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Anharmonic phonon quasiparticle theory of zero-point and thermal shifts in insulators: Heat capacity, bulk modulus, and thermal expansion

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The quasiharmonic (QH) approximation uses harmonic vibrational frequencies $\omega_{Q,H}(V)$ computed at volumes V near V_0 where the Born-Oppenheimer (BO) energy $E_{\rm el}(V)$ is minimum. When this is used in the harmonic free energy, QH approximation gives a good zeroth order theory of thermal expansion and first-order theory of bulk modulus, where $n^{\rm th}$-order means smaller than the leading term by ϵ^n, where $\epsilon = \hbar\omega_{\rm vib}/E_{\rm el}$ or $k_BT/E_{\rm el}$, and $E_{\rm el}$ is an electronic energy scale, typically 2 to 10 eV. Experiment often shows evidence for next-order corrections. When such corrections are needed, anharmonic interactions must be included. The most accessible measure of anharmonicity is the quasiparticle (QP) energy $\omega_Q(V,T)$ seen experimentally by vibrational spectroscopy. However, this cannot just be inserted into the harmonic free energy F_H. In this paper, a free energy is found that corrects the double-counting of anharmonic interactions that is made when F is approximated by $F_H(\omega_Q(V,T))$. The term "QP thermodynamics" is used for this way of treating anharmonicity. It enables $(n+1)$-order corrections if QH theory is accurate to order n. This procedure is used to give corrections to the specific heat and volume thermal expansion. The QH formulas for isothermal (B_T) and adiabatic (B_S) bulk moduli are clarified, and the route to higher-order corrections is indicated.

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I. INTRODUCTION

In nonmagnetic, insulating materials, thermodynamic behavior is controlled by vibrational excitations, which are often close to harmonic. There is a unique and correct version of harmonic theory, based on Taylor-expanding the Born-Oppenheimer (BO) energy $E_{\rm el}(\{\vec{R}_\ell\})$ around the atomic coordinates $\{\vec{R}_{\ell,0}\}$ of a crystal with volume V. The BO energy is a "ground-state" property, and the main target of density functional theory (DFT). This gives normal mode eigenvectors and frequencies $\omega_{Q,H}(V)$, where the index $Q=\{\vec{Q},j\}$ labels the states; $\vec{Q}$ runs over the N wave vectors of the Brillouin zone, and j runs over the $3n$ branches. These states can be called "noninteracting quasiparticles." However, in this paper, the term quasiparticle (QP) will be reserved for the vibrational resonances seen experimentally. These differ from harmonic eigenfrequencies because higher-order ("anharmonic") terms in the Taylor expansion are not negligible.

In this paper, the term "harmonic" will refer to the unique correct harmonic limit, further specialized to the case when the volume is chosen to be V_0, where the BO energy is minimum. It is useful also to know the harmonic normal modes [and their frequencies $\omega_{Q,H}(V)$] at other volumes; this is the "quasiharmonic" (QH) theory. The harmonic approximation is a good starting point, successfully implemented by "*ab initio*" DFT calculations [1], and gives a good zeroth-order approximation for things like specific heat, $C_P(T)$. Vibrational spectroscopy [2] of reasonably pure crystals most often sees reasonably sharp Lorentzian resonances. They can be assigned a wave vector $\vec{Q}$, and are expected to show a one-to-one correspondence with the harmonic normal modes. They are the QP's of this paper. The central frequency ω_Q (the QP frequency, or energy) is T dependent. There is good evidence from theory-experiment comparisons [3] that the QH energy $\omega_Q(V)$, evaluated at the correct thermally expanded volume $V(T)$ at higher T, does not reproduce well the measured thermal shifts $\Delta\omega_Q$ of QP energies $\omega_Q(V,T)$. There is an anharmonic thermal shift, additional to and different from, the pure volume-related shift of QH theory, and it is often significant at higher T.

Terminology is not universally agreed upon. Cowley [4], in his seminal paper, derived the modern Matsubara perturbation theory for anharmonic effects. He occasionally uses the word "quasiharmonic" to denote what is here called "quasiparticle." In recent literature, QH most often denotes use of $\omega_{Q,H}(V)$ from $T=0$ DFT. Occasionally, papers about anharmonic theory still use "QH" and "QP" interchangeably when referring to approximate normal modes, $\omega_Q(V,T)$, which are here called QP.

The QP relaxation rate $1/\tau_Q$ is the full width at half maximum of the spectroscopic Lorentzian line. In pure crystals, it lies outside harmonic theory, and is also T dependent. This paper is about extracting additional thermodynamic information from the temperature dependence of ω_Q, ignoring $1/\tau_Q$. This suffices for most low-order thermal corrections. I will call this "quasiparticle thermodynamics." It differs from "quasiharmonic thermodynamics." Deviations from harmonic vibrations are responsible for thermal shifts of many properties. The ones of prime concern in this paper are C_P and C_V (constant pressure and constant volume), bulk modulus B_T and B_S (isothermal and adiabatic), and volume expansion $V(T)$ and $\alpha=(1/V)dV/dT$ (constant pressure). Good general discussions can be found in older literature [4–8].

There are two main ideas in QP theory: (1) low-lying excitations correspond 1-to-1 with a noninteracting single-particle picture; they have QP energies $\hbar\omega_Q(V,T)$ and mode occupancies $\langle\hat{n}_Q\rangle$. (2) The low-energy dynamics can be described as the dynamics, in space and time, of the mode occupancy. QP theory can fail in at least two ways. (a) The resonance can be very non-Lorentzian so that ω_Q is poorly defined. (b) Correlated occupancy $\langle\hat{n}_Q\hat{n}_{Q'}\rangle - \langle\hat{n}_Q\rangle\langle\hat{n}_{Q'}\rangle$ may

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become important. In this paper, n_Q denotes the equilibrium (Bose-Einstein) mean occupancy $[\exp(\hbar\omega_Q(V,T)/k_BT)-1]^{-1}$, $n_{Q,H}$ its harmonic or QH version, and $\langle\hat{n}_Q\rangle$ denotes the actual occupancy in a general ensemble, not necessarily equilibrium. Entropy plays a special role [9], since it is just $1/N$ times the logarithm of the number of ways of distributing $\langle n\rangle N\hbar\omega$ of excitation energy into N oscillators of frequency ω,

$$\hat{S} = k_B \sum_Q [(\langle\hat{n}_Q\rangle + 1)\ln(\langle\hat{n}_Q\rangle + 1) - \langle\hat{n}_Q\rangle \ln\langle\hat{n}_Q\rangle]. \quad (1)$$

The equilibrium occupancy n_Q is the one that maximizes Eq. (1) at fixed energy, and the thermodynamic entropy $S(T)$ is given by Eq. (1) with $\langle\hat{n}_Q\rangle \to n_Q$. When harmonic frequencies $\omega_{Q,H}$ are used in n_Q, the result is the harmonic entropy S_H. When the T-dependent QP energies are used in n_Q, and inserted in $S(T)$, an accurate improvement of the thermodynamics is achieved. This will be denoted $S_{\rm QP}$. The same replacement does not work for the harmonic free energy. If $\omega_Q(T)$ is inserted into F_H, the resulting F does not obey $-dF/dT = S_{\rm QP}$. A "correct" QP free energy that does agree with $S_{\rm QP}$ is found as follows. The thermodynamic energy $U(T) = F + TS$ in harmonic theory is

$$U_H = \sum_Q \hbar\omega_{Q,H}(n_{Q,H} + 1/2). \quad (2)$$

When normal mode frequencies acquire an anharmonic correction, $\omega_{Q,H} \to \omega_Q(T)$, the energy acquires a correction [10],

$$U_{\rm QP} = \sum_Q \hbar\omega_Q(T)(n_Q + 1/2) - (1/2)\sum_Q \hbar[\omega_Q(T) - \omega_{Q,H}](n_Q + 1/2). \quad (3)$$

This corrects for the double-counting of the interaction, but only in leading anharmonic approximation where [7]

$$\omega_Q(T) - \omega_{Q,H} \equiv \Delta_Q^{(2)} = \frac{1}{N}\sum_{Q'}\left(\frac{\partial\omega_Q}{\partial n_{Q'}}\right)_0\left(n_{Q'} + \frac{1}{2}\right), \quad (4)$$

where the superscript $\Delta^{(2)}$ indicates the lowest-order correction (second-order perturbation theory), which comes from third- and fourth-order anharmonicity. Further details are in Appendix. Here, $\partial\omega_Q/\partial n_{Q'}$ is a T-independent anharmonic interaction function. In higher-order perturbation theory, there are presumably additional shifts of the type

$$\Delta_Q^{(3)} = \frac{1}{N^2}\sum_{Q',Q''}\left(\frac{\partial^2\omega_Q}{\partial n_{Q'}\partial n_{Q''}}\right)_0\left(n_{Q'} + \frac{1}{2}\right)\left(n_{Q''} + \frac{1}{2}\right) \quad (5)$$

involving anharmonic interactions up to sixth-order in displacement u_Q. We assume these can be omitted, and this approximation enables the correction in Eq. (3) to be sufficient. Then an accurate and consistent thermodynamic free energy is $F_{\rm QP} = U_{\rm QP} - TS_{\rm QP}$. Notice that the anharmonic shift, Eq. (4), does not vanish at $T = 0$, but has a zero-point component where $n_{Q'} + 1/2 \to 1/2$. The quasiparticle frequencies are shifted from the harmonic frequencies even at $T = 0$.

QH thermodynamics is a limiting case. It uses only the volume dependence of $\omega_{Q,H}(V)$. The correction factor in $U_{\rm QP}$, Eq. (3), vanishes, and the quasiharmonic free energy is just the harmonic free energy with a volume-dependent harmonic frequency. It improves pure harmonic theory and gives correct lowest-order thermal shifts for properties such as the bulk modulus, which are volume derivatives of F. The reason it works to lowest order is because $d\omega_Q/dV$ differs from $d\omega_{Q,H}/dV$ only in next order. QH theory is computationally accessible, but QP theory much less so. QP theory suffers from the difficulty that the anharmonic shift is not usually measured except at a few temperatures. It can be numerically computed using DFT for the anharmonic forces. It is not yet computed routinely, but this is changing [11–16].

The exact theory associates the vibrational resonances with the poles of a phonon Green's function, a correlation function describing the dynamics on the BO energy surface. The exact thermodynamics should be computed from a corresponding theory for the free energy. This can be computed perturbatively [4,17]. At high T, classical molecular dynamics (MD) describes the dynamics nonperturbatively, if the BO forces are known. This is called *ab initio* MD, or AIMD. Thermodynamics generally then requires a tricky "thermodynamic integration" [15,18–21]. To do a correct nonperturbative computation at lower T, requires quantum corrections, as in path-integral MD [22].

Zero-point and related thermal nuclear motions cause shifts and isotope dependencies in many measured physical properties [4–7,23–28]. Explicit formulas are given here for the first-order shifts of C_P, B_T, B_S, and α. If no specification (adiabatic *versus* isothermal) is made, isothermal is implied. The adiabatic shift can be found by thermodynamic rules, as shown in Sec. VI. Many of these results can be found in some form in the literature. There is a lot of correct [4–7], plus much partially correct, as well as incorrect or confusing literature on this subject. There are semiempirical formulas that have a long history of enabling useful fitting, even though the formulas do not seem to be justifiable in detail [29,30]. The aim of this paper is a simplified, possibly less confusing, derivation of correct formulas.

The paper is organized as follows. In Sec. II, examples of thermal shifts from experiments are given. In Sec. III, extra complexities of noncubic crystals, and crystals with internal coordinates, are discussed. In Sec. IV, the QH approximation and the QP approximation are discussed. Specific heat formulas are presented, showing that the QP theory provides a thermal correction inaccessible in the QH approximation. In Sec. V, two orders of thermal correction to the volume are discussed. This gives a Grüneisen theory of thermal expansion α_0 plus a first-order correction. In Sec. VI, the leading correction to the bulk modulus is derived (from QH theory). The Appendix reviews the microscopic theory of Eqs. (1)–(4).

II. EXPERIMENTAL EXAMPLES

Figures 1–3 illustrate the thermal shifts under discussion. Figure 1 shows that the bulk modulus has surprisingly large vibrational corrections [31–40]. These have serious significance for geoscience, for example [23,24]. The leading-order bulk modulus B_0 comes from electronic stiffness. The product B_0V_a ($V_a = V_0/Nn$ is the volume per atom in leading order

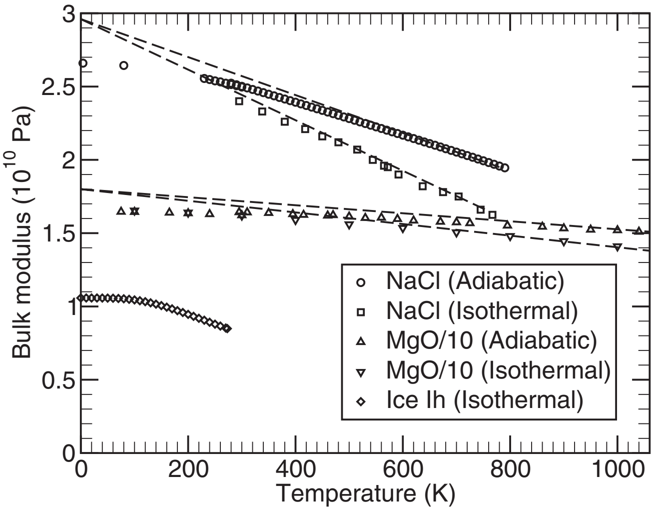

FIG. 1. Experimental bulk modulus B vs temperature. The isothermal data for ice Ih are from Ref. [31]. For NaCl, the low-T adiabatic data are from Ref. [32], and the high-T data are from Ref. [33]. The isothermal data for NaCl are from Ref. [34]. For MgO, the adiabatic low-T data are from Ref. [35] and the high-T data from Ref. [36]. The isothermal data for MgO are from Ref. [37]. The MgO data are larger by 10 than the others, and have a weaker thermal shift. Many metals (Al, Cu, Ni, *etc.*, Ref. [38]) have bulk moduli similar in magnitude to MgO, with large thermal shifts (similar to NaCl, for $\Delta T \sim \Theta_D$). Covalent materials, like carbon [39] and silicon [40], are more similar to MgO, showing weaker T dependence. The dashed lines are approximate extrapolations suggesting that the zero-temperature, frozen-lattice values of B are larger than the measured zero-temperature values by ∼15% (NaCl) and ∼9% (MgO). The extrapolation for ice Ih is not given, and would require detailed calculations as explained in the text.

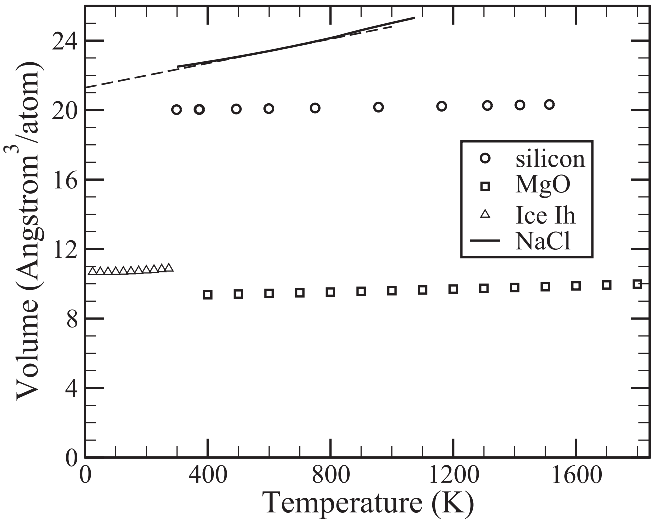

FIG. 2. Experimental volume V_a per atom vs temperature. The data for silicon are from Ref. [43]. The data for MgO are from Ref. [44]. The data for ice Ih are from Ref. [31]. The data for NaCl were constructed by integrating the polynomial expressions for linear thermal expansion given in Ref. [45]. The dashed curve extrapolates the NaCl $V(T)$ using the quasiharmonic high-T slope (valid for $T > \Theta_D$) $dV_a/dT = 3k_B\bar{\gamma}/B_0$, with experimental values $\bar{\gamma} = 1.57$ and $B_0 = 23.7$ GPa, as tabulated in Ref. [46]. This suggests that the zero-point expansion $\Delta V(T=0)/V_0$ of NaCl is about 5%. Crude extrapolations for MgO and silicon suggest zero-point expansions of less than 2% and 1%, respectively. The extrapolation for ice Ih is not given. Detailed calculations for ice show that (as is true for silicon as well) Grüneisen parameters are negative for some modes and positive for others; the theoretical zero-point expansion of ice Ih was computed to be ≈1% in Ref. [47].

theory) has order of magnitude 10 eV, a characteristic electron energy. Vibrational energies are two orders of magnitude smaller. I will define ϵ as the dimensionless ratio of phonon to electron energies. This will appear explicitly in the form $\hbar\omega/BV_a$ or k_BT/BV_a in various results. A parameter like $\epsilon \approx 0.01$ controls the size of the vibrational corrections under discussion. Figure 1 shows ≈10% shifts, indicating that there can be a significant prefactor multiplying ϵ.

The small parameter ϵ can be estimated as $\epsilon \approx k_B\Theta_D/B_0V_a$, where Θ_D is the Debye temperature. Experimental B and V_a may be used. Rough values are $\epsilon = 0.0045$ (silicon [40]), 0.0087 (MgO [41]), 0.0072 (NaCl [41]), and 0.042 (ice Ih [31,42]). However, the parameter ϵ for ice Ih is poorly defined. The number $\epsilon = 0.042$ used the low-T $\Theta_D \approx 300$ K. This measures only thermally excited (acoustic and librational) vibrations at $T \leqslant 273$ K. The "O-H stretch" vibrations at the opposite end of the spectrum have $\hbar\omega/k_B$ larger by 11. These modes also contribute to the zero-point shifts in ice. If optic modes are used to define ϵ, the value of this "small parameter" increases to 0.5.

It is perhaps worth mentioning that the representation of a physical property P as an expansion in ϵ ($P = P_0 + P_1\epsilon + P_2\epsilon^2 + \ldots$) is not forced to have universally defined coefficients. Especially because the expansion is truncated after the P_1 or possibly P_2 term, it is normal that the last coefficient may (or may not, depending on the source) contain some higher effects ($P_1 = P_{10} + P_{11}\epsilon$, for example.) The only rule is that $P_n\epsilon^n$ should contain nothing of lower order than ϵ^n. This will be mentioned again in Secs. V and VI.

The volume shifts [31,43–47] shown in Fig. 2 are smaller in relative size. Figure 3 shows that α, the temperature derivative of the volume [48], roughly follows a harmonic specific heat (C_{H}) type of T dependence. This is the result of Grüneisen theory [49]. However, at higher T, there is a very significant thermal shift of both $C_P(T)$ and $\alpha(T)$ away from the $C_{\mathrm{H}}(T)$ form.

Figures 1 and 2 also illustrate zero-point shifts. Mean square thermal lattice displacements of the ith atom, in harmonic theory, are [5]

$$\langle u_i^2\rangle = \sum_Q \frac{\hbar}{M_i\omega_{Q,H}}|\langle i|Q\rangle|^2\left(n_{Q,H} + \frac{1}{2}\right), \tag{6}$$

where $\langle i|Q\rangle$ is the component of the phonon eigenvector $|Q\rangle$ on the ith atom, and where n_Q is the equilibrium occupation number. The zero-temperature value $\langle u^2\rangle \sim \hbar/2M\omega$ is the quantum zero-point motion, which depends on nuclear mass, whereas the high-T value $k_BT/M\omega^2$ is classical and depends only on the force constant $M\omega^2$, not on the nuclear mass M. The low-T $\langle u^2\rangle$ causes zero-point shifts of atomic volume $V(T=0)$ and bulk modulus, which differ for different

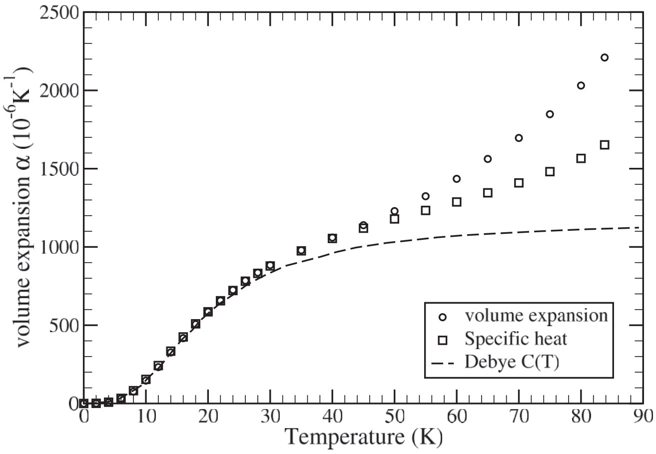

FIG. 3. Experimental volume expansion $\alpha(T)$ and specific heat $C_P(T)$, for crystalline argon, at $P = 1$ atmosphere, up to the melting temperature (82.3 K). The data were compiled by Bodryakov [48], who analyzed ≈10 different experiments. Shown for comparison is the Debye model with $\Theta_D = 81.2$ K fitted to C_P data. Both experimental and Debye-model specific heats were scaled, by the same factor, to lie on top of the volume expansion curve at lower T.

isotopes. Therefore the DFT ("frozen-lattice") value V_0 or B_0 should differ from the actual value $V(0)$ or $B(0)$. It is interesting that the frozen-lattice value can sometimes be deduced from experiment [28]. This is because the thermal factor $n + 1/2$ at high T becomes $x(1 - 1/12x^2 + \cdots)$, where $x = k_BT/\hbar\omega$. An asymptotic linear-in-T fit to $n + 1/2$ at high T passes through 0 at $T = 0$. It is of course difficult to find the "correct" experimental asymptote, since thermal corrections enter to alter it. However, the bulk modulus simplifies the fit if both isothermal and adiabatic versions are available, because each should extrapolate to the same $T = 0$ value B_0, as is shown on Fig. 1. Curves of this type are in the review of Leibfried and Ludwig [6].

We have already seen that the anharmonic shift $\Delta\omega_Q = \omega_Q - \omega_{Q,H}$ of phonon frequencies has a similar form, Eq. (4). The T-independent coupling parameter $\partial\omega_Q/\partial n_{Q'}$ has contributions like V_4 and $|V_3|^2/\hbar\omega$; see Appendix, Eq. (A3). They have order-of-magnitude $\epsilon\hbar\omega_Q$. For example, the term of the type $|V_3|^2/\hbar\omega$ involves a third-order anharmonic coupling coefficient V_3, of structure $u^3\partial^3E_{\rm el}/\partial u^3$, and of order $(u/a)^3E_{\rm el}$. The ratio $(u/a)^2$ of lattice displacement to interatomic distance is of order $\hbar\omega/M\omega^2a^2 \approx \epsilon$. Putting all these factors together, we see that $\partial\omega_Q/\partial n_{Q'} \approx \epsilon\omega_Q$ (or $\Delta\omega_Q/\omega_Q \approx \epsilon$).

The smallness of the anharmonic shift is only a crude estimate which sometimes may fail. A failure is likely to cause anharmonic broadening Γ_Q of vibrations to be bigger than the spacing of vibrational levels ω_Q. In such cases, phonon quasiparticles are poorly defined, perturbative treatments may fail, and thermal shifts may not be described well by quasiparticle theory.

The validity of perturbative computation beyond harmonic approximation for thermodynamic properties is not a closed issue. Wallace [26] summarizes evidence for failure of anharmonic perturbation theory to reproduce apparently reliable MD. However, Boltzmann equation treatments of thermal conductivity are now very successful [50–52], and are based on the third-order term in the same perturbation theory. Computations based on DFT anharmonic forces are becoming more common, and generally claim decent agreement with experiment. A nice example is theory and experiment for aluminum by Tang *et al.* [53]. A thermal conductivity $\kappa > 5$ W/mK is a good hint that phonon quasiparticles are mostly well behaved. This crude estimate comes from $\kappa \sim Cv\ell/3$ where the specific heat is $C = 3k_B/\Omega_a$, Ω_a is the volume per atom, $v \sim \pi\omega_{\rm max}/a$ is the sound velocity, a the lattice constant, and ℓ the phonon mean free path. Quasiparticle theory requires ℓ large compared to a, or κ large compared to $\kappa_{\rm min} = Cva/3$. If we choose $\hbar\omega_{\rm max}/k_B \sim \Theta_D$ to be 300 K, and a to be 5 Å, then $\kappa_{\rm min} \sim 1$ W/mK, and $\kappa > 5\kappa_{\rm min}$ should be sufficient to trust the quasiparticle theory for most of the phonons of the material. However, Θ_D may be significantly bigger or smaller than 300 K, and the criterion could be scaled to $\kappa > (\Theta_D/300\ \text{K}) \times 5$ W/mK.

III. NONCUBIC CRYSTALS AND INTERNAL COORDINATES

Pressure, volume, and temperature are not the only thermodynamic variables in crystals. One can also have anisotropic stress $\sigma_{\alpha\beta}$ and anisotropic strains $\epsilon_{\alpha\beta}$. Pressure and volume change are the traces of these tensors. This paper looks only at pressure and volume. The generalization to tensor properties complicates notations and results, but the principles are not changed. Consider hexagonal structures as a simple example of noncubic. The separate $a(T)$ and $c(T)$ lattice parameters are relevant thermodynamic variables. They are also not considered in this paper, only $V(T) = \sqrt{3}a^2c/2$ is considered. When T changes, not only does V change, but also c/a. This can not be ignored, but is kept hidden in this paper. The volume-dependent phonon frequency $\omega_{Q0}(V)$ is treated as a well-defined variable. There is a hidden assumption that this has been computed at various volumes, and for each volume, the correct c/a ratio has been found and used in the phonon calculation. Finally, consider the wurtzite crystal structure (hexagonal symmetry and four atoms per cell). There is one "internal coordinate" $u(T)$, which determines the c-axis offset between the cation and anion sublattices. This also cannot be ignored. However, it is hidden by the assumption that for a particular choice of V, the correct $u(T)$ as well as c/a have been computed, and used to find $\omega_{Q,H} = \omega_Q(V_0)$, and $\partial\omega_{Q,H}/\partial V$, etc. Cubic crystals can also have internal coordinates not fixed by symmetry, which need to be treated the same way.

IV. QUASIPARTICLE THERMODYNAMICS

Even when the harmonic approximation is seriously perturbed by anharmonic effects, there may still be phonon quasiparticles, with effective interactions not too strong. Thermodynamics is then approximated by using the QP frequencies $\omega_Q(V,T)$ in the noninteracting entropy formula [9],

$$S_{\rm QP} = k_B\sum_Q[(n_Q + 1)\ln(n_Q + 1) - n_Q\ln n_Q]. \qquad (7)$$

Because of the V and T dependence of the QP energy, $S_{\rm QP}$ has altered V and T derivatives, which give corrections in thermodynamic calculations [7,25,54–56]. The corresponding free energy is

$$F_{\rm QP} = E_{\rm el}(V) + F_{\rm vib,H}(V,T) + \Delta F_{AH}, \tag{8}$$

$$F_{\rm vib,H} = k_B T \sum_Q \ln\left[2\sinh\left(\frac{\hbar\omega_Q(V,T)}{2k_B T}\right)\right], \tag{9}$$

$$\Delta F_{AH} = -\frac{\hbar}{2}\sum_Q \Delta_Q^{(2)}(n_Q + 1/2), \tag{10}$$

where $\Delta_Q^{(2)} = \omega_Q(V,T) - \omega_{Q,H}$ was defined in Eq. (4). The part $F_{\rm vib,H}$ has the standard form of the harmonic free energy, but here the quasiparticle frequency $\omega_Q(V,T)$ is inserted. The double-counting correction ΔF_{AH} is nominally smaller by ϵ than the part $F_{\rm vib,H}$. This version of F_{QP} is the same as $U_{QP} - TS_{QP}$ and Eq. (3) for U_{QP}. The quasiharmonic formulas S_{QH} and F_{QH} are the same except that $\omega_Q(V,T)$ is replaced by $\omega_Q(V)$, usually calculated by DFT. In that case, the anharmonic term, Eq. (10), vanishes. In a metal or a magnetic material, one should include additional terms in $F_{\rm QP}$ for thermal excitation of electrons or magnons. Such effects are omitted here. The QH procedure of using just a volume-dependent QP energy in the harmonic free-energy formula, does give correct first-order V derivatives, but fails to give thermal shifts, which depend on T derivatives. In this sense, it can be regarded as an incomplete, rather than an incorrect, theory, and as a partially correct simplification of QP theory. It correctly contains the information available from DFT calculations of the frequency-spectra at different volumes. Ramirez *et al.* [57] made a careful study of the accuracy of the QH approximation by comparison with well-converged path-integral MD for three phases of ice. They find generally very good agreement between QH and PIMD

As an example of QP thermodynamics, consider the specific heat, $C = TdS/dT$. The free energy is not needed; the correct QP entropy is Eq. (7) with QP frequencies in the equilibrium occupation functions

$$C_X = T\left(\frac{\partial S}{\partial T}\right)_X \approx \sum_Q \hbar\omega_Q\left(\frac{\partial n_Q}{\partial T}\right)_X. \tag{11}$$

Here, X is pressure P or volume V. This gives

$$C_{X,\rm QP} = \sum_Q \hbar\omega_Q\left(\frac{dn_Q}{dT}\right)_{\rm H}\left[1 - \frac{T}{\omega_Q}\left(\frac{\partial\omega_Q}{\partial T}\right)_X\right], \tag{12}$$

where the subscript "H" means $(dn_Q/dT)_{\rm H} = (\hbar\omega_Q/k_B T^2)n_Q(n_Q+1)$, obtained by differentiating n_Q by the explicit T in the Bose function, but not by the implicit T contained in $\omega_Q(V,T)$. The first term of Eq. (12) is a harmonic specific heat $C_{\rm H}$, but not the purely harmonic C_0, because the frequencies ω_Q appearing in the formula are the renormalized T-dependent quasiparticle frequencies. The difference between $C_{\rm H}$ and C_0 is a gentle T-dependent stretching of the harmonic $C_0(T)$ curve along the T axis. This does not affect the high-T classical limit, $3Nnk_B$. A serious high-T deviation from harmonic theory (see the measurement for Ar, Fig. 3) must be caused by the second term of Eq. (12).

In QH theory, $(\partial\omega_Q/\partial T)_V = 0$, so $C_{V,\rm QH} = C_{\rm H}$. Also in QH theory, $(\partial\omega_Q/\partial T)_P = (\partial\omega_Q/dV)_T(\partial V/\partial T)_P$, so there is a significant QH correction to C_P. QH theory gives the correct difference, $C_P - C_V$, but it misses the anharmonic correction, which appears in the correct QP theory for both C_V and C_P. Computational evidence [55] shows that QH theory shifts $C_P(T)$ away from the harmonic value C_0, but that experiment exhibits different shifts [58].

V. VOLUME EXPANSION

The aim is to get corrections to one higher order than the standard Grüneisen theory [49]. The method is to use Eq. (8) for the free energy, calculate $P(V,T) = -\partial F/\partial V$, and then find the volume $V(T)$ at which the pressure is zero. It is convenient to have a notation for the dimensionless volume expansion ζ:

$$\zeta = (V - V_0)/V_0, \tag{13}$$

where V_0 is as usual the volume that minimizes the frozen lattice (Born-Oppenheimer) energy. For results to order ϵ^2, it is necessary to know the DFT frozen lattice energy $E_{\rm el}$ to third order in ζ,

$$E_{\rm el}(V) = E_{\rm el}(V_0) + \tfrac{1}{2}B_0V_0\zeta^2 + \tfrac{1}{6}\dot{B}_0V_0\zeta^3 + \cdots. \tag{14}$$

Here, $B_0 = V_0(d^2E_{\rm el}/dV^2)_{V_0}$ is the order ϵ^0 electronic contribution to the bulk modulus, and $\dot{B}_0$ is the third derivative, $V_0^2(d^3E_{\rm el}/dV^3)_{V_0}$. $\dot{B}_0$ is similar in order of magnitude to B_0. The notation $\dot{B}$ is used because the notation B' means $dB/dP = -1 - \dot{B}/B$ in the equation-of-state theory [23,24]. Normally, $\dot{B}_0 < 0$ is found. Crystals are softer when expanded and stiffer when compressed. From the volume derivative, we get an "equation of state,"

$$P(V,T) = -B_0\zeta - \frac{1}{2}\dot{B}_0\zeta^2 - \sum_Q \frac{\partial F_H}{\partial\omega_Q}\frac{\partial\omega_Q}{\partial V} + \frac{\hbar}{2}\sum_Q\left[\frac{\partial\Delta_Q^{(2)}}{\partial V}(n_Q + 1/2) + \Delta_Q^{(2)}\frac{\partial n_Q}{\partial\omega_Q}\frac{\partial\omega_Q}{\partial V}\right]. \tag{15}$$

Making the substitutions $\partial F_H/\partial\omega_Q = \hbar(n_Q + 1/2)$ and $\partial n_Q/\partial\omega_Q = -(\hbar/k_BT)n_Q(n_Q+1)$, and setting $P = 0$, this becomes

$$\zeta = -\frac{\dot{B}_0}{2B_0}\zeta^2 + \sum_Q \frac{\hbar\omega_Q}{B_0V}(\gamma_Q - \delta_Q/2)(n_Q + 1/2) + \frac{1}{2}\sum_Q \frac{\hbar\omega_Q}{B_0V}\frac{\hbar\Delta_Q^{(2)}}{k_BT}\gamma_Q n_Q(n_Q+1). \tag{16}$$

Here, the following definitions have been introduced:

$$\gamma_Q = -\frac{V}{\omega_Q}\frac{\partial\omega_Q}{\partial V}, \tag{17}$$

$$\delta_Q = -\frac{V}{\omega_Q}\frac{\partial\Delta_Q^{(2)}}{\partial V}, \tag{18}$$

where γ_Q is the "mode Grüneisen parameter," and δ_Q is the analogous volume derivative of the correction $\omega_Q - \omega_{QH}$.

Therefore $\delta_Q = \gamma_Q - (\omega_{QH}/\omega_Q)\gamma_{QH}$, where

$$\gamma_{QH} = -\frac{V}{\omega_{QH}}\frac{\partial \omega_{QH}}{\partial V}. \tag{19}$$

A. Lowest-order (Grüneisen) theory

Grüneisen parameters γ_Q are of order 1, while $\Delta_Q^{(2)}$ is a small anharmonic correction of order $\epsilon\omega_Q$. Therefore δ_Q is of order $\epsilon\gamma_Q$. All the terms on the right of Eq. (16) except the first term involving γ_Q are higher order in ϵ. Therefore the leading-order relation for the thermal shift of the volume $[\zeta \equiv (V - V_0)/V_0]$ is

$$\zeta_G \equiv \left(\frac{V - V_0}{V_0}\right)_G = \sum_Q \left(\frac{\hbar\omega_Q}{B_0 V}\right)\gamma_Q\left(n_Q + \frac{1}{2}\right), \tag{20}$$

$$\alpha_G \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_G = \frac{1}{B_0}\sum_Q C_{QH}(T)\gamma_Q, \tag{21}$$

where $C_{QH}(T) = (\hbar\omega_Q/V)\partial n_Q/\partial T$ is the specific heat per harmonic mode. These are the famous Grüneisen relations. Grüneisen's papers [49] of 1912 and 1918 were a remarkable advance, simultaneous with the first true understanding of crystals that came from Rutherford and Bohr, von Laue and the Braggs, Born and von Karman, Eucken, and Debye. Geophysicists and others like to define an average Grüneisen parameter γ and to write Eq. (15) as $P = P_{\rm el} + \gamma U_{\rm vib}/V$, where $U_{\rm vib}$ is the harmonic vibrational energy, see Eq. (2). This is called the "Grüneisen equation of state." It omits the higher-order corrections, which are now to be discussed.

B. Quasiharmonic theory

The need for corrections is evident from Fig. 3, showing large high-T deviations of thermal expansion relative to the specific heat. If Eq. (21) were correct, this would require unphysically large T dependence of Grüneisen constants. To correctly find the volume shift ζ to next order, it is necessary to solve Eq. (16) self-consistently. The job is complicated by the fact that γ_Q as defined in Eq. (17), and γ_{QH} as defined in Eq. (19), are volume dependent.

An interesting example is the computation by Skelton *et al.* [59] of $\alpha(T)$ for PbS, PbSe, and PbTe. Above the Debye temperature, α shows strong T dependence, similar to argon in Fig. 3. These computations had no anharmonic corrections. This shows that a good quasiharmonic theory does in fact have important corrections beyond the lowest-order Grüneisen theory. The volume-dependent electron and vibrational free energy in Eq. (8) are included, omitting the correction term involving $\Delta_Q^{(2)}$. The resulting $F_{QH}(V,T)$ is minimized at fixed T, giving $V_{QH}(T)$. This is equivalent to a self-consistent solution of Eq. (16), omitting the terms involving δ_Q and $\Delta_Q^{(2)}$.

C. Full second-order theory

It is rather messy to do the full solution to second order. To simplify things, consider just the high-T limit, where $n_Q + 1/2$ is $\approx k_BT/\hbar\omega_Q$ and $n_Q(n_Q+1)$ is $\approx (k_BT/\hbar\omega_Q)^2$. The quantum corrections are factors $[1 \pm (\hbar\omega/k_BT)^2/12 + 4^{\rm th}\text{order} + \cdots]$. Then, to order ϵ^2, Eq. (16) becomes

$$\zeta = -\frac{\dot{B}_0}{2B_0}\zeta_0^2 + \frac{k_BT}{B_0V_0(1+\zeta_0)}\sum_Q\left(\gamma_Q(V) - \frac{\delta_{Q0}}{2} + \frac{\Delta_{Q0}^{(2)}}{2\omega_{Q0}}\gamma_{Q0}\right). \tag{22}$$

The subscript 0's indicate that quantities are all (except the first appearance of γ_Q) evaluated at the frozen-lattice $T = 0$ minimum volume V_0. The lowest-order volume expansion, ζ_0, at high T, from Eq. (20) or from Eq. (22) is

$$\zeta_0 = \frac{k_BT}{V_0B_0}\sum_Q \gamma_{Q0}. \tag{23}$$

The definition of γ_{Q0} is

$$\gamma_{Q0} = -\frac{V_0}{\omega_{Q0}}\left(\frac{\partial\omega_{QH}}{\partial V}\right)_{V_0}, \tag{24}$$

and the phonon frequencies ω_{Q0} are similarly the $T = 0$ harmonic frozen lattice values.

We now need to expand the fully anharmonic γ_Q around γ_{Q0}, to first order in ζ. This is done in two stages. First, we expand around γ_{QH},

$$\gamma_Q(V) \equiv -\frac{V}{\omega_{QH} + \Delta_Q^{(2)}}\frac{\partial\left(\omega_{QH} + \Delta_Q^{(2)}\right)}{\partial V}$$

$$\approx \left(1 - \frac{\Delta_{Q0}^{(2)}}{\omega_{Q0}}\right)\gamma_{QH}(V) + \delta_{Q0}. \tag{25}$$

Subscripts 0 indicate sufficient accuracy for a first-order result. Next, we expand $\gamma_{QH}(V)$ around the volume V_0 where γ_{Q0} is defined. To do this, we need to know the harmonic frequencies to second order in ζ around V_0,

$$\omega_{QH}(V) = \omega_{Q0}[1 - \gamma_{Q0}\zeta - \dot{\gamma}_{Q0}\zeta^2/2 + \cdots], \tag{26}$$

$$\dot{\gamma}_{Q0} \equiv -\frac{V_0^2}{\omega_{Q0}}\left(\frac{\partial^2\omega_{QH}}{\partial V^2}\right)_{V_0}. \tag{27}$$

The notation $\dot{\gamma}_Q$ used here [Eq. (27)] is not the same as $V(\partial\gamma_Q/\partial V) = \gamma_Q + \gamma_Q^2 + \dot{\gamma}_Q$. The volume dependence of $\gamma_Q(V)$ has often been neglected. If the mode Grüneisen parameter were independent of volume, one could integrate to find $\omega_Q(V) = \omega_Q(V_0)(V/V_0)^{\gamma_Q}$. As observed previously [60,61], there is no justification for this except unwarranted optimism. After some algebra, the relation between γ_{QH} and γ_{Q0} is

$$\gamma_{QH}(V) = \gamma_{Q0} + [\gamma_{Q0} + \gamma_{Q0}^2 + \dot{\gamma}_{Q0}]\zeta. \tag{28}$$

Combining the two stages, the result is

$$\gamma_Q = \gamma_{Q0} + [\gamma_{Q0} + \gamma_{Q0}^2 + \dot{\gamma}_{Q0}]\zeta_0 - \frac{\Delta_Q^{(2)}}{\omega_{Q0}}\gamma_{Q0} + \delta_{Q0} + \cdots. \tag{29}$$

Finally, we insert this into Eq. (22) and keep only the first-order corrections. The result is

$$\zeta = \zeta_0 - \frac{\dot{B}_0}{2B_0}\zeta_0^2 + \frac{k_B T}{B_0 V_0}\sum_Q \Big[\left(\gamma_{Q0}^2 + \dot{\gamma}_{Q0}\right)\zeta_0 + \frac{\delta_{Q0}}{2} - \frac{\Delta_{Q0}^{(2)}}{2\omega_{Q0}}\gamma_{Q0}\Big]. \tag{30}$$

The corresponding high-T formula for the volume thermal expansion coefficient is

$$\alpha = \alpha_0 + \Delta\alpha_{QH} + \Delta\alpha_{AH}. \tag{31}$$

The leading term, α_0, is just the Grüneisen formula evaluated with frozen-lattice parameters. Its high-T form is

$$\alpha_0 = \frac{k_B}{B_0 V_0}\sum_Q \gamma_{Q0}. \tag{32}$$

The high-T quasiharmonic correction is explicitly linear in T,

$$\Delta\alpha_{QH} = 2T\alpha_0\left(\frac{k_B}{B_0 V_0}\sum_Q \left(\gamma_{Q0}^2 + \dot{\gamma}_{Q0}\right)\right) - \frac{\dot{B}_0 T}{B_0}\alpha_0^2. \tag{33}$$

These are smaller than the leading term α_0 by a factor like $T\alpha_0 \sim \epsilon$. The high-T anharmonic correction is

$$\Delta\alpha_{AH} = \frac{k_B}{B_0 V_0}\sum_Q \left(\delta_{Q0} - \frac{\Delta_{Q0}^{(2)}}{\omega_{Q0}}\gamma_{Q0}\right). \tag{34}$$

This is also smaller than α_0 by one power of ϵ. The anharmonic factors $\delta - (\Delta/\omega)\gamma$ vary linearly with T at high T. This is why the factors of 1/2 multiplying δ_{Q0} and $(\Delta_{Q0}^{(2)}/\omega_{Q0})\gamma_{Q0}$ in Eq. (30) disappear in Eq. (34) after taking the temperature derivative.

The QH calculations of Karki *et al.* [58] for MgO show that QH corrections, Eq. (33), can cause a large effect, even exceeding the experimental linear rise in α. The calculations of Mounet and Marzari [39] also show a significant QH linear increase of $\alpha(T)$ in diamond, but less than the shift observed experimentally by Slack and Bartram [62]. These results indicate that the anharmonic part of Eq. (31) is as important as the QH part. A path integral Monte Carlo study by Herrero and Ramirez [22] confirms this.

VI. THERMAL CORRECTION TO BULK MODULUS

The literature about $B(T)$ is large because of its importance in geoscience. The bulk modulus is the simplest and most accessible part of the elastic constant matrix C_{ij}, all components of which show related zero-point and thermal alterations. This paper focuses on B for simplicity, but generalization to the full elasticity tensor is not hard [6,7,38,39,58,63–69]. The bulk modulus is dominated by the large electronic contribution B_0. Corrections to first and second order in ϵ can be found from the quasiparticle free energy, Eq. (8), and pressure, Eq. (15). The first-order shift of the isothermal bulk modulus uses only the first two correction terms in Eq. (15),

$$P(V,T) = -B_0\zeta - \frac{1}{2}\dot{B}_0\zeta^2 - \sum_Q \frac{\hbar\omega_Q}{V}\gamma_Q(n_Q + 1/2). \tag{35}$$

There is no anharmonic contribution to $B = -V\partial P/\partial V$ in first order. The simulations by Ramirez *et al.* [57] [using a fluctuation formula [9] for $B(T)$] confirm the accuracy of quasiharmonic theory for phases of ice. For cases like ice, where volume shifts are relatively large, it is insufficient to compute only low-order derivatives of energy and vibrational frequency. However, QH theory, with $\gamma_Q(V)$ computed separately for different volumes along the QH $V(T)$ curve, has been shown to work [57].

Taking the volume derivative of Eq. (35),

$$B_{T,QH}(T) = \frac{V}{V_0}(B_0 + \dot{B}_0\zeta) - B_0\sum_Q\left(\frac{\hbar\omega_Q}{B_0 V}\right) \times\left[T\left(\frac{\partial n_Q}{\partial T}\right)_{\mathrm{H}}\gamma_Q^2 + \left(n_Q + \frac{1}{2}\right)\dot{\gamma}_Q\right]. \tag{36}$$

The last term uses the identity $\partial(\omega_Q\gamma_Q/V)/\partial V = \omega_Q\dot{\gamma}_Q/V^2$. The next to last term uses the fact that $V\partial n_Q/\partial V$ equals $T(\partial n_Q/\partial T)_{\mathrm{H}}\gamma_Q$. The first term of Eq. (36) is the purely electronic term, B_{el}. To first order in ϵ it can be written as $B_0 + (B_0 + \dot{B}_0)\zeta_0$. The high-$T$ version of ζ_0 is given in Eq. (23), and the general expression is the same as the Grüneisen version, Eq. (20), except frequencies and derivatives are evaluated at $(V,T) = (V_0,0)$. Then Eq. (36) becomes

$$\left(\frac{\Delta B}{B_0}\right)_T = \sum_Q\left(\frac{\hbar\omega_{Q0}}{B_0 V_0}\right)\Big[-T\left(\frac{\partial n_{Q0}}{\partial T}\right)_{\mathrm{H}}\gamma_{Q0}^2 + \left(n_{Q0} + \frac{1}{2}\right)\left(\gamma_{Q0}\left[1 + \frac{\dot{B}_0}{B_0}\right] - \dot{\gamma}_{Q0}\right)\Big]. \tag{37}$$

This equation is contained in somewhat hidden form in Leibfried and Ludwig [6]. Born and Huang [5] and Wallace [7] also give this result, except altered because frequencies and derivatives are evaluated at (V,T). The paper of Karch *et al.* [65] gives an alternate derivation. Many simplified versions exist [70].

The parameter ϵ is not truly small for ice Ih. For this reason, Eq. (37) does not work particularly well [57,71]. Direct computation and minimization of the QH free energy [Eq. (8) without the last term] may work. This was used for many years, even in cases where the shifts are small enough that Eq. (37) should be adequate [38,39,64,66,72,73]. In cases, like ice Ih, where ϵ is too large to use Eq. (37), there is no guarantee that truly anharmonic terms of order ϵ^2 and higher are not as important as QH terms found by direct minimization.

It is important to distinguish between adiabatic (B_S) and isothermal (B_T) conditions [63]. The definitions are

$$B_T = -V(\partial P/\partial V)_T = V(\partial^2 F/\partial V^2)_T, \tag{38}$$

$$B_S = -V(\partial P/\partial V)_S = V(\partial^2 U/\partial V^2)_S, \tag{39}$$

where U and F are the internal energy and Helmholz free energy, respectively. Thermodynamics gives exact relations [6,7,23,24,38,63,74–76],

$$\frac{B_S}{B_T} - 1 = \frac{C_P}{C_V} - 1 = \frac{T\alpha^2 B_T V}{C_V} = \frac{T\alpha^2 B_S V}{C_P}, \tag{40}$$

where C_V/V is the heat capacity per volume. The product αT is of order ϵ, and $C_V T/B_T V$ is also of order ϵ, so the shift $(B_S - B_T)/B$ is positive and of order ϵ. The full tensor version also is available [7,76–78]. The vibrational corrections δ_S (adiabatic) and δ_T (isothermal) are both first order in ϵ, and they differ from each other in the same order. The leading order value of $T\alpha^2 B_T V/C_V$ is sufficient for correcting isothermal to adiabatic. Using Eq. (21) and the harmonic specific heat, the result is

$$B_S - B_T = \frac{T}{V}\frac{\left[\sum_Q \hbar\omega_{Q0}\left(\frac{\partial n_{Q0}}{\partial T}\right)_{\rm H}\gamma_{Q0}\right]^2}{\sum_Q \hbar\omega_{Q0}\left(\frac{\partial n_{Q0}}{\partial T}\right)_{\rm H}}. \tag{41}$$

Figure 1 shows approximate high-T slopes (dB/dT) of both B_S and B_T for NaCl. In the high-T limit where $\hbar\omega_Q(dn_Q/dT) \to k_B$, Eq. (41) reduces to $d(B_S - B_T)/dT = 3k_B\bar{\gamma}^2/V_a$, where $\bar{\gamma} = \sum_Q \gamma_Q/3N$. The slopes shown in Fig. 1 then require $\bar{\gamma} \approx 1.5$, in good agreement with other estimates of $\bar{\gamma}$ for NaCl.

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APPENDIX

This appendix tries to illuminate the quasiparticle thermodynamics of Eqs. (1)–(4) by using anharmonic thermal perturbation theory. According to Cowley [4], the vibrational thermal Green's function matrix, in the basis of harmonic eigenstates $|\lambda\rangle$ with frequencies $\omega_{\lambda,H}$, is

$$(G^{-1})_{\lambda\lambda'} = \left(\omega_{\lambda,H}^2 - \omega^2\right)\delta_{\lambda\lambda'} + 2(\omega_\lambda\omega_{\lambda'})^{1/2}[\Delta_{\lambda\lambda'} - i\Gamma_{\lambda\lambda'}]. \tag{A1}$$

The eigenvalues ω^2 of the matrix $\hat{G}^{-1} + \omega^2\hat{1}$, with the imaginary part $\hat{\Gamma}$ omitted, are denoted ω_λ^2. They are the renormalized squared normal mode frequencies. If anharmonicity is weak, then in the leading approximation, these eigenvalues are $\omega_\lambda^2 = \omega_{\lambda,H}^2 + 2\omega_\lambda\Delta_{\lambda\lambda}$. At the same level of approximation, $\omega_\lambda = \omega_{\lambda,H} + \Delta_{\lambda\lambda}$. Cowley gives an explicit formula from the lowest-order perturbation theory, for the anharmonic shift $\Delta_{\lambda\lambda}^{(2)} = \Delta_Q^{(2)} = \omega_Q - \omega_{Q,H}$. The normal mode index λ is now replaced by $Q = (\vec{Q},j)$. Cowley's formula can be written in the form

$$\Delta_Q^{(2)} = \frac{1}{N}\sum_{Q'}\frac{\partial\omega_Q}{\partial n_{Q'}}(n_{Q'} + 1/2), \tag{A2}$$

$$\begin{aligned}\frac{\partial\omega_Q}{\partial n_{Q'}} = {}& \frac{24}{\hbar}V^{(4)}(QQ,Q'Q') \\ & - \frac{36}{\hbar^2}\sum_{Q''}|V^{(3)}(QQ'Q'')|^2\left(\frac{1}{\omega_{Q''}+\omega_{Q'}+\omega_Q}\right. \\ & + \frac{1}{\omega_{Q''}+\omega_{Q'}-\omega_Q} + \frac{1}{\omega_{Q''}-\omega_{Q'}+\omega_Q} \\ & \left. + \frac{1}{\omega_{Q''}-\omega_{Q'}-\omega_Q}\right).\end{aligned} \tag{A3}$$

This is an explicit form for Eq. (4). Here, $V^{(3)}$ and $V^{(4)}$ are third and fourth derivatives of the BO potential taken around the periodic sites of the crystal of volume V_0, and the frequencies ω_Q and the occupation number $n_{Q'}$ use anharmonic renormalization (computed self-consistently).

Cowley also derives the anharmonic free energy at the same level of perturbation theory. His answer can be written as

$$F = F_{H,0} + \frac{\hbar}{2}\sum_Q \Delta_Q^{(2)}(n_Q + 1/2) + F_{A0}, \tag{A4}$$

$$\begin{aligned}F_{A0} = {}& -\frac{3}{2\hbar}\sum_{QQ'Q''}|V^{(3)}(QQ'Q'')|^2 \\ & \times\left(\frac{1}{\omega_{Q''}+\omega_{Q'}+\omega_Q} - \frac{3}{\omega_{Q''}+\omega_{Q'}-\omega_Q}\right),\end{aligned} \tag{A5}$$

where $F_{H,0}$ is the free energy of noninteracting (harmonic) quasiparticles. Now find the corresponding entropy, $S = -dF/dT$. The noninteracting part gives the harmonic entropy

$$S_{H,0} = k_B\sum_Q[(n_Q + 1)\ln(n_Q + 1) - n_Q\ln n_Q]. \tag{A6}$$

Consider what happens if the "quasiparticle entropy" is constructed by replacing the harmonic frequencies in Eq. (A6) by the anharmonic frequencies $\omega_{Q,H} + \Delta_Q^{(2)}$. Taylor expanding to first order in Δ_Q, the answer is

$$\Delta S = S_{QP} - S_{H,0} = -\hbar\sum_Q\frac{\partial n_Q}{\partial T}\Delta_Q^{(2)}. \tag{A7}$$

This is the same as the entropy dF/dT from Eq. (A4). The factor 1/2 in (A4) disappears when using Eq. (A2), while differentiating Eq. (A4) for ΔF, because $\partial\omega_Q/\partial n_{Q'}$ is symmetric in Q and Q'. An alternate derivation using a variational principle is given in Ref. [55]. This suggests that the use of QP energies in the harmonic entropy formula may be valid somewhat beyond low-order perturbation theory.

Consider then what happens if the same substitution $\omega_{Q,H} \to \omega_Q$ is done in the harmonic free energy $F_H = \sum_Q \hbar\omega_{Q,H}(n_Q + 1/2) - TS_H$. The answer is $\Delta F_H = \hbar\sum_Q \Delta_Q^{(2)}(n_Q + 1/2) - T\Delta S$. This differs from the correct anharmonic free energy, Eq. (A4), by not having the correct factor of $1/2$. This is a proof of the double-counting correction that was added to the internal energy in Eq. (3). The correct formula, Eq. (A4), does differ from the QP theory of Eqs. (1)–(4) by a small T-independent term F_{A0}.

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