Richards (1907) and his coworkers Stull, Brink and Bonnet have shown through a large number of compressibility measurements 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. Confirmation 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

\[ \sum m u^2 + \sum r f(r) = 3 p v \]

(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 \( 3\alpha \) is the cubic thermal expansion coefficient, and \( \kappa \) is the isothermal compressibility, the *pressure coefficient*\(^2\) is given by the relation

\[ \]
\[
\frac{\partial p}{\partial T} = \frac{8\alpha}{\kappa}.
\]

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

\[
\frac{3\alpha v}{\kappa} = \frac{1}{3} \frac{\partial}{\partial T} \left\{ \sum \overline{mu^2} + \sum f(r) \right\}.
\]

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

\[
\sum \frac{1}{2} mu^2 = \frac{3}{2} RT,
\]

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 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

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

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

\[
\sum \overline{rf_2}(r) = \beta \sum \overline{\Phi_2(r)} = \beta U_2,
\]

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 \(\beta\), Grüneisen took \(\nu\); 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

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

thus after eqn.5

$$\frac{\partial}{\partial T} \left( \sum r f_2(r) \right)_v = \beta \left[ C_v - \frac{3}{2} R \right]. \tag{6}$$

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 $\beta$ 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 $\beta$ 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

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

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 $\kappa$ 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. 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.

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<td>atomic heat $C_p \cdot \frac{10^6}{\kappa}$ (CGS)</td>
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</table>

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 $\frac{3\alpha v}{\kappa}$ shows low variability, compared with $3\alpha$, $v$ and $\kappa$, especially if Antimony and Bismuth 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

$$\frac{3\alpha v}{\kappa} = 5.9 \cdot 10^{18} \text{ [cm}^2 \text{ g sec}^{-2}], \text{ or } \frac{3\alpha v}{\kappa C_v} = 2.3.$$ 

---

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 \(3\alpha = 19 \cdot 10^{-6}\), and its atomic heat at 18°C was found to be 25.5\(\cdot\)10\(^7\) [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

\[
\kappa = 0.28 \cdot 10^{-12} \text{[CGS]}. 
\]

Thus Iridium would be the least compressible one of all metals so far. The value \(\kappa\) given here and the value \(E = 51.5 \cdot 10^{11}\) [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 \(\mu\) (Grüneisen 1908a)\(^6\). After all, Iridium is the hardest of all metals listed here (Grüneisen 1907a).

In the context of measuring of \(\mu\) I had called attention on a relation according to which \(\mu\) 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

\[
\frac{2\alpha v}{\kappa c_p s} \equiv \frac{\alpha E_a}{c_p s (1-2\mu)}
\]

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 \(3\alpha v/\kappa = 5.9 \cdot 10^8\) and would require a \(\beta\) 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 \(\mu\) 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 $\kappa/\kappa_a = C_p/C_v$.

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

<p>| | | | |</p>
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<tr>
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<td>Bi</td>
<td>1.012</td>
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</table>

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 $7 \times 10^8$, $5 \times 10^8$ for Cl, whereas for the metals with higher atomic weight we arrived at a mean value of $5.9 \times 10^8$. 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$^3$ as was observed for metals.

Charlottenburg, April 1908. (Submitted 5 May 1908)

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$^7$ $\alpha/C_v$ increases only moderately with temperature (cf. Anonymous 1908), the same must be concluded for $\kappa$ from the experiments so far; $\nu$ 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) Öfversigt af Finska Vet.-Soc. Förh. 35, 16
Slotte KF (1900) Acta Soc. Scient. Fennicae 26, No.5
Slotte KF (1906) Öfversigt af Finska Vet.-Soc. Förh. 48, No.8