I. INTRODUCTION

Quasi-harmonic (QH) thermodynamics uses volume (V) dependence of “bare” quasiparticle (QP) energies $\omega_Q(V)$ and $\epsilon_K(V)$ of phonons and electrons to compute the approximate free energy $F(V, T)$. It ignores the effect of interactions which introduce temperature ($T$) dependence measured in QP energies $\omega_Q^{QP}(V, T)$ and $\epsilon_K^{QP}(V, T)$. These interactions cause the free energy to be shifted from the QH approximation. The question is, how big is this shift compared to the influence of the QH shifts?

Standard electronic structure theory ($\epsilon, g, \text{DFT}$ and density functional perturbation theory DFT+$\text{Q}$) give single-particle electron and phonon energies (the “bare” QP energies), which will also be called “QH energies” $\epsilon_K(V)$ and $\omega_Q(V)$. The symbol $K$ is short for $(\vec{k}, n)$, the electron wavevector and band index. The symbol $Q$ is short for $(\vec{q}, j)$, the phonon wavevector and branch index. The symbol $V$ (and for more clarity, sometimes $\{V\}$) will mean the complete set of parameters ($\vec{a}, \vec{b}, \ldots$) needed to define the structure, including any internal parameters. Cubic crystals like rocksalt and zincblende have only one structure parameter, volume. A general crystal has $n$ parameters, all varying with temperature $T$. To compute $V(T)$ requires setting all external and internal strains $\{P\} = -\partial F\{\{V\}, T\}/\partial \{V\}$ to zero. This determines the $T$-dependent structure $\{V\}(T)$. The symbol $V_0$ or $\{V_0\}$ denotes the “frozen lattice” parameters, not quite the same as zero temperature parameters $\{V\}(T = 0)$ which contain zero-point corrections.

For phonons, the first QH correction, where $\omega_Q(V_0 + \Delta V) - \omega_Q(V_0)$ is approximated by $-\gamma_Q\omega_Q\Delta V/V$, gives Gr"uneisen\cite{gruneisen} theory of thermal expansion. The code GIBBS$^\text{2}$\cite{gibbs} implements full quasiharmonic theory using density functional theory (DFT). It is quite successful for equation-of-state and related thermodynamic calculations. QH calculations for MgO, Al, and C\cite{ccarbon} fit experiment very well, especially when $V$ values are taken from experiment rather than DFT. The methodology involves computing $V$-dependent phonon densities of states, without explicit evaluation of mode Gr"uneisen parameters $\gamma_Q$, and going beyond low-order $V$-derivatives.

QH theory puts $\omega_Q(V)$ and $\epsilon_K(V)$ in the standard formulas for thermal free energy $F(V, T)$, of bare (or QH) phonons $F^{\text{QH}}$ and bare (or QH) electron single particle excitations $E^{\text{el}}$. It is unfortunately incorrect to insert the full renormalized energies into the noninteracting free energy $F_{\text{QH}}$. For electrons, the first order Taylor expansion of $\epsilon_K(V)$ in $\Delta V$ gives Mikiura’s theorem\cite{mikiura} (rediscovered by Visvanathan\cite{visvanathan}) of the electronic contribution to thermal expansion.

The terminology “quasi-harmonic” should be carefully distinguished from “truly” anharmonic. In this paper, “true anharmonicity” is defined as the consequences of inter-atomic forces beyond harmonic, at fixed volume. True anharmonicity shifts the phonon free energy $F(V, T) = F_{\text{QH}}(V, T) + \Delta F_{\text{anhar}}(V, T)$. It therefore causes thermal expansion to deviate from the QH result contained in $F_{\text{QH}}$. This paper examines corrections to QH theory from QP renormalization. The result is that QH theory does give correctly the leading volume dependence of $F(V, T)$ needed for a correct lowest-order theory of thermal expansion. How safe is it to ignore the higher-order corrections from true anharmonicity? A very care-
fial study by Erba et al. illuminates this issue. For rocksalt-structure MgO, a weakly anharmonic material, the QH answer is 1000K and starts to fail at higher T. For isostructural CaO, with softer phonons and therefore significant anharmonicity, breakdown of the QH prediction is seen already at 100K. Silicon (see Ref. 12 and references therein) is another weakly anharmonic material where QH theory does well. There is evidence that breakdown is very significant in NaBr material where QH theory does well. There is evidence that breakdown is very significant in NaBr material where QH theory does well.
element $|v_C|$ is of order $E_{el}$, so the fractional shift is of order 1. But it is the job of DFT to include all relevant $T = 0$ Coulomb renormalization in the bands $\epsilon_K$. Only the thermal alteration of Coulomb renormalization is left to include in $\Delta \epsilon_K^{QP}(V, T)$, and this is usually unnecessary. The lifetime broadening caused by Coulomb scattering is smaller by $(\hbar/\tau_C)/E_{el} \sim (k_BT/E_{el})^2$. A similar, and negligible thermal Coulomb shift of the QP energy can be expected.

Finally, consider electron-phonon interactions. For both electron and phonon renormalization, the energy denominator in second order perturbation theory is $\sim E_{el}$. The numerator is $|V_{ep}|^2 \sim (dU/du)^2 < u^2 > \sim E_{el}\hbar\omega_{ph}$. Therefore the result is

$$\Delta_{ep}^{QP} \sim \Delta_{ep}\hbar\omega_Q^{QP} \sim \hbar\omega_{ph}.$$  \hspace{1cm} (5)

For electronic states $\epsilon_K$, this is a small effect. It is omitted in band structure calculations, but appears in experiment as zero-point and thermal shifts of band gaps.\(^{22,23}\) These can be measured and computed, and gives a correction of order $\hbar\omega_{ph}$ or a few $k_BT$. However, in metals at low $T$ (i.e. when thermal excitation of electrons $E_{ph}^{el} \sim k_BT$ is significantly smaller than $\hbar\omega_{ph}$), there is an important, additional, non-adiabatic effect caused by the singularity at the sharp Fermi edge $\epsilon_K \approx E_F$. This causes a “mass renormalization” $\epsilon_K \rightarrow \epsilon_K/(1 + \lambda_K(T))$. The parameter $\lambda \equiv < \lambda_K(T = 0) >$ is the superconducting coupling constant, usually in the range $0.1 < \lambda < 2.0$. As $T$ increases, $\lambda_K(T)$ decreases rapidly; it becomes negligible before $T = \Theta_B$.\(^{24}\) This mass renormalization is actually a shift of bands of the expected order ($\sim \hbar\omega_{ph}$), but only for electron states within $\sim \hbar\omega_{ph}$ of $E_F$. This enhances the electron density of states at $T = 0$ (at the Fermi level), which in turn causes the familiar $(1 + \lambda)$ enhancement of the low-$T$ electronic specific heat. It should also appear in low-$T$ thermal expansion of metals. It is the only common case where QH theory gets an order 1 correction from QP renormalization.

For phonons, however, the electron-phonon renormalization ($\sim \omega_{ph}$) is a shift of order 1. It is the job of DFT (more specifically, density-functional perturbation theory, DFPT\(^{24}\)) to include $T = 0$ electron-phonon renormalization in the calculation of “bare” phonon bands. Additional thermal renormalization also occurs, with both lifetime broadening and phonon energy shifts. The lifetime broadening of phonons in metals is $\sim (\hbar\omega_{ph}/E_{el})k_BT$, similar in size to (but usually smaller than) anharmonic lifetime broadening. Therefore the residual thermal shift $\Delta\omega_Q^{QP}(T)$ of phonon QP energy from electron-phonon interactions, omitted in phonon band calculations, is similar in magnitude to anharmonic shifts. Both effects give higher-order corrections to thermal expansion.

### IV. QUASI-HARMONIC THERMAL EXPANSION

Some thermodynamic relations are

$$P(V, T) = -\left(\frac{\partial F}{\partial V}\right)_T; \quad V(P, T) = \left(\frac{\partial G}{\partial P}\right)_T,$$  \hspace{1cm} (6)

where $F$ and $G$ are the Helmholtz and Gibbs free energies. These are versions of the equation of state. Further relations are

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V} \left(\frac{\partial^2 G}{\partial T \partial P}\right)_P,$$  \hspace{1cm} (7)

$$B_T = -V \left(\frac{\partial P}{\partial T}\right)_V = V \left(\frac{\partial^2 F}{\partial V^2}\right)_T.$$  \hspace{1cm} (8)

where $\alpha$ is the coefficient of volume thermal expansion and $B_T$ is the isothermal bulk modulus. A curious connection is the relation

$$\alpha B_T = -\left(\frac{\partial^2 F}{\partial V^2}\right)_{TV},$$  \hspace{1cm} (9)

which is given as Eq. 1.35 of ref.\(^{21}\).

The QH energies generate QH free energies,

$$F_{QH} = -k_BT\ln(Z_{el}^{bare} \times Z_{ph}^{bare}) = F_{el}^{QH} + F_{ph}^{QH}.$$  \hspace{1cm} (10)

Technically, the electron part is not $F(V, T, N)$ but the “grand potential” $\Omega(V, T, \mu)$. For the phonon part, there is no difference ($N_{ph}$ is not conserved, so there is no $\mu_{ph}$), and for the electron part, in this paper the difference is irrelevant. The symbol $F$ will be used instead of $\Omega$. The electron part is

$$F_{el}^{QH}(V, T) = k_BT \sum_K \ln(1 - f_{K0}(V, T))$$

$$= \sum_K (\epsilon_K(V) - \mu(V)) + k_BT \sum_K \ln \frac{1 - f_{K0}(V, T)}{1 - f_{K0}(V, 0)}$$

$$\rightarrow E_{el}(V) + k_BT \sum_K \ln \frac{1 - f_{K0}(V, T)}{1 - f_{K0}(V, 0)}$$

$$\equiv E_{el}(V) + \Delta\epsilon_{el}^{QH}(V, T).$$  \hspace{1cm} (11)

Here $f_K$ is the Fermi-Dirac distribution. The additional subscript 0 indicates that the energy $\epsilon_K(V)$ appearing in $f_{K0}$ is the QH energy, independent of $T$. The phonon part is

$$F_{ph}^{QH}(V, T) = \sum_Q \frac{\hbar\omega_Q(V)}{2} - k_BT \sum_Q \ln(1 + n_{Q0}(V, T)).$$  \hspace{1cm} (12)

Here $n_{Q0}$ is the Bose-Einstein distribution. The subscript 0 indicates that the energy $\omega_Q(V)$ appearing in $n_{Q0}$ is the QH energy, independent of $T$.\(^{2,3}\)
The first term in Eq. 12 is the zero-point phonon energy. In the second line of Eq. 11 the zero temperature part has been added and subtracted in order to make the zero-point electronic contribution explicit. In the third and fourth lines of Eq. 11 the zero-point electronic contribution has been replaced by a more accurate electronic \( T = 0 \) frozen lattice energy, \( E_{el}(V) \). This is computed, for example, by DFT. It contains additional energy, beyond the single-particle zero-point part of the first two lines of Eq. 11.

Now Taylor-expands in powers of the lattice displacements around the frozen lattice structure \( V_0 \). The zeroth order term, \( F_{QH}(V_0, T) \), contains the large \( T \)-independent piece \( E_{el}(V_0) \), plus thermal shifts \( \Delta F_{el}^{QH}(V_0, T) + \Delta F_{ph}^{QH}(V_0, T) \). This \( (V-V_0) \)-independent term does not affect thermal expansion. The first contributing terms in the expansion are

\[
F_{QH}(V, T) - F_{QH}(V_0, T) = \frac{B_0 V_0}{2} \left( \frac{V - V_0}{V_0} \right)^2 + V_0 \left[ \frac{\partial^2 F_{el}^{QH}}{\partial V^2} \right] \left( \frac{V - V_0}{V} \right) + \ldots \tag{13}
\]

By definition, the large term \( E_{el}(V) \) is minimum at \( V = V_0 \), so does not contribute in first order in \( (V-V_0) \). Its second derivative gives \( B_0 \),

\[
B_0 = V_0 \left( \frac{\partial^2 E_{el}}{\partial V^2} \right)_{V=V_0}. \tag{14}
\]

Here \( B_0 \) is the leading-order strain tensor, equal to a scalar, the bulk modulus, in simple crystals. It is uncertain what volume \( V^* \) should be used when the derivatives are taken. The convenient choice \( V^* = V_0 \) will be used here. The corrections from different \( V^* \) choices are small. The second derivatives of \( \Delta F_{el}^{QH}(V, T) + \Delta F_{ph}^{QH}(V, T) \) are omitted because they are small compared to \( B_0 V \). Stopping the expansion here gives the standard Gr"uneisen theory. Recent advances in computation have allowed reliable evaluation of higher-order effects, beyond Gr"uneisen. These give noticeable corrections at higher \( T \), as will be mentioned below.

The quasiharmonic equation of state is given by

\[
P(V, T) = -(\partial F_{QH}/\partial V)_{T}. \tag{15}
\]

Zero pressure \( P = 0 \) structure parameters minimize the free energy \( (\partial F/\partial V)_{T} = 0 \). This gives the first-order QH result,

\[
\left( V_1^{QH}(T) - V_0 \right)_{V_0} = -\frac{1}{B_0} \left[ \left( \frac{\partial F_{el}^{QH}}{\partial V} \right)_T + \left( \frac{\partial F_{ph}^{QH}}{\partial V} \right)_T \right] V_0. \tag{15}
\]

For the \( P > 0 \) result, add \( P \) to the terms inside \( [ ] \). That gives the first-order QH equation of state. Now introduce electron and phonon Gr"uneisen parameters. They are in general vectors, and \( 1/B_0 \) is a tensor. Gr"uneisen\textsuperscript{a} already recognized the vector nature of his parameters:

\[
\gamma_k \equiv -\frac{V}{(\epsilon_k - \mu)} \frac{d(\epsilon_k - \mu)}{dV} \tag{16}
\]

These are computed from the bare QP (i.e. the QH) energies. Then the two parts of the QH thermal expansions are

\[
\begin{align*}
\left( \frac{V_1 - V_0}{V_0} \right)_{el}^{QH} & = \frac{1}{B_0 V_0} \sum_k (\epsilon_k - \mu) \gamma_k (f_{K0}(V, T) - f_{K0}(V, 0)) \\
\left( \frac{V_1 - V_0}{V_0} \right)_{ph}^{QH} & = \frac{1}{B_0 V_0} \sum Q \hbar \omega Q \gamma_Q (n_Q + 1/2). \quad (18)
\end{align*}
\]

This is Gr"uneisen limit of QH theory\textsuperscript{a}. Equation 18 is the Mikura theory\textsuperscript{e} and Eq. 19 is the Gr"uneisen theory\textsuperscript{a}. The electronic part is usually omitted. It dominates in metals at low \( T \), but is otherwise much smaller than the vibrational part, especially in non-metals. The full expression for \( \Delta V \) (which includes zero-point effects) is not usually given in the literature; Refs. 18, 26, 30 give parts or all of the answer. More often the \( T \) derivative \( \alpha(T) = (dV/dT)/V \) is given,

\[
\alpha_{QH}(T) = \frac{1}{B_0} \left[ \sum_k C_k^{el}(T) \gamma_k + \sum Q C_Q^{ph}(T) \gamma_Q \right], \tag{20}
\]

where \( V_0 C_k^{el} = (\epsilon_k - \mu) \partial f/K/\partial T \) is the mode \( K \) contribution to the electron specific heat, and \( V_0 C_Q^{ph} = \hbar \omega_Q \gamma_Q / \partial T \) is the mode \( Q \) contribution to the phonon specific heat. The corresponding formula for the first \( T \)-dependent correction to the bulk modulus is

\[
B_{QH}(T) - B_0 = \sum Q \left[ [U_Q(T) \gamma_Q - T C_Q \gamma_Q^2] \right. \\
+ \sum_k \left[ [U_K(T) - U_K(0)] \gamma_k - T C_K \gamma_k^2 \right) \tag{21}
\]

\[
\gamma_Q \equiv \left( \frac{V^2}{\omega_Q} \frac{d^2 \omega_Q}{dV^2} \right)_{V_0} \gamma'_Q \equiv \left( \frac{V^2}{(\epsilon_k - \mu)} \frac{d^2(\epsilon_k - \mu)}{dV^2} \right)_{V_0}. \tag{22}
\]

where \( V_0 U_Q \equiv \hbar \omega_Q (n_Q + 1/2) \) is the mode \( Q \) contribution to the volumetric thermal vibrational energy, and \( V_0 U_K \equiv \epsilon_k f_K \) is the mode \( K \) contribution to the non-interacting volumetric thermal electron energy. I did not find these leading order formulas for \( \Delta B \) in previous literature. Wu and Wentzovitch\textsuperscript{f} give general formulas for the tensor elastic constants in QH theory and classical approximation. Davies\textsuperscript{h} and others have done it with quantized lattice vibrations.

At \( T > \Theta_D \), the phonon part of Eq. 20 (Gr"uneisen theory) gives a thermal expansion \( \alpha(T) \) that saturates at \( (k_B / B_0 V_0) \sum_Q \gamma_Q \), similar to the behavior of the harmonic specific heat \( C(T) \). Experimental \( C(T) \) usually saturates fairly cleanly. However, \( \alpha(T > \Theta_D) \) is often
less constant than \( C(T > \Theta_D) \). This does not necessarily indicate that true anharmonic corrections have begun entering. The lowest order version, Eq. 13 of QH theory needs to be extended to higher powers of \( \Delta V \). Rather than further terms in Taylor series, it is more common simply to do the full calculation in Eqs. 11 and 12 numerically. At each chosen volume, the QH free energy is calculated versus \( T \). The value of \( T \) that minimizes \( F_{QH} \) gives a discreet point on the QH \( V(T) \) curve. It was done, for example, with the help of model equations of state, by Kantorovich\(^{23} \) in 1995 for KCl and NaCl. Advances in computation now allow reliable model-free calculations of this kind; for example, the work by Skelton et al.\(^{11} \) for PbTe and Erba et al.\(^{11} \) for MgO and CaO. Deviations from constant \( \alpha(T > \Theta_D) \) are often quite well described.

The full QH theory shows that anharmonic corrections may be unnecessary for a weakly anharmonic material like MgO until \( T \) is significantly higher than \( \Theta_D \). The only advantage of using the Grüneisen expansion is that Eqs. 18 and 19 have an appealing simplicity that disappears in the more complete version of QH theory.

V. QUASIPARTICLE THERMODYNAMICS

The aim is to compute renormalization corrections (anharmonic and electron-phonon) beyond QH to the \( V \)-dependence of \( F(V, T) \). This problem has been addressed by many authors, for example, Werthamer\(^{34} \), and Götzte and Michl\(^{35} \). The straightforward route is to use Feynman-Dyson-Matsubara perturbation theory for such corrections. For anharmonic phonon interactions, the answer derived by Liebfried and Ludwig\(^{36} \) can be used for this purpose. Unfortunately, the corresponding correction to \( F(V, T) \) from electron-phonon interactions double-counts the electron-phonon renormalization effects on phonons, which were already included in \( F_{QH} \). Therefore an alternate route is needed. One can find the desired corrections to entropy \( S \), and then integrate to get \( F \).

For gases of independent quasiparticles obeying Fermi-Dirac or Bose-Einstein statistics, entropy can be evaluated by counting the number of ways of distributing their occupation. The formulas are\(^{37} \)

\[
S_{el} = -k_B \sum_K [f_K \ln f_K + (1 - f_K) \ln (1 - f_K)].
\]

\[
S_{ph} = k_B \sum_Q [(n_Q + 1) \ln (n_Q + 1) - n_Q \ln n_Q],
\]

Although rigorously true only for non-interacting particles, there is justification for using these formulas for gases with reasonably well-defined quasiparticles. The distributions \( f_K \) and \( n_Q \) then have \( T \)-dependent energies\(^{31,37} \). The renormalization corrections to \( S \) are given correctly to lowest order, and effects of higher order in perturbation theory are partially captured. Then the \( T \)-dependent part of the free energy can be obtained from

\[
F(V, T) - F(V, 0) = - \int_0^T dT' S(V, T').
\]

If QH energies (independent of \( T \)) are used in the distributions \( f_K \) and \( n_Q \) in Eqs. 23 and 24, the \( dT' \) integrals can be done explicitly, and give Eqs. 11 and 12 except that the zero-point contributions have been subtracted off. In other words, they are exactly as expected from Eq. 11. As a reality check, a method for doing the integration is explained in the appendix.

VI. CORRECTIONS TO QH THEORY FROM QP RENORMALIZATION

QH theory puts the first two terms of the energies in Eqs. 1 and 2 into the free energy Eqs. 11 and 12. To get the renormalization corrections \( \Delta F_{renorm} \) from \( \Delta \epsilon_{QP} \) and \( \Delta \omega_{QP} \), use the entropy formulas 23 and 24 with the full QP energies in Eqs. 1 and 2. Then Taylor expand to first order in \( \Delta \epsilon_{QP} \) and \( \Delta \omega_{QP} \). The zeroth order terms can be integrated over \( T' \) as in Eq. 43 to reproduce the QH results. The first order terms can then be numerically integrated over \( T' \) to give the corrections \( \Delta F_{renorm}(V, T) \). Then the volume derivative gives the correction to \( (V - V_0)/V_0 \).

To be specific, here is the electronic contribution from QP renormalization:

\[
\frac{\partial \Delta F_{QP}^{el}}{\partial V} = \int_0^T dT' \sum_K \frac{\partial [(1 - f_K) \ln (1 - f_K) + f_K \ln f_K]}{\partial (\epsilon_K - \mu)} \times k_B \frac{\partial \Delta (\epsilon_K - \mu)_{QP}}{\partial V}.
\]

The shift \( \Delta (\epsilon_K - \mu)_{QP} \) is the renormalization \( \Delta \epsilon_{QP}^{el} \) in Eq. 1 minus the shift \( \Delta \mu \) of the chemical potential. A Grüneisen-like parameter \( \Delta \gamma_K \) can be defined,

\[
\Delta \gamma_K = - \left( \frac{V}{(\epsilon_K - \mu)} \frac{\partial \Delta (\epsilon_K - \mu)_{QP}}{\partial V} \right)_{V^*=V_0}.
\]

This is smaller than the analogous Eq. 16 for the ordinary electronic Grüneisen parameter. The fractional volume shift \(-V[\partial \Delta (\epsilon_K - \mu)_{QP}/\partial V]/(\epsilon_K - \mu)_{QP}\) of the quasiparticle renormalization is probably similar in size to the ordinary Grüneisen parameter, the fractional volume shift \(-V[\partial \Delta (\epsilon_K - \mu)_0/\partial V]/(\epsilon_K - \mu)_0\). But since both are normalized to \((\epsilon_K - \mu)_0\), \( \Delta \gamma_K \) is smaller than \( \gamma_K \). Once again, there is uncertainty about the volume \( V^* \) to be used, but the convenient value \( V_0 \) is chosen here. Then Eq. 26 can be written

\[
\frac{\partial \Delta F_{QP}^{el}}{\partial V} = - \int_0^T dT' \sum_K C_K(T') \Delta \gamma_K(T'),
\]

\[
\Delta \gamma_K = - \left( \frac{V}{(\epsilon_K - \mu)} \frac{\partial \Delta (\epsilon_K - \mu)_{QP}}{\partial V} \right)_{V^*=V_0}.
\]
This can now be compared to the corresponding QH formula (compare Eqs. 15 and 18),
\[
\frac{\partial F_{\text{el}}^{\text{QH}}}{\partial V} = -\frac{1}{V_0} \sum_K (\epsilon_K - \mu) \gamma_K (f_{K0}(V, T) - f_{K0}(V, 0))
\]  
(29)

These formulas are very similar. If Grüneisen-type parameters are ignored, then Eq. 29 is the thermal electron energy per volume, while Eq. 28 is the T-integrated electronic specific heat (the same thing, except for slightly different volume normalizations). But the Grüneisen-type parameters are quite different. The ratio \( \Delta \gamma_K/\gamma_K \) is expected to be similar in size to \( \Delta (\epsilon_K - \mu)QP/(\epsilon_K - \mu) \), a small number. Therefore, the QP correction to the QH \( dF/dV \) is small, and (except for the low-T mass renormalization) QH theory is justified for the electron part.

The phonon contribution from QP renormalization is
\[
\frac{\partial \Delta F_{\text{ph}}^{\text{QP}}}{\partial V} = -\int_0^T dT' \sum_Q \frac{\partial [(n_Q + 1) \ln(n_Q + 1) + n_Q \ln n_Q]}{\partial \omega_Q} \cdot k_B \left( \frac{\partial \Delta \omega_Q^{\text{QP}}}{\partial V} \right)_{V*,=V_0}
\]
(30)
The shift \( \Delta \omega_Q^{\text{QP}} \) is the renormalization \( \Delta \omega_Q^{\text{QP}}(V, T') \) in Eq. 2. Define a Grüneisen-like parameter \( \Delta \gamma_Q \).
\[
\Delta \gamma_Q = -\left( \frac{V}{\omega_Q} \frac{\partial \Delta \omega_Q^{\text{QP}}}{\partial V} \right)_{V*,=V_0}
\]
(31)
This is smaller than the analogous Eq. 17 for the ordinary phonon Grüneisen parameter. The fractional volume shift \( -V (\partial \Delta \omega_Q^{\text{QP}}/\partial V) / \Delta \omega_Q^{\text{QP}} \) should be similar in size to \( \gamma_Q \). But \( \Delta \gamma_Q \) is normalized to the larger harmonic frequency \( \omega_Q \). There is another important difference between this Grüneisen-like parameter and the ordinary Grüneisen parameter of Eq. 17. \( \Delta \gamma_Q \) is \( T \)-dependent (increases with \( T \) as anharmonicity increases), while \( \gamma_Q \) is a constant, independent of \( T \). The same may be true of the electronic versions.

Then Eq. 28 becomes
\[
\frac{\partial F_{\text{ph}}^{\text{QP}}}{\partial V} = -\int_0^T dT' \sum_Q C_Q(T') \Delta \gamma_Q(T'),
\]
(32)
This can now be compared to the corresponding QH formula (compare Eqs. 15 and 18),
\[
\frac{\partial F_{\text{ph}}^{\text{QH}}}{\partial V} = -\frac{1}{V_0} \sum_Q h \omega_Q \gamma_Q (n_Q + 1/2)
\]
(33)
These two equations are parallel to Eqs. 28 and 29 except that Eq. 33 has an extra zero-point energy contribution (the 1/2). This does not alter the observation that Eqs. 32 and 33 are very similar in magnitude except that \( \Delta \gamma_Q/\gamma_Q \) has the magnitude of \( \Delta \omega_Q^{\text{QP}}/\omega_Q \), based on similar sensitivity to volume change. This demonstrates that QP corrections to the phonon QH volume derivative of \( F \) are small.

Similar results can be found for the QP corrections to the QH thermal shift of \( B = V_0^2 F/\partial V^2 \). Except for the low \( T \) electronic mass renormalization correction, the QP corrections to \( B \) are normally smaller than the QH corrections given in Eq. 21.

The explicit quasiparticle correction formulas (28 and 29) have not been published before. They have potential use for thinking about or computing higher order thermal expansion or \( B(T) \) corrections. Consider the next order corrections to the expansion of Eq. 13
\[
F(V, T) - F(V_0, T) = B_0 V_0 \left( \frac{V - V_0}{V_0} \right)^2 + B_1 V_0 \left( \frac{V - V_0}{V_0} \right)^3
\]
\[
+ V_0 \left[ \frac{\partial F_{\text{el}}^{\text{QH}}}{\partial V} + \frac{\partial F_{\text{ph}}^{\text{QH}}}{\partial V} \right] \left( \frac{V - V_0}{V_0} \right) + \ldots
\]
(34)
Three new terms have been added. (1) The frozen lattice electron energy \( E_{\text{el}}(V) \) now has a third derivative term \( B_3 = V_0 (\partial B_0/\partial V)_{V_0} \). (2) The QH electron energy \( \epsilon_K(V) \) and QH phonon energy \( \omega_K(V) \) volume dependence is now expanded to second order. (3) The quasiparticle corrections of Eqs. 28 and 29 are now kept in first order. The volume that minimizes this expression (or, for \( P > 0 \), that satisfied \( \partial F/\partial V \) in Eq. 21) the low \( T \) thermal shift of the bulk modulus is
\[
\left( \frac{V - V_0}{V_0} \right)(T) = -\frac{1}{V_0} \left[ \frac{\partial F_{\text{el}}^{\text{QH}}}{\partial V} + \frac{\partial F_{\text{ph}}^{\text{QH}}}{\partial V} \right].
\]
(35)
The corresponding formula for thermal expansion is
\[
\alpha(T) = \alpha_{\text{el}} + \Delta \alpha_{\text{QP}}
\]
(36)
where \( \Delta \alpha_{\text{QP}} = \Delta \alpha_{\text{el}}^q + \Delta \alpha_{\text{ph}}^q \), and
\[
\Delta \alpha_{\text{QP}}(T) = \frac{1}{B_0} \left[ \sum_K C_K^q(T) \Delta \gamma_K + \sum_Q C_Q^q(T) \Delta \gamma_Q \right].
\]
(37)
This is the analog of Eq. 27. The renormalization corrections are smaller, as suggested by a \( \Delta \) in their formulas.

VII. CONCLUSION

Except in metals at low \( T \), QH theory gives the correct leading order \( V \) derivatives of \( F(V, T) \). Therefore thermal expansion and thermal shift of the bulk modulus are
accurately described in leading order. QH should not be considered a theory of anharmonic effects. In a hypothetical purely harmonic crystal, the frequencies \( \omega_Q \) are independent of \( V \), but a non-zero \( \gamma_Q \) does not require explicit anharmonic forces. The insistence that this is “anharmonic” only causes confusion. The computed harmonic frequencies \( \omega_{QH}(V) \) are usually close to the measured quasiparticle frequencies \( \omega_{QP}(V, T) \), but differ increasingly at high \( T \). However, the volume derivative needed for \( \partial F/\partial V \) is dominated by the volume dependence of the harmonic frequency \( \omega_Q(V) \). The correction from the volume derivative of \( \omega_{QP}(V, T) - \omega_Q(V) \) is higher order, but not negligible at high \( T \).

**VIII. APPENDIX**

The aim is to do integrals

\[
I_{el}(T) = -k_B \sum_{K} \int_{0}^{T} dT'[f_K(T') \ln f_K(T') + (1 - f_K(T')) \ln(1 - f_K(T'))].
\]  
(38)

\[
I_{ph}(T) = -k_B \sum_{Q} \int_{0}^{T} dT'[n_Q(T') \ln n_Q(T') - (n_Q(T') + 1) \ln(n_Q(T') + 1)].
\]  
(39)

The trick is to write for electrons

\[
T = \frac{\epsilon_K - \mu}{k_B} \frac{1}{\ln((1 - f_K)/f_K)}
\]  
(40)

and for phonons

\[
T = \frac{\hbar \omega_Q}{k_B} \frac{1}{\ln((1 + n_Q)/n_Q)}.
\]  
(41)

Then the integrals become

\[
I_{el}(T) = -k_B \sum_{K} \int_{f_K(0)}^{f_K(T)} df_K [f_K \ln f_K + (1 - f_K) \ln(1 - f_K)] \frac{dT}{df_K}
\]  
(42)

and

\[
I_{ph}(T) = -k_B \sum_{Q} \int_{n_Q(0)}^{n_Q(T)} dn_Q [n_Q \ln n_Q
\]

\[
- (n_Q + 1) \ln(n_Q + 1)] \frac{dT}{dn_Q}.
\]  
(43)

Because the QH energies \( \epsilon_K \) and \( \omega_Q \) do not depend on \( T \), the derivatives \( dT/df_K \) and \( dT/dn_Q \) are easy. The resulting formulas can be integrated by parts, and yield the answers shown in Eqs. 11 and 12.

**IX. ERRATUM**

The text above was already published in Modern Physics Letters B Vol. 34, No. 2 (2020) 2050025. Three interesting papers [35, 36] should have been cited.

Stimulated by Varma et al., I noticed an important error in this paper, which invalidates some of the results, but is easily corrected. The underlying method is to find temperature \((T)\)-dependent corrections from electron-phonon interactions to the free energy \( F(V, T) \). The starting point is the quasiparticle (QP) energy \( \epsilon_{k, QP} = \epsilon_k(V) + \Delta \epsilon_{k, EP}(T) \) of electron bands. When the electron-phonon shift \( \Delta \epsilon_{k, EP} \) is omitted, the volume \((V)\) dependence of band energies \( \epsilon_k(V) \) gives the quasiharmonic approximation (QHA). The QP corrections to \( \epsilon_k \) are then used to find corrections beyond QHA to properties like thermal expansion. Another correction not given by \( \Delta \epsilon_{k, EP} \) should be included.

It is argued that the entropy \((S(V, T))\) of interacting quasiparticles is given (provided quasiparticle energies are not too badly smeared by lifetime broadening) by using renormalized (and generally \( T \)-dependent) quasiparticle energies in the formulas for the entropy of noninteracting particles.

The free energy is then obtained from the entropy using

\[
F(V, T) = F(V, 0) - \int_{0}^{T} dT' S(V, T').
\]  
(44)

This is Eq. 25 of the main text. The error is failure to note that the zero-temperature piece \( F(V, 0) \) contains an additional correction related to quasiparticle renormalization. Here I argue that this correction can be easily constructed using density-functional theory (DFT) results. At \( T = 0 \), \( F(V, 0) = E(V, 0) \rightarrow E_{DFT}(V) + \Delta E_{EP}(V, 0) \). The electron-phonon correction \( \Delta E_{EP} \) to lowest order is found from the effective Hamiltonian

\[
H_{eff} = \sum_k \epsilon_k(V) c_k \dagger c_k + \sum_Q \hbar \omega_Q (a_Q \dagger a_Q + 1/2) + V_{ep}
\]  
(45)

\[
V_{ep} = \sum_{kQ} V^{(1)}(kQ) c_k \dagger c_{k+Q} (a_Q + a_{-Q} \dagger)
\]

\[
+ \sum_{kk'Q'Q''} V^{(2)}(kQQ') c_k c_{k+Q+Q'} (a_Q a_{-Q'} \dagger a_{-Q''}) + \cdots
\]  
(46)

where \( V^{(1)} \) and \( V^{(2)} \) are the lowest order Taylor expansion of the DFT energy at distorted atom coordinates \( \hat{R}_i = \hat{\ell} + \hat{u_i} \). The electron excitation energies \( \epsilon_k(V) \) for ordinary metals align well with the DFT energies \( \epsilon_{k, DFT}(V) \), and the phonon excitations \( \omega_Q \) are ordinarily given by density-functional perturbation theory (DFPT). Then the perturbative correction to the ground state en-
energy is
\[
\Delta E_{EP}(V, 0) = \sum_{k} \left[ (k|V^{(2)}|k) + \sum_{Q} \frac{(k|V^{(1)}|k + Q)|^2}{\epsilon_k - \epsilon_{k+Q}} (1 - f_{k+Q}) \right] f_k, \tag{47}
\]
where \(f_k\) is the Fermi distribution, here at \(T = 0\). This result has the same structure as the sum of electron-phonon energy shifts \(\Delta \epsilon_{k,EP}\) of occupied states \(k\), given by the Allen-Heine formula. But it differs because of the factor \(1 - f_{k+Q}\) in the second term, which is not present in the QP energy shifts. The additional lowest-order electron-phonon correction (eq. 47) to the free energy is of similar magnitude to the corrections already discussed in the main text. In particular, eqs. 26, 28, 30, 32, and 37 need corrections easily derivable from eq. 47.

**X. ACKNOWLEDGEMENTS**

I thank S. Baroni and M. L. Klein for help with the literature, and B. Fultz, P. Ordejon, and N. K. Ravichandran for discussions. This work was supported in part by DOE grant No. DE-FG02-08ER46550.

---

1. R. M. Martin, L. Reining, and D. M. Ceperley, *Interacting Electrons: Theory and Computational Approaches* (Cambridge University Press, 2016).
2. S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, “Phonons and related crystal properties from density-functional perturbation theory,” Rev. Mod. Phys. 73, 515–562 (2001).
3. S. Baroni, P. Giannozzi, and E. Isaev, “Density-functional perturbation theory for quasi-harmonic calculations,” Rev. Mineral. Geochem. 71, 39 (2010).
4. E. Gruneisen, “Theorie des festen Zustandes einatomiger Elemente,” Annalen der Physik 344, 257–306 (1912).
5. E. Gruneisen, “Zustand des festen Körpers,” in *Handbuch der Physik*, edited by H. Geiger and K. Scheel (Springer, Berlin, 1926) pp. 1–52. An English translation is available at http://www.dtic.mil/dtic/tr/fulltext/u2/215056.pdf.
6. A. Otero-de-la-Roza, D. Abbassi-Pérez, and V. Luaña, “GIBBS2: A new version of the quasiharmonic model code. II. Models for solid-state thermodynamics, features and implementation,” Computer Physics Communications 182, 2232–2248 (2011).
7. A. Otero-de-la-Roza and V. Luaña, “Treatment of first-principles data for predictive quasiharmonic thermodynamics of solids: The case of MgO,” Phys. Rev. B 84, 024109 (2011).
8. A. Otero-de-la-Roza and Víctor Luaña, “Equations of state and thermodynamics of solids using empirical corrections in the quasiharmonic approximation,” Phys. Rev. B 84, 184103 (2011).
9. Z. Mikura, “Contribution of the conduction electrons in a metal to the thermal expansion,” Proc. Phys. Math. Soc. Japan 23, 390 (1941).
10. S. Viswanathan, “Thermal expansion at low temperatures,” Phys. Rev. 81, 626–627 (1951).
11. A. Erba, M. Shahrokh, R. Moradian, and R. Dovesi, “On how differently the quasi-harmonic approximation works for two isostructural crystals: Thermal properties of periclase and lime,” J. Chem. Phys. 142, 044114 (2015).
12. D. S. Kim, O. Hellman, J. Herriman, H. L. Smith, J. Y. Y. Lin, N. Shulumba, J. L. Niedziela, C. W. Li, D. L. Abernathy, and B. Fultz, “Nuclear quantum effect with pure anharmonicity and the anomalous thermal expansion of silicon,” Proc. Nat. Acad. Sci. 115, 1992–1997 (2018).
13. Y. Shen, C. N. Saunders, C. M. Bernal, D. L. Abernathy, M. E. Manley, and B. Fultz, “Anharmonic origin of the giant thermal expansion of nabl,” Phys. Rev. Lett. 125, 085504 (2020).
14. O. Delaire, J. Ma, K. Marty, A. F. May, M. A. McGuire, M. H. Du, D. J. Singh, A. Podlesnyak, G. Ehlers, M. D. Lumsden, and B. C. Sales, “Giant anharmonic phonon scattering in PbTe,” Nature Materials 10, 614 – 619 (2011).
15. J. M. Skelton, S. C. Parker, A. Togo, I. Tanaka, and A. Walsh, “Thermal physics of the lead chalcogenides PbS, PbSe, and PbTe from first principles,” Phys. Rev. B 89, 205203 (2014).
16. B. Houston, R. E. Strakna, and H. S. Belson, “Elastic constants, thermal expansion, and Debye temperature of lead telluride,” J. Appl. Phys. 39, 3913–3916 (1968).
17. T. H. K. Barron, “Equation of state and thermodynamic properties,” in *Proceedings of the VIIth International Conference on Low Temperature Physics*, edited by G. M. Graham and A. C. Hollis Hallett (U. of Toronto Press, Toronto, 1961) pp. 655 – 670.
18. G. Leibfried and W. Ludvig, “Theory of anharmonic effects in crystals,” in *Solid State Physics*, Vol. 12, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1961) pp. 276 – 444.
19. E. R. Cowley, R. A. Cowley, and Cochran W., “Anharmonic interactions in alkali halides I,” Proc. R. Soc. Lond. A 287, 259–280 (1966).
20. R. A. Cowley, “Anharmonic crystals,” Rep. Progr. Phys. 31, 123 (1968).
21. D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972) , reprinted by Dover Publications, 1998.
22. P. B. Allen and V. Heine, “Theory of the temperature dependence of electronic band structures,” J. Phys. C: Solid State Physics 9, 2305–2312 (1976).
23. S. Poncé, Y. Gillet, J. Laffamme Janssen, A. Marini, M. Verstraete, and X. Gonze, “Temperature dependence of the electronic structure of semiconductors and insulators,” J. Chem. Phys. 143, 102813 (2015).
24. G. Grimvall, *The Electron-Phonon Interaction in Metals (Selected Topics in Solid State Physics XVI)* (North Holland, Amsterdam, 1981).
25. G. Grimvall, *Thermophysical Properties of Materials* (North Holland, Amsterdam, 1986).
E. A. Stern, “Theory of the anharmonic properties of solids,” Phys. Rev. 111, 786–797 (1958).

J. Ziman, Electrons and Phonons (Oxford University Press, New York, 1960).

P. Pavone and S. Baroni, “Dependence of the crystal lattice constant on isotopic composition: Theory and ab initio calculations for C, Si, and Ge,” Solid State Commun. 90, 295–297 (1994).

Liang-Feng Huang, Xue-Zeng Lu, E. Tennesen, and J. M. Rondinelli, “An efficient ab-initio quasiharmonic approach for the thermodynamics of solids,” Computational Materials Science 120, 84–93 (2016).

D. C. Wallace, Statistical Physics of Crystals and Liquids (World Scientific, Singapore, 2002).

Zhongqing Wu and Renata M. Wentzcovitch, “Quasiharmonic thermal elasticity of crystals: An analytical approach,” Phys. Rev. B 83, 184115 (2011).

G. F. Davies, “Effective elastic moduli under hydrostatic stress - I. quasi-harmonic theory,” J. Phys. Chem. Solids 35, 1513–1520 (1974).

L. N. Kantorovich, “Thermoelastic properties of perfect crystals with nonprimitive lattices. II. Application to KCl and NaCl,” Phys. Rev. B 51, 3535–3548 (1995).

N. R. Werthamer, “Self-consistent phonon formulation of anharmonic lattice dynamics,” Phys. Rev. B 1, 572–581 (1970).

W. Götz and K. H. Michel, “Elastic constants of nonionic anharmonic crystals,” Z. Phys. B 217, 170–187 (1968).

E. M. Lifshitz and L. P. Pitaevsky, Statistical Physics, 3rd Edition (Pergamon Press, Oxford, 1980).

T. H. K. Barron, “Thermodynamic properties and effective vibrational spectra of an anharmonic crystal,” in Lattice dynamics: Proceedings of the international conference held at Copenhagen, edited by R. F. Wallis (Pergamon Press, Oxford, 1963) pp. 247 – 254.

O. Delaire, M. S. Lucas, J. A. Muñoz, M. Kresch, and B. Fultz, “Adiabatic electron-phonon interaction and high-temperature thermodynamics of A15 compounds,” Phys. Rev. Lett. 101, 105504 (2008).

N. Bock, D. Coffey, and Wallace D. C., “Nonadiabatic contributions to the free energy from the electron-phonon interaction in Na, K, Al, and Pb,” Phys. Rev. B 72, 155120 (2005).

N. Bock, Wallace D. C., and D. Coffey, “Adiabatic and nonadiabatic contributions to the free energy from the electron-phonon interaction for Na, K, Al, and Pb,” Phys. Rev. B 73, 055114 (2006).

A. R. Varma, S. Paul, A. Itale, P. Pable, R. Tibrewala, S. Dodal, H. Yerunkar, S. Bhaumik, V. Shah, M. P. Gururajan, and T. R. S. Prasanna, “Electron-phonon interaction contribution to the total energy of group IV semiconductor polymorphs: Evaluation and implications,” arXiv:2204.08321.