CHAPTER 4.

EXPERIMENTAL PROCEDURE AND DATA ANALYSIS

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The typical X-ray diffraction photographs for the unoriented and oriented nematic phase (CPHB at 34°C) are shown in the Fig. 4.1 and Fig. 4.2 respectively.

Generally, randomly oriented nematic phase consists of a large number of domains, the molecules being ordered within each domain in a preferred direction i.e. along the director, but there is no preferred direction for the specimen as a whole so that the X-ray diffraction pattern has a symmetry of rotation around the direction of the X-ray beam which is evident from the uniform diffuse outer halo or ring as in fig. 4.1, which is similar to the X-ray diffraction photograph from isotropic liquid. The diffraction photograph also contains a diffuse inner halo (in case of isotropic phase inner ring is generally more diffuse).

Nematic and isotropic phases can be distinguished by X-ray diffraction by using an oriented nematic sample. Fig. 4.2 shows the photograph of sample CPHB in the supercooled oriented nematic phase at 34°C in presence of a magnetic field of 5.8 K. Gauss. The outer halo splits up into two crescents along the equator for each of which the intensity is a maximum in the equatorial ~~na~~ section which is absent in case of isotropic or randomly oriented mesophase. The inner ring is also splitted into two crescents for which the intensity has a maximum in the meridian section.

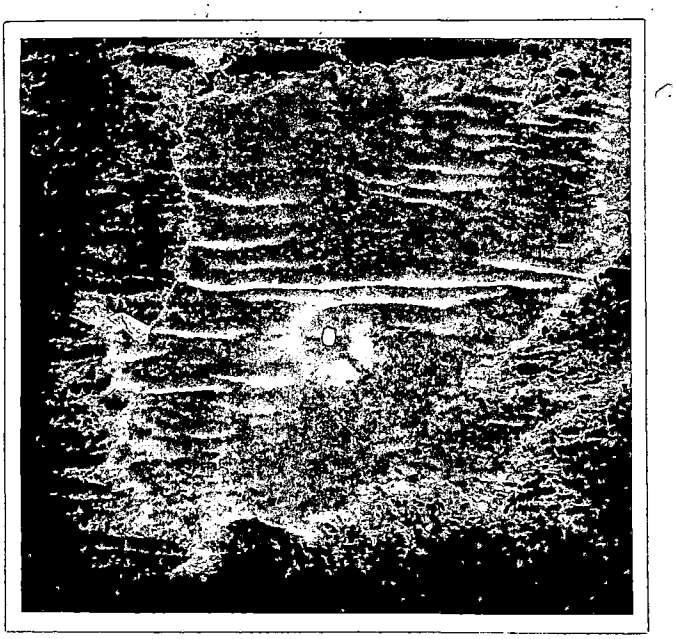

Fig. 4.1. Photograph of unoriented CPHB (nematic phase) at 34°C

Fig. 4.2. Photograph of oriented CPHB (Nematic phase) at 34°C.

In order to determine the various parameters the film containing the X-ray diffraction patterns were scanned (both linearly and circularly) by an optical densitometer (ECIL Model DM 803), with the help of a linear cum rotatory stage designed by us and constructed in our workshop.

Optical density obtained from the densitometer readings were converted to X-ray intensities wherever necessary with the help of a calibration curve [Fig. 2.3] prepared by the method as described in chapter 2.

It is found that intensity (I) is linear with O. D. values in the lower region of the curve and for this reason in case of determination of the diameters of the halos or crescents, the optical density values have not been converted to X-ray intensity values.

Linear scanning is required for the calculation of different molecular parameters.

In order to calculate the average intermolecular distance the diameter of the outer diffuse halo in case of unoriented sample and the diameter of the outer crescents at its maxima in case of oriented nematics is to be determined. The optical densities obtained from the linear scanning of the outer ring through the centre (central spot) is plotted against the linear scale readings (L in cm.). A typical graph (linear scan) for the diffraction photograph (Fig. 4.1) is shown in the Fig. 4.3(a).

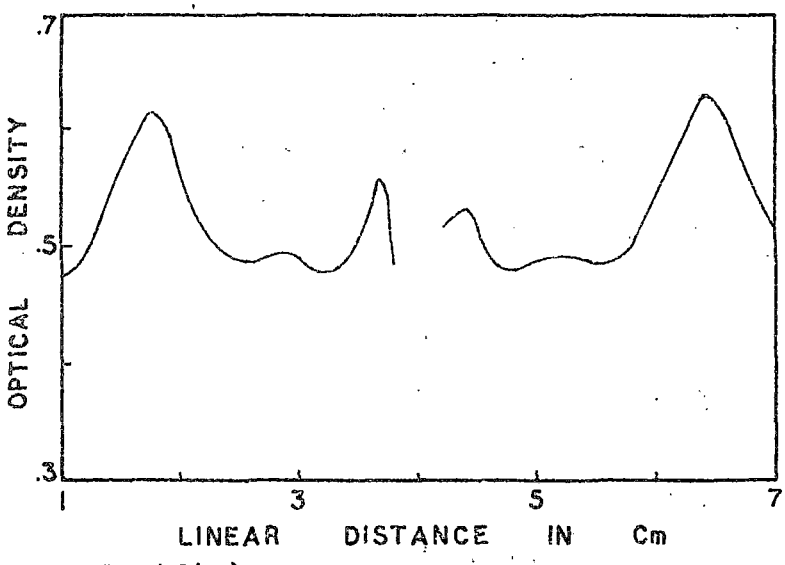

FIG. 4.3(a).

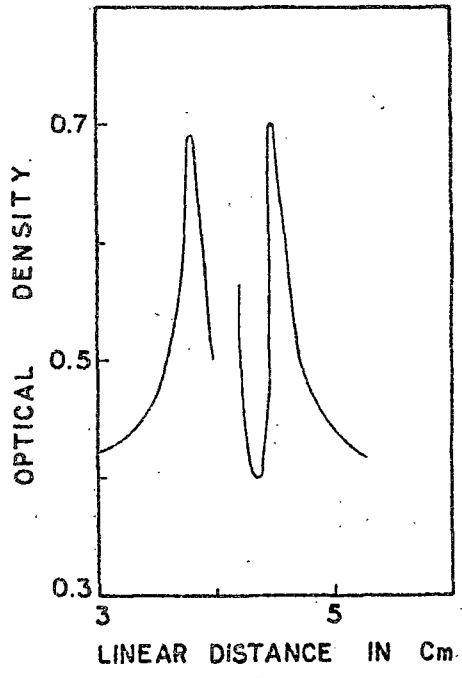

FIG. 4.3(b).

The difference between the two peak points of the outermost halo gives the diameter of the outer halo, (which is necessary for the determination of the half angle between the incident X-ray beam and diffracted beam).

Location of peak position:-

There are different methods[1] for locating the peak position from L-O.D. curve as shown in Fig. 4.3(A). P_o is the apperent maximum of the line profile. It has the drawback that statistical uncertainity in the intensity values at and in the immediate vicinity of the maximum makes its precise location uncertain. In order to avoid this problemm a commonly employed device is to locate the peak of P_x, the point of intersection of two straight lines projected from the most nearly linear portions of the sloping sides of the profile. Another method is to assign the peak position to the mid points of a chord drawn parallel to the background and located at one half of the maximum peak intensity ~~at~~ $P_{1/2}$, or better at higher levels such $P_{2/3}$ or $P_{3/4}$.

Some times different methods give somewhat different values for the peak position despite the relative sharpness of the line profile.

In our case the peak position is located by one of the above mentioned methods, taking care that the method is convenient for the particular case. Generally, where the peak is well defined we simply take the P_o position but in some cases we used the other methods.

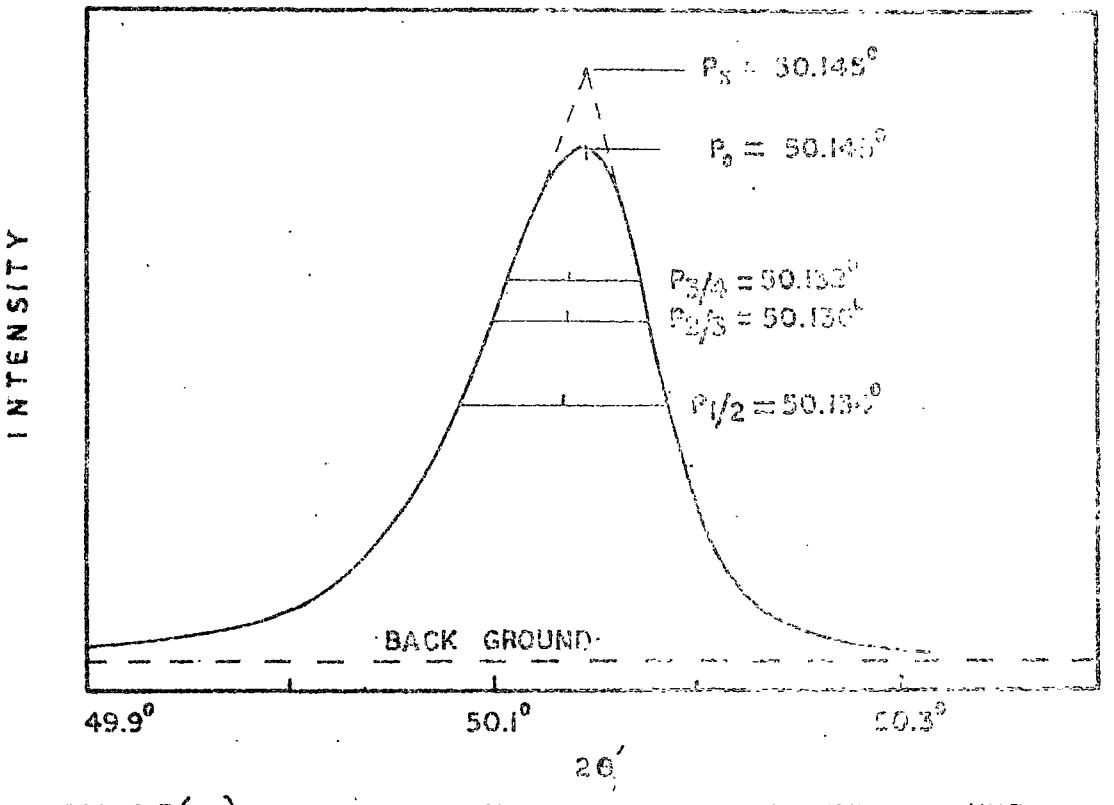

FIG. 4.3(A). VARIOUS METHODS OF LOCATING THE PEAK POSITION OF A LINE PROFILE.

The diameter of the outer crescents or halo is determined by taking the linear distance between the two peaks. The exact distance between the sample to film is determined as described in Chapt. 2 and value of the Bragg angle is determined.

Then the average intermolecular distance is calculated by using the formula 3.1 following the theory described in Chapter 3. As described in Chapt. 3, the diameter of the inner ring or halo (shown in fig. 4.1) is also to be determined in order to get the apparent molecular length.

A typical linear scanning through the diameter of the inner ring (halo) is shown by plotting O.D. against linear distance (L in cm.) as shown in Fig. 4.3 (b). The peak positions are located by the methods described earlier, though here the peaks are well defined and it is easy to locate.

Knowing the diameter of the inner halo the apparent molecular length is determined by calculating the Bragg angle α with the help of the actual distance between sample and film as given by deVries (Eqn. 3.1 in Chapt. 3).

Now let us consider the case of diffraction pattern of oriented sample (as in Fig. 4.2). Here both linear and angular scanning are required. Angular scanning is required for getting the intensity distribution.

The average intermolecular distance and the apparent length of the molecule are determined by the same process described in case of unoriented sample.

In order to get the diameter of the outer crescents accurately the linear scanning was made on different angular positions (θ values), [Fig. 4.4].

Considering $\theta = 0°$ at the maximum intensity position the linear scanning is done [Fig. 4.5(a)]. The peak difference between the two maxima is obtained i.e. the diameter of the outer halo is obtained at maximum intensity. Then linear scanning is done at two other positions at $\theta = 30°$, [Fig.4.5(b)] and $\theta = -30°$, [Fig. 4.5(c)]. The difference between the two peaks positions are obtained from both the θ positions and it was found that diameter of the outer most halo (crescents) of the diffraction pattern are same in all the three cases.

Linear scanning is done at $\theta = 90°$ and the nature of the curve is shown in the Fig. 4.5 (d). A smooth line is obtained without any prominent peak position at the diameter of the outer halo. The O.D. at the maxima of the outer ring positions for the scanning at $\theta = 90°$ is corrected for fogging factor by subtracting a factor which is the optical density of the unexposed portion called the background O.D. After correction the O.D. value at maxima of the outer ring position (at $\theta = 90°$) is converted to intensity value I with the help of calibration curve described earlier.

The values of optical density obtained from the densitometeric circular scanning (scanned along the arc of main equatorial reflection) of the diffraction pattern are converted to X-ray intensity value with the help of the calibration curve. The converted intensity is then plotted against

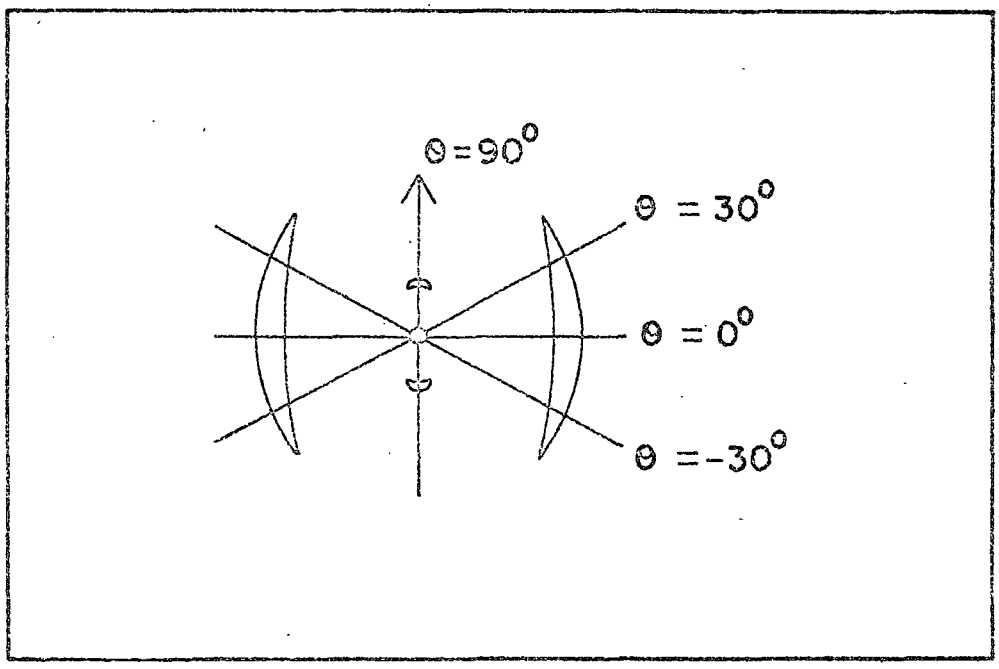

FIG. 4.4.

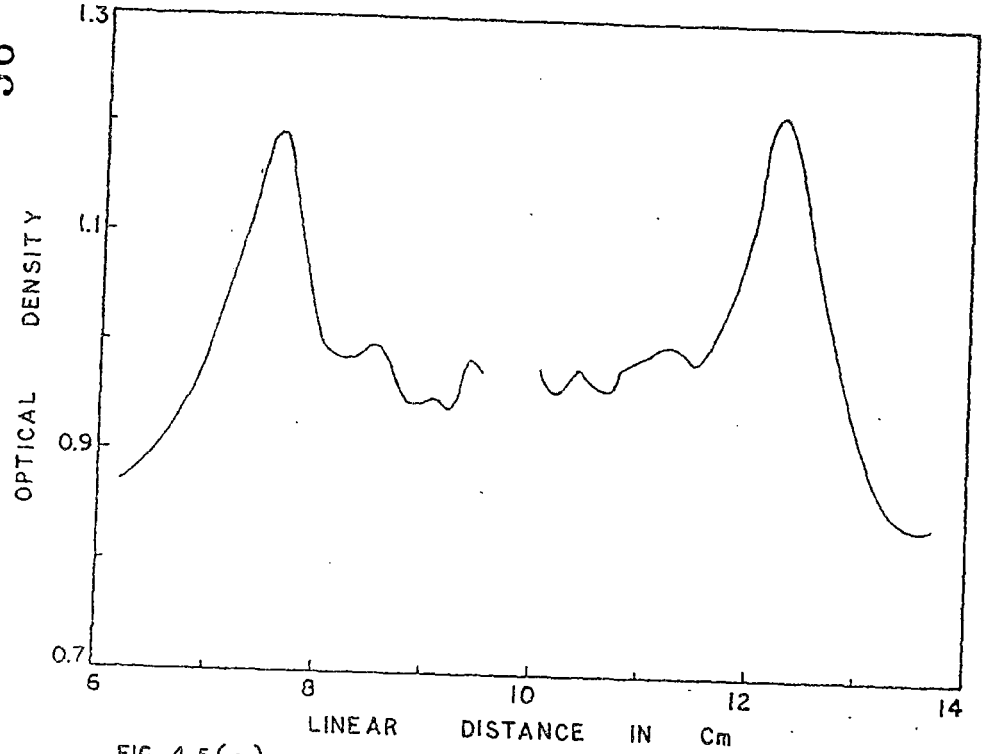

FIG. 4.5(a).

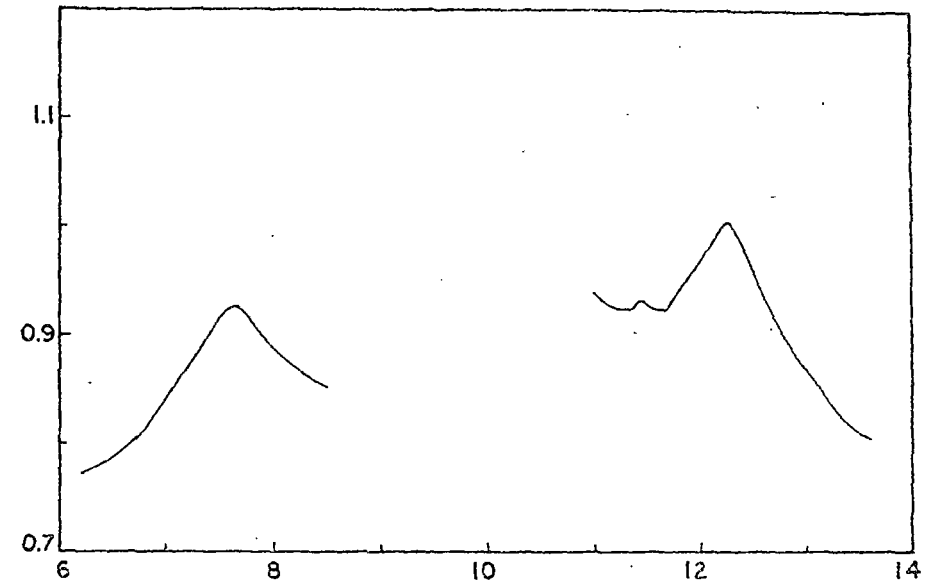

FIG. 4.5(c).

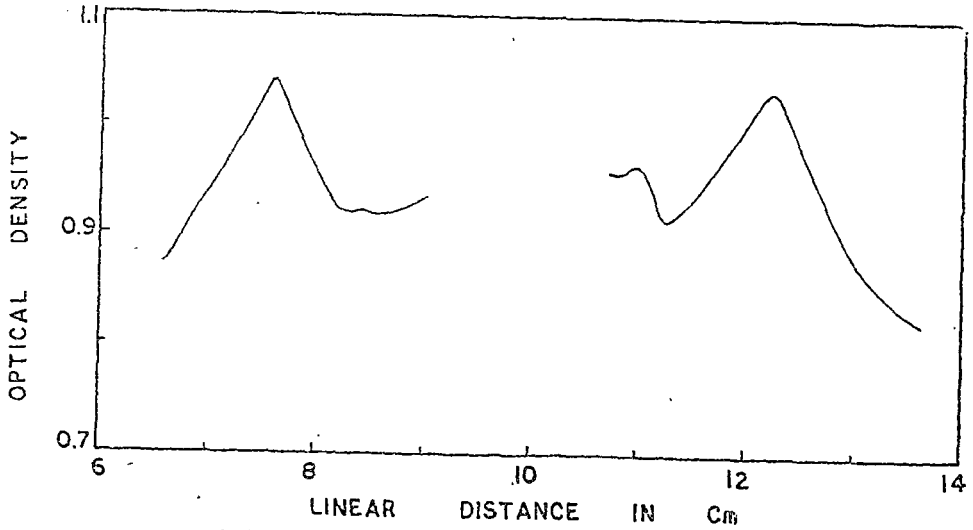

FIG. 4.5(b).

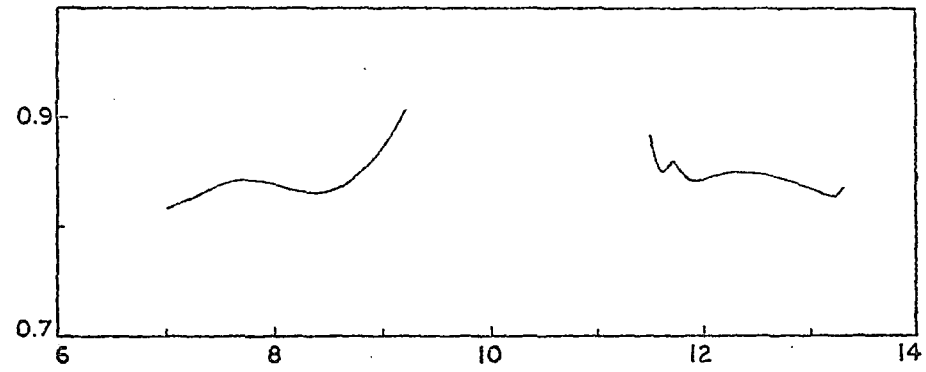

FIG. 4.5(d).

different angular positions θ.). The background intensity arising due to the thermal vibration of the molecule and air scattering is eliminated by subtracting the converted intensity value of the O.D. at the smooth curve obtained at $\theta = \frac{\pi}{2}$ position from the converted intensity values of the corrected optical density value of the angular scanning at the diametrical position of the outer halo.

The scanning of the photograph then gives the background intensity which is normally a tangent at $\theta = \frac{\pi}{2}$ i.e. minimum of the intensity distribution curve, [I (θ) versus θ curve] .

Leadbetter et al[2] also had similar intensity distribution with their X-ray diffraction photograph of the aligned sample.

The typical plot of I (θ) against θ is shown in the Fig. 4.6. Four equivalent sets of data from the four quadrants i.e. ($\theta = 0$ to 2π) are shown separately in fig. 4.6(a) and 4.6 (b) and the average I (θ) of these four quadrants is also plotted against θ as shown in fig. 4.6(c).

The dotted lines show the level of the background scattering intensity.

For our calculation the angular scanning for four quadrants (i.e. $\theta = 0$ to $\theta = \pi/2$) is required. We have obtained I (θ) vs θ distribution for all four quadrants separately and calculated order parameters for each of the four quadrants separately and then took the average.

We have at the same time calculated order parameter values by using the mean I (θ) values for the four quadrants.

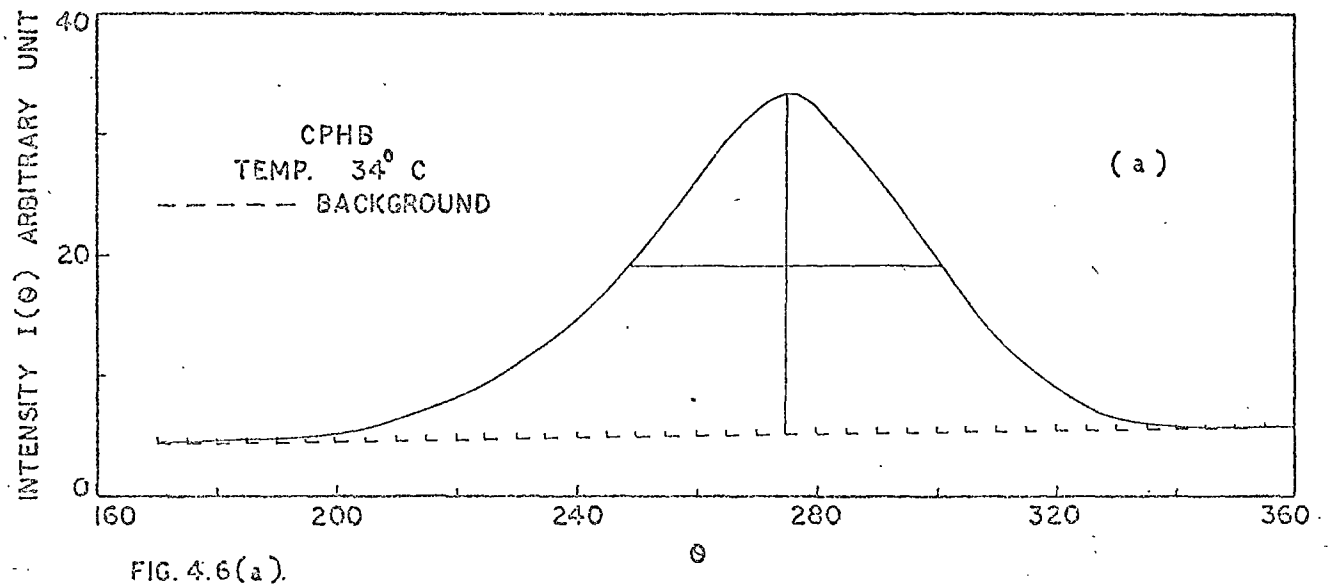

FIG. 4.6(a).

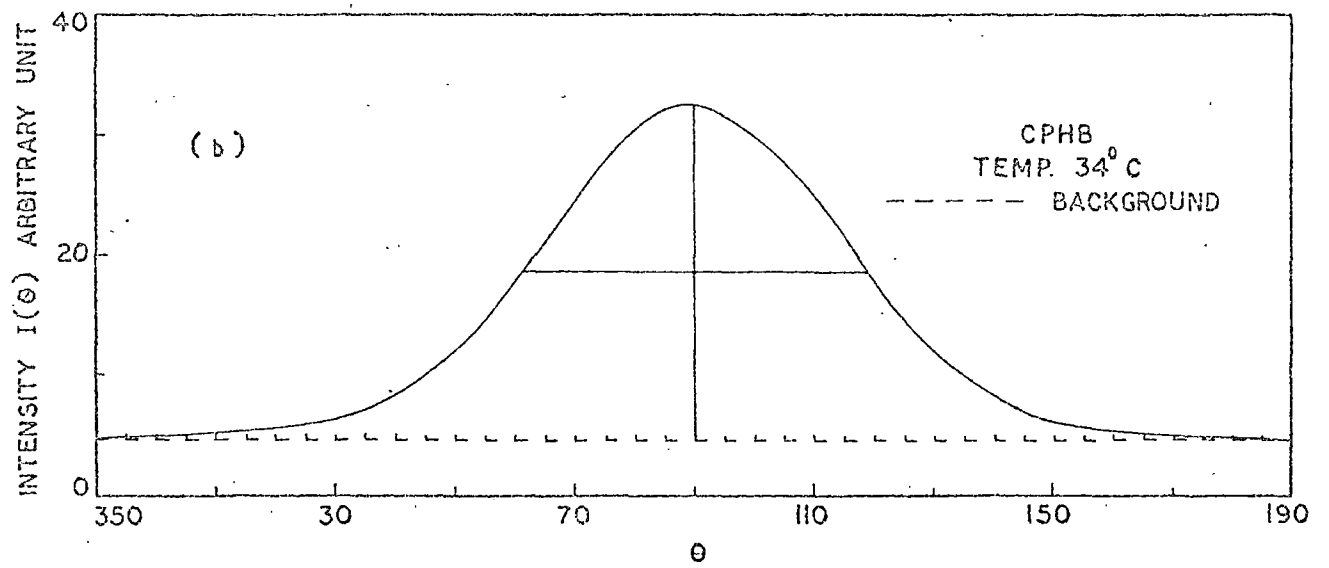

FIG. 4.6(b)

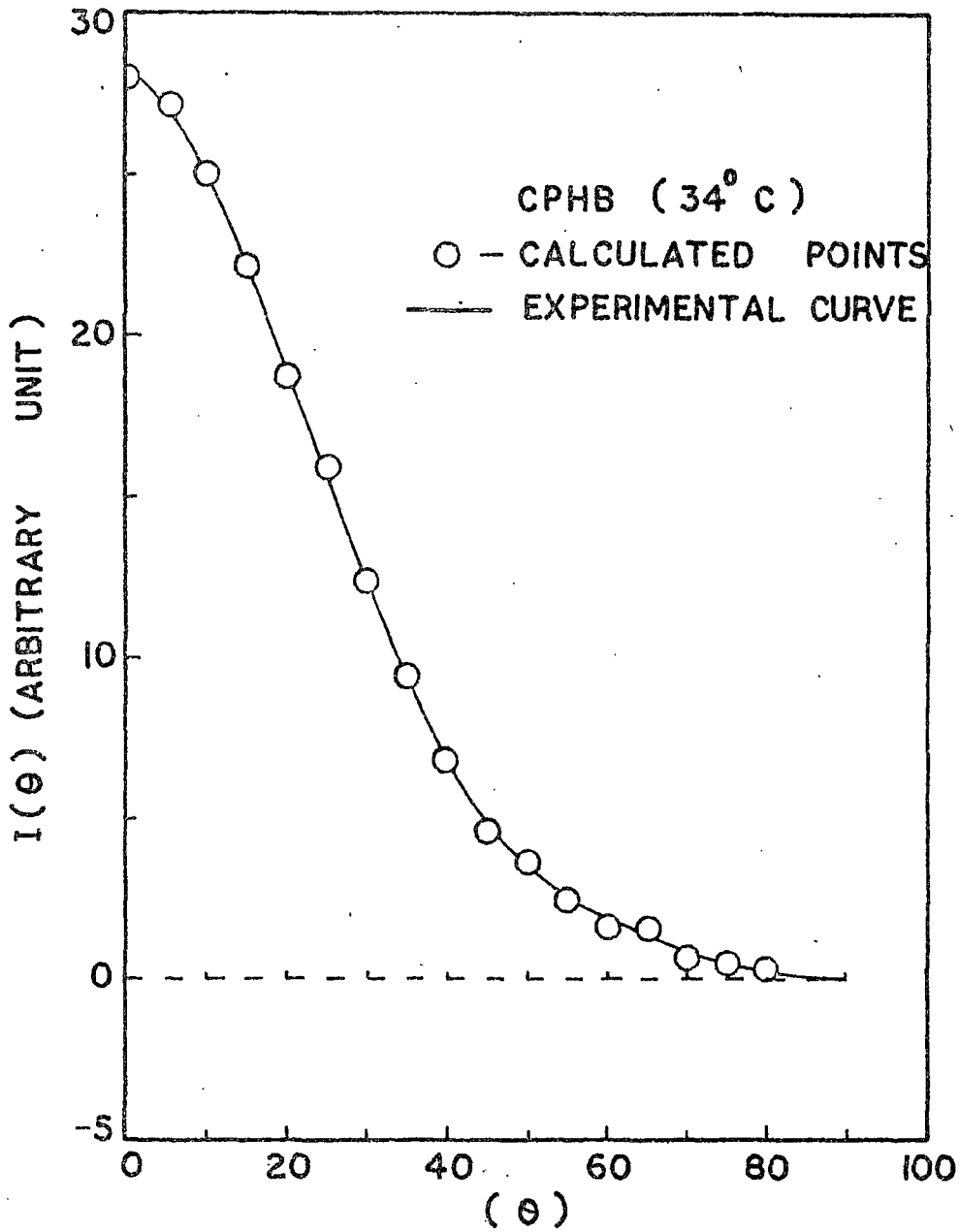
CPHB (34° C)
O – CALCULATED POINTS
EXPERIMENTAL CURVE
I(θ) (ARBITRARY UNIT)
30
20
10
0
-5
0
20
40
60
80
100
(θ)

FIG. 4.6(c).

The difference between the two methods gave nearly equal results for the order parameters, better than the experimental uncertainity. Therefore, we have calculated the distribution functions and order parameters (as described in chapt. 3) from only the mean I (θ) value of the four quadrants.

The calculated intensity values are shown in the fig. 4.6 (c) by points inside the circles (chap 3, equ 4, eight terms).

Calculating $f(\beta)$ values from I (θ) values by a programme from the computer the $f(\beta)$ values are plotted against (β) at different temperatures [Fig. 4.7] . The programme used has been given at the end of this chapter.

The results were analysed (as described in chapt.3) to give $f(\beta)$ from which order parameters i.e. $\langle P_L \rangle$ values [$\langle P_2 \rangle$ & $\langle P_4 \rangle$] were calculated.

Uncertainity in O. D. value obtained from our densitometric scanning is .0025 which gives rise to the uncertainity in intensity value is 0.3.

Three different curves are obtained by plotting I (θ), (I+0.3) (θ) and (I - 0.3) (θ) against θ . $f(\beta)$ values were calculated from these three different intensity values (by the method described earlier) and $f(\beta)$ values were plotted against (β). The uncertainity in distribution function obtained in this way is only 1%.

The order parameters obtained from these three values are found to be accurate within 0.02.

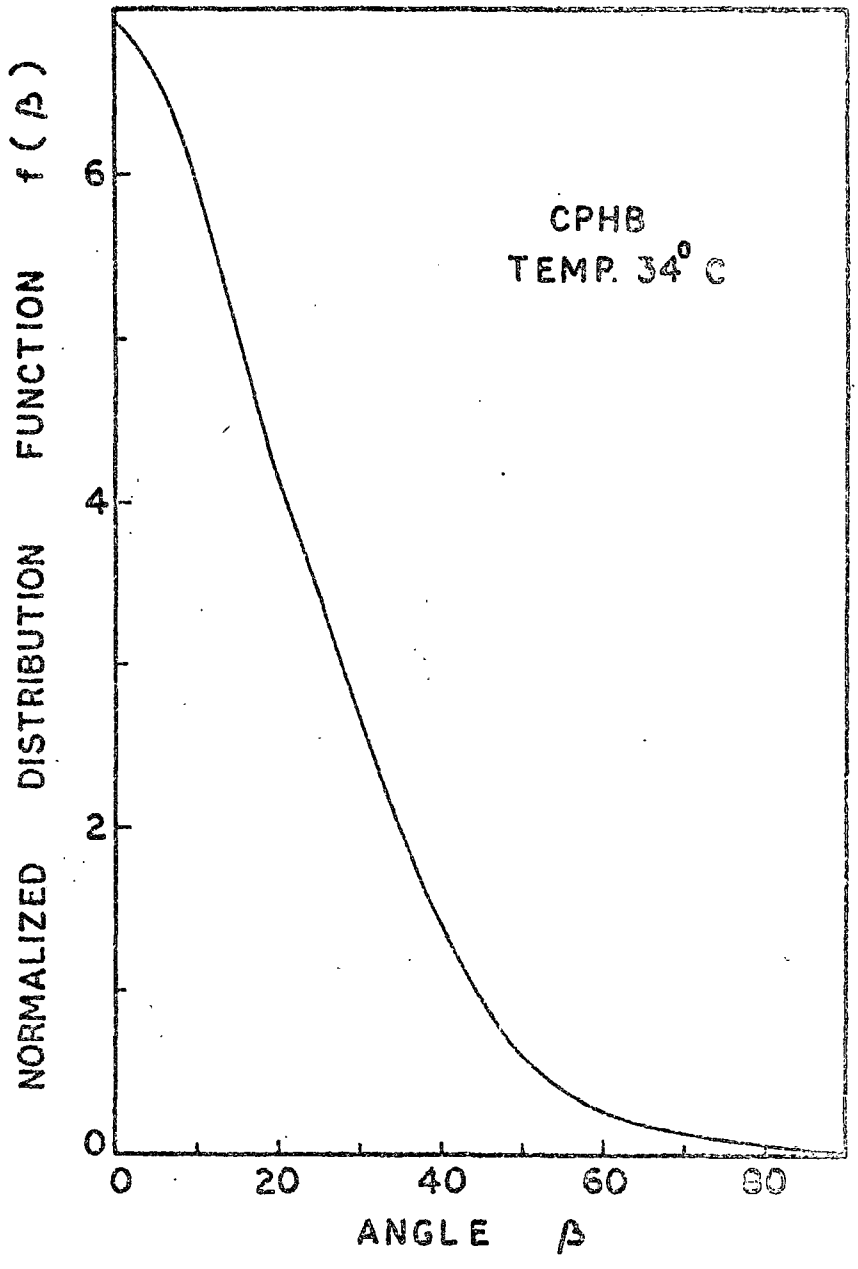
NORMALIZED DISTRIBUTION FUNCTION f (β)
6
4
2
0
CPHB
TEMP. 34° C
0
20
40
60
80
ANGLE β

FIG. 4.7.

REFERENCES

1. H. P. Klug and L.E. Alexander, - X-ray Diffraction Procedures. p. 308, John Wiley & Sons (1954).

2. A. J. Leadbetter and E. K. Norris, Mol. Phys. 38 669 (1979).

COMPUTER PROGRAMME

The calculations for the order parameters and distribution functions were done with a DCM (India) Spectrum 1 Microcomputer incorporated with a slightly different form of BASIC Language (HI-BASIC), and situated in the Research Service Centre, North Bengal University. The programmes are given below:

I. KAPALØ1.BAS

```
1:        REM CALCULATION OF ORDER PARAMETERS
2:   1    INPUT"MORE JOB?"; YØ
3:        IF YØ="N" THEN STOP
4:        INPUT"IDENTIFICATION"; ID$
5:        INPUT"NO. OF POINTS";NP
6:        DIM IN(NP)
7:        NY=NP-1:JA=Ø
8:        CONSOLE
9:        FOR I = Ø TO NY
1Ø:       PRINT IN(I):INPUT "INTENS VAL="; IN(I)
11:       NEXT I
12:2.Ø1   INPUT"NO. OF VARIABLES";NV
13:       LPRINTER WIDTH 4Ø
14:       IF JA > .5 THEN GOTO 2.11
15:       PRINT TAB(5); ID$
16:       PRINT "INTENSITY VALUES"
17:       FOR I=Ø TO NY
18:       PRINT USING"-####.##   ";IN(I);
19:       NEXT I
2Ø:2.11.  IF NV> NP THEN PRINT"TOO MANY VARIABLES"
          ELSE GOTO 2.Ø2
21:       GOTO 2.Ø1
22:2.Ø2   CON=ATN(1)/9:NX=NV-1:NS=2+NX
23:       DIM C(NS),D(NS),B(NX),A(NX,NX),X(NX)
```

```
24:        I=1 TO NS
25:        D(I)=ϕ
26:        IF I LE NX THEN B(I) =ϕ
27:        NEXT I
28:        C(ϕ)=1:D(ϕ)=NP:B(ϕ)=ϕ
29:        FOR M=ϕ TO NY
3ϕ:        ANG=CON+M:CSQ=COS(ANG):CSQ=CSQ+CSQ
31:        B(ϕ)=B(ϕ)+EN(M)
32:        FOR K = 1 TO NS
33:        C(K)=C(K-1)+CSQ
34:        D(K)=D(K)+C(K)
35:        IF K LE NX THEN B(K)=B(K)+C(K)+IN(M)
36:        NEXT, K,M
37:        FOR I =ϕ TO NX
38:        FOR J = ϕ TO NX
39:        A(I,J)= D(I+J)
4ϕ:        NEXT J,I
41:        FOR NL=NX TO 1.ϕ STEP -1.ϕ
42:1.ϕ4    TERM=A(ϕ,NL):IMAX=ϕ
43:        FOR I=1 TO NL
44:        IF A(I,NL) < TERM THEN 1.ϕ5
45:        TERM=A(I,NL):IMAX=I
46:1.ϕ5    NEXT I
47:        FOR K=ϕ TO NL
48:        P=A(IMAX,K):A(IMAX,K)=A(NL,K):A(NL,K)=P
49:        NEXT K
5ϕ:        P=B(IMAX):B(IMAX)=B(NL):B(NL)=P:NK=NL-1
51:        FOR I=ϕ TO NK
52:        PT=A(I,NL)/TERM
53:        FOR J=ϕ TO NK
54:        A(I,J)=A(I,J)-A(NL,J)*PT
55:        NEXT J
```

```
56:        B(I)=B(I)-B(NL)*PT
57:        NEXT I,NL
58:        X(Ø)=B(Ø)/A(Ø,Ø)
59:        PRINT TAB(5);"COEFFICIENT";PRINT"X Ø=";X(Ø)
6Ø:        FOR I = 1 TO NX
61:        SUM = Ø
62:        FOR J=Ø TO (I-1)
63:        SUM=A(I,J)*X(J)+SUM
64:        NEXT J
65:        X(I)=(B(I)-SUM)/A(I,J)
66:        PRINT"X";I;"=";X(I):NEXT I
67:        PRINT
68:        IF JA > Ø THEN 1.Ø7
69:        PL$="VAINSHTEIN"
7Ø:        FOR IK=Ø TO 1
71:        GOSUB 3.Ø1
72:         GOSUB 4.Ø1
73:        IF IK > .5 THEN 1.Ø6
74:        GOSUB 5.Ø1
75:        PL$="LEADBETTER"
76:        NEXT IK
77:1.Ø6    JA=1:GOTO 2.Ø1
78:1.Ø7    IK=2
79:        GOSUB 4.Ø1
8Ø:1.Ø9    GOSUB 6.Ø1
81:        GOSUB 7.Ø1
82:        INPUT "CONVERGENCE?"; X$
83:        IF X$="Y" THEN 2.Ø1
84:          PRINT:PRINT:PRINT:GOTO 1
85:3.Ø1    DIM  SI(2)
86:        FOR I=Ø TO 2
87:        SI(I)=Ø
88:        NEXT I
89:        FOR I=Ø TO 2
9Ø:        FOR N=Ø TO NX
```

```
91:      SI(I)=X(M)/(2+(M+I)+1)+SI(I)
92:      NEXT M,I
93:      PRINT:PRINT"INTEGRALS":PRINT SI(ϕ),SI(1),SI(2)
94:      P2=1.5+SI(1)/SI(ϕ)-.5
95:      P4=((35+SI(2))/SI(ϕ)-(3ϕ+SI(1)/SI(ϕ))+3)/8
96:      PRINT PL$;" ORDER PARAMETERS"
97:      PRINT"P2=";P2;" P4= ";P4
98:      RETURN
99:4:ϕ1  DIM Z(NY)
1ϕϕ:     IF IK < .5 THEN PRINT"CALCULATED INTENSITY VALUES":
         GOTO 4.11
1ϕ1:     PRINT "DISTRIBUTION FUNCTION VALUES"
1ϕ2:4:11 FOR M=ϕ TO NY
1ϕ3:      ANG=CON+M:CSQ=COS (ANG):CSQ=CSQ+CSQ
1ϕ4:     SUM=ϕ
1ϕ5:     FOR J=MX TO 1.ϕ STEP -1.ϕ
1ϕ6:     SUM=(SUM+X(J))+CSQ
1ϕ7:     NEXT J
1ϕ8:     Z(M)=SUM+X(ϕ)
1ϕ9:     NEXT M
11ϕ:     IF IK < 1.5 THEN 4.ϕ2
111:     FOR M=ϕ TO NY
112:     Z(M)=EXP(Z(M))
113:     NEXT M:GOTO 4.ϕ3
114:4.ϕ2  IF IK < .5 THEN 4.ϕ3
115:     FOR M=ϕ TO NY
116:     Z(M)=Z(M)/SI(ϕ)
117:     NEXT M
118:4.ϕ3 FOR M=ϕ TO NY
119:      PRINT USING"-###.### ";Z(M);
12ϕ:     NEXT M:PRINT
121:     IF IK NE 1 THEN ϕ.ϕ4.
122:     FOR M=ϕ TO NY
123:     IF Z(M) < ϕ THEN 4.ϕ5
124:     LN(M)=LOG (Z(M))
125:     NEXT M
```

```
126:4.Ø4   RETURN
127:4.Ø5   NP=M:NY=NP-1:GOTO 1.06
128:5.Ø1   PRO=1:PRINT:PRINT"COEFFICIENT" PRINT"X 0 =";X(Ø)
129:       FOR M=1 TO NX
13Ø:       PRO=PRO+(M+.5)/M
131:       X(M)=PRO+X(M):PRINT X(M)
132:       NEXT M
133:       RETURN:STOP
134:6.Ø1   DIM T(NX,NX)
135:       T(Ø,Ø)=1
136:       FOR I=1 TO NX
137:       T(I,Ø)=-T(I-1,Ø)+(I-.5)/I
138:       NEXT I
139:       FOR I=1 TO NX
14Ø:       FOR J=1 TO I
141:       T(I,J)=T(I,J-1)+(1+J-.5)+(J-I-1))/(J+J-.5+J)
142:       NEXT J,I.
143:       RETURN
144:7.Ø1   DIM Y(NX)
145:       Y(NX)=X(NX)/T(NX,NX).
146:       FOR J=(NX-1) TO Ø.Ø STEP -1.Ø
147:       SUM =Ø
148:       FOR I=(J+1) TO NX
149:       SUM=SUM+T(I,J)+Y(I)
15Ø:       NEXT I
151:       Y(J)=(X(J)-SUM)/T(J,I)
152:       NEXT J
153:       PRINT:PRINT "COEFFS OF LEGENDRE POLYNOMIALS"
154:       FOR I =Ø TO NX
155:       PRINT"Y";I;"=";Y(I)
156:       NEXT I
157:       RETURN
```

II. R.PAL06.BAS

```
1:        REM CALCULATION FOR NORMALISED DISTRIBUTION FUNCTION
2:1.01    INPUT "MORE JOB?"Y$
3:        IF Y$="N" THEN STOP
4:        INPUT "IDENTIFICATION"; ID$
5:        INPUT  "NO OF TERMS";NP
6:        NX=NP-1
7:        DIM A (NX), B(NX), FUN (18)
8:        FOR I=0 TO NX
9:        INPUT "A(I) =";A(I)
10:       NEXT I
11:       LPRINTER WIDTH 40
12:       PRINT TAB(5);ID$
13:       CON=ATN(1)/9
14:       GO SUB 6.01
15:       FOR NY =0 TO NX
16:       SUM =0
17:       FOR I=NY TO NX
18:       SUM=SUM+A(I)+I(I,NY)
19:       NEXT I
20:       B(NY)=SUM
21:       NEXT NY
22:       FOR M=0 TO 18
23:       ANG=CON+M:CSQ:COS(ANG):CSQ:CSQ+CSQ
24:       SUM=B(NX)
25:       FOR N=(NX-1) TO 0.0 STEP -1.0
26:       SUM=SUM+CSQ+B(N)
27:       NEXT N
28:       FUN(M)=EXP(SUM)
29:       NEXT M
30:       DIM W(6)
31:       W(0)=1:W(1)=5:W(2)=1:W(3)=6:W(4)=1:W(5)=5:W(6)=1
32:       PRINT "NO OF TERMS =  ";NP
33:       PRINT "COEFFS"
34:       FOR I=0 TO NX
35:       PRINT "X";I;"=";A(I)
36:       NEXT I
37:       PRINT
```

```
38:        PRINT "DISTRIBUTION FUNCTION VALUES"
39:        FOR M=Ø 18
4Ø:        PRINT USING "-###.### "; FUN(M);
41:        NEXT M
42:        PRINT
43:        SUM=Ø
44:        FOR M=Ø TO   2
45:        FOR N=Ø TO 6
46:        PA=6+M+N
47:        SUM=SUM+W(N) +FUN(PA)+SIN(PA+CON)
48:        NEXT N,M
49:        SUM=SUM+Ø.3+CON:SUM=1/SUM
5Ø:        PRINT "NORMALISING CONSTANT= ";
51:        PRINT "NORMALISED DISTRIBUTION FUNCTION"
52:        FOR M=Ø TO 18
53:        FUN(M)=SUM+FUN(M)
54:        PRINT USING "-###.### ";FUN(M);
55:        NEXT M
56:        PRINT:PRINT:PRINT
57:        GO TO 1.Ø1
58:6.Ø1    DIM T(NX,NX)
59:        T(Ø,Ø)=1
6Ø:        FOR I=1 TO NX
61:        T(I,Ø)=-T(I-1,Ø)+(I-Ø.5)/I
62:        NEXT I
63:        FOR I=1 TO NX
64:        FOR J=1 TO 1
65:        T(I,J)=T(I,J-1)+(I+J-.5)+(J-I-1)  /(J+J-.5+J)
66:        NEXT J,I
67:        RETURN.
```