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Instabilities in adiabatic transformations of first-order phase transitions in a model with bistable units

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Abstract

In this paper we study adiabatic transformations in a model of first-order phase transformations made of superposition of bistable units. A differential equation with hysteresis operators is derived and how to compute numerically the $T(H)$ trajectories is discussed. The numerical method is applied to an idealized phase transformation displaying an instability. We discuss the differences of the temperature change between the controlled magnetic field case and the controlled phase transformation case.

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1. Introduction

The recent developments of magnetic materials with giant magneto-caloric effect (GMCE) for magnetic refrigeration [1] require a better understanding of their thermodynamic aspects. GMCE materials display a first-order magneto-structural phase transformation with hysteresis that can be approximately described as rate independent and in which the entropy change achievable by the application of the magnetic field and the entropy produced by the hysteresis irreversibility are both present.

Here we face the problem of first-order magneto-structural phase transformations with hysteresis from the viewpoint of hysteresis model based on the superposition of bistable units. The two states of the units correspond to one of the two stable thermodynamic phases 0 or 1 (see Fig. 1) and the driving force of the switching is the difference between the Gibbs free energies g_0 and g_1 of the pure ideal phases [2]. The expressions for the entropy change and the entropy production rate are derived by using the equivalence between the superposition and the thermodynamic approaches with *internal variables* [3].

In this paper we study this model in the case of adiabatic transformations for the magnetic body. This is a rather interesting situation for several reasons. (i) Since the model is defined with H and T as controlled variables, in order to obtain adiabatic transformations one has to include explicitly in the description the role of the part of the system (phonons, electrons, etc.) contributing to the specific heat. This is valid if we assume thermal equilibrium between magnetic and structural parts. (ii) When the magnetic field H is varied, the adiabatic temperature change is given by the solution of a differential equation containing hysteresis operators of Preisach type. This kind of equation has its own interest for the mathematical aspects it involves. (iii) To go deeper into the physics of the phase transformation process, we envisage the possibility of predicting instabilities in the phase transformation that occurs under adiabatic conditions, but not under isothermal ones. These model conditions may be realized in real materials.

We derive a numerical scheme for the integration of the differential equation for the adiabatic transformation and we apply it to a limit case in which the balance between the

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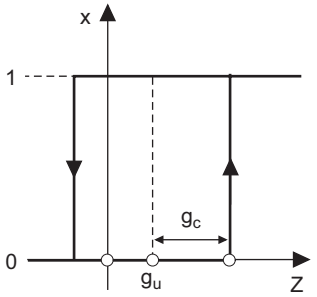

Fig. 1. Bistable loop for the first-order phase transformation.

entropy production due to hysteresis and the entropy change is such that, after a threshold, the transformation is self-sustained without any change of the external magnetic field. We show that the numerical scheme proposed provides a solution in which the magnetic field H is recoiling back, then representing the trajectory $T(H)$ with controlled transformation speed. The result is that the controlled magnetic field trajectory would display an instability at a critical field value and would result in a different temperature of the final state because of the kinetics involved. The instability we predict by the model may be found in adiabatic transformations of magnetic alloys with AF–F phase transformations [4].

2. The model

The model represents a phase transformation with hysteresis. It is a superposition of bistable units, of Preisach type, with states 0 and 1 (see Fig. 1) corresponding to two thermodynamic phases of a magnetic alloy (for example, 0 = anti-ferromagnetic state, 1 = ferromagnetic state). The input of the unit is the difference in the Gibbs free energies of the two pure phases $g_0(H,T)$ and $g_1(H,T)$, denoted by the symbol Z:

$$Z = \frac{g_0 - g_1}{2} \tag{1}$$

and depending on the two intensive variables H and T.

The superposition of the units is taken with weight function $p(g_c, g_u)$. The state of the system is given by the same rules of the Preisach model of hysteresis. The regions of the plane (g_c, g_u) in the 0 or 1 state depends on the time history of $Z(t)$ and are separated by a borderline function $b(g_c)$ which is determined by enforcing the inequality $|b(g_c) - Z(t)| \leqslant g_c$ at each instant of time (see Ref. [5] for a detailed discussion of this evolution rule).

We assume that the non-equilibrium Gibbs free energy $\hat{g}$ of the system is a superposition of bistable contributions [5]:

$$\hat{g} = A + \int_0^\infty \mathrm{d}g_c \left[\int_{-\infty}^{b(g_c)} (g_u - Z) p(g_c, g_u)\, \mathrm{d}g_u - \int_{b(g_c)}^{\infty} (g_u - Z) p(g_c, g_u)\, \mathrm{d}g_u \right], \tag{2}$$

where $A = (g_0 + g_1)/2$ and we have used the equilibrium-specific Gibbs free energies of the pure phases g_0 and g_1 per unit mass. Then the out-of-equilibrium thermodynamics of the system is derived consequently by making use of known results for the thermodynamics with *internal variables* [3]. We take a distribution $p(g_c, g_u)$ that does not depend on H and T, then the borderline $b(g_c)$ takes the role of the internal state variable. Using the results of Ref. [3] we obtain:

(1) The phase fraction per unit mass $\hat{X}$ of phase 1:

$$\hat{X} = \int_0^\infty \mathrm{d}g_c \int_{-\infty}^{b(g_c)} p(g_c, g_u)\, \mathrm{d}g_u. \tag{3}$$

(2) The extensive variables: the magnetization $\hat{M}$ and the specific entropy $\hat{s}$ (both per unit mass):

$$\mu_0 \hat{M} = -\left.\frac{\partial \hat{g}}{\partial H}\right|_{T, b(g_c)}, \tag{4}$$

$$\hat{s} = -\left.\frac{\partial \hat{g}}{\partial T}\right|_{H, b(g_c)}, \tag{5}$$

where the internal variable, the function $b(g_c)$, is kept constant.

(3) The rate of entropy production $\mathrm{d_i}\hat{s}/\mathrm{d}t$:

$$T\frac{\mathrm{d_i}\hat{s}}{\mathrm{d}t} = -\left.\frac{\partial \hat{g}}{\partial t}\right|_{H,T}, \tag{6}$$

where the variation of the Gibbs free energy in time is due to a variation $\delta b(g_c)$ of the internal state under constant H and T. By the fact that the system is not in the equilibrium state, every transformation with a change in the state line corresponds to an internal generation of entropy.

The previous expressions are easily computed giving

$$\hat{M} = \hat{X} M_1 + (1 - \hat{X}) M_0 = \Delta M \hat{X} + M_0, \tag{7}$$

$$\hat{s} = \hat{X} s_1 + (1 - \hat{X}) s_0 = \Delta s \hat{X} + s_0, \tag{8}$$

where $\mu_0 M_1 = -\partial g_1/\partial H$, $\mu_0 M_0 = -\partial g_0/\partial H$, $s_1 = -\partial g_1/\partial T$, $s_0 = -\partial g_0/\partial T$, $\Delta M = M_1 - M_0$, $\Delta s = s_1 - s_0$ and $\hat{X}$ is the phase fraction given by the Preisach model expression, Eq. (3), with $Z(H,T)$ as input. The rate of entropy production $\mathrm{d_i}\hat{s}/\mathrm{d}t$ results:

$$T\frac{\mathrm{d_i}\hat{s}}{\mathrm{d}t} = 2\int_0^\infty [Z - b(g_c)] p(g_c, b(g_c)) \frac{\partial b}{\partial t}\, \mathrm{d}g_c \tag{9}$$

which is a definite positive quantity.

3. Adiabatic transformations

In adiabatic transformations the system is isolated and its temperature T may change. The variation of the entropy of the body $\hat{s}$ is given by the entropy balance