1 Introduction

The quasi-continuum (QC) method [1–3] is a multiscale approach that was originally developed to solve molecular statics problems at a reduced computational cost. Several similar methods have since been developed, many of which are reviewed in Refs. [4,5] and in Chapter 12 of Ref. [6]. These methods fall into the class of coupled domain approaches in which one region of the system is modeled atomistically (where the degrees of freedom are the positions of all atoms in that region) while the rest of the system is modeled using a computational approximation to continuum mechanics (usually finite elements). In the case of QC, the method was designed to study crystalline solids amenable to the Cauchy–Born rule (see for example Ref. [6]), which is used to define the underlying constitutive behavior for the continuum region.

In all such static coupled domain models, the goal is “MS without all the atoms,” that is to say, to produce the predictions of molecular statics (MS) without explicitly treating all the atoms in the system. The idea is to identify a small subset of the system which is treated explicitly using full atomistics (the atomistic region), while most of the atoms in the surrounding continuum region are eliminated by a “coarse-graining” procedure in which the positions of the atoms are approximated by a continuous displacement field that is interpolated from discrete solution points. A significant gain in terms of computational cost is expected from the fact that the method involves much fewer degrees of freedom in comparison with a complete atomistic description.

As noted above, the original QC is a static method (or so-called “zero temperature” method). This is because the atoms and finite element nodes have no kinetic energy associated with them. It can be used to find zero-temperature equilibrium structures of crystalline bodies (possibly containing defects) under static loads. It can also be used, to a reasonable approximation, to predict the low temperature, low strain rate deformation behavior of such systems by using a quasi-static program of loading. However, temperature and dynamics cannot be treated by the static QC method or any of its close (i.e., zero temperature) cousins. In response, many authors have developed dynamic and/or finite temperature coupled domain methods. The goal of such methods could be summed up as “MD without all the atoms,” that is, to make the same predictions as molecular dynamics (MD) simulations without explicitly treating every atom (and therefore, again, hopefully at a lower computational cost).

Extending static methods to take into account dynamical and/or finite temperature effects is not straightforward. There are additional difficulties that make the problem much more complex. For example, there is only one “goal” to MS and static multiscale
methods: one seeks an equilibrium configuration of atoms. MD, on the other hand, embodies a wider variety of goals, and it is important to use the appropriate formulation for each. In this case, there are two main categories of interest:

(1) We might be interested in equilibrium properties of a system at finite temperature.

(2) We may want to study rapid, nonequilibrium processes that are an important part of the phenomenon of interest.

Both cases are dynamic processes in the sense that atoms are at finite temperature and therefore in constant motion. However, in the first case, the boundary conditions are changing slowly (in principle, infinitely slowly) on the atomic scale. This usually means a situation where it is valid to assume a nearly constant, spatially uniform, temperature and one can introduce a conceptual heat bath to simplify the computations. For short, we refer to these simply as “equilibrium MD” (EMD) simulations. Central to EMD simulations is the concept of a thermostat [6–9] in which the equations of motion are modified to mimic the effect of coupling the atoms to a large external heat bath at a constant, uniform temperature. The result is an additional drag force on each atom, which tends to slow the atoms down if their temperature is too high, or accelerate them if their temperature is too low. In order to be useful, thermostats usually need to do more than simply maintain a constant average temperature. The goal is a system that correctly reproduces the thermal fluctuations of the canonical ensemble (Holian et al. [10] discuss this in more detail). Of course, thermostats are limited to studying EMD problems because they are driving the system to remain in thermodynamic equilibrium by design.

In the second case (nonequilibrium MD or NEMD), both the atomic positions and the boundary conditions are time-dependent. This includes processes like fracture where localized heating due to bond-breaking or plastic flow, which are inherent to the process, implies that an approach predicated on constant temperature may no longer be applicable.

A multiscale approximation to the NEMD case is more challenging than EMD, in a way, because it requires a model for the transfer of heat between the partitioned domains. The very nature of the concepts of temperature and heat introduce fundamental questions about nonequilibrium multiscale methods. At the level of individual atoms, there is no well-defined temperature or heat flow; there are only atomic velocities and collisions. On the other hand, the continuum theories that we hope to use to effect our coarse-graining are often predicated on the notion of a temperature field and properties that depend, pointwise, on that temperature.

Despite these challenges, several multiscale methods have been proposed to tackle NEMD problems, although many open questions remain before a robust multiscale theory can be established. In these methods, a key problem is that of spurious wave reflections from the interface between the region modeled atomistically and the region modeled using the more coarsely represented continuum. By design, the continuum region has a reduced density of nodes compared to the density of atoms, so that there is a range of short-wavelength phonons that propagate freely through the atomistic region but which are not supportable by the continuum. When these phonons reach the interface, it appears to them as a rigid boundary. They are thus reflected back into the atomistic region. A second problem arises if the constitutive behavior is significantly different in the two regions. For example, a linear elastic continuum region coupled to the inherently nonlinear atomistic region also creates an artificial impedance to wave transmission at the interface. In the example of nonsodientation that we will study later, for instance, wave reflections could mean that a large part of the energy imparted by the indenter would be artifically trapped in the small atomistic region beneath the indenter tip, heating it and destroying the accuracy of the results. The wave reflection problem is made worse by what is the essential goal in multiscale models: to make the atomistic region as small as possible and to represent the continuum as coarsely as we can.

One solution to the wave reflection problem is the use of so-called “absorbing boundary conditions.” Methods of this type start from the generalized Langevin equation (GLE) [13,14], which makes it possible to describe the motion of the atomistic region and replace the effect of the coarse-grained atoms in the continuum region by a kernel function integrated over time

$$m_i \ddot{q}_i = -\frac{\partial V}{\partial q_i} - \sum_j a \int_0^t \beta_j(t-t') \dot{q}_j(t-t') dt + \text{initial conditions terms}$$

(1)

where $j$ runs only over atoms inside the atomistic region and a superscripted dot denotes time differentiation. In this equation, the familiar equation of motion (Newton’s law) for each atom $i$ represented by the mass, $m_i$, acceleration, $\ddot{q}_i$ and force, $-\partial V/\partial q_i$, is augmented by a complicated integral function and subject to initial conditions. The integral essentially represents all the indirect interactions between atoms $i$ and $j$, as transmitted through the missing atoms from the continuum region. This integral is extremely complicated to compute exactly for all but the simplest of systems. Consequently, various approximations are used which can confine the computational effect to a few atoms near the atomistic/continuum interface and to only a few time steps (i.e., in Eq. (1), the sum over $j$ only runs over a small subset of the atoms, and the integral in time only extends from $t - \Delta t$ to $t$ for some small $\Delta t$). Cai et al. [15] computed $\beta_j$ exactly (but numerically) in 1D and 2D examples to demonstrate that the wave reflections can be almost completely eliminated by this formulation. Weinan and co-workers [16,17] introduced an approximation that allows the integral term to be evaluated with a handful of discrete contributions to each atom near the atomistic/continuum interface, and showed that although the integral in Eq. (1) is in principle over all time, wave reflections can be largely eliminated by considering only a few previous time steps in the evaluation. Wagner et al. [18,19] studied a simple 1D case where $\beta_j$ can be computed analytically, and then showed how Laplace transforms can be used to efficiently obtain $\beta_j$ for a given crystal structure. Mathew et al. [20] extended the absorbing boundary condition idea by dividing the atomistic phonon spectrum into a long-and short-wavelength regime, allowing the long wavelengths to pass as deformation and the short wavelengths to be absorbed and converted to an equivalent continuum heat flux.

Until recently, these GLE methods were effectively “zero temperature” dynamic methods: while the atomistic region naturally has some nonuniform temperature due to atomic motion, the temperature and entropy of the missing atoms in the continuum is not considered. In effect, the atomistic/continuum interface acts as a damper, efficiently preventing waves from being reflected back into the atoms but also not permitting heat flow between the two coupled domains. However, Karpov et al. [21] have shown that an effective Langevin thermostat can be implemented in such methods using a naturally-occurring random force term in the GLE (left out of Eq. (1) for brevity) that is associated with the random initial conditions of the missing atoms in the continuum. This term approximates the flow of heat to and from the continuum.

As an alternative to GLE, several authors have implemented NEMD methods using an approach that can be generically described as a damping band: essentially thermostats applied to only some of the degrees of freedom in the problem. The thermostat is the essential component of most equilibrium (EMD) simulations, and therefore it seems strange that it can be used in a method designed to multiscale NEMD problems. However, damping-band methods apply additional forces only to the atoms...
located in a narrow band of the atomistic region immediately adjacent to the continuum. The forces on the damping band atoms are derived from an underlying thermostat so that the temperature in the band is strictly controlled. Damping bands of this type regulate the temperature in the entire atomistic region, although the rate of thermal equilibration depends on the relative size of the damping band compared to the total atomistic region. For the same time, disturbances in atomic velocities can propagate through the atomistic region without being artificially suppressed by a global thermostat since a local temperature fluctuation deep within the atomistic region is not sensed by the thermostat until phonons propagate to the atomistic/continuum interface where the damping band resides. This provides a realistic multiscale model for the study of NEMD phenomena. Damping-band methods also do an adequate job of mitigating the problem of wave reflections, although the parameters must typically be tuned and tweaked for a specific problem and/or material.

One disadvantage of damping-band methods (and for that matter, absorbing boundary conditions as well) is that they are really only applicable to insulators. This is because metals conduct most of their heat through the electrons that are not explicitly accounted for in empirical interatomic models. So, while the damping band equilibrates the entire atomistic region to a predetermined temperature, the rate of equilibration is much slower than it would be in real metals due to the absence of electronic heat conduction. Of course this is a disadvantage inherited from the underlying atomistics, as opposed to something emerging from the multiscale approach, but it must nonetheless be kept in mind. In contrast, global thermostats are more amenable to metals. One can view the thermostat forces as being the result of the electron-phonon coupling mechanisms that transfer heat from the vibrating atoms to the mobile electrons. For example, Finnis et al. [28] have proposed a thermostat that is derived from explicit considerations of the ion-electron interactions.

GLE methods, damping-bands and absorbing boundary conditions prevent spurious heating of the atomistic region, but they do not include a robust theory of heat transfer to and from the continuum. They mainly act as a means to dissipate the heat from the system. Several groups have tried to develop methods that fully couple mechanical and thermal responses [29-34]. Kulkarni et al. [33] have developed a novel approach to multiscale NEMD based on the maximum entropy principle of equilibrium thermodynamics. Their method leads to a local (pointwise) statement of thermoelasticity. Their method is coupled with a heat equation to model nonequilibrium behavior. Fish and co-workers [31] have attempted to shed light on the nature of the connection between heat and atomic motion (and how to sensibly implement a coupled NEMD code) using homogenization theory. Liu and Li [32] have sought to develop a multiscale NEMD approach whereby each continuum node has its own thermostat, permitting different temperatures at different spatial locations. They then derive a heat flow equation that couples neighboring thermostats. Wagner et al. [33] have developed a method to systematically coarse-grain atomic motion in order to make a connection to temperature. Using multiple thermostats set to various (and time-dependent) temperatures, they implemented an atomistically informed heat flow model. Jolley and Gill [34] investigated the effectiveness of several thermostats in a similar type of multiscale heat flow analysis.

As summarized above, a great deal of effort has been invested in developing NEMD methods. Various approaches addressing the issue from different viewpoints have been proposed and it seems that there is still no real consensus on this difficult subject. Our aim in this paper is not to propose a new NEMD formulation, but rather to derive a more limited EMD formulation as rigorously as possible. With such a formulation in hand, it will be possible to place the more ambitious goals of NEMD on a more secure footing. For example, one would expect a rigorous NEMD formulation to reduce to the EMD formulation in the equilibrium limit. Thus, we turn our attention to EMD methods and describe how we have extended them to a multiscale paradigm.

Since, as stated above, EMD problems are normally studied using a thermostat, some authors have sought to develop a multiscale method by extending the concept of an MD thermostat to a coupled domain setting. One approach is to “convert” an essentially static multiscale method to a dynamic one and then apply a thermostat to the entire system (both atoms and continuum nodes). For example, Luan et al. [35] use a Langevin thermostat on their model of two-dimensional contacts. This approach has the advantage of being relatively straightforward to implement but the disadvantage that the atomistic region does not inherently include temperature-dependent properties (which would need to be introduced “by hand” into the continuum constitutive law). In addition certain pathologies may emerge in the continuum region, such as the “mesh entropy” effect we describe later in this article (see Sec. 2.5.1). An alternative approach that can impart temperature-dependence on the continuum is the “coarse-grained molecular dynamics (CGMD)” model developed by Rudd and Broughton [36,37]. Kobayashi et al. [38,39] have extended CGMD by improving the wave-passing abilities of the atomistic/continuum interface, while a similar approach based on a meshless method to discretize the continuum appears in [40]. To et al. [41] have developed a form of the finite-temperature Cauchy-Born rule that is closely related to that which we describe below.

Our work was presented in preliminary form in Ref. [42]. Here, we provide the full details and the latest developments of the finite temperature QC model (or simply “hot-QC” for short). Hot-QC is a rigorous EMD method in the sense that all approximations are clearly defined and the overall accuracy of the method is established. It has a second advantage in that the continuum regions in the model are “atomistically-informed,” and thus seamlessly capture the temperature dependence of the material properties (for example, thermal expansion and the change in elastic constants with temperature) to within the accuracy of the approximations inherent to the method. This is accomplished by accounting for the missing entropy of the removed atoms at finite temperature through use of the so-called “local harmonic approximation” [43].

In this manner, a finite element constitutive law—essentially a temperature-dependent Cauchy-Born model similar to that developed in Ref. [42] and more recently in To et al. [41] (see also Ref. [6])—can be derived and subsequently coupled to the atomistic region.

Since the publication of our preliminary model, other researchers have made important advances in the understanding of coarse-grain dynamics and thermostats in this context. For example, Gill et al. [27] demonstrate the effectiveness of the Nosé and Poincaré thermostats in a multiscale setting. They show how methods such as “partial thermostating” in the atomistic region can be an effective way to mitigate nonphysical perturbations of the atom dynamics due to the thermostat forces. They also discuss so-called “recursive multiple thermostats” and how they can be used to improve thermostat performance in systems with multiple length scales. These issues are not the main focus of the work we present here, but in principle they could be applied to our model in future work.

Our article is organized as follows. In Sec. 2, we describe the theoretical derivation of the hot-QC formulation. The derivation is couched in terms of Hamiltonian mechanics. The final result will be a temperature-dependent Hamiltonian for the coupled system. In Sec. 2, we go step-by-step through the Hamiltonian derivation, first showing how a formally exact (but computationally impractical) Hamiltonian can be written in a form that eliminates any direct dependence on the coarse-grained degrees of freedom. This derivation is closely related to the concept of the potential of
mean force introduced by Kirkwood [44]. Then, in Secs. 2.2.1 and 2.2.2, we take two levels of approximation (first the quasi-harmonic approximation and next the local harmonic approximation) to render the formulation computationally tractable while keeping account of the level of error introduced at each step.4 In Sec. 2.3, we introduce the continuum-based coarsing familiar from the static QC method, and use finite elements and the Cauchy–Born rule to capture spatial variations due to nonuniform deformation. Section 2 closes with a presentation of two alternative approaches to finding solutions within the hot-QC framework: (i) “hot-QC-static” where a fully dynamic atomistic region is embedded into a static continuum, and (ii) “hot-QC-dynamic,” a possibly more efficient alternative where the entire system is solved dynamically.

In Sec. 3, we discuss several practical points about implementing the model including the detailed equations required for the model for a pair functional interatomic potential [6] such as the embedded-atom method (EAM) [47] and the choice of thermostat. We close out the paper in Sec. 4 with a series of numerical studies to explore the accuracy and performance of the hot-QC methodology. We investigate the effectiveness of several thermostats (Landevin, Nosé–Poincaré and Nosé–Hoover) in maintaining a global set temperature and temperature uniformity across the continuum and atomistic regions. We then apply the methodology with a realistic application problem: the effect of temperature on nonindention into an initially perfect single crystal film.

2 Theoretical Derivation of the Hot-QC Formulation

We consider a system consisting of a large number of atoms N whose positions and momenta are given by \( q_1, \ldots, q_N \) and \( p_1, \ldots, p_N \), where \( q_i \) and \( p_i \) are the position and momentum of the atom \( i \). Within the framework of classical MD, the Hamiltonian of this system can be written as

\[
H(q, p) = V(q) + K(p)
\]

where \( V(q) \) is the potential energy and \( K(p) \) is the kinetic energy of the system, which is given by

\[
K(p) = \sum_{i=1}^{N} \frac{\|p_i\|^2}{2m_i}
\]

Equilibrium statistical properties at temperature \( T \) of such systems are given by phase space averages in the canonical ensemble. We are considering solid systems and therefore adopt a restricted ensemble view where the phase averages are restricted to the portion of phase space accessible to the solid system [48–50]. We assume that the particles remain close to their mean positions, \( q = q_\text{c} + w \), so that

\[
q = q_\text{c} + w
\]

where \( w = (w_1, \ldots, w_N) \) are the vibration displacements of the atoms relative to their mean positions.\(^5\) Later, the mean positions will be determined by the condition that the free energy of the system is at a minimum when the atoms occupy these positions (see Eq. (26) below). As such, we can think of the mean positions as functions of the temperature and boundary conditions of the problem. We will sometimes make this explicit by writing \( \bar{q}(T) \).

The restriction keeping the atoms close to their mean positions is imposed by a characteristic function, \( \chi(w) \), which is equal to one when the system is within the restricted ensemble and zero otherwise. For example, if the atoms are constrained to lie within a distance \( r_c \) of their mean positions, then

\[
\chi(w) = \begin{cases} 1 & \text{if, for all } i \in [1,N], \|w_i\| \leq r_c \\ 0 & \text{otherwise} \end{cases}
\]

The restricted phase average (or observable) \( A \) of a phase function \( A(q, p) \) is given by (see Ref. [6])

\[
A(T) = \langle A \rangle_T = \frac{1}{h^{3N}} \int Z(T)^{1/2} A(q(T) + w, p) \exp[-\beta H(q(T) + w, p)] \, dw \, dp
\]

where \( \beta = (k_B T)^{-1} \), \( k_B \) is the Boltzmann’s constant, \( h \) is Planck’s constant, and \( Z(T) \) is the partition function of the restricted canonical ensemble

\[
Z(T) = \frac{1}{h^{3N}} \int \exp[-\beta H(q(T) + w, p)] \, dw \, dp
\]

In practice, the observable Eq. (6) can be computed by running an MD simulation of the system, and evaluating the time-average of the phase function \( A \) along the simulated trajectory (see Sec. 3.3 below), but this is potentially a simulation of great computational expense. Our goal here is to describe viable methods for approximating the evaluation of Eq. (6) at a significantly reduced computational effort.

In many cases, the phase functions of interest do not depend on all the variables of the system, but only on a subset located in a region of interest. Examples include the study of a dislocation in a crystal or an atomically-sharp crack tip (shown in Fig. 1) where only the atoms near the defect are important. Consequently, our coarse-graining strategy begins with the selection of this atomistic region, which we denote \( \Omega^a \). The remaining part of the system, \( \Omega^c \), is called the continuum region (see Fig. 1(a)). The role of this region is to provide appropriate mechanical and thermal boundary conditions for the atomistic region. For definiteness, the superscripts “a” and “c” refer to the atomistic and continuum regions throughout this article.

We renumber the atoms so that the \( N_a \) atoms lying within the atomistic region appear first followed by the \( N_c \) atoms in the continuum region, so that \( N_a + N_c = N \). The coordinates of the atoms are then given by

\[
q = (q_1, \ldots, q_{N_a}, q_{N_a+1}, \ldots, q_N)
\]

\[
\equiv (q^a_1, \ldots, q^a_{N_a}, q^c_1, \ldots, q^c_N) = (q^a, q^c)
\]

Similarly, the momenta are given by

\[
p = (p^a_1, \ldots, p^a_{N_a}, p^c_1, \ldots, p^c_N) = (p^a, p^c)
\]

We continue to employ a restricted ensemble, so that Eq. (4) holds with

\[
\bar{q} - (q^a, q^c), \quad w = (w^a, w^c)
\]

We are interested in phase functions that depend only on the positions and momenta of atoms in the atomistic region, \( A = A(q^a, p^a) \). Hence, our aim is to compute

\(^5\)Note that Kimmor and Jones [45] have recently done a critical comparison of the computational cost and accuracy of both the quasi-harmonic and local harmonic approximations over a range of temperatures. This work sheds further light on the level of approximation inherent in our formulation, and is largely consistent with our observations discussed in Sec. 2. Khot et al. [46] have also examined the stability (as a function of strain) of the temperature-dependent Cauchy–Born rule, showing that care must be taken at large strains where the eigenvalues of the crystal’s dynamical matrix can become negative.

\(^6\)We distinguish between vibrational displacements from the changing mean position (\( w = q - \bar{q} \)) and absolute displacement from a fixed reference position (\( u = q - Q \)).
considering the integral in the numerator of Eq. (8). This integral can be separated out into atomic and continuum parts:

\[ \int \int \int \exp(-\beta H(q^a + w^a, \bar{q}, w^c, p^a, p^c)) \times \chi(w^c) dw^c dp^c \]

where \( \chi(w^c) \) and \( \chi(w^c) \) are the characteristic functions for the atomic and continuum regions separately. We have used the fact that \( \chi(w) = \chi(w^a) \chi(w^c) \), which is correct since the system is confined to its restricted configuration space only if both the atomic and continuum regions satisfy their respective constraints. We now define the effective Hamiltonian for the atomic region, \( H^a(q^a, p^a, \bar{q}) \), by making the following connection to the expression in the square brackets in Eq. (9):

\[ \exp[-\beta H^a(q^a, p^a, \bar{q}, T)] = \frac{1}{h^{N_a}Z^a(T)} \int \chi(w^c) dw^c dp^c \]

from which we obtain the desired definition:

\[ H^a(q^a, p^a, \bar{q}, T) \equiv -\kappa_a T \ln \frac{1}{h^{N_a}Z^a(T)} \int \chi(w^c) dw^c dp^c \]

In this discussion, we will often use the presence or absence of a \( \bar{ } \) to emphasize that a function has been modified only through a change of variables.

Substituting Eq. (10) into Eq. (9) and then back into Eq. (8) and applying a similar procedure to the denominator, we have:

\[ A(T) = \frac{1}{h^{N_a}Z^a(T)} \left[ A(q^a(T) + w^a, p^a) \times \exp(-\beta H^a(q^a(T) + w^a, p^a, T)) \right] \times \chi(w^c) dw^c dp^c \]

with the reduced partition function:

\[ Z^a(T) = \frac{1}{h^{N_a}} \left[ \int \exp(-\beta H^a(q^a + w^a, p^a, T)) \times \chi(w^c) dw^c dp^c \right] \]

In Eq. (13), we now have an expression for the average of the phase function \( A(q^a, p^a) \) at a given temperature \( T \) directly in terms of the atomic variables (although it depends indirectly on the continuum region through the effective Hamiltonian \( H^a(T) \)). To explore how this expression can be computed efficiently, we note that since the Hamiltonian can be separated into potential energy and kinetic energy, the effective Hamiltonian has a similar separation:

\[ H^a(q^a, p^a, T) = V^a(q^a, T) + K^a(p^a, T) \]
\[ \Psi^\text{at}(q^\text{at}, T) = -k_B T \ln \frac{1}{h_q} \int \exp[-\beta V(q^\text{at}, \bar{q} + w^\text{c})] \chi^c(w^\text{c}) dw^\text{c} \tag{16} \]

where we recall that \( \bar{q} = \bar{q}(q^\text{at}, T) \), and

\[ K^\text{at}(p^\text{at}, T) = -k_B T \ln \frac{1}{h_p} \int \exp[-\beta K(p^\text{at}, p^\text{p})] dp^\text{p} \tag{17} \]

In Eqs. (16) and (17), \( h_q \) and \( h_p \) are constants with units of position and momentum, respectively, that satisfy the relation \( h_q h_p = h \), where \( h \) is the Planck’s constant. Note that different choices for \( h_q \) lead to effective potential energies \( V^\text{at}(q^\text{at}, T) \) that only differ by an additive constant.

The effective kinetic energy \( K^\text{at}(p^\text{at}, T) \) in Eq. (17) can be evaluated analytically by substituting in the expression for \( K \) in Eq. (3) and integrating each momentum degree of freedom from \( -\infty \) to \( \infty \). The result is

\[ K^\text{at}(p^\text{at}, T) = \sum_{i=1}^{N_q} \frac{\| p_i^\text{at} \|^2}{2m_i^\text{at}} - \frac{3}{2} \sum_{j=1}^{N_q} \ln \frac{2 \pi k_B T m_j^\text{cont}}{h_p^2} \tag{18} \]

where \( m_i^\text{at} \) is the mass of atom \( i \) in the atomistic region, and \( m_j^\text{cont} \) is the mass of atom \( j \) in the continuum region. In the case where all atoms in the system are of the same species with mass \( m \), then all \( m_i^\text{at} = m_j^\text{cont} = m \).

While the effective kinetic energy is analytically computable, the calculation of the effective potential energy \( V^\text{at}(q^\text{at}, T) \) is more challenging. It involves the integration of a complex, generally anharmonic, potential energy function over all degrees of freedom in the continuum region. As such, it is similar to the concept of the potential of mean force introduced by Kirkwood [44]. Direct calculation of this term would be more demanding than the calculation of the complete potential energy \( V(q) \) and the forces on all atoms, making this coarse-grained approach potentially much slower than a full MD simulation. Therefore, the purpose of the next section is to demonstrate how it is possible to expedite this calculation using a quasi-harmonic approximation (and eventually a local harmonic approximation).

### 2.2 Efficient Calculation of the Effective Potential Energy

In the next step of the derivation, we recognize that the effective potential energy \( V^\text{at} \) in Eq. (16) is in fact the Helmholz free energy \( \Psi^\text{at} \) of the system when the atoms in the continuum region are under conditions of thermodynamic equilibrium at the specified temperature \( T \). More precisely, in view of Eq. (16),

\[ V^\text{at}(q^\text{at}, T) = \Psi^\text{at}(q^\text{at}, \bar{q}^\text{at}(q^\text{at}, T), T) \tag{19} \]

where

\[ \Psi^\text{at}(q^\text{at}, \bar{q}; T) = -k_B T \ln \frac{1}{h_{q^\text{at}}} \int \exp[-\beta V(q^\text{at}, \bar{q} + w^\text{c})] \chi^c(w^\text{c}) dw^\text{c} \tag{20} \]

and \( \bar{q} \) (defined in Eq. (26) below) is the value that (essentially) minimizes \( \Psi^\text{at} \) at given positions of the atoms in the atomistic region \( q^\text{at} \) and temperature \( T \).

#### 2.2.1 Quasi-Harmonic Approximation

We begin by computing the free energy in Eq. (20) using the quasi-harmonic approximation [6,52–55]. Specifically, the lattice dynamics of the system associated with the vibrations of the atoms in the continuum region are treated within the harmonic approximation. This means that the potential energy of the system is expanded about a given equilibrium structure of the crystal defined by \( \bar{q} \), which will be determined at the end of this process by ensuring that the corresponding Helmholz free energy, \( \Psi^\text{c} \), is minimal with respect to these coordinates.

More precisely, we first estimate the free energy of the system by expanding the potential energy function to second order around a candidate crystal structure defined by the coordinates \( \bar{q} \):

\[ V(q^\text{at}, \bar{q}^\text{at} + w^\text{c}) \approx V(q^\text{at}, \bar{q}^\text{c}) + \sum_{j=1}^{N_q} \frac{W_{ij}}{2} (q^\text{at} - \bar{q}^\text{at} - \bar{q}^\text{c}) \cdot (q^\text{at} - \bar{q}^\text{at} - \bar{q}^\text{c}) \]

\[ + \frac{1}{2} \sum_{i,j} w_{ij}^c \cdot \Phi_{ij}(q^\text{at} - \bar{q}^\text{at} - \bar{q}^\text{c}) \tag{21} \]

where \( w_{ij}^c = q_{ij}^c - \bar{q}_{ij}^c \) is the displacement of atom \( i \) relative to \( \bar{q}_{ij}^c \), and \( \Phi_{ij}^c \) is the \( 3 \times 3 \) force constant matrix, or “Hessian,” associated with atoms \( i \) and \( j \) in the continuum region, defined as

\[ \Phi_{ij}^c(q^\text{at} - \bar{q}^\text{at} - \bar{q}^\text{c}) \]
The mean positions, $\vec{q}$, are now determined by minimizing $\Psi_{QH}$ with respect to the trial positions

$$\vec{q} = \arg\min_{\vec{q}} \Psi_{QH}(q^a, \vec{q}; T)$$

(26)

We therefore see that under the assumption of small temperature (which is equivalent to performing the harmonic approximation of Eq. (21) on $\phi$), the restriction imposed by $\chi'$ naturally drops out and that

$$V^H(q^a, T) = \Psi_{QH}(q^a, \vec{q}(q^a, T), T) + O((k_B T)^2)$$

(27)

The approximation $\Psi_{QH}$ that we have constructed is hence accurate to second order in temperature. In what follows, we will use the notation

$$\tilde{V}(q^a, T) = \Psi_{QH}(q^a, \vec{q}(q^a, T), T) = \min_{\vec{q}} \Psi_{QH}(q^a, \vec{q}; T)$$

(28)

Thus, we are using the low-temperature regime to obtain a tractable approximation of the effective potential $V^H(q^a, T)$.

### 2.2.2 Local Harmonic Approximation

In view of Eq. (27), the quasi-harmonic approximation in Eq. (24) provides a good estimate for $V^H$. Unfortunately, this expression is computationally intractable for most systems, since $\Psi_{QH}$ includes the determinant of the full $3N_c \times 3N_c$ force constant matrix. We therefore go one step further and adopt the local harmonic model proposed by LeSer et al. [43] in which all of the off-diagonal coupling terms in Eq. (25) are set to zero, i.e., $\Phi_a^{\vec{q}} := 0$ for $i \neq j$. Although this is a drastic simplification of the total force constant matrix (which, for example, precludes phonons), this assumption was shown to be valid for the calculation of complex structure at finite temperature from 0 K up to half of the melting temperature of the crystal [57].

In addition, we note that this assumption is invoked only in the continuum region. It should therefore hold with reasonable accuracy, since the atoms are expected to be located close to their mean positions in a defect-free crystal. Using the local harmonic approximation, the determinant of the force constant matrix can be written as the product of the determinants of the local $3 \times 3$ force constant matrices, $\Phi_a^{\vec{q}}$ (no sum on $i$), of the atoms $i = 1, \ldots, N_c$ in the continuum region

$$\det \Phi_{LH} = \prod_{i=1}^{N_c} \det \Phi_a^{\vec{q}}$$

(29)

The Helmholtz free energy in Eq. (24) is therefore approximated by

$$\Psi_{LH}(q^a, \vec{q}; T) = V(q^a, \vec{q})$$

$$+ \frac{k_B T}{2} \sum_{i=1}^{N_c} \ln \left[ \frac{h^2}{2k_B T} \det \Phi_a^{\vec{q}}(q^a, \vec{q}) \right]$$

(30)

As was done in Eqs. (26) and (27), we approximate the effective potential energy, $V^L(q^a, T)$, as the minimum of the free energy in Eq. (30) with respect to the trial positions $\vec{q}$.

$$\tilde{V}^L(q^a, T) = \min_{\vec{q}} \Psi_{LH}(q^a, \vec{q}; T)$$

(31)

The approximate effective Hamiltonian for the atomistic region is then

$$\tilde{H}^L(q^a, p^a, T) = \tilde{V}^L(q^a, T) + K^d(p^a, T)$$

(32)

where $\tilde{V}^L$ is given above and $K^d$ is given in Eq. (18).

#### 2.3 Finite Element Discretization and the Cauchy–Born Rule

The effective Hamiltonian defined in Eq. (32) requires the calculation of the free energy in Eq. (30). This is difficult since $\Psi_{LH}$ depends on a large number of degrees of freedom (as many as the original potential energy), and also involves a sum over all the atoms which have been integrated out. To reduce the cost of this computation, we adopt the QC strategy of representing the deformation in the continuum region in terms of a discretized displacement field and then applying the Cauchy–Born rule to obtain an approximation for $\Psi_{LH}$.

The first step in constructing the hot-QC framework is the introduction of a reference configuration relative to which deformations are measured. We denote the mean positions of the atoms in this reference configuration as $\vec{Q} = (\bar{Q}_1, \ldots, Q_N)$. The choice of a reference configuration is problem specific. For example, for a single crystal, the reference configuration can be taken as the unstressed crystal with the mean positions equal to the ideal lattice positions. The fact that one can define this reference configuration is related to our assumption that the system remains in a metastable basin, which is itself consistent with the use of a restricted ensemble viewpoint. We relate the mean positions of the atoms, $\vec{q} = (q_1, \ldots, q_N)$, to their mean reference positions by

$$\vec{q}_i = \vec{Q}_i + \bar{u}_i, \quad i = 1, \ldots, N$$

(33)

where $\bar{u}_i$ is the mean displacement of atom $i$.

The second step in constructing the hot-QC framework is to make the assumption that the mean displacement field in the continuum region is spatially slowly varying and can be accurately approximated by an interpolation based on a discretized representation. As in 0 K QC, we select a subset of all atoms in the model to be representive atoms or “repatoms” for short. The set of repatoms includes all atoms in the atomistic region and a small number of atoms in the continuum region. Criteria for repatom selection are discussed for example in [3,58–62].

The repatoms serve as the nodes in a finite element mesh, as shown in Fig. 1(b). In two dimensions (resp. three dimensions), linear triangular elements (resp. linear tetrahedral elements) are used. We assume that the mesh is “fully-refined” near the atomistic-continuum interface, i.e., that the mesh has been refined down to the atomic scale there. This means that no element with a node in the atomistic region contains any internal atom. This is not a requirement of the method, but is done to improve accuracy [5] and to simplify the implementation. The number of nodes in the atomistic and continuum regions, respectively, are $n_{nodes}$ (which is equal to $N_{at}$) and $n_{nodes}^c$, such that $n_{nodes} + n_{nodes}^c = n_{nodes}$, where $n_{nodes}$ is the total number of nodes (which is equal to the number of repatoms, $n_R$).

The mean position of any atom in the continuum region (defined for all atoms in Eq. (33)) is now approximated using finite element interpolation of the mean positions of the repatoms,\(^8\)

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\(^8\)In standard QC parlance, the repatoms in the atomistic region are called nonlocal repatoms and those in the continuum region are local repatoms.\(^9\)

\(^9\)There is no need to use interpolation to obtain the positions of atoms in the atomistic region, since all atoms are represented there. In fact, the finite element mesh is not needed in the atomistic region (except for the elements spanning the interface with the continuum region). It is retained to facilitate meshing and to enable easy expansion and shrinking (i.e., adaption) of the atomistic region.
Here $S_j(X)$ and $\hat{q}_i$ are the finite element shape function and mean displacement associated with node $i$ in the continuum region. Note that we use uppercase letters to denote nodal indices as opposed to lowercase letters for atom indices. Recall that finite element shape functions possess the “Kronecker $\delta$ property,” whereby $S_j(\hat{q}) = 1$ if atom $i$ is co-located with node $j$, and zero if atom $i$ is co-located with node $j \neq I$. Therefore, if the sum in Eq. (34) is evaluated at a nodal position, it simply returns the mean displacement of that node.

We are now ready to revisit the calculation of $\hat{V}^{at}$ in Eq. (31). Rather than minimizing $\Psi_{LH}^{at}$ with respect to the full set of positions $\hat{q}^c = (\hat{q}_i^c)_{1 \leq i \leq N_c}$, we will minimize this function over configurations that can be obtained from the smooth displacement field defined by the nodal displacements, $\vec{u} = (\vec{u}_i^c)_{1 \leq i \leq N_c}$. In this way, the number of degrees of freedom in the continuum region is reduced from $3N_c$ to $3n_{ nodes}$. To make this explicit, let us recast the Helmholtz free energy in Eq. (30) as a function of the nodal displacements,

$$\tilde{\Psi}_{LH}^{at}(q^a, \vec{u}^c, T) = \mathcal{V}(q^a, \hat{q}^c(\vec{u}^c)) + \frac{k_BT}{2} \ln \left[ \frac{h_0^2 \det \Phi_{c}^e(q^a, \hat{q}^c(\vec{u}^c))}{(2\pi k_BT)^3} \right]$$

where, as in Eq. (34), we have

$$\hat{q}_i^c = \hat{q}_i^c(\vec{u}^c) = \hat{Q}_i^c + \sum_{j=1}^{n_{nodes}} S_j(\hat{Q}) u_j^c \quad i = 1, \ldots, N_c$$

Later (see Eq. (43) below), we will chose a precise value for $\vec{u}^c$, namely that which minimizes the free energy, which is denoted $\vec{u}^c$.

To proceed, we write the potential energy term as a sum over the energies of the individual atoms

$$\mathcal{V}(q^a, \hat{q}^c) = \sum_{i=1}^{N_c} E_i^a(q^a, \hat{q}^c) + \sum_{j=1}^{N_i} E_j^a(q^a, \hat{q}^c)$$

where $E_i^a$ is the energy of atom $i$ in the atomistic region, and $E_j^a$ is the energy of atom $j$ in the continuum region. Both functions depend on $q^a$ and $\hat{q}^c$ since atoms in one region can have neighbors that lie in the other. We also define the atom energy functions in terms of the nodal displacements,

$$\tilde{E}_i^a(q^a, \vec{u}^c) \equiv E_i^a(q^a, \hat{q}_i^c, \vec{u}^c)$$

$$\tilde{E}_j^a(q^a, \vec{u}^c) \equiv E_j^a(q^a, \hat{q}_j^c, \vec{u}^c)$$

Next, let us define $\psi_j^a$ as the free energy of atom $j$ in the continuum region

$$\psi_j^a(q^a, \vec{u}^c, T) \equiv \tilde{E}_j^a(q^a, \vec{u}^c) + \frac{k_BT}{2} \ln \left[ \frac{h_0^2 \det \Phi_{c}^e(q^a, \hat{q}_j^c(\vec{u}^c))}{(2\pi k_BT)^3} \right]$$

We can now write Eq. (35) as

$$\tilde{\Psi}_{LH}^{at}(q^a, \vec{u}^c, T) = \sum_{i=1}^{N_c} \tilde{E}_i^a(q^a, \vec{u}^c) + \sum_{j=1}^{N_i} \psi_j^a(q^a, \vec{u}^c, T)$$

The free energy now depends on a small number of degrees of freedom. However, we still require an efficient method for computing $\tilde{\Psi}_{LH}^{at}$ and its gradient without having to visit every atom in the problem as implied by the sum in the second term of Eq. (39) We invoke the slow variation of the displacement field and make use of the Cauchy–Born approximation. We assume that the atomic neighborhood of each atom in the continuum region is uniform, and consequently its free energy contribution can be computed as if it were in an infinite crystal homogeneously strained by the deformation gradient $\mathbf{F}$ at its position. We use the finite element interpolation to compute the deformation gradient at a position $X$ in the continuum region

$$\mathbf{F}(X) = I + \sum_{j=1}^{n_{nodes}} u_j^c \otimes \nabla S_j^e(X)$$

where $I$ is the identity tensor, $\otimes$ denotes the tensor (outer) product, and $\nabla$ denotes the gradient with respect to $X$. Since we have opted to use linear shape functions, the deformation gradient is constant within each element. We therefore replace the sum in Eq. (39) over all atoms in the continuum region with a sum over the elements spanning this region with appropriate weighting

$$\sum_{i=1}^{N_i} \psi_i^a \approx \sum_{i=1}^{n_{elem}} \nu_i \psi_{CB}(F, T)$$

Here $n_{elem}$ is the number of elements that have at least one node in the continuum region, $F$, is the deformation gradient in element $e$, and $\psi_{CB}(F, T)$ is the “Cauchy–Born” free energy density, i.e., the free energy per atom in an infinite crystal subjected to a uniform deformation gradient $F$. The weighting factor $\nu_i$ is the number of atoms “associated” with element $e$. If all of the nodes of element $e$ are inside the continuum region, then $\nu_i = V_e/\Omega$, where $V_e$ is the volume of element $e$ and $\Omega$ is the crystal unit cell volume in the reference configuration. For elements crossing into the atomistic region, $\nu_i$ must be proportionally reduced to prevent double counting of atoms in the atomistic region (see Ref. [3] for details).

Now the Helmholtz free energy in Eq. (39) is simply the sum of element free-energies for the continuum region plus the energy of the atoms in the atomistic region. It can be written as

$$\tilde{\Psi}_{LH}^{at}(q^a, \vec{u}^c, T) = \sum_{i=1}^{N_c} E_i^a(q^a, \vec{u}^c) + \sum_{e=1}^{n_{elem}} \nu_e \psi_{CB}(F, T)$$

We note the similarity between this expression and the calculation of the potential energy at 0 K using the Static QC method [3]. The only difference is that the free energy density function $\psi_{CB}(F, T)$ now replaces the 0 K strain energy density function $W(F)$. Using this framework, the approximate effective potential in Eq. (31) is estimated by minimizing the free energy $\tilde{\Psi}_{LH}^{at}(q^a, \vec{u}^c, T)$ with respect to $\vec{u}^c$ subject to the appropriate continuum boundary conditions

$$\tilde{\Psi}^{at}(q^a, \vec{u}^c, T) = \min_{\vec{u}^c} \tilde{\Psi}_{LH}^{at}(q^a, \vec{u}^c, T)$$

The value of $\vec{u}^c$ that minimizes Eq. (43) is $\vec{u}^c$ which appears in Eq. (34). In the next section, we describe how Eq. (43) can be used in hot-QC simulations.

2.4 Hot-QC-Static: Atomic Dynamics Embedded in a Static Continuum. The approximate effective potential energy in Eq. (43) and the effective kinetic energy in Eq. (18) can be combined to give an approximation to the effective Hamiltonian, defined in Eq. (15).

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For a two-dimensional QC model, the volume of an element is equal to its area multiplied by the length of the periodic cell in the out-of-plane direction.
This function can be used to perform an equilibrium MD simulation of the atomistic region at a given temperature $T$, with the continuum region maintained at its free energy minimum. We refer to this approach as hot-QC-static, noting that only the continuum region is "static."

In practice, a hot-QC-static simulation proceeds by numerically integrating the equations of motion for the atoms in the atomistic region (see Sec. 3.3 for precise expressions),

$$m_i^a \ddot{q}_i^a = f_i^a, \quad i = 1, \ldots, N_a$$

(45)

with the temperature imposed using a suitable thermostat. In Eq. (45), $q_i^a$ is the acceleration of atom $i$ in the atomistic region, and $f_i^a$ is the time-dependent, temperature-dependent force acting on it, given by

$$f_i^a = -\frac{\partial \tilde{V}_{at}}{\partial q_i^a} + f_i^{\text{ext},at}$$

(46)

In this relation, $f_i^{\text{ext},at}$ is the external force acting on atom $i$ due to external fields and due to the thermostat used to maintain the temperature $T$ (see, e.g., Eq. (150) below).

The equilibrium MD simulation described above can be used to compute time average analogs to phase averages of the form

$$\langle A \rangle_T^{\text{approx}} \equiv \frac{1}{h^{3N_a} Z(T)} \int A(q^a(T) + w^a, p^a) \times \exp \left[ -\beta \tilde{H}_{at}(q^a(T) + w^a, p^a, T) \right] \times \chi^a(w^a) dw^a dp^a$$

(47)

with the approximate reduced partition function

$$\tilde{Z}(T) = \frac{1}{h^{3N_a} Z(T)} \int \exp \left[ -\beta \tilde{H}_{at}(q^a(T) + w^a, p^a, T) \right] \times \chi^a(w^a) dw^a dp^a$$

(48)

It is worth noting that in a typical MD simulation, it is not necessary to impose the restriction $\tilde{V}(w^a)$, which is designed to keep the atoms from moving too far from their mean positions in the original solid structure. This occurs naturally due to the short time scale (on the order of nanoseconds) accessible in current-day MD for realistic system sizes. At the relative low temperatures considered in hot-QC, the probability of a solid system escaping from its initial metastable state is very low. The mean positions $\bar{q}(T)$ then emerge from the MD simulation as outputs.

In view of Eq. (13), and since $\tilde{H}_{at}$ is an approximation of $\tilde{H}$ at the atomistic scale, the approximate phase averages computed from MD should satisfy

$$\langle A \rangle_T^{\text{approx}} (T) \approx \langle A \rangle_T(T)$$

(49)

where $A$ is a property of the system which depends only on the positions and momenta of the atoms in the atomistic region, and where $\langle A \rangle_T(T) = \mathcal{A}(T)$ is the phase average of Eq. (8) computed with the full system (at temperature $T$). Of course, the simplifications that were performed in the construction of the coarse-grained potential, $\tilde{V}_{at}$ will obviously limit the accuracy of the approximation in Eq. (49). The errors due to finite-element interpolations have been described in the context of the QC method at 0K and will persist here. In the present description, we have added the use of the quasi-harmonic approximation and ultimately its local variant, the local harmonic approximation. The quasi-harmonic assumption limits the accuracy of the calculation of properties such as the partition function and phase averages of $\tilde{A}(q^a, p^a)$ to second order in temperature as

$$\tilde{Z}(T) = Z(T) + O((k_B T)^2)$$

(50)

$$\langle A(q^a, p^a) \rangle_T^{\text{approx}} = \langle A(q^a, p^a) \rangle_T + O((k_B T)^2)$$

(51)

This is a consequence of Eq. (27). Several studies have shown that the quasi-harmonic approximation remains valid for temperatures up to half the melting temperature of the crystal (see for example Ref. [63]). Strictly speaking, the local harmonic model does not guarantee the same accuracy, but as noted earlier, it has been shown in numerical tests to provide accuracy comparable to that of the quasi-harmonic approximation over the same temperature range for various systems (see, e.g., Ref. [57]).

2.5 Hot-QC-Dynamic: Atomic and Continuum Dynamics. The hot-QC-static approach described in the previous section is efficient in the sense that it involves a limited number of degrees of freedom $q^a$ and $p^a$. However, at each time step, this approach requires the calculation of the force in Eq. (46), which involves the minimization of the free energy in the continuum region according to Eq. (43). While the QC formulation significantly reduces the number of degrees of freedom (from $3N_c$ to $3N_{\text{nodes}}$), this may still be computationally expensive. Another limitation of hot-QC-static is that since nodes in the continuum region always occupy positions that minimize its free energy, macroscopic dynamics is precluded in this region.

Building on the effective Hamiltonian of Eq. (44), we now demonstrate that it is possible to restore a form of dynamics in the continuum region while maintaining our initial objective. We will refer to the resulting formulation as hot-QC-dynamic. The idea is to introduce equations of motion for the macroscopic system, so that the system essentially samples configurations close to the one that minimizes the Helmholtz free energy. This modification has several advantages. First, there is no longer a need to perform a free energy minimization at each time step. Second, the atomistic and continuum region evolve simultaneously in time, reducing in part (although not entirely canceling) spurious wave reflection effects that may exist at the interface between the atomistic and the continuum regions [64]. The outcome of this coarse-graining procedure is the definition of a global Hamiltonian that allows us to use the same integration scheme in the entire system.

The method is as follows. Rather than calculating at every time step the displacement field $\bar{u}$ that minimizes the Helmholtz free energy $\tilde{\Psi}_{1H}^L(q^a, \bar{u}, T)$ in order to obtain the effective potential energy $\tilde{V}^L$ (see Eq. (43)), we let the entire system evolve in time based on $\tilde{\Psi}_{1H}^L$. This strategy leads to an effective finite-temperature QC Hamiltonian, $\tilde{H}_{QC}$, which depends on both the positions of atoms in the atomistic region and the displacement field in the continuum region. For definiteness, we use the “QC” subscript to refer to this final formulation. We discuss the derivation of $\tilde{H}_{QC}$ in the remainder of this section.

Before proceeding, we recall that in the derivation above, we first introduced a quasi-harmonic approximation to the effective potential energy in Sec. 2.2.1. Then to simplify the computations, we introduced a local harmonic approximation in Sec. 2.2.2. In the following, we take the same approach and therefore take a...
step back and assume that we have only performed the quasi-harmonic approximation. Our starting expression is thus Eq. (27), rather than Eq. (43).

Our first task is to introduce a kinetic energy for the continuum region. We use the following definition:

\[ K^c(\bar{u}^c) \equiv \frac{1}{2} \bar{u}^c \cdot M^c \bar{u}^c \]  

(52)

where \( M \) is the mass matrix. In order to unify this continuum approach with MD, we choose a diagonal matrix \( M^c \), hence

\[ K^c(\bar{u}^c) = \sum_{i=1}^{Nc} \frac{\|\bar{u}^c_i\|^2}{2M^c_i} \]  

(53)

where \( \bar{u}^c_i = M^c_i \bar{q}^c_i \) is the momentum of node \( i \) and \( M^c_i \) is its mass. Measures sampled in terms of the atomistic degrees of freedom, \( q^a \) and \( p^a \), do not depend on the choice of masses of the nodes in the coarse-grained region. However, the numerical efficiency of the approach can depend on how \( M^c_i \) are chosen. A particular choice that ensures that the coarse-grained system has the same total mass and the same kinetic free energy as the full system is given in Ref. [42]. Next, we turn to the definition of \( \mathcal{H}_{QC} \).

2.5.1 A “Naive” Choice for \( \mathcal{H}_{QC} \). A natural first guess for \( \mathcal{H}_{QC} \) would be to combine the kinetic energy of the atomistic and continuum regions with the effective free energy expression derived earlier. We refer to this as a “naive” choice and we show below that this definition loses the second-order accuracy in temperature of the hot-QC-static method. The naive definition is

\[ \mathcal{H}^{naive}_{QC}(q^a, \bar{u}^a, p^a, \bar{u}^c, T, I, \mathbf{F}) = \bar{\Psi}_{QC}^{naive}(q^a, \bar{u}^a, T) + K^c(\bar{u}^c) + K^a(q^a) \]  

(54)

where \( K^a \) and \( K^c \) are the respective kinetic energies in Eqs. (18) and (53) for the atomistic and the continuum regions, and \( \bar{\Psi}_{QC}^{naive}(q^a, \bar{u}^a, T) \) is the quasi-harmonic, free energy in Eq. (24) written as a function of the mesh variables (see Eq. (36))

\[ \bar{\Psi}_{QC}^{naive}(q^a, \bar{u}^a, T) = \mathcal{V}(q^a, \bar{u}^c) + \frac{k_B T}{2} \ln \left[ \frac{h_{hc}^{\mathcal{V}(q^a, \bar{u}^c), T}}{(2\pi k_B T)^{Nc}} \right] \]  

(55)

Our objective is to perform MD simulations with the effective Hamiltonian energy defined in Eq. (54) and to compute phase averages of the form

\[ \langle \mathcal{A}(q^a, p^a) \rangle_{Z_{QC}^{naive}} = \frac{1}{h_{hc}^{Z_{QC}^{naive}(T)}} \int \mathcal{A}(q^a + w^a, p^a) \exp \left[ -\beta \mathcal{H}^{naive}_{QC}(q^a + w^a, \bar{u}^c + \bar{w}^a, p^a, \bar{u}^c, T) \right] \times \chi^a(w^a) \chi^c(w^c) d\mathbf{w}^a d\mathbf{w}^c dp^a \]  

(56)

with

\[ Z_{QC}^{naive}(T) = \frac{1}{h_{hc}^{Z_{QC}^{naive}(T)}} \int \exp \left[ -\beta \mathcal{H}^{naive}_{QC}(q^a, \bar{u}^a, \bar{w}^a, p^a, \bar{u}^c, T) \right] \times \chi^a(w^a) \chi^c(w^c) d\mathbf{w}^a d\mathbf{w}^c dp^a \]  

(57)

Again, \( \bar{u}^c = \bar{u}^c(q^a, T) \) is a function of \( q^a = \bar{q}^a + w^a \), which will be defined later by minimization (see Eq. (62)). In Eqs. (56) and (57), \( \chi^a(w^a) \) is a characteristic function limiting the movement of the nodes. For example, a possible definition is to have \( \chi^a(w^a) = 1 \) for all perturbations \( w^a \) that do not cause elements to turn inside out (i.e., that do not cause a change in the sign of the volume of the element), and zero otherwise.

Let us now estimate the accuracy of \( \langle \mathcal{A}(q^a, p^a) \rangle_{Z_{QC}^{naive}} \). Following the procedure outlined in Sec. 2.1, Eqs. (56) and (57) can be rewritten as

\[ \langle \mathcal{A}(q^a, p^a) \rangle_{Z_{QC}^{naive}} = \frac{1}{h_{hc}^{Z_{QC}^{naive}(T)}} \int \exp \left[ -\beta \mathcal{H}^{naive}_{QC}(q^a, \bar{u}^c \bar{w}^a, \bar{u}^c, T) \right] \times \chi^a(w^a) d\mathbf{w}^a dp^a \]  

(58)

with

\[ Z_{QC}^{naive}(T) = \frac{1}{h_{hc}^{Z_{QC}^{naive}(T)}} \int \exp \left[ -\beta \mathcal{H}^{naive}_{QC}(q^a, \bar{u}^c \bar{w}^a, \bar{u}^c, T) \right] \times \chi^a(w^a) d\mathbf{w}^a dp^a \]  

(59)

The effective Hamiltonian for the atomistic region appearing in these relations is

\[ \mathcal{H}^{naive}_{QC}(q^a, \bar{w}^a, T) = \mathcal{V}_{QC}(q^a, \bar{u}^c \bar{w}^a) \]  

(60)

In turn, the kinetic energy is given by

\[ K^{naive}_{QC}(p^a, T) = -k_B T \ln \left( \frac{1}{h_{hc}^{\mathcal{V}(q^a, \bar{u}^c \bar{w}^a), T}} \right) \]  

(61)

In the low temperature regime, we can apply a quasi-harmonic approximation to Eq. (60), as outlined in Sec. 2.2, to obtain

\[ \bar{\Psi}_{QC}^{naive}(q^a, \bar{u}^a, T) = \min_{\bar{u}^a} \left\{ \bar{\Psi}_{QC}^{naive}(q^a, \bar{u}^a, T) \right\} + \frac{k_B T}{2} \ln \left( \frac{h_{hc}^{\mathcal{V}_{QC}(q^a, \bar{u}^c \bar{w}^a), T}}{(2\pi k_B T)^{Nc}} \right) \]  

(62)

where the quasi-harmonic stiffness matrix of the continuum region, \( D_{\mathcal{V}_{QC}} \), is defined by

\[ D_{\mathcal{V}_{QC}} = \left[ \frac{\partial^2 \bar{\Psi}_{QC}^{naive}}{\partial \bar{u}^c \partial \bar{u}^c} \right]_{\bar{u}^c} \]  

(63)

The value of \( \bar{u}^c \) that minimizes Eq. (62) is denoted \( \bar{u}^c \).

Finally, we recall from Eqs. (26) and (27) that the exact effective potential satisfies

\[ \mathcal{V}^{eff}(q^a, T) = \min_{\bar{u}^c} \bar{\Psi}_{QC}^{naive}(q^a, \bar{u}^c) + O(k_B T) \]  

(64)
Comparing this relation with Eq. (62), we see that
\[ \
\gamma_{\text{naive}}^{Q\text{C}}(q^a, T) = \gamma^a(q^a, T) + O(k_b T) \]  

(65)

Thus, we have lost the second-order accuracy in temperature when we use \( \mathcal{H}^{\text{naive}}_{Q\text{C}} \) to perform MD.

Physically, we can interpret this loss of accuracy in the following way. The coupling between the atomistic and continuum regions introduced by \( \mathcal{H}^{\text{naive}}_{Q\text{C}} \) causes the nodes in the continuum region to vibrate, leading to an additional, unphysical contribution to the entropy of the system that we refer to as mesh entropy, \( S_{\text{mesh}} \). This ultimately modifies both the kinetic and potential parts of the free energy of the system leading to spurious effects in its equilibrium properties. As an illustration, the average kinetic energy carried by each node is
\[ 
\left\langle \frac{1}{2M_I^2} \right\rangle_Q^{\text{naive}} = \frac{3}{2} k_b T, \quad I = 1, \ldots, n^c \]  

(66)

whereas the effective Hamiltonian \( \mathcal{H}^a \) is built on the premise that the nodes do not carry any kinetic energy. Another example is seen in Fig. 11 where the thermal expansion of a perfect single crystal is calculated using the effective Hamiltonian \( \mathcal{H}^a \), the naïve Hamiltonian \( \mathcal{H}^{\text{naive}}_{Q\text{C}} \), and the final finite-temperature Hamiltonian \( \mathcal{H}_{Q\text{C}} \) described below. This figure shows that \( \mathcal{H}^{\text{naive}}_{Q\text{C}} \) does not yield satisfactory results. Similar observations have been made by Marion et al. [65], who studied another finite temperature extension of the QC method.

2.5.2 An Accurate Choice for \( \mathcal{H}_{Q\text{C}} \). We now come to the strategy we propose for maintaining both the dynamics in the continuum region and accurate equilibrium properties. It consists of correcting the naïve \( \mathcal{H}^a \) by subtracting off a second-order term for the spurious mesh entropy from the total free energy \( \mathcal{V}_{Q\text{C}} \) of the system. Formally, we write
\[ 
\mathcal{H}_{Q\text{C}}(q^a, u^c, p^a, \Pi^a, T) = \mathcal{H}^{\text{naive}}_{Q\text{C}}(q^a, u^c, p^a, \Pi^a, T) + \mathcal{V}_{\text{mesh}}(q^a, u^c, T) 
\]  

(67)

where \( \mathcal{V}_{\text{mesh}} = TS_{\text{mesh}} \) is the mesh free energy associated with the mesh entropy. We will determine \( \mathcal{V}_{\text{mesh}} \) from the condition
\[ 
\mathcal{H}^a_{Q\text{C}}(q^a, p^a, T) = \mathcal{H}^a(q^a, p^a, T) + O\left((k_b T)^2\right) 
\]  

(68)

where \( \mathcal{H}^a \) is defined in Eq. (12) and
\[ 
\mathcal{H}^a_{Q\text{C}}(q^a, p^a, T) = -k_b T \ln \frac{1}{h_{p_{\text{nodes}}}} \times \left[ \exp[-\beta \mathcal{H}_{Q\text{C}}(q^a, u^c, p^a, \Pi^a, T)] \times \Pi^a \right] 
\]  

(69)

As previously, in the above equation \( \Pi^a = \Pi^a(q^a, T) \) minimizes the free energy. To facilitate the calculation of \( \mathcal{H}^{\text{naive}}_{Q\text{C}} \), we separate \( \mathcal{H}_{Q\text{C}} \) into its potential energy and kinetic energy parts,
\[ 
\mathcal{H}_{Q\text{C}}(q^a, u^c, p^a, \Pi^a, T) = \mathcal{V}_{Q\text{C}}(q^a, u^c, T) + \mathcal{K}_{Q\text{C}}(p^a, \Pi^a, T) 
\]  

(70)

where, using Eqs. (67) and (54),
\[ 
\mathcal{V}_{Q\text{C}}(q^a, u^c, T) = \mathcal{V}_{Q\text{C}}(q^a, u^c, T) - \mathcal{V}_{\text{mesh}}(q^a, u^c, T) 
\]  

(71)

\[ 
\mathcal{K}_{Q\text{C}}(p^a, \Pi^a, T) = \mathcal{K}^a(p^a, T) + \mathcal{K}^c(\Pi^a) - \mathcal{V}_{\text{mesh}}(T) 
\]  

(72)

In Eqs. (71) and (72), \( \mathcal{V}_{Q\text{C}} \) and \( \mathcal{K}_{Q\text{C}} \) are the potential and kinetic parts of the mesh free energy, such that
\[ 
\mathcal{V}_{Q\text{C}} = \mathcal{V}_{\text{mesh}} + \mathcal{V}_q 
\]  

(73)

Given the separation in Eq. (70), the condition in Eq. (68) divides into two conditions
\[ 
\mathcal{V}_{Q\text{C}}(q^a, T) = \mathcal{V}^a(q^a, T) + O\left((k_b T)^2\right) 
\]  

(74)

\[ 
\mathcal{K}_{Q\text{C}}(p^a, T) = \mathcal{K}^a(p^a, T) + O\left((k_b T)^2\right) 
\]  

(75)

where \( \mathcal{V}_{Q\text{C}} \) and \( \mathcal{K}_{Q\text{C}} \) are obtained from \( \mathcal{V}_{Q\text{C}} \) and \( \mathcal{K}_{Q\text{C}} \) in analogous fashion to the calculation of \( \mathcal{V}^a \) and \( \mathcal{K}^a \) in Eqs. (16) and (17).

The following choice for \( \mathcal{V}_{\text{mesh}} \) satisfies Eq. (73):
\[ 
\mathcal{V}_{\text{mesh}}(q^a, u^c, T) = \frac{k_b T}{2} \ln \left( \frac{\det D_0^q(q^a, u^c)}{\det D_0^q(\beta\gamma_{\text{naive}}^{Q\text{C}})} \right) 
\]  

(76)

Note that \( D_0^q \) is easier to compute than \( D_{Q\text{C}}^q \) appearing in Eq. (62), since we only need second derivatives of the potential energy \( \gamma \) (not higher-order ones). To show that \( \mathcal{V}_{\text{mesh}} \) defined above satisfies Eq. (73), it is necessary to show that
\[ 
\min_{u^c} \left\{ -k_b T \ln \frac{1}{h_{p_{\text{nodes}}}} \left[ \exp[-\beta \mathcal{V}_{Q\text{C}}(q^a, u^c + w^c, T)] X^c(w^c)dw^c \right] 
\]  

\[ 
\mathcal{V}^a(q^a, T) + O\left((k_b T)^2\right) 
\]  

(77)

This can be done by expanding \( \mathcal{V}_{Q\text{C}}(q^a, u^c, T) \) around \( u^c \). The contribution coming from the second derivative of \( \mathcal{V}_{Q\text{C}} \) with respect to \( u^c \) cancels with \( \mathcal{V}_{\text{mesh}} \). The only contribution left (up to second order corrections) is hence \( \mathcal{V}_{Q\text{C}}(q^a, u^c, T) \). In view of Eq. (64), we then obtain the approximation in Eq. (77).

The following choice for \( \mathcal{V}_{\text{mesh}} \) satisfies Eq. (74):
\[ 
\mathcal{V}_{\text{mesh}}(T) = -3k_b T \ln \frac{\sum_{i=1}^{\nu^c} \ln \left( \frac{h_{p_{\text{nodes}}}}{h_p} \right)}{2} 
\]  

(78)

Actually, with this choice, \( \mathcal{K}_{Q\text{C}}(p^a, T) = \mathcal{K}^a(p^a, T) \). This is easy to see by analytically integrating the left-hand side of the following condition (see Eq. (74)):
\[ 
-k_b T \ln \frac{1}{h_{p_{\text{nodes}}}} \left[ \exp[\beta \mathcal{K}_{Q\text{C}}(p^a, \Pi^a, T)] \right] \frac{\Pi^a}{\Pi^a} 
\]  

(79)

where \( \mathcal{K}^a(p^a, T) \) is the exact coarse-grained kinetic energy in Eq. (18).

We now have a complete formulation. The potential energy and kinetic energy parts of the hot-QC Hamiltonian with the definition of the mesh free energy given above are
\[ 
\mathcal{V}_{Q\text{C}}(q^a, u^c, T) = \mathcal{V}_{Q\text{C}}(q^a, u^c, T) - \mathcal{V}_{\text{mesh}}(q^a, u^c, T) 
\]  

(80)

\[ 
\mathcal{K}_{Q\text{C}}(p^a, \Pi^a, T) = \mathcal{K}^a(p^a, T) + \mathcal{K}^c(\Pi^a) - \mathcal{V}_{\text{mesh}}(T) 
\]  

(81)

With these definitions, \( \mathcal{H}_{Q\text{C}} = \mathcal{V}_{Q\text{C}} + \mathcal{K}_{Q\text{C}} \) satisfies the condition in Eq. (68). As a consequence, canonical averages of phase
functions \( A(q^d, p^d) \) can be computed as canonical averages with respect to \( \mathcal{H}_{\text{QC}} \) with far less computational expense than full MD simulations, and with second order accuracy in temperature. We therefore have a relation similar to Eq. (51)

\[
(A(q^d, p^d)_{iz})_{\text{QC}}(T) = (A(q^d, p^d)_{iz}(T) + O\left(k_B T^2\right)) \tag{82}
\]

where

\[
(A(q^d, p^d)_{iz})_{\text{QC}} \equiv \frac{1}{h_{\text{QC}}^{\text{QC}}(T)} \sum \sum A(q^d, p^d) \times \exp[-\beta \mathcal{H}_{\text{QC}}(q^d, p^d, \mathbf{u}^d, \mathbf{w}^d, \mathbf{p}^d, \mathbf{I}^F, T)] \times \chi^d(w^d) X^c(w^d) dw^d dp^d d\mathbf{I}^F \tag{83}
\]

and

\[
Z_{\text{QC}}(T) = \frac{1}{h_{\text{QC}}^{\text{QC}}(T)} \sum \sum \exp[-\beta \mathcal{H}_{\text{QC}}(q^d, p^d, \mathbf{u}^d, \mathbf{w}^d, \mathbf{p}^d, \mathbf{I}^F, T)] \times \chi^d(w^d) X^c(w^d) dw^d dp^d d\mathbf{I}^F \tag{84}
\]

Finally, we discuss the practicality of the definition of \( \mathcal{V}_{\text{QC}} \) in Eq. (80). This expression includes the quasi-harmonic approximation to the free energy, \( \mathcal{V}_{\text{QC}} \). However, as discussed at the beginning of Sec. 2.2.2, calculation of this expression is impractical since it involves the full stiffness matrix \( \Phi \) (see Eq. (24)). As there, we thus resort to a local harmonic approximation together with the Cauchy–Born approximation, and use the local approximation for \( \mathcal{V}_{\text{QC}} \) in Eq. (42), which can be computed in practice. In addition, it is also convenient to apply a local harmonic approximation to the stiffness matrix \( D_\delta \) defined by Eq. (76)

\[
(D_\delta^{\text{LH}}(q^d, u^d))_{IJ} = \begin{cases} [D_\delta]_{IJ}(q^d, u^d) & \text{if } I = J \\ 0 & \text{otherwise} \end{cases} \tag{85}
\]

Hence, in practice, we will use

\[
\mathcal{V}_{\text{QC}}(q^d, u^d, T) = \mathcal{V}_{\text{LH}}(q^d, u^d, T) - k_B T \ln \left[ \frac{\det(D_\delta^{\text{LH}}(q^d, u^d))}{(2\pi k_B T)^n} \right] \tag{86}
\]

where \( \mathcal{V}_{\text{LH}} \) is the free energy in Eq. (42). Note that since \( D_\delta \) is a sparse \( n_{\text{nodes}} \times n_{\text{nodes}} \) matrix, it would also not be difficult to compute its determinant exactly.

3 Practical Implementation

In Secs. 2.4 and 2.5, we derived expressions for the effective Hamiltonian for the hot-QC-static (\( \mathcal{H}_{\text{QC}} \) in Eq. (44)) and hot-QC-dynamic (\( \mathcal{H}_{\text{QC}} \) in Eq. (70)) formulations. We now discuss some of the practical issues associated with these methods including explicit expressions for an EAM potential and details of the thermosets used to control temperature.

3.1 Calculation of Continuum-Region Properties. In this section, we present the formulae used in the practical implementation of the hot-QC method. We focus only on the continuum region using the Cauchy–Born approximation since the energy and forces in the atomistic region are computed in the same way as in a conventional atomistic simulation. We recall that the Cauchy–Born framework deals with an infinite periodic lattice so that the potential energy and the free energy of a crystal can be decomposed per atom.

3.1.1 Preliminary Notation. For an element \( e \) with \( N_{\text{en}} \) nodes (e.g., \( N_{\text{en}} = 3 \) for linear triangular elements in 2D), the nodal displacements are denoted by \( \mathbf{u}_i = [u_{i1}, u_{i2}, u_{i3}]^T (l = 1, \ldots, N_{\text{en}}) \), where \( \mathbf{u}_i \) is the component along the \( x_i \) direction (\( i = 1, 2, 3 \)) of node \( l \). We use a sans serif font to denote finite element matrices. Note that in the above, \( l \) refers to the local node numbering of a single element. When we wish to refer to global node numbers, we will use an upper case roman index, e.g., \( \mathbf{u}_l \) where \( l = 1, \ldots, n_{\text{nodes}} \). All the quantities in this section refer to the continuum region, but we drop the usual "c" superscript for simplicity.

The deformation gradient \( \mathbf{F} \) of the element is given by

\[
\mathbf{F} = \mathbf{I} + \mathbf{UB}^T \tag{87}
\]

where \( \mathbf{I} \) is the identity matrix

\[
\mathbf{U} = \begin{bmatrix} u_{11} & u_{12} \ldots & u_{1N_{\text{en}}} \\ u_{21} & \ldots & u_{2N_{\text{en}}} \\ u_{31} & \ldots & u_{3N_{\text{en}}} \end{bmatrix}, \quad \mathbf{B} = \begin{bmatrix} \frac{\partial S_1}{\partial x_1} & \frac{\partial S_{N_{\text{en}}}}{\partial x_1} \\ \frac{\partial S_1}{\partial x_2} & \frac{\partial S_{N_{\text{en}}}}{\partial x_2} \\ \frac{\partial S_1}{\partial x_3} & \frac{\partial S_{N_{\text{en}}}}{\partial x_3} \end{bmatrix} \tag{89}
\]

where \( S_j \) is the finite element shape function associated with node \( j \). We use only linear shape functions so that \( \mathbf{B} \) is a constant matrix for each element.

The basic procedure for computing continuum properties is (a) to apply \( \mathbf{F} \) to a cluster comprised of an atom and its environment in an infinite crystal, (b) to compute the properties per atom experienced by this cluster, and (c) to obtain the element property by multiplying the cluster property per atom by the number of atoms associated with the element (see, e.g., Eq. (41)). We assume that the cluster includes only identical atoms and the center atom is located at the origin of the coordinate system. Then, by symmetry, we need to consider only the atoms whose distances from the center atom are within the cutoff radius \( r_{\text{cut}} \) in the deformed configuration. The reference and deformed positions of atom \( x \) in the cluster are denoted by \( \mathbf{R}_x = [r_{1x} r_{2x} r_{3x}]^T \) and \( \mathbf{r}_x = \mathbf{F} \mathbf{R}_x = [r_{1x} r_{2x} r_{3x}]^T \).

The corresponding distances from the center atom are given by

\[
R_x = ||\mathbf{R}_x|| = \sqrt{r_{1x}^2 + r_{2x}^2 + r_{3x}^2} \tag{90}
\]

\[
r_x = ||\mathbf{r}_x|| = \sqrt{r_{1x}^2 + r_{2x}^2 + r_{3x}^2} \tag{91}
\]

In the following sections we will present the formulae for an EAM potential [47].

3.1.2 Zero-Temperature Static QC. For completeness we begin with the original zero-temperature static QC method.

Energy. The energy of an element \( e \), which is a function of its deformation gradient \( \mathbf{F} \), is defined by

\[
E_{\text{static}}^e = \nu_e \mathcal{E}_{\text{static}}(\mathbf{F}) \tag{92}
\]

where \( \nu_e \) is the number of atoms associated with the element and \( \mathcal{E}_{\text{static}}(\mathbf{F}) \) is the energy per atom of the cluster subject to the deformation gradient \( \mathbf{F} \). For an EAM potential, we have

\[
\mathcal{E}_{\text{static}} = \frac{1}{3} \sum_{r_{x} < R_{\text{cut}}} \mathcal{E}(r_{x}) + U(\tilde{\rho}) \tag{93}
\]

\[
\tilde{\rho} = \sum_{r_{x} < R_{\text{cut}}} \rho(r_{x}) \tag{94}
\]
where $\phi$, $U$, and $\rho$ are the pair interaction energy, the embedding energy, and the electron density function, respectively.

**Force.** We define the nodal force matrix for element $e$ as

$$f_e = \begin{bmatrix} f_{1e} & f_{2e} & \cdots & f_{Ne} \end{bmatrix}$$

where

$$f_{ie} = -\frac{\partial E_e}{\partial u_i} = -v_e \frac{\partial E_{\text{static}}}{\partial u_i}$$

(96)

Each column of the nodal force matrix represents the force contribution to the corresponding node from $E_{\text{static}}$ (the energy of element $e$). The total force on a node is obtained by a finite element assembly process (associating the local node index to the global node index) where the contributions of all elements touching the node are summed.

For an EAM potential, we can show that

$$\frac{\partial E_{\text{static}}}{\partial u_i} = [J_0s]_{ij} f_{ej}$$

(97)

where

$$J_0 = \begin{bmatrix} 1 & \frac{\partial U}{\partial \rho} \end{bmatrix}$$

(98)

and

$$[J_{\text{pair}}]_{ij} = \sum_{r_{ij} < \text{cut}} \frac{\partial \phi}{\partial r_{ij}}$$

(99)

$$[J_{\text{embed}}]_{ij} = \sum_{r_{ij} < \text{cut}} \frac{\partial \rho}{\partial r_{ij}}$$

(100)

$$B_0 = F^{-1} B$$

(101)

Note that $J_0s$ is the Kirchhoff stress $\tau_{\text{static}}$, where $s$ is the volume per atom in the reference configuration. Thus, we have

$$f_e = -v_e \Omega_s \tau_{\text{static}} B_0$$

(102)

### 3.1.3 Hot-QC Without Mesh Entropy Correction

**Energy.** In hot-QC we include the free energy contribution given by

$$\epsilon_{\text{hot}}(F,T) = \begin{cases} \frac{k_B T}{4} \ln[(\det \Phi)^2 + \delta^2] & \text{for } \det \Phi > 0 \\ \frac{k_B T}{4} \ln[\delta^2] & \text{otherwise} \end{cases}$$

(103)

where

$$\Phi = M_{\text{pair}} + 2 \frac{dU}{d\rho} M_{\text{embed}} + \frac{d^2U}{d\rho^2} M_{2\text{embed}}$$

(104)

$$+ \left( \epsilon_{\text{pair}} + 2 \frac{dU}{d\rho} \epsilon_{\text{embed}} \right) I$$

(105)

**Force.** We have a nonzero force vector from the free energy term only when $\det \Phi > 0$, which is given by

$$f_{e,\text{hot}} = -v_e \Omega_s \tau_{\text{hot}} B_0$$

(115)

where

$$\Omega_s = \frac{k_B T}{2} \left[ \frac{(\det \Phi)^2}{(\det \Phi)^2 + \delta^2} \right] + \frac{2}{\delta^2} \left( \text{pair} + 2 \frac{dU}{d\rho} \text{embed} \right) \Phi^{-1}$$

(116)

$$+ \frac{2dU}{d\rho} M_{2\text{embed}} + \frac{d^2U}{d\rho^2} M_{2\text{embed}}$$

(117)

$$K = \frac{d^2U}{d\rho^2} M_{2\text{embed}} + \epsilon_{\text{pair}} + 2 \frac{dU}{d\rho} \epsilon_{\text{embed}}$$

(118)

$$[N_{\text{pair}}]_{ijkl} = \sum_{r_{ij} < \text{cut}} \left[ \frac{d^2\phi}{d\rho^2} \frac{1}{r_{ij}^3} - 3 \frac{d^2\phi}{d\rho^2} \frac{1}{r_{ij}^2} \frac{d\phi}{d\rho} \right] r_{i k} r_{j l}$$

(120)

$$[N_{1\text{embed}}]_{ijkl} = \sum_{r_{ij} < \text{cut}} \left[ \frac{d^2\rho}{d\rho^2} \frac{1}{r_{ij}^3} - 3 \frac{d^2\rho}{d\rho^2} \frac{1}{r_{ij}^2} \frac{d\rho}{d\rho} \right] r_{i k} r_{j l}$$

(121)

$$[N_{2\text{embed}}]_{ijkl} = \sum_{r_{ij} < \text{cut}} \left[ \frac{d\rho}{d\rho} \frac{1}{r_{ij}^3} \frac{d^2\rho}{d\rho^2} - \frac{d\rho}{d\rho} \frac{d\rho}{d\rho} \right] r_{i k} r_{j l}$$

(122)
\[ P_2 = \frac{d^2 U}{dp^2} M_1^{\text{embed}} + \frac{d^2 U}{dp^2} M_2^{\text{embed}} \]  

(123)

As such the total nodal force matrix \( \mathbf{f}_e \) is the sum of \( f_{\text{static}}^e \) and \( f_{\text{hot}}^e \) given in Eqs. (95) and (115).

Note that computing the energy and the force of the hot-QC method is more demanding than that of the conventional simulations because it requires the second and third derivatives of the interatomic potential.

### 3.1.4 Hot-QC With Mesh Entropy Correction

**Energy.** The mesh entropy correction using the local harmonic approximation is given by

\[ E_{\text{mesh}} = -\psi_{j}^{\text{mesh}} = -\sum_{j} \psi_{j}^{\text{mesh}} \]  

(124)

where \( I \) runs over the nodes in the continuum region (\( I = 1, \ldots, n_{\text{nodes}} \)). \( \psi_{j}^{\text{mesh}} \) is given by

\[
\psi_{j}^{\text{mesh}} = \begin{cases} 
\frac{k_B T}{4} \ln[(\det \mathbf{D}_I)^2 + \delta^2] & \text{for } \det \mathbf{D}_I > 0 \\
\frac{k_B T}{4} \ln[\delta^2] & \text{otherwise}
\end{cases}
\]  

(125)

where

\[ [\mathbf{D}_I]_{ij} = \frac{\partial^2 E_{\text{static}}}{\partial u_{ij} \partial u_{ij}} \]  

(126)

\[ E_{\text{static}} = \sum_{e} E_{e,\text{static}} \]  

(127)

Here \( \mathbf{D}_I \) is a \( 3 \times 3 \) submatrix of \( \mathbf{D}_{1,\text{hot}} \) and \( e \) runs over all elements in the continuum region. Note that \( \delta \) appearing in Eq. (125) serves the same purpose as that in Eq. (103), but may be numerically different. A similar procedure to that outlined in footnote 13 is used to choose the value.

Since only the elements touching node \( I \) can contribute to \( \mathbf{D}_I \), we have the following relation:

\[ [\mathbf{D}_I]_{ij} = \sum_{\text{touching node}} [\mathbf{d}_I]_{ij} \]  

(128)

where

\[ [\mathbf{d}_I]_{ij} = \frac{\partial^2 E_{\text{static}}}{\partial u_{ij} \partial u_{ij}} \]  

(129)

We can show that

\[ [\mathbf{d}_I]_{ij} = \nu_e \left( \delta_{ij} [\mathbf{B}_I]_{i\text{local}}+ [\mathbf{A}_I]_{i\text{local}} + \frac{d^2 U}{dp^2} [B_0]_{i\text{local}}[B_0]_{j\text{local}} \right) \]  

(130)

where

\[ [\mathbf{A}_I]_{i\text{local}} = \sum_{k} \sum_{l} [\mathbf{A}_{ijkl}]_{i\text{local}} [\mathbf{B}_0]_{i\text{local}} [\mathbf{B}_0]_{j\text{local}} \]  

(131)

\[ \mathbf{B}_I = \mathbf{B}_I^{\text{embed}} \]  

(132)

\[ \mathbf{A} = \frac{1}{2} \mathbf{N}_2^{\text{pair}} + \frac{d \mathbf{F}}{dp} \mathbf{N}_3^{\text{embed}} \]  

(133)

\[ [\mathbf{N}_2^{\text{pair}}]_{ijkl} = \sum_{r<s < i} \frac{d^2 \phi}{dr^2} \frac{1}{r_a^2} \frac{d \phi}{dr} r_{as} r_{ia} r_{ia} \]  

(134)

\[ [\mathbf{N}_3^{\text{embed}}]_{ijkl} = \sum_{r<s < i} \frac{d^2 \phi}{dr^2} \frac{1}{r_a^2} \frac{d \phi}{dr} r_{as} r_{ia} r_{ia} \]  

(135)

and \( I_{\text{local}}(\in \{1, \ldots, N_{\text{local}}\}) \) is the local node index corresponding to the global node index \( I \).

The total energy of the continuum region is thus given by

\[ E = E_{\text{static}} + E_{\text{hot}} + E_{\text{mesh}} \]  

(136)

where

\[ E_{\text{hot}} = \sum_{e} E_{e,\text{hot}} = \sum_{e} \nu_e \delta_{I}^{\text{hot}} \]  

(137)

and \( \delta_{I}^{\text{hot}} \) is given in Eq. (103).

**Force.** The force vector contributions from \( -\psi_{j}^{\text{mesh}} \) can be obtained by taking the derivatives with respect to \( u_{ij} \), where \( J \) runs over all the nodes belonging to the elements touching node \( I \). For \( \det \mathbf{D}_I > 0 \), we have a nonzero force given by

\[
(\psi_{j}^{\text{mesh}})_{ij} = -\frac{\partial(\psi_{j}^{\text{mesh}})}{\partial u_{ij}} = \frac{k_B T}{2} \left( \frac{(\det \mathbf{D}_I)^2}{(\det \mathbf{D}_I)^2 + \delta^2} \right)
\]  

(138)

and

\[ \frac{\partial \mathbf{D}_I}{\partial u_{ij}} = \sum_{\text{touching node}} \frac{\partial \mathbf{d}_I}{\partial u_{ij}} \]  

(139)

Thus to calculate the force vector, we require the derivatives of \( [\mathbf{d}_I]_{ij} \) with respect to the nodal displacement \( u_{ij} \)

\[
\frac{\partial [\mathbf{d}_I]_{ij}}{\partial u_{ij}} = \nu_e \left( \delta_{ij} [\mathbf{B}_I]_{i\text{local}} + [\mathbf{A}_I]_{i\text{local}} + \frac{d^2 U}{dp^2} [B_0]_{i\text{local}}[B_0]_{j\text{local}} \right)
\]  

(140)

where \( \delta \) is the Kronecker \( \Delta \) and

\[ \mathbf{C} = \frac{1}{2} \mathbf{L}^{\text{pair}} + \frac{d U}{dp} \mathbf{L}^{\text{embed}} \]  

(141)

\[ [\mathbf{L}^{\text{pair}}]_{ijklm} = \sum_{r<s < i} \frac{d^3 \phi}{dr^3} \frac{1}{r_a^3} \frac{d \phi}{dr} r_{as} r_{ia} r_{ia} \]  

(142)

\[ [\mathbf{L}^{\text{embed}}]_{ijklm} = \sum_{r<s < i} \frac{d^3 \phi}{dr^3} \frac{1}{r_a^3} \frac{d \phi}{dr} r_{as} r_{ia} r_{ia} \]  

(143)

\[ [\mathbf{S}]_{i\text{local} j\text{local}} = \sum_{k} [\mathbf{N}_3^{\text{embed}}]_{ijkl} [\mathbf{B}_0]_{i\text{local}} [\mathbf{B}_0]_{j\text{local}} \]  

(144)
\[
[A]_{\text{local}} = \sum_j \sum_k \sum_i [A]_{ijkl} [B]_{jk} [B]_{kl} [B]_{l} \tag{146}
\]

The total force on repton \( I \) then follows by the assembly over elements \( \varepsilon \) of the nodal force matrices \( f_j \) (which are the sum of \( f_{\text{static}} \) and \( f_{\text{cubic}} \) defined in Eqs. (95) and (115)) together with the sum over \( f_{\text{cubic}}^{\text{int}} \) defined in Eq. (138) over all nodes belonging to elements in contact with repton \( I \).

### 3.2 Interatomic Potentials

The expressions given in the previous section show that care must be taken when selecting an interatomic potential to be used with the hot-QC formulation. In contrast to a fully-atomistic calculation, the behavior of the continuum region in hot-QC is governed by thermodynamic variables such as the free energy and its derivatives. In practice, these quantities are calculated using a local harmonic approximation which involves the first, second, and third derivatives of the interatomic potential. All these quantities must therefore be well-behaved in order to prevent numerical difficulties.

The above condition is not satisfied by all interatomic potentials. Indeed, many potentials are constructed by interpolation from piecewise polynomials (splines). For example, consider the cubic spline technique. This technique uses the discretized values of a function to compute a discretized set of a first, second, and third derivatives assuming the actual function in a piecewise cubic spline. From these values, it provides consistent expressions of the first, second, and third derivatives of the functions. There is, however, no guarantee that these values correspond to the actual function unless the discretization step tends to zero. In addition, in the case of a cubic spline, the third derivative is piecewise constant and there is no guarantee that there are no discontinuities that may result in numerical instabilities—even in the case where the third derivative of the exact function is continuous. In mathematical terms, we say that the interpolated function is only \( C^2 \) continuous (i.e., the function itself is continuous, differentiable, and its first and second derivatives are continuous). The situation can be mitigated to some extent by reducing the grid spacing used in the interpolation. However, ideally one should work with interatomic potentials of class \( C^3 \). This can be achieved for example by using a quartic spline interpolation. The EAM potentials used in the numerical examples of Sec. 4 were modified to use cubic splines.

### 3.3 Thermostats

The hot-QC formulation is designed to reproduce equilibrium phase averages under conditions of constant uniform temperature. For hot-QC-dynamic, this means evaluating phase averages of the form given in Eq. (83). We assume that the restriction imposed by the constraints \( \sum_{\varepsilon} \mathcal{P}_\varepsilon = 0 \). For hot-QC dynamics, which is very challenging to assess, symplectic integration, it has limitations as well. First, as mentioned above, there is no drift in the energy, which is in contrast to explicit or implicit Euler algorithms for which the energy normally diverges or vanishes. On the other hand, if the dynamics is not Hamiltonian but still preserves some quantity (which is the case for Nosé–Hoover dynamics), then designing an algorithm which does not show any drift in this quantity is a challenging task (see Refs. [69] and [70] for some studies along this line).

Although the Nosé–Pöncärè method enjoys the advantage of symplectic integration, it has limitations as well. First, as mentioned above, Eq. (149) is based on an ergodicity assumption of the Nosé–Pöncärè dynamics, which is very challenging to assess, both from the theoretical and numerical viewpoints (see Refs. [71,72] for some theoretical studies in the case of the Nosé–Hoover thermostat, which is simpler to analyze, and Ref. [73] for some careful numerical studies of the Nosé–Pöncärè thermostat). To our knowledge, there is no clear link between ergodicity and the dynamics being Hamiltonian. In addition, even if the exact dynamics is ergodic, designing an algorithm such that this ergodicity property still holds on the discrete trajectory (possibly for a modified measure \( \mu_\text{NP}(q,p) \), which is an approximation of the Boltzmann measure \( \mu_\text{NP}(q,p) \), is difficult. Second, the selection of the artificial mass, \( M \), can be tricky. This variable scales the coupling

\[\mathcal{A}(q,p) \text{ with } \mathcal{H}_{\text{NP}}(q,p,T) \] (where the argument \( T \) is expected to coincide with the thermostat set temperature).

The idea of the Nosé–Pöncärè method [67] is to couple the physical variables with a thermostat such that, at equilibrium, the physical variables are distributed according to the Boltzmann measure. In the Nosé–Pöncärè method, the thermostat is modeled by an additional fictitious particle added to the physical system that plays the role of a heat reservoir. The state of this fictitious particle is described by its position \( Q \) and its momentum \( P \). The Nosé–Pöncärè dynamics is the Hamiltonian dynamics generated by the Hamiltonian

\[
\mathcal{H}_{\text{NP}}(q,p,Q,P) = Q \left( \mathcal{H}(q,P) + \frac{P^2}{2M} + g_k T \ln Q - \mathcal{H}_0 \right) \tag{148}
\]

where \( \mathcal{H} \) is given by Eq. (2), \( g \) is the number of degrees of freedom to thermalize (usually \( g = 3N \), where \( N \) is the number of atoms), \( \mathcal{H}_0 \) is chosen such that \( \mathcal{H}_{\text{NP}} = 0 \) for the initial conditions, and \( M \) is a free parameter that the user has to choose that represents the mass of the additional particle, or the strength of coupling between this particle and the physical system. Under strong ergodicity assumptions, it can be shown that time averages computed along the Nosé–Pöncärè trajectory converge to the canonical phase average

\[
\lim_{t \to \infty} \frac{1}{t} \int_0^t A(q(s),\dot{q}(s)) ds = \langle A \rangle \tag{149}
\]

The Nosé–Pöncärè method is one of many methods that have been proposed for sampling the canonical measure. Another approach is the popular Nosé–Hoover thermostat. An interesting feature of the Nosé–Pöncärè method, and the reason we chose to use it, is the fact that it yields a Hamiltonian feature of the Nosé–Pöncärè method, and the reason we chose to use it, is the fact that it yields a Hamiltonian dynamics, which is well-known for Hamiltonian dynamics, there exists a class of algorithms, called symplectic algorithms, that have good properties in the long time limit [68]. These properties are of paramount importance when computing long time averages such as in Eq. (149).

More precisely, when the dynamics is integrated with a symplectic algorithm, the energy (which is preserved along the exact trajectory) fluctuates around its initial value within a band of size \( \Delta p \) (where \( p \) is the order of the scheme) for extremely long times (of the order of \( \exp(c/\Delta t) \)). In other words, there is no drift in the energy, which is in contrast to explicit or implicit Euler algorithms for which the energy normally diverges or vanishes. On the other hand, if the dynamics is not Hamiltonian but still preserves some quantity (which is the case for Nosé–Hoover dynamics), then designing an algorithm which does not show any drift in this quantity is a challenging task (see Refs. [69] and [70] for some studies along this line).

13Note that \( Q \) is dimensionless, \( P \) has units of energy \( \times \) time, and \( M \) has units of energy \( \times \) time \(^2 \); therefore strictly speaking \( Q, P, \) and \( M \) are not actually variables of position, momentum and mass. Yet they play a similar role in the equations.
between the physical system and the heat reservoir. As such, it has an influence on the speed of convergence of Eq. (149) (see Ref. [74] for a similar study in the case of the Nose–Hoover thermostat). It is also possible that Eq. (149) does not hold for values of \( M \) that are either too small or too large. This is why we have used different values of \( M \) in the numerical tests described in Sec. 4.

An alternative to using Nose–Poincaré dynamics is to use the Langevin equation, which can be proved to be ergodic for the Boltzmann measure under some very mild assumptions [75,76]. The Langevin equation reads

\[
\dot{q}_i = \frac{p_i}{m_i}, \quad \dot{p}_i = -\nabla_q V(q) - \frac{\zeta_i}{m_i} p_i + \sqrt{2\xi_i / \beta G_i}
\]  

(150)

where \( (G_i)_{1 \leq i \leq N} \) is a set of \( N \), three-dimensional, random variables, such that for any \( t_1 > t_0 \), the quantity \( \int_{t_0}^{t_1} G dt \) is a vector of dimension \( 3N \), whose components are independent and identically distributed according to a Gaussian distribution of zero mean value and variance \( t_1 - t_0 \). The two last terms of the second expression in Eq. (150) represent a dissipative term and a fluctuation term, whose magnitude is scaled by the adjustable “friction” parameter \( \zeta_i \). For any \( \zeta_i > 0 \), and for any initial conditions, the time average of any phase function (which is a random number) converges to the phase space average

\[
\lim_{t \to \infty} \frac{1}{t} \int_0^t A(q(t), p(t)) dt = \langle A \rangle
\]

(151)

Of course, the speed of convergence (and hence the numerical efficiency of the method) depends on \( \xi \). Note that we retain the convergence in Eq. (151) even if different friction parameters, \( \zeta_i \), are used for the different particles, i.e., if we replace Eq. (150) by

\[
\dot{q}_i = \frac{p_i}{m_i}, \quad \dot{p}_i = -\nabla_q V(q) - \frac{\zeta_i}{m_i} p_i + \sqrt{2\xi_i / \beta G_i}
\]

(152)

This flexibility is very useful when the particle masses (or the eigenvalues of the potential energy Hessian) vary over a large range, as is the case in a QC model. Consider indeed the oversimplified case of a one-dimensional system, with the harmonic potential energy \( V(q) = kq^2 / 2 \) (for some stiffness \( k \). The Langevin Eq. (150) then reads

\[
\dot{q} = \frac{p}{m}, \quad \dot{p} = -kq - \frac{\zeta}{m} p + \sqrt{2\xi / \beta G}
\]

(153)

On this simple example, the convergence to equilibrium can be analytically assessed. It is the fastest when

\[
\zeta = 2\sqrt{km}
\]

(154)

We thus observe that the optimal choice of the friction depends on the mass and stiffness in the system. In our context, repatoms have different masses, and the stiffness of the coarse-grained potential is also very different from one repatom to the other. In Sec. 4 below, we have tested different strategies for the selection of \( \zeta_i \) as a function of the masses \( m_i \) of the particles.

Several schemes are available to integrate the Langevin equations. We have chosen to work with the following scheme (see Ref. [77]):

\[
p_i^{n+1/2} = p_i^n - \frac{1}{2}\Delta t \left( \nabla_r V(q^n) + \frac{\zeta_i}{m_i} p_i^n \right) + \frac{1}{2}\sqrt{2\Delta t / \beta G_i^n}
\]

\[
q_i^{n+1} = q_i^n + \Delta t p_i^{n+1/2} / m_i
\]

\[
p_i^{n+1} = p_i^{n+1/2} - \frac{1}{2}\Delta t \nabla_q V(q^{n+1}) + \frac{1}{2}\sqrt{2\Delta t / \beta G_i^n}
\]

Here \( n \) is the time step counter. As noted above, the components of the random variable \( G_i^n \) are independent and identically distributed according to a normalized Gaussian distribution. In addition, for different time steps \( n \neq m \), any component of \( G_i^n \) is independent of any component of \( G_i^m \).

4 Numerical Results: Tests and Applications

We now turn to the verification of the hot-QC-static and hot-QC-dynamic formulations described in Sec. 2. We explore the predictions of these methods and the effectiveness of different thermostats for two basic tests:

- global thermalization and temperature uniformity
- thermal expansion and mesh dependence

We then apply hot-QC-dynamic to a more realistic application problem: the effect of temperature on nanoindentation into a nickel thin film.

4.1 Global Thermalization and Temperature Uniformity. In this section, we study the effectiveness of three different thermostats (Nose–Poincaré, Langevin and Nosé–Hoover chains) at maintaining a hot-QC system at a global temperature of 300 K and the uniformity of the resulting temperature distribution.

We consider a face-centered cubic (fcc) crystal of Ni atoms modeled using an EAM potential due to Angelo et al. [78]. The \( x \), \( y \), and \( z \) directions are oriented along the crystallographic directions [100], [010], and [001]. The crystal is of size 200 Å × 200 Å in the \( x-y \) plane and two layers thick in the \( z \) direction for a total of about 13,000 atoms. Free boundary conditions are applied in the \( x \) and \( y \) directions and periodic boundary conditions in the \( z \) direction. This configuration corresponds to a nanobar with a square cross-section which is infinite in the out-of-plane direction. The nanobar is modeled using a 2D hot-QC mesh which includes a fully-refined region of size 40 Å × 40 Å consisting of 121 repatoms surrounded by a coarser mesh of 1248 repatoms for a total of 1369 repatoms as shown in Fig. 2. The repatoms are free to move in the \( x \), \( y \), and \( z \) directions.

Fig. 2 Hot-QC mesh used to study thermalization and temperature distribution. In the outside zone, the continuum approximation is applied and the repatoms are local. In the central square, the repatoms are either local (simulation 1) or nonlocal (simulations 2 and 3).
Three different simulations were performed: In the first case, only the continuum limit is applied and all 1369 repatoms are taken to be local repatoms (nodes). In the second and third cases, the 121 repatoms in the central fully-refined region are taken to be nonlocal repatoms (atoms), while the remaining 1248 repatoms are local (nodes). The difference between cases 2 and 3 is related to the handling of ghost forces. In case 2, ghost force corrections in the form of dead loads are applied as described in Refs. [3,6], whereas in case 3, no corrections are applied.

For each of the three simulations, the momenta of the repatoms are initialized according to the Boltzmann distribution at 300 K. Subsequently the system is evolved according to the Nosé–Poincaré and Langevin equations (see Sec. 3.3) with T = 300 K. For Nosé–Poincaré dynamics, the simulations are performed using three different values of the fictitious particle “mass” M in Eq. (148)

\[ M = 0.01 k_B T, \quad M = 0.1 k_B T, \quad M = k_B T \]  

(155)

where \( k_B \) is the Boltzmann constant (\( k_B = 8.6173 \times 10^{-5} \text{ eV/K} \)) and M is in units of \( \text{eV} \cdot \text{ps}^2 \). For Langevin dynamics, three different strategies were tested for the choice of the friction coefficients \( \xi_i \) in Eq. (152) as a function of the masses \( m_i \) of the particles

\[ \xi_i = \xi^0 m_i, \quad \xi_i = \xi^0 \sqrt{m_i}, \quad \xi_i = \xi^0 \]  

(156)

In addition, four different choices for \( \xi^0 \) were explored: \( 10^{-1}, 1, 10, \) or 100. Note that \( \xi^0 \) has units of mass/time (\( \text{eV} \cdot \text{ps}^2/\text{Å}^2 \)) in the simulations therefore \( \xi^0 \) has different units for the different scenarios: time \(^{-1} \), mass \(^{1/2} \cdot \) time \(^{-1} \), and mass \cdot \) time \(^{-1} \). (The units of mass in the simulations are \( \text{eV} \cdot \text{ps}^2/\text{Å}^2 \)) The second strategy in Eq. (156) is directly motivated by the optimality condition in Eq. (154). In all simulations, an MD time step of \( \Delta t = 0.001 \text{ ps} \) was used and the dynamical equations were integrated over \( 5 \times 10^6 \) steps.

4.1.1 Global Thermalization. Our objective is to compare the ability of the methods to sample the canonical measure

\[ Z_{\text{QC}}^{-1} \exp(-\beta H_{\text{QC}}(q^0, p^0, u^0, \Omega^0, T)) \]

As a first criterion, we compare their ability to thermalize the system, i.e., maintain the global set temperature (\( T = 300 \text{ K} \)). To this end, we define the following functions for each repatom \( i \):

\[ A_i(t) = \frac{1}{t} \int_0^t \frac{\|p_i(s)\|^2(s)}{2m_i} ds \]  

(157)

\[ B_i(t) = \frac{1}{t} \int_0^t \left( \frac{p_i^x(s)^2(s) + p_i^y(s)^2(s) + p_i^z(s)^2(s)}{(2m_i)^2} \right) ds \]  

(158)

where \( p_i \) belongs to the concatenated set of nonlocal and local repatoms \( p^\text{rep} \) as explained in Sec. 3.3 and \( p_i^x, p_i^y, \) and \( p_i^z \) are the x, y, and z components of \( p_i \).

In this section, we monitor the average values of \( A_i \) and \( B_i \) over all repatoms

\[ A_{\text{rep}}(t) = \frac{1}{n_R} \sum_{i=1}^{n_R} A_i(t), \quad B_{\text{rep}}(t) = \frac{1}{n_R} \sum_{i=1}^{n_R} B_i(t) \]  

(159)

We expect that, for any repatom \( i \),

\[ \lim_{t \to \infty} A_i(t) = \frac{3}{2} k_B T, \quad \lim_{t \to \infty} B_i(t) = \frac{9}{2} (k_B T)^2 \]  

(160)

\(^{16}\)The QC potential in Eq. (86) involves the free energy given by Eq. (42), which is the sum of a 0K contribution and of a temperature-dependent contribution. The former is exactly the 0K QC potential whose gradient may be corrected to remove so-called ghost forces [3] which introduce spurious effects at the interface between the local and the nonlocal regions.

In contrast to the observables \( A_{\text{rep}} \) and \( B_{\text{rep}} \), the exact result for \( \lim_{t \to \infty} C(t) \) (independently of the choice of thermostat) is a priori different for cases 1, 2, and 3, which each have a different potential energy contribution to the QC Hamiltonian.

We start with Nosé–Poincaré dynamics for the first test case (all repatoms are local) and monitor \( A_{\text{rep}}(t), B_{\text{rep}}(t), \) and \( C(t) \). The results are presented in Fig. 3. We observe that the smaller the

---

**Fig. 3** For Nosé–Poincaré dynamics, evolution as a function of \( t \) of (a) \( A_{\text{rep}}(t) \), (b) \( B_{\text{rep}}(t) \), and (c) \( C(t) \) for different choices of \( M \) (note the different scales for the horizontal axes in the three figures)
value of $M$, the faster the convergence of $A_{\text{rep}}(t)$ and $B_{\text{rep}}(t)$ to equilibrium (additionally, oscillations in this convergence are also smaller when $M$ is smaller). The conclusions are similar for the two other test cases (nonlocal central region with or without ghost force corrections). We therefore choose to work with smaller when equilibrium (additionally, oscillations in this convergence are also results are presented in Fig. 4. We observe that, the larger value of $M$, $\text{limit } t \to \infty$ of $C(t)$ when $t \to \infty$. This function is plotted in Fig. 5 where we observe that $\xi^0 = 10$ appears to be the optimal choice. The same result is also obtained for the other two test cases where some repatoms are nonlocal.

A similar analysis can be performed when the systems are thermalized with the Langevin equation with the friction parameters chosen according to $\xi = \xi^0$ where $\xi^0$ is a constant. In that case, the optimal value of $\xi^0$ appears to lie between 0.1 and 1. Likewise, when the friction parameters are chosen according to $\xi = \sqrt{m_i}/m_i$, the optimal value is found to be about $\xi^0 = 1$.

We have now identified the optimal parameter, for each of the thermalizing models being considered. In Fig. 6, we compare these thermalizing models, again for the system where all repatoms are local repatoms (similar conclusions hold for the two other cases). We observe that the Nosé–Poincaré method converges faster to equilibrium for the computation of the average temperature of the system and the thermal expansion (observables $A_{\text{rep}}$ and $C$). On the other hand, the variance of the temperature (observable $B_{\text{rep}}$) is better captured by the Langevin dynamics with the choices $\xi_i = \sqrt{m_i}$ and $\xi_i = 10 m_i$.

4.1.2 Temperature Uniformity. We now look more closely at the ability of the different schemes to uniformly thermalize the system. In the canonical ensemble, we expect that

$$\lim_{t \to \infty} A_i(t) = \frac{3}{2} k_B T, \quad \lim_{t \to \infty} B_i(t) = \frac{9}{2} (k_B T)^2$$

for each repatom $i$. In the previous section, we only looked at values that were averaged over all repatoms. To explore temperature uniformity, we consider (i) the Nosé–Poincaré method with $M = 0.01 k_B T$, (ii) Langevin dynamics with $\xi_i = 10 m_i$, (iii) Langevin dynamics with $\xi_i = \sqrt{m_i}$, and (iv) Langevin dynamics with $\xi_i = 1$. The set temperature is $T = 300$ K. The results for each of these methods for the case where all repatoms are local are plotted in

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Figure 4: For Langevin dynamics, evolution as a function of $t$ of (a) $A_{\text{rep}}(t)$, (b) $B_{\text{rep}}(t)$, and (c) $C(t)$ for different values of $\xi^0$ (with the choice $\xi_i = \xi^0 m_i$). Note the different scales for the horizontal axes in the three figures.

Figure 5: For Langevin dynamics, evolution as a function of $t$ of $\text{err}(t)$ defined by Eq. (162) for different choices of $\xi^0$ (with the choice $\xi_i = \xi^0 m_i$).
We clearly observe from Figs. 7 and 8 that the system is uniformly thermalized when Langevin thermostat is applied using any of the three different strategies that were tested. In contrast, the temperature is not uniform when the Nosé–Poincaré method is used. The temperature is clearly higher in the corners of the simulation even though all the repatoms in the outer zone are identical. The same conclusions hold for simulations where some repatoms are nonlocal.

To quantify the observations in Figs. 7 and 8, we gather in Table 1 the minimum and maximum values (over the system) of the observable $A_i$ at the end of the simulation. For all the simulations using Langevin dynamics, we see that the temperature is very uniform in the system, the ratio between the maximum and minimum values being close to 1 with an error of 3% or less. For the Nosé–Poincaré method, this error is about 8%. Similar conclusions are reached for the observable $B_i$ (see Table 2). Again, results are similar in the cases when some repatoms are nonlocal (results not shown).

Finally, as an alternative choice of thermostat, we explore the effectiveness of the Nosé–Hoover chain method [79] at
maintaining a uniform temperature. In this approach, a series of Nose–Hoover thermostats are coupled together to control the temperature. Figure 9 shows the average temperature in the continuum and atomistic regions for four different thermostating strategies with the nominal temperature set to $T = 100$ K. We note in accordance with the results discussed above that the Langevin thermostat (Fig. 9(a)) exhibits a better capacity to uniformly control temperature relative to Nose–Poincaré (Fig. 9(b)). The results for the Nose–Hoover chain thermostat with 10 link parameters are shown in Fig. 9(c). While there is definitely an improvement relative to the Nose–Poincaré thermostat, the results are still not as good as those obtained with the Langevin thermostat. Further improvement is obtained by using two separate Nose–Hoover chain thermostats to independently control the temperatures of the continuum and atomistic regions (Fig. 9(d)). This strategy results in the tightest temperature control, although it comes at the expense of a larger number of thermostat parameters (20 for the two chains) that need to be selected and tuned.

4.2 Thermal Expansion. As in Sec. 4.1, we consider a Ni fcc crystal oriented along [100], [010], and [001] in the x, y, and z directions with a size of $40 \times 40 \times 1$ unit cells (140.8 Å × 140.8 Å × 3.52 Å at zero temperature). The in-plane (x and y) directions are free and periodic boundary conditions with the minimum repeat distance of two layers is applied in the z directions. The atomic interactions are modeled using an EAM potential for Ni due to Angelo et al. [78].

Four different meshes of increasing refinement were tested as shown in Fig. 10. The coarsest $10 \times 10$ mesh (Fig. 10(a)) has 121 nodes and the finest $80 \times 80$ mesh (Fig. 10(d)) has 6561 nodes. The latter mesh is fully-refined in the sense that all atoms in the crystal are represented. In all cases, the local limit of the hot-QC formulation is used which means that the effective potential energies are calculated using the Cauchy–Born rule. Each system is simulated at 10 different temperatures ranging from 100 K to 1000 K (the 0 K lattice parameter, 3.52 Å, was determined by minimizing the energy of an fcc lattice with respect to the periodic cell size). Constant temperature is maintained using a

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Method & $\min A_i(t_{\text{max}})$ & $\max A_i(t_{\text{max}})$ & $\max A_i(t_{\text{max}})$ \\
\hline
Nose–Poincaré, $M = 0.01 k_B T$ & 0.03774 & 0.04090 & 1.084 \\
Langevin dynamics, $\zeta = 10 m_i$ & 0.03844 & 0.03917 & 1.019 \\
Langevin dynamics, $\zeta = \sqrt{m_i}$ & 0.03818 & 0.03935 & 1.031 \\
Langevin dynamics, $\zeta = 1$ & 0.03841 & 0.03917 & 1.020 \\
\hline
\end{tabular}
\caption{Minimum and maximum values of $A_i(t_{\text{max}})$ for the different thermalizing schemes at the end of the simulation (for the case where all repatoms are local). In the units we use, $3k_B T^2 = 0.03878$.}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Method & $\min B_i(t_{\text{max}})$ & $\max B_i(t_{\text{max}})$ & $\max B_i(t_{\text{max}})$ \\
\hline
Nose–Poincaré, $M = 0.01 k_B T$ & 0.002843 & 0.003356 & 1.180 \\
Langevin dynamics, $\zeta = 10 m_i$ & 0.002941 & 0.003073 & 1.045 \\
Langevin dynamics, $\zeta = \sqrt{m_i}$ & 0.002915 & 0.003099 & 1.063 \\
Langevin dynamics, $\zeta = 1$ & 0.002940 & 0.003083 & 1.049 \\
\hline
\end{tabular}
\caption{Minimum and maximum values of $B_i(t_{\text{max}})$ for the different thermalizing schemes at the end of the simulation (for the case where all repatoms are local). In the units we use, $9 k_B T^2 / 2 = 0.03007$.}
\end{table}

\footnotesize{\textsuperscript{17}The masses for the Nose–Hoover chain are selected based on the natural frequency of the system and through trial and error (see Ref. [79] for details). In the current simulations, the same value of $8.62 \times 10^{-3}$ eV ps$^{-2}$ was used for all links in the Nose–Hoover chain. Note that similarly to the friction coefficient in Langevin thermostat, the masses of the Nose–Hoover chain thermostat only affect the equilibration time scale. Thus the simulation results eventually converge to the equilibrium values regardless of the mass values.}
The lattice parameter at each temperature $a(T)$ is measured separately from the average length changes in the two diagonal directions ($y = \pm x$). This yields two estimates for $a(T)$ which allows us to explore the effect of element orientation on the thermal expansion. The results obtained from the hot-QC simulations were compared with a fully-atomistic MD simulation using the same EAM potential.

Figure 11 shows the lattice parameters as a function of temperature. Results are shown for the MD simulation (which is taken to be the “exact” solution), hot-QC-static and hot-QC-dynamic with and without mesh entropy corrections. The hot-QC-static results were in best agreement with the MD results and did not exhibit mesh dependence. The error for this model ranged from 0.03% at 200 K to 0.34% at 1000 K. These errors arise from the local harmonic approximation and cannot be avoided in the current framework of the hot-QC method. An improvement in accuracy may be obtained by adopting a quasi-harmonic approximation [6] or self-consistent approach [80,81]. However this is left for future work.

In contrast to hot-QC-static, the hot-QC-dynamic method does exhibit a dependence on both the element size and orientation. The error is much larger in the “naive” implementation of hot-QC-dynamic (i.e., the implementation which does not include the mesh entropy correction as explained in Sec. 2.5.1). With regards

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Fig. 10 Meshes of the model: (a) $10 \times 10$ mesh with 121 nodes and 200 elements, (b) $20 \times 20$ mesh with 441 nodes and 800 elements, (c) $40 \times 40$ mesh with 1681 nodes and 3200 elements, and (d) $80 \times 80$ mesh with 6561 nodes and 12,800 elements

Fig. 11 Lattice parameters as function of temperature: (a) $10 \times 10$ mesh, (b) $20 \times 20$ mesh, (c) $40 \times 40$ mesh, and (d) $80 \times 80$ mesh
to element size, it is found that the error increases with decreasing element size, with the largest error obtained for the fully-refined mesh (Fig. 11(d)). The orientation dependence manifests itself in the fact that different estimates for the lattice parameter are obtained along $y = +x$ and $y = -x$. Again the differences increase with decreasing element size.

As noted above, the errors in the hot-QC-dynamic formulation are significantly larger for the "naıve" implementation. This suggests that these errors are at least partly associated with the loss of second-order accuracy in temperature as explained in Sec. 2.5.1. Figure 12 explicitly shows how the situation improves with the mesh entropy correction. Not only does the correction term move the mean of the $x$ displacement of the bottom left node close to the static solution (as borne out in Fig. 11), but it also reduces the magnitude of thermal fluctuation. The latter result is consistent with the idea that the mesh entropy correction reduces the spurious vibrations of the continuum nodes.

Although the mesh entropy correction improves accuracy, it does not completely resolve the mesh dependence as seen in Fig. 11, especially with the fully-refined mesh. The development of more effective schemes for addressing this problem is an important topic for future research.

### 4.3 A Nanoindentation Test

As a final example, we apply the hot-QC method to simulate a nanoindentation experiment at finite temperature in which a thin film of single crystal Ni deposited on a rigid substrate is indented by a cylindrical indenter. The objective is to determine how the temperature affects the initial nucleation of dislocations from under the indenter (preliminary results were reported in Ref. [42]). Nanoindentation is an ideal problem for hot-QC because the long-range stress field of the indenter can drive nucleated dislocations far into the film. This makes the problem computationally expensive for conventional fully-atomistic methods such as MD. We will see below that the number of degrees of freedom needed to accurately simulate this problem is significantly reduced by applying the hot-QC methodology.

The simulation model shown in Fig. 13 consists of an fcc crystalline rectangular-shaped block of size $2000 \times 1000 \text{ Å}$ comprised of Ni atoms. The atomic interactions are modeled by an EAM potential due to Angelo et al. [78]. The crystal is oriented such that the $x$ and $y$ axes line along the crystallographic [111] and [110] directions. Thus, the $y$ and $z$ axes lie in a (111) slip plane. As in the previous simulations, periodic boundary conditions are applied in the out-of-plane ($z$) direction with a minimum repeat distance of two atomic layers. (The spacing in the $z$-direction is adjusted to accommodate the thermal expansion of the crystal at the simulated temperature.) Fixed displacement boundary conditions are applied to the left, right and bottom of the model. The top surface is free. An indenter of radius of 70 $\text{ Å}$ modeled as a repulsive potential [82] is driven into the top surface in the negative $y$-direction at a velocity of $0.05 \text{ Å}/\text{ps}=5 \text{ m/s}$. This is a large velocity but it is necessary in order for dislocation nucleation to occur within the time scale reachable to the molecular dynamics in the atomistic region. The hot-QC model consists of an atomistic (nonlocal) semicircular region (Fig. 13(b)) embedded in a surrounding continuum (Fig. 13(a)). The mesh is fully-refined in the atomistic region and gradually coarsens out to fixed size in the continuum region. The system includes 3048 atoms (nonlocal repatoms) in the atomistic region and 1494 nodes (local repatoms) in the continuum region for a total of 4542 repatoms. Thus, a significant reduction in the number of degrees of freedom is achieved in comparison to the 790,000 atoms needed to model the same system with a fully-atomistic simulation.

The first decision that needs to be made is the selection of a thermostat. The tests described in Sec. 4.1 suggest that overall the Langevin thermostat exhibited the best mix of ease of use and effectiveness. However, care needs to be taken when applying thermostats designed for sampling equilibrium states to a nonequilibrium process such as nanoindentation. We therefore perform preliminary nanoindentation simulations at $T=100 \text{K}$ using both a Langevin thermostat and a Nose–Poincaré thermostat with

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\[ \text{Fig. 12 Thermal fluctuation in the } x\text{-displacement of the bottom left node of the hot-QC-dynamic mesh} \]

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\[ \text{Fig. 13 Mesh of the nanoindentation model: (a) entire system, and (b) zoomed view of the fully-refined mesh under the indenter} \]
dentation simulations. The system was tested at five temperatures:

\[ T = 0 \text{ K}, 100 \text{ K}, 200 \text{ K}, 300 \text{ K}, \text{ and } 400 \text{ K}. \]

For the 0 K test, the conventional static QC method was used. In the finite temperature simulations, the hot-QC-dynamic method with mesh entropy correction was used. At the start of each simulation, the system was equilibrated for 100 ps with the indenter position held fixed. Following the equilibration process, the cylindrical indenter was lowered at a constant velocity of 0.05 Å/ps. The simulation stopped when the indentation depth reached 20 Å. Dislocation nucleation occurred at all temperatures before this indentation depth was reached.

Figure 15 shows the hot-QC mesh after the first dislocation is nucleated. The dislocation nucleates on the (111) slip plane and dissociates into two Shockley partial dislocations separated by an intrinsic stacking fault. The initial nucleation positions are shown as circles. One partial then moves upward to the surface while the other moves downward and stops inside the atomistic region. Figure 16 shows the load versus indentation depth curves at different temperatures and the curve obtained at 0 K using the static QC method. In Fig. 16(a), all curves are superposed which shows the softening of the initial elastic response due to the increasing temperature. In Fig. 16(b), the curves are shifted apart horizontally to help view them and the location of the first dislocation nucleation is indicated. The nucleation event is associated with a small drop in the load which is sometimes difficult to discern due to the thermal fluctuations. It is clear from the figure that the nucleation load decreases with increasing temperature. This is expected since at finite temperature dislocation nucleation is a thermally-activated process. At higher temperatures the probability of a transition increases. This dependence is made explicit in Fig. 17 which shows the dislocation nucleation load plotted as a function of temperature. The error bars indicate the standard error obtained from 10 separate runs at each temperature.

The nonlinear response shown in Fig. 17 can be rationalized using a modified Tomlinson model which was originally introduced to account for the velocity and temperature dependence of atomic-scale friction [84,85]. In this model, dislocation nucleation under the indenter is assumed to occur via a thermally-activated process involving a unidirectional transition between two states. The energy barrier governing this transition is assumed to decrease linearly with increasing driving force (i.e., the indentation load). The barrier vanishes when the driving force reaches a critical value. At zero temperature, a dislocation can nucleate only when the load reaches the critical value. However, at finite temperature nucleation can occur below the critical load with the nucleation load and temperature related as follows:

\[ \frac{\Delta U}{kT} = \frac{1}{n} \left( \frac{n}{n+1} \right) \frac{1}{\xi_0} \frac{1}{C_0} \eta \left( \frac{\eta}{C_0} \right)^{1/n} \chi \eta \left( \frac{\xi_0}{\eta} \right)^{1/n} \]

where \( n \) is the parameter of the model, \(\eta\) is the friction coefficient, \(\xi_0\) is the characteristic length scale, \(C_0\) is the elastic modulus, and \(\chi\) is the dislocation mobility.

For comparison, we also perform the simulations using the Nose–Poincaré thermostat with \(M/k_B T = 0.01,0.1,1,10\) ps\(^{-1}\). The results are shown in Fig. 14(b). We see that in contrast to the Langevin thermostat, Nosé–Poincaré does not exhibit a strong dependence on the mass parameter (over the range of masses tested).

Based on the above results, a Nosé–Poincaré thermostat (using the parameter \(M = 0.01k_B T\)) was used for the remaining nanoinindentation simulations. The system was tested at five temperatures:

\[ T = 0 \text{ K}, 100 \text{ K}, 200 \text{ K}, 300 \text{ K}, \text{ and } 400 \text{ K}. \]

It is well-known that the time step in integrating the Langevin dynamics must be reduced when the friction coefficient is increased. It is standard to require that the time step \( \Delta t \) is much smaller than \( 1/\xi_0 \) (for \( \zeta = \xi_0 m_0 \)) [83]. In our simulations \( \Delta t = 10^{-13} \text{ ps} \), while the smallest value of \( 1/\xi_0 \) is 0.1 ps, so this condition is satisfied.

![Figure 14](http://appliedmechanicsreviews.asmedigitalcollection.asme.org/)

**Fig. 14** Force as a function of indentation depth for (a) the Langevin thermostat, and (b) the Nosé–Poincaré thermostat.

![Figure 15](http://appliedmechanicsreviews.asmedigitalcollection.asme.org/)

**Fig. 15** Mesh after dislocation nucleation at \( T = 100 \text{ K} \). The figure shows a closeup of the region under the indenter (which is embedded in a larger continuum region as shown in the inset). The nucleated dislocation dissociates into a pair of Shockley partial dislocations. See text for discussion.
The fit based on Eq. (163) is shown as the red dashed curve in Fig. 17. It is clear that the Tomlinson model describes the data well. Note that the underlying assumption of the unidirectional transition in the Tomlinson model means that all the dislocation sites in our nanoindentation system (at least the most probable sites) behave largely in the same way as the indenter moves down. The verification of this conjecture remains for future work.

5 Conclusions

We have presented a new method for finite temperature multiscale mechanics referred to as “hot-QC.” This is a coupled continuum and atomistic approach which is designed to reproduce equilibrium phase averages of the corresponding fully-atomistic system for functions that depend only on the atomistic region. The method is suitable for studying processes under equilibrium or near equilibrium (quasi-static) conditions which are localized to regions that can be treated atomistically. Examples include phenomena at atomically-sharp cracks or under nanoindenters. It is demonstrated that the method is accurate to second-order in temperature.

The key step in developing hot-QC is the derivation of an effective Hamiltonian that adequately approximates the contributions of the unrepresented atoms in the continuum region. This is solved, in essence, by computing the missing entropy associated with those atoms using a local harmonic approximation at the nominal set temperature. The effect of nonuniform deformation on the local harmonic model is included using a finite element discretization, the Cauchy–Born rule, and a piecewise constant deformation within each finite element. The dynamics of the atomistic region can then be evolved using MD with forces computed from the effective Hamiltonian.

Two variants of hot-QC were described which differ in the way that the continuum region is treated. In “hot-QC-static,” the free energy of the continuum is minimized at each MD time step of the atomistic region. In “hot-QC-dynamic,” the nodes in the continuum region are evolved dynamically together with the atoms in the atomistic region. The hot-QC-dynamic approach is computationally more efficient; however, in order to maintain the same level of accuracy, it is necessary to correct for an artifact we refer to as mesh entropy. This is an artificial contribution to the total entropy of the system due to the motion of the nodes storing the discretized field of mean atom positions. A simple correction is introduced to restore the second-order accuracy of the approach.

Constant temperature is maintained in the hot-QC formulation by an external thermostat which is tied to the system. In hot-QC-static only, the atomistic region is thermostated while in hot-QC-dynamic both the atoms and nodes are controlled. Three different thermostating strategies were explored: Langevin, Nosé–Poincaré, and Nosé–Hoover chains. Generally, it was found that the Langevin thermostat provided the best mix of ease of use and effective temperature control. This was particularly true for hot-QC-dynamic where simultaneously thermalizing an atomistic and coarse-grained continuum region was a challenge for the Nosé–Poincaré thermostat which was not able to achieve temperature uniformity. The Nosé–Hoover chain thermostat performed better than Nosé–Poincaré but required more parameters to set than Langevin. On the other hand, we found that the results of our indentation simulations were more sensitive to the choice of parameters for the Langevin thermostat than they were to the Nosé–Poincaré parameters. As such, we used the Nosé–Poincaré thermostat for the indentation simulations.

As a first test, the hot-QC methodology was used to compute the thermal expansion of an Ni fcc crystal. The lattice parameter calculations demonstrate that the hot-QC-static method does not exhibit mesh dependence and has errors as small as 0.34% at 1000 K compared with an MD simulation result. In contrast, the thermal expansion in hot-QC-dynamic simulations does depend on element size and orientation, with greater error introduced as
the mesh size becomes smaller and approaches the atomic scale. The error is significantly reduced by the inclusion of the mesh entropy correction, but some discrepancies remain.

Finally, the hot-QC method was applied to a nanoindentation problem. A 2000 Å × 1000 Å thin film of single crystal Ni was indented by a cylindrical indenter of radius 70 Å. This system, which contains 790,000 atoms, is represented by a hot-QC dynamic model consisting of just 4500 representative atoms. The simulations show the softening of the indenter load-displacement curve due to temperature effects. In addition, the critical load for dislocation nucleation is seen to decrease nonlinearly with increasing temperature. This behavior is well characterized by a modified Tomlinson model which accounts for the reduction in the activation energy for dislocation nucleation due to an increasing driving force.

Although more limited than some dynamic multiscale approaches, hot-QC has the benefit of a well-defined design goal (reproducing equilibrium phase averages) and analytic estimates for its accuracy (second-order in temperature). Further research and development is warranted in a number of areas:

• As noted above, hot-QC-dynamic exhibits mesh dependence. The analytical mesh entropy correction proposed in this article reduces the error but does not eliminate it. The development of improved expressions for mesh entropy correction is of interest.

• The second-order accuracy cited for the method is strictly true only for the quasi-harmonic approximation. Numerical studies show that similar accuracy is also observed for the local harmonic approximation which is currently used in hot-QC. However, it is expected that accuracy will improve in a quasi-harmonic hot-QC formulation. The development of a computationally-efficient implementation of such an approach should be pursued.

• The hot-QC-static formulation was shown to be more accurate than hot-QC dynamic for the thermal expansion calculations. In particular, it does not exhibit the mesh dependence of the latter approach. However, hot-QC-static requires a full minimization of the free energy of the continuum region at each MD time step which makes it computationally expensive. The development of efficient solvers for hot-QC-static that perform an approximate minimization at each step could make this a viable computational method.

• In the current implementation of hot-QC-dynamic, a single thermostat is normally used to control the temperature of the entire system (atomistic and continuum). The possibility of separate temperature control for the continuum and atomistic regions was also briefly explored and found to improve temperature uniformity. The latter approach requires more study. In particular recent work on thermostatting coarse-grained systems, such as that of Gill et al. [27], including concepts like “partial thermo-stating” and “recursive multiple thermostats” may improve the performance of hot-QC-dynamic and should be explored.

• The current implementation of hot-QC is “2.5D.” This means that a 2D finite element mesh is used but nodes and atoms can move in the x, y, and z directions. All atomistic calculations are performed in 3D. This is comparable to a plate-like 3D atomistic system in which periodic boundary conditions with a minimal repeat distance are applied in the out-of-plane direction. The 2.5D kinematics places certain limitations on the allowed deformation mechanisms; for example, only dislocation with lines perpendicular to the simulation plane can nucleate, but otherwise gives realistic results. Extension of hot-QC to full 3D involves no new physics but is nontrivial from an implementation standpoint.

• The current hot-QC framework is limited to simple lattice crystals. The extension to multilattices (i.e., lattices with a basis) introduces in the continuum region a dependence on the shifts of the basis atoms in addition to the deformation gradient. The appropriate manner in which shift fields should be treated from a thermodynamic perspective remains an area of current research (see for example the discussion in Sec. 11.3.4 of Ref. [6]).

• Finally, the extension of hot-QC to a nonequilibrium setting, where the temperature is nonuniform, and heat flux can occur between different parts of the model is a natural next step in the development of the QC framework.

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Nomenclature

\[ A = \text{phase average (observable)} \]

\[ A(q, p) = \text{phase function} \]

\[ D_0 = \text{zero temperature stiffness matrix of the continuum region} \]

\[ D_{0,H}^c = \text{local harmonic approximation to } D_0, \text{ stiffness matrix of the continuum region} \]

\[ E_i^a = \text{energy of atom } i \text{ in the atomic region} \]

\[ E_i^q = \text{energy of atom } i \text{ in the continuum region} \]

\[ F = \text{deformation gradient} \]

\[ k_B = \text{Boltzmann’s constant} \]

\[ H(q, p) = \text{Hamiltonian of all atoms in system} \]

\[ H^a(q, p, T) = \text{effective Hamiltonian of atomic region} \]

\[ \tilde{H}^a(q^a, p^a, T) = \text{harmonic approximation to } H^a \]

\[ \tilde{H}_I^a(q^a, p^a, T) = \text{finite element and Cauchy-Born approximation to } \tilde{H}^a \]

\[ \mathcal{H}_{QC}(q^a, p^a, T) = \text{hot-QC-dynamic Hamiltonian} \]

\[ \mathcal{H}_{QC}^a(q^a, p^a, T) = \text{hot-QC approximation to } \tilde{H}_I^a \]

\[ \mathcal{K}(p) = \text{kinetic energy of all atoms in system} \]

\[ \mathcal{K}^a(p^a, T) = \text{effective kinetic energy of atomic region} \]

\[ \mathcal{K}^c(\Gamma) = \text{kinetic energy of the continuum region} \]

\[ \mathcal{K}_{QC}(p^a, \Gamma, T) = \text{hot-QC-dynamic kinetic energy} \]

\[ M_l = \text{mass of node } l \text{ in the continuum region} \]

\[ m_i = \text{mass of atom } i \]

\[ N = \text{number of atoms}, N = N_{at} + N_c \]

\[ N_{at} = \text{number of atoms in the atomic region} \]

\[ N_c = \text{number of atoms in the continuum region} \]

\[ N_{chem} = \text{number of elements in the continuum region} \]


