Admittedly, this approximation neglects specifically anharmonic contributions to the thermodynamic functions, detailed estimates of which have recently been undertaken for some simple force models,[19,20] but the available evidence, to be discussed in Section 5, suggests that these contributions are unimportant in the temperature range of utmost interest for our analysis.

A general consequence of the quasi-harmonic approximation is that, at temperatures sufficiently close to the absolute zero, the heat capacity at constant volume of a cubic non-metal is simply proportional to $[T/\Theta_D(V)]^3$, where $\Theta_D(V)$ is the elastic Debye characteristic temperature. At somewhat higher temperatures, however, the (quasi-harmonic) heat capacity contains additional terms in higher odd powers of T, originating from the dispersion of the acoustic modes and involving each the ratio between the absolute temperature and a purely volume-dependent characteristic temperature appropriate to the term and generally different from $\Theta_D(V)$.[17] This result, when combined with the thermodynamic theorem involving the heat capacity given in Section 2, allows one to state that *the T^3 region is, in general, the only low-temperature region where the thermal formulation of the Mie–Grüneisen approximation is valid, and where γ does not depend explicitly on temperature*. BORN[11] and BARRON[12,13] had already pointed out that in the T^3 region γ and γ'' are both given by the logarithmic derivative of $\Theta_D(V)$. *The vibrational formulation of the Mie–Grüneisen approximation*, instead, *is not valid in the T^3 region*, contrary to what was assumed by HUANG[4], since the vibrational free energy could have the form (6a) in this region only if the zero-point energy were simply proportional to $\Theta_D(V)$; namely, if the Debye form for the vibrational spectrum were appropriate for the entire vibrational spectrum of the solid. Finally, the Hildebrand approximation for the thermal or vibrational energy is clearly not valid at low temperatures.

Another general consequence of the quasi-harmonic approximation for a cubic non-metal, pertinent to the region of moderate and high temperatures where the Thirring–Stern expansions of the thermodynamic functions converge, is easily established by inspection of these expansions, which are given in the Appendix. This is that the vibrational energy becomes explicitly independent of volume and the vibrational free energy takes the form (6a) only at temperatures somewhat above the Debye characteristic temperature $\Theta_2(V)$ for the high temperature heat capacity at constant volume, where they approach, respectively, $3kT$ per particle and the high temperature Debye functional form $T \ln [T/\Theta_0(V)]$. On the other hand, the thermal energy per particle approaches $3kT$, and the thermal free energy approaches the high temperature Debye functional form, $T \ln [T/\Theta_0(V)]$, only at the significantly higher temperatures where the zero-point energy per particle is negligible compared to $3kT$. These results, when combined with the thermodynamic theorem given in Section 2, connecting these particular functional forms for the energies and free energies, lead one to the following conclusions: (1) *The vibrational formulation of the Mie–Grüneisen approximation becomes valid, in general, when and only when the vibrational energy per particle approaches $3kT$, namely, when and only when the Hildebrand approximation for the vibrational energy becomes valid; and (2) the thermal formulation of the Mie–Grüneisen approximation would generally become valid in the high-temperature region only at the very high temperatures, hardly ever attained by a solid, where the Hildebrand approximation for the thermal energy becomes valid.* BORN[11] indicated long ago that γ is a function only of the volume of the solid in the temperature range where the law of Dulong and Petit is obeyed, and BARRON[12] has pointed out that for $T \to \infty$, γ'' and γ approach a common value given by the logarithmic derivative of the Debye characteristic temperature for the entropy for $T \to \infty$. BARRON's calculations[12] of the temperature variation at constant volume of γ and γ'' for a particular quasi-harmonic model, a face-centered cubic solid with central forces between nearest neighbors, provide also an illustration of the general result, implicit in (1) and (2), that γ'' *approaches the common limit*, γ_∞, *of the γs at high temperatures more slowly than* γ.

In the region of intermediate temperatures, where the Thirring–Stern expansions converge but the vibrational energy per particle has not yet attained the value $3kT$, the validity of the Hildebrand approximation for the vibrational energy requires that the pertinent even moments μ_{2n} of the frequency distribution of the normal modes of the solid be independent of the volume of the solid. On