

Short Research Article

Maxwell Relations for Substances with Negative Thermal Expansion and Negative Compressibility

ABSTRACT

It is shown that taking into account the negative compressibility of substances changes Maxwell relations. The earlier results of the author indicating that these relations differ for substances with negative thermal expansion have received additional confirmation. Universal Maxwell relations have been derived. The results obtained have been confirmed experimentally by a number of authors.

Keywords: Maxwell relations, thermodynamics, negative thermal expansion, negative compressibility, heat exchange, compression

1. INTRODUCTION

Recently, negative compressibility materials were discovered [1–9]. For them, isothermal compressibility $\beta = -1/V (\partial V / \partial P)_T$ is negative. In this paper, it is shown that the Maxwell relations for such substances differ from normal relations. Moreover, additional evidences are found that Maxwell relations differ for substances with a negative thermal expansion coefficient $\alpha = 1/V (\partial V / \partial T)_P$. General Maxwell relations have been derived which take into account the sign of compressibility and thermal expansion. Experiments show that the first and third general Maxwell relations are correct.

2. THEORY

The first Maxwell relation is:

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad (1)$$

where S is entropy. This relation stems from the first law of thermodynamics. This law for *heat exchange* can be written as:

$$\delta Q = T dS = dU + P dV \quad (2)$$

where δQ is the heat introduced into the system and U is internal energy. One introduces a quantity of heat into the system and it turns into the change in internal energy and work produced by the system. On the left-hand side, the motive force of the process is written, and its effect is written on the right-hand side. In [10–16] the general form of the first law of thermodynamics for the *heat exchange* was obtained:

$$\delta Q = T dS = dU + \text{sign}(\alpha) P dV. \quad (3)$$

However, for the heating of substance *by compression*, the first law of thermodynamics cannot be derived from Eq. (2) and must be derived independently [10, 12]:

$$P dV = -dU. \quad (4)$$

Again, the motive force of the process is written on the left-hand side, and its effect is written on the right-hand side. One can prove this result very easily. Equation (2) cannot describe the compression of the substances with negative compressibility. The equation for that is:

$$P dV = dU. \quad (5)$$

One can adduce another good argument. According to tables of thermodynamic derivatives [17],

$$\left(\frac{\partial U}{\partial V} \right)_P = -P + \frac{C_P}{\alpha V}. \quad (6)$$

46 This is the derivative for the heat exchange process. However, for mechanical compression this
47 derivative must be obtained from Eq. (4), and it is:

$$48 \quad \left(\frac{\partial U}{\partial V} \right)_P = -P. \quad (7)$$

49 Therefore, the thermodynamics of compression differs from the thermodynamics of the heat
50 exchange.

51
52 From Eq. (3) it follows that the first Maxwell relation will be as follows:

$$53 \quad \left(\frac{\partial T}{\partial V} \right)_S = -\text{sign}(\alpha) \left(\frac{\partial P}{\partial S} \right)_V. \quad (8)$$

54 In the Appendix it is shown that this has been confirmed by many experiments and that Eq. (1)
55 contradicts them.

56
57 The second Maxwell relation is:

$$58 \quad \left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P. \quad (9)$$

59 Its traditional derivation is the following [18]. One introduces dU from Eq. (2) into the differential of
60 enthalpy:

$$61 \quad dH = dU + PdV + VdP \quad (10)$$

62 and obtains:

$$63 \quad dH = TdS + VdP. \quad (11)$$

64 From this equation, Eq. (9) results.

65
66 One can notice a mistake in this derivation. Let us prove that Eq. (2) is valid only for a constant
67 pressure. Let us assume that the pressure is not constant in it. One can notice that $\delta Q = TdS = dH_P$ in
68 Eq. (2) is a full differential, where dH_P is the enthalpy change at a constant pressure. Therefore, the
69 derivatives $(\partial H/\partial V)_U$ and $(\partial P/\partial U)_V$ must be equal. However, for the ideal gas, they equal 0 and

70 $2/3V$, respectively. In reality, these derivatives must also be taken at a constant pressure, thus both
71 are equal to zero. The differential dU from Eq. (2) does not equal dU from Eq. (10) because in Eq. (2)
72 it is for constant pressure, but in Eq. (10) it is for varying pressure. (In Eq. (4), of course, the pressure
73 can vary.) The correct derivation must be the following. For heat exchange with varying pressure and
74 volume [19]:

$$75 \quad \delta Q = TdS = dU + PdV + VdP. \quad (12)$$

76
77 One can see that:

$$78 \quad TdS = TdS_1 + TdS_2 \quad (13)$$

79 where

$$80 \quad \delta Q_1 = TdS_1 = dU_1 + PdV \quad (14)$$

81 is the heat exchange at a constant pressure, and

$$82 \quad \delta Q_2 = TdS_2 = dU_2 + VdP \quad (15)$$

83 is the heat exchange at a constant volume [19, 20]. From Eq. (15), omitting the subscripts, the second
84 Maxwell relation can be derived:

$$85 \quad \left(\frac{\partial T}{\partial P} \right)_S = - \left(\frac{\partial V}{\partial S} \right)_P. \quad (16)$$

86 This equation has a different sign compared with Eq. (9).

87
88 From the well-known thermodynamic identity [21], it follows that:

$$89 \quad dP = \left(\frac{\partial P}{\partial T} \right)_V dT = - \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial V} \right)_T dT = \frac{\alpha}{\beta} dT. \quad (17)$$

90 This means that Eq. (15) will look like:

$$TdS = dU + \text{sign}(\alpha\beta)VdP. \quad (18)$$

From this equation the general second Maxwell relation follows:

$$\left(\frac{\partial T}{\partial P}\right)_S = -\text{sign}(\alpha\beta)\left(\frac{\partial V}{\partial S}\right)_P. \quad (19)$$

The third Maxwell relation is:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T. \quad (20)$$

Consider its traditional derivation [18]. One introduces dU from Eq. (2) into the differential of Helmholtz energy:

$$dF = dU - TdS - SdT \quad (21)$$

which results in:

$$dF = -PdV - SdT. \quad (22)$$

From this, Eq. (20) is obtained. However, this derivation is non-strict: an equation which describes the heat exchange at a constant pressure with varying volume is introduced into the equation which describes a process with a constant volume and varying pressure. A more strict derivation should be one such as:

$$dF = dF_1 + dF_2 \quad (23)$$

where

$$dF_1 = dU_1 - TdS_1 - SdT_1 = -SdT_1 \quad (24)$$

corresponds to the quantity of heat introduced into the system at a constant volume (we introduce into Eq. (24) dU from Eq. (2) with $dV = 0$), and

$$dF_2 = dU_2 - TdS_2 - SdT_2 = -PdV - SdT_2. \quad (25)$$

corresponds to the expansion/compression of the system due to the heat exchange at a constant pressure (into Eq. (25) we introduce dU from Eq. (2)). Summing up Eqs. (24) and (25), one gets Eq. (22).

Let us take the thermal expansion coefficient into account. Introducing Eq. (3) into Eq. (25), and summing Eqs. (24) and (25), one obtains:

$$dF = -\text{sign}(\alpha)PdV - SdT \quad (26)$$

and the third Maxwell relation becomes:

$$\text{sign}(\alpha)\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T. \quad (27)$$

In the Appendix it is shown that this equation has been confirmed by many experiments and that Eq. (20) contradicts them.

The fourth Maxwell relation is:

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T. \quad (28)$$

Consider its traditional derivation [18]. One introduces dU from Eq. (2) into the differential of Gibbs energy:

$$dG = dU + PdV + VdP - TdS - SdT \quad (29)$$

and obtains:

$$dG = VdP - SdT. \quad (30)$$

From this, Eq. (28) results.

One can see that this derivation is non-strict: dU from Eq. (2) is at a constant pressure and does not equal dU from Eq. (29), which is at a varying pressure. Let us try to derive Eq. (28) more strictly. One introduces a quantity of heat (TdS) into the system at varying volumes and pressures and the Gibbs energy of the system changes:

$$dG = dG_1 + dG_2 \quad (31)$$

where dG_1 is the change in the Gibbs energy at a constant pressure:

$$dG_1 = dU_1 + PdV - TdS_1 - SdT_1 \quad (32)$$

and dG_2 is the change in it at a constant volume:

$$dG_2 = dU_2 + VdP - TdS_2 - SdT_2. \quad (33)$$

Introducing Eq. (14) into Eq. (32), we obtain:

$$dG_1 = -SdT_1. \quad (34)$$

One can note that one can obtain Eq. (20) from Eq. (34), assuming that

$$SdT_1 = -PdV. \quad (35)$$

Introducing Eq. (15) into Eq. (33), we obtain:

$$dG_2 = -SdT_2. \quad (36)$$

We can note that one can obtain Eq. (28) from Eq. (36), assuming that:

$$SdT_2 = VdP. \quad (37)$$

For substances with negative thermal expansion or negative compressibility, it follows from Eqs. (17) and (37) that:

$$SdT_2 = \text{sign}(\alpha\beta)VdP \quad (38)$$

and that the fourth Maxwell relation is:

$$\text{sign}(\alpha\beta) \left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T. \quad (39)$$

3. CONCLUSION

It has been shown that the negative compressibility of substances effects the Maxwell relations. The earlier results of the author indicating that negative thermal expansion also effects these relations have been strongly confirmed. General Maxwell relations have been obtained which take into account the sign of compressibility and thermal expansion: Eqs. (8), (19), (27), and (39). The first and third general Maxwell relations have been supported experimentally. It is shown that their previous versions fail to describe the experiments of a number of authors.

REFERENCES

1. Baughman RH, Fonseca AF. Straining to expand entanglements. *Nat Mater.* 2016;15(1):7–8. DOI: 10.1038/nmat4436
2. Rodney D, Gadot B, Martinez OR, Roscoat SR, Org  as L. Reversible dilatancy in entangled single-wire materials. *Nat Mater.* 2016;15(1):72–8. DOI: 10.1038/nmat4429
3. Rozsa VF, Strobel TA. Triple guest occupancy and negative compressibility in hydrogen-loaded β -hydroquinone clathrate. *J Phys Chem Lett.* 2014;5(11):1880–4. DOI: 10.1021/jz5005895
4. Lakes R, Wojciechowski KW. Negative compressibility, negative Poisson's ratio, and stability. *Phys Status Solidi B.* 2008;245(3):545–51. DOI: 10.1002/pssb.200777708
5. Moore B, Jaglinski T, Stone DS, Lakes RS. On the bulk modulus of open cell foams. *Cell Polym.* 2007;26(1):1–10.
6. Moore B, Jaglinski T, Stone DS, Lakes RS. Negative incremental bulk modulus in foams. *Phil Mag Lett.* 2006;86(10):651–9. DOI: 10.1080/09500830600957340
7. Baughman RH. Avoiding the shrink. *Nature.* 2003;425(6959):667. DOI: 10.1038/425667a
8. Baughman RH, Stafstr  m S, Cui C, Dantas SO. Materials with negative compressibilities in one or more dimensions. *Science.* 1998;279(5356):1522–4.
9. Kornblatt JA. Materials with negative compressibilities. *Science.* 1998;281(5374):143a.
10. Stepanov IA. The isochoric heat capacity of ZrW_2O_8 and $Sc_2W_3O_{12}$ is greater than their isobaric

- one. Mater Lett. 2016;177:112–5.
DOI: j.matlet.2016.04.153
11. Stepanov IA. Compression of substances with negative thermal expansion. Mater Lett. 2015;161:365–7.
DOI: j.matlet.2015.08.150
12. Stepanov IA. Anomalous dependence of the heat capacity of supercooled water on pressure and temperature. Results Phys. 2014;4:28–30. (Free online).
DOI: 10.1016/j.rinp.2014.02.003
13. Stepanov IA. The first law of thermodynamics for auxetic materials. J Non-Cryst Solids. 2013;367:51–2.
DOI: 10.1016/j.jnoncrysol.2013.02.017
14. Stepanov IA. Thermodynamics of substances with negative thermal expansion and negative compressibility. J Non-Cryst Solids. 2010;356(23–24):1168–72.
DOI: 10.1016/j.jnoncrysol.2010.03.013
15. Stepanov IA. The first law of thermodynamics for materials with negative thermal expansion. Mater Res Innov. 2008;12(1):28–9.
DOI: 10.1179/143307508X270794
16. Stepanov IA. Thermodynamics of iodine under high pressure at low temperatures. Physica B. 2004;349(1–4):251–3.
DOI: 10.1016/j.physb.2004.03.177
17. Karapetyants MKh. Himicheskaja termodinamika. Moscow: Vysshaja Shkola; 1974, pp. 108–110. Karapetyants MKh. Chemical thermodynamics. (Translated by Leib G.). Moscow: Mir; 1978.
18. Daniels F, Alberty RA. Physical chemistry. 4th ed. New York: John Wiley and Sons, Inc; 1975.
19. Stepanov IA. The second Maxwell relation must have a different sign. Phys Chemistry: An Indian J. 2015;10(6):199–200. (Free online).
20. Guy AG. Crucial experimental verification that the heat capacities C_V and C_P are equal for a perfect gas. Appl Phys Commun. 1984;4(4):259–77.
21. Atkins PW. Physical chemistry. Vol. 1. Oxford: Oxford University Press; 1977.
22. Carroll HB, Eisner M, Henson RM. Rubber band experiment in thermodynamics. Am J Phys. 1963;31(10):808.
23. Roundy D, Rogers M. Exploring the thermodynamics of a rubber band. Am J Phys. 2013;81(1):20–3.
DOI: 10.1119/1.4757908
24. Borgnakke C, Sonntag RE. Fundamentals of thermodynamics. 7th ed. Wiley, 2009; p. 94.

APPENDIX

In [22, 23] and references therein, the tension of a rubber band as a function of temperature and length was measured. The tension τ is proportional to $-P$; hence the first Maxwell relation, Eq. (8), will be expressed as:

$$\left(\frac{\partial T}{\partial V}\right)_S = \text{sign}(\alpha) \left(\frac{\partial \tau}{\partial S}\right)_V. \quad (\text{A1})$$

The sign of the left part must be negative because when one increases the temperature of a system, its entropy increases and for the entropy to remain constant the volume must decrease. The derivative in the right part of Eq. (A1) describes the change in the tension during heating and has the same sign as $(\partial \tau / \partial T)_V$, which was found experimentally to be positive. The rubber band contracts when heated under tension (the Gough–Joule effect) [22, 23]; hence α is negative. One can see that the traditional Maxwell relation, Eq. (1), contradicts the experiment.

The third Maxwell relation, Eq. (27), in this case will have the following form:

$$-\text{sign}(\alpha) \left(\frac{\partial \tau}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T. \quad (\text{A2})$$

The left part of it is positive. Its right part describes the following process: one introduces a quantity of heat into the system ($dS > 0$) and its volume decreases. If one wants to keep the temperature

constant, one has to increase the volume, and hence this derivative is greater than zero. Again, the traditional Maxwell relation, Eq. (20), contradicts the experiment.

Let us introduce a quantity of heat into a substance (Eq. (2)) and let us suppose that it expands. According to the definition of work in thermodynamics, P in Eq. (2) is the internal pressure (produced by the substance) and is positive in our case because it expands the substance [24]. Its absolute value equals the sum of the pressure caused by surface tension and atmospheric pressure, with the latter being negligibly small compared to the former. If the substance possesses negative thermal expansion, then the pressure produced by the substance is negative and Eq. (2) can be rewritten as:

$$\delta Q = dU + (-|P|)(-|dV|) = dU + \text{sign}(\alpha)|P|dV \quad (\text{A3})$$

which coincides with Eq. (3).