E. Grüneisen

Relation between compressibility, thermal expansion, atom volume and atomic heat of the metals

Richards (1907) and his coworkers Stull, Brink and Bonnet have shown through a large number of compressibility measurments using a large number of chemical elements that the compressibility is a periodical function of the atomic weight, similar to atomic volume, [thermal] expansion coefficient and other properties. Since the maximal or minimal values, respectively, of all these periodical properties approximately coincide, the periodicity causes a certain parallelism among them. Richards basically constrained himself to demonstrate this qualitatively, although there are attempts to derive quantitative relations theoretically.

The theoretical concepts are based on the assumption of *monatomic* solid or fluid bodies. Cofirmation of their prediction could thus be used as a criterium for the monatomic nature of such bodies, provided that the other theoretical assumptions are valids. Subsequent to the compressibility measurements (Grüneisen 1907a+b, 1908a+b) I therefore tested the theory on *metals* who are occasionally considered monatomic.

Theoretical relation

To my knowledge, the first attempt to demonstrate a relation between compressibility and other physical properties using a kinetic theory of monatomic bodies was made by Slotte (1893, 1900, 1906). Here I bypass his work since the relation of the temperature coefficient of the compressibility to thermal expansion coefficient is of tantamount importance in his considerations, but it is as yet insufficiently known. Provided that this relation is small near 1, Slottes's relation is going to be similar to that of the kinetic theory of monatomic bodies by Mie (1903, section 11, eqn.37). Here we follow Mie's line of thought in deriving the relation in question in most succinct form, reducing the necessary assumptions to a minimum since some points required for a more comprehensive treatise are not of importance for the purpose of this paper.

Under the assumption that the atoms can be taken as mass points which exert central forces upon one another, the virial law of Clausius (1870) for disorderly heat motion is valid in the original form

$$\sum m\overline{u^2} + \sum \overline{rf(r)} = 3pv \tag{1}$$

where m is the atomic mass, u is its velocity, r is the interatomic distance, $f(r)$ is the force acting between them, p is the external pressure, and v is its volume, taken to be the molar volume.

If 3α is the cubic thermal expansion coefficient, and κ is the isothermal compressibility, the *pressure coefficient*[2] is given by the relation

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{8\alpha}{\kappa}.$$

T is the absolute temperature. By taking the derivative of eqn.1 for T at constant volume we get

$$\frac{3\alpha v}{\kappa} = \frac{1}{3}\frac{\partial}{\partial T}\left\{\sum \overline{mu^2} + \sum \overline{rf(r)}\right\}_v. \tag{2}$$

We have to make certain assumptions if we want to conclude on the temperature dependence of the term in parentheses.

The first assumption which is commonly done is: the average kinetic energy of the molar volume for solids, as for gases, is proportional to the absolute temperature, hence

$$\sum \frac{1}{2}\overline{mu^2} = \frac{3}{2}RT, \tag{3}$$

where R is the gas constant $(8{,}3{\cdot}10^7)$.

In the second assumption we follow Mie: let the interatomic forces be comprised of an attractive part $-f_1(r)$ and a repulsive part $+f_2(r)$. We know from the behavior of elastic solids that the the repulsive part decreases much faster with distance than the attractive part. Thus it is assumed that, regarding the attractive forces, both the virial $-\sum \overline{rf_1(r)}$ and the respective part of the molar internal potential energy U_1 will not change significantly with temperature at constant volume. Hence we assume

$$\frac{\partial}{\partial T}\left(\sum \overline{rf_1(r)}\right)_v = 0, \quad \left(\frac{\partial U_1}{\partial T}\right)_v = 0 \tag{4}$$

The third assumption is the most deliberate one: the repulsive interatomic force is to have a potential of the form[3]

$$\Phi_2(r) = \frac{\alpha}{r^\beta},$$

so

$$f_2(r) = -\frac{\partial}{\partial r}\Phi_2(r) = \frac{\beta}{r}\Phi_2(r),$$

hence the virial of the repulsive forces is

$$\sum \overline{rf_2(r)} = \beta\sum \Phi_2(r) = \beta U_2, \tag{5}$$

where U_2 is that part of the internal potential energy of the molar volume which relates to the repulsive effect between the atoms.

The temperature dependence of U_2 can now be easily found. For the entire energetic content of the molar volume at temperature T and negligible external pressure we get, possibly excepting an additive constant,

$$\int_0^T C_P dT = \sum \frac{1}{2}\overline{mu^2} - U_1 + U_2$$

---

[3] [Instead of β, Grüneisen took v; but this is too similar to a lower case italic v in the font used here. v stands for volume.]

where C_P is the atomic heat at constant pressure. If the temperature is changed *at constant volume*, the energetic content on the LHS will be changed by $C_v dT$ whereas U_1 is constant (eqn.4). If the above equation is differentiated for T at constant volume, and considering eqn.3, we get

$$C_v = \frac{3}{2}R + \left(\frac{\partial U_2}{\partial T}\right)_v,$$

thus after eqn.5

$$\frac{\partial}{\partial T}\left(\sum \overline{rf_2(r)}\right)_v = \beta\left[C_v - \frac{3}{2}R\right]. \tag{6}$$

Finally, from eqns.2, 4 and 6, and considering eqn.3 there follows

$$\frac{3\alpha v}{\kappa} = R + \beta\left[\frac{1}{3}C_v - \frac{1}{2}R\right]. \tag{7}$$

Apart from the gas constant R and the unknown exponent β there are only terms in this equation that can be measured. For metals it will be found that $3\alpha v/\kappa$ is much larger than R, hence the magnitude of the exponent β in the potential of the repulsive force is quite significant.

Assuming that the distance law of repulsion for the atoms of all elements is the same (cf. Mie), hence that it is an universal constant, eqn.7 states that *the product of pressure coefficient and atomic volume of monatomic bodies is a linear function of the atomic heat.*

Mie introduced the Dulong-Petit law in the form

$$C_v = 3R$$

which was already found theoretically by Boltzmann (1871). Thus from eqn.7 follows

$$\frac{3\alpha v}{\kappa} = \frac{\beta+2}{2}R. \tag{8}$$

This relation between compressibility, thermal expansivity and atomic volume (resp. number of atoms) is indeed very simple and can be expressed as follows: *The pressure coefficient of monatomic solids and fluids is a definite multiple of the number of atoms in the volume unit.*

The change of temperature upon adiabatic compression is given by

$$\frac{dT}{T} = \frac{dv}{v}\left(\frac{3\alpha v}{\kappa C_v}\right).$$

Considering the constant value of C_v, Mie's relation eqn.8 permits the conclusion that *all monatomic solids and fluids undergo similar temperature change upon similar adiabatic compression.*

Check of the theoretical relation

Since metals indeed have almost the same atomic heat (=3 R) at common temperature, eqn.8 would suggest that the terms $3\alpha v/\kappa$ and $3\alpha v/\kappa C_v$ are approximately constant. In Table 1 (column 6 and 7) both terms have been calculated for as many metals as possible; however, instead of C_v, C_p was used because it can be experimentally found, and the difference is very small (cf. Table 2).

For ease of comparison the numerical values are given that were used in the calculation. For the compressibility κ I used either the data by Richards (1907) and his coworkers or the data found by myself; to Richard's data a probably correction of $+0{,}2{\cdot}10^{-12}$ was applied.[4] Clearly, given the uncertainty of the experimental data, or of the thermal expansivity of some metals, the expectations for the correlation of theoretical prediction and experimental data should be low. An uncertainty of 10% in the numbers of column 6 and 7 is easily possible.

Table 1

	1	2	3	4	5	6	7
	atomic weight A	atomic volume v	thermal expansion coefficient $3\alpha{\cdot}10^6$	compress-ibility $\kappa{\cdot}10^{12}$ (CGS)	atomic heat $C_{p}{\cdot}10^{-7}$ (CGS)	$\dfrac{3\alpha v}{\kappa}{\cdot}10^{-8}$ (CGS)	$\dfrac{3\alpha v}{\kappa C_p}$
Na	23,0	23,5	210	15,6	29	3,2	1,1
Mg	24,4	14,4	76	2,9	23,9	3,8	1,6
Al	27,1	10,0	72	1,4	24,4	5,0	2,1
K	39,1	45	250	32	26,1	3,5	1,3
Fe	55,9	7,2	33	0,61	25,1	3,9	1,6
Ni	58,7	6,6	37	0,57	26,4	4,3	1,6
Cu	63,6	7,1	48	0,75	24,2	4,5	1,9
Zn	65,4	9,2	78	(1,7)	24,9	(4,2)	(1,7)
Pa	106	8,9	35	0,57	25,4	5,5	2,2
Ag	108	10,3	55	0,98	24,8	5,8	2,3
Cd	112	13,0	86	2,1	25,8	5,3	2,1
Sn	119	16,3	64	1,9	26,2	5,5	2,1
Sb	120	17,9	29	2,4	24,0	2,2	0,9
Pt	195	9,1	27	0,40	26,1	6,1	2,4
Au	197	10,3	41	0,64	25,6	6,6	2,6
Hg	200	14,7	181	3,9	28,0	6,8	2,4
Tl	204	17,2	84	2,8	27,3	5,2	1,9
Pb	207	18,3	82	2,4	26,7	6,2	2,3
Bi	208	21,2	38	3,0	25,4	2,7	1,1

All data valid for ca.18°C

It turns out that the variability of the numbers go way beyond that margin, thus it can be said with certainty that Mie's relation is not strictly valid for all metals. Still, a certain success cannot be denied. The term $3\alpha v/\kappa$ shows *low* variability, compared with 3α, v and κ, especially if Antimony and Bismut are excluded; their behavior differs strongly of that of other metals. Also, a certain systematic pattern in the deviations from Mie's relation since the product of pressure coefficient and atomic volume at first increases faster with the atomic weight, then slower. Thus the metals with an atomic weight above 100 – excepting Sb and Bi – can be approximated relatively successfully by

$$\frac{3\alpha v}{\kappa} = 5{,}9{\cdot}108 \ [\text{cm}^2 \text{ g sec}^{-2}], \text{ or } \frac{3\alpha v}{\kappa C_v} = 2{,}3.$$

---

[4] Cf. Grüneisen (1908a). The attempted justification of the correction was based on an erroneous assumption on my part. Richards did eliminate the lengthening of the tube which probably occurred due to pressure increase in the apparatus. Still, his data may contain a constant additive observation error, which indeed Richards himself considers to be possible (Richards 1907, p.181, 194, 195). – For the soft metals Cd, Sn, Pb, Bi I took the corrected data of Richards, for Ni I preferred my own; in all other cases I took the mean if data were available from both of us.

The fluid Hg is no exception. Thus it might be possible to calculate the compressibilities of other metals.

Take Iridium as an example. Its thermal expansion coefficient was found by Benoit[5] to be $3\alpha = 19\cdot10^{-6}$, and its atomic heat at 18°C was found to be $25,5\cdot10^{7}$ [CGS]; the number was kindly provided by Jaeger and Diesselhorst. The atomic volume is $v = 8,6$. These numbers plugged into the two mentioned equations yields

$$\kappa = 0{,}28\cdot10^{-12} \text{ [CGS]}.$$

Thus Iridium would be the least compressilbe one of all metals so far. The value κ given here and the value $E = 51{,}5\cdot10^{11}$ [CGS] observed by myself before would correlate, according to the formula

$$\kappa = \frac{3(1-2\mu)}{E},$$

with the number

$$\mu = 0{,}26.$$

Thus it appears that a strong hardness is correlated with a small μ (Grüneisen 1908a)[6]. After all, Iridium is the hardest of all metals listed here (Grüneisen 1907a).

In the context of measuring of μ I had called attention on a relation according to which μ usually is the larger the smaller the term $\alpha E_a/c_p s$ is found to be. Here, E_a indicates the adiabatic elastic modulus, c_p the specific heat of the mass unit, and s the density. This relation is evidently assured by the observation that the term

$$\frac{2\alpha v}{\kappa C_v} \equiv \frac{\alpha E_a}{c_p\, s\,(1-2\mu)}$$

is constant, thus it is merely a somewhat more general relation as that of Mie.

Meyer (1884) and Richarz (1893) have shown that the change of the specific heat as a function of temperature, and thus the deviations from the Dulong-Petit law which are so notable at lower temperatures, vary with the atomic weight and volume. Thus the similarities in the validities of this law and Mie's relation appear to be related. This is best demonstrated by comparing the values for the mean atomic heat between –186° and –79° (Behn 1989, 1900) with those of column 6 in Table 1. Their patterns are in part identical. However, without a theoretical basis it would be meaningless to use this observation for the development of an empirical extension of Mie's relation.

Why isn't Mie's relation strictly valid for metals? Two answers are possible. Either the metals are not monatomic, or the other assumptions in the theory are too restricted. Provisionally I tend towards the second answer. Especially the assumption of a potential for the repulsive forces of the form $\Phi(r) = a/r^{\beta}$ appears to deserve little confidence. The value for metals with high atomic weight is $3\alpha v/\kappa = 5{,}9\cdot10^{8}$ and would require a β of ca.12.

The data for antimony and bismut deviate completely. I tend to take that as an indication of a very different molecular structure.

---

[5] [No reference given]
[6] The statement must not be reversed. A small μ may occur in soft metals.

Relation of the specific heats C_p:C_v

Above the insignificant difference of C_p to C_v was mentioned. In Table 2 below the values of C_p:C_v were calculated using the well-known thermodynamic equation

$$\frac{C_p}{C_v} = 1 + 3\alpha T\left(\frac{3\alpha v}{\kappa C_v}\right)$$

for 18°C where the expression in parentheses was taken from Table 1, column 7, thereby ignoring the difference of C_p and C_v. The values are nearly constant from material to material, and the temperature dependence is small[7]; it follows that *the ratio of the two specific heats of most metals is mainly determined by the product of the absolute temperature and the thermal expansion coefficient at that temperature*. The same holds for the ratio of isothermal to adiabatic compressibility which is $\kappa_i/\kappa_a = C_p/C_v$.

Table 2: Ratio of specific heats C_p:C_v at 18°C

Na	1,06$_7$	Ag	1,03$_7$
Mg	1,03$_5$	Cd	105$_2$
Al	1,04$_4$	Sn	1,03$_9$
K	1,08$_7$	Sb	1,00$_8$
Fe	1,01$_4$	Pt	1,01$_9$
Ni	1,01$_7$	Au	1,03$_1$
Cu	1,02$_6$	Tl	1,04$_6$
Zn	1,03$_9$	Pb	1,05$_5$
Pa	1,02$_1$	Bi	1,01$_2$

Finally, I would like to comment on the *non-metallic* elements; Richards has explored some of them. I pick two very different ones: Silicium and liquid Chlor; their compressibilities have the ratio 1:20 (corrections necessary for Richards' data are applied). If $3\alpha v/\kappa$ is calculated[8], the result for Si is $7\cdot10^8$, $5\cdot10^8$ for Cl, whereas for the metals with higher atomic weight we arrived at a mean value of $5,9\cdot10^8$. *Thus there exists the interesting fact that the pressure coefficient for a number of non-metallic elements is approximately the same multiple of the atomic number/cm^3 is as was observed for metals.*

Charlottenburg, April 1908. (Submitted 5 May 1908)

---

[7] α/C_v increases only moderately with temperature (cf. Anonymous 1908), the same must be concluded for κ from the experiments so far; v is inversely proportional to the density, so it increases only very little.
[8] The thermal expansion coefficient of Silicium was determined by Fizeau, that of Chlor by Knietsch. See Landolt-Börnsteins Tabellen, 3rd edition, p.198, 1905.

References

Anonymous (1908) Annalen der Physik **26**, 211
Behn U (1898) Wiedemanns Annalen **66**, 237
Behn U (1900) Annalen der Physik **1**, 257
Boltzmann L (1871) Wiener Sitzungsberichte **63**, 731
Clausius R (1870) Poggendorffs Annalen **141**, 125
Grüneisen E (1907a) Annalen der Physik **22**, 801
Grüneisen E (1907b) Zeitschrift für Instrumentenkunde 27, 38
Grüneisen E (1908a) Annalen der Physik **25**, 825
Grüneisen E (1908b) Zeitschrift für Instrumentenkunde **28**, 89
Meyer L (1884) Moderne Theorien, p.167
Mie G (1903) Annalen der Physik **11**, 657
Richards TW (1907) Zeitschrift für physikalische Chemie **61**, 77.171.183
Richarz F (1893) Wiedemanns Annalen **48**, 708
Slotte KF (1893) Öfversight af Finska Vet.-Soc. Förh. **35**, 16
Slotte KF (1900) Acta Soc. Scient. Fennicae **26**, No.5
Slotte KF (1906) Öfversight af Finska Vet.-Soc. Förh. **48**, No.8