

Editorial Comment

What Would J. Willard (Gibbs) Do?

When flipping through the inaugural issue of *International Journal of Wettability Science and Technology*, my attention was drawn to an article by Makkonen titled “Faulty Intuitions of Wetting.”

For years I have been in awe of J. Willard Gibbs, who over years of careful analysis and intuition came up with the foundations of thermodynamics. Gibbs’ work has provided a firm foundation upon which subsequent scientists and technologists have built not only theories, but also practical equipment and engines that power our modern society. So the question arises, if thermodynamics has been so reliable, why do researchers such as Makkonen keep stumbling across situations where those concepts do not seem to work for contact angle and wettability issues? I wonder what Gibbs would be thinking if he were to read articles published in the last 60 years in this academic discipline.

When first reading Makkonen’s article, my reaction was relief. I was pleased to be able to read a studied explanation of aspects that had been bothering me since 2015, when I was in a group that wrote an article titled “Contact angles and wettability of cellulosic surfaces: A review of proposed mechanisms and test strategies” (*BioResources* 10(4), 8657, 2015). When I had started working on that review article, my thinking was something like “This is a mature field. All that’s needed is a review article showing how the concepts apply in the case of cellulosic surfaces.” But my expectations were soon dashed once I began to read the literature. In particular, I was struck by the work of Fowkes and co-authors, whose 1990 article “Interfacial interactions between self-associated polar liquids and squalene used to test equations for solid-liquid interfacial interactions” (*Colloids Surf.* 42, 367) pretty much destroyed my confidence in any of the prevailing analyses based on such concepts as acid-base components of surface energy, among others. Also I sensed an alarming disconnect between some researchers who paid attention to surface roughness issues (including the Wenzel equation) and those who ignored such issues while attempting to fit data to ever-more com-

plicated equations based on the purported free energy of perfectly smooth surfaces, which they assumed could be relevant for real situations.

Makkonen raises troubling questions about some issues that are yet more fundamental than those we mainly considered in our 2015 article. He makes the point that contact angles often represent situations where a contact angle “gets stuck”. As Gibbs would be quick to note, his thermodynamic theories apply only when processes occur in a reversible manner, not when things get stuck or build up until they undergo sudden change. Makkonen suggests that the free energy of a solid surface can be used as the basis of the Young equation, which governs contact angles. But is there a reversible way to form a solid surface? As yet, there does not seem to be a way to separately evaluate the interfacial free energy between (a) a droplet and a solid, together with (b) the interfacial free energy between the same solid and an atmosphere. My hunch is that Gibbs would accept the existence of a difference between those two terms (as in Dupré’s definition of the thermodynamic work of adhesion), but probably not either of those terms as a separate thermodynamic quantity.

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