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# A universal mathematical expression for multi-phase X-ray diffraction in several polymers

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## Summary

This paper proposes a transcendental function as a common expression of the forms of the X–ray diffraction of three phases in several typical polymers, which is a indispensable supplement of the Gaussian–Cauchy function in actual application. The function includes five special examples (Gaussian–Cauchy function etc.); satisfies eight requests in application, such as very high fitting accuracy, better flexibility and generality etc.; possesses theoretical completeness and logicality; and reflects out the dialectical relation of the unity of opposites between different phases in polymers. When studying the relation between structure and properties of complex polymers by means of the resolution of X–ray diffraction peak of the superposition, the function not only can give accurate data but also can carry out many valuable exploration for crystal grain size, lattice distortion and transitive state in polymers.

## Introduction

Earlier scholars in some countries described the X–ray diffraction of three phases in polymers in the following way[1–6]: a symmetrical function was used to describe crystalline and transitive X–ray diffraction multipeaks; some asymmetrical functions were used to describe amorphous X–ray diffraction multipeaks. The defects of described method are that relative error of fit (diffraction curve and calculated curve) is larger and it does not reflect the contact between three phases (crystalline, amorphous and transitive states) in polymer. So that it can not provide accurate results for the study of the structure of polymers. According to the view of the unity of opposites in philosophy, we think that the X–ray diffraction of different phases in polymer possesses the law of the diffraction of the unity, i. e. the separate mathematical expressions may be replaced by a common expression. For this purpose, the author had explored the problem in the previous work[7], and had obtained some elementary results being imperfect, there are reciprocal restraint conditions between principal parameters P, Wl and Wr; goodness of fit is insufficient; the formula only apply to smaller interval of angle of diffraction and so on. To meet the need for application, the common expression of the forms of the X–ray diffraction of different phases in various polymers is necessary and must satisfy some requirements as follows: (1) there are not reciprocal restraint conditions between principal parameters P, Wl and Wr; (2) accuracy of fit is high–grade; (3) applied range is extensive; (4) the function has only a maximum value in choosed interval of angle; (5) initial values of the parameters are choosed easily; (6) it may apply to larger interval of angle of diffraction; (7) the independent variable x may represent $\Theta$, $2\Theta$ and other independent variable besides diffraction angle; (8) it is applicable to all curves having more or less experimental error.

The authors have proposed further a formula by the above mentioned requirements as a common expression of the forms of the X–ray diffraction of three phases (amorphous, crystalline and transitive states) in various polymers. This fact explains forcefully that the X–ray diffraction of three phases in polymer possesses the law of diffraction of the unity. The formula will be considerably useful for the study of the structure and performance of polymers.

## Experimental

### I. The new function proposed by the authors

To remedy some defects of the old formulae, a new function form is created (course of derivation omitted). Its general form is

$$y(x)=fA\ \exp[-(\ln 2)Q(x)]+(1-f)A/[1+Q(x)]; \qquad (1)$$

where

$$Q(x)=[(x-P)/(WlWr)]^2\exp\{a\ \exp[-(x-x_0)^2k^2]+b\},$$
$$a=2\ln(Wr/Wl)/\{\exp[-(P-Wl-x_0)^2k^2]-\exp[-(P+Wr-x_0)^2k^2]\},$$
$$b=\ln(WlWr)-(a/2)\{\exp[-(P-Wl-x_0)^2k^2]+\exp[-(P+Wr-x_0)^2k^2]\};$$

$y(x)$, $A$, $P$, $f$, $x$, $Wl$, $Wr$, $x_0$ and $k$ are respectively the strength of every diffraction of the X–ray diffraction multipeak (crystalline, amorphous or transitive state), the height of peak, the position of peak, the factor of peak shape, the angle of diffraction (denoted by $2\Theta$), the left half–peak breadth, the right half–peak breadth, the angular coordinate of the top point of convex (concave) locus of the diffraction multipeak and convex (concave) extent scale.

Next, it should be proved that Eq. (1) is suitable to the X–ray diffraction of the polymers with the different phases.

### II. Expounding and proving

Up to the present, the expression used for the symmetrical, multipeaks of the crystalline state is the Gaussian–Cauchy function, i. e.

$$y(x)=fA\ \exp\{-(\ln 2)[2(x-P)/W]^2\}+(1-f)A/\{1+[2(x-P)/W]^2\}, \qquad (2)$$

where W represents the half–peak breadth of the diffraction multipeak of the crystalline state, and the rest symbols are the same as in the above Eq. (1). It was feasible through inspecting in practice for quite pure crystalline state. In fact, Eq. (2) is a special case of Eq. (1). Thence Eq. (1) is suitable to mathematical description of the crystalline state. Because former objective conditions were restricted (testing means and mathematical model), polymers were divided artificially and arbitrarily into two kinds: crystalline polymers and amorphous state polymers. In fact, this division is not quite right, because there is no strict boundary of phases between crystalline state and amorphous state, and there is also another kind of state between them: the transition state of half–and–half order [6]. The X–ray diffraction peaks of the pure transitive state or crystalline state with transitive state are not quite symmetric, therefore it is evidently unsuitable to describe the diffraction peaks by symmetrical Gaussian–Cauchy function. The description can not reflect out original appearances of the diffraction peaks and error of fit is large. The formula (1) is most applicable for the diffraction peaks. Now we are going to prove that Eq. (1) is also valid as a mathematical description of the X–ray diffraction of the amorphous state by taking the amorphous specimens of three rather typical polymers as examples, and for further examining the suitability of Eq. (1), it is applied to the multipeak resolution of specimens of undrawn polypropyrene fibers in both crystalline state with transitive state of half–and–half order and amorphous state. To start with, we explain the symbol

$$\delta = \{ (\sum_{i=1}^{m} (y_i - Y_i)^2) / (\sum_{i=1}^{m} Y_i^2) \}^{1/2} \times 100\% \quad , \qquad (3)$$

which is called the relative error of fit. It reflects the exact degree of mutual fitting between the experimental curve and the calculated curve (where $y_i$ and $Y_i$ stand for the calculated values and the measured values of the diffraction strength corresponding to the angles of diffraction $x_i$; m is the sum of the points of division of angular interval).

(a) Amorphous polypropyrene specimen

Angles of diffraction x(2Θ) take values between 10.2° and 24°, sum of points of division m=70, value of each point of division $x_i=10.2°+(i-1)h$ (where i=1, 2, 3, ..., 70; h=0.2°). Through calculating by Eq. (1) and Eq. (3), we obtain the calculated values $y_i$ (i=1, 2, 3, ..., 70; see Fig. 1); parametric values f=0.25, A=69.574637, P=16.323217°, Wl=4.188987°, Wr=6.015576°, k=0.285 and $x_o$ =11.1°, and the relative error of fit δ=0.68% (see Table 1).

(b) Amorphous polyethylene glycol terephthalate specimen

Angles of diffraction x(2Θ) take values between 6.2° and 30°, sum of points of division m=120, value of each point of division $x_i=6.2°+(i-1)h$ (where i=1, 2, 3, ..., 120; h=0.2°). Through calculating by Eq. (1) and Eq. (3), we obtain the calculated values $y_i$ (i=1, 2, 3, ..., 120; see Fig. 1); parametric values f=0.35, A=63.8, P=20.97°, Wl=7.36°, Wr=6.98°, k=0.216 and $x_o$ =19.8°, and the relative error of fit δ=0.75% (see Table 1).

(c) Amorphous polymethyl methacrylate specimen

Angles of diffraction x(2Θ) take values between 10.2° and 24°, sum of points of division m=70, value of each point of division $x_i=10.2°+(i-1)h$ (where i=1, 2, 3, ..., 70; h=0.2°). Through calculating by Eq. (1) and Eq. (3), we obtain the calculated values $y_i$ (i=1, 2, 3, ..., 70; see Fig. 1); parametric values f=0.98, A=108.02, P=13.68°, Wl=4.22°, Wr=5.38°, k=0.32 and $x_o$ =11.37°, and the relative error of fit δ=0.62% (see Table 1).

(d) Specimen of undrawn polypropyrene fibers containing both crystalline state with a little transitive state of half—and—half order (Note α*) and amorphous state

Angles of diffraction x(2Θ) take values between 10.2° and 24°, sum of points of division m=70, value of each point of division $x_i=10.2°+(i-1)h$ (where i=1, 2, 3, ..., 70; h=0.2°). Through calculating by Eq. (1) and Eq. (3), we obtain the values as follows: (i) the parametric values and the calculated values of the diffraction strength for amorphous diffraction peak: P=16.55°, A=46, Wl=3.9°, Wr=5.25°, f=0.75, k=0.285, $x_o$ =12° and $y_{i(a)}$ (i=1, 2, 3, ···, 70; see Table 2 and Fig. 2); (ii) for (110) face diffraction peak: P=14.0248°, A=167, Wl=0.5606°, Wr=0.4852°, f=1, k=1.99, $x_o$ =13.882° and $y_{i(110)}$ (i=1, 2, 3, ..., 70; see Table 2 and Fig. 2); (iii) for (040) face diffraction peak: P=16.87°, A=189, Wl=0.55°, Wr=0.475°, f=1, k=2.0, $x_o$ =16.726° and $y_{i(040)}$ (i=1, 2, 3, ..., 70; see Table 2 and Fig. 2); (iv) for (130) face diffraction peak: P=18.52°, A=109, Wl=0.5812°, Wr=0.5005°, f=0.5, k=1.75, $x_o$ =18.36° and $y_{i(130)}$ (i=1, 2, 3, ..., 70; See Table 2 and Fig. 2); (v) the sum of calculated values of the diffraction strength: $y_i=y_{i(a)}+y_{i(110)}+y_{i(040)}+y_{i(130)}$ (i=1, 2, 3, ..., 70; see Fig. 2); (vi) the relative error of fit: δ=2.2% (see Table 2).

Note: a) Computational procedure omitted; b) Measured values (in Fig. 1 and Fig. 2) are introduced from the references [1] and [7].

Now to sum up the results computed with various formulae for the same specimen in Table 1 and Table 2, we discover that the errors arise from the Eq. (1) are the smallest. At the same time, we drew the diagrams (Fig. 1 and Fig. 2) based on the calculated values and measured values. As shown in the Fig. 1 and Fig. 2 that the diffraction curve and calculated curve are almost coincident. All these suggest that Eq. (1) possesses better suitability.

Table 1. The Comparisons of the Results Computed with Various Formulae for Amorphous Specimens (a), (b) and (c).

| Formulary Types | Specimens | A | P | f | Wl | Wr | k | $x_{\circ}$ | $\delta$(%) |
|---|---|---|---|---|---|---|---|---|---|
| Gaussian–Cauchy Function (1) | (a) | – | – | – | – | – | – | – | above 6.3 |
| Polynomial of Degree3 (1) | (a) | – | – | – | – | – | – | – | above 10.0 |
| First Characteristic Function (1) | (a) | 68.91 | 16.43° | – | 4.486° | 5.979° | – | – | 2.0 |
| | (b) | 64.198 | 20.92° | – | 7.548° | 7.061° | – | – | 2.9 |
| | (c) | 107.24 | 14.01° | – | 4.385° | 4.987° | – | – | 1.8 |
| Second Characteristic Function (1) | (a) | 69.57 | 16.44° | – | 4.432° | 5.915° | – | – | 1.5 |
| | (b) | 64.933 | 20.75° | – | 7.168° | 7.204° | – | – | 2.2 |
| | (c) | 107.45 | 14.10° | – | 4.651° | 4.844° | – | – | 2.5 |
| Synthetic Function (7) | (a) | 68.912 | 16.437° | 0.7 | 4.4868° | 5.9790° | – | – | 1.80 |
| | (b) | 64.1984 | 20.922° | 0.65 | 7.5483° | 7.0612° | – | – | 2.46 |
| | (c) | 107.246 | 14.015° | 0.99 | 4.3852° | 4.9875° | – | – | 1.88 |
| The Present Formula (1) | (a) | 69.574 | 16.323° | 0.25 | 4.1889° | 6.0155° | 0.285 | 11.1° | 0.68 |
| | (b) | 63.8000 | 20.970° | 0.35 | 7.3600° | 6.9800° | 0.216 | 19.8° | 0.75 |
| | (c) | 108.020 | 13.680° | 0.98 | 4.2200° | 5.3800° | 0.32 | 11.37° | 0.62 |

## Results and Discussion

1. According to the above evaluation, the formula (1) may be used in description of the X–ray diffraction multipeak of the quite pure crystalline state, amorphous state and crystalline state with a little transitive state of half–and–halt order successfully. We think that it may also describe the X–ray diffraction multipeak of the pure transitive state. In fact, the degree of order in the transitive state stands between the pure crystalline state and the amorphous state, and deflects to the former. The half–peak breadths at left and right show inequality on X–ray diffraction multipeak. Its symmetry is not as good as the pure crystalline state, but is far better than the amorphous state. The degree of asymmetry can be calculated in the formula (1), even a little difference can be identified. From the examination and calculation for specimens of undrawn polypropyrene fibers in both crystalline state with a little transitive state of half–and–half order and amorphous state, it can be seen that the difference of left and right half–peak breadth is 0.076° in (110) face diffraction peak, 0.075° in (040) face, 0.080° in (130) face respectively, and the higher the peak, the smaller the difference of left and right half–peak breadth (see Table 2). In short, the formula (1) can be used to distinguish the difference between left and right half–peak breadth, so that, it may well describe X–ray diffraction multipeak of the pure transitive state.

2. There are reciprocal restraint conditions between principal parameters P, Wl and Wr in former formulae, for example, Wl must be smaller than Wr; position of P also affects Wl and Wr. Thus, P, Wl and Wr can not be taken as arbitrary values and the former formulae have its limitations in application. Now judging from the configuration of formula (1), P, Wl and Wr don't restrict mutually, therefore the limitations have been eliminated.

3. As shown in the configuration of formula (1), the interval of diffraction angle may be

increased or decreased at will; the starting values of parameters A, P, Wl, Wr may also be taken at will. The suitable values can be found finally by iterative calculation of computer.

Table 2. The Comparisons of the Results Computed with Various Formulae for the Specimen (d)

| Formulary Types | Types of Crystalline State | Diffra–ction Peaks | A | f | P | W | Wl | Wr | k | $x_0$ | $\delta$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Gaussian –Cauchy Function | α* Crystalline State | 110 | 171.7 | 0.98 | 14.00° | 1.01° | | | | | 5.9 |
| | | 040 | 204.5 | 0.81 | 16.84° | 0.99° | | | | | |
| | | 130 | 110.6 | 0.71 | 18.56° | 1.04° | | | | | |
| Polynomial of Degree4 (8) | Amorphous State | | | | | | | | | | |
| Gaussian –Cauchy Function | α* Crystalline State | 110 | 171.07 | 0.98 | 13.99° | 1.01° | | | | | 5.1 |
| | | 040 | 192.62 | 0.99 | 16.83° | 0.98° | | | | | |
| | | 130 | 110.02 | 0.71 | 18.50° | 0.98° | | | | | |
| First Char–acteristic Function (1) | Amorphous State | | 46.20 | | 17.03° | | 4.40° | 4.84° | | | |
| Gaussian –Cauchy Function | α* Crystalline State | 110 | 175.000 | 0984 | 13.992° | 1.000° | | | | | 4.7 |
| | | 040 | 196.600 | 0.999 | 16.839° | 0.972° | | | | | |
| | | 130 | 110.027 | 0.715 | 18.504° | 0.987° | | | | | |
| Synthetic Function (7) | Amorphous State | | 46.205 | 0.650 | 17.033° | | 4.405° | 4.848° | | | |
| The Present Formula (1) | α* Crystalline State | 110 | 167.000 | 1.000 | 14.025° | | 0.561° | 0.485° | 1.990 | 13.882° | 2.2 |
| | | 040 | 189.000 | 1.000 | 16.870° | | 0.550° | 0.475° | 2.000 | 16.726° | |
| | | 130 | 109.000 | 0.500 | 18.520° | | 0.581° | 0.501° | 1.750 | 18.360° | |
| | Amorphous State | | 46.000 | 0.750 | 16.550° | | 3.900° | 5.250° | 0.285 | 12.000° | |

Note: Melting extruding temperature 270°C

If a starting value taken is away from true value too far, the number of times of iteration will be increased, and the process of calculation will be prolonged, therefore the starting values taken should be as near the true value as possible.

4. Since there is a parametric factor k in the formula (1), the independent variable x may represent $\Theta$ or $2\Theta$; x may also represent other independent variables besides diffraction angle. So the similar diagrams can adequately be described by the formula (1).

5. The formula (1) can also describe the peaks with varied shape, thus it is applicable to curves which have large or small experimental error. When error of fitting equals to experimental error, the computation finished. The formula (1) possesses greater flexibility in its application.

6. In view of shape of X–ray diffraction multipeak of some polymers, the left half–peak breadth Wl is smaller than right half–peak breadth Wr in X–ray diffraction multipeak of the amorphous state in the great majority of cases. The same phenomenon also appears in X–ray diffraction multipeaks of the crystalline state with a little transitive state of half–and–half order or the pure transitive state. But the left half–peak breadth Wl is larger than right Wr in the three states sometimes. Moreover, in general there is always a convex or concave section at the left half–peak. Therefore when constituting the formula (1), we must consider these specialities of peak shape. For this reason, the authors have added two parameters $x_0$ and k into the formual (1). The $x_0$ represents the angular coordinate of the concave or convex

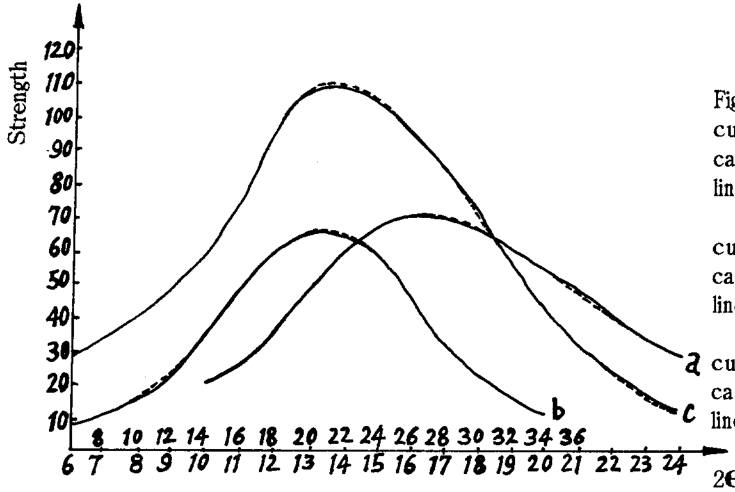

Fig. 1. a, X-ray diffraction curve (solid line) and calculated curve (dotted line) of specimen (a); b, X-ray diffraction curve (solid line) and calculated curve (dotted line) of specimen (b); c, X-ray diffraction curve (solid line) and calculated curve (dotted line) of specimen (c).

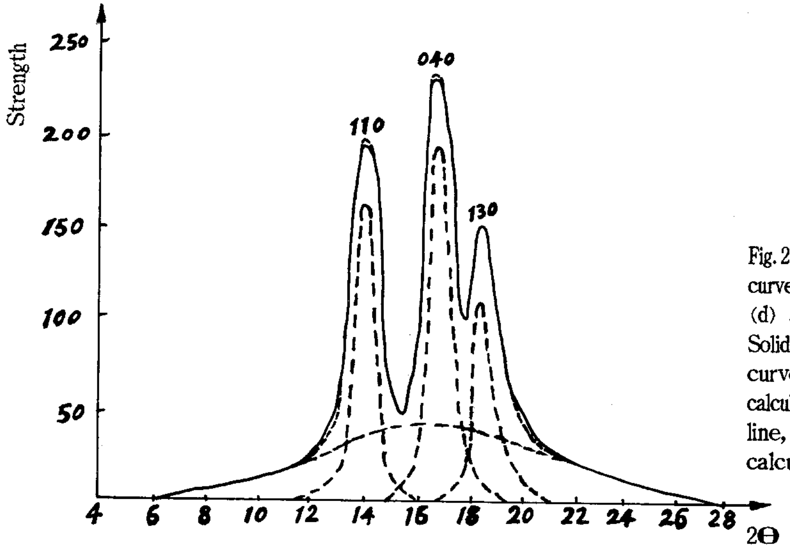

Fig. 2. X-ray diffraction curve of the specimen (d) and its division. Solid line, diffraction curve; dashed line, calculated curve; dotted line, combined calculated curve.

top; the k represents the concave or convex extent. The concave or convex extent is determined by the experimental curve of certain sample. To make the left half-peak increase and the right half-peak decrease, $x_o$ and k must take suitable values satisfying the following differential inequalities on the actual experimental curve:

$$\frac{dy(A, P, f, Wl, Wr, x_o, k, x)}{dx} > 0 \text{ (when } x<P\text{)}, \qquad (4)$$

$$\frac{dy(A, P, f, Wl, Wr, x_o, k, x)}{dx} < 0 \text{ (when } x>P\text{)} \qquad (5)$$

So long as the optimal values of $x_o$ and k are taken according to the conditions of inequalities(4) and (5), it may be ensured fitting mutually between the calculated and experimental curves well enough. Only when x=P, the following equality holds:

$$\frac{dy(A, P, f, Wl, Wr, x_o, k, x)}{dx} = 0 \qquad (6)$$

Thus, it may be ensured that the formula(1) is a single extremal function in the choosed interval.

7. However the actual experimental curve deviates either to the function of first term of formula (1) or to second, it is determined by the peak shape factor f. In the light of experience the factor f takes value in $|f| \leqslant 1$. This should be effected by the transformation $f=\sin f^*$ in the calculation, otherwise the strength of X–ray diffraction is a negative value sometimes, it is unreasonable.

8. There are some special cases of Eq. (1): (i) when Wl=Wr, and $0<f<1$, Eq. (1) is exactly a combined Gaussian–Cauchy function, i. e. Eq. (2); (ii) when Wl=Wr and f=1, Eq. (1) is just a Gaussian function; (iii) when Wl=Wr and f=0, Eq. (1) is just a Cauchy function; (iv) when $Wl \neq Wr$ but f=1, Eq. (1) is called a generalized Gaussian function; and (v) when $Wl \neq Wr$ but f=0, Eq. (1) is called a generalized Cauchy function.

9. The Gaussian function is a symmetric function of index type; the Cauchy function is a symmetric function of fraction type. The curve of the Gaussian function decreases fast at the left and right of peak, but the curve of the Cauchy function decreases rather slowly. With the change of parameters A, P, W, they can represent many symmetric curves. If they are combined by the combinatorial coefficient f and constituting a function $fG+(1-f)C$, it can represent more symmetric curves with the changes of f, A, P, W. But the three functions can only represent symmetric curves, they are not able to represent asymmetric curves. Thus, they possess large limitation in the application, because the peaks of many curves are asymmetrical in practice. The formula(1) created by the authors has not such limitation. It includes the above five special cases and can characterize the curves of both symmetric and asymmetric peaks. Consequently its application is very extensive.

10. From the Table 1 and Table 2, it is seen that the strength(A) of X–ray diffraction multipeak of amorphous state is small, the left and right half–peak breadth(Wl, Wr) is wide, and the difference between Wl and Wr is larger; the strength (A) of X–ray diffraction multipeak of crystalline state with a little transitive state of half–and–half order is large, the left and right half–peak breadth(Wl, Wr) is narrow, and the difference between Wl and Wr is extremely small which is smaller than 0.1°. Because the degree of order in the amorphous state is far smaller than that in the crystalline state, the above cases take place. Therefore, the three numerical values(the peak height A; magnitude of half–peak breadth Wl, Wr; the difference between Wl and Wr) can serve as an important mark of the degree of order in polymers intuitively.

11. It should be stressed that because the specimen of undrawn polypropyrene fibers contains a little transitive state of half–and–half order in crystalline region, the X–ray diffraction peaks of the crystalline portion are slightly asymmetric(see Fig. 2 and Table 2).

12. The k is far smaller than 1 for the amorphous state, but the k is far larger than 1 for the crystalline state with a little transitive state of half–and–half order, and transitive state. This is determined by magnitude of the value of $\ln(Wr/Wl)$. Thus, it may be ensured that the inequalities (4) and (5) hold. The value of $\ln(Wr/Wl)$ may be used as a reference for selecting the starting value of k.

13. If the number of resolved peaks can be seen on the diffraction curve of a specimen, the separation of curve is unique; if it can not be seen, the separation may not be unique. In latter case the selection of a correct solution should be determined by some analyses of the concrete experiment.

## Conclusions

From what is proven and discussed above, we may obtain following conclusions:

1. The X–ray diffraction of three phases (crystalline, transitive and amorphous) of some polymers possesses unified law of diffraction, it may be characterized by same equation.
2. Since fitting accuracy of the formula (1) is very high, it can reflect X–ray diffraction law of three phases precisely.
3. The formula (1) satisfies eight requests in application and includes five special examples, therefore it possesses better flexibility and generality in application.
4. The formula (1) possesses theoretical completeness and logicality. It reflects the dialectical relation of the unity of opposites between different phases in polymers, and the relation of gradual transformation from quantitative to qualitative change between different phases is seen visually from formula (1). Its principal mark is changed extent of some key parameters.
5. When studying the relation between structure and properties of complex polymers by means of the resolution of X–ray diffraction peak of the superposition, the formula (1) can give accurate data of quantitative and qualitative relation. To use some parameter values computed by the formula (1) not only can compute out accurately crystallinity, distance between crystal faces and unit cell parameters in polymers, but also can carry out many valuable exploration for crystal grain size, lattice distortion and transitive state in polymers.
6. The formula (1) is a indispensable supplement of the Gaussian–Cauchy function in actual application.

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