Statistical characteristics of coefficients of a cubic approximation of isotherms of surface active substance films

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Abstract. We explore possibilities for polynomial approximation of the isotherms (the dependence of the pressure, exerted by the film, on the concentration of the substance per unit area) of films of surface active substances in marine environment. The analysis is based on isotherms for samples from the nearshore of the Black Sea and the coasts of the USA. The isotherms are approximated using cubic polynomials. The constant term and the coefficients of this polynomial have a reasonable scatter: their average values are comparable with their standard deviation. The standard deviations of the coefficients at the quadratic and the cubic term exceed the relevant average values by two orders of magnitude. This property signals that it is evidently not possible to approximate the isotherms of surface active films using one universal polynomial function even for one location and that it is necessary to account for the described scatter in estimates of the properties and impact of surface films. We provide cumulative distributions of the coefficients of the cubic approximation for the use in probabilistic express models of properties of surface films in the marine environment.

Key words: surface active substances, surface film, surface tension, film pressure, elastic modulus, isotherms.

1. INTRODUCTION

Films of various surface-active substances often play a crucial role in the formation and interpretation of the signal emitted or reflected from the ocean surface and detected in the remote sensing of lakes, seas, and oceans. While in some occasions such films may considerably damp the useful signal (Gade et al., 1998), on other occasions their occurrence highlights the presence of various otherwise non-observable phenomena for remote sensing devices (Bakhanov et al., 1989; Ermakov et al., 1999; Ermakov, 2010). The common property of such films is that they substantially increase the damping rate of short (capillary and gravity-capillary) surface waves (wind ripples) and considerably smooth the appearance of the water surface, especially in areas where the film is relatively thick (Garrett, 1967;

Ermakov et al., 1980, 1982; Ermakov and Pelinovsky, 1984; Ermakov, 2010).

Changes in the concentration of surface-active substances and associated films are significantly modified by the field of local surface currents, created by various sources (Bulgakov et al., 1988; Kozlov et al., 1987, 1991; Kozlov and Talipova, 1991). As a result, variations in the concentration of such substances or in the thickness of the films in question (normally created by convergence and divergence of flows caused by certain large-scale phenomena) are often clearly distinguishable from space. This effect makes it possible to remotely detect meso- and submesoscale features such as fronts, (synoptic) eddies, trapped edge waves (Averbukh et al., 2014) or internal waves (Ermakov, 2010). As the interpretation of the remote sensing data crucially depends on the adequacy of the understanding of the effects created by surface films, the analysis of the physics and appearance of such effects has been in the

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focus of researchers for decades (Dorrestein, 1951; Jarvis et al., 1967; Barger et al., 1974; Ermakov et al., 1986; Frew and Nelson, 1992) and continues to be an important topic today (Ermakov, 2010). Moreover, such films, both anthropogenic and natural (e.g. created via algal blooms) may greatly modify the fluxes of energy and mass at the sea surface and in this way contribute to the effects of climate change and impact the entire status of the ecosystem.

Theoretical and numerical analysis of the process of damping of surface waves by films of surface active substances (Lamb, 1932; Levich, 1959; Ermakov et al., 1980; Ermakov, 2010) has shown that the key parameter governing the rate of damping of ripples is the elasticity of the film. This parameter is often characterized in terms of surface pressure–area $(\pi - A)$ isotherms (Frew and Nelson, 1992), equivalently, in terms of the dependence of the surface tension on the concentration of the surface active substances or the local thickness of the film. Research towards quantification of various properties of natural surface films had already started in the 1960s (Jarvis et al., 1967). The results reflect, among other features, the dependence of the elasticity of the film on the chemical properties of the film (Barger et al., 1974), concentration of organic substances in the subsurface microlayer (Frew and Nelson, 1992), and on the wind speed (Hühnerfuss et al., 1977), as well as hysteresis phenomena (Ermakov and Talipova, 1985), elasticity (Demin et al., 1985), stress-relaxation analysis (Pogorzelski and Kogut, 2001), the analysis of the decay of ripples owing to the presence of various films (Ermakov et al., 1986), and methods of evaluation of ripple wave parameters (Fernandez et al., 1992). Similar efforts for the Baltic Sea include construction of a specific device for 'cutting out' a section, an undisturbed portion of sea surface layer (Pogorzelski, 1992), and performing isotherm analyses without the microlayer material being transferred or chemically processed (Pogorzelski and Kogut, 2001).

We focus on the possibilities of express estimates of the basic properties of surface films using the governing parameters of the films. We rely on the reanalysis of the collection of data, originally presented by Demin et al. (1985), Ermakov and Talipova (1985), and Ermakov et al. (1986) in the co-authorship of T. Talipova. Also, we partially use the classical data sets published by Jarvis et al. (1967) and Barger et al. (1974). This data set covers examples of isotherms of films, evaluated in greatly different conditions in the nearshore of Crimea, the Black Sea, in San Diego Bay, California, and in the nearshore of the eastern (Atlantic) coast of the USA, and therefore is likely to be representative of films in the nearshore areas of various seas and oceans. Data sets from the coastal waters of the Baltic Sea (Pogorzelski et al., 1994; Pogorzelski, 2001; Pogorzelski and Kogut, 2001) and from the Mediterranean (Pogorzelski et al.,

1994) reveal a qualitatively similar appearance of the isotherms. The collection used in this study has been recently re-used for the evaluation of statistical properties of elasticity of surface active substances under various deformations (Talipova et al., 2013a) and statistical properties of contrasts and gradients of the intensity of ripples in slicks associated with films (Talipova et al., 2013b). Although some properties of films, measured in laboratory conditions, may differ from those established directly at the sea surface (Pogorzelski, 1992), the qualitative appearance of the isotherms is largely invariant.

Although parts of the isotherms are approximately linear or can be approximated by a quadratic function (Barger and Means, 1985), in the general case isotherms often contain an inflection point and both concave and convex sections (Pogorzelski and Kogut, 2001) and therefore require more elaborated treatment. In this paper we aim at the construction and validation of a higher order polynomial (cubic) approximation of the dependence of the properties of such films on their governing parameters. The focus is on the statistical distributions of the coefficients of such an approximation. The goal is to provide a first-order express method for the evaluation of the pressure in the film and its elastic modulus under the impact of large-scale fields of surface motions.

2. MEASUREMENTS OF ISOTHERMS OF MARINE SURFACE FILMS

An isotherm of a marine surface film is defined as the dependence of the pressure π exerted by the film on the concentration Γ of the relevant substance per unit area (for simplicity called concentration of the film in the following) or the area of the film $A \sim 1/\Gamma$ for a finite amount of surface active substance. The pressure of a film is understood here as the difference between the surface tension $\sigma_0(S,T)$ of pure water and this tension $\sigma(S,T)$ for the water covered by the film. Both these variables depend on the local salinity S and temperature T. An isotherm expresses this dependence

$$\pi(\Gamma) = \sigma_0 - \sigma(\Gamma) \qquad (1)$$

for constant temperature and salinity.

The properties of isotherms are usually measured using a Wilhelmy plate or a Langmuir balance (also called Langmuir trough). In the latter system the surface pressure is measured directly as the force exerted on a moveable barrier separating film-covered water from pure water (Chechel and Nikolaev, 1991). The properties of films in samples, taken from the Black Sea, were measured using a rectangular container (often called ditch) with a height of 10 cm and area of 320 cm^2.

The ditch was separated into two sections by a barrier and initially filled with the sample water, in which the concentration Γ_0 of the film is to be measured. This concentration generally deviates by less than 10% from the initial concentration on the sea surface (Demin et al., 1985). The idea is to vary the water surface area in one of the sections and to measure the force exerted to the barrier by the film. The concentration Γ_0 in the other section does not change. Doing so makes it possible to measure the variation of the pressure $\Delta\pi(\Gamma)$ with respect to its initial value $\pi(\Gamma_0)$:

$$\Delta\pi(\Gamma) = \pi(\Gamma_0) - \pi(\Gamma). \qquad (2)$$

Here Γ is the concentration of the film in the variable-area section that is obtained from the ratio of the original and deformed surface areas. This method is not able to evaluate the original value of pressure $\pi(\Gamma_0)$ and only gives its rate of change $\Delta\pi(\Gamma)$, which is the crucial variable in the following discussion. Combining its values with the elastic modulus of the film at a characteristic (state) point, it is possible to evaluate, for example, the damping rate of wave ripples caused by the film (Talipova et al., 2013b).

A selection of isotherms of films on the surface of water samples is presented in Fig. 1. This collection reflects properties of 17 samples of films from the nearshore of the Black Sea taken in September–October 1981 (Fig. 1a), the eight most characteristic isotherms out of a total of 28 samples, taken in June–July 1982 in the same area (Fig. 1b), and ten characteristic isotherms out of 104 samples, taken in May–June 1983 (Fig. 1c).

The overall appearance of the isotherms presented in Fig. 1 generally matches the appearance of the isotherms in other regions of the world ocean. For example, Fig. 2 provides a selection of isotherms from classical studies measured for samples taken in the nearshore of the USA (Jarvis et al., 1967) and in the San Diego Bay, California (Barger et al., 1974). Differently from the procedure used for the analysis of samples from the Black Sea, in these experiments the ditch of a Langmuir balance was filled with distilled water and the samples of films from the marine environment were placed on the surface of this water in one section of the balance. This means that the results of measurements reflect the total pressure $\pi(\Gamma)$ by the film. This difference, however, does not change the appearance of the isotherm and only leads to its shift along the vertical coordinate in Figs 1 and 2. A description of the shape of isotherms for samples from the coastal waters of the Baltic Sea is presented by Pogorzelski and Kogut (2001).
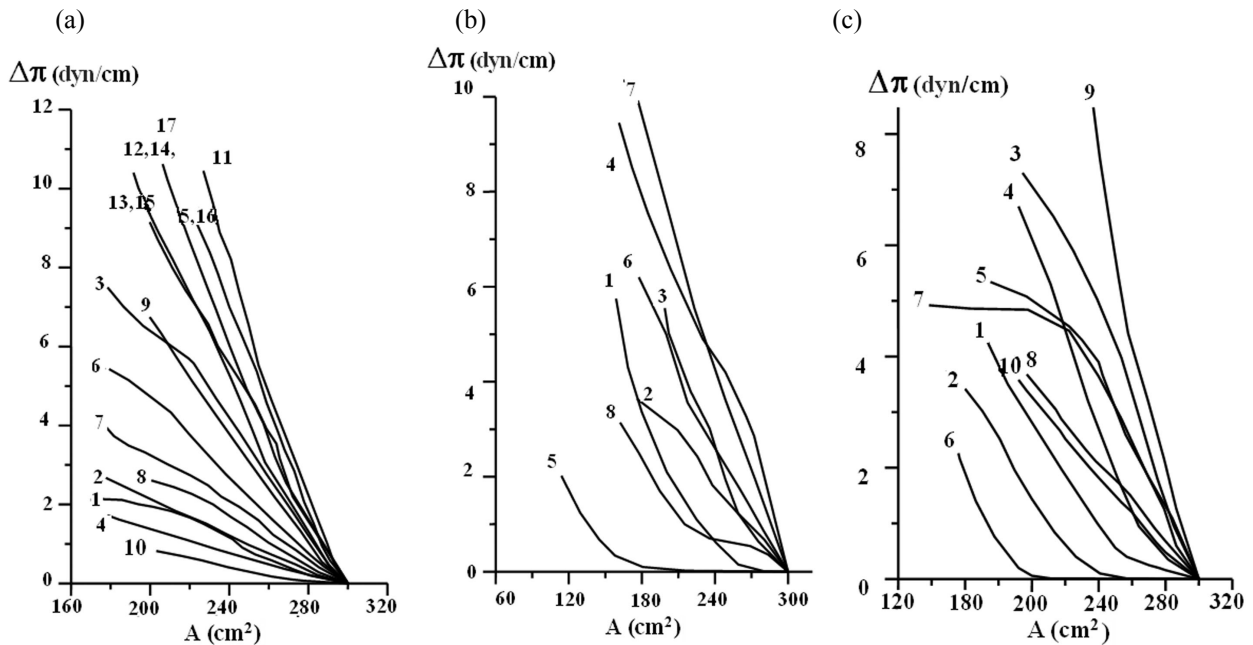
Fig. 1. Isotherms of films from samples taken from the Black Sea: (a) Sept–Oct 1981, (b) June–July 1982, (c) May–June 1983 (Ermakov and Talipova, 1985; Ermakov et al., 1986).
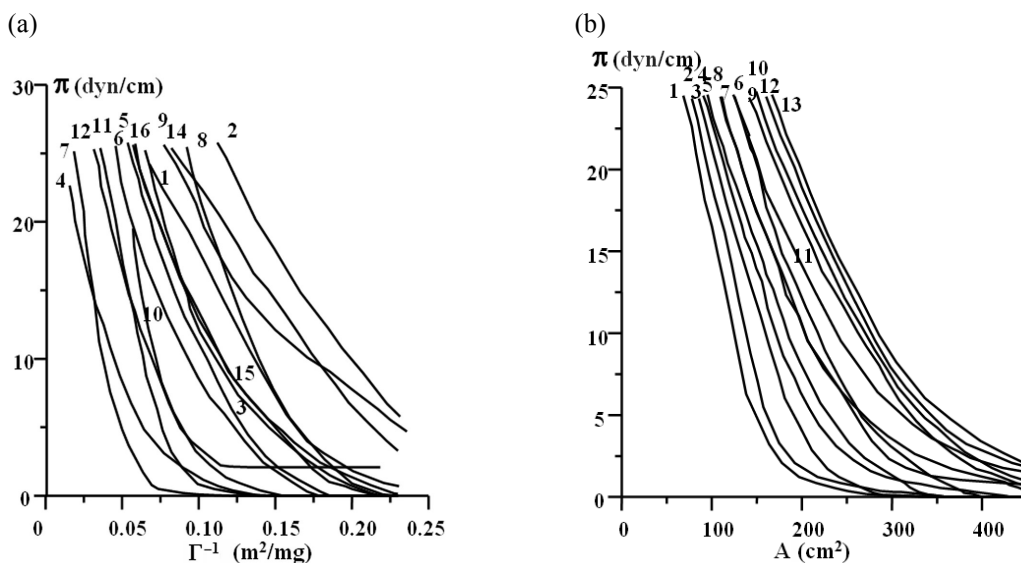
Fig. 2. Isotherms of films from samples taken from: (a) the Atlantic Ocean (Jarvis et al., 1967), (b) in the San Diego Bay, California (Barger et al., 1974).

3. CUBIC APPROXIMATION OF ISOTHERMS

The shape of an isotherm (the dependence of the pressure of film on its surface area) is a common input in calculations of the elastic modulus of surface active substances. There have been several attempts towards approximation of this shape using simple (e.g. quadratic) functions (Barger and Means, 1985; Pogorzelski and Kogut, 2001). The material in Figs 1 and 2 vividly demonstrates that the isotherms often contain an inflection point and both concave and convex sections. This complexity has led to efforts towards approximation of the isotherms using higher-order polynomials. For example, Fernandez et al. (1992) developed a cubic approximation of isotherms and calculated the average optimum values of the relevant coefficients.

The approach, employed by Fernandez et al. (1992), is not particularly convenient for the use in marine conditions and/or under the impact of wave fields because of uncertainties in the definition of the surface area, covered by a film. A proper quantity to substitute for the film area in field conditions is the rate of relative deformation of the surface active substance film. It is straightforward to derive a balance equation for this quantity under the impact of currents and waves. The relative deformation e depends on the surface area A as follows:

$$e = \frac{A_0 - A}{A_0}, \quad (3)$$

where A_0 is the initial area covered by the film. As the concentration of the film $\Gamma \sim 1/A$ is inversely proportional to its surface area, Eq. (3) means that

$$e = \frac{\Gamma - \Gamma_0}{\Gamma}. \quad (4)$$

The elastic modulus of a film is defined as

$$P = \Gamma \frac{d\pi}{d\Gamma} = \Gamma \frac{d\Delta\pi}{d\Gamma}. \quad (5)$$

By definition, the theoretical or measured shapes of the isotherms provide us with the values of $\Delta\pi(e)$ and $\pi(e)$ at each point of the isotherms; consequently,

$$P = (1-e)\frac{d\pi}{de} = (1-e)\frac{d\Delta\pi}{de}. \quad (6)$$

The measured isotherms in Figs 1 and 2, presented as the dependences $\Delta\pi(\Gamma)$ or $\Delta\pi(A)$, can be recalculated into functions $\Delta\pi(e)$ or $\pi(e)$ (Figs 3 and 4) in a straightforward manner.

Following Fernandez et al. (1992) we approximate each empirical isotherm, presented in terms of the elastic modulus $\pi(e)$ (or its variations $\Delta\pi(e)$), using a cubic polynomial:

$$\Delta\pi(e) = C_{00} + \sum_{n=1}^{3} C_n e^n,$$
$$\pi(e) = C_{01} + \sum_{n=1}^{3} C_n e^n. \quad (7)$$

The coefficients in Eq. (7) were calculated using the least squares method. It is obvious that the representations of isotherms in terms of $\Delta\pi(e)$ and $\pi(e)$ only differ by the value of the constant additive C_{00} or

(a) (b) (c)
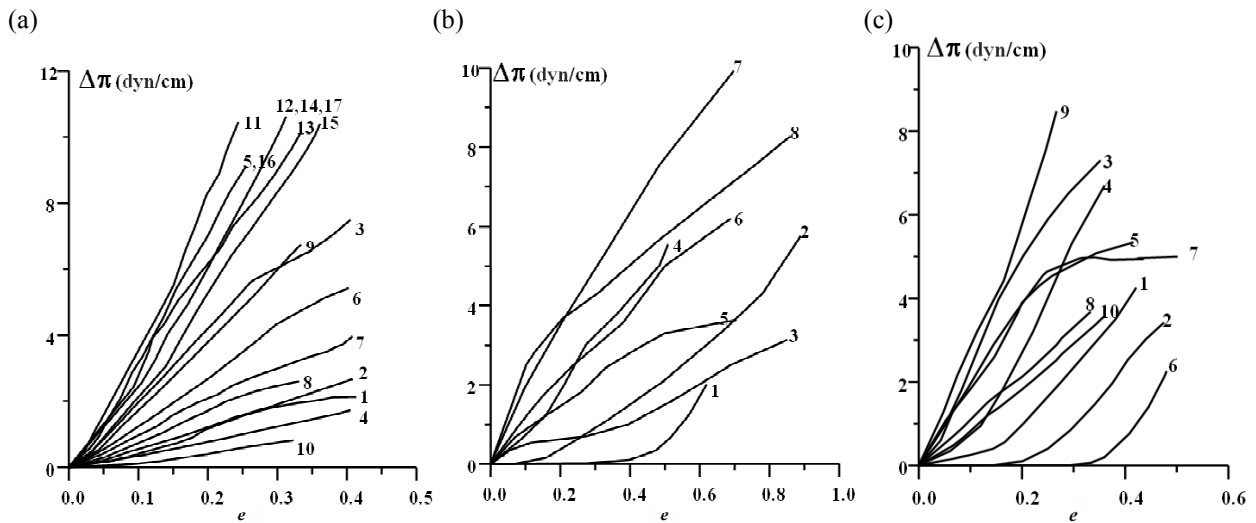
Fig. 3. Recalculated isotherms of films in terms of $\pi(e)$ from samples taken from the Black Sea: (a) Sept–Oct 1981, (b) June–July 1982, (c) May–June 1983 (Ermakov and Talipova, 1985; Ermakov et al., 1986).

(a) (b)
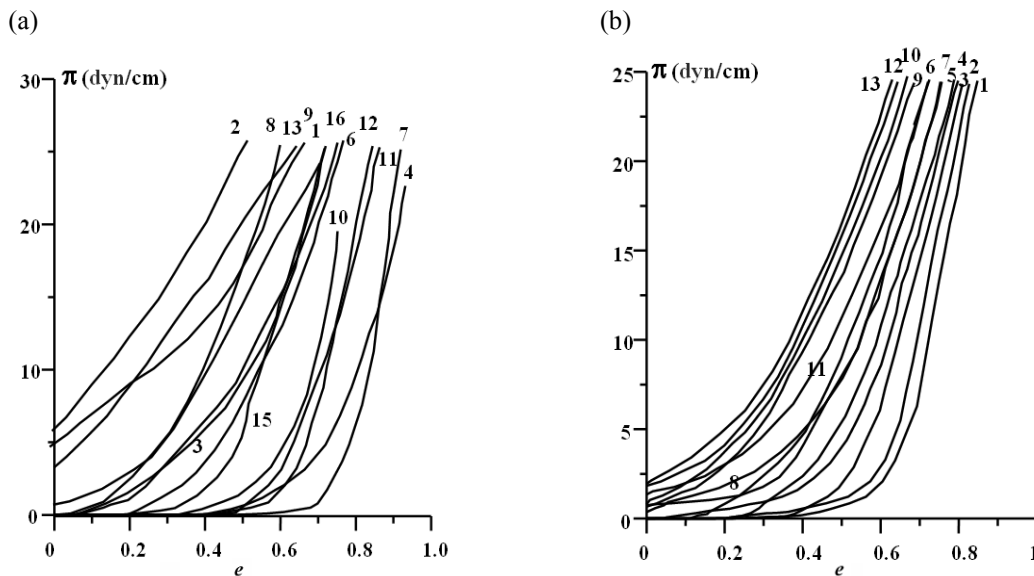
Fig. 4. Recalculated isotherms in terms of $\pi(e)$ of films from samples taken from: (a) the Atlantic Ocean (Jarvis et al., 1967), (b) in the San Diego Bay, California (Barger et al., 1974).

C_{01}. This difference does not affect the elastic modulus that can be expressed as follows:

$$P = (1-e)\sum_{n=1}^{3} nC_n e^{n-1}. \qquad (8)$$

The particular values of the coefficients C_1, C_2, and C_3 for isotherms of samples, taken from the Black Sea, are presented in the Appendix, Tables 1–3. Similar coefficients for isotherms of samples, taken from the nearshore of the Atlantic coast of the USA (Jarvis et al., 1967), are presented in Table 4 of the Appendix and the

coefficients for samples taken from the San Diego Bay, California (Barger et al., 1974) – in Table 5 of the Appendix. As Eqs (7) and (8) express the pressure and elasticity as polynomial functions of nondimensional deformation e, all coefficients C_1, C_2, and C_3 in these equations have the dimension of pressure and elasticity (dyn/cm).

As the polynomial approximation only roughly follows the isotherms, Eq. (7) may give small negative (non-physical) values of π or $\Delta\pi$ for small relative deformations. This is a typical feature of many similar approaches in which, in particular, the end parts of the

empirical curves are not exactly represented. Such occasions are commonly resolved by setting the negative values to zero in further calculations. In this particular case such negative values occur only for gas-like isotherms, that is, in situations when the film pressure is almost zero for small relative deformations.

## 4. STATISTICS OF COEFFICIENTS OF THE CUBIC APPROXIMATION

The possibilities and reliability of the proposed approach can be, to a first approximation, evaluated using distributions of the coefficients C_{00}, C_{01}, C_1, C_2, and C_3 for isotherms taken from different locations. As coefficients C_{00} and C_{01} have different physical mean-

ing for the Black Sea samples and samples from the nearshore of the USA, the relevant values and distributions are not comparable and are analysed separately.
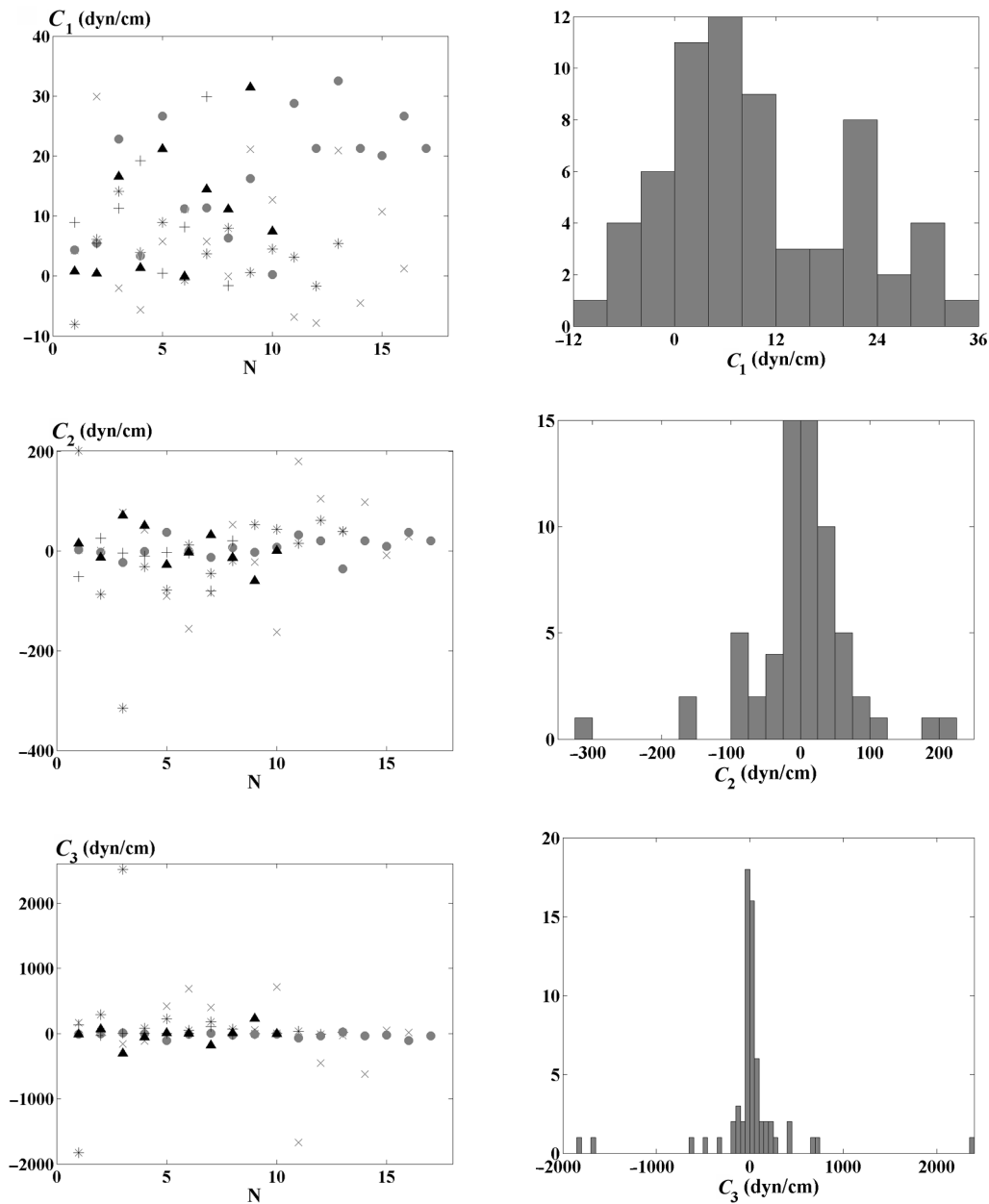
The values of coefficient C_{00} for the Black Sea samples are in the range from -0.22 to 0.067 dyn/cm (Fig. 5). The values for different years vary to some extent whereas relatively large negative values occurred in 1981 and larger positive values were common in 1983. However, the overall distribution (Fig. 5b) has a clearly defined peak for the range $[-0.04, 0]$. It is expected that the values of C_{01} (Fig. 6) are quite different from those of C_{00}. The particular values of C_{01} lie in the range from -0.2 to 6 dyn/cm for the Atlantic nearshore of the USA and from -0.2 to 2.6 dyn/cm for San Diego Bay. The average over all isotherms in Fig. 4 is 0.79 dyn/cm (standard deviation (std) 1.53 dyn/cm).
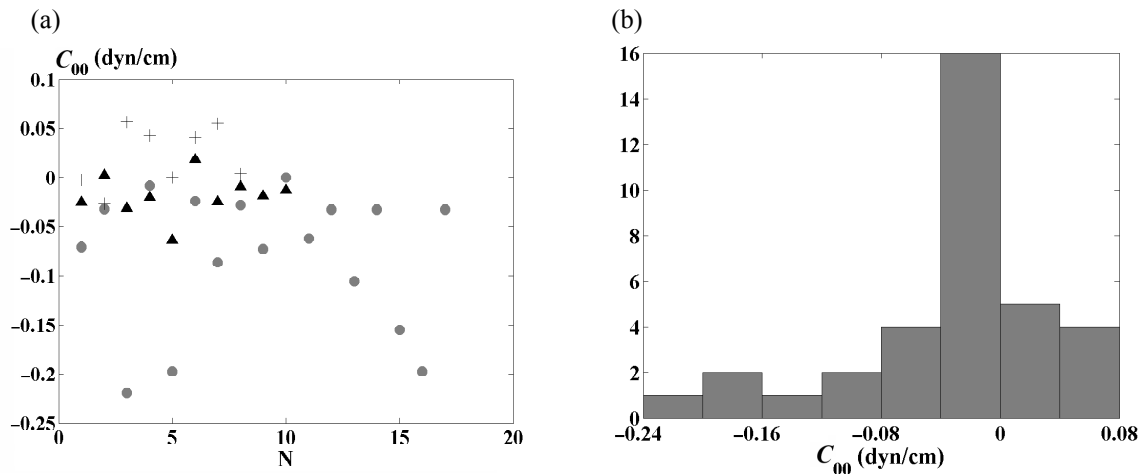
Fig. 5. (a) Coefficients C_{00} for the Black Sea isotherms (N is the sequential number of an isotherm in Fig. 3) in different years: ● – 1981, ✚ – 1982, ▲ – 1983; (b) histogram of different values of coefficients C_{00} for all years.
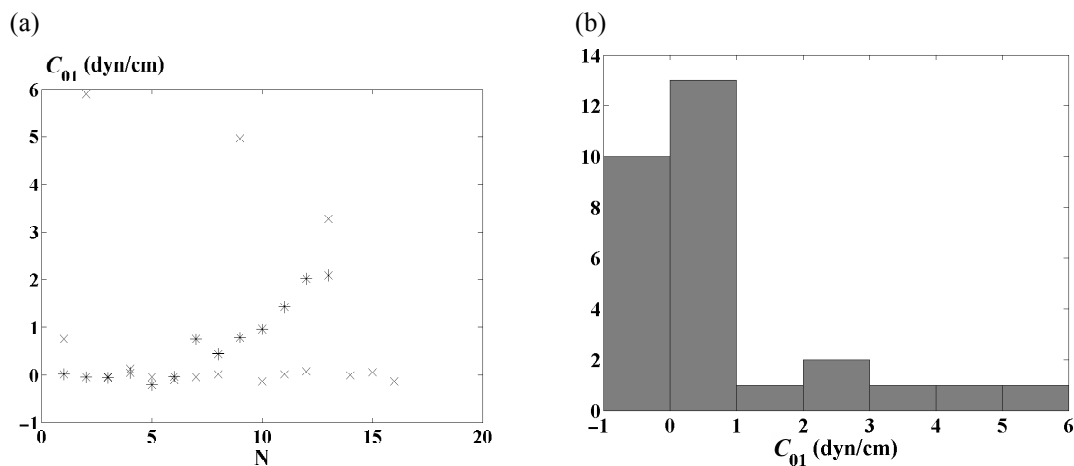
Fig. 6. (a) Coefficients C_{01} for the isotherms in Fig. 4 (N is the sequential number of an isotherm): ✖ – Atlantic coast of the USA, ✳ – San Diego Bay; (b) histogram of different values of coefficients C_{01} for all isotherms in Fig. 4.

Fig. 7. Left column: single values of coefficients C_1, C_2, and C_3 for the isotherms in Figs 3 and 4 (N is the sequential number of an isotherm). Shown are the coefficients for the Black Sea isotherms in different years: ● – 1981, ✚ – 1982, ▲ – 1983 and for the nearshore of the USA; ✖ – Atlantic coast of the USA, ✱ – San Diego Bay. Right column: histograms of different values of coefficients C_1, C_2, and C_3 for all isotherms in Figs 3 and 4.

Similar distributions for C_1, C_2, and C_3 are presented in Fig. 7 for all isotherms in Figs 3 and 4. The values of C_1 are highly scattered between −10 dyn/cm and 30 dyn/cm, with no obvious outliers, but still a more or less clear peak exists for values in the range 4–8 dyn/cm. The pool of values of C_2 contains five outliers whereas the rest of this pool is more or less uniformly scattered in the range from −100 to 100 dyn/cm. Similarly, the set of coefficients C_3 contains three

outliers but the rest of the values are in the range from −700 to 700 dyn/cm.

Histograms of the values of coefficients C_1, C_2, and C_3 (Fig. 7) demonstrate that these quantities have a clearly defined peak; however, the formal average does not necessarily match the location of this peak. For example, the average of the values of C_1 (which has a two-peak distribution) is 9.6 dyn/cm (std 10.5 dyn/cm). The average values of C_2 and C_3 match the locations of

the relevant peaks in the empirical histograms in Fig. 7. The averages of C_2 and C_3 are 0.7 and 10.8 dyn/cm (std 72 and 468 dyn/cm), respectively.

These results indicate that the scatter of coefficients C_2 and C_3 around their average values is extremely large, which may rise questions of reliability of the resulting express estimates. A natural step towards improving our estimates is to ignore outliers of C_2 and C_3. The diagrams in Fig. 7 suggest that realistic values of C_2 and C_3 are in the range ±200 dyn/cm and ±700 dyn/cm, respectively. If the values of C_2, exceeding ±200 dyn/cm, are ignored, the improved estimate of its average is 2.5 dyn/cm (std 56 dyn/cm). A further narrowing of the values of C_2 used in the calculation of the average to ±120 dyn/cm leads to the estimate of the average of 5 dyn/cm (std 43 dyn/cm). Similar narrowing of the values of C_3 in the evaluation of the average to ±700 dyn/cm leads to an estimate of its average 16 dyn/cm (std 179 dyn/cm). The corresponding value

of the average for the values of C_3 in the range of ±700 dyn/cm is 0.7 dyn/cm (std 97 dyn/cm).

On the one hand, the described scatter of the values of the coefficients of the cubic polynomial approximation signals that the use of their single representative values is generally not justified. On the other hand, Fig. 7 also reveals that the basic features of the values for these coefficients apparently are universal for various locations of the World Ocean. A possible way forward is to construct probabilistic methods for express estimates of the elastic modulus, $P(C_i)$, $i = 1, 2, 3$, of the films based on probability distributions of the occurrence of the discussed coefficients.

The cumulative distribution functions for constants C_{00} (for the Black Sea samples) and C_{01} (for the samples from the nearshore of the USA) are quite different (Fig. 8a, b), apparently because of the difference in their physical background. In both cases, however, a high proportion of the values of these
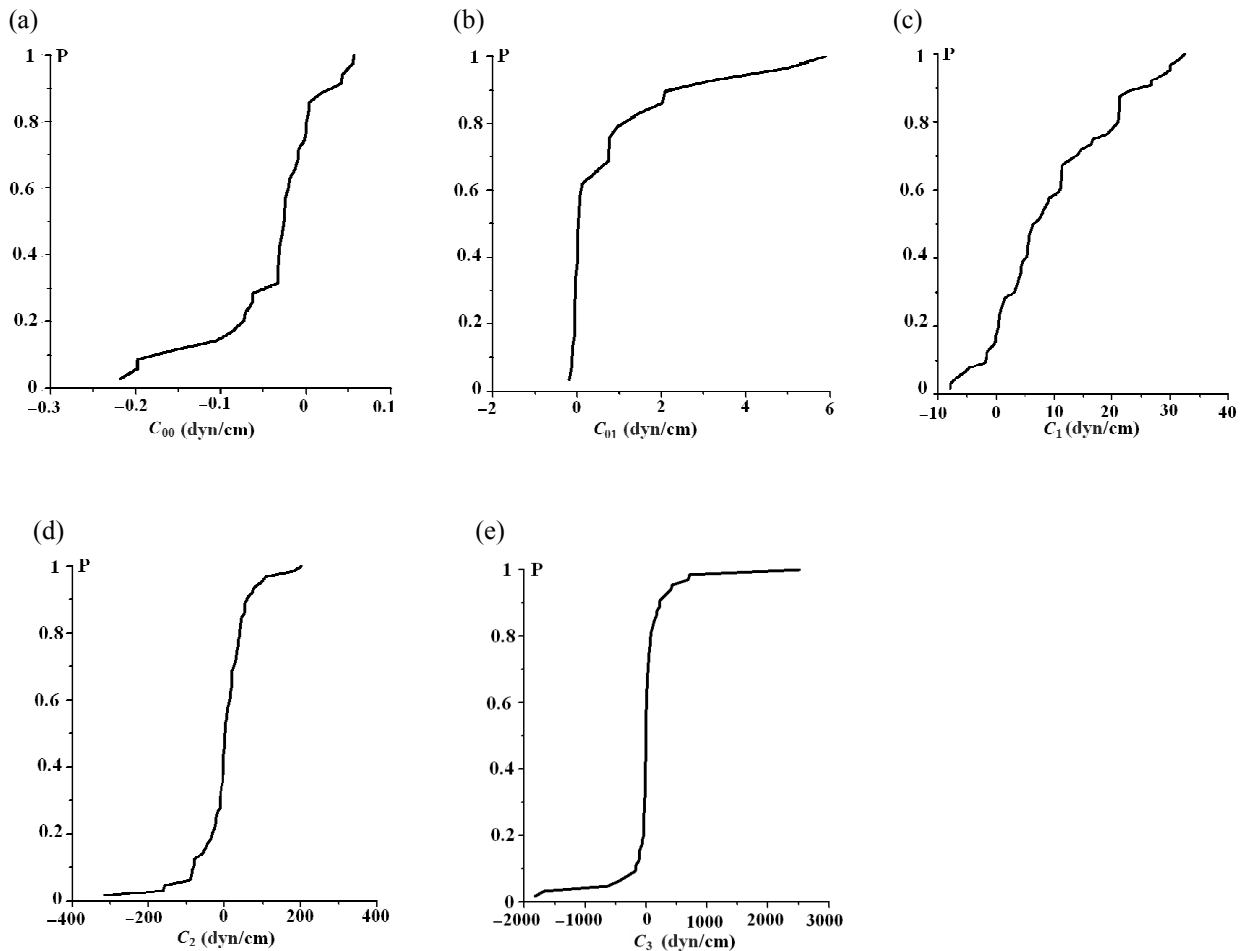
Fig. 8. Cumulative distribution functions for constants C_{00} (for the Black Sea samples) and C_{01} (for the samples from the nearshore of the USA) and for coefficients C_1, C_2, and C_3.

coefficients are concentrated in a relatively narrow range, as discussed above. The probability for C_{00} to be smaller than 0.04 dyn/cm is about 30% whereas this quantity lies in the range from −0.04 to 0.04 dyn/cm with a probability of about 60%. Similarly, the probability of C_{01} to be in a relatively narrow range from −0.05 to 0.05 dyn/cm is also about 60%. Although quite large values of this coefficient occasionally occur, the probability of having $C_{01} > 4$ dyn/cm is less than 8%.

Cumulative distribution functions for constants C_1, C_2, and C_3 (Fig. 8c, d, e) substantially differ from each other. While the values of C_1 are more or less homogeneously scattered and have no clear outliers, the values of C_2 and C_3 are largely concentrated around certain values and contain a few extremely large negative and positive values. As a result, the cumulative distribution function of C_1 can be adequately approximated by a straight line. None of the distributions for C_1, C_2, and C_3 is close to a Gaussian distribution. The probability of the values of C_1 to be within one standard deviation from the average (9.6 ± 10.5 dyn/cm) is about 80% while for the values of C_2 (0.7 ± 70 dyn/cm) this probability is even larger, about 85%. A high proportion (about 60%) of values of C_3 is concentrated in a narrow range of ± 50 dyn/cm from its average whereas the std is as large as 468 dyn/cm.

5. CONCLUDING REMARKS

The presented analysis of the cubic approximation of the dependence of the pressure $\pi(e)$ of films of surface active substances on the relative deformation vividly demonstrates extremely large scatter of the coefficients of this approximation. This scatter, expressed in terms of the standard deviation, is relatively modest (1.5–2 times as large as the average value) for the constant terms of the relevant cubic polynomials. Similarly, the scatter for the coefficient at the linear term of the cubic polynomial is approximately the same as its average value. The coefficients at the quadratic and cubic terms have the largest scatter. The standard deviation of the values of the coefficient at the quadratic term exceeds by about 100 times the average of these values; for the coefficient at the cubic term the standard deviations exceeds the average by about 50 times. The described property signals that it is evidently not possible to approximate the dependence in question (equivalently, the shape of the isotherms of surface active films) using one universal polynomial function, even for one location of the world ocean. Consequently, it is necessary to account for the described scatter in various estimates of the shape of the isotherms and in calculations of the properties of surface active films in the marine environment.

APPENDIX

Table 1. Coefficients of the cubic approximation of the isotherms of films sampled in September–October 1981 in the nearshore of the Crimea Peninsula, the Black Sea. All coefficients have the dimension of dyn/cm. The first column (*N*) indicates the sequential number of the isotherm in Fig. 1a

N	C_0	C_1	C_2	C_3
1	−0.070812	4.34528	3.12312	−7.0271
2	−0.031888	5.44817	−1.93491	−0.427674
3	−0.219127	22.8315	−22.3808	7.602
4	−8.13E−03	3.31484	−0.789816	−0.541852
5	−0.197843	26.6612	37.5108	−106.19
6	−0.024216	11.2048	0.72405	−7.99007
7	−0.08652	11.3453	−12.4623	6.34307
8	−0.028244	6.29944	7.52098	−19.4005
9	−0.072867	16.2281	−2.10729	−6.38015
10	8.84E−05	0.242918	8.00215	−10.3169
11	−0.062318	28.7752	33.1252	−65.84
12	−0.032549	21.2681	20.4675	−35.211
13	−0.105362	32.5091	−35.1046	21.414
14	−0.032549	21.2681	20.4675	−35.211
15	−0.155224	20.071	9.8995	−22.9787
16	−0.197843	26.6612	37.5108	−106.19
17	−0.032549	21.2681	20.4675	−35.211

Table 2. Coefficients of the cubic approximation of the isotherms of films sampled in June–July 1982 in the nearshore of the Crimea Peninsula, the Black Sea. All coefficients have the dimension of dyn/cm. The first column (*N*) indicates the sequential number of the isotherm in Fig. 1b

N	C_0	C_1	C_2	C_3
1	−2.31E−03	8.91202	−50.704	135.151
2	−0.026757	5.4873	25.8575	−30.8747
3	0.0567599	11.2733	−4.16497	1.18066
4	0.0431125	19.2165	−9.77448	3.66516
5	1.88E-04	0.477883	−2.21199	3.23835
6	0.0412789	8.19917	−4.24155	1.93968
7	0.0550191	29.8905	−79.3925	110.474
8	0.0039055	−1.59128	20.6994	−18.2993

Table 3. Coefficients of the cubic approximation of the isotherms of films sampled in May–June 1983 in the nearshore of the Crimea Peninsula, the Black Sea. All coefficients have the dimension of dyn/cm. The first column (N) indicates the sequential number of the isotherm in Fig. 1c

N	C_0	C_1	C_2	C_3
1	−0.0253497	0.804049	15.6141	−11.9524
2	2.68E-03	0.44705	−12.035	70.0713
3	−0.0313464	16.5996	71.7163	−305.652
4	−0.0202374	1.37004	51.304	−57.8233
5	−0.06377	21.1888	−26.9119	10.8705
6	0.0183053	−0.07325	−1.94532	5.06762
7	−0.0245494	14.5034	32.3287	−179.004
8	−9.43E-03	11.1483	−12.1382	9.26849
9	−0.0189165	31.4458	−59.3629	229.346
10	−0.01274	7.4372	0.916046	−5.08233

Table 4. Coefficients of the cubic approximation of the isotherms of films sampled near the Atlantic coast of the USA. All coefficients have the dimension of dyn/cm. The first column (N) indicates the sequential number of the isotherm in Fig. 2a

N	C_0	C_1	C_2	C_3
1	0.753209	4.27577	2.98273	167.87
2	5.90588	29.9257	1.53255	31.6557
3	−0.04607	−2.04188	78.0544	−161.611
4	0.124727	−5.65259	43.3647	−115.562
5	−0.04533	5.73662	−89.7281	423.695
6	−0.10043	11.1319	−156.004	685.066
7	−0.04279	5.75844	−83.8342	401.374
8	0.01853	−0.02622	53.32	28.473
9	4.96458	21.1286	−21.9914	57.716
10	−0.1351	12.6903	−162.275	713.102
11	0.016464	−6.8421	180.084	−1667.82
12	0.070993	−7.85164	105.016	−453.331
13	3.27873	20.8802	41.1937	−31.3015
14	0.001107	−4.50739	98.3015	−623.074
15	0.051688	10.7204	−8.02981	52.3153
16	−0.12879	1.20796	29.2334	18.8837

Table 5. Coefficients of the cubic approximation of the isotherms of films sampled from the San Diego Bay, California. All coefficients have the dimension of dyn/cm. The first column (N) indicates the sequential number of the isotherm in Fig. 2b

N	C_0	C_1	C_2	C_3
1	0.021071	−8.06171	201.78	−1828.9
2	−0.04355	6.1025	−86.2109	291.731
3	−0.05293	14.0843	−315.129	2519.58
4	0.042961	3.95007	−31.4275	82.921
5	−0.20178	8.9551	−78.4571	224.553
6	−0.03366	−0.67124	12.3053	50.2661
7	0.752762	3.72828	−45.0101	180.216
8	0.438799	7.94578	−19.3229	67.859
9	0.776994	0.599861	53.6059	−6.07971
10	0.959237	4.46952	43.4386	4.15521
11	1.43285	3.10969	15.6867	33.5567
12	2.01757	−1.68001	61.8243	−7.52556
13	2.09176	5.40447	39.8677	13.6112

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Pindaktiivsete ainete isotermide lähendamine kuupfunktsiooniga

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On analüüsitud võimalusi lähendada pindaktiivsete ainete poolt mere pinnal moodustatud kilede isoterme kuup-funktsiooniga. Isotermideks nimetatakse selliste kilede tekitatud rõhu sõltuvust pindaktiivsete ainete kontsent-ratsioonist. Analüüsis on kasutatud Musta mere ja Kalifornia ranniku lähedal mere pinnakihist võetud veeproove. Erinevate proovide jaoks leitud kuuppolünoomide vabaliikmete väärtused erinevad kõigi proovide keskmisest enamasti vähem kui ühe standardhälbe võrra. Polünoomide ruut- ja kuupliikme kordajate üksikväärtuste standard-hälve seevastu ületab vastava keskmise enam kui kahe suurusjärgu võrra. Seega ei tohi pindaktiivsete ainete isoterme lähendada ühe universaalse kuupfunktsiooniga isegi samast kohast võetud proovide puhul ja kõnesolevate kilede omaduste ning mõju hindamisel tuleb arvestada isotermide omaduste varieerumisega. On arvutatud kuupfunktsiooni vabaliikme ja kordajate tõenäosusjaotused, mis on mere pinnal leiduvate kilede omaduste statistiliste mudelite sisendiks.