A truncated quasiharmonic method for free energy calculations and finite-temperature applications

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Abstract

Harmonic-based finite-temperature calculation methods play an important role in the study of thermodynamic properties of materials. In this study, we propose a truncated quasiharmonic (TQH) method to approximate the Helmholtz free energy by truncating the high-order terms of finite-temperature vibrational energy. To evaluate the efficacy of the TQH method against other established finite-temperature methods, i.e. the quasiharmonic (QH), the modified local harmonic (MLH) and the local quasiharmonic (LQH) methods, analysis of a homogeneous and vacancy-containing atomic system is performed with each method and compared. We found that the TQH method provides improved accuracy over the MLH and LQH methods for a system containing defects while requiring less computational time than the QH method to achieve convergence.

1. Introduction

Correct computing of free energy and its derivatives is essential for calculating the thermodynamic properties of materials [1]. Free energy calculations in molecular systems using ab initio and molecular dynamics simulations have been particularly improved by the work of Bonomi et al [2]. Nevertheless, the computational cost associated with such detailed methods is inherently high, which limits their potential applicability. The quasiharmonic (QH) method, which is based on quantum-mechanical lattice dynamics, is a less intensive alternative approach for calculating free energy and its derivatives [3]. Provided that the anharmonic vibrational contribution is negligible, the QH method is capable of very accurately calculating free energy [4].
The QH method has gained widespread use in the study of the temperature dependence of material properties. Nevertheless, the computational cost associated with the QH approach prohibits its use in studying thermodynamic properties of relatively large systems [4]. To overcome this computational barrier, LeSar et al. invoked a local assumption on the QH method (local quasiharmonic method, LQH) to study the atomic volume of copper at different pressures and temperatures [5]. They also extended their model to study the free energy of copper vacancy formation. Zhao et al. used both the QH and LQH methods to investigate the free energy and the entropy of vacancy formation at various temperatures in six different metals [6]. Rickman et al. developed the modified local harmonic (MLH) method from the QH method and related the computed eigenvalues to those obtained from LQH by cleverly correcting for vibrational energy [7]. Zhao et al. assumed that the QH method can be solved in \( k \)-space (the quasiharmonic method in \( k \)-space, QHK) [8]. They highlighted that the QHK method provides efficient and accurate analysis of a perfect system. Until now, the QH-based finite-temperature theories have been developed and widely used by researchers to study a variety of materials [9–13].

The QH method can correctly describe the harmonic interaction between atoms of an \( N \)-atom system at a finite temperature, but for a significant computational cost. This is because it requires the determination of the eigenvalues of a \( 3N \times 3N \) matrix, which becomes computationally prohibitive as \( N \) increases. By contrast, the LQH method is very computationally efficient since it invokes a local assumption on the QH approach. Nevertheless, the LQH local assumption can sometimes lead to a larger error when calculating the free energy and its derivatives. The MLH method works particularly well for perfect crystals and relates the matrix eigenvalues to those obtained from LQH. However, the use of MLH may potentially lead to a poorer result than LQH in the determination of free energy for a system containing defects. Solving the QH problem in \( k \)-space gives the same results obtained from the QH method without the need for intense computation. However, the QHK method assumes that the system under consideration is perfect (the \( k \)-space) and therefore, it cannot account for the presence of defects. Owing to the aforementioned limitations, the QH-based finite-temperature method needs to be improved to more correctly and efficiently perform free energy calculations.

We introduce the truncated quasiharmonic (TQH) method as an alternative approach to the QH method. The TQH approach allows for the consideration of both homogeneous and defect-containing systems without the introduction of any local assumptions. In the development of the TQH method, we seek to avoid the computational expense, which limits the efficacy of the QH method. In the following, we briefly introduce the QH, LQH and MLH methods in section 2. The TQH method is then introduced in section 3. Finally, in section 4, numerical examples are provided to compare the accuracy and efficiency of the different harmonic-based finite-temperature methods.

2. QH, LQH, MLH methods: an overview

2.1. The QH method

The QH method uses a harmonic potential to describe interatomic interactions in a finite-temperature system. For an \( N \)-atom system, the Hamiltonian is

\[
H = U(x) + \sum_{i=1}^{N} \frac{p_i^2}{2m_i}, \tag{1}
\]

where \( U \) is the potential energy, \( x \) describes the system’s configuration, and \( p_i \) and \( m_i \) are the \( i \)th atom’s momentum and mass, respectively. Based on quantum-mechanical lattice dynamics,
the Helmholtz free energy of a harmonic crystal can be obtained from [3]

\[ A = U(x^0) + \frac{\tilde{h}}{2} \sum_{i=1}^{3N-3} \omega_i + k_B T \sum_{i=1}^{3N-3} \ln(1 - e^{-\tilde{h} \omega_i/k_B T}), \]  

(2)

where \( x^0 \) corresponds to the equilibrium configuration, \( \tilde{h} = h/2\pi \), \( h \) is the Planck constant, \( \omega_i \) is the \( i \)th system’s vibrational frequency, \( k_B \) is the Boltzmann constant and \( T \) is the system’s temperature. The vibrational frequencies of a system can be obtained using a normal mode analysis. Thus, the vibrational frequencies of an \( N \)-atom system will correspond to the square root of the eigenvalues of the system’s dynamical matrix:

\[ D_{\alpha\beta} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 U}{\partial x_{\alpha} \partial x_{\beta}}, \]  

(3)

The dynamical matrix is a \( 3N \times 3N \) matrix with \( 3N \) eigenvalues. The occurrence of 3 zero eigenvalues is indicative of rigid body motion in three translational directions. The temperature dependence of the system can be easily described by the QH method.

2.2. The LQH method

As highlighted above, the QH method is computationally expensive as obtaining the 3\( N \) vibrational frequencies involves solving for the eigenvalues of a \( 3N \times 3N \) matrix. The computational effort increases rapidly with increasing number of atoms in the system under consideration. Consequently, a local assumption that ignores the vibrational correlation between atoms is commonly invoked in the LQH method to reduce the computational expense of the QH method. With this assumption, the vibrational frequency of each atom corresponds to the eigenvalues of a \( 3 \times 3 \) matrix. Equation (2) can thus be rewritten as

\[ A = U(x^0) + \frac{\tilde{h}}{2} \sum_{i=1}^{N} \sum_{\alpha=1}^{3} \omega_{i\alpha} + k_B T \sum_{i=1}^{N} \sum_{\alpha=1}^{3} \ln(1 - e^{-\tilde{h} \omega_{i\alpha}/k_B T}). \]  

(4)

where \( \omega_{i\alpha} \) are three vibrational frequencies of atom \( i \). The computational cost is evidently reduced in the LQH approach as the Helmholtz free energy is obtained by solving for the eigenvalues of a \( 3 \times 3 \) matrix \( N \) times as opposed to solving for the eigenvalues of a \( 3N \times 3N \) matrix.

2.3. The MLH method

The MLH method combines the zero-point and finite-temperature vibrational energy to a hyperbolic sine function:

\[ A = U(x^0) + k_B T \sum_{i=1}^{3N-3} \ln \left( 2 \sinh \left( \frac{\tilde{h} \omega_i}{2k_B T} \right) \right) \]  

(5)

and strives to retain the simplicity of the LQH methodology. The MLH method defines a vibrational correction effect, \( \Delta \), between the QH and LQH methods:

\[ A_{QH} = A_{LQH} + \Delta \]  

(6)

with

\[ \Delta = k_B T \sum_{i=1}^{3N-3} \ln \left( 2 \sinh \left( \frac{\tilde{h} \omega_i}{2k_B T} \right) \right) - k_B T \sum_{i=1}^{N} \sum_{\alpha=1}^{3} \ln \left( 2 \sinh \left( \frac{\tilde{h} \omega_{i\alpha}}{2k_B T} \right) \right). \]
The method further assumes that $k_B T \gg h \omega_\alpha$, which simplifies the correction term to
\[
\Delta = \frac{k_B T}{2} \ln \left[ \frac{\hbar}{k_B T} \right]^6 \frac{\det D'_{\text{QH}}}{\det D_{\text{LQH}}} ,
\]
where $D_{\text{LQH}}$ is the dynamical matrix formulated by the LQH method and $D'_{\text{QH}}$ is the sub-matrix of $D_{\text{QH}}$, which corresponds to the QH dynamical matrix formulated by removing an arbitrary choice of an atom’s contribution inside the dynamical matrix $D_{\text{QH}}$. The aforementioned rationale is the formulation of a $3N - 3 \times 3N - 3$ non-singular dynamical matrix.

The MLH method further relates the eigenvalues to those obtained from LQH. For the dynamical matrix $D'_{\text{QH}}$ with eigenvalues $\lambda_i$ ($i = 1, 3N - 3$), these values can be correlated with a referenced value, $\lambda_0$, with an offset magnitude value $a_i$, i.e. $\lambda_i = \lambda_0 + a_i$ for a perfect system or $\lambda_i \approx \lambda_0 + a_i$ for a system with defects. From this relation, the correction term, $\Delta$, can be written in terms of $a_i$:
\[
\Delta = \frac{k_B T}{2} \sum_{i=1}^{3N-3} \ln \left[ 1 + \frac{a_i}{\lambda_0} \right] + \frac{k_B T}{2} \ln \left[ \frac{\hbar}{k_B T} \right]^6 \frac{\det D_{\text{LQH}}}{\det D'_{\text{QH}}} .
\]
After expanding the first term using a Taylor expansion, the correction term becomes
\[
\Delta = \frac{k_B T}{2} \sum_{k=1}^{\infty} \sum_{i=1}^{3N-3} (-1)^k \left( \frac{a_i}{\lambda_0} \right)^k + \frac{k_B T}{2} \ln \left[ \frac{\hbar}{k_B T} \right]^6 \frac{\det D_{\text{LQH}}}{\det D'_{\text{QH}}} .
\]
(7)
Since $a_i$ is related to the eigenvalue, $\lambda_i$, we obtain the following relation:
\[
\sum_{i=1}^{3N-3} a_i = \text{Tr}(D'_{\text{QH}} - \lambda_0 I).
\]
From the above, the summation of the power of $a_i$ will decay rapidly while the $\lambda_0$ value is close to the diagonal value of $D'_{\text{QH}}$. The MLH method suggests that $\lambda_0$ can be selected from the LQH eigenvalues for a perfect system, and as the average of the diagonal value of $D'_{\text{QH}}$ for a system containing defects. In addition, the contribution of the second term can be neglected for large systems. Finally, the MLH free energy calculation is reduced to a form of additional LQH vibrational contributions:
\[
\Delta_{\text{MLH}} = \Delta_{\text{LQH}} - \frac{k_B T}{2} \left( \frac{\Gamma_2}{2} - \frac{\Gamma_3}{3} + \frac{\Gamma_4}{4} \right)
\]
(8)
\[
\Gamma_k = \sum_{i=1}^{3N-3} \left( \frac{a_i}{\lambda_0} \right)^k .
\]

3. The TQH method

In this section, we introduce a new finite-temperature approach, referred to as the TQH method. Conceptually, TQH starts from the finite-temperature vibrational energy and strives for consistent approximation of the QH method via a pure mathematical Taylor expansion. TQH approximates the third term in equation (2). To this end, we decompose equation (2) into a series form so that the Helmholtz free energy can be obtained by truncating the high-order terms.

Starting from the second and the third terms of equation (2):
\[
\frac{\hbar}{k_B T} \sum_{i=1}^{N} a_0 + k_B T \sum_{i=1}^{N} \ln(1 - e^{-\hbar \omega_\alpha / k_B T}) .
\]
The trace of a matrix is equal to the summation of all its eigenvalues:

$$Dx = \lambda x$$

$$\text{Tr}(D_{3N \times 3N}) = \sum_{i=1}^{3N} \lambda_i.$$  

(9)

Thus, the second term can be rewritten as

$$\frac{\hbar}{2} \text{Tr}(D^{0.5}),$$

(10)

which is a function of the system’s dynamical matrix.

To solve the third term of equation (2),

$$k_B T \sum_{i=1}^{3N} \ln(1 - e^{-\frac{\hbar \omega_i}{k_B T}})$$

we expand \( \ln \) and \( \exp \) components using a Taylor series, i.e.

$$\ln(1 + f(x)) = \sum_{\alpha = 1}^{\infty} (-1)^{\alpha+1} \frac{f(x)^\alpha}{\alpha}, \quad -1 \leq f(x) \leq 1$$

$$\exp(g(x)) = \sum_{\beta = 0}^{\infty} \frac{g(x)^\beta}{\beta!}.$$  

(11)

The third term can then be expanded as

$$-k_B T \sum_{i=1}^{3N} \sum_{\alpha = 1}^{\infty} \frac{(-\alpha h \omega_i / k_B T)^{\beta}}{\alpha \times \beta!} \times \text{Tr}(D^{\beta/2}).$$

From the above, the relation between the trace and eigenvalues shown in equation (9) can be used to rewrite equation (11) as follows:

$$-k_B T \sum_{i=1}^{3N} \sum_{\alpha = 1}^{\infty} \frac{(-\alpha h / k_B T)^{\beta}}{\alpha \times \beta!} \times \text{Tr}(D^{\beta/2}).$$

(12)

Equation (12) is also a function of the dynamical matrix. From equations (2), (10) and (12), the Helmholtz free energy in the TQH method is given by

$$A = U(x^0) + \frac{\hbar}{2} \text{Tr}(D^{1/2}) - k_B T \sum_{\alpha = 1}^{\infty} \sum_{\beta = 0}^{\infty} \frac{(-\alpha \hbar \omega_i / k_B T)^{\beta}}{\alpha \times \beta!} \times \text{Tr}(D^{\beta/2}).$$

(13)

To obtain the Helmholtz free energy by the TQH method, we need to determine the trace of the dynamical matrix to the power of \( \beta/2 \). We herein employ a Taylor expansion to expand the \( D^{\beta/2} \) at \( \xi I \):

$$D^{\beta/2} = \xi^{\beta/2} I + \sum_{\gamma = 1}^{\infty} \frac{(D - \xi I)^\gamma}{\gamma!} (D^{\beta/2})^{(\gamma)} \big|_{D=I}.$$  

(14)

From equations (13) and (14), it is evident that the TQH method simply re-organizes equation (2) to a series form.

The TQH method described above uses three Taylor expansions to obtain the Helmholtz free energy. The result converges to an exact value when more terms in the series are considered. However, because the contribution of the higher order terms is usually small, they can often be truncated. In our application of the TQH method, we truncate the \( \ln \) component after \( n \) terms,
truncate the exp component after $m$ terms and truncate the $D^{\beta/2}$ component after $k$ terms. Equations (13) and (14) can then be combined and rewritten as

$$A = U(x^0) + \frac{\hbar}{2} \text{Tr}(D^{1/2}) - k_B T \sum_{\alpha=1}^{n} \sum_{\beta=0}^{m} \frac{(-\alpha)^\beta}{\alpha! \beta!} \left( \frac{\hbar}{k_B T} \right) \text{Tr}(D^{\beta/2})$$

$$D^{\beta/2} = \xi^{\beta/2} I + \sum_{\gamma=1}^{k} \frac{(D - \xi I)^\gamma}{\gamma!} \left( D^{\beta/2} \right)^{(\gamma)} \bigg|_{D=\xi I}.$$  

(15)

4. Numerical examples

4.1. Homogeneous argon system

To evaluate the validity of the proposed methodology, a simple homogeneous argon system is first considered. From equation (15), it is evident that the $n$ and $m$ values are coupled and only affect the accuracy of the third term. The $k$ value affects the accuracy of $D^{\beta/2}$, which in turn affects the values of both the second and third terms of equation (15). Let us consider the $n$ and $m$ values more closely. To compare the approximating error of the third term of equation (15), a vibrational frequency, $\omega$, is substituted into the third term of equation (2) and into the third term of equation (15). The approximating error can thus be obtained from

$$\text{Error} = \frac{|P_{QH} - P_{TQH}|}{P_{QH}}$$

$$P_{QH} = k_B T \ln(1 - e^{-\hbar\omega/k_B T})$$

$$P_{TQH} = -k_B T \sum_{\alpha=1}^{n} \sum_{\beta=0}^{m} \frac{(-\alpha)^\beta}{\alpha! \beta!} \left( \frac{\hbar\omega}{k_B T} \right)^\beta.$$  

The contribution of the $\alpha$ and $\beta$ terms in $P_{TQH}$ increases with vibrational frequency, which leads to a subsequent increase in the difference between $P_{QH}$ and $P_{TQH}$. If the difference exceeds the change in $P_{QH}$, the approximation error increases with increasing $\omega$. The opposite result is obtained if the aforementioned condition is not satisfied. The largest approximating error, therefore, occurs at the highest or the lowest vibrational frequencies.

We apply the TQH method to a $5 \times 5 \times 5$ homogeneous argon system to determine how the $n$ and $m$ values affect the accuracy of the calculated Helmholtz free energy. The system temperature was set to 50 K and the Lennard-Jones potential was used to describe atomic interactions [14]. We use normal mode analysis to obtain the relation of the lowest and highest vibrational frequencies to the error. In figure 1, the error contribution is divided into two main regions: the bottom-right region with a relatively larger error and the upper-left region with a relatively smaller error. With regard to the former, the error is produced by the expansion of the exponential function. As the $m$ value increases, the error initially rises to a maximum value, after which it decreases. While the $m$ value is large enough to reach the boundary of the upper-left region, the error will reduce to a small value, indicating that the $(n, m)$ pair can produce a converged result in the TQH approach. By considering the convergence reached for different $n$ values, we find that the error does not always decrease with increasing $n$. The value of $m$ needed to obtain a converged result dramatically increases when $n$ is increased. Therefore, we can say that the value of $m$ used is dependent on $n$. By comparing the results of the highest and lowest frequency analysis, it is evident that the former makes the most significant contribution to the error. From the selected $(n, m)$ pair in this case, we notice that the vibrational frequencies of the system are coupled and cannot be considered individually. The $(n, m)$ pair should thus, in general, be chosen such that an allowable tolerance is provided for both the lowest frequency result and the highest frequency result.
In the following, we conduct the same analysis as performed above on the argon system at temperatures of 30 and 70 K. The dependence of the error on the values of the \((n, m)\) pairs are shown in figures 2 and 3, respectively. The highest vibrational frequency analysis again makes the most significant contribution to the generated error. When the system temperature decreases, the upper-left region shrinks, which indicates that the TQH method cannot converge under the given conditions. However, if an \((n, m)\) located in the upper-left region is chosen, the error is large at elevated temperatures. By comparing the error results computed at 30, 50 and 70 K, \(n = 10\) and \(m = 90\) were determined as the optimal values for the TQH analysis of the homogeneous argon system.

The final parameter that needs to be assigned in the TQH method is the \(k\) value. Again, we consider the argon system at 50 K to determine the effect of the free energy error on the \(k\) value. The value of \(\xi\) in equation (14) is set equal to \(D_{1,1}\) and the error analysis results are plotted in figure 4(a). If \(k = 1\), a result similar to that obtained with the LQH approach is obtained. As \(k\) increases, the TQH results converge with the QH results. For instance, when \(k = 10\), the TQH method yields a sufficiently accurate result. We therefore use this particular \(k\) value in the following study of the homogeneous argon system.

The TQH method can now be applied to study the volumetric thermal expansion of the argon system at different temperatures. Volumetric thermal expansion is defined as

\[
\frac{1}{V} \frac{\partial V}{\partial T}.
\]

The errors obtained by the LQH, MLH and TQH methods compared with the QH method are shown in figure 4(b). The TQH method provides similar results to the QH method. However, at high temperatures, the error becomes appreciable which agrees well with the above error.
Figure 2. Error (%) associated with truncating terms in the TQH method for the homogeneous argon system at 30 K at the lowest frequency (left) and the highest frequency (right) considered.

Figure 3. Error (%) associated with truncating terms in the TQH method for the homogeneous argon system at 70 K at the lowest frequency (left) and the highest frequency (right) considered.
Figure 4. $5 \times 5 \times 5$ homogeneous argon system with lattice spacing $= 5.425$ Å. (a) Comparison of TQH ($n = 10$, $m = 90$) calculated free energy at 50 K and different $k$ values with results obtained from the QH, LQH and MLH methods. (b) Error of calculated thermal expansion by LQH, MLH and TQH ($n = 10$, $m = 90$ and $k = 10$) methods.

4.2. Au vacancy formation (point defect)

We apply the TQH method to a system containing vacancies. The initial model consists of $5 \times 5 \times 5$ face centered cubic (fcc) lattice of Au atoms. To create the vacancy, the central atom is removed. The Buckingham potential was used to treat atomic interactions. To compare the accuracy and efficiency of the QH, LQH, MLH and TQH methods, the conjugate gradient (CG) method was employed to obtain the equilibrium structure of the defect system.

We consider the vacancy system under two different conditions using these finite-temperature methods. The first system consists of the initial model described above with a lattice spacing of $a = 4.1312$ Å at a temperature of 300 K. Once the atoms are placed in their equilibrium positions, we slice the (1 0 0) plane through the vacancy to compare the difference of the equilibrium models yielded from these different finite-temperature methods. Figure 5 includes the analysis obtained using the QH, LQH, MLH and TQH methods with two different truncating terms. The results of each method differ significantly for atoms close to the vacancy, and less for atoms away from the vacancy. The LQH method produces a larger difference error than the TQH method. The difference in atomic positions decreases when more high-order terms in the TQH method are considered. Finally, the results from the MLH method produce the largest error and the observations agree well with those concluded from [7]. Owing to the approximation of $\lambda_i$ in the defect system, MLH can sometimes lead to a worse result than LQH in the calculation of free energy and its derivatives for a defected system.

For the second case study, we consider the vacancy system at zero pressure and a temperature of 300 K. The free energy and entropy of formations of this system in particular were analyzed. To measure the properties of the vacancy, it is necessary to make comparisons with that of an ideal system. Thus, the vacancy formation free energy is given by $G_v = G_0 - G_p$, where $G_0$ and $G_p$ correspond to the Gibbs free energy of the vacancy system and the ideal
Figure 5. Difference of the equilibrium structure determined by (a) the LQH method, (b) the MLH method, (c) the TQH method for \( n = 10, m = 35, k = 10 \) and (d) the TQH method for \( n = 20, m = 50, k = 10 \). All the results are compared with the QH method (unit in Å).

Table 1. Error produced by the different methods considered.

| Method        | \( G_v \) (eV)/error(%) | \( S \) (eV K\(^{-1}\))/error(%) |
|---------------|--------------------------|-----------------------------------|
| QH            | 2.2256/—                 | 0.1313/—                          |
| LQH           | 2.2334/0.35              | 0.1196/8.86                        |
| MLH           | 2.2644/1.74              | 0.1319/0.42                        |
| TQH \( (n = 10, m = 35, k = 10) \) | 2.2306/0.22 | 0.1299/1.05                        |
| TQH \( (n = 20, m = 50, k = 10) \) | 2.2283/0.12 | 0.1315/0.21                        |

system, respectively. The vacancy formation entropy is obtained from the system’s internal energy, \( U \), free energy, \( A \), and temperature, \( T \): \( S = (U - A)/T \). The results obtained are listed in Table 1. The LQH method produces a larger error than the TQH method. The MLH method also interestingly produces a larger error in the computation of the vacancy formation free energy, but not for the vacancy formation entropy.

Upon comparing the accuracy of these finite-temperature theories, we focus now on their respective efficiency. Table 2 shows the total CG steps and total time required for the
Table 2. CG steps and required CPU time of the different methods of interest.

| Method   | CG steps | CPU time (min) |
|----------|----------|----------------|
| QH       | 20       | 3365.67        |
| LQH      | 19       | 0.05           |
| TQH ($n = 10, m = 35, k = 10$) | 20/90.17 |
| TQH ($n = 20, m = 50, k = 10$) | 23/102.14 |

determination of the equilibrium structure of the vacancy model in the QH, LQH and TQH methods, respectively. The CG steps needed by these methods are different since the LQH method and the TQH method employ distinct approaches to mimic the QH method. The potential curves are therefore also distinct. Table 2 shows that the TQH method requires less time than the QH method but more time than the LQH method to arrive at the equilibrium structure. The computational cost of the TQH method is significantly less than that of the QH method and therefore, the TQH approach is an efficient choice for finite-temperature case studies.

The computational time and the number of CG steps required for the TQH method depend on the number of truncating terms selected. The total computational time is a sum of the preparation time, the energy minimization time and the finalization time. We cannot unfortunately determine the exact time needed for each CG step, which would interestingly allow for a comparison of the additional time required for varying the number of truncating terms. However, from the derivation of the TQH method, it is evident that the majority of the computational cost arises from the determination of the trace of the dynamical matrix of different order $\text{Tr}(D^{\beta/2})$ in equation (15). The selection of different $n$ and $m$ values only affects the factor in equation (15) which is multiplied with $\text{Tr}(D^{\beta/2})$. Therefore, choosing an efficient algorithm to obtain $\text{Tr}(D^{\beta/2})$ can render the TQH method highly efficient in the future.

5. Conclusions

In this study, we introduced a new harmonic-based method to study the thermodynamic properties of various materials. The TQH method re-organizes the free energy equation into series expansions and approaches the desired result by truncating higher order terms. The truncating terms are determined by considering their relation to the computed accuracy. The QH, LQH, MLH and TQH methods were herein applied in the analysis of a homogeneous argon system and a defect gold system. The results of each approach were compared in order to determine the efficacy and validity of the TQH method. From the analysis, it is evident that the TQH method generally affords an improved accuracy over the LQH method as well as the MLH method in the consideration of systems bearing defects. Additionally, the TQH approach affords improved efficiency over the QH method. Therefore, the TQH method is indeed a strong choice for finite-temperature system analysis.

Although the TQH method can be highly effective, care must be taken when choosing truncating terms. Due to the expansion process, the TQH method will have a larger error at both high and low temperatures. In selecting the truncating terms, the $n$ value is the most sensitive to temperature change and the $m$ value, which depends on the $n$ value, must be sufficiently large to yield a converged result. Note that too large an $m$ value cannot ensure greater accuracy. The $k$ value determines the computational cost of the TQH method and it is expected that future algorithm optimization can lead to an even more improved TQH efficiency.
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