

the other hand, the validity of the Mie-Grüneisen approximation for the vibrational free energy, as well as the condition that γ be a purely volume-dependent function, require only that the volume dependence of the roots $(\mu_{2n})^{1/2n}$ of the pertinent even moments of the vibrational spectrum be the same as that of the geometric means of the normal-mode frequencies, a less restrictive condition than the validity of the Debye functional form for the vibrational free energy (see Appendix). The corresponding conditions for the validity of the thermal formulations involve also the moment μ_1 . Clearly, one cannot make any general statement on the actual validity of either formulation of the Mie-Grüneisen or Hildebrand approximation, but one has some reason to expect either formulation of the Mie-Grüneisen approximation to be less inaccurate than the corresponding formulation of the Hildebrand approximation in the region of moderate temperatures. One can also state that within the region of convergence of the Thirring-Stern expansions, the temperature ranges in which γ and γ' do not depend on temperature at constant volume coincide. Thus the calculations of the temperature variation at constant volume of the parameter γ for simple quasi-harmonic models of rare-gas solids, performed by BARRON⁽¹²⁾ and by HORTON and LEECH⁽¹⁸⁾, which show that in these cases γ remains practically constant down to temperatures of the order of one third of the Debye characteristic temperature, do confirm that in these cases the vibrational Mie-Grüneisen approximation is in fact less inaccurate than the vibrational Hildebrand approximation at these temperatures.

The Thirring-Stern expansions for the entropy and the vibrational free energy allow one also to show that the rates of approach of γ and γ' to γ_∞ are equal in absolute value but opposite in sign. This result, together with equation (4), allows one to predict that for any model for which γ increases monotonically with temperature from 0°K upwards (and in which one neglects the effect of thermal expansion on the vibrational frequencies), as is the case, for example, for most of the quasi-harmonic models of rare-gas solids treated by BARRON⁽¹²⁾ and by HORTON and LEECH⁽¹⁸⁾, γ' will be larger than γ_∞ and will increase steadily with decreasing temperature down to 0°K, where $(\partial\gamma'/\partial T)_V$ must vanish. One can envisage this result as a particularly dramatic illustration of the general

result that γ' differs from γ at very low temperatures.

A condition for the validity, within the quasi-harmonic approximation, of both formulations of the Mie-Grüneisen approximation over the entire range of temperatures has recently been given by BLACKMAN⁽¹⁴⁾. If one rewrites the quasi-harmonic expressions

$$\gamma' = - \sum_j \frac{d \ln \nu_j}{d \ln V} W_{\text{vib}}^{(j)} / W_{\text{vib}}$$

and

$$\gamma'' = - \sum_j \frac{d \ln \nu_j}{d \ln V} W_{\text{th}}^{(j)} / W_{\text{th}}$$

in integral form, it is in effect apparent that the condition in question is that the arithmetic average of $d \ln \nu / d \ln V$ for all vibrations lying between ν and $\nu + \Delta \nu$ be a constant, independent of the frequency. This is clearly more restrictive than the conditions for the validity of either formulation of this approximation at intermediate temperatures, that we have given above.

4. THE MIE-GRÜNEISEN AND HILDEBRAND EQUATIONS OF STATE

The formulations (1) and (2) of the equation of state of a cubic solid under hydrostatic pressure, and their first volume derivatives at constant temperature:

$$-\frac{1}{K} + V \frac{d^2 W_L}{dV^2} = \frac{\gamma'^2}{V} (TC_V - W_{\text{vib}}) + \gamma' \frac{W_{\text{vib}}}{V} \left[\frac{V}{\gamma'} \left(\frac{\partial \gamma'}{\partial V} \right)_T + T \left(\frac{\partial \gamma'}{\partial T} \right)_V - 1 \right] \quad (13)$$

$$-\frac{1}{K} + V \frac{d^2 W_C}{dV^2} = \frac{\gamma''^2}{V} (TC_V - W_{\text{th}}) + \gamma'' \frac{W_{\text{th}}}{V} \left[\frac{V}{\gamma''} \left(\frac{\partial \gamma''}{\partial V} \right)_T + T \left(\frac{\partial \gamma''}{\partial T} \right)_V - 1 \right] \quad (14)$$

can be easily reduced to the special forms appropriate in the Mie-Grüneisen and Hildebrand approximations. One uses the Mie-Grüneisen and Hildebrand approximations to $\gamma'(V, T)$ and $\gamma''(V, T)$, together with the thermodynamic