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Interatomic force constants from first principles: The case of α-quartz

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We describe a method for calculating the interatomic force constants in crystalline insulators, from first principles, with explicit inclusion of the long-ranged anisotropic dipole-dipole interaction. Using this technique, the dynamics of α-quartz, a model for tetrahedrally bonded silica, is investigated: we examine the range of interatomic forces, their anisotropy, their longitudinal and transverse character, and the importance of the dipole-dipole contribution. These force constants provide an extensive database for testing semiempirical interatomic potentials used in silica molecular-dynamics simulations.

The description of dynamical properties of solids,[1] within the Born-Oppenheimer approximation, makes central use of the quantities known as interatomic force constants (IFC's) $\Phi_{\alpha\beta}(i\kappa;j\kappa')$, second derivatives of the ground-state energy of the solid with respect to nuclear displacements (α and β run on the three spatial directions, i and j on all unit cells, κ and κ' on all nuclei within a given unit cell, $\vec{R}_{i\kappa}=\vec{R}_i+\vec{\tau}_\kappa$ are the nuclear positions). IFC's can also be thought as the coefficients describing, at linear order, the force created on one nucleus by the displacement of another from its equilibrium position.

First-principles calculations of dynamical matrices, the Fourier transform of interatomic force constants

$$A_{\alpha\beta}(\kappa\kappa'|\vec{q})=\sum_j \Phi_{\alpha\beta}(0\kappa;j\kappa')\ e^{i\,\vec{q}\cdot\vec{R}_j}, \qquad (1)$$

have benefited from recent advances[2,3] in the density functional perturbation theory (DFPT).[4] Using pseudopotentials coupled with plane waves[3,5] or linear muffin-tin orbital[6] or linearized augmented plane wave[7] basis sets, such calculations are now feasible for solids with a periodic unit cell containing up to ten atoms. Even if the calculation of one dynamical matrix is still computationally very demanding, applications on many solids (semiconductors, metals, oxides, surfaces, alloys, superlattices[3,5–12]) have been presented. Calculated phonon frequencies agree with experimental data within a few percent.

From dynamical matrices, one should be able to compute the IFC's by inverse Fourier transform:

$$\Phi_{\alpha\beta}(0\kappa;j\kappa')=\frac{1}{\Omega_{\rm BZ}}\int_{\rm BZ} A_{\alpha\beta}(\kappa\kappa'|\vec{q})\ e^{-i\,\vec{q}\cdot\vec{R}_j}\,d^3q. \qquad (2)$$

The integral over the Brillouin zone, in Eq. (2), is problematic, because the dynamical matrices can be calculated only for a few wave vectors. Under the hypothesis of *short-ranged* IFC's with respect to the distance between nuclei $\delta=|\vec{R}_{i\kappa}-\vec{R}_{j\kappa'}|$, one can use the information provided by the dynamical matrices on a regular grid of points in the Brillouin zone[13] to build approximate IFC's in a large box, by a discrete Fourier transform; outside of this box, the IFC's are constrained to vanish:

$$\Phi_{\alpha\beta}(0\kappa;j\kappa')=\frac{1}{N_{\vec{q}}}\sum_{\vec{q}\ \in\ {\rm grid}(lmn)} A_{\alpha\beta}(\kappa\kappa'|\vec{q})e^{-i\,\vec{q}\cdot\vec{R}_j}$$
$$\text{if}\quad \vec{R}_j+\vec{\tau}_\kappa-\vec{\tau}_{\kappa'}\ \in\ {\rm box}(lmn). \qquad (3)$$

Unfortunately, this technique[8] does not work in the general case. Indeed, for all metals or insulators, the interatomic force constants are *long-ranged*: they do not decrease exponentially fast, but like the inverse of some power of the interatomic distance (at most the seventh power). For insulators, the displacement of nuclei will usually induce a dipole (with proportionality coefficient given by the Born effective charge tensor $Z^*_{\kappa,\alpha\beta}$). The associated dipole-dipole interaction contributes to IFC's as the inverse of the third power of the distance between nuclei.[14] It is related to the well-known LO-TO splitting of the phonon frequencies for zone-center wave vector.[1] Forgetting the associated nonanalytic behavior will create Gibbs oscillations instead of LO-TO splitting.[15]

In order to bypass this problem, one can try to decompose the dynamical matrices into the dipole-dipole contribution and the remaining "short-ranged" part, which could be treated by Fourier transform in a large box. The trouble-making dipole-dipole interaction has to be dealt with in an *analytical* way. Such an analytical expression is available for isotropic dielectric and effective charge tensors.[9,10]

In the present paper, we first give the general expression for the treatment of dipole-dipole interactions for materials with anisotropic effective charge tensors and anisotropic di-

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electric tensor, thus allowing treatment of *any insulator* along the lines previously described. Then we describe the application of this technique to the calculation of IFC's in α-quartz, a solid with a complicated crystalline structure (nine atoms per unit cell, four internal degrees of freedom), complicated lattice dynamics,[16,17] and large anisotropy of effective charges.[5]

The nonanalytical dipole-dipole term present in the dynamical matrix at the zone-center wave vector $\vec{q}=\vec{0}$ depends on the limiting direction of the wave vector:

$$A^{dd}_{\alpha\beta}(\kappa\kappa'|\vec{q}\to\vec{0})=\frac{4\pi}{\Omega}\frac{(\Sigma_\gamma Z^*_{\kappa,\alpha\gamma}\,q_\gamma)(\Sigma_\gamma Z^*_{\kappa',\beta\gamma}\,q_\gamma)}{\Sigma_{\alpha\beta}q_\alpha\,\epsilon_{\alpha\beta}\,q_\beta}\,.$$

In this expression, ϵ can be identified as a metric in reciprocal space. This limiting value is correctly reproduced by the following ansatz for dipole-dipole interatomic force constants, with ϵ^{-1} used as a metric in real space:

$$\Phi^{dd}_{\alpha\beta}(0\kappa;j\kappa')=\sum_{\alpha'\beta'} Z^*_{\kappa,\alpha\alpha'}\,Z^*_{\kappa',\beta\beta'}\left(\frac{(\epsilon^{-1})_{\alpha'\beta'}}{D^3}-3\frac{\Delta_{\alpha'}\Delta_{\beta'}}{D^5}\right)(\det\epsilon)^{-\frac{1}{2}},\qquad(4)$$

where $\Delta_\alpha=\Sigma_\beta(\epsilon^{-1})_{\alpha\beta}\,\delta_\beta$ is the conjugate of the vector relating nuclei $\vec{\delta}=\vec{R}_j+\vec{\tau}_{\kappa'}-\vec{\tau}_\kappa$, and the norm is $D=\sqrt{\vec{\Delta}\cdot\vec{\delta}}$. The $j=0$ and $\kappa=\kappa'$ case is obtained by imposing the translational symmetry sum rule on the first or the second indices.[1] The contribution of these dipole-dipole IFC's to the dynamical matrix can be calculated using the Ewald summation technique[1] as follows: (1) translational invariance gives $A^{dd}_{\alpha\beta}(\kappa\kappa'|\vec{q})=\tilde{A}_{\alpha\beta}(\kappa\kappa'|\vec{q})-\delta_{\kappa,\kappa'}\,\Sigma_{\kappa''}\tilde{A}_{\alpha\beta}(\kappa\kappa''|\vec{q}=\vec{0})$;[18] (2) the effective charge tensors can be factored out $\tilde{A}_{\alpha\beta}(\kappa\kappa'|\vec{q})=\Sigma_{\alpha'\beta'}Z^*_{\kappa,\alpha\alpha'}\,Z^*_{\kappa',\beta\beta'}\,\tilde{A}_{\alpha'\beta'}(\kappa\kappa'|\vec{q})$; (3) the remaining quantity can be split into three parts, a rapidly convergent sum in reciprocal space, a rapidly convergent sum in real space, and the limiting contribution, as usual in Ewald summation techniques:

$$\begin{aligned}\tilde{A}_{\alpha'\beta'}(\kappa\kappa'|\vec{q})=&\sum_{\vec{G}\text{ with }\vec{K}=\vec{G}+\vec{q}}\frac{4\pi}{\Omega}\frac{K_{\alpha'}K_{\beta'}}{\Sigma_{\gamma\gamma'}K_\gamma\epsilon_{\gamma\gamma'}K_{\gamma'}}\\&\times e^{i\vec{K}\cdot(\vec{\tau}_\kappa-\vec{\tau}_{\kappa'})}\exp\left(-\sum_{\gamma\gamma'}\frac{K_\gamma\epsilon_{\gamma\gamma'}K_{\gamma'}}{4\Lambda^2}\right)\\&-\sum_j\Lambda^3\,e^{i\vec{q}\cdot\vec{R}_j}H_{\alpha'\beta'}(\Lambda\vec{\Delta},\Lambda D)\,(\det\epsilon)^{-\frac{1}{2}}\\&-\frac{4}{3\sqrt{\pi}}\Lambda^3\,\delta_{\kappa\kappa'}\,(\epsilon^{-1})_{\alpha'\beta'}\,(\det\epsilon)^{-\frac{1}{2}}\qquad(5)\end{aligned}$$

with

$$\begin{aligned}H_{\alpha\beta}(\vec{x},y)=&\frac{x_\alpha x_\beta}{y^2}\left[\frac{3}{y^3}\mathrm{erfc}(y)+\frac{2}{\sqrt{\pi}}e^{-y^2}\left(\frac{3}{y^2}+2\right)\right]\\&-(\epsilon^{-1})_{\alpha\beta}\left(\frac{\mathrm{erfc}(y)}{y^3}+\frac{2}{\sqrt{\pi}}\frac{e^{-y^2}}{y^2}\right).\end{aligned}$$

The parameter Λ can assume any value, and is adjusted to obtain the fastest convergence of both reciprocal and real

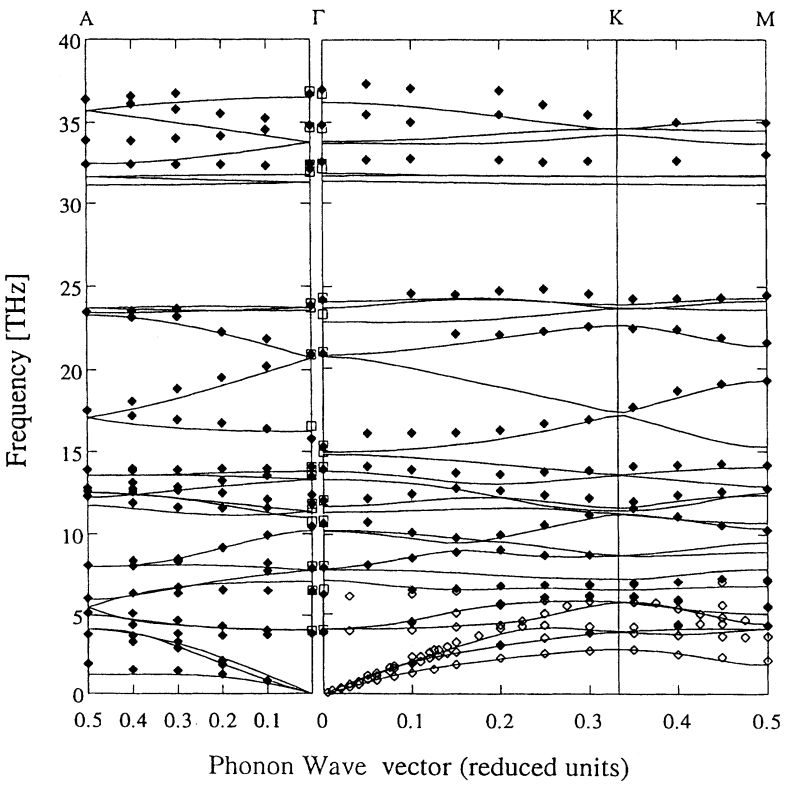

FIG. 1. Phonon band structure of α-quartz along selected directions. Filled and open diamonds: experimental data from Refs. 16 and 17, respectively; open squares, experimental data from Table II of Ref. 5; lines: present results.

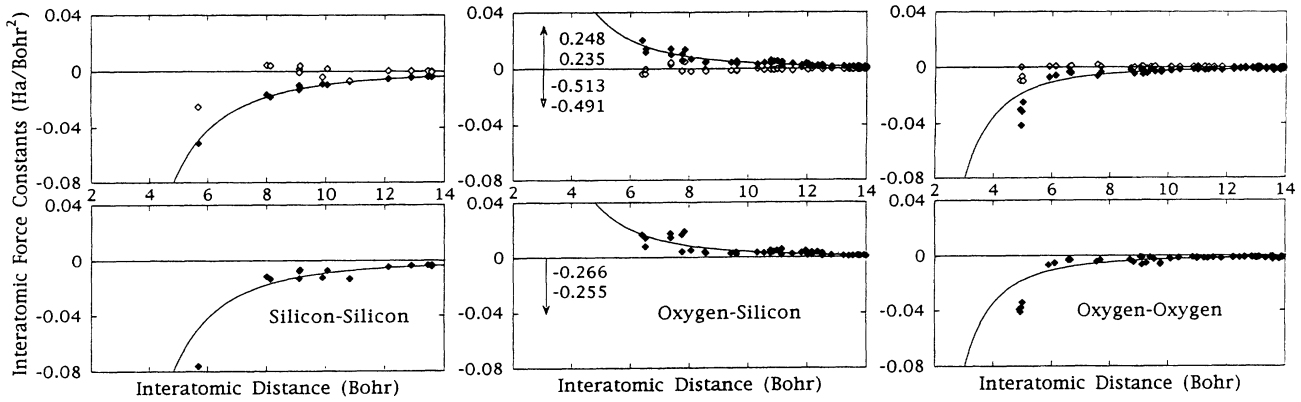

FIG. 2. Longitudinal interatomic force constant versus the distance between atoms. From left to right: Si-Si, O-Si, and O-O pairs. Upper panels: filled diamonds, anisotropic dipole-dipole contribution; open diamonds, short-ranged contribution; line, fitted isotropic dipole-dipole functional form (see text). Lower panels: filled diamonds, total interatomic force constants; line, same fitted isotropic dipole-dipole functional form as in the upper panel.

space sums. Effective charge tensors and dielectric constants can be obtained easily in the framework of DFPT.[3,5,19]

To find the IFC's, the dipole-dipole part of a set of dynamical matrices is subtracted using this Ewald technique, the short-ranged part is treated analytically, using (3), and the analytical dipole-dipole contribution (4) is added.

For the application of this technique to α-quartz, we have chosen the same variational approach to DFPT and technical details as in a previously published study of the dielectric tensor, effective charges, and zone-center dynamical matrix of α-quartz.[5] The mean deviation of phonon frequencies at Γ with respect to experimental data is 1.7%, with standard deviation of 2.6% with respect to this mean value.

In order to test the convergence of the IFC's with respect to the coarseness of the wave-vector grid, we have calculated dynamical matrices for α-quartz for five different grids[13] corresponding to real space boxes containing, respectively, 9, 72, 162, 144, and 324 atoms [the two last boxes correspond, respectively, to a $3\times3\times2$ grid, with 4 points in the Irreducible Brillouin zone (IBZ) and a $3\times3\times4$ grid, with 10 points in the IBZ]. The convergence of the interatomic force constants of the $3\times3\times2$ grid was found adequate for obtaining the phonon band structure (on average, less than 1% convergence error), except for the acoustic branches in the region close to the zone center, that are likely influenced by the remaining quadrupole-dipole interaction, not treated analytically. This band structure is shown in Fig. 1, with available experimental data.

We analyze now the large database[20] of IFC's obtained from the $3\times3\times4$ grid. Relative to each pair of atoms for which the three-by-three IFC matrix is analyzed, a system of coordinates is chosen as follows: (1) the first unit vector $\vec{e}_1$ is along the vector relating the two atoms; (2) when the first atom is displaced along $\vec{e}_1$, the second atom feels a force that has some part parallel to the first unit vector, and some part perpendicular to it, that defines the direction of the second unit vector $\vec{e}_2$; (3) the third unit vector is perpendicular to the first and second vector. Note that in general the three-by-three IFC matrices are not symmetric. In these systems of coordinates, the elements Φ_{13} vanish. If the IFC matrices were derived from two-body central interatomic potentials they would be diagonal, with $\Phi_{22}=\Phi_{33}$. We refer to the latter elements as the transverse IFC's, while Φ_{11} is referred to as the longitudinal IFC.

Figure 2 presents the longitudinal IFC as a function of the distance, for the O-O, Si-Si, and O-Si pairs, as well as their decomposition into dipole-dipole contribution and the "short-ranged" part. The continuous line is a least-squares fit of functional form β/δ^3 (it is the form that would be obtained if the IFC's were only due to electrostatic interaction of pointlike charges in an isotropic medium) to the anisotropic dipole-dipole part, weighted by the cube of the distance. Note the positive coefficient for O-Si and negative coefficient for Si-Si and O-O, as expected from the opposite charges. From the statistical analysis of these data (up to the 200th neighbor), we note that the isotropic functional form fits the global behavior of the longitudinal IFC well, except for the nearest-neighbor O-Si; with respect to the isotropic form, the "short-ranged" corrections and anisotropic dipole-dipole corrections, respectively, have standard deviation with respect to that isotropic form of 27.0% and 6.3% for the Si-Si pairs, 25% and 28.8% for the O-Si pairs (excluding the nearest-neighbor pairs), and 10.1% and 44.7% for the O-O pairs, respectively.

TABLE I. Interatomic force constant matrix elements, for the Si and O atom, as well as the nearest O-Si, Si-Si, and O-O pairs. The systems of coordinates are described in the text. Force constants are given in Ha/bohr^2.

	Si	O	O-Si	Si-Si	O-O
Diagonal elements					
Φ_{11}	0.4648	0.5886	−0.2658	−0.0763	−0.0391
Φ_{22}	0.5060	0.1279	−0.0329	0.0170	0.0074
Φ_{33}	0.4936	0.0557	−0.0331	0.0064	0.0076
Nondiagonal elements					
Φ_{12}	0.0000	−0.0056	0.0042	0.0129	0.0078
Φ_{21}	0.0000	−0.0056	0.0016	−0.0131	0.0043
Φ_{23}	0.0193	−0.0015	−0.0005	0.0003	0.0007
Φ_{31}	0.0000	−0.0011	−0.0020	−0.0006	−0.0033
Φ_{32}	0.0193	−0.0015	0.0006	0.0012	0.0013

Let us now present the results for short-range IFC's, including second derivatives of total energy with respect to the position of *one* atom (the potential well felt by one atom) referred to as the "self-IFC." For the self-IFC, no obvious local system of coordinates is available. Thus, for the Si self-IFC, we choose the atom at (u 0 1/6), located on the mirror plane (x-z), as the generic silicon atom, and keep the cartesian coordinate system, while for the O self-IFC the local coordinate system is as follows: first unit vector along the line connecting the two nearest-neighbor Si atoms, second vector in the Si-O-Si plane, third vector perpendicular to the others. The self-IFC matrix is symmetric, and in these local coordinate systems, it nearly diagonalizes, as shown in Table I. Note that the Si self-IFC is nearly isotropic, while the O self-IFC is strongly anisotropic, as expected from the anisotropy of its local environment.

The values of the three-by-three IFC's matrices for O-Si, Si-Si, and O-O closest pairs are also mentioned in Table I. The longitudinal component is the largest one. The IFC for the nearest-neighbor Si-O pair could be well described by a central two-body interatomic potential,[21] while nondiagonal contributions as well as the difference between transverse IFC's can be significant for O-O and Si-Si pairs (up to 20%). Although non-negligible, this inadequacy of the central potentials is smaller than in the case of SiO_2-stishovite,[11] a high-pressure form of silica. By contrast, three-body interatomic potentials may describe these noncentral contributions.

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