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ADDENDUM

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Abstract. Theory given previously, in a series of papers, relating surface phenomena to the electric double layer by a continuum theory of electrostatic forces in a fluid medium, has been found to be affected by a systematic error due to the attachment of the wrong sign to the mean curvature of the surface. In the present note, one of the main results of that theory, namely, the formula given for surface tension, is corrected and a discussion given of the corrected result.

The direct, as distinct from energy, approach to the theory of electrostatic force in a continuum, given by Brown (1951), was further developed by the present author (Cade 1954) to take into account the effect of the boundary layer which may be considered to separate a body from its ambient medium and be host of an electric double layer.

The original objective of the latter work was to investigate whether any significant modification was incurred to the classical force and torque formulae for the mechanical action on an isolated or immersed body, formulae in terms of the Maxwell stress tensor and which are reproduced in Brown's theory. Negative results were obtained with regard to *total* force and torque, but, when there is a double layer, the stress formulae themselves are quite different.

This fact is of significance if the body is non-rigid and, in a series of papers (Cade 1963, 1964, 1965, 1966), this aspect was studied and led to new developments. In the first place, since the double layer is an inherent physical attribute, present with or without an applied field, the existence of electrostatic stresses at a liquid surface is a normal physical property, and in this way the stress theory led to an electrostatic theory of surface tension, a formula being given (Cade 1963) identifying surface tension as a functional of the double-layer field. In the second place, if there is an applied field, the stresses, through containing their modification due to the double layer, predict the deformation of the liquid surface differently from what would be the case with the classical theory, although this would include surface tension added in an *ad hoc* manner (it is now present naturally, as part of the electrical action).

However, at the stage of the development of the surface-tension theory, a major systematic error entered which affected everything subsequently, namely, in the sign given to the mean curvature K_m of the surface.

The object of this note is to correct the surface-tension theory and discuss briefly the corrected result. The surface-deformation theory is defective on additional, independent, grounds, and will not be dealt with on this occasion.

The error we are presently concerned with was not a superficial one and had its origin in the fact that the sign of the mean curvature K_m of a surface, in contrast to that of the Gaussian curvature K, is arbitrary until a rule is decided upon for fixing it. In pure differential geometry it matters little what the rule is, and if K_m evolves from a certain prior formula (say in terms of the fundamental tensors of the surface, as in our case), it is the custom to accept it with the sign it comes out with, something which could itself be thought of as one of the possible rules. This is what we did and was the mistake. For in physics the convention is to regard the sign of mean curvature as positive if the liquid surface (or the surface of the denser one if there are two in contact) is locally convex†, and this convention has to be obeyed if we are to use a formula containing mean curvature for the purpose of making an identification with something in conventional physics. This then should have been our rule, and a quick review of the previous general theory (Cade 1963–1966) will show that it requires everywhere reversal of the sign before K_m.

We suppose that there is no externally applied field, the only field being that due to the double layer, and by what we have just said, the correct identification of the surface tension is by the previous expression (Cade 1963, equation (9)) preceded by a minus sign; that is,

$$T = -\frac{1}{4\pi}\int_{c_A}^{c_B} E_0 D_0 \, \mathrm{d}x_0. \tag{1}$$

We recall that x_0 is distance increasing in the outward-normal direction, 'outward' being from the liquid, or (if there are two) denser liquid, A into its environment B, and that otherwise, the suffix 0 refers to the outward-normal components of the electric intensity E_λ and electric displacement D_λ. The values c_A and c_B of the coordinate x_0 represent the sides of the boundary layer in A and B, respectively.

An inconsistency with the previous, erroneous, formula for T appears first to have been discovered by Devillez *et al* (1967) through their thermodynamical study of the double layer around a spherical colloidal particle, and the new result (1) is compatible with their theory. It deserves some comment, appearing intuitively suspect since surface tension must be positive and we tend to think of D_0 as having the same sign as E_0. But this is a prejudice which comes from our experience of matter in bulk and was partly responsible for an easy acceptance of the expression with the wrong sign. In fact, a closer intuitive look makes the present version more reasonable. For, E_0 and D_0 being related to the dielectric polarisation vector P_λ by $D_0 = E_0 + 4\pi P_0$, it indicates that the condition where $P_0 = 0$ is impossible, which is what we would expect since two layers of opposite free charge would tend to coalesce under their mutual attraction. It is, on the other hand, a self-consistent picture to imagine a layer of dipoles with the same orientation (towards or away from the surface) and maintaining a layer of positively charged particles (free charge) on the negative side and a negative one on the positive side, and elementary continuum electrostatics (in which we 'smooth out' the particles) shows that E_0 and D_0 have opposite signs if the dipole part of the double layer is strong enough relative to the free-charge part.

Description of surface tension by a continuum stress theory in a boundary layer is not new, ideas on these lines going back to G Bakker and K Fuchs in the last century; Defay and Sanfeld (1967) give a comprehensive citation of literature, and a review of the more classical approach is given by Buff (1960). The novel feature of the present

† More precisely, since a surface need be neither convex nor concave, a principal radius of curvature is positive if the curve (a section of the surface) of which it is the radius of curvature is locally convex with respect to the (or, if there are two, the denser) liquid; this determines the sign of the mean curvature.

theory is that, instead of making *ad hoc* assumptions concerning the nature of a purely hydrostatic stress tensor, it is based upon an electrohydrostatic stress tensor whose derivation assumes nothing beyond the ordinary generally accepted principles of physics.

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