

OCTA

Integrated simulation system for soft materials

Multi-Phase Dynamics Program

Muffin

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User's Manual

- Volume VII -

Light Transmittance Simulator

Turban

OCTA User's Group

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Chapter 1

Theoretical Background of TURBAN

1.1 What's TURBAN?

According to the size distribution of spherulite in the solid polymeric material, the material which is originally transparent becomes muddy. Although these phenomena become a serious bottleneck when we apply the polymeric materials to a wrapping material where the transparency is required, the control of transparency has been fulfilled by changing of experiential conditions, and the accurate theoretical prediction of transparency has not been succeeded.

We have developed a simulator named as TURBAN (TURBidity ANalyzer) which serves to predict the transparency of polymeric material having spherulite structures. Here we explain the theoretical background of the our developed the simulation program: TURBAN.

1.2 Theoretical background of a light-transmittance simulator

1.2.1 Propagation of the light to a medium

When a light passes through a material, a reflection, scattering, and adsorption take place. When a light

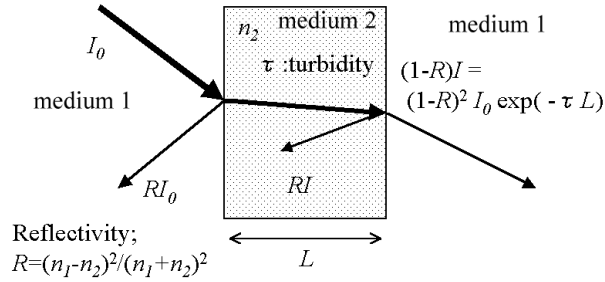


Figure 1.1: The optical progress conceptual diagram to a medium.

propagates from a medium of a refractive index n_1 to a medium of n_2 , a reflection occurs at the interface according to these two values of refractive indices. The reflectance R is given by

$$R = \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2}. \quad (1.1)$$

Thereby, when an incident-light intensity is set to I_0 , an intensity $I_{int(1 \rightarrow 2)}$ of the light which propagates to a medium 2 without reflecting by the interface is

$$I_{int(1 \rightarrow 2)} = (1 - R)I_0 = \frac{4n_1 n_2}{(n_1 + n_2)^2} I_0. \quad (1.2)$$

The intensity also decreases by the adsorption and scattering as the light goes through the medium 2. When the light with a intensity I propagates only by a distance dL , the decrease rate of the light intensity, dI/dL is proportional to the intensity at the position L . Then we can derive the Lambert's equation,

$$I_{bulk(1 \rightarrow 2)}(\tau, L) = I_{int(1 \rightarrow 2)} \exp(-\tau L). \quad (1.3)$$

The value τ in this equation is called as a turbidity, and it is an important material constant.

When the light arrives at the other side of interface, a reflection of the light takes place again due to the change of the refractive indices between two medium. The reflectance is the same as that when the light goes to $1 \rightarrow 2$. Therefore, the equation of the intensity of light which passes through this interface is

$$I_t = I_{int(2 \rightarrow 1)} = (1 - R)I_{bulk(1 \rightarrow 2)}(\tau, L) = \frac{16n_1^2 n_2^2}{(n_1 + n_2)^4} I_0 \exp(-\tau L). \quad (1.4)$$

Therefore, the intensity of the direct transmitted light I_t/I_0 becomes,

$$\frac{I_t}{I_0} = \frac{16n_1^2 n_2^2}{(n_1 + n_2)^4} \exp(-\tau L). \quad (1.5)$$

1.2.2 Turbidity

Here we consider a solid polymeric material with a spatially non-uniform structure whose characteristic size is comparable to the wave length of the incident beam. In order to simplify the following explanation, we assume the structure of the solid polymeric material to be that of polyethylene. Due to the heterogeneity of the spatial structure, the permittivity field also becomes spatially non-uniform, which strongly influences the optical property of the system. For polyethylene solids, the heterogeneity of this structure originates from the nucleus formation at the time of creation of the solid phase. The statistical property of the spatial distribution of spherulites and the size distribution are determined by the process of the solidification. The whole system is occupied by spherulites and it is assumed that the interior of spherulite consists of the crystal and amorphous part.

When the light propagates from the air to such material, there are (1) a reflection by the surface, (2) (a) a scattering loss, (b) an adsorption loss of the light inside solids and (3) a reflection when the light goes from the solid side into the air. (1) and (3) can be estimated by the refractive index of the solid as described in the previous section. Optical properties peculiar to the material are based on (2). However, since the polyethylene consists only of non-polar molecules, the absorption of the light coming from the retardation of the induced polarization does not occur, and therefore it is not taken into consideration in this simulator.

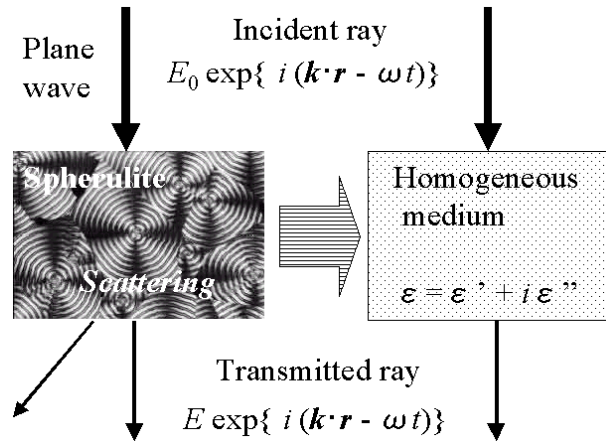


Figure 1.2: The model figure about the light which penetrates polyethylene.

Now we consider such a situation that the plane waves with a wave number \mathbf{k} goes and is scattered at the inside of the material occupied by spherulite as shown in Figure 1.2. In order to consider only the

property of bulk, we do not consider the effect of the interface where the refractive index changes. If an incident plane wave $\mathbf{E}_0 \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$ propagates into the solid occupied by spherulites, a dipole moment will be induced and electromagnetic waves will be emitted by the oscillation of the dipole moment. The scattered electromagnetic waves and plane waves induce another dipole moments, and repeat scatterings. In order to estimate the decrease of the light intensity by the multiple scattering described above, we have to solve the Maxwell equation for propagating waves in a medium with a spatial distribution of permittivity $\epsilon_{\alpha\beta}(\mathbf{r})$. However, since this method requires a big computer resources, it is difficult to apply this method to a cheap material like the polyethylene. So, we regard this problem as that of estimation of the complex effective dielectric constant of the uniform system (right-hand side in Figure 1.2) which gives an equivalent propagation of the system on the left hand side of Figure 1.2.

Suppose that the value of the field of a dielectric tensor $\epsilon_{\alpha\beta}(\mathbf{r})$ is now known at the arbitrary positions \mathbf{r} in the material. Since the system as a whole is isotropic, the spatial average of $\langle \epsilon_{\alpha\beta}(\mathbf{r}) \rangle$ is turned out to be $\epsilon_0 \delta_{\alpha\beta}$. After a perturbative calculation, the following macroscopic effective dielectric tensors is obtained as

$$\bar{\epsilon}_{\alpha\beta} = \frac{1}{V} \int \langle \epsilon_{\alpha\beta}(\mathbf{r}) \rangle + \frac{1}{(2\pi)^d} \int d^d \mathbf{q} G_{\mu\nu}(\mathbf{q}, \omega = \frac{ck}{\sqrt{\epsilon^0}}) T_{\alpha\mu\nu\beta}(\mathbf{k} - \mathbf{q}), \quad (1.6)$$

where $G_{\mu\nu}(\mathbf{q}, \omega)$ is defined as

$$G_{\mu\nu}(\mathbf{q}, \omega) = -\frac{q_\mu q_\nu - \mathbf{k}^2 \delta_{\mu\nu}}{q^2 - \mathbf{k}^2}. \quad (1.7)$$

$T_{\alpha\mu\nu\beta}(\mathbf{q})$ is the Fourier transformation of the correlation function of the dielectric tensor field, and is defined as

$$T_{\alpha\mu\nu\beta}(\mathbf{q}) = \frac{1}{V} \frac{1}{\epsilon^0} \langle \delta \epsilon_{\alpha\mu}(\mathbf{q}) \delta \epsilon_{\nu\beta}(-\mathbf{q}) \rangle. \quad (1.8)$$

The first term of the right-hand side of eq.(1.6) is corresponding to the intrinsic birefringence, the real part of the second term corresponds to the form birefringence, and the imaginary part corresponds to the form dichroism. The turbidity τ is expressed by the following equations,

$$\tau \cong \frac{\mathbf{k}}{2\epsilon^0} (\delta_{\alpha\beta} - \hat{k}_\alpha \hat{k}_\beta) \text{Im}[\bar{\epsilon}_{\alpha\beta}]. \quad (1.9)$$

The operator $(\delta_{\alpha\beta} - \hat{k}_\alpha \hat{k}_\beta)$ serves to extract the component perpendicular to the direction of the wave propagation.

It is known that the roughness of the material surface mainly affects on the transparency of polyethylene. Since the surface roughness comes from the mechanical problems in the polymer processing, and it is very difficult to consider the transparency including this effect. So, the scattering at a material surface is not considered here, but only the transparency based on the internal structure is discussed.

1.2.3 Spherulite growth simulator

When we observe the process of crystallization with spherulite structure of polymeric materials such as polyethylene under a constant temperature, spherulites grow up toward the directions of their radii at a constant velocity, collides and their growth stop. When a spherulite grows up from the melt, the apparent crystallinity is the volume fraction of spherulites and the true crystallinity has to be calculated from crystal structure in spherulites. At a time t in the crystallization process, the apparent crystallinity X can be determined by the number of nuclei N , the line growth rate $G(r = Gt)$ of the spherulite at radii r and the collision of spherulites. This equation is called the equation of Avrami and can be written as

$$X = 1 - \exp\{-kt^n\}, \quad (1.10)$$

where k is called the rate constant, n is called the Avrami index. In the three dimensional growth and the spatially non-uniform nucleation which all nuclei generate at the time $t = 0$, the values n and k are $n = 3$ and $k = (4\pi/3)NG^3$, in the case of the uniform nucleation which the number of nucleus increases with time in the form of $N = It$, $n = 4$ and $k = (\pi/3)IG^3$ are taken.

Since what is required for the light transmittance simulator is the filled structure by spherulites, we obtain such a filled structure by a simulation based on the equation of Avrami in the three dimensional space.

In the case of the spatially non-uniform nucleation, the actual procedure of simulation is as follows.

1. Generate coordinates of nuclei at random and with a given density.
2. Grow up spherulites with a constant growth velocity from each position of nuclei.
3. When a spherulite collides with the other spherulite, stop the growth for this direction here.
4. If all space is filled with spherulites, this simulation stops.

In the case of a uniform nucleation, nuclei generate at a fixed rate with time in the space where the material has not been crystallized. The others are same as the case in the spatial non-uniform nucleation. The growth image is shown in Figure 1.3.

The information acquired by this simulation is the coordinate of the nucleus of the spherulite which occupies an arbitrary position in the systems. Using this information, the orientation of basic axes of crystallite at an arbitrary position can be known. And the turbidity calculation described below is performed.

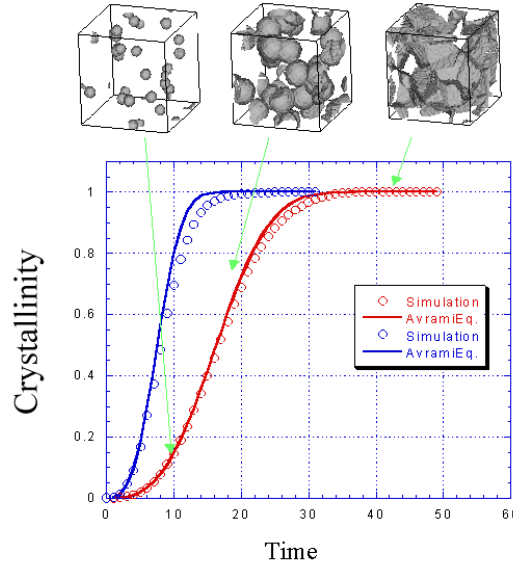


Figure 1.3: The real image of the spherulite growth simulator.

1.2.4 The spatial distribution of a dielectric tensor

In order to calculate the turbidity, it is necessary to obtain the spatial distribution of the dielectric tensor. It becomes important what a spatial distribution is estimated from the data obtained from a spherulite growth simulator. However, since the detail of the structure inside the polyethylene spherulite is still not clear experimentally and theoretically, the structure explained below is used for our calculation. It is well known experimentally for the polyethylene spherulite that the polymer crystal lamellae grow radially from a nucleus and are twisted in a constant pitch. We summarize the experimentally known evidences for the interior of polyethylene spherulite.

1. The normal direction of a lamella is perpendicular to radius vector direction.
2. The lamella is twisted in a constant pitch to the direction of radius.

The normal direction to the surface of lamella and the molecular orientation axis of a lamella are assumed to be the same. At a point inside a spherulite (P :positional vector \mathbf{r}), the crystallinity is set to a constant ϕ_c , the dielectric tensor of the crystal part is set to $\epsilon_{\alpha\beta}^{(cryst)}(\mathbf{r})$, and the dielectric tensor of the amorphous part set to $\epsilon^{(a)}\delta_{\alpha\beta}$, the dielectric tensor at the point \mathbf{r} is given by

$$\epsilon_{\alpha\beta}(\mathbf{r}) = \phi_c \epsilon_{\alpha\beta}^{(cryst)}(\mathbf{r}) + (1 - \phi_c) \epsilon^{(a)} \delta_{\alpha\beta}. \quad (1.11)$$

Suppose that a point \mathbf{r} is in the interior of the spherulite i . The relative unit vector from the position \mathbf{r}_i of

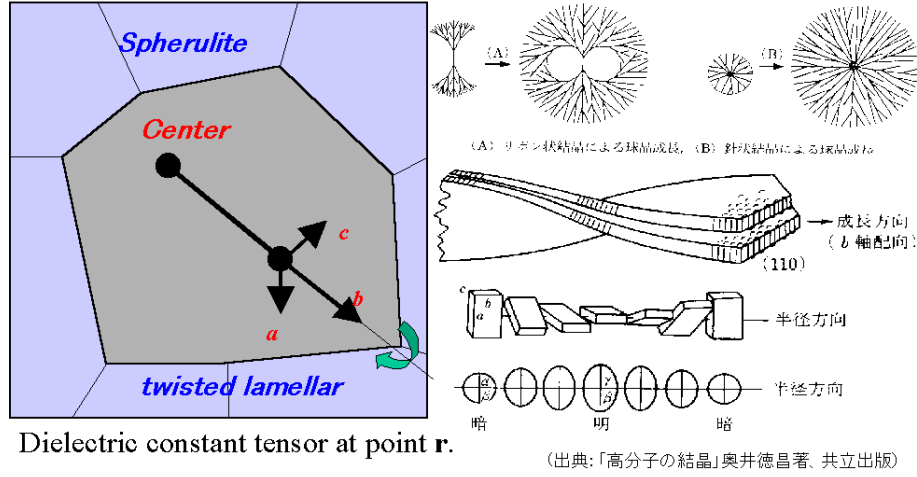


Figure 1.4: The conceptual diagram of the dielectric tensor inside spherulite.

the nucleus of spherulite i to a point \mathbf{r} is give by

$$\mathbf{e}_b = \frac{(\mathbf{r} - \mathbf{r}_i)}{|\mathbf{r} - \mathbf{r}_i|}. \quad (1.12)$$

This direction of \mathbf{e}_b is in agreement with that of the b axis of a crystal. The a axis and the c axis are perpendicular to the b axis. Since the lamella is twisted, the a and c axis are rotating around the direction of b axis. From the above discussion, we can obtain the following expression for the unit vector along a axis at a position \mathbf{r} as

$$\mathbf{e}_a(\mathbf{r}) = \cos\left(\frac{|\mathbf{r} - \mathbf{r}_i|}{L_t}\right) \mathbf{e}_a(\mathbf{0}) - \sin\left(\frac{|\mathbf{r} - \mathbf{r}_i|}{L_t}\right) \mathbf{e}_c(\mathbf{0}) \quad (1.13)$$

where L_t is a constant pitch. The c axis automatically determined by the following equation using the unit vectors for other two axes as

$$\mathbf{e}_c(\mathbf{r}) = \mathbf{e}_a(\mathbf{r}) \times \mathbf{e}_b(\mathbf{r}). \quad (1.14)$$

If we take the directions of crystallographic axes as the bases, the dielectric tensor is expressed as

$$\epsilon_{\alpha\beta} = \begin{bmatrix} n_a^2 & 0 & 0 \\ 0 & n_b^2 & 0 \\ 0 & 0 & n_c^2 \end{bmatrix} \quad (1.15)$$

where (n_a, n_b, n_c) are refractive indices for each axis of polyethylene crystal, the value are (1.514, 1.519, 1.575) or (1.517, 1.520, 1.582). Since directions of the crystallographic axis (base directions of three axis $\{\mathbf{e}_a(\mathbf{r}), \mathbf{e}_b(\mathbf{r}), \mathbf{e}_c(\mathbf{r})\}$) at a point \mathbf{r} is known now, the transformation to the laboratory coordinate system of the base $\{\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z\}$ is given by the following second order tensor, \mathcal{R} :

$$\mathcal{R} = \begin{bmatrix} (\mathbf{e}_x \cdot \mathbf{e}_a(\mathbf{r})) & (\mathbf{e}_y \cdot \mathbf{e}_a(\mathbf{r})) & (\mathbf{e}_z \cdot \mathbf{e}_a(\mathbf{r})) \\ (\mathbf{e}_x \cdot \mathbf{e}_b(\mathbf{r})) & (\mathbf{e}_y \cdot \mathbf{e}_b(\mathbf{r})) & (\mathbf{e}_z \cdot \mathbf{e}_b(\mathbf{r})) \\ (\mathbf{e}_x \cdot \mathbf{e}_c(\mathbf{r})) & (\mathbf{e}_y \cdot \mathbf{e}_c(\mathbf{r})) & (\mathbf{e}_z \cdot \mathbf{e}_c(\mathbf{r})) \end{bmatrix}. \quad (1.16)$$

Using this transformation tensor, the dielectric-tensor field in a laboratory coordinate system will be given as

$$\epsilon_{\alpha\beta}(\mathbf{r}) = R_{\alpha\alpha}(\mathbf{r}) \epsilon_{\alpha\beta}(\mathbf{r}) ({}^t R(\mathbf{r}))_{b\beta}. \quad (1.17)$$

Since the value of the dielectric tensor in each point is known by eq.(1.17), if the Fourier transformation of a dielectric-tensor field is performed by

$$\epsilon_{\alpha\beta}(\mathbf{q}) = \int d^d \mathbf{r} e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \epsilon_{\alpha\beta}(\mathbf{r}), \quad (1.18)$$

we can obtain the fourth order tensor $T_{\alpha\mu\nu\beta} = \langle \epsilon_{\alpha\mu}(\mathbf{q}) \epsilon_{\nu\beta}(-\mathbf{q}) \rangle$. Using value of tensor, the turbidity τ can be found from eq.(1.9).

Chapter 2

Sample Problems of TURBAN

2.1 Application operation of the light-transmittance simulator TURBAN

This chapter shows the application of the light-transmittance simulator TURBAN. The input file and output file for the application are in the directory MUFFIN3/sample/TURBAN of MUFFIN3.

2.1.1 Application: Calculation of the turbidity spectrum of a polyethylene film, and turbidity analysis for a visible ray of light

Set a problem and process

1. We shall carry out light-transmittance prediction of a polyethylene blown film.
2. We perform a simulation in the cubic cell (This corresponds to $(4\mu m)^3$ system) of 128x128x128.
3. We set the wavelength of a visible ray of light to $400 - 700nm$.
4. We assume that the primary nucleation velocity of spherulite is sufficiently faster than the spherulite growth rate (= non-uniform nucleation).
5. We use the well experimentally known values for physical-properties of polyethylene film.

A generation of an input file

The filename of sample input for TURBAN is MUFFIN3/sample/TURBAN/sample.inp. This can be edited as a simple text file. All you can change in the input file are the left end number in rows. The number and explanation of a sample input file are shown in the following table.

Numeric values	Variable names	Meanings
128	<i>xaxis</i>	The number of mesh of one side. (The total number of mesh is the 3rd power of this value.)
1.514	<i>na</i>	The refractive index of crystal a-axis direction
1.519	<i>nb</i>	The refractive index of crystal b-axis direction
1.575	<i>nc</i>	The refractive index of crystal c-axis direction
1.510	<i>n_amorphous</i>	The refractive index of the amorphous section
1.0	<i>nejireshuki</i>	The lamella torsion period in spherulite (μm)
300	<i>nucle_num</i>	The nuclear number in a simulation box (numbers)
500.0	<i>max_time</i>	The maximum step number of spherulite growth simulators (times)
1.0	<i>dt</i>	Time of 1step (<i>sec</i>)
0.03	<i>dr</i>	Line growth rate of spherulite ($\mu m/sec$)
0.3	<i>crystallinity</i>	Crystallinity (0.0 – 1.0)
4.0	<i>cell_length</i>	The length of one side of simulation boxes (μm)

Run of a simulation

The following commands are executed from the command prompt of UNIX (True64, Cygwin, and Linux). The pass to the directory with an execution file (turban) must be set into the environment variable "PATH". The arguments are a input file name, a name of a spherulite growth simulation result file, a turbidity spectrum calculation result file name, turbidity integration result file name for a visible ray of light and a log file name after a redirect symbol as shown in the following line:

```
% turban sample.inp out1.txt out2.txt out3.txt>sample.log&
```

An ellipsis of a file name is not permitted. All file names can be changed.

Analysis of results

The explanation of the file outputted by TURBAN is described below. The obtained data are divided by blanks.

- Output file 1 (spherulite growth simulation result) : the output file where the information obtained by a spherulite growth simulation is written. The index of the spherulites to which a certain point (x, y, z) belongs is given as

1'st row	2'nd row	3'rd row	4'th row
x coordinate	y coordinate	z coordinate	spherulite index

- Output file 2 (turbidity spectrum calculation result) : it is an output file where a result of the turbidity calculation for each incident-light wavelength using the result of a spherulite growth simulator is written.

1'st row	2'nd row
Incident-light wavelength (μm)	Turbidity (μm^{-1})

- Output file 3 (turbidity integration result for a visible ray of light) : the calculation result of the integration in the visible ray of light area (wavelength of $400 - 700nm$) using the turbidity spectrum acquired above in the output file 2. This is the turbidity of a visible ray of light with wavelength $400 - 700nm$.

1'st row	2'nd row
Number	Total Turbidity
The number of spherulite (number)	The turbidity integration value for a visible ray of light (μm^{-1})

The turbidity spectrum calculation result by sample

We show a result of calculation of the turbidity spectrum using a sample file in Figure 2.1. The peak of turbidity is seen from Figure 2.1 around the wavelength equivalent to the average size (about $0.8\mu m$) of the spherulites. For example, we can obtain the relation between the spherulite size and the turbidity integration value for a visible ray of light by changing the average size of the spherulites, i.e., the number of the nucleus in a simulation box.

Next, we show the result calculated by changing the number (i.e., the average spherulite diameter) of the nucleus in a simulation box for the conditions mentioned above. In Figure 2.2, the peak of turbidity is seen near the wavelength of the incident light which is in agreement with each average spherulite diameter. In Figure 2.3, we plot the result of the integration in the visible ray of light area (wavelength $400 - 700nm$) using the calculated turbidity spectra for each average spherulite diameters. It turns out that the peak of a turbidity integration value is in the range of a visible light region. Therefore the turbidity increases around the average diameter of spherulite which corresponds with the wavelength of a visible ray of light. These calculations are in good agreement with experimental results.

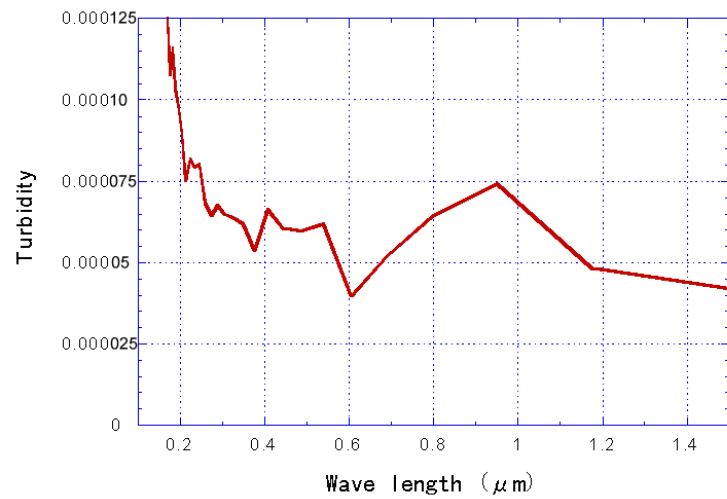


Figure 2.1: The turbidity spectrum calculation result by sample.inp (out2.txt).

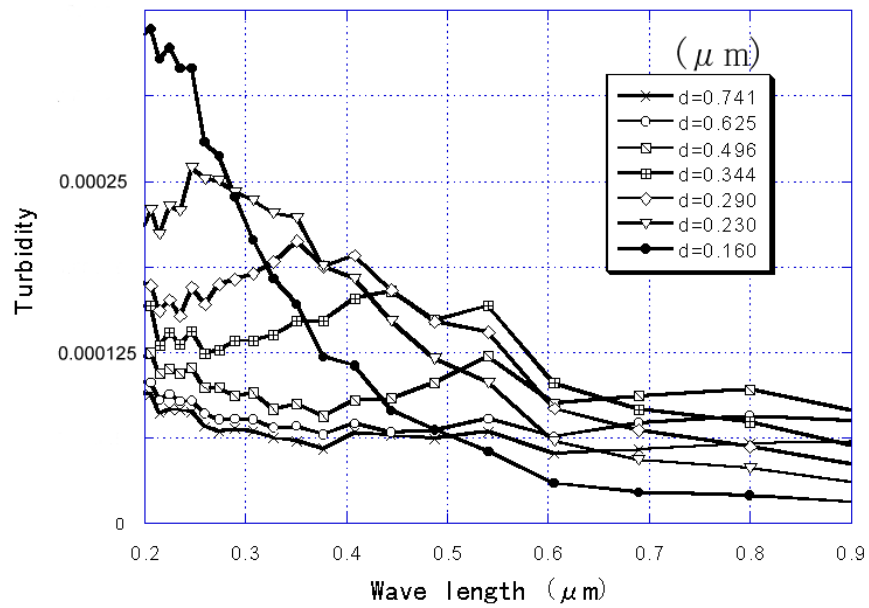


Figure 2.2: The turbidity spectra for system with the various average spherulite diameters.

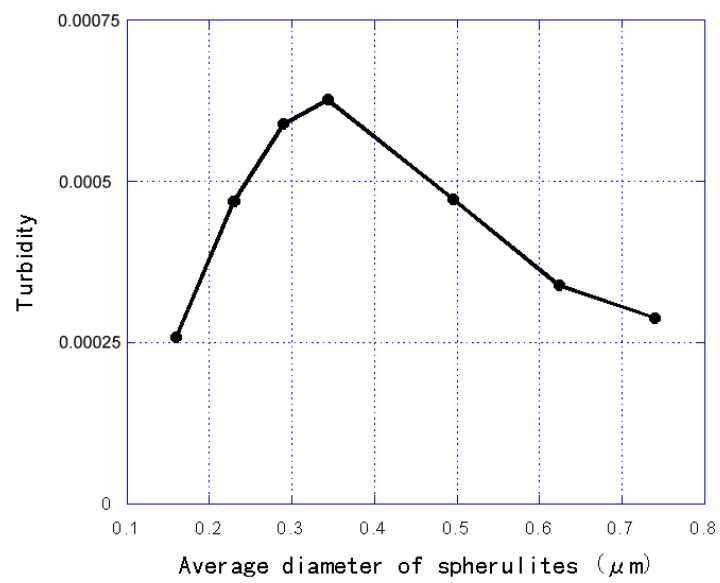


Figure 2.3: The turbidity integration value for the visible ray of light in each spherulite diameter.

Chapter 3

Operation Guide of TURBAN

3.1 Input parameters of TURBAN

Line number	Variable names	Meanings and guide
1	<i>xaxis</i>	The number of mesh of one side. (The total number of mesh is the 3rd power of this value.) You must set to 2^n . We recommend to set 128.
2	<i>na</i>	The refractive index of crystal a-axis direction. (Polyethylene is 1.514.)
3	<i>nb</i>	The refractive index of crystal b-axis direction. (Polyethylene is 1.519.)
4	<i>nc</i>	The refractive index of crystal c-axis direction. (Polyethylene is 1.575.)
5	<i>n_amorphous</i>	The refractive index of the amorphous section. (Polyethylene is about 1.510.)
6	<i>nejireshuki</i>	The lamella torsion period in spherulite (μm). (Polyethylene is about $1 - 4\mu m$. not important matter.)
7	<i>nucle_num</i>	The nuclear number in a simulation box (numbers). The range is about $10^2 - 10^4$ order.
8	<i>max_time</i>	The maximum step number of spherulite growth simulators (times). Any large number (for example 500).
9	<i>dt</i>	Time of 1step (<i>sec</i>). For example 1.
10	<i>dr</i>	Line growth rate of spherulite ($\mu m/sec$). For example 0.03.
11	<i>crystallinity</i>	Crystallinity (0.0 – 1.0). Polyethylene is about 0.3.
12	<i>cell_length</i>	The length of one side of simulation box (μm). You must set to two times and over of the wavelength of visible light.

3.2 Appendix

An average spherulite diameter

d ; An average spherulite diameter, L ; The length of one side of the simulation box, n ; The nuclear number in the simulation box,

$$d = 2 \times \left\{ \frac{3}{4\pi} \cdot \frac{L^3}{n} \right\}^{\frac{1}{3}} \quad (3.1)$$