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## TEMPERATURE DEPENDENCE OF HYSTERESIS IN PSEUDOELASTICITY

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### Abstract

This paper proposes to consider the existence of hystereses in phase transitions as a consequence of interfacial energies. Given such an energy, the size of the hysteresis and its dependence on temperature are then calculated. This paper extends the ideas that were previously described in MÜLLER [1] and BORNERT [2].

### 1. Pseudoelasticity - Phenomenon and Landau Model.

Pseudoelasticity is a phenomenon that occurs in shape memory alloys. It is characterized by load-deformation diagrams with hysteresis loops in the first and third quadrants. Fig. 1 shows schematic plots of three load-deformation curves for increasing temperatures. The material is elastic, because during a loading-unloading cycle it returns to its original state. The material is also pseudoelastic, because during such a cycle it returns to this original state by way of a hysteresis loop.

In the first quadrant of the diagram, the upper horizontal line represents a phase transition from the austenitic to the martensitic phase, while the lower horizontal line represents the reverse transition.

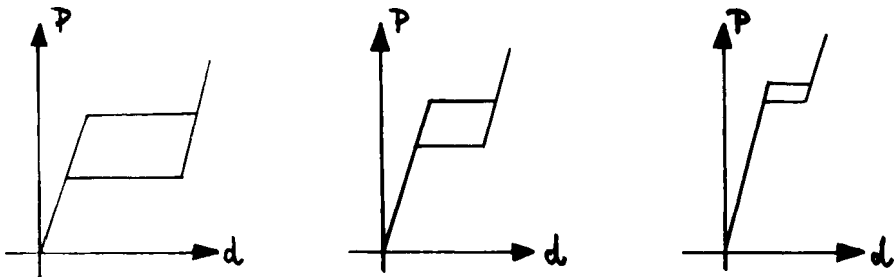


Figure 1: Schematic load-deformation curves of a pseudoelastic body.

Attempts to model such hysteretic behavior invariably result in a non-monotone, load-deformation curve instead of a hysteresis. The best known among such models is the purely phenomenological Landau model which is characterized by free energy of the form

$$f(d, t) = f_0(T) + \frac{1}{2}a(T-T_0)d^2 - \frac{1}{4}bd^4 + \frac{1}{6}cd^6 \quad (1.1)$$

where all coefficients are positive. With the proper choice of coefficients, and, within a certain temperature range, this free energy function is non-convex, and its derivative--the load  $P$ --is non-monotone. Fig. 2 shows a number of possibilities covered by the expression (1.1) for  $f(d, T)$ , and for its derivative  $P(d, T)$ . In this paper we are especially interested in the temperature range  $T_f < T < T_e$ , which we call the pseudoelastic range.

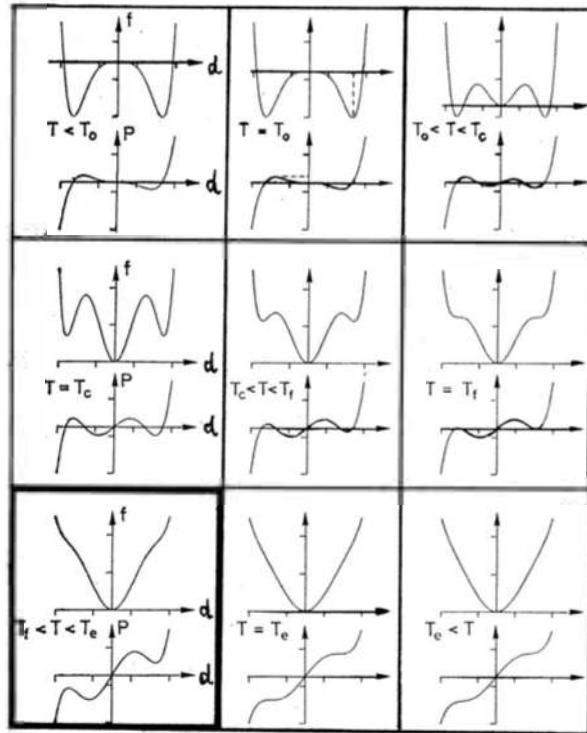


Figure 2. Specific free energy and load as functions of specific deformations

## 2. The Problem

We assume that a statistical or phenomenological theory--as Landau's--has provided us non-monotone free energies. The next step is to ask in what way such a theory can help us understand hysteresis.

The non-monotone character of the load-deformation curve dictated by a non-convex free energy is often argued to imply a hysteresis--at least in a load-controlled experiment. Indeed, when a load is applied, the resulting deformation increases smoothly for small loads until the maximum of the (P,d)-curve is reached. Upon further loading, however, a breakthrough occurs towards the right ascending branch of the curve, along which further loading can take place. During unloading, the deformation will change abruptly at that point where the load falls below the minimum. This sequence of events is illustrated in Fig. 3a.

There are certain phase transitions, however, that occur reversibly along a single horizontal line as shown in Fig. 3c. The prototype of such a phase transition is provided by the liquid-vapor phase transition of a van der Waals gas.

Now, if the situations depicted in Fig. 3a and 3c are both possible, then it is obviously possible for an intermediate state as shown in Fig. 3b to occur.

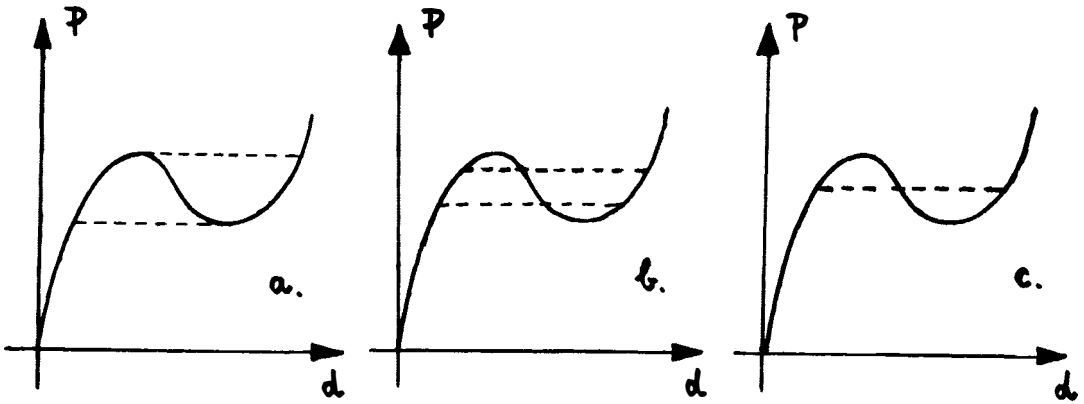


Figure 3: Possible sizes of the hysteresis.

The problem we will discuss in this paper is as follows: given a non-convex energy, and therefore, a non-monotone load-deformation curve, what is the size of the hysteresis? And, in addition, how does the hysteresis depend on temperature?

## 3. A Possible Answer - Phase Equilibrium

### 3.1 Minimization of Free Energy

If we have a separation of two phases, ('') and (''), we may assume that the free energy of the phase mixture is the sum of the free energies of the phases. Conceivably, there is also an interfacial energy such that

$$F = F' + F'' + A m' m'' / m. \quad (3.1)$$

The last term is a reasonable specific assumption for the interfacial energy. Indeed, from a statistical standpoint, the expected number of interfaces between the regions of the phases can be assumed to be proportional to  $m'm''/m$ .  $A$  is assumed to be positive constant of proportionality. Such an approximation for the free energy as (3.1) was first made, to our knowledge, by CAHN and LARCHE [3], albeit in a different context.

We divide (3.1) by  $m$  and introduce the phase fraction  $z=m'/m$  to obtain

$$f = (1-z)f(d') + zf(d'') + Az(1-z) \quad (3.2)$$

where  $d'$  and  $d''$  are the specific deformations of the phases, and  $f=F/m$  is the specific free energy of the phase mixture. The specific deformation of the phase mixture is assumed to be given in terms of  $d'$  and  $d''$  by

$$d = (1-z)d' + zd'' \quad (3.3)$$

$f$  in (3.2) is a function of three variable:  $z$ ,  $d'$ , and  $d''$ . We find the equilibrium values of these variables by minimizing  $f$  under the constraint (3.3). Thus, we obtain

$$z_E = \frac{d - d'_E}{d''_E - d'_E} \quad (3.4)$$

$$\left. \frac{\partial f}{\partial d} \right|_{d'_E} = \left. \frac{\partial f}{\partial d} \right|_{d''_E} = \frac{f(d''_E) - f(d'_E) + A(1 - 2z_E)}{d''_E - d'_E} \quad (3.5)$$

### 3.2. The Case Without Interfacial Energy.

In the case  $A=0$ , the equations of (3.5) indicate that  $d'_E$  and  $d''_E$  are independent of  $z_E$ , or  $d$ . Their values are found as abscissae of points on the  $(f,d)$ -curve, which have the same slope as well as a difference quotient equal to that slope. Points are then easily found by the "common tangent construction" as illustrated in Fig. 4a.

There is an alternative, graphical method for determining  $d'_E$  and  $d''_E$ --one that uses the  $(P,f)$ -diagram. We first note that  $(3.5)_1$  implies that the loads  $P=\partial f/\partial d$  on the two phases are equal in equilibrium, and we denote this common load by  $P_E$ . Next, we write  $f(d''_E)-f(d'_E)$  in  $(3.5)_2$ --with  $A=0$ --which may be expressed in the form

$$f(d''_E) - f(d'_E) = \int_{d'_E}^{d''_E} \partial f / \partial u du = \int_{d'_E}^{d''_E} P(u) du \quad (3.6)$$

Now the equation  $(3.5)_2$ --still with  $A=0$ --may be expressed in the form

$$P_E(d''_E - d'_E) = \int_{d'_E}^{d''_E} P(u) du \quad (3.7)$$

This means that the rectangle with sides  $P_E$  and  $d''_E-d'_E$  must be equal in area to the area below the  $(P,d)$ -curve between  $d'_E$  and  $d''_E$ . Equivalently, the two shaded areas in Fig. 4b must be equal. It is obvious that this requirement now identifies  $P_E$ , in addition to  $d'_E$  and  $d''_E$  as we can see in Fig. 4b. This construction is known as the "equal area rule".

Once  $d'_E$  and  $d''_E$  have been determined, we may calculate  $z_E$  from (3.4) and, hence, from (3.2) and (3.4):

$$f_E = f(d'_E) + \frac{f(d''_E) - f(d'_E)}{d''_E - d'_E}(d - d'_E) \quad (3.8)$$

This is a linear function of  $d$ ; in fact, it is the equation for the tangent shown in Fig. 4a. It is now obvious why the body separates into two phases: in this

way it can assume a smaller free energy, and indeed,  $f_E(d)$  is smaller than  $f(d)$  within the range  $d_E^1 < d < d_E^2$ .

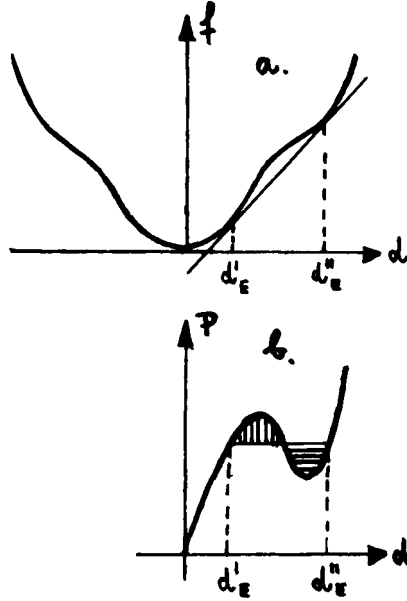


Figure 4: Common tangent construction and equal area rule

From the above discussion we conclude that  $d_E^1$  and  $d_E^2$  are independent of  $z_E$ , and hence, of  $d$ . Therefore, the individual phases do not change their specific deformations as the phase transition proceeds from  $z_E=0$  to  $z_E=1$ . Also as a result of the above argument, there is no hysteresis observed. Rather, the phase transition proceeds reversibly at load  $P_E$ . This is not what we want, of course, since in pseudoelasticity we do in fact observe hysteresis. Therefore, we now proceed to investigate the case  $A \neq 0$  in the hope that this general case will permit hysteresis.

### 3.3 The Case with Interfacial Energy.

From (3.5), we conclude that even if  $A \neq 0$  holds true, the loads on the two phases remain equal, and we continue to denote the common load as  $P_E$ . The two equations (3.5) now show that  $d_E^1$  and  $d_E^2$  depend on  $z_E$ , and, by (3.4), on  $d$  as well. This is due to the interfacial energy, and we will now proceed to determine the functions  $d_E^1(d)$  and  $d_E^2(d)$  graphically.

Of course (3.6) is still valid, and therefore,  $(3.5)_2$  may be written in the form

$$P_E(d_E^2 - d_E^1) - \int_{d_E^1}^{d_E^2} P(u) du = A(1 - 2z_E). \quad (3.9)$$

For  $z_E=0$  we have

$$P_E(0) (d_E''(0) - d_E'(0)) - \int_{d_E'(0)}^{d_E''(0)} P(u) du = A. \quad (3.10)$$

For  $z_E=1$  we have

$$P_E(1) (d_E''(1) - d_E'(1)) - \int_{d_E'(1)}^{d_E''(1)} P(u) du = -A, \quad (3.11)$$

where the arguments 0 and 1 refer to  $z_E=0$  and  $z_E=1$  respectively.

Equation (3.10) implies that  $P_E(0)$ ,  $d_E''(0)$ ,  $d_E'(0)$  assume values such that the rectangle with sides  $P_E(0)$  and  $d_E''(0) - d_E'(0)$  is larger than the area below the  $(P,d)$ -curve between  $d_E'(0)$  and  $d_E''(0)$  by  $A$ . Equation (3.10) identifies the values  $P_E(0)$ ,  $d_E''(0)$ , and  $d_E'(0)$  uniquely as shown in Fig. 5a. Similarly, equation (3.11) identifies  $P_E(1)$ ,  $d_E''(1)$ ,  $d_E'(1)$  graphically as shown in Fig. 5b. It is therefore obvious that the interfacial energy stabilizes the pure phases. Indeed, with  $A>0$ ,  $P_E(0)$  is greater than  $P_E$  when  $A=0$ , and  $P_E(1)$  is, in turn, smaller than this  $P_E$ . This implies a hysteresis in a load-controlled, loading-unloading experiment. A breakthrough from the austenitic to the martensitic phase occurs when  $P$  exceeds  $P_E(0)$ , and a breakthrough in the reverse direction occurs when  $P$  falls below  $P_E(1)$ . The shaded region in Fig. 5c is the region bounded by the hysteresis loop, and, it follows from Fig. 5a and 5b, that this area is equal to  $2A$ .

Thus, we have partially answered the question concerning the size of the hysteresis. We now proceed to determine its dependence on temperature.

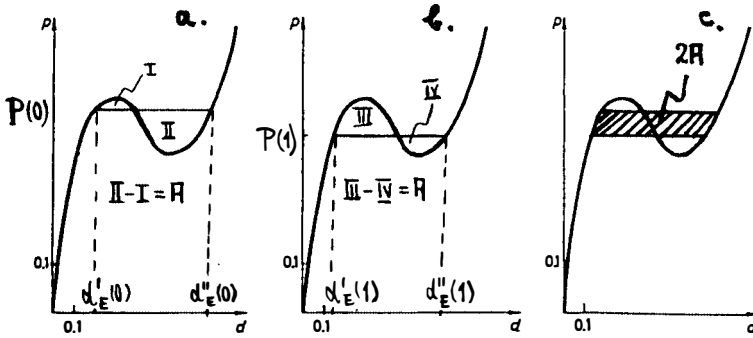


Figure 5: Breakthrough lines and hysteresis.

### 3.4 The Size of the Hysteresis as Function of Temperature.

According to (1.1) the "wobble" in the  $(P,d)$ -curves observed in the pseudoelastic range becomes less pronounced, i.e., shallower and narrower as the temperature increases, (see Fig. 6). If a breakthrough were to occur, as Fig. 3a suggests, we would therefore expect a steady decrease in the vertical width of the hysteresis. In Fig. 7 this width has been calculated from (1.1) as a function of temperature. The width is represented by the vertical distance between the two dotted lines.

If, on the other hand, the hysteresis is determined by the area  $2A$  as suggested in the previous section, we would initially expect a slight increase in the width of the hysteresis as  $\tau$  grows. This is due to the fact that as the

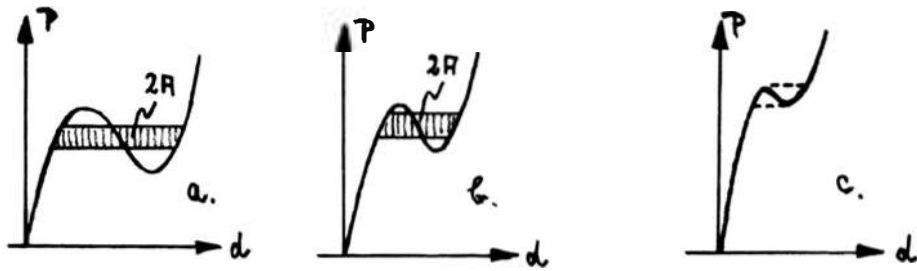


Figure 6:  $(P,d)$ -curves of the Landau model for increasing temperature in the pseudoelastic range.

"wiggle" becomes narrower, the hysteresis necessarily becomes wider to accommodate the area  $2A$  (see Fig. 6b). The vertical width has been calculated for some  $A$  and is represented in Fig. 7 by the vertical distance between the two solid lines.

Of course, once the "wiggle" becomes too small to accommodate the area  $2A$ , that area becomes irrelevant in determining transitions. Rather, the transitions between phases will pass through the extrema of the  $(P,d)$ -curve (see Fig. 6c). The hysteresis should then become thinner rapidly as the temperature increases. Fig. 7 shows the eventual disappearance of the hysteresis as predicted by the Landau model.

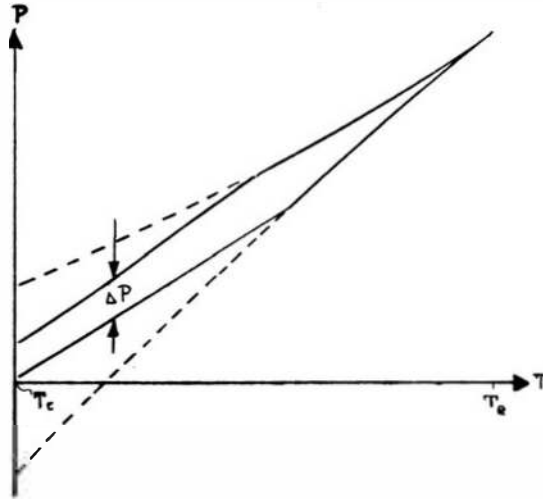


Figure 7: On the vertical width  $\Delta P$  of the hysteresis. Dotted curves: Transition passes through extrema. Solid curves: Hysteresis corresponds to the area  $2A$  as long as possible.



Fig. 8 depicts measurements of the hysteresis for the memory alloy CuZnAl at different temperatures. These curves seem to support graphically the heretofore discussed conclusions. In particular, we note that a rapid decrease in the width of the hysteresis begins at 60°C. We may therefore interpret this temperature as the boundary temperature, beyond which the area 2A is no longer relevant in regard to the size of the hysteresis.

#### 4. The Stability of Phase Equilibrium.

In the case without interfacial energy, we have seen that the phase transition occurred along a horizontal line in the (P,d)-diagram. We may say that along this line the body exists in states of indifferent equilibrium which are distinguished only by a different phase fraction  $z$ .

The situation is quite different when we take the interfacial energy into account. Indeed, if we graphically determine  $P_E$ ,  $d_E^L$ , and  $d_E^H$  from (3.9), we will obtain values within the ranges of

$$d_E^L(1) < d_E^L(z_E) < d_E^L(0) \quad \text{and} \quad d_E^H(1) < d_E^H(z_E) < d_E^H(0) \quad (4.1)$$

for values of  $z_E$  between 0 and 1.

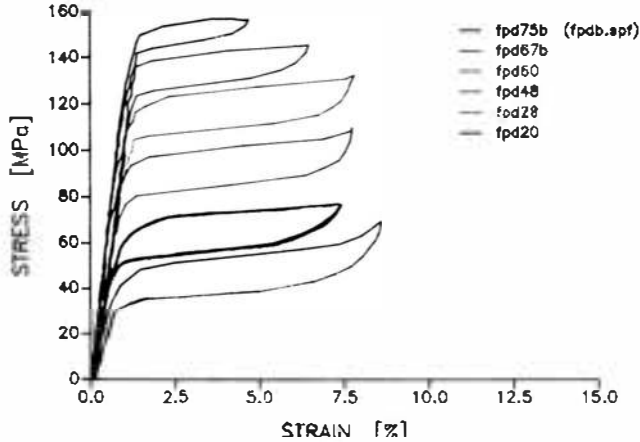


Figure 8: Measured hysteresis in CuZnAl.

The corresponding value of  $d$  follows from (3.4), and the curve  $f_E(d)$  is derived by inserting  $z_E$ ,  $d_E^L$ , and  $d_E^H$  into (3.2). Fig. 9 shows qualitative plot of  $f_E(d)$  and  $P_E(d)$ .

It is important to note that the free energy  $f_E(d)$  within the range  $d_E^L(0) < d < d_E^H(1)$  where phase equilibrium is able to prevail is depicted as concave in Fig 9. Also within this range, the load  $P_E(d)$  slopes downward. This indicates that all phase equilibria are unstable.

At this time it is an open question how the states inside the hysteresis loop are to be characterized. Experiments have demonstrated that such states exist, that a load-deformation path of the type shown in Fig. 10 is possible. However, from the foregoing analysis, it is clear that the states inside the hysteresis loop cannot exist in phase equilibrium.

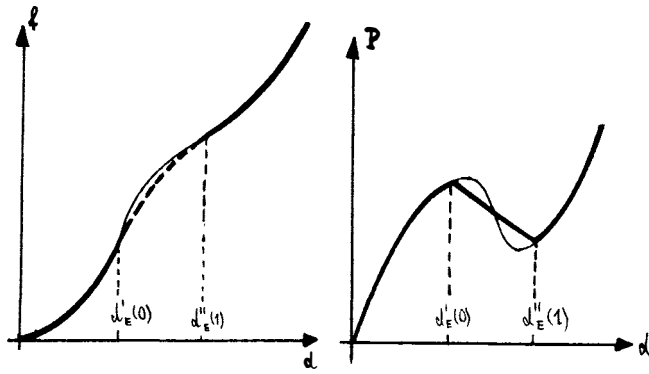


Figure 9: Free energy and load as functions of deformation in phase equilibrium.

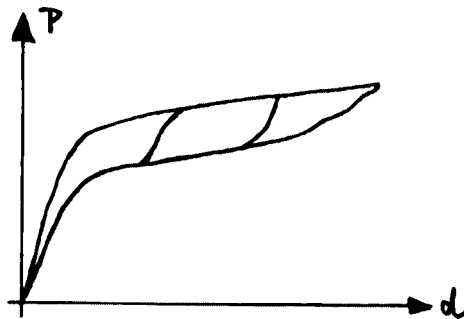


Figure 10: Possible states inside the hysteresis loop.

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