

# Diffuse scattering from large-angle, thermally induced, orientational disorder in molecular crystals

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Large-angle rotational motion (libration) characteristic of molecular solids has not been properly included in many scattering calculations because of the need to develop scattering theory through small-angle approximations. A simple but effective approach to calculating the influence of large-angle librations on the thermal disorder scattering given by molecular solids is to treat the molecules as independent librators, each in a harmonic potential well, using the mathematics appropriate for large-angle rotations. The resulting probability distribution for angular misorientations is Gaussian and this distribution can be used to smear the molecular form factor, enabling the librational influence on the scattering to be calculated. It is shown how to apply this direct approach quite generally and by way of examples the technique is used with the molecular solids sulfur hexafluoride (SF<sub>6</sub>), adamantane (C<sub>10</sub>H<sub>16</sub>) and buckminsterfullerene (C<sub>60</sub>). For these materials, the molecular Fourier transform (*i.e.* the molecular form factor) have been calculated in selected planes in reciprocal space, followed by the separate effects of librational and translational smearing. It is found that the librational smearing produces a large effect on the form factor, particularly at larger scattering vectors, that is not sensitive to approximations in the argument. Additionally, the Debye–Waller effect of vibrational motion is included in the calculations, showing quantitatively the decreasing influence of vibrations on the scattering with increasing scattering vector. Both effects illustrate with pedagogic clarity how different processes modify the basic molecular scattering.

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## 1. Introduction

Solids made from comparatively rigid globular molecules that are relatively weakly bound to their neighbours typically exhibit a phase transition from an ordered to a plastic phase (*e.g.* Rapcewicz & Przystawa, 1995). Their behaviour is interesting in this context alone but they are also useful because they form a system that is sufficiently simple to enable the different contributions to X-ray scattering to be shown clearly. This study presents a development of the X-ray scattering produced by such systems, which takes into account the large-angle librations shown by globular molecules. The theory is used to calculate X-ray scattering contours for a set of molecules of increasing size to illustrate how both thermal libration and vibration modify the basic molecular scattering in reciprocal space. Our calculations do not include the highly localized Bragg scattering and the accompanying strongly peaked scattering from low-frequency acoustic modes. These modifications to scattering that are conspicuous over the rest of reciprocal space arise

from well known causes that supplement our considerations here.

The characteristic of molecular solids is that their long-range coupling is weak, making the independent-molecule approximation realistic for librational motion. The reasons for keeping to globular molecules are to obtain the simplifications of describing reciprocal space with respect to cubic axes and to enable the librations to be treated as isotropic, meaning that there is no preferred rotation axis. A similar treatment can be applied to all molecular solids. The ideas are also relevant to large molecular systems, such as proteins, where part of the molecule may be comparatively well oriented and part show a large angular movement. The same technique can be developed for molecules whose libration is anisotropic.

We have chosen to illustrate the scattering from SF<sub>6</sub>, adamantane (C<sub>10</sub>H<sub>16</sub>) and buckminsterfullerene (C<sub>60</sub>). The results will show quantitatively how increasing libration angles smear out the molecular scattering and also the effect of molecular vibration as incorporated *via* the Debye–Waller-factor term.

The technique we have used is simple enough to allow it to be readily applied to quite large molecules, yet realistic enough that the results are meaningful. For example, both the molecular dynamic study of Lonie (1997) and the neutron scattering results of Windsor *et al.* (1981) show that the librational motion in adamantane exhibits little correlation between neighbouring molecules. The novelty of our approach is that we have incorporated the effects of large angles of libration with relative simplicity.

## 2. Librations

The X-ray scattering is calculated by averaging over the probability distribution, in the whole of rotational space, that a molecule is rotated away from its equilibrium position as a consequence of its thermal energy. For the purposes of calculating the X-ray scattering, the assumption is made that librational motion can be represented by a superposition of independent classical harmonic oscillators. This is effectively the Einstein specific heat argument applied to rotational motion, where it is a better match to reality for the molecular solids considered here than the equivalent vibrational assumption. The 'classical' assumption is valid for molecular crystals, where the librational modes are sufficiently low in frequency that the energy per mode is simply ' $kT$ ' at temperatures of interest. For large-amplitude librations, the potential well within which the librations are taking place may depart from this ideal harmonic case. See Dove & Pawley (1984) for a specific example with SF<sub>6</sub> and Michel *et al.* (1995) for C<sub>60</sub>. Such departures can be very substantial but the important point is that they are confined to the wings of the probability distribution and only a small percentage of the molecules in an ensemble are affected. This will not alter the major effects shown by our calculations.

The following result is not new but is central to subsequent discussion. The (unpublished) argument given by Moore (1973) shows briefly that, for an ensemble of independent angular simple harmonic oscillators with energies distributed according to the Boltzmann distribution, the probability of being displaced by an angle  $\psi$  is given by a Gaussian distribution. This result is not limited to small angles.

Let  $P_A(\psi)$  be the probability of finding a simple harmonic oscillator at a position  $\psi$  for a fixed amplitude of oscillation,  $A$ .

$$P_A(\psi) = \frac{1}{\pi(A^2 - \psi^2)^{1/2}}, \quad |\psi| < A. \quad (1)$$

The probability that a particular oscillator from an ensemble of uncoupled oscillators will have amplitude  $A$  ( $A \geq 0$ ), assuming that the oscillators have a Boltzmann distribution of energies,  $E$ , is  $P(A)$  given by

$$P(A) = \frac{2A}{A_0} \exp\left(\frac{-A^2}{A_0^2}\right), \quad (2)$$

where

$$\frac{A^2}{A_0^2} = \frac{E}{kT}.$$

$2^{1/2}A_0$  is the r.m.s. vibrational amplitude. Finally,  $P(\psi)$  is the probability of finding an oscillator at position  $\psi$  (where the oscillators have a Boltzmann distribution of energies). Using (1) and (2),

$$\begin{aligned} P(\psi) &= \int_0^\infty P(A)P_A(\psi) dA \\ &= \frac{1}{\pi} \int_\psi^\infty \frac{P(A) dA}{(A^2 - \psi^2)^{1/2}} \\ &= \frac{1}{\pi^{1/2}A_0} \exp\left(\frac{-\psi^2}{A_0^2}\right), \end{aligned} \quad (3)$$

a Gaussian probability distribution. This result simplifies the scattering calculations.

## 3. Treatment of molecular orientations

The fundamental feature of a librating molecule is that it moves (rapidly) through angular misorientations that are too large to be treated by a small-angle approximation. A proper treatment of librations must therefore be based on the mathematics of finite rotations. Our development uses quaternions to represent rigid-body rotations of the whole molecule. Quaternion algebra involves only sines and cosines, which is computationally simple and effective, and there are no singular points such as arise with the use of Euler angles.

Quaternions were introduced by William R. Hamilton in the first half of the 19th century and popularized by P. G. Tait in a treatise that showed their usefulness for formulating many physical problems. Computational convenience has revived their use. Quaternions are not yet commonly introduced in mechanics textbooks but a number of articles such as that by Spina (1993) give an outline of their important properties. The following introduction is intended to provide enough background to explain our approach.

The quaternion  $\mathbf{q}$  representing a rotation can be treated as a 4-component entity ( $q_0, q_1, q_2, q_3$ ) lying on the hypersphere  $q_0^2 + q_1^2 + q_2^2 + q_3^2 = 1$ .  $q_0$  can be interpreted as a scalar component and the remaining  $q_i$  as the components of a 3-vector. This distinction can be shown explicitly by writing  $\mathbf{q}$  as  $(a, \mathbf{u})$ , or

$$\mathbf{q} = a + \mathbf{u},$$

where  $a$  is  $q_0$  and  $\mathbf{u}$  represents  $(q_1, q_2, q_3)$ . All rigid-body rotations can be represented by a unit vector  $\mathbf{n}$  and an angle of rotation ( $\theta$ ) about  $\mathbf{n}$ . The corresponding quaternion  $\mathbf{q}$  is

$$\mathbf{q} = \cos(\theta/2) + \mathbf{n} \sin(\theta/2), \quad (4)$$

*i.e.*  $q_0 = \cos(\theta/2)$ ,  $q_1 = n_1 \sin(\theta/2)$ ,  $q_2 = n_2 \sin(\theta/2)$ ,  $q_3 = n_3 \sin(\theta/2)$ .

Any vector  $\mathbf{r}$  is moved by rotation  $\mathbf{q}$  to vector  $\mathbf{r}'$  given by

$$\mathbf{r}' = \mathbf{q} * \mathbf{r} * \mathbf{q}^{-1}, \quad (5)$$

where

$$\mathbf{q}^{-1} = \cos(\theta/2) - \mathbf{n} \sin(\theta/2)$$

and  $\mathbf{r}$  is treated as a quaternion  $(0, \mathbf{r})$  of zero scalar component in the  $*$  product. This product is defined by

$$(a + \mathbf{u}) * (b + \mathbf{v}) = ab - \mathbf{u} \cdot \mathbf{v} + a\mathbf{v} + b\mathbf{u} + \mathbf{u} \times \mathbf{v},$$

where  $(b, \mathbf{v})$  represents the components of the second quaternion in the same way that  $(a, \mathbf{u})$  represents the first. Finally, if a rotation  $\mathbf{q}_1$  is first applied and then followed by a rotation  $\mathbf{q}_2$ , the effect of the consecutive rotations is achieved by quaternion  $\mathbf{q}_3$ , where

$$\mathbf{q}_3 = \mathbf{q}_2 * \mathbf{q}_1.$$

Orientation space is large, being described by the surface of the hypersphere. The number of orientations making an angle between  $\psi$  and  $\psi + d\psi$  to any orientation increases as  $\sin^2(\psi/2) d\psi$ . One consequence of this is that the average angle made by orientations at random to a given direction can be calculated to be  $(\pi/2 + 2/\pi)$  rad, namely  $126.48^\circ$ . (This is more than twice the average angle between a reference direction and random directions on a hemisphere centred on the reference direction, which is 1 rad.) If a dynamical model of the system, or the result of measurements, shows that the average angle of molecules to a specific orientation is less than  $126.48^\circ$ , then the molecules show preferential orientation.

Suppose that a molecule is librating around an orientation, represented by a rotation ( $\mathbf{q}$ ) from a standard configuration, in a potential well that allows (large amplitude) misorientation by angle  $\psi$ . The previous section has shown that the probability ( $P$ ) of the molecule being misoriented by angle  $\psi$  is Gaussian, namely

$$P(\psi) = \frac{1}{(2\pi)^{1/2}\sigma} \exp(-\psi^2/2\sigma^2), \quad (6)$$

where  $\sigma$  is the standard deviation of the isotropically distributed libration.

#### 4. Librational smearing of the structure factor

The form factor  $F(\mathbf{K}, \mathbf{q})$  of any molecule depends on its orientation  $\mathbf{q}$ , where  $\mathbf{K}$  is the scattering vector and  $\mathbf{q}$  is given by (4). The effect of the libration on the structure factor is to smear it over the range of orientations given with probability  $P(\mathbf{q})$ :

$$\langle F \rangle = \int_{\text{librational range}} P(\mathbf{q})F(\mathbf{q}) d\mathbf{q}.$$

$P(\mathbf{q})$  depends only on the misorientation angle  $\psi$  in the isotropic case. Remembering from (4) that  $q_0 = \cos(\psi/2)$  and  $q_1, q_2, q_3 = \sin(\psi/2)\mathbf{n}$ ,  $\mathbf{n}$  can be specified as lying on the surface of a unit sphere. Hence  $d\mathbf{n} = \sin\theta d\theta d\phi$  and the average becomes

$$\langle F \rangle = \int_0^{\psi_{\max}} P(\psi) \sin^2(\psi/2) d\psi \int_0^\pi \sin\theta d\theta \int_0^{2\pi} F(\mathbf{q}) d\phi / D$$

and  $q_0 = \cos(\psi/2)$ ,  $q_1 = \sin(\psi/2)\sin\theta\cos\phi$ ,  $q_2 = \sin(\psi/2)\sin\theta\sin\phi$ ,  $q_3 = \sin(\psi/2)\cos\theta$ .  $D$  is the normalizing denominator, see below.

Globular molecules may from time to time flip between symmetry-related orientations as well as librating about their current mean orientation. More generally, the libration will not be centred on the reference quaternion orientation but on orientation  $\mathbf{q}_A$ . In this case, we have to apply  $\mathbf{q}_A$  to every value of  $F$  first and then apply the misorientation integral in  $\mathbf{q}$ :

$$\langle F \rangle = \int_0^{\psi_{\max}} P(\psi) \sin^2(\psi/2) d\psi \int_0^\pi \sin\theta d\theta \int_0^{2\pi} F(\mathbf{q} * \mathbf{q}_A) d\phi / D, \quad (7a)$$

with

$$\begin{aligned} D &= \int_0^{\psi_{\max}} P(\psi) \sin^2(\psi/2) d\psi \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \\ &= 4\pi \int_0^{\psi_{\max}} P(\psi) \sin^2(\psi/2) d\psi. \end{aligned} \quad (7b)$$

The smearing of the structure factor by librations is therefore given by (7), with (6) giving the function  $P(\psi)$ . The method requires one orientational integration per  $\mathbf{K}$  value.

#### 5. Vibrational smearing of the structure factor

The spectrum of thermal vibrations necessarily gives rise to sharp peaks of diffuse scattering centred on Bragg reflections, due to the dominant effect of low-frequency ‘acoustic’ vibrations on the scattering in these locations. If we set aside for the moment this localized structure, the broad effect of vibrational motion on the structure factor is to introduce a multiplicative Debye–Waller term of  $[1 - \exp(-2M)]$  into the scattered intensity. Thus,

$$|F_{\text{vib}}|^2 = |F_{\text{molecule}}|^2 [1 - \exp(-2M)], \quad (8)$$

where

$$M = 8\pi^2 \langle u^2 \rangle \sin^2\theta / \lambda^2.$$

$\langle u^2 \rangle$  is the mean square displacement. James (1948) discusses this Debye–Waller term in the context of independent vibrations for each molecule. The term accounts for the effects of random phases at each molecular site removing the coherence in the scattering from separate molecules. The result cuts out the scattering peak at the origin of reciprocal space and gives small-angle scattering proportional to  $\sin^2\theta/\lambda^2$ . At larger scattering vectors, the scattering from the molecular structure factor is virtually unaffected.

#### 6. Calculations

Evaluation of the X-ray scattering is achieved through evaluating the smearing integral (7) over the surface of the hypersphere of rotations, with the Gaussian sampling probability function (6). The effect of translational smearing is applied through (8). The  $\psi$  integral was truncated at  $\pm 3\sigma$  for the libration probability distribution. Trials were made using adaptive subdivision integration strategies for both a seventh-degree rule and a Monte Carlo technique, *via* NAG Fortran library subroutines. The two techniques produced comparable

results in comparable times. Integral convergence takes longest to achieve at larger  $|\mathbf{K}|$  values and with a modest convergence criterion a little integration noise can be seen on some of the contours. Minor irregularities in some contours do not hide the general conclusions.

For a given resolution in reciprocal space, the time of the calculation looks as if it should increase in proportion to the number of atoms in the molecule, making the technique viable in principle for molecules containing many thousands of atoms. However, there is a hidden run-time scaling factor that arises because for larger molecules the form factor is increasingly sensitive to orientation.

The form factor  $F(\mathbf{K}, \mathbf{q})$  of the molecule after rotation by  $\mathbf{q}$  depends on scattering vector  $\mathbf{K}$  and all the rotated coordinates of each atom in the molecule,  $\mathbf{r}'$  from (5). This dependence is highlighted by writing the scattering factor as  $F(\mathbf{K}, \mathbf{r}')$ . Instead of rotating each atom within the molecule, the same scattering factor is found by providing the inverse rotation to  $\mathbf{K}$ , written  $\mathbf{K}'$ , *i.e.* the calculation uses the relationship

$$F(\mathbf{K}, \mathbf{r}') = F(\mathbf{K}', \mathbf{r}), \quad \text{where } \mathbf{K}' = \mathbf{q}^{-1} * \mathbf{K} * \mathbf{q}, \quad (9)$$

in an analogous way to (5). The purpose of this transformation is to enable the calculations to be made with a single inverse rotation of  $\mathbf{K}$  in place of  $n$  rotations of the atomic coordinates  $\mathbf{r}$ , where  $n$  is the number of atoms in the molecule.

We present calculations for three materials whose rotational dynamics have been investigated by other authors: the small molecule sulfur hexafluoride, SF<sub>6</sub>, a larger molecule adamantane, C<sub>10</sub>H<sub>16</sub>, and the comparatively large 'inorganic' molecule buckminsterfullerene, C<sub>60</sub>. Their appearances are shown in Fig. 1.

## 7. Results and comment

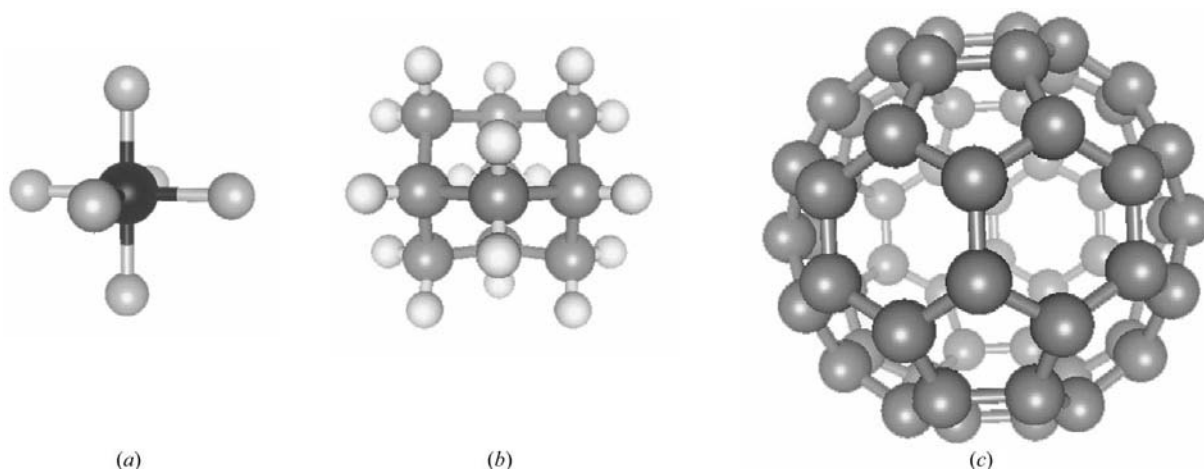
Fig. 2 shows the scattering for the three molecules **without libration or translation** for scattering vectors  $\mathbf{K}$  in the  $(\bar{1}\bar{1}0)$  plane. Values of  $\mathbf{K}$  are in units of  $2\pi/a$ , where  $a$  is the lattice constant of the material in the solid plastic phase, and the calculations have been made for a  $\mathbf{K}$  interval of 0.05. For the

three materials, the lattice constants are  $a = 5.926 \text{ \AA}$  for sulfur hexafluoride,  $a = 9.455 \text{ \AA}$  for adamantane and  $a = 14.17 \text{ \AA}$  for C<sub>60</sub>. No integration is involved and no approximating expansions. The contours are scattering intensities in electron units. The molecules are in standard orientations relative to the crystal axes of their solid plastic phase.

The contour features reflect the point-group symmetry of the molecules, their size and the distribution of atoms within the molecule. The larger the molecule, the greater is the ratio of peak heights to troughs and the fine structure of the pattern becomes more complex. These features are conspicuous for the much larger C<sub>60</sub> molecule of around  $10 \text{ \AA}$  in diameter. Of course, in the solid phase constructive interference between unit cells will enhance the scattering at integer reciprocal-lattice vectors. It is helpful to remember that this process only builds on what is already provided by the molecular form factor.

If we look more closely at the adamantane results, the 'hole' around 555 is consistent with the adamantane structure. Most of the scattering is generated by the C atoms which, in adamantane, are arranged like a ten C-atom fragment of diamond. The well known forbidden 222 reflection in diamond manifests itself here as the 'hole' near 555, the change in the  $\mathbf{K}$  value being due simply to the difference in lattice constants between diamond ( $3.567 \text{ \AA}$ ) and adamantane ( $9.455 \text{ \AA}$ ). In adamantane, the molecules are preferentially oriented around two possible configurations. Both configurations of molecule produce the same scattering in any plane, since the molecular form factors differ in phase but not in modulus.

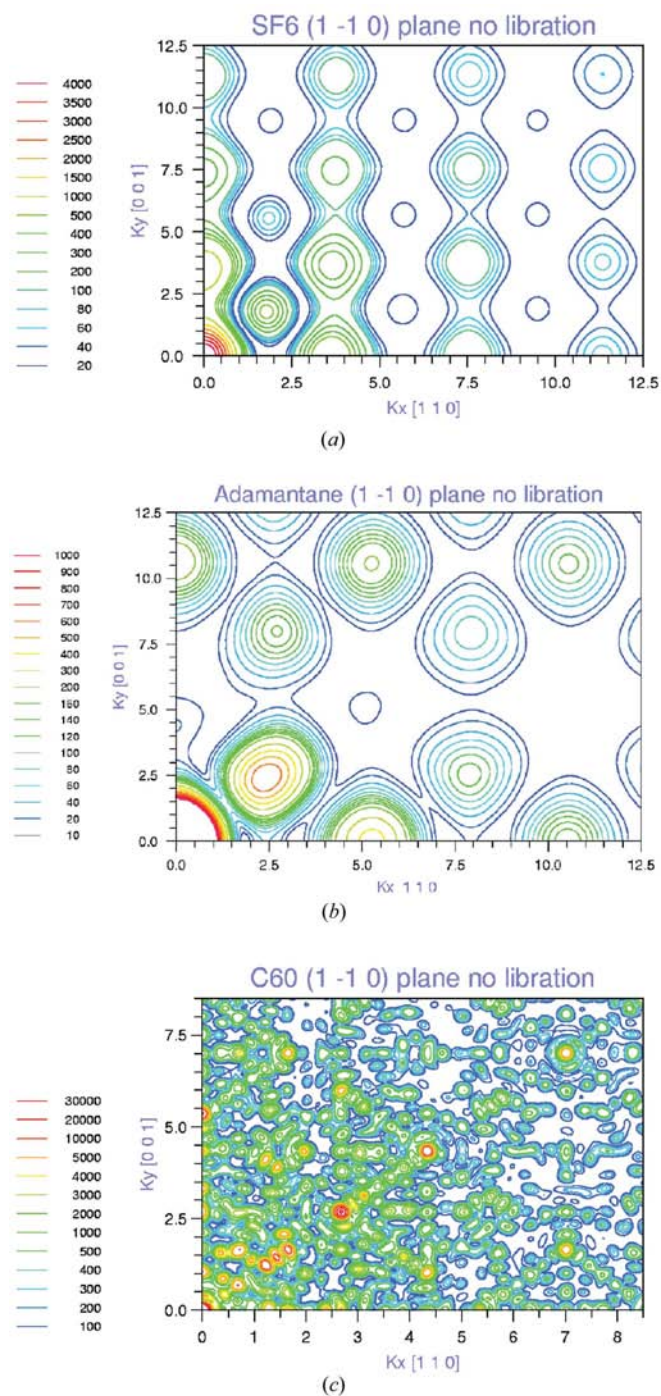
Fig. 3 shows scattering for all molecules with added libration. The general effect of smearing the intensities is not particularly sensitive to the standard deviation of the libration angle for the large angles shown by our materials. For SF<sub>6</sub>, a standard deviation of  $14.4^\circ$  was suggested by Dolling *et al.* (1979). For adamantane, we have used  $8^\circ$ , following the molecular dynamics simulation result of Lonie (1997), which is in keeping with the earlier results of Nordman & Schmitkons (1965). For C<sub>60</sub>, we have chosen  $15^\circ$  in keeping with the potential energy well (Michel *et al.*, 1995) but the exact value is



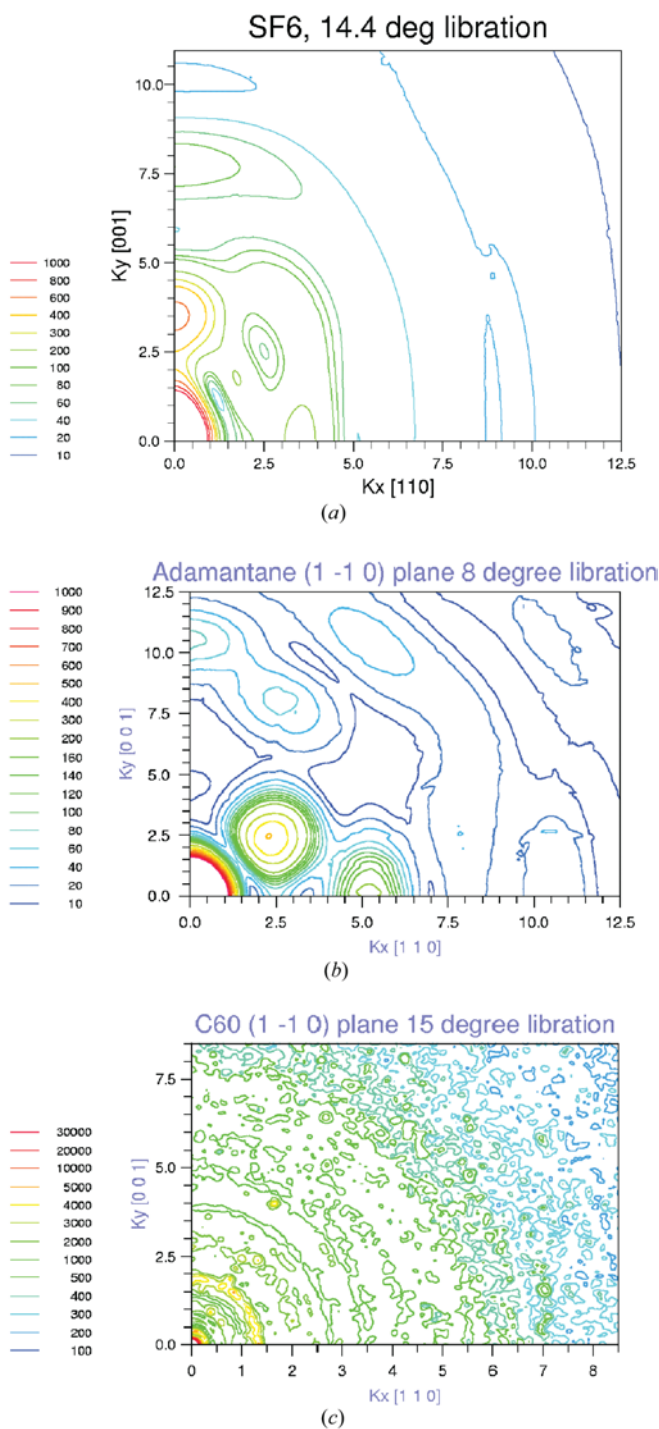
**Figure 1**  
The three molecules used in the illustrative calculations: (a) SF<sub>6</sub>; (b) adamantane, C<sub>10</sub>H<sub>16</sub>; (c) buckminsterfullerene, C<sub>60</sub>.

not important since much of the fine detail in Fig. 2 is reduced to fluctuations that can be considered as ‘molecular size noise’. If  $15^\circ$  seems small for a molecule that is highly orientationally disordered, remember that rotations up to  $\pm 3\sigma$  are included in the integration and, in addition, there are some 60 rotational orientations of the  $C_{60}$  molecule that reproduce the standard configuration of atoms. Hence larger rotations are always

equivalent to smaller rotations from a symmetry-equivalent orientation. In general, libration flattens peaks and raises minima. For larger scattering vectors, maxima disappear to be replaced by contours that tend to follow lines of constant  $|\mathbf{K}|$ . It is worth noticing in passing that isotropic librations do not imply isotropic diffuse scattering in reciprocal space, even for large rotational motion.



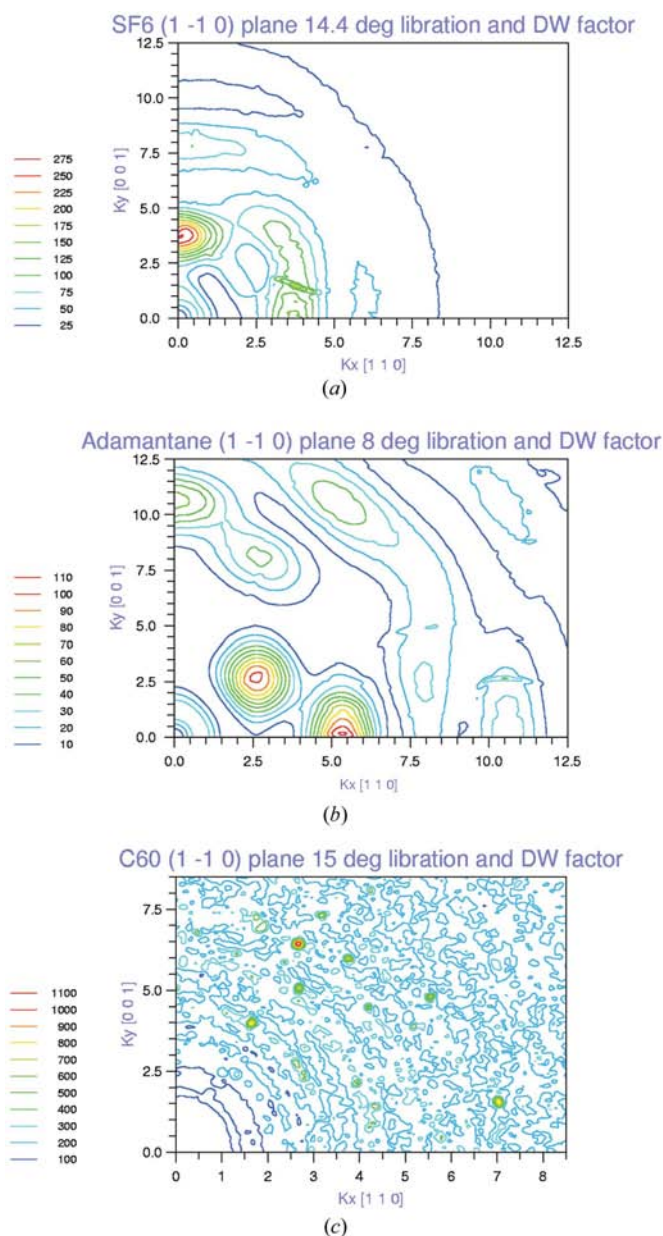
**Figure 2** (110) plane X-ray scattering in electron units given by the molecules in their standard orientations: (a)  $SF_6$ ; (b) adamantane,  $C_{10}H_{16}$ ; (c) buckminsterfullerene,  $C_{60}$ . The scattering vector coordinates are in units of  $2\pi/a$ , where  $a$  is the lattice constant of the material. These units are also used in subsequent figures.



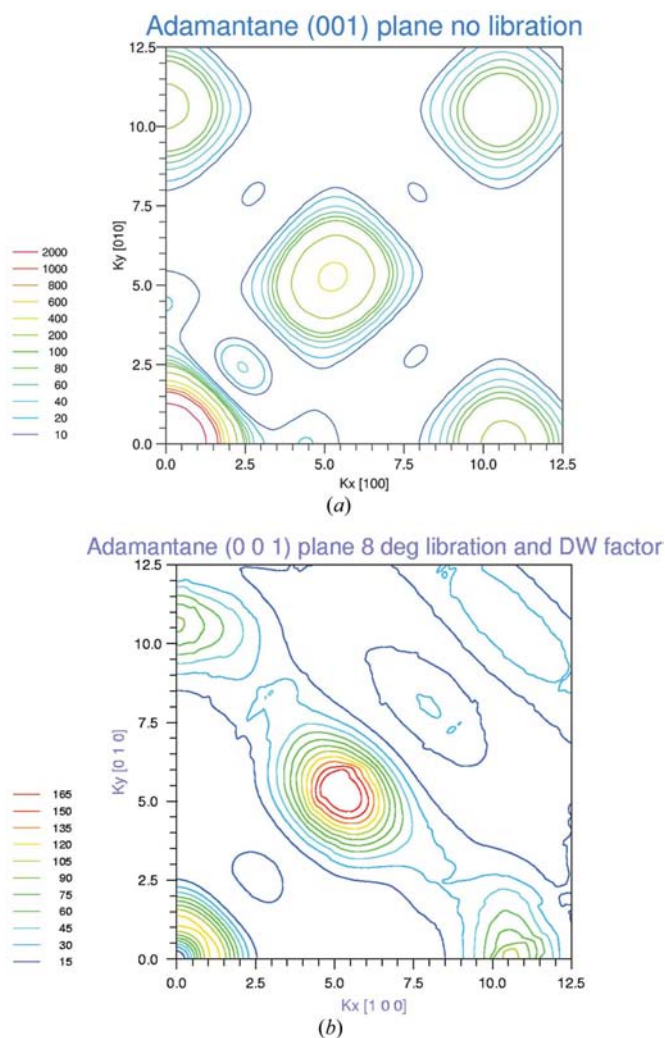
**Figure 3** (110) plane X-ray scattering in electron units given by librating molecules: (a)  $SF_6$ , with libration standard deviation  $14.4^\circ$ ; (b) adamantane,  $C_{10}H_{16}$ , with libration standard deviation  $8^\circ$ ; (c) buckminsterfullerene,  $C_{60}$ , with libration standard deviation  $15^\circ$ .



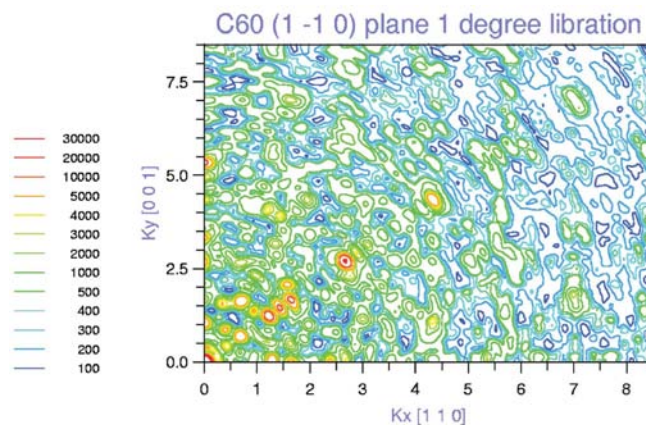
It is worth commenting that the fine detail visible in the  $C_{60}$  contours does not represent a failure of the integration routine to converge satisfactorily. It represents the residue of the basic molecular scattering intensity variations in reciprocal space after inclusion of the effects of libration. Variations in scattering vector  $\mathbf{K}$  by  $0.1 \times (2\pi/a)$  are quite sufficient to change the intensity by tens of %. This is the effect referred to above as ‘molecular size noise’. One is reminded of the speckle pattern of a laser shining on a painted wall, where small movements of the beam or even changes in the angle of observation produce fine changes in the intensity from each small region.



**Figure 4**  
 (110) plane X-ray scattering in electron units given by librating and vibrating molecules: (a) SF<sub>6</sub>; (b) adamantane, C<sub>10</sub>H<sub>16</sub>; (c) buckminsterfullerene, C<sub>60</sub>. (a) and (b) show some small features introduced by the numerical integration that could not be removed in the time available for the calculation.



**Figure 5**  
 Example of X-ray scattering contours in electron units in (001) plane: (a) from a stationary adamantane molecule; (b) with libration and vibration, as in Fig. 4.



**Figure 6**  
 Example showing how quickly libration smears the structure of the scattering for larger molecules. C<sub>60</sub> with a standard deviation of 1°. Compare Figs. 2(c) and 3(c).

Fig. 4 shows the scattering with both libration and translation included. We have used mean square vibrational amplitudes of  $0.09 \text{ \AA}^2$  for  $\text{SF}_6$ , from the neutron scattering results of Dolling *et al.* (1979),  $0.0281 \text{ \AA}^2$  for adamantane, used by Moore (1973) and others and originating from Lucas (1965), and  $0.022 \text{ \AA}^2$  for  $\text{C}_{60}$  (Chow *et al.*, 1992). The Debye–Waller term removes the large forward scatter peak for all materials. For increasing  $|\mathbf{K}|$ , it has progressively less effect. The overall reduction in contour levels highlights how much well defined structure in reciprocal space is lost by the combined effects of libration and translational motion.

The technique allows scattering to be calculated equally easily for any plane. A particularly simple example showing clearly the effect of librational smearing is illustrated by the contours for adamantane in the (001) plane in Figs. 5(a) and 5(b).

Decreasing temperature reduces librational amplitude and here anharmonicity may significantly influence the temperature dependence of the mean square amplitude. To illustrate how sensitive the effect of librational smearing is, Fig. 6 shows the  $\text{C}_{60}$  form factor smeared with only  $1^\circ$  r.m.s. librational amplitude. This is well below the actual amplitude at any temperature that  $\text{C}_{60}$  remains in its plastic phase. Compare Fig. 6 with Fig. 2 to see the substantial loss of scattering structure that such a small libration causes.

## 8. Conclusions

We have demonstrated an effective way of including large-angle librations in the calculation of diffuse X-ray scattering intensities. The calculations here include only processes that arise in an ensemble of independent molecules. Processes involving coherent scattering from two or more molecules are not included. For adamantane, our results are very similar to intensities calculated from the molecular dynamic simulation by Lonie (1997), where no such independent-atom simplification was made. This gives us confidence that, for the kind of

materials we have considered, our approximations are realistic.

The effect of librations and vibrations in modifying the scattering that would be produced from stationary molecules is very clearly shown in Figs. 2–4.

A comparison of our contours with experimental data requires the measurement of well determined absolute scattering intensities over an extended region of reciprocal space. Such data have not yet been published. We shall make a comparison of our calculations with experiment in a later paper.

The authors would like to thank Dr Sandra Lonie, whose first principles calculations of the thermal motion in adamantane in particular and the scattering that resulted provided a strong foundation on which to base the methods outlined in this paper.

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