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THERMODYNAMIC STABILITY OF DIA- AND PARAMAGNETIC MATERIALS

Péter Ván

Department of Chemical Physics
Technical University of Budapest
H–1521 Budapest, Hungary

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Abstract

According to the present theories of magnetic media the intrinsic stability is violated. Dia- and paramagnetic materials cannot be stable with the usage of the same extensive variables. Two different energy-momentum tensors are proposed to resolve the problem.

Keywords: thermodynamic stability, energy-momentum tensors, dia- and paramagnetic materials.

1. Introduction

According to the Second Law the intrinsic stability criteria in thermostatics requires a concave entropy function. If the entropy depends on the extensive variables, the second derivative of the specific entropy, $D^2 s$ must be a negative definite matrix.

For magnetic materials the most widely accepted treatment introduces the magnetic polarization as an extensive variable

$$s(\ldots, \mathbf{m})$$

If we accept the magnetic work in the form $\mathbf{B}d\mathbf{m}$, that is the intensive quantity for magnetic interactions is the magnetic induction $\mathbf{B}$ then the Gibbs relation can be written as

$$du = Tds - pdv + \ldots + \mathbf{B}d\mathbf{m}\,.$$

So the corresponding derivative of the entropy function is

$$\frac{\partial s}{\partial \mathbf{m}} = -\frac{\mathbf{B}}{T}$$

and the second partial derivative according to $\mathbf{m}$

$$\frac{\partial^2 s}{\partial \mathbf{m}^2} = -\frac{\mu}{T\chi_m}.$$

where χ_m is the magnetic susceptibility and μ is the relative permeability.

Therefore the specific entropy is a concave function of the extensive variables if and only if χ_m is a positive number (function). However, we know that the magnetic susceptibility is a negative quantity for diamagnetic materials, and positive for para- and ferromagnetic materials. You can see clearly the contradiction.

Common textbooks containing the thermostatic theory of magnetic materials reflect this confusion. Different forms of the magnetic work are introduced by different authors [1], [2] and most of the authors simply avoid the treatment of diamagnetic materials [3], [4], [5].

In this short paper we give a possible resolution of the problem, however, to this end we should go back to the origin of the different work terms in the first law, we should take into account the energy-momentum tensors of the different electromagnetic media. The theory of electromagnetism is essentially a special relativistic theory, therefore we will investigate this problem considering special relativistic spacetime.

2. Electromagnetic Energy-Momentum Tensors for Magnetic Materials

First of all we introduce some notations:

The electromagnetic field is an asymmetric cotensor denoted by F, the polarization N and displacement G are asymmetric tensors. To see the clue with the usual time and space splitted notations we give these quantities in a momentary rest frame.

The time-like component of the electromagnetic field is the $\mathbf{E}$ electric field, the space-like component is the magnetic field

$$F_0 = \begin{pmatrix} 0 & \mathbf{E} \\ -\mathbf{E} & -\mathbf{B} \end{pmatrix}.$$

The time-like component of the polarization is the electric polarization and the space-like component is the magnetic polarization:

$$N_0 = \begin{pmatrix} 0 & \mathbf{P} \\ -\mathbf{P} & \mathbf{M} \end{pmatrix}.$$

The time-like component of the displacement is the electric displacement and the space like component is the magnetic field strength:

$$G_0 = \begin{pmatrix} 0 & \mathbf{D} \\ -\mathbf{D} & -\mathbf{H} \end{pmatrix}.$$

Here we considered that the tensors and the cotensors can be identified with the help of the Lorentz form. The relation of the field quantities:

$$G = F + N \rightarrow \left\{ \begin{array}{ll} \mathbf{D} & = \mathbf{P} + \mathbf{E}, \\ \mathbf{B} & = \mathbf{H} + \mathbf{M}. \end{array} \right.$$

We can find a lot of different energy-momentum tensors in the literature, a proper form of the electromagnetic field energy-momentum for a polarizable medium is a well discussed problem from the beginning of the century. Here we give some tensors and cite their assumptions. We gave two different forms: first the relativistic four-vector notation is used (with indexes) after that we give the expression in a momentary rest frame.

The first and well known form is due to MINKOWSKI (1908) [6]. He gave this expression requiring the form invariance of the field energy-momentum. This is the one that appears in most of the textbooks [3], [7], [8], [9].

$$T_M^{\alpha\beta} = F^{\alpha\gamma} G_\gamma^\beta - \frac{1}{4} F_{\gamma\epsilon} G^{\gamma\epsilon} g^{\alpha\beta},$$

$$T_M = \begin{pmatrix} \frac{1}{2}(\mathbf{E}\cdot\mathbf{D} + \mathbf{B}\cdot\mathbf{H}) & \mathbf{E}\times\mathbf{H} \\ \mathbf{D}\times\mathbf{B} & -\mathbf{E}\circ\mathbf{D} - \mathbf{H}\circ\mathbf{B} + \frac{1}{2}(\mathbf{E}\cdot\mathbf{D} + \mathbf{B}\cdot\mathbf{H})\mathbf{I} \end{pmatrix}.$$

After that ABRAHAM gave the following expression in 1909-1910 [10]. He supposed that the field energy-momentum should be symmetric.

$$\begin{aligned} T_A^{\alpha\beta} &= \frac{1}{2}(F^{\alpha\gamma} G^\beta_{\cdot\gamma} + F^{\beta\gamma} G^\alpha_{\cdot\gamma}) - \frac{1}{4} F_{\gamma\epsilon} G^{\gamma\epsilon} g^{\alpha\beta} + \\ &\quad + \frac{1}{2} c^{-2} \left[U^\beta (F^{\alpha\gamma} M_{\gamma\epsilon} - M^{\alpha\gamma} F_{\gamma\epsilon}) + U^\alpha (F^{\beta\gamma} M_{\gamma\epsilon} - M^{\beta\gamma} F_{\gamma\epsilon}) \right] U^\epsilon, \end{aligned}$$

$$T_A = \begin{pmatrix} \frac{1}{2}(\mathbf{E}\cdot\mathbf{D} + \mathbf{B}\cdot\mathbf{H}) & \mathbf{E}\times\mathbf{H} \\ \mathbf{E}\times\mathbf{H} & -(\mathbf{E}\circ\mathbf{D})^s - (\mathbf{H}\circ\mathbf{B})^s + \frac{1}{2}(\mathbf{E}\cdot\mathbf{D} + \mathbf{B}\cdot\mathbf{H})\mathbf{I} \end{pmatrix}.$$

Some decades later DE GROOT and SUTTORP realized that a macroscopic field energy expression should be based on a covariant statistical derivation [11]. From the microscopic field equations they have the following formulas:

$$\begin{aligned} T_{GS} &= -F\cdot G - \frac{g}{2} F : F + [F, N]\cdot U\circ U - U\circ U\cdot N\cdot F\cdot U\circ U = \\ &= -F^{\alpha\gamma} G_\gamma^{\cdot\,\beta} - \frac{1}{4} F_{\gamma\epsilon} G^{\gamma\epsilon} g^{\alpha\beta} + c^{-2}(F^{\alpha\gamma} M_{\gamma\epsilon} U^\epsilon - \\ &\quad -(g^{\alpha\gamma} + c^{-2} U^\alpha U^\gamma) M_{\gamma\epsilon} F^{\epsilon\chi} U_\chi) U^\beta; \end{aligned}$$

$$T_{GS} = \begin{pmatrix} \frac{1}{2}(\mathbf{E}^2 + \mathbf{B}^2) & \mathbf{E}\times\mathbf{H} \\ \mathbf{E}\times\mathbf{H} & \begin{array}{c} -\mathbf{E}\circ\mathbf{D} - \mathbf{H}\circ\mathbf{B} + \\ + \left(\frac{1}{2}(\mathbf{E}\cdot\mathbf{D} + \mathbf{B}\cdot\mathbf{H}) - \mathbf{M}\cdot\mathbf{B}\right)\mathbf{I} \end{array} \end{pmatrix} \qquad (1)$$

Here the expression is given in three different forms, before the usual four vector formulation I give the expression in a frame independent notation, too [12], [13].

In thermodynamics, where the different balances have a practical application, different authors suggested a different form of the field energy density. For example DE GROOT and MAZUR [14], VERHÁS [15] and MAUGIN [4] applied a different field energy densities. After that MATOLCSI [16] realized that this energy density can be given in a covariant form

$$\begin{aligned} T_{GM} &= -F\cdot G - \frac{g}{2}F:F - ([F,N] - g(F:N))\cdot U\circ U = \\ &\quad -F^{\alpha\gamma}G^{\beta}_{\gamma} - \frac{1}{4}F_{\gamma\epsilon}G^{\gamma\epsilon}g^{\alpha\beta} - c^{-2}(F^{\alpha\gamma}M_{\gamma\epsilon}U^{\epsilon}U^{\beta} - \\ &\quad -g^{\alpha\gamma}M_{\gamma\epsilon}F^{\epsilon\chi}U_{\chi}U^{\beta}) + \frac{1}{2}F_{\gamma\epsilon}M^{\gamma\epsilon}U^{\alpha}U^{\beta}; \end{aligned}$$

$$T_{GM} = \begin{pmatrix} \frac{1}{2}(\mathbf{E}^2 + \mathbf{B}^2 - \mathbf{M}\cdot\mathbf{B}) & \mathbf{E}\times\mathbf{H} \\ \mathbf{E}\times\mathbf{H} & \begin{array}{c} -\mathbf{E}\circ\mathbf{D} - \mathbf{H}\circ\mathbf{B} + \\ +\left(\frac{1}{2}(\mathbf{E}\cdot\mathbf{D} + \mathbf{B}\cdot\mathbf{H}) - \mathbf{M}\cdot\mathbf{B}\right)\mathbf{I} \end{array} \end{pmatrix}. \tag{2}$$

Let us note that the last two expressions differ only in their electromagnetic field energy (in a momentary rest frame).

3. Thermodynamic Considerations

The electromagnetic field energy is a part of the whole energy balance. To get the work terms in the First Law we should write the internal energy balance and from the expression of the source of the internal energy (the dissipation) we can conclude the polarization work terms. Using the expression of DE GROOT and SUTTORP [11] the source of the internal energy can be written as

$$\sigma_u = \mathbf{j}\cdot\mathbf{E} + \mathbf{E}\cdot\frac{\partial\mathbf{P}}{\partial t} - \mathbf{M}\cdot\frac{\partial\mathbf{B}}{\partial t}.$$

Therefore the extensive quantity appearing as an independent variable in the entropy function is $\mathbf{B}$. So the Gibbs relation is:

$$du = Tds + \mathbf{E}d\mathbf{P} - \mathbf{m}d\mathbf{B},$$

and the corresponding derivatives of the entropy are:

$$s(u,\mathbf{p},\mathbf{B}) \rightarrow \frac{\partial s}{\partial\mathbf{B}} = \frac{\mathbf{m}}{T} \rightarrow \frac{\partial^2 s}{\partial\mathbf{B}^2} = \frac{\chi_m}{T\mu}. \tag{3}$$

The requirement of the intrinsic stability criteria suggests that the corresponding medium is a *diamagnetic* one.

Similarly, from the expression of the thermodynamic field energy momentum we can get for the dissipation density:

$$\sigma_u = \mathbf{j}\cdot\mathbf{E} + \mathbf{E}\cdot\frac{\partial\mathbf{P}}{\partial t} + \mathbf{B}\cdot\frac{\partial\mathbf{M}}{\partial t}.$$

Therefore the extensive quantity in this case is the specific magnetization $\mathbf{m}$. The appropriate form of the Gibbs relation is the one given in the introduction:

$$du = Tds + \mathbf{E}d\mathbf{P} + \mathbf{B}d\mathbf{m}.$$

The derivatives of the entropy:

$$s(u,\mathbf{p},\mathbf{m}) \rightarrow \frac{\partial s}{\partial\mathbf{m}} = -\frac{\mathbf{B}}{T} \rightarrow \frac{\partial^2 s}{\partial\mathbf{m}^2} = -\frac{\mu}{T\chi_m}. \tag{4}$$

The requirement of the intrinsic stability criteria shows that the corresponding medium is a *paramagnetic* one.

Investigation of the field energy densities suggests a similar interpretation as the thermodynamic considerations. Let us consider the energy expressions of the different electromagnetic media separately. The energy density of the pure field without any polarization is

$$\epsilon^{(f)}_{EM} = \frac{1}{2}(\mathbf{E}\cdot\mathbf{D} + \mathbf{B}\cdot\mathbf{H}).$$

The energy density of the electric dipoles is

$$\epsilon^{(el)}_{EM} = -\frac{1}{2}(\mathbf{E}\cdot\mathbf{P}).$$

The energy density of the magnetic dipoles is

$$\epsilon^{(ma)}_{EM} = -\frac{1}{2}(\mathbf{B}\cdot\mathbf{M}).$$

The last two expressions require some further considerations. In polarizable media we distinguish two different dipole types: permanent and induced. The behaviour of the two electric and magnetic dipole types in an external field is different. While both the induced and the permanent electric dipoles turn to the same direction in an external field, the different magnetic dipoles turn to the opposite direction. In view of this fact we should change the sign of the field energy of induced magnetic dipoles, when no permanent ones are present.

If we add the three terms above we get the thermodynamic energy density in (2):

$$\epsilon^{(para)}_{EM} = \frac{1}{2}(\mathbf{E}\cdot\mathbf{D} + \mathbf{B}\cdot\mathbf{H}) - \frac{1}{2}(\mathbf{E}\cdot\mathbf{P}) - \frac{1}{2}(\mathbf{B}\cdot\mathbf{M}) = \frac{\mathbf{E}^2}{2} + \frac{\mathbf{B}^2}{2} - \mathbf{M}\cdot\mathbf{B}.$$

If we change the sign of the energy of the magnetic dipoles and we add the three terms again, then we get the de Groot–Suttorp form energy density

$$\epsilon^{(dia)}_{EM} = \frac{1}{2}(\mathbf{E}\cdot\mathbf{D} + \mathbf{B}\cdot\mathbf{H}) - \frac{1}{2}(\mathbf{E}\cdot\mathbf{P}) + \frac{1}{2}(\mathbf{B}\cdot\mathbf{M}) = \left(\frac{\mathbf{E}^2}{2} + \frac{\mathbf{B}^2}{2}\right).$$

4. Discussion

In the usual considerations on the electromagnetic field energy-momentum of polarizable media people expect a unique expression for different materials. Now we have seen that at least two basic expressions have to exist if we require the intrinsic stability. In this case the two most widely accepted expressions do not compete any more, they can be valid for different media.

Different energy-momentum tensors for different materials are quite common in continuum physics. However, those are based on different constitutive laws. Here no constitutive laws were considered yet: we gave two equivalent *basic* forms of the field energy momentum.

Some immediate consequences of the above considerations are applied in the relaxation theory of para- and diamagnetic materials [17].

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EQUIPARTITION OF FORCES: REVIEW OF A NEW PRINCIPLE FOR PROCESS DESIGN AND OPTIMIZATION

Signe KJELSTRUP, Erik SAUAR and Kristian M. LIEN*

Department of Physical Chemistry
* Department of Chemical Engineering
Norwegian University of Science and Technology
N-7034 Trondheim, Norway

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Abstract

We present a general proof for a design principle developed during the last two years: The principle of equipartition of forces. The principle is derived for parallel, coupled transport processes without restrictions on the phenomenological coefficients. Minimum entropy production is obtained for the total system, when the thermodynamic forces of transport are the same over all parallel paths in the system. We review some of the results obtained so far by application of the principle to distillation columns.

Keywords: entropy production, energy efficiency, irreversible thermodynamics, distination.

1. Introduction

Energy optimization is important in the process industry. Energy optimization of a process means determination of minimum entropy production. Already in his works on the symmetry relations, ONSAGER stated (1931a, b) that entropy production is minimum in the stationary state, that is a state with constant fluxes. BEJAN (1982) has described how minimum entropy production can be obtained in practice for several cases of heat and mass transfer. In a heat exchanger for example, he found a sharp minimum for the entropy production for certain flow conditions in the tube. For constant transport coefficients, TONDEUR – KVAALEN (1987) showed that minimum entropy production is obtained when the entropy production rate is constant through the apparatus. As a consequence of this, a heat exchanger with countercurrent flow dissipates less energy than one with concurrent flow; a well-known engineering observation.

The results of TONDEUR – KVAALEN are in accordance with the results from finite time thermodynamics. In a recent review on finite time thermodynamics, ANDRESEN (1996) states: Constant rate of entropy production is the path or operating strategy which produces the least overall entropy in the system. In his elaboration on the topic in 1990, TONDEUR