pression

$$(\partial^3 u/\partial r^3)_0 = -54\gamma_{DM}K_0, \qquad (27)$$

obtained by Druyvesteyn and Meyering from prior work of Ornstein and Zernike.[30]

For a solid with a simple cubic lattice, in which the potential energy U of an atom in the interatomic force field is given, in terms of the interatomic distance r, by

$$U = -A/r^m + B/r^n, \qquad (28)$$

where m and n are constants, and A and B are lattice sums which are computed for pairwise interaction of the atom with all others (considered fixed), and which are constant for deformation without distortion, Grüneisen[20] determined the characteristic frequency directly to obtain the expression

$$(m+n+3)/6 = \gamma_{DM} \qquad (29)$$

for the Grüneisen constant at normal volume. The equation of state corresponding to the potential energy (28) can be evaluated as

$$P = 3K_0(n-m)^{-1}[(V_0/V)^{n/3+1} - (V_0/V)^{m/3+1}], \quad (30)$$

where K_0 is the bulk modulus corresponding to the normal volume V_0. If the bulk modulus K is determined from this equation, one verifies that Eq. (24) for γ_{DM} reproduces correctly Grüneisen's value of Eq. (29) for the parameter at normal volume. Slater[3] has given the value $(n+6)/6$ for the Grüneisen constant at normal volume of a solid for which $m=1$ in Eq. (28); the difference from the value $(n+4)/6$ corresponding to Eq. (29) of Grüneisen is due to the fact that Slater based his result on Eq. (15) for the Debye model.

A solid of the type of Druyvesteyn and Meyering shows thermal vibrations corresponding to the single frequency given by Eq. (17). Hence, thermodynamic functions, such as the thermal energy E_l of Eq. (6), can be expressed in terms of $h\nu_{DM}/kT$ by making use of results from Einstein's theory[23] of the heat capacity of solids. The properties discussed above, depending on the cubic term in the interatomic potential energy, are consistent with the usual thermodynamic functions derived directly from the partition function $Q = \sum_n \times \exp[-(n+\frac{1}{2})h\nu_{DM}/kT]$, since the energy levels of an anharmonic oscillator are independent of the cubic term within first-order perturbation theory.[31]

Lattices more general than the simple cubic can be treated by following Slater's procedure,[3] used in his heuristic representation of the metallic bond by a diatomic molecule, of writing the volume per atom as cr^3 in terms of the interatomic distance r of nearest-neighbor atoms, where the constant c is characteristic of the lattice type. In such a case, Eq. (20) remains

[30] L. S. Ornstein and F. Zernike, Proc. Roy. Acad. Amsterdam 19, 1289, 1304 (1916).

[31] L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 160.

valid, since each oscillator introduces a generalized coordinate $q_i = r - r_0$ to describe the solid, which has $3N$ degrees of freedom. Taylor expansion of $V = Ncr^3$ changes the constant factor in Eq. (21) for u, however. For the more general lattices in question, therefore, the value of s_{DM} in Eq. (23) for ν_{DM} becomes $3^{1/2}c^{1/3}/2^{1/2}\pi$, but Eq. (24) for γ_{DM} remains unchanged. For such lattices, Grüneisen's law in the form (26) can be verified by means of Eq. (25).

The preceding results can be generalized directly to the case of a simple cubic lattice where the mass of an atom differs from the common mass of its six nearest neighbors, as in the structure of the alkali halides. If the mass ratio is significantly different from unity, the value of s_{DM} approaches $\sqrt{3}/2\pi$. This value is quite close to the corresponding coefficient, as noted above, obtained by Einstein; in point of fact, both Madelung and Einstein had ionic crystals of the type of the alkali halides in mind in their treatments. For the degenerate case of mass ratio very different from unity, the Druyvesteyn-Meyering solid can be viewed as a solid of independent (light) atoms, where the coupling to the heavy atoms serves the function of providing an interatomic force field for the light atoms. The Grüneisen parameter γ_{DM} is independent of the mass ratio.

C. Ideal Harmonic Solid

An ideal harmonic solid will be defined as one in which the oscillator frequencies ν_i are strict constants. The constancy of the frequencies demands that the Grüneisen parameter vanish, from Eq. (4). It follows from Grüneisen's law (7) that the coefficient of thermal expansion vanishes, and, from Eq. (5), that the thermal pressure P_l vanishes. The latter conclusion is in agreement with the virial theorem, which one derives as[32]

$$\langle \sum_i \tfrac{1}{2}p_i^2 \rangle_{Av} - \langle \sum_i 2\pi^2\nu_i^2 q_i^2 \rangle_{Av} = \tfrac{3}{2}P_l V, \qquad (31)$$

for an ensemble of purely harmonic oscillators; since the average kinetic and average potential energies which enter are equal, one has $P_l = 0$. As will appear, the Debye and the Druyvesteyn-Meyering models make different predictions on the equation of state of an ideal harmonic solid.

From Eq. (24) for the Grüneisen parameter of a Druyvesteyn-Meyering solid, the condition $\gamma_{DM} = 0$ yields

$$K = K_0(V_0/V), \qquad (32a)$$

$$P = K_0[(V_0/V) - 1], \qquad (32b)$$

for the bulk modulus and equation of state (corresponding to $P = 0$ for $V = V_0$) of an ideal harmonic solid on this model. In this case, Eq. (18) or Eq. (21) yields the potential energy u of a bond oscillator as

$$u = (3/2)K_0 v_0^{1/3}(r-r_0)^2 + O[(r-r_0)^4], \qquad (33)$$

[32] H. C. Corben and P. M. Stehle, *Classical Mechanics* (John Wiley and Sons, Inc., New York, 1950), p. 202.