

depend only on the ratio of  $v$  to its value  $v_0$  at zero pressure. It follows that  $\gamma$  at low pressure is a function only of  $v$  to the extent that the temperature-dependent term in Eq. (49), which is proportional to the ratio  $p/k$ , can be neglected. Accordingly, the prescription of Eq. (15) for including the effect of temperature on the pressure should yield approximately the same results in practice as the method of Walsh and associates,<sup>18,19</sup> who use the Mie-Grüneisen relation (43) directly, on the assumption that the Grüneisen parameter is a function only of the volume  $v$ . It follows also that the approximate constancy assumed for the Murnaghan exponent  $n$  of Eq. (8) represents a consistent assumption for  $P$  small.

The equation of state as an explicit function of volume and temperature can be found from Eq. (15) for a solid obeying the Debye theory at sufficiently low temperature. In this case,  $C_V$  and  $E_T$  vary with temperature as  $T^3$  and  $T^4$ , respectively, and thus the last term can be ignored in Eq. (45), which reduces to the usual form of Grüneisen's law. Hence, the temperature dependence of the coefficient  $\alpha$  of thermal expansion becomes the same as that of the heat capacity  $C_V$ , when one neglects the small temperature dependence of the Grüneisen parameter, the bulk modulus, and the volume (under isobaric conditions) specified by Eqs. (49), (48), and (47), respectively. The Debye expression for the heat capacity is

$$C_V = (12\pi^4/5)NR(T/\Theta)^3, \quad (52)$$

where  $R$  is the gas constant,  $N$  is the number of moles in the solid, and  $\Theta$  (proportional to the maximum lattice frequency and thus a function of volume) is the Debye temperature in the limit of zero temperature.<sup>15</sup> Grüneisen's law yields

$$\alpha = (12\pi^4/5)NR(\gamma_0/kv)(T/\Theta)^3, \quad (53)$$

where  $\gamma_0$  is given by Eq. (50). Expressing the pressure differentiation in the definition (20) of  $\eta$  in terms of one with respect to the volume  $v$ , one obtains

$$\eta = 5\gamma_0 - \frac{2}{3} + d \ln \gamma_0 / d \ln v \quad (54)$$

by using Eqs. (42) and (53); the derivative appearing corresponds to that of Eq. (51). Hence, for a Debye solid at low temperature, the parameters  $\mathcal{U}$  and  $\mathcal{K}$  can be written through first-order terms in the exponentials involved, as

$$\mathcal{U} = v_0 [1 + (3\pi^4/5)NR(\gamma_0/k_0v_0)T^4/\Theta_0^3], \quad (55a)$$

$$\mathcal{K} = k_0 \left[ 1 - \pi^4 NR \left( 3\gamma_0 - \frac{2}{3} + \frac{d \ln \gamma_0}{d \ln v} \right) \left( \frac{\gamma_0}{k_0v_0} \right) \frac{T^4}{\Theta_0^3} \right], \quad (55b)$$

where  $k_0$  and  $\Theta_0$  represent values of  $k$  and  $\Theta$ , respectively, evaluated at  $v=v_0$ , to which point  $\gamma_0$  and the derivative appearing also correspond. The value of  $\gamma_0$  is given by Eq. (14), and the value of the derivative follows as

$$d \ln \gamma_0 / d \ln v = nm(n+m-\frac{1}{3})^{-1}, \quad (56)$$

from Eq. (51). Substitution of the results of Eqs. (55) into Eq. (15) yields the explicitly temperature-dependent equation of state. It is seen that the thermal component  $P_T$  of pressure varies as  $T^4$  in this limit.

The results obtained can be applied to the case of an ideal harmonic solid which, because of the absence of anharmonicity of the lattice vibrations, shows no thermal pressure and no thermal expansion. In this case, the lattice frequencies are strict constants, so that the Grüneisen constant  $\gamma$  vanishes. It is clear from Eq. (46) or Eq. (51) that  $\gamma$  can be constant only if at least one of the exponents  $n$  and  $m$  vanishes. Selecting  $m=0$ , one obtains  $\gamma = \frac{1}{2}(n - \frac{1}{3})$ , which vanishes only for  $n = \frac{1}{3}$ . In the general case,  $\mathcal{U}$  and  $\mathcal{K}$  of Eqs. (27) and (32) can be independent of the temperature only for  $\alpha_0$  equal to zero, and this value of  $\alpha_0$  follows from Grüneisen's law (45) when  $\gamma$  vanishes. For the Debye model, Eqs. (55) show that  $\mathcal{U}$  and  $\mathcal{K}$  reduce to  $v_0$  and  $k_0$ , respectively, for  $\gamma_0$  equal to zero. Hence, the entire development is consistent with the expression

$$P = 3k_0[(v_0/v)^3 - 1] \quad (57)$$

for the equation of state of an ideal harmonic solid, as established previously by the author for this case.<sup>22</sup> This equation corresponds to Eq. (9), derived by Murnaghan from the linear theory of finite strain.

As noted, the generalized equation of state predicts that the Grüneisen parameter should be independent of temperature at zero pressure. On this point, direct evidence from experimental data for temperatures higher than normal is available from values of  $\gamma$  computed by Birch for compounds<sup>8</sup> and by the author for elements.<sup>30</sup> The results of the author show no more than a small or moderate decrease, in general, of the parameter over the range of temperature from normal to the fusion point; the decrease might be interpreted as a consequence of anharmonicity, since the temperatures involved exceed the Debye temperature, in general. For low temperature, the experimental evidence is conflicting. In this case, Bijl and Pullan found an anomalously large decrease relative to its normal value in the parameter for copper,<sup>31</sup> but Figgins *et al.* observed an increase for aluminum.<sup>32</sup> However, Baluffi and Simmons recently have reported measurements of the thermal expansion of copper from 102° down to 8°K, and have concluded that no evidence exists for a real variation of  $\gamma$  in this temperature range.<sup>33</sup> Their results are in agreement with those of Rubin *et al.*<sup>34</sup> for temperatures down to about 110°K. These considerations tend to justify the assumption that the exponent  $n$  of Murnaghan's Eq. (7) with  $n$  evaluated

<sup>30</sup> J. J. Gilvarry, *Phys. Rev.* 102, 308 (1956).

<sup>31</sup> D. Bijl and H. Pullan, *Physica* 21, 285 (1955).

<sup>32</sup> Figgins, Jones, and Riley, *Phil. Mag.* 1, 747 (1956).

<sup>33</sup> R. W. Baluffi and R. O. Simmons, *Bull. Am. Phys. Soc. Ser. II*, 2, 137 (1957).

<sup>34</sup> Rubin, Altman, and Johnston, *J. Am. Chem. Soc.* 76, 5289 (1954).