The Grüneisen parameter — computer calculations via lattice dynamics

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ABSTRACT

Full lattice dynamical calculations on a monatomic cubic lattice have confirmed the linear relationship between the Grüneisen parameter and the first derivative of incompressibility with respect to pressure. The exact expressions are dependent upon the details of the simulation, but generally take the form

$$\gamma = a \frac{dK}{dP} - b \tag{1}$$

where γ is the Grüneisen parameter, K is the bulk modulus, P is pressure and a and b are constants. In our atomistic simulation we considered pairwise additive Lennard–Jones and Morse potential models. We found that if we only considered short-range nearest neighbour forces, a and b take the values 0.50 and 0.90, respectively. This result differs from the forms of the well-known definitions of the Slater, Dugdale–Macdonald and Vaschenko–Zubarev (or free-volume) γ, but provides an exact confirmation of the approximations used to obtain the Barron γ. In order to determine the wider validity of such a simple model, further calculations considered long-range forces and the NaCl lattice. This resulted in a reduction in the values of both a and b in the case of the long-range interactions thereby approaching the free-volume fomulation. However, no simple relation could be found in the case of the more complex NaCl structure, with no linearity existing between γ and the pressure dependence of the shear modulus.

1. Introduction

The Grüneisen parameter, γ, is a valuable quantity in solid-state geophysics because it can be used to set limitations on the pressure and temperature dependence of the thermal properties of the mantle and core, and to constrain the adiabatic temperature gradient. It is dimensionless and, for a wide range of solids, has an approximately constant value, varying only slowly with the pressure and temperature (Anderson, 1989).

The Grüneisen parameter has both a microscopic and macroscopic definition (Grüneisen, 1912), yet the physical connection between them has been the source of much confusion. The

macroscopic definition is in terms of familiar thermodynamic properties, which in principle may be evaluated experimentally. The microscopic definition arises from a consideration of the motion of atoms in a solid and their vibrational frequencies. If both descriptions are calculated accurately for a particular structure, they should take the same value under the limitations of the quasi-harmonic approximation (Gillet et al., 1991).

Unfortunately the experimental determination of the macroscopic Grüneisen parameter for many geophysically relevant materials is very difficult, requiring prohibitively high temperatures and pressures which are inaccessible in most laboratories. Furthermore, the microscopic definition may not be used to evaluate γ precisely for real lower mantle systems since it requires a knowledge of

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the dispersion of the phonon frequencies in the first Brillouin zone. To allow estimates of γ to be obtained where little experimental data exist, alternative, approximate formulations, relating γ to the first derivative of bulk modulus (K) with respect to pressure, dK/dP, and other thermodynamic quantities, have been constructed and used to evaluate γ in the Earth's interior (see Poirier, 1991, for a review). However, such expressions may only be valid if the alternative formulations used (e.g. Slater 1939; Dugdale and MacDonald 1953; Barron, 1955; Vaschenko and Zubarev, 1963) are supported by a strong theoretical underpinning. This can be achieved by comparing the results of the approximate solutions with those of computer modelling of the lattice dynamics of a model system. In order to enable us to compare our conclusions directly with those of previous workers, we have used the computer code PARAPOCS (Parker and Price, 1989) to calculate γ from the predicted phonon frequencies for a monatomic cubic lattice as a function of volume. The program uses interatomic potentials (e.g. Lennard–Jones, Morse, etc.) to describe the interactions between atoms in the lattice. For sufficiently simple potentials, the necessary thermodynamic properties (such as dK/dP) can also be evaluated analytically and hence a link between the microscopic definition and approximate formulations.

In the following sections, the background is given to the Grüneisen parameter and a brief description of the potential models and methodology used in the computer simulations is presented. Results are given for simple nearest-neighbour pairwise additive interactions within a monatomic cubic lattice, and for less idealized systems involving firstly longer range interactions and then for materials with the more complex NaCl structure.

2. Definitions of the Grüneisen parameter

The thermal or macroscopic formulation of the Grüneisen parameter is given by

$$\gamma_{th} = \frac{\alpha V K_T}{C_V}$$ (2)

where α is the thermal expansion, V is the molar volume, K_T is the isothermal bulk modulus and C_V is the heat capacity at constant volume. The microscopic definition of γ was in fact the original definition proposed by Grüneisen (1912), who postulated that the vibrational frequencies of the individual atoms in a solid, varied with the volume, V, via the relation

$$\gamma_i(\boldsymbol{q}) = -\frac{\partial \ln \omega(\boldsymbol{q})_i}{\partial \ln V}$$ (3)

where $\omega(\boldsymbol{q})_i$ is the frequency of the ith mode of vibration, which itself is a function of wavevector $(\boldsymbol{q})$ in the first Brillouin zone, and V is the volume. Unfortunately, except for $\gamma_i(0)$, it is impossible in general to evaluate $\gamma_i(\boldsymbol{q})$ without either using some lattice dynamical model or using high-pressure inelastic neutron scattering data. Under certain circumstances, the microscopic definition of γ can be related to the thermal definition. It can be shown (e.g. Barron, 1957) that at high temperatures but within the quasi-harmonic approximation, $\gamma_{th} = (1/n)\Sigma\gamma_i(\boldsymbol{q})$, where n is the number of vibrational modes (equivalent to 3 Nm, where N is the number of atoms in the crystal and m is the number of Brillouin zone points sampled). At lower temperatures the low-frequency modes dominate and the thermodynamic γ is given by $\gamma_{th} = (1/C_V)\Sigma C_{Vi}\gamma_i$, where C_{Vi} is the heat capacity at constant volume contributed by each mode i. However, the high-temperature approximation is found to give values which are too small when applied to real materials (e.g. Chopelas, 1990). It has been suggested (Price et al., 1987) that this may result from the intrinsic anharmonicity of the atomic vibrations at high temperatures. Gillet et al. (1991) have derived an expression for the high-temperature Grüneisen parameter $(T \gg \theta_D)$, which includes intrinsic anharmonic contributions, that reduces to the low-temperature relation when the system is within the limitations of the quasi-harmonic approximation.

To circumvent the intractable nature of $\gamma_i(\boldsymbol{q})$, there have been many approximate formulations of the Grüneisen parameter, all of which may be written (in their zero pressure form) in the style

of Eq. (1). One of the oldest is from Slater (1939) and is given by

$$\gamma_S = \frac{1}{2}\frac{dK}{dP} - \frac{1}{6} \tag{4}$$

This relation is valid only if Poissons ratio, ν, is independent of volume, and therefore pressure, and if all $\gamma_i(q)$ are equal, which is a direct consequence of the Debye model from which it is derived.

However, it has been suggested (Knopoff and Shapiro, 1969) that the Grüneisen parameter does, in fact, have a significant shear modulus dependence, especially when considering more complex structures such as the NaCl structure. They suggest the following relation for the thermal Debye Grüneisen parameter, which is similarly derived from Debye theory, but in this case the average acoustic wave velocity is replaced by a weighted average of the longitudinal and shear velocities

$$v_{\mathrm{m}} = \left(\frac{3}{\dfrac{1}{v_{\mathrm{P}}^3} + \dfrac{2}{v_{\mathrm{S}}^3}} \right)^{1/3} \tag{5}$$

giving

$$\gamma_{\mathrm{D}} = -\frac{1}{6} + \frac{1}{2}\frac{dK}{dp} - g(1 - 2\nu)\frac{dK}{dP}$$
$$+ \frac{2g}{3}(1 + \nu)\frac{d\mu}{dP} \tag{6}$$

where K and μ are the bulk and shear modulus, respectively, and $g(\nu)$ is an arithmetic function of Poisson's ratio.

If γ is independent of Poisson's ratio, implying that all elastic constants have the same pressure or volume dependence, Eq. (6) reduces to the original γ_S derived from Debye theory (Eq. (4)). However, Falzone and Stacey (1980) suggest that this independence is fundamentally impossible for purely geometric reasons, therefore invalidating Slater's formulation of γ. If, however, $d\nu/dP$ is non-zero, then this has a significant effect on γ, depending upon the relative values of $d\mu/dP$ and dK/dP (Knopoff and Shapiro, 1969).

By defining the average acoustic velocity differently, thus

$$v_{\mathrm{m}} = \left(v_{\mathrm{P}} v_{\mathrm{S}}^2 \right)^{1/3} \tag{7}$$

the acoustic Grüneisen parameter is obtained (Stacey, 1992)

$$\gamma_{\mathrm{ac}} = \frac{1}{2}\frac{dK}{dP} - \frac{4 - 5\nu}{(1+\nu)(1-\nu)(1-2\nu)}\frac{K}{3}\frac{d\nu}{dP}$$
$$- \frac{1}{6} \tag{8}$$

This also reduces to γ_S if Poisson's ratio is independent of pressure. The difference between the above two expressions for γ lies only in the definition of the average acoustic velocity.

Dugdale and MacDonald (1953) also considered a simple cubic lattice of independent pairs of nearest-neighbour atoms undergoing harmonic oscillations. Implicit in their analysis is the relation: $\partial\nu/\partial V = -1/3\ V_0^{-1/3}V^{-2/3}$ (Pastine, 1965). The model assumes one-dimensional oscillations, and so by implication only a one-dimensional lattice, which can therefore only take into account longitudinal vibrational modes and at zero pressure the model gives

$$\gamma_{\mathrm{DM}} = \frac{1}{2}\frac{dK}{dP} - \frac{1}{2} \tag{9}$$

In contrast, Barron (1955) derived an expression for γ based upon an approximate lattice dynamical solution to the frequency spectrum where the nth moment between nearest neighbours in a simple cubic lattice is given by $\mu_n = \int^{\max} \omega^n g(\omega)\,d\omega$. The theory behind this approach is significantly different from those using the Debye approximation and resulted in

$$\gamma_{\mathrm{Barron}} = \frac{1}{2}\frac{dK}{dP} - 0.94 \tag{10}$$

When extended to include all neighbours, the linear approximation becomes

$$\gamma_{\mathrm{Barron}} = \frac{1}{2}\frac{dK}{dP} - 1.12 \tag{11}$$

Vaschenko and Zubarev (1963) derived their formulation of the Grüneisen parameter, γ_{VZ}, from free-volume theory based on anharmonic central

pairwise potentials between nearest-neighbour atoms in a three-dimensional cubic lattice, and obtained (at zero pressure)

$$\gamma_{vz} = \frac{1}{2}\frac{dK}{dP} - \frac{5}{6} \tag{12}$$

This model automatically incorporates the volume dependence of Poisson's ratio and reduces to γ_{DM} for one-dimensional vibrations.

Many variations on the above formulations have been put forward, each trying to reduce the assumptions and approximations inherent in their derivation (e.g. Pastine, 1965; Leibfried and Ludwig, 1961; Knoppoff and Shapiro, 1969; Irvine and Stacey, 1975; Quareni and Mulargia, 1989). However, such approximate derivations of the Grüneisen parameter usually consider only first-order elastic interactions which are greatly simplified by radial symmetry and elastic isotropy and neglect any adiabatic corrections, however small; some neglect optical modes and consider acoustic modes as being independent of each other and non-dispersive—an assumption valid only at low temperatures. Of the models considered, all but Barron's approach are based upon Debye theory; the differences between the approximate formulations are generally just the differences in the treatment of averaging out the acoustic velocities, and therefore how Poisson's ratio varies with volume.

To assess the shortcomings in these previous analyses it is essential to compare their results with the complete and strictly defined γ that can be obtained from the exact analysis of the lattice dynamics of a model system.

3. Computer modelling

One of the first attempts at the computer simulation of γ was by Welch et al. (1978) who simulated the motion of atoms via molecular dynamics in which the potential range was effective within second neighbours at constant volume. Each computer experiment determined pressure as a function of temperature and energy for an individual atom at constant volume and a γ was derived which was found to be equivalent to the

γ of Leibfried and Ludwig (1961), which reduced to the free-volume γ when only nearest-neighbour interactions were considered.

Barton and Stacey (1985) also used molecular dynamics to obtain values for γ using potential models such as the Born–Mie potential function. They found no agreement with existing theoretical relations for the Grüneisen parameter and proposed a modified free-volume theory as the closest approximation which, at zero pressure, has a value approaching that of Barron.

In this paper, attempts have been made to provide a microscopic underpinning of the relation between γ and dK/dP, using lattice dynamical computer modelling employed in the code PARAPOCS. As with previous theoretical models, our simulations deal firstly with a simple monatomic cubic lattice and then the more complex NaCl structure. In both cases, simulations were performed at zero pressure and temperature and were constrained within the quasi-harmonic approximation.

4. Potential models

The four potential forms used in our calculations, based on the PARAPOCS code (Parker and Price, 1989), were

(1) the simple harmonic potential which takes the form

$$\Psi(r) = \frac{1}{2}k(r - r_0)^2 \tag{13}$$

where k is the harmonic spring constant, r is the interatomic separation and r_0 is the equilibrium separation at zero pressure—a full discussion of the properties of this special case is given by Stacey (1993);

(2) the Lennard–Jones potential with the form

$$\Psi(r) = \frac{A}{r^n} - \frac{B}{r^m} \tag{14}$$

where A and B are constants, n and m are integers and r is the interatomic separation: to within a constant term, the harmonic potential is equivalent to a Lennard–Jones potential with $n = -1$ and $m = -2$;

(3) the Morse potential with the form

$$\Psi(r) = A\{1 - \exp[-B(r - r_0)]\}^2 - A \qquad (15)$$

where A and B are constants and r_0 is the equilibrium interatomic separation;

(4) the Buckingham potential with the form

$$\Psi(r) = A \exp\left(-\frac{r}{B}\right) - \frac{C}{r^6} \qquad (16)$$

where A, B and C are constants and r is the interatomic separation. It can be shown analytically that for an harmonic potential at zero pressure $dK/dP = 1$. By setting the equilibrium interatomic separation to unity, it can be shown that for a Morse potential, $dK/dP = (1 + B)$ and is independent of the energy scaling factor A; and for the Lennard–Jones potential, $dK/dP = (m + n + 6)/3$, and $nA = mB$. In order to model dynamically stable equilibrated structures, the

harmonic potential was used to sample the $dK/dP = 1$ region, the Morse potential with suitably chosen values of B was used to sample the $dK/dP = 2$–4 region. For the Lennard–Jones potential we set $A = m$ and $B = n$, and chose suitable values of m and n to sample the $dK/dP \geqslant 4$ region.

5. Results

5.1. Pairwise interactions

The Grüneisen parameter was calculated at zero pressure by perturbing the volume of a monatomic cubic lattice and calculating the subsequent frequency shifts via Eq. (3). Special points $(q_x > q_y > q_z)$ in the first asymmetric Brillouin zone (Chadi and Cohen, 1973) were sampled, and
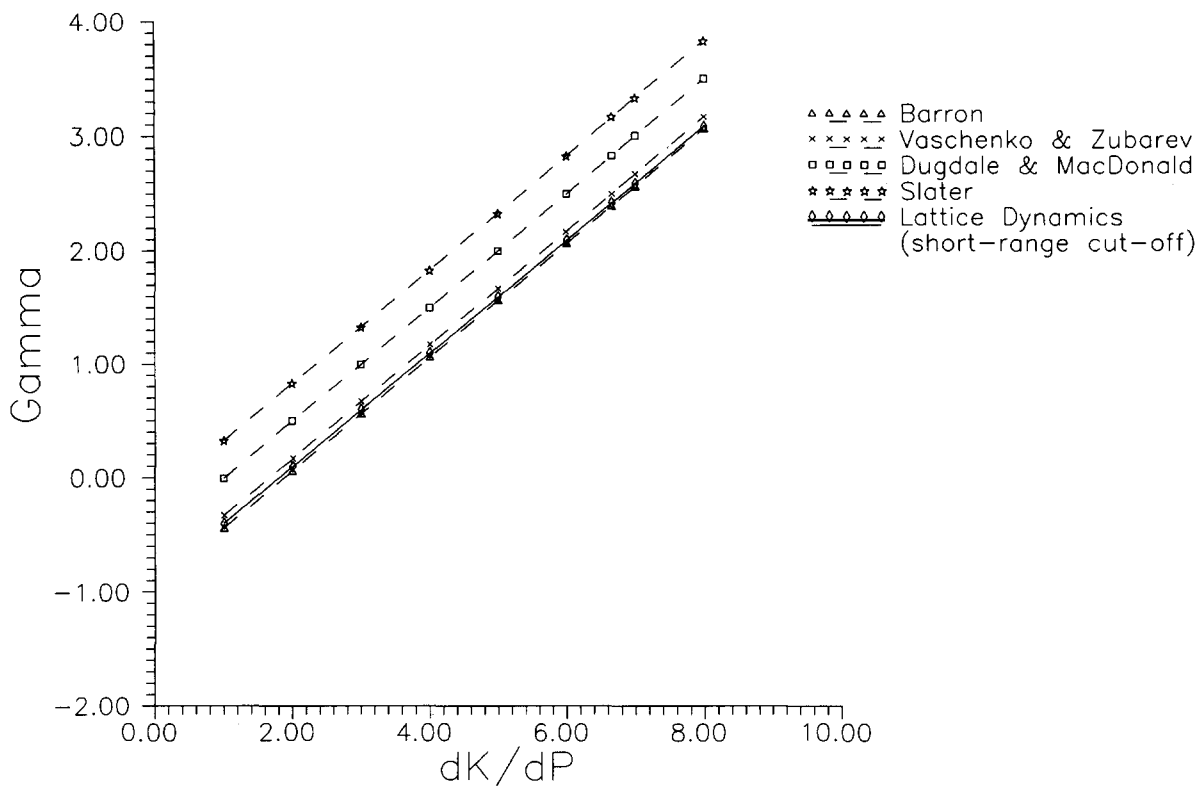

Fig. 1. Comparison of various approximations to γ with lattice dynamical γ (cut-off 1.3 lattice units).

only first nearest-neighbour interactions (cut-off range of 1.3 lattice units) were considered (see Table 1 and Fig. 1). Our calculations of $\gamma_{LD1.3}$, based on lattice dynamics, are in close agreement with Barron's approximate formulation and result in a linear relation of the form

$$\gamma_{LD1.3} = 0.5 \pm 0.02 \frac{dK}{dP} - 0.90 \pm 0.02 \qquad (17)$$

5.2. Long-range interactions

Having established an exact expression for γ for a system determined by first-neighbour interactions, we investigated the effect of including longer range interactions as would be found in real materials, and summed the potentials up to a cut-off of 15.0 lattice units. Although still based upon a simple lattice model, we would expect

TABLE 1

Comparison of various approximations to γ with the lattice dynamical Grüneisen parameter, γ_{LD} (cut-off 1.3 lattice units).

dK/dP	γ_{LD}	γ_S	γ_{DM}	γ_{VZ}	γ_{Barron}
1	−0.402	0.33	0.00	−0.33	−0.44
2	0.098	0.83	0.50	0.17	0.06
3	0.597	1.33	1.00	0.67	0.56
4	1.095	1.83	1.50	1.17	1.06
5	1.592	2.33	2.00	1.67	1.56
6	2.089	2.83	2.50	2.17	2.06
6.7	2.419	3.17	2.83	2.50	2.39
7	2.584	3.33	3.00	2.67	2.56
8	3.079	3.83	3.50	3.17	3.06

that such a simulation would better approximate real materials than considering nearest-neighbour interactions alone. If we were to find any significant effect in this case, then the result would undermine the usefulness of the simple free-
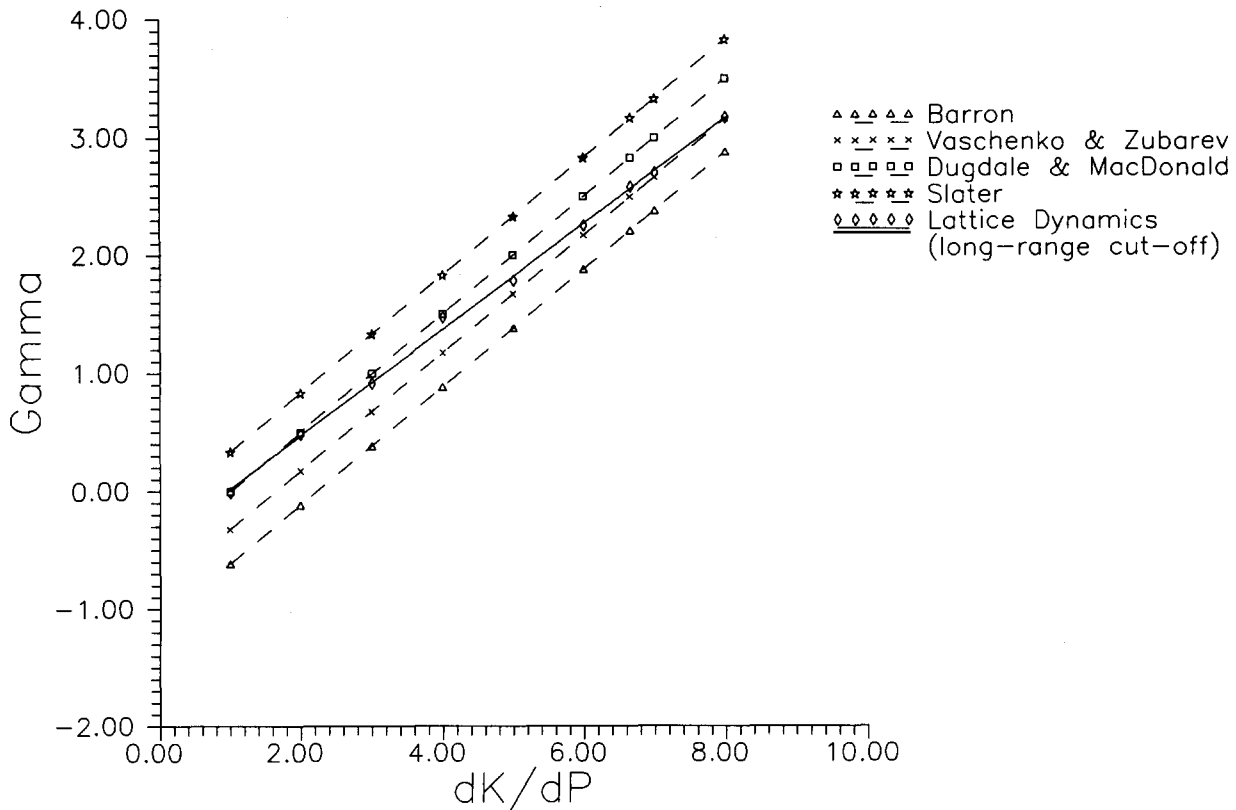

Fig. 2. Comparison of various approximations to γ with lattice dynamical γ (cut-off 15.0 lattice units).

TABLE 2

The variation of γ with dK/dP and $d\mu/dP$ for NaCl-type structures as a function of Buckingham potential parameters A and B ($C = 0$), with the ion charge magnitude maintained at $q = \pm 1$

A(eV)	B(Å)	γ	dK/dP	$d\mu/dP$
500	0.30	1.590	5.006	1.947
800	0.30	1.599	5.192	1.775
1000	0.30	1.613	5.260	1.719
2500	0.30	1.704	5.958	1.591
5000	0.30	1.792	5.958	1.562
800	0.35	1.629	5.266	1.831
1000	0.35	1.645	5.515	1.782
2500	0.35	1.743	5.914	1.676
5000	0.35	1.834	6.262	1.662
800	0.40	1.660	5.406	1.909
1000	0.40	1.679	5.825	1.865
2500	0.40	1.783	6.217	1.778
5000	0.40	1.878	6.668	1.781

volume theory which does not address the influence of long-range interactions upon γ. We found that $\gamma_{LD15.0}$ is significantly larger than $\gamma_{LD1.3}$, and in fact lies somewhere between γ_{DM} and γ_{VZ} (see Fig. 2) and takes the following linear form

$$\gamma_{LD15.0} = 0.45 \pm 0.03 \frac{dK}{dP} - 0.43 \pm 0.03 \qquad (18)$$

In this case our result is significantly different from Barron's long-range relation, presumably because of the greater uncertainty in the method of moments technique when extended to include long-range interactions. If our, albeit simple, long-range interaction model has some similarity to reality, our results could give credence to the relatively successful application of the free-volume formulation to real systems, for which
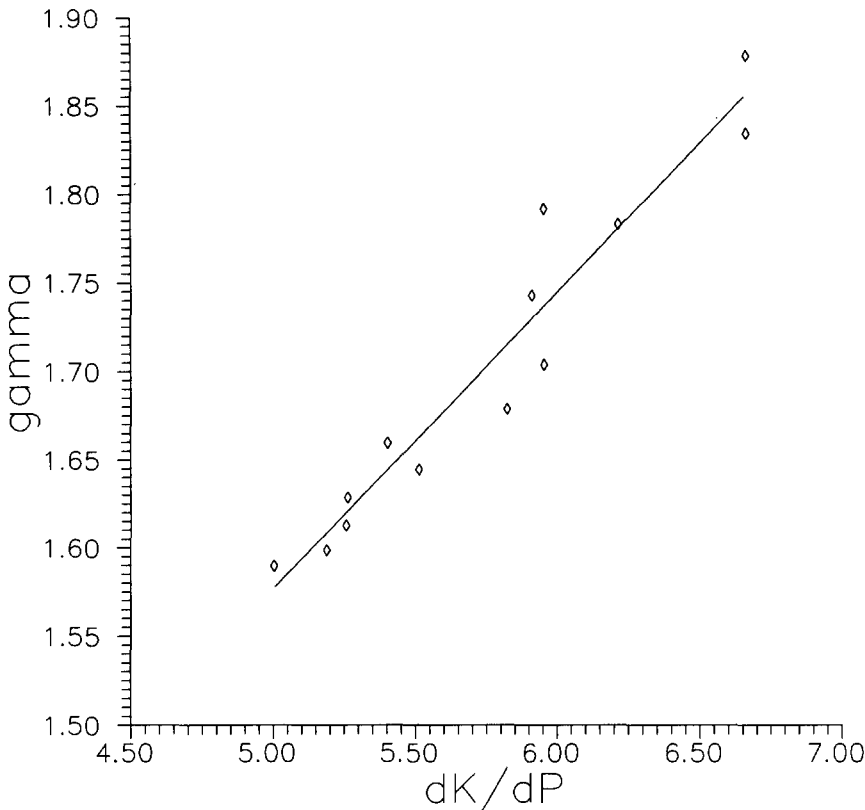

Fig. 3. γ vs. dK/dP for NaCl-type structures.

dK/dP usually lies between 3 and 6 (Anderson, 1989), since in this range our results are reasonably comparable with those of the free-volume approach. However, the free–volume theory was derived under the assumption that only nearest-neighbour interactions occur, so its universal success when applied to real materials is a result of good fortune since the effect of long-range interactions in real systems are not negligible.

5.3. The NaCl structure and the role of the shear modulus

The above calculations considered a monatomic simple cubic lattice, which, for short-range interactions has, by definition, a zero shear strength. Knopoff and Shapiro (1969) suggested, however, that the Grüneisen parameter should

have a significant shear modulus dependence (Eq. (6) above). Geophysically, this would be a vital consideration, since all real materials have a non-zero shear modulus.

In this section therefore, we consider the effect of the shear modulus on γ for a NaCl-type structure in order to establish the validity of the approximate expression given in Eq. (6). Using the PARAPOCS computer code and the Buckingham potential model, the structure was perturbed about its equilibrium position by slightly adjusting the ambient pressure, within the constraints described in the last section, such that $P \ll K$. The pressure dependence of both the incompressibility and shear modulus was then obtained from the resulting calculated elastic constants. The simulations were based on monovalent ions interacting via a Buckingham poten-
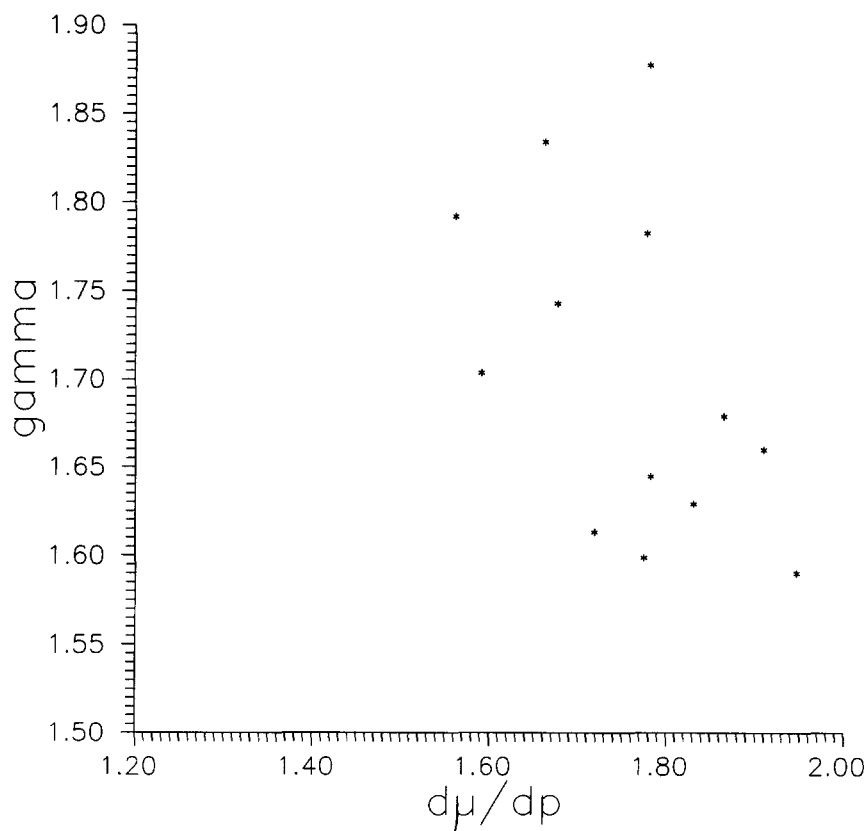

Fig. 4. γ vs. dμ/dP for NaCl-type structures.

tial model (Eq. (16)), set to include nearest neighbours only. By varying the parameters A and B of the potential different regions of dK/dP and $d\mu/dP$ space were sampled, and therefore the variation of γ with both dK/dP and $d\mu/dP$ could be investigated. The results are given in Table 2 and are illustrated in Figs. 3 and 4, where we note that the relationship between γ and dK/dP for the NaCl lattice is quite different from that for a simple cubic lattice. Futhermore, from these results it would appear that there is no obvious form for the dependence of γ on the $d\mu/dP$ as suggested by Knopoff and Shapiro (1969).

6. Summary

Computer calculations of the lattice dynamics of a monatomic cubic lattice with short-range nearest-neighbour, pairwise additive potentials have resulted in a linear relation between the Grüneisen parameter and dK/dP which confirms that found by Barron (1955) in preference to free-volume and other formulations. However, a different conclusion is reached for the long-range calculations where the free-volume approach is the closest approximation and that of Barron differs significantly. The possible success of the free-volume formulation may be because it gives similar results to lattice dynamics irrespective of the cut-off range in the $dK/dP = 3$-6 region—where most real materials lie. In addition, we have failed to find any simple relationship between γ and $d\mu/dP$ as suggested by Knoppoff and Shapiro, and, to a first approximation, this dependence may be ignored.

We conclude that it is not viable to use any of the approximations for γ described in this paper when making assumptions about the lower mantle or planetary interiors. We have found that γ is lattice dependent since the variation of γ with dK/dP for a simple cubic lattice is significantly different to that for NaCl-type structures. Therefore, there is no reason to expect that any of these approximations for γ would be valid for complex lower mantle oxides such as $MgSiO_3$-perovskite. In order to be able to predict how γ

varies within planetary interiors, we need either accurate experimental data at high P and T conditions or full computer calculations on the dynamics of the appropriate phases.

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