

A Unified Approach to Line-Shape Analysis in Polymer Crystallography

BY M. THAKUR,* S. K. TRIPATHY* AND J. B. LANDO

Case Western Reserve University, University Circle, Cleveland, OH 44106, USA

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Abstract

General line shapes in the diffraction patterns of polymeric crystalline systems have been investigated on the basis of the interaction among the scattering units. A perturbation term has been incorporated into the Hamiltonian of the harmonic molecular lattice and the corresponding intensity distribution has been deduced from first principles with the assumption of elastic scattering. The various line broadenings, formerly interpreted as results of microlattice strains within a crystal or paracrystallinity, have been shown to be special cases of the general consequence of the higher-order interactions. Finally, the explicit temperature dependence of a line width was deduced and verified against experimental work on polyethylene single crystals.

Introduction

Extensive studies have been made in the past on line-shape analysis of the diffraction patterns of crystalline polymeric systems (Buchanan, McCullough & Miller, 1966; Hosemann, 1951; Hosemann & Nilke, 1964; Guinier, 1963; Ziman, 1972). Two consistent observations have been made in these studies, and these studies are not limited to polymeric crystals alone. Firstly, the peak heights decrease with increasing magnitude of the corresponding reciprocal-lattice vector $[s]$ and, secondly, the line widths increase as $[s]$ increases. The first of these effects has been successfully described by harmonic approximation of the interaction potential leading to the well-known Debye-Waller effect (Debye, 1914; Waller, 1923, 1928). The second effect, however, does not lend itself to such general interpretation. The increase in line width as a function of $[s]$ has been variously explained as a manifestation of paracrystallinity (Hosemann, 1981; Hosemann & Wilke, 1964), or the presence of strain in the crystal lattice (Buchanan *et al.*, 1966; Guinier, 1963; Wilson, 1949). Although these broadenings can be interpreted in terms of a more generalized interaction, scant attention has been paid to such a treatment. In fact, most interpretations of line-width broadening are based on direct-space analysis using

various statistical models. This *ad hoc* description of the arrangement of scattering units leaves out any discussion related to the nature of interaction among these particles leading to line-shape changes. Also, no explicit temperature dependence of the line width is obtainable from these treatments.

The Debye-Waller effect, which is a direct consequence of harmonic interaction of the lattice, is manifested in a decrease of diffraction intensities as the scattering angle and temperature increases (Guinier, 1963; Debye, 1914; Waller, 1923, 1928). Changes in line shapes, however, are not accounted for by such harmonic effects (Guinier, 1963; Vainshtein, 1966). Extensive theoretical studies have been made to arrive at the observed line-shape broadening in the diffraction patterns on the basis of static disorders (Hoseworth, 1951; Hosemann & Wilke, 1964; Guinier, 1963). In these treatments, displacement from equilibrium lattice position are selected in an *ad hoc* manner.

In the present paper an investigation is made on the line shapes that can be expected when the individual scattering units 'see' an effective higher-order interaction potential. Although the special cases of paracrystallinity, finite crystal size and lattice strain will be explored, the treatment will be kept very general. The specific goal is not only to put the two types of effects discussed earlier on the same footing, but to arrive at relevant correction terms that can be used in structure calculations. Finally, an explicit temperature dependence of line width will be deduced and compared to experiment.

Theory

The effective electron density $\rho(\mathbf{r})$ of the molecular crystal lattice is given by convoluting the molecular electron density $\rho_m(\mathbf{r})$ with the disposition functions $A(\mathbf{r})$ (Vainshtein, 1966). As outlined in this treatment, one can express $\rho(\mathbf{r}) = \rho_m(\mathbf{r})A(\mathbf{r})$. Ideally, the disposition function for a static point lattice is a series of delta functions. This results in delta-function line shapes in the diffraction pattern. However, in conjunction with an anharmonic force field at higher temperature, such point lattice approximation fails. The disposition function in that case can be chosen as

$$A(\mathbf{r}) = \sum_{j=1}^N a(\mathbf{r} - \mathbf{r}_j),$$

* Present address: GTE Laboratories, Incorporated, 40 Sylvan Road, Waltham, MA 02254, USA.

where N = number of scattering units present in the crystal and $a(\mathbf{r})$ is an arbitrary function dependent on the interaction potential. The structure amplitude, the Fourier transform of $\rho(\mathbf{r})$, will be given by

$$F(\mathbf{s}) = F_m(\mathbf{s})b(\mathbf{s}), \quad (1)$$

where $F_m(\mathbf{s}) = F[\rho_m(\mathbf{r})]$, $F \equiv$ Fourier transform

$$b(\mathbf{s}) = F[A(\mathbf{r})] = \sum_{j=1}^N \exp(2\pi i \mathbf{s} \cdot \mathbf{r}_j) F[a(\mathbf{u})] \quad (2)$$

$$\mathbf{u} = \mathbf{r} - \mathbf{r}_j.$$

Evidently, the choice of $a(\mathbf{u})$ will determine the nature of $b(\mathbf{s})$ and hence $F(\mathbf{s})$. The term $a(\mathbf{u})$, on the other hand, depends on the choice of the interaction potential. The simplest, most tractable, and yet general form of this potential we can use is similar to the one proposed by Einstein, where no dispersion is envisaged. Each scattering unit sees an effective potential $V(\mathbf{r}_j)$, which is independent of the position of every other unit. The Hamiltonian then assumes the form

$$H = \sum_{j=1}^N [p_j^2/2m + V(\mathbf{r}_j)],$$

where p_j = momentum of the j th scattering unit and m = mass of the scattering unit.

Using the Maxwell-Boltzmann distribution we can define $a(\mathbf{r})$ as

$$a(\mathbf{r}) = \frac{\int d\mathbf{p}^N \int d\mathbf{r}^N \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j) \exp(-\beta H)}{\int d\mathbf{p}^N \int d\mathbf{r}^N \exp(-\beta H)}$$

$$= \frac{N \exp[-\beta V(\mathbf{r})]}{\int d\mathbf{r} \exp[-\beta V(\mathbf{r})]} = L \exp[-\beta V(\mathbf{r})], \quad (3)$$

where $\beta = 1/kT$ and $L = N/\int d\mathbf{r} \exp[-\beta V(\mathbf{r})]$. Putting this back in (2), one obtains

$$b(\mathbf{s}) = L \sum_{j=1}^N \exp(2\pi i \mathbf{s} \cdot \mathbf{r}_j) F\{\exp[-\beta V(\mathbf{u})]\}. \quad (4)$$

In general, for one dimension, $V(\mathbf{u})$ can be written in the form

$$V(\mathbf{u}) = \underbrace{\frac{1}{2}\gamma_0 u^2}_{\text{harmonic term}} + \underbrace{\gamma(u)}_{\text{all other terms}} \quad (5)$$

As mentioned earlier, the harmonic term $1/2\gamma_0 u^2$ leads to the Debye-Waller factor, which affects the total intensity of the diffraction maxima. However, the harmonic term does not result in any modification of the line shapes. It is the second term, $\gamma(u)$, on the other hand, which is responsible for the line broadening and henceforth it will be referred to as the anharmonic term. It is assumed that $\gamma(u)$ is analytic over the whole range of u . Thus, substituting in (3), we get

$$a(u) = L_1 \exp[-\frac{1}{2}\gamma_0 \beta u^2 - \beta \gamma(u)],$$

where L_1 is the proper front factor in one-dimension

$$\exp[-\beta \gamma(u)] = \sum_{n=0}^{\infty} \frac{u^n}{n!} \frac{d^n}{du^n} \exp[-\beta \gamma(u)] \Big|_{u=0}$$

$$= \sum_{n=0}^{\infty} \frac{u^n}{n!} \sum_{l=0}^{\infty} p_l^n(T),$$

where

$$\frac{d^n}{du^n} \exp[-\beta \gamma(u)] \Big|_{u=0} = \sum_{l=0}^{\infty} p_l^n(T)$$

are the position-independent constants.

Thus,

$$a(u) = L_1 \exp(-\frac{1}{2}\gamma_0 \beta u^2) \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} \frac{p_l^n}{n!} u^n$$

$$Fa(u) = L_1 \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \frac{p_l^n (-1)^n (2\pi)^{n/2}}{n! (2\pi)^{n/2} (\gamma_0 \beta / 2\pi)^{(n+1)/2}}$$

$$\times \exp[-2\pi^2 s^2 / \gamma_0 \beta] H_n[2\pi s / (\gamma_0 \beta)^{1/2}]$$

where $H_n[2\pi s / (\gamma_0 \beta)^{1/2}]$ is the Hermite polynomial of degree n .

$$b(s) = L_1 \sum_{j=1}^N \exp(2\pi i s x_j)$$

$$\times \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \frac{p_l^n (-1)^n}{n! i^n (\gamma_0 \beta)^{(n+1)/2}}$$

$$\times \exp[-2\pi^2 s^2 / \gamma_0 \beta] H_n[2\pi s / (\gamma_0 \beta)^{1/2}].$$

The quantity of interest is $[b(s)]^2$, which is proportional to the intensity recorded on the film or collected by the relevant detector.

$$|b(s)|^2 = L_1^2 \sum_{j=1}^N \sum_{k=1}^N \exp[2\pi i s (x_j - x_k)]$$

$$\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n'=0}^{\infty} \sum_{m'=0}^{\infty} \frac{p_n^n q_m^m \times 2\pi \exp(-4\pi^2 / \gamma_0 \beta) s^2}{n! m! i^{m+n} (\gamma_0 \beta)^{(m+n+2)/2}}$$

$$\times H_m(\zeta) H_n(\zeta),$$

where $\zeta = 2\pi s / (\gamma_0 \beta)^{1/2}$.

Substituting

$$r_n^n = \frac{p_n^n (2\pi)^{1/2}}{i^n (\gamma_0 \beta)^{(n+1)/2}},$$

$$t_m^m = \frac{q_m^m (2\pi)^{1/2}}{i^m (\gamma_0 \beta)^{(m+1)/2}}$$

$$|b(\zeta)|^2 = L_1^2 \sum_{j=1}^N \sum_{k=1}^N \exp[2\pi i s (x_j - x_k)]$$

$$\times \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n'=0}^{\infty} \sum_{m'=0}^{\infty} \frac{r_n^n t_m^m}{n! m!}$$

$$\times \exp(-\zeta^2) H_m(\zeta) H_n(\zeta).$$

Using the generating function for Hermite polynomials (Arfken, 1966):

$$\sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \exp(-\zeta^2) H_m(\zeta) H_n(\zeta) \frac{r_{n'}^n t_{m'}^m}{n! m!} \\ = \exp(\zeta - r_{n'} - t_{m'})^2 + 2r_{n'} t_{m'}.$$

It is easy to show for a periodic lattice that

$$\sum_{j=0}^N \sum_{k=0}^N \exp[2\pi i s(x_j - x_k)] = \frac{\sin^2 \pi N a s}{\sin^2 \pi a s},$$

where the lattice periodicity $a = x_j - x_{j+1}$.

Thus,

$$|b(s)|^2 = L_1^2 \frac{\sin^2 \pi N a s}{\sin^2 \pi a s} \\ \times \sum_{n'=0}^{\infty} \sum_{m'=0}^{\infty} \exp[-(\zeta - r_{n'} - t_{m'})^2 + 2r_{n'} t_{m'}]. \quad (6)$$

The derivation of $[b(s)]^2$ has been completely general so far. The first term in the expression of $[b(s)]^2$, that is $\sin^2 \pi N a s / \sin^2 \pi a s$, is the familiar interference function. It is the second term, however, that contains the modulation effect that is added to the ideal first term owing to the nature of the potential. Below we derive the detail implication and the specified special cases from the second term.

Special cases. To extract the full meaning of the second term, let us make the following choices for $r_{n'}$ and $t_{m'}$,

$$\frac{1}{\gamma_0 \beta} (r_{n'} + t_{m'}) = \frac{4\pi(n' + m')/a}{[V_0 + W_0(n' + m')^2]^2} \quad (7)$$

$$(r_{n'} - t_{m'})^2 - \ln(l + n' + m') = \frac{(n' + m')^2/a^2}{[V_0 + W_0(n' + m')^2]^2} \quad (8)$$

and

$$\frac{4\pi^2}{A_0 \beta} + \frac{1}{(V_0 W_0 h^2)^2} = \frac{4\pi^2}{\gamma_0 \beta}, \quad (9)$$

where n' , m' and h are all integers, V_0 , W_0 and A_0 are constants. The sole purpose of making such choices has been to cast the general expression in (6) into a familiar form [(10)] without introducing any redundancies. In other words, no new parameter has been introduced.

With this choice of terms and further algebraic simplification (see Appendix), we obtain

$$|b(s)|^2 = L_1^2 \frac{\sin^2 \pi N a s}{\sin^2 \pi a s} \exp(-4\pi^2/\beta A_0 s^2) \\ \times \sum_{h=0}^{\infty} \exp[-(s - h/a)^2/(V_0 + W_0 h^2)^2]. \quad (10)$$

The various terms in this expression can be interpreted as follows:

1. The first term, which is the interference term, has maxima at $s = h/a$, where h is an integer. The peak heights are of the order of N^2 , where N is the number of molecular units in the crystal and line width (Δ_1) is of the order of $1/Na$, where a is the lattice parameter.

2. $\exp(-4\pi^2 s^2/A_0 \beta)$ is due to the harmonic vibrations and it reduces the peak heights in an exponential fashion. A comparison with the Debye-Waller temperature factor $\exp(-2B \sin^2 \theta/\lambda^2)$ gives $(4\pi^2/\beta A_0) = B/2$. Note that this term *does not* affect the line widths of the peaks.

3. The third term, $\sum_{h=0}^{\infty} \exp[-(s - h/a)^2/(V_0 + W_0 h^2)^2]$, is contributed by the additional term in the potential (other than harmonic). It has maxima at $s = h/a$ just as in the first term. The effective peak height of a reflection is not affected at all by this term. The line widths, however, are considerably increased by its presence. The contribution to line widths from this term for a reflection $h00$ is given by

$$\Delta_2 = \frac{\int_{\text{reflection}} I(s') ds'}{I(0)} = \frac{V_0 + W_0 h^2}{s\pi^{1/2}}. \quad (11)$$

Thus, Δ_2 apparently increases as h^2 .

Finally, the *total* line width obtained by combining contributions from the first and third term,

$$\Delta^2 = U_1 + (V_1 h^2 + W_1 h^4), \quad (12)$$

where U_1 , V_1 and W_1 are a new set of constants defined in terms of Δ_1 , V_0 and W_0 . If F_1 , $W_1 = 0$, then $\Delta^2 = U_1$, which relates to the familiar crystal size effect (Sherrer, 1918) $U_1 = 1/L_1^2$, where L_1^2 is the mean-square size of the crystal. If, on the other hand, W_1 , $U_1 = 0$, then $\Delta^2 = V_1 h^2$. At constant temperature, this type of dependence of Δ^2 on h is identical with what is observed when there is lattice strain in the crystal (Buchanan *et al.*, 1966; Wilson, 1949).

If, on the other hand, $U_1 = 0$, $V_1 = 0$, then $\Delta^2 = W_1 h^4$. Comparison with Hosemann's analysis shows that this h^4 dependence is similar to that of a paracrystalline crystal at a given temperature (Hosemann, 1951; Hosemann & Wilke, 1964; Guinier, 1963).

Thus, in the above three special cases, we have been able to arrive at the experimentally observed functional relationship between the line width and the reciprocal-lattice vector. This was achieved by choosing a suitable set of transformations given by (7), (8) and (9). In other words, (7), (8) and (9) are relationships describing the physical nature of the system leading to the experimentally observed features in the diffraction pattern. To investigate the temperature dependence of the line width, let us analyze one of these relationships further. Dimensional analysis of (9) shows that V_0 and W_0

will have a temperature dependence of $T^{-1/2}$ since γ_0 is temperature independent (force constant, characteristic of the system). Hence, V_1 and W_1 will have a temperature dependence of T^{-1} . Thus, the functional dependence of line width on temperature can be expressed as

$$\Delta^2 = U_1 + C/T,$$

where C is a constant independent of temperature. Hence, within a reasonable range, the line width is expected to decrease with increasing temperature. An experimental verification of this correlation has been made employing the data from detailed work by Krenzer & Ruland (1981) on single crystals of polyethylene. Their resulting width-temperature correlation curve for the 110 line is shown in Fig. 1. The general shape of the curve remains almost the same for all other lines (010, 200, 100 *etc.*). In the correlation curve the three zones are related to changes caused by the β and γ relaxations. For any specific zone, as the plot shows, the width (Δ^2) maintains a linear relationship with the reciprocal temperature ($1/T$), in excellent accord with the theoretical prediction. For other lines (100, 010, 200 *etc.*) the agreement is equally good. This agreement between the experiment and the theory further implies that the relaxation (β , γ) processes are primarily assisted by anharmonic motions.

Results and discussions

We have shown in a very general manner that the line-width broadening in polymer diffraction patterns is caused by the complex nature of the interaction potential. The harmonic term alone is not sufficient to explain these effects. Detailed interpretation for line-width broadening has been presented by Hosemann, Guinier and others by a consideration of long-range disorder. We have shown here that adequate descriptions can be furnished on the basis of an anharmonic interaction potential alone. It is important to note that the potential that was used in

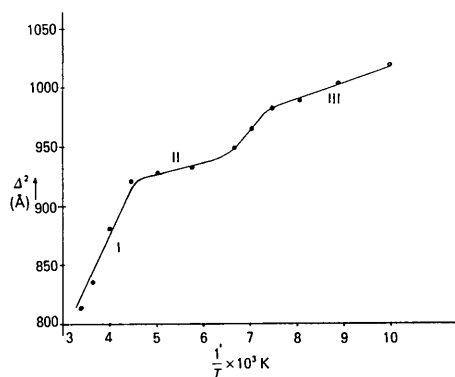


Fig. 1. Temperature dependence of the line width for polyethylene. (Data from Krenzer & Ruland, 1981).

this treatment, although similar, is not identical to that of Einstein since the harmonic force constant (γ_0) for any set of planes has been assumed to be a function of the corresponding interplanar spacing [see (9)]. In this analysis, although no specific form of the additional term in the potential [$\gamma(u)$] was assumed (except that it should be well behaved), a comprehensive and unified correlation between line width and the interaction potential was established. The explicit temperature dependence of a line width was also deduced and successfully verified against experimental work on polyethylene. In principle, the nature of the interaction potential can be established as a measure of the temperature dependence of the line widths. In a subsequent paper we will show how the inclusion of a specific high-order term in the interaction potential can lead to very specific anomalies in the observed diffraction patterns. This may provide an avenue for solving crystal structures where such anomalies are observed in the diffraction pattern.

The nature of anharmonicity, if it can be established, may lead to an understanding of the nature of the crystal itself at the molecular level. Criteria can be established between the existence of a specific higher-order term in the anharmonic interaction potential and the nature of the electron cloud that participates in the scattering process. In short, the unified nature of the present approach opens up many new possibilities. In a subsequent paper, this possibility will be explored in the specific cases of some polydiacetylene crystal diffraction patterns.

Finally, it should be noted that the emphasis has been to probe the various anharmonic effects on the diffraction intensities from 'first principles'. The expression in (6), containing anharmonic contributions, is completely general. With proper choices of the expansion coefficients (r_n , t_m), we hope it will be possible to account for other important observations related to crystalline solids. Some specific work in this direction is presently under way.

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APPENDIX

Using (7), (8) and (9), it is fairly simple to show that (6) transforms to

$$|b(s)|^2 = L_1^2 \frac{\sin^2 \pi N a s}{\sin^2 \pi a s} \exp \left[-\frac{4\pi^2}{\beta A_0} s^2 \right] \\ \times \sum_{n'=0}^{\infty} \sum_{m'=0}^{\infty} \exp [-\ln(l+n'+m')] \\ - \frac{[s - (n' + m')/a]^2}{[V_0 + W_0(n' + m'')^2]^2}$$

Now

$$\sum_{n'=0}^{\infty} \sum_{m'=0}^{\infty} \exp[-\ln(l+n'+m')] - \frac{[s - (n'+m')/a]^2}{[V_0 + W_0(n'+m')^2]^2} = \sum_{h=0}^{\infty} (h+1)f_h$$

where h is an integer and

$$f_{n'+m'} = \exp[-\ln(l+n'+m')] - \frac{[s - (n'+m')/a]^2}{[V_0 + W_0(n'+m')^2]^2}$$

However, $(h+1) \exp[-\ln(l+h)] = 1$. Hence,

$$|b(s)|^2 = L_1^2 \frac{\sin^2 \pi N a s}{\sin^2 \pi a s} \exp\left(-\frac{4\pi^2}{\beta A_0} s^2\right) \times \sum_{h=0}^{\infty} \exp\left[-\frac{(s-h/a)^2}{(V_0 + W_0 h^2)^2}\right]$$

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The Significance of Anharmonic Motion in Polymer Crystal Structure Analysis

BY M. THAKUR,* S. K. TRIPATHY,* C. W. BURKHART AND J. B. LANDO

Case Western Reserve University, University Circle, Cleveland, OH 44106, USA

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Abstract

Nonsystematic absences along certain reciprocal-lattice directions have been observed in the diffraction patterns of the macroscopic single crystals of various materials, both in our laboratory and in the literature. These extinctions are not space-group related nor are they the result of secondary scattering. Incorporation of the lowest-order anharmonic interaction terms, cubic and quartic in displacement, into the Hamiltonian of the molecular lattice, has made it possible to give a complete interpretation of these observations. A general intensity distribution was deduced with the assumption of elastic scattering. The final result provides new insight into the interaction of molecular units within a crystal and reveals new avenues for the solution of some unsolved crystal structures. A general procedure for the application of the required correction term to the intensity distribution is outlined, along with appropriate examples.

Introduction

The functional dependence of the line shape in a diffraction pattern on the nature of the interaction potential among the scattering entities has been established (Thakur, Tripathy & Lando, 1985). It has been shown that the monotonic decrease in the peak intensities is a consequence of the harmonic part of the interaction potential (Debye-Waller effect). The changes in the line shape, on the other hand, were generally interpreted to be a function of the nonharmonic aspect of the interaction potential. The paracrystallinity, finite crystal size and presence of lattice strain were investigated using a very general form of the potential.

It has been observed in our laboratory that certain macroscopic crystalline systems have nonsystematic absences in their diffraction patterns, although intensities calculated from their crystal structures should be observed. Similar observations, not accounted for in detail, were made by various other workers (Akiyama, Tanaka & Iitaka, 1970; Shannon & Katz, 1970; Srivastava & Przybylska, 1970; Mazhar-ul-Haque & Caughlan, 1970; Torii & Iitaka, 1970). In

* Present address: GTE Laboratories, Incorporated, 40 Sylvan Road, Waltham, MA 02254, USA.

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