MATTERS ARISING

Dielectric constant of ice

ADAMS has recently considered the dielectric constant of ice[1]. His Monte Carlo calculations fill a gap in the literature and complement previous calculations. However, his theoretical discussion, while displaying an important constraint on the Kirkwood–Frohlich (K–F) theory, falls short of the 'simple resolution' claimed.

Adams' primary equation[1] is

$$\langle \mu_1 \Sigma \mu_i \rangle_{\varepsilon'} N/9\varepsilon_0 kTV = (\varepsilon - 1)(2\varepsilon' + 1)/3(\varepsilon + 2\varepsilon') \qquad (1)$$

The right hand side (RHS) of equation (1) is obtained using macroscopic electrostatic theory for a spherical system of ice of dielectric constant ε surrounded by a much larger sphere of dielectric constant ε'. The left hand side (LHS) of equation (1) is obtained using microscopic statistical mechanics for a system of water dipoles in the central sphere which interact with each other as well as with the material in the outer sphere, whence the subscript ε'. The internal field E_{int} which acts on the dipoles in the calculation of the LHS of equation (1) is interpreted to be the cavity field which would have existed if the ice sphere were removed, whereas the polarization P is computed from the field actually present in the electrostatic calculation before the ice sphere is removed. The first problem is to determine specifically which intermolecular interactions are required in the calculation of the LHS to make it correspond to the RHS for which the cavity field is used. This has not been *a priori* obvious as evidenced by the fact that several researchers[1–7], including Adams, have performed calculations assuming only short range interactions which Adams correctly concludes is an inconsistent model in the context of equation (1).

For the ideal ice-rules model the numerical results for the correlation sums g_K and G for the LHS appear to agree with the RHS for the respective cases of $\varepsilon' = \varepsilon$ and $\varepsilon' = \infty$. However, as Adams acknowledges, for a finite concentration of Bjerrum defects, which is a necessary feature of real ice, equation (1) becomes inconsistent because statistical mechanics requires that the two correlations sums G and g_K are equal when the ideal ice rules are broken and only short range interactions are included. Adams tries to eliminate this dilemma by the proposal that dipolar interactions, previously left out of all but one primitive calculation[8], will restore the numerical values of G and g_K to those given by the ideal ice-rules. As Adams admits, this proposal cannot be exact because the ice rules determine G/g_K to be independent of the dipole moment and temperature which cannot be true for dipolar interactions. He also admits that dipolar interactions are likely to raise the numerical value of G which would reduce the calculated dipole moment below the value $\mu = 3.0$ D quoted in his paper. Therefore, Adams' simple resolution leaves us with a theory for which neither G nor g_K has been calculated and for which such calculations may be practically impossible due to the difficulty of doing statistical mechanical calculations on systems with long range dipolar interactions. Adams' real conclusion, also emphasized by Stillinger[10], is that G and g_K must satisfy a relation (Adams' equation (9)) if the proper interactions consistent with the internal cavity field are included in the calculation of the LHS of equation (1).

Adams' theory is essentially an extension of the K–F theory to include the cases $\varepsilon' \neq \varepsilon$ and this allows him to connect the K–F equation, given by equation (1) when $\varepsilon' = \varepsilon$ for which the LHS has a factor g_K, to an equation which is derived from equation (1) by setting $\varepsilon' = \infty$ for which the LHS has a factor which Adams identifies as G. If this last identification is made, then the Onsager–Slater (O–S) equation is recovered and must be equivalent to the K–F equation because they both come from the same unified derivation. However, this identification is incorrect because to calculate the G required by Adams' theory it is necessary to include dipolar interactions; in contrast dipolar interactions are completely absent in the calculation of G appropriate for the O–S theory. This astonishing feature has caused many to dismiss the O–S theory too lightly. However, elsewhere I have shown that the O–S theory consists of a renormalization of the electrostatic interactions in ice into a dipole-free effective Hamiltonian[9]. Therefore, the G required for the O–S theory cannot be the same as the quantity required for the LHS of equation (1) which should henceforth be called by a different name, $g_{\infty=\varepsilon'}$. It then follows that the use of equation (1) does not permit a derivation of the O–S theory which is fundamentally different from the K–F theory[2,3,9]; in particular, the internal field in the O–S theory is not the cavity field. A major advantage of the O–S theory to the K–F theory is that extant calculations of G, which do not include dipolar interactions, can be applied immediately and unambiguously to the O–S theory. However, it is to be hoped that the more difficult calculation of g_∞ necessary for the K–F theory may also be performed and that this might indeed result in complete resolution of the theory of the dielectric constant of ice.

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ADAMS REPLIES—The 'simple resolution' which I claim is the observation that it is not necessary to choose between either the Onsager–Slater equation or the Kirkwood equation. The Onsager–Slater equation, $\varepsilon - 1 = 3yG$, becomes equivalent to the exact Kirkwood equation when G is identified with g_∞ which is obtained with $\varepsilon' = \infty$ (that is, the 'tin-foil' case) and when all the dipole–dipole and other interactions of the model hamiltonian are included in the calculation[1,2]. The approximation of the Onsager–Slater theory is that the dipole–dipole interactions are to be ignored in the calculation of G.

Perfect ice-rules ice is a very simple hamiltonian which despite having no dipole–dipole interactions produces long-range dipole–dipole correlations of the sort to be expected in real dielectrics. I have calculated unambiguous values of $G = g_\infty$ and g_K for this model. The identification of such a model with real ice must be done with caution and I have tried to make an informed guess as to the direction of the error. One major approximation of the model is that all configurations allowed under the ice rules have the same energy. This cannot be too drastic an approximation or the observed residual entropy of ice would not be predicted so well.[3]

The other major approximation I have made is to ignore the Bjerrum defects which undoubtedly occur in real ice. However, when non-interacting defects are introduced into the model then the long-range correlations are destroyed and $g_K = G = g_\infty$ which cannot be true for a real dielectric. I argue that to introduce defects without also including the long-range electrostatic interactions which occur in all real dielectrics is to make the model worse and not better. I agree with Nagle that complete resolution requires making difficult calculations with all electrostatic interactions included and using the formally exact expressions for the dielectric constant of the Kirkwood type.

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