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ANALYSIS OF THERMAL EXPANSIVITY BASED ON INTRINSIC ANHARMONICITY

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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 quality is the intrinsic anharmonicity parameter a, which can derived from vibrational spectroscopy or computer simulation. Advantages of our approach include (l) 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.

I. INTRODUCTION

The quasiharmonic approximation traditionally plays a central role in thermodynamic modeling and theory of equations of state of solids. In this approximation, thermodynamic properties are calculated from the vibrational spectrum. This 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). 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 [1]. One can see that above 2000k 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 behavior in the low and high temperature limits and can be readily used in fitting equations state and extrapolating thermodynamic properties of solids.

II. TREATMENTS OF INTRINSIC ANHARMONICITY

Thermal expansion on MgO. Results are presented for 0, 50, 100 and 150 GPa (from top to bottom) solid curves- calculations with intrinsic anharmonicity [1], dashed curvers- quasiharmonic model [1], Crosses- quasiharmonic calculations [2,3] circles- experimental data at 1 bar [4].

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 in quadratic [5-7]. Ignoring higher order terms one writes.

$$\frac{F_{anh}(V,T)}{3nk_B} = \frac{1}{2}aT^2 \tag{1}$$

Where is the number of atoms in crystal, kB is the Boltzmonn 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].

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

Where a_0 is the intrinsic anharmonicity parameter at standard conditions, and

$$m = \frac{d\ln a}{d\ln v} \text{ is a constant} \tag{3}$$

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

$$\frac{S_{anh}}{3nK_B} = -aT, \qquad \frac{E_{anh}}{3nK_B} = -\frac{1}{2}aT^2, \tag{4}$$

$$\frac{C_{Vanh}}{3nK_B} = -aT, \qquad \frac{P_{anh}}{3nK_B} = -\frac{1}{2}a\frac{m}{v}T^2, \tag{5}$$

$$KT_a = P_a(1-m) \tag{6}$$

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 performed molecular dynamics simulations [1] of MgO at a series of temperatures and constant volume corresponding to the experimental volume of ambient conditions. Such simulations are fully anharmonic and give direct access to the intrinsic anharmonic internal energy. From which we calculated the free energy. 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 Fanh stile can be fitted well by a quadratic function (1). For the internal energy, higher terms amount to more than a half of the quadratic term at 3 000k.

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 Eq. (5) would over whelm the harmonic term at low temperatures, leading to large errors in the thermal expansion coefficient and the Gruneisen below ~ 100k. The problem is the equations (1) and (5) are classical 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}~T^4, and not C_{va}~T as it was in the classical equation (5). We are interested in a formalism that would include quantum effects and would lead to the correct classical limit (1) and high temperatures.

2.2 Quantum Treatment

Wallace [8] has shows that in the first approximation in intrinsic an harmonic effects can be incorporated by using the true (i.e.) temperature dependent) vibrational frequencies w (or characteristic temperatures $\Theta VT=hw/k_B$ and substituting them into the quasiharmonic expression for the entropy of a harmonic oscillator. In the Einstein model with 3nKB oscillators one has.

$$\frac{S(V.T.)}{3nk_B} = -In\left(1-\exp\frac{-\Theta_{VT}}{T}\right)+\frac{\Theta_{VT}}{T\left(\exp\Theta_{VT}/T\right)-1} \qquad (6)$$

Eg. (6) contains quasiharmonic and intrinsic anharmonic contributions both of which include the desired quantum effects. Gillet et
al. [7] and define the temperature dependent characteristic temperature as

$$\Theta_{VT}=\theta\exp(aT) \qquad (7)$$

Where θ is the quasiharmonic (only volume dependent) characterstic temperature, and the exponential factor contains the intrinsic anharmonicity parameter the same as in equation (1-5). Equation (7) thus defines the physical meaning of this parameter as the logarithmic derivative of the virbational frequency (or characteristic temperature) with respect to volume.

$$a=\left(\frac{\partial\ln w_{VT}}{\partial T}\right)_V=\left(\frac{\partial\ln\Theta_{VT}}{\partial T}\right)_V \qquad (8)$$

From eq. (6) one calculate the heat capacity Cy and (by integration) all the other themodynamic properties. In the classical limit $\left(\frac{\Theta_{VT}}{T}\right)\to 0$ eqa, (1) and (5) are easily derived from (6) for the anharmonic free energy, wallace's approach gives only the T^2 term, higher terms are absent. Only S and Cv can be determined analytically in this approach all the other functions have to be calculated using numerical integration. Due to this in convenience, 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), show the physical meaning of the intrinsic anharmonicity are approximately additive; it would be more convenient if one could use quasiharmonic equations (eqs) with temperature dependent vibrational frequencies, but starting from the Helmholtz free energy, instead of the entropy-thus avoiding n on-analytical integrals. This approach lacks the rigor of Wallace's theory and inevitably leads to slightly different results [8/ 10], but has been widely used [11]. We [10] found that, in order to give the correct classical limit (1), the temperature dependence of the frequencies should be modified.

$$\left(\frac{\Theta_{VT}}{T}\right) = \theta \exp\left(\frac{1}{2}\alpha T\right) \tag{9}$$

Then for the free energy one has

$$\frac{F(V.T.)}{3nK_B} = \frac{1}{2}\Theta_{VT} + TIn\left(1-\exp\frac{-\Theta_{VT}}{T}\right) \tag{10}$$

From which all the other thermodynamic functions can be derived (40) from 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 $\left(\frac{\Theta_{VT}}{T}\right) \to 0$

Apart from the already mentioned problems, both approaches share one problem, for a>0, the ratio $\frac{\Theta_{VT}}{T}(or\ \frac{\Theta_{VT}}{T}\ \text{in the F-model})$ does not decay to zero as $T \to \infty$, 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 T<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.

III. NEW APPPROACH

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

$$U = \frac{1}{2}kx^2 + a_3x^3 + a_4x^4 + \ldots\ldots\ldots \tag{11}$$

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

As a reference system we consider a harmonic oscillator.

$$U_0 = \frac{1}{2}kx^2 \tag{12}$$

Using first-order thermodynamic perturbation theory [6]^3 , an harmonic free energy can be calculated as follows.

$$f_{anh} = U - U_0 > 0 \qquad (13)$$

Where averaging is performed over configurations sampled by the harmonic oscillator. Eqns. (13) suggests that effects of intrinsic anharmonicity can be described by additive corrections to quasiharmo nic results.

3.1 Expressions in Terms of Displacement Moments

By applying first order thermodynamic perturbation theory, one obtains

$$f_{anh} = U - U_0 > 0 = \left(a_3 x^3 + a_4 x^4 + \ldots\ldots\ldots\right)0 = a_4 x^4 0 + a_6\left(x^6\right)0 + a_8\left[x^8\right]0 + \qquad (14)$$

This expression is remarked in that the moments of atomic displacements used are those of a harmonic oscillator and can be easily calculated. Since the harmonic reference potential (12) is symmetric, only even-order terms are retained in (14). Higher- order moments becomes 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 higher temperature $\left(x^4\right)0 \sim T^2$, so the an harmonic free energy is quadratic in temperature in the first approximation. Further terms in (14) are proportional to T^3, T^4 etc.

3.2 Expressions in Terms of Temperature

One has to calculate the moments $(x^4)_0$, $(x^6)_0$, $(x^8)_0$ …. for a harmonic oscillator.

The integral energy E of a harmonic oscillator is a sum of kinetic (k) and potential (U) terms.

$$E=K+U \qquad (15)$$

The time-averaged integral energy at constant T is given by Einstein's formula.

$$E = \frac{1}{2} K_B \theta + \frac{K_B \theta}{\exp\,(\theta / T) - 1} = 2(U) = 2(k) \qquad (16)$$

Where the last equalities. Follows from the virial theorem. As

$$(U) = \frac{1}{2} K \left(x^2\right)_0 \text{, one can seen that} \qquad (17)$$

$$\left(x^2\right)_0 = \frac{1}{2}(E) = \frac{1}{2}\left(\frac{1}{2} K_B \theta + \frac{K_B \theta}{\exp\left(\theta / T - 1\right)}\right)$$

One can easily calculate higher-order moments. Below we derive (x^4) 0 using simple manipulations.

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

And the well known (see e.g.)

And the well known [12] relation.

$$\left(E^2\right)=\left\{E^2\right\}+K_B C_V T^2$$

We arrive at the equality

$$\left(U^2\right)=\frac{1}{4}\left(E^2\right)+\frac{1}{2}K_B C_V T^2$$

And than

$$\left(x^4\right)_0=\frac{4}{k^2}\left(U^2\right)=\frac{1}{K^2}\left[\left(E^2\right)+2k_B C_V T^2\right] \tag{18}$$

From (14) and (18), the harmonic part of the free energy of an Einstein model to order T^2 can be written as follows.

$$\frac{F_{anh}}{3n}=\frac{a_4}{K^2}\left[(E)^2+2k_B C_V T^2\right] \tag{19}$$

To make sure that (19) 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 (aharmonicity) parameter.

$$\frac{F_{anh}}{3n}=\frac{a}{6K_B}\left[(E)^2+2k_B C_V T^2\right] \tag{20}$$

From (20), one trivially obtains anharmonic zero point energy in the first approximation.

$$\frac{E_{anh}^{ZP}}{3n}=\frac{a}{24}k_B\theta^2 \tag{21}$$

That the expression in brackets contains thermal energy and heat capacity of a harmonic oscillator with the characteristic temperature θ(not Θ_{VT} or Θ_{VT}). For typical values of parameters ($a=2.0 \times 10^{-5}k^{-1}$) $\theta=1000k$. This value amounts to only 0.17% of the harmonic zero-point energy. Eq (20), the central equation of their paper, has been derived with in 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 $(x^6)_0$. However the practical purposes of fitting equation of state (20) 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.

IV. NUMERICAL TESTS- COMPARISON BETWEEN DIFFERENT APPRAOCHES

Let us write explicitly the expressions for the most important functions, starting with the free energy of (20).

$$\frac{F_{anh}}{3nk_B}=\frac{a}{6}\left[\left(\frac{1}{2}\theta+\frac{\theta}{\exp\left(\frac{\theta}{T}\right)-1}\right)^2+2\left(\frac{\theta}{\mathrm{T}}\right)^2\frac{\exp\left(\frac{\theta}{\mathrm{T}}\right)}{\left(\exp\left(\frac{\theta}{\mathrm{T}}\right)-1\right)^2}T^2\right] \qquad (22)$$

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. 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 temperature. Already at the characteristic temperature there is hardly any difference between our approach and the classical one, 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

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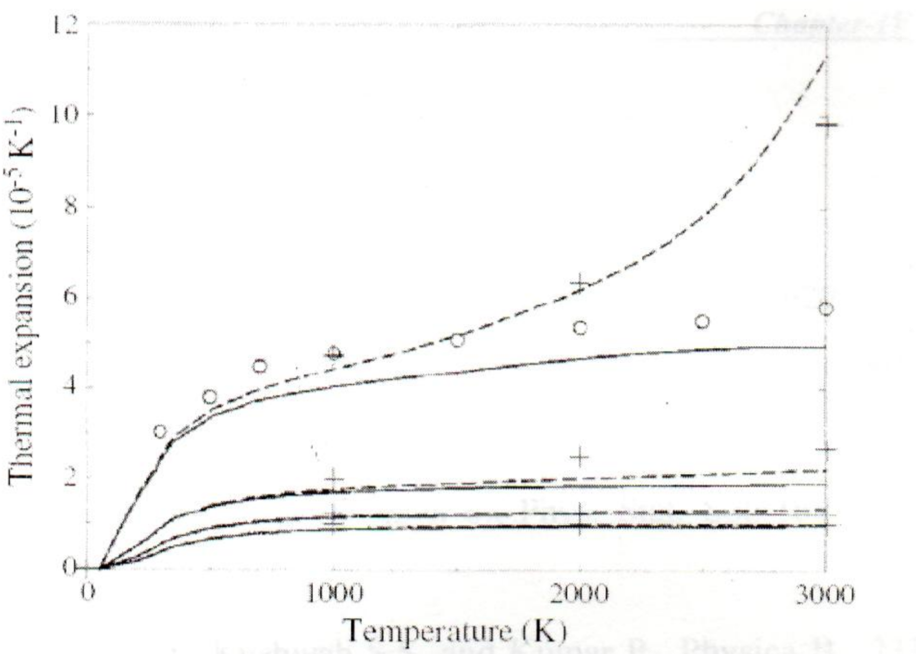

Figure 4.1 Thermal expansion of MgO. Graph is presented for 0, 50, 100, and 150 GPa (from top to bottom): solid curves - calculation with intrinsic anharmonicity [31]; dashed curves – quasiharmonic model [1]; crosses – quasiharmonic calculations [32, 33], circles – experimental data at 1 bar.

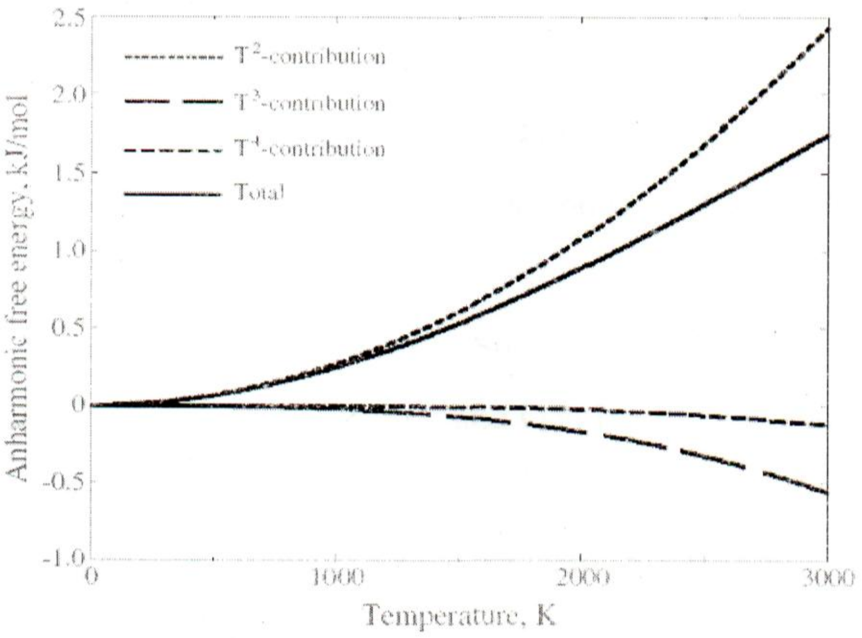

Figure 4.2 Intrinsic anharmonic free energy of MgO.

V. DISCUSSION

The present formalism was developed mainly for application to equation of state of solids. The importance of intrinsic anharmonicity for equation of state has been stressed in many ways.

Some mentioned (solids with soft models and liquids are intrinsically anharmonic at a very fundamental level. It is not possible to account for their stability within 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. Our discussion will be illustrated by results on MgO.

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