Neutron and X-ray scattering cross sections of orientationally disordered solid C_{60}

Neutron and x-ray scattering cross sections of orientationally disordered solid C_{60}

J R D Copley† and K H Michel‡

† Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
‡ Department of Physics, Universitaire Instelling Antwerpen, B-2610 Wilrijk, Belgium

Abstract. Differential cross sections for neutron and x-ray scattering have been derived for the orientationally disordered phase of solid C_{60}. Interaction centres are placed at nuclei and at the centres of interatomic bonds. Bragg and diffuse scattering cross sections, for single crystals and for powders, are formulated using symmetry-adapted rotator functions. Thermal averages are calculated taking account of crystal field effects. Thermally averaged orientational distribution functions have also been calculated.

1. Introduction

C_{60}-fullerite is an unusual molecular crystal (Krätschmer *et al* 1990) which undergoes a phase change at about 255 K (Dworkin *et al* 1991, Heiney *et al* 1991), from a high-temperature face-centred cubic (FCC) structure (Fleming *et al* 1991) with orientational molecular disorder (Yannoni *et al* 1991, Tycko *et al* 1991, Neumann *et al* 1992), to a low-temperature $Pa\bar{3}$ structure where the molecules are differently oriented on four simple cubic sublattices (Sachidanandam and Harris 1991, David *et al* 1991). An understanding of diffraction experiments on this material requires a detailed theoretical description of its various scattering cross sections, taking into account the orientational degrees of freedom of the C_{60} molecule.

Orientation-dependent properties of molecular crystals are best formulated in terms of symmetry-adapted multipolar rotator functions. In this way the symmetries of the molecule and of the crystalline site are fully incorporated. Rotator functions were first introduced by James and Keenan (1959) in formulating a theory of the phase transitions in solid CD_4. Press and Hüller (1973) and Press (1973) used and extended these concepts in presenting a method for the analysis of orientational structure in molecular solids. A general method of constructing rotator functions, taking full advantage of group theory, was subsequently described by Yvinec and Pick (1980), while Michel and Parlinski (1985) formulated a general method of calculating the free energy of orientationally disordered crystals on the basis of atom–atom intermolecular potentials. Due to the high symmetry of the C_{60} molecule and the complexity of the molecular structure, a theoretical description of the macroscopic properties of solid C_{60}, on the basis of a microscopic theory, is a significant challenge.

In a recent theoretical study of the orientationally disordered phase and the phase transition in solid C_{60} (Michel *et al* 1992), orientational ordering is described using molecular and site symmetry adapted rotator functions belonging to the manifolds $\ell = 6$ and $\ell = 10$. The active mode with $\ell = 10$ is found to dominate, and the relevant rotator

functions form a basis of irreducible T_{2g} representations of the cubic site group. The fact that the only orientational modes that occur are those with $\ell = 6, 10, 12...$ is a consequence of the very high symmetry of the C_{60} molecule, that of a truncated icosahedron (Kroto *et al* 1985). In the aforementioned microscopic theory, the C_{60} molecule was treated as a rigid structure with interaction centres located at the sites of the sixty carbon atoms. Analysis of low-temperature (T) structural data suggests that the so-called double bonds that fuse adjacent hexagons on a molecule act as repulsive centres of interaction between neighbouring molecules (David *et al* 1991). This idea has been implemented in molecular dynamics calculations (Sprik *et al* 1992) where the inclusion of double bonds is found to be necessary to stabilize the observed cubic low-T structure. The microscopic theory has recently been extended to the case of a more complex molecular structure (Michel 1992a) in which interaction centres are located not only at atoms but at the centres of both double and 'single' bonds. The latter bonds fuse a pentagon and a hexagon and their importance was recently emphasized (Zhang *et al* 1991, Saito and Oshiyama 1991). The set of rotator functions used by Michel *et al* (1992) is sufficient to describe orientation-dependent properties in the case of the more complex molecular structure. In comparison with the atomic model, molecular interactions are modified, but the basic form of the theory remains unchanged. In the present work we assume the more complex molecular structure.

Given the connection between molecular structure and orientation-dependent interactions, it is important to extend the formulation of differential scattering cross sections to the case of a complex molecular structure. In this paper we derive cross sections for both neutrons and x-rays; whereas neutrons couple to nuclei, x-rays interact with the electronic structure of the molecule. An interpretation of the observed differential scattering cross sections should therefore provide useful information about the molecular structure. In the following we derive expressions for the Bragg and diffuse scattering cross sections and for the nuclear and electronic orientational density distribution functions. The thermal averages entering these experimentally measurable quantities are related to the microscopic interaction potentials, in particular to the crystal field in the orientationally disordered phase. This work extends the results of previous work on molecular liquids (Sears 1966, Lovesey 1984), and on molecular crystals (Yvinec and Pick 1980, Seymour and Pryor 1970, Rowe *et al* 1973, Press and Hüller 1973), in which small molecules have generally been considered.

Previously the orientational part of the scattering length density and the rotational structure factor were expanded in terms of symmetry-adapted functions, taking into account the symmetry of the molecule and of the site within the crystal. Up to now the expansion coefficients have been obtained as temperature-dependent empirical parameters. In the present paper the expansion coefficients are related to the molecular interaction potential. This formulation should be very useful to test new theoretical concepts against experiment. It is particularly needed in the case of solid C_{60}, where the electronic structure of the molecule is related to orientational properties.

2. Molecular structure factor

We consider a crystal which consists of N rigid molecules with centres rigidly located at FCC lattice sites $X(n), n = 1 - N$. Molecules may rotate about their centres of mass, but we exclude inter- and intra-molecular vibrations. Each molecule is represented by sixty atom centres, thirty double-bond centres, and sixty single-bond centres. Centres are labelled ν_A, where $A = $ a, b and s denotes atoms, double bonds, and single bonds respectively and the number of centres of type A is denoted N_A; $\nu_A = 1,..N_A$, with $N_a = 60$, $N_b = 30$, and

$N_s = 60$. The position of the centre ν_A belonging to the molecule at lattice site n is written

$$X(n, \nu_A) = X(n) + d(n, \nu_A) \tag{2.1}$$

where the direction of $d(n, \nu_A)$, for a given molecule n, is described by two polar angles $\Omega(\nu_A) = (\theta(\nu_A), \phi(\nu_A))$, and the length of the vector $d(n, \nu_A)$ is d_A.

2.1. Molecular and site symmetries

We start with a molecule in its 'standard' orientation, such that three of its twofold axes coincide with the three cubic axes of the crystal as shown in figure 1, and we introduce coefficients

$$c_\ell^{nA} = \sum_{\nu_A} Y_\ell^n(\Omega(\nu_A)) \tag{2.2}$$

where $Y_\ell^n(\Omega)$ are spherical harmonics, defined according to Bradley and Cracknell (1972) and Altmann and Cracknell (1965). Molecular symmetry implies that the only non-zero coefficients c_ℓ^{nA} are those with $\ell = 0, 6, 10, 12, ...$ and that all coefficients with odd n are identically zero. Coefficients for bond centres are related to coefficients for atomic sites by the equations (Michel 1992a)

$$c_\ell^{nb} = \xi_\ell c_\ell^{na} \tag{2.3}$$

and

$$c_\ell^{ns} = \zeta_\ell c_\ell^{na} \tag{2.4}$$

where ξ_ℓ and ζ_ℓ are numerical constants, independent of n.

We now consider *molecular* symmetry-adapted functions appropriate to the identity representation of molecules with icosahedral (I) symmetry (such as C$_{60}$),

$$S_{\ell(I)}^A(\Omega) = \sum_{n=-\ell}^{\ell} \alpha_{\ell(I)}^{nA} Y_\ell^n(\Omega) \tag{2.5}$$

which have orthonormalized coefficients

$$\alpha_{\ell(I)}^{nA} = c_\ell^{nA}/g_\ell^A \tag{2.6}$$

where

$$g_\ell^A = \sqrt{\sum_n (c_\ell^{nA})^2}. \tag{2.7}$$

We regard the latter quantity as a 'molecular shape factor' (it is sometimes called a 'molecular form factor'), since it follows from equations (2.2), (2.5), and (2.6) that

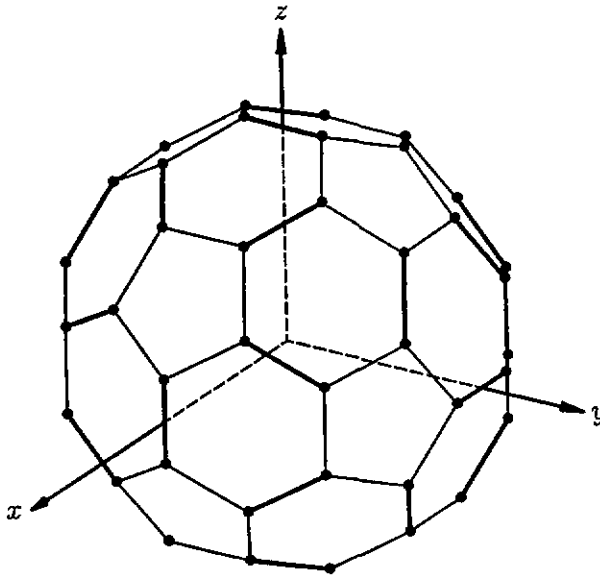$$g_\ell^A = \sum_{\nu_A} S_{\ell(I)}^A[\Omega(\nu_A)]. \tag{2.8}$$

Figure 1. A C_{60} molecule is shown in its 'standard' orientation. Molecular twofold axes lie along the Cartesian x, y and z directions. 'Single' and 'double' bonds are shown as fine and bold lines respectively. An equivalent (but distinct) 'standard' orientation is obtained if the molecule is rotated through $90°$ about one of the Cartesian axes.

Using the well-known identity

$$\sum_n Y_\ell^{n*}[\Omega(\nu_A)]Y_\ell^n[\Omega(\nu_A')] = \frac{(2\ell+1)}{4\pi}P_\ell[\cos(\alpha_{\nu_A\nu_A'})] \tag{2.9}$$

where $\alpha_{\nu_A\nu_A'}$ is the angle between the directions $\Omega(\nu_A)$ and $\Omega(\nu_A')$, we also find that

$$(g_\ell^A)^2 = \frac{(2\ell+1)}{4\pi}\sum_{\nu_A,\nu_A'}P_\ell[\cos(\alpha_{\nu_A\nu_A'})]. \tag{2.10}$$

This result is used in section 3.

Calculated values of g_ℓ^A, for $\ell = 6, 10$, and 12, and for three different models of the structure of the C_{60} molecule, are given in table 1; note that $g_0^A = N_A/\sqrt{4\pi}$. Equations (2.3), (2.4), and (2.7) imply that

$$g_\ell^b = |\xi_\ell|g_\ell^a \tag{2.11}$$

and that

$$g_\ell^s = |\zeta_\ell|g_\ell^a. \tag{2.12}$$

Table 1. Calculated values of the molecular shape factors g_ℓ^A, for three models of the structure of a C_{60} molecule. In models 1 and 2, atoms are placed at the vertices of a truncated icosahedron. In model 1 all bond distances are the same but in model 2 the ratio of 'single' to 'double' bond distances is 1.45:1.40. In model 3 atoms are located according to table 1 of David *et al* (1991); these atom positions do not strictly satisfy icosahedral symmetry.

	Model 1	Model 2	Model 3
g_6^a	3.19	2.56	2.43
g_{10}^a	18.89	19.35	19.46
g_{12}^a	8.85	7.89	7.67
g_6^b	6.33	6.33	6.33
g_{10}^b	13.75	13.75	13.74
g_{12}^b	17.54	17.54	17.53
g_6^s	12.00	11.39	11.24
g_{10}^s	4.20	4.37	4.41
g_{12}^s	23.64	24.08	24.16

Thus, using equation (2.6), we obtain

$$\alpha_{\ell(I)}^{nb} = \text{sgn}(\xi_\ell)\alpha_{\ell(I)}^{na} \tag{2.13}$$

and

$$\alpha_{\ell(I)}^{ns} = \text{sgn}(\zeta_\ell)\alpha_{\ell(I)}^{na} \tag{2.14}$$

with $\text{sgn}(\xi_6) = -1$, $\text{sgn}(\xi_{10}) = +1$, $\text{sgn}(\xi_{12}) = -1$, $\text{sgn}(\zeta_6) = +1$, $\text{sgn}(\zeta_{10}) = +1$, and $\text{sgn}(\zeta_{12}) = +1$. These relationships will shortly be used to simplify our expression for the molecular structure factor.

To describe orientational fluctuations at a site with average cubic symmetry we now introduce *site* symmetry adapted functions (Bradley and Cracknell 1972, Altmann and Cracknell 1965):

$$S_\ell^\tau(\Omega) = \sum_{m=-\ell}^{\ell} \alpha_\ell^{m\tau} Y_\ell^m(\Omega). \tag{2.15}$$

Here the index τ represents the combination (Γ, μ, i), where Γ denotes the irreducible representation of the site cubic group O_h, μ distinguishes between representations that occur more than once within a given manifold, and i labels rows of the representation; the coefficients $\alpha_\ell^{m\tau}$ are tabulated by Bradley and Cracknell (1972) and by Altmann and Cracknell (1965).

A rotation from the standard orientation $\{\Omega(\nu_A)\}$ to an arbitrary molecular orientation $\{\Omega'(\nu_A)\}$ may be described by the Euler angles ω. It is then found from equation (2.15), using equations (2.6) and (2.8), that

$$\sum_{\nu_A} S_\ell^\tau[\Omega'(\nu_A)] = g_\ell^A U_\ell^{\tau A}(\omega) \tag{2.16}$$

where rotator functions for centres of type A read

$$U_\ell^{\tau A}(\omega) = \sum_{n,m} \alpha_{\ell(I)}^{nA} \mathcal{D}_\ell^{nm}(\omega)\alpha_\ell^{m\tau} \tag{2.17}$$

and $\mathcal{D}_\ell^{\prime m}(\omega)$ are the Wigner matrices which govern the transformation of spherical harmonics under rotation. It follows from the proportionality of the coefficients $\alpha_{\ell(l)}^{nA}$, expressed in equations (2.13) and (2.14), that orientation-dependent quantities (when the C_{60} molecule is treated as a rigid body with atoms, double-bond centres and single-bond centres as constituting elements) can be described by a *single* set of rotator functions which take into account both the molecule's symmetry and that of the molecular site within the crystal.

2.2. *Scattering cross sections*

We will now apply these concepts to a formulation of the differential scattering cross section per unit solid angle Ω_Q (or 'scattering law') (Lovesey 1984),

$$\frac{d\sigma}{d\Omega_Q} = \sum_{n,n'} \sum_{A,A'} \sum_{\nu_A,\nu_{A'}} \rho_A \rho_{A'} \langle \exp\{iQ \cdot [X(n,\nu_A) - X(n',\nu_{A'})]\} \rangle \qquad (2.18)$$

where $\hbar Q$ is the momentum transferred in the scattering process, ρ_A is the (identical) scattering length for centres of type A, and angle brackets denote a thermal average. In the case of neutron scattering $\rho_a = \lambda_C$, the scattering length of carbon (which is independent of Q), whereas $\rho_b = \rho_s = 0$. For x-rays all centres contribute so that ρ_a, ρ_b and ρ_s are in general non-zero, decreasing with increasing $|Q|$; at $Q = 0$, $\rho_A = z_A r_e$, where z_A is the charge at a site of type A in units of the electronic charge, and r_e is the classical electron radius.

The total differential scattering cross section, equation (2.18), may be rewritten

$$\frac{d\sigma}{d\Omega_Q} = \sum_{n,n'} \exp\{iQ \cdot [X(n) - X(n')]\} \sum_{A,A'} \langle F_n^A(Q) F_{-n}^{A'}(Q') \rangle \qquad (2.19)$$

where the molecular structure factor is given by

$$F_n^A(Q) = \rho_A \sum_{\nu_A} \exp\{iQ \cdot d(n,\nu_A)\}. \qquad (2.20)$$

This expression is an extension to a complex molecular structure of the rotational structure factor described by *Press* and *Hüller* (1973), *Seymour* and *Pryor* (1970), and *Rowe et al* (1973).

Following the procedure of Pick and Yvinec (1980) we now expand the molecular structure factor in terms of molecular rotator functions and obtain

$$F_n^A(Q) = 4\pi\rho_A \sum_\ell \sum_\tau j_\ell(Qd_A) i^\ell g_\ell^A S_\ell^\tau(\Omega_Q) U_\ell^{\tau A}(n) \qquad (2.21)$$

where j_ℓ denotes a Bessel function, and the argument of U_ℓ^τ stands for $\omega(n)$. Note that (for a centrosymmetric molecule such as C_{60}) $F_n^A(Q)$ is real, and therefore $F_n^A(Q) = F_n^A(-Q)$, since the allowed values of ℓ are all even.

The task of computing molecular structure factors $F_n^A(Q)$ is considerably simplified because the coefficients $\alpha_{\ell(l)}^{nA}$ are proportional to one another for different A. All of the

structure factors can therefore be written in terms of 'atomic' rotator functions $U_\ell^{\tau a}$; from now on we shall drop the superscript a. From equation (2.21) we obtain

$$F_n^A(Q) = 4\pi \sum_\ell \sum_\tau \rho_\ell^A j_\ell(Qd_A) i^\ell S_\ell^\tau(\Omega_Q) U_\ell^\tau(n) \tag{2.22}$$

where

$$\rho_\ell^A = \rho_A \, \text{sgn}(\xi_\ell^A) g_\ell^A \tag{2.23}$$

and we have introduced the conventions $\xi_\ell^a = 1$, $\xi_\ell^b = \xi_\ell$, and $\xi_\ell^s = \zeta_\ell$.

3. Differential scattering cross sections

Having expressed the molecular structure factor $F_n^A(Q)$ in terms of rotator functions (equation (2.22)), we now take advantage of symmetry to obtain various contributions to the total differential scattering cross section. Equation (2.19) may be rewritten as the sum of two terms:

$$d\sigma/d\Omega_Q = (d\sigma/d\Omega_Q)|_B + (d\sigma/d\Omega_Q)|_d \tag{3.1}$$

where the subscripts B and d denote Bragg and diffuse scattering cross sections respectively. The Bragg term is

$$\frac{d\sigma}{d\Omega_Q}\bigg|_B = \left| \sum_n \exp\{iQ \cdot X(n)\} \sum_A \langle F_n^A(Q) \rangle \right|^2 \tag{3.2}$$

which reduces to

$$\frac{d\sigma}{d\Omega_Q}\bigg|_B = \frac{N(2\pi)^3}{V_c} \sum_G \delta(Q - G) \left| \sum_A \langle F_n^A(Q) \rangle \right|^2 \tag{3.3}$$

where G is a reciprocal lattice vector and V_c is the volume of the primitive unit cell. The remaining diffuse term may be broken into a single-molecule 'self' component

$$\frac{d\sigma}{d\Omega_Q}\bigg|_{d,\text{self}} = N \sum_{A,A'} \left[\langle F_n^A(Q) F_n^{A'}(-Q) \rangle - \langle F_n^A(Q) \rangle \langle F_n^{A'}(-Q) \rangle \right] \tag{3.4}$$

which is independent of n, and a 'distinct' component

$$\frac{d\sigma}{d\Omega_Q}\bigg|_{d,\text{dist}} = \sum_n \sum_{n' \neq n} \exp\{iQ \cdot [X(n) - X(n')]\} \sum_{A,A'} \bigg[\langle F_n^A(Q) F_{n'}^{A'}(-Q) \rangle$$

$$- \langle F_n^A(Q) \rangle \langle F_{n'}^{A'}(-Q) \rangle \bigg] \tag{3.5}$$

associated with orientational correlations between molecules at different sites.

In order to proceed we need to calculate the thermal averages which appear in equations (3.3)–(3.5). The intermolecular potential may be written as the sum of a rotation–rotation interaction term which is quadratic in the rotator functions U_ℓ^τ, and a crystal field term which is linear in these functions. In actual calculations the potential is treated within the molecular field approximation. In the disordered phase the single-particle potential at any molecular site then reduces to the crystal field potential, which has full cubic symmetry (i.e. $\Gamma = A_{1g}$, the unit representation), and can therefore be expanded in cubic rotator functions (Michel *et al* 1992a). For $\ell \geqslant 12$ there is more than one A_{1g} representation and we shall use the symbol τ_{1g} to denote the combination (A_{1g}, μ); μ labels the A_{1g} representations. The expansion of the crystal field now reads (writing n for $\omega(n)$)

$$V_{CF}(n) = \sum_\ell \sum_{\tau_{1g}} w_\ell^{\tau_{1g}} U_\ell^{\tau_{1g}}(n) \tag{3.6}$$

where the coefficients are calculated from microscopic theory. For a complex molecular structure with several types of interaction centre they may be written as

$$w_\ell^{\tau_{1g}} = 12 \sum_{A,A'} v_{\ell 0}^{AA'\tau_{1g}} g_\ell^A g_0^{A'} \operatorname{sgn}(\xi_\ell^A). \tag{3.7}$$

The definition of the quantity $v_{\ell 0}^{AA'\tau_{1g}}$ follows from equation (3.17) of Michel (1992a).

The thermal average of a function $\Phi(\omega)$ is defined by

$$\langle \Phi \rangle = Z^{-1} \int d\omega \, \Phi(\omega) \exp[-V_{CF}(\omega)/T] \tag{3.8}$$

where the partition function

$$Z = \int d\omega \exp[-V_{CF}(\omega)/T]. \tag{3.9}$$

It follows that

$$\langle U_\ell^\tau \rangle = \delta_{\tau,\tau_{1g}} \langle U_\ell^{\tau_{1g}} \rangle \tag{3.10}$$

so that

$$\langle F_n^A(Q) \rangle = 4\pi \sum_\ell \sum_{\tau_{1g}} \rho_\ell^A j_\ell(Q d_A) i^\ell K_\ell^{\tau_{1g}}(\Omega_Q) \langle U_\ell^{\tau_{1g}} \rangle. \tag{3.11}$$

Note that in this and subsequent equations the function $S_\ell^{\tau_{1g}}(\Omega)$ is replaced by the well known cubic harmonic $K_\ell^{\tau_{1g}}(\Omega)$ (von der Lage and Bethe 1947, Bradley and Cracknell 1972, Altmann and Cracknell 1965). Since the crystal field has cubic symmetry, we apply a group theoretical matrix element theorem (Tinkham 1964) to obtain

$$\langle U_\ell^{\Gamma\mu i} U_{\ell'}^{\Gamma'\mu'i'} \rangle = \delta_{\Gamma\Gamma'} \delta_{ii'} \langle U_\ell^{\Gamma\mu i} U_{\ell'}^{\Gamma\mu'i} \rangle \tag{3.12}$$

so that

$$\langle F_n^A(Q) F_n^{A'}(-Q) \rangle = 16\pi^2 \sum_{\ell,\ell'} \sum_\Gamma \sum_{\mu,\mu'} \sum_i \rho_\ell^A \rho_{\ell'}^{A'} j_\ell(Q d_A) j_{\ell'}(Q d_{A'})$$
$$\times S_\ell^{\Gamma\mu i}(\Omega_Q) S_{\ell'}^{\Gamma\mu'i}(\Omega_Q) \langle U_\ell^{\Gamma\mu i} U_{\ell'}^{\Gamma\mu'i} \rangle. \tag{3.13}$$

3.1. Bragg scattering

The Bragg scattering intensity for a single crystal is readily obtained by substituting equation (3.11) into equation (3.3). The result is that

$$\left.\frac{d\sigma}{d\Omega_Q}\right|_B = \frac{N(2\pi)^3}{V_c} \sum_G \delta(Q - G) \left| 4\pi \sum_\ell \sum_{\tau_{1g}} i^\ell K_\ell^{\tau_{1g}}(\Omega_Q) \langle U_\ell^{\tau_{1g}} \rangle \sum_A \rho_\ell^A j_\ell(Qd_A) \right|^2. \quad (3.14)$$

Whether or not single crystals are available, useful structural information can also be obtained from *powder* samples, in which the scattered intensity is averaged over all directions of Q. We shall denote powder averages by an overbar, i.e.,

$$\overline{f(\Omega_Q)} = \frac{1}{4\pi} \int d\Omega_Q \, f(\Omega_Q) \quad (3.15)$$

where $f(\Omega_Q)$ represents any function which depends on the direction of Q. The powder-averaged Bragg scattering intensity is then

$$\overline{\left.\frac{d\sigma}{d\Omega_Q}\right|_B} = \frac{N(2\pi)^3}{V_c} \sum_G 4\pi \frac{\delta(Q - G)}{G^2} \left| \sum_\ell \sum_{\tau_{1g}} i^\ell K_\ell^{\tau_{1g}}(\Omega_G) \langle U_\ell^{\tau_{1g}} \rangle \sum_A \rho_\ell^A j_\ell(Qd_A) \right|^2 \quad (3.16)$$

which reduces, in the absence of a crystal field, to

$$\overline{\left.\frac{d\sigma}{d\Omega_Q}\right|_B^{V_{CF}=0}} = \frac{N(2\pi)^3}{V_c} \sum_G \frac{\delta(Q - G)}{G^2} \left[\sum_A \rho_0^A j_0(Qd_A) \right]^2. \quad (3.17)$$

This expression accounts well for the observed Bragg intensities in room-temperature x-ray and neutron powder diffraction experiments on C_{60} (Heiney *et al* 1991, Fischer *et al* 1991, Copley *et al* 1992a,b); in the case of neutron scattering $\rho_0^A = (60\lambda_C/\sqrt{4\pi})\delta_{A,a}$. Notice that one should not conclude from these experiments that the crystal field is strictly zero. Indeed recent single-crystal x-ray diffraction experiments (Chow *et al* 1992) conclusively show that the distribution of orientations of C_{60} molecules in the disordered phase is not completely spherical.

3.2. Diffuse scattering

Inserting equations (3.11) and (3.13) into equation (3.4), we find that

$$\left.\frac{d\sigma}{d\Omega_Q}\right|_{d,self} = 16\pi^2 N \sum_{\ell,\ell'}' \sum_{A,A'} \rho_\ell^A \rho_{\ell'}^{A'} j_\ell(Qd_A) j_{\ell'}(Qd_{A'}) \left\{ \sum_\Gamma \sum_{\mu,\mu'} \sum_i S_\ell^{\Gamma\mu i}(\Omega_Q) S_{\ell'}^{\Gamma\mu' i}(\Omega_Q) \right.$$

$$\left. \langle U_\ell^{\Gamma\mu i} U_{\ell'}^{\Gamma\mu' i} \rangle - i^{\ell-\ell'} \sum_{\mu,\mu'} K_\ell^{A_{1g},\mu}(\Omega_Q) K_{\ell'}^{A_{1g},\mu'}(\Omega_Q) \langle U_\ell^{A_{1g},\mu} \rangle \langle U_{\ell'}^{A_{1g},\mu'} \rangle \right\}. \quad (3.18)$$

The prime on the sum over ℓ and ℓ' indicates that the $\ell = \ell' = 0$ term is omitted; this term vanishes because $U_0^\tau(\omega) = \delta_{\tau,A_{1g}}$. All thermal averages in equation (3.18) refer to a

single molecular site, and translational invariance of the crystal implies that all sites are equivalent. Equation (3.18) is a very general formulation of the single-molecule diffuse differential scattering cross section in an orientationally disordered single crystal.

Since the site symmetry adapted functions S_ℓ^τ are orthonormalized, we obtain from equation (3.18) that the powder-averaged single-molecule diffuse scattering intensity is

$$\overline{\frac{d\sigma}{d\Omega_Q}\Big|_{d,self}} = 4\pi N \sum_{\ell \neq 0} \left\{ \sum_\tau \langle (U_\ell^\tau)^2 \rangle - \sum_{\tau_{1g}} \langle U_\ell^{\tau_{1g}} \rangle^2 \right\} \left[\sum_A \rho_\ell^A j_\ell(Qd_A) \right]^2. \tag{3.19}$$

The temperature dependence of this scattering is determined by the strength of the crystal field (see equation (3.8)).

In the absence of a crystal field, the orthogonality of the rotator functions implies that $\langle U_\ell^{\tau_{1g}} \rangle = 0$ for $\ell \neq 0$, and that

$$\langle (U_\ell^\tau)^2 \rangle_{V_{CF}=0} = 1/(2\ell + 1). \tag{3.20}$$

Since there are $2\ell + 1$ components of τ for a given manifold ℓ, equation (3.19) reduces to

$$\overline{\frac{d\sigma}{d\Omega_Q}\Big|_{d,self}^{V_{CF}=0}} = 4\pi N \sum_{\ell \neq 0} \left[\sum_A \rho_\ell^A j_\ell(Qd_A) \right]^2. \tag{3.21}$$

Using equation (2.23) this expression may be rewritten as follows:

$$\overline{\frac{d\sigma}{d\Omega_Q}\Big|_{d,self}^{V_{CF}=0}} = 4\pi N \sum_{\ell \neq 0} \left[\sum_A \rho_A \operatorname{sgn}(\xi_\ell^A) j_\ell(Qd_A) g_\ell^A \right]^2. \tag{3.22}$$

In the case of x-rays all scattering centres contribute, but for neutrons the only interaction is with nuclei and $\rho_A = \delta_{A,a}\lambda_C$. In this case, using equation (2.10), we find that

$$\overline{\frac{d\sigma}{d\Omega_Q}\Big|_{d,self}^{V_{CF}=0}} = N\lambda_C^2 \sum_{\ell \neq 0} (2\ell + 1) j_\ell^2(Qd_a) \sum_{\nu_a,\nu_a'} P_\ell[cos(\alpha_{\nu_a\nu_a'})]. \tag{3.23}$$

This is the diffuse neutron differential scattering cross section in the absence of a crystal field (see also Neumann *et al* 1992, Copley *et al* 1992a).

We now turn to the 'distinct' diffuse term, equation (3.5). The principal contributions to this scattering arise from order parameter fluctuations which build up as the phase transition is approached from above. In view of previous work (Michel *et al* 1992) we shall restrict our attention to the three components of the dominant T_{2g} mode belonging to the manifold $\ell = 10$. The following discussion also holds for T_{2g} modes belonging to the manifold $\ell = 6$, and can be extended to linear combinations of T_{2g} modes with $\ell = 6$ and $\ell = 10$. In the disordered phase $\langle U_\ell^{\tau_{2g}} \rangle = 0$ so that only the 'correlated' part of equation (3.5) remains. The leading contribution to the 'distinct' term is therefore given by

$$\frac{d\sigma}{d\Omega_Q}\Big|_{d,dist} = 16\pi^2 N \left[\sum_A \rho_{10}^A j_{10}(Qd_A) \right]^2 \sum_{i,j} S_{10}^i(\Omega_Q) S_{10}^j(\Omega_Q) \langle U_{10}^i(q) U_{10}^j(-q) \rangle. \tag{3.24}$$

Here $U_{10}^i(q)$ are the Fourier transforms of the order parameter variables, the indices i and j refer to the three components of the dominant T_{2g} representation, and $q = Q - G$. The correlation function in equation (3.24) is related to the collective order parameter susceptibility $\chi(q)$ by

$$\langle U_{10}^i(q)U_{10}^j(-q)\rangle T^{-1} = \chi^{ij}(q) \tag{3.25}$$

with (Michel 1992b)

$$\chi(q) = x_{10}^{(2)}[T + x_{10}^{(2)}J(q)]^{-1}. \tag{3.26}$$

Here $J(q)$ is a 3×3 interaction matrix and $x_{10}^{(2)}$ is the single-particle expectation value

$$x_{10}^{(2)} = \langle(U_{10}^i)^2\rangle. \tag{3.27}$$

The interaction matrix $J(q)$ becomes diagonal and has its maximum negative eigenvalue at the X point of the Brillouin zone, i.e. for $q = k^X$. Here k^X stands for any of the vectors $k_x^X = (2\pi/a, 0, 0)$, $k_y^X = (0, 2\pi/a, 0)$, and $k_z^X = (0, 0, 2\pi/a)$, where a is the crystal lattice constant. Explicitly we find that

$$J(q) = 4\begin{pmatrix} \gamma C_{yz} + \alpha(C_{zx} + C_{xy}) & -\beta S_{xy} & -\beta S_{zx} \\ -\beta S_{xy} & \gamma C_{zx} + \alpha(C_{xy} + C_{yz}) & -\beta S_{yz} \\ -\beta S_{zx} & -\beta S_{yz} & \gamma C_{xy} + \alpha(C_{yz} + C_{zx}) \end{pmatrix} \tag{3.28}$$

where $C_{ij} \equiv \cos(q_i a/2)\cos(q_j a/2)$ and $S_{ij} \equiv \sin(q_i a/2)\sin(q_j a/2)$. The quantities α, β and γ in equation (3.28) were originally determined by numerical calculation for the case of atom–atom Lennard–Jones potentials between nearest-neighbour molecules (Michel *et al* 1992). Extension of the theory to a more complex structure, including double- and single-bond interactions as well as Coulomb interactions within a distribution of electronic charges, shows that the structure of the matrix $J(q)$ is unaltered (Michel 1992a). Depending on the strengths of the various interactions the coefficients α, β and γ take different values, but in all cases $\gamma \gg \alpha, \beta$. The structure of the matrix $J(q)$ is the same for T_{2g} modes belonging to the manifold $\ell = 6$.

4. Orientational distribution functions

Orientational density distribution functions can in principle be determined in diffraction experiments (Press and Hüller 1973, Seymour and Pryor 1970, Rowe *et al* 1973). Neutron diffraction data can be analysed to yield information regarding the thermal average of the instantaneous orientational distribution function for *nuclei*, which may be written (Michel and Parlinski 1985) as

$$f^n(\Omega; \omega) = \sum_\ell \sum_\tau g_\ell^a U_\ell^\tau(\omega)S_\ell^\tau(\Omega) \tag{4.1}$$

where Ω is the direction of observation, the instantaneous orientation of the molecule is described by Euler angles ω, and the superscript n denotes nuclear density. This expression

generalizes an earlier formulation of the scattering length density which was expanded in terms of cubic rotator functions (Press and Hüller 1973). The thermally averaged distribution function is then given by

$$f^n(\Omega) = \langle f^n(\Omega; \omega)\rangle. \tag{4.2}$$

Using equation (3.10) we obtain

$$f^n(\Omega) = \sum_\ell \sum_{\tau_{1g}} \gamma_\ell^{n\tau_{1g}} K_\ell^{\tau_{1g}}(\Omega) \tag{4.3}$$

where

$$\gamma_\ell^{n\tau_{1g}} = g_\ell^a \langle U_\ell^{\tau_{1g}}\rangle. \tag{4.4}$$

Since $K_0 = 1/\sqrt{4\pi}$ and $g_0^a = 60/\sqrt{4\pi}$, the first term in equation (4.3) is simply $60/4\pi$. The coefficients $\gamma_\ell^{n\tau_{1g}}$ can be determined from neutron diffraction experiments since the thermal averages $\langle U_\ell^{\tau_{1g}}\rangle$ appear in the Bragg differential scattering cross section, equations (3.14) and (3.16). On the other hand they can also be calculated if the crystal field, equation (3.6), is obtained from a theoretical model.

We now consider the thermally averaged *electron* density distribution function, which is relevant to the analysis of x-ray experiments, and we start with the charge distribution for a molecule in its standard orientation (figure 1):

$$\sum_A \sum_{\nu_A} z_A \delta(\Omega - \Omega(\nu_A)) = \sum_A \sum_{\nu_A} \sum_{\ell,\tau} z_A S_\ell^\tau[\Omega(\nu_A)] S_\ell^\tau(\Omega). \tag{4.5}$$

Applying the rotation operation $\Omega'(\nu_A) \equiv R(\omega)\Omega(\nu_A)$, we obtain the instantaneous charge distribution function

$$f^e(\Omega; \omega) = \sum_A \sum_{\nu_A} z_A \delta(\Omega - \Omega'(\nu_A)) \tag{4.6}$$

where the superscript e denotes electron density. Using concepts developed in section 2 we find that

$$f^e(\Omega; \omega) = \sum_A \sum_{\ell,\tau} z_\ell^A U_\ell^\tau(\omega) S_\ell^\tau(\Omega) \tag{4.7}$$

where

$$z_\ell^A = z_A \,\mathrm{sgn}(\xi_\ell^A) g_\ell^A \tag{4.8}$$

is the 'electron molecular shape factor' for sites of type A (cf equation (2.23)). The thermally averaged electron density distribution is then

$$f^e(\Omega) = \sum_\ell \sum_{\tau_{1g}} \gamma_\ell^{e\tau_{1g}} K_\ell^{\tau_{1g}}(\Omega) \tag{4.9}$$

where

$$\gamma_\ell^{c\tau_{1g}} = \sum_A z_\ell^A \langle U_\ell^{\tau_{1g}} \rangle. \tag{4.10}$$

The first term in the expansion of $f^e(\Omega)$, equation (4.9), is $\sum_A z_A N_A/4\pi = 360/4\pi$, since there are six electrons per atom of carbon.

Our formulation of the thermally averaged nuclear and electronic density distributions, $f^n(\Omega)$ and $f^e(\Omega)$, enables their calculation for a specific microscopic potential model, but in practice our current (first-principles) understanding of the intermolecular potential is still somewhat incomplete. Molecular dynamics calculations (Cheng and Klein 1992) and energy minimization calculations (Guo *et al* 1991) have shown that Lennard–Jones potentials based on atom–atom interactions alone result in non-cubic lattice structures at low temperature. (This shortcoming has been avoided in the analytical theory (Michel *et al* 1992) by restricting attention to a rigid lattice structure and only allowing the C_{60} molecule to have orientational degrees of freedom.) Following molecular dynamics calculations with improved potentials (Sprik *et al* 1992), it is now commonly accepted that the inclusion of double bonds as repulsive interaction centres (David *et al* 1991) ensures that the low-T structure is cubic. The electronic charge distribution of the molecule, which contributes an electrostatic multipole component to the intermolecular potential, may also be taken into account (Lu *et al* 1992). It has recently been shown (Michel 1992a) that the theory can be extended to intermolecular potentials associated with a complex molecular structure. Application of the extended theory to various models of the molecular structure shows that numerical values of the multipolar intermolecular interaction constants and of the crystal field coefficients depend strongly on details of the molecular structure such as the distribution of electric charge among bonds and atoms, and the location and strength of Lennard–Jones interactions. Given the inherent uncertainties in this parametrization of the molecular structure, we prefer here not to use a particular molecular model but rather to discuss the dependence of $f^n(\Omega)$ on parameters of the crystal field itself. By parametrizing the crystal field we obtain results which can be compared with the results of experiments. Such an analysis provides information which can in turn be used to improve our description of the molecular interaction potential.

We have numerically calculated the coefficients $\gamma_\ell^{n\tau_{1g}}$ for various choices of the crystal field parameters w_6 and w_{10} in equation (3.6), using equation (3.8) to calculate the thermal averages entering equation (4.4). Representative results are shown in table 2 and in figure 2, expressed in terms of the dimensionless variables $\hat{w}_\ell \equiv w_\ell/T$ ($\ell = 6$ and 10). To a good approximation we find that γ_6^n decreases linearly with increasing $\hat{w}_6$, and is relatively insensitive to $\hat{w}_{10}$. On the other hand γ_{10}^n is mostly quadratic in $\hat{w}_6$, and increases with decreasing $\hat{w}_{10}$. The behaviour of the coefficients in equation (4.3) is such that $f^n(\Omega)$ becomes more isotropic as the temperature is increased. Very similar conclusions apply to γ_ℓ^e and to $f^e(\Omega)$, since z_ℓ^A, equation (4.8), is dominated by the contribution from atomic centres.

In figure 3 we show the dependence of $f(\Omega)$, e.g. $f^n(\Omega)$ or $f^e(\Omega)$, on the corresponding coefficients γ_6 and γ_{10}. The orientational density distribution is clearly deficient close to the (111) direction when γ_6 is negative and γ_{10} is positive. Furthermore the density in the (110) direction depends on γ_6 but is almost independent of γ_{10}. Scattering experiments provide important information about the coefficients γ_ℓ, information which in turn improves our understanding of the intermolecular potential.

Table 2. The coefficients γ_6^n and γ_{10}^n, calculated for the indicated values of the dimensionless parameters $\hat{w}_6 \equiv w_6/T$ and $\hat{w}_{10} \equiv w_{10}/T$. Note that $\gamma_0^n = 60/\sqrt{4\pi} = 16.926$.

$\hat{w}_6$	$\hat{w}_{10}$	γ_6^n	γ_{10}^n
−4.0	−0.4	0.64	1.58
	0.0	0.62	1.31
	0.4	0.59	1.04
−2.0	−0.4	0.38	0.73
	0.0	0.36	0.43
	0.4	0.34	0.13
0.0	−0.4	0.00	0.38
	0.0	0.00	0.00
	0.4	0.00	−0.36
2.0	−0.4	−0.41	1.05
	0.0	−0.38	0.51
	0.4	−0.36	−0.02
4.0	−0.4	−0.72	2.50
	0.0	−0.68	1.79
	0.4	−0.64	1.14

The crystal field coefficient w_6 is sensitive to certain aspects of our model of the molecular interaction potential. From equation (3.7) we obtain the result, for $\ell = 6$ or 12, that

$$w_\ell^{\tau_{1g}} = \left(360/\sqrt{4\pi}\right)[2g_\ell^a v_{\ell 0}^{aa\tau_{1g}} - g_\ell^b v_{\ell 0}^{bb\tau_{1g}} + 2g_\ell^s v_{\ell 0}^{ss\tau_{1g}} + (g_\ell^a - 2g_\ell^b)v_{\ell 0}^{ab\tau_{1g}} + 2(g_\ell^a + g_\ell^s)v_{\ell 0}^{as\tau_{1g}}$$

$$+ (g_\ell^s - 2g_\ell^b)v_{\ell 0}^{bs\tau_{1g}}]. \tag{4.11}$$

(The same expression holds for $\ell = 10$, except that all signs are positive.) Inserting numerical values of the molecular shape factors g_6^A from table 1 (model 2), we find that

$$w_6 = \left(\frac{360}{\sqrt{4\pi}}\right)[5.12v_{60}^{aa} - 6.33v_{60}^{bb} + 22.78v_{60}^{ss} - 10.10v_{60}^{ab} + 27.90v_{60}^{as} - 1.27v_{60}^{bs}]; \tag{4.12}$$

the superscript τ_{1g} is dropped because there is only one A_{1g} representation for $\ell = 6$. Since the C_{60} molecule is electrically neutral, Coulomb interactions do not contribute to the crystal field. Furthermore the Lennard–Jones potential is such that all elements $v_{\ell 0}^{AA'}$ have the same (negative) sign. Thus w_6 is always negative in the absence of double-bond interaction centres whereas such centres give a positive contribution to w_6 because of the negative signs in equation (4.11). In the absence of single-bond centres, and under the plausible assumption (Sprik *et al* 1992) that double-bond centres contribute strongly to the repulsive interaction, the latter centres cause w_6 to be positive. Since single-bond centres always produce a negative contribution to w_6, we see that the sign of w_6 largely depends on the interplay between double- and single-bond centre interactions. The coefficients $v_{60}^{AA'}$ are very sensitive to parameters of the corresponding Lennard–Jones potentials. On the other hand we find that for all models studied, and for all plausible choices of potential parameters, w_{10} is negative.

Recently Chow *et al* (1992) have measured x-ray Bragg peak intensities in a single crystal of C_{60} at 300 K. The measurements were analysed to extract the coefficients $\gamma_\ell^{e\tau_{1g}}$
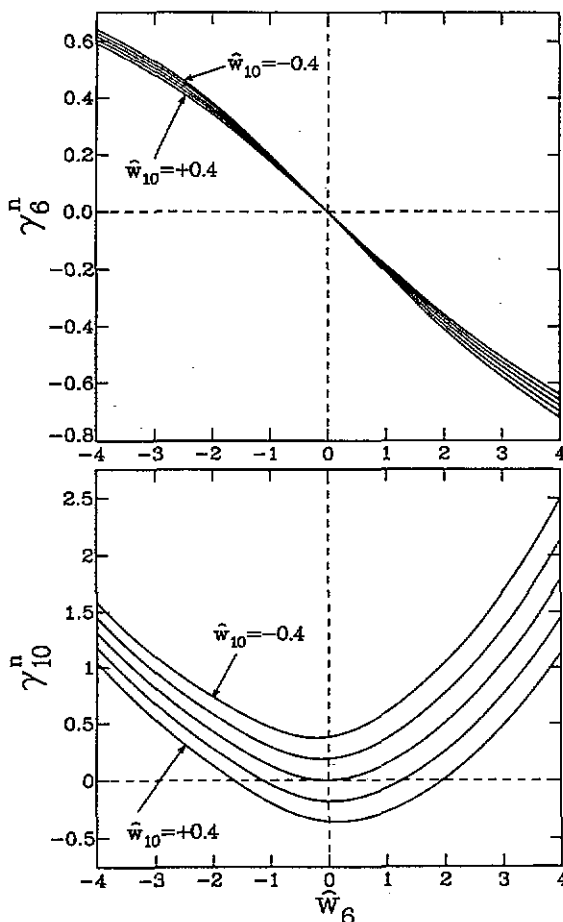
Figure 2. The coefficients γ_6^n and γ_{10}^n, plotted as a function of $\hat{w}_6 \equiv w_6/T$ for the following values of $\hat{w}_{10} \equiv w_{10}/T$: -0.4, -0.2, 0, 0.2, and 0.4.

in the expansion of the electron orientational distribution function, equation (4.9). It was found that γ_6^c is negative, which suggests that the coefficient w_6 in the effective crystal field potential is positive, confirming the importance of double-bond centres in our model of the intermolecular potential. With $w_{10} < 0$ and $w_6 > 0$, we deduce from figure 2 that γ_{10} is positive, in agreement with Chow *et al* (1992).

5. Concluding remarks

Using the formalism of molecular and site symmetry adapted rotator functions, we have derived expressions for differential cross sections for neutron and x-ray scattering in the orientationally disordered phase of solid C$_{60}$. We have given expressions for Bragg scattering and diffuse scattering for the cases of single crystals and powder samples. The single-particle orientational distribution function has been discussed, and the dependence of its first two coefficients on crystal field parameters has been examined.

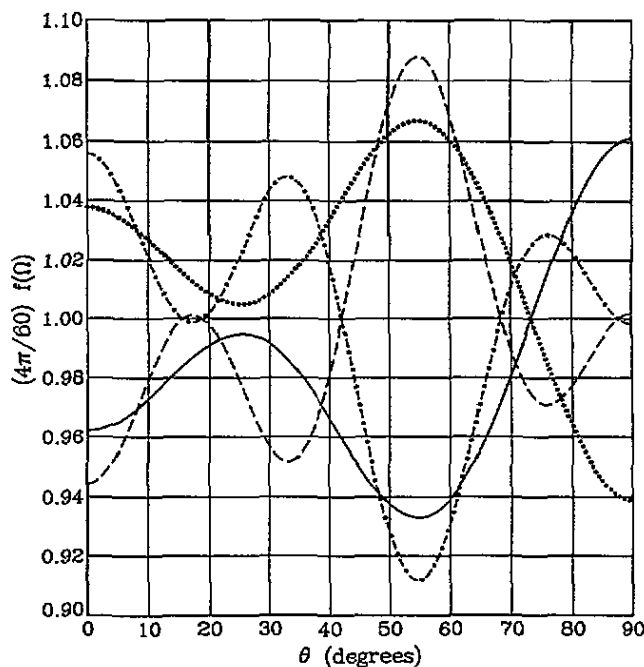We have restricted our treatment to orientational degrees of freedom and have assumed

Figure 3. Plots of the normalized orientational distribution function, $(4\pi/60)f(\Omega)$, for four choices of the coefficients γ_ℓ: $\gamma_0 = 60/\sqrt{4\pi}$. Full curve, $\gamma_6 = -0.4$, $\gamma_{10} = 0.0$; dotted curve, $\gamma_6 = +0.4$, $\gamma_{10} = 0.0$; broken curve, $\gamma_6 = 0.0$, $\gamma_{10} = -0.4$; chain curve, $\gamma_6 = 0.0$, $\gamma_{10} = +0.4$. The function is plotted in the $[1\ \bar{1}0]$ plane as a function of the polar angle θ, with $\phi = 45°$. The crystallographic directions (001), (111) and (110) correspond to $\theta = 0°$, $54.7°$ and $90°$ respectively.

that molecular centres lie on a rigid lattice. This assumption is certainly justified as a first approximation. Indeed at the X point of the Brillouin zone there is no coupling between acoustic lattice displacements and orientational order parameter fluctuations. (Acoustic lattice displacements couple to the square of the T_{2g} order parameter fluctuations (Lamoen and Michel 1993), causing the cubic cell constant to contract at the first-order phase transition (David *et al* 1992, Heiney *et al* 1992).) The absence of bilinear coupling implies that we do not need to include mixed translation–rotation correlation functions in the scattering cross sections.

As we have pointed out in section 4, the orientational distribution function in the disordered phase of C_{60} is determined by the coefficients $w_\ell^{\Gamma|s}$ of the crystal field. We have given expressions for $w_\ell^{\Gamma|s}$ in terms of the distribution and strength of the interaction centres of the molecule. Since our knowledge in this matter is somewhat incomplete, *ab initio* calculations of the electronic structure of the molecule should help to provide a more reliable parametrization of the intermolecular potential. However even at present our analysis indicates that double-bond interaction centres, which were initially introduced to explain structural data at low temperature (David *et al* 1991), play an important role in determining the orientational distribution in the high-T phase.

There is a fundamental reason why a theoretical calculation of the single-particle orientational distribution function is an extremely difficult challenge. The field experienced by a rotating molecule within a crystal actually includes contributions from all degrees of freedom in the crystal. In particular the self-energy of a rotating molecule in a

deformable lattice yields important contributions to the effective crystal potential, in addition to those obtained in the case of a rigid lattice (Michel and Rowe 1985). On the other hand characteristic properties at phase transitions only depend on a few relevant degrees of freedom. As a more direct test of theoretical concepts (Michel *et al* 1992, Michel 1992b), and in particular of expression (3.24), we encourage and look forward to a detailed investigation of the static collective orientational susceptibility in a single crystal of C$_{60}$ at a temperature close to that of the orientational phase transition.

Acknowledgments

References

Altmann S L and Cracknell A P 1965 *Rev. Mod. Phys.* **37** 19
Bradley C J and Cracknell A P 1972 *The Mathematical Theory of Symmetry in Solids* (Oxford: Clarendon Press)
Cheng A and Klein M L 1992 *Phys. Rev.* B **45** 1889
Chow P C, Jiang X, Reiter G, Wochner P, Moss S C, Axe J D, Hanson J C, McMullan R K, Meng R L and Chu C W 1992 *Phys. Rev. Lett.* **69** 2943
Copley J R D, Neumann D A, Cappelletti R L and Kamitakahara W A 1992a *J. Phys. Chem. Solids* **53** 1353
Copley J R D, Neumann D A, Cappelletti R L, Kamitakahara W A, Prince E, Coustel N, McCauley J P Jr, Maliszewskyj N C, Fischer J E, Smith A B III, Creegan K M and Cox D M 1992b *Physica* B **180 & 181** 706
David W I F, Ibberson R M, Dennis T J S, Hare J P and Prassides K 1992 *Europhys. Lett.* **18** 219; **18** 735 (addendum)
David W I F, Ibberson R M, Matthewman J C, Prassides K, Dennis T J S, Hare J P, Kroto H W, Taylor R and Walton D R M 1991 *Nature* **353** 147
Dworkin A, Szwarc H, Leach S, Hare J P, Dennis T J S, Kroto H W, Taylor R and Walton D R M 1991 *C. R. Acad. Sci., Paris* II **312** 979
Fischer J E, Heiney P A, McGhie A R, Romanow W J, Denenstein A M, McCauley J P Jr and Smith A B III 1991 *Science* **252** 1288
Fleming R M, Siegrist T, Marsh P M, Hessen B, Kortan A R, Murphy D W, Haddon R C, Tycko R, Dabbagh G, Mujsce A M, Kaplan M L and Zahurak S M 1991 *Mater. Res. Soc. Symp. Proc.* vol 206, ed R S Averback, J Bernholc and D L Nelson, 691
Guo Y, Karasawa N and Goddard W A III 1991 *Nature* **351** 464
Heiney P A, Fischer J E, McGhie A R, Romanow W J, Denenstein A M, McCauley J P Jr, Smith A B III and Cox D E 1991 *Phys. Rev. Lett.* **66** 2911
Heiney P A, Vaughan G B M, Fischer J E, Coustel N, Cox D E, Copley J R D, Neumann D A, Kamitakahara W A, Creegan K M, Cox D M, McCauley J P Jr and Smith A B III 1992 *Phys. Rev.* B **45** 4544
James H M and Keenan T A 1959 *J. Chem. Phys.* **31** 12
Krätschmer W, Lamb L D, Fostiropoulos K and Huffman D R 1990 *Nature* **347** 354
Kroto H W, Heath J R, O'Brien S C, Curl R F and Smalley R E 1985 *Nature* **318** 162
Lamoen D and Michel K H 1993 *Phys. Rev.* B at press
Lovesey S W 1984 *Theory of Neutron Scattering from Condensed Matter* vol 1 (Oxford: Clarendon)
Lu J P, Li X-P and Martin R M 1992 *Phys. Rev. Lett.* **68** 1551
Michel K H 1992a *J. Chem. Phys.* **97** 5155
——— 1992b *Z. Phys.* B **88** 71
Michel K H, Copley J R D and Neumann D A 1992 *Phys. Rev. Lett.* **68** 2929
Michel K H and Parlinski K 1985 *Phys. Rev.* B **31** 1823
Michel K H and Rowe J M 1985 *Phys. Rev.* B **32** 5827

Neumann D A, Copley J R D, Cappelletti R L, Kamitakahara W A, Lindstrom R M, Creegan K M, Cox D M, Romanow W J, Coustel N, McCauley J P Jr, Maliszewskyj N C, Fischer J E and Smith A B III 1992 *Phys. Rev. Lett.* **67** 3808

Pick R M and Yvinec M 1980 *J. Physique* **41** 1053

Press W 1973 *Acta Cryst.* A **29** 257

Press W and Hüller A 1973 *Acta Cryst.* A **29** 252

Rowe J M, Hinks D G, Price D L, Susman S and Rush J J 1973 *J. Chem. Phys.* **58** 2039

Sachidanandam R and Harris A B 1991 *Phys. Rev. Lett.* **67** 1467

Saito S and Oshiyama A 1991 *Phys. Rev. Lett.* **66** 2637

Sears V F 1966 *Can. J. Phys.* **44** 1279

Seymour R S and Pryor A W 1970 *Acta Cryst.* B **26** 1487

Sprik M, Cheng A and Klein M L 1992 *J. Phys. Chem.* **96** 2027

Tinkham M 1964 *Group Theory and Quantum Mechanics* (New York: McGraw-Hill) p 80

Tycko R, Haddon R C, Dabbagh G, Glarum S H, Douglass D C and Mujsce A M 1991 *J. Phys. Chem.* **95** 518

von der Lage F C and Bethe H 1947 *Phys. Rev.* **71** 617

Yannoni C S, Johnson R D, Meijer G, Bethune D S and Salem J R 1991 *J. Phys. Chem.* **95** 9

Yvinec M and Pick R M 1980 *J. Physique* **41** 1045

Zhang Q-M, Yi J-Y and Bernholc J 1991 *Phys. Rev. Lett.* **66** 2633