \sigma_3 - \gamma_{12} - \sigma_{13} - \sigma_{123} \quad (87a)
\]

\[
W_{123}^{(I)} = \gamma_1 + \gamma_2 + \sigma_3 - \gamma_1 - \sigma_3 - \sigma_{13} \quad (87b)
\]

When phase 1 is immersed in phases 2 and 3 the interfacial contacts 1–2 and 1–3 remain and the work of adhesion is dramatically simplified (should be 3 in 1 and 2, process II):

\[
W_{123}^{(II)} = \gamma_2 + \sigma_3 \quad (88a)
\]

\[
W_{123}^{(II)} = \gamma_2 + \sigma_2 + \sigma_3 \quad (88b)
\]
If all three phases are separated simultaneously, we find (process III)

\[ W_{(III)}_{123} = 2\gamma_1 + 2\gamma_2 + 2\gamma_3 - \sigma_{12} - \sigma_{13} - \sigma_{23} \]  

\[ W_{(III)}_{123} = W_{12} + W_{13} + W_{23} - \sigma_{123} \]  

The process considered is obviously of prime importance for the surface tension–surface energy balance found. The energy balance at the tpcp should equal zero at equilibrium.

Two processes are offered as a standard for the work of adhesion in textbooks on surface and colloid chemistry [16, 31]. The reason for the particular averaging scheme is probably to maintain the symmetry of the geometric averaging rule.

First we consider that a liquid (L) and a solid (S) initially in contact are separated from each other and brought into cohesive contact (Fig. 1.16):

\[ W_{(IV)}_{SLS} = C_{LL} + C_{SS} - 2W_{SL} \]  

Written in terms of interfacial tensions, this equation reduces to

\[ W_{(IV)}_{SL} = 2\sigma_{SL} \]  

The second is the separation between two phases (S and K) initially in contact with the medium (L) to form a contact with the two phases and the third phase internally.
Converted into binary work of cohesion and adhesion (Fig. 1.17) [16, 31]:

$$W(V)_{SLK} = C_{LL} + W_{SK} - W_{KL} - W_{SL}$$  \(92\)

Written in terms of interfacial tensions:

$$W(V)_{SLK} = \gamma_{KL} + \sigma_{SL} - \sigma_{SK}$$  \(93\)

The latter process is illustrated in terms of the triangular sphere in Fig. 1.18. As shown, the latter two-phase \([W(IV)_{SL}]\) and three-phase \([W(V)_{SKL}]\) work of adhesion correspond to only a fraction of the total work of adhesion \([W(III)_{PLK}]\). They therefore all represent different thermodynamic realities.
1.4.1

**Preferential Spreading at Three-component Interfaces**

Dispersing a solid (S) and a liquid (K) in small amounts in an immiscible liquid (L) may lead to a full dispersion (rejection) of all the phases or an *engulfment* (preferential wetting) of the solid into the K liquid. The intervening situation when all phases partially wet each other is denoted a *funicular state*. In order to determine these limiting states, we derive the ternary work of adhesion and spreading denoting the dispersion medium between the dispersed phases in the lower index. We select the traditional process (Eq. 86) and permute the liquid (K) and the dispersion medium (L) maintaining the solid (S).

With reference to the binary processes (Fig. 1.14), we may write the ternary work of spreading and the work of adhesion in terms of interfacial tensions. For the first case, we find

\[
\begin{align*}
S_{SLK} = & \sigma_{SL} - \gamma_{LK} - \gamma_{SK} \\
W_{SLK} = & \sigma_{SL} + \gamma_{LK} - \gamma_{SK}
\end{align*}
\]

\[S_{SLK} = W_{SLK} - 2\gamma_{LK} \tag{94}\]

Considering L as the dispersed liquid and K as the dispersion medium, we find

\[
\begin{align*}
S_{SKL} = & \sigma_{SK} - \gamma_{KL} - \gamma_{SL} \\
W_{SKL} = & \sigma_{SK} + \gamma_{KL} - \gamma_{SL}
\end{align*}
\]

\[S_{SKL} = W_{SKL} - 2\gamma_{KL} \tag{95}\]

The ternary work of spreading may thus be expressed as the difference between the ternary work of adhesion and the two times the interfacial tension between the liquids (Fig. 1.19).

![Fig. 1.19](image)

**Fig. 1.19** The preferential wetting of two non-miscible liquids on a solid may be expressed by the ternary work of spreading expressed in terms of interfacial tensions. The work of spreading represents the difference between the ternary work of adhesion and two times the interfacial tension between the liquids.

Likewise as for the binary case, the spreading coefficient is expected to be positive (negative Gibbs free energy) for spontaneous preferential spreading to occur. Three limiting cases can be distinguished:

1. The dispersed liquid (K) cannot spread on the solid (S) since the dispersion liquid (L) preferentially wets the particles, i.e. \( S_{SLK} \geq 0 \), but \( S_{SKL} < 0 \).
2. The dispersed liquid (K) partially forms (liquid bridges between) the solids (S) if both \( S_{SLK} < 0 \) and \( S_{SKL} < 0 \).
3. The dispersed liquid (K) preferentially wets the solid particles (S), displacing the dispersion liquid (L), if $S_{SKL} > 0$, but $S_{SLK} < 0$.

Note that the interfacial tension between the liquids determine whether the ternary work of spreading has a positive or negative sign (Fig. 1.20).

We may measure directly the work of adhesion by the introduction of a ternary Young-Dupré equation:

$$W_{SLK} = \gamma_{KL} (\cos \Theta_{SLK} + 1) \quad (96 \text{a})$$

$$W_{SKL} = \gamma_{LK} (\cos \Theta_{SKL} + 1) \quad (96 \text{b})$$

In the former case the contact angle between the solid (S) and the droplet (K) is measured immersed in liquid (L) and in the latter case the liquids are reversed. Owing to density differences, one measurement is usually made from a sessile drop and the other from a pendant drop.

The ternary work of adhesion can be related to the binary work of adhesion as discussed previously [8]:

---

Fig. 1.20 Preferential wetting of oil on hydrophobic particles dispersed in an aqueous dispersion. The particles are the more efficiently removed the smaller the interfacial tension between the water and the oil is and the larger the difference $\sigma_{SK} > \sigma_{SL}$ grows.
The liquid (interfacial) tensions are measured as usual and the binary work of adhesion for the solid as

\[ W_{SL} = \gamma_{LV}(\cos \Theta_{SL} + 1) \] (98 a)

\[ W_{SK} = \gamma_{KV}(\cos \Theta_{SK} + 1) \] (98 b)

Since \( C_{LL} - W_{LK} = -S_{LK} \) and \( C_{KK} - W_{KL} = -S_{KL} \), we may rearrange the equations:

\[ W_{SLK} = \gamma_{KL}(\cos \Theta_{SLK} + 1) - \gamma_{LV}(\cos \Theta_{SL} + 1) - S_{LK} \] (99 a)

\[ \gamma_{KL} \cos \Theta_{SLK} = \gamma_{LV} \cos \Theta_{SL} - \gamma_{KV} \cos \Theta_{SK} \] (99 b)

\[ W_{SKL} = \gamma_{LK}(\cos \Theta_{SKL} + 1) - \gamma_{LV}(\cos \Theta_{SL} + 1) - \gamma_{SV}(\cos \Theta_{SK} + 1) - S_{KL} \] (99 c)

\[ \gamma_{LK} \cos \Theta_{SKL} = \gamma_{LV} \cos \Theta_{SL} - \gamma_{KV} \cos \Theta_{SK} \] (99 d)

This so-called Bartell-Osterhof equation [47] shows that the ternary contact angle (solid–liquid–liquid) may be related to the binary one (solid–liquid–vapor) in a straightforward way. It may be considered as a Cassie equation for a multicomponent system.

1.4.2 Models for Dispersive Solid–Liquid–Liquid Interaction

When considering the two standard processes for the work of cohesion and adhesion, we introduce the geometric average of the dispersive component:

\[ C_{SS}^d = 2(\sqrt{\sigma_{SV}^d \sigma_{SV}^d}) \] and \( C_{LL}^d = 2(\sqrt{\gamma_{LV}^d \gamma_{LV}^d}) \) (100)

\[ W_{SL}^d = 2(\sigma_{SV}^d \sigma_{SV}^d)^{1/2} \] (101)

Then we may write the work of adhesion for the extended (SLS) binary system defined by the equation [8, 17, 18]

\[ W_{SLS}^d = 2[(\gamma_{LV}^d \gamma_{LV}^d)^{1/2} + (\sigma_{SV}^d \sigma_{SV}^d)^{1/2} - 2(\gamma_{LV}^d \sigma_{SV}^d)^{1/2}] \] (102 a)

\[ W_{SLS}^d = 2(\sqrt{\sigma_{SV}^d} - \gamma_{LV}^d)^2 = 2\sigma_{SL}^d \] (102 b)

As shown, the extended binary system produces, as expected from the process considerations, a double dispersive interfacial tension. For both versions the equation shows that only when \( \sqrt{\sigma_{SV}^d} = \gamma_{LV}^d \) does \( W_{SLS}^d = 0 \). Otherwise \( W_{SLS}^d \) is
always positive. For the three-component system we may write for the work of adhesion

\[ W_{\text{SLK}}^d = 2[(\gamma_{LVI})^{1/2} + (\sigma_{SV}^d)^{1/2} - (\sigma_{SV}^d)^{1/2} - (\gamma_{KV}^d)^{1/2}] \]  
\[ W_{\text{SLK}}^d = 2[(\gamma_{KV}^d - \gamma_{LVI}^d)(\gamma_{SV}^d - \gamma_{LVI}^d)] \]  

(103a)  
(103b)

The equation indicates that the dispersive interaction is repulsive if \( \sigma_{SV}^d > \gamma_{LVI}^d \) or \( \sigma_{SV}^d < \gamma_{LVI}^d \).

Since \( \gamma \approx A_H/(k_A d_0^2) \), where \( k_A \approx 75.40 \) for van der Waals liquids, 100.5 for pure hydrocarbons and 10.47 for semi-polar liquids, we may also write the equations in terms of Hamaker constants (\( A_H \)) [16, 31]:

\[ A_{\text{SLK}} = A_{LL} + A_{SK} - A_{SL} - A_{KL} \]  
\[ A_{SKL} = A_{KK} + A_{SL} - A_{SK} - A_{KL} \]  

(104a)  
(104b)

The same geometric averaging rules have been applied to these interfacial Hamaker constants. Owing to the definition of the work of adhesion for three-component systems without the \( t_{pcl}(p) \), the interfacial tension cannot be derived in a straightforward way.

The three-phase systems offer an interesting alternative to measure contact angles of, e.g., a solid (S) immersed in a hydrocarbon (oil, O). If a drop of water (W) is placed as a sessile drop on the solid immersed in the oil, we may write for the ternary Young equation [8]

\[ \sigma_{SO} = \sigma_{SW} + \gamma_{OW} \cos \Theta_{SOW} \]  

(105)

We assume that the hydrocarbon interacts with the solid solely through London-van der Waals forces and write the interfacial energy in terms of the Dupré-Fowkes equation:

\[ \sigma_{SO} = \sigma_{SV} + \gamma_{OV} - 2(\sigma_{SV}^d \gamma_{OV}^d)^{1/2} \]  

(106)

On the other hand, the \( \sigma_{SW} \) component is assumed to be polar, hence the interaction is both dispersive and specific (polar) in origin (\( W_{SW} = W_{SW}^d - W_{SW}^p \)) [48]:

\[ \sigma_{SW} = \sigma_{SV} + \gamma_{WV}^p - 2(\sigma_{SV}^d \gamma_{WV}^d)^{1/2} - W_{SW}^p \]  

(107)

Inserted into Eq. (105), we obtain the Schultz equation [49]:

\[ \gamma_{WV}^p - \gamma_{OV}^p \cos \Theta_{SOW} = 2\sqrt{\sigma_{SV}^d(\sqrt{\gamma_{WV}^p} - \sqrt{\gamma_{OV}^p}) + W_{SW}^p} \]  

(108)
A Schultz plot of $\gamma_{WV} - \gamma_{OV} + \gamma_{OW} \cos \Theta_{SOW}$ against $\sqrt{\gamma_{WV}^d - \gamma_{OV}^d}$ is expected to give a straight line with slope $2\sqrt{\sigma_{SV}^d}$ and intercept $W_{SW}^p$. The extraction of $W_{SW}^p$ can be improved by choosing octane as the immersion liquid, since its surface tension equals the dispersion component of water. The accuracy of the measurement is frequently fairly low, but it can be confirmed by measuring the contact angle from the pendant hydrocarbon drop against the solid immersed in water [8, 48].

1.4.3 Contribution from the Surface Pressure of a Monomolecular (Gaseous) Film

The preferential spreading of a liquid (K) dispersed in small amounts in an immiscible liquid (L) on an equally dispersed solid (S) may lead to a phenomenon similar to preferential adsorption of one component from a mixed solvent. However, as discussed before, the state of the film considered should be specified, i.e. whether it is a molecular vapor (given by the surface pressure), an unstable intermediate or a bulk (immiscible) liquid (given by the work of spreading). Since $\pi_{S(K)} = \sigma_{SV} - \sigma_{S(S)}$, it is realized that the anticipated process is correct. It is obvious from Eqs. (31) and (32) that the spreading coefficient equals the negative surface pressure of a duplex film, i.e. when the liquid fully wets the solid surface as a duplex film. Exchanging the vapor (gas) for the liquid (K), we obtain the following permutative ternary spreading coefficients between K, component L (liquid) and S (substrate), i.e. $S_{SLK}$ and $S_{SKL}$, respectively.

The preferential spreading of the liquid probe (K) on the solid (S) displacing the dispersion liquid (L) may be assumed to occur via an intermediate state where both liquids are preadsorbed on the solid represented by the surface pressures before immersion in the other liquid. Neglecting the surface pressures on the liquids, we obtain

$$\pi_{S(K)} = \pi_{S(L)} - \pi_{S(S)}$$

We obtain for the work of adhesion for competing surface pressures (Eq. 12a)

$$W_{S(K,L)K} = C_{LL} + W_{S(L)K} - W_{S(K)L} - W_{LK}$$

$$= 2\gamma_{LV} + [\sigma_{SV} + \gamma_{KV} - \sigma_{S(L)K}] - [\sigma_{SV} + \gamma_{LV} - \sigma_{S(K)L}] - (\gamma_{LV} + \gamma_{KV} - \gamma_{LK})$$

$$W_{S(K,L)K} = \gamma_{LK} + \sigma_{SL} - \sigma_{SK} - \pi_{S(K)L} + \pi_{S(L)K}$$

where $C_{LL} = C_{L(L)} = 2\gamma_{L(L)} = \gamma_{LV}$. We find the following work of spreading:

$$S_{S(K,L)K} = W_{S(K,L)K} - 2\gamma_{LK} = \sigma_{SL} - \sigma_{SK} - \gamma_{LK} - \pi_{S(K)L} - \pi_{S(L)K}$$
The preferential spreading of the liquid (K) occurs in parallel with the retreat of liquid L (negative spreading, opposite signs). Clearly, the preferential wetting may be treated as preferential adsorption from a mixed solvent system to produce a film pressure! For non-miscible liquids the basic phenomena is, however,' more favorably described by an adsorption isotherm.

1.4.4
Models for Lewis (Polar) Solid–Liquid–Liquid Interaction

When considering the two standard processes for the work of cohesion and adhesion, we introduce the geometric average of the acid–base component:

\[ W_{ij}^{AB} = W_{ij}^{LW} = 2[(\gamma_{ij}^{L1})^{1/2} + (\gamma_{ij}^{L2})^{1/2}] = 2(\sqrt{\gamma_{ij}^{L1}} \cdot \sqrt{\gamma_{ij}^{L2}}) \]  

(113)

Additionally, for bidentate (one acidic and one basic site) probe liquids, we find

\[ \sigma_{Si}^{AB} = \sigma_{Si}^{LW} = 2(\sigma_{Si}^{LW})^{1/2} = 2(\sqrt{\sigma_{Si}^{LW} \cdot \sigma_{Si}^{LW}}) \]  

(114 a)

\[ \gamma_{Li}^{AB} = \gamma_{Li}^{LW} = 2(\gamma_{Li}^{LW})^{1/2} = 2(\sqrt{\gamma_{Li}^{LW} \cdot \gamma_{Li}^{LW}}) \]  

(114 b)

The symmetry rule also applies for the work of cohesion, being \( W_{ii}^{AB} = C_{ii}^{AB} = 2\gamma_{i}^{AB} \). The work of adhesion and cohesion indicated above thus takes the form [8, 17, 18]

\[ W_{SLK}^{AB} = W(4)_{SLK}^{AB} = C_{SS}^{AB} + W_{LK}^{AB} - W_{SL}^{AB} - W_{SK}^{AB} \]  

(115 a)

\[ W_{SLK}^{AB} = 2\{2(\sqrt{\sigma_{SV}^{LW} / \sigma_{SV}^{LW}}) + [(\sqrt{\gamma_{LV}^{LW} / \gamma_{KV}^{LW}}) + (\sqrt{\gamma_{KV}^{LW} / \gamma_{KV}^{LW}})] - [(\sqrt{\sigma_{SV}^{LW} / \gamma_{KV}^{LW}}) + (\sqrt{\sigma_{SV}^{LW} / \gamma_{KV}^{LW}})\} \]  

(115 b)

\[ W_{SLK}^{AB} = 2\{[(\sqrt{\sigma_{SV}^{LW} - \gamma_{LV}^{LW}})(\sqrt{\sigma_{SV}^{LW} - \gamma_{KV}^{LW}})] + [(\sqrt{\sigma_{SV}^{LW} - \gamma_{KV}^{LW}})(\sqrt{\sigma_{SV}^{LW} - \gamma_{KV}^{LW}})] \]  

(115 c)

\[ W_{SLK}^{AB} = 2\{[(\sqrt{\gamma_{KV}^{LW} - \gamma_{LW}^{LW}})(\sqrt{\sigma_{SV}^{LW} - \gamma_{KV}^{LW}})] + [(\sqrt{\gamma_{KV}^{LW} - \gamma_{LW}^{LW}})(\sqrt{\sigma_{SV}^{LW} - \gamma_{KV}^{LW}})]\} \]  

(115 d)

The LW and AB interactions in the three-component system may be written in a more illustrative way [8]:

\[ W_{SLK}^{LW} = W_{SK}^{LW} - 2(\sqrt{\gamma_{LV}^{LW}}(\sqrt{\sigma_{SV}^{LW} / \gamma_{KV}^{LW}} - \gamma_{LW}^{LW})) \]  

(116 a)

\[ W_{SLK}^{AB} = W_{SK}^{AB} - 2(\sqrt{\gamma_{LV}^{LW}}(\sqrt{\sigma_{SV}^{LW} + \gamma_{KV}^{LW}} - \gamma_{LW}^{LW})) - 2(\sqrt{\gamma_{LV}^{LW}}(\sqrt{\sigma_{SV}^{LW} + \gamma_{KV}^{LW}} - \gamma_{LW}^{LW})) \]  

(116 b)
In both cases the binary work of adhesion between the dispersed components may be separated from the interaction between the medium liquid and the dispersed components. Thus the LW component of the medium liquid interacts with (is multiplied with) the dispersed S and K components, while the interaction with itself is subtracted from the balance. In a similar way, the acidic site interacts with the basic sites of the dispersed S and K components, while the interaction between the acidic and basic sites of the liquid is subtracted from the balance. Conversely, the basic sites of the liquid interact with the acidic sites of the S and K components, while the interactions with its own acidic sites are subtracted from the balance.

An interesting opportunity to evaluate the work of ternary interaction is provided by the atomic force microscope (AFM), utilized as such or as a colloidal probe [50]. According to the Derjaguin-Muller-Toporov (DMT) theory [51] for a small-radius solid (tip, T) interacting with a flat solid (S) in a liquid (L), the force of adhesion is given by

$$F_A = 2\pi RW_{TLS}$$

where \( R \) is the radius of curvature of the tip (or colloid). Since

$$W_{TLS} = C_{LL} + W_{TS} - W_{TL} - W_{SL}$$

on combining the equations we obtain

$$W_{TS} = \left(\frac{F_A}{2\pi R}\right) + W_{TL} + W_{SL} - C_{LL}$$

Now \( W_{TL} \) and \( W_{SL} \) may be determined from contact angle measurements and \( C_{LL} = 2\gamma_{LV} \). Using standard vOOG liquids, the surface energy components were determined for a number of solid substrates using an Si\(_3\)N\(_4\) AFM tip [50]. However, in the colloidal probe procedure a roughly spherical particle (ca. 1 \( \mu \)m) is glued on the cantilever and then just about any combination of T–L–S and T–S interactions can be measured.

1.5 Adsorption from Solution

As indicated earlier, the preferential adsorption of a liquid component from a mixture cannot be determined from wetting experiments, e.g. from the work of spreading. However, the determination of the adsorption of probe molecules on the sites offers a straightforward way to determine the molecular surface pressure. In this section we discuss the Lewis type and the Brønsted type of acid–base interaction separately, since the mechanism and energy involved differ. We shall also distinguish between adsorption from an undefined medium resembling the gas adsorption. The difference is, however, that in a hydrocarbon solu-
Adsorption provides the proper mean to evaluate the surface states of the solid. In the first model the process involves two steps. First, the adsorption of probe molecules to the surface which is determined separately providing the number of sites. Second, the ability to transfer electrons from the adsorbed basic absor- 
te to the acidic surface sites provides the strength of the surface sites. Assuming that the adsorbed probe molecule is an almost pure Lewis base ($B_0$) reacting on the surface with acidic surface sites ($A$) to form an adduct ($AB$) we may write the equilibrium and the equilibrium constant as [52]:

$$A + B \leftrightarrow (AB) \Rightarrow 1/K_B^s = K_{ads}^s = (a_{AB}^s)/(a_A^s a_B^s) = (x_{AB}^s/x_A^s) (f_{AB}^s/f_A^s a_B^s)$$ (120)

where $a =$ activity, $x =$ mole fraction, $f =$ activity coefficient, $s =$ surface and $b =$ (equilibrium) bulk solution. We may now introduce the Hammett function ($H_0$):

$$H_0 = -\log K_B^s + \log(x_B^s/x_{AB}^s) = -\log(a_A^s) - \log(f_B^s/f_{AB}^s)$$ (121 a)

$$H_0 = pK_B^s + \log(x_B^s/x_{AB}^s) = p(a_A^s) - \log(f_B^s/f_{AB}^s)$$ (121 b)

When $x_{AB}^s = x_B^s$ then $H_0 = pK^s$. Since a mole fraction ratio is considered, it may be exchanged for any other concentration scale. A slight excess of acidic and basic indicator probes has been adsorbed on solids of opposite nature dispersed in a saturated hydrocarbon solvent. After equilibration, the indicators are desorbed using even stronger acids and bases. The amount acid and base needed for changing the color of the adsorbed indicator ($x_{AB}^s = x_A^s$) gives the number of sites and then $H_0 = pK^s = pK_a$ (indicator).

The fraction of acidic surface sites ($A$) occupied by the basic probe molecules ($B$) dispersed in indifferent oil (O) for low surface site occupancy (surface coverage) may be related to the surface film pressure [53]:

$$\pi_{S(B)O} = \pi_{S(K)O} = \sigma_{SO} - \sigma_{S(B)O} = (RT/A_m) \ln(a_{AB}^s/a_A^s) \approx (RT/A_m) (x_{AB}^s/x_A^s)$$ (122)

where the molar surface area $A_m = N_A a$ and $a$ is the surface area occupied by each B or rather each site area. The number of surface sites $N_m^s = N_A (n_{AB}^s)_m$ and the area occupied by one site $s = A/N^s = wS_A/N_m^s$. The monolayer surface excess is $\Gamma_m = (n_{AB}^s)_m/A = N_m^s/AN_A$. In this calculation, it is assumed that the solvent is a fully inert oil (O) and that there is no (surface or concentration) potential against which the adsorption occurs. It may not be possible to
identify \( n_{AB}^s \) the end-point, but rather the equivalence point where \( x_{AB}^s / x_A^s = 1 \). This can conveniently be identified, e.g. from spectroscopic measurements (spectral or color changes).

For ideal surfaces, the term in Eq. (121) involving activity coefficients can be omitted. The relationship with the energy exchange upon adsorption can be confirmed with the Boltzmann equation:

\[
 n_{AB}^s = n_B^b \exp(\Delta \mu_{SB}^O / RT) \tag{123}
\]

Introduced in Eq. (117) we obtain:

\[
 \pi_{SB}^O = \sigma_{SO} - \sigma_{SB}^O = (RT/A_m)(\Delta \mu_{SB}^O / RT) = (\Delta \mu_{SB}^O / A_m) \tag{124}
\]

since \( n_{AB}^s / n_B^b = x_{AB}^s / x_B^b \).

Thus, for dilute solutions depletion measurements may be used.

Calorimetry can also be used to determine the degree of adsorption. Figure 1.21 illustrates the amount of an adsorbed basic (probe) molecule on acidic silica silanol (Si–OH) groups plotted against increasing basicity (left) and increasing acidity (right) of a number of solvents. The adsorption is considered to be dependent on the relative degree of (specific) interaction, being greatest from neutral solvents. The strength of the basic solvent is plotted as \( \Delta H_{BL}^{BA} \), the heat of interaction of the basic solvents with \( t \)-BuOH. The choice of this alcohol is due to the assumption that it has acidic properties similar to those of the surface Si–OH sites of silica [43]. The strength of the acidic solvents is plotted as...
\( \Delta H_{\text{AL}}^{A(B)} \), the heat of interaction of the solvents with ethyl acetate. It is considered as an oxygen base which models the oxygen basicity of the basic probe.

The left side of Fig. 1.21 shows that as the solvent becomes more basic (e.g. aromatic or oxygenated substances) it forms acid–base complexes with the Si–OH sites. A smaller amount of basic probes is then adsorbed because of reduced exothermicity of adsorption to the SiOH–solvent complex sites [43]. Similarly, the right side of Fig. 1.21 shows that as the solvent becomes more acidic (e.g. halogenated hydrocarbons) and forms acid–base complexes with the basic probe molecule, less probe–solvent complex is adsorbed on the acidic Si–OH surface sites of silica owing to decreased exothermicity of adsorption.

### 1.5.2 Determination of Brønsted (Charge) Interactions with Surface Sites

A Brønsted acid–base interaction is activated if the Lewis interaction is strong enough, e.g. for hydrogen bonds a protolysis occurs. Then in water both the adsorbate (probe) and the adsorbent (solid substrate) become charged. The Brønsted acidity and basicity thus interlink the Lewis electron acceptor and donor activity into true Coulomb charge interactions. Since the distance over which this interaction is active supersedes the extension of the van der Waals interactions by orders of magnitude, they should be kept apart. However, the considerations of proton and electrolyte distributions as a function of the distance from the surface (given, e.g., by the DLVO theory) is not considered here since the discussion is focused on the surface properties alone.

The clear difference between Lewis and Brønsted acid–base interactions has, however, not always been recognized when selecting molecules for surface probing. In order to avoid complications, nearly ideal polymers are then used as model surfaces. However, in particular when using water as a vOCG probe liquid on inorganic polar surfaces, the Brønsted activity must be considered.

It may be difficult to detect proton transfer at surface sites if the surface area is not sufficient for detectable adsorption to occur. In the simplest form, the adsorption of a proton (acid) on a basic surface site may be described by the Hammett parameter \( (H_0) \) [52]:

\[
\begin{align}
AH^a + B^a & \leftrightarrow A^a + (BH^+)^a \\
1/K_s^a &= K_{\text{ads}}^a = (a_A^a)(a_B^a)/(a_{AH}^a a_{BH}^a) = (a_A^a x_B^a / a_{AH}^a x_{BH}^a)(f_B^a / f_{BH}^a)
\end{align}
\]

where \( a = \) activity, \( x = \) mole fraction, \( f = \) activity coefficient, \( s = \) surface. Assuming the surface to be ideal \( (a_A^a=1) \) we obtain:

\[
H_0 = -\log K_s^a + \log(x_B^a / x_{BH}^a) = -\log(a_A^a) - \log(f_B^a / f_{BH}^a)
\]

\[
H_0 = pK_s^a + \log(x_B^a / x_{BH}^a) = p(A)H^a - \log(f_B^a / f_{BH}^a)
\]
where \( p(A)H^s \) represents the proton activity at the surface sites. At the equivalence point when \( x_{BH}^s = x_H^s \) then \( H_0 = pK_a^s \), the acidity constant.

The reaction does not necessarily have to be in water. It is sufficient that a proton exchange between the surface and the basic probe (indicator) molecules occur. Figure 1.22 illustrates the titration of titania (anatase and rutile) powders dispersed in cyclohexane using \( n \)-butylamine as the base titrant for acidic surface sites and trichloroacetic acid as the acidic titrant for basic surface sites [54].

The indicator probe molecules chosen for the acidic surface sites have increasing, but low, \( pK_a^s \). They are all weaker bases than \( n \)-butylamine. The strength of the surface sites is determined by \( H_0 < pK_a^s \) and the number of sites is determined by the amount of \( n \)-butylamine consumed in order to reach the equilibrium point (color change of indicator). For the basic surface sites, indicators with a rather high \( pK_a^s \) are used and trichloroacetic acid is used to desorb these indicators from the surface until the equivalence point. As shown in Fig. 1.22, the titania samples have both acidic and basic sites which can be identified both in number and in \( (H_0) \) strength.

In water, neglecting the activity coefficients (ideal surface conditions), the equation may be rewritten in the form

\[
H_0 - p(A)H^s = pK_a^s + \log(x_{BH}^s/x_H^s)
\]

(127)
It is obvious that the Hammett function may be expressed as a corrected pH scale. However, in non-aqueous solvents the pH concept is not clear. All critical values $H_{0,\text{max}}, \text{pH}_{\text{PZC}}$ and $\text{pH}_{\text{IEP}}$ usually match (~6.2 for anatase and ~5.3 for rutile) fairly well, but as shown they diverge in the present case [54]. This is indicative of surface impurities. The corresponding equation may be written for the adsorption of the hydroxyl ions on acidic surface sites. Since the surface is charged in aqueous dispersions, it is customary to relate the pH of the solution with the surface concentration with the Boltzmann relation:

$$n_s^H = n_b^H \exp(-F\psi_0/RT)$$  \hspace{1cm} (128)

where $x_s^H/x_b^H = n_s^H/n_b^H$.

The previous equations do not make any explicit consideration of the proton exchange equilibrium at the surface. According to the Partial Charge Model, the degree of hydrolysis ($h$) of a cation can be estimated from [55]

$$h = \frac{1}{1 + 0.41 \text{pH}} \left\{ \left[ (1.36z - N_C)(0.236 - 0.08 \text{pH}) \right] - \left[ (2.621 - 0.02 \text{pH} - \chi_M^*)/\sqrt{\chi_M^*} \right] \right\}$$  \hspace{1cm} (129a)

where $h$ = the number of protons spontaneously released by the coordinated complex $[\text{M(OH}_2\text{N}]^{z^+}$ in solution, $z$ = valency (charge number), $N_C$ = coordination number and $\chi_M^*$ = Mulliken type electronegativity of the metal. At pH = 0, the equation reduces to [55]

$$h = (1.36z - 0.24N_C) - \left[ (2.621 - \chi_M^*)/\sqrt{\chi_M^*} \right]$$  \hspace{1cm} (129b)

and at pH = 14 to [55]

$$h = (1.14z - 0.25N_C) - \{0.836[(2.341 - \chi_M^*)]/\sqrt{\chi_M^*} \}$$  \hspace{1cm} (129c)

The most important parameter is the formal valency ($z$, charge number) of the metal cation; $N_C$ and $\langle \chi_M^* \rangle$ are of lesser importance. The type of coordination can be approximated as the $z$–pH dependence (Fig. 1.23).

Assuming initially that the metal maintains its coordination complex at the surface, the ligands may reside in the oxo (M–O–), the hydroxo (M–OH) and the aquo (M–OH$_2^+$) form. The charging of the surface is then due to a single type of (average metal) surface sites. The hydrolysis may then be expressed in terms of the surface charge density:

$$\sigma_\pm = F(G_H - G_{\text{OH}}) = (F/w_S A_w)[(n_H - n_{\text{OH}}) - (n_{\text{H}} - n_{\text{OH}})]$$  \hspace{1cm} (130)

where $F$ = Faraday constant, $w_S$ = mass of the solid powder sample, $A_w$ = specific surface area, $n_i$ = acid or base added to the suspension and $n_{ib}^i$ = acid or base added to the separated supernatant. Of course, other acids and bases may com-
pete for the adsorption sites. The point where the charges are neutralized ($\sigma_0 = 0$) is denoted the point of zero charge, $\text{pH}_{PZC}$.

The $\text{pH}_{PZC}$ values can be used to determine the ratio of OH groups attached to hydrolyzable surface species (metals) such as Al or Ti. The surface site dissociation can be written as [56]

$$
M\text{OH}_2^+ \leftrightarrow M\text{OH} + H^+ \quad K_{M,2}^{\text{int}} = \frac{[M\text{OH}][H^+]}{[M\text{OH}_2^+]} \quad (131\ a)
$$

$$
M\text{OH} \leftrightarrow M\text{O}^- + H^+ \quad K_{M,1}^{\text{int}} = \frac{[M\text{O}^-][H^+]}{[M\text{OH}]} \quad (131\ b)
$$

where $K_{X,m}$ is the equilibrium constant for the metal oxide (M) and $m$ = number of protons. $[H^{+,s}]$ denotes the activity of the protons at the Bronsted surface sites, which is related to the bulk proton activity ($[H^{+,b}]$) through the Boltzmann relation (Eq. 128):

$$
[H^{+,s}] = [H^{+,b}] \exp(-F\psi_0/RT) \quad (132)
$$

where $\psi_0$ = surface potential, $R$ = gas constant and $T$ = absolute temperature.

At $\text{pH}_{PZC}$, when $\psi_0 = 0$, Eq. (132) states that $[H^{+,s}] = [H^{+,b}]$, i.e. the intrinsic constant, $K_{X,m}^{\text{int}}$ represents the proton equilibrium constant (acidity constant of the surface sites) in a chargeless environment. They are assumed to be independent of the concentrations of the species and the surface potential.
The site number \( N_{s}^{\pm} \) and the total number of OH groups at the surface sites \( N_{m}^{s} \) is given by

\[
N_{m}^{s} = [M-OH] + [M-OH^{+}] + [M-O^{-}]
\]  

Using these site number definitions, the surface charge density can be defined as

\[
\sigma_{\pm} = (F/A)N_{m}^{s}\{(M-OH^{+})/[M-O^{-}]\}/\{(M-OH) + [M-OH^{+}] + [M-O^{-}]\}
\]  

Introducing the equilibrium constants [56]:

\[
\sigma_{\pm} = F(N_{m}^{s}/A)\{(\exp(-F_{0}/RT)/k_{M,1}^{\text{int}}) - (k_{M,2}^{\text{int}}exp(-F_{0}/RT))/[\mathcal{H}^{+,b}])\}/\{1 + (\exp(-F_{0}/RT)/k_{M}^{\text{int}}) + (k_{M,1}^{\text{int}}exp(-F_{0}/RT))/[\mathcal{H}^{+,b}]\}
\]

The total number of OH per nm\(^{2}\) can be determined by, e.g., titration or adsorption experiments. The site density is very dependent on the experimental method and model of analyzing the data [56].

Formally, the charged surfaces are subdivided into non-polarizable and polarizable surfaces. The polarizable surfaces do not share potential-determining ions (PDI's) with the liquid. Non-polarizable surfaces are characterized by one common species for the surface matrix and the intervening solution. This is typical for most solids where potential-determining cations dissolve partially from the surface, thus determining the surface charge \( \psi_{0} \). Assuming the metal oxide surface to be fully polarizable (insoluble) at constant ionic strength (i.e. neglecting the ion contribution), we may relate the electrochemical potential to the interfacial energy by adding the electrical work to the Gibbs-Duhem equation (Eq. 3a). At constant \( T \) and \( P \) we obtain

\[
(n_{H}^{s})d\mu_{H} + (n_{OH}^{s})d\mu_{OH}) + Ad\sigma_{SL} + N_{m}^{s}d\psi_{0} = 0
\]  

\[
(I_{H}^{s} - I_{OH}^{s})d\mu_{H} + d\sigma_{SL} + \sigma_{\pm}d\psi_{0} = (\sigma_{\pm}/F)d\mu_{H} + d\sigma_{SL} + \sigma_{\pm}d\psi_{0} = 0
\]

where \( \sigma_{\pm} \) is the surface charge density. This is the Lippmann equation:

\[
-d\sigma_{SL} = \sigma_{\pm}d\psi_{0} + (\sigma_{\pm}/F)d\mu_{H} = \sigma_{\pm}d\psi_{0} + (I_{H}^{s} - I_{OH}^{s})d\mu_{H}
\]

This quasi-thermodynamic relation defines an electrical and a chemical contribution to the interfacial energy. The difference between the solid and liquid phases may be varied by an externally applied electrical potential \( V \). The electrical potential difference \( U = \Delta V \) can be used to replace \( \Delta \psi_{0} \). Deriving the surface charge density with respect of the surface potential at constant chemical potential for the protons, \( \mu_{H} \):

\[
-(d\sigma_{SL}/dV)_{P,T,\mu} = (\sigma_{\pm})_{L} = -(\sigma_{\pm})_{S} \Rightarrow (\sigma_{\pm})_{L} = F(I_{H}^{s} - I_{OH}^{s})
\]
This is the electrocapillarity equation (Fig. 1.23), which shows that when \( \frac{d \sigma_{SL}}{dV} > 0 \), then \( \Gamma_H^s > \Gamma_H^o \) and when \( \frac{d \sigma_{SL}}{dV} < 0 \), then \( \Gamma_H^s > \Gamma_{OH}^o \). A maximum surface energy occurs at pH\(_{PZC}\), when \( \frac{d \sigma_{SL}}{dV} = 0 \):

\[
\left( \frac{d \sigma_{SL}}{d \psi_0} \right)_{P,T,\mu} = 0 \Rightarrow \Gamma_H^s = \Gamma_{OH}^o
\]  

(138)

Thus, at the pH\(_{PZC}\), \( \sigma = 0 \) and thence \( \Gamma_H^s = \Gamma_{OH}^o \) as expected. In the absence of specifically adsorbing ions, \( \sigma_{SL} \) is at a maximum at pH\(_{PZC}\). A shift from this position due to the presence of specifically adsorbing ions is denoted the Esin-Markov effect [57]. The chemical contribution may be evaluated assuming Langmuir isotherm conditions for the chemical potential (e.g. for protons alone) [58]:

\[
d\mu_H = RT \ln \left[ \frac{\theta}{(1 - \theta)} \right]
\]  

(139 a)

Again, assuming that only M–O\(^-\) and M–OH\(_2^+\) sites exist, we may write

\[
\theta = \frac{\sigma_{max} + \sigma_\pm}{2 \sigma_{max}}
\]  

(139 b)

where \( \sigma_{max} = 2F\Gamma_{PZC} \) and \( \Gamma_{PZC} \) is the surface excess at pH\(_{PZC}\) (\( \sigma = 0 \) and \( \psi_0 = 0 \)) and \( \Gamma_H = \Gamma_{OH} = 1/2 \Gamma_{max} \). The equation shows that the interfacial tension is maximum at pH\(_{PZC}\) and that both chemical and charge factors contribute to the decrease in surface energy from PZC. Since the adsorption causes a decrease in interfacial energy and since spontaneous dispersion of the system occurs for \( \sigma_{SL} < 0 \), a point of zero interfacial tension pH\(_{PZIT}\) may be identified. In the presence of PDIs, two pH\(_{PZIT}\) may be identified on both sides of the maximum. In the presence of electrolytes, a range (pH > pH\(_{PZIT}\)) has been identified where the surface charge becomes saturated [58].

In addition to a complete account of electrolytes in the double layer provided by the Gouy-Chapman approach [16, 31], Stol and de Bruyn offer the following simplified solution to the integrated interfacial energy [58]:

\[
\Delta \sigma_{SL} \approx 2 \left( RT/F \right) (\sigma_- - \sigma_+) - \left( RT/F \right) (\sigma_+^2 / \sigma_{max})
\]  

(140)

where \( \sigma_- \) and \( \sigma_+ \) are the charge densities of the anions and cations, respectively, in the diffuse part of the double layer.

Recalling equation (136 c) \( (d\mu_H = RT \ln \sigma_H \approx 2.3 RT dpH) \), the Lippmann equation may be rewritten in the form

\[
d\sigma_{SL} = -\sigma_\pm d\psi_0 + 2.3 \sigma_\pm (RT/F) dpH
\]  

(141)

Barthes-Labrousse and Joud derived two limiting conditions from this equation [48].

First, when the pH of the aqueous solution is close to pH\(_{PZC}\) of the metal oxide surface, a parabolic dependence of the integrated \( \sigma_{SL} \) on pH is observed (Fig. 1.24):
\[ \Delta \sigma_{SL} = -8RT(c_{1:1}/\kappa_d)(pH_{PZC} - pH)^2 \]  
\(142\)

where \(c_{1:1}\) is the concentration of possible supporting aqueous 1:1 electrolyte solution and \(1/\kappa_d\) is the Debye screening length of the Gouy-Chapman equation. The ratio expresses the amount of ions per unit surface area.

Second, if it is assumed that the mineral acid or base used to adjust the pH does not influence the components (e.g. \(\sigma_{SO}\) and \(\gamma_{OW}\)) other than the solid in contact with water, they may derive the Young equation (cf. Eq. 106):

\[
\frac{d\sigma_{SW}}{dpH} = -\gamma_{OW}(d \cos \Theta_{SOW})/dpH = \gamma_{OW} \sin \Theta_{SOW}(d \Theta_{SOW}/dpH)
\]  
\(143\)

In the presence of electrolytes, \(\gamma_{OW}\) is, however, expected to change but is easily measurable. When the surface charge density is close to the maximum value \((\sigma_{max})\), the interfacial surface energy is linearly dependent on pH (cf. Eq. 141):

\[
\frac{d\sigma_{SW}}{dpH} = 4.6(RT/F)(\sigma_{\pm})_{max}
\]  
\(144\ a\)

\[
(\sigma_{\pm})_{max} = -(F/4.6RT)\gamma_{WO}(d \cos \Theta_{SOW}/dpH)
\]  
\(144\ b\)

\[
(\sigma_{\pm})_{max} = (F/4.6RT)\gamma_{WO} \sin \Theta_{SOW}(d \Theta_{SOW}/dpH)
\]  
\(144\ c\)

Note that, in order to avoid the development (adsorption and spreading) of an aqueous surface film \([\sigma_{S(W)}]\), the measurements were made in a hydrocarbon \((O)\) liquid. Hence \(\gamma_{OW}\) represents the interfacial tension between an aqueous solution \((W)\) and a hydrocarbon (oil, \(O\)) and \(\Theta_{SOW}\) the contact angle of the sessile aqueous drop on the solid \((S)\) immersed in the hydrocarbon.

The influence of the electrolyte concentration and of pH on the surface tension of water and on its contact angle with the hydrophilic silica in air (Table 1.12) may be related to the previous equations by replacing the oil medium by air.
Assuming that $pH_{PZC} \approx 2$ and that the number of surface sites were $N_s/A \approx 1.5 \text{ nm}^2$ \cite{56}, the surface charge density was calculated using Eq. (145) and the change in surface energy using Eq. (142), where $RT(c_{1,1}/K_d) \approx kT(N_s/A)$. The results were not realistic and are not listed in Table 1.12. The change in contact angle and the change in $pH$ (Eq. 146b) also did not balance. Obviously, there must be some other effects that are not included in the models offered. One reason may be the enhanced surface pressure of electrolyte solution or that the $pH_{PZC}$, assumed to be 2, is shifted upon electrolyte addition. Therefore, the calculations were repeated assuming the $pH_{PZC}$ to be 6, but this did not improve the results. The underlying assumption that the concepts of a fully polarizable surface can be applied is not supported by the experiments.

In the absence of a water film on the surface, the equations should apply also in the absence of the hydrocarbon liquid. The slopes are proportional to $\sigma_{\text{max}}$. Bain and Whitesides related the contact angle to the $pK_a$ values of the carboxyl groups in a film \cite{60}. The model can be modified to apply to the surface M–OH groups with a single acid constant:

$$\cos \theta_{SL} = \cos \theta_{SL}(PZC) - (N_s kT/A \gamma_{LV}) \ln[c_H/(c_H - K_a)] \quad (146a)$$

Since $pH_{PZC} = pK_a$, the equation takes the form ($c_H << K_a$)

$$\gamma_{LV}[\cos \theta_{SL} - \cos \theta_{SL}(PZC)] = 2.3kT(N_s/A)(pH - pH_{PZC}) \quad (146b)$$

Obviously, when $pH = pH_{PZC} = K_{M,1}^{\text{int}} = pK_a$ then $\cos \theta_{SL} = \cos \theta_{SL}(PZC)$ and the contact angles of water showed the typical maximum. The derivative $[\gamma_{LV} \cos \theta_{SL} - (\gamma_{LV}(PZC) \cos \theta_{SL}(PZC))] / 2.3kT(pH - pH_{PZC})$ should thus give the change in the number of surface sites ($N_s/A$) produced by the change in $pH$

<table>
<thead>
<tr>
<th>[NaCl] (mol dm$^{-3}$)</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>pH</td>
<td>2.05</td>
</tr>
<tr>
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<td>$\theta_{SW}$ (°)</td>
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</tr>
<tr>
<td></td>
<td>$\theta_{SW}$ (°)</td>
<td>45.31</td>
</tr>
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(Table 1.12). Assuming that $\text{pH}_{\text{PZC}} \approx 2$ and that the number of surface sites were originally $(N^s/A) \approx 4/\text{nm}^2$ the change in surface charge density calculated using Eq. (146b) is of the order of only 1–5%.

1.5.3

Adsorption Isotherms for Competitive Interaction at Surface Sites

The adsorption isotherms discussed so far can be extended to include the displacement of e.g. previously adsorbed liquid (solvent, $L$) molecules by base molecules ($B$) from solution:

\[
(AL)^s + B^b \leftrightarrow (AB)^s + L^b
\]

\[
K_L = (a_{AB}^s a_L^b)/(a_{AL}^s a_B^b) = [(x_{AB}^s/x_{AL}^s)(x_B^b/x_L^b)(f_{AB}^a f_B^b/f_{AL}^a f_L^b)]
\]

where $K_L = K_{ads}$ in previous equations.

Assuming ideal conditions both at the surface and in the bulk (dilute) solution, we may omit the term including the activity coefficients. If we additionally introduce $x_{AL}^s = 1 - x_{AB}^s$ and $x_L^b/x_B^b = c_L^b/c_B^b$ (molar concentrations) into the equilibrium constant, then

\[
K_L = [x_{AB}^s/(1 - x_{AB}^s)](c_L^b/c_B^b)
\]

Rearrangement gives

\[
x_{AB}^s = [c_B^b K_L/(c_L^b + c_B^b K_L)]
\]

This is one form of the Langmuir adsorption isotherm where $x_{AB}^s$ represents the surface site occupancy ($\theta$) of equal non-communicating ideal surface sites. Note that $c_L^b$ has been maintained in the equation in order to keep $K_L$ dimensionless.

Two limiting cases can be anticipated:

1. If $a_{AB}^b << 1$, i.e. when $c_L^b >> c_B^b$, we find $\theta = x_{AB}^s = (c_B^b/c_L^b)K_L$, representing dilute solutions.

2. If $a_{AB}^b >> 1$, i.e. when $c_L^b << c_B^b$, we find $\theta = x_{AB}^s = 1$, representing a monolayer of adsorbate molecules.

The experimental data are linearized by inverting the equation:

\[
1/x_{AB}^s = [c_B^b/(c_B^b K_L)] + 1
\]

A plot of $1/x_{AB}^s$ against $1/c_B^b$ should result in a straight line with intercept equal to unity and a slope of $c_B^b/K_L$. 

---

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Recognizing that \( x_{AB}^{s} = n_{AB}^{s}/(n_{AB}^{s})_m \) \((m = \text{maximum number of surface sites})\) and multiplying both sides by \( c_B^b \), we obtain

\[
c_B^b/n_{AB}^{s} = c_L^b/(n_{AB}^{s})_m K_L + c_B^b/(n_{AB}^{s})_m
\]

which is the typical form used (Fig. 1.25). A plot of \( c_B^b/n_{AB}^{s} \) against \( c_B^b \) is expected to give a straight line with an intercept \( c_L^b/(n_{AB}^{s})_m K_L \) and a slope of \( 1/(n_{AB}^{s})_m \). Since the total volume \( (V) \) is known for dilute solutions, \( n_{AB}^{s} = n_B^b - c_B^b V \) and \( n_L^b = c_L^b V \). The number of surface sites is \( N_m^{s} = N_A(n_{AB}^{s})_m \) and the area occupied by one site is \( a = A/N_m^{s} = w_A A_w/N_m^{s} \). In this calculation, it is assumed that there is no (surface or concentration) potential against which the adsorption occurs.

The molar Gibbs free energy of adsorption is given by

\[
\Delta G_{m,\text{ads}}^{s} = -RT \ln K_L = \Delta H_{m,\text{ads}}^{s} - T \Delta S_{m,\text{ads}}^{s}
\]

For spontaneous adsorption, \( \Delta G_{m,\text{ads}}^{s} \) must be negative. \( \Delta S_{m,\text{ads}}^{s} \) is also negative since the motion in three dimensions is restricted to bound molecules in two dimensions. Self-evidently, \( \Delta H_{m,\text{ads}}^{s} \) must be negative, corresponding to an exothermic process.

Suppose that the solid is homogeneous and that the dispersion solvent \( (L) \) and the base \( (B) \) molecules adsorb on acidic surface sites \( (A) \) of equal average molar surface areas \( A_m(= N_A a, \text{where} \ a \ \text{is the average area occupied by each site}) \). Suppose, further, that both the bulk and the surface phases are ideal. Under these circumstances, at adsorption equilibrium, we find for the fractional adsorption from dilute solutions of \( B \) in indifferent (non-adsorbing) liquid \( L \)

\[
\pi_{S(B):L} = \sigma_{SL} - \sigma_{S(B):L} = (RT/A_m) \ln(x_{AB}^{s}/x_B^{b})
\]

Correspondingly, we find for the fractional adsorption of \( L \) in non-adsorbing \( B \)

\[
\pi_{S(L):L} = \sigma_{SL} - \sigma_{S(L):L} = (RT/A_m) \ln(x_{AL}^{s}/x_A^{b})
\]

The latter equation serves as an illustration of the partial coadsorption of the indifferent dispersion medium. Obviously \( (x_{AB}^{s} + x_A^{s}) = (x_{AB}^{s})_{\text{max}} = (x_A^{s})_{\text{max}} \). We may therefore write formally for the replacement of adsorbed \( L \) by \( B \) in an indifferent medium:

\[
\pi_{S(B,L)} - \pi_{S(B):L} = \pi_{S(L):L} - \pi_{S(L):L} = RT/A_m \ln(x_{AB}^{s} x_B^{b}/x_A^{s} x_{AL}^{b})
\]

We define the molar Gibbs free energy of adsorption of monodentate bases on monodentate acid surface sites thus replacing preadsorbed solvent molecules in terms of surface pressure for the adsorbed molecules:
Fig. 1.25 Linearized Langmuir adsorption isotherms for phenol, benzylamine and 3-phenylpropionic acid (3-PPA) on porous silica powder from cyclohexane. Fits using both the Freundlich and the Langmuir isotherms to draw the line through the experimental points for phenol are also shown (from [61], with permission).
\[ \Delta G_{m, \text{ads}}^s = -RT \ln K_{\text{ads}}^s = -RT \ln \left( \frac{x_{AB}^s}{x_{AL}^s} \frac{x_{PB}^b}{x_{PA}^b} \right) \]  
\[ \Delta G_{m, \text{ads}}^s = -(RT/A_m) \ln \left( \frac{x_{AB}^s}{x_{PB}^b} \right) + \ln \left( \frac{x_{PB}^b}{x_{AL}^s} \right) \]  
\[ \Delta G_{m, \text{ads}}^s = -\pi_{S(B)\ell} + \pi_{S(L)\ell} = \Delta \mu_{S(B)\ell} - \Delta \mu_{S(L)\ell} \]

Utilizing Boltzmann equation the overall Gibbs free energy can thus be subdivided into its components.

The surface pressure can be determined \( [x_{AB}^s = n_{AB}^s/(n_{AB}^s)_{\text{max}} = x_{AB}^s/(x_{AB}^s)_{\text{max}}] \) as a depletion from the solution or an adsorption on the surface with different (e.g. spectroscopic) techniques. We define a bidentate surface \((S^{AB})\) with predominantly acidic \((S^{(A)}B = A^s)\) and basic \((S^{(A)}B = B^s)\) interactions, respectively. Likewise, for a bidentate probe \((P^{AB})\) we denote \((P^{A(B)} = P^A)\) and \((P^{A(B)} = P^B)\). For a bidentate probe adsorbing from an indifferent solution onto a bidentate surface we may then write:

\[ (P^B)^b + (P^A)^b + A^s + B^s \leftrightarrow (P^B)^s \times (P^A)^s \]

\[ K_{\text{ads}} \approx \left( \frac{x_{PB}^s x_{PB}^b}{x_{PA}^s x_{PA}^b} \right) \left( a_A^s a_B^b \right) \]

Assuming that the surface may be assumed ideal \((a_A^s = a_B^b = 1)\) we find for the fractional adsorption of \(P^A\) and \(P^B\) in the indifferent liquid \((L)\):

\[ \pi_{S(PB)\ell} = \sigma_{SL} - \sigma_{S(PB)\ell} = (RT/A_m) \ln \left( \frac{x_{PB}^s}{x_{PA}^s} \right) \]

\[ \pi_{S(PA)\ell} = \sigma_{SL} - \sigma_{S(PA)\ell} = (RT/A_m) \ln \left( \frac{x_{PA}^b}{x_{PB}^b} \right) \]

The sum of these reactions in indifferent media gives:

\[ \pi_{S(PA, PB)\ell} = \pi_{S(PA)\ell} + \pi_{S(PB)\ell} = \sigma_{S(L)\ell} + \sigma_{S(B)\ell} + 2\sigma_{SL} \]

\[ \pi_{S(PA, PB)\ell} = RT/A_m \ln \left( \frac{x_{PB}^s x_{PA}^b}{x_{PA}^s x_{PB}^b} \right) + \ln \left( \frac{x_{PB}^s x_{PA}^b}{x_{PA}^s x_{PB}^b} \right) \]

The molar Gibbs free energy of adsorption then takes the form:

\[ \Delta G_{m, \text{ads}}^s = -RT \ln K_{\text{ads}}^s = -RT \ln \left[ \frac{x_{PB}^s x_{PA}^b}{x_{PA}^s x_{PB}^b} \right] \]

\[ \Delta G_{\text{ads}}^s = -\pi_{S(PA)\ell} + \pi_{S(PB)\ell} = \Delta \mu_{S(B)\ell} + \Delta \mu_{S(L)\ell} \]

where all terms may be determined experimentally as discussed previously. The mass balance is recovered when summing the contributions:

\[ n_p = n_{PA} + n_{PB} = (n_{PA}^s + n_{PB}^s) + (n_{PA}^b + n_{PB}^b) \]

\[ n_p = n_{PA}^b (k_{PAB}^s + 1) + n_{PB}^b (k_{PBA}^s + 1) \]

since \( k_{PBA}^s = (n_{PBA}^s/n_{PB}^b) \) and \( k_{PBA}^s = (n_{PBA}^s/n_{PA}^b) \).
There is another way of evaluating the competitive adsorption of basic molecules with the solvent molecules or with a competing base for the same surface sites [62–64]. The preferential adsorption \( n_B^b \) (= surface excess, \( n_B^b \), per unit mass of solid substrate powder, \( w_S \)) from a mixed solvent on a solid surface (specific surface area \( A_w \)) may also be quantified by considering the following limiting cases [65]:

1. The total amount of competing components (B and L = solvent) before adsorption: \( n_O = n_{BO}^b + n_{LO}^b \).
2. The total amount of competing components in bulk solution at adsorption equilibrium: \( n_T^b = n_B^b + n_L^b \).
3. The total number of competing components adsorbed per unit mass of solid at adsorption equilibrium: \( m_{AT}^s = m_{AB}^s + m_{AL}^s \), where \( m_B^s = n_B^b/w_S \) and \( n_B^b = w_B/M_B \) and \( c_B = n_B/V \).

Note that \( n_{AB}^s = n_{BO}^b - n_B^b \). Consequently, \( n_O = (n_B^b + w_S m_B^s) + (n_L^b + w_S m_L^s) \).

Since \( n_B^b/n_L^b = x_B^b/x_L^b \), the mass balance may be described by

\[
\begin{align*}
    n_{BO}^b &= n_L^b x_B^b/x_L^b + w_S m_B^s \\
    n_{LO}^b &= n_A^b x_L^b/x_A^b + w_S n_L^s
\end{align*}
\] (157 a)

Multiplication with \( x_L^b \) and \( x_B^b \), respectively, gives

\[
\begin{align*}
    n_{BO} x_L^b &= n_L^b x_B^b + w_S m_B^s x_L^b \\
    n_{LO} x_B^b &= n_B^b x_L^b + w_S m_L^s x_B^b
\end{align*}
\] (158 a)

Subtraction of Eq. (158 b) from Eq. (158 a) and considering that \( n_L^b x_B^b = n_B^b x_L^b \), yields

\[
    n_{BO} x_L^b - n_{LO} x_B^b = w_S (m_B^s x_L^b - m_L^s x_B^b)
\] (159)

Substitution of \( x_L^b = 1 - x_B^b \) and \( n_{LO} = n_O - n_{BO} \) and recalling that \( n_{BO} = n_O x_{BO} \) gives the equation for the surface excess isotherm [62–64]:

\[
    n_O^b x_B^b - w_S = m_B^s x_L^b - m_L^s x_B^b
\] (160)

where \( \Delta x_B = x_{BO} - x_B \), which is frequently determined as depletion, e.g. through the change in refractive index or by separate sampling using gas chromatography. The plot of \( n_O^b x_B^b - w_S \) against \( x_B \) indicates, for positive values (i.e. when \( x_{BO} > x_B \)), a preferential adsorption of component B over L on the solid S. It then follows that a negative plot of \( n_O^b x_B^b - w_S \) indicates that the liquid component L is negatively adsorbed and the surface phase is less rich than the bulk in L. Figure 1.26 shows the subdivision of the composite isotherm into two general classes.

Provided that a linear section can be identified in the composite isotherm, the thickness of the adsorbed layer can be estimated in the following way. Exchanging \( x_L = 1 - x_B \) in Eq. (160) gives
Evidently the extrapolated value at $x_B^0 = 0$ gives $(m_B^s)_{xL=1}$ and the extrapolated value at $x_B^1 = 1$ gives $-(m_L^s)_{XB=1}$. Monolayer adsorption is indicated if [63]

$$
(m_B^s)_{crit}/(m_B^s)_{max} + (m_L^s)_{crit}/(m_L^s)_{max} = 1
$$

Assuming that the probe molecules change surface tension and that all depleted molecules adsorb on the solid surface, the Gibbs adsorption equation can be used to determine the surface excess:

$$
n_0 \Delta x_B^b / \omega_S = m_B^s - (m_B^s + m_L^s)x_B^b
$$
The influence of the composition on the surface energy (σ_{SV}) tension of the mixed liquid may also be derived in the following way. Since \( n_b^s = n_{BO} - n_b \), the composite isotherm Eq. (160) may be written in the form

\[
n_o \Delta x^b_b / A = \Gamma - \Gamma_L x^b_b
\]

Introducing \( x^L_b = 1 - x^b_b \), we obtain

\[
n_o \Delta x^b_b / A = \Gamma - (\Gamma_B + \Gamma_L) x^b_b \approx \Gamma^{(L)} x^b_L
\]

\[
\Gamma^{(L)} = (n_o \Delta x^b_b / A x^b_L)
\]

The latter equality assumes that the phase boundary is normalized to erase the surface excess of the dispersion liquid and to account only for the surface excess of the solute probe (B). Replacing \( \Gamma^{(L)} \) with the Gibbs adsorption equation [64]:

\[
-x^b_L (1/RT) [d\sigma_{S(b)L} / d \ln a_b] = \Gamma_B - (\Gamma_B + \Gamma_L) x^b_L = \Gamma_B - \Gamma_{\max} x^b_B
\]

It is thus possible to quantify the preferential adsorption on the L/V surface by simply measuring the surface tension of the liquid as a function of the composition. Since \( n_o \Delta x^b_b / A \) represents the change in surface tension with the base probe concentration (B), a positive deviation should indicate preferential adsorption and a negative deviation competitive desorption of component (B). For U-shaped isotherms, the component with the lower surface tension (B) adsorbs preferentially on the liquid surface (positive surface excess). In dilute solutions, \( x_b = 0 \) and hence \( \Gamma_B = \Gamma^{(L)} \).

The model introduced may be combined with the adsorption equilibrium, i.e. when a liquid (L) in contact with the solid (S) is replaced by the basic component B [64]:

\[
\pi_{S(b)L} = \sigma_{S(b)L} = \frac{(RT / A) \int_{a_b=1}^{a_B} (n_o \Delta x^b_b / x_L) d \ln a_B^b}{\ln K_{AB}}
\]

\( \Delta \) plot of \( (n_o \Delta x^b_b / x_L) \) against \( \ln a_B^b \) may thus be graphically integrated to give \( \pi_{S(b)L} \).

We now have all the elements required to relate the key parameters of adsorption to the molecular models described in Table 1.7: \( \Delta G^{a\text{ads}}_{AB} = -RT \ln K_I \) should be proportional to \( \ln K_{AB} \) of the Edwards, Maria and Gal, Handcock and Marcianno models, and \( \Delta H_{\text{ads}} \) should equal \( \Delta H_{AB} \) of the Drago and Wayland and Kroeger and Drago models. The implicit condition is that the equilibrium constant refers to adsorption from a fully dispersive solvent and that the enthalpy of wetting the solid with the dispersive solvent has been subtracted from the total enthalpy of adsorption to give \( \Delta H_{AB} \). No consideration has been given, however,
to whether the process is considered to occur solely at the interface or at an interface in equilibrium with the bulk solution. Tentatively, the molecular models relate to interactions at surfaces, whereas the adsorption concerns an equilibrium of the probe molecules between the bulk solution and the surface. The thermodynamic function relating to the surface alone is the surface pressure. Moreover, since no $PV$ work has been considered, the proper state function would, as shown, be the internal energy. If salient specific (AB) interactions are aimed for, the third-order derivatives from the free energies ($F$ or $G$) should probably be superior state functions for the correlation.

1.6 Contributions from Surface Heterogeneities

The surface of a solid substrate differs considerably from that of a liquid in that the heterogeneities are not equilibrated by the rapid molecular motions. In reality the solid surface is not molecularly smooth, but consists of surface heterogeneities, such as asperities, dislocations (steps, kinks, adatoms and vacancies) and different crystal habits (crystal planes) and other physico-chemical surface heterogeneities (Fig. 1.27). At each heterogeneous site an energy is stored (e.g., as broken bonds) providing the surface with specific binding sites, which influence the wetting phenomena.

Two cases are considered which influence the properties of the system. First, the surface may be of a chemically heterogeneous character, for which the Brønsted interaction and adsorption isotherm are discussed. Self-evidently, there is an even more extensive influence on the Lewis interaction sites, exemplified, e.g., by the dislocations found at the molecular level on the surface. Second, the surface may at the macroscopic level be structurally rough, which influences the wetting for extremely hydrophobic and hydrophilic surfaces. In the latter case, the effect of line tension must be considered.

Fig. 1.27 Solid surfaces may be discontinuous on both the molecular and the macroscopic scale. At the molecular level the dislocations (steps, kinks, adatoms and vacancies) liberate energetic bonds, the number of which depends on the direction of cleavage.
1.6.1 Non-ideal Solid–Liquid Brønsted (Charge) Interactions

Jolivet strongly criticizes the naivistic treatment of solid surfaces described previously and claims that no group may in reality exhibit an amphoteric character, in spite of the fact that they may be positively or negatively charged as a function of pH [55]. Instead, a single equilibrium occurs for each site with $pK_{X,m}^{\text{int}} = pH_{PZC}$. This means that the successive involvement of two protons on the same surface site appears completely unrealistic. Instead, for the equilibria in Eq. (131) to apply, they must all be assigned to different surface groups. The latter view is fully possible, since the surfaces contain in reality imperfections representing different crystal planes with the surface elements being involved in different degrees of binding [66]. Following the multisite complexation (MUSIC) model and the formal bond valence concept, we extend our focus on silica and titania to include alumina in order to illustrate the capabilities of this model. For alumina, having the $z = +3$ and coordination numbers 4 and 6, we find the following sequence for singly coordinated OH ligands $n = 1$ and $m = 1$ [55, 56]:

\[
\begin{align*}
\text{Al} - \text{OH} & \quad v = 3/4 = 3/4 \quad \delta = 3/4 - 2 + 1 = -1/4 \quad \text{Al(4)} - \text{OH}^{1/4-} \\
\text{Al} - \text{OH} & \quad v = 3/6 = 1/2 \quad \delta = 1/2 - 2 + 1 = -1/2 \quad \text{Al(6)} - \text{OH}^{1/2-}
\end{align*}
\]

However, there are also doubly and triply coordinated OH ($n = 2, 3; m = 1$) [55]. The dissociation equilibria should therefore be written in the generalized form (cf. Eq. 132):

\[
\begin{align*}
\text{Al}_n\text{OH}^{(nv-1)} & \leftrightarrow \text{Al}_n\text{O}^{(nv-2)} + \text{H}^+ & K_{n,1}^{\text{int}} = \frac{[\text{Al}_n\text{O}^{(nv-2)}][\text{H}^+]}{[\text{Al}_n\text{OH}^{(nv-1)}]} & (167\ a) \\
\text{Al}_n\text{OH}_2^{(nv)} & \leftrightarrow \text{Al}_n\text{O}^{(nv-1)} + \text{H}^+ & K_{n,2}^{\text{int}} = \frac{[\text{Al}_n\text{O}^{(nv-1)}][\text{H}^+]}{[\text{Al}_n\text{OH}_2^{(nv)}]} & (167\ b)
\end{align*}
\]

For gibbsite, Al(OH)$_3$, the large 001 faces (13.8 OH per nm$^2$) are characterized by doubly coordinated OH groups ($n = 2$) while the sides of the platelets ($hk0$ faces) contain singly (9.6 OH per nm$^2$) and doubly (4.8 OH per nm$^2$) coordinated OH groups (Fig. 1.28).

For these groups, Jolivet [55] estimates ($N_C = 6$) that for the dissociations

\[
\begin{align*}
\text{Al} - \text{OH}_2^{1/2+} & \leftrightarrow \text{Al} - \text{OH}^{1/2-} + \text{H}^+ & pK_{1,2}^{\text{int}} = 10 & (168\ a) \\
\text{Al}_2 - \text{OH}^0 & \leftrightarrow \text{Al}_2 - \text{O}^- + \text{H}^+ & pK_{2,1}^{\text{int}} = 12.3 & (168\ b) \\
\text{Al}_2 - \text{OH}_2^+ & \leftrightarrow \text{Al}_2 - \text{OH} + \text{H}^+ & pK_{2,2}^{\text{int}} = -1.5 & (168\ c)
\end{align*}
\]
The pK$_{1,m}^\text{int}$ of the [Al–OH]$^{1/2–}$/[Al–O$^–$] equilibrium (pK$_{1,1}^\text{int} = 23.88$) is very high and the singly coordinated groups are therefore present only as Al–OH$^{1/2–}$ or Al–OH$^2_1^{+}$, depending on the pH. James and Parks report (C. P. Huang, PhD Thesis, 1971) for γ-Al$_2$O$_3$ pK$_{1,2}^\text{int} = 7.89$ (0.42 OH per nm$^2$) and pK$_{1,1}^\text{int} = 9.05$ (0.39 OH per nm$^2$) and for α-Al$_2$O$_3$ pK$_{1,1}^\text{int} = 8.50$ and pK$_{2,2}^\text{int} = 9.70$ (2.7 OH per nm$^2$) in the presence of 0.1 mol dm$–3$ NaCl. Doubly coordinated groups exist only as Al$^2–$OH within the normal pH range. For Al$_2$O$_3$, the following dissociation constants pK$_{n,1}^\text{int}$ were calculated: pK$_{1,1}^\text{int}$ (–Al–OH$^{1/2–}$) = 24, pK$_{2,1}^\text{int}$ (–Al$_2$–OH$^0$) = 12.3 and pK$_{3,1}^\text{int}$ (–Al$_3$–OH$^{1/2+}$) = 1.6. The increased acidity or weakened strength of the O–H bond with increased degree of coordination of the hydroxyl ligand is clearly reflected.

If one or more of the pK$_{M,m}^\text{int}$ is outside the available pH range, only a single equilibrium occurs where pH$_{PZC} = \text{pK}_{M,m}^\text{int}$. Jolivet [55] also compared the experimental pH$_{PZC}$ with those calculated with the MUSIC model: Al$_2$O$_3$ (z = 3, C N=6, $\text{pK}_{M,1}^\text{int} = 9.1$). This compares well with the experimentally found value (9.1) and with those reported by James and Parks for γ-Al$_2$O$_3$ (pH$_{PZC} = 8.47$) and for α-Al$_2$O$_3$ (pK$_{PZC} = 9.10$). According to Jolivet, we may write [55, 56]

\[
\Sigma pK_{X}^\text{int} - 2p[H^+] = pK_{1,1}^\text{int} + pK_{1,2}^\text{int} - 2p[H^+] = \log([\text{XOH}^+_2]/[\text{XO}^–]) \quad (169)
\]

At the pH$_{PZC}$ where $\psi_0 = 0$, [H$^+$] = [H$^{+}$] and [XOH$^2_2$] $\approx$ [XO$^–$], we find

\[
\text{pH}_{PZC} = 1/2(pK_{1,1}^\text{int} + pK_{1,2}^\text{int}) = 1/2\Sigma pK_{X}^\text{int} \quad (170a)
\]

\[
\text{pH}_{PZC}(\text{Al}_2\text{O}_3) = 1/2\Sigma pK_{\text{Al}}^\text{int} = 1/2(pK_{1,1}^\text{int} + pK_{1,2}^\text{int}) = 9.1 \quad (170b)
\]

Obviously, the pH$_{PZC}$ values compare favorably with the values found experimentally and calculated with the MUSIC model. The equilibria can also be written in the following way:

\[
\Delta pK_{\text{Al}}^\text{int} = pK_{1,1}^\text{int} - pK_{1,2}^\text{int} = \log([\text{AlOH}]/[\text{AlOH}_2^+/\text{AlO}^–]) = 1.2 \quad (171)
\]

We may draw the following general conclusions regarding any single metal (M) surface sites [55]:

- If $\Delta pK_{X}^\text{int} > 4$ (high), then [XOH] $\gg$ [XOH$^2_2$] $\approx$ [XO$^–$] and the acid [XOH$^2_2$] is much stronger than the acid [XOH] and the base [XO$^–$] is much stronger than...
the base [XOH]. The predominant species is XOH and the number of ionized species is very small.

- If $\Delta pK_{i}^{\text{int}} < 4$ (small), the XOH$^+$ and XOH acids and XO$^-$ and XOH bases, respectively, have similar strengths. Then the number of charged groups XOH$^+$ and XO$^-$ is large.

These predictions seem, however, not to be met by a number of acidic and basic groups listed by James and Parks [67], indicating a variable hydroxyl group density for oxides. A more refined analysis of the MUSIC model shows that the dissociation equilibrium must be considered separately for each surface group. The pH at which the net charge is zero depends on the relative fractions of each type of group, and also on their respective $pK_{i}^{\text{int}}$. For many oxides, cancelation of the global charge may take place through compensation. Moreover, the influence of neighboring hydroxyl groups must be taken into account. The hydroxyl groups decrease linearly with increase in temperature [68]. However, when the communication between the –OH groups ceases, the dependence on temperature is strongly reduced. In this case the rehydroxylation becomes much slower. In porous matrices doubly (geminal) and triply coordinated hydroxyl groups exist [66] which are not described by the MUSIC model and they are only fractionally available for chemical reactions.

1.6.2
Surface Energy of Coexisting Crystal Planes

Since the crystal habit of gibbsite is fairly symmetrical (Fig. 1.28), we may derive a simple model to resolve the surface energy for the two dominant crystal planes, i.e. the surface (face = F) and the sides (edge = E) in equilibrium with the saturated solution. The surface area, the volume and the thickness of the particle may be expressed in terms of the width ($w$) and a constant $k$ as follows:

$$A = 2kw^2 + 6tw$$

$$V = kw^2t$$

$$t = V/kw^2$$

where $k = (3/2)\sqrt{3} = 2.598$. The density ($\rho$) and molar mass ($M$) of gibbsite are known and we define the molar surface energy $G_m^s$ of the particle as

$$G_m^s = 2/3\{[2kw^2\sigma_{SV}(F) + 6wt\sigma_{SV}(E)]M\}/V\rho$$

Introducing the thickness, the equation takes the form

$$G_m^s = 2/3\{2kw^2\sigma_{SV}(F) + 6[\sigma_{SV}(E)/kw]M\}/V\rho$$
Keeping \( V \) and \( \rho \) constant, we derive the molar surface energy with respect to \( w \):

\[
\frac{dG_m}{dw} = 2/3\left\{4[kw\sigma_{SV}(F)] - 6[V\sigma_{SV}(E)/kw^2)]M]\right\}/V\rho \tag{173c}
\]

Since also the second derivative is positive, the extreme point is a minimum. For this equilibrium, we set the free energy derivative equal to zero and reintroduce the thickness:

\[
4[kw\sigma_{SV}(F)] = 6[V\sigma_{SV}(E)/kw^2)] = 6t\sigma_{SV}(E) \tag{174a}
\]

\[
\sigma_{SV}(E) = \frac{2kw\sigma_{SV}(F)}{3t} \tag{174b}
\]

We reintroduce this relationship into the original equation for the molar free energy and eliminate \( V \):

\[
\begin{aligned}
\sigma_{SV}(F) &= \frac{G_m^s tp}{4M} \\
\sigma_{SV}(E) &= \frac{kwG_m^s \rho}{6M}
\end{aligned}
\Rightarrow \frac{\sigma_{SV}(E)}{\sigma_{SV}(F)} = \frac{2kw/3t = 3.46}{} \tag{175}
\]

The ratio has been found to agree with electron microscope-measured ratios. For intermediate aging times, \( \sigma_{SV}(F) = 140 \pm 24 \) mJ m\(^{-2}\) and \( \sigma_{SV}(E) = 483 \pm 84 \) mJ m\(^{-2}\), which agree with experimentally determined values. It has been shown that the ratio of a variable mixture of hydrophilic and hydrophobic particles was linearly related to the contact angle determined with the Cassie model [69, 70]. Consequently, the measured average surface energy determined for gibbsite particles can be subdivided into the surface energy contributions of each crystal plane knowing the fraction of each partial surface. The opposite is also true: from the total surface energy the contributions of each crystal plane can be calculated.

1.6.3 Competing Multi-site Adsorption

The nature of these surface sites has been characterized using attributes such as polar, acid, basic, etc. In medium and high dielectric media, the surface sites may develop charges which are enhanced by surface reactions and isomorphic substitutions of the constituent atoms (ions). The driving force for the adsorption is to neutralize the excess energy of these surface sites. For adsorption on these surface sites a “generalized Langmuir equation” (GL) has been developed from the localized Langmuir (L) isotherm [71]:

\[
n_A^s/(n_A^s)_m = [(K_{GL}n_A)^q/(1 + K_{GL}n_A)^q]^r \tag{176}
\]

The constants \( q \) and \( r \) are assumed to characterize the width of the distribution function and lie within the range 0–1. The constant \( q \) characterizes the distribution widening in the direction of the lower adsorption energies and \( r \) represents this widening towards higher adsorption energies. For \( q = r = 1 \) the equation is
transformed back into the local Langmuir equation for adsorption on homogeneous solids. However, when $q = 1$ and $r = 1/k$ is between 0 and 1, a generalized Freundlich isotherm is obtained. This corresponds to an asymmetric, quasi-Gaussian energy distribution, with widening occurring in the direction of lower adsorption energies. When both $q$ and $r$ lie between 0 and 1, the equation describes the Langmuir-Freundlich isotherm, having a symmetrical quasi-Gaussian energy distribution of the sites. Alternatively, the adsorption energy determined with the Freundlich isotherm can be considered to be dependent on the degree of surface coverage (the lateral interaction between the adsorbate molecules). Empirically, the Freundlich adsorption equation is expressed as [16, 31]

$$m_{AB}^s = k_F (n_B^b)^{1/k}$$  \hspace{1cm} (177a)

$$\ln m_{AB}^s = \ln k_F + 1/k \ln n_B^b$$  \hspace{1cm} (177b)

where $k_F$ and $k$ are experimental constants. The logarithm of the amount adsorbed per unit mass of solid ($m_{AB}^s = n_{AB}^s/w_S$) is plotted against the logarithm of equilibrium concentration ($\ln n_B^b$) to give the constant $1/k$ as the slope and the constant $\ln k_F$ as the intercept. The enhanced fit over the Langmuir adsorption isotherm is illustrated for phenol on silica in Fig. 1.24.

For uniform sites ($k = 1$), the Freundlich isotherm is comparable to the Langmuir isotherm for dilute solutions:

Freundlich isotherm: $n_{AB}^s = k_F (n_B^b)^{1/k} \Rightarrow k_F = n_{AB}^s/n_B^b$

Langmuir isotherm: $n_{AB}^s = (n_{AB}^s)_L (n_B^b/n_L^b) K_L \Rightarrow K_L = n_{AB}^s/[(n_{AB}^s)_L (n_B^b/n_L^b)]$

Consequently, the constants used are related to each others as $k_F = K_L[(n_{AB}^s)_L/n_L^b]$.

According to Perkel and Ullman, the adsorption saturation $[(m_{AB}^s)_{\text{max}}]$ for polymers fits the equation [72]

$$w_{AB}^s/w_S = k_F M^k$$  \hspace{1cm} (177c)

The exponent can be related to the conformation that the polymer takes at the surface: $k = 0$ (in plane), $k = 1$ (upright), $k = 0.5$ (tangled and intertwined), $0 < k < 0.1$ (spherical threads).

The indifferent adsorption in excess of the Langmuir adsorption can be accounted for by setting the exponential constant of the Freundlich isotherm equal to one ($k = 1$). The resulting isotherm is then called a Henry isotherm. The Langmuir-Henry isotherm then takes the form [61]

$$(m_A^s)_{\text{LH}} = (m_A^s)_{\text{exp}} - k_H n_A = (m_A^s)_{\text{LH}} (K_{\text{LH}} n_A^b)/(1 + K_{\text{LH}} n_A^b)$$  \hspace{1cm} (178)

The Freundlich equation is particularly usable for the characterization of the concurrent adsorption on the different crystal planes. It may also be used for
characterizing the adsorption in multilayers. Since the degree of adsorption may continue infinitely with increasing \( n_B \), the equation is not suitable for high coverages. Assume that the probe molecules first adsorbed form a monolayer \((k=0)\) on the surface. In such cases, the multilayer adsorption may be described by the following equation:

\[
m_{AB}^* = (k_F)_m + k_F n_B^{1/k}
\]

The constant \((k_F)_m\) represents the monolayer adsorption \((k = 0)\) and the last term \(k_F n_B^{1/k}\) the multilayer adsorption.

1.6.4 Structural Heterogeneities of the Surface

The dependence of the contact angle on chemical heterogeneities at the surface was studied by Cassie and Baxter [70]. As discussed previously, the contribution of known crystal planes to the average total surface energy is linearly dependent on their fractional surface area. This observation can be rationalized with the well-known Cassie equation being related to the work of adhesion as

\[
W_{SLV} = -\left(\frac{\Delta G}{\Delta A}\right) = f_1(\sigma_{SL1} - \sigma_{SV}) + f_2(\sigma_{SL2} - \sigma_{SV})
\]

where the function \(f_i\) denotes the probability of finding (fractional) surface area with the property \(i\) characterized by the contact angle \(\theta_{SLi}\). Applying the Young equation, we may write for the contact angle

\[
\cos(\theta_{SL}) = f_1 \cos \theta_{SL1} + f_2 \cos \theta_{SL2}
\]

where \(\langle \theta_{SL} \rangle\) is the average contact angle. Multiplying each term by the surface tension, one obtain the arithmetic surface energy dependence on the fractional surface energy of each diverging property. For porous surfaces, the fractional porc area covered by the liquid (e.g. \(f_2\)) may be accounted for by setting \(\theta_{SL2} = 0\) to give

\[
\cos(\theta_{SL}) = f_1 \cos \theta_{SL1} + f_2
\]

Wenzel reported on the interdependence of wettability and surface roughness for polar surfaces as early as 1936 [73]. The so-called Wenzel equation can be derived from the Young equation [74]:

\[
dG = \sum_i \gamma_i dA_i = \sigma_{SV} dA - \gamma_{LV} dA \cos \theta_{SL} - \sigma_{SL} dA
\]

where \(i\) represents \(V = \) vapor, \(L = \) liquid, \(S = \) solid. Realizing that the real surface area is much greater than the projected (Young) surface area \(q = A_{\text{real}} / A_{\text{projected}}\), we obtain the work of adhesion:
\[ W_{SLV} = -(\Delta G/\Delta A) = q(\sigma_{SL} - \sigma_{SV}) + \gamma_{LV} \cos \Theta_{SL}^e \] (183)

Introducing the Young equation \((\sigma_{SL} - \sigma_{SV}) = -\gamma_{LV} \cos \Theta_{SL}\) at equilibrium \((\Delta G/\Delta A = 0)\) we obtain the well-known Wenzel equation:
\[ \cos \Theta_{SL}^e = q \cos \Theta_{SL} \] (184)

where \(q \geq 1\) relates the Young contact angle \((\Theta_{SL})\) to the effective contact angle \((\Theta_{SL}^e)\) of the real surface.

Four basic wetting behaviors of a corrugated surface can be identified:

1. the Imbition range
2. the Wenzel range
3. the Cassie range
4. the Lotus range
5. and two transition zones (2) and (5) (Fig. 1.29).

Above the limit of imbition, the liquid is modeled to be sucked into the porous surface structure leaving the top of the asperities in contact with air [75]. The surface area fraction in contact with air is denoted \(f_1 = \phi_{SV}^s\). However, we also have to consider the extended real surface by multiplying the solid surface by \(q\), but subtracting the fraction of surface not in contact with the liquid \((\phi_{SV}^e)\). Finally, as discussed above, we find a fraction of the surface area covered with liquid for which \(f_2 = 1 - \phi_{SV}^s\). The work of adhesion thus takes the form \((\cos \Theta_{LV} = 1)\)
\[ W_{SLV} = -(\Delta G/\Delta A) = q(\sigma_{SL} - \sigma_{SV}) - \phi_{SV}^s(\sigma_{SL} - \sigma_{SV}) + \gamma_{LV}(1 - \phi_{SV}^s) \] (185)

Introducing Young equation at equilibrium, we find
\[ \cos \Theta_{SL}^e = q \cos \Theta_{SL} = \phi_{SV}^s \cos \Theta_{SL} + (1 - \phi_{SV}^s) \] (186)

\[ \text{Fig. 1.29 Relationship between the effective contact angle (cos } \Theta_{SL}^e \text{) and the ideal (Young) contact angle (cos } \Theta_{SL} \text{) can be divided schematically into four basic ranges (1, 3, 4 and 6) and two transition zones (2 and 5). The influence of the surface structure on wetting is illustrated for each range.} \]
Therefore, if $\cos \theta_{SL}^c$ is plotted against $\cos \theta_{SL}$ for the imbition range, the line extrapolates to $1 - \phi_{SV}^c$ with a slope $\phi_{SV}^c$ when $\cos \theta_{SL} = 0$. The critical contact angle for imbition is [75]

$$\cos \theta_{c}^I = (1 - \phi_{SV}^c)/(q - \phi_{SV}^c)$$

(187)

which may be found as a break point above the $\cos \theta$ axis. Imbition occurs when $\theta_{SL} < \theta_c$, i.e. the surface roughness is flooded by the liquid. For a flat surface $q = 1$, i.e. $\cos \theta_c = 1$. Common for both the Wenzel and Imbition ranges is that $\theta_{SL} < 90^\circ$. When $\theta_{SL} > \theta_c$ the rough surface remains dry ahead of the drop.

Considering the surface asperities as a powder applied as a layer on a plate for the wicking experiments, but assuming full contact of all surfaces with the wetting liquid, White derived an expression for the suction (Laplace like) pressure due to wetting [76]:

$$\Delta P = [2(\sigma_{SV} - \sigma_{SL})/R_{eff}] + (\rho_v - \rho_L)gh = [2\gamma_{LV} \cos \theta_{SL}/R_{eff}] + (\rho_v - \rho_L)gh$$

(188)

where $R_{eff} = 2(1 - \phi_S)/(\rho_S A_w \phi_S)$, $\rho_S$ the density of the particles, $A_w$ the specific surface area of the particles and $\phi_S$ the volume fraction of the particles in the wetting space considered.

The transition from complete to partial wetting of the surface as a function of changing shape of the solid surface (slope of the surface asperities) was demonstrated by Wapner and Hoffman [77]. Their paper actually demonstrates how certain topographical features may give rise to the birth of air pockets and thereby, for example, explains the formation of nanobubbles when such a surface is covered by a liquid. This transition is opposite to the Wenzel range, but now the air pockets form below the drop on top of the asperities. Hence maintaining the surface fractions, the same the Cassie range is defined by [78]

$$W_{SLV} = -(\Delta G/\Delta A) = q(\sigma_{SL} - \sigma_{SV}) - \phi_S (\sigma_{SL} - \sigma_{SV}) - \gamma_{LV}(1 - \phi_S)$$

(189)

since $\cos \theta_{LV} = -1$ on the liquid-air pockets. Hence, at equilibrium, the Young equation gives

$$\cos \theta_{SL}^c = q \cos \theta_{SL} = -1 + \phi_S(\cos \theta_{SL} + 1) = (\phi_S - 1) + \phi_S \cos \theta_{SL}$$

(190)

Therefore, if $\cos \theta_{SL}^c$ is plotted against $\cos \theta_{SL}$ for the imbition range, the line extrapolates to $\phi_S - 1$ with slope $\phi_S$ when $\cos \theta_{SL} = 0$. The critical contact angle for the Lotus surface is [79]

$$\cos \theta_{c}^L = (\phi_S - 1)/(q - \phi_S)$$

(191)

Hence it is through the interdependence of topography and enhanced hydrophobicity that a surface turns from “normal” hydrophobic to superhydrophobic.
Nature utilizes this phenomenon, for example, in self-cleaning plant leaves (the so-called Lotus effect) [78, 79]. Bico et al. assumed a discontinuity between the Wenzel and Lotus (i.e. the Cassie) ranges; however, this was not supported by the experimental results presented [79], but is more an artifact due to the assumption of only purely vertical surface asperities. For hemispherical asperities, Bico et al. derived the equation [78]

$$\cos \Theta^*_SL = -1 + \phi_B^e (\cos \Theta_{SL} + 1)^2$$ (192)

where $\phi_B^e$ is the ratio of the base over the total surface area of the asperities. This type of representation is in agreement with experimental findings and may probably be used to represent the transition ranges (2) and (5). For example, in the transition range between the Imbition (1) and Wenzel (3) ranges a liquid collar may be found around the drop in the surface heterogeneities as described by Apel-Paz and Marmur [80].

Tsujii's group has demonstrated that even molecular-scale topography contributes to contact angle hysteresis [81]. Topographical characterization has to be carried out with high resolution and at scales of different lengths, which is characteristic for the surface structure [81]:

$$\cos \Theta^*_SL = (L/l)^{D-2} \cos \Theta_{SL}$$ (193)

where $L$ and $l$ are the upper and lower limit step lengths, respectively, over which the fractal dimension was analyzed and $D$ ($2 < D < 3$) is the fractal dimension of the surface (Fig. 1.30). However, in their presentation they made a fit only to the data within the Wenzel range, leaving the analysis of the Cassie range uncompleted [82].

Compared with artificial textured surfaces, the description of the form and shape of real surfaces with complex topography sets high requirements on sur-

Fig. 1.30 Plot of $\cos \Theta^*_SL$ against $\cos \Theta_{SL}$ for an alkylketene dimer (AKD)/dialkyl ketone (DAK) surface. The line drawn according to Eq. (193) is characteristic only for part of the surface structure (bold line) relating to the Wenzel region (from [81], with permission).
face microscopy and especially image analysis. Obviously, root mean square (RMS) roughness or peak-to-valley height parameters may be regarded as only indicative when considering, for example, surface porosity or topography-corrected wetting behavior. Peltonen et al. applied a set of topographical parameters for the description of amplitude, spatial and hybrid properties of surfaces for a versatile 3D surface characterization of sol–gel samples with different topography [83]. It was demonstrated that different sets of parameters describe and identify surfaces of different character. They also demonstrated the topography-dependent functionality of the studied surfaces. The 3D image data were captured by atomic force microscopy (AFM). The challenge to be met is to quantify a real surface not only by RMS roughness, but also, for example, by the effective surface area, height asymmetry, surface porosity and the number, size and form of local maxima. In this way, the understanding of the role of topography in phenomena such as wetting, adsorption/precipitation and liquid penetration can be considerably enhanced.

1.7 Contributions from External Stimuli

Many wetting experiments are performed under uncontrolled conditions, e.g. under the influence of external electrostatic potentials and intensive light. It may therefore be of value to consider some not immediately obvious dependences of wetting on external stimuli. The discussion on the relationship between the surface energy and the surface potential showed that electromagnetism may have a profound influence on the surface states of a solid. This is particularly true for semiconductors, in which the electron distribution within the space charge region may be considered to be a (negative) mirror image of the ions in the aqueous double layer outside the surface.

1.7.1 External Electrostatic Potential

For conductive polarizable or non-polarizable surfaces, the distribution of excess cations or anions near the surface is represented by the surface charge density. The Lippmann or electrocapillarity equation discussed previously shows that the surface energy may be adjusted by applying an external electrostatic potential (E) over the surface (Eq. 137):

$$\Delta \sigma_{SL} = \int_0^d \sigma_{SL} \, dV - \int_0^d \sigma_{\pm} \, dV$$  \hspace{1cm} (194)

From the Young equation, we obtain

$$\cos \Theta_{SL} = (1/\gamma_{LV})[\sigma_{\pm} \, dV + \sigma_{SV}]$$  \hspace{1cm} (195)
Alternatively, the electrowetting can be derived by way of the minimum free energy requirement for thermodynamic equilibrium conditions for a droplet of conducting liquid (e.g. water, W) on a solid (S) immersed in a insulating oil (O) [84]:

\[
\cos \theta_{SOW} = \cos \theta_{SOW}^0 + (\varepsilon_r \varepsilon_0 \Delta V^2 / 2 \gamma_{OW} \delta)
\]

\[
\gamma_{OW} \cos \theta_{SOW} = \sigma_{SO} - \sigma_{SW} + (\varepsilon_r \varepsilon_0 \Delta V^2 / 2 \delta)
\]

where \( \theta_{SOW}^0 \) is the contact angle in the absence and \( \theta_{SOW} \) that in the presence of the applied external electrical potential \( (\Delta V) \), \( \varepsilon_r (= \varepsilon_{SW}) \) the relative dielectric constant of the conductive liquid close to the solid and \( \delta \) is the thickness of the dielectric layer. The latter is typically of the order of micrometers whereas size of the droplet is of the order of millimeters.

Kang identified the Maxwell stress \( (F_e) \) and the perpendicular force components acting at the three-phase contact line (tpcl) as (Fig. 1.31) [84]

\[
F_e = (\varepsilon_r \varepsilon_0 \Delta V^2 / 2 \delta) \cos \theta_{SOW}
\]

\[
F_{ex} = (\varepsilon_r \varepsilon_0 \Delta V^2 / 2 \delta)
\]

\[
F_{ey} = (\varepsilon_r \varepsilon_0 \Delta V^2 / 2 \delta) \cot \theta_{SOW}
\]

It is interesting that the horizontal force component is independent of the contact angle. This very localized point force would pull the tpcl until it balances with the dragging force of surface tension. The macroscopic balance of the horizontal force components is given by the electrocapillary equation (Eq. 137).

In simple terms, the surface potential gradient is related to the surface charge density \( \sigma_\pm (= N_\pm^s / A) \)

\[
(d\psi / dx) \approx (\Delta \psi / \delta) = \sigma_\pm / \varepsilon_r \varepsilon_0
\]

\( \Delta V = \Delta \psi = \psi_0 - \psi_\delta \) is the potential drop between two plates at a distance \( \delta \) with a medium characterized by the relative dielectric constant \( \varepsilon_r \) and \( \Delta V \) is the

![Fig. 1.31 Electrostatic force and its influence of horizontal and vertical balance of forces acting on the three-phase contact line (tpcl) (from [84], with permission).](image-url)
externally applied potential. We may now proceed to relate the electrostatic potential across the interface, being represented by the differential capacity of the double layer in the liquid phase using the electrocapillary equation:

\[
C_{SL} = (d\sigma_{\pm}/dV)_{P,T,\mu} = -(d^2\sigma_{SL}/dV^2)_{P,T,\mu}
\] (199)

where \(\varepsilon_r\varepsilon_0 = \delta C_{SL}\). The major difference between differential capacity and the capacity of an electric condenser is that it depends on the potential across the double layer, whereas that of the electric condenser does not. For the purpose of integration the potential difference is referred to the electrocapillary maximum \(U_{ECM}\), which for pH scales occurs at pH_{PZC} (see Fig. 1.24).

1.7.2
External Illumination

Let \(V_{hv}\) be the electrical potential generated by photonic energy. Then the potential difference in relation to an arbitrary reference potential \((\Delta V_{hv} = V_{hv} - V_0)\) is [85]

\[
d\sigma_{SL}/d\psi \approx d\sigma_{SL}/dV_{hv}
\] (200)

We have defined the work of immersion at constant \(P\), \(T\) and \(\mu\) (Eq. 6d), which is also termed the adhesion tension:

\[
l_{SL} = \sigma_{SV} - \sigma_{SL} = \gamma_{LV} \cos \Theta_{SL}
\] (201)

The Young equation is utilized to define the surface charge density difference between the SV and the SL interfaces [85]:

\[
\Delta\sigma_{\pm} = d(l_{SL})/dV_{hv} = d(\sigma_{SV} - \sigma_{SL})/dV_{hv}
\] (202a)

\[
\Delta\sigma_{\pm} = \gamma_{LV}[d(\cos \Theta_{SL})/dV_{hv}] = -\gamma_{LV} \sin \Theta_{SL}(d\Theta_{SL}/dV_{hv})
\] (202b)

The latter expression is symmetrical with Eq. (144c) and shows that the change in the contact angle on illumination is proportional to the charge density difference.

Table 1.13 illustrates the dependence of the contact angle on illumination. As shown, the contact angle decreases slowly with time, indicating that the solid may store the optical energy.

As shown in Fig. 1.32, the hydrophilization (reduction in contact angle) is related to the degradation time of stearic acid reflected as a reduced absorbance which is characteristic for hydrocarbon groups [87]. It is assumed that the hydrophilization is due to the (radical?) formation of hydroxyl groups at the surface [86]. This activation is obviously also related to the degradation mechanism. When energy-rich UV light was used, the time needed to reduce the contact
angle was shortened. The UV irradiance was measured [87] as $1.1 \text{ mW cm}^{-2} = 11 \text{ J m}^{-2} \text{s}^{-1}$, which when multiplied by the irradiation time gives the illumination energy at the surface $E_{\text{ill}}$ reported in Table 1.13.

By differentiation, we obtain the differential capacity difference between the SV and SL interfaces [85]:

$$\Delta C_{SL} = \frac{d^2(I_{SL})}{d(V_{hv})^2} = \frac{d(\Delta \sigma_{\pm})}{dV_{hv}} \quad (203)$$

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>60</th>
<th>180</th>
<th>360</th>
<th>540</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescent visible light</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contact angle, $\theta_{SW}$ ($^\circ$)</td>
<td>33</td>
<td>30</td>
<td>24</td>
<td>18</td>
<td>17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ultraviolet light</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contact angle, $\theta_S$ ($^\circ$)</td>
<td>49</td>
<td>32</td>
<td>26</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{\text{ill}}$ (kJ m$^{-2}$)</td>
<td>0</td>
<td>10</td>
<td>20</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 1.13** Dependence of the contact angle of water on mesoporous titania (anatase) surfaces on the UV and fluorescent visible illumination as a function of time (from [86, 87], with permission).

**Fig. 1.32** Reduction in the characteristic infrared peaks for stearic acid as a function of time due to catalytic degradation by titania. Pilkington glass, atomic layer deposition and (sol–gel) surfaces under illumination (from [87], with permission).
where $I_{\text{SL}}$ is denoted adhesion tension. Recalling that the process is carried out at constant $P$, $T$ and $\mu$, we replace $\sigma_{\pm}$ and $C_{\text{SL}}$ by $\Delta \sigma_{\pm}$ and $\Delta C_{\text{SL}}$ (Eqs. 199 and 203), respectively, to give [85]

$$
\Delta \psi_0 = \Delta V_{hv} = (\Delta \sigma_{\pm} / \Delta C_{\text{SL}})_{T,P,\mu}
$$

A plot equivalent to the electrocapillary curve should be obtained on plotting $I_{\text{SL}}$ against $\Delta \psi_0$ or $\Delta V_{hv}$ (Fig. 1.33).

![Schematic illustration of the dependence of the work of immersion ($I_{\text{SL}}$) on the photonic potential ($V_{hv}$), resembling an electrocapillary curve.](image)

The left-hand side from the maximum refers to n-type semiconductor solids and the right-hand side to p-type. The maximum corresponds to $V_{hv} = V_0 \propto U_{\text{ECM}}$, i.e. the point of zero charge (cf. pH$_{\text{PZC}}$) or the flat band potential. It is assumed that at PZC both the space charge layer and the electrical double layer vanish.

The energy gap of intrinsic semiconductors, $\langle E_g \rangle$, approximately equals twice the equivalent heat of formation ($-\Delta H_{\text{eq}}^f \propto -\Delta G_{\text{eq}}^f$) for several binary inorganic substances. For defect-free (intrinsic) semiconductors, we find that [88]

$$
\frac{1}{2} \langle E_g \rangle \approx -\Delta H_{\text{eq}}^f = E_F = \langle E_h \rangle - k
$$

where $\langle E_h \rangle$ is the average bond energy and $k = 2.7$ eV for a large number of solids. Using this equation, Vijh [88] found an energy gap of 4.7 eV for titania, which is not far from the values reported below.

The band gap can also be determined spectroscopically through the transmittance (Fig. 1.34). First the refractive index ($n$) and extinction coefficient ($k$) are determined. The following relationship has been defined for the photonic energy [89]:

$$
E_{hv} = h\nu = \kappa_e / kn
$$

where $\kappa_e$ is the conductivity of the solid. The absorption coefficient ($a$) is then determined as [90]

$$
ahv = l(h\nu - \langle E_g \rangle)^m
$$
where \( l \) is a model-dependent constant relating to the transition considered and is determined by \( \langle E_g \rangle \) and \( m \). The exponent \( m \) equals 1/2 for allowed direct, 2 for allowed indirect, 3/2 for forbidden direct and 3 for forbidden indirect transitions. Extrapolating the linear part of \((a\hbar v)^m\) against \( h\nu \) (both in eV) to the abscissa gives \( m \) as the slope and \( \langle E_g \rangle \) at \((a\hbar v)^m = 0\) [87].

The bulk value for rutile is 3.0 eV and for anatase 3.2 eV, which correspond favorably with the values found (3.3–3.4 eV) in Fig. 1.34.

![Graph](image_url)

Fig. 1.34 Band gap \( \langle E_g \rangle \) determinations of TiO\(_2\) films for an allowed direct transition \( (m = 1/2) \) (from [87], with permission).
Since the Hamaker constant is also described in terms of refractive indices and dielectric constants, including a characteristic frequency in the ultraviolet region ($\nu \approx 8 \times 10^{15} \text{ s}^{-1}$), the relationship between the photonic energy parameters is obvious [16, 31]. Converting the band gap energies to thermodynamic energy units, we obtain for the 3.0–3.4 eV range $(48.1–54.5) \times 10^{-20}$ J, which is not far from published Hamaker constant values for titania in air (vacuum) [90]: $(15.5–16.8) \times 10^{-20}$ J, representing the cohesive energy of the solid (Eq. 12b).

1.8 Conclusions

It has been demonstrated that nearly all phenomena occurring at solid surfaces can be related to and investigated by the use of different work of wetting. This holds true for the adsorption isotherms, which can be considered as representing the surface pressure in liquids competing for surface sites.

Despite their sensitivity to salient molecular interactions, higher order thermodynamic parameters, such as heat capacity, expansivity and compressibility, are not determined. In contrast, first-order parameters such as enthalpy are (unsuccessfully) related to the Gibbs free energy.

The relationships between wetting models currently considered have been presented and evaluated. Although the absolute values vary between the models, the overall trends remain the same, frequently being dependent on the probe liquids used. Since the choice is to a large extent a matter of convenience, simplification of most current models is suggested.

The equations presented are restricted to equilibrium conditions excluding considerations on dynamic wetting, hysteresis effects and differences in advancing and retreating (receding) contact angles. Moreover, only the interfaces between pure solids, liquids and probe molecules are evaluated. The properties of aqueous electrolyte solutions at a distance from the solid surfaces is discussed only to a limited extent.

The influence of chemical and structural heterogeneity of the surface has been considered with a few examples. Moreover, it has been shown that external stimuli influence the surface energy and contact angle. All models can, however, be rationalized in a straightforward way.

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