A supercooled water layer on ice—Reply

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ABSTRACT

The comments of Turner on the present author's earlier work on the existence of a quasi-liquid surface layer on ice are discussed. Reasons are given for accepting the approximations given in the 1973 version of the theory rather than reverting to the 1968 version as argued by Turner.

I am grateful to G. J. Turner (Turner 1983, preceding paper) for maintaining interest in this problem. As he remarks, there is a tendency for experimenters to regard the theory as established when they should really be more cautious than this.

My original semi-quantitative theory (Fletcher 1962) ascribed the driving force for liquid-layer formation to an energy difference ε_1 between two possible orientations (*protons in* or *protons out*) for water molecules at an ice or water surface. This treatment gave results which were reasonable in terms of liquid film thickness and its temperature dependence, but omitted certain important electrostatic effects (Fletcher 1963). The second version of the theory (Fletcher 1968) corrected these omissions and gave a treatment in which dipole–quadrupole coupling was the major driving force. The predictions were again reasonable and not very different from those of the first version. However, I became convinced that this second version had wrongly included the spherically symmetrical part of the quadrupole moment. This was corrected in the third version of the theory (Fletcher 1973) while retaining proper treatment of the other electrostatic effects. The major driving force then became once more the surface orientation energy ε_1. Numerical predictions were again altered only in detail.

In his paper, Turner (1983) argues for a return to the second (1968) version of the theory, and supplies two numerical corrections. His final eqn. (14) is identical with eqn. (21) of Fletcher (1968) except for these numerical factors, which do not significantly affect the final result. I remain convinced however, recognizing that all versions are at best first-order approximations, that the treatment given in Fletcher (1973) is most nearly correct.

A major difficulty with the development is, as Turner recognizes, a proper calculation of the dipole–quadrupole interaction energy. This calculation itself begs the question of the convergence of the multipole expansion for molecules in such close proximity as the water molecules in the quasi-liquid surface phase, and the legitimacy of truncating the expansion at quadrupole terms. If this is accepted, however, then certainly $\mathbf{V} \cdot \mathbf{E} = 0$ where $\mathbf{E}$ is the field at any molecular site due to its neighbours. The dipole–quadrupole interaction energy is then as given in Turner's eqn. (3) and, after averaging over configurations in the (x, y) plane containing the molecules, leaving the z configuration constant,

$$\Delta U_q \approx -\tfrac{1}{6} N_{zz} \, \partial E_z / \partial z.$$

The discussion of Turner's eqns. (5) and (6) is complicated by the inclusion of the self-energy of each molecular multipole, but leads to the same result if we accept that $\mathbf{V} \cdot \mathbf{E} = 0$. This can be seen by substituting (4) in (6) and using appropriate axes. It is thus essentially N_{zz} rather than Q that should appear in (8) and, since $|N_{zz}| \ll |Q|$, the magnitude of the dipole–quadrupole energy is small, as argued by Fletcher (1973).

The fact that in the development of each version of the theory $\partial E_z/\partial z \neq 0$ is meant to imply only the ensemble-average property of this quantity and not that $\mathbf{V} \cdot \mathbf{E} \neq 0$, at least within the multipole approximation.

The discussion set out above for point multipoles applies also to molecules of finite size, provided that their charge distributions do not interpenetrate. I concede that in a properly detailed quantum-mechanical calculation of molecular interactions the conclusions may be rather different, but such a calculation has not been attempted either by Turner or by me. Even a semi-classical treatment using molecular polarizabilities is probably impractical at present.

Within the framework of the multipole model, therefore, I do not think that the treatment in Fletcher (1973) has been shown to be significantly in error. The preferred surface orientation is probably that with protons buried in the liquid.

REFERENCES

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