Reply to Bordewijk's comment "On the relationship between Kirkwood correlation factor and the dielectric permittivity"

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(Received 4 March 1980; accepted 18 March 1980)

The apparent simplicity of Bordewijk's conclusions[1] rests upon three modelistic hypotheses, and one approximation about local order in liquids. The "polarization model" which he suggests should be re-examined in the light of those conclusions[2-4] does not satisfy the hypotheses, and the approximation has doubtful validity specifically for those substances that the polarization model was created to describe.

(1) The most important of Bordewijk's hypotheses (though not articulated in his comment) is that the molecules are geometrically rigid. By contrast the polarization model permits molecular deformation. These deformations include normal modes of vibration, static nuclear deformations under the influence both of internal and of external fields, and even ionic dissociation of molecules. Needless to say the incorporation of this molecular nonrigidity is mandatory for any model that seeks to describe the full frequency dependence of dielectric response.

(2) Bordewijk's second hypothesis is that changes in molecular dipole moments induced by local electric fields are strictly linear in those fields. Without such linearity the rearrangement of the expression for total system moment into a sum of "effective" molecular moments is not possible. While the polarization model does indeed take *electronic* polarizability to be linear, the finite deformation of molecules (at fixed positions and orientations) by finite fields automatically introduces a nonlinearity of induced moments.

(3) The third hypothesis is that electronic polarizability is isotropic. The polarization model in its general form attributes an isotropic electronic polarizability to each *atom*. Polyatomic species then will exhibit anisotropic electronic polarizability except in special configurations of high symmetry. This situation can be aggravated furthermore by molecular deformability, which can introduce anisotropy of nuclear response even in situations where electronic response is isotropic.

(4) Finally Bordewijk finds it convenient to neglect fluctuations in the effective moments which are always present even if the above three hypotheses are fulfilled. As supporting evidence he cites "the small depolarized Rayleigh scattering in carbon tetrachloride." Such evidence of course does not exclude fluctuations in the *length* of the effective moment vector, at fixed direction, attributable to local isotropic density fluctuations. Nor does it exclude fluctuations in real fluids stemming from molecular deformations that occur well below optical frequencies. In those hydrogen bonding liquids (NH_3, H_2O, HF) that the polarization model was primarily designed to describe these deformations in large part will be associated with formation and destruction of hydrogen bonds, a form of interaction considerably stronger than that encountered in carbon tetrachloride. In any event, upon restoring fluctuations to the Bordewijk approach as dictated by the molecular physics of the problem, an "orientational correlation factor" g for effective moments can only be defined as a ratio of fluctuating quantities, just as was done for the Kirkwood factor g_K in Ref. 4.

The correlation factors g and g_K, respectively, for effective moments and for direct molecular moments, are distinct quantities. Kirkwood was only concerned with the latter in his pioneering work on polar dielectrics,[5] and it has a vivid pedagogical value in showing geometrically how local molecular order in polar fluids affects the static dielectric constant. In contrast the delocalization of effective moments over many molecules reduces the corresponding pedagogical value of g, whose interpretation is structurally less obvious.

In view of these points it is doubtful that the Bordewijk approach is generally "preferable" to that ultimately attributable to Kirkwood. However this does not exclude some modest interest in effective moments. With proper interpretation, their evaluation in future computer simulations of polar dielectrics could form a useful addition to the list of properties evaluated.

[1] P. Bordewijk, J. Chem. Phys. **73**, 595 (1980), preceding comment.
[2] F. H. Stillinger and C. W. David, J. Chem. Phys. **69**, 1473 (1978).
[3] F. H. Stillinger, Int. J. Quantum Chem. **14**, 649 (1978).
[4] F. H. Stillinger, J. Chem. Phys. **71**, 1647 (1979).
[5] J. G. Kirkwood, J. Chem. Phys. **7**, 911 (1939).