## METHODOLOGICAL NOTES

PACS number: 77.22.-d

# Methodological aspects of the thermodynamics of dielectrics

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<u>Abstract.</u> Some methodological aspects of the thermodynamics of dielectrics are discussed. In particular, it is noted that in the general case neither the electric displacement D nor the electric field strength E can be taken as the thermodynamic parameter defining the state of a polarized medium and that the electric polarization P is the appropriate choice. The relation between D and E as defined by the material equation of a medium is shown to be valid only in the state of thermodynamic equilibrium and hence is violated by fluctuations of P. In such an event, the material equation of a dielectric is not an analogue of the equation of state of the substance, which relates the pressure to the volume.

## 1. Introduction

A system which is a dielectric medium positioned in an electric field  $\mathbf{E}^{\text{ex}}$  of external charges (the field of external charges in a vacuum) is considered here from the thermodynamic point of view. The conditions of thermodynamic equilibrium of such a system are analyzed; in this case the state of the medium is defined by the spatial distribution of the polarization vector  $\mathbf{P}(\mathbf{x})$ . Within the context of thermodynamics, such a system may be associated with the 'gas under a piston' system for which  $p_0$  (the piston pressure on the gas) is taken as the external pressure (as it is termed in thermodynamics); under such an analogy, the polarization  $\mathbf{P}$  is the counterpart of the gas volume v, and the external field  $\mathbf{E}^{\text{ex}}$  corresponds to the external pressure  $p_0$  (more precisely,  $-p_0$ , see below).

This paper is primarily aimed at a thermodynamic consideration of the 'medium in an external field' system, a consideration that would be exactly analogous to that used to analyze the 'gas under a piston' system. Our intention derives from the fact that the approaches employed in the thermodynamics of dielectrics frequently differ in form from the

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Received 17 September 1996, revised 5 June 1998 Uspekhi Fizicheskikh Nauk **168** (12) 1331–1339 (1998) Translated by M V Tsaplina; edited by A Radzig standard scheme of the thermodynamic method. We shall clarify this assertion.

1. The prime element of the thermodynamic consideration is the expression for the work done on a system. If the work is done quasi-statically and isothermally, it determines the variation of the free energy of the system and, as follows from the second law of thermodynamics, in the case of a 'system in a thermostat' the thermodynamic equilibrium corresponds to minimality of the indicated quantity on a set of states characterized by a temperature equal to the thermostat temperature. In the case of interest, the work done on the system is the work on the charges of the medium itself, and the mutual displacements of these charges determine the polarization vector P(x). It is however of importance that the charges of the medium are microscopic objects, whereas the traditional construction of thermodynamics is based on the concept of work done 'by us', that is, work done on the objects that can in principle be regarded as macroscopic. As applied to the system in question, the 'cost' of such an approach appears to be the necessity of a preliminary consideration of so-called extended systems (the term is due to Leontovich [1]). In an extended system the free energy is described by the known expression [2]:

$$\mathcal{F} = \frac{1}{4\pi} \int \mathbf{E} \, \mathrm{d}\mathbf{D} \,, \qquad \mathcal{F}^{\,\mathrm{tot}} = \int \mathcal{F} \, \mathrm{d}\mathbf{x} \,, \tag{1}$$

where  $d\mathbf{x} = dx dy dz$ , and the superscript 'tot' refers here and below to the system as a whole†; in Eqn (1), the electric displacement **D** and the field **E** are related to each other by the static material equation

$$\mathbf{D} = f(\mathbf{E}, \mathbf{x}), \tag{2}$$

the dependence on  $\mathbf{x}$  reflecting the possible inhomogeneity of the medium. Expression (1) has the sense of the free energy of a 'medium + external charges' system because it arises as the work done (quasi-statically and isothermally) on the external charges (not the charges of the medium itself) whose interaction with one another is altered by the presence of the

<sup>&</sup>lt;sup>†</sup>We follow the terminology used by Landau and Lifshitz [2]: the energy quantities that refer to the system as a whole are called total; in this paper, such quantities are marked by a superscript 'tot'. If not marked, they refer to unit volume.

medium. As to the free energy of the medium itself, it is obtained by subtraction from  $\mathcal{F}^{\text{tot}}$  of the two summands which have nothing in common with polarization as such, i.e. the energy of the external-charge field  $\mathbf{E}^{\text{ex}}$  in a vacuum [2], and the energy of interaction of this field with the polarized medium [3–6].

Another example of an extended ('less extended') system is the system which can be identified as the 'medium + external field'. Its free energy is given by the expression

$$F = -\int \mathbf{P} \, \mathrm{d}\mathbf{E}^{\,\mathrm{ex}} \,, \qquad F^{\,\mathrm{tot}} = \int F \, \mathrm{d}\mathbf{x} \,, \tag{3}$$

which arises as the work done on the medium when it moves (quasi-statically and isothermally) from infinity to a given place in space, where there exists a fixed field  $\mathbf{E}^{\text{ex}}(\mathbf{x})$  [a field of a rigid conglomerate of external charges, which corresponds to a fixed  $\rho^{\text{ex}}(\mathbf{x})$ ] [3]. Formally, *F* is the volume density of the quantity obtained by subtracting from  $\mathcal{F}^{\text{tot}}$  (1) the energy of the external-charge field  $\mathbf{E}^{\text{ex}}$  in a vacuum [2]; the free energy *V* of the medium itself is obtained by subtraction from *F* of the interaction energy with the field  $\mathbf{E}^{\text{ex}}$  [3–6]:

$$V = F - (-\mathbf{E}^{\mathrm{ex}}\mathbf{P}).$$
<sup>(4)</sup>

A preliminary consideration of extended systems hampers the analysis of some points in the general form. So, the wellknown investigations of thermodynamic stability of dielectrics (for which the notion of a free energy is the crucial point) are always associated with a specific manner of the action on the medium, which appears to be responsible for the form of the obtained thermodynamic inequalities for the permittivity (these inequalities express the stability of the medium under fluctuations of **P**). It is true that in the scientific literature one can also find studies of the general issues, in which the minimality of  $\mathcal{F}^{\text{tot}}$  (1) is taken as the criterion of thermodynamic equilibrium [2, 7, 8]. As has been noticed by Kirzhnits [4], such an approach is not justified. Indeed,  $\mathcal{F}^{\text{tot}}$ occurs as work done on external charges in the presence of a medium, and therefore the minimality of this quantity corresponds to an equilibrium spatial distribution of the external charge relative to the medium [i.e.  $\rho^{\text{ex}}(\mathbf{x})$ ] rather than an equilibrium state of the medium [i.e. the value of P(x) relative to a fixed distribution of the external charge.

In Section 2, the free energy V of a polarized medium is determined through the work done directly on the charges of the medium itself; although these charges are microscopic objects, it is their displacements relative to one another that determine the thermodynamic parameter P(x) of the medium. The addition to V of the interaction energy with a fixed external field  $E^{ex}$  yields the free energy of the 'medium in an external field' system, and the requirement of the minimum total value of this quantity in the equilibrium state under arbitrary variations of P(x) leads to the thermodynamic inequalities for the permittivity [9] (see Section 3). These inequalities characterize the medium as such because their form does not depend on the way in which the medium is affected.

**2.** The remark to follow concerns the erroneous interpretation of the material equation (2) for a dielectric as a direct analogue of the equation of state in thermodynamics proper. The latter equation relates the pressure and the volume (for a given temperature):

$$p = p(v) , \tag{5}$$

and holds not only for equilibrium, but for nonequilibrium states as well. We shall illustrate this assertion on an example of the 'gas under a piston' system, for which an external parameter is  $p_0$  (the piston pressure on the gas) which is fixed by the mass of the load lying on the piston. Let the external pressure  $p_0$  (the mass of the load lying on the piston) change instantaneously; the state of the system becomes nonequilibrium (after which the nonequilibrium process of gas density evolution begins). However, in view of the rapid change of  $p_0$ , the p and v values have not got enough time to change, and hence the relation of these quantities, given by the equation of state (5), holds true. The situation is different with the material equation of a dielectric, which refers to equilibrium states only. Indeed, let an external field  $\mathbf{E}^{ex}$ change instantaneously (it is  $\rho^{ex}$  that changes; to make sure that the procedure is correct, see the footnote<sup>†</sup>); the state of the system becomes nonequilibrium [after which the nonequilibrium process of evolution of the polarization P(x)begins]. In view of the rapidity of the E<sup>ex</sup> variation, the polarization P(x) does not have enough time to change, and therefore the depolarizing field of the medium, which is due to the polarization charge with volume density  $-\text{div }\mathbf{P}$ , remains unchanged. As a result, we have: the field E (equal to the sum of the external and depolarizing fields) undergoes a change (equal to the variation of  $\mathbf{E}^{ex}$ ), while the polarization  $\mathbf{P}$ remains unaltered. Thus, on a set of arbitrary nonequilibrium states the E and P values are in no way correlated with each other, i.e. there exists no relation between them, including consequently the relation between E and P specified by the material equation (2) with the substitution

$$\mathbf{D} \equiv \mathbf{E} + 4\pi \mathbf{P} \,. \tag{6}$$

In Section 3, the material equation of a dielectric is derived as the condition of thermodynamic equilibrium of the 'medium in an external field' system, namely, as the extremality condition of the total free energy of the above-mentioned system. This condition defines the relation of the equilibrium value of the polarization with a fixed external field (which is an analogue of the relation between the equilibrium value of gas volume and a fixed external pressure), from which after identity transformations one obtains a material equation of the form (2).

**3.** Another remark regards the choice of the thermodynamic parameter (generalized coordinate) specifying the state of a polarized medium. Instead of the polarization **P** the electric displacement **D** (or the field **E**) is frequently taken as such a parameter. In Section 4 it is shown that different states of the medium [i.e. different values of the polarization P(x)whose functional is the total free energy of the medium] may correspond to one and the same values of D(x) [the same as E(x)]. Consequently, in the general case neither the electric

† If the current **j** responsible for the variation of  $\rho$  is longitudinal (rot **j** = 0), the right-hand side of the equation

$$\operatorname{rot} \mathbf{H} = \frac{4\pi}{c} \,\mathbf{j} + \frac{1}{c} \,\frac{\partial \mathbf{E}}{\partial t}$$

vanishes and neither the magnetic field nor the radiation occur; according to the electrostatic equations, the field **E** 'obediently' follows the variations of  $\rho$ . As concerns the infinitely rapid change of  $\rho$ , the procedure does not contradict the fundamental principles of relativity theory because charge motion does not necessarily cause mass motion [15] and, moreover, we mean a preliminary prepared experiment and not therefore the propagation of a signal.

displacement **D** nor the field **E** can be taken as parameters identifying the state of a polarized medium.

The thermodynamic consideration of the 'medium in an external field' system undertaken in this paper corresponds to the case of 'conventional' electrodynamics without spatial dispersion. From the phenomenological point of view this is the case where the material equation (2) is a spatially local relation, i.e. f is an arbitrary function rather than a functional.

## 2. Free energy of a polarized medium

The primary element of a thermodynamic consideration is the expression for elementary work on a system whose state in the general case is specified by the temperature T and a certain set of parameters  $\{a\}$ . In the case under consideration, the system is a polarized medium and  $\{a\} = \mathbf{P}$ ; proper thermodynamic parameters like volume will not be written down for the sake of brevity. The elementary work on the system is correspondingly the work on the charges  $q_i$  of the medium itself, whose displacements d $\mathbf{r}_i$  determine the vector d $\mathbf{P}$ .

In particular, if the polarization is generated by the external field  $\mathbf{E}^{\text{ex}}$  (the field of external charges in a vacuum), the elementary work done by this field in unit volume is given by the expression

$$\delta A = \frac{1}{\Omega} \sum_{i} (q_i \mathbf{E}^{\text{ex}}) \,\mathrm{d}\mathbf{r}_i \,, \tag{7}$$

where the summation is taken over the charges of the medium, contained in a physically infinitesimal volume  $\Omega$ . As mentioned above, we restrict our consideration to the case of 'conventional' electrodynamics without spatial dispersion, which from the microscopic point of view corresponds to the situation where the microscopic parameters of the substance, including displacements  $d\mathbf{r}_i$  of charged particles, change radically only at distances appreciably exceeding the characteristic dimension of the microscopic structure of the substance (the radius of the 'effective region', the radius of the molecular action, etc. [10]); the latter is called the size of the spatial dispersion and for dielectrics coincides in order of magnitude with the interatomic distance  $a_0$  [2, 10]. Note [10] that the well-known procedure of averaging over a physically infinitesimal volume is mathematically correct only if this condition holds. The polarization vector will then be specified by the relation

$$\mathbf{P} = \frac{1}{\Omega} \sum_{i} q_{i} \mathbf{r}_{i} , \qquad (8)$$

with allowance for which expression (7) for the elementary work assumes the form

$$\delta A = \mathbf{E}^{\,\mathrm{ex}} \,\mathrm{d}\mathbf{P} \,. \tag{9}$$

In view of what has been said, the polarization defined by Eqn (8) meets the condition

$$\left|\frac{\nabla P}{P}\right|^{-1} \gg a_0 \,, \tag{10}$$

which has, accordingly, the sense of intrinsic consistency of the macroscopic description of the medium, which ignores spatial dispersion. Drawing the analogy with the 'gas under a piston' system, we see that an analogue of (9) is the expression

$$\delta A = -p_0 \,\mathrm{d}v\,,\tag{11}$$

the comparison of which with (9) implies the following correspondence formulae:

$$\mathbf{P} \leftrightarrow v, \qquad \mathbf{E}^{\mathrm{ex}} \leftrightarrow -p_0. \tag{12}$$

If the polarization in a medium is due to a quasi-static and isothermal increase of  $\mathbf{E}^{\text{ex}}$ , the work done on the medium will determine its free energy for which, with allowance for (9), we obtain

$$V = \int \mathbf{E}^{\text{ex}} \, \mathrm{d}\mathbf{P} \,, \qquad V^{\text{tot}} = \int V \, \mathrm{d}\mathbf{x} \,. \tag{13}$$

The expression written for V with allowance made for (3) is identical to expression (4) which occurred in the preliminary consideration of the extended 'medium + external field' system.

A distinguishing feature of dielectric thermodynamics is the presence of long-range (electromagnetic) forces. A manifestation of this is, in particular, the dependence of the free energy of a homogeneously polarized body on its geometrical form. We shall consider a dielectric ellipsoid of unit volume. The medium will be thought of as homogeneous (the material equation (2) does not involve the dependence on **x**), but generally anisotropic and nonlinear; then the polarization **P** in a homogeneous external field  $\mathbf{E}^{\text{ex}}$  is also homogeneous. The field  $\mathbf{E}^{\text{ex}}$  in sum with the proper (depolarizing) field of the ellipsoid

$$E_i^{dep} = -4\pi n_i P_i, \qquad i = x, y, z \tag{14}$$

(there is no summation over *i*;  $n_i$  are depolarizing factors of the ellipsoid, and  $n_x + n_y + n_z = 1$ ) yields the field **E** in the medium. Accordingly, for **E**<sup>ex</sup> we have

$$E_i^{\text{ex}} = E_i + 4\pi n_i P_i, \quad i = x, y, z.$$
 (15)

Let the polarization of the ellipsoid be created by a quasistatic and isothermal increase of  $\mathbf{E}^{\text{ex}}$ . Substituting (15) into the first relation (13), we obtain

$$V(\mathbf{P}) = V_0(\mathbf{P}) + 2\pi (n_x P_x^2 + n_y P_y^2 + n_z P_z^2), \qquad (16)$$

where

$$V_0(\mathbf{P}) = \int_0^{\mathbf{P}} \mathbf{E}(\mathbf{P}') \,\mathrm{d}\mathbf{P}'\,,\tag{17}$$

and  $\mathbf{E} = \mathbf{E}(\mathbf{P})$  is the material equation of the medium in the form of the relation between  $\mathbf{E}$  and  $\mathbf{P}$ , determined by (2) with the substitution of (6). In the expansion (16), the dependence on the type of the medium is given by the summand  $V_0$  (17); the dependence on the sample shape is given by the depolarizing factors  $n_i$  which are expressed in the wellknown manner through the ratios between the lengths of the ellipsoid axes. The quantity  $V_0$  is the free energy of the 'needle' type of ellipsoid polarized along its axis (the x-axis): the substitution of  $n_x = 0$  and  $P_y = P_z = 0$  into (16) yields  $V = V_0$ .

Note that since the work of a force does not depend on the physical nature of the force, the calculation of V by formula (13) corresponds to a particular mode of generating polarization, namely, by means of an electric field. If the polarization is created by an extraneous force ('by hand'), then  $V_0(\mathbf{P})$ 

appears (by definition) as work done by this force in unit volume in the creation of homogeneous polarization inside the 'needle' along its axis [11]. Indeed, if we mentally divide a homogeneously polarized ellipsoid into needles parallel to **P** (Fig. 1), then the first term in (16) corresponds to the work on polarization of these needles and the second term corresponds to the work against the depolarizing field  $-\int \mathbf{E}^{dep} d\mathbf{P}$  (where  $\mathbf{E}^{dep}$  is given by expression (14)) common for the whole sample.



Figure 1. Homogeneously polarized dielectric ellipsoid is divided into 'needles' parallel to the polarization vector **P**.

If the medium is homogeneous, the quantity  $V_0(\mathbf{P})$  is the free energy of a homogeneously polarized infinite medium. To motivate this assertion, one should divide the medium into needles (or, which is the same, into infinite cylinders) parallel to  $\mathbf{P}$  and take into account that  $\mathbf{E}^{dep} = 0$  (because of the absence of a polarization charge:  $-\text{div } \mathbf{P} \equiv 0$ ) and no additional work is done against the depolarizing field. If the medium is inhomogeneous, this case can be interpreted as a variation of the type of the medium from point to point with  $V_0$  depending explicitly on the spatial coordinate:

$$V_0 = V_0(\mathbf{P}, \mathbf{x}) \,. \tag{18}$$

The quantity  $V_0(\mathbf{P}, \mathbf{x})$  can be taken [instead of the material equation (2)] as a primary element in the phenomenological description of the medium; it is either defined phenomenologically (for example, in the form of a power series in the spirit of the Landau theory) or is calculated from microscopic considerations.

Let us turn to the general case, when the medium (either an infinite medium or a finite sample) is polarized in an arbitrary inhomogeneous way. Suppose the polarization is generated by an extraneous force ('by hand') so that its current value is equal to

$$\mathbf{P}'(\mathbf{x}) = \alpha \mathbf{P}(\mathbf{x}), \tag{19}$$

where P(x) is its final value, and  $\alpha$  grows infinitely slowly from zero to unity. Since the process is quasi-static, the field **E** is described by the static Maxwell equations

$$\operatorname{div} \mathbf{D} = 4\pi \rho^{\operatorname{ex}}, \quad \operatorname{rot} \mathbf{E} = 0, \qquad (20)$$

which are known to be equivalent [with allowance made for (6)] to the Coulomb law

$$\mathbf{E} = \int \rho^{\text{tot}}(\mathbf{x} - \boldsymbol{\xi}) \frac{\boldsymbol{\xi}}{\boldsymbol{\xi}^3} \, \mathrm{d}\boldsymbol{\xi} \equiv \rho^{\text{tot}} * \frac{\mathbf{x}}{x^3} \,, \tag{21}$$

where the symbol '\*' implies a convolution of two functions, and  $\rho^{\text{tot}}$  is the total charge density equal to the sum of densities of the external and polarization (induced) charges:

$$\rho^{\text{tot}} = \rho^{\text{ex}} + \rho^{\text{in}}, \quad \rho^{\text{in}} = -\text{div}\,\mathbf{P}.$$
(22)

Substituting (22) into (21), we come to\*

$$\mathbf{E} = (\rho^{\text{ex}} - \operatorname{div} \mathbf{P}) * \frac{\mathbf{x}}{x^3}.$$
 (23)

In our case  $\rho^{\text{ex}} = 0$  and the field **E**, which is described by (23) and has the sense of a depolarizing field, is equal to

$$\mathbf{E}^{dep} = -\operatorname{div} \mathbf{P} * \frac{\mathbf{x}}{x^3} \tag{24}$$

[in the particular case of a homogeneously polarized ellipsoid, -div **P** is a  $\delta$ -function on the ellipsoid boundary, and (24) has the form of Eqn (14)]. Since **E**<sup>dep</sup> specified by (24) is a linear functional of **P**(**x**), after the substitution of (19) we have for its current value

$$\mathbf{E}^{\operatorname{dep}'}(\mathbf{x}) = \alpha \mathbf{E}^{\operatorname{dep}}(\mathbf{x}) \,. \tag{25}$$

We shall mentally divide the medium into infinitely small needles which at each point of the medium are parallel to **P**. The work on polarization of these needles per unit volume corresponds to the summand  $V_0$ , and the work against the depolarizing field common to the entire medium corresponds to the summand which, with allowance made for (19) and (25), is equal to

$$-\int_0^{\mathbf{P}} \mathbf{E}^{\operatorname{dep}'} \, \mathrm{d}\mathbf{P}' = -\mathbf{E}^{\operatorname{dep}} \mathbf{P} \int_0^1 \alpha \, \mathrm{d}\alpha = -\frac{\mathbf{E}^{\operatorname{dep}} \mathbf{P}}{2}$$

Finally, for the total free energy as a functional of  $\mathbf{P}(\mathbf{x})$  we arrive at

$$V^{\text{tot}}[\mathbf{P}(\mathbf{x})] = \int \left[ V_0(\mathbf{P}) - \frac{\mathbf{E}^{\text{dep}}\mathbf{P}}{2} \right] d\mathbf{x} , \qquad (26)$$

where  $\mathbf{E}^{dep}$  is a functional of  $\mathbf{P}(\mathbf{x})$  specified by (24); the additional dependence of  $V_0$  on  $\mathbf{x}$  [see Eqn (18)] corresponds to the case of an inhomogeneous medium.

It is noteworthy that as distinct from the case of thermodynamics proper, the free energy of a medium, given by the integrand of (26)

$$V = V_0(\mathbf{P}) - \frac{\mathbf{E}^{dep}\mathbf{P}}{2}, \qquad (27)$$

is not a function, but a functional of its thermodynamic parameter [ $\mathbf{E}^{dep}$  is the functional of  $\mathbf{P}(\mathbf{x})$  defined by Eqn (24)]. This fact reflects the long-range character of electromagnetic forces and as applied to a homogeneously polarized ellipsoid it manifests itself in the dependence of its free energy on its geometrical form [see formula (16) which can be derived by the substitution of (14) into (27)].

Let us now proceed to the situation when a given polarization P(x) is generated (quasi-statically and isother-

<sup>&</sup>lt;sup> $\dagger$ </sup> Being an integral relation, Eqn (23) is equivalent to the differential Maxwell equations (20) (in which **D** is given by (6)) together with the boundary conditions at infinity. More precisely, the latter equations are written on the basis of relation (23).

mally) in a medium which is already in a fixed external field  $\mathbf{E}^{ex}(\mathbf{x})$ . The work done on the charges of the medium then has the meaning of the work done on the 'medium in an external field' system. The force field which polarizes the medium in the presence of a fixed  $\mathbf{E}^{ex}$  is either an external electric field complementary to the one already existing (this is the role that the field  $\mathbf{E}^{ex}$  played above when it was complementary to the fixed zero external field) or else it may be a field of extraneous forces of nonelectromagnetic nature. The elementary work done on the charges of the medium and determining the change of its free energy dV is the sum of the elementary works of the force field  $\delta A$  polarizing the medium and the fixed external field  $\mathbf{E}^{ex} d\mathbf{P}$  [see Eqn (9)]; accordingly, for  $\delta A$  we have

$$\delta A = \mathrm{d}V - \mathbf{E}^{\mathrm{ex}} \,\mathrm{d}\mathbf{P}$$

Integrating this expression over **P** (assuming  $\mathbf{E}^{\text{ex}}$  to be fixed) and bearing in mind that  $\delta A$  determines the free energy variation dW of the 'medium in an external field' system, we are led to

$$W = V - \mathbf{E}^{\mathrm{ex}} \mathbf{P} \,. \tag{28}$$

Substituting (27) into (28) and integrating the latter expression over the volume occupied by the medium, for the total free energy of a 'medium in an external field' system we have

$$W^{\text{tot}}[\mathbf{P}(\mathbf{x})] = \int \left[ V_0(\mathbf{P}) - \frac{\mathbf{E}^{\text{dep}}\mathbf{P}}{2} - \mathbf{E}^{\text{ex}}\mathbf{P} \right] d\mathbf{x}, \qquad (29)$$

where  $\mathbf{E}^{dep}$  is the functional of  $\mathbf{P}(\mathbf{x})$  given by (24); the additional dependence of  $V_0$  on  $\mathbf{x}$  [see Eqn (18)] corresponds to the case of an inhomogeneous medium.

We note that the 'medium in an external field' system differs from that identified in the Introduction as the 'medium + external field' system. For the latter system, the thermodynamic parameter (the generalized coordinate) is the distance between the medium and the rigid conglomerate of external charges or, which is the same, the distribution  $\mathbf{E}^{ex}(\mathbf{x})$ in the volume occupied by the medium; correspondingly, the distribution  $\mathbf{P}(\mathbf{x})$  and along with it the total free energy  $F^{\text{tot}}$ [see Eqn (3)] of this system turn out to be functionals of  $\mathbf{E}^{\text{ex}}(\mathbf{x})$ . On the contrary, to the 'medium in an external field' system corresponds a fixed mutual position of the medium and the conglomerate of external charges and, therefore, a fixed distribution  $\mathbf{E}^{ex}(\mathbf{x})$  in the volume occupied by the medium; the thermodynamic parameter of such a system is the distribution P(x) whose functional is  $W^{tot}$  (29). We shall emphasize that W(28) coincides with F defined by (4) only for equilibrium **P** values.

## 3. The material equation of a dielectric and the thermodynamic inequalities for permittivity as conditions of thermodynamic equilibrium of a 'medium in an external field' system

Considering a medium (an infinite medium or a finite sample) in an external field, we shall distinguish in it a physically infinitesimal ellipsoid whose characteristic dimension L satisfies the inequalities

$$a_0 \ll L \ll \left|\frac{\nabla P}{P}\right|^{-1}$$
 (30)

Fulfillment of the left inequality leaves us within the framework of a macroscopic description of the medium, while fulfillment of the right inequality allows us to assume this ellipsoid to be homogeneously polarized and to apply the corresponding formulae of Section 2; the possibility for the double inequality (30) to hold is provided by the condition of disregard for the spatial dispersion (10). The field external to the indicated ellipsoid,  $\mathbf{E}^{ex}$ , is the field which, when extracted from the medium, would occur in the cavity thus formed;  $\mathbf{E}^{ex}$ in sum with  $\mathbf{E}^{dep}$  (14) gives the field  $\mathbf{E}$  and is hence defined by (15). Thermodynamic equilibrium of the 'dielectric ellipsoid in a homogeneous external field' system (a particular case of the 'medium in an external field' system) corresponds to minimality of the quantity

$$U - T_0 S - \mathbf{E}^{\mathrm{ex}} \mathbf{P}, \qquad (31)$$

where U is the internal energy of the ellipsoid, S is its entropy, and  $T_0$  is the temperature of the surrounding medium. We do not present the proof of this because it repeats literally the proof known from thermodynamics [12], where the expression for elementary work has the form (11) instead of (9) and where instead of (31) the minimum quantity is

$$U - T_0 S + p_0 v \,, \tag{32}$$

where v is the volume of a small part of the medium, and  $p_0$  is the pressure external relative to this part. Minimality of the quantity (31) over an entire set of states implies its minimality over any of its subsets, including that corresponding to constant values of temperature T (which is equal to the temperature of the thermostat whose role is played by the part of the medium surrounding the ellipsoid) and of thermodynamic parameters proper (which are not written explicitly). Putting  $T_0 = T$  in (31) and omitting the thermodynamic part proper in the free energy U - TS, we come to the quantity

$$W = V - \mathbf{E}^{\mathrm{ex}} \mathbf{P}, \qquad (33)$$

which is the free energy of a 'medium in an external field' system [see Eqn (28)]. The necessary conditions of the minimum of W have the form

$$(dW)_T = 0, \quad (d^2W)_T \ge 0.$$
 (34)

As concerns the medium as a whole, or more precisely the 'medium in an external field' system, one can readily show in an analogous manner that thermodynamic equilibrium corresponds to fulfillment of the following conditions for the first and second variations of the total free energy  $W^{\text{tot}}$  (29):

$$(\delta W^{\text{tot}})_T = 0, \qquad (\delta^2 W^{\text{tot}})_T \ge 0.$$
(35)

After the substitution of (33), the first of the conditions (34) yields

$$\mathbf{E}^{\,\mathrm{ex}} = \frac{\mathrm{d}\,V(\mathbf{P})}{\mathrm{d}\,\mathbf{P}} \,. \tag{36}$$

Substituting here  $\mathbf{E}^{\text{ex}}$  (15) and V (16), we obtain a material equation in the form of a relation between **E** and **P**:

$$\mathbf{E} = \frac{\mathrm{d}V_0(\mathbf{P})}{\mathrm{d}\mathbf{P}};\tag{37}$$

the additional dependence of  $V_0$  on **x** [see Eqn (18)] corresponds to the case of an inhomogeneous medium. This is the general notation of the material equation in terms of the quantity  $V_0(\mathbf{P})$  which, as mentioned in Section 2, can be taken (instead of the material equation) as a primary element in the phenomenological description of a medium. Notice that the material equation can of course also be obtained in the general form, that is, from the first condition (35).

A material equation in the form (37) was first written by Ginzburg [13] for a ferroelectric:

in the isotropic case we have

$$V_0 = -\frac{a}{2} P^2 + \frac{b}{4} P^4 \quad (a > 0, \ b > 0),$$
(38)

and the material equation takes the form

$$\mathbf{E} = (-a + bP^2)\mathbf{P}.\tag{39}$$

A material equation in the form of a relation between **D** and **E** can, with allowance made for (37) and (6), be given parametrically (**P** is the parameter):

$$\mathbf{E} = \frac{\mathrm{d}V_0(\mathbf{P})}{\mathrm{d}\mathbf{P}}, \quad \mathbf{D} = \frac{\mathrm{d}V_0(\mathbf{P})}{\mathrm{d}\mathbf{P}} + 4\pi\mathbf{P}.$$
(40)

When (37) and (6) are involved, the tensors of the inverse electric susceptibility and permittivity are as follows:

$$\alpha_{ik}^{-1} \equiv \frac{\partial E_i}{\partial P_k} = \frac{\partial^2 V_0}{\partial P_i \,\partial P_k} \,, \tag{41}$$

$$\varepsilon_{ik} \equiv \frac{\partial D_i}{\partial E_k} = \delta_{ik} + 4\pi\alpha_{ik} \,. \tag{42}$$

We shall emphasize that a material equation appears as a thermodynamic equilibrium condition, and therefore for nonequilibrium P(x) values the relation between **D** and **E** specified by this equation turns out to be violated. This was mentioned in the Introduction where it was also noted that a material equation can be regarded as an analogue of the functional relation between the equilibrium value of the gas volume v and a fixed external pressure  $p_0$ . Indeed, in thermodynamics proper, over a set of states characterized by a temperature equal to the thermostat temperature  $(T = T_0)$ , Eqn (32) assumes the form

$$F + p_0 v \,, \tag{43}$$

where  $F \equiv U - TS$  is the free energy of the gas<sup>†</sup>. In equilibrium state, the minimality of this quantity corresponds to the condition

$$p_0 = -\left(\frac{\partial F}{\partial v}\right)_T,\tag{44}$$

which relates the equilibrium value of v to a fixed  $p_0$ . Obviously, an analogue of (44) is relation (36) [see Eqn (12)] which, after identity transformations, just gives the material equation (37).

As to the equation of state of matter (5), relating the system volume not to the external pressure  $p_0$  but to the

pressure p of the gas itself, it is valid, as mentioned in the Introduction, both for equilibrium and nonequilibrium states. Its analogue in the thermodynamics of dielectrics is the relation between the polarization **P** and the internal forces acting on the charges of the medium on the side of the medium itself; so, in the framework of the oscillator model, these are forces acting, firstly, on the side of oscillator 'springs' and, secondly, on the side of the so-called acting field from which the external field  $\mathbf{E}^{\text{ex}}$  is subtracted.

We shall now proceed to an examination of the thermodynamic stability of dielectrics [9]. A significant contribution to the comprehension of this issue was made by D A Kirzhnits [4–6] who systematically considered the various ways of an electromagnetic affecting a medium; it was shown in particular that in the presence of spatial dispersion the longitudinal (relative to **k**) permittivity can take on negative values. The indicated papers were concerned with linear (homogeneous, isotropic) media; we are on the contrary dealing with the opposite case of arbitrary nonlinear (inhomogeneous, anisotropic) media, but without spatial dispersion. The latter corresponds to fulfillment of condition (10), which allows consideration of physically infinitesimal homogeneously polarized volumes.

The thermodynamic stability of a physically infinitesimal ellipsoid mentally distinguished in the medium is governed by the second condition (34) which, after the substitution of (28), means that the quadratic form

$$\left(\frac{\partial^2 V}{\partial P_i \partial P_k}\right)_T \mathrm{d} P_i \mathrm{d} P_k$$

is nonnegative. In this case, for the eigenvalues (e.v.) of the tensor  $(\partial^2 V / \partial P_i \partial P_k)_T$  we have

e.v. 
$$\left(\frac{\partial^2 V}{\partial P_i \partial P_k}\right)_T \ge 0$$
. (45)

Let the ellipsoid be so chosen that in the coordinate system connected with its major axes the tensor  $\partial^2 V_0 / \partial P_i \partial P_k$  is diagonal; then the tensor  $\partial^2 V / \partial P_i \partial P_k$ , where V is specified by (16), appears to be diagonal, too. Substituting (16) into (45), we obtain three inequalities for the eigenvalues of the inverse electric susceptibility tensor (41):

$$\alpha_{ii}^{-1} \equiv \frac{\partial^2 V_0}{\partial P_i^2} \geqslant -4\pi n_i \tag{46}$$

(there is no summation over *i*), each of which expresses stability under fluctuations of the corresponding component  $P_i$ . Since stability of the medium as a whole implies stability of all the ellipsoids distinguished mentally in it, the choice of the strongest inequalities in (46) corresponds to the resulting conditions of stability; in view of  $n_i \ge 0$ , the latter inequalities are due to an alternate choice of needle-shaped ellipsoids parallel to the coordinate axes  $(n_i = 0)$ :

$$\alpha_{ii}^{-1} \equiv \frac{\partial^2 V_0}{\partial P_i^2} \ge 0 \tag{47}$$

(there is no summation over *i*). These inequalities imply that the eigenvalues of the inverse electric susceptibility tensor  $\alpha_{ik}^{-1}$  (41)

e.v. 
$$\left(\frac{\partial E_i}{\partial P_k}\right)_T \ge 0$$
 (48)

<sup>&</sup>lt;sup>†</sup> The quantity  $F + p_0 v$  can be obtained as work done quasi-statically and isothermally on a gas at a fixed external pressure  $p_0$ . This quantity is accordingly the free energy of the system which could be identified as a 'gas under external pressure' (an analogue of the 'medium in an external field' system).

are nonnegative. Accordingly, the eigenvalues of the electric susceptibility tensor  $\alpha_{ik}$  itself are negative too, and for the eigenvalues of the permittivity tensor  $\varepsilon_{ik}$  (42) we therefore have

e.v. 
$$\left(\frac{\partial D_i}{\partial E_k}\right)_T \ge 1$$
. (49)

Our derivation of thermodynamic inequalities, as is seen from the derivation itself, involves the case of anisotropic and nonlinear media; it also however includes the case of inhomogeneous media because the ellipsoids distinguished in the medium were assumed to be infinitesimal and their size was hence assumed to be much smaller than the characteristic size of inhomogeneity of the medium. We shall also notice that such thermodynamic inequalities can also be obtained in the general form, i.e. from the second condition (35).

Notice that the inequalities (49) are analogous to the wellknown thermodynamic inequality

$$\left(\frac{\partial p}{\partial v}\right)_T \leqslant 0. \tag{50}$$

Indeed, the inequalities (49) arise as a result of identity transformations of the conditions (45) whose analogue in thermodynamics proper is the inequality  $(\partial^2 F/\partial v^2)_T \ge 0$  [see Eqn (12)] which, with allowance made for (44), looks like

$$\left(\frac{\partial p_0}{\partial v}\right)_T \leqslant 0\,,\tag{51}$$

where  $p_0$  and v are related to each other as in Eqn (44). At equilibrium  $p = p_0$ , and (51) takes the form (50).

We shall specially point out the case of an isotropic medium:  $V_0 = V_0(P)$ . The material equation (37) and the inverse electric susceptibility tensor  $\alpha_{ik}^{-1}$  (41) have the form

$$\mathbf{E} = \frac{E(P)\mathbf{P}}{P}, \qquad E(P) = \frac{\mathrm{d}V_0(P)}{\mathrm{d}P}, \tag{52}$$

$$\frac{\mathrm{d}E_i}{\mathrm{d}P_k} = \frac{\mathrm{d}E(P)}{\mathrm{d}P} \frac{P_i P_k}{P^2} + \frac{E(P)}{P} \left(\delta_{ik} - \frac{P_i P_k}{P^2}\right),\tag{53}$$

where we have used the relations

$$\frac{\partial P}{\partial P_i} = \frac{P_i}{P}$$
 and  $\frac{\partial P_i}{\partial P_k} = \delta_{ik}$ .

The quantities dE/dP and E/P have the sense of longitudinal and transverse (relative to the vector **P**) inverse electric susceptibilities, respectively. The conditions (48) as applied to the tensor (53) imply feasibility of the inequalities

$$\frac{\mathrm{d}E(P)}{\mathrm{d}P} \ge 0, \qquad \frac{E(P)}{P} \ge 0, \tag{54}$$

of which the first expresses stability of the medium under fluctuations of the absolute value of the polarization vector  $\mathbf{P}$ , and the second specifies the same property depending on its direction.

It is particularly noteworthy that the second condition (54) establishes co-alignment of the vectors  $\mathbf{E}$  and  $\mathbf{P}$  (the material equation (52) gives only their collinearity). From this, with allowance made for (6), it follows that the vectors  $\mathbf{E}$  and  $\mathbf{D}$  are also aligned in one direction.

We shall illustrate what has been done with an example of an isotropic ferroelectric for which  $V_0$  is given by Eqn (38). We shall locally (at a given point of the space) choose the xaxis to be collinear to the vector **P**. Then the material equation (39) and the stability conditions (54) have the form

$$E_x = (-a + bP_x^2)P_x, \qquad (55)$$

$$\frac{\mathrm{d}E_x}{\mathrm{d}P_x} \ge 0\,,\qquad \frac{E_x}{P_x} \ge 0\,. \tag{56}$$

Graphically, (55) is given by the well-known loop shown in Fig. 2. Its portion M0N fails to meet the first condition (56) [13, 14]. However, a still larger portion AM0NB is forbidden by the second condition (56) which expresses stability under fluctuations of the direction of the vector **P**. The latter fact means that no hysteresis is observed in an isotropic ferroelectric. Physically, this corresponds to the absence of an energy barrier between states with opposite orientations of the vector **P** (rotating without a change of the absolute value, this vector goes around the energy barrier 'along the valley'). Note that all this equally refers to an isotropic ferroelectric.



**Figure 2.** Material equation of an isotropic ferroelectric in the form of a relation between **E** and **P**. The portion M0N corresponds to states unstable 'in the absolute value', and the portion AM0NB to those unstable 'in the direction';  $P_0 = \sqrt{a/b}$ ,  $P_1 = \sqrt{a/(3b)}$ .

#### 4. The thermodynamic parameter of a dielectric

The state of a polarized medium is specified by the spatial distribution of the polarization vector  $\mathbf{P}(\mathbf{x})$  whose functional is the free energy of the medium, which is the crucial point in the analysis of conditions of thermodynamic equilibrium. In spite of this, the field  $\mathbf{E}$  (or electric displacement  $\mathbf{D}$ ) is frequently taken as the thermodynamic parameter (generalized coordinate) of the medium. Obviously, such an approach is rightful only under condition that the polarization P can be expressed in terms of the field E (or electric displacement D). In the general case this however is impossible. Indeed, this can be attained using a material equation, but the latter does not suit the purpose because it refers to equilibrium states only. Consequently, one should use relation (23) specified by the Maxwell equations and valid for both equilibrium and nonequilibrium states. This relation is however 'irreversible' because P(x) cannot be expressed in terms of  $\mathbf{E}(\mathbf{x})$  in the general case: the solenoidal (transverse in the k-space) component of the polarization

P(x) does not contribute to the divergence and is not thus determined by the E(x) value.

We shall illustrate our assertion with an example of a thin (infinitely thin in the limit) plate homogeneously polarized in the absence of an external field; the equality  $\rho^{\text{ex}} = 0$ corresponds to this condition and (23) takes the form of formula (24) which, when applied to the case under consideration, has the form (14), where  $n_x = 1$ ,  $n_y = n_z = 0$  (the *x*-axis is orthogonal to the plate faces):

$$E_x = -4\pi P_x$$
,  $E_t = 0$ ,  $t = (y, z)$ . (57)

The same relations written for the electric displacement  $\mathbf{D}$  (6) look as follows:

$$D_x = 0$$
,  $\mathbf{D}_t = 4\pi \mathbf{P}_t$ ,  $t = (y, z)$ . (58)

From (57) and (58) it is seen that the polarization **P** cannot be expressed in terms of **E** alone or **D** alone except in the particular cases of 'x-consideration', where it is expressed in terms of the field [see the first relation in (57)], and 't-consideration', where it is expressed in terms of the electric displacement [see the second relation in (58)].

It is of importance to notice that both the field **E** and the electric displacement D can however be taken as thermodynamic parameters in a whole number of cases. In view of what has been said above, these are cases where the material equation 'works', that is, the P(x) values are equilibrium. We are then dealing with states which are equilibrium in the parameter P but generally nonequilibrium in other parameters, including thermodynamic ones proper. An example may be the situation when we are interested in the equilibrium distribution of the external charge with respect to the medium, which corresponds to minimality of  $\mathcal{F}^{\text{tot}}$  (1) (see Introduction). The set of competing states corresponds here to the various distributions of the external charge  $\rho^{\text{ex}}(\mathbf{x})$ , which are assumed to be created quasi-statically. This means that over the indicated set of states the distributions P(x) are equilibrium [and are each time associated with the corresponding distributions  $\rho^{\text{ex}}(\mathbf{x})$ ; accordingly, the material equation of the medium holds, which allows, in turn, the expression of **P** in terms of both **E** and **D**.

## 5. Conclusions

The thermodynamic consideration presented above is based on the concept of work done directly on charges of the medium itself; although these charges are microscopic objects, it is nonetheless their spatial displacements that determine the state of a polarized medium. Such a construction corresponds in form to the standard scheme of the thermodynamic method and is exactly analogous to that used in thermodynamics proper; it does not appeal to a preliminary consideration of the extended systems, which, as mentioned in the Introduction, is due to the desire to deal exclusively with macroscopic objects.

The state of a polarized medium is governed by the spatial distribution of the polarization P(x) which in the general case cannot be expressed in terms of **D** or **E** alone; in other words, different distributions P(x) may correspond to identical distributions D(x) and E(x). Thus, neither the electric displacement **D** nor the field **E** can in the general case identify the state of a polarized medium.

It should be stressed that the Maxwell equations in no way restrict the possible values of polarization, that is, the set of competing states correspond to all possible distributions  $\mathbf{P}(\mathbf{x})$ . The role of the Maxwell equation comes down to only a specification of the field  $\mathbf{E}(\mathbf{x})$  [and also the electric displacement  $\mathbf{D}(\mathbf{x})$ ] which corresponds to a given  $\mathbf{P}(\mathbf{x})$ . Indeed, thermodynamics considers only such nonequilibrium states that can be generated in an equilibrium manner, i.e. quasi-statically (infinitely slowly); accordingly, on a set of arbitrary nonequilibrium states the static Maxwell equations (20) hold, which are equivalent to the Coulomb law (23):

$$\mathbf{E} = (\rho^{\mathrm{ex}} - \operatorname{div} \mathbf{P}) * \frac{\mathbf{x}}{x^3} \,.$$

The Coulomb law just allows the determination of the field E(x) corresponding to a given (arbitrary) P(x).

In the approach presented, instead of the material equation the expression for the free energy of a homogeneously polarized infinite medium,  $V_0(\mathbf{P})$ , was taken as the primary element of the phenomenological description of a dielectric; this quantity is either defined phenomenologically (for instance, as a power series in the spirit of the Landau theory) or is calculated from microscopic considerations. The total free energy  $V^{\text{tot}}[\mathbf{P}(\mathbf{x})]$  of the medium (an infinite medium or a finite sample) polarized in an arbitrary inhomogeneous way is written in the general form in terms of this quantity. An addition to  $V^{\text{tot}}$  of the interaction energy with a fixed external field gives the total free energy  $W^{\text{tot}}[\mathbf{P}(\mathbf{x})]$  of the 'medium in an external field' system, and as follows from the second law of thermodynamics, this quantity assumes the minimum value in the equilibrium state. This minimum value is mathematically expressed by the conditions  $\delta W^{\text{tot}} = 0$  and  $\delta^2 W^{\text{tot}} \ge 0$ . The former determines the material equation of the medium, which appears to be written in the general form in terms of  $V_0(\mathbf{P})$ ; occurring as the equilibrium condition, the material equation refers therefore to equilibrium states only, which means, in particular, that it is not an analogue of the equation of state of matter in thermodynamics proper. The latter condition determines the thermodynamic inequalities for permittivity, which express stability of the medium under fluctuations of the polarization P. In application to the 'conventional' electrodynamics without spatial dispersion, these are the following inequalities: for an arbitrary (inhomogeneous, anisotropic, nonlinear) medium the eigenvalues of the permittivity tensor are greater than or equal to unity; these inequalities are an analogue of the well-known thermodynamic inequality  $(\partial p/\partial v)_T \leq 0$  which expresses stability of the medium under fluctuations of its volume.

In the particular case of an isotropic medium, stability under fluctuations of the direction of the vector **P** corresponds to co-alignment of the vectors **E** and **P**; accordingly, the vectors **E** and  $\mathbf{D} \equiv \mathbf{E} + 4\pi\mathbf{P}$  are also co-aligned. What has been said implies, in particular, the prohibition of the existence of states with a spontaneous field **E** (for  $\mathbf{D} = 0$ ) in isotropic media: the equality  $\mathbf{D} \equiv \mathbf{E} + 4\pi\mathbf{P} = 0$  implies counter-alignment of the vectors **E** and **P**. Another illustration of co-alignment of **E** and **P** may be the absence of hysteresis in an isotropic ferroelectric (it can be shown that this assertion also holds for the magnetic analogue of an isotropic ferroelectric, i.e. for an isotropic ferromagnetic).

The author is thankful to A M Ignatov, V P Makarov and A A Rukhadze for fruitful discussions of the results. This work was sponsored by the Russian Foundation for Basic Research (project No. 96-02-16256-a).

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