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Checking the Triple Product Rule for the Compression and Stretching of Materials

Igor A. Stepanov
Institute of Science and Innovative Technologies,
Liepaja University, Liepaja, LV–3401, Latvia

ABSTRACT

It is shown here that the well-known thermodynamic relation which stems from the triple product rule is not valid for descriptions of the compression and stretching of almost all materials.

Keywords: Euler's Chain Relationship, Cyclic relation, Cyclic chain rule, Compression, Expansion: Elastomers, Rubber.

INTRODUCTION

Functions theory includes the triple product rule, as follows:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \quad (1)$$

There is a well-known thermodynamic relation that follows from Eq. (1):

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1 \quad (2)$$

where P, V, T, are pressure, volume and temperature, respectively. this relation, The relation in, Eq. (2) is traditionally checked with the equation of an ideal gas [1]:

$$PV = RT\ . \quad (3)$$

Indeed, if one introduces Eq. (3) into Eq. (2), it can be seen that Eq. (2) is correct. However, Eq. (2) describes only the heating of a gas with heat exchange. More specifically, a quantity of heat is introduced into a gas, and both its temperature and volume increase, meaning that the second derivative in Eq. (2) is positive. The third derivative in Eq. (2) is positive and the first is negative. In [2], it was shown that Eq. (2) fails to describe processes of compression; for a gas under compression, the first and second derivatives in Eq. (2) are negative, while the third derivative is positive. It is therefore of interest to check whether Eq. (2) is valid for the compression of materials.

THEORY

In materials science, the tension σ is used instead of the pressure P.

The authors of [3] state: "The derivative $(\partial T/\partial V)^{-1}{}_P$ is negative for almost all substances except for elastomers under expansion. Thus, the temperature of the sample increases under compression, Analogously, the temperature of the sample decreases under stretch". The first derivative in Eq. (2) is negative for a solid, as its volume decreases under compression and increases under stretching. (since expansion pressure is negative.) The third derivative in Eq. (2) is positive for a solid, meaning that the product of the derivatives is positive.

In [4,5] an attempt was made to check the validity of the triple product rule for the stretching of rubber bands. The results from [4] are given in Table 1, where T is temperature, L is length and σ is tension. The authors of [4] considered Eq. (2) in the following form:

$$\left(\frac{\Delta\sigma}{\Delta L}\right)_T \left(\frac{\Delta L}{\Delta T}\right)_\sigma \left(\frac{\Delta T}{\Delta\sigma}\right)_L = -1 \tag{4}$$

Table 1: Experimental results from [4] and corrections

Derivative [4]	Value from [4]	corrected value
$\left(\frac{\Delta\sigma}{\Delta L}\right)_T$	50.1g/cm	–50.1g/cm
$\left(\frac{\Delta L}{\Delta T}\right)_\sigma$	–0.0023 cm/°C	0.0023 cm/°C
$\left(\frac{\Delta T}{\Delta\sigma}\right)_L$	≈7.65 °C/g	≈–7.65 °C/g

It can be seen that some of the results in Table 1 are incorrect. The derivative in the first row is positive, as the authors of [4] assumed that an expanding tension is positive. This is a mistake: in solid state physics, a compressing tension is positive, whereas an expanding tension is negative. The derivative in the second row is negative, since the authors heated the bands with an infrared lamp and found that they had a negative thermal expansion coefficient; however, if the bands are stretched mechanically, their temperature increases [5]. Since the experiments in [4,5] involved mechanical expansion of the bands, it should be assumed that the derivative in the second row is positive. The derivative in the third row is positive, since the authors of [4] assumed that an expanding tension is positive. If the correct sign of the expanding tension is assumed, this derivative will be negative. The product of these three derivatives will be approximately equal to 0.88.

In [6], Hilgeman and Alcaraz checked the triple product rule for the deformation latex elastomer, and their results are given in Table 2. These authors checked this rule in the following form:

$$\left(\frac{\Delta\sigma}{\Delta T}\right)_L \left(\frac{\Delta L}{\Delta\sigma}\right)_T \left(\frac{\Delta T}{\Delta L}\right)_\sigma = -1 \tag{5}$$

Some of the results in Table 2 are incorrect for the same reasons as those in Table 1. If the corrected data from Table 1 are introduced into Eq. (5), the product of the derivatives is approximately equal to 1.13.

If the corrected data from Table 2 are introduced into Eq. (5), the product of the derivatives is equal to 1.11, whereas if they are introduced into Eq. (4), the product is equal to 0.90.

Table 2: Experimental results from [6] and corrections

Derivative [6]	Value from [6]	corrected value
$\left(\frac{\Delta\sigma}{\Delta T}\right)_L$	0.2852 g/°C	–0.2852 g/°C
$\left(\frac{\Delta L}{\Delta\sigma}\right)_T$	0.0178 cm/g	–0.0178 cm/g
$\left(\frac{\Delta T}{\Delta L}\right)_\sigma$	– 219.23 °C/cm	219.23 °C /cm

CONCLUSION

It has been shown here that for almost all materials, the thermodynamic identity given in Eqs. (4) and (5) fails to describe the processes of compression and mechanical expansion. More specifically, the right-hand sides of Eqs. (4) and (5) are positive rather than negative, and it can be assumed that the values on the right-hand sides must be equal to +1 rather than –1. Further research will be necessary to confirm this hypothesis.

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