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The Thermal Expansion of Solids

J. S. Dugdale* and D. K. C. MacDonald
National Research Council, Ottawa, Canada

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Under appropriate conditions, the thermal expansion of a solid is closely related to the Grüneisen parameter γ. This in turn may be derived from the variation of the characteristic frequency of the lattice with volume. If, however, this variation is calculated from the usual expressions for the velocity of sound in solids at zero pressure, the γ does not agree with that predicted from lattice theory, and an anomalous thermal expansion is predicted for a solid with a purely harmonic atomic potential.

General expressions for the dependence on volume of the velocity of plane waves in one-, two-, and three-dimensional lattices are obtained, and hence the corresponding Grüneisen γ's. The three-dimensional γ differs by a numerical constant from that used by Slater. All three expressions are now consistent when applied to a body with a purely harmonic atomic potential and predict no thermal expansion.

If it is possible to express the specific heat at constant volume of a solid as $f(T/\Theta)$, where Θ is a function only of volume, then, as was shown by Grüneisen, the thermal expansion coefficient α is given by

$$\alpha=\gamma C_V\chi/V, \tag{1}$$

where $\gamma=-d\log\Theta/d\log V$ and χ is the compressibility. This is, in fact, equivalent to assuming that the frequency ν_i of each normal mode of vibration of the solid has the same volume dependence, $\nu\sim 1/V^{\gamma}$.

Although the small vibrations of any lattice may in principle be resolved into its normal modes, such a calculation is in general a cumbersome procedure. In Debye's theory of specific heats these are therefore replaced by the appropriate number of normal modes of a three-dimensional continuum.

For a linear lattice, however, the normal modes and dispersion are well known, and we shall first consider this case. In an infinite linear chain of identical particles of mass m separated by a distance b, in which only nearest neighbor interaction is considered, the velocity of waves of length λ and frequency ν is given by the expression[1]

$$v=\nu\lambda=b\left(\frac{\partial^2u/\partial r^2}{m}\right)^{\frac{1}{2}}\cdot\frac{\sin(\pi b/\lambda)}{\pi b/\lambda},\quad\text{for}\quad\lambda\geqslant 2b, \tag{2}$$

in which the energy of interaction between two particles, u, depends only on their instantaneous mutual separation, r. There is thus a limiting frequency,

$$\nu_m=\frac{1}{\pi}\left(\frac{\partial^2u/\partial r^2}{m}\right)^{\frac{1}{2}}, \tag{3}$$

which may be used to characterize the spectrum of frequencies. If, however, more than nearest neighbor interaction is envisaged, it is no longer possible to represent the spectral behavior by a limiting frequency. From Eq. (3),

$$\gamma=-\frac{d\log\nu_m}{d\log l}=-\frac{l}{2}\frac{\partial u''/\partial l}{u''}, \tag{4}$$

where l is the length of the chain, and we have written u'' for $\partial^2u/\partial r^2$.

For the one-dimensional continuum, moreover, the velocity of longitudinal waves (the only kind of vibration logically possible in one dimension) is

$$v=(E/\rho)^{\frac{1}{2}}, \tag{5}$$

where E is the elastic modulus of the continuum and ρ its mass per unit length. Thus, the frequency corresponding to a wavelength λ is

$$\nu=\lambda^{-1}(E/\rho)^{\frac{1}{2}}, \tag{6}$$

and so

$$\gamma=-\frac{l}{2}\frac{\partial E/\partial l}{E}. \tag{7}$$

This is quite equivalent to Eq. (4) for a linear chain and, in particular, it vanishes if E is strictly constant.

The behavior of a two-dimensional lattice is already too complex to be capable of brief calculation. However, the velocity of propagation of plane waves in, say, a monatomic triangular lattice with nearest neighbor interactions may readily be evaluated for certain particular directions, and the calculation could in principle be extended to any arbitrary direction. The results again indicate that the velocity depends on u'' in the form

$$v=kb\left(\frac{u''}{m}\right)^{\frac{1}{2}}\cdot\frac{\sin\pi b/\lambda}{\pi b/\lambda}, \tag{8}$$

where b is now a lattice parameter dependent on the direction of propagation, and k is a geometrical constant depending on the direction of the wave and its type (i.e., longitudinal or transverse).

This leads directly to a value of γ:

$$\gamma=-\frac{d\log\nu_m}{d\log A}=-\frac{l}{4}\frac{\partial u''/\partial l}{u''}=-\frac{3}{4}-\frac{A}{2}\frac{\partial^2P/\partial A^2}{\partial P/\partial A}\quad(\text{for } P=0), \tag{9}$$

where l is now a linear dimension of the lattice, P is the force/unit length, and A is the area of the lattice.

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* National Research Laboratories Postdoctorate Fellow.

[1] L. Brillouin, *Wave Propagation in Periodic Structures* (McGraw-Hill Book Company, Inc., New York, 1946), Chap. IV.

For the corresponding two-dimensional continuum the formula for the velocity usually quoted in texts is

$$v=\left(\frac{\chi}{\rho(1+\sigma)}\right)^{\frac{1}{2}}, \tag{10}$$

where $\chi=-A\partial P/\partial A$, $\rho=M/A$, and σ is the two-dimensional Poisson's ratio. If this expression is then used to derive γ, one gets

$$\gamma=-\frac{1}{2}-\frac{A}{2}\frac{\partial^2 P/\partial A^2}{\partial P/\partial A}, \tag{11}$$

using the fact that σ (the limiting value of Poisson's ratio for small deformations) in a monatomic lattice does not change with a homogeneous areal change.[2] It will be seen that this does not agree with Eq. (9). Moreover, if the continuum is to correspond to a lattice in which the atoms oscillate purely harmonically [i.e., the atomic potential is the form $u\propto(r-r_0)^2$], then the total internal energy U_0 at absolute zero (Roberts,[3] Slater[4]) must have the form

$$U_0\propto(A^{\frac{1}{2}}-A_0^{\frac{1}{2}})^2;$$

and hence, for $T\rightarrow 0$ from Eq. (11),

$$\gamma=-\tfrac{1}{2}+\tfrac{3}{4}=\tfrac{1}{4}.$$

The predicted thermal expansion thus presents a dilemma, since for a purely harmonic atomic potential no atomic mechanism is present to produce such an expansion.

These difficulties persist in the case of a three-dimensional continuum where (see Slater[5]) a value for the Grüneisen parameter,

$$\gamma=-\frac{2}{3}-\frac{V}{2}\frac{\partial^2 p/\partial V^2}{\partial p/\partial V}, \tag{12}$$

is then predicted, and an ideal harmonic body with

$$U_0\propto(V^{\frac{1}{3}}-V_0^{\frac{1}{3}})^2,$$

would then have

$$\gamma=-\tfrac{2}{3}+1=\tfrac{1}{3}.$$

The error arises from the use of formulas for the vibrational velocity which are in fact only valid when $P=0$, and $p=0$ in the two-dimensional and three-dimensional cases, respectively.

The correct expressions follow at once from the fact that the velocity of "plane" waves in a monatomic lattice of any dimensions with nearest-neighbor interaction is always of the form

$$v\propto l(u''/m)^{\frac{1}{2}},$$

where l is the lattice constant and u the interatomic potential.

Alternatively, by extending elasticity theory to the case of small deformations under a finite applied pressure, it is readily shown that for a three-dimensional solid the instantaneous Young's modulus is related to the bulk modulus by

$$E=3(1-2\sigma)\{V\partial p/\partial V+\tfrac{2}{3}p\}. \tag{13}$$

Either mode of attack then yields

$$v\propto l(-\partial F/\partial l)^{\frac{1}{2}}, \tag{14}$$

$$v\propto A(-\partial P/\partial A-P/2A)^{\frac{1}{2}}, \tag{15}$$

$$v\propto V(-\partial p/\partial V-\tfrac{2}{3}p/V)^{\frac{1}{2}}. \tag{16}$$

These expressions evidently reduce to the conventional formulas for the particular case of zero "pressure." However, when differentiated to yield γ, we now have

$$\gamma=-\frac{l}{2}\frac{\partial^2 F/\partial l^2}{\partial F/\partial l}, \tag{17}$$

$$\gamma=-\frac{3}{4}-\frac{A}{2}\left\{\frac{\partial^2 P/\partial A^2-3P/4A^2}{\partial P/\partial A+P/2A}\right\}, \tag{18}$$

$$\gamma=-1-\frac{V}{2}\left\{\frac{\partial^2 p/\partial V^2-10p/9V^2}{\partial p/\partial V+2p/3V}\right\}, \tag{19}$$

which for zero "pressure" reduce to

$$\gamma=-\frac{l}{2}\frac{\partial^2 F/\partial l^2}{\partial F/\partial l}, \tag{20}$$

$$\gamma=-\frac{3}{4}-\frac{A}{2}\left\{\frac{\partial^2 P/\partial A^2}{\partial P/\partial A}\right\}, \quad \text{(see Eq. (9))} \tag{21}$$

$$\gamma=-1-\frac{V}{2}\left\{\frac{\partial^2 p/\partial V^2}{\partial p/\partial V}\right\}, \tag{22}$$

and for a "body" of n dimensions,

$$\gamma=-\frac{3}{2}\left(\frac{n-1}{n}\right)-\frac{\mathcal{V}}{2}\left\{\frac{\partial^2\mathcal{P}/\partial\mathcal{V}^2}{\partial\mathcal{P}/\partial\mathcal{V}}\right\},$$

where $\mathcal{P}$ and $\mathcal{V}$ are the generalized pressure and volume, respectively. If now these expressions are applied to the case of "bodies" with purely harmonic potentials, γ (and hence the expansion coefficient) is *always* zero, as we should expect.

So long as we consider only equations of state at absolute zero, the derivatives $\partial p/\partial V$ and $\partial^2 p/\partial V^2$ are determined without ambiguity, since then the p, V relationships only involve purely mechanical quantities.

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[2] Indeed, under these conditions, for any given axis in the lattice, the ratio of the differential orthogonal displacements is a purely geometrical constant dependent on the specific lattice type.

[3] J. K. Roberts, *Heat and Thermodynamics* (Blackie and Son, Ltd., London, 1951), pp. 534–5.

[4] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), p. 212.

[5] See reference 4, p. 239.

In general, however, these derivatives must be evaluated under the physical conditions obtaining when a sound wave is propagated through the body. For example, at low enough temperatures a perfect infinite lattice without impurity will have a thermal conductivity tending to infinity. Consequently, the changes which occur during the propagation of a sound wave will be isothermal, and $(\partial p/\partial V)_T$ is the appropriate derivative. At higher temperatures, however (and this will usually include room temperature), the processes will be practically adiabatic so that $(\partial p/\partial V)_S$ should be employed.

At intermediate temperatures the conditions for the first derivative will be neither isothermal nor adiabatic but lie between. Then within the limitations of the theory $\partial p/\partial V$, and hence the wave velocity and Θ, depend only on the volume. Under these circumstances, the second differentiation with respect to volume presents no ambiguity.

Comparing Eq. (22) with Eq. (12), it follows that Slater's values[6] based on experimental $p:V$ data must be diminished by 0.33. This correction then slightly improves the over-all agreement.

This work forms part of a general investigation of the effects of anharmonicity on the thermodynamic properties of simple solids and the electrical resistance of metals.

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[6] See reference 4, pp. 393, 451.

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Multiple Scattering Corrections to the Impulse Approximation in the Two-Body System*

K. A. Brueckner
Indiana University, Bloomington, Indiana

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Exact solutions for the scattering of a fast particle by two heavy scatterers are obtained and compared with the usual treatment of the impulse approximation in which multiple scattering is neglected. It is found that the multiple scattering qualitatively changes the solution except in the extreme Born approximation limit. The methods developed are applied to the isotopic spin dependent, but spin independent, scattering of mesons in the deuteron. It is found that if high energy scattering is assumed to be in the isotopic spin $\frac{3}{2}$ state, a considerable depression in the total cross section can be expected for phase shifts larger than 45 degrees.

I. INTRODUCTION

THE impulse approximation[1-3] has been developed to deal with the scattering of a fast particle by a system of heavy scatterers where the motion of the scattering centers can be neglected during the scattering process. This approximation leads to simplified theoretical evaluations of many processes and has been applied in particular to a variety of phenomena in deuterium.[4] In these applications, it has been argued that multiple scattering effects can be neglected if the free-particle scattering amplitudes are small compared with the deuteron radius. It will be shown, however, that this criterion is incorrect and that the neglect of multiple scattering is valid only in the limit where the Born approximation is valid for the single scattering center, leading otherwise to qualitatively incorrect results. The exact solutions, in the framework of the impulse approximation, will be discussed first for the simple case of S-state scattering and secondly in the case of P-state meson scattering. In the latter case, spin independent but isotopic spin dependent scattering will be considered.

We shall not discuss the validity of the impulse approximation as such, since this has been discussed in detail particularly by Chew and Wick,[2] and by Chew and Goldberger.[3] We shall also not attempt to consider the effects of scatterings which do not conserve energy since, although such processes undoubtedly give corrections to the impulse approximation, they are distinct from the effect we wish to consider here.

The methods developed here will be applied to the evaluation of spin dependent scattering and to photomesonic phenomena in a forthcoming paper.

II. THE IMPULSE APPROXIMATION FOR S-STATE SCATTERING

We shall consider this very simple case to illustrate the consequences of an exact treatment of the impulse approximation. For the case of S-state scattering from

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[1] G. F. Chew, Phys. Rev. **80**, 196 (1950).

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[4] Fernbach, Green, and Watson, Phys. Rev. **82**, 980 (1951); B. Segall, Phys. Rev. **83**, 1247 (1951); W. B. Cheston, Phys. Rev. **85**, 952 (1952); Y. Fujimoto and Y. Yamaguchi, Prog. Theoret. Phys. **6**, 166 (1951); G. F. Chew and H. W. Lewis, Phys. Rev. **84**, 779 (1951); Isaacs, Sachs, and Steinberger, Phys. Rev. **85**, 803 (1952).