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

$$P_l=\gamma E_l/V, \tag{5}$$

where the thermal energy E_l of the lattice is defined by

$$E_l=\langle\sum_i \tfrac{1}{2}p_i^2\rangle_{Av}+\langle\sum_i 2\pi^2\nu_i^2 q_i^2\rangle_{Av}, \tag{6}$$

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

$$K\alpha=\gamma C_V/V, \tag{7}$$

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

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

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

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

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

$$K=-V\partial P/\partial V \tag{10}$$

yields the result

$$K=\lambda+\tfrac{2}{3}\mu \tag{11}$$

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

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

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

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

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

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

Thermodynamic functions on the Debye model, such as the thermal energy E_l of Eq. (6), are given directly by standard results[23] 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

$$\gamma_D=-\tfrac{1}{6}-\tfrac{1}{2}\partial\ln K/\partial\ln V \tag{15}$$

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 defined[24]; 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

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