Appendix A

The Geometry of Strained Diamond and Graphite

> My attempts to establish a universally acceptable notation were not very successful. In the course of time I was compelled to change my own notation, and thus I cannot complain that others felt the same need.
>
> – Max Born [70]

In this appendix we compute changes in bond lengths and angles, accurate to second order in strain, for the diamond and graphitic crystal structures (and, of course, we use our own unconventional notation). These results supply geometrical information needed in computing analytic formulae for elastic constants.

A.1 Diamond Lattice

A.1.1 First Neighbors

To be specific about the displacement of each atom under strain, center a Cartesian coordinate system on a representative atom at the origin, and number the (tetrahedral) first neighbors as follows,

$$\begin{aligned} \vec{r}_1 = &\ \tfrac{a_d}{4}(1,1,1)\,, \quad \vec{r}_2 &= \frac{a_d}{4}(-1,-1,1) \\ \vec{r}_3 = &\ \tfrac{a_d}{4}(-1,1,-1)\,, \vec{r}_4 &= \frac{a_d}{4}(1,-1,-1), \end{aligned}$$

where a_d is the lattice constant. Denote the common first neighbor bond length by $r = \sqrt{3}a_d/4$. The volume per atom is $a_d^3/8$.

Appealing to cubic lattice symmetry, we thankfully need only consider the strain components $\varepsilon_1 = \varepsilon_{xx}$, $\varepsilon_2 = \varepsilon_{yy}$ and $\gamma_6 = 2\varepsilon_{xy}$ [75]. (Since $c_{66} = c_{44}$, γ_6 has the same effect on the energy as γ_4). In terms of these dimensionless strains, the distorted bond lengths are

$$\frac{\Delta r_i}{r} = \frac{1}{3}(\varepsilon_1 + \varepsilon_2) \pm \frac{1}{3}\gamma_6 + \frac{1}{9}(\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1\varepsilon_2) + \frac{1}{36}\gamma_6^2, \tag{A.1}$$

accurate to second order in the strain, where the upper sign applies to $i = 1, 2$ and the lower to $i = 3, 4$. At leading order, the uniaxial strains lengthen all four bonds, while the shear strain lengthens two and shortens the other two (consistent with volume conservation). The distorted angles are,

$$\Delta l_{12,34} = \frac{1}{9}\left[-4\left(\varepsilon_1 + \varepsilon_2 \pm \gamma_6\right) + \frac{2}{3}\left(\varepsilon_1^2 + \varepsilon_2^2 + 8\varepsilon_1\varepsilon_2\right) + \frac{5}{3}\gamma_6^2\right], \tag{A.2}$$

$$\Delta l_{13,24} = \frac{1}{9}\left[-4\varepsilon_1 + 8\varepsilon_2 + \frac{1}{3}\left(2\varepsilon_1^2 - 4\varepsilon_2^2 - 8\varepsilon_1\varepsilon_2\right) - \frac{1}{6}\gamma_6^2\right], \tag{A.3}$$

$$\Delta l_{14,23} = \frac{1}{9}\left[8\varepsilon_1 - 4\varepsilon_2 + \frac{1}{3}\left(-4\varepsilon_1^2 + 2\varepsilon_2^2 - 8\varepsilon_1\varepsilon_2\right) - \frac{1}{6}\gamma_6^2\right], \tag{A.4}$$

where in the first expression the upper sign refers to atoms 1 and 2 and lower to atoms 3 and 4. At first order, uniaxial tension opens four angles ($\Delta l < 0$) and closes two ($\Delta l > 0$), while the shear strain opens the angle between atoms 1 and 2 along the symmetry axis, closes the angle between atoms 3 and 4 perpendicular to the axis, and does not change the other four cross angles.

Using Eqs. (A.1) - (A.4), we can evaluate the expressions that arise in Taylor expansion of interatomic potentials to second order in the independent strains:

$$\sum_{i=1}^{4} \frac{\Delta r_i}{r} = \frac{4}{9}(\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1\varepsilon_2) + \frac{1}{9}\gamma_6^2, \tag{A.5}$$

$$\sum_{i=1}^{4} \left(\frac{\Delta r_i}{r}\right)^2 = \frac{4}{9}\left[(\varepsilon_1 + \varepsilon_2)^2 + \gamma_6^2\right], \tag{A.6}$$

$$\sum_{i=1}^{3}\sum_{j=i+1}^{4} \left(\frac{\Delta r_i}{r}\right)\left(\frac{\Delta r_j}{r}\right) = \frac{2}{9}[3(\varepsilon_1 + \varepsilon_2)^2 - \gamma_6^2] \tag{A.7}$$

$$\sum_{i=1}^{3}\sum_{j=i+1}^{4} \left(\frac{\Delta r_i}{r} + \frac{\Delta r_j}{r}\right) = \frac{4}{3}(\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1\varepsilon_2) + \frac{1}{3}\gamma_6^2, \tag{A.8}$$

$$\sum_{i=1}^{3}\sum_{j=i+1}^{4} \left[\left(\frac{\Delta r_i}{r}\right)^2 + \left(\frac{\Delta r_j}{r}\right)^2\right] = \frac{4}{3}\left[(\varepsilon_1 + \varepsilon_2)^2 + \gamma_6^2\right] \tag{A.9}$$

$$\sum_{i=1}^{3}\sum_{j=i+1}^{4} \Delta l_{ij} = \frac{8}{27}\gamma_6^2, \tag{A.10}$$

$$\sum_{i=1}^{3}\sum_{j=i+1}^{4} \Delta l_{ij}^2 = \frac{32}{81}\left[6\left(\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1\varepsilon_2\right) + \gamma_6^2\right], \tag{A.11}$$

$$\sum_{i=1}^{3}\sum_{j=i+1}^{4} \Delta l_{ij}\left(\frac{\Delta r_i}{r} + \frac{\Delta r_j}{r}\right) = -\frac{16}{27}\gamma_6^2. \tag{A.12}$$

A.1.2 Internal Relaxation

For C_{44} (or equivalently C_{66} here) we must allow internal relaxation of the interpenetrating FCC lattices. By symmetry the relaxation can only occur by moving the central atom at the origin along the z axis to the point $(0, 0, z)$. Following Kleinman [81] and Harrison [76], we express the relaxation distance in terms of a parameter ζ via, $z = a\gamma_6\zeta/4$. With internal relaxation, the first neighbor bond lengths for the shear strain are,

$$\frac{\Delta r_i}{r} = \pm\frac{1}{3}(1-\zeta)\gamma_6 + \frac{1}{36}\left(3 + 6\zeta^2 - 2(1-\zeta)^2\right)\gamma_6^2, \tag{A.13}$$

where the upper sign refers to $i = 1, 2$ and the lower to $i = 3, 4$. If $\zeta = 1$, the first order change in all bond lengths vanishes. For simplicity, we only compute strained first neighbor bond angles to first order with internal relaxation. In that case,

$$\Delta l_{12} = -\Delta l_{34} = -\frac{4}{9}(1 + 2\zeta)\gamma_6, \tag{A.14}$$

and all other first order angular variations vanish.

A.1.3 Second Neighbors

The second neighbors in the diamond structure are the same as 12 first neighbors in an FCC crystal with the same lattice constant, *i. e.* $R(\pm 1, \pm 1, 0)$, $R(\pm 1, 0, \pm 1)$ and $R(0, \pm 1, \pm 1)$, where $R = a_d/\sqrt{2}$ is the second neighbor distance. The strained bond lengths are given by,

$$\frac{\Delta R}{R} = \frac{1}{2}(\varepsilon_1 + \varepsilon_2) + \frac{1}{8}(\varepsilon_1^2 + \varepsilon_2^2 - 2\varepsilon_1\varepsilon_2) \pm \frac{1}{2}\gamma_6, \tag{A.15}$$

for $(1, 1, 0), (-1, -1, 0)$ (upper sign) and $(1, -1, 0), (-1, 1, 0)$ (lower sign),

$$\frac{\Delta R}{R} = \frac{1}{2}\varepsilon_1 + \frac{1}{8}\varepsilon_1^2 + \frac{1}{16}\gamma_6^2, \tag{A.16}$$

for $(\pm 1, 0, \pm 1)$, and

$$\frac{\Delta R}{R} = \frac{1}{2}\varepsilon_2 + \frac{1}{8}\varepsilon_2^2 + \frac{1}{16}\gamma_6^2, \tag{A.17}$$

for $(0, \pm 1, \pm 1)$. The contributions from second neighbors to the expressions needed for (pair potential) elastic formulae are:

$$\sum_{i=1}^{12} \left(\frac{\Delta R_i}{R}\right) = \varepsilon_1^2 + \varepsilon_2^2 - 2\varepsilon_1\varepsilon_2 + \frac{1}{2}\gamma_6^2, \tag{A.18}$$

$$\sum_{i=1}^{12} \left(\frac{\Delta R_i}{R}\right)^2 = 2(\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_1\varepsilon_2) + \gamma_6^2. \tag{A.19}$$

We do not consider angles involving second neighbors.

A.2 Graphitic Lattice

Now we repeat the same exercise for the graphitic structure. Here we only consider first neighbors, and hence restrict ourselves to covalent bonds within a single hexagonal plane. Relative to an atom at the origin, the first neighbors (all in the $z = 0$ plane) are

$$\vec{r}_1 = r(1,0),\ \vec{r}_2 = r\left(-\frac{1}{2}, \frac{\sqrt{3}}{2}\right),\ \vec{r}_3 = r\left(-\frac{1}{2}, -\frac{\sqrt{3}}{2}\right), \tag{A.20}$$

where $r = a_h/\sqrt{3}$ is the bond length and a_h is the in-plane lattice constant of the hexagonal array. The area per atom is $a_h^2\sqrt{3}/4$. We only consider the in-plane tensile strains ε_1 and ε_2. The γ_6 in-plane shear-strain dependence is related to ε_1 and ε_2 through $C_{66} = (C_{11} - C_{12})/2$ [85]. The deformed bond lengths and angles are

$$\Delta r_1/r = \varepsilon_1 + \frac{1}{2}\gamma_4^2, \tag{A.21}$$

$$\frac{\Delta r_i}{r} = \frac{1}{4}(\varepsilon_1 + 3\varepsilon_2) + \frac{3}{32}(\varepsilon_1^2 + \varepsilon_2^2 - 2\varepsilon_1\varepsilon_2) + \frac{1}{8}\gamma_4^2, \tag{A.22}$$

$$\Delta l_{1i} = \frac{3}{64}[8(\varepsilon_2 - \varepsilon_1) + 3\varepsilon_1^2 - 5\varepsilon_2^2 - 2\varepsilon_1\varepsilon_2] - \frac{3}{16}\gamma_4^2, \tag{A.23}$$

$$\Delta l_{23} = \frac{3}{4}(\varepsilon_1 - \varepsilon_2 + \varepsilon_2^2 - \varepsilon_1\varepsilon_2) + \frac{3}{8}\gamma^2, \tag{A.24}$$

where $i = 2, 3$. The expressions needed for interatomic potential elastic constants are:

$$\sum_{i=1}^{3} \frac{\Delta r_i}{r} = \frac{3}{2}(\varepsilon_1 + \varepsilon_2) + \frac{3}{16}(\varepsilon_1^2 + \varepsilon_2^2 - 2\varepsilon_1\varepsilon_2) + \frac{3}{4}\gamma_4^2, \tag{A.25}$$

$$\sum_{i=1}^{3} \left(\frac{\Delta r_i}{r}\right)^2 = \frac{3}{8}\left[3(\varepsilon_1 + \varepsilon_2)^2 + 2\varepsilon_1\varepsilon_2\right], \tag{A.26}$$

$$\sum_{i=1}^{2}\sum_{j=i+1}^{3} \left(\frac{\Delta r_i}{r}\right)\left(\frac{\Delta r_j}{r}\right) = \frac{3}{16}[3(\varepsilon_1 + \varepsilon_2)^2 + 10\varepsilon_1\varepsilon_2], \tag{A.27}$$

$$\sum_{i=1}^{2}\sum_{j=i+1}^{3} \left(\frac{\Delta r_i}{r} + \frac{\Delta r_j}{r}\right) = 3(\varepsilon_1 + \varepsilon_2) + \frac{3}{8}(\varepsilon_1^2 + \varepsilon_2^2 - 2\varepsilon_1\varepsilon_2) + \frac{3}{2}\gamma_4^2, \tag{A.28}$$

$$\sum_{i=1}^{2}\sum_{j=i+1}^{3} \left[\left(\frac{\Delta r_i}{r}\right)^2 + \left(\frac{\Delta r_j}{r}\right)^2\right] = \frac{3}{4}\left[3(\varepsilon_1 + \varepsilon_2)^2 + 2\varepsilon_1\varepsilon_2\right], \tag{A.29}$$

$$\sum_{i=1}^{2}\sum_{j=i+1}^{3} \Delta l_{ij} = \frac{3}{32}[3(\varepsilon_1^2 + \varepsilon_2^2) - 10\varepsilon_1\varepsilon_2], \tag{A.30}$$

$$\sum_{i=1}^{2} \sum_{j=i+1}^{3} \Delta l_{ij}^2 = \frac{27}{32}(\varepsilon_1^2 + \varepsilon_2^2 - 2\varepsilon_1\varepsilon_2), \tag{A.31}$$

$$\sum_{i=1}^{2} \sum_{j=i+1}^{3} \Delta l_{ij} \left(\frac{\Delta r_i}{r} + \frac{\Delta r_j}{r} \right) = -\frac{9}{16}(\varepsilon_1^1 + \varepsilon_2^2 - 2\varepsilon_1\varepsilon_2). \tag{A.32}$$

The formulae in this section are somewhat tedious to compute and write down, but they are the starting point for the derivation of elastic constant formulae for wide classes of interatomic potentials.