# Quasiharmonic free energy and derivatives for three-body interactions

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Quasiharmonic lattice dynamics applied to crystals of atoms interacting via general rotationally and translationally invariant short-ranged three-body forces is considered. Expressions for the static energy and its first and second derivatives, and the free energy and its first derivatives, are presented, where the differentiation is with respect to internal (atomic positions) and external (macroscopic deformation) strains. Some results of applying the theory to $\alpha$-quartz are given. The paper extends the work of Taylor et al. [M. B. Taylor et al, Phys. Rev. B **56**, 14380 (1997)] in which more careful consideration of the basic theory has been given, and detailed expressions for pairwise short-ranged and Coulombic interactions were presented.

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## I. INTRODUCTION

In principle lattice dynamics is an attractive route for the theoretical calculation of the thermodynamic properties of crystals with periodic symmetry[1]. Quantum effects are readily taken into account and the method does not rely on long runs for high precision. Unstable vibrational modes provide a sensitive test for interionic potentials and interpretation of the normal modes is straightforward, revealing, for example, the mechanisms of phase transitions or thermal expansion. Given the optimised geometry of a crystal, calculations of the free energy, heat capacity, thermal expansion and other equilibrium thermodynamic properties is rapid and accurate[2]. The kinetic barriers and critical slowing-down effects suffered by Monte Carlo (MC) and molecular dynamics (MD) techniques are avoided. Not only

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does lattice dynamics allow the calculation of equilibrium structures of crystals as a function of temperature and pressure, but it is also a very efficient route to the free energy of particular configurations of *disordered* solids. This is the basis of a recently proposed methodology[3] for obtaining the free energy of disordered solids, which is quite different from standard approaches[7,8]. Not only can the new methodology prove much less expensive than classical MC and MD simulations, but it can also be used below the Debye temperature where these fail due to their neglect of quantum effects.

With lattice dynamics the bulk of the computational effort is generally expended in the optimization problem of finding the equilibrium geometry of the crystal[9] at a given temperature and pressure. For efficient optimization it is necessary to use the derivatives of the appropriate thermodynamic potential with respect to the geometrical coordinates (or strains). Until very recently the small number of existing generally available lattice dynamics codes[4–6] either neglected vibrational contributions to these derivatives or generated them *numerically* which is prohibitively expensive for large unit cells with many internal coordinates. In ref. 1 we developed the general theory, using lattice statics and lattice dynamics within the quasiharmonic approximation, for the *analytic* calculation of the free energy and its first derivatives with respect to parameters of the crystal geometry. Careful consideration was also given to the problem of the best use of these quantities to perform the full structure optimization of systems with large unit cells containing hundreds of ions. Detailed expressions were presented[1] for all the lattice sums required for particles assumed to interact via long-ranged Coulomb forces and arbitrary short-ranged spherically-symmetric pair potentials. These expressions have formed the basis for a new code[10] developed at Bristol designed for the efficient study of periodic structures with many internal strains. Applications to ionic solids have included phase transitions in $MgF_2$[11], defect free energies[12], surface energies[13] and the thermal expansion of complex oxides[13].

Although most simulations in solid state physics have used pairwise interatomic potentials, it is clear that three-body forces play an important role in the dynamics and stability of many systems. Three-body interactions are very important for instance for compounds containing polyatomic ions such as silicates[14] and sulphates[15] and are an essential part of the forcefields for organic systems[16]. In this paper we present the additional expressions required for general short-ranged three-body potentials, and give an example of the application of the theory to a silicate material.

We do not repeat here the details of the discussions given in ref. 1, but in the next section we summarise the essential points of the general theory of quasiharmonic free energy minimization needed for our present purposes. In section III the expressions required for calculating the free energy and its derivatives, assuming a general three-body potential, are presented and the final expressions for an example potential form are given. Since derivation of these formulae is time-consuming and error-prone, we have taken care to present here, in a form which requires a minimum of additional algebraic work, all the expressions required for efficient implementation of the theory in a computer program. Finally section IV presents the results of applying the theory to $\alpha$-quartz.

## II. THEORETICAL BACKGROUND

### A. Crystal geometry

Geometrical optimization of a crystal structure involves finding the most stable state given a set of thermodynamic constraints, and hence the minimization of the appropriate thermodynamic potential. At finite temperature $T$ and fixed volume $V$ the appropriate potential is the Helmholtz free energy $F$. At temperature $T$ under an applied hydrostatic pressure $P_0$ the appropriate potential is an availability $\widetilde{G}$, defined

$$\widetilde{G} = F + P_0 V = \Phi_{\text{stat}} + F_{\text{vib}} + P_0 V \tag{1}$$

where $F$ has static and vibrational parts $\Phi_{\text{stat}}$ and $F_{\text{vib}}$ respectively. In order to proceed further, $F$ must be expressed as a function of the geometrical parameters, or coordinates in a configuration space, of the structure, with respect to which it can be minimised. These coordinates may be classfied into two types: *external* ones which describe macroscopic deformation of the crystal, and *internal* ones which describe the positions of the atoms within the crystal lattice.

The positions of all the particles (which in a shell model[17] may be massive "cores" or massless "shells") in a macroscopically strained crystal may be given by Cartesian coordinates

$$r^{\alpha}_{i\mathbf{x}} = \sum_{\gamma} (\delta_{\alpha\gamma} + e^{\alpha\gamma})(x^{\gamma} + \rho^{\gamma}_{i}) \tag{2}$$

where Greek superscripts are Cartesian indices $1\ldots3$ (as throughout this paper), $\mathbf{x}$ is a lattice vector of the unstrained crystal labelling a unit cell, $i = 1\ldots n$ is an index that labels a specific particle within a unit cell, and $\delta_{\alpha\beta}$ is the

Kronecker delta. Components of the tensor $e^{\alpha\beta}$ are then a set of external strains which determine both the orientation and the macroscopic state of strain of the crystal[18]. The vector components $\rho_i^\alpha$ are internal coordinates determining the positions of particles within a unit cell.

It can be convenient, if a symmetrical structure is being considered, to define the coordinates $\boldsymbol{\rho}_i$ in terms of a set of offsets of magnitude $w_m$ in directions $\mathbf{h}_{m,i}$ from base positions $\mathring{\boldsymbol{\rho}}_i$:

$$\rho_i^\alpha = \mathring{\rho}_i^\alpha + \sum_m w_m h_{m,i}^\alpha \tag{3}$$

or equivalently, expressing the directions as vectors $\mathbf{g}_{m,i}$ in unit cell space

$$\rho_i^\alpha = \mathring{\rho}_i^\alpha + \sum_m w_m \left( g_{m,i}^1 a_1^\alpha + g_{m,i}^2 a_2^\alpha + g_{m,i}^3 a_3^\alpha \right) \tag{4}$$

where $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the unit cell vectors. In this way it may be possible to parameterise the state of internal strain of the crystal using considerably fewer than the $3n-3$ coordinates which would otherwise be required. An example of such parameterization is given in section IV.

If the vector of derivatives of the free energy with respect to all the strains of interest can be generated then various methods may be used to iterate towards a free energy minimum. The function can of course be differentiated numerically, but this is prohibitively slow for large unit cells. In sections II B and III we show how the free energy derivatives can be generated analytically. The method we have found to be most efficient is a variant of the quasi-Newton method[19] which uses the static energy Hessian as an approximation to the free energy Hessian, and we therefore give expressions below for the static second derivatives as well as the static and dynamic first derivatives. Parameterisation of the crystal structure, and the optimization algorithms, are discussed in more detail in refs. 1 and 10.

### B. Lattice dynamics

The static energy $\Psi$ of an entire crystal as defined in section II A is assumed to be a function of the positions $\mathbf{r}_{i\mathbf{x}}$ of the particles comprising the crystal. Each particle $i$ will be either a core of mass $m_i > 0$ or a shell of mass $m_i = 0$. Information about the restoring forces acting on each ion is given by the matrix $B(\mathbf{q})$, defined as the Fourier transform of the second derivatives of the energy with respect to particle position. Assuming translational invariance of the crystal, $B(\mathbf{q})$ can be written

$$B_{ij}^{\alpha\beta}(\mathbf{q}) = \sum_{\mathbf{x}} e^{i\mathbf{q}.\mathbf{x}} \frac{\partial^2 \Psi}{\partial r_{i\mathbf{0}}^\alpha \partial r_{j\mathbf{x}}^\beta} \tag{5}$$

In this section we use Greek *sub*scripts to refer to Cartesian components of particle positions, i.e. each represents a pair of indices such as ${}_i^\alpha$ such that the coordinates ranged over are those of certain types of particle:

$\chi,\ \chi',\ \ldots$ — cores only
$\sigma,\ \sigma',\ \ldots$ — shells only
$\tau,\ \tau',\ \ldots$ — both cores and shells

Additionally, $m_\chi$ is the mass of the particle corresponding to the coordinate $\chi$. Equation (5) can therefore be expressed instead

$$B_{\chi\chi'}(\mathbf{q}) = \sum_{\mathbf{x}} e^{i\mathbf{q}.\mathbf{x}} \frac{\partial^2 \Psi}{\partial r_{\chi\mathbf{0}} \partial r_{\chi'\mathbf{x}}} \tag{6}$$

We consider first the situation (*rigid ion*) in which there are only cores and no shells. In this case (here and subsequently the $(\mathbf{q})$ dependence is implicit) the *dynamical matrix* $D$ may be constructed[20,21] from $B$

$$D_{\chi\chi'} = m_\chi^{-1/2} B_{\chi\chi'} m_{\chi'}^{-1/2} \tag{7}$$

Then solving the characteristic equation

$$\sum_{\chi'} D_{\chi\chi'} f_{\chi',\chi''} = \omega^2_{\chi''} f_{\chi,\chi''} \tag{8}$$

gives the set of $3n$ vibrational frequencies $\omega_{\chi''}$ allowed in the crystal for each wave vector $\mathbf{q}$, and their associated eigenvectors $\mathbf{f}_{\chi''}$. First order perturbation theory can then be applied to yield the derivatives of the eigenvalues:

$$\left[\omega^2_{\chi}\right]' = \sum_{\tau\tau'} b^*_{\tau,\chi} B'_{\tau\tau'} b_{\tau',\chi} \tag{9}$$

where a primed quantity (other than an index) indicates the derivative of that quantity with respect to a general strain, and where $b_{\tau,\chi'}$ is the mass-adjusted eigenvector

$$b_{\tau,\chi'} = b_{\chi,\chi'} = f_{\chi,\chi'} m_{\chi}^{-1/2} \tag{10}$$

From the frequencies $\omega_{\chi}(\mathbf{q})$ and their strain derivatives it is then straightforward to obtain the vibrational parts of the free energy at a wave vector $\mathbf{q}$ and its strain derivatives. Integrating numerically over the Brillouin zone then gives the quantities required for geometrical optimization[1].

This theory may be extended to the shell model case[17], in which some of the particles have zero mass, by making two changes to these expressions: the frequencies are obtained from (8) if (7) is generalised to

$$D_{\chi\chi'} = m_{\chi}^{-1/2}\left[B_{\chi\chi'} - \sum_{\sigma\sigma'} B_{\chi\sigma} B^{-1}_{\sigma\sigma'} B_{\sigma'\chi'}\right] m_{\chi'}^{-1/2} \tag{11}$$

and the frequency derivatives are obtained from (9) if (10) is generalised by defining also elements for the shell coordinates:

$$b_{\tau,\chi'} = \begin{pmatrix} b_{\chi,\chi'} \\ b_{\sigma,\chi'} \end{pmatrix} = \begin{pmatrix} f_{\chi,\chi'} m_{\chi}^{-1/2} \\ -\sum_{\sigma'\chi''} B^{-1}_{\sigma\sigma'} B_{\sigma'\chi''} f_{\chi'',\chi'} m_{\chi''}^{-1/2} \end{pmatrix} \tag{12}$$

This discussion, although less thorough, is equivalent to the one given in ref. 1; the expressions (9) and (12) however are somewhat more elegant than equations (32) and (34) from that paper.

## III. THREE BODY INTERACTIONS

### A. Theory for general interaction form

The theory developed in ref. 1 and applied there to pairwise interactions can also be used to treat three body interactions. The static energy per unit cell of a translationally invariant crystal of infinite extent may be written in terms of two- and three-body translationally invariant potentials $\hat{\phi}$ and $\hat{\zeta}$ respectively as

$$\Phi_{\mathrm{stat}} = \Phi_2 + \Phi_3 = \sum_{\mathbf{x}}\sum_{ij} \hat{\phi}_{ij}\left(\mathbf{r}_{i\mathbf{0}}, \mathbf{r}_{j\mathbf{x}}\right) + \sum_{\mathbf{xy}}\sum_{ijk} \hat{\zeta}_{ijk}\left(\mathbf{r}_{i\mathbf{0}}, \mathbf{r}_{j\mathbf{x}}, \mathbf{r}_{k\mathbf{y}}\right) \tag{13}$$

The pairwise part of $\Phi_{\mathrm{stat}}$, $\Phi_2$, is treated in ref. 1; for the rest of this paper we concern ourselves only with the three-body part $\Phi_3$. Assuming additionally rotational invariance of the interactions, $\Phi_3$ may be expressed without loss of generality

$$\Phi_3 = \sum_{\mathbf{xy}}\sum_{ijk} \zeta_{ijk}\left(r_1\begin{bmatrix}\mathbf{0xy}\\ ijk\end{bmatrix}, r_2\begin{bmatrix}\mathbf{0xy}\\ ijk\end{bmatrix}, \cos\theta\begin{bmatrix}\mathbf{0xy}\\ ijk\end{bmatrix}\right) \equiv \sum_{\mathbf{xy}}\sum_{ijk} \zeta\begin{bmatrix}\mathbf{0xy}\\ ijk\end{bmatrix} \tag{14}$$

where

$$\mathbf{r}_1\begin{bmatrix}\mathbf{0xy}\\ ijk\end{bmatrix} = \mathbf{r}_{j\mathbf{x}} - \mathbf{r}_{i\mathbf{0}} \tag{15}$$

$$\mathbf{r}_2\begin{bmatrix}\mathbf{0xy}\\ ijk\end{bmatrix} = \mathbf{r}_{k\mathbf{y}} - \mathbf{r}_{i\mathbf{0}} \tag{16}$$

$$\cos\theta\begin{bmatrix}\mathbf{0xy}\\ ijk\end{bmatrix} = \frac{\mathbf{r}_1\begin{bmatrix}\mathbf{0xy}\\ ijk\end{bmatrix} . \mathbf{r}_2\begin{bmatrix}\mathbf{0xy}\\ ijk\end{bmatrix}}{r_1\begin{bmatrix}\mathbf{0xy}\\ ijk\end{bmatrix} r_2\begin{bmatrix}\mathbf{0xy}\\ ijk\end{bmatrix}} \tag{17}$$

It is helpful to label the arguments of the function $\zeta$ as the elements of a vector $\mathbf{z}$:

$$\begin{pmatrix} z_1 \\ z_2 \\ z_3 \end{pmatrix} \equiv \begin{pmatrix} r_1 \\ r_2 \\ \cos\theta \end{pmatrix} \tag{18}$$

Here and subsequently, where the bracketed sextuples have been omitted for clarity they are assumed to be $\begin{bmatrix} \mathtt{0xy} \\ i\,j\,k \end{bmatrix}$. Then if we define the partial derivatives of $\zeta$ using the notation

$$Z = \zeta\ , \quad Z^a = \frac{\partial\zeta}{\partial z_a}\ , \quad Z^{ab} = \frac{\partial^2\zeta}{\partial z_a \partial z_b}\ , \quad \cdots \tag{19}$$

first and second derivatives of the potential with respect to arbitrary strains $\mathcal{E}_A$ are given by

$$\frac{\partial\zeta}{\partial\mathcal{E}_A} = \sum_a Z^a \frac{\partial z_a}{\partial\mathcal{E}_A} \tag{20}$$

$$\frac{\partial^2\zeta}{\partial\mathcal{E}_A\partial\mathcal{E}_B} = \sum_a Z^a \frac{\partial^2 z_a}{\partial\mathcal{E}_A\partial\mathcal{E}_B} + \sum_{ab} Z^{ab} \frac{\partial z_a}{\partial\mathcal{E}_A}\frac{\partial z_b}{\partial\mathcal{E}_B} \tag{21}$$

In this way different forms of interaction can be implemented by the relatively straightforward use of (19) to generate different geometric derivatives of $\zeta$. The general part of the derivative expressions $(\partial^n\mathbf{z}/\partial\mathcal{E}^n)$ on the other hand need be derived only once regardless of the form of (translationally and rotationally invariant) three body interaction.

The derivatives of $\zeta$ with respect to internal strains contain many Kronecker delta functions, since $\zeta\begin{bmatrix} \mathtt{0xy} \\ i\,j\,k \end{bmatrix}$ will depend on $\rho_u^\alpha$ only in the case that $u$ is equal to one of $i$, $j$ or $k$. It is convenient to define a set of quantities by factorizing out the delta functions where they occur in some of the required expressions. These quantities $(\mathbb{B}, \mathbb{G}, \ldots)$, expressions for which are given later (eqs. 53–60), are defined as follows

$$\left(\frac{\partial^2\cos\theta}{\partial\rho_u^\alpha\partial\rho_v^\beta}\right)_0 = \sum_{LM} \Delta_{uL}\Delta_{vM}\mathbb{B}_{LM}^{\alpha\beta} \tag{22}$$

$$\left(\frac{\partial\zeta}{\partial\rho_u^\alpha}\right)_0 = \sum_L \Delta_{uL}\mathbb{G}_L^\alpha \tag{23}$$

$$\left(\frac{\partial\zeta}{\partial e^{\mu\nu}}\right)_0 = \mathbb{P}^{\mu\nu} \tag{24}$$

$$\left(\frac{\partial^2\zeta}{\partial\rho_u^\alpha\partial e^{\mu\nu}}\right)_0 = \sum_L \Delta_{uL}\mathbb{H}_L^{\alpha\mu\nu} \tag{25}$$

$$\left(\frac{\partial^2\zeta}{\partial e^{\mu\nu}\partial e^{\sigma\tau}}\right)_0 = \mathbb{Q}^{\mu\nu\sigma\tau} \tag{26}$$

$$\left(\frac{\partial^2\zeta}{\partial\rho_u^\alpha\partial\rho_v^\beta}\right)_0 = \sum_{LM} \Delta_{uL}\Delta_{vM}\mathbb{D}_{LM}^{\alpha\beta} \tag{27}$$

$$\left(\frac{\partial\mathbb{D}_{LM}^{\alpha\beta}}{\partial\rho_t^\gamma}\right)_0 = \sum_N \Delta_{tN}\mathbb{E}_{LMN}^{\alpha\beta\gamma} \tag{28}$$

$$\left(\frac{\partial\mathbb{D}_{LM}^{\alpha\beta}}{\partial e^{\mu\nu}}\right)_0 = \mathbb{F}_{LM}^{\alpha\beta\mu\nu} \tag{29}$$

where subscripts $\begin{bmatrix} \mathtt{0xy} \\ i\,j\,k \end{bmatrix}$ as usual are implicit on everything except the differentiation variables and the summation variables, and the symbol $()_0$ indicates that derivatives are taken at zero external strain $(e^{\mu\nu} = 0)$. In the above each of the summation variables takes the values 1 and 2, and $\Delta$ is defined in terms of Kronecker deltas:

$$\Delta_{uL} \equiv \Delta_{uL}\begin{bmatrix} \mathtt{0xy} \\ i\,j\,k \end{bmatrix} = \begin{cases} \delta_{uj} - \delta_{ui} & L = 1 \\ \delta_{uk} - \delta_{ui} & L = 2 \end{cases} \tag{30}$$

In the final quantities of interest many of the delta functions are eliminated by the $i, j, k$ summations required for $\Phi_3$ and its derivatives. This also eliminates some of the summations so that the resulting expressions can be calculated more efficiently. For example, using (14) and (23) the derivative of the static energy with respect to internal strains is

$$\left(\frac{\partial \Phi_3}{\partial \rho_u^\alpha}\right)_0 = \sum_{\mathbf{xy}} \sum_{ijk} \left( \Delta_{u1}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,k\end{smallmatrix}\right] \mathbb{G}_1^\alpha\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,k\end{smallmatrix}\right] + \Delta_{u2}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,k\end{smallmatrix}\right] \mathbb{G}_2^\alpha\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,k\end{smallmatrix}\right] \right) \tag{31}$$

Because of the delta signs (30) the computation is reduced from a triple to a double summation over particles in the unit cell:

$$\left(\frac{\partial \Phi_3}{\partial \rho_u^\alpha}\right)_0 = \sum_{\mathbf{xy}} \left( \sum_{ik} \mathbb{G}_1^\alpha\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,u\,k\end{smallmatrix}\right] - \sum_{jk} \mathbb{G}_1^\alpha\left[\begin{smallmatrix}\mathbf{0xy}\\ u\,j\,k\end{smallmatrix}\right] + \sum_{ij} \mathbb{G}_2^\alpha\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,u\end{smallmatrix}\right] - \sum_{jk} \mathbb{G}_2^\alpha\left[\begin{smallmatrix}\mathbf{0xy}\\ u\,j\,k\end{smallmatrix}\right] \right) \tag{32}$$

$$= \sum_{\mathbf{xy}} \sum_{ij} \left( \mathbb{G}_1^\alpha\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,u\,j\end{smallmatrix}\right] + \mathbb{G}_2^\alpha\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,u\end{smallmatrix}\right] - \mathbb{G}_*^\alpha\left[\begin{smallmatrix}\mathbf{0xy}\\ u\,i\,j\end{smallmatrix}\right] \right) \tag{33}$$

where we have introduced a notation in which a subscripted $*$ indicates a summation of the terms formed by replacing it by a 1 and a 2, so that for instance

$$\mathbb{G}_*^\alpha\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,k\end{smallmatrix}\right] \equiv \mathbb{G}_1^\alpha\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,k\end{smallmatrix}\right] + \mathbb{G}_2^\alpha\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,k\end{smallmatrix}\right] \tag{34}$$

$$\mathbb{E}_{*2*}^{\alpha\beta\gamma}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,k\end{smallmatrix}\right] \equiv \mathbb{E}_{121}^{\alpha\beta\gamma}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,k\end{smallmatrix}\right] + \mathbb{E}_{122}^{\alpha\beta\gamma}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,k\end{smallmatrix}\right] + \mathbb{E}_{221}^{\alpha\beta\gamma}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,k\end{smallmatrix}\right] + \mathbb{E}_{222}^{\alpha\beta\gamma}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,k\end{smallmatrix}\right] \tag{35}$$

Similar manipulations may be applied to equations (24–27) to give expressions for the other static energy derivatives as follows:

$$\left(\frac{\partial \Phi_3}{\partial e^{\mu\nu}}\right)_0 = \sum_{\mathbf{xy}} \sum_{ijk} \mathbb{P}^{\mu\nu}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,k\end{smallmatrix}\right] \tag{36}$$

$$\left(\frac{\partial^2 \Phi_3}{\partial e^{\mu\nu}\partial e^{\sigma\tau}}\right)_0 = \sum_{\mathbf{xy}} \sum_{ijk} \mathbb{Q}^{\mu\nu\sigma\tau}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,k\end{smallmatrix}\right] \tag{37}$$

$$\left(\frac{\partial^2 \Phi_3}{\partial \rho_u^\alpha \partial e^{\mu\nu}}\right)_0 = \sum_{\mathbf{xy}} \sum_{ij} \left( \mathbb{H}_1^{\alpha\mu\nu}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,u\,j\end{smallmatrix}\right] + \mathbb{H}_2^{\alpha\mu\nu}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,u\end{smallmatrix}\right] - \mathbb{H}_*^{\alpha\mu\nu}\left[\begin{smallmatrix}\mathbf{0xy}\\ u\,i\,j\end{smallmatrix}\right] \right) \tag{38}$$

$$\left(\frac{\partial^2 \Phi_3}{\partial \rho_u^\alpha \rho_v^\beta}\right)_0 = \delta_{uv} \sum_{\mathbf{xy}} \sum_{ij} \left( \mathbb{D}_{11}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,u\,j\end{smallmatrix}\right] + \mathbb{D}_{22}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,j\,u\end{smallmatrix}\right] + \mathbb{D}_{**}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{0xy}\\ u\,i\,j\end{smallmatrix}\right] \right)$$

$$+ \sum_{\mathbf{xy}} \sum_{i} \left( \mathbb{D}_{12}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,u\,v\end{smallmatrix}\right] + \mathbb{D}_{21}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{0xy}\\ i\,v\,u\end{smallmatrix}\right] - \mathbb{D}_{1*}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{0xy}\\ v\,u\,i\end{smallmatrix}\right] - \mathbb{D}_{2*}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{0xy}\\ v\,i\,u\end{smallmatrix}\right] - \mathbb{D}_{*1}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{0xy}\\ u\,v\,i\end{smallmatrix}\right] - \mathbb{D}_{*2}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{0xy}\\ u\,i\,v\end{smallmatrix}\right] \right) \tag{39}$$

(40)

Derivatives with respect to the symmetric internal strains $w_m$ can be derived from those with respect to the basis internal strains $\rho_u^\alpha$ using (3).

Using (6), (14) and (27) and an extension of the $\Delta$ notation of (30):

$$\Delta_{vM}^{\mathbf{z}}\left[\begin{smallmatrix}\mathbf{wxy}\\ i\,j\,k\end{smallmatrix}\right] = \begin{cases} \delta_{vj}\delta_{\mathbf{zx}} - \delta_{vi}\delta_{\mathbf{zw}} & M = 1 \\ \delta_{vk}\delta_{\mathbf{zy}} - \delta_{vi}\delta_{\mathbf{zw}} & M = 2 \end{cases} \tag{41}$$

(where the Kronecker $\delta$ has been extended in an obvious way to apply to vectors) the massless part $B$ of the dynamical matrix can be written

$$B_{uv}^{\alpha\beta}(\mathbf{q}) = \sum_{\mathbf{z}} e^{i\mathbf{q}.\mathbf{z}} \sum_{\mathbf{wxy}} \sum_{ijk} \sum_{LM} \Delta_{uL}^{\mathbf{0}}\left[\begin{smallmatrix}\mathbf{wxy}\\ i\,j\,k\end{smallmatrix}\right] \Delta_{vM}^{\mathbf{z}}\left[\begin{smallmatrix}\mathbf{wxy}\\ i\,j\,k\end{smallmatrix}\right] \mathbb{D}_{LM}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{wxy}\\ i\,j\,k\end{smallmatrix}\right] \tag{42}$$

and applying the same manipulations which led to (39) then gives

$$B_{uv}^{\alpha\beta}(\mathbf{q}) = \delta_{uv} \sum_{\mathbf{xy}} \sum_{ij} \left( \mathbb{D}_{11}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{x0y}\\ i\,u\,j\end{smallmatrix}\right] + \mathbb{D}_{22}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{xy0}\\ i\,j\,u\end{smallmatrix}\right] + \mathbb{D}_{**}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{0xy}\\ u\,i\,j\end{smallmatrix}\right] \right)$$

$$+ \sum_{\mathbf{xy}} \sum_{i} e^{i\mathbf{q}.\mathbf{x}} \left( \mathbb{D}_{12}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{y0x}\\ i\,u\,v\end{smallmatrix}\right] + \mathbb{D}_{21}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{yx0}\\ i\,v\,u\end{smallmatrix}\right] - \mathbb{D}_{1*}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{x0y}\\ v\,u\,i\end{smallmatrix}\right] - \mathbb{D}_{2*}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{xy0}\\ v\,i\,u\end{smallmatrix}\right] - \mathbb{D}_{*1}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{0xy}\\ u\,v\,i\end{smallmatrix}\right] - \mathbb{D}_{*2}^{\alpha\beta}\left[\begin{smallmatrix}\mathbf{0yx}\\ u\,i\,v\end{smallmatrix}\right] \right) \tag{43}$$

For an efficient computational implementation it is convenient to express this equation in a form which gathers together contributions from the same unit cell triples. This can be done by exchanging variables and shifting the origins of the $\mathbf{xy}$ summations to give

$$
\begin{aligned}
B_{uv}^{\alpha\beta}(\mathbf{q}) = {} & \delta_{uv} \sum_{\mathbf{xy}} \sum_{ij} \left( \mathbb{D}_{11}^{\alpha\beta} \begin{bmatrix} \mathbf{0xy} \\ i\,u\,j \end{bmatrix} + \mathbb{D}_{22}^{\alpha\beta} \begin{bmatrix} \mathbf{0xy} \\ i\,j\,u \end{bmatrix} + \mathbb{D}_{**}^{\alpha\beta} \begin{bmatrix} \mathbf{0xy} \\ u\,i\,j \end{bmatrix} \right) \\
& + \sum_{\mathbf{xy}} \sum_{i} \left( e^{i\mathbf{q}.(\mathbf{y}-\mathbf{x})} \mathbb{D}_{12}^{\alpha\beta} \begin{bmatrix} \mathbf{0xy} \\ i\,u\,v \end{bmatrix} + e^{i\mathbf{q}.(\mathbf{x}-\mathbf{y})} \mathbb{D}_{21}^{\alpha\beta} \begin{bmatrix} \mathbf{0xy} \\ i\,v\,u \end{bmatrix} - e^{i\mathbf{q}.(-\mathbf{x})} \mathbb{D}_{1*}^{\alpha\beta} \begin{bmatrix} \mathbf{0xy} \\ v\,u\,i \end{bmatrix} - e^{i\mathbf{q}.(-\mathbf{y})} \mathbb{D}_{2*}^{\alpha\beta} \begin{bmatrix} \mathbf{0xy} \\ v\,i\,u \end{bmatrix} \right. \\
& \left. - e^{i\mathbf{q}.\mathbf{x}} \mathbb{D}_{*1}^{\alpha\beta} \begin{bmatrix} \mathbf{0xy} \\ u\,v\,i \end{bmatrix} - e^{i\mathbf{q}.\mathbf{y}} \mathbb{D}_{*2}^{\alpha\beta} \begin{bmatrix} \mathbf{0xy} \\ u\,i\,v \end{bmatrix} \right)
\end{aligned} \qquad (44)
$$

The dynamical matrix derivatives can then be expressed in terms of $\mathbb{E}$ and $\mathbb{F}$ (27–29) as follows:

$$
\begin{aligned}
\left( \frac{\partial B_{uv}^{\alpha\beta}(\mathbf{q})}{\partial e^{\mu\nu}} \right)_0 = {} & \delta_{uv} \sum_{\mathbf{xy}} \sum_{ij} \left( \mathbb{F}_{11}^{\alpha\beta\mu\nu} \begin{bmatrix} \mathbf{0xy} \\ i\,u\,j \end{bmatrix} + \mathbb{F}_{22}^{\alpha\beta\mu\nu} \begin{bmatrix} \mathbf{0xy} \\ i\,j\,u \end{bmatrix} + \mathbb{F}_{**}^{\alpha\beta\mu\nu} \begin{bmatrix} \mathbf{0xy} \\ u\,i\,j \end{bmatrix} \right) \\
& + \sum_{\mathbf{xy}} \sum_{i} \left( e^{i\mathbf{q}.(\mathbf{y}-\mathbf{x})} \mathbb{F}_{12}^{\alpha\beta\mu\nu} \begin{bmatrix} \mathbf{0xy} \\ i\,u\,v \end{bmatrix} + e^{i\mathbf{q}.(\mathbf{x}-\mathbf{y})} \mathbb{F}_{21}^{\alpha\beta\mu\nu} \begin{bmatrix} \mathbf{0xy} \\ i\,v\,u \end{bmatrix} - e^{i\mathbf{q}.(-\mathbf{x})} \mathbb{F}_{1*}^{\alpha\beta\mu\nu} \begin{bmatrix} \mathbf{0xy} \\ v\,u\,i \end{bmatrix} \right. \\
& \left. - e^{i\mathbf{q}.(-\mathbf{y})} \mathbb{F}_{2*}^{\alpha\beta\mu\nu} \begin{bmatrix} \mathbf{0xy} \\ v\,i\,u \end{bmatrix} - e^{i\mathbf{q}.\mathbf{x}} \mathbb{F}_{*1}^{\alpha\beta\mu\nu} \begin{bmatrix} \mathbf{0xy} \\ u\,v\,i \end{bmatrix} - e^{i\mathbf{q}.\mathbf{y}} \mathbb{F}_{*2}^{\alpha\beta\mu\nu} \begin{bmatrix} \mathbf{0xy} \\ u\,i\,v \end{bmatrix} \right)
\end{aligned} \qquad (45)
$$

$$
\begin{aligned}
\left( \frac{\partial B_{uv}^{\alpha\beta}(\mathbf{q})}{\partial \rho_t^{\gamma}} \right)_0 = {} & \delta_{tu}\delta_{tv} \sum_{\mathbf{xy}} \sum_{ij} \left( \mathbb{E}_{111}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ i\,u\,j \end{bmatrix} + \mathbb{E}_{222}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ i\,j\,u \end{bmatrix} - \mathbb{E}_{***}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ u\,i\,j \end{bmatrix} \right) \\
& + \delta_{uv} \sum_{\mathbf{xy}} \sum_{i} \left( -\mathbb{E}_{11*}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ t\,u\,i \end{bmatrix} - \mathbb{E}_{22*}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ t\,i\,u \end{bmatrix} + \mathbb{E}_{**2}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ u\,i\,t \end{bmatrix} + \mathbb{E}_{**1}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ u\,t\,i \end{bmatrix} + \mathbb{E}_{112}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ i\,u\,t \end{bmatrix} + \mathbb{E}_{221}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ i\,t\,u \end{bmatrix} \right) \\
& + \delta_{tv} \sum_{\mathbf{xy}} \sum_{i} \left( -e^{i\mathbf{q}.\mathbf{x}} \mathbb{E}_{*11}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ u\,v\,i \end{bmatrix} - e^{i\mathbf{q}.\mathbf{y}} \mathbb{E}_{*22}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ u\,i\,v \end{bmatrix} + e^{i\mathbf{q}.(-\mathbf{x})} \mathbb{E}_{1**}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ v\,u\,i \end{bmatrix} \right. \\
& \left. + e^{i\mathbf{q}.(-\mathbf{y})} \mathbb{E}_{2**}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ v\,i\,u \end{bmatrix} + e^{i\mathbf{q}.(\mathbf{y}-\mathbf{x})} \mathbb{E}_{122}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ i\,u\,v \end{bmatrix} + e^{i\mathbf{q}.(\mathbf{x}-\mathbf{y})} \mathbb{E}_{211}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ i\,v\,u \end{bmatrix} \right) \\
& + \delta_{tu} \sum_{\mathbf{xy}} \sum_{i} \left( -e^{i\mathbf{q}.(-\mathbf{x})} \mathbb{E}_{1*1}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ v\,u\,i \end{bmatrix} - e^{i\mathbf{q}.(-\mathbf{y})} \mathbb{E}_{2*2}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ v\,i\,u \end{bmatrix} + e^{i\mathbf{q}.\mathbf{x}} \mathbb{E}_{*1*}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ u\,v\,i \end{bmatrix} \right. \\
& \left. + e^{i\mathbf{q}.\mathbf{y}} \mathbb{E}_{*2*}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ u\,i\,v \end{bmatrix} + e^{i\mathbf{q}.(\mathbf{y}-\mathbf{x})} \mathbb{E}_{121}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ i\,u\,v \end{bmatrix} + e^{i\mathbf{q}.(\mathbf{x}-\mathbf{y})} \mathbb{E}_{212}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ i\,v\,u \end{bmatrix} \right) \\
& + \sum_{\mathbf{xy}} \left( -e^{i\mathbf{q}.(\mathbf{y}-\mathbf{x})} \mathbb{E}_{12*}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ t\,u\,v \end{bmatrix} - e^{i\mathbf{q}.(\mathbf{x}-\mathbf{y})} \mathbb{E}_{21*}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ t\,v\,u \end{bmatrix} - e^{i\mathbf{q}.(-\mathbf{x})} \mathbb{E}_{1*2}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ v\,u\,t \end{bmatrix} \right. \\
& \left. - e^{i\mathbf{q}.(-\mathbf{y})} \mathbb{E}_{2*1}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ v\,t\,u \end{bmatrix} - e^{i\mathbf{q}.\mathbf{x}} \mathbb{E}_{*12}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ u\,v\,t \end{bmatrix} - e^{i\mathbf{q}.\mathbf{y}} \mathbb{E}_{*21}^{\alpha\beta\gamma} \begin{bmatrix} \mathbf{0xy} \\ u\,t\,v \end{bmatrix} \right)
\end{aligned} \qquad (46)
$$

$$(47)$$

Making use of the further definitions

$$s_L^{\alpha} = r_L^{-1} r_L^{\alpha} \qquad (48)$$

$$\mathbb{A}_L^{\alpha} = r_L^{-1} \left( s_{\overline{L}}^{\alpha} - s_L^{\alpha} \cos\theta \right) \qquad (49)$$

$$\mathbb{C}_L^{\alpha\beta} = r_L^{-1} \left( \delta_{\alpha\beta} - s_L^{\alpha} s_L^{\beta} \right) \qquad (50)$$

$$\mathbb{S}_L^{\alpha\mu\nu} = \mathbb{C}_L^{\alpha\mu} s_L^{\nu} \qquad (51)$$

$$\mathbb{K}^{\mu\nu} = \left( s_1^{\mu} r_1 \mathbb{A}_1^{\nu} + s_2^{\mu} r_2 \mathbb{A}_2^{\nu} \right) \qquad (52)$$

the terms defined in (22–29) can be shown using the general formulae (20) and (21) to be

$$\mathbb{B}_{LM}^{\alpha\beta} = r_L^{-1} r_M^{-1} \left( \delta_{LM} \left[ (3 s_L^{\alpha} s_L^{\beta} - \delta_{\alpha\beta}) \cos\theta - s_L^{\alpha} s_{\overline{L}}^{\beta} - s_{\overline{L}}^{\alpha} s_L^{\beta} \right] + \delta_{L\overline{M}} \left[ s_L^{\alpha} s_M^{\beta} \cos\theta - s_L^{\alpha} s_L^{\beta} - s_M^{\alpha} s_M^{\beta} + \delta_{\alpha\beta} \right] \right) \qquad (53)$$

$$\mathbb{G}_L^{\alpha} = Z^L s_L^{\alpha} + Z^3 \mathbb{A}_L^{\alpha} \qquad (54)$$

$$\mathbb{P}^{\mu\nu} = Z^1 r_1 s_1^{\mu} s_1^{\nu} + Z^2 r_2 s_2^{\mu} s_2^{\nu} + Z^3 \mathbb{K}^{\mu\nu} \qquad (55)$$

$$\mathbb{H}_L^{\alpha\mu\nu} = Z^L \left[ \delta_{\alpha\mu} s_L^{\nu} + \delta_{\alpha\nu} s_L^{\mu} - s_L^{\alpha} s_L^{\mu} s_L^{\nu} \right] + Z^3 \left[ r_L \mathbb{A}_L^{\mu} \mathbb{C}_L^{\alpha\nu} + r_L \mathbb{A}_L^{\nu} \mathbb{C}_L^{\alpha\mu} - \mathbb{A}_L^{\alpha} ( s_L^{\mu} s_L^{\nu} + s_{\overline{L}}^{\mu} s_{\overline{L}}^{\nu} ) \right]$$

$$
+ s_L^\alpha \left[Z^{L1} r_1 s_1^\mu s_1^\nu + Z^{L2} r_2 s_2^\mu s_2^\nu + Z^{L3}\mathbb{K}^{\mu\nu}\right] + \mathbb{A}_L^\alpha \left[Z^{31} r_1 s_1^\mu s_1^\nu + Z^{32} r_2 s_2^\mu s_2^\nu + Z^{33}\mathbb{K}^{\mu\nu}\right] \tag{56}
$$

$$
\begin{aligned}
\mathbb{Q}^{\mu\nu\sigma\tau} &= Z^1 r_1^2 s_1^\nu s_1^\tau \mathbb{C}_1^{\mu\sigma} + Z^2 r_2^2 s_2^\nu s_2^\tau \mathbb{C}_2^{\mu\sigma} + Z^3 \Big( \left[s_1^\mu s_1^\nu (3 s_1^\sigma s_1^\tau + s_2^\sigma s_2^\tau) + s_2^\mu s_2^\nu (3 s_2^\sigma s_2^\tau + s_1^\sigma s_1^\tau)\right] \cos\theta \\
&\quad - \left[(s_1^\mu s_1^\nu + s_2^\mu s_2^\nu)(s_1^\sigma s_2^\tau + s_2^\sigma s_1^\tau) + (s_1^\mu s_2^\nu + s_2^\mu s_1^\nu)(s_1^\sigma s_1^\tau + s_2^\sigma s_2^\tau)\right] + \delta_{\mu\sigma}\mathbb{K}^{\nu\tau} \Big) \\
&\quad + Z^{11} r_1 s_1^\mu s_1^\nu r_1 s_1^\sigma s_1^\tau + Z^{12} r_1 s_1^\mu s_1^\nu r_2 s_2^\sigma s_2^\tau + Z^{21} r_2 s_2^\mu s_2^\nu r_1 s_1^\sigma s_1^\tau + Z^{22} r_2 s_2^\mu s_2^\nu r_2 s_2^\sigma s_2^\tau \\
&\quad + \mathbb{K}^{\mu\nu}\left[Z^{31} r_1 s_1^\sigma s_1^\tau + Z^{32} r_2 s_2^\sigma s_2^\tau\right] + \mathbb{K}^{\sigma\tau}\left[Z^{13} r_1 s_1^\mu s_1^\nu + Z^{23} r_2 s_2^\mu s_2^\nu\right] + \mathbb{K}^{\mu\nu}\mathbb{K}^{\sigma\tau} Z^{33}
\end{aligned} \tag{57}
$$

$$
\mathbb{D}_{LM}^{\alpha\beta} = \delta_{LM} Z^L \mathbb{C}_L^{\alpha\beta} + Z^3 \mathbb{B}_{LM}^{\alpha\beta} + Z^{LM} s_L^\alpha s_M^\beta + Z^{L3} s_L^\alpha \mathbb{A}_M^\beta + Z^{3M}\mathbb{A}_L^\alpha s_M^\beta + Z^{33}\mathbb{A}_L^\alpha \mathbb{A}_M^\beta \tag{58}
$$

$$
\begin{aligned}
\mathbb{E}_{LMN}^{\alpha\beta\gamma} &= \delta_{LM}\delta_{LN}\Big(r_L^{-2} Z^3 \left[\mathbb{C}_N^{\alpha\gamma}(3 s_M^\beta \cos\theta - s_{\overline{M}}^\beta) + \mathbb{C}_N^{\beta\gamma}(3 s_L^\alpha \cos\theta - s_{\overline{L}}^\alpha)\right] - r_N^{-1} Z^N \left[s_L^\alpha \mathbb{C}_N^{\beta\gamma} + s_M^\beta \mathbb{C}_N^{\alpha\gamma} + s_N^\gamma \mathbb{C}_N^{\alpha\beta}\right]\Big) \\
&\quad - \delta_{LM}\delta_{L\overline{N}} r_L^{-2} Z^3 \left[s_L^\alpha \mathbb{C}_N^{\beta\gamma} + s_M^\beta \mathbb{C}_N^{\alpha\gamma}\right] + \delta_{LM}\left[r_L^{-2} Z^3 \mathbb{A}_N^\gamma (3 s_L^\alpha s_M^\beta - \delta_{\alpha\beta}) + Z^{LN} s_N^\gamma \mathbb{C}_L^{\alpha\beta} + Z^{L3}\mathbb{A}_N^\gamma \mathbb{C}_L^{\alpha\beta}\right] \\
&\quad + \delta_{L\overline{M}} r_L^{-1} r_M^{-1} Z^3 \left[s_L^\alpha s_M^\beta \mathbb{A}_N^\gamma - \delta_{LN}(r_M \mathbb{A}_M^\beta \mathbb{C}_N^{\alpha\gamma} + \mathbb{C}_N^{\beta\gamma} s_L^\alpha) - \delta_{MN}(\mathbb{C}_N^{\alpha\gamma} s_M^\beta + r_L \mathbb{A}_L^\alpha \mathbb{C}_N^{\beta\gamma})\right] \\
&\quad + \delta_{LN}\left[\mathbb{C}_N^{\alpha\gamma}(Z^{LM} s_M^\beta + Z^{L3}\mathbb{A}_M^\beta) - r_N^{-1}(s_L^\alpha \mathbb{A}_N^\gamma + s_N^\gamma \mathbb{A}_L^\alpha + \mathbb{C}_N^{\alpha\gamma}\cos\theta)(Z^{3M} s_M^\beta + Z^{33}\mathbb{A}_M^\beta) - r_N^{-1} s_N^\gamma Z^3 \mathbb{B}_{LM}^{\alpha\beta}\right] \\
&\quad + \delta_{MN}\left[\mathbb{C}_N^{\beta\gamma}(Z^{LM} s_L^\alpha + Z^{3M}\mathbb{A}_L^\alpha) - r_N^{-1}(s_M^\beta \mathbb{A}_N^\gamma + s_N^\gamma \mathbb{A}_M^\beta + \mathbb{C}_N^{\beta\gamma}\cos\theta)(Z^{L3} s_L^\alpha + Z^{33}\mathbb{A}_L^\alpha) - r_N^{-1} s_N^\gamma Z^3 \mathbb{B}_{LM}^{\alpha\beta}\right] \\
&\quad + \delta_{L\overline{N}} r_L^{-1}\left[\mathbb{C}_N^{\alpha\gamma} - s_L^\alpha \mathbb{A}_N^\gamma\right]\left[Z^{3M} s_M^\beta + Z^{33}\mathbb{A}_M^\beta\right] + \delta_{M\overline{N}} r_M^{-1}\left[\mathbb{C}_N^{\beta\gamma} - s_M^\beta \mathbb{A}_N^\gamma\right]\left[Z^{L3} s_L^\alpha + Z^{33}\mathbb{A}_L^\alpha\right] \\
&\quad + s_N^\gamma \left[Z^{3N}\mathbb{B}_{LM}^{\alpha\beta} + Z^{LMN} s_L^\alpha s_M^\beta + Z^{L3N} s_L^\alpha \mathbb{A}_M^\beta + Z^{3MN}\mathbb{A}_L^\alpha s_M^\beta + Z^{33N}\mathbb{A}_L^\alpha \mathbb{A}_M^\beta\right] \\
&\quad + \mathbb{A}_N^\gamma \left[Z^{33}\mathbb{B}_{LM}^{\alpha\beta} + Z^{LM3} s_L^\alpha s_M^\beta + Z^{L33} s_L^\alpha \mathbb{A}_M^\beta + Z^{3M3}\mathbb{A}_L^\alpha s_M^\beta + Z^{333}\mathbb{A}_L^\alpha \mathbb{A}_M^\beta\right]
\end{aligned} \tag{59}
$$

$$
\begin{aligned}
\mathbb{F}_{LM}^{\alpha\beta\mu\nu} &= \delta_{LM}\Big(-Z^L \left[\mathbb{S}_L^{\alpha\mu\nu} s_L^\beta + s_L^\alpha \mathbb{S}_L^{\beta\mu\nu} + s_L^\mu s_L^\nu \mathbb{C}_L^{\alpha\beta}\right] + \mathbb{C}_L^{\alpha\beta}\left[Z^{L1} s_1^\mu s_1^\nu r_1 + Z^{L2} s_2^\mu s_2^\nu r_2 + Z^{L3}\mathbb{K}^{\mu\nu}\right] \\
&\quad + Z^3 r_L^{-2}\Big[\mathbb{K}^{\mu\nu}(3 s_L^\alpha s_L^\beta - \delta_{\alpha\beta}) + r_L \mathbb{S}_L^{\alpha\mu\nu}(3 s_L^\beta \cos\theta - s_{\overline{L}}^\beta) + r_L \mathbb{S}_L^{\beta\mu\nu}(3 s_L^\alpha \cos\theta - s_{\overline{L}}^\alpha) \\
&\quad - r_{\overline{L}} \mathbb{S}_{\overline{L}}^{\beta\mu\nu} s_L^\alpha - r_{\overline{L}} \mathbb{S}_{\overline{L}}^{\alpha\mu\nu} s_L^\beta\Big]\Big) \\
&\quad + \delta_{L\overline{M}} Z^3 \left[r_L^{-1} r_M^{-1}\mathbb{K}^{\mu\nu} s_L^\alpha s_M^\beta - \mathbb{A}_L^\alpha \mathbb{S}_M^{\beta\mu\nu} - \mathbb{S}_L^{\alpha\mu\nu}\mathbb{A}_M^\beta - r_M^{-1} s_L^\alpha \mathbb{S}_M^{\beta\mu\nu} - r_L^{-1}\mathbb{S}_M^{\alpha\mu\nu} s_M^\beta\right] \\
&\quad - Z^3 \mathbb{B}_{LM}^{\alpha\beta}\left[s_L^\mu s_L^\nu + s_M^\mu s_M^\nu\right] + r_L \mathbb{S}_L^{\alpha\mu\nu}\left[Z^{LM} s_M^\beta + Z^{L3}\mathbb{A}_M^\beta\right] + r_M \mathbb{S}_M^{\beta\mu\nu}\left[Z^{LM} s_L^\alpha + Z^{3M}\mathbb{A}_L^\alpha\right] \\
&\quad + r_L^{-1}\left[r_{\overline{L}}\mathbb{S}_{\overline{L}}^{\alpha\mu\nu} - r_L \mathbb{S}_L^{\alpha\mu\nu}\cos\theta - s_L^\alpha \mathbb{K}^{\mu\nu} - r_L s_L^\mu s_L^\nu \mathbb{A}_L^\alpha\right]\left[Z^{3M} s_M^\beta + Z^{33}\mathbb{A}_M^\beta\right] \\
&\quad + r_M^{-1}\left[r_{\overline{M}}\mathbb{S}_{\overline{M}}^{\beta\mu\nu} - r_M \mathbb{S}_M^{\beta\mu\nu}\cos\theta - s_M^\beta \mathbb{K}^{\mu\nu} - r_M s_M^\mu s_M^\nu \mathbb{A}_M^\beta\right]\left[Z^{L3} s_L^\alpha + Z^{33}\mathbb{A}_L^\alpha\right] \\
&\quad + r_1 s_1^\mu s_1^\nu \left[Z^{31}\mathbb{B}_{LM}^{\alpha\beta} + Z^{LM1} s_L^\alpha s_M^\beta + Z^{L31} s_L^\alpha \mathbb{A}_M^\beta + Z^{3M1}\mathbb{A}_L^\alpha s_M^\beta + Z^{331}\mathbb{A}_L^\alpha \mathbb{A}_M^\beta\right] \\
&\quad + r_2 s_2^\mu s_2^\nu \left[Z^{32}\mathbb{B}_{LM}^{\alpha\beta} + Z^{LM2} s_L^\alpha s_M^\beta + Z^{L32} s_L^\alpha \mathbb{A}_M^\beta + Z^{3M2}\mathbb{A}_L^\alpha s_M^\beta + Z^{332}\mathbb{A}_L^\alpha \mathbb{A}_M^\beta\right] \\
&\quad + \mathbb{K}^{\mu\nu}\left[Z^{33}\mathbb{B}_{LM}^{\alpha\beta} + Z^{LM3} s_L^\alpha s_M^\beta + Z^{L33} s_L^\alpha \mathbb{A}_M^\beta + Z^{3M3}\mathbb{A}_L^\alpha s_M^\beta + Z^{333}\mathbb{A}_L^\alpha \mathbb{A}_M^\beta\right]
\end{aligned} \tag{60}
$$

### B. Application to harmonic exponential potentials

Given the above framework, the contributions to the static and dynamical parts of the free energy and its derivatives can be calculated for a general translationally and rotationally invariant three-body potential, as long as the $Z$ functions defined in (19) can be calculated. This is usually fairly straightforward; in this section we give an example of a potential which combines a harmonic dependence on angle and an exponential decay with distance:

$$
\zeta(r_1, r_2, \cos\theta) = k e^{-r_1/R_1} e^{-r_2/R_2} (\theta - \theta_0)^2 \tag{61}
$$

This leads to the derivative functions

$$Z = ke^{-r_1/R_1} e^{-r_2/R_2} (\theta - \theta_0)^2 \tag{62}$$
$$Z^3 = -2 \csc\theta \, ke^{-r_1/R_1} e^{-r_2/R_2} (\theta - \theta_0) \tag{63}$$
$$Z^{33} = \csc^2\theta \left( 2ke^{-r_1/R_1} e^{-r_2/R_2} + \cos\theta Z^3 \right) \tag{64}$$
$$Z^{333} = \csc^2\theta \left( Z^3 + 3\cos\theta Z^{33} \right) \tag{65}$$

The others are formed by multiplying a factor of $-1/R_L$ to introduce a superscript of $L = 1$ or 2, for instance

$$Z^{12} = \frac{1}{R_1 R_2} Z \ , \quad Z^{331} = -\frac{1}{R_1} Z^{33} \ , \quad \cdots \tag{66}$$

Assuming a well-behaved potential $\zeta$ it is clear from (19) that the order of the superscripts is immaterial.

Note that for the case of the potential (61) most of the $Z$ functions diverge for $\cos\theta = \pm 1$. This is not an indication of unphysical behaviour but simply an undesirable consequence of using $\cos\theta$ as an intermediate differentiation variable. To treat three body interactions between particles which may be collinear therefore, a different form of potential $\zeta$ must be used, e.g. one harmonic in $(\cos\theta - \cos\theta_0)$. Alternatively a set of expressions for the free energy and its derivatives which avoids the use of $\cos\theta$ may be derived.

## IV. EXAMPLE APPLICATION TO $\alpha$-QUARTZ

We end with a brief example, our treatment here being illustrative rather than comprehensive. The thermal expansion of $\alpha$-quartz has received considerable experimental[22] and theoretical[23–25] attention, and so it serves as an excellent example of our methodology. Quartz is optically active, the laevo- and dextro-rotatory form of $\alpha$-quartz belonging to the space groups $P3_121$ and $P3_221$ respectively. The structure consists of approximately regular $SiO_4$ tetrahedra sharing oxygen atoms at each vertex. The unit cell is hexagonal with nine atoms in the primitive cell. There are six structural parameters: the lattice parameters $a$ and $c$, and four internal coordinates $u$, $x$, $y$ and $z$ which parameterise the internal strain state of the atoms, according to equation (3), except we have renamed the $w_m$ as $u$, $x$, $y$, $z$. The position vectors in unit cell space of each atom can therefore be written as in table I. At 846 K $\alpha$-quartz undergoes a phase transition to $\beta$-quartz, which is a special case of the $\alpha$ structure, with hexagonal symmetry and retaining only one internal degree of freedom.

We start with a set of shell-model potential parameters due to Gale[25] listed in table II, which includes two-body interactions and a standard three-body harmonic-angle potential, of the form

$$\zeta = \frac{1}{2} k_\theta (\theta - \theta_0)^2 \tag{67}$$

where $\theta$ is the O-Si-O angle, $\theta_0 = 109.47°$ and both oxygen atoms are bonded to the same silicon.

### A. Thermal expansion

Figure 1 (full lines) shows values of $a$ and $c$ over the temperature range 0–400 K, calculated as outlined in the previous sections of this paper, together with experimental values for comparison[22]. Inclusion of the vibrational terms expands the lattice (estimated dilations at $T = 0$ are $\delta a = 0.25\,\%$ and $\delta c = 0.18\,\%$). At temperatures above 400 K the full free-energy minimisation fails, due to the appearance of imaginary modes which appear to be associated with low frequency modes associated with the rotation of the $SiO_4$ tetrahedra. The same occurs with all the three-body potentials we have tested, including the two sets of potentials tabulated in ref. 25.

### B. Comparison with strut potentials

For comparison, we also present calculations employing a commonly-used alternative to the three-body term involving the Si-O-Si angle. Instead, a harmonic strut is placed between the O atoms which are part of the same $SiO_4$ tetrahedron, i.e. (67) is replaced with the two-body potential

$$\phi = \frac{1}{2} k_s (r_{O-O} - r_s)^2 \tag{68}$$

where $r_{\mathrm{O-O}}$ is the oxygen-oxygen distance and $r_{\mathrm{s}}$ a constant. Strut potentials of this form have recently been used for silicates with success by Gale[25]. Equations (67) and (68) are clearly inequivalent since the bond angle is a function of the two Si-O bond lengths and the O-O distance. Nevertheless it is possible to expand (68) as a Taylor series in $r_{\mathrm{O-O}}$, in which the first term is of the same form as the right hand side of (67), and

$$k_{\mathrm{s}} = k_\theta \frac{2}{r^2_{\mathrm{Si-O}}\,(1+\cos\theta_0)} \tag{69}$$

To assess the importance of higher order terms in (67), we used (69) to determine the value of $k_{\mathrm{s}}$ corresponding to the value of $k_\theta$ used in (67) (putting $r_{\mathrm{Si-O}} = 1.625\,\mathrm{\AA}$). The resulting values of $k_{\mathrm{s}}$ and $r_{\mathrm{s}}$ are listed as set 1 in table II. The calculation of the thermal expansion of $\alpha$-quartz was then repeated replacing the harmonic-angle term with a strut. The dashed lines in figure 1 show the resulting values of the lattice parameters as a function of temperature. It is clear that higher-order terms are not negligible with differences in the calculated lattice parameters, for example, of the order of 0.01 Å. From figure 1 it is clear that the differences between quantities calculated using three-body potentials and those using struts can be of the same order as the total change in the quantities between 0 and 400 K. As with the three-body potentials the full free energy minimizations fail at 400 K. Figure 2 shows calculated values of the dimensionless Grüneisen function $\gamma$ ($= \beta V/\chi_T C_V$ where $\beta$ is the coefficient of volumetric thermal expansion and $\chi_T$ the isothermal compressibility) determined using both the three-body and strut potentials. Whereas the differences in the calculated lattice constants differ by less than 1%, the Grüneisen functions differ in the two models at low and high temperatures by more than 10%, showing the effect of a proper consideration of three body forces.

An alternative procedure for the strut potential parameters is to fix $r_{\mathrm{s}}$ and obtain $k_{\mathrm{s}}$ by requiring that the new potential set reproduces the same static energy as the potential set which includes the three-body term. We used a value of 2.65359 Å for $r_{\mathrm{s}}$, which is the value corresponding to $r_{\mathrm{Si-O}} = 1.625\,\mathrm{\AA}$ and $\theta_0 = 109.47°$, and the resulting parameters are collected together in table II as set 2. The corresponding calculated thermal expansion is shown by dot-dashed lines in figure 1. Again, these do not quite reproduce the three-body potential results. Compared with strut potential set 1, the values of $a$ are closer and the values of $x$ further from the three-body results.

Comparison between experiment and theory shows that there is considerable scope for improvement of the potentials. Potential parameters for a given solid have often been obtained by fitting to observed properties of the solid such as the lattice parameters and elastic constants. However, the calculations have been largely restricted to the static limit. Our new methodology makes it straightforward to fit the parameters using calculations at finite temperature, and in particular at the same temperature as the experimental measurements, including thermal effects explicitly.

### C. ZSISA

Finally we comment on previous approaches to the modelling of thermal effects[4] which have used the zero static internal stress approximation (ZSISA); in this approximation only the external strains ($\mathcal{E}_l^{\mathrm{ext}}$) are relaxed using fully dynamic free energy derivatives, while the internal strains ($\mathcal{E}_k^{\mathrm{int}}$) are relaxed using static energy derivatives[26]. This approach is popular since static energy derivatives can be calculated analytically, and rapidly, while only a small number of free energy derivatives is required, which are readily obtained numerically. The ZSISA optimization condition is

$$\left(\frac{\partial \widetilde{G}}{\partial \mathcal{E}_l^{\mathrm{ext}}}\right)_{\mathcal{E}^{\mathrm{ext}\prime},\tau^{\mathrm{int}}} = 0\ , \quad \tau_k^{\mathrm{int}} \equiv \left(\frac{\partial \widetilde{G}_{\mathrm{stat}}}{\partial \mathcal{E}_k^{\mathrm{int}}}\right)_{\mathcal{E}^{\mathrm{ext}},\mathcal{E}^{\mathrm{int}\prime}} = 0 \tag{70}$$

It is worthwhile emphasizing the variables which are kept constant in (70). ZSISA involves the minimisation of $\widetilde{G}$ with respect to the external strains at constant internal *stress* $\tau^{\mathrm{int}}$ and not at constant internal *strain*[27] $\mathcal{E}^{\mathrm{int}}$. For $\alpha$-quartz the difference is crucial, as has been pointed out by Gale[25]: for example, keeping the internal strain constant predicts an erroneous large negative volumetric thermal expansion coefficient for $\alpha$-quartz.

Figure 3 also shows results for the crystallographic parameters $a$, $c$, $u$ and $x$ of $\alpha$-quartz obtained using ZSISA and the set of potential parameters used earlier including the O-Si-O three-body term. For comparison, the full minimisation results are also included in these figures. A previous study[11] showed that for $MgF_2$ the results obtained using this approximation with two-body potentials are in very good agreement with those obtained by carrying out a full minimization. In contrast, for our present example, values using ZSISA agree with those from the full minimization only at very low temperatures. At temperatures higher than 400 K indeed the ZSISA results fail to show the instability of the $\alpha$-quartz structure as predicted by the full minimization. Very similar conclusions are obtained using any of the potentials in ref. 25. These results call into question the commonly-used assumption that ZSISA is a good approximation to full free energy minimization for $\alpha$-quartz and related silicates.

## V. CONCLUSIONS

We have extended the theory of ref. 1 to apply to general rotationally and translationally invariant three-body interactions, enabling fully dynamic geometrical optimisation of a wider range of crystals. Detailed expressions, in a form suitable for efficient incorporation into a computer program, have been given, and such a program has been written[10,28]. By way of example, we present the results of applying the theory to $\alpha$-quartz, comparing the fully dynamic three-body potential optimisations both with dynamic pseudo-three-body ("strut") potential optimisations and with semi-dynamic (ZSISA) three-body potential optimisations; in both cases the predictions of the approximate treatments differ significantly from the exact one.

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[27] In our earlier work[1,11] we were not sufficiently careful in making this distinction, which, though pointed out in ref. 26, was not made in refs. 1 and 11. The systems studied in these earlier papers were of high symmetry and the numerical errors arising were negligible.

[28] The code is intended to be available for use by other groups; academic users interested in obtaining a copy should contact N. L. Allan. Further information may also be found at http://dougal.chm.bris.ac.uk/programs/shell/.

FIG. 1. Calculated variation of $a$ and $c$ with temperature for $\alpha$-quartz using the potential sets listed in table II. Full lines denote calculations using the three-body O-Si-O angle term. Dashed and dot-dashed lines show values obtained using strut potentials set 1 and set 2 respectively. Filled squares show experimental values[22].

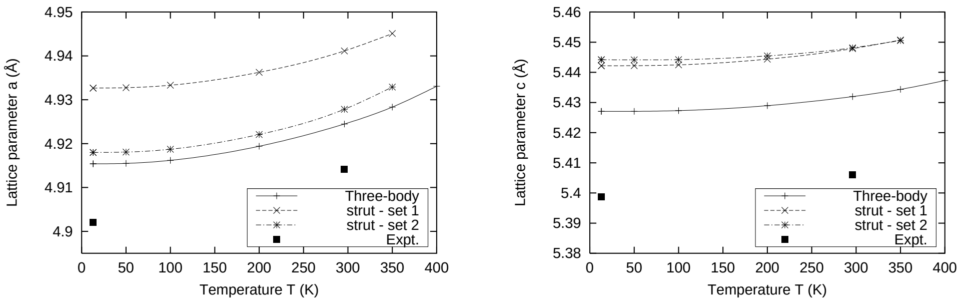


FIG. 2. Calculated variation of Grüneisen $\gamma$ function for $\alpha$-quartz using the potential sets listed in table II. Full lines denote calculations using the three-body O-Si-O angle term. Dashed and dot-dashed lines show values obtained using strut potentials set 1 and set 2 respectively.

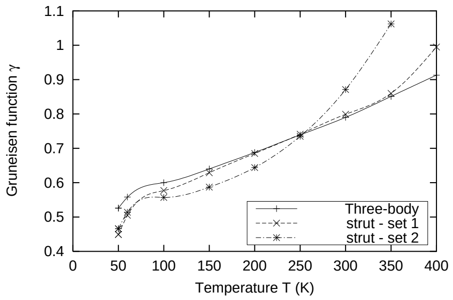

FIG. 3. A comparison of full free-energy minimisation and ZSISA results for $a$, $c$, $u$ and $x$. Full lines denote full free-energy minimisations of all external and internal variables. Dashed lines show values obtained using ZSISA. All calculations used the three-body potential set listed in table II.

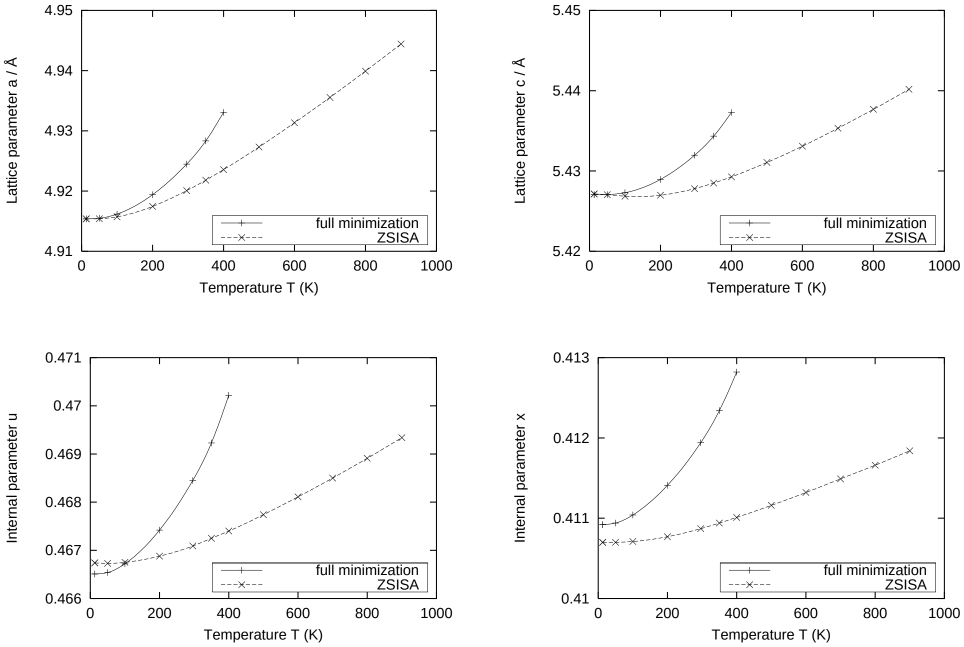

TABLE I. Arrangement of atomic cores in the unit cell of $\alpha$-quartz, defined using the notation in (4), with $(w_1, w_2, w_3, w_4) \equiv (u, x, y, z)$. The unlisted $\mathbf{g}_{m,i}$ vectors are zero.

| $i$ | Type | | $+u$ | $\mathbf{g}_{1,i}$ | $+x$ | $\mathbf{g}_{2,i}$ | $+y$ | $\mathbf{g}_{3,i}$ | $+z$ | $\mathbf{g}_{4,i}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Si | $(0\ 0\ 0)$ | $+u$ | $(-1\ -1\ 0)$ | | | | | | |
| 2 | Si | $(0\ 0\ 1/3)$ | $+u$ | $(1\ 0\ 0)$ | | | | | | |
| 3 | Si | $(0\ 0\ 2/3)$ | $+u$ | $(0\ 1\ 0)$ | | | | | | |
| 4 | O | $(0\ 0\ 0)$ | | | $+x$ | $(1\ 0\ 0)$ | $+y$ | $(0\ 1\ 0)$ | $+z$ | $(0\ 0\ 1)$ |
| 5 | O | $(0\ 0\ 1/3)$ | | | $+x$ | $(0\ 1\ 0)$ | $+y$ | $(-1\ -1\ 0)$ | $+z$ | $(0\ 0\ 1)$ |
| 6 | O | $(0\ 0\ 2/3)$ | | | $+x$ | $(-1\ -1\ 0)$ | $+y$ | $(1\ 0\ 0)$ | $+z$ | $(0\ 0\ 1)$ |
| 7 | O | $(0\ 0\ 0)$ | | | $+x$ | $(0\ 1\ 0)$ | $+y$ | $(1\ 0\ 0)$ | $+z$ | $(0\ 0\ -1)$ |
| 8 | O | $(0\ 0\ 1/3)$ | | | $+x$ | $(-1\ -1\ 0)$ | $+y$ | $(0\ 1\ 0)$ | $+z$ | $(0\ 0\ -1)$ |
| 9 | O | $(0\ 0\ 2/3)$ | | | $+x$ | $(1\ 0\ 0)$ | $+y$ | $(-1\ -1\ 0)$ | $+z$ | $(0\ 0\ -1)$ |

TABLE II. The shell model parameter set for $\alpha$-quartz. The parameters $A$, $r_0$ and $C$ are the coefficients for Buckingham potentials of the form $A\exp(-r/r_0) - Cr^{-6}$. $K_{\rm cs}$ is a core-shell spring constant. $k_\theta$ and $\theta_0$ are the parameters for the three-body O-Si-O potential defined in (67). $k_{\rm s}$ and $r_{\rm s}$ are the parameters for the strut potential (68), which, as described in the text, replaced the three-body term in some calculations. Two sets of strut potentials are listed (see the text). In all cases the atomic charges are +4.0 for Si, considered as a rigid ion, +0.86902 for the O core ($\mathrm{O_c}$) and -2.86902 for the O shell ($\mathrm{O_s}$). The cut-off used for the Buckingham potentials is 12.0 Å while that for the struts is 2.8 Å.

| Interaction | $A$ / eV | $r_0$ / Å | $C$ /eV Å$^6$ | $K_{\rm cs}$ / eVÅ$^{-2}$ | $k_\theta$ / eV rad$^{-2}$ | $\theta_0$ / ° | $k_{\rm s}$ / eVÅ$^{-2}$ | $r_{\rm s}$ / Å |
|---|---|---|---|---|---|---|---|---|
| Si-$\mathrm{O_s}$ | 1316.374 | 0.3205 | 10.66 | | | | | |
| $\mathrm{O_s}$-$\mathrm{O_s}$ | 22764.00 | 0.1490 | 27.879 | | | | | |
| $\mathrm{O_c}$-$\mathrm{O_s}$ | | | | 74.92 | | | | |
| $\mathrm{O_s}$-Si-$\mathrm{O_s}$ (3-body) | | | | | 2.09724 | 109.47 | | |
| $\mathrm{O_s}$-Si-$\mathrm{O_s}$ (strut: set 1) | | | | | | | 1.23277 | 2.65359 |
| $\mathrm{O_s}$-Si-$\mathrm{O_s}$ (strut: set 2) | | | | | | | 2.38277 | 2.65359 |