On the Definition of the Excess Permittivity of a Fluid Mixture: Molecular Formalism

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Permittivity is a magnitude not included in the thermodynamical formalism and in the literature different assumptions on its ideal behaviour can be found. Most of the authors consider the ideal permittivity to be a sum of the permittivities of the pure components weighted either by the mole- [1] or by the volume fractions (see for instance [2-3]). Sometimes they also appear weighted by the weight fractions (for example [4]). In this work we propose a molecular formalism that shows that the second option appears to be the correct one, i.e. the permittivities of the pure components should be weighted by their volume fractions.

An ideal fluid mixture is assumed to be a homogeneous linear and isotropic system. The following conditions are considered:

(I) no interaction between molecules,
(II) point-like molecules,
(III) under fixed temperature and pressure conditions the number of molecules per unit volume is the same for both the individual components and the mixture.

The formal demonstration for a binary mixture arrives to:

a) Under hypothesis I and II the excess permittivity of the mixture, ε^E, is given in terms of volume fractions

$$\varepsilon^E = \varepsilon_m - (\phi_1\varepsilon_1 + \phi_2\varepsilon_2) \quad (1)$$

ε_m represents the permittivity of the mixture ε_i and ϕ_i are the permittivity and the volume fraction of the component *i* of the mixture with $\phi_1 + \phi_2 = 1$ (assuming the excess molar volume is zero, $V_m{}^E = 0$).

b) Under hypothesis I, II and III the excess permittivity is given in terms of the mole fraction

$$\varepsilon^E = \varepsilon_m - (x_1\varepsilon_1 + x_2\varepsilon_2) \quad (2)$$

where x_i is the mole fraction of the component *i*.

Assumption III, however, implies that mole and volume fractions coincide, $x_i = \phi_i$ so that equation (2), valid for ideal gases, can be considered a particular case of the more general result where the permittivities of the components are to be weighted by their volume fractions.

Although the proof is given for a binary mixture, it is a simple exercise to extend it to any multi-component mixture.

Accepting equation (1), a mixture with $\varepsilon^E > 0$ exceeds Wiener's upper bound ($\varepsilon = \phi_1\varepsilon_1 + \phi_2\varepsilon_2$,). Indeed there are some observational results of this kind [5], [6], [1].

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