Thermodynamic potentials in anisotropic and nonlinear dielectrics

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ABSTRACT

The variation of total energy, entropy, Helmholtz free energy due to the application of a static electric field is calculated and discussed, under suitable conditions, in the case of a dielectric with either anisotropic or nonlinear response. The proposed approach starts from Fröhlich's theory of dielectric thermodynamics and, by analyzing its assumptions, provides a method to generalize it. The obtained relationships can be employed for describing the thermodynamics of different classes of dielectric materials, also in experimental investigations. Specifically, the anisotropy and nonlinearity conditions are considered and relative examples are indicated and discussed.

1. Introduction

The issue of developing a thermodynamics of ideal dielectrics was considered in few seminal studies carried out by important physicists. Although relationships connecting dielectric and thermodynamic quantities were proposed in the thirties and in the forties in the context of the studies on the electrocaloric effects [1,2], the first general theory was developed by H. Fröhlich [3,4], followed by R. Becker [5], L. Landau [6], V. Daniel [7], C. Böttcher [8], and B. Scaife [9]. These last ones provided considerations which are still based on the first treatise of Fröhlich: he obtained specific relationships which, under suitable conditions, correlate the physical quantities usually involved in dielectrics- i.e. static dielectric function ε_s, dielectric displacement field **D**, and applied electric field **E**- with the main thermodynamic state functions- i.e. total thermodynamic energy U, entropy S, and Helmholtz free energy F. Fröhlich demonstrated that, when a reversible isothermal transformation is considered, the variation of the main thermodynamic potentials can be written as

$$U(T, \mathbf{E}) = U_0(T) + U_E(T, \mathbf{E}), \tag{1a}$$

$$S(T, \mathbf{E}) = S_0(T) + S_E(T, \mathbf{E}), \tag{1b}$$

$$F(T, \mathbf{E}) = F_0(T) + F_E(T, \mathbf{E}), \tag{1c}$$

where T is the considered temperature, U_0, S_0, F_0 are the change of respectively thermodynamic total energy, entropy, Helmholtz free energy in absence of field, while U_E, S_E, F_E are their respective field-induced change. We note that the condition of considering reversible transformations requires that at each temperature the involved physical quantities do not depend on the time [10]; this implies that, strictly speaking, relationships (1) hold for static fields. It is worth noting that the field-dependent terms of (1) also display a dependence on temperature which can not be decoupled from the dependence on the field: this is due to the intrinsic dependence of the dielectric permittivity on the temperature. In his treatise Fröhlich starts from the electromagnetic energy U_e correlated with the application of **E** to an ideal loss-free dielectric medium. Therefore U_e, for unit of volume, is given by

$$U_e = \frac{1}{2}\mathbf{E} \cdot \mathbf{D}. \tag{2}$$

When **D** changes with the temperature T, from Eq. (2) we can obtain the energy difference (per unit volume) of the considered dielectric, although such relationship apparently does not contain thermodynamic quantities. If the variation of **D** is due to some thermodynamic process occurring to the dielectric, the effective energy provided by the above expression will depend on the feature of the occurring transformation. In particular Becker stressed that for an adiabatic process the variation of electric energy dU_e coincides with the variation of the total thermodynamic energy dU [5]; this implies that when an isothermal process is considered dU_e coincides with the variation of the Helmholtz free energy dF [3–5,11]. We note that in this treatise the volume variation of the system is assumed negligible (no electrostriction effects are considered), therefore the changes of Helmholtz and Gibbs free

energies coincide. While adiabatic conditions are difficult to be treated [5], isothermal transformations were more easily treated and discussed by the Fröhlich's theory. In his treatise, Fröhlich considers a system whose volume is maintained constant and the sole independent variables are the temperature T and the external electric field E. Moreover, he assumes D linearly depending on E, $D = \varepsilon\, E$ (we here employ the absolute dielectric function $\varepsilon \equiv \varepsilon_0 \varepsilon_s$, where ε_0 is the vacuum dielectric permittivity and ε_s is the static relative permittivity), with the further hypotheses of considering both an isotropic medium and a scalar approximation. In such conditions, relations (1) are expressed by

$$U(T,E) = U_0(T) + \frac{1}{2}\left(\varepsilon + T\frac{\partial \varepsilon}{\partial T}\right)E^2, \tag{3a}$$

$$S(T,E) = S_0(T) + \frac{1}{2}\frac{\partial \varepsilon}{\partial T}E^2, \tag{3b}$$

$$F(T,E) = F_0(T) + \frac{1}{2}\varepsilon E^2, \tag{3c}$$

which are the *Fröhlich's thermodynamic relationships* [3,4], where the energy, entropy, free energy of the dielectric as provided by such expressions are *Fröhlich total energy*, *Fröhlich entropy*, *Fröhlich free energy* (all for volume unit) [12]. We note that (3) show that the standard expression (2) actually does not provide the total energy but just the free energy. The form of (3) is very transparent: namely it allows to immediately highlight the connection between dielectric and thermodynamic variables. Even better, such a connection is expressed through a simple mathematical form, where the free energy is proportional to the dielectric susceptibility and the entropy is proportional to its derivative. However, the elegant formulation of (3) requires the above-mentioned specific hypotheses. Summarizing, beyond the condition of considering a loss-free (ideal) dielectric, Fröhlich adopts four assumptions, two *assumptions about the thermodynamics* of the considered process, i.e.

- reversibility,
- isothermal conditions,

and two *assumptions about the* features of the *dielectric*, i.e.

- linear dependence of **D** on **E**,
- scalar approximation (isotropic dielectric).

We note that the requirement of considering an independent-on-time field (static condition) is a consequence of the reversibility assumption and Boltzmann's ergodic conditions. In fact, in the assumed hypothesis the considered thermodynamic potentials are also state functions [10,13]. On the other hand, the dielectric assumptions concern the specific features of the dielectric response, which is determined by the considered material.

Actually, mathematical relationships correlating thermodynamic and dielectric quantities were theoretically and experimentally treated in the context of electrocaloric, pyroelectric and piezocaloric effects [2,14–18]. In these studies the dependence of scalar thermodynamic variables on vectors and tensors -electric and magnetic fields, susceptivity and susceptibility tensors, dielectric displacement and magnetization fields, stresses and strains tensors, etc.- was extensively discussed [6,13,15,16,19], this allows us, inter alia, to extend Maxwell's thermodynamic relations for media with dielectric, magnetic, and elastic anisotropies [15,20]. However, although the significance of the Fröhlich's thermodynamic approach, whose relationships (3) were published in 1949 [3], was emphasized by founders of the physics of dielectrics [5–7,9], no experimental studies specifically involving his theory have been accomplished for more than forty years. The first experimental uses of Fröhlich's equations and interpretation have been carried out in 2003 by GB. Parravicini et al. for the investigation of melting processes in metallic nanoparticles [21–23]. Subsequently, Fröhlich's arguments have been applied e.g. on nematic compounds [24–28], molecular crystals [29,30], ferroelectric and glassy perovskites [12,31,32],

polar glasses [33], polar and glass-forming liquids [34–38], polymeric films [39], enzymes [40].

The use of Fröhlich's theory in describing so different systems raises the issue about the conditions under which the above-listed four assumptions are effectively satisfied. Actually, in experimental domain the validity of Fröhlich relationships was demonstrated in less stringent conditions with respect to the formal ones. Namely, relationships (3) were experimentally found to hold in quasi-equilibrium states [12,29,30] and quasi-static conditions [21–23,38], i.e. they still experimentally hold when relaxation phenomena are negligible: this implies that quasi-static fields (frequencies until $\simeq 100$ MHz [24]) can be handled. On the other hand, the validity of hypotheses on dielectric features strongly depends on the investigated material. Namely, the investigation of systems whose response is intrinsically directional such as anisotropic crystals [12,32] and nematic compounds [24–27], naturally rises the problem of a formulation of (3) taking into account anisotropy. Furthermore, the study of dielectric dipolar liquids [34], recalls that the linearity assumed by Fröhlich strictly holds only for $E \to 0$, making mandatory to consider the problem of nonlinear corrections.

In this work we address these issues in order to treat a thermodynamic description of anisotropic and nonlinear dielectrics. The employed approach is based on a generalization of Fröhlich's thermodynamic theory for dielectrics. Namely, we report the steps to obtain the equivalent of expressions (3) when either anisotropy or nonlinearity are not negligible. The obtained results permit not to assume the two Fröhlich's hypotheses about the features of the dielectric. Therefore, the final generalized relationships provide a useful tool to be applied in the evaluation of total energy, entropy, and free energy from experimental data of a generic dielectric material. We will discuss the physical meaning of the obtained equations and provide examples of physical systems where they can be usefully employed in experimental investigations.

2. Anisotropic linear media

In developing the calculations we consider all physical quantities for unit of volume. First we assume a linear correlation between the applied static electric field **E** and the displacement vector **D**, as in Fröhlich's relationships. In the most general case, ε of (4) is a 2-rank tensor, i.e. $\varepsilon \equiv \varepsilon_{ij}$. So, the relation between **E** and **D** has the general form $\mathbf{D} = \boldsymbol{\varepsilon} \cdot \mathbf{E}$, i.e.

$$D_i = \sum_j \varepsilon_{ij}E_j \tag{4}$$

for $i, j = 1, 2, 3$, with the x, y, z components of the field labeled as $E_x = E_1$, $E_y = E_2$, $E_z = E_3$, and similarly for **D**. For treating thermodynamic transformations, we consider the variation of U_e as provided by Ref. [4]:

$$dU_e = \mathbf{E} \cdot d\mathbf{D}, \tag{5}$$

which is the energy variation of the dielectric (per unit volume) if **D** is infinitesimally varied. By combining Eq. (5) with the first principle of thermodynamics, we can obtain the energy variation dU for a reversible transformation, i.e. during a process where the field or the temperature, or both, are varied, per unit volume, in the form

$$dU = dQ + dU_e = dQ + \mathbf{E} \cdot d\mathbf{D}. \tag{6}$$

where dQ is the amount of exchanged heat (for unit of volume) during the considered reversible transformation. We note that the structure of (6) is analogous to the relationship giving the first principle of thermodynamics for a gas, $dU = dQ - p\,dv$, if **E** and **D** are respectively replaced by the pressure p with changed sign and the volume v [4]. The differential of the dielectric displacement vector **D** in the case of an anisotropic dielectric can be written as

$$dD_i = d\left(\sum_j \varepsilon_{ij}dE_j\right) = \sum_j \left(\varepsilon_{ij}dE_j + E_j\frac{\partial \varepsilon_{ij}}{\partial T}dT\right). \tag{7}$$