Orthogonal polynomial fitting method applied to contact angle data variations

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Abstract. We discuss our method of constructing orthogonal polynomials (orthonormal polynomial expansion method - OPEM) for fitting experimental data. The method is in use to approximate a set of data when both the dependent and independent variables are measured with errors. We review its main principles and analyze the orthonormal and "usual" coefficients in the expansions of the approximating function. The method is applied to the variations of the wetting angle of a water drop in the process of its evaporation in the air. The wetting properties of liquids are at present of high interest for research, due to applications and still unsolved topics in the theory of wetting.

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INTRODUCTION

In the paper a new application of our orthonormal polynomial expansion method-OPEM[1] to wetting angle variations of a water drop is proposed. Our method is a generalization of Forsythe [2] three-term recurrence equation for constructing orthonormal polynomials. Some special characteristics of the approximations and two types of coefficients in the expansions for approximating curves are demonstrated for this purpose.

Here we discuss the kinetics of the contact angle [3] of water drop of deionized water placed on a non wetting substrate (hostaphan).

PHYSICAL DATA

In the course of evaporation of the drop, as the drop's contact angle changes, we measure the frequency of appearance of such angles within prescribed angle intervals. One can say that in this way the "state spectrum" with respect to the contact (wetting) angle is obtained of the corresponding thermodynamically open system. For this purpose one measures at regular time intervals (here every 5 minutes) the values for several drops (to enable drawing statistical conclusions). One determines the variations of contact angle by microscope observations using the optical method of Antonov [4].

One measures the width a of a light refraction pattern in the form of a dark ring produced around the drop (Figure 1) by light beams 1 passing near the boundary of the drop 2 which is situated on the non wetting folio 3 and kept at a constant room temperature. The folio is situated on a glass plate 4 having a refraction index n and thickness d. The width a is measured by microscope observations. The laws of geometric

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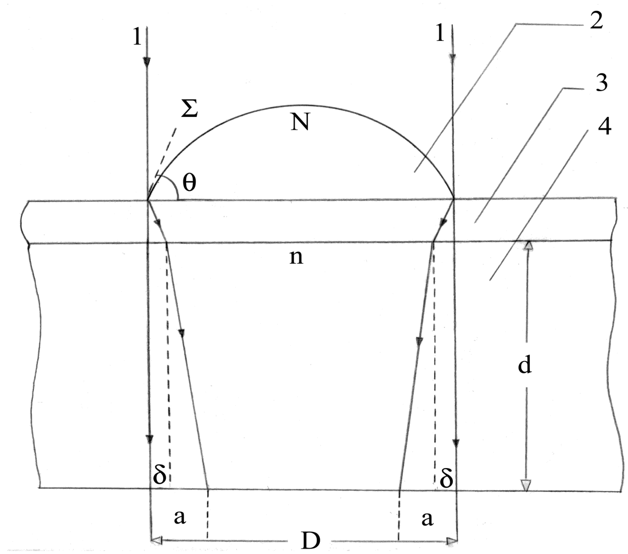

FIGURE 1. Experimental setup of contact angle wetting

optics give tan of θ as a function of a by the formula

$$\tan\theta = n/[(N^2\Delta - n^2])^{12} - \Delta]^{1/2}; \delta = 1 + d^2(a-\delta)^2, \tag{1}$$

where N is the water refraction index and the δ dimension denoted on Figure 1 is usually neglected in the above formula since $\delta << a$. In this way one obtains a set of discrete values $\{f_i\}$- the frequencies of occurrence of $\{\theta_i\}$. On the graphs-(Figure 2) we give f versus θ with the corresponding errors on both variables. On the Figure 2 two curves of deionized water are given. The first curve (with squares) corresponds to the treated by γ-rays water sample . The second one (with circles) corresponds to the non treated water sample. The source of γ rays is Co-60 (65 krad/h). The period of treatment is 2 minutes.

MATHEMATICAL APPROACH

Here one defines the total variance at $i-th$ point (θ_i, f_i) in the form

$$S_i^2 = {\sigma_{f_i}}^2 + (\frac{\partial f_i}{\partial\theta_i})^2 {\sigma_{\theta_i}}^2, \tag{2}$$

where σ_{f_i} and σ_{θ_i} are the errors in both variables, $i = 1, 2, \ldots M$ and M is the number of measured pairs $\{\theta_i, f_i\}$. In the formula (2) the Bevington's [5] proposal to combine both variable uncertainties and assign them to dependent variable is used.

The generalized OPEM

We develop some points of our algorithm [6]. The principal relation for one-dimensional generation of orthonormal polynomials $\{P_i^{(0)}, i = 1, 2, \ldots\}$ and their derivatives

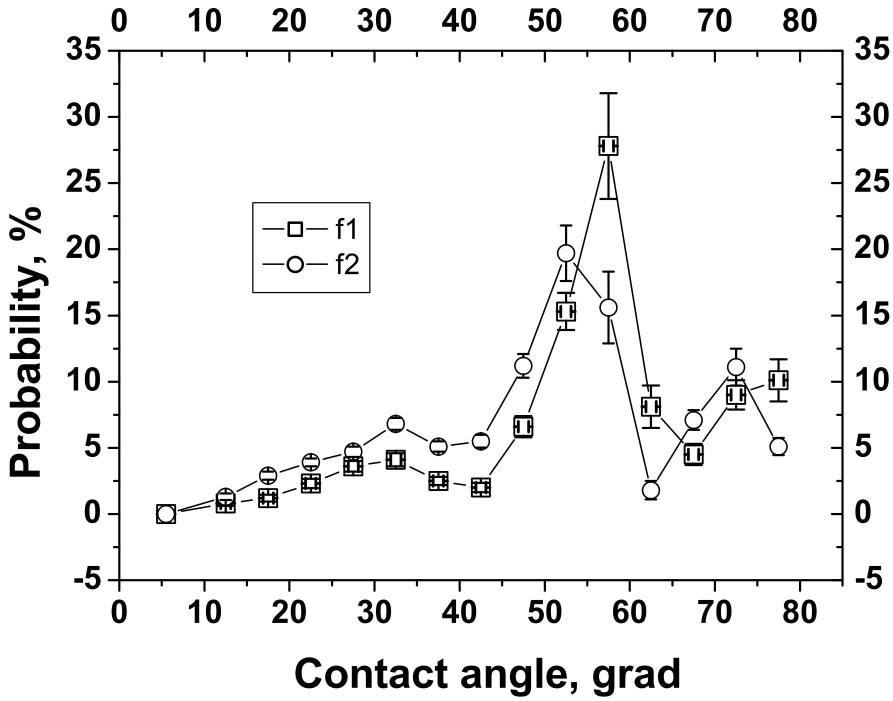

FIGURE 2. Measured probability of contact angle - deionized treated (squares) $f1$ and non treated (circles) $f2$ water data

$\{P_i^{(m)}, m = 1, 2, \dots\}$, in OPEM is:

$$P_{i+1}^{(m)}(\theta) = \gamma_{i+1}[(\theta - \mu_{i+1})P_i^{(m)}(\theta) - (1 - \delta_{i0})\nu_i P_{i-1}^{(m)}(\theta) + mP_i^{(m-1)}(\theta)]. \qquad (3)$$

Here the normalization coefficient γ_i and the recurrence coefficients μ_i, ν_i are given as scalar products of the polynomials in the given data. One can generate $P_i^{(m)}(\theta)$ recursively. The polynomials satisfy the following orthogonality relations

$$\sum_{i=1}^{M} w_i P_k^{(0)}(\theta_i) P_l^{(0)}(\theta_i) = \delta_{kl}$$

over the discrete point set $\{\theta_i, i = 1, 2, \dots\}$, where $w_i = 1/(\sigma_{f_i}^2)$ are the corresponding weights. The approximation function f^{appr} and its m-th derivative $f^{(m)appr}$ are constructed as follows:

$$f^{(m)appr}(\theta) = \sum_{k=0}^{L} a_k P_k^{(m)}(\theta) = \sum_{k=0}^{L} c_k \theta^k. \qquad (4)$$

The coefficient matrix in the least square method becomes an identity matrix and due to orthogonality conditions a_k are easily computed by

$$a_k = \sum_{i=1}^{M} f_i w_i P_k^{(m)}(\theta_i). \qquad (5)$$

The knowledge of a_k enables to calculate c_k by the help of the coefficients μ_i, ν_i from formula (3). We remark that all the calculations for the sake of uniformity are carried out for θ in [-1,1] , i.e. after the input data θ_i in the interval $[\theta_1, \theta_M]$,$\theta_1 \leq \theta_i \leq \theta_M$ are transformed to the unit interval $[-1,1]$. The inherited errors in usual coefficients are given by the inherited errors in orthogonal coefficients (see equation (6) in [7] for details).

It is worth noting the following advantages of OPEM: a) It avoids recomputing the polynomial coefficients of the current highest degree polynomial using unchanged the coefficients of the lower-order polynomials b) it avoids the procedure of inversion of the coefficient matrix to obtain the solution and this shortens the computing time. For appropriate classes of examples this diminishes the number of iterations required to reach a prescribed numerical precision. Two criteria are used here to select the optimum series length in equation (4).

First criterion

(i) Here one neglects the errors in θ variable, the graph of the fitting curve lies inside the "usual" error corridor $[f-\sigma, f+\sigma]$.

(ii) After calculating the derivatives at any point θ_i using equations (3) and (4) the fitting curve has to lie inside the total error corridor $[f-S, f+S]$.

Second criterion

We extend the above algorithm to include S_i^2 in OPEM in two stages:

(i). i.e. the following χ^2 is minimized

$$\chi^2 = \sum_{i=1}^{M} w_i [f^{appr}(\theta_i) - f(\theta_i)]^2/(M-L-1),$$

where the weights are $w_i = 1/\sigma_{f_i}^2$.

(ii): The next approximation is calculated with the weight function $w_i = 1/S_i^2$.

The results of calculations in (i) gives the first approximation. The procedure is iterative and the result of the consequent k-th iteration, $k > 1$, is called below the **k-th approximation**. The preference is given to the first criterion and when it is satisfied, the search for the minimal chi-squared stops. Based on the above features the algorithm selects the optimal solution for a given set $\{\theta, f\}$.

APPROXIMATION DETAILS AND RESULTS

Treated water data

1. The approximation of 15 given point data of treated water with errors in both variables was carried out with different degrees of polynomials. The optimal degree

TABLE 1. OPEM approximation of contact water drop angle - experimental and approximating values

No.	θ	f	σ_θ	σ_f	$f_{a_k}^{appr,9}$	$f_{c_k}^{appr,9}$	$f_{a_k}^{appr,13}$
1	7.5	0.1	0.6	0.001	0.01165	0.01381	0.1046
2	12.5	0.8	0.6	0.200	0.79651	0.78957	0.8137
3	17.5	1.2	0.6	0.250	1.21521	1.23927	1.1931
4	22.5	2.3	0.6	0.350	2.16775	2.08592	2.3082
5	27.5	3.6	0.6	0.400	3.80385	3.86199	3.5592
6	32.5	4.1	0.6	0.500	3.97455	4.04787	4.1987
7	37.5	2.5	0.6	0.300	2.42583	2.34459	2.4305
8	42.5	2.0	0.6	0.300	2.19333	2.16459	2.0902
9	47.5	6.6	0.6	0.800	6.01824	6.79850	5.8362
10	52.5	15.3	0.6	1.400	15.71836	14.51524	16.9840
11	57.5	27.8	0.6	4.000	19.41744	18.08124	24.8242
12	62.5	8.1	0.6	1.600	12.15988	12.22944	8.7655
13	67.5	4.5	0.6	0.800	2.92818	3.92818	4.3741
14	72.5	9.0	0.6	1.100	9.91328	9.81663	9.1634
15	77.5	10.1	0.6	1.600	9.23731	9.23587	9.1049

was chosen between 1 to 12 to be 9 with $\chi^2 = 1.42$ at $k = 3$-rd approximation (if k=1 then $\chi^2 = 1.59$, if $k = 2$ then $\chi^2 = 1.43$). The given points on new Figure 3 are chosen in legend as $f1$ (open squares). The approximating curve with orthogonal polynomials is denoted as E (full squares). The approximating curve with usual coefficients is not distinguishable from E on the Figure 3.

Note 1. It is important to notice, that the evaluated of our algorithm point numbers 11 and 12 are out of the given "usual" and total corridors of dependent variables. For the 11-th point in orthonormal expansion the σ_f is 4., $S = 4$. (the first derivative is zero) and the calculated function is $f^{appr} = 19.41$. For the 12-th point the σ_f is 1.6, $S = 1.94$ and calculated function is $f^{appr} = 12.15$ (see Table 1). The preference is given to second criterion- minimum of χ^2.

2. A different approximation is carried out with $L = 13$-th degree, chosen by the algorithm between 2 to 14 with $\chi^2 = 0.94$ at $k = 3$-rd approximation (if $k = 1$ then $\chi^2 = 1.20$, if $k = 2$ then $\chi^2 = 0.95$). The approximating curve F is given by rhombuses.

We present in the next Table 1 the comparative values of the given experimental data $\{f_i, \theta_i\}$ (with their errors σ_{f_i} and σ_{θ_i}) and three approximating curves at $L = 9$-th degree in orthogonal $f_a^{appr,9}$ and usual $f_c^{appr,9}$ expansions and the approximating curve $f_a^{appr,13}$ in orthogonal expansion at $L = 13$-th degree. The curves, constructed by 9-th degrees are very close till 3-rd numbers after decimal point, but the last one by 13-th degree is more close to the given points.

CONCLUSION

The approximation results with OPEM for contact angle variation show a good accuracy for obtained optimal polynomials with 3-rd iteration step by the orthogonal and usual coefficients.

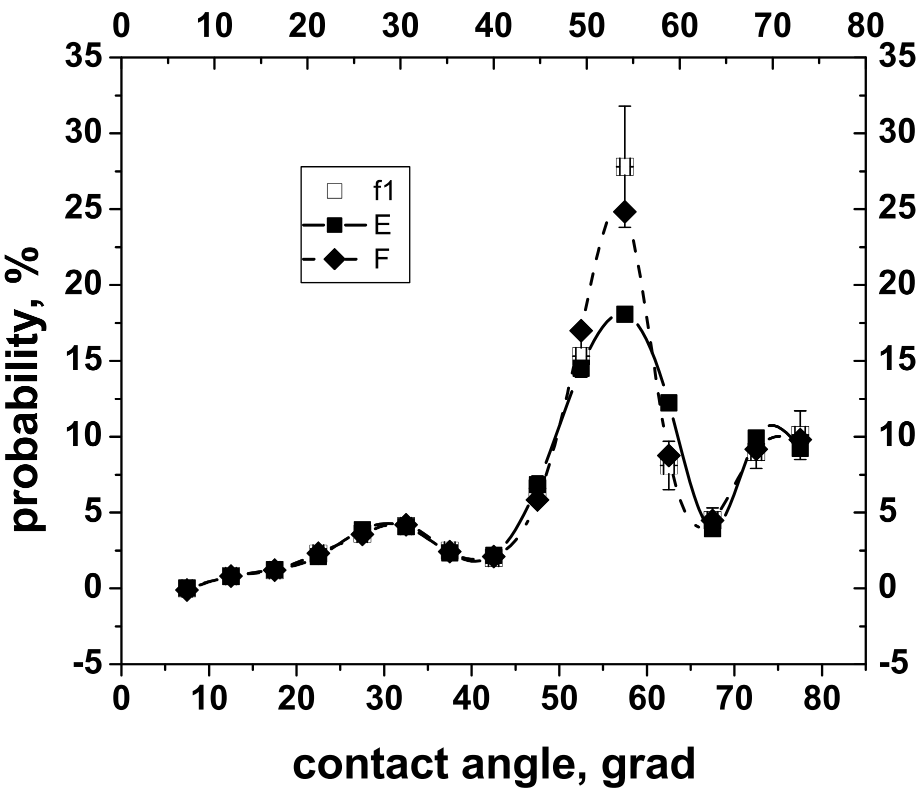

FIGURE 3. OPEM approximation by 9-th degree E (full squares) and 13-th degree F (rhombuses) polynomials of measured contact angle probability of treated water $f1$ (open squares).

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