# Why some things are darker when wet

John Lekner and Michael C. Dorf

Ångstrom has proposed that rough absorbing materials are darker when wet because their diffuse reflection makes possible total internal reflection in the water film covering them, increasing the likelihood of the absorption of light by the surface. His model is extended here in two ways: the probability of internal reflection is calculated more accurately, and the effect on absorption of the decrease of the relative refractive index (liquid to material instead of air to material) is estimated. Both extensions decrease the albedo of the wetted surface, bringing the model into good agreement with experiment.

## I. Introduction

From early childhood we learn to distinguish wet from dry, not just by touch, but also by sight. Most objects, especially those with rough and absorbing surfaces, are darker when wet: they reflect less light. In a model for this phenomenon proposed by Ångstrom,[1] the surface roughness leads to diffuse reflection, and thus to total internal reflection at the liquid–air interface of the thin film of liquid covering the surface. This reflection gives an increased probability of the absorption of light by the surface, and thus a darker surface.

Ångstrom's model is extended in the following two sections. The results are then compared with experiment. In the final section we also compare Ångstrom's approach to that of Bohren[2] and Twomey et al.[3] (TBM), in which the darkening is taken to be due to the increase in the forward scattering on wetting.

## II. Diffuse Scattering and Internal Reflection

An optically smooth surface reflects specularly, whether or not the surface is covered by a film of liquid. A ray of light reflecting at a smooth surface will not be totally reflected at the liquid–air interface. If the surface is rough, its diffuse reflection sends some light out obliquely enough to be totally internally reflected at the liquid–air interface. This increases the chance of absorption at the surface.

Consider a rough absorbing surface, such as a blackboard. We treat the surface as an array of randomly oriented facets, each of which reflects specularly. When wet, a thin liquid layer covers the surface. Light incident on this layer has probability $1 - R_l$ of reaching the surface, where $R_l$ is the reflectance at the air–liquid interface. Some fraction of the transmitted light is absorbed by the surface. Call this fraction $a$. Of the light which is reflected by the surface, let $p$ be the fraction which is then reflected back at the liquid–air interface, so that it is once again incident on the surface. The process is illustrated in Fig. 1.

Continuing the process illustrated *ad infinitum*, the total probability of absorption by the rough surface is

$$A = (1 - R_l)[a + a(1 - a)p + a(1 - a)^2 p^2 + \ldots]$$

$$= \frac{(1 - R_l)a}{1 - p(1 - a)}. \tag{1}$$

Ångstrom evaluates $p$ as follows: all the light with an angle of incidence greater than the critical angle $\theta_c$ ($= \arcsin 1/n_l$) onto the liquid–air interface will be totally reflected. Thus $p$ may be estimated as the fraction of diffusely reflected light which lies outside the cone generated by rays whose reflection angle is $\theta_c$. For a Lambertian surface, the intensity reflected at angle $\theta$ is proportional to $\cos\theta$. Light emerging at angles $\theta$ to $\theta + d\theta$ subtends a solid angle $2\pi \sin\theta d\theta$. Thus

$$p \approx \frac{2\pi \displaystyle\int_{\theta_c}^{\pi/2} d\theta \, \sin\theta \, \cos\theta}{2\pi \displaystyle\int_0^{\pi/2} d\theta \, \sin\theta \, \cos\theta} = \cos^2\theta_c = 1 - 1/n_l^2. \tag{2}$$

Equations (1) and (2) are together equivalent to the last equation in Ångstrom's Sec. 4(ii), except that he omits the $1 - R_l$ factor.
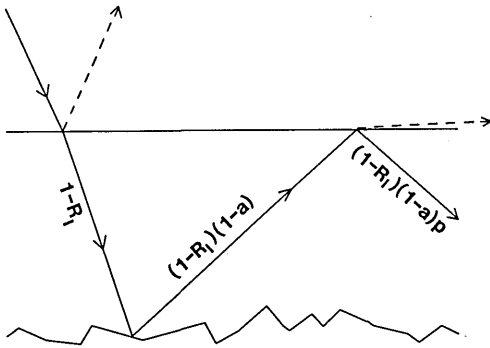
Fig. 1. Liquid layer over a rough surface. The coefficients represent the fraction of the incident light intensity which is transmitted along each path.

Equation (2) underestimates $p$: the reflectivities for both polarizations are generally small but not zero for $\theta < \theta_c$; see, for example, Ref. 4, Sec. 1.5, or Ref. 5, Figs. 1-3 and 1-4. For a surface which reflects diffusely according to Lambert's law, the probability reflection at the liquid–air interface is

$$p = \frac{\int_0^{\pi/2} d\theta \, \sin\theta \, \cos\theta R(x,1/n_l)}{\int_0^{\pi/2} d\theta \, \sin\theta \, \cos\theta} = \int_0^1 dx R(x, 1/n_l), \qquad (3)$$

where $x = \sin^2\theta$ and $R(x,n)$ is the reflectance at an interface between media 1 and 2, with $n = n_2/n_1$. Here $n = 1/n_l < 1$ and $R$ is unity for $x > n^2$ so

$$p = 1 - n^2 + \int_0^{n^2} dx R(x,n). \qquad (4)$$

For both polarizations, the reflectances have the property that

$$R(x,n) = R(x/n^2, 1/n) \qquad (5)$$

(this was noted by Stern[6] for the transmittances). On changing to the variable $y = x/n^2$, the integral in Eq. (4) may be written as

$$n^2 \int_0^1 dy R(n^2 y, n) = n^2 \int_0^1 dy R(y, 1/n) = n^2 \bar{R}(1/n). \qquad (6)$$

The last equality expressed the integral in terms of the average reflectance of an isotropically illuminated surface,

$$\bar{R}(n) = \frac{\int_0^{\pi/2} d\theta \, \sin\theta \, \cos\theta R(x,n)}{\int_0^{\pi/2} d\theta \, \sin\theta \, \cos\theta} = \int_0^1 dx R(x,n) \qquad (7)$$

(in correspondence with the average transmittance defined by Stern[6]). For unpolarized light, Stern's formulas (9a) and (9b) lead to

$$\bar{R}(n) = \frac{3n^2 + 2n + 1}{3(n + 1)^2} - \frac{2n^3(n^2 + 2n - 1)}{(n^2 + 1)^2(n^2 - 1)} + \frac{n^2(n^2 + 1)}{(n^2 - 1)^2} \log n$$

$$- \frac{n^2(n^2 - 1)^2}{(n^2 + 1)^3} \log \frac{n(n + 1)}{n - 1} \qquad (n > 1). \quad (8)$$

From Eqs. (4) and (6) we have the result

$$p = 1 - \frac{1}{n_l^2} [1 - \bar{R}(n_l)]. \qquad (9)$$

For water, this formula gives a $p$ larger by $\sim 9\%$ than the Ångstrom estimate (0.475 instead of 0.437).

## III. Probability of Absorption by a Wetted Surface

The parameter $a$ in Eq. (1) is the fraction of the light incident on the surface which is absorbed. (The above refers to a single interaction: the total probability of absorption, allowing for reflections at the liquid–air interface, is $A$.) Ångstrom takes $a$ to have the same value for the wet as for the dry surface. We expect $a_w$ (the value when wet), to be greater than $a_d$ (the value when dry), since the absorbing medium will normally have the real part of its refractive index greater than unity. Since reflection is caused by wave vector mismatch, and since wave vectors are determined by refractive indices, covering the surface with a layer of liquid (with $n_l > 1$) results in less reflection.

The value of $a_d$ is in principle determined by the complex refractive index $n_r + i n_i$ of the material, and by the roughness of the surface (which influences the average angle of incidence on its randomly oriented facets, and the probability of multiple interactions, as in a crevice). The value of $a_w$ is in addition a function of $n_l$, the refractive index of the liquid film covering it. For the purpose of comparing the albedos $1 - a_d$ and $1 - A$ of the dry and wetted surfaces, we estimate $a_w$ in terms of $a_d$, $n_l$, and $n_r$ as follows.

For small absorption ($n_i \ll n_r$), $a_d \approx 1 - \bar{R}(n)$ where $\bar{R}(n)$ is the average reflectance of an isotropically illuminated surface, defined in Eq. (7). The assumption made here is that the angle of incidence on facets of the rough surface (for, say, normal illumination) has the same distribution as would be obtained for a plane surface illuminated isotropically. Similarly, $a_w \approx 1 - \bar{R}(n_r/n_l)$ when $n_i \ll n_r$. Thus when the absorption is small,

$$a_w \approx a_d[1 - \bar{R}(n_r/n_l)]/[1 - \bar{R}(n_r)] \equiv a_w^{(0)}. \qquad (10)$$

When the absorption is large, on the other hand, and $a_d \to 1$, we expect $a_w \approx a_d \equiv a_w^{(1)}$. We will use an interpolation formula which incorporates these limiting forms by giving $a_w^{(0)}$ and $a_w^{(1)}$ the weights $1 - a_d$ and $a_d$:

$$a_w \approx (1 - a_d)a_w^{(0)} + a_d a_w^{(1)},$$

or $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (11)$

$$\frac{a_w}{a_d} \approx (1 - a_d)\frac{1 - \bar{R}(n_r/n_l)}{1 - \bar{R}(n_r)} + a_d.$$

Because $\bar{R}(n)$ is a monotonically increasing function of $n$ (for $n > 1$), $\bar{R}(n_r/n_l) < \bar{R}(n_r)$ for $n_l < n_r$, and so $a_w \geq a_d$, with the greatest percentage increase occurring at low absorption. For small $a_d$ and $n_l = 4/3$ (water), the ratio of $a_w/a_d$ takes the values 1.07, 1.08, and 1.10 for $n_r = 1.5$, 2, and 2.5 (most minerals have refractive indices within this range). When we put $a_w$, as defined by (11), for $a$ in Eq. (1), we can find the ratio of the total absorption by a wetted surface to the absorption by the dry surface, $A/a_d$. This provides one measure of how much darker a given surface becomes when wetted.

The ratio $A/a_d$ is plotted as a function of $n_l$ (for two values of $a_d$) in Fig. 2.

We note from Fig. 2 that the darkening effect is strongest when the absorption is weak. When the absorption is strong the contribution of internal reflections is less important, since a larger fraction of the light is absorbed on first contact with the surface.

The interpolation formula (11) gives $a_w \geq a_d$. We expect this to be true for all cases where the refractive index of the liquid film lies between that of air and the real part of the index of the surface. Now from Eq. (1) it follows that

$$\frac{dA}{da} = \frac{(1-p)(1-R_1)}{[1-p(1-a)]^2} > 0 \tag{12}$$

for all physical values of $a$, $p$, and $R_l$. Thus taking $a_w = a_d$ provides a lower bound for $A$. This is shown by the dashed curves in Fig. 2, which neglect the increase in absorption due to the change in relative refractive index at the surface on wetting. As such, they isolate the effect of internal reflection, which is seen to be dominant for a weakly absorbing rough surface.

## IV. Comparison with Experimental Data and Discussion

Albedo is defined and measured as the ratio of the light intensity incident on a surface to that diffusely reflected back by the surface. For example, Ångstrom measured albedo by taking the reading ($\alpha$) of his upward facing pyranometer, then the reading ($\beta$) of the same pyranometer facing the ground. The albedo is $\beta/\alpha$. His Table III lists albedo comparisons for dry and wet sand (0.182 and 0.091) and for dry and wet black mold (0.141 and 0.084). The variability is indicated by the last value being an average of 0.091, 0.081, and 0.081. These are plotted as circles in Fig. 3, on which we compare theoretical albedos ($1 - a_d$ for the dry surface, $1 - A$ for the wet). Other data available are those listed by Sellers,[7] Table IV, for dry and wet sand dunes, and dry and wet savanna (grassland). These appear, respectively, as the large and small crosses in Fig. 3, the size of the crosses indicating the range of values observed.

The agreement of Ångstrom's theory (as extended here) with the data is similar to that obtained by Twomey *et al.*[3] (TBM), as shown in their Fig. 5. Ångstrom's original theory, incorporating only the possibility of internal reflection (and that approximately) is seen to show the same trend, but agreement with the data is not quite so good. [However, the variation in the darkening of sand with the refractive index of the wetting liquid is not so strong in the Ångstrom model as in the experimental data of TBM (Ref. 3, Fig. 7).]

The fact that the two theories, based on such different models, both agree with the (very limited) wet and dry albedo data is surprising. Ångstrom's theory would seem to apply best to rough solid surfaces, such as blackboards, asphalt, or concrete. The TBM theory, based on the idea of enhanced forward scattering when the interstitial space in the medium is filled with liquid, would seem to apply best to finely divided media, such as sand. An intermediate case is that of
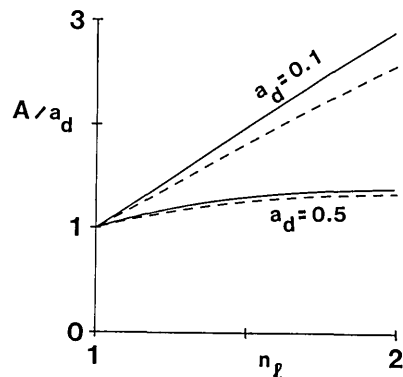


Fig. 2. Ratio of average absorption by a wet surface to that of the dry surface, for varying refractive index of the wetting liquid. For the solid curves $a_w$ is given by (11), with $n_r = 2$. The dashed curves are drawn for $a_w = a_d$ (Ångstrom). In all cases we have set $R_l = (n_l - 1)^2/(n_l + 1)^2$ (normal illumination).
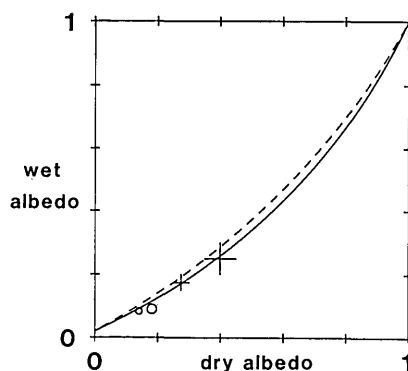


Fig. 3. Wet albedo as a function of dry albedo, for a layer of water over a rough surface. Normal illumination is assumed. Dry albedo is given by $1 - a_d$ and wet albedo by $1 - A$, the latter calculated using $n_r = 2$. $A$ is given by Eq. (1); the solid line has $a = a_w$ as given by (11), and $p$ by Eq. (9). The dashed line has $a = a_d$ and $p$ given by (2) (Ångstrom's approximations). The experimental data are as described in the text.

clothing fabric. Further work, both experimental and theoretical, is surely needed on this fascinating everyday phenomenon.

## References

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