A method for predicting non-equilibrium thermal expansion using steepest-entropy-ascent quantum thermodynamics

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Abstract
Steepest-entropy-ascent quantum thermodynamics (SEAQT) is an intriguing approach that describes equilibrium and dynamic processes in a self-consistent way. To date, it has been applied primarily to gas phase systems because of the difficulty in generating the complex eigenstructures (eigenvalues and eigenfunctions) associated with solid or liquid phases. In this contribution, the SEAQT modeling is extended to the solid phase by constructing a so-called pseudo-eigenstructure, and its applicability is demonstrated by calculating the thermal expansion of metallic silver for three cases: (a) stable equilibrium, (b) along three irreversible paths from different initial non-equilibrium states to stable equilibrium, and (c) along an irreversible path between two stable equilibrium states. The SEAQT framework with an anharmonic pseudo-eigenstructure predicts reasonable values for the equilibrium thermal expansion. For the irreversible cases considered, the SEAQT approach makes it possible to predict the time-dependence of lattice relaxations from the initial state to the final equilibrium state.

Keywords: thermal expansion, steepest entropy ascent, nonequilibrium thermodynamics, first-principles calculation

(Some figures may appear in colour only in the online journal)
and provides a link between quantum mechanics and thermodynamics. This dissipation term provides an equation of motion that captures the effects of irreversibility and makes it possible to describe the detailed time evolution of all non-equilibrium states of the system.

Energy eigenstructures in the SEAQT theoretical framework can be constructed from appropriate quantum mechanical models. For instance, an eigenstructure for a gas phase can be constructed with a manageable number of degrees of freedom by assuming that gas molecules move independently with translational, rotational, and vibrational modes (the ideal gas approximation). For a condensed phase, however, the interactions between molecules greatly affect physical properties, so they cannot be neglected. These interactions complicate the energy eigenstructure for solids or liquids (and real gases as well). Furthermore, for sufficiently large systems (from the micro- to the macro-scale) and regardless of phase, infinite-dimensional state spaces are present, which make solving the equation of motion computationally intractable. Nevertheless, these difficulties can be overcome by using simple models to construct a so-called ‘pseudo-eigenstructure’ and by using the density operator method developed by Li and von Spakovsky [14] to replace infinite-dimensional spaces. Together, these strategies make it possible to solve the equation of motion for a condensed phase.

The SEAQT framework for solids has two distinct benefits: first, it provides a method to explore kinetic behavior in a thermodynamic system (non-equilibrium paths and evolution with time) that is consistent with classical mechanics. Second, when a simple pseudo-eigenstructure is available, the SEAQT framework is remarkably efficient from a computational standpoint.

To demonstrate the approach, we apply the SEAQT framework to calculate the thermal expansion of solid silver. The presentation is organized as follows. The basis of the SEAQT equation of motion is described in section 2.1, while in section 2.2, the system pseudo-eigenstructure is constructed by treating the crystal as a collection of anharmonic oscillators. Section 2.3 calculates the thermal expansion coefficient treating the crystal as a collection of anharmonic oscillators. Section 3.1 validates the approach with a comparison between the calculated (equilibrium) paths and experimental data. Finally, sections 3.2 and 3.3 apply the approach to investigate lattice relaxation associated with several different irreversible (non-equilibrium) paths.

2. Theory

2.1. Equation of motion

Following Beretta and others [10, 11, 26–28], a general equation of motion for a quantum system is taken to be composed of reversible and irreversible terms. In the SEAQT framework, the form of this equation of motion for an assembly of indistinguishable particles is [8, 9, 14]

\[
\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar}[\hat{\rho}, \hat{H}] - \frac{1}{\tau(\hat{\rho})} \hat{D}(\hat{\rho}),
\]

where \( \hat{\rho} \) is the density operator, \( t \) the time, \( \hbar \) the reduced Planck constant, \( \hat{H} \) the Hamiltonian operator, \( \tau \) the relaxation time (which reflects the speed of the time evolution of states of the system in Hilbert space), and \( \hat{D} \) the dissipation operator. The left-hand side of the equation and the first term on the right corresponds to the time-dependent von Neumann equation. The second term on the right is the irreversible contribution that accounts for relaxation processes in the system. This dissipation term is derived via a constrained gradient in Hilbert space [8, 9, 14] that causes the system to follow the direction of steepest entropy ascent when the energy and occupation probabilities are conserved. When \( \rho \) is diagonal in the Hamiltonian eigenvector basis, \( \rho \) and \( \hat{H} \) commute and the von Neumann term in the equation of motion disappears so that equation (1) simplifies to [14]:

\[
\frac{d\rho_j}{dt} = -\frac{1}{\tau} \left[ \sum_i \frac{\rho_i \ln \frac{\rho_i}{g_i}}{\rho_i} \frac{\rho_j}{g_j} \right] \frac{\rho_j}{g_j} \left( \frac{\rho_i}{g_i} \right) \frac{\rho_i}{g_i} \left( \frac{\rho_j}{g_j} \right) \left( \frac{\rho_i}{g_i} \right),
\]

where the \( \rho_j \) are the diagonal terms of \( \hat{\rho} \), each of which represents the occupation probability of a particle being in the \( j \)th energy level, \( \epsilon_j \). The \( g_j \) are the degeneracies of \( \epsilon_j \). Equation (2) is a system of differential equations involving the ratio of determinants. An example application to a particularly simple system—four energy level particles—can be found in [8]. In general, the density operator is diagonalized when there are no quantum correlations or in classical cases [15, 16, 18]. In this work, the density operator is diagonalized with respect to the energy eigenstates basis (section 2.2) so that equation (2) is applicable rather than equation (1).

When there is a heat interaction between the system and a heat reservoir at temperature \( T_R \), the SEAQT equation of motion, equation (2), transforms, using the concept of hypo-equilibrium state, into [14, 15]

\[
\frac{d\rho_j}{dt} = \frac{1}{\tau} \rho_j \left[ \left( -\ln \frac{\rho_j}{g_j} \right) - \beta^R (\epsilon_j - \langle \epsilon \rangle) \right],
\]

where \( \beta^R = 1/k_B T_R \) (\( k_B \) is the Boltzmann constant), and \( \langle \epsilon \rangle \) and \( \langle \epsilon \rangle \) are the expected values of the system energy and entropy, which are, respectively, defined as

\[
e = \langle \epsilon \rangle = \sum_i \epsilon_i \rho_i \quad (4)
\]

and

\[
s = \langle \epsilon \rangle = -\sum_i \rho_i \ln \frac{\rho_i}{g_i} \quad (5)
\]

Equation (5) is the von Neumann expression for the entropy. Provided the density operator is based on a homogeneous ensemble [1], this expression satisfies all the characteristics of
entropy required by thermodynamics without making entropy a statistical property of the ensemble [23, 24].

2.2. Pseudo-eigenstructure: anharmonic oscillator

To model thermal expansion of a crystalline solid, we treat atoms in the lattice as coupled anharmonic oscillators vibrating about equilibrium positions. Two problems must be resolved in this context. The first is one of computational scale. The envisioned oscillators have an infinite number of energy levels, and using such an eigenstructure with equation (2) requires solution of an infinitely large system of equations. This difficulty is circumvented by replacing the infinite-level state space with an approximate, finite, state space of several hundred or thousand energy levels through a density of states approach. The second problem involves developing a representation for the energy levels of the anharmonic oscillators. Unlike for the simple case of harmonic oscillators, the eigenvalues and eigenfunctions of anharmonic oscillators generally cannot be solved analytically. They can, however, be found numerically. The details of how this is done are found in [29], and the essential points are described below.

To determine the anharmonic eigenstates, a Morse potential for the pair interaction energy is assumed, i.e.

\[ V_{\text{Morse}}(x) = A + D(1 - e^{-\lambda(x-x_0)})^2 \]  

(6)

where \( A, D, \lambda, \) and \( x_0 \) are fitting parameters. Since there are four fitting parameters and the potential is nonlinear in two of them, the fitting procedure is operationally difficult. The fitting procedure, however, can be simplified with the approach suggested by Moruzzi et al. [30]. To obtain a realistic Morse potential for silver, the parameters in equation (6) are fitted to electronic total energy calculations for silver performed using the projector augmented-wave (PAW) method [31] as implemented in the Vienna Ab Initio Simulation Package (VASP). A description of the ab initio calculations and the resulting Morse potential parameters are provided in appendix A.

Substituting the Morse potential into the time-independent Schrödinger equation (i.e. the energy eigenvalue problem),

\[ \hat{H}\psi_n(x) = \epsilon_n \psi_n(x), \]

\[ -\frac{\hbar^2}{2m} \frac{d^2\psi_n(x)}{dx^2} + V_{\text{Morse}}(x)\psi_n(x) = \epsilon_n \psi_n(x). \]  

(7)

With the ladder operators, \( a_+ \) and \( a_- \), the Hamiltonian can be rewritten as

\[ \hat{H} = \hbar \omega \left\{ \frac{1}{2} \left( a_- a_+ + \frac{1}{2} \right) - \frac{1}{4} \left[ (a_-)^2 + (a_+)^2 \right] \right\} + \zeta \left( 1 - 2\tilde{F}(\lambda^0) + \tilde{F}(2\lambda^0) \right), \]  

(8)

where

\[ \tilde{F}(\lambda^0) = e^{-\lambda^0(a_- + a_+)} , \]

\[ \tilde{F}(2\lambda^0) = e^{-2\lambda^0(a_- + a_+)} , \]

\[ \zeta = \frac{\partial}{\partial \omega} , \quad \text{and} \quad \lambda^0 = \frac{1}{2} \sqrt{\frac{\hbar \omega}{m}} = \frac{i}{2} \sqrt{\frac{\omega}{\zeta}} . \]

The eigenfunctions, \( \psi_n(x) \), for the anharmonic oscillator are then given by [29]

\[ \psi_n(x) = \sum_{k=0}^{n_{\text{max}}-1} C_{kn}\psi_k^{\text{HO}}(x), \]  

(9)

where the \( C_{kn} \) are coefficients of the expansion, the \( \psi_n^{\text{HO}}(x) \) are the eigenfunctions of a related harmonic oscillator, and \( n_{\text{max}} \) is the largest quantum number of eigenvalues used for the numerical calculation. The latter is chosen to include enough energy eigenlevels to adequately represent the thermal expansion of the system with the available computational resources. The procedure for determining the harmonic oscillator eigenfunctions, \( \psi_n^{\text{HO}}(x) \), and selecting \( n_{\text{max}} \) is described in appendix B.

The vibrational frequencies, \( \omega \), in equation (8), are obtained from the Debye approximation [32] in which the velocity of sound is taken to be a constant and the lattice vibrates with frequencies up to the Debye frequency, \( \omega_D \). Adopting a definition suggested by Moruzzi et al. [30], the constant velocity of sound at the ground state, \( v_0 \), is given by

\[ v_0 = 0.617 \sqrt{\frac{B_0}{\rho_0}} , \]  

(10)

where \( B_0 \) and \( \rho_0 \) are, respectively, the bulk modulus and the density of the specimen evaluated with the lattice constant at 0 K, \( a_0 \). The coefficient, 0.617, comes from the fact that there are two wave modes, transverse and longitudinal, whose velocities have different dependencies on the bulk modulus [30]. The bulk modulus at the ground state is given as

\[ B_0 = -V_0 \left( \frac{\partial P}{\partial V} \right)_v = \frac{4}{9 a_0} \left( \frac{\partial^2 E_{\text{total}}}{\partial\omega^2} \right)_{a_0} = \frac{4}{9 a_0} 6(2D\lambda^0) , \]  

(11)

where \( P \) is the system pressure, \( V \) is the volume (\( V_0 \) is the volume evaluated at \( a_0 \)), \( E_{\text{total}} \) is the total energy of the system, and \( D \) and \( \lambda \) are the fitting parameters in the Morse potential. The factor of 6 in equation (11) is related to the number of first-nearest-neighbor pairs (as seen in equation (A.1)). The Debye frequency, \( \omega_D \), and the density of states, \( g_0(\omega) \), evaluated at \( a_0 \) are given by [32]

\[ \omega_D = \frac{6\pi^2 N_s}{V_s} \]  

(12)

and

\[ g_0(\omega) = \frac{9N_s\omega^2}{\omega_D^3} , \]  

(13)

where \( N_s \) and \( V_s \) are, respectively, the number of primitive cells in a specimen and the volume of the specimen (\( V_s = N_s a_0^3 / 4 \)). \( N_s \) is set equal to Avogadro’s number.

The incorporation of vibrational frequencies below the Debye frequency cannot be done in a straightforward manner because the density of states is not discrete as is evident from
equation (13). To avoid this difficulty, the density of states method developed by Li and von Spakovsky [14] within the SEAQT framework is applied. This strategy combines similar energy eigenvalues into discrete bins and significantly reduces the computational burden without losing the accuracy of the result. By using this method, which is based on a quasi-continuous assumption, the vibrational frequency and degeneracy in the pseudo-system becomes (see appendix C)

\[ \bar{\omega}_i = \frac{1}{G_i} \int_{\bar{\omega}_i}^{\omega_{i+1}} \bar{\omega} g_0(\bar{\omega}) d\bar{\omega} \]

and

\[ G_i = \int_{\bar{\omega}_i}^{\omega_{i+1}} g_0(\bar{\omega}) d\bar{\omega} , \]

where \( \bar{\omega} \) is the vibrational frequency of the original system and \( \bar{\omega}_i \) is the interval of the frequency. The vibrational frequencies, equation (14), are used in equation (8) to derive the eigenvalues and eigenfunctions of the crystal of anharmonic oscillators.

2.3. Thermal expansion

The expected lattice constant, \( a \), at time, \( t \), is determined from the probability of a particle at a given position and time, \( \Phi(x,t) \), and its position, \( x_i \), such that

\[ a = \langle x \rangle = \sum \Phi(x_i) x_i , \]

where the position probability of a particle, \( \Phi(x,t) \), can be described as [33]

\[ \Phi(x,t) = \sum p_i(t) | \psi_i(x) |^2 , \]

and the position of the oscillator, \( x \), corresponds to the interatomic distance in the present application.

The values of the occupation probabilities, \( p_i \), in equation (17) reflect the distribution of the oscillators in the crystal among the various energy eigenvalues of the eigenstructure. If a solid is at thermal equilibrium, a natural choice for the occupation probabilities is given by the canonical distribution:

\[ p_i^{\text{eq}} = \frac{G_i e^{-\beta E_i}}{\sum_j G_j e^{-\beta E_j}} = \frac{G_i e^{-\beta E_i}}{Z} , \]

where \( Z \) is the partition function, \( \beta = 1/k_B T \), and \( s \) denotes stable equilibrium. We denote the occupation probability, energy eigenvalue, and energy degeneracy, respectively, as \( p_i \), \( E_i \), and \( G_i \) (instead of \( p_j \), \( \epsilon_j \), and \( g_j \)) in order to emphasize that these quantities apply to the pseudo-system, which closely approximates the real system.

Figure 1 shows how the oscillator position affects the occupation probability for silver oscillators at a series of different temperatures. The peak in the position probability is the same at all temperatures and corresponds to the ground state lattice parameter and the minimum pair interaction energy (see figure A1 in appendix A). Nevertheless, the distribution becomes broader with increasing temperature and the asymmetric pair potential distributes energy to energy eigenvalues corresponding to larger interatomic distances.

Equation (16) in conjunction with the pseudo-eigenstructure and equation (18) provides a means to calculate the lattice constant at any temperature. The coefficient of thermal expansion, \( \alpha \), is obtained from the temperature-dependent lattice constants via the relationship:

\[ \alpha(T) = \frac{a(T) - a(T_{0K})}{a(T_{0K})} . \]

Here, \( a(T_{0K}) \) includes zero-point vibrations and is different from \( a_0 \). The estimated lattice constant for \( a(T_{0K}), 1.002a_0 \) [34], is used here because it is difficult to satisfy the quasi-continuous condition, equation (C.1), at very low temperatures.

It is important to note that a pseudo-eigenstructure can be constructed from any reasonable solid-state model. The one employed here for thermal expansion arises from anharmonic oscillators. It evaluates the phonon dispersion relation (or the Debye frequency) at the ground state (corresponding to \( a_0 \)) and determines the thermal expansion from the intrinsic asymmetry of the pair-potential curve in an intuitive way. A useful pseudo-eigenstructure could be built just as easily from the harmonic oscillator approximation with a volume-dependent phonon dispersion relation (i.e. the quasi-harmonic approximation; see, for example, [30, 35]). Also, additional contributions to thermal expansion, such as electronic contributions, can be incorporated into the pseudo-eigenstructure if desired. The Debye model is used here for the sake of simplicity to calculate the density of states of vibrational frequencies. For more accurate calculations, a more detailed description of the density of states—such as one obtained from density functional theory (DFT)—would be required.

3. Results

3.1. Thermal expansion at stable equilibrium

Calculated equilibrium lattice constants for silver over a range of temperatures using the occupation probabilities given by
The temperature dependence of the Ag lattice constant. The red/yellow lines are calculated using the GGA/LDA functionals. The solid black circles are experimental data [36]. The lattice constant at 0 K is estimated as 4.002\(a_0\), where \(a_0\) is the ground state lattice constant without zero-point vibrations [34].

The solid curves in figure 3 calculated from the anharmonic model with the SEAQT framework show that the thermal expansion obtained from the GGA functional is an overestimate, whereas that from LDA is quite close to the experimental results up to a fairly high temperature (~800 K). The improved agreement of the LDA thermal expansion arises from the fact that the LDA functional overestimates both the Debye temperature and Gr"uneisen constant, which are, respectively, related to the potential curvature and asymmetry/softening effect, and these errors offset each other (see appendix D). The qualitative agreement between experimental thermal expansion and predicted values from the SEAQT framework suggests that the pseudo-eigenstructure built from an anharmonic oscillator model is reasonable. Because the LDA thermal expansion is closer to experiment than the GGA thermal expansion, only the LDA functional is used in the calculations of the following sections (sections 3.2 and 3.3).

### 3.2. Nonequilibrium lattice evolution

In this section, the SEAQT model is used to explore how the state of the silver lattice evolves from an initial, non-equilibrium state to a stable equilibrium state with an equilibrium lattice constant. An initial state can be generated in a variety of ways. Two different approaches are used here. The first selects an initial occupation distribution described by an appropriate probability distribution. For example, Li and von Spakovsky [14, 15] generated initial states with a gamma function distribution of the form

\[
P_j^0 = \frac{G_j E_j^0 e^{-\beta E_j}}{\sum_i G_i E_i^0 e^{-\beta E_i}},
\]

where \(\beta\) is as defined above and \(\theta\) represents an adjustable parameter that shifts the initial state away from the canonical distribution. In the second approach, the initial state can be generated using an ad hoc description of the initial occupation distribution. For example, an occupation distribution generated by pumping energy into the silver lattice with a laser might be approximated by assuming that the injected photons excite silver atoms out of the lower energy states. To numerically determine such an initial state, the procedure developed by Beretta [8] is used here. The initial probability distribution, \(P_j^0\), is expressed in terms of the following perturbation function:

\[
P_j^0 = (1 - \lambda_{\text{const}}) P_j^{\text{pe}} + \lambda_{\text{const}} P_j^{\text{se}},
\]

where \(P_j^{\text{pe/se}}\) are the partially canonical and stable equilibrium probability distributions and \(\lambda_{\text{const}}\) is the perturbation constant (assumed to be 0.1 here) that describes the initial departure from the partially canonical state. For the partially canonical distribution, it is assumed that the atoms do not occupy the lowest three quantum levels.

Now, in order to determine the maximum vibrational quantum number and apply the quasi-continuous condition of the density of states method [14], equations (B.2) and (C.1) given in appendices B and C must be satisfied at stable equilibrium as well as at non-equilibrium. Both conditions are satisfied rigorously at stable equilibrium but require an additional concept at non-equilibrium, namely, that of a hypoequilibrium state [14]. With this concept, equations (B.2) and (C.1) can be satisfied rigorously at non-equilibrium. A discussion of this concept is beyond the scope of the present paper and, thus, the reader is referred to [14].

Figure 4 shows an example of how the position probability distribution varies with interatomic distance at three different times for the irreversible thermodynamic path determined for the initial state generated using the partially canonical distribution of equation (21). Figure 5 shows the time dependence of the silver lattice parameter for three different initial states, one generated based on equation (21) and two based
on equation (20). For the former, the change in the lattice parameter is quite small because the total energy remains fixed throughout the evolution. For the other two, the system energy varies since the system is allowed to interact with a heat reservoir at 800 K. All three evolutions arrive at the same stable equilibrium state of 800 K. An interesting feature of the evolution based on equation (21) is that a non-monotonic change of the lattice parameter with time is observed. Note that the lattice parameter at stable equilibrium for all three evolutions corresponds to the lattice constant at 800 K derived from the canonical distribution in section 3.1 (see figure 2).

In these results, the time scales are normalized by the relaxation time, $\tau$, as $t^* = t/\tau$. The dimensionless time, $t^*$, can be correlated to real time via comparisons with experimental data [13, 19] or from ab initio calculations based on quantum or classical mechanical considerations [10, 15, 21]. The latter approach is used in the following section (section 3.3). Regardless of how $\tau$ is scaled to real time, though, the SEAQT framework predicts a unique kinetic path in state space. The relaxation time, $\tau$, simply determines how fast along that path the state of the system changes.

3.3. Thermal expansion along an irreversible path between equilibrium states

The real-time dependence of the lattice parameter can be estimated by correlating the relaxation time, $\tau$, to the phonon contribution of thermal conductivity. This is done by allowing the system to interact with a heat reservoir in an irreversible process in which the system starts at an initial temperature $T_0$ and ends up in thermal equilibrium with the reservoir at $T_R$. The calculated time dependence of the lattice parameter for $T_0 = 300$ K and $T_R = 800$ K is shown in figure 6. Here, the real time scale is determined using the following equation (derived in appendix F):

$$\tau = \frac{N}{24L K_{\text{phonon}}(T_R - T_C)} \frac{dE}{dr^*}$$ (22)

where $N$ is the number of atoms in the sample, $L = 10$ mm is the edge length of the sample with an assumed cube shape, $K_{\text{phonon}}$ is the phonon component of the thermal conductivity coefficient, $T_C$ is the temperature at the center of the sample, and $dE/dr^*$ is the energy change rate per atom, which can be determined from the SEAQT framework (the determined relaxation time, $\tau$, is shown in figure F3 in appendix F).

From figure 6, it is apparent that the steepest part of the lattice change happens at the first half of the relaxation process (i.e. from 0 to 2 min) and slows as the temperature of the sample, $T_C$, approaches the temperature of the reservoir, $T_R$. Note that, however, the equation (22) is derived based on
some assumptions; e.g. only the Fourier type heat transfer is considered, and a spatially uniform system is assumed. For a more reliable estimation of the relaxation time, $\tau$, a more realistic system description would be required.

4. Conclusions

The SEAQT model can reliably estimate the thermal expansion of face-centered-cubic silver with a pseudo-eigenstructure based on a crystal of anharmonic oscillators. The accuracy of the approach is quite good for anharmonic oscillators determined from band calculations. It has the added advantage that the thermal expansion can be calculated not only at stable equilibrium but also along a path from some initial non-equilibrium state to stable equilibrium.

In the present work, the following three calculations are provided: (a) at stable equilibrium, (b) along three irreversible paths from different initial non-equilibrium states to stable equilibrium, and (c) along an irreversible path between two stable equilibrium states. For each calculation, it is confirmed that

(a) the SEAQT framework with an anharmonic pseudo-eigenstructure predicts reasonable values for equilibrium thermal expansion;
(b) the time dependence of the lattice parameter has a non-monotonic behavior for one particular choice of initial state prepared by a method that uses partial occupation probabilities, equation (21), to approximate energy injection from a laser. A lattice parameter that monotonically increases or decreases with time can result from initial states prepared using equation (20);
(c) the real-time dependence of the lattice parameter is found using the phonon component of thermal conductivity and shows that the most significant lattice change occurs at the earlier stages of the relaxation process.

It is noteworthy that the SEAQT model with an anharmonic pseudo-eigenstructure based on a coupled anharmonic oscillator is much more computationally efficient than quasi-harmonic models. The latter require volume dependent phonon dispersion relations which are computationally demanding using DFT, but our approach evaluates the phonon dispersion relation only at the ground state and thermal expansion is calculated from the pseudo-eigenstructure by solving the time-independent Schrödinger equation of anharmonic oscillators. This involves solving a modest size system of ordinary differential equations—a comparatively small computational problem.

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Appendix A. Ab initio calculations

To obtain a realistic Morse potential for silver, the parameters in equation (6) are fitted to electronic total energy calculations for silver performed using the projector augmented-wave (PAW) method [31] as implemented in VASP. For the exchange-correlation functional, both the localized density approximation (LDA) of Ceperley and Alder [37, 38] and the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [39] are employed. Supercells in the present DFT calculations contain four atoms in the face-centered cubic (fcc) structure, and the plane wave cut-off energy is set to 400 eV. Integration over the Brillouin zone is done with $11 \times 11 \times 11$ $k$-points, and the tetrahedron method [40] is applied for the $k$-space integrals.

The pair interaction energy, $E_{\text{pair}}$, employed in the Morse potential, equation (6), is extracted from the total energies, $E_{\text{total}}$, derived from the band calculation by considering only first-nearest-neighbors, i.e.

$$E_{\text{total}} = \frac{N_c z}{2} E_{\text{pair}} \Rightarrow E_{\text{pair}} = \frac{1}{6N_c} E_{\text{total}},$$  \hspace{1cm} (A.1)

where $N_c$ is the number of atoms in the supercell and $z$ is the coordination number ($z = 12$ for the fcc structure). The pair potentials are fitted in the range from 3.8 to 5.2 Å for GGA and 3.6–4.8 Å for LDA. The pair interaction energy and fitting parameters are, respectively, shown in figure A1 and table A1 for the GGA and the LDA functionals.

Appendix B. The maximum vibrational quantum number and the harmonic oscillator

The vibrational quantum number can be infinite. Thus, the maximum value, which does not underestimate the thermal expansion of the lattice, must be determined. A value as small as possible that does not change the result is sought. The probability of phonons, $X_n$, whose quantum number is labeled as $n$, can be derived from the Maxwell–Boltzmann distribution as [32]

$$X_n = \frac{N_v}{\sum_{i=0}^{n} N_v} = \exp\left(\frac{-n \omega \delta}{k_B T}\right) \sum_{i=0}^{\infty} \exp\left(-\frac{i \omega \delta}{k_B T}\right)^i,$$  \hspace{1cm} (B.1)

where $N_v$ is the number of phonons with quantum number $n$. Checking whether or not the summation of the above probabilities from $n = 0$ to $n_{\text{max}}$ is approximately one determines the maximum vibrational value, $n_{\text{max}}$, i.e. when

$$\delta = 1 - \sum_{j=0}^{n_{\text{max}}} X_j \approx 0.$$  \hspace{1cm} (B.2)

In this work, $n_{\text{max}}$ is set in order to satisfy the condition $\delta < 0.01$.

To determine the eigenvalues, $\epsilon_n^{\text{HO}}$, and eigenfunctions at a position $x$, $\psi_n^{\text{HO}}(x)$, for the quantum harmonic oscillator, the following analytical expressions are used [41]:

$$\epsilon_n^{\text{HO}} = \left(n + \frac{1}{2}\right) \hbar \omega$$  \hspace{1cm} (B.3)
where $c_j$ is the $j$th eigenvalue in the original system in the $i$th energy interval and $g_j^i$ is its degeneracy. The degeneracy of $E_i$, $G_i$, is defined as

$$G_i = \sum_j g_j^i. \quad (C.3)$$

The length of each energy interval is given by $(\epsilon_{cut} - \epsilon_{ground})/R$, where $\epsilon_{cut}$ and $\epsilon_{ground}$ are, respectively, the cutoff and ground state energies and $R$ is the number of intervals.

The above procedure is now extended to the vibrational frequency. For simplicity, an harmonic oscillator is assumed here to derive the analogous expression for the quasi-continuous condition of the vibrational frequency. For the harmonic oscillator, the vibrational frequency is directly related to the energy eigenvalue as shown in equation (B.3). Thus, equations (C.1)–(C.3) can be rewritten as

$$\frac{1}{\beta} \gg \hbar \left( \langle n \rangle_{\omega_{i+1}} + \frac{1}{2} \right) \omega_{i+1} - \left( \langle n \rangle_{\omega_i} + \frac{1}{2} \right) \omega_i \right|, \quad (C.4)$$

$$\omega_i = \frac{1}{G_i} \int_{\tilde{\omega}_i}^{\tilde{\omega}_{i+1}} \tilde{\omega}g(\tilde{\omega})d\tilde{\omega}, \quad (C.5)$$

and

$$G_i = \int_{\tilde{\omega}_i}^{\tilde{\omega}_{i+1}} g(\tilde{\omega})d\tilde{\omega}, \quad (C.6)$$

where $\omega_i$ and $G_i$ are the vibrational frequency and its degeneracy in the pseudo-system, $\langle n \rangle_{\omega_i}$ is the average number of phonons with vibrational frequency $\omega_i$, $\tilde{\omega}$ is the vibrational frequency in the original system, and $\tilde{\omega}_i$ is the interval of the vibrational frequency, which is specified as

$$\tilde{\omega}_i = (i - 1)\frac{\omega_D}{R}, \quad (C.7)$$

where $R$ is the number of intervals, $\omega_D$ is the Debye frequency, and $i$ is an integer ($i = 1, 2, \ldots, R$). Since the Debye frequency is the maximum frequency with which the lattice can vibrate, it can be regarded as the cutoff energy (cutoff vibrational frequency). The average number of phonons at temperature, $T$, can be expressed as

$$\langle n \rangle_{\omega} = \frac{1}{\exp(h\omega/k_B T) - 1}. \quad (C.8)$$

The above quasi-continuous condition is valid at stable equilibrium but can be extended to non-equilibrium via the hypo-equilibrium concept [14].

### Appendix D. Analysis of GGA/LDA thermal expansion

The origin of the difference between the calculated thermal expansion and that given by experiments (figure 3) can be inferred from three characteristics of the interatomic potential energy: its curvature, its asymmetry about the minimum bonding energy, and its width at large displacements from the minimum point (i.e. the softening effect [32]). Note that the first and third contributions do not have an impact on the
The Debye temperature, $\Theta_{D,0}$, and Grüneisen constant, $\gamma_0$, for Ag evaluated at $a_0$ from the GGA and LDA functionals with experimental data [42, 43]. The normalized Grüneisen constant, $\gamma'_0 = \gamma_0/a_0$, is shown as well. The lattice constant in table A1 ($a_0^{\text{GGA}} = 4.149$ Å and $a_0^{\text{LDA}} = 4.003$ Å) and [36] ($a_0^{\text{Exp}} = 4.076$ Å) are used, respectively, for the normalization.

|                | GGA  | LDA  | Exp. |
|----------------|------|------|------|
| $\Theta_{D,0}$ (K) | 221.9 | 266.9 | 226.5 [43] |
| Error in $\Theta_{D,0}$ | $-2.03\%$ | $+17.8\%$ | — |
| $\gamma_0$ (1/Å) | 2.623 | 2.664 | 2.46 [42] |
| Error in $\gamma'_0$ | $+4.74\%$ | $+10.4\%$ | — |

Thermal expansion for the symmetry potential of the harmonic oscillators, but do strongly affect it for the asymmetry potential. The Debye temperature, $\Theta$, and the Grüneisen constant, $\gamma$, can be used to evaluate the magnitude of each of these contributions. These constants evaluated at $a_0$ are obtained from band calculations using the following relationships [30, 32]:

$$\Theta_{D,0} = \frac{\hbar \omega_{D,0}}{k_B} \quad (D.1)$$

and

$$\gamma_0 = \left(\frac{\partial \ln \Theta}{\partial \ln V}\right)_{\omega_0} = \frac{\lambda a_0}{2} \quad (D.2)$$

where $\omega_{D,0}$ is given in equation (12). The calculated values of these constants are shown in table D1 and compared with experimental results [42, 43]. The normalized Grüneisen constant, $\gamma'_0 = \gamma_0/a_0$, is used because $\gamma_0$ depends on $a_0$ ($x_0$), which does not contribute to the thermal expansion (see appendix E; hereafter, we call the normalized constant, simply the Grüneisen constant). In general, the lattice expansion becomes smaller or larger when it has a larger or smaller Debye temperature and a smaller or larger Grüneisen constant (appendix E). As seen in table D1, the Debye temperature and Grüneisen constant are overestimated by the LDA functional, while only the Grüneisen constant is overestimated by the GGA functional. For this reason, it is concluded that the GGA functional overestimates the thermal expansion because it does not accurately represent the asymmetry/softening effect in the potential energy. The closer agreement of the LDA thermal expansion to experimental values arises from the fact that the LDA functional overestimates both the Debye temperature and the Grüneisen constant and these errors offset each other.

Appendix E. The relationship of the Debye temperature and Grüneisen constant to thermal expansion

A simple anharmonic potential is given as [29, 32]

$$V(x) = V_0 + c(x - x_0)^2 - g(x - x_0)^3 + f(x - x_0)^4 \quad (E.1)$$

where $V_0$ is the energy at the equilibrium point, $x_0$, and $c$, $g$, and $f$ are all positive coefficients. The second and fourth terms in this potential, respectively, are related to the inverse of the curvature and the width of the potential at large amplitudes, while the third term represents the asymmetry [32]. It is expected that a thermal expansion becomes smaller or larger when $c$ and $f$ in the potential are smaller or larger and $g$ in the potential is larger or smaller. Furthermore, a Taylor series expansion of the Morse potential, equation (6), is written as

$$V_{\text{Morse}}(x) \approx A + D \lambda^2 (x - x_0)^2 - D \lambda^3 (x - x_0)^3 \quad + \frac{7}{12} D \lambda^4 (x - x_0)^4 + \cdots$$

where

$$\gamma_0 = \frac{6}{7} \frac{f}{g} \quad (E.2)$$

A comparison of the coefficients between equations (E.1) and (E.2) leads to the following relations: $c = D \lambda^2$, $g = D \lambda^3$, and $f = \frac{7}{12} D \lambda^4$. From these relations and equations (10)–(12), the Debye temperature and the Grüneisen constant (equations (D.1) and (D.2)) are written as

$$\Theta_{D,0} = \frac{\hbar}{k_B} C \sqrt{c} \quad (E.3)$$

and

$$\gamma'_0 = \frac{\gamma_0}{x_0} = \frac{6f}{7g} \quad (E.5)$$

From the above equations, it is inferred that the lattice expansion becomes smaller or larger when the Debye temperature, $\Theta_{D,0}$, is larger or smaller and the normalized Grüneisen constant, $\gamma'_0$, is smaller or larger.

Appendix F. Real-time scaling

In this appendix, it is shown how the SEAQT relaxation time, $\tau$, can be correlated to real time through the phonon component of the thermal conductivity. If the process of heating a block of silver from an initial temperature to a higher temperature through contact with a heat reservoir is considered, the kinetics of this process can be described by solving the SEAQT equation of motion, or the process can be treated as a transport problem whose kinetics are described by Fourier’s law. The transport problem is readily verified by experiment and its time scale can be directly compared with the SEAQT relaxation time, $\tau$.

One can question the validity of this strategy given the system in the SEAQT framework is spatially uniform whereas the block in the transport problem is not (the center is cooler than the surfaces). A more rigorous approach would be to make the SEAQT system spatially nonuniform by arranging a network of subsystems with different energies that exchange heat with each other in the manner of [19, 21]. This approach has been extended to coupled transport processes as well [18, 21]. However, the added complexity is avoided here for...
the sake of simplicity and because the rate of the spatially-dependent transport processes should provide a rough bound for the SEAQT relaxation time.

For the case of a cube-shaped sample experiencing irreversible heating from a uniform initial temperature to the temperature of a surrounding reservoir, energy conservation during thermal conduction requires that

$$\frac{\partial E_V}{\partial t} = -\nabla \cdot J,$$

(F.1)

where $E_V$ is the energy density of the substance at a point $(x, y, z)$ and $J$ is the heat flux. Using Fourier’s law for the flux, $J = -K \nabla T$ where $K$ is the thermal conductivity coefficient, and assuming $K$ is constant (independent of position or temperature), equation (F.1) becomes

$$\frac{\partial E_V}{\partial t} = K \nabla^2 T.$$

(F.2)

The laplacian can be replaced by expressing the temperature on each of the six surfaces of the cube as a Taylor series expanded about the temperature at the cube center and summing the series (up to the quadratic terms). With this approximation, equation (F.2) becomes

$$\frac{\partial E_V}{\partial t} = K \left( \frac{L}{2} \right)^2 (T_R - T_C).$$

(F.3)

where $L$ is the edge length of the cube-shaped sample, and $T_C$ and $T_R$ are the temperatures of the center and the surface of the sample, respectively (the surface is maintained at the reservoir temperature).

For the equivalent SEAQT system, the energy change rate per volume, $\partial E_V/\partial t$, is

$$\frac{\partial E_V}{\partial t} \approx N \frac{dE}{dt}.$$

(F.4)

where $N$ is the number of atoms in the sample and $dE/dt$ is total energy change rate per atom. Converting $t$ in equation (F.4) to $t'$ (i.e., $\frac{dt}{dt'} = \frac{1}{\tau}$) and equating equations (F.3) with (F.4) yields an expression for the relaxation time in terms of measurable quantities. If only the phonon contribution of the thermal conductivity is considered, the relaxation time, $\tau$, is

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\[ \tau = \frac{N}{24 L K_{\text{phonon}}(T^R - T^C)} \frac{dE}{dr^*}. \]  

(F.5)

Note that since the transient case is considered here, \( T^C \) is a function of time, and \( K_{\text{phonon}} \) is a function of \( T^C \).

To apply equation (F.5), a cube-shaped block of silver with edge length \( L = 10 \) mm and initial temperature \( T_0 = 300 \) K is considered to interact with a heat reservoir maintained at \( T^R = 800 \) K. The calculated time dependences of lattice parameter, temperature, and energy change rate per atom \((dE/dr^*)\) using the SEAQT model are shown in figure F1 where the time dependence of the temperature in the system is estimated using the relation between the lattice constant and temperature derived in the stable equilibrium calculation of section 3.1 (figure 2). The temperature dependence of the phonon thermal conductivity coefficient, \( K_{\text{phonon}} \), calculated from first-principles by Jain et al [44] (taking into account electron–phonon and phonon–phonon interactions) are used here by fitting to the following expression:

\[ K_{\text{phonon}}(T) = A' + B' \exp\left(\frac{C'}{T}\right), \]  

(F.6)

where \( T \) is temperature and \( A', B', \) and \( C' \) are fitting parameters. The fitting result is shown in figure F2 with the original data [44]. Equation (F.6) closely reproduces the original values although the reliability of the fitted function above 500 K cannot be verified because there is no calculated data above this temperature. The determined time dependence of the relaxation time for the cube-shaped sample is shown in figure F3.

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