mechanics then yields the expression

$$\frac{\alpha B_T V}{C_V} = \gamma_{Gr} = \frac{\sum_{j=1}^{3N} \gamma_j C_{Vj}}{\sum_{j=1}^{3N} C_{Vj}} \tag{1}$$

in which C_{Vj} is the heat capacity of the jth normal mode of the crystal at the temperature of observation, and the sum is over all normal modes. Thus each individual mode γ is seen to be weighted by the heat capacity of that mode. It is the changes of these weighting factors with temperature along with differences of mode gammas which give rise to a temperature dependence of γ_{Gr}.

In the limit of temperatures high compared with $h\nu_{max}/k$ where ν_{max} is the highest frequency of the distribution, each mode has a heat capacity k and the expression for γ_{Gr} reduces to

$$\gamma_\infty = \frac{\sum \gamma_j}{3N},$$

the simple average of the γ_j over all normal modes. If one had a knowledge of the frequency distribution of the $3N$ normal modes, and of the value of γ_j associated with each, it would be possible to calculate the value of the γ_{Gr} or of the thermal expansion at any temperature (within the small changes expected in B_T and V as well as the fundamental limitations of a quasi-harmonic oscillator model). It would be possible in principle to do very careful neutron diffraction studies on samples at high pressures to measure the pressure dependence of the normal mode frequencies and thence the volume dependences. A complete set of these data would of course provide the crucial test of the model. In practice the difficulties associated with such a procedure seem formidable, especially for such materials as germanium and silicon which are relatively incompressible, e.g. a mode whose γ_j had the large value 2 would exhibit a total change of less than 3% in 10 kB for Ge, 2% in Si, which would push present neutron diffraction techniques near their limit to see the change, even without the problems associated with the additional background scattering due to the thick walled pressure vessel. The implication is that the check on the limitations of the quasi-harmonic *model* used had best be made on one of the more compressible materials such as rubidium iodide which should exhibit interesting behaviour, or on the very compressible sodium.

Since we do *not* know the numerical values of all the γ_j, let us review the information which is available about the volume dependence of various normal mode frequencies. Consider the dispersion curve, frequency ν plotted against wave vector $\mathbf{k}$ for waves propagating in a particular direction in the reciprocal lattice.

The curve may change as pressure is applied to the crystal, reducing its volume. The frequency of a normal mode j (defined as a wave having an intergral number of wavelengths per unit distance fixed to the lattice, i.e. compressing with the lattice) changes for two reasons: (i) the value of k changes due to dimensional change of the lattice, (ii) the curve proper shifts due to changes in the interatomic interactions. Since the slope of the curve in the non-dispersive region is the velocity of sound waves of the appropriate polarization $-\gamma_j = d(\ln v)/d(\ln V) + d(\ln k_j)/d(\ln V)$ applies to modes in the non-dispersive region of the spectrum.

2. Gamma of an anisotropic continuum

Recently measurements have been made (McSkimmin 1957, Chapman 1959) of the pressure dependence of all three independent elastic constants of germanium and silicon, making it possible to eliminate two of the assumptions of the Slater model, the assumption of elastic isotropy and that of independence of Poisson's ratio of volume. For each direction of propagation in the crystal an expression for the velocities of each of the three independent polarizations of sound waves will appear in the form $v = (C/\rho)^{1/2}$, where C is an elastic stiffness, ρ is the crystal density.

The gamma of each of these modes then appears in the form $\gamma = -\frac{1}{2}d(\ln C)/d(\ln V) - \frac{1}{6}$. The quantities $d(\ln C)/d(\ln V)$ are related to the measured pressure derivatives of the elastic constants by the relation $d(\ln C)/d(\ln V) = -(B_T/C)(dC/dP)$ where B_T is the isothermal bulk modulus. The high temperature limit of γ_{Gr} on the anisotropic continuum model is an average of the γ's of the longitudinal and two transverse modes over all directions of propagation in the crystal. This averaging process has been carried out by Sheard (1958) using a machine calculation for a number of crystals. The averaging may be performed approximately by using a process such as that of Houston (1948). Values obtained in Ge and Si using the Houston approximation and data on pressure dependence of elastic constants of Ge by McSkimmin (1957) and of Si by Chapman (1959) yield $\gamma_\infty = 0{\cdot}72$ in Ge, $0{\cdot}51$ in Si, comparing almost too well with the experimental values of γ_{Gr} found by Gibbons, $0{\cdot}73$ in Ge, $0{\cdot}45$ in Si in the high temperature limit. Table 1 contains the individual values of γ for modes propagating along [100], [110] and [111] in Ge and Si. Note that the Slater gamma is much higher than the average gamma because of the excessive weight it gives to the longitudinal modes.

Table 1. γ's of long wavelength acoustic modes propagating along various crystallographic directions.

Direction of propagation	γ_L	C_{11}'	γ_{T1}	C_{T1}	γ_{T2}	C_{T2}
[100]	1·37	(1·67)	0·33	(0·80)	0·33	(0·80)
Si [110]	1·33	(1·96)	0·33	(0·80)	−0·12	(0·51)
[111]	1·32	(2·05)	0·08	(0·61)	0·08	(0·61)
	γ_L	$\rho N_L^2/C_{11}'$	γ_{T1}	$\rho N_{1T}^2/C_{T1}$	γ_{T2}	$\rho N_{2T}^2/C_{2T}$
[100]	1·29	(1·29)	0·584	(0·67)	0·584	(0·67)
Ge [110]	1·28	(1·56)	0·584	(0·67)	0·170	(0·40)
[111]	1·27	(1·65)	0·36	(0·49)	0·36	(0·49)

To obtain the low temperature limit γ_0 of γ_{Gr} on this continuum model, one must weight the individual mode gammas by the inverse cube of the velocity of waves of that mode type, and again average over all directions of propagation. This is equivalent to determining $-d(\ln \Theta_0)/d(\ln V)$ where Θ_0 is the low temperature limit of the Debye temperature. This may most easily be accomplished by using de Launay's (1960) tables of Θ_0 (C_{11}, C_{12}, C_{44}, ρ) together with the values of dC_{ij}/dP, with the results $\gamma_0 = 0{\cdot}49$ in Ge, $0{\cdot}25$ in Si (Daniels 1962). These points are plotted on the T = 0 ordinate of figures 1 and 2. Note the high degree of similarity then apparent between the behaviour of Ge and Si. It might seem then as if the continuum model fits quite well the behaviour of