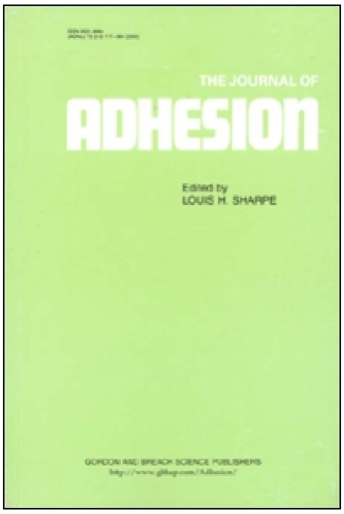

**The Journal of Adhesion**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

# Comments to J. R. Huntsberger: Surface Chemistry and Adhesion—A Review of Some Fundamentals

A. W. Neumann[a]; A. V. Rapacchietta[a]
[a] Department of Mechanical Engineering, University of Toronto,

**To cite this Article** Neumann, A. W. and Rapacchietta, A. V.(1977) 'Comments to J. R. Huntsberger: Surface Chemistry and Adhesion—A Review of Some Fundamentals', The Journal of Adhesion, 9: 1, 87 — 91

**To link to this Article: DOI:** 10.1080/00218467708075102

**URL:** http://dx.doi.org/10.1080/00218467708075102

*J. Adhesion*, 1977, Vol. 9. pp. 87–91

Printed in Scotland

# Letters

## COMMENTS TO J. R. HUNTSBERGER: SURFACE CHEMISTRY AND ADHESION— A REVIEW OF SOME FUNDAMENTALS

Dear Sir,

In a recent paper, J. R. Huntsberger[1] made a number of assertions which require comment. Essentially, the paper is based on Good's interaction parameter which the author introduces with the following statement:

> What follows is based on the premise that the interaction parameter $\phi$ makes Eq. (1) exact.

$$W_{\text{adh}} = 2\phi(\gamma_1\gamma_2)^{\frac{1}{2}} \tag{1}$$

Although the average reader may know proper definitions for $W_{\text{adh}}$ and $\phi$ and therefore not need them here, we object to the lack of procedural concern, combined with misleading allusions to "exactness" of his Eq. (1). Exactness, after all, is a concept in the area of differential equations, but the above relation is not a differential equation and $\phi$ is certainly not an integrating factor.

This, by itself, is of course very minor, and indeed might be hardly worth mentioning, would it not reveal a trend: The author gives just about any proposition which he deems useful a special aura of importance, irrespective of its general scientific status. The most important case in question is that he refers to six specific equations as "fundamental equations" or "fundamental relations". Dr. Huntsberger's article deals with quantities like surface tensions, free energies and work and hence with thermodynamics. But since Gibbs[2] "fundamental" has had only one meaning: a relation (equation) linking the internal energy of the system with the entropy and the other appropriate independent extensive parameters, and the Legendre transformed versions of such a relation. These fundamental equations are "fundamental" because they contain all thermodynamic information relevant to the system.

Turning then to Dr. Huntsberger's equations (3)–(8) (to be denoted here by H3, H4, . . . etc.)

$$\gamma_{SL} = \gamma_{SO}+\gamma_{LV}-2\phi(\gamma_{SO}\gamma_{LV})^{\frac{1}{2}} \tag{H3}$$

$$\gamma_{SV}-\gamma_{SL} = \gamma_{LV}\cos\theta \tag{H4}$$

$$\gamma_{SO}-\pi_{e} = \gamma_{SV} \tag{H5}$$

$$\pi_{SL}-\pi_{e} = \gamma_{LV}\cos\theta \tag{H6}$$

$$\pi_{SL} = \gamma_{SO}-\gamma_{SL} \tag{H7}$$

$$\gamma_{SO}-\pi_{e}-\gamma_{SL} = \gamma_{LV} \text{ when } \theta = 0 \tag{H8}$$

it is apparent that they are not fundamental equations, and Dr. Huntsberger is not free to designate them as such: H(3) is the definition of Good's interaction parameter, and should of course have appeared prior to its use in Eq. (H1); Eqs. (H5) and (H7) are definitions of equilibrium spreading pressures, Eq. (H4) is an equilibrium condition and Eqs. (H6) and (H8) are equations derived in some manner from the others.

The author then uses these relations to generate a series of parameterized figures using a variety of quantities as dependent and independent coordinates, respectively, for various values of Good's interaction parameter. This procedure cannot be faulted, although we again doubt the significance of the whole operation: quantitative insight into the behaviour of a thermodynamic system can be derived only either by microscopic–molecular considerations (strictly speaking from microscopic thermodynamics) or from experiments, seeking, e.g., equation of state relationships. In the area of interest here, Good's calculations of $\phi$ from intermolecular forces[3] is an example of the former and Zisman's well known plots is an example for the latter. The author seems to be oblivious of this fact and introduces instead, by implication, the dogma that all relevant plots of surface tension quantities have relevance or significance only if they are curves of constant $\phi$. While it is indeed often desirable in a thermodynamic argument to keep at least one variable constant, it is usually only a matter of convenience to choose a particular one. There is certainly no reason to assume that in the wide area of solid/liquid interactions only curves of constant $\phi$ have physical significance. The fact that a Zisman plot or our plot does not represent curves of constant $\phi$ cannot be construed as a deficiency.

In the most recent of our papers,[4] criticized by Dr. Huntsberger, we have dealt in considerable detail with the proposition $\gamma_{SL} = 0$ in the limiting case when the contact angle approaches zero. In order to deal with any objections, we would need more of an argument than Dr. Huntsberger's statement that we make unwarranted assumptions. His next claim, that our $(\gamma_{LV})^*$ value is identical with Zisman's long established $\gamma_c$ we dealt with over ten years ago.[5] The values are not equal, and hence not identical. We would, however, be agreeable to the statement that there is an operational similarity between the two values, and that we have, through the years, been strongly influenced by Zisman's work.

Dr. Huntsberger next claims that we substituted $(\gamma_{SV})^* = \gamma_c$ into Eq. (H6). The fact is that we did not define nor otherwise introduce a quantity $(\gamma_{SV})^*$, nor did the quantity $\gamma_c$ enter the paper at any stage. The latter fact, we had hoped, would be obvious to the reader of our paper,[4] particularly in conjunction with the paper immediately preceding[6]: We are attempting a thermodynamic approach to a quantitative interpretation of contact angles, and $\gamma_c$ is defined operationally, but not thermodynamically.

Unfortunately, Dr. Huntsberger's further arguments are incorrect due to faulty logic and mathematics, even if we retain $\gamma_{SV}$, as in our paper,[4] rather than $\gamma_c$. First of all our relation

$$\phi = 1 - 0.0075\,\gamma_{SL} \tag{H18}$$

is essentially an empirical one. The fact that $\phi = \phi(\gamma_{SV})$ under certain circumstances, which the author fails to specify, does not contradict Eq. (H18) in any way: Basically we have, from the definition of $\phi$

$$\phi = \phi(\gamma_{SV}, \gamma_{LV}, \gamma_{SL}).$$

For the type of curve considered, it is implied that $\gamma_{SV} = \text{const.}$, and the existence of an equation of state implies $\gamma_{SL} = \gamma_{SL}(\gamma_{LV})$, so that $\phi = \phi(\gamma_{SL})$ is *a priori* possible. That this relation is given by a straight line and that the slope is, within the limitations of experimental contact angle data presently available, approximately independent of $\gamma_{SV}$ cannot be proven nor disproven by any amount of reorganizing of experimental data and defining relations. This is so in spite of the author's assertion that it can be easily shown from the "fundamental" relationships that $d\phi/d\gamma_{SL}$ is linear only at constant $\gamma_{LV}/\gamma_{SO}$, and that the slope varies with changes in $\gamma_{LV}/\gamma_{SO}$ substantially, say by a factor of 5 over the range of systems considered in our paper.[4]

Since the author felt it unnecessary to prove his claims, it may be appropriate to prove them mathematically wrong here. First of all it must be realized that the result of a differentiation of $\phi$ will depend on whether or not $\gamma_{SV}$, $\gamma_{LV}$ and $\gamma_{SL}$ are all considered independent or not. If they are independent, we have

$$\frac{d\phi}{d\gamma_{SL}} = \left(\frac{\partial\phi}{\partial\gamma_{SL}}\right)_{\gamma_{SV},\gamma_{LV}} = -\frac{1}{2(\gamma_{SV}\gamma_{LV})^{\frac{1}{2}}}$$

It is this result which Dr. Huntsberger probably meant to obtain. This derivative is constant when $\gamma_{SV}\gamma_{LV}$ is constant and not, as the author claims, when $\gamma_{LV}/\gamma_{SV}$ is constant. However, if we are to keep $\gamma_{SV}$ and $\gamma_{LV}$ constant, this derivative cannot be applied to the experimental curves of $\phi$ versus

$\gamma_{SL}$ which are developed from systems with no such specific restrictions on $\gamma_{SV}$ and $\gamma_{LV}$. To obtain a physically reasonable formulation for $d\phi/d\gamma_{SL}$, we have to consider that $\gamma_{SV}$, $\gamma_{LV}$ and $\gamma_{SL}$ are not independent, but that a relation

$$\gamma_{SL} = \gamma_{SL}(\gamma_{SV}, \gamma_{LV})$$

exists as proven in one of our papers (6). With this constraint, the above derivative becomes

$$\frac{d\phi}{d\gamma_{LS}} = \left(\frac{\partial\phi}{\partial\gamma_{SL}}\right)_{\gamma_{SV},\gamma_{LV}} + \left(\frac{\partial\phi}{\partial\gamma_{SV}}\right)_{\gamma_{LV},\gamma_{SL}} \left(\frac{\partial\gamma_{SV}}{\partial\gamma_{SL}}\right)_{\gamma_{LV}} + \left(\frac{\partial\phi}{\partial\gamma_{LV}}\right)_{\gamma_{SV},\gamma_{SL}} \left(\frac{\partial\gamma_{LV}}{\partial\gamma_{SL}}\right)_{\gamma_{SV}},$$

or, after evaluation of the partial derivatives of $\phi$:

$$\frac{d\phi}{d\gamma_{SL}} = -\frac{1}{2(\gamma_{SV}\gamma_{LV})^{\frac{1}{2}}} + \frac{1}{4\gamma_{SV}(\gamma_{SV}\gamma_{LV})^{\frac{1}{2}}}(\gamma_{SV}-\gamma_{LV}+\gamma_{SL})\left(\frac{\partial\gamma_{SV}}{\partial\gamma_{SL}}\right)_{\gamma_{LV}} + \frac{1}{4\gamma_{LV}(\gamma_{SV}\gamma_{LV})^{\frac{1}{2}}}(\gamma_{LV}-\gamma_{SV}+\gamma_{SL})\left(\frac{\partial\gamma_{LV}}{\partial\gamma_{SL}}\right)_{\gamma_{SV}}$$

This relation obviously does not allow any general inferences, but it certainly does not preclude the correctness of our deduction[4] as given in Eq. (H18) above.

It is, in principle, desirable to study the questions at hand in situations where all the interfacial tensions are directly measurable, e.g. for liquid/liquid/vapour systems. While it is difficult to study a possible correlation between $\phi$ and the interfacial tension between two liquids in the case of low molecular weight substances because of problems with the mutual solubility,[7] such a study is possible for pairs of polymer melts. Clearly, the surface tensions of two polymer melts can be determined by conventional techniques, just as the interfacial tensions between polymeric melts. Thus all the quantities in the defining equation for $\phi$ are measurable directly. Plots of $\phi$ versus the polymer/polymer interfacial tension for a variety of combinations have been given.[8, 9] The data satisfy a linear relationship between $\phi$ and the liquid/liquid interfacial tension rather well. It is interesting that the slope for these systems is larger than the slope for the solid/liquid systems by approximately a factor of 2, whereas the intercept is also $\phi = 1$ at zero liquid/liquid interfacial tension. Overall the behaviour of liquid/liquid polymer systems provides strong support for our work with solid/liquid systems: For both types of systems, there is an approximately linear relationship between $\phi$ and the interfacial tension. The only difference is that the polymeric liquid/liquid systems have a substantially larger slope $d\phi/d\gamma_{L_1L_2}$.

Finally, we should like to point out that probably the best way of testing the merit of approaches like ours is to apply them to the description of independent phenomena and processes. We have, over the years, applied our approach to a variety of problems,[10] including a comparison of calorimetric heats of immersion with heats of wetting obtained from temperature dependent contact angles,[11] phagocytosis and cellular adhesiveness,[12] and particle engulfment by solidifying melts.[13] We have not found an inconsistency yet.

A. W. NEUMANN
A. V. RAPACCHIETTA

Department of Mechanical Engineering
University of Toronto

(*Received April 19, 1977*)

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