First Ten Ångstroms

Surface Energy Methods Summary

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The following table summarizes the common surface energy methods. The underlying problem is that there is no definitive "combining rule." A combining rule is an equation that tells you the *interfacial* tension across the *interface* in terms of the original *substance-vapor surface* tensions of the materials forming the interface. More recent formulations analyze (break down) the total surface tension into a sum of components, each component having some chemical specificity. The equations we use are approximations, for better or worse. Each has their place in history and application.

Name	Liquid contact angles required	Surface energy γ_{SV} components computed	Combining rule equation	Comments
Wetting Tension	1	$\gamma_{SV} - \gamma_{LS}$	None Uses right hand side of Young's equation: $\gamma_{LV} \cos(\theta)$	Alternative to combining rule approaches; has same units (mN/m, etc.); varies from $-\gamma_{LV}$ (say, -72) for non-wetting surfaces to $+\gamma_{LV}$ (+72) for fully wetting surfaces. To the degree Young's equation is valid, wetting tension = $\gamma_{SV} - \gamma_{LS}$, rather than γ_{SV}. Primary application is in biochemistry and biomaterials.
Zisman	2 or more	γ_{CWT}, critical wetting tension $\gamma_{CWT} \approx \gamma_{SV}$	None Extrapolation of γ_{LV} for $\cos(\theta)$ values to the γ_{LV} value for $\cos(\theta) = 1$ ($\theta=0$)	Earliest attempt to assign a specific value to surfaces based on contact angles. Dates from just after WWII. A liquid with $\gamma_{LV} = \gamma_{CWT}$ should just completely wet out on surface.
Girifalco-Good-Fowkes-Young (GGFY)	1	$\gamma_{SV} = $ total γ	Geometric mean Interaction parameter $\Phi=1$ $\pi = $ vapor pressure (≈ 0) $(1 + \cos(\theta)) \gamma_{LV} =$ $\quad 2 \sqrt{(\gamma_{SV}\gamma_{LV})} - \pi$	The earliest combining rule and still probably the most used in manufacturing. Tends to be low for non-wetting surfaces. Close to Zisman's γ_{CWT} for wetting surfaces. Water is the most common test liquid.

Name	Contact angles	Surface energy γ_{SV} components	Combining rule equation	Comments
Extended GGFY	1	γ_{SV} = total γ	Geometric mean Interaction parameter Φ set by measured θ on low-energy (PTFE) surface. π = vapor pressure (≈ 0) $(1 + \cos(\theta))\,\gamma_{LV} = 2\,\sqrt{(\gamma_{SV}\gamma_{LV})} - \pi$	Ad-hoc method by FTA to improve GGFY results on low energy surfaces. Water is typically used for GGFY. For water, 112° for 72.8 is used to set Φ. Vapor pressure π is included in the solution but rarely used, as it is rarely known.
Neumann (and Dwok) Equation of State	1	γ_{SV} = total γ	Geometric mean Interaction parameter Φ effectively set by averaged measurements by Neumann to give "beta" $\beta = .0001247$ $(1 + \cos(\theta))\,\gamma_{LV} = 2\,\sqrt{(\gamma_{SV}\gamma_{LV})} \times \exp(-\beta(\gamma_{LV} - \gamma_{SV})^2)$	Empirically set β gives good results on low energy surfaces, but not remarkably different from the above Extended GGFY. Suffers same limitations as other 1-liquid systems that the choice of test liquid profoundly affects the resulting γ. Single liquid methods are used as convenience to obtain a quick result.
Owens-Wendt	2	$\gamma_{SV}^{LW} = \gamma_{SV}^{D} =$ London-van der Waals/ non-polar/ dispersive γ_{SV}^{P} = polar/ hydrogen bonding $\gamma_{SV} = \gamma_{SV}^{D} + \gamma_{SV}^{P}$	Geometric mean $(1 + \cos(\theta))\,\gamma_{LV} = 2\,\sqrt{(\gamma_{S}^{D}\gamma_{L}^{D})} + 2\sqrt{(\gamma_{S}^{P}\gamma_{L}^{P})}$ for notational compactness from here on, $\gamma_{SV} = \gamma_{S}$ and $\gamma_{LV} = \gamma_{L}$ if there n liquids, a set of n equations must be solved	First method to use two liquids and compute two components: decomposes solid γ_{SV} into dispersive and polar components. Most widely used method in industrial research. Water and methylene iodide are common liquid choices.
Wu	2	$\gamma_{SV}^{LW} = \gamma_{SV}^{D} =$ London-van der Waals/ non-polar/ dispersive γ_{SV}^{P} = polar/ hydrogen bonding $\gamma_{SV} = \gamma_{SV}^{D} + \gamma_{SV}^{P}$	Harmonic mean $(1 + \cos(\theta))\,\gamma_{LV} = 4[\gamma_{S}^{D}\gamma_{L}^{D}/(\gamma_{S}^{D} + \gamma_{L}^{D}) + \gamma_{S}^{P}\gamma_{L}^{P}/(\gamma_{S}^{P} + \gamma_{L}^{P})]$	Alternative 2-liquid, 2-component formulation, primarily applied to polymers. Wu wrote a useful book on polymers with much data. Note, all choices for a combining rule work relatively well on non-wetting (hydrophobic) surfaces because most bonding is dispersive and these assumptions work well.

Name	Contact angles	Surface energy γ_{SV} components	Combining rule equation	Comments
Lewis acid-base/ van Oss-Good-Chaudhury	3	$\gamma_{SV}^{LW} = \gamma_{SV}^{D} =$ London/ dispersive $\gamma_{SV}^{A} = \gamma_{SV}^{+} =$ acid $\gamma_{SV}^{B} = \gamma_{SV}^{-} =$ base $\gamma_{SV} = \gamma_{SV}^{D} + \gamma_{SV}^{A} + \gamma_{SV}^{B}$	Geometric mean $(1+ \cos(\theta))\, \gamma_{LV} =$ $2\,\sqrt{(\gamma_S^D \gamma_L^D)} + 2\sqrt{(\gamma_S^A \gamma_L^B)} +$ $2\sqrt{(\gamma_S^B \gamma_L^A)}$	This logical extension analyzed the surface tension into dispersive, acid, and base components. It requires contact angles from three liquids. Note acids bond to bases. This method is widely used in the automotive paint industry to design paints that adhere to particular polymers. Also used extensively in academic work.
Over-determined equations	same as combining rule selected	same as combining rule selected	same as combining rule selected	Uses *extra* liquids and contact angles to sample a wider chemical space. For example, rather than use the minimum of 2 liquids for Owens-Wendt, one might use three or four *different* liquids. Equations are solved by a minimization technique.
Peterson	many, number set as results unfold	$\gamma_{SV}^{LW} = \gamma_{SV}^{D} =$ London/ dispersive $\gamma_{SV}^{A} = \gamma_{SV}^{+} =$ acid $\gamma_{SV}^{B} = \gamma_{SV}^{-} =$ base $\gamma_{SV} = \gamma_{SV}^{D} + \gamma_{SV}^{A} + \gamma_{SV}^{B}$	Geometric mean derivative Various solutes are added to test solutions and contact angles measured over a range of temperatures. The method presumes "cross-talk" between components and competition for binding sites.	This is an alternative philosophy, put forth in 2005 by I R Peterson (e-mail i.peterson@coventry.ac.uk) published in **Surface Coatings International Part B: Coatings Transactions**, Vol.88 Others are working on similar extensions. The term "corresponding states" is sometimes used. These are likely to remain academic pursuits until their benefit as predictive methods can be established.

For introductory information, see

http://www.firsttenangstroms.com/pdfdocs/SurfaceEnergy.pdf

and, for an example application,

http://www.firsttenangstroms.com/pdfdocs/TPOsinAutomotive2000.pdf

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