The Cassie-Baxter Equation

The Cassie-Baxter wetting, model introduced in Refs. 1-2, deals with the wetting of *flat chemically heterogeneous* surfaces. Suppose that the surface under the drop is flat, but consists of *n* sorts of materials randomly distributed over the substrate as shown in Figure 1. The radius of the wetted area is supposed to be much larger than the characteristic length scale of heterogeneities. This corresponds to the assumptions of the Cassie-Baxter wetting model.[1-3] Each material is characterized by its own surface tension coefficients $\gamma_{i,SL}$ and $\gamma_{i,SA}$, and by the fraction f_i in the substrate surface, $f_1 + f_2 + ... + f_n = 1$. The Cassie equilibrium apparent contact angle θ^* in this wetting situation will be given by following equation:

$$\cos\theta^* = \frac{\sum_{i=1}^{n} f_i(\gamma_{i,SA} - \gamma_{i,SL})}{\gamma}, \qquad (1)$$

predicting the so-called Cassie apparent contact angle θ^* on flat chemically heterogeneous surfaces. When the substrate consists of two kinds of species, the Cassie-Baxter equation obtains the form:

$$\cos\theta^* = f_1\cos\theta_1 + f_2\cos\theta_2, \qquad (2)$$

which is widespread in the scientific literature dealing with the wetting of heterogeneous surfaces. It is noteworthy that Eq. (2) was based by Cassie and Baxter on semi-qualitative considerations.[1,2] More rigorous derivation of the Cassie-Baxter equation exploiting the principle of virtual works can be found in Refs. 4-5. The most general variational approach to the wetting of *flat chemically heterogeneous* surfaces demonstrates that the Cassie-Baxter equation represents the transversality condition of the variational problem of wetting.[6] The variational approach demonstrates that the Cassie equilibrium apparent contact angles are insensitive to the volume and shape of droplets and external fields (including gravity).[6]

The Israelachvili and Gee criticism of the Cassie-Baxter model

Israelachvili and Gee criticized the traditional Cassie-Baxter equation and proposed instead of it the following equation[7]:

$$(1+\cos\theta^*)^2 = f_1(1+\cos\theta_1)^2 + f_2(1+\cos\theta_2)^2 . \qquad (3)$$

Cassie-Baxter wetting in a situation where a droplet partially sits on air

The peculiar form of the Cassie-Baxter equation given by Eq. (1) was successfully used for the explaining the phenomenon of superhydrophobicity. Consider a situation where the mixed surface is comprised of solid surface and air pockets, with the contact angles θ_Y (which is the Young contact angle of the solid substrate) and π respectively. We denote by f_s and $1-f_S$ relative fractions of solid and air respectively. Thus we deduce from Eq. (2):

$$\cos\theta^* = -1 + f_S(\cos\theta_Y + 1)\,. \qquad (4)$$

Formula (4) predicts the apparent contact angle in the situation where a droplet sits partially on solid and partially on air, and it was shown experimentally that it does work for a diversity of porous substrates.[8] It is noteworthy that switching from Eq. (4) to Eq. (2) is not straightforward, because the triple (three phase) line could not be at rest on pores.[9] The reasonable explanation for the success of the Cassie-Baxter Eq. (4), perhaps, may be related to considering the fine structure of the triple line, considering a thin precursor film, surrounding a droplet[9].

The Cassie-Baxter wetting of curved surfaces

The Cassie-Baxter equation has been successfully generalized for curved surfaces[10].

Cassie-Baxter impregnating wetting

There exists one more possibility of the heterogeneous wetting: this is the so-called Cassie-Baxter impregnating wetting state first introduced in Ref. 4 and well explained in Ref. 5. In this case liquid penetrates into the grooves of the solid and the drop finds itself on a substrate viewed as a patchwork of solid and liquid (solid ‘‘islands’’ ahead of the drop are dry, as shown in Figure 3. The Cassie-Baxter Eq. (1) can be applied to the mixed surface depicted in Figure 3, with contact angles θ_Y and zero respectively. We then derive for the apparent contact angle θ^*:

$$\cos\theta^* = 1 - f_S + f_S\cos\theta_Y\,. \qquad (5)$$

We denote here by f_s and $1-f_S$ the relative fractions of the solid and liquid phases underneath the droplet.[4-5] Eq. (5) may be obtained from the first variational principles for the composite surface comprised of two species, characterized by the Young angles of θ_Y and zero.[6]

The use of Cassie-Baxter Eqs. 1-2, 4 needs some care. It should be taken into account that only an area of the substrate adjacent to the triple line exerts an influence on the Cassie apparent contact angle θ^*.[3, 11-12]

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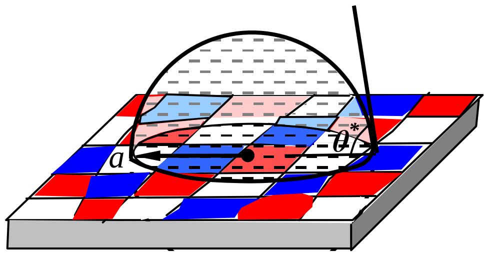

Figure 1. Cassie-Baxter wetting of flat chemically heterogeneous surfaces (various colors correspond to different chemical species).

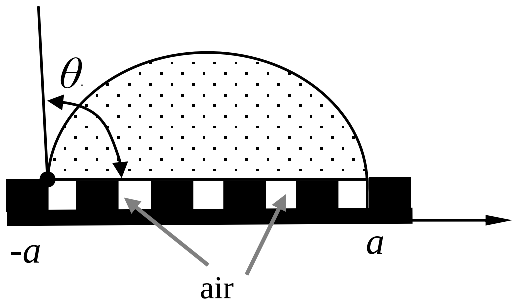

Figure 2. The particular case of the Cassie wetting: a droplet is partially supported by solid and partially by air cushions.

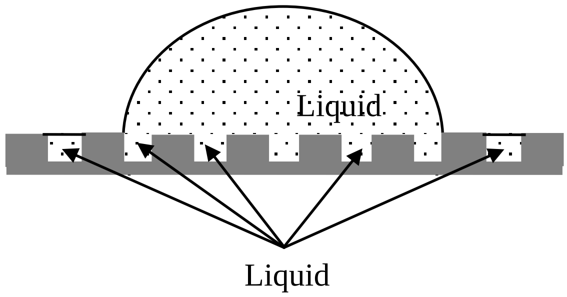

Figure 3. The Cassie-Baxter impregnating wetting state.