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### Some comments on cylindrical distribution functions, with special reference to X-ray studies of liquid crystals.\*

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A fundamental problem of cylindrical distribution functions is that they deal with the numbers of units in cylindrical shells. The height of these shells is undefined. Consequently, the numbers of units in these shells are also undefined.

During recent years a considerable number of papers have appeared in which cylindrical distribution functions (cdf's) are used for the analysis of X-ray diffraction data from liquid crystals (Chistyakov, 1964; Chistyakov & Chaikovskii, 1967, 1969; Chistyakov & Vainshtein, 1963; Delord, 1969; Delord & Falgueirettes, 1968*a, b*; Delord & Malet, 1970; Gusakova & Chistyakov, 1968; Kosterin & Chistyakov, 1968, 1969; Vainshtein, Chistyakov, Kosterin & Chaikovskii, 1967, 1969). All these papers refer to Vainshtein (1966)† for more details on the cdf's, but, unfortunately, Vainshtein does not give a detailed derivation of the cdf's. Some other papers (Oster & Riley, 1952; Alexander & Michalik, 1959) discuss a particular case of cylindrical symmetry in more detail, but their models, valuable as they are, are too far removed from the reality of a liquid crystalline medium. As a result of this, one has generally been unaware of a particular fundamental difference between radial distribution functions (rdf's) and cdf's. The rdf's deal with the numbers of units in spherical shells; the volumes of these shells are defined, and so are the numbers of units in the shells. The cdf's deal with cylindrical shells. The volumes of these shells are undefined because the heights of the shells are undefined; consequently, the numbers of units in these shells are also undefined. As far as we know, this has not been recognized, and the data obtained often have been interpreted incorrectly.

To demonstrate this lack of definition in the cdf's, we shall present here very briefly some of the main steps in the derivation of the atomic cdf (acdf). For simplicity, we shall assume all atoms to have equal scattering factors.

In the calculation of cdf's one uses only the intensity diffracted in the equatorial plane (the plane perpendicular to the axis of cylindrical symmetry of the sample). We shall take this plane as the *xy* plane of an orthogonal set of axes, the *z* axis being parallel to the axis of cylindrical symmetry. Both the incident and the diffracted beam (defined by the unit vectors  $\mathbf{S}_0$  and  $\mathbf{S}$  respectively) are in the *xy* plane, and the *x* axis will be chosen along  $\mathbf{s} = 2\pi(\mathbf{S} - \mathbf{S}_0)/\lambda$ .

The total intensity of the scattering from an assembly of *N* equal atoms is

$$\bar{I}_t(s) = \sum_{p=1}^N \left\langle f^2 + \sum_{q \neq p} f^2 \exp(i\mathbf{s} \cdot \mathbf{r}_{pq}) \right\rangle \equiv \sum_{p=1}^N \bar{I}_p(s)$$

where the angular brackets indicate averaging over time. For the calculation of each  $\bar{I}_p(s)$  we take the origin of the coordinate system (described above) at the center of the atom *p*, and define the position of each atom *q* by the following param-

eters:  $z_q$  = the height above the *xy* plane,  $a_q$  = the distance from the *z* axis, and  $\varphi_q$  = the angle between the *x* axis and the plane through the atom and the *z* axis. Using these cylindrical coordinates, and performing the usual operations (see, e.g. James, 1958) of replacing the summation over *q* by an integral over the volume and introducing the atomic density  $\rho$  and the average atomic density  $\rho_0$ , one obtains (under the assumption of cylindrical symmetry)  $\bar{I}_t(s) = N\bar{I}(s)$ , where

$$\bar{I}(s) = f^2 + f^2 \int_{a_q=0}^{\infty} \int_{z_q=-h}^{+h} \int_{\varphi_q=0}^{2\pi} \{\rho(a_q, z_q) - \rho_0\} \times \exp(isa_q \cos \varphi_q) a_q da_q dz_q d\varphi_q.$$

For larger values of  $a_q$  and/or  $z_q$  the value of  $\rho(a_q, z_q)$  will become equal to  $\rho_0$  and the integrand will become zero. Thus the actual limits for the integrations over  $a_q$  and  $z_q$  are unimportant as long as they include the whole region in which  $\rho$  varies. For the integration over  $z_q$  we can write

$$\int_{-h}^{+h} \{\rho(a_q, z_q) - \rho_0\} dz_q \equiv \Delta \rho'(a_q). \quad (1)$$

Note that  $\Delta \rho'(a_q)$  is independent of the value of *h*, as long as *h* is large enough to satisfy the above mentioned condition that  $\rho(a_q, z_q) = \rho_0$  for  $|z_q| \geq h$ . The integration of the exponential factor over  $\varphi_q$  yields  $2\pi J_0(sa_q)$ , where  $J_0$  is the Bessel function of zero order. Leaving off the now unnecessary subscripts *q*, we find as final formula

$$\bar{I}(s) = f^2 + 2\pi f^2 \int_0^{\infty} \Delta \rho'(a) J_0(sa) a da. \quad (2)$$

This equation is equivalent to equation (5) of Alexander & Michalik (1959).

A Fourier-Bessel transformation (Margenau & Murphy, 1950) yields

$$\Delta \rho'(a) = \frac{1}{2\pi} \int_0^{\infty} i(s) J_0(sa) s ds. \quad (3)$$

$\Delta \rho'(a)$  is, according to equation (1), the projection of an atomic density difference and has the dimension of atoms per unit area. Formally it can be written as the difference between a density  $\rho'(a)$  and an average density  $\rho'_0$  (both in atoms per unit area):

$$\Delta \rho'(a) = \rho'(a) - \rho'_0. \quad (4)$$

From equations (3) and (4), and with  $\{\bar{I}(s) - f^2\}/f^2 \equiv i(s)$ , we obtain

$$2\pi a \rho'(a) = 2\pi a \rho'_0 + a \int_0^{\infty} i(s) J_0(sa) s ds. \quad (5)$$

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† The Russian papers refer to the original Russian text of this book, published in 1963.

This equation is the acdf of Vainstein (1966) and is equivalent to his equation (152).

The aim of this note is to draw attention to the lack of definition of the  $\varrho'_0$  in the acdf (equation 5). It will be clear that equation (4) does not define  $\varrho'_0$ . From equation (1) the most logical choice of  $\varrho'_0$  would appear to be

$$\varrho'_0 = \int_{-h}^{+h} \varrho_0 dz = 2h\varrho_0 \quad (6)$$

but this still does not define  $\varrho'_0$ , since the value of  $h$  is not fixed. This lack of definition of  $\varrho'_0$  has, to our knowledge, not been recognized. Because of it, the usefulness of equation (5) is limited, and certainly *the areas under the peaks of the acdf cannot be interpreted in terms of the numbers of neighbors* as has been done in the literature (Chistyakov, 1964; Chistyakov & Vainshtein, 1963). That it is incorrect to do so follows from the fact that by varying  $\varrho'_0$  one can arbitrarily change the areas under the peaks. Putting it another way, since the acdf deals with the numbers of atoms in cylindrical shells of undefined height ( $2h$ ), these numbers are not defined either. Moreover, the term 'neighbors' loses its meaning for atoms in a cylindrical shell: some of these atoms (those with small  $z$ ) may be rather close to the reference atom  $p$ , whereas others (with large  $z$ ) are quite far away from it.

For these reasons it is preferable to use equation (3), or  $2\pi a$  times equation (3), for acdf studies; unlike  $\varrho'(a)$  and  $\varrho_0$ ,  $\Delta\varrho'(a)$  is a well defined quantity, not dependent upon the choice of  $h$ .

For the *molecular* cylindrical distribution function (mcdf) the same argument holds: here too, the areas under the peaks should not be correlated with the number of neighbors of a molecule, as done in the literature (*e.g.* Kosterin & Chistyakov, 1969). There also appear to be other serious problems connected with the mcdf. These require a detailed analysis of the mcdf and its derivation, and will be discussed elsewhere (De Vries, 1972).

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**Comments on the paper, *The determination of cyclicity hexagonality and other properties of polytypes by Dornberger-Schiff, Schmittler and Farkas-Jahnke: Erratum.*** By J. KAKINOKI, E. KODERA and T. AIKAMI, *Department of Physics, Faculty of Science, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka, Japan*

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Corrections are given to *Acta Cryst.* (1972). A28, 292.

(1) Page 292, column 2, line 14: '  $\gamma$  ' and '  $\delta$  ' should be read as '  $\rho$  ' and '  $\lambda$  '.

(2) Page 293, column 2, the first term in the larger parentheses in expression of  $D_m^*$  for  $m=3r-1$ : The summa-

tion should be performed over  $s$  not from 2 but from 0 to  $t-1$ .

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