

Principal component analysis and multicomponent surface free energy theories

C. Della Volpe and S. Siboni*

*Department of Materials Engineering and Industrial Technologies, University of Trento,
Mesiano di Povo, 38050 Povo, Trento, Italy*
E-mail: stefano.siboni@ing.unitn.it

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The same underlying mathematical structure characterizes some of the most popular multicomponent models for the prediction of surface free energies and adhesion works. After a brief illustration of the general methods for the computation of liquid and solid components in typical multicomponent theories, it is shown that both model definition and component estimate may take great advantage from application of Principal Component Analysis techniques, owing to the very peculiar structure of adhesion work equations. It is also put into evidence that a problem of scale multiplicity arises as a consequence of the symmetries involved in the model equations for adhesion work and surface free energy. A special discussion is devoted to the specific cases of van Oss–Chaudhury–Good acid–base theory, Qin–Chang model and extended Drago theory, which constitute the most common multicomponent models usually applied in the analysis of adhesion phenomena.

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1. Multicomponent surface free energy theories

It is widely recognized that multicomponent models play an important role in the analysis of the interfacial interactions of many materials and, more specifically, in the prediction of the solid–liquid work of adhesion and surface free energy of solid surfaces. The description of the surface interaction of two materials in terms of an appropriate number of “components” pertaining to contributions of different physico-chemical nature is a approach shared by many models proposed in different years. One of the most widely recognized and successful multicomponent models is van Oss–Chaudhury–Good (vOCCG) theory [1–6], which expresses the work of adhesion of a liquid l on a solid s by the formula

* Corresponding author.

$$W^{\text{adh}} = 2 \left[\sqrt{\gamma_s^{LW} \gamma_l^{LW}} + \sqrt{\gamma_s^+ \gamma_l^-} + \sqrt{\gamma_s^- \gamma_l^+} \right] \quad (1.1)$$

whereas the surface tension of the liquid and the surface free energy of the solid take the form

$$\gamma_l = \gamma_l^{LW} + 2\sqrt{\gamma_l^+ \gamma_l^-} \quad \gamma_s = \gamma_s^{LW} + 2\sqrt{\gamma_s^+ \gamma_s^-} \quad (1.2)$$

respectively. In the previous equations the superscript LW denotes the Lifshitz–van del Waals components of the materials, related to dispersive interactions, while $+$ and $-$ label the acidic and the basic components, which take into account the acid–base interactions between electron-donor (basic) and electron-acceptor (acidic) sites of the interacting molecules – acidity and basicity are thus understood in a Lewis’ sense. All the model equations reflect the intrinsic complementarity of acid–base interactions. Although nowadays it constitutes one of the most commonly used, vOCG theory was not the first multicomponent model introduced in adhesion science. In the late 60s, long before vOCG, a prototype of multicomponent theory was already proposed by Owens and Wendt [7] (OW), whose aim was to estimate the specific contribution of dispersive and “polar” interaction to the overall work of adhesion by the definition of suitable dispersive and polar contributions for each material, in such a way that

$$\gamma_l = \gamma_l^d + \gamma_l^p \quad \gamma_s = \gamma_s^d + \gamma_s^p \quad (1.3)$$

for liquids and solids, respectively. A sort of geometric-mean rule separately applied to dispersive and polar components provides then, accordingly, the work of adhesion between the liquid and the solid in contact

$$W^{\text{adh}} = 2 \left[\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p} \right]. \quad (1.4)$$

The theory can be easily extended, for instance to take specifically into account hydrogen-bonding interactions:

$$W^{\text{adh}} = 2 \left[\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p} + \sqrt{\gamma_s^H \gamma_l^H} \right] \quad (1.5)$$

$$\gamma_l = \gamma_l^d + \gamma_l^p + \gamma_l^H \quad \gamma_s = \gamma_s^d + \gamma_s^p + \gamma_s^H$$

by introducing, for each chemical species involved, the appropriate further component labeled by the superscript H . Although relatively aged, OW theory is still currently applied with satisfactory results, even in very sophisticated and intriguing experimental contexts [8]. More recently [9–11], Qin and Chang (QC)

have revised vOCG theory and proposed a new, in principle more general three-parameter model whose equations can be put into the form

$$\begin{aligned} \gamma_l &= \frac{1}{2}(P_l^d)^2 - P_l^a P_l^b & \gamma_s &= \frac{1}{2}(P_s^d)^2 - P_s^a P_s^b \\ W^{\text{adh}} &= P_s^d P_l^d - (P_s^a P_l^b + P_s^b P_l^a) \end{aligned} \quad (1.6)$$

for liquid surface tension, solid surface free energy and solid-liquid work of adhesion, the superscripts d , a and b corresponding to LW -dispersive, Lewis-acidic and Lewis-basic components, respectively. Although developed not to predict adhesion work or surface free energy, other models present a structure very similar to those previously described. Drago's theory [12–14] provides a very well-known example. Drago distinguishes “acidic” and “basic” solvents (electron acceptors and donors), each characterized by two variables in such a way that the enthalpy of adduct formation for any acceptor-donor pair is written as

$$-\Delta H = C_A C_B + E_A E_B \quad (1.7)$$

where the subscripts A and B indicate acceptor and donor and E and C represent electrostatic and covalent contributions, respectively. Similar empirical relationships, but for free energy, have been obtained by electrochemical techniques by Edwards [15], Mulliken [16] and Foss [17]. Drago's theory for enthalpy of adduct formation can be readily extended [18] to take into account the possible co-existence of acidic and basic sites in the same molecule, by envisaging an equation of the form

$$-\Delta H = C_A C'_B + C_B C'_A + E_A E'_B + E_B E'_A. \quad (1.8)$$

Even more general models, with an analogous formulation, are provided by the Linear Free Energy Relationships (LFERs). In recent papers [19, 20] it has been emphasized that from a mathematical point of view the GvOC theory can be classified in the realm of Linear Free Energy or Solvation Energy Relationships (LFER or LSER) [21, 22], where a thermodynamical quantity Q , pertaining in this case to Lewis acid–base properties of two materials X and Y , is expressed as a sum of pairwise products of some material coefficients

$$Q = \sum_i X_i Y_i. \quad (1.9)$$

The quantity Q may assume a different meaning according to the kind of application, for instance it may be a free energy or an enthalpy, but this is not mandatory. Typically the index i specifies the class of the coefficient: dispersive, acidic, basic, etc, whereas symbols X and Y denote the interacting materials. These kinds of relations are widely employed in physical organic chemistry [21, 22], as it is done in the acid–base theory by Drago [12].

All the multicomponent models previously listed can be expressed as *bilinear or quadratic forms* of components, for adhesion work and surface free energy, respectively. Not all the multicomponent theories are constructed in this way; an interesting exception is for instance the model by Wu [23, 24], who distinguishes dispersive and “polar” contributions to adhesion work, as in WO, but assuming a harmonic-mean combining rule instead of a geometric-mean approximation

$$W^{\text{adh}} = 4 \left[\frac{\gamma_l^d \gamma_s^d}{\gamma_l^d + \gamma_s^d} + \frac{\gamma_l^p \gamma_s^p}{\gamma_l^p + \gamma_s^p} \right]. \tag{1.10}$$

The general mathematical form of almost all the above multicomponent models is immediately recognized. For a set of s solids, labeled by the index i , and l liquids, denoted with the index j , the adhesion work W_{ij}^{adh} of the solid i on the liquid j is written as

$$W_{ij}^{\text{adh}} = 2 \sum_{h,k=1}^c \xi_i^{(h)} S_{hk} \lambda_j^{(k)} \quad \forall i = 1, \dots, s \quad j = 1, \dots, l \tag{1.11}$$

while the surface tension γ_j of the liquid j , susceptible of a direct measurement, holds

$$\gamma_j = \sum_{h,k=1}^c \lambda_j^{(h)} S_{hk} \lambda_j^{(k)} \quad j = 1, \dots, l \tag{1.12}$$

where:

- $\lambda_j^{(k)}$, with $k = 1, \dots, c$, stand for the components of the liquid j ;
- $\xi_i^{(h)}$, for $h = 1, \dots, c$, denote the components of the solid i ;
- $S = \{S_{hk}\}_{h,k=1,\dots,c}$ is a $c \times c$ structure matrix, characteristic of the multicomponent model, which we will assume real, symmetrical and non-singular.

With the assumed prescriptions on S , equations of the form (1.11)–(1.12) are certainly valid for all the multicomponent models previously listed, provided that the “components” are identified with the square roots of surface free energy parameters:

$$\xi = \sqrt{\gamma_s} \quad \lambda = \sqrt{\gamma_l}, \tag{1.13}$$

on having introduced the obvious vector notation. The only exception is QC theory, where parameters P_s, P_l coincide with components up to a constant scale factor

$$\xi = \frac{1}{\sqrt{2}} P_s \quad \lambda = \frac{1}{\sqrt{2}} P_l. \tag{1.14}$$

If d_1, \dots, d_c are the (real and non-vanishing) eigenvalues of S and $\text{sgn}(x)$ denotes the sign function, an orthogonal matrix C exists such that

$$S = C^T \begin{pmatrix} \sqrt{|d_1|} & & \textcircled{0} \\ & \ddots & \\ \textcircled{0} & & \sqrt{|d_c|} \end{pmatrix} \begin{pmatrix} \text{sgn}(d_1) & & \textcircled{0} \\ & \ddots & \\ \textcircled{0} & & \text{sgn}(d_c) \end{pmatrix} \begin{pmatrix} \sqrt{|d_1|} & & \textcircled{0} \\ & \ddots & \\ \textcircled{0} & & \sqrt{|d_c|} \end{pmatrix} C \tag{1.15}$$

and therefore the multicomponent model can always be reduced to the standard form

$$W_{ij}^{\text{adh}} = 2 \sum_{h=1}^c \text{sgn}(d_h) \xi_i^{(h)} \lambda_j^{(h)} \quad \gamma_j = \sum_{h=1}^c \text{sgn}(d_h) \left(\lambda_j^{(h)} \right)^2 \tag{1.16}$$

by applying the same linear transformation to the components of the solids

$$\begin{pmatrix} \sqrt{|d_1|} & & \textcircled{0} \\ & \ddots & \\ \textcircled{0} & & \sqrt{|d_c|} \end{pmatrix} C \begin{pmatrix} \xi_i^{(1)} \\ \vdots \\ \xi_i^{(c)} \end{pmatrix} = \begin{pmatrix} \xi_i^{(1)} \\ \vdots \\ \xi_i^{(c)} \end{pmatrix} \quad \forall i = 1, \dots, s \tag{1.17}$$

and to those of the liquids. Multicomponent models of the form (1.11)–(1.12) are thus actually different if their structure matrices do not share the same signature $\{\text{sgn}(d_1), \dots, \text{sgn}(d_c)\}$, otherwise they should be regarded as mathematically equivalent up to a linear gauge of components [18].

The main goal of multicomponent theories is to provide reliable estimates of solid and liquid components, in such a way that equations (1.11) and (1.12) hold true with a satisfactory accuracy for the largest set of liquids and solid surfaces. More specifically, since no unquestionable direct measurement technique is available in this respect, one of the most important skills of multicomponent theories is the prediction of surface free energy of solids by means of relationships analogous to (1.12), involving the components of the solids

$$\gamma^i = \sum_{h,k=1}^c \xi_i^{(h)} S_{hk} \xi_i^{(k)} \quad i = 1, \dots, s. \tag{1.18}$$

The problem can be numerically tackled in essentially three different ways, according to the available data and the application purposes.

2. Methodologies for component estimate

The calculation of components may be carried out by adopting different approaches. Indeed the conceivable methods for component estimate, by using only adhesion work and surface tension data, can be classified as follows:

- (a) linear method;
- (b) linear best-fit method;
- (c) nonlinear best-fit method.

The approach (a), as well as (b), provides a strategy for the calculation of solid components and assumes the components of an appropriate set of test liquids as *a priori* known. In this sense the application of both of them appears conditioned by the actual availability of such a set of known components. Such an occurrence is far from being obvious, owing to the difficulties in gathering an adequate number of reliable adhesion work or contact angle data, and to the nonunivocal interpretation of the components eventually calculated by contact angle measurements, which is intrinsic to this kind of models. In this respect see section 6, devoted to the problem of scale multiplicity in the definition of components. It is worthy of note that even in the domain of the vOCG model, maybe one of the most classical and successful multicomponent theories, different scales of acid–base strength have been proposed [20]. Method (c) faces up to the problem of component calculation in the most complete way, since it assumes no known component. Nevertheless, it requires a large number of high-quality data and numerical calculations are more cumbersome and time-consuming than for the previous approaches (a) and (b).

(a) *Linear method.* If the components and adhesion works, on a given solid i , of c liquids specified by appropriate values of the index $j \in \Lambda \subseteq \{1, 2, \dots, l\}$ are known, then there holds

$$\sum_{h=1}^c \left(\sum_{k=1}^c S_{hk} \lambda_j^{(k)} \right) \xi_i^{(h)} = W_{ij}^{\text{adh}} \quad \forall j \in \Lambda. \quad (2.1)$$

The latter is a linear set of algebraic equations to be solved in the solid components $\xi_i^{(h)}$, $h = 1, \dots, c$. Solution exists and is unique provided that the square matrix

$$A_{jh} = \sum_{k=1}^c S_{hk} \lambda_j^{(k)}, \quad j \in \Lambda, \quad h = 1, \dots, c \quad (2.2)$$

is nonsingular. Even in this case, however, the possible ill-conditioning of the matrix may seriously affect the accuracy of the estimated components [25].

(b) *Linear best-fit method.* When the number of probe liquids is larger than c , the linear set (2.1) consists of more equations than the unknown components, so that it is expected that no solution generally exists in a proper sense. If this is the case, one may anyway look for a best-fit solution in a least-square sense, always defined. The latter may turn out to be unique or not, but the smallest-Euclidean norm solution can be written as

$$\begin{pmatrix} \xi_i^{(1)} \\ \vdots \\ \xi_i^{(c)} \end{pmatrix} = A^+ \begin{pmatrix} W_{ij}^{\text{adh}} \\ \vdots \\ j \in \Lambda \end{pmatrix} \tag{2.3}$$

in terms of the Moore-Penrose pseudoinverse matrix A^+ [26]. Troubles arising from ill-conditioning are similar to those of method (a) [25].

(c) *Nonlinear best-fit method.* The most general approach to the problem of component calculation consists in searching a best-fit solution for the whole set of adhesion work and surface tension equations. Out of a set of s solids and l liquids there are sl equations for the adhesion work and l further equations for surface tension. The s equations for the surface free energies of solids are not considered in the calculation, since the surface free energies $\gamma^i, i = 1, \dots, s$ are not experimentally known. The number of components to be determined is then $c(s + l)$, versus a whole of $sl + l$ equations. As c is fixed, there certainly holds $sl + l > c(s + l)$ for s and l large enough. In this hypothesis there is only a remote possibility that equations (1.11) and 1.12 can be solved exactly, so that a best-fit solution may represent a reasonable compromise. For instance, one can minimize the sum of squares or residuals

$$\Phi(\xi, \lambda) = \sum_{i=1}^s \sum_{j=1}^l \left[2 \sum_{h,k=1}^c \xi_i^{(h)} S_{hk} \lambda_j^{(k)} - W_{ij}^{\text{adh}} \right]^2 + \sum_{j=1}^l \left[\sum_{h,k=1}^c \lambda_j^{(h)} S_{hk} \lambda_j^{(k)} - \gamma_j \right]^2, \tag{2.4}$$

an appropriate weighted sum of squares of residuals or any other suitable residual-dependent merit function. The calculations involved are much more cumbersome than in the linear approach (a) or (b), and more delicate appears the problem of error propagation. But the method requires no *a priori* estimate of or assumption on the components of the test liquids used [25].

3. Principal Component Analysis

Principal Component Analysis (PCA) can be viewed as a particular technique to filter data which are arranged in an array [27, 28]. Let X be a $n \times p$ matrix of data. One can assume that each of its rows corresponds to a point in the space \mathbb{R}^p of vectors with p components, one per each column; the matrix X specifies then a set of n points x_i in \mathbb{R}^p :

$$X = \begin{pmatrix} \overline{x_1^T} \\ \vdots \\ \overline{x_n^T} \end{pmatrix} \quad x_i \in \mathbb{R}^p \quad \forall i = 1, \dots, n. \tag{3.1}$$

It may happen that the points x_i are not distributed at random in \mathbb{R}^p , but along a particular subset of \mathbb{R}^p . More specifically, it may be that the data approximately lie on a linear space \mathbb{S}_k of dimension $k \leq p$, spanned by an orthonormal set $\{h_1, h_2, \dots, h_k\}$ of vectors in \mathbb{R}^p (see figure 1)

$$h_j^T h_q = \delta_{jq} \quad \forall j, q = 1, \dots, k, \tag{3.2}$$

which will form the columns of a $p \times k$ matrix H

$$H = (h_1 | h_2 | \dots | h_k). \tag{3.3}$$

The orthogonal projections of the vectors x_i 's on \mathbb{S}_k are given by the column vectors (see figure 2)

$$HH^T x_i \quad \forall i = 1, \dots, n \tag{3.4}$$

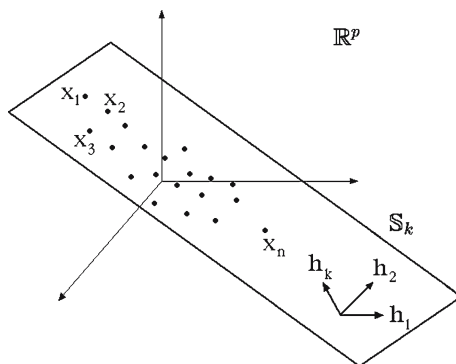


Figure 1. The points $x_i \in \mathbb{R}^p, i = 1, \dots, n$, representative of the rows of matrix X , almost aligned along a linear space \mathbb{S}_k of dimension $k < p$.

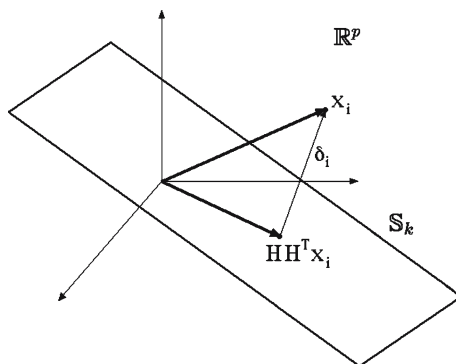


Figure 2. The orthogonal projection $HH^T x_i$ of a generic point $x_i \in \mathbb{R}^p$ on the linear space \mathbb{S}_k . The distance of x_i from \mathbb{S}_k is denoted with δ_i and defined as the difference $x_i - HH^T x_i$.

or, equivalently, by the row vectors

$$x_i^T H H^T \quad \forall i = 1, \dots, n \tag{3.5}$$

and the matrix of orthogonal projections holds therefore

$$X H H^T \tag{3.6}$$

so that the orthogonal projections of x_i 's on \mathbb{S}_k coincide with the rows of $X H H^T$. The distances of the points x_i from \mathbb{S}_k – the “residuals” – can be written

$$\delta_i = x_i - H H^T x_i = (\mathbb{I} - H H^T)x_i \quad i = 1, \dots, n \tag{3.7}$$

and the sum of their squares turns out to be

$$\begin{aligned} SS &= \sum_{i=1}^n \delta_i^2 = \text{tr}[X(\mathbb{I} - H H^T)X^T] = \text{tr}[X X^T] - \text{tr}[X H H^T X^T] \\ &= \text{tr}[X X^T] - \text{tr}[H^T X^T X H] \end{aligned} \tag{3.8}$$

on having denoted with $\text{tr}(A)$ the trace of a generic square matrix A . In PCA the matrix H , and the corresponding linear space \mathbb{S}_k , are determined by using a least-square fitting strategy: H must be chosen in such a way that the residual sum of squares is minimum or, equivalently, that the trace

$$\text{tr}[H^T X^T X H] \tag{3.9}$$

is maximum, with the constraint that the columns h_1, \dots, h_k of H constitute an orthonormal set. An algebraic calculation shows that the vectors h_1, \dots, h_k coincide with the first k vectors of the orthonormal basis

$$h_1, h_2, \dots, h_p \tag{3.10}$$

of eigenvectors of the real, symmetric and semipositive defined matrix $X^T X$

$$X^T X h_i = \lambda_i h_i \quad \forall i = 1, \dots, p \tag{3.11}$$

with eigenvalues arranged in decreasing order

$$\lambda_1 \geq \lambda_2 \geq \dots \geq \lambda_p \geq 0. \tag{3.12}$$

The corresponding (residual) sum of squares holds then

$$\text{tr}[X(\mathbb{I} - H H^T)X^T] = \sum_{i=k+1}^p \lambda_i. \tag{3.13}$$

If we assume that the data x_i are principally located along \mathbb{S}_k , we replace the points x_i with their orthogonal projections on \mathbb{S}_k

$$x_i \longrightarrow HH^T x_i \tag{3.14}$$

so that the data matrix X is approximated by the k -principal component model

$$XHH^T = \sum_{j=1}^k (Xh_j)h_j^T, \tag{3.15}$$

where h_i is known as the *loading* of the i -th principal component and Xh_i denotes the i -th *score*. An alternative interpretation of the result is that the sum of squares of data – also known as the “deviance of the sample”

$$\sum_{i=1}^n \sum_{j=1}^p (x_{ij})^2 = \sum_{i=1}^n \sum_{j=1}^p X_{ij}^2 = \text{tr}(X^T X) = \sum_{j=1}^p \lambda_j \tag{3.16}$$

can be expressed as the sum of a “deviance explained by the k -PC model”

$$\text{tr}[XHH^T X^T] = \text{tr}[H^T X^T XH] = \sum_{j=1}^k \lambda_j \tag{3.17}$$

and of an “unexplained deviance” (3.13). PCA is strictly related to the Singular Value Decomposition (SVD) of the data matrix X [29]. Indeed, one can easily verify that the k -PC model is no more than a truncation to the largest k singular values of the SVD of X

$$X = V \begin{pmatrix} \Sigma & \mathbb{O} \\ \mathbb{O} & \mathbb{O} \end{pmatrix} U^T = \sum_{j=1}^r \sigma_j v_j u_j^T \tag{3.18}$$

where:

- (i) $r = \text{rank}(X) = \text{rank}(X^T X) \leq \min(n, p)$ is the rank of X ;
- (ii) $U = (u_1 | u_2 | \dots | u_p)$ with $u_1, u_2, \dots, u_p \in \mathbb{R}^p$ an orthonormal basis of eigenvectors of $X^T X$

$$X^T X u_i = \sigma_i^2 u_i \quad i = 1, \dots, p$$

for eigenvalues $\sigma_i^2 \geq 0$ arranged in a decreasing order – $\sigma_1^2 \geq \sigma_2^2 \geq \dots \geq \sigma_p^2$;

- (iii) $V = (v_1 | v_2 | \dots | v_n)$ with v_1, v_2, \dots, v_n any orthonormal basis of \mathbb{R}^n such that

$$v_i = \frac{1}{\sigma_i} X u_i \quad \forall i = 1, \dots, r \tag{3.19}$$

As a consequence, if $k \leq r$ – the only interesting case – there holds

$$\sum_{j=1}^k \sigma_j v_j u_j^T = \sum_{j=1}^k \sigma_j \frac{1}{\sigma_j} (X u_j) u_j^T = \sum_{j=1}^k (X u_j) u_j^T \tag{3.20}$$

and to obtain the k -PC model it is enough to pose $h_j = u_j \ \forall j = 1, \dots, k$. Moreover, $\lambda_j = \sigma_j^2 \ \forall j = 1, \dots, k$.

4. PCA and multicomponent theories

From a purely computational/statistical point of view, multicomponent theories are strictly related to PCA. Indeed multicomponents equations can be interpreted as PC models of adhesion work data, although in an indirect way. The number of components coincides with the number of PC taken into account. Any multicomponent theory describes the work of adhesion between a solid – denoted by the index $i = 1, \dots, s$ – and a liquid – specified by $j = 1, \dots, l$ – by expressions of the form (1.11), which can be collected into the matrix relationship

$$W^{adh} = 2 \sum_{k=1}^c \sigma^{(k)} \lambda^{(k)T} \tag{4.1}$$

on having introduced the $s \times l$ adhesion work matrix

$$W^{adh} = \begin{pmatrix} W_{11}^{adh} & \dots & W_{1l}^{adh} \\ \vdots & & \vdots \\ W_{s1}^{adh} & \dots & W_{sl}^{adh} \end{pmatrix}, \tag{4.2}$$

the solid and liquid component column vectors

$$\xi^{(k)} = \begin{pmatrix} \xi_1^{(k)} \\ \vdots \\ \xi_s^{(k)} \end{pmatrix} \quad \lambda^{(k)} = \begin{pmatrix} \lambda_1^{(k)} \\ \vdots \\ \lambda_l^{(k)} \end{pmatrix} \quad \forall k = 1, \dots, c \tag{4.3}$$

and the auxiliary solid component column vectors

$$\sigma^{(k)} = \begin{pmatrix} \sigma_1^{(k)} \\ \vdots \\ \sigma_s^{(k)} \end{pmatrix} = \sum_{h=1}^c S_{hk} \xi^{(h)} = \sum_{h=1}^c S_{kh} \xi^{(h)} = \sum_{h=1}^c S_{kh} \begin{pmatrix} \xi_1^{(h)} \\ \vdots \\ \xi_s^{(h)} \end{pmatrix}. \tag{4.4}$$

Throughout the paper, the vectors $\lambda^{(1)}, \dots, \lambda^{(c)}$ will be assumed linearly independent, and so will $\sigma^{(1)}, \dots, \sigma^{(c)}$ – or $\xi^{(1)}, \dots, \xi^{(c)}$ due to invertibility of the matrix S .

Principal components of the adhesion work matrix are obtained from the eigenvectors of the $l \times l$ real symmetric and semipositive definite matrix

$$W^{\text{adh}T} W^{\text{adh}} = 4 \sum_{h=1}^c \lambda^{(h)} \sigma^{(h)T} \sum_{k=1}^c \sigma^{(k)} \lambda^{(k)T} = 4 \sum_{h,k=1}^c \sigma^{(h)T} \sigma^{(k)} \lambda^{(h)} \lambda^{(k)T} \quad (4.5)$$

which maps the vector space \mathbb{R}^l into the linear subspace of \mathbb{R}^l spanned by $\lambda^{(1)}, \dots, \lambda^{(c)}$

$$W^{\text{adh}T} W^{\text{adh}} x \in \text{span} \left\{ \lambda^{(1)}, \dots, \lambda^{(c)} \right\} \quad \forall x \in \mathbb{R}^l \quad (4.6)$$

since

$$W^{\text{adh}T} W^{\text{adh}} x = 4 \sum_{h,k=1}^c \sigma^{(h)T} \sigma^{(k)} \lambda^{(h)} \lambda^{(k)T} x = 4 \sum_{h,k=1}^c [\sigma^{(h)T} \sigma^{(k)}] [\lambda^{(k)T} x] \lambda^{(h)}. \quad (4.7)$$

Obviously the linear space $\text{span} \left\{ \lambda^{(1)}, \dots, \lambda^{(c)} \right\}$ has dimension l

$$\dim \text{span} \left\{ \lambda^{(1)}, \dots, \lambda^{(c)} \right\} = l \quad (4.8)$$

due to the assumed linear independency of $\lambda^{(1)}, \dots, \lambda^{(c)}$. As a consequence, the real non-negative spectrum of $W^{\text{adh}T} W^{\text{adh}}$ consists of

- (i) c positive eigenvalues $\sigma_1, \dots, \sigma_c$, whose eigenvectors belong to $\text{span} \left\{ \lambda^{(1)}, \dots, \lambda^{(c)} \right\}$ and define an orthonormal basis therein;
- (ii) a 0 eigenvalue with multiplicity $l - c$ and eigenvectors forming an arbitrary (orthonormal) basis in the orthogonal complement of $\text{span} \left\{ \lambda^{(1)}, \dots, \lambda^{(c)} \right\}$.

\mathbb{R}^l is thus decomposed into a direct sum of the corresponding subspaces

$$\mathbb{R}^l = \text{span} \left\{ \lambda^{(1)}, \dots, \lambda^{(c)} \right\} \oplus \text{span} \left\{ \lambda^{(1)}, \dots, \lambda^{(c)} \right\}^\perp \quad (4.9)$$

each of which is invariant through $W^{\text{adh}T} W^{\text{adh}}$:

$$\begin{aligned} W^{\text{adh}T} W^{\text{adh}} \left(\text{span} \left\{ \lambda^{(1)}, \dots, \lambda^{(c)} \right\} \right) &\subseteq \text{span} \left\{ \lambda^{(1)}, \dots, \lambda^{(c)} \right\} \\ W^{\text{adh}T} W^{\text{adh}} \left(\text{span} \left\{ \lambda^{(1)}, \dots, \lambda^{(c)} \right\}^\perp \right) &\subseteq \text{span} \left\{ \lambda^{(1)}, \dots, \lambda^{(c)} \right\}^\perp. \end{aligned} \quad (4.10)$$

The eigenvalues $\sigma_1, \dots, \sigma_c$ are also the positive singular values of the matrix W^{adh} . The loadings $p^{(1)}, \dots, p^{(c)}$ of the c first principal components constitute

an orthonormal basis of the linear subspace $\text{span}\{\lambda^{(1)}, \dots, \lambda^{(c)}\}$, so that appropriate constants α_{kh} defining a non-singular $c \times c$ matrix α allow us to write

$$\lambda^{(k)} = \sum_{h=1}^c \alpha_{kh} p^{(h)} \quad \forall k = 1, \dots, c. \quad (4.11)$$

The works of adhesion become then

$$W^{\text{adh}} = 2 \sum_{k=1}^c \sigma^{(k)} \lambda^{(k)T} = 2 \sum_{k,h=1}^c \sigma^{(k)} \alpha_{kh} p^{(h)T} = 2 \sum_{h=1}^c \left(\sum_{k=1}^c \alpha_{kh} \sigma^{(k)} \right) p^{(h)T} \quad (4.12)$$

and the scores of the first c principal components can be expressed as

$$t^{(h)} = \sum_{k=1}^c \alpha_{kh} \sigma^{(k)} \quad \forall h = 1, \dots, c, \quad (4.13)$$

whence we deduce the inverse relationships

$$\sigma^{(k)} = \sum_{h=1}^c (\alpha^{-1})_{hk} t^{(h)} \quad \forall k = 1, \dots, c \quad (4.14)$$

and coming back to the solid component vectors

$$\xi^{(r)} = \sum_{k=1}^c (S^{-1})_{rk} \sigma^{(k)} = \sum_{h,k=1}^c (S^{-1})_{rk} (\alpha^{-1})_{hk} t^{(h)}. \quad (4.15)$$

As a conclusion, the vectors $\lambda^{(k)}$ and $\xi^{(k)}$ of liquid and solid components can be written as appropriate linear combinations of loadings $p^{(k)}$ and scores $t^{(k)}$ of the c principal components of W^{adh} . *A necessary condition for a multicomponent model to be adequate to describe the works of adhesion of the materials considered is that adhesion work matrix W^{adh} admits a good principal component representation, with the same number of PCs as the number of components per each compound* (the residual, unexplained deviance of adhesion work data must be small). Noticeably, this statement is independent on the estimate of components, i.e., it provides an *a priori* criterion.

5. The nonlinear best-fit estimate of components revisited

The PC loadings and scores entering formulas (4.11) and (4.15) are easily calculated through SVD of the data matrix W^{adh} , for which standard and efficient algorithms are available. For any choice of the nonsingular $c \times c$ matrix α , the liquid component vectors $\lambda^{(k)}$ and the solid component vectors $\xi^{(k)}$ given by (4.11) and (4.15), respectively, provide formally equivalent models of the adhesion work matrix, with the same residual sum of squares. The matrix α has a fixed number c^2 of entries, independent on the number of solids and liquids involved in the calculations. Such entries can be used as free variables to match, at least approximately, the surface tension equations of all the liquids (1.12), for instance by minimizing the sum of squares

$$\sum_{j=1}^l \left[\sum_{h,k=1}^c \lambda_j^{(h)} S_{hk} \lambda_j^{(k)} - \gamma_j \right]^2 \quad (5.1)$$

thus leading to an optimization problem with a number of free variables independent on l . This means that as a first approximation a tentative solution of equation (1.12) is searched in the known linear space $\text{span}\{p^{(1)}, \dots, p^{(c)}\}$. The result will provide a reasonable initial guess to reckon a nonlinear best-fit solution for the set of both adhesion work and liquid surface tension equations, (1.11) and (1.12).

6. Scale multiplicity

By definition, equations (4.11) and (4.15) leave invariant the adhesion work matrix W^{adh} for any choice of the nonsingular matrix α . For a nonsingular $\tilde{\alpha}$ in place of α the liquid and solid component vectors become

$$\tilde{\lambda}^{(k)} = \sum_{h=1}^c \tilde{\alpha}_{kh} p^{(h)} \quad \tilde{\xi}^{(r)} = \sum_{k=1}^c (S^{-1})_{rk} \sigma^{(k)} = \sum_{h,k=1}^c (S^{-1})_{rk} (\tilde{\alpha}^{-1})_{hk} t^{(h)} \quad (6.1)$$

and define a new set of components as accurate as the original one in what concerns the only adhesion works. If we consider the arbitrary nonsingular $c \times c$ matrix β defined by $\tilde{\alpha} = \beta\alpha$, the new components are related to the old ones by the linear transformations

$$\tilde{\lambda}^{(k)} = \sum_{h=1}^c \tilde{\alpha}_{kh} p^{(h)} = \sum_{h,a=1}^c \beta_{ka} \alpha_{ah} p^{(h)} = \sum_{a=1}^c \beta_{ka} \lambda^{(a)} \quad k = 1, \dots, c \quad (6.2a)$$

and

$$\begin{aligned}
 \tilde{\xi}^{(r)} &= \sum_{h,k=1}^c (S^{-1})_{rk} (\tilde{\alpha}^{-1})_{hk} t^{(h)} = \sum_{h,k=1}^c (S^{-1})_{rk} [(\tilde{\alpha}^T)^{-1}]_{kh} t^{(h)} \\
 &= \sum_{h=1}^c [S^{-1}(\tilde{\alpha}^T)^{-1}]_{rh} t^{(h)} = \sum_{h=1}^c [S^{-1}(\alpha^T \beta^T)^{-1}]_{rh} t^{(h)} \\
 &= \sum_{h=1}^c [S^{-1}(\beta^T)^{-1}(\alpha^T)^{-1}]_{rh} t^{(h)} = \sum_{h=1}^c [S^{-1}(\beta^T)^{-1} S S^{-1}(\alpha^T)^{-1}]_{rh} t^{(h)} \\
 &= \sum_{h,k=1}^c [S^{-1}(\beta^T)^{-1} S]_{rk} [S^{-1}(\alpha^T)^{-1}]_{kh} t^{(h)} = \sum_{k=1}^c [S^{-1}(\beta^T)^{-1} S]_{rk} \xi^{(k)} \quad (6.2b)
 \end{aligned}$$

$\forall r = 1, \dots, c$. The further requirement that the transformation (6.2) does not affect equation (1.12) of the liquid surface tensions implies that the matrix β is no more arbitrary but obeys $\beta^T S \beta = S$, since $\forall j = 1, \dots, l$

$$\begin{aligned}
 \gamma_j &= \sum_{h,k=1}^c \tilde{\lambda}_j^{(h)} S_{hk} \tilde{\lambda}_j^{(k)} = \sum_{h,k=1}^c \sum_{a,b=1}^c \beta_{ha} \lambda_j^{(a)} S_{hk} \beta_{kb} \lambda_j^{(b)} \\
 &= \sum_{a,b=1}^c \sum_{h,k=1}^c (\beta^T)_{ah} S_{hk} \beta_{kb} \lambda_j^{(a)} \lambda_j^{(b)} = \sum_{a,b=1}^c (\beta^T S \beta)_{ab} \lambda_j^{(a)} \lambda_j^{(b)} \\
 &= \sum_{a,b=1}^c S_{ab} \lambda_j^{(a)} \lambda_j^{(b)}, \quad (6.3)
 \end{aligned}$$

so that liquid and solid components undergo the same transformation

$$\tilde{\lambda}^{(k)} = \sum_{h=1}^c \beta_{kh} \lambda^{(h)} \quad \tilde{\xi}^{(k)} = \sum_{h=1}^c \beta_{kh} \xi^{(h)} \quad \forall k = 1, \dots, c. \quad (6.4)$$

We conclude that surface tensions and works of adhesion do not specify components in a unique way, but only up to a transformation (6.4), thus allowing a multiplicity of scales for the multicomponent model. In order to remove multiplicity and specify a unique well-defined scale, a conventional assignment of component values to some reference compounds is needed. The most general matrix β is completely determined by $c(c - 1)/2$ parameters, thus the reference components must be chosen accordingly. It is easily verified that the set of matrices β

$$\mathbb{G} = \{ \beta \text{ real } c \times c \text{ non-singular matrix} : \beta^T S \beta = S \} \quad (6.5)$$

constitutes a non-Abelian group with respect to the usual matrix product, because $\mathbb{I}^T S \mathbb{I} = S$, while $\beta^T S \beta = S$ implies $(\beta^{-1})^T S \beta^{-1} = S$ and finally

$$\beta^T S \beta = S, \quad \gamma^T S \gamma = S \implies (\beta\gamma)^T S \beta\gamma = \gamma^T \beta^T S \beta\gamma = \gamma^T S \gamma = S. \tag{6.6}$$

Up to isomorphisms, \mathbb{G} can also be identified with the generalized orthogonal group $O(d_+, d_-; \mathbb{R})$, on having denoted with d_+ and d_- respectively the number of positive and negative eigenvalues of the symmetric matrix S [30]; as an analytical manifold, the group $O(d_+, d_-; \mathbb{R})$ has dimension $c(c - 1)/2$. Matrices $\beta \in \mathbb{G}$ show very peculiar spectral properties, because equality $\beta^T S = S \beta^{-1}$ implies for any $\mu \in \mathbb{C}$

$$(\beta^T - \mu \mathbb{I}) S = S (\beta^{-1} - \mu \mathbb{I}) \tag{6.7}$$

and therefore

$$\det(\beta^T - \mu \mathbb{I}) \det S = \det S \det(\beta^{-1} - \mu \mathbb{I}) \tag{6.8}$$

or, equivalently,

$$\det(\beta - \mu \mathbb{I}) = \det(\beta^{-1} - \mu \mathbb{I}) \tag{6.9}$$

so that if $\mu \in \mathbb{C}$ is an eigenvalue of β , so is μ^{-1} . Moreover, any matrix of \mathbb{G} infinitesimally close to the identity can be written into the form

$$\mathbb{I} + \varepsilon \Gamma + o(\varepsilon) \quad (\varepsilon \rightarrow 0) \tag{6.10}$$

in terms of the scalar $\varepsilon \in \mathbb{R}$ and of any $c \times c$ real matrix Γ which satisfies the relationship

$$[\mathbb{I} + \varepsilon \Gamma^T + o(\varepsilon)] S [\mathbb{I} + \varepsilon \Gamma + o(\varepsilon)] = S \quad (\varepsilon \rightarrow 0) \tag{6.11}$$

i.e.,

$$S \Gamma + \Gamma^T S = 0. \tag{6.12}$$

By using the symmetry of the structure matrix S , equation (6.12) reduces to

$$S \Gamma + (S \Gamma)^T = 0 \tag{6.13}$$

and therefore the most general form of Γ must be

$$\Gamma = S^{-1} \Omega \tag{6.14}$$

on having denoted with Ω any real skewsymmetric $c \times c$ matrix, which depends on $c(c - 1)/2$ parameters. Vice versa, a simple calculation shows that whenever (6.12) is satisfied the exponential of Γ

$$\exp(\Gamma) = \sum_{n=0}^{\infty} \frac{1}{n!} \Gamma^n = \lim_{n \rightarrow +\infty} \left(\mathbb{I} + \frac{\Gamma}{n} \right)^n \tag{6.15}$$

belongs to \mathbb{G} . Consistently, the spectrum of matrices Γ obeying (6.14) is symmetrical with respect to zero, owing to the chain of equalities

$$\begin{aligned} \det(\Gamma - \mu\mathbb{I}) &= \det(S^{-1}\Omega - \mu\mathbb{I}) = \det(S^{-1})\det(\Omega - \mu S) \\ &= \det(S^{-1})\det(\Omega^T - \mu S^T) = \det(S^{-1})\det(-\Omega - \mu S) \\ &= (-1)^c \det(S^{-1})\det(\Omega + \mu S) = (-1)^c \det(S^{-1}\Omega + \mu\mathbb{I}) \\ &= (-1)^c \det(\Gamma + \mu\mathbb{I}) \end{aligned} \tag{6.16}$$

so that if μ is an eigenvalue of Γ , so is $-\mu$. Finally, it is easily checked that the whole set of matrices of type (6.14) forms a Lie algebra with respect to matrix product. The general theory of Lie groups and algebras [30] ensures that elements of \mathbb{G} can be conveniently expressed by exponentiation of matrices (6.14).

Scale multiplicity due to the invariance transformation group (6.5) leads to the important consequence that the material parameters (components) of a multicomponent theory do not necessarily admit a direct interpretation, as they are obtained by surface tension and contact angle data *only*, unless it is possible to establish a correlation with other scales of surface energetics admitting a direct measurement of the model parameters [25].

7. Scale multiplicity in some special multicomponent models

In the very special case of vOCG theory, the $c = 3$ components can be more satisfactorily identified with the square roots of the dispersive, acidic and basic parameters

$$\sqrt{\gamma^{LW}}, \quad \sqrt{\gamma^+}, \quad \sqrt{\gamma^-}. \tag{7.1}$$

The structure matrix is given by

$$S = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tag{7.2}$$

and has signature $\{1, 1, -1\}$, which is also its spectrum. For matrices of the invariance group \mathbb{G} close to unity according to (6.10), condition (6.14) provides

$$\Gamma = S \begin{pmatrix} 0 & \omega_1 & \omega_2 \\ -\omega_1 & 0 & \omega_3 \\ -\omega_2 & -\omega_3 & 0 \end{pmatrix} = \begin{pmatrix} 0 & \omega_1 & \omega_2 \\ -\omega_2 & -\omega_3 & 0 \\ -\omega_1 & 0 & \omega_3 \end{pmatrix} \tag{7.3}$$

since S is clearly idempotent. Arbitrary choices of the real scalars $\omega_1, \omega_2, \omega_3$ allow us to write the elements of group \mathbb{G} in the exponential form

$$\beta = \exp \begin{pmatrix} 0 & \omega_1 & \omega_2 \\ -\omega_2 & -\omega_3 & 0 \\ -\omega_1 & 0 & \omega_3 \end{pmatrix}. \tag{7.4}$$

As already outlined, the $c = 3$ components of the QC model coincide with the Qin and Chang parameters up to a constant scale factor

$$\frac{1}{\sqrt{2}}P^d, \quad \frac{1}{\sqrt{2}}P^a, \quad \frac{1}{\sqrt{2}}P^b \quad (7.5)$$

with a structure matrix of the form

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} \quad (7.6)$$

and signature $\{1, 1, -1\}$ as in vOCG theory. Owing to idempotency of S , the group generators Γ take then the general form

$$\Gamma = S \begin{pmatrix} 0 & \omega_1 & \omega_2 \\ -\omega_1 & 0 & \omega_3 \\ -\omega_2 & -\omega_3 & 0 \end{pmatrix} = \begin{pmatrix} 0 & \omega_1 & \omega_2 \\ \omega_2 & \omega_3 & 0 \\ \omega_1 & 0 & -\omega_3 \end{pmatrix} \quad (7.7)$$

and the matrices of the connected component of \mathbb{G} containing the identity are expressed as

$$\beta = \exp \begin{pmatrix} 0 & \omega_1 & \omega_2 \\ \omega_2 & \omega_3 & 0 \\ \omega_1 & 0 & -\omega_3 \end{pmatrix} \quad \forall \omega_1, \omega_2, \omega_3 \in \mathbb{R}. \quad (7.8)$$

Extended Drago model describes surface energetics in terms of $c = 4$ parameters per compound

$$C_A, \quad C_B, \quad E_A, \quad E_B, \quad (7.9)$$

the idempotent structure matrix being given by

$$S = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad (7.10)$$

with signature $-$ and spectrum $\{1, 1, -1, -1\}$. Invariance group transformations are generated by the matrices

$$\Gamma = S \begin{pmatrix} 0 & \omega_1 & \omega_2 & \omega_3 \\ -\omega_1 & 0 & \omega_4 & \omega_5 \\ -\omega_2 & -\omega_1 & 0 & \omega_6 \\ -\omega_4 & -\omega_5 & -\omega_6 & 0 \end{pmatrix} = \begin{pmatrix} -\omega_1 & 0 & \omega_4 & \omega_5 \\ 0 & \omega_1 & \omega_2 & \omega_3 \\ -\omega_4 & -\omega_5 & -\omega_6 & 0 \\ -\omega_2 & -\omega_1 & 0 & \omega_6 \end{pmatrix} \quad (7.11)$$

and can then be put into the exponential form

$$\beta = \exp \begin{pmatrix} -\omega_1 & 0 & \omega_4 & \omega_5 \\ 0 & \omega_1 & \omega_2 & \omega_3 \\ -\omega_4 & -\omega_5 & -\omega_6 & 0 \\ -\omega_2 & -\omega_1 & 0 & \omega_6 \end{pmatrix} \quad \forall \omega_i \in \mathbb{R}, \quad i = 1, 2, \dots, 6. \quad (7.12)$$

It is worthy of note that in the original Drago model it is not mandatory to apply the same linear transformation to both acids and bases, since the inclusion of a compound in the class of acids or in that of bases must be *a priori* decided and the two classes appear predefined and disjoint. Therefore, no constraint of the form $\beta^T S \beta = S$ applies and the matrix β is simply requested to be non-singular – $\mathbb{G} \in GL(c, \mathbb{R})$, the general linear group of real $c \times c$ matrices.

8. Conclusions

It has been proved that PCA techniques may be helpful, firstly, in determining whether a multicomponent model is actually adequate to account for adhesion work data of a certain set of liquids and solids and, secondly, in the calculation of material parameters. The approach can be applied to multicomponent theories reducible to a bilinear/quadratic structure, which are those most commonly used in adhesion science and technology. The necessary precondition to do that is the availability of a full and reliable set of adhesion works between given test liquids and solids, to which the nonlinear best-fit approach may be applied. An interesting by-product is the general occurrence of scale multiplicity, due to the possibility of changing the whole set of components by an appropriate group of linear transformations which leave all the multicomponent model equations invariant. Selection of a specific scale requires the arbitrary definition of a suitable number of components for appropriately chosen reference compounds. This circumstance prevents the direct chemico-physical interpretation of material components as they are estimated from surface tension and adhesion work equations, that is from surface tension and equilibrium contact angle data only. Such an interpretation could come only from an eventual theoretical or empirical correlation between a particular scale of a multicomponent theory and other models of surface energetics where the material parameters are susceptible of a direct measurement.

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