

ν_i vary with volume in the same manner.²⁰ The thermal pressure P_t of the lattice is given by

$$P_t = \gamma E_t / V, \quad (5)$$

where the thermal energy E_t of the lattice is defined by

$$E_t = \langle \sum_i \frac{1}{2} p_i^2 \rangle_{Av} + \langle \sum_i 2\pi^2 \nu_i^2 q_i^2 \rangle_{Av}, \quad (6)$$

in which the averages of the kinetic and potential energies which appear must be computed from quantum statistical mechanics. The volumetric coefficient α of thermal expansion for a harmonic solid can be found from Grüneisen's law

$$K\alpha = \gamma C_V / V, \quad (7)$$

in which K is the bulk modulus (inverse compressibility) and C_V is the heat capacity at constant volume. This result follows directly from Eq. (5), on the Grüneisen assumption that γ is a function only of volume.

The thermal oscillators, whose coordinates appear in Eq. (3) for H , may be the virtual oscillators of the acoustic field as in a Debye solid (which shows a spectrum of frequencies), or they may be material oscillators, as in the Druyvesteyn-Meyering solid (where only one frequency appears) discussed below. Such harmonic solids stand in contrast to the anharmonic solids treated by Born and Brody,²¹ or by Hooton.²²

A. Debye Solid

For purposes of later reference, a prefatory discussion of a Debye solid will be given.

The Debye frequency ν_D of an isotropic monatomic solid is defined by

$$3N = (4/3)\pi V(c_l^{-3} + 2c_t^{-3})\nu_D^3, \quad (8)$$

where N is Avogadro's number, V is the atomic volume, and c_l and c_t are the velocities of longitudinal and transverse elastic waves, respectively; this definition corresponds to the Debye assumption of an average wave velocity for the two types of waves. The wave velocities are given for an isotropic solid by

$$c_l^2 = (\lambda + 2\mu)/\rho, \quad c_t^2 = \mu/\rho, \quad (9)$$

if ρ is the density and λ and μ are the Lamé parameters. The definition of the bulk modulus by

$$K = -V\partial P/\partial V \quad (10)$$

yields the result

$$K = \lambda + \frac{2}{3}\mu \quad (11)$$

on the infinitesimal theory of elasticity. Use of this relation and the definition,

$$\sigma = \frac{1}{2}\lambda/(\lambda + \mu), \quad (12)$$

of Poisson's ratio σ permits one to write Eq. (8), in the form of I and II, as

$$\nu_D = s_D N^{1/3} M^{-1/2} K^{1/2} V^{1/6}, \quad (13)$$

where M is the atomic weight and $s_D(\sigma)$ is defined by

$$s_D = \left[\frac{3}{2(1+\sigma)} \right]^{1/2} \left[\frac{9/4\pi}{[2(1-\sigma)]^{-3} + 2[1-2\sigma]^{-3}} \right]^{1/2}. \quad (14)$$

Thermodynamic functions on the Debye model, such as the thermal energy E_t of Eq. (6), are given directly by standard results²³ in terms of $h\nu_D/kT$, where h and k are the Planck and Boltzmann constants respectively, and T is the absolute temperature.

To satisfy Grüneisen's postulate,²⁰ that all the frequencies vary with volume in the same manner, it is essential that the Poisson ratio σ be constant; otherwise the frequencies of the longitudinal and transverse waves show different variations.³ With this assumption, use of Eq. (13) in Eq. (4) yields

$$\gamma_D = -\frac{1}{6} - \frac{1}{2}\partial \ln K / \partial \ln V \quad (15)$$

for the Grüneisen parameter γ_D on the Debye model. This form for γ_D is essentially that of Lorentz; by Eq. (10), it is equivalent to Eq. (1) of Slater, which, one notes, does not contain explicitly the Lamé parameters λ and μ characteristic of the infinitesimal theory of elasticity.

It is common in the theory of elasticity of solids to consider only adiabatic and isothermal processes, in which cases a strain-energy function can be defined²⁴; thus, the distinction between the energy and the Helmholtz free energy will be ignored, in general. It is known that the bulk modulus for a solid can be taken indifferently as adiabatic or isothermal at low pressure,²⁵ and the result for a solid at high pressure follows from the Thomas-Fermi atomic model, for temperatures low in the sense of the model.²⁶ Hence, qualification of a partial derivative with respect to volume as adiabatic or isothermal will be omitted, on the basis above, and on the basis of Grüneisen's assumption that the characteristic frequency is a function only of volume.

B. Druyvesteyn-Meyering Solid

In this section, the Grüneisen parameter given by Druyvesteyn and Meyering will be obtained from an atomistic model. Consider a monatomic solid with a simple cubic lattice. Assume that each atom shares a bond with each of its six nearest neighbors, and with no neighbors more remote. Let each bond be represented

²⁰ E. Grüneisen, in *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1926), pp. 1-59.

²¹ M. Born and E. Brody, *Z. Physik* 6, 132 (1921).

²² D. J. Hooton, *Phil. Mag.* 46, 422, 433 (1955).

²³ J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), pp. 243, 251.

²⁴ A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (Dover Publications, New York, 1944), fourth edition, pp. 94, 99, 104.

²⁵ H. Jeffreys, *Proc. Cambridge Phil. Soc.* 26, 101 (1930).

²⁶ J. J. Gilvarry, *Phys. Rev.* 96, 934 (1954).