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Intrinsic anharmonicity in equations of state and thermodynamics of solids

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Abstract

Using thermodynamic perturbation theory, we derive a simple formalism for treating intrinsic anharmonic effects in solids. In this formalism, the central quantity is the intrinsic anharmonicity parameter a , which can be derived from vibrational spectroscopy or computer simulation. Advantages of our approach include (1) correct low- and high-temperature behaviour, (2) analyticity of all the thermodynamic functions and (3) the possibility of systematic incorporation of higher-order anharmonic effects. This approach can be used in studying equations of state and thermodynamics of solids in a wide temperature range. A detailed comparison with other approaches is given.

1. Introduction

The quasiharmonic approximation traditionally plays a central role in thermodynamic modelling and theory of equations of state of solids. In this approximation, thermodynamic properties are calculated from the vibrational spectrum, which is assumed to depend only on volume and not on temperature. However, the intrinsic anharmonic effects, ignored in this approximation and leading to the temperature dependence of phonon frequencies, become important at high temperatures (especially at low pressures). To illustrate this point, figure 1 shows experimental thermal expansion of MgO at 1 bar (circles) and *ab initio* calculations at 0, 50, 100, and 150 GPa in the quasiharmonic approximation and with the inclusion of intrinsic anharmonic effects. One can see that above 2000 K quasiharmonic theory grossly overestimates thermal expansion, but inclusion of intrinsic anharmonic effects restores agreement with experiment.

The treatment of intrinsic anharmonicity is a non-trivial problem, with no well established solution. Here we propose a simple approach based on thermodynamic perturbation theory of an anharmonic oscillator, derive the necessary equations, and perform numerical tests comparing results of our present approach with other approaches. The present formulation has correct behaviour in the low- and high-temperature limits and can be readily used in fitting equations of state and extrapolating thermodynamic properties of solids.

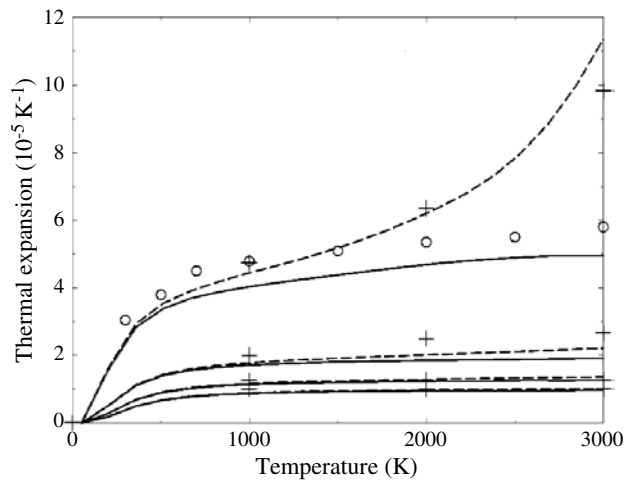


Figure 1. Thermal expansion of MgO. Results are presented for 0, 50, 100, and 150 GPa (from top to bottom): solid curves—calculations with intrinsic anharmonicity [1]; dashed curves—quasiharmonic model [1]; crosses—quasiharmonic calculations [2, 3]. Circles—experimental data at 1 bar [4].

2. Treatments of intrinsic anharmonicity

2.1. Classical treatment

The simplest way of treating intrinsic anharmonicity takes advantage of the fact that in the high-temperature expansion of the anharmonic free energy the lowest-order term is quadratic [5–7]. Ignoring higher-order terms, one writes

$$\frac{F_{\text{anh}}(V, T)}{3nk_{\text{B}}} = \frac{1}{2}aT^2, \quad (1)$$

where n is the number of atoms in crystal, k_{B} is the Boltzmann constant, and a is the so-called intrinsic anharmonicity parameter. Equation (1) contains an assumption that intrinsic anharmonic contributions from different modes are additive. This is clearly a simplification, but it has roots in physically sound arguments of Wallace [8]. To account for the strong decrease of intrinsic anharmonicity with pressure, the following volume dependence is usually assumed [5]:

$$a = a_0 \left(\frac{V}{V_0} \right)^m, \quad (2)$$

where a_0 is the intrinsic anharmonicity parameter at standard conditions, and $m = \frac{d \ln a}{d \ln V}$ is a constant.

One can easily find other anharmonic thermodynamic properties, such as the entropy, energy, isochoric heat capacity, thermal pressure, and bulk modulus:

$$\begin{aligned} \frac{S_{\text{anh}}}{3nk_{\text{B}}} &= -aT, & \frac{E_{\text{anh}}}{3nk_{\text{B}}} &= -\frac{1}{2}aT^2, & \frac{C_{V_{\text{anh}}}}{3nk_{\text{B}}} &= -aT, \\ \frac{P_{\text{anh}}}{3nk_{\text{B}}} &= -\frac{1}{2}a\frac{m}{V}T^2, & K_{Ta} &= P_a(1 - m). \end{aligned} \quad (3)$$

In equation (1), third- and higher-order terms are neglected. The validity of restricting the anharmonic free energy to the quadratic term can easily be tested. For this purpose we have

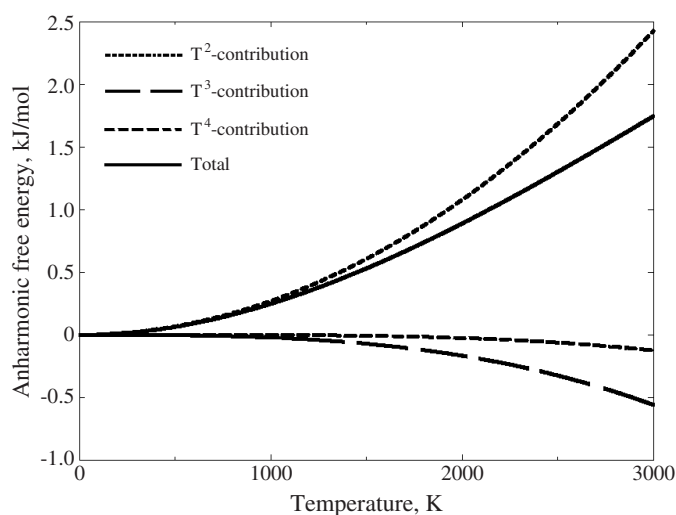


Figure 2. Intrinsic anharmonic free energy of MgO. Simulations were based on a rigid-ion pair potential model with atomic charges of +1.74 and -1.74 for Mg and O, respectively, and Buckingham short-range potentials (Oganov, unpublished) that were fitted to experimental data, but proved to describe *ab initio* energy surfaces well. A short-range cut-off of 8.4 \AA and long-range corrections were used. Simulations were performed on the cubic 512-atom supercell, with 1 fs timestep, 10 ps equilibration, and 20 ps production time. Calculations were performed at temperatures between 0 and 3000 K, with a 250 K interval. Tests with more accurate computational settings (4096-atom cell, 14.6 ps equilibration, 50 ps production, 10 \AA cut-off) indicate that errors of our calculated anharmonic energies are about 3%.

performed molecular dynamics simulations of MgO at a series of temperatures and *constant volume* corresponding to the experimental volume at ambient conditions. Such simulations are fully anharmonic and give direct access to the intrinsic anharmonic internal energy, from which we calculated the free energy. As can be seen from figure 2, quadratic term (1) is indeed dominant in the anharmonic free energy up to the melting point. Third- and fourth-order terms become non-negligible at very high temperatures, but F_{anh} still can be fitted well by a quadratic function (1). For the internal energy, higher-order terms amount to more than a half of the quadratic term at 3000 K.

The model just discussed works well at high temperatures and has been widely used [1, 5, 9]. However, there are problems: the linear anharmonic heat capacity equation (3) would overwhelm the harmonic term at low temperatures, leading to large errors in the thermal expansion coefficient and the Grüneisen parameter below $\sim 100 \text{ K}$.

The problem is that equations (1) and (3) are classical and completely ignore quantum vibrational effects, which determine low-temperature thermodynamics. Inclusion of quantum effects should suppress anharmonicity at low temperatures; e.g., for Debye crystals $C_{Va} \sim T^4$, and not $C_{Va} \sim T$ as it was in the classical equation (3). We are interested in a formalism that would include quantum effects and would lead to the correct classical limit (1) at high temperatures.

2.2. Quantum treatments

Wallace's theory. Wallace [8] has shown that in the first approximation intrinsic anharmonic effects can be incorporated by using the true (i.e. temperature-dependent) vibrational frequencies ω (or characteristic temperatures $\Theta_{VT} = \hbar\omega/k_B$) and substituting them into the (quasi)harmonic expression for the entropy of a harmonic oscillator. In the Einstein model

with $3nk_B$ oscillators one has

$$\frac{S(V, T)}{3nk_B} = -\ln\left(1 - \exp\frac{-\Theta_{VT}}{T}\right) + \frac{\Theta_{VT}}{T(\exp(\Theta_{VT}/T) - 1)}. \quad (4)$$

Equation (4) contains quasiharmonic and intrinsic anharmonic contributions, both of which include the desired quantum effects. We follow Gillet *et al* [7] and define the temperature-dependent characteristic temperature as

$$\Theta_{VT} = \theta \exp(aT), \quad (5)$$

where θ is the quasiharmonic (only volume-dependent) characteristic temperature, and the exponential factor contains the intrinsic anharmonicity parameter, the same as in equations (1)–(3). Equation (5) thus defines the physical meaning of this parameter as the logarithmic derivative of the vibrational frequency (or characteristic temperature) with respect to volume:

$$a = \left(\frac{\partial \ln \omega_{VT}}{\partial T}\right)_V = \left(\frac{\partial \ln \Theta_{VT}}{\partial T}\right)_V. \quad (6)$$

From equation (4) one can calculate the heat capacity C_V and (by integration) all the other thermodynamic properties. In the classical limit ($\frac{\Theta_{VT}}{T} \rightarrow 0$) equations (1) and (3) are easily derived from (4). For the anharmonic free energy, Wallace's approach gives only the T^2 -term; higher-order terms are absent.

Unfortunately, only S and C_V can be determined analytically in this approach—all the other functions have to be calculated using numerical integration. Due to this inconvenience, Wallace's approach has not been used as widely as it deserves (see [7] for some applications). On a fundamental level, Wallace's theory justifies equation (1), shows the physical meaning of the intrinsic anharmonicity parameter, and indicates that mode anharmonic contributions are approximately additive.

F-model. It would be more convenient if one could use quasiharmonic equations with temperature-dependent vibrational frequencies, but starting from the Helmholtz free energy, instead of the entropy—thus avoiding non-analytical integrals. This approach lacks the rigour of Wallace's theory and inevitably leads to slightly different results [8, 10], but has been widely used (see, e.g., [11]). We [10] found that, in order to give the correct classical limit (1), the temperature dependence of the frequencies should be modified:

$$\tilde{\Theta}_{VT} = \theta \exp\left(\frac{1}{2}aT\right). \quad (7)$$

Then for the free energy one has

$$\frac{F(V, T)}{3nk_B} = \frac{1}{2}\tilde{\Theta}_{VT} + T \ln\left(1 - \exp\frac{-\tilde{\Theta}_{VT}}{T}\right), \quad (8)$$

from which all the other thermodynamic functions can be derived (see [10] for analytical expressions).

Like Wallace's theory, this model (which we call the *F-model*, because it starts with the Helmholtz free energy F) incorporates quantum effects both in the quasiharmonic and intrinsic anharmonic contributions and has the correct classical limit (at $\frac{\tilde{\Theta}_{VT}}{T} \rightarrow 0$).

Deficiencies of the existing quantum treatments. Apart from the already mentioned problems, both approaches share one problem: for $a > 0$, the ratio $\frac{\Theta_{VT}}{T}$ (or $\frac{\tilde{\Theta}_{VT}}{T}$ in the *F-model*) does not decay to zero as $T \rightarrow \infty$, but at very high temperatures grows to infinity, and therefore the classical limit of equation (1) is never achieved. Both Wallace's approach and the *F-model* give meaningful results only at $aT < 0.05$.

Below we suggest an approach based on thermodynamic perturbation theory [6], which includes quantum vibrational effects, is computationally convenient (all the expressions are analytical), and is well behaved at high temperatures.

3. New approach

Let us consider a weakly anharmonic oscillator, described by the potential

$$U = \frac{1}{2}kx^2 + a_3x^3 + a_4x^4 + \dots, \quad (9)$$

with $k > 0$ and where x is the displacement from equilibrium.

As a reference system we consider a harmonic oscillator:

$$U_0 = \frac{1}{2}kx^2. \quad (10)$$

Using first-order thermodynamic perturbation theory [6],³ anharmonic free energy can be calculated as follows:

$$F_{\text{anh}} = \langle U - U_0 \rangle_0, \quad (11)$$

where averaging is performed over configurations sampled by the harmonic oscillator. Equation (11) suggests that effects of intrinsic anharmonicity can be described by additive corrections to quasiharmonic results.

3.1. Expressions in terms of displacement moments

By applying first-order thermodynamic perturbation theory, one obtains

$$F_{\text{anh}} = \langle U - U_0 \rangle_0 = \langle a_3x^3 + a_4x^4 + \dots \rangle_0 = a_4 \langle x^4 \rangle_0 + a_6 \langle x^6 \rangle_0 + a_8 \langle x^8 \rangle_0 + \dots \quad (12)$$

This expression is remarkable in that the moments of atomic displacements used are those of a harmonic oscillator, and can be easily calculated. Since the harmonic reference potential (10) is symmetric, only even-order terms are retained in (12). Higher-order moments become significant only at very high temperatures, so within the limits of applicability of the first-order perturbation theory it should be safe to consider only the first terms (often, the first term alone is sufficient). At high temperatures $\langle x^4 \rangle_0 \sim T^2$, so the anharmonic free energy is quadratic in temperature in the first approximation. Further terms in (12) are proportional to T^3 , T^4 , etc.

3.2. Expressions in terms of temperature

To make our expressions useful, one has to calculate the moments $\langle x^4 \rangle_0$, $\langle x^6 \rangle_0$, $\langle x^8 \rangle_0$, \dots , for a harmonic oscillator. Classical calculation of the moments would result in classical expressions for the free energy; however, if the moments are derived using quantum mechanics, the resulting thermodynamic quantities would automatically include the proper quantum corrections.

The internal energy E of a harmonic oscillator is a sum of kinetic (K) and potential (U) terms:

$$E = K + U. \quad (13)$$

The time-averaged internal energy at constant T is given by Einstein's formula:

$$\langle E \rangle = \left(\frac{1}{2}k_B\theta + \frac{k_B\theta}{\exp(\theta/T) - 1} \right) = 2\langle U \rangle = 2\langle K \rangle, \quad (14)$$

where the last two equalities follow from the virial theorem. As $\langle U \rangle = \frac{1}{2}k \langle x^2 \rangle_0$, one can see that

³ Here we use classical perturbation theory. However, in our case first-order quantum perturbation theory leads to exactly the same results.

$$\langle x^2 \rangle_0 = \frac{1}{k} \langle E \rangle = \frac{1}{k} \left(\frac{1}{2} k_B \theta + \frac{k_B \theta}{\exp(\theta/T) - 1} \right). \quad (15)$$

One can easily calculate higher-order moments. Below we derive $\langle x^4 \rangle_0$. Using simple manipulations,

$$\begin{aligned} \langle E^2 \rangle &= \langle (U + K)^2 \rangle = \langle U^2 \rangle + 2\langle UK \rangle + \langle K^2 \rangle \\ &= 2\langle U^2 \rangle + 2\langle U \rangle \langle K \rangle = 2\langle U^2 \rangle + 2\langle U \rangle^2 = 2\langle U^2 \rangle + 2\frac{1}{4} \langle E \rangle^2 \end{aligned}$$

and the well known (see e.g. [12]) relation

$$\langle E^2 \rangle = \langle E \rangle^2 + k_B C_V T^2,$$

we arrive at the equality

$$\langle U^2 \rangle = \frac{1}{4} \langle E \rangle^2 + \frac{1}{2} k_B C_V T^2,$$

and then

$$\langle x^4 \rangle_0 = \frac{4}{k^2} \langle U^2 \rangle = \frac{1}{k^2} [\langle E \rangle^2 + 2k_B C_V T^2]. \quad (16)$$

From (12) and (16), the anharmonic part of the free energy of an Einstein model to order T^2 can be written as follows:

$$\frac{F_{\text{anh}}}{3n} = \frac{a_4}{k^2} [\langle E \rangle^2 + 2k_B C_V T^2]. \quad (17)$$

To make sure that (17) in the high-temperature limit reduces exactly to (1), one has to set $\frac{a_4}{k^2} = \frac{a}{6k_B}$, where a is the intrinsic anharmonicity parameter, so we finally have:

$$\frac{F_{\text{anh}}}{3n} = \frac{a}{6k_B} [\langle E \rangle^2 + 2k_B C_V T^2]. \quad (18)$$

From (18), one trivially obtains anharmonic zero-point energy in the first approximation:

$$\frac{E_{\text{anh}}^{\text{zp}}}{3n} = \frac{a}{24} k_B \theta^2. \quad (19)$$

Note that the expression in brackets contains thermal energy and heat capacity of a *harmonic oscillator* with the characteristic temperature θ (not Θ_{VT} or $\tilde{\Theta}_{VT}$). For typical values of parameters ($a = 2 \times 10^{-5} \text{ K}^{-1}$, $\theta = 1000 \text{ K}$), this value amounts to only 0.17% of the harmonic zero-point energy.

Equation (18), the central equation of this paper, has been derived within the first-order thermodynamic perturbation theory. In the second order of thermodynamic perturbation theory one obtains an additional order T^2 contribution, proportional to a_3^2 and $\langle x^6 \rangle_0$ [13]. However, for practical purposes of fitting equations of state (18) is fully sufficient as it has correct limiting behaviours and effectively mimics the full order T^2 expression by using the correct intrinsic anharmonicity parameter.

4. Numerical tests—comparison between different approaches

Let us write explicitly the expressions for the most important functions, starting with the free energy of (18):

$$\frac{F_{\text{anh}}}{3nk_B} = \frac{a}{6} \left[\left(\frac{1}{2} \theta + \frac{\theta}{\exp(\theta/T) - 1} \right)^2 + 2 \left(\frac{\theta}{T} \right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) - 1)^2} T^2 \right]. \quad (20)$$

Based on this, in the appendix we list expressions for anharmonic contributions to other important thermodynamic functions.

Assuming some ‘typical’ values of parameters, we can estimate these functions and compare the results with those obtained using Wallace’s theory and the F -model (figure 3). At low temperatures all these approaches display the correct quantum behaviour. It can be seen that the present approach is the only one truly reducing to the classical limit at high temperatures. Already at the characteristic temperature there is hardly any difference between our approach and the classical one (figure 3), whereas the F -model and Wallace’s approach remain distinctly different even at temperatures twice as high. In fact, the F -model and Wallace’s approach never strictly attain the classical limit because of the pathological increase of $\frac{\Theta_V T}{T}$ at very high temperatures. The present approach has the advantages of giving correct low- and high-temperature limits and of being analytical and easily extendable to incorporate T^3 -, T^4 -, and higher-order terms. For fitting equations of state and thermodynamic properties of crystals, the simple form (20) (or its generalization to an arbitrary phonon spectrum) should usually be sufficient.

5. Discussion

The present formalism was developed mainly for applications to equations of state of solids. The importance of intrinsic anharmonicity for equations of state has been stressed in many works [1, 5, 7, 10, 14–16], but as some authors [17] maintain an opposite view, a clear discussion is useful.

Some materials (solids with soft modes and liquids) are intrinsically anharmonic at a very fundamental level: it is not possible to account for their stability within the quasiharmonic approximation. However, most solids seem to be ‘weakly anharmonic’ and describable to some extent by the quasiharmonic approximation; our perturbative approach is intended exactly for this case, and only for these materials does a discussion of the importance of intrinsic anharmonicity make sense. Our discussion will be illustrated by results on MgO.

The intrinsic anharmonicity parameter a is usually small (for MgO theoretical and experimental values are in the range $(1-2) \times 10^{-5} \text{ K}^{-1}$ at ambient conditions) and, consequently, the anharmonic contribution to $F(V, T)$ is small. In the case of MgO, we find that the anharmonic part of the thermal pressure is also small (for MgO, at most -2 to -3 GPa near the melting point [1]). However, for higher-order derivatives of $F(V, T)$ intrinsic anharmonicity can be significant. Thermal expansion is a good example: as shown in figure 1, intrinsic anharmonicity makes a major contribution to thermal expansion at 1 bar and high temperatures. However, on compression intrinsic anharmonicity decreases, and in MgO its contribution to thermal expansion becomes small at 50 GPa (see figure 1).

When fitting a P - V - T equation of state, it is highly desirable to include all available experimental data, especially at 1 bar, where precise determinations can be made for many properties. Ignoring intrinsic anharmonicity, one would either fail to reasonably describe high-temperature data, or be forced to ignore these data.

As shown by Holzapfel [11], the three common definitions of the Grüneisen parameter γ (via the thermal pressure P_{th} , thermal expansion α , and volume derivatives of the characteristic temperatures)

$$\gamma_{\alpha}(V, T) = \alpha \frac{K_T V}{C_V} \quad (21a)$$

$$\gamma_P(V, T) = \frac{P_{\text{th}}}{E_{\text{th}}} V \quad (21b)$$

$$\gamma_{\text{qh}}(V) = \left\langle -\frac{d \ln \theta_i}{d \ln V} \right\rangle \quad (21c)$$

(where E_{th} is thermal energy, and K_T is the bulk modulus) are different whenever

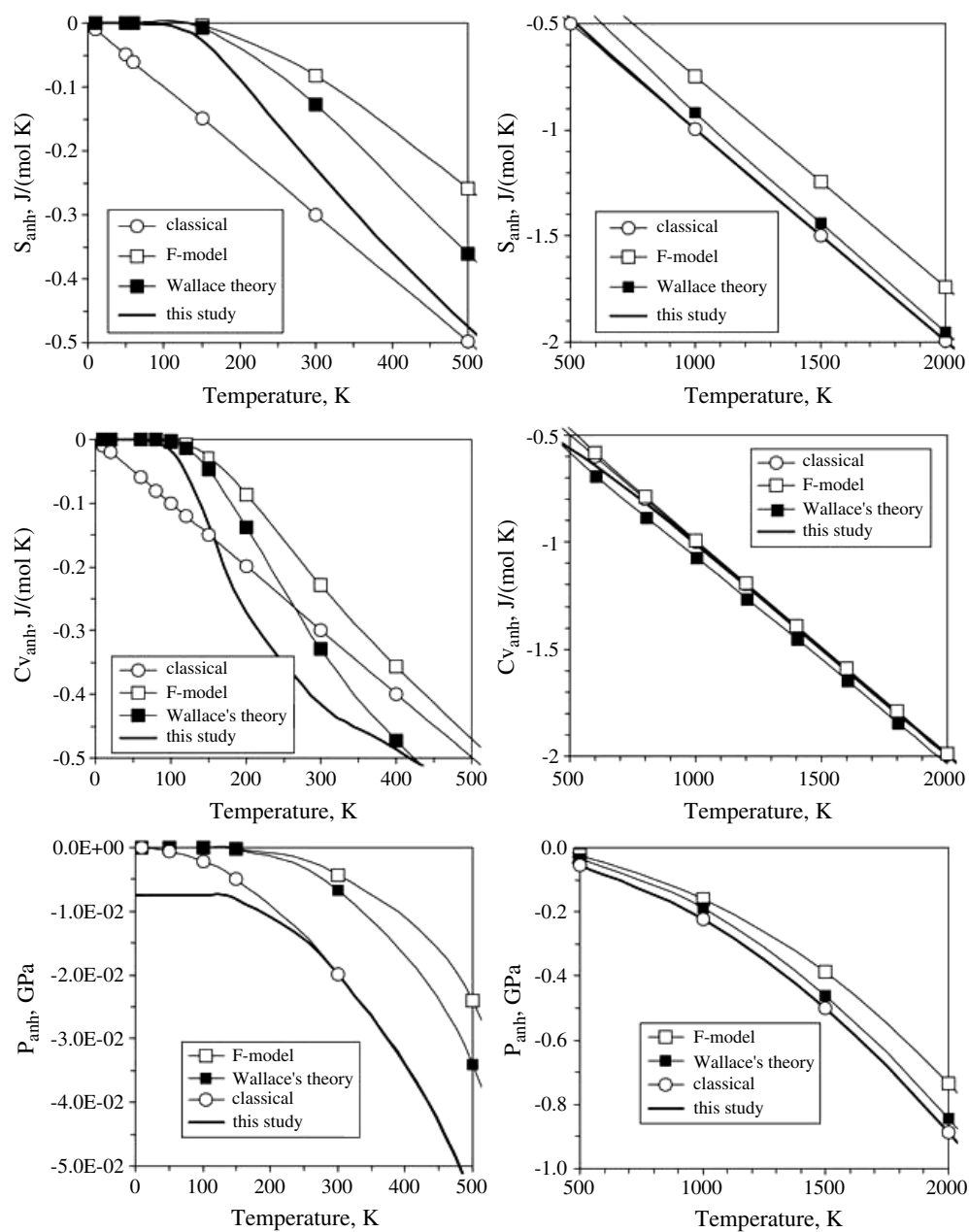


Figure 3. Anharmonic thermodynamic functions. These calculations are for a crystal with two atoms in the unit cell and constant $V = 11.248 \text{ cm}^3 \text{ mol}^{-1}$. Other parameters used are $a = 2 \times 10^{-5} \text{ K}^{-1}$, $m = 5$, $\gamma = 1.5$, and $\theta = 1000 \text{ K}$. One can see a small anharmonic zero-point pressure in the present approach (this is physically correct); this pressure component was neglected in *F*-model and Wallace's theory-based calculations, and is absent by definition in classical treatment.

intrinsic anharmonicity is present⁴. The differences increase with temperature: note that definitions (21a) and (21b) are now temperature dependent, whereas (21c) is not. The different

⁴ Except for the rather artificial case when intrinsic anharmonicity is volume-independent.

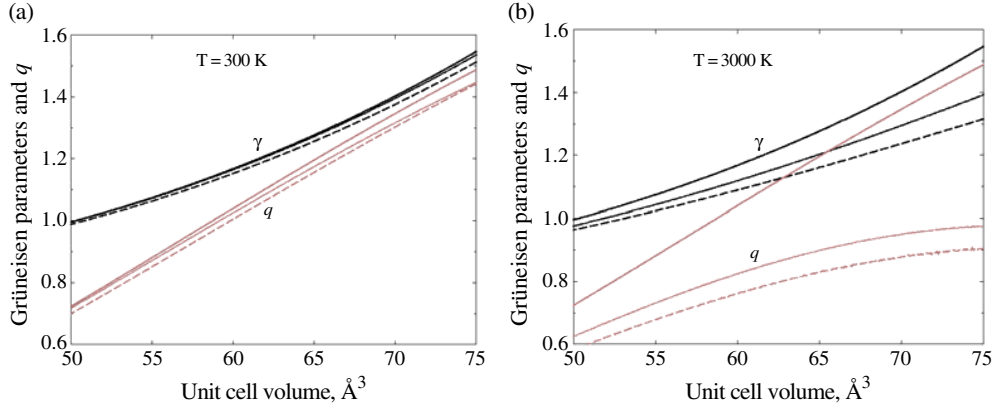


Figure 4. Grüneisen parameters and q of MgO (a) at 300 K and (b) at 3000 K. Results of *ab initio* simulations [1]. Black curves— γ ; grey curves— q . Solid curves— γ_{qh} ; dotted curves— γ_p ; dashed curves— γ_α .

(This figure is in colour only in the electronic version)

definitions of the Grüneisen parameter, along with the corresponding logarithmic volume derivatives,

$$q = \left(\frac{\partial \ln \gamma}{\partial \ln V} \right)_T, \quad (22)$$

are shown in figure 4. One can see a significant temperature dependence (at constant volume) of γ_α and γ_p . The corresponding q manifest a very strong temperature dependence even at pressures as high as ~ 150 GPa—quite contrary to the expectation of Stacey and Isaak [17] that ‘ q is also effectively independent of T at constant V ’.

To summarize, in certain situations (for liquids, soft-mode materials, or for high-order properties such as α , γ , or q , especially at high temperatures) intrinsic anharmonicity can play an important role. It is often necessary to account for intrinsic anharmonicity when constructing accurate thermal equations of solids. The conventional classical approximation (equations (1) and (3)) works well at high temperatures, but produces unphysical results in the low-temperature region. Here we have derived a simple analytical formalism with correct low- and high-temperature limits. This formalism can be used for constructing equations of state of solids in a wide temperature range.

Acknowledgments

Calculations used for figure 2 were performed with the DL-POLY code, a package of molecular simulation routines written by W Smith and T R Forester, copyright The Council for the Central Laboratory of the Research Councils, Daresbury Laboratory at Daresbury, Nr Warrington (1996). Useful discussions with W B Holzappel and R Monnier and funding from RFBR (grant No 02-05-64062) are gratefully acknowledged.

Appendix. Anharmonic thermodynamic functions

$$\frac{S_{anh}}{3nk_B} = -\frac{a}{2} \times \frac{\theta^3}{T^2} \times \frac{\exp \frac{\theta}{T} (\exp \frac{\theta}{T} + 1)}{(\exp \frac{\theta}{T} - 1)^3} \quad (A.1)$$

$$\frac{E_{\text{anh}}}{3nk_{\text{B}}} = \frac{a}{24} \times \frac{\theta^2}{T} \times \frac{T \exp \frac{3\theta}{T} + 9T \exp \frac{2\theta}{T} - 12\theta \exp \frac{2\theta}{T} - 9T \exp \frac{\theta}{T} - 12\theta \exp \frac{\theta}{T} - T}{(\exp \frac{\theta}{T} - 1)^3}, \quad (\text{A.2})$$

$$\frac{Cv_{\text{anh}}}{3nk_{\text{B}}} = -\frac{a}{2} \times \left(\frac{\theta}{T}\right)^3 \times \frac{\exp \frac{\theta}{T} (\theta \exp \frac{2\theta}{T} - 2T \exp \frac{2\theta}{T} + 4\theta \exp \frac{\theta}{T} + 2T + \theta)}{(\exp \frac{\theta}{T} - 1)^4}, \quad (\text{A.3})$$

$$\frac{P_{\text{anh}}}{3nk_{\text{B}}} = \frac{a}{24} \times \frac{m\theta^2(-\exp \frac{3\theta}{T} - 9\exp \frac{2\theta}{T} + 9\exp \frac{\theta}{T} + 1)}{V(\exp \frac{\theta}{T} - 1)^3} + \frac{a}{12} \times \frac{\gamma\theta^2(T \exp \frac{3\theta}{T} + 9T \exp \frac{2\theta}{T} - 6\theta \exp \frac{2\theta}{T} - 9T \exp \frac{\theta}{T} - 6\theta \exp \frac{\theta}{T} - T)}{VT(\exp \frac{\theta}{T} - 1)^3}. \quad (\text{A.4})$$

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