THE SPECIFIC HEAT OF SOLIDS AND THE PRINCIPLE OF SIMILITUDE.

By Richard Chace Tolman.

The writer has already presented\(^1\) a number of derivations in widely different fields of physical science, all of which are based on a single postulate which may be called the principle of similitude. In the present article we shall make use of this same principle in deriving a formula for the specific heat of homogeneous, isotropic, elastic substances.

We shall find that the formula thus obtained for specific heat agrees with that of Debye\(^2\) for the specific heat of solids and liquids at low temperatures. In our proof, however, it will not be necessary to make use of any of the various forms of quantum theory. In particular, the derivation of Debye rests on the special assumption borrowed from the quantum theory of Planck that

\[
E_r = \frac{h\nu}{e^{h\nu/kT} - 1} \, d\nu
\]

is the energy in an elastic sphere at temperature \(T\) associated with modes of vibration whose frequencies lie between \(\nu\) and \(\nu + d\nu\). In our derivation, however, we shall make no assumptions as to the form of the relation connecting energy with temperature and frequency of vibration.

This possibility of deriving a satisfactory formula for the specific heat of solids and liquids without the special assumptions of the quantum theory is of particular interest at the present time, since in spite of brilliant justification from the experimental standpoint, the theoretical foundation of the quantum theory must still be regarded as a field where further research is necessary.

It is also interesting to point out that the derivation of the Debye formula which we shall present will necessitate no new investigations in the field of elasticity theory, but will merely make use of the well-known expressions for the velocity of wave motions in elastic solids.

PART I. THE PRINCIPLE OF SIMILITUDE.

The principle of similitude may be stated as follows:—The fundamental entities of which the physical universe is constructed are of such a nature

\(^1\) Tolman, Phys. Rev., 3, 244 (1914).

that from them a miniature universe could be constructed exactly similar in
every respect to the present universe. For a discussion of this new postulate
we must refer the reader to the article already mentioned, and shall here
confine ourselves merely to a recapitulation of those deductions from
the principle which are necessary for our immediate purpose.

Let us consider two observers, $O$ and $O'$, provided with instruments
for making physical measurements. $O$ is provided with ordinary meter
sticks, clocks and other measuring apparatus of the kind and size which
we now possess, so that he can duplicate all our measurements in the
present physical universe. $O'$, on the other hand, is provided with a
shorter meter stick, and correspondingly altered clocks and other appar-
atus so that he can make measurements in the miniature universe of which
we have spoken and in accordance with our postulate obtain exactly
the same numerical results in all his experiments as does $O$ in the analogous
measurements made in the real universe.

If now $O$ and $O'$, instead of each remaining in his own universe, should
both make measurements of the same physical objects and occurrences,
it is evident that they would not obtain the same results, since their
units of measurement are different. Let us suppose that $O$ and $O'$ both
measure the same length, then if $O$'s meter stick is $x$ times as long as that
of $O'$, it is evident that their measurements of the given length would be
connected by the equation $l' = xl$.

In the article already referred to it was found possible to obtain a
whole series of transformation equations of the type $l' = xl$, connecting
the measurements made by $O$ and $O'$ of given lengths, time, intervals,
masses, forces, charges, etc. These relations were derived by combining
with the postulate of similitude, certain principles taken from the Einstein
theory of the relativity of motion and from the electron theory. We
shall now present for future reference a table of such transformation

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<td>For energy ....................................... $E' = E/x$ ....................................................... (13)</td>
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For energy density \( u' = u/x^4 \)  \hspace{1cm} (14)
For absolute temperature \( T' = T/x \) \hspace{1cm} (15)
For the coefficient of compressibility \( \chi' = \chi x^2 \) \hspace{1cm} (16)
For Poisson's Ratio \( \sigma' = \sigma \) \hspace{1cm} (17)

Of these transformation equations the only ones not already derived in the article referred to are those for the coefficient of compressibility and for Poisson's ratio. The coefficient of compressibility may be defined by the equation

\[ \chi = \frac{1}{V} \frac{dV}{dP} \]

while Poisson's ratio, \( \sigma \), is that between the longitudinal and transverse strain of an elastic substance. The derivation of the transformation equations for these two quantities is obviously merely a matter of substituting equations already given above.

PART II. APPLICATION OF THE PRINCIPLE OF SIMILITUDE TO DETERMINE THE FORM OF THE FUNCTION.

The general method of applying the principle of similitude to determine the form of functional relations connecting physical magnitudes is to consider some construct which could exist either in the actual universe or in the miniature universe which to observer \( O' \) appears the same as the actual universe. It is evident from the principle of similitude that the properties of a construct which has the same general character in both universes will have to obey the same general laws, whether measured by observer \( O \) or by observer \( O' \), while a further condition will be imposed upon the magnitude of these measurable properties by the transformation equations which we have just developed. These two sets of conditions will permit the attainment of definite information as to the necessary form of the functional relation connecting the measurements of different properties of the construct.

In the article already mentioned this method was used for deriving the law of Charles for an ideal gas, for showing that the specific heat of such an ideal gas would be independent of the temperature, for deriving Stefan's law for the energy density of a hohlraum, for obtaining a relation between energy density and frequency in a hohlraum, and for deriving various relations in the fields of electromagnetic and gravitational theory. We may now apply the method to obtain information as to the form of the functional relation connecting the energy density of an elastic substance with its temperature and elastic constants.

In the first place it is evident that a given homogeneous, isotropic, elastic substance is a construct which would appear to be homogeneous, isotropic and elastic both to observer \( O \) and to observer \( O' \), and hence by the principle of similitude experiments made on it by either observer would have to lead to the same general laws. It is also evident that the energy density \( u \), of such a substance will be completely determined by
its temperature $T$ and the three constants—density $\rho$, compressibility $\chi$, and Poisson's ratio $\sigma$—which completely determine its elastic properties.\(^1\) Suppose now the measurements of $O$ have led to the following relation, between the energy density and the elastic properties and temperature of the substance,

$$u = F(\rho, \chi, \sigma, T)$$  \(18\)

then by the principle of similitude the measurements of $O'$ will have to lead to a similar relation,

$$u' = F(\rho', \chi', \sigma', T')$$  \(19\)

where $F$ must have the same form as in the previous equation.

We have, however, already found transformation equations, Nos. (14), (15), (16), and (17), connecting the measurements of energy density, temperature and elastic constants made by $O'$ with those made by $O$. Substituting in equation (19) we have

$$\frac{u}{x^i} = F\left(\frac{\rho}{x^i}, \frac{x^i\chi}{x}, \frac{\sigma}{x}, \frac{T}{x}\right)$$

or solving for $u$ and combining with (18) we obtain,

$$u = x^i F\left(\frac{\rho}{x^i}, x^i\chi, \frac{\sigma}{x}, \frac{T}{x}\right) = F(\rho, \chi, \sigma, T)$$  \(20\)

Since the total energy of an elastic body will be proportional to its volume we may write,

$$E = Vx^i F\left(\frac{\rho}{x^i}, x^i\chi, \frac{\sigma}{x}, \frac{T}{x}\right) = VF(\rho, \chi, \sigma, T)$$  \(21\)

Since $x$ may be any number we have thus obtained from the principle of similitude an equation which imposes very definite conditions on the form of the functional relation connecting the energy content of an elastic body with its temperature and elastic properties.

By considering some familiar results of the theory of elasticity we may complete the solution of our problem.

**PART III. APPLICATION OF ELASTICITY THEORY.**

In the previous section we have derived from the principle of similitude a functional equation, No. 21, which presents certain necessary relations between the energy content of an elastic body and its volume, elastic constants, and temperature. Let us now see what conclusions we can draw from the *theory of elasticity* as to the energy content of an elastic body.

\(^1\) We shall assume a substance in which the elastic properties are independent of the temperature.
Let us consider an elastic body of some definite shape and size, fixed at its outer surface. At a given temperature such a body will contain a certain amount of energy and we may think of this energy as due to the presence of systems of standing waves which undergo continual reflection at the fixed boundary. These waves may either transverse or longitudinal. In the former case the theory of elasticity has shown that their velocity will be $\sqrt{\frac{\mu}{\rho}}$ and in the latter case $\sqrt{\frac{(\lambda + 2\mu)}{\rho}}$, where $\rho$ is the density of the material and $\mu$ and $\lambda$ its elastic constants. These constants are connected with the measurable quantities compressibility, $\chi$, and Poisson’s ratio, $\sigma$, by the equations

$$\mu = \frac{1}{\chi} \frac{3(1 - 2\sigma)}{2(1 + \sigma)}$$

and

$$\lambda = \frac{1}{\chi} \frac{3\sigma}{1 + \sigma}.$$  \hfill (22)

If now we should change the dimensions of the body or its elastic properties, it is evident that we should also change the frequency of the standing waves which it contains at thermal equilibrium.

If we consider changes in the volume of the body without alteration of shape, it is evident that the linear dimensions of the body will always be proportional to the cube root of the volume, $V^{\frac{1}{3}}$. Hence the wave lengths of the different standing waves which the body contains will be proportional to the cube root of the volume or their frequencies to its reciprocal.

On the other hand, if we change the elastic properties of the body we should also change the frequencies of the different standing waves since we change the velocity of propagation. For transverse waves the frequencies will be proportional to the velocity of transverse waves, $\sqrt{\frac{\mu}{\rho}}$; and similarly for longitudinal waves the frequencies will be proportional to $\sqrt{\frac{(\lambda + 2\mu)}{\rho}}$.

Hence we may write for the frequencies of the different standing waves which a body of given shape will contain

$$\nu_1 = \frac{a_1}{V^{\frac{1}{3}}} \sqrt{\frac{\mu}{\rho}}, \ \nu_2 = \frac{a_2}{V^{\frac{1}{3}}} \sqrt{\frac{\mu}{\rho}}, \ \nu_3 = \frac{a_3}{V^{\frac{1}{3}}} \sqrt{\frac{\mu}{\rho}}, \text{ etc.,}$$

$$\nu_1' = \frac{a_1'}{V^{\frac{1}{3}}} \sqrt{\frac{\lambda + 2\mu}{\rho}}, \ \nu_2' = \frac{a_2'}{V^{\frac{1}{3}}} \sqrt{\frac{\lambda + 2\mu}{\rho}}, \ \nu_3' = \frac{a_3'}{V^{\frac{1}{3}}} \sqrt{\frac{\lambda + 2\mu}{\rho}} \text{ etc.,} \hfill (24)$$

where $\nu_1, \nu_2, \nu_3$, etc., are the frequencies of the various transverse, and $\nu_1', \nu_2', \nu_3'$, etc., are the frequencies of the various longitudinal standing waves. $a_1, a_2, a_3$, etc., and $a_1', a_2', a_3'$, etc., are constants which depend
on the shape of the body but are independent of its volume or elastic properties.

Now let us assume that at thermal equilibrium the average energy associated with each loop of a standing wave is determined merely by its frequency and the temperature. Then in the case of our elastic body we may write for the energy associated with a standing wave of frequency \( \nu \),

\[
E_{\nu} = nF'(\nu, T)
\]

where \( n \) is the number of loops in the standing wave under consideration, and \( F' \) is the unknown functional relation connecting energy with frequency and temperature.

For the total energy of the body we may write

\[
E = \Sigma E_{\nu} = \Sigma nF'(\nu, T)
\]

where the summation \( \Sigma \) is to include all the different waves in the body.

We have already seen, however (equation 24), that the frequencies of the different waves are determined by equations either of the form

\[
\nu = \frac{a}{\sqrt{\nu/a}} \sqrt{\frac{\mu}{\rho}}
\]

or

\[
\nu = \frac{a'}{\sqrt{\nu/a}} \sqrt{\frac{\lambda + 2\mu}{\rho}},
\]

where \( a \) and \( a' \) are constants depending on the shape of the body. Hence we may write for the total energy of the body

\[
E = \Sigma E_{\nu} = \Sigma nF'(\nu, T) = \Sigma nF'\left( \left[ \frac{a}{\sqrt{\nu/a}} \sqrt{\frac{\mu}{\rho}} \right], T \right) + \Sigma' n'F'\left( \left[ \frac{a'}{\sqrt{\nu/a}} \sqrt{\frac{\lambda + 2\mu}{\rho}} \right], T \right), \quad (25)
\]

where the summation \( \Sigma \) includes all the transverse waves and \( \Sigma' \) includes all the longitudinal waves. In this equation \( n, n', a \) and \( a' \) are constants independent of the volume or elastic properties of the body.

Let us now transform this equation by substituting for \( \mu \) and \( \lambda \) their values in terms of compressibility and Poisson’s ratio as given in equations (22) and (23). We shall obtain

\[
E = \Sigma E_{\nu} = \Sigma nF'(\nu, T) = \Sigma nF'\left( \left[ \frac{a}{\sqrt{\nu/a}} \left( \frac{1}{\rho_X} \frac{3(1 - 2\sigma)}{2(1 + \sigma)} \right)^{1/2} \right], T \right) + \Sigma' n'F'\left( \left[ \frac{a'}{\sqrt{\nu/a}} \left( \frac{1}{\rho_X} \frac{3(1 - \sigma)}{1 + \sigma} \right)^{1/2} \right], T \right). \quad (26)
\]

We thus have obtained from the theory of elasticity a functional relation.
between the energy of an elastic body, and its volume, density, elastic constants \( \chi \) and \( \sigma \), and its temperature.

We have already obtained, however, from the principle of similitude another functional relation, equation 21, between these same quantities. This equation was

\[
E = Vx^4F\left(\frac{\rho}{x^4}, \frac{x^4\chi}{x}, \frac{T}{x}\right) = VF(\rho, \chi, \sigma, T).
\]

By comparing these two expressions we see since the \( x \)'s must cancel and since volume must enter to the first power, that \( F'(\rho, \chi, T) \), which occurs in equation (26) must be of the form,\(^1\)

\[
E_x = k \frac{T^3}{\rho^b} = k \frac{T^3}{x^b},
\]

where \( k \) is some constant.

The total energy of the body will then be given by the equation

\[
E = A V \rho^{b/2} \chi^{3/2} \left\{ B \left( \frac{2(1 + \sigma)}{3(1 - 2\sigma)} \right)^{3/2} + \left( \frac{1 + \sigma}{3(1 - \sigma)} \right)^{3/2} \right\} T^3,
\]

or differentiating with respect to \( T \) we obtain for the heat capacity of any elastic isotropic body,

\[
C = 4A V \rho^{b/2} \chi^{3/2} \left\{ B \left( \frac{2(1 + \sigma)}{3(1 - 2\sigma)} \right)^{3/2} + \left( \frac{1 + \sigma}{3(1 - \sigma)} \right)^{3/2} \right\} T^3.
\]

\( A \) and \( B \) are numerical constants which are the same for all materials and their values may be determined once for all by measurements on two substances.

We have thus derived from the principle of similitude and the theory of elasticity not only the important fact that the heat capacity of an elastic substance is proportional to the third power of the temperature but also the complete form of the equation connecting heat capacity with temperature and elastic properties.

**PART IV. COMPARISON WITH THE EQUATION OF DEBYE.**

It can be shown that the above equation agrees with the form taken at low temperatures by Debye's equation for the specific heat of monatomic elastic substances. Debye's equation No. 13\(^2\) reads

\[
\frac{C}{C_\infty} = 77.938(T^3/\theta^3).
\]

Substituting for \( \theta \) the value given by Debye's equations (7), (3\(^1\)) and (2), and for \( C_\infty \) the value \( 3Nk \), we may rewrite his formula in the form

\[
C = \frac{326}{h^3} k^4 V \rho^{b/2} \chi^{3/2} \left\{ 2 \left( \frac{2(1 + \sigma)}{3(1 - 2\sigma)} \right)^{3/2} + \left( \frac{1 + \sigma}{3(1 - \sigma)} \right)^{3/2} \right\} T^3,
\]

which agrees in form completely with our equation No. 29.

\(^1\) Since \( \rho \) and \( \chi \) occur to the same power, \( T \) has to enter to the fourth power in order that the \( x \)'s cancel.

\(^2\) Loc. cit.
The undetermined factor $B$ which occurs in our equation is seen to have the numerical value 2 in Debye's formula. From our derivation it is evident that $B$ is the ratio of the total energy associated with transverse waves to that associated with longitudinal waves. Our considerations however, were not sufficient for a theoretical determination of the magnitude of this ratio.

The factor $326(k^4/h^2)$ in Debye's formula corresponds with our undetermined numerical factor $4A$. $k$ and $h$ in this factor have the usual significance; $k$ is the so-called gas constant for a single molecule, and $h$ is Planck's Wirkungsquantum.

Debye's calculations have led to a definite numerical value of $A$ since he has made the definite assumption that the energy associated with a mode of vibration of frequency $v$ is

$$\frac{h v}{e^{v/kT} - 1}$$

We, on the other hand, have merely assumed that the energy associated with each loop of a stationary wave is some function of frequency and temperature, and then determined, except for a constant numerical factor, what this function must be (see equation 27).

With regard to the temperature range over which we can expect our formula for specific heat to hold, we can merely say that at low temperatures where the amplitudes of wave motions are small we may expect actual substances to behave like homogeneous media, and hence to obey this formula. For comparison with experimental data we may refer to the article of Debye or to an article by Nernst and Lindemann. We may call attention to the fact that from our derivation we shall expect the same formula to apply to all substances and not merely to monatomic substances as Debye's derivation suggested. As a matter of fact this appears to be true in the case of the measurements of Nernst and Lindemann on potassium and sodium chlorides.

At moderately high temperatures, where there will be a freer motion of the individual atoms, we shall no longer expect that solid bodies will behave like homogeneous media, and hence shall expect increasing deviations from the formula which we have derived. According to Debye,

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1 The possibility that actual substances behave like continua at very low temperatures was first suggested to the writer by Professor G. N. Lewis. This idea also forms the basis of the considerations of Debye and of Born and Karman, Phys. Zeitschrift, 13, p. 297 (1912). In the case of anisotropic substances we might provisionally take an average value of $\tau$.

2 Loc. cit.


4 Loc. cit.
however, we may expect the specific heat to be proportional to the third power of the temperature within one per cent. up to temperatures as high as $T = \theta/12$ where $\theta$ varies for different substances from 72 to 467.\footnote{Loc. cit., pp. 802 and 817.}

At high temperatures we know that the specific heat of solid substances will obey the law of Dulong and Petit (or of Kopp in the case of polyatomic substances). Hence we might devise as Debye has done a formula which would give a smooth connection between the two known ends of the specific heat curve. For the present, however, we cannot see any satisfactory theoretical derivation for this intermediate part of the curve.

\footnotetext{\textit{University of California, Berkeley, Cal., U.S.A.} May 12, 1914.}