finite strain may not modify Eq. (1) at high pressure. On the basis of Duhem's formulation[7] of the theory of finite strain, Druyvesteyn and Meyering[8] have obtained a value γ_{DM} for the Grüneisen parameter of a solid as evaluated from the equation of state, which can be expressed as

$$\gamma_{DM}=\gamma_D-\tfrac{1}{3}, \tag{2}$$

in terms of γ_D of Eq. (1). The presumption in their work is that the conflict of Eq. (2) with Eq. (1) arises from consideration of finite strain. Further, Druyvesteyn[9] has used Murhaghan's theory[10,11] of finite strain, with some drastic assumptions, to evaluate the Grüneisen parameter of a solid in terms of its Poisson ratio alone. In later work,[12] however, he pointed out that values of the Grüneisen constant obtained from Grüneisen's law show only poorly the predicted correlation with Poisson ratio; hence, this result of Druyvesteyn will not be considered further in what follows.

Of late, this question of the possible effect of finite strain has been reopened by Dugdale and MacDonald.[13] These authors point out that Eq. (1) yields a value $\gamma_D=\frac{1}{3}$ when applied to the equation of state of a solid which they believe should show no thermal expansion; since γ_D does not vanish, Grüneisen's law implies a thermal expansion. Dugdale and MacDonald ascribe the paradox to neglect of finite strain in the derivation of Eq. (1). They attempt to resolve the paradox by postulating (apparently without formal derivation from the theory of finite strain) an expression for the Grüneisen parameter as evaluated from the equation of state, which coincides with Eq. (2) of Druyvesteyn and Meyering at zero pressure, and thus yields a vanishing Grüneisen parameter for the case in question.

The infinitesimal theory of elasticity describes an isotropic solid by means of two elastic parameters, which can be taken as the two Lamé constants or as the bulk modulus and the Poisson ratio. These coefficients yield directly the values of such derivatives as $\partial P/\partial V$ or $\partial^2 E/\partial V^2$, where E is the total energy. To evaluate the corresponding higher derivatives, the formal theory of finite strain introduces three additional coefficients for an isotropic solid, which can be taken as the three Brillouin[14,15] or the three Murnaghan[10,11] parameters. These parameters yield directly the values of such derivatives as $\partial^2 P/\partial V^2$ or $\partial^3 E/\partial V^3$. Since Eq. (1) contains $\partial^2 P/\partial V^2$, though not expressed in terms of Brillouin or Murnaghan parameters, it involves consideration of finite strain. Hence, Eq. (1) for the Grüneisen parameter on the Debye model should contain no restriction to infinitesimal strain (a point which has also been made by Slater[16]).

In this paper, Eq. (2) for γ_{DM} will be derived without recourse to the formal mechanics of the theory of finite strain. The derivation brings out clearly the area of physical validity of the result; it applies to a model of independent pairs of nearest neighbor atoms. Druyvesteyn and Meyering obtained the expression by virtue only of tacit limitation to such a solid. Hence, the difference between Eqs. (1) and (2) lies in the model employed. The former equation corresponds to a Debye solid, in which coupling of the vibrations of the individual atoms is taken into account. These considerations yield an immediate resolution of the paradox of Dugdale and MacDonald.

Murnaghan has reduced the theory of finite strain to a form very tractable for physical applications.[17] The consistency of his results with the very extensive earlier work has been shown by Truesdell.[18] The formalism of the Murnaghan theory will be used in this paper to derive the value of the Grüneisen parameter under finite strain, as evaluated from the equation of state for a Debye solid, on the basis of an assumption corresponding to that of constant Poisson ratio. The result is identical with that of Eq. (1), as one should expect on the usual assumption that the presence of a uniform finite pressure affects the velocities of elastic waves of infinitesimal amplitude only through its effect upon the density and the elastic parameters. In point of fact, this assumption has been justified by Biot[19] on his formulation of the theory of finite strain, by a general argument. The value of Eq. (2) is found for the Grüneisen parameter of a Druyvesteyn-Meyering solid under finite strain.

II. HARMONIC SOLIDS

A harmonic solid is one in which the thermal behavior can be represented by a set of lattice oscillators whose Hamiltonian H is

$$H=\tfrac{1}{2}\sum_i(p_i^2+4\pi^2\nu_i^2 q_i^2), \tag{3}$$

where the range of i corresponds to all normal modes of oscillation, p_i is the generalized momentum corresponding to the oscillator coordinate q_i, and ν_i is an oscillator frequency. The Grüneisen parameter γ of the solid is defined by

$$\gamma=-\partial\ln\nu_i/\partial\ln V, \tag{4}$$

on the Grüneisen postulate that all lattice frequencies

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