

Fowkes F M. Attractive forces at interfaces. *Ind. Eng. Chem.* **56**:40-52, 1964

The various intermolecular attractions in a liquid contribute independently to the surface tension γ . The dispersion force contribution γ^d , measurable for any liquid or solid, may be used to calculate the dispersion force contribution to the work of adhesion between immiscible phases, permitting precise calculation of interfacial tensions and contact angles. [The SC[®] indicates that this paper has been cited over 195 times since 1964.]

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"Graduate research with W.D. Harkins at Chicago set me on a career in surface chemistry, which I was pursuing at Shell Development Company when I became very interested in intermolecular forces because of a course on solubility given by Joel Hildebrand from the nearby Berkeley campus of the University of California. I dreamed of applying Hildebrand's methods to interfacial phenomena. So, when in 1961 the Association of California Chemistry Teachers asked me to speak on surface chemistry, I took the opportunity to try the Hildebrand approach; this synthesis turned out to be more successful than I imagined.

"This approach involved two fairly reasonable assumptions. The surface tension of a pure liquid γ is known to be a direct measure of its intermolecular forces; it was assumed that the surface tension is the sum of the contributions of the dispersion

forces γ^d (which operate between all substances) and the contributions of specific interactions (such as hydrogen bonds, γ^h). The second assumption was that the dispersion force attraction between immiscible phases (1 and 2) could be predicted by $2\gamma_1^d\gamma_2^d$, an energy-average similar to that used by Hildebrand or by Girifalco and Good.¹ It was found that γ^d values could be determined for all liquids and solids and that interfacial tensions and contact angles could be predicted as accurately as they can be measured.

"The work was first presented to the Association of California Chemistry Teachers in 1961 and first published in 1962.² The highly cited 1964 article was a contribution to an ACS symposium on surface chemistry. It summarized the work done since 1961 and included a novel extension to calculation of Hamaker constants for calculation of long-range dispersion force interactions.

"This work has stimulated much theoretical and experimental work by others. R.J. Good defended this work and popularized it.³ Soon experimentalists discovered γ^d anomalies with the higher n-alkanes, which have been resolved just recently.⁴

"In the field of solubility my proposal for the separation of intermolecular forces into separate terms led to 'multidimensional' solubility parameters, and in surface studies several investigators tried to calculate the contribution of specific intermolecular interactions with a term such as $2\gamma^h\gamma^d$. I take exception to these approaches and prefer to use Drago's equations for hard and soft Lewis acid-base interactions.⁵

"This article is highly cited because it publicized the discovery of \bar{a}^d , the dispersion force contribution to surface tension, a useful property of liquids and solids."

1. Girifalco LA & Good R J. A theory for the estimation of surface and interfacial energies. *J Phys. Chem.* **61**:904-9, 1957.
2. Fowkes F M. Determination of interfacial tensions, contact angles, and dispersion forces in surfaces by assuming additivity of intermolecular interactions in surfaces. *J. Phys. Chem.* **66**:382, 1962.
3. Good R J. Estimation of surface energies from contact angles. *Nature* **212**:276-7, 1966.
4. Fowkes F M. Surface effects of anisotropic London dispersion forces in n-alkanes. *J. Phys. Chem* **84**:510-12, 1980.
5. Fowkes F M & Mostafa M A. Acid-base interactions in polymer adsorption. *Ind. Eng. Chem Prod. Res. Develop* **17**:3-7, 1978.