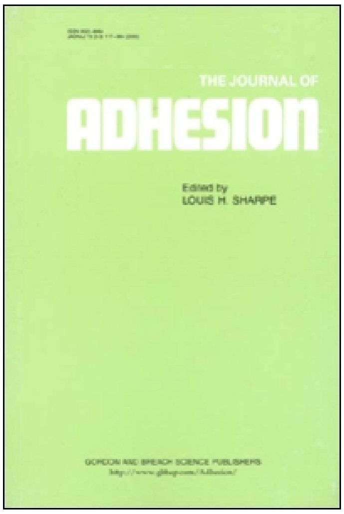

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Letter

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Letter

Sir,

The criticism[1] of my paper[2] entitled "Capillary Attraction and Hysteresis of Wetting" is based on the assumption that systems, which are not in equilibrium even in one respect, cannot be treated by classical thermodynamics: "free energy should be calculated for the *equilibrium* states of the system". That this view is erroneous, is shown, for instance, by the adiabatic expansion of gases, which gave rise to an early triumph of thermodynamics, although the gas is not in equilibrium with the surroundings.[3]

Another example is closely related to the subject of my previous note.[2] If a drop is deposited on a horizontal plate, it may assume the profile indicated in Figure 1, continuous line. If a droplet is added to the larger drop, the new profile will look like the line of dashes; and if a small droplet is removed from the initial drop, the profile may be represented by the dotted line. Because the three-phase line (in which the vapor, the liquid, and the solid meet) did not shift, the visible contact angles θ are different for the three drops.

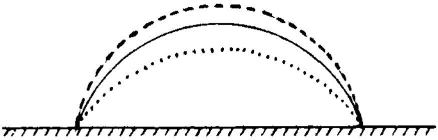

Figure 1.

Thus, the region of the system adjacent to the three-phase line is, or seems to be, not in equilibrium. Nevertheless, equilibrium reigns everywhere else. All three profiles shown in Figure 1 are determined by the equilibrium between the gravitation which tends to flatten the drop and the capillary pressure which tends to achieve a spherical symmetry. The shape of each drop can, in principle, be derived either by calculating the free energy (Gauss, 1829) or by considering the forces acting on its surface (Laplace, 1805). As a matter of fact, the θ often is used as the limit of integration of the differential equation for the drop profile. The apparent absence of equilibrium along the 3-phase line has no effect on these calculations.

Many additional examples of systems which behave in a reversible manner in some, but not all, changes, come to mind but are omitted here to save space. However, the two following remarks deserve publication, in my opinion.

Visible contact angles were mentioned above. The real θ may be different from the visible θ and may correspond to an equilibrium even in the presence of hysteresis of wetting. This uncertainty is caused by surface roughness.[4] When the edge of the drop rests on a slope and the slope forms an angle α with the horizontal, the visible angle is θ–α, while the true contact angle remains equal to the equilibrium angle θ.

The reference to Bakker (1928) in the letter[1] may lead a reader to the conclusion that Bakker derived the equations for capillary attraction. In reality, they are due to Laplace. A history of the theories of capillary attraction has recently been published.[5]

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