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A Thermodynamic Pressure Demagnetization

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Abstract: For paramagnetic and elastic materials in the presence of quasi-static magnetic field, there is correspondingly quasi-static magnetic pressure, in contrast to the radiational electromagnetic pressure associated with electromagnetic momentum density. A thermodynamic pressure demagnetization is demonstrated. For the elastic dielectrics in the presence of quasi-static electrical field, its dual effect can be easily obtained by variable transformation.

Keywords: piezomagnetism; magnetostriction; electrostriction; piezoelectricity; pressure; thermodynamics

I. Introduction

Thermodynamics for materials in the presence of electromagnetic fields is the crucial part of the discipline and has wide applications ranging from superconductivity to blackbody radiation, from magnetic cooling to magnetostriction (electrostriction), etc. However there are still issues beyond our full understanding. For instance, how the electromagnetic energy or work enters thermodynamics and becomes a proper thermodynamic quantity are still under controversy, [1] see also the discussion in section III. Usually, the fundamental thermodynamics equation for a paramagnetic and elastic electromagnetic material takes the following form, [2,3]

$$dU = TdS - pdV + \varepsilon_0 EdP + \mu_0 HdM \tag{1}$$

in which U, T, S, p, V are internal energy, temperature, entropy, pressure and volume, respectively, and E and P denote the electric strength and total electric moment, respectively, and H and M symbolize the magnetic strength and total magnetic moment, respectively, and μ_0 is the vacuum permeability and ε_0 is the vacuum dielectric constant.

Many other forms different from Eq. (1) are also frequently used. For instance, once the energy of the field energies are also included, we have, [4,5]

$$dU = TdS - pdV + VEdD + VHdB. \tag{2}$$

A distinctive feature of this form is that two natural variables D and B are intensive quantities. Assuming that a thermodynamic system contains not only the magnetizable and polarizable materials but also the un-magnetizable and un-polarizable space with field distribution even the source area of field, the internal energy could be, see the Eq. (29) of reference [1],

$$dU = TdS - pdV + \frac{1}{2}d(VED) + \frac{1}{2}d(VHB). \tag{3}$$

Evidently, we are lacking a correspondence rule to uniquely map electromagnetic energies to thermodynamic works. In this sense, thermodynamics bears some phenomenological feature from which the specific system must be treated case-by-case. When the materials are taken as a thermodynamic system, the Eq. (2) is proper form to start with.

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The main concern of present study is to show *a thermodynamic pressure demagnetization* which seems to have been long gone unnoticed. The pressure demagnetization is well-established phenomena in rocks and minerals, [6–9] and was also experimentally confirmed in condensed matter physics. [10] However, there is no thermodynamic analogue yet. We will point out in section II that such an effect exists in thermodynamics, and briefly discuss why it has been overlooked for long times in section III.

We are limited ourself within the equilibrium thermodynamics, in which the electrical or magnetic field are both quasi-static can be treated separately. We explicitly deal with magnetic materials only, for all results apply for the dielectrics by merely change of symbols.

II. Thermodynamics for PARAmagnetic and homogeneous materials

The electrodynamics gives the full magnetic energy density element $d\omega$ for paramagnetic materials in the following, [11]

$$d\omega = HdB = \mu_0 Hd\left(H+m\right) = \mu_0\left(d\frac{H^2}{2}+Hdm\right) = \mu_0 d\left(\frac{H^2}{2}+Hm\right)-\mu_0 mdH, \tag{4}$$

where B is the magnetic flux density, and $m\,(=M/V)$ is the magnetization strength, and induced magnetic fields is along the direction of the applied magnetic field such that $\mathbf{H}\cdot d\mathbf{B} = HdB$. The volume of the magnetic material is V, and the energy element dW_B along with the increase of the magnetic strength m or magnetic strength H is,

$$dW_B = \int_V d\omega dV = \mu_0 V\left(d\frac{H^2}{2}+Hdm\right) = \mu_0 Vd\left(\frac{H^2}{2}+Hm\right)-\mu_0 MdH. \tag{5}$$

One must be very careful that the volume V here is not a constant in presence of the magnetostriction. Precisely, it is function of the magnetic strength m or magnetic strength H, and also the temperature T. In light of the first principle of the thermodynamics, we must add these terms into dU at very beginning step of introducing them into thermodynamics,

$$dU = TdS - pdV + \mu_0 Vd\left(\frac{H^2}{2}+Hm\right)-\mu_0 MdH. \tag{6}$$

The Euler homogeneous function theorem for $U = U(S, V, \left(\frac{H^2}{2}+Hm\right), H)$, in which $\frac{H^2}{2}+Hm$ and H are both intensive quantities, gives,

$$U = TS - pV. \tag{7}$$

It shows the a free energy $G \equiv U - TS + pV$ is identically zero. This G is nothing but a new thermodynamic function obtained by the Legendre transform, and one do not confuse this G with the usual Gibbs free function which can not apply for internal energy (6) in which two natural variables are intensive quantities. Thus, we have the Gibbs-Duhem relation,

$$SdT = Vd\left(p+\mu_0\frac{H^2}{2}+\mu_0 Hm\right)-\mu_0 MdH. \tag{8}$$

It is an important relation from which following consequences are in order.

1. We have a generalized pressure p_H, defined by,

$$p_H \equiv p + \mu_0\frac{H^2}{2}+\mu_0 Hm. \tag{9}$$

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in which $\mu_0 H^2/2$ is the magnetic pressure [11,12] and the rest part $\mu_0 Hm$ is seldom treated as a part of pressure, but both are reasonable and transparent. We can define the static magnetic pressure p_{HM},

$$p_{HM} \equiv \mu_0 \frac{H^2}{2} + \mu_0 Hm. \tag{10}$$

2. From the Gibbs-Duhem relation (8), only two variables in three intensive quantities (p_H, H, T) are independent and we can conveniently choose them as (H, T). Once $dT = 0$, we have from Eq. (8),

$$d\left(p + \mu_0 \frac{H^2}{2} + \mu_0 Hm\right) = \mu_0 m dH. \tag{11}$$

It clearly indicates a *pressure demagnetization*,

$$\left(\frac{\partial m}{\partial p}\right)_T = -\frac{1}{\mu_0 H}\left(1 + \left(\frac{\partial H}{\partial m}\right)_T\right)^{-1} < 0, \tag{12}$$

provided that the materials are paramagnetic,

$$\left(\frac{\partial m}{\partial H}\right)_T > 0. \tag{13}$$

When the magnetic field $H \longrightarrow \infty$, the magnetization becomes saturation and the influence of the applied mechanical pressure has little effect to demagnetize, i.e. $(\partial m/\partial p)_T \to 0$. However, when $H \to 0$, we have a nonphysical result $(\partial m/\partial p)_{H,T} \to \infty$, which must be excluded from the application. However, it shows qualitatively in opposite limit $H \to 0$, the demagnetization becomes more easily.

3. Once $dH = 0$, we have from Eq. (8),

$$SdT = Vdp + V\mu_0 Hdm. \tag{14}$$

We have in consequence,

$$\left(\frac{\partial p}{\partial T}\right)_H = \frac{S}{V} - \mu_0 H \left(\frac{\partial m}{\partial T}\right)_H > 0, \tag{15}$$

provided that the materials are paramagnetic in the way of Curie's law $(\partial m/\partial T)_H < 0$. It shows that when materials are compressed, their temperature increases. It is understandable that for constant H the pV-work done to the system transforms into the internal energy.

4. We have two Maxwell relations from Eq. (8),

$$\left(\frac{\partial V}{\partial H}\right)_{p_H} = -\mu_0 \left(\frac{\partial M}{\partial p_H}\right)_H, \tag{16a}$$

$$\left(\frac{\partial S}{\partial H}\right)_T = \mu_0 \left(\frac{\partial M}{\partial T}\right)_H, \tag{16b}$$

in which Eq. (16a) offers the correct relation between the magnetostriction (left-hand side) and the piezomagnetism (right-hand side), and Eq. (16b) is the usual relation accounting for the magneto-caloric effect. Some author [5] obtains the relation (16a) together with a condition of constant temperature, which would be identically zero from (8),

$$\left(\frac{\partial V}{\partial H}\right)_{T,p_H} = -\mu_0 \left(\frac{\partial M}{\partial p_H}\right)_{T,H} = 0. \tag{17}$$

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5. There is a *self-piezomagnetism* by which we mean that for constant mechanical pressure $p = const.$, the applied external field can act as an effective *"external"* pressure to cause a change of the magnetic moment. Considering the right-hand side of Eq. (16a), we have,

$$\mu_0 \left(\frac{\partial M}{\partial p_H}\right)_{H,p} = \mu_0 \left(\frac{\partial M}{\partial m}\right)_{H,p} \left(\frac{\partial m}{\partial p_H}\right)_{H,p} = \frac{1}{H}\left(V + m\left(\frac{\partial V}{\partial m}\right)_H\right) \neq 0. \tag{18}$$

It is in general nonvanishing.

In completely similar manner, we can deal with the electrical dielectrics. Also a novel quantity is the generalized pressure now becomes,

$$p_E \equiv p + \varepsilon_0 \frac{E^2}{2} + \varepsilon_0 E\rho \tag{19}$$

in which $\rho \equiv P/V$ is the polarization density, and $\varepsilon_0 E^2/2$ is the electrical pressure [11,12] and the rest part $\varepsilon_0 EP$ is also seldom treated as a part of pressure, but both are reasonable and transparent, too. We can define the static electrical pressure p_{EP},

$$p_{EP} \equiv \varepsilon_0 \frac{E^2}{2} + \varepsilon_0 E\rho. \tag{20}$$

All results for magnetic materials can be transformed to the electric ones by replacement of variables,

$$\{M, m, \mu_0, H\} \longrightarrow \{P, \rho, \varepsilon_0, E\}. \tag{21}$$

Similarly, we have *a thermodynamic pressure depolarization*,

$$\left(\frac{\partial \rho}{\partial p}\right)_T = -\frac{1}{\mu_0 E}\left(1 + \left(\frac{\partial E}{\partial \rho}\right)_T\right)^{-1} < 0. \tag{22}$$

It must be emphasized that the crucial steps leading to the pressure demagnetization are first the introduction of static magnetic pressure (9), and secondly the utilization of the Gibbs-Duhem relation (8).

III. Conclusions and discussions

From calculations in section II, we see that a thermodynamic pressure demagnetization exists, which is quite easily accessible. The reasons why it has been overlooked for long times might be in the following: 1, it may not be completely independent from the magnetostriction and the piezomagnetism; and 2, we *do not* have a correct relation between the magnetostriction and the piezomagnetism in thermodynamics, for instance, the relation reported in literature [13–16] is enormous. Let us now sketch how this relation is derived. Once intensive variables such as T, p, E and H are more convenient to be taken as natural variables, a Legendre transform of the internal energy U (1) into a free energy must be performed, for instance, [16]

$$G \equiv U - TS + pV - \varepsilon_0 EP - \mu_0 HM. \tag{23}$$

The differential of G is,

$$dG = -SdT + Vdp - \varepsilon_0 PdE - \mu_0 MdH. \tag{24}$$

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Then the Maxwell relations give, [13–16]

$$\left(\frac{\partial V}{\partial E}\right)_{p,T,H} = -\varepsilon_0\left(\frac{\partial P}{\partial p}\right)_{E,T,H}, \tag{25a}$$

$$\left(\frac{\partial V}{\partial H}\right)_{p,T,E} = -\mu_0\left(\frac{\partial M}{\partial p}\right)_{H,T,E}, \tag{25b}$$

Apparently, we have the relation (25a) between the electrostriction (left-hand side) and the piezoelectricity (right-hand side), and Eq. (25b) does so between the magnetostriction (left-hand side) and the piezomagnetism (right-hand side). In fact, these two relations are dubious. This is because, in electrodynamics, [11] only when V is constant can it be absorbed into the differential dm such that $Vdm = d(Vm) = dM$ and the fundamental form of the electromagnetic energy element is $EdD + HdB$. However, once V is a constant, $dV = 0$ in Eq. (1), thus the left-hand side of relations (25a) and (25b) vanish and these two relations are meaningless.

Some historical remarks are needed. It is possibly Professor Zhuxi Wang (1911/7/7-1983/1/30, the founder of teaching school of thermodynamics in China, and also one of the founding fathers of the modern physics education in China) who first found in 1964 that $\mu_0 HM$ and $\varepsilon_0 EP$ are *formally* existent for the electrical and magnetic materials, respectively, but he did not pay attention whether $\mu_0 HM$ and $\varepsilon_0 EP$ might have physical significance. [5]

In sum, we have demonstrated that the static magnetic pressure and the static electrical pressure are two physically significant quantities, from which an experimentally testable effect, *a thermodynamic pressure demagnetization* and its dual for dielectrics as *a thermodynamic pressure depolarization*, are identified. The static electromagnetic pressures are in contrast to the radiational electromagnetic pressure associated with electromagnetic momentum density $\varepsilon_0 \mathbf{E} \times \mathbf{B}$. However, the present exploration is limited for the ideal materials. For more realistic situation our results are not applicable, which will be further studied in the further.

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