

The Thermal-Motion Correction for Bond Angles

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(Received 10 November 1977; accepted 10 December 1977)

Expressions for the thermal-motion correction of bond angles are derived by determining the mean angle. Thus the joint distribution of the three relevant nuclei is used in the harmonic approximation of the nuclear vibrations. To calculate the correction in practice, the coupling tensors among the three relevant atoms must be known, these being a characteristic feature of the joint distribution. Since the coupling tensors cannot be measured, they must be determined from simple models of motion or from the interatomic force constants. The model of rigid-body motions can be applied in many cases, and for this model it is shown that the angle correction can be calculated from the corrected bond lengths. Approximate expressions for upper and lower bounds of the angle correction are derived.

1. Introduction

At the end of a refinement, bond lengths and angles are calculated, as a rule, from the mean positions of the atoms. It is known, however, that a better assessment of the bond lengths is given by the mean distances between the atoms and it is on their calculation that the bond-length correction is based (Busing & Levy, 1964; Johnson, 1970; Scheringer, 1972). Similarly, we regard the mean angle as a better assessment of the bond angle when the joint distribution of the three relevant atoms is taken into account. Likewise, Busing & Levy (1964) consider the mean angle as a 'sensible measure', but they find it difficult to derive the relevant expressions. Johnson (1970) derived a correction formula for the model of rigid-body motions of a molecule, but we found that his approach cannot be applied to the general case. In this paper we derive the bond-angle correction by calculating the mean angle from the joint distribution of the three relevant atoms. Thus we restrict ourselves to the harmonic approximation of the atomic motions.

2. The calculation of the mean angle

We consider three atoms r – t – s and denote the bond vectors rt , st and rs between the mean positions of the atoms by \mathbf{a} , \mathbf{b} , and \mathbf{c} respectively. Then $\mathbf{c} = \mathbf{a} - \mathbf{b}$. Let the angle at t be φ , and let the instantaneous thermal displacement vectors of the atoms from their mean positions be \mathbf{u}_r , \mathbf{u}_s and \mathbf{u}_t . For an instantaneous thermal configuration we have

$$\begin{aligned} \mathbf{a}_u &= \mathbf{a} + \mathbf{u}_r - \mathbf{u}_t, & \mathbf{b}_u &= \mathbf{b} + \mathbf{u}_s - \mathbf{u}_t, \\ \mathbf{c}_u &= \mathbf{a}_u - \mathbf{b}_u = \mathbf{c} + \mathbf{u}_r - \mathbf{u}_s. \end{aligned} \quad (2.1)$$

The subscript u denotes the instantaneous interatomic vectors. For the difference between the instantaneous angle φ_u and the angle φ , we can write

$$\varphi_u - \varphi = \arcsin(\cos \varphi \sin \varphi_u - \cos \varphi_u \sin \varphi). \quad (2.2)$$

In the following we calculate the average $\langle \varphi_u - \varphi \rangle = \langle \varphi_u \rangle - \varphi$ as a function of the atomic displacement vectors \mathbf{u}_r , \mathbf{u}_s , \mathbf{u}_t . We consider only first and second powers of the displacements (harmonic approximation). We apply the series expansion of the arcsin function and, since the second-order terms are zero, obtain

$$\varphi_u - \varphi \simeq \cos \varphi \sin \varphi_u - \cos \varphi_u \sin \varphi, \quad (2.3)$$

which corresponds to the approximation $\varphi_u - \varphi \simeq \sin(\varphi_u - \varphi)$. For $\cos \varphi_u$ we write

$$\cos \varphi_u = (\mathbf{a}_u \cdot \mathbf{b}_u) / (a_u b_u). \quad (2.4)$$

We put $a_u b_u = [(\mathbf{a}_u \cdot \mathbf{a}_u)(\mathbf{b}_u \cdot \mathbf{b}_u)]^{1/2}$, insert (2.1) into (2.4), multiply out all terms and obtain

$$\cos \varphi_u = \cos \varphi (1 + D)^{-1/2} + (ab)^{-1} (1 + D)^{-1/2} G, \quad (2.5)$$

where

$$\begin{aligned} G &= \mathbf{a} \cdot (\mathbf{u}_s - \mathbf{u}_t) + \mathbf{b} \cdot (\mathbf{u}_r - \mathbf{u}_t) + (\mathbf{u}_r - \mathbf{u}_t) \cdot (\mathbf{u}_s - \mathbf{u}_t), \\ D &= Aa^{-2} + Bb^{-2} + AB(ab)^{-2}, \\ A &= 2\mathbf{a} \cdot (\mathbf{u}_r - \mathbf{u}_t) + |\mathbf{u}_r - \mathbf{u}_t|^2, \\ B &= 2\mathbf{b} \cdot (\mathbf{u}_s - \mathbf{u}_t) + |\mathbf{u}_s - \mathbf{u}_t|^2. \end{aligned} \quad (2.6)$$

To work with $\sin \varphi_u$, we put $\sin \varphi_u = (1 - \cos^2 \varphi_u)^{1/2}$. Moreover, a representation:

$$(1 - \cos^2 \varphi_u)^{1/2} = (1 - \cos \varphi)^{1/2} (1 + X)^{1/2} (1 + D)^{-1/2} \quad (2.7)$$

proves to be expedient. With (2.5) we find

$$\begin{aligned} X &= [D - 2 \cos \varphi (ab)^{-1} G - (ab)^{-2} G^2] (\sin \varphi)^{-2} \\ &\equiv E (\sin \varphi)^{-2}. \end{aligned} \quad (2.8)$$

(2.8) defines E . With these results, (2.3) becomes

$$\varphi_u - \varphi = \{\cos \varphi [(1 + X)^{1/2} - 1] - G(ab)^{-1}\} \times (1 + D)^{-1/2} \sin \varphi. \quad (2.9)$$

Now we expand the square-root expressions in (2.9) into the corresponding series up to second-order terms, multiply out all terms and obtain

$$\begin{aligned} \varphi_u - \varphi = & \cos \varphi (2 \sin \varphi)^{-1} E - \sin \varphi (ab)^{-1} G \\ & - \cos \varphi (2 \sin \varphi)^{-3} E^2 - \cos \varphi (4 \sin \varphi)^{-1} \\ & \times [D^2 - 2 \cos \varphi (ab)^{-1} DG] + \sin \varphi (2ab)^{-1} DG. \end{aligned} \quad (2.10)$$

If we neglect third and higher-order terms in E^2 , we find

$$E^2 \simeq D^2 - 4 \cos \varphi (ab)^{-1} DG + (2 \cos \varphi G)^2 (ab)^{-2}. \quad (2.11)$$

We insert (2.11) into (2.10), reorder the terms, and finally obtain

$$\begin{aligned} \varphi_u - \varphi = & \cos \varphi (2 \sin \varphi)^{-1} D - (ab \sin \varphi)^{-1} G \\ & - [(2 \sin \varphi)^{-3} + (4 \sin \varphi)^{-1}] \cos \varphi D^2 \\ & - (ab)^{-2} (\sin \varphi)^{-3} \cos \varphi G^2/2 \\ & + (2ab)^{-1} (\sin \varphi)^{-3} DG. \end{aligned} \quad (2.12)$$

If we insert D and G from (2.6) into (2.12), we would obtain $\varphi_u - \varphi$ as a function of the atomic displacements \mathbf{u}_r , \mathbf{u}_s , \mathbf{u}_t . We shall not write down this lengthy expression, but rather proceed to the thermal average $\langle \varphi_u \rangle - \varphi$. With (2.6), the averages $\langle A \rangle$, $\langle B \rangle$, $\langle AB \rangle$ and $\langle G \rangle$ will appear. To express these averages by way of the atomic displacements, we introduce the vibration tensors \mathbf{U}_r , \mathbf{U}_s , \mathbf{U}_t of the three atoms r , s , t respectively and the coupling tensors \mathbf{U}_{rp} , \mathbf{U}_{sp} , \mathbf{U}_{rs} , with

$$U_{rt}^{ik} = \langle U_r^i U_t^k \rangle; \quad i, k = 1, 2, 3; \quad \mathbf{U}_{ir} = \mathbf{U}_{rt}^T; \quad (2.13)$$

(Scheringer, 1972). To shorten our description we use the symmetric tensors \mathbf{A}_{rt} , \mathbf{A}_{st} , \mathbf{A}_{rs} , with

$$\mathbf{A}_{rt} = \mathbf{U}_r + \mathbf{U}_t - \mathbf{U}_{rt} - \mathbf{U}_{tr}, \quad (2.14)$$

and the tensor

$$\mathbf{P} = (\mathbf{A}_{rs} - \mathbf{A}_{rt} - \mathbf{A}_{st})(2ab)^{-1} + (\mathbf{A}_{rt} a^{-2} + \mathbf{A}_{st} b^{-2}) \frac{1}{2} \cos \varphi. \quad (2.15)$$

With (2.6) and (2.12–15) we finally obtain

$$\begin{aligned} \langle \varphi_u \rangle - \varphi = & (\sin \varphi)^{-1} \text{trace } \mathbf{P} - (\sin \varphi)^{-3} [\mathbf{a}^T \mathbf{P} \mathbf{a} a^{-2} \\ & + \mathbf{b}^T \mathbf{P} \mathbf{b} b^{-2} - 2 \cos \varphi \mathbf{a}^T \mathbf{P} \mathbf{b} (ab)^{-1}] \\ & - (\sin \varphi)^{-1} \{ \cos \varphi [\mathbf{a}^T \mathbf{A}_{rt} \mathbf{a} a^{-4} + \mathbf{b}^T \mathbf{A}_{st} \mathbf{b} b^{-4}] \\ & - \mathbf{a}^T [\mathbf{A}_{rt} a^{-2} + \mathbf{A}_{st} b^{-2}] \mathbf{b} (ab)^{-1} \}. \end{aligned} \quad (2.16)$$

(2.13–16) are valid in a general metric. We can simplify (2.16) if we refer to a special Cartesian coordinate system which is symmetric to \mathbf{a} and \mathbf{b} . Let the Z axis be perpendicular to the plane \mathbf{ab} , the Y axis be the bisector of the angle φ , the positive Y axis point to side \mathbf{c} , and the positive X axis to the atom s (Fig. 1). Then we have $-a_x/a = b_x/b = \sin(\varphi/2)$, $a_y/a = b_y/b = \cos(\varphi/2)$ and (2.16) reduces to

$$\langle \varphi_u \rangle - \varphi = (\sin \varphi)^{-1} P^{33} + \frac{1}{2} \sin \varphi [(A_{rt}^{22} - A_{rt}^{11}) a^{-2} + (A_{st}^{22} - A_{st}^{11}) b^{-2}] + \cos \varphi (A_{rt}^{12} a^{-2} - A_{st}^{12} b^{-2}). \quad (2.17)$$

The first term in (2.17) refers only to out-of-plane motions; the two other terms only to in-plane motions (*i.e.* motions for which the atoms vibrate only in the plane \mathbf{abc}). For isotropic in-plane motions, we have $A_{rt}^{11} = A_{rt}^{22}$, $A_{st}^{11} = A_{st}^{22}$, $A_{rt}^{12} = A_{st}^{12} = 0$, and the two final terms in (2.17) vanish. In (2.16) the quadratic and mixed forms represent only in-plane contributions.

We can interpret the first term in (2.17), $(\sin \varphi)^{-1} P^{33}$, as a correction that can be calculated from the three sides that were corrected only for out-of-plane motions of the relevant triangle. Let φ_{corr} be the angle that is obtained from the three corrected sides, and we have

$$P^{33} = \cos \varphi - \cos \varphi_{\text{corr}} \quad (2.18)$$

The proof of (2.18) is as follows. In the coordinate system of (2.17) (Fig. 1), the side a , being corrected for out-of-plane motions, is

$$a_{\text{corr}} = a + A_{rt}^{33} (2a)^{-1}; \quad (2.19)$$

the same is true for b and c (Scheringer, 1972, equations 3.1 and 3.6). We ignore all quadratic terms of A_{rt}^{33} , A_{st}^{33} and A_{rs}^{33} , and obtain

$$\cos \varphi_{\text{corr}} = \frac{a^2 + b^2 - c^2 + A_{rt}^{33} + A_{st}^{33} - A_{rs}^{33}}{2[a + A_{rt}^{33} (2a)^{-1}][b + A_{st}^{33} (2b)^{-1}]} \quad (2.20)$$

In the denominator of (2.20) we extract the factor $2ab$, expand the remainder into a series and obtain (2.18) in the linear terms of A_{rt}^{33} , A_{st}^{33} and A_{rs}^{33} .

The factors of $(\sin \varphi)^{-1}$ and $(\sin \varphi)^{-3}$ in (2.16), and of $(\sin \varphi)^{-1}$ in (2.17) suggest that the correction will diverge for $\sin \varphi \rightarrow 0$. In truth, this is not the case, although divergence may occur in the first term of (2.17), because, for $\sin \varphi \rightarrow 0$, P^{33} cannot be determined well enough experimentally. The transition from (2.16) to (2.17) has shown that the divergence of the in-plane contributions [terms with $(\sin \varphi)^{-1}$ and $(\sin \varphi)^{-3}$ in (2.16)] vanishes with the choice of a special coordinate system. For the external motions of a molecule (rigid-body motions), we shall show (3.6 below) that the first term of (2.17), $(\sin \varphi)^{-1} P^{33}$, tends towards zero for $\sin \varphi \rightarrow 0$. For the internal motions, we first state that the sides \mathbf{a} , \mathbf{b} , \mathbf{c} no longer define a plane for $\sin \varphi = 0$. Hence, in this case, any vibration of the three atoms, which are on a straight line, can be regarded as an in-plane motion for which no divergence occurs. With the example of the linear triatomic

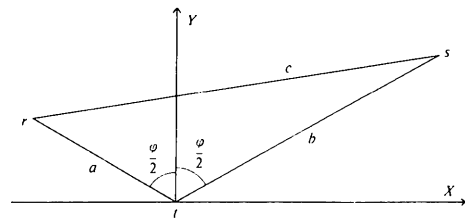


Fig. 1. Cartesian coordinate system in which (2.17), (2.18), (3.6), and (4.3) are valid. Z axis perpendicular to the plane \mathbf{abc} .

molecule, which is known to remain linear on the thermal average, the vanishing of the divergence and the zero correction are obtained as follows: For the external vibrations, the correction is zero with (3.6); for the internal (in-plane) vibrations, the second term in (2.17) vanishes with $\sin \varphi = 0$, and the third term with $A_{rt}^{12} = A_{st}^{12} = 0$ since the molecular axis \mathbf{a} represents a principal axis of the internal motions.

With (2.17) and (2.18) the angle correction $\langle \varphi_u \rangle - \varphi$ consists of two parts: the first part can be obtained from the sides of the relevant triangle which have been corrected for out-of-plane motions, the second part arises from the anisotropic remainder of the in-plane motions. Obviously, it does not hold that the corrected angle can generally be calculated from those three sides of the relevant triangle that have been corrected for all types of motions.

The main difficulty in the application of (2.16) and (2.17) consists of the fact that the coupling tensors \mathbf{U}_{rt} , \mathbf{U}_{st} , \mathbf{U}_{rs} cannot be derived from diffraction data, and, thus, are usually unknown. For their calculation, five simple models of motion are at hand: complete in-phase motion, complete anti-phase motion, uncorrelated motion, riding motion, and rigid-body motion (Scheringer, 1972). Only the model of rigid-body motions presents a useful approximation of reality, particularly at higher temperatures. The other four models will rarely correspond to the real situation, and even if they do this cannot be convincingly shown. Furthermore, for each of the three sides of the relevant triangle, a different model of motion must usually be applied (except for rigid-body motions); this implies a careful consideration of the actual situation.

There is a possibility of calculating the coupling tensors, which is likely to produce the most accurate results but requires much effort. The motions of the molecule are separated (to a good approximation) into internal and external modes, and the coupling tensors are calculated separately for each type of motion. For the internal modes, they can be derived from the interatomic force constants which must be known from IR and Raman measurements; for the external modes, they will be determined from the model of rigid-body motions after the experimentally determined vibration tensors have been corrected for the contributions of the internal modes (Scheringer, 1977).

Generally, the corrected sides and angles of a triangle will not fit together into a closed triangle. Hence one has to decide for which quantities a correction can reasonably be applied and for which it cannot. If, for example, the sides a and b represent chemical bonds but c only a distance, then the correction of a , b and the angle between a and b is reasonable, but not the correction of c . However, the situation is not always as clear cut, for example, for bonds and angles among atoms which belong to different molecules.

3. Rigid-body motions

The model of rigid-body motions signifies that the configuration of the molecule is the same in every thermal state. The coordinates of the atoms determined in the refinement do not represent this configuration, since the mean bond lengths are larger than the distances between the mean nuclear positions. The mean positions thus conceal the true configuration of the (rigid) molecule, and the purpose of the thermal-motion correction is to recover this configuration. Since it is uniquely determined by the bond lengths, it should be possible to gain the corrected bond angles from the corrected bond lengths. We shall show that this is the case, but we now derive the angle correction for the model of rigid-body motions from (2.16) and (2.17); this is the simpler procedure and yields a better insight into the characteristic features of the correction.

The model of rigid-body motions is described by the tensors \mathbf{TLS} , but only the libration tensor \mathbf{L} is needed for the correction. This follows from

$$\mathbf{A}_{rt} = (\mathbf{V}_r - \mathbf{V}_t) \mathbf{L} (\mathbf{V}_r - \mathbf{V}_t)^T \equiv \mathbf{V}_a \mathbf{L} \mathbf{V}_a^T \quad (3.1)$$

(Scheringer, 1972, equation 4.5), where the tensor

$$\mathbf{V}_r = \begin{pmatrix} 0 & -Z_r & Y_r \\ Z_r & 0 & -X_r \\ -Y_r & X_r & 0 \end{pmatrix} \quad (3.2)$$

contains the coordinates of atom r in a Cartesian system. Since $\mathbf{a}^T \mathbf{V}_a = \mathbf{a} \times \mathbf{a} = \mathbf{0}$, for rigid-body motions, all quadratic and mixed forms in (2.16) vanish and it reduces to

$$\langle \varphi_u \rangle - \varphi = (\sin \varphi)^{-1} \text{trace } \mathbf{P}. \quad (3.3)$$

If one considers that, in a Cartesian coordinate system,

$$\text{trace } (\mathbf{V}_a \mathbf{L} \mathbf{V}_a^T) = a^2 \text{trace } \mathbf{L} - \mathbf{a}^T \mathbf{L} \mathbf{a}, \quad (3.4)$$

etc., one finally obtains with (3.1–4)

$$\langle \varphi_u \rangle - \varphi = (\sin \varphi)^{-1} [(\mathbf{a}^T \mathbf{L} \mathbf{a} + \mathbf{b}^T \mathbf{L} \mathbf{b} - \mathbf{c}^T \mathbf{L} \mathbf{c})(2ab)^{-1} - \frac{1}{2} \cos \varphi (\mathbf{a}^T \mathbf{L} \mathbf{a} a^{-2} + \mathbf{b}^T \mathbf{L} \mathbf{b} b^{-2})]. \quad (3.5)$$

Although \mathbf{V}_r of (3.2) is referred to a Cartesian coordinate system, (3.5) is valid in a general crystal metric (with $a^2 = \mathbf{a}^T \mathbf{g} \mathbf{a}$, \mathbf{g} = metric tensor). This follows from the fact that (3.5) is invariant with respect to a transformation of the base vectors. The simplest form of the correction is obtained in the special coordinate system of (2.17) (Fig. 1)

$$\langle \varphi_u \rangle - \varphi = \frac{1}{2} \sin \varphi (L_{22} - L_{11}). \quad (3.6)$$

Since the correction is dependent only upon the difference $L_{22} - L_{11}$, the absolute magnitude of the librations is not of primary importance, but rather the extent of the anisotropy of \mathbf{L} . Hence, an isotropic libration tensor gives a zero correction. Since L_{33} does not appear in (3.6), in-plane motions (which are described

by L_{33} in this coordinate system) do not contribute to the correction. Note that with (3.6) both positive and negative corrections can be obtained, since, for the different angles in the molecule, the special coordinate system of Fig. 1 has different orientations and, hence, the ascertainment of what L_{11} and L_{22} are changes with the angle.

Now we show that the corrected angle which is obtained from (3.5) and (3.6) is equal to the angle which is obtained from the triangle of the three corrected sides. Since, for the rigid-body model, in-plane motions do not contribute to the angle correction, it follows from § 2, that the corrected angle is obtained if it is calculated from the triangle of the three sides corrected for out-of-plane motions. However, for the rigid-body model, in-plane motions give a non-zero contribution to the corrected sides. The corresponding calculation performed in the coordinate system of (3.6) (Fig. 1) shows that all three sides are enlarged by multiplication by the same factor, $(1 + L_{33}/2)$, so that there is no effect of the in-plane motions on the angle.

Johnson's (1970) formula (20) agrees with our results in the linear terms of the libration tensor \mathbf{L} . In order to show this, the square-root expressions in Johnson's equation (20) must be expanded into a series and then reformulated, a procedure that is so cumbersome that we do not show it here.

Finally, we give some numerical results of the angle correction for maleic anhydride (MAL) and 5-chloro-1,4-naphthoquinone (5CIN), where we had made use of our earlier TLS analysis of these compounds (Scheringer, 1973). For MAL, the corrections for the various angles lie between -0.0182 and 0.0107 ; for 5CIN, between -0.1646 and 0.1580° . Although the MAL molecules carry out much stronger librations in the crystal because of the loose packing, the angle corrections for MAL are smaller by about a factor of 10. This can be explained with (3.6): In the principal inertial system of MAL, L_{22} is nearly equal to L_{11} , so that only a small angle correction is obtained.

4. Lower and upper bounds

Although the condition for calculating the bounds can be exactly formulated, an explicit expression for the bounds can only approximately be derived. The bounds are gained from the condition that the covariance matrix of the joint Gaussian distribution of the atomic displacements must be positive definite. For the three atoms r, s, t , the relevant part of the covariance matrix is a 9×9 diagonal block \mathbf{M} , and the condition reads

$$\mathbf{M} = \begin{pmatrix} U_r & U_{rs} & U_{rt} \\ U_{sr} & U_s & U_{st} \\ U_{tr} & U_{ts} & U_t \end{pmatrix}, P(\mathbf{M}) \geq 0, \lambda(\mathbf{M}) \geq 0 \quad (4.1)$$

for the 511 principal minors $P(\mathbf{M})$ and 9 eigenvalues $\lambda(\mathbf{M})$. The bounds would be obtained by varying the coupling tensors within the limits set by (4.1), calculating the correction for each set of tensors, and selecting the extreme values of the corrections so obtained. Obviously this procedure cannot be applied in practice with the 27 parameters given by the components of the coupling tensors. Without loss of generality we can reduce the number of parameters to five, if we express the condition (4.1) in the coordinate system of (2.17) (Fig. 1). Transformation to this system implies a congruence transformation of the covariance matrix by which the eigenvalues are changed but not the positive-definiteness. Still, five parameters are too many, and we confine ourselves to a calculation of the bounds with the approximation that the in-plane motions are isotropic. Then we are left with a 3×3 covariance matrix of the three parameters $U_{rt}^{33}, U_{st}^{33}, U_{rs}^{33}$. There are now three principal 2×2 minors and the 3×3 determinant. Since it is difficult algebraically to exploit the condition given by the 3×3 determinant, we make use only of the 2×2 principal minors, and thus obtain the explicit condition

$$|U_{rt}^{33}| \leq (U_r^{33} U_t^{33})^{1/2}. \quad (4.2)$$

The same is true for U_{st}^{33} and U_{rs}^{33} . The bounds for the angle φ are now obtained from (2.17) by adding and subtracting respectively the extremes given by (4.2) to a basic term for which the coupling tensors are zero, *i.e.*

$$\begin{aligned} \varphi(\text{bounds}) &= \varphi + (K_1 \pm K_2)/\sin \varphi, \\ K_1 &= \frac{1}{2} \cos \varphi [U_r^{33} + U_t^{33}]a^{-2} + (U_s^{33} + U_t^{33})b^{-2} \\ &\quad - U_t^{33} (ab)^{-1}, \\ K_2 &= |\cos \varphi a^{-2} - (ab)^{-1}| (U_r^{33} U_t^{33})^{1/2} + |\cos \varphi b^{-2} \\ &\quad - (ab)^{-1}| (U_s^{33} U_t^{33})^{1/2} + (ab)^{-1} (U_r^{33} U_s^{33})^{1/2}. \end{aligned} \quad (4.3)$$

The smaller the out-of-plane motions, the narrower the bounds are. Since K_1 is generally not zero, the bounds are not symmetrical with respect to φ . The bounds (4.3) are, on the one hand, too wide, since we did not use the condition given by the 3×3 determinant, and, on the other hand, too narrow, since we neglected anisotropic in-plane motions. Neglect of both will, at least partially, compensate for each other, so that (4.3) will be a reasonable approximation to the true bounds.

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