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Inherent anharmonicity of harmonic solids

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ABSTRACT

Atomic vibrations, in the form of phonons, are foundational in describing the thermal behavior of materials. The possible frequencies of phonons in materials are governed by the complex bonding between atoms, which is physically represented by a spring-mass model that can account for interactions (spring forces) between the atoms (masses). The lowest order, *harmonic*, approximation only considers linear forces between atoms and is thought incapable of explaining phenomena like thermal expansion and thermal conductivity, which are attributed to non-linear, *anharmonic*, interactions. Here we show that the kinetic energy of atoms in a solid produces a pressure much like the kinetic energy of atoms in a gas does. This vibrational or *phonon pressure* naturally increases with temperature, as it does in a gas, and therefore results in a thermal expansion. Because thermal expansion thermodynamically defines a Grüneisen parameter γ , which is a typical metric of anharmonicity, we show that even a harmonic solid will necessarily have some anharmonicity. A consequence of this phonon pressure model is a harmonic estimation of the Grüneisen parameter as $\gamma \approx (3/2)(3 - 4x^2)/(1 + 2x^2)$, where $x = v_t/v_l$ is the ratio of the transverse and longitudinal speeds of sound. We demonstrate the immediate utility of this model by developing a high-throughput harmonic estimate of lattice thermal conductivity that is comparable to other state-of-the-art estimations. By linking harmonic and anharmonic properties explicitly, this study provokes new ideas about the fundamental nature of anharmonicity, while also providing a basis for new materials engineering design metrics.

Broader Context

Non-linear “anharmonic” forces between atoms are responsible for many behaviors of thermoelectric, battery, fuel cell, and photovoltaic materials, because they govern diverse phenomena ranging from the thermodynamics of heat to the propagation of earthquakes. Yet, the ubiquity of anharmonicity does not mean that it is well-understood. Without a detailed study of the vibrational properties of a material (i.e. phonons) it is nearly impossible to make any prediction about the magnitude of thermal expansion, thermal conductivity, or other so-called anharmonic properties of solids. Here, we demonstrate a fundamental relation between harmonicity (e.g. elasticity), which is well-characterized in every kind of solid, and anharmonicity, which is not well-characterized and is a highly active field of research. We show how anharmonicity can be interpreted as the result of mechanical pressure exerted by vibrating atoms on the rest of the solid, and contextualize this perspective with the current quantum mechanical interpretation. This work provides a new framework by which anharmonicity may be characterized from harmonic properties of solids, subsequently leading to metrics of anharmonicity useful for materials screening and design.

The characterization and understanding of atomic bonding has been the subject of solid state physics and physical chemistry for more than a century, and even still there are new notions about the nature of chemical bonds in solids¹. Fundamental to the description of a bond is how it deforms when a force is applied. Although most materials exhibit Hookean elastic behavior (i.e. a linear stress-strain relation) for small atomic displacements, this often breaks down at larger displacements. And yet, this non-linear or anharmonic behavior is essential to the material properties relevant to modern energy technologies, such as thermal conductivity², atomic/ionic diffusion³, thermal stability⁴, defect formation⁵, ferroelectricity⁶, and superconductivity⁷. For thermoelectric materials in

particular, anharmonicity is seen as crucial for low thermal conductivity and high thermoelectric performance^{2,8–10}.

The spring-mass model of atomic bonding has been an indispensable tool, providing a clear conceptual link between classical and quantum mechanics¹¹. In this model, the complicated interactions between atoms (masses) are attributed to spring-like forces. Specifically, the key aspects of bonding are described by an n -degree Taylor expansion of the interatomic potential about the equilibrium position of the atoms. Then the total potential energy of the material can be written in terms of the displacement u of atoms α , β , etc. from their equilibrium positions in cartesian coordinates (indexed by

i, j, k) as¹²

$$U = U_0 + \sum_{\alpha} \sum_i (-f_i^{\alpha}) u_i^{\alpha} + \frac{1}{2!} \sum_{\alpha, \beta} \sum_{i, j} C_{ij}^{\alpha\beta} u_i^{\alpha} u_j^{\beta} + \frac{1}{3!} \sum_{\alpha, \beta, \gamma} \sum_{i, j, k} C_{ijk}^{\alpha\beta\gamma} u_i^{\alpha} u_j^{\beta} u_k^{\gamma} + \dots \quad (1)$$

Here, U_0 accounts for any initial potential energy already contained by the bonds (springs) at equilibrium and the linear term $(-f_i^{\alpha} = (\partial U / \partial u_i^{\alpha})_{u_i^{\alpha}=0})$ is zero since there is no net force on any atom at equilibrium (by definition). The “harmonic” term (with force constants $C_{ij}^{\alpha\beta}$) is the lowest order term that describes changes in the potential energy when an atom is displaced from its equilibrium position and can be used to obtain the fundamental frequencies of vibration (i.e. phonon eigenmodes). Cubic (i.e. $C_{ijk}^{\alpha\beta\gamma}$) and higher order “anharmonic” terms account for non-linear forces between atoms. Implicitly, each term (U_0 , f , C and u) in Eq. 1 is temperature dependent since the force constants and equilibrium positions of the atoms can change with temperature.

The generality of Eq. 1 has made it the starting point for theoretical and computational assessments of diverse material behaviors^{11–13}. But, it becomes computationally expensive to consider both higher order terms in atomic displacement and the temperature dependence of the potential. The thermodynamic Maxwell relation, however, between entropy S , pressure P , volume V and temperature T ,

$$(\partial S / \partial V)_T = (\partial P / \partial T)_V, \quad (2)$$

subsequently shows that isothermal material properties can be related to temperature dependent properties (the subscripts indicate which variable is held constant). It is not surprising then that a description of thermal expansion (i.e. the quasi-harmonic model¹⁴) can be obtained using the Taylor expansion (Eq. 1) at 0 K, since $(\partial P / \partial T)_V$ is directly related to the bulk modulus $B = -(\partial P / \partial \ln V)_T$ and thermal expansion coefficient $\alpha = (\partial \ln V / \partial T)_P$ as

$$(\partial P / \partial T)_V = -(\partial P / \partial \ln V)_T (\partial \ln V / \partial T)_P = B\alpha. \quad (3)$$

In the quasi-harmonic approximation, the change in vibrational entropy with volume is attributed to changes in phonon frequencies ω_i with volume, i.e. $(\partial S / \partial V)_T = \sum_i (\partial S / \partial \omega_i)_T (\partial \omega_i / \partial V)_T$. From this perspective (e.g. Fig. 1) anharmonic terms are necessary in Eq. 1 for $(\partial \omega_i / \partial V)_T \neq 0$ ¹⁵, leading to the conclusion that harmonic solids cannot have thermal expansion.

Utilizing the phonon entropy (e.g. the quasi-harmonic approximation) however, is but one approach to modeling the physics of anharmonicity (Fig. 1). Alternatively, a mechanistic description of the pressure in solids could be used. This is easily done for an ideal gas but has not been considered for solids. The pressure exerted by an ideal gas is due to its kinetic energy. Atoms in a solid have the same form of kinetic energy as an ideal gas and should therefore have a

similar pressure. Importantly, the kinetic energy of atoms inside a solid will change with temperature with or without any change in the vibrational frequencies. This is to say that a mechanical model of pressure in solids would not necessarily require anharmonic terms to be included in the potential.

Herein, we provide an intuitive (mechanical) understanding of thermal expansion that also suggests an inherent connection between harmonic and anharmonic aspects of bonding in real solids. The specific nature of thermal expansion, thermal conductivity, and other “anharmonic” material properties is at the forefront of solid-state materials research¹⁶, as are methods to predict/calculate these properties *en masse*^{17–19}. Consequently, a mechanistic understanding of vibrational pressure in solids has broad implications for engineering design metrics of diverse material phenomena, such as negative thermal expansion, ultralow thermal conductivity and superconductivity. We demonstrate this utility by developing a harmonic estimate of the lattice thermal conductivity that is suitable for high-throughput screening of materials.

Results and discussion

It is well-known that a monatomic ideal gas at volume V exerts a pressure P (force/area) that is proportional to its average internal energy, $PV = 2E/3$. When combined with the equipartition theorem ($E \sim k_B T$), this relation gives the microscopic origin of the ideal gas law, $PV = NRT$. In general, pressures arise as a result of the confinement of kinetic energy. Consequently, diverse physical systems from ideal gases to laser beams²⁰ and ultrasound acoustic waves²¹ all produce pressures that are proportional to their kinetic energy density. A connection with the Umov-Poynting vector should also be noted. Each of these pressures can be determined by considering the flux of linear momentum (i.e. kinetic energy) through an arbitrary plane representing a confining surface (Fig. 2a and Supplemental Note 1). In the realistic case where the kinetic particles are actually confined by an elastic medium, there is an associated pressure (stress) provided by the medium as it deforms (i.e. strain $\neq 0$) in response to interacting with the particles.

For the same reasons, the kinetic energy of atomic vibrations gives rise to pressures in solids that can be thought of as phonon pressure. In fact, analogous to the ideal gas pressure, this phonon pressure is temperature dependent due to the change in kinetic energy with temperature. This is to say that, even for a harmonic solid, there is a pressure that can mechanistically facilitate thermal expansion (see Methods). For the sum of forces inside the solid to be zero at equilibrium (e.g. the linear term f_i^{α} in Eq. 1), the divergence of the stress tensor must be zero. Thus, the force exerted by the atomic vibrations must be compensated by an elastic restoring force that is proportional to the change in the equilibrium position. This is essentially the same physics that describes mechanical equilibrium in an elastic balloon-like container filled with an ideal gas.

To illustrate, consider a gas kept at a finite pressure in

Figure 1. Two different paths to understanding thermal expansion. While thermodynamically equivalent (Eq. 2), the current explanation of thermal expansion is through the perspective that vibrational modes shift as the volume changes (top panel). In this picture, anharmonicity is required for vibrational states to shift. Alternatively, the change in pressure due to changes in temperature can be considered (bottom panel), as is often done for gases. Pressure is related to the kinetic energy (velocity) of the atoms and anharmonicity is not required in the lowest order description of atomic movement in solids.

equilibrium with an elastic container (Fig. 2b). An important distinction here is that the elasticity of the container is defined by radially distributed springs originating at the center of the container, and not by the surface of the container. The elastic response of the container is characterized by the bulk modulus B so that the total pressure of the system at volume V can be related as

$$P_{\text{total}} = P_{\text{kinetic}} + P_{\text{elastic}} = \frac{NRT}{V} - \frac{B(V - V_0)}{V} = 0. \quad (4)$$

The volume that satisfies this equilibrium condition is $(V - V_0) = NRT/B$, which increases linearly with temperature. This is known to be the case according to Charles' law (i.e. at constant pressure) and also holds for the case of elastic pressure considered here. Experimentally, it is well-demonstrated that the volume of solids is linearly proportional to temperature (Fig. 2c) when the kinetic energy of atomic vibrations increases linearly with temperature (i.e. at high temperature).

The expansion of a balloon-like container with temperature is the natural result of balancing the temperature-dependent pressure of the kinetic gas with the elastic pressure in the container (Eq. 4 and Fig. 2b). This condition of static equilibrium (i.e. $P_{\text{total}} = 0$) is determined by minimizing the internal energy of a system with an interface (comprised of the temperature dependent kinetic energy plus total elastic energy) at a given temperature (Fig. 2b and Supplemental Note 2). Because vibrating atoms in a solid have the same form of momentum flux (kinetic energy) as a gas they must also produce an outward pressure to expand. Unlike a gas, which needs external confinement (e.g. the balloon), the balancing force creating the mechanical equilibrium (net force = 0) in

a solid must be from the interatomic forces (represented by springs).

This is to say that thermal expansion can be described within the harmonic approximation. Specifically, the present theory uses the phonons found from the harmonic approximation to calculate the pressure exerted by atoms on the rest of the solid. There is a corresponding volume (strain) that satisfies the equilibrium condition at each temperature (analogous to Eq. 4). The thermal expansion coefficient is found from summing the individual contributions of all the vibrational modes (see Methods).

Remarkably, this intuitive picture of thermal expansion largely captures both the magnitude and temperature dependence of experimental observations (Fig. 3a). It should be reiterated that this estimation of the thermal expansion coefficient is determined solely using harmonic vibrational states in conjunction with the mechanical concept of phonon pressure (e.g. see inset of Fig. 3a). The relevance of lead telluride, PbTe, as a high-efficiency thermoelectric material makes this example particularly interesting, since understanding its vibrational properties is fundamental to engineering its thermal conductivity²⁶. As PbTe is considered an archetype of anharmonic materials⁸ and is known to have complex (higher order) bonding interactions²⁷, it is unexpected that a harmonic model could capture an anharmonic property like the thermal expansion behavior so well. In the quasi-harmonic approximation, the large thermal expansion coefficient is attributed to the relatively large positive mode Grüneisen parameters ($\gamma_i = -(\partial \ln \omega_i / \partial \ln V)_T$) at all frequencies (Fig. 3b). Here, the phonon pressure makes the solid expand, corresponding to $\gamma_i > 0$. The close agreement between the two perspectives (compare "harmonic γ " and "average γ_i " in Fig. 3b) is indica-

Figure 2. Depiction of pressure due to kinetic energy and its effect on equilibrium volume with temperature. (a) The pressure due to kinetic energy can be derived by considering the momentum flux through a fixed imaginary surface (e.g. pink and green planes in figure). Since the (time averaged) flux of momentum is equal in both directions, the (thermodynamic) pressure exerted on both sides of the surface is also equal. From this perspective, vibrating atoms in a solid exert a pressure on the rest of the solid just as gas particles exert a pressure on their container. (b) An elastic balloon-like container filled with an ideal gas, which corresponding to the case described by Eq. 4. Here, radially distributed springs define the elasticity of the container. The temperature dependence of the equilibrium volume is due to the balance between the temperature-dependent kinetic energy of the gas (blue balls) and the corresponding elastic response of the material. As an analogy, the elastic balloon-like container represents the bonding between atoms holding the material together and the ideal gas represents the atomic vibrations pushing the solid outward. (c) The equilibrium volume of solids^{22,23} increases linearly with increasing temperature (at high temperature) and can be attributed to an analogous mechanical mechanism as the thermal expansion of the ideal gas in an elastic medium.

tive of an underlying connection (e.g. Fig. 1). In the present perspective, the large thermal expansion coefficient in PbTe is thus explained by the large ratio of phonon pressure to the elastic restoring force.

It should be noted that, in the present calculations, atoms were considered to vibrate independent of each other. However, the coordinated movements of neighboring atoms are likely important in some cases, particularly in negative or anomalous thermal expansion materials^{28,29}. The influence of higher order anharmonicity may also contribute to the behavior of thermal expansion¹⁴. Thus, further considerations of atomic structure and bonding could lead to a better understanding of the relation between the present phonon pressure perspective and the mode Grüneisen parameters found from quantum mechanics, which may provide insights to the origin of negative thermal expansion in some solids.

Complex bonding interactions in real solids necessarily include anharmonic terms (i.e. non-linear forces). Here we show

that the lowest-order harmonic description is related to those higher order effects (Figs. 3 and 4), but does not preclude additional anharmonic considerations that may be important. Specifically, the harmonic theory of thermal expansion is thermodynamically connected to anharmonicity through the Grüneisen relation. The thermodynamic Grüneisen parameter γ is a restatement of Eq. 2 that can be written as¹⁵

$$\gamma = \frac{\alpha B}{c_V}, \quad (5)$$

where the heat capacity c_V approaches the Dulong-Petit value ($3k_B/\text{atom}$) at high temperature. Then the “harmonic Grüneisen parameter” can be calculated in the high temperature limit using the phonon pressure model of thermal expansion in conjunction with the bulk modulus determined by density functional theory (see Methods). This scalar “harmonic Grüneisen parameter” is compared with the scalar “DFT Grüneisen parameter” found by averaging the mode Grüneisen parameters γ_i (Fig. 4a). The overall agreement

Figure 3. Thermal expansion coefficient and Grüneisen

parameters of lead telluride, PbTe. (a) Coefficient of linear thermal expansion α_L for PbTe estimated using the “phonon pressure model” of thermal expansion (see Methods) calculated from harmonic eigenmodes and eigenvectors found from density functional theory (solid orange line) compared with experimental results (triangles²⁴, diamonds²², dashed-line²⁵). The “high temperature approximation” is found from a simplified analytical model (See Methods) and is defined as $\alpha_L = 3k_B/2\bar{m}v_s^2$, where k_B is Boltzmann’s constant, $\bar{m} = 2.8 \times 10^{-25}$ kg atom⁻¹ is the average atomic mass and $v_s = 1850$ m s⁻¹ is the average speed of sound. The inset illustrates how phonon modes contribute to the vibrational pressure exerted by an atom differently at different temperatures due to the number of phonons that are excited. Here the real space direction of the atom vibrations (i.e. phonon eigenvectors) is shown by arrows. The length of the arrows is scaled by the heat capacity of the phonon mode. **(b)** Mode Grüneisen parameters γ_i of PbTe calculated from density functional theory (gold diamonds) and their average value, compared with the estimated “Harmonic Grüneisen parameter” (see Methods).

(within a factor of ~ 2) corresponds to the agreement between their respective thermal expansion estimations. The important point, however, is that the vibrational properties of harmonic phonon modes can be related to their own anharmonicity at the thermodynamic level.

Using the theory of phonon pressure, it is also possible to show that the thermodynamic Grüneisen parameter (average γ) can be estimated from the ratio of the bulk-averaged transverse and longitudinal speeds of sound ($x = v_t/v_l$) (Fig. 4b), or equivalently the isotropic Poisson’s ratio. The connection is plausible given that Poisson’s ratio is a fundamental metric of materials behavior when strained elastically³⁰. To arrive at this analytic result, we use a simplified form of the vibrational pressure model (see Methods) to obtain the thermal expansion coefficient α in terms of the heat capacity c_V , density ρ and speed of sound v_s , as

$$\alpha \approx \left(\frac{3}{2}\right) \frac{c_V}{\rho v_s^2}. \quad (6)$$

Substituting this result into the thermodynamic definition of the Grüneisen parameter (Eq. 5) yields

$$\gamma \approx \frac{3}{2} \frac{B}{\rho v_s^2}, \quad (7)$$

which, when v_s is considered to be the root mean square speed of sound (i.e. $v_s^2 = (2v_t^2 + v_l^2)/3$), can be written as (Supple-

mental Note 3)

$$\gamma \approx \frac{3}{2} \frac{(3 - 4x^2)}{(1 + 2x^2)}, \quad (8)$$

where $x = v_t/v_l$. This form of the Grüneisen parameter (Eqs. 7 and 8) has been obtained previously^{31,32} but was based on a different assumption about the nature of vibrational pressure. In that work, the temperature dependence of vibrational pressure was not considered³¹.

It is easily acknowledged that this approximation for the Grüneisen parameter (Eq. 8, dark blue line in Fig. 4b) is quite crude given the scatter in the data (grey circles in Fig. 4b). But its usefulness is more apparent when comparing with the average Grüneisen parameter of materials with similar speed of sound ratios (yellow-green circles in Fig. 4b), demonstrating that there is an intimate connection between material chemistry, elasticity, and anharmonicity that has not been fully explored. For one, Eq. 8 indicates that solids that are more “liquid-like” (i.e. $x \rightarrow 0$) are expected to be more anharmonic. This corresponds to the large Grüneisen parameter in metals like gold, silver and lead, where the atomic structure and bonding is often described as positively charged ions held together by a sea of negatively charged electrons – the reason being that the electrons are delocalized and can be easily rearranged like a liquid. Conversely, the Grüneisen parameter is much lower in highly directional, covalently bonded materials

Figure 4. Apparent relations between “anharmonic” and harmonic properties of solids. (a) An equal plot comparing the ‘DFT Gruneisen parameter’ (i.e. the average mode Grüneisen parameter) with the ‘Harmonic Gruneisen Parameter’ (i.e. the thermodynamic Grüneisen parameter estimated from the harmonic model of thermal expansion) for 119 compounds. Light grey dashed lines indicate a factor of 2 from the equal line. (b) The thermodynamic Grüneisen parameter estimated from Eq. 7 in terms of the speed of sound ratio $x = v_t/v_l$ (using the RMS speed of sound, which is Eq. 8, gives the dark blue line and using the bulk modulus and v_s described by Anderson³³, gives the purple line, which diverges as $x \rightarrow 0$ and can be found in Supplemental Note 3) compared with a previous theory given by Druyvesteyn³⁴ (dashed blue line) and the DFT calculated thermodynamic Grüneisen parameters (average γ_i) of individual materials (light grey circles) as well as the average Grüneisen parameters (yellow-green circles) of materials binned according to their speed of sound ratio (bins: [0.2,0.3], [0.3,0.4], [0.4,0.5], [0.5,0.6], [0.6,0.7]). The area of the marker is related to the number of materials it represents and the color represents the average density of those materials (Supplemental Note 4). The “liquid” limit for this model of solids is the case where the transverse speed of sound goes to zero (Poisson’s ratio = 0.5). The other thermodynamic limit ($v_t/v_l = \sqrt{3}/2$, Poisson’s ratio = -1) is the point where Eq. 8 gives $\gamma = 0$.

like diamond and silicon, when x is closer to the upper thermodynamic limit of $\sqrt{3}/2$. In this respect, beryllium, which has unusual elastic properties for a metallic element³⁵, also has a Grüneisen parameter that is in good agreement with the model. Another relation between γ and Poisson’s ratio³⁴, derived from analytical considerations of an anharmonic interatomic potential, indicates γ diverges as $x \rightarrow 0$, but gives similar estimates as Eq. 8 for most materials ($0.4 < x < 0.7$, dashed blue line in Fig. 4b). Using a different average v_s (i.e. a harmonic mean³³) in Eq. 7 will also cause γ to diverge since $v_s \rightarrow 0$ as $v_t \rightarrow 0$ (purple line in Fig. 4b, Supplemental Note 3), suggesting that the root mean square speed of sound better captures the nature of the elastic pressure.

Altogether, this relation (Eq. 8) provides a simple physical justification for the chemist’s intuition that the anharmonicity of solids is related to the type of bond and atomic coordination (density)^{9,36,37}. Nor would it be surprising if more intricate connections were found between elasticity, atomic structure and anharmonicity through modern machine learning methods.

This profound connection of the thermodynamic Grüneisen parameter with harmonic properties of solids means that transport phenomena like thermal conductivity and atomic diffusion may also be explained in terms of a harmonic potential. The temperature dependence of vibrational

pressure corresponds to a temperature dependent potential energy landscape such that interactions between vibrational modes (e.g. phonon-phonon scattering) may be accounted for within perturbation theory. However, further investigations are needed to reconcile the relations between harmonic and anharmonic terms in the interatomic potential. Nevertheless, having accessible estimates for thermal expansion (e.g. Eq. 6) and the thermodynamic Grüneisen parameter allows for higher accuracy descriptions of the temperature dependent molar volumes and constant pressure heat capacity³⁸ needed for the thermodynamic modeling that is crucial to the design of next generation materials³⁹. For example, the harmonic Grüneisen parameter can be used in conjunction with a semi-empirical model (see Methods) for high-throughput screening of lattice thermal conductivity (Fig. 5 and Supplemental Note 5). Thus, the consideration of phonon pressure in solids is not an esoteric exercise, but provides a new basis for engineering design metrics that do not require the computationally-expensive anharmonic calculations currently employed.

The concept of phonon pressure provides a physical mechanism for “anharmonic” behavior (i.e. thermal expansion) that thermodynamically relates harmonic and anharmonic aspects of bonding in solids. That is, harmonic solids have an inherent anharmonicity. In this perspective, the harmonic potential shifts with temperature to be centered around the

Figure 5. Harmonic estimation of lattice thermal conductivity. Here, the experimental values of lattice thermal conductivity κ_L at 300 K for 53 previously reported compounds³⁶ were estimated using only harmonic descriptors in a semi-empirical model (Eq. 15 and Supplemental Note 5). The grey shaded region spans a factor of 3 from the equal line and represents the approximate accuracy of the semi-empirical model reported by Miller, et al.³⁶.

equilibrium position determined by the force balance between vibrational pressure and the elasticity of the material (analogous to Eq. 4). The success of the Temperature Dependent Effective Potential (TDEP) method developed by Hellman and coworkers^{40,41} further supports the idea that there are aspects of anharmonicity that can be represented by a harmonic potential that changes with temperature. In the TDEP method, the equilibrium atomic position also changes with temperature through a force balance procedure. Instead of explicitly using the theory of vibrational pressure, the residual forces between those calculated from the model potential and those obtained by molecular dynamics simulation are minimized. The necessity of a temperature dependent potential is apparent given that the Taylor expansion around equilibrium at 0 K is unable to reproduce finite temperature observations in some materials^{40,42}.

Conclusion

Although the concept of energy flux as a pressure in elastic materials was first shown by Umov⁴³ and, somewhat later, Brillouin⁴⁴ proposed that thermal expansion in solids may be due to the vibrational pressure of elastic waves, the field of lattice dynamics largely left this mechanistic idea behind. As a result, it is commonly thought that harmonic solids cannot have thermal expansion and other properties assumed to be due entirely to anharmonic effects⁴⁵. Here, the physical mechanism of phonon pressure leads to an explanation for thermal expansion based on only the lowest-order, harmonic approximation of solids. The connection of thermal expansion to the thermodynamic Grüneisen parameter, as well as other anharmonic behavior in solids, suggests that harmonic material

descriptors may correlate with anharmonic properties more generally. The insights gained from this fundamental shift in thought-paradigm may be used to better understand both basic thermodynamic properties of solids, including melting (e.g. the Lindemann melting criteria), as well as the mechanisms of complex transport phenomena like superconductivity, ionic transport, and heat transport in defective materials.

Methods

Phonon Pressure Model

The divergence of the stress tensor must be zero at equilibrium. In many cases, this can be described by the balance of forces in a free body diagram. Here, we consider the sum of forces (normalized by a unit area) acting on atom α due to each phonon mode (having frequency ω , wave vector $\mathbf{k}$ and branch index s). We consider mechanical equilibrium to occur when the normal component (in the $\hat{n}$ -direction) of the vibrational (kinetic) stress $\sigma_{\mathbf{k}s}^{\text{kinetic}}$ is exactly compensated by the normal component of the elastic stress $\sigma_{\mathbf{k}s}^{\text{elastic}}$, such that the total normal stress $\sigma_{\mathbf{k}s}^{\text{total}}$ (a scalar) due to the $\mathbf{k}s$ vibrational mode is

$$\sigma_{\mathbf{k}s}^{\text{total}} = \sigma_{\mathbf{k}s}^{\text{kinetic}} + \sigma_{\mathbf{k}s}^{\text{elastic}} = \quad (9)$$

$$\frac{\hbar\omega_{\mathbf{k}s}}{V_a} f_{\text{BE}}(\omega_{\mathbf{k}s}, T) |\hat{e}_{\mathbf{k}s} \cdot \hat{n}|^2 - \rho v_p^2 |\hat{e}_{\mathbf{k}s} \cdot \hat{n}| \epsilon_{\mathbf{k}s} = 0,$$

where $\epsilon_{\mathbf{k}s}$ is the corresponding normal component of the strain. The strain is defined by the displacement of the atom from a 0 K reference position. The vibrational stress $\sigma_{\mathbf{k}s}^{\text{kinetic}}$ due

to the $\mathbf{k}_s$ phonon mode (having the unit eigenvector $\hat{\mathbf{e}}_{\mathbf{k}_s}$ that determines the motion of atom α) is proportional to the kinetic energy of each phonon ($\hbar\omega_{\mathbf{k}_s}/2$) as well as the number of phonons that are excited according to the Bose-Einstein distribution,

$$f_{\text{BE}}(\omega_{\mathbf{k}_s}, T) = \left[\exp\left(\frac{\hbar\omega_{\mathbf{k}_s}}{k_B T}\right) - 1 \right]^{-1}, \quad (10)$$

and V_a is the atomic volume. Note the explicit temperature dependence of f_{BE} . Also note that the vibrational stress due to each phonon mode is found by considering its contribution to the normal component of the flux of linear momentum of atom α (Fig. 2 and Supplemental Note 1).

The elastic stress $\sigma_{\mathbf{k}_s}^{\text{elastic}}$ acting against (compensating) the vibrational stress is defined by the elastic modulus (ρv_p^2) governing the vibration, where ρ is the mass density of the solid and $v_p = \omega_{\mathbf{k}_s}/|\mathbf{k}|$ is the magnitude of the phase velocity of the phonon. The normal component of the strain $\epsilon_{\mathbf{k}_s}$ (i.e. the strain in the $\hat{n}$ -direction due to the $\mathbf{k}_s$ vibrational mode) that results in mechanical equilibrium (Eq. 9) is

$$\epsilon_{\mathbf{k}_s} = \frac{\hbar\omega_{\mathbf{k}_s}}{V_a} \frac{f_{\text{BE}}(\omega_{\mathbf{k}_s}, T)}{\rho v_p^2} |\hat{\mathbf{e}}_{\mathbf{k}_s} \cdot \hat{n}|. \quad (11)$$

The contribution of the $\mathbf{k}_s$ vibrational mode to the normal component of the thermal expansion coefficient tensor is found using Eq. 9 and the thermodynamic relation

$$\left(\frac{\partial \epsilon_{\mathbf{k}_s}}{\partial T} \right)_{\sigma_{\mathbf{k}_s}} = - \frac{(\partial \sigma_{\mathbf{k}_s} / \partial T)_{\epsilon_{\mathbf{k}_s}}}{(\partial \sigma_{\mathbf{k}_s} / \partial \epsilon_{\mathbf{k}_s})_T} \quad (12)$$

and the total thermal expansion coefficient in the $\hat{n}$ -direction is found by summing over all vibrational modes,

$$\left(\frac{\partial \epsilon}{\partial T} \right)_{\sigma} = \sum_{\mathbf{k}_s} \left(\frac{\partial \epsilon_{\mathbf{k}_s}}{\partial T} \right)_{\sigma_{\mathbf{k}_s}}. \quad (13)$$

It should be noted that the rank 2 thermal expansion coefficient tensor can be constructed using appropriate values of $\hat{n}$. When $\hat{n}$ points only in the x -, y -, or z -direction, Eq. 13 corresponds to the linear thermal expansion coefficient α_L in that direction. The volumetric thermal expansion coefficient is the summation of the three linear thermal expansion coefficients, or in the case of materials with cubic symmetry like PbTe, $\alpha = 3\alpha_L$.

Note that the above derivation is written explicitly for materials with one atom per primitive unit cell, but is easily generalized to many-atom unit cells by considering the partial pressures contributed by each atom.

The Grüneisen parameter can be calculated from the volumetric thermal expansion coefficient according to Eq. 5 and can be used to renormalize the frequencies $\omega_{\mathbf{k}_s}$ within the single Grüneisen parameter approximation (i.e. all vibrational modes have the same γ_i). This process can be done iteratively with temperature and, thus, phenomenologically accounts for the gentle increase in the thermal expansion coefficient at high temperatures (as shown in Fig. 3a).

The "harmonic Grüneisen parameter" used in Fig. 4 did not consider any renormalization of vibrational frequencies and was calculated using Eqs. 9, 12 and 13 in the $T \rightarrow \infty$ limit.

A simplified analytic description of thermal expansion can also be derived from the concept of vibrational pressure (Eq. 6). Here, an approximation for the frequency distribution of vibrational modes must be made (if the density of states is unknown), as well as the vibration direction. The Debye model of phonons as a dispersive continuum is often used to approximate the distribution of vibrational modes in solids and is applicable here. In the isotropic approximation the elastic properties of the solid are independent of direction and the atoms vibrate equally in all directions (i.e. the average incidence cosine $|\hat{\mathbf{e}}_{\mathbf{k}_s} \cdot \hat{n}|$ is $1/2$). Making use of these approximations, the linear thermal expansion coefficient α_L can be written as

$$\alpha_L \approx \frac{3k_B}{4\pi^2 \rho v_s^5} \int_0^{\omega_D} \omega^2 \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{\exp\left(\frac{\hbar\omega}{k_B T}\right)}{\left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right)^2} d\omega, \quad (14)$$

where ρ is the density (kg m^{-3}), v_s is the average speed of sound (m s^{-1}), and $\omega_D = (6\pi^2 n)^{1/3} v_s$ is the Debye frequency, which uses v_s and the number density of atoms n (atoms m^{-3}) to approximate the maximum frequency of vibration in the solid.

Density Functional Theory Calculations

Harmonic eigenmodes (phonons) and corresponding mode Grüneisen parameters γ_i were found using density function theory methods. The compounds shown in Fig. 4a were previously reported¹⁸. Additional calculations were undertaken to calculate thermodynamically averaged Grüneisen parameter for compounds with varied v_t/v_l ratios as shown in Fig. 4b. The isotropically averaged speed of sounds (v_t and v_l) were calculated using the christoffel code.⁴⁶ The elastic modulus tensor input for the code was calculated from the Density Functional Perturbation Theory (DFPT)^{47,48} capabilities implemented in the VASP code.⁴⁹ We used the PBEsol⁵⁰ formulation of the exchange–correlation energy functional derived under a generalized-gradient approximation (GGA).⁵¹ Plane-wave basis sets were truncated at an energy cutoff of 500 eV, and a Γ -centered k -point mesh with a density of ~ 8000 k -points per reciprocal atom (KPPRA) was used. The electronic degrees of freedom in the self-consistent loop were converged to 10^{-8} eV. All structures were relaxed with respect to cell vectors and their internal degrees of freedom until forces on all atoms were less than 0.1 eV nm^{-1} . "DFT Grüneisen parameters" were found by thermodynamically averaging the mode Grüneisen parameters γ_i in the high temperature limit such that they are weighted equally at all frequencies. The mode Grüneisen parameters were calculated using a finite difference method as implemented in Phonopy.¹² For this,

the phonon calculations of the compounds were performed on structures where the cell parameters were strained by $\pm 0.02\%$.

Semi-empirical model of thermal conductivity

The same form of the semi-empirical model used by Miller, et al.³⁶ was used in this study (Fig. 5), but the exponents were re-optimized (using a gradient decent algorithm) since we use different definitions of v_s and γ . Explicitly, the experimental lattice thermal conductivity κ_L at 300 K is estimated as

$$\kappa_L = 2.69 \times 10^{-3} \frac{\bar{m} v_s^{4.169}}{\gamma V_a^{0.498} N^{0.935}} + \frac{3}{2} \left(\frac{\pi}{6} \right)^{1/3} \frac{k_B v_s}{V_a^{0.695}} \left(1 - \frac{1}{N^{2/3}} \right) \quad (15)$$

where $\bar{m}$ is the average atomic mass, v_s is the RMS speed of sound, γ is the harmonic Grüneisen parameter found from the speed of sound ratio (Eq. 8), V_a is the average atomic volume and N is the number of atoms per primitive unit cell. All quantities were found from the Materials Project⁵² database and need to be in SI units for Eq. 15. The longitudinal and transverse speeds of sound were obtained from the theoretical density ρ and Voigt-Reuss-Hill values⁵³ of bulk modulus B_{VRH} and shear modulus G_{VRH} through the relations:³³

$$v_t = \sqrt{\frac{G_{VRH}}{\rho}}, \quad (16)$$

$$v_l = \sqrt{\frac{B_{VRH} + (4/3)G_{VRH}}{\rho}}. \quad (17)$$

Since only structural and harmonic material descriptors are used, Eq. 15 can be referred to as a "harmonic thermal conductivity." A similar equation was also found to reasonably estimate the 300 K values of lattice thermal conductivity calculated by DFT (Supplemental Note 5).

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Contributions

G.J.S. and M.T.A. conceived the project. M.T.A. developed the model and drafted the manuscript. S.A. provided additional computational data. All authors revised and commented on the manuscript.

Data Availability

Any relevant data not contained within this publication is available from the corresponding authors upon reasonable request.

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