CORRESPONDENCE

Surface Structure of Water and Ice—A Reply and a Correction

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IN a recent note Watts-Tobin (1963) criticizes the present author's paper with the title given above (Fletcher 1962) and states, without presenting any detailed discussion, that its shortcomings are sufficient to invalidate its conclusions. He maintains that the oriented layer whose existence was discussed in the original paper cannot possibly be stable because of electrostatic depolarizing effects.

It must be conceded at the outset that the model used in discussing water and ice surfaces was extremely crude and that a really good treatment should include the long-range electrostatic forces. However, a little consideration shows that inclusion of these forces affects only the numerical results and leaves the conclusions about the existence of the surface layer unaltered.

In the first place Watts-Tobin suggests that the depolarizing field is essentially the same as that in a spherical cavity in a thin dielectric slab. This is an oversimplification and is no longer true if the molecular dipoles are of finite size. Indeed a calculation with a thin slab of ' dipoles ' of finite size arranged on a cubic lattice shows that the depolarizing field may be much smaller than predicted from the ' point-dipole ' model, and may even have the opposite sign when the dipole length becomes comparable with the lattice spacing.

Suppose that the depolarizing field is of magnitude θP, where P is the polarization. Then the energy of a parallel dipole μ is $\theta P \mu$, and calculation shows that this energy is at most of order 10^{-13} erg, which is comparable with other energies involved in the calculation.

If θ is known, then, since P is proportional to the net orientation $(\alpha - \frac{1}{2})$ in the notation of the original paper, the depolarization energy per molecule is proportional to $(\alpha - \frac{1}{2})^2$. There is already a term of this form in the free energy expression so that the result of including the depolarization energy is simply to modify the numerical results. If $\theta > 0$ the film will be less stable than originally calculated, giving a thinner but still finite equilibrium layer.

It might be useful to note that this sort of difficulty has arisen before in connection with certain treatments of ferroelectricity (Megaw 1957)

where indeed the situation is in some ways quite comparable. From an empirical viewpoint one might also point out that monomolecular oil films on water surfaces orient their dipoles in parallel array normal to the surface despite the influence of any depolarizing forces.

In addendum it should be remarked that eqn. (26) of the original paper has been found to contain an error : the third term on the right hand side should contain an additional factor $[1 - \exp(-2\gamma d)]$. Minimization of this free energy expression by numerical methods gives a curve closely similar to that of fig. 2, above $-5°\text{c}$, but below this temperature the film thickness decreases more rapidly and the film vanishes at $-12°\text{c}$.

REFERENCES

FLETCHER, N. H., 1962, *Phil. Mag.*, **7**, 225.
MEGAW, H. D., 1957, *Ferroelectricity in Crystals* (Methuen), pp. 176–7, 183–8.
WATTS-TOBIN, R. J., 1963, *Phil. Mag.*, **8**, 333.