***Graphical Abstract (for review)**

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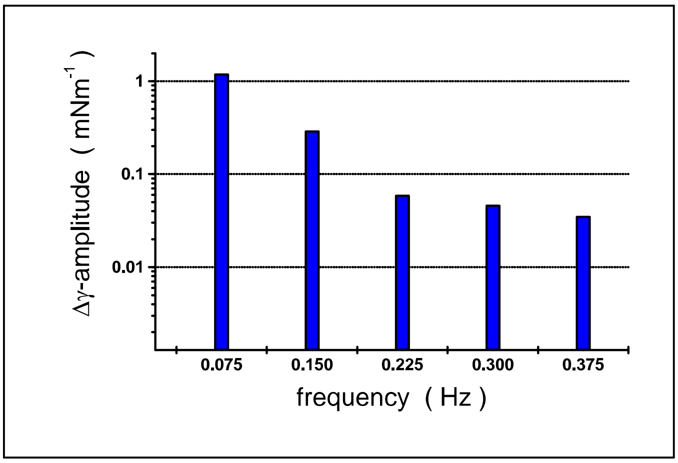

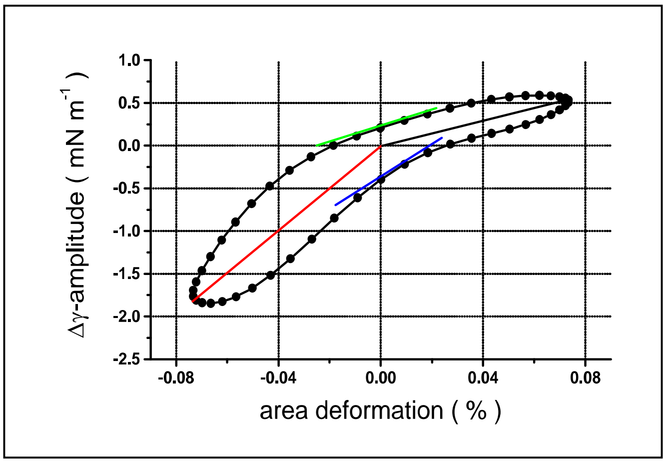

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Highlights

- ► Application of mathematical methods effectively describes nonlinearity magnitude.
- ► Spectrum characterizes the nonlinear interfacial response in oscillation experiments.
- ► Lissajous plot quantifies the degree of nonlinearity in interfacial periodic responses.
- ► Complex substances give rise to notable nonlinear interfacial rheological properties.

Surface dilational rheological properties in the nonlinear domain

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ABSTRACT

The interfacial tension response to dilational deformation of interfacial area exhibits a (more or less) nonlinear behaviour, depending on the amplitude of the deformation. Studies of such observable interfacial properties in the nonlinear domain suggest valuable information about the two-dimensional micro-structure of the interfacial layer, as well as about the structure time-evolution.

In this article, the emphasis is centered on the available mathematical methods for quantitatively analyzing and describing the magnitude and the characteristics of the nonlinear interfacial viscoelastic properties. Specifically, in periodic oscillation experiments the nonlinear behaviour can be represented by the combination of a linear part (the surface dilational modulus), with an additional complementary Fourier analysis parameterising the non-linearity. Also asymmetric Lissajous plots, of interfacial tension versus deformation, are useful tools for expanding the response nonlinearity into four distinct components relevant to significant points of the cyclic loop.

In connection with the mathematical methods, nonequilibrium thermodynamic formulations provide a powerful theoretical framework for investigating the interfacial dynamic properties of multiphase systems.

Experimental results for adsorption layers of complex components, available in the literature, show notable nonlinear interfacial viscoelastic behavior. In particular in this review, data are illustrated for solutions of polymers and of polyelectrolyte/surfactant complexes.

The observed nonlinear findings reveal formation of complexes, patches, and other different interfacial structures.

Keywords: Nonlinear interfacial rheology, Surface dilational modulus, Surface dilational viscoelasticity, Fourier spectral analysis, Lissajous plots, Stress decomposition .

& This article is dedicated to Dr. habil. Reinhard Miller on the occasion of his 65th birthday.

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Surface dilational rheological properties in the nonlinear domain

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1. Introduction

Multiphase disperse systems, belonging to a wide variety of categories, are basic material assemblages in numerous industrial products [1, 2], living organisms [3] and natural compartments [4]. The composition, microstructure and conformation of such systems are now explored under different aspects and their properties are determined by a multitude of measurement methods.

In liquid/liquid multiphase systems the thermodynamic and the rheological properties of the interfacial layer (i.e., the quasi-bidimensional region separating the adjoining phases) have an increasing effective influence on the overall system behaviour, upon decreasing the dispersion size from the sub-millimetric to the sub-micrometric level [5].

A specific relevant property of the above-mentioned interfacial layers is the dilational viscoelasticity, which is manifested when the interfacial area is subjected to extension or compression. Among all possible causes of the stability of disperse systems, these surface viscoelastic properties are now well identified as ones of the principal physical quantities governing the long-term stability or the time-evolution of emulsions and foams [6].

The magnitude and the characteristics of the dilational interfacial viscoelasticity essentially depend on *i*) the chemical nature of the components; *ii*) the adsorption equilibrium composition of the surface layer or the instantaneous transient composition; *iii*) the extent of the interfacial area change. Hence in real systems, depending on the particular circumstances, the interfacial dilational viscoelasticity may assume different characteristics, from a steady-state linear behaviour (exhibited for small area perturbation in proximity of the adsorption equilibrium state) to a steady-state nonlinear behaviour and arriving to the most general case of the transient non-equilibrium nonlinear behaviour in case of large area disturbances of a freshly-formed interface.

Up to now the dynamic interfacial rheological properties (specifically the dilational interfacial viscoelastic properties) have been intensively studied during the last decades. A great part of the obtained results, described in the literature, are related to the systems at or near equilibrium. In this case the methods of the analysis of experimental data are well established. All of them are based on the assumption that the response amplitude is proportional to the disturbance amplitude.

However, real interfaces actually manifest a more or less nonlinear dynamic response, with memory, as a result of the changes of interfacial area. In practice, most technological operations involve violent hydrodynamic conditions, far from a quiescent equilibrium state, resulting in wide and fast area extension/compression of the interfacial layers, which are present inside the processed heterogeneous body. In such hydrodynamic circumstances an amplitude dependence of the rheological properties may be expected, that is, the viscoelastic response may become nonlinear.

Obviously, in case of nonlinearity, the linear models cannot be adopted as a good description of the stress response. Hence, from a practical point of view, it is advantageous to theoretically and experimentally investigate the interfacial rheological parameters related to strong deviations from equilibrium, as the observable nonlinear behaviour conveys additional information, in respect to the linear behaviour, closely manifesting the real condition of the processed system. Moreover the interfacial nonlinear rheology can be used to link the information on the macroscopic dynamics of the system to the molecular structure.

Various available nonequilibrium thermodynamic formulations allow the interfacial response-stress phenomenology to be interpreted either for small and large area deformations, providing a powerful theoretical framework to investigate the dynamics of disperse multiphase systems. The formalism of nonequilibrium thermodynamics can be used to construct a wide range of admissible nonlinear models, conveying an insight on the interfacial layer microstructure at large deformations [7, 8] .

Note that all the results under discussion below relate to the thermodynamic branch and thereby not to the large deviations from equilibrium. When parameters of the system deviate further from equilibrium values the thermodynamic branch can become unstable and completely new and unexpected types of behaviour can occur [9]. The conditions of the stability of the thermodynamic branch are discussed in ref. [10] for a two-phase system with the account of surface phenomena. The violation of these conditions results in the spontaneous growth of the amplitude of surface waves and consequently to the surface convection and turbulence.

In addition to nonequilibrium thermodynamics, several mathematical tools (namely, Volterra series, Fourier transform operation, Fourier expansion series, stress decomposition method, Lissajous plots and polynomial series) can be applied for a quantitative characterization of the nonlinear interfacial rheological behaviour, estimating the limits of the linear approximation and parameterizing the deviations from a linear response.

The aim of the present work is twofold: A) to present an overview of the above-mentioned mathematical tools, complementing the nonlinear thermodynamics; and B) to provide examples of recent experimental results, for different classes of adsorption layer components, with particular focus on the applied mathematical methods for the characterization of the observed nonlinear dilational viscoelastic behaviour.

2. Interfacial dilational modulus

Considering a linear viscoelastic regime, the interfacial dilational modulus, ε(ω), is the physical property that quantitatively describes the viscoelastic behaviour of adsorption layers. Such a physical quantity was earlier defined in the frequency domain by Lucassen et al. [11; 12, 13, 14, 15]. Later on, Loglio et al. [16] extended in the time domain the definition of the interfacial dilational modulus. Essentially, limiting to appropriately-small disturbances of interfacial area under not-far-from-equilibrium conditions, the dilational modulus can be defined either in the time domain or in the frequency domain, within the mathematical framework of systems theory, as shown in the following expressions,

$$\Delta\gamma(t) \;=\; \gamma(t)-\gamma_0 \;=\; \int_0^t \mathrm{F}^{-1}\{\varepsilon(\omega),\tau\}\Delta A(t-\tau)/A_0\,d\tau \tag{1}$$

$$\Delta\gamma(\omega)=\varepsilon(\omega)\Delta A(\omega)/A_0 \tag{2}$$

where $\Delta\gamma(\omega)=F\{\Delta\gamma(t)\}$, $\Delta A(\omega)=F\{\Delta A(t)\}$, F is the Fourier transform operator, τ is the dummy time in the convolution integral, ω is the angular frequency, Δγ is the surface tension change and $\Delta A/A_0$ is the relative area change.

According to Eq.(2), ε(ω) can be conceived as the frequency response function of the interfacial system, which quantitatively describes the viscoelastic behaviour in the linear regime. Also from Eq.(1), the impulse response function (transfer function) is formulated as the inverse Fourier transformation F^{-1} of the frequency-response function of the system $k_1(t)=\mathrm{F}^{-1}\{\varepsilon(\omega,t)\}$.

Eq. (1) implies that the viscoelastic system under consideration has memory and the surface tension depends not only on the surface area at the given time but on the surface area in all the preceding times. From the pure mathematical point of view this means that the surface tension is not a function of ΔA but a functional of ΔA(t). In the case of small surface deformations one can apply a general representation of linear functionals [17]

$$\Delta\gamma(t) \;=\int_{-\infty}^{t} \mathrm{G}(\mathrm{t}-\tau)(\mathrm{d}\Delta A(\tau)/A_0\;d\tau)d\tau \tag{2a}$$

where G is the surface relaxation function.

Application of the Fourier transform to Eq. 2a results in Eq. 2 and the relations between the components of the complex modulus ε and the relaxation function

$$\varepsilon(\omega)=G_0+\int_0^{\infty}G(\eta)\sin(\omega\eta)d\eta+i\omega\int_0^{\infty}G(\eta)\cos(\omega\eta)d\eta \tag{3}$$

It is assumed here that the relaxation function consists of a constant part G_0 and a part which depends on time.

Adopting a linear model, the basic conceptual proposition is now well-established that the interfacial dilational modulus, $\varepsilon(\omega)$, is an intrinsic constitutive property of a system which characterises the dynamics of adsorption layers, linking the interfacial response, $\Delta\gamma(t)$, to the interface excitation, $\Delta A(t)/A_0$, forced with any functional form [16, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33].

3. Mathematical methods for nonlinearity characterization

The nonlinear viscoelastic behaviour of the interface becomes progressively more and more dominant on increasing the amplitude and the time scale (or the frequency) of the interfacial input perturbation. Also, the interfacial response depends on the inherent relaxation mechanisms of the interfacial layer, i.e., bulk-to-interface material transport and molecular conformation or reorganization at the interface. Such relaxation mechanisms may occur at a comparable time scale as the time scale of the interfacial perturbation. It is just these relaxation processes which impart the memory effect to the interfacial behaviour.

From a general point of view, the behaviour of nonlinear systems with memory cannot easily be described in explicit mathematical terms.

Relying on a time-invariance assumption (that is, assumption of a steady-state condition), in the following sections a review is reported on the possible mathematical approaches for processing the measurement results and characterizing the behaviour of real interfacial systems.

3.1. Thermodynamic approach

Almost all thermodynamic descriptions of the non-equilibrium interfacial layer are based on the ideas of Gibbs and formulated in terms of surface excesses [5, 6, 8, 10, 34]. This method neglects the thickness of the interfacial layer and considers it as a mathematical surface with the prescribed values of extensive properties per unit surface area (surface excesses).

The main attention in nonlinear two-phase systems with large strains and rates of strain has been paid to shear surface properties until now and thereby these results are irrelevant in the work on dilational surface rheology [5, 8, 35]. The neglect of the influence of shear deformations and consideration of a frequent case of the two-dimensionally isotropic interface facilitates significantly the mathematical description. All tensors and vectors disappear in the expression for the entropy production d_iS/dt and one can write for an open system consisting of the surface layer and a thin layer of the adjacent bulk phase (subsurface layer) [9]

$$\frac{\mathrm{d_i}S}{Tdt} = \sum_i A_i^a \frac{d\xi_i^a}{dt} + \sum_j A_j \frac{d\xi_j}{dt} \geq 0 \tag{4}$$

where T is the absolute temperature, A_i^a is the affinity of adsorption of component i from the bulk phase to the surface, ξ_i^a is the extent of adsorption, A_j is the affinity of the chemical reaction j between the components in the surface layer or the corresponding thermodynamic force for a structural transition in the surface layer, ξ_j is the corresponding extent of reaction or a structural parameter.

Relation (4) assumes that the set of independent variables apart from the usual thermodynamic parameters (temperature, pressure, concentrations in the bulk phase and adsorbed amounts) contains also the internal variables ξ_i^a and ξ_j. The structure of relation (4) indicates that for small deviations from equilibrium all the thermodynamic fluxes $d\xi_l/dt$ are connected with thermodynamic forces A_k by the following linear relations

$$\frac{d\xi_l}{dt} = \sum_k L_{lk} A_k \tag{5}$$

where L_{lk} is the matrix of kinetic coefficients.

The combination of kinetic equations (5) with balance equations in the bulk phase (diffusion equations for all the components, hydrodynamic equations), some boundary conditions and kinetic models for the processes in the surface layer lead to a general expression for the interfacial dilational modulus [36]. One can obtain compact forms of this expression in the case of simplified kinetic models, for example, when the only relaxation processes are the diffusion of a surfactant from the bulk phase to the surface and the transition through an adsorption barrier at the surface [36], the adsorption of two surfactants with the diffusion controlled adsorption kinetics [37], the surfactant adsorption from micellar solutions [17, 38] the formation of loops and tails in the polymer adsorption layer [39].

One can extend the linear models mentioned above to the weakly non-linear domain by expanding the thermodynamic fluxes in Eq. (5) to higher order. This formal approach, however, increases strongly the number of phenomenological kinetic coefficients. On the other hand, in the case of shear deformations it describes the surface rheological behavior adequately only for a very limited range of stain rates [35]. It is hardly possible to expect that the account of higher orders terms in Eq. (5) results in a significantly better description of a nonlinear system with dilational deformations.

The classic approach based on the relations of type (4) and (5) is not the only possible formalism in the modern nonequilibrium thermodynamics. Other thermodynamic formalisms like the extended irreversible thermodynamics based on another choice of independent variables or extended rational thermodynamics based on the assumption of the conservation of fluxes give no significant advantages at the description of nonlinear phenomena as compared with the classic formalism [5, 8]. A more perspective formalism is the GENERIC (General Equation for the Non-Equilibrium Reversible Irreversible Coupling), which is more suitable for the description of the far from equilibrium behaviour [40]. It has been applied to surface phenomena only recently [7, 8]. This approach is characterized by the serious mathematical complexity. The incorporation of the models of relaxation processes in the surface layer in GENERIC and its application to the interpretation of experimental data on the surface dilational rheological properties are still the tasks for future.

3.2. *Volterra series and Fourier analysis*

The Volterra series appears as a good theoretical modelling tool, in the time domain or in the frequency domain, for (weakly) nonlinear dynamic systems [41]. In case of interfacial layers, in which $\Delta A(t)/A_0$ is the input perturbation and $\gamma(t)$ is the output response, the Volterra series reads in the time domain [42] :

$$\gamma(t) = \gamma_0 + \sum_{n=1}^{n=\infty} \frac{1}{n!} \int_0^t \ldots\ldots \int_0^t k_n(\tau_1, \tau_2, \ldots \tau_n) \times \prod_{i=1}^{n} \Delta A(t - \tau_i)/A_0 \, \mathrm{d}\tau_1 \, \mathrm{d}\tau_2 \ldots\ldots \mathrm{d}\tau_n \qquad (6)$$

where γ_0 is the equilibrium surface tension at the instant $t = 0$ and the mathematical *n*-th order Volterra kernel k_n can be physically interpreted as the *n*-th higher-order impulse response of the system.

As seen in Eq. (6), the Volterra series includes the first-order impulse response of the interfacial system, which has been already introduced in refs. [18, 19] on the basis of the dilational viscoelastic modulus $\varepsilon(\omega)$, that is, the frequency-response function of the interfacial layers, earlier defined by Lucassen et al. [11, 13, 14].

It is noticeable that Eq. (6) is a generalisation of the Taylor's series, because it includes the memory. Also, Eq. (6) is an extension of the previous linear treatment as Eq.(1) can be obtained by truncating the series at the zeroth-order plus the first-order terms. In addition, Eq.(6) defines the higher-order impulse responses k_n of the interfacial layers.

Thus Eq. (6) in principle is an appropriate mathematical resource for the representation and identification of the real interfacial systems which are more or less non-linear.

However, the Volterra series has a serious drawback, because at present in the literature no efficient numerical algorithm, especially tailored for the interfacial layers, can be found. Another hindrance is the lack of experimental techniques for the kernel measurement relevant to the non-linear contribution of interfacial tension responses.

In order to circumvent the above-mentioned inconveniences of Volterra series, the nonlinear interfacial behaviour can be represented and characterised by a consecutive combination of a linear part followed by an additional Fourier analysis parameterising the non-linearity in periodic oscillation experiments.

Essentially, at experiment conditions of steady-state responses to forced sinusoidal perturbations, the nonlinearity behaviour is phenomenologically described by giving the amplitude spectrum of the fundamental frequency and of the higher harmonics frequency multiples [28, 31]. To this purpose, the amplitude spectrum of periodic phenomena are properly analysed by expansion into Fourier series. In principle, a single cycle of a periodic phenomenon contains all the necessary physical information. In practice, in the harmonic oscillation experiments, the acquisition of data during a time interval longer than the single-oscillation period appears advantageous for a convenient experimental redundancy as well as for a verification of the transient or steady-state regime. The essential aspects of this technique, as it applies to interfacial rheology, was recently reviewed in ref. [42].

As concerns the frequency content of time-varying signals, the amplitude spectrum is practically determined with the powerful algorithms of the Fast Fourier Transform (FFT), available in widespread computer programmes. For a more detailed consideration, the interested reader is directed to Ref. [43].

An index of the non-harmonic contribution, occurring in the interfacial response, is expressed by the Total Harmonic Distortion (THD), that is, the ratio of the higher harmonics amplitude to the amplitude at the measured fundamental frequency.

In the following equation, a_1 is the amplitude value at the fundamental frequency and a_2, a_3, …, a_n are amplitude values of the higher harmonics :

$$\mathrm{THD} = (a_2^2 + a_3^2 + \ldots + a_n^2)^{1/2} / a_1 \qquad (7)$$

Thus, the THD index can easily be computed from the amplitude values of the fundamental frequency and of the higher order harmonic frequencies. THD is also expressed as a percentage of the fundamental-frequency amplitude.

Alternatively, the non-linearity extent can be quantitatively expressed by defining THD as the ratio of the higher harmonics power to the power at the fundamental frequency [42]

For small-amplitude perturbations, the THD value becomes vanishingly small (linearity approximation). At constant-amplitude perturbation, THD depends on the excitation frequency (frequency dispersion of THD).

Note that the dynamic surface elasticity cannot be described by a single number for surface deformations of large amplitude and one has to consider a particular surface elasticity for any harmonics. Warszynski, Wantke and Fruhner proposed to use the geometrical mean value of the particular elasticities to characterize the dynamic surface properties in this case [44].

3.3. *Stress decomposition*

Relation (2) defines unequivocally the interfacial dilational modulus only in the case of infinitesimal surface deformations ΔA. A possible approach in the case of large deformations consists in the application of the Fourier analysis and the use of the main harmonics to calculate the “global” or intracycle interfacial dilational modulus as described above. In this case the obtained value of the modulus relates to the whole cycle of compression/expansion. At the same time, the surface stress Δγ in a non-linear system is not a linear function of the surface strain during the whole cycle. This means that if we take small enough values of ΔA, much less the amplitude of the surface area oscillations, the applications of relation (2) will give different values of the surface elasticity in different steps of surface deformation. These “local” intercycle values can differ strongly from the “global” value and can contain information disappearing in the course of the standard Fourier analysis. The problem of the distinctions between intercycle and intracycle surface elasticities was realized first in the studies of the bulk shear rheology and a few methods were proposed to analyze the intercycle nonlinearities [45, 46, 47, 48]. Only very recently van Kempen et al. have applied a graphic method based on Lissajous plots to estimate the intracycle dilational surface elasticity of solutions of oligofructose fatty acid esters [49]. The surface rheological properties of these systems were very different from those of the solutions for surfactants of low molecular weight and fairly elastic Lissajous plots displayed asymmetric behavior with strain hardening during compression and strain softening during expansion. The analysis of nonlinear dilational rheology allowed the authors to conclude on the formation of two-dimensional glass phase in the surface layer.

The graphic method gives both the real and imaginary components of the interfacial dilational modulus characterizing the adsorption layer, for example, in the ranges of maximal and minimal surface deformations. In this case the real component for the minimal deformation equals the tangent slope to the Lissajous plot at zero strain and the real component for the maximal deformation equals the slope of the secant at maximum strain. Fig. 1 represents this plot for mixed solutions of polyacrylic acid (PAA) and dodecyltrimethyl ammonium bromide (DTAB) at pH 9.2 [51]. One can estimate the corresponding imaginary components from the analysis of the surface stress dependence on the strain rate. The application of this graphic method of the analysis of experimental data of the surface rheological methods showed that the intercycle moduli of the surface elasticity at minimal and maximal deformations can differ for the compression and expansion and thereby depend not only on the strain absolute value but also on the strain direction [49].

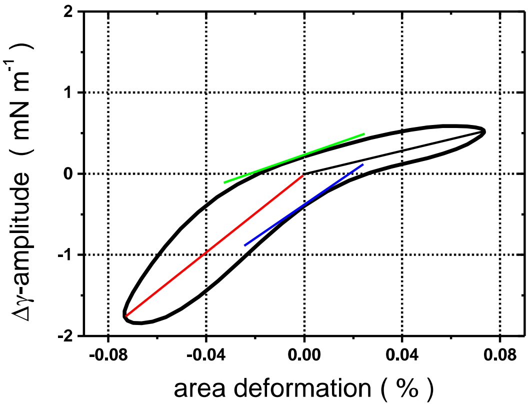

Fig. 1. The dependence of the surface tension on relative changes of the surface area (Lissajous plot) for mixed solutions of polyacrylic acid and dodecyltrimethyl ammonium bromide at pH 9.2. The tangent slope of the lines corresponds to the real part of the interfacial dilational modulus at maximal compression (black line), maximal expansion (red line), and at minimum strain in the course of compression (blue line), in the course of expansion (green line).

The simple method under consideration above of the analysis of nonlinear surface rheological data is a graphic realization of the well-known stress decomposition method, which is widely used together with the Fourier analysis in the studies of the bulk shear rheology to characterize the nonlinear system response to large deformations [48]. In the case of shear strains only odd high harmonics contribute usually to the system response and as a consequence the change of the strain direction leads only to the change of the stress sign but not its absolute value. As a result the elastic stress component for shear strains is an odd function of the relative shear strain x and an even function of the strain rate y. At the same time, the viscous component on the contrary is an even function of x and an odd function of y. Using the properties of these functions Cho et al. presented the whole system response as a sum of two contributions [45]

$$\Delta\gamma(t) \equiv f(x,y) = \frac{f(x,y)-f(-x,y)}{2} + \frac{f(x,y)-f(x,-y)}{2} \equiv \tau_1 + \tau_2 \tag{8}$$

The dependencies of τ_1 on the strain and τ_2 on the strain rate are linear functions unlike the corresponding dependencies of the general response f(x,y) which are the Lissajous plots. This means that τ_1 depends only on x and τ_2 depends only on y at the given strain amplitude, and consequently τ_1 corresponds to the real component of the system response and τ_2 to the viscous component.

Cho et al. also proposed to use polynomial fitting to approximate the elastic and viscous components [45]. However, in this case the increase of polynomial order results in the change of the coefficients of lower order. To avoid this inconvenience Ewoldt et al. applied orthogonal Chebyshev polynomials to the fitting [46]

$$\tau_1(x) = \sum_{n:odd} b_n T_n(x) = b_1 x + b_3(4x^3 - 3x) + \cdots \tag{9}$$

$$\tau_2(y) = \sum_{n:odd} a_n T_n(y) = a_1 x + a_3(4x^3 - 3x) + \cdots \tag{10}$$

where the coefficients a_n and b_n does not change at the account of higher order terms.

The sign of the coefficients in the third order terms in Eq. (9) and Eq. (10) has a clear physical meaning [46]. For example, the positive sign of b_3 indicates the strain stiffening while the negative sign corresponds to the strain softening. The application of the Chebyshev polynomials gives also a possibility to obtain easily the intercycle viscoelastic moduli. The elastic moduli at minimal (E_r^{min}) and maximal (E_r^{max}) can be represented by the following expressions

$$E_r^{max} \equiv \frac{f_{x=x_{max}}}{x_{max}} = b_1 + b_3 + \cdots$$

$$E_r^{min} \equiv \left(\frac{df}{dx}\right)_{x=0} = b_1 - 3b_3 + \cdots \qquad (11)$$

This approach cannot be applied directly to the case of compression/expansion, in particular to the surface dilational rheology where one has to take into account the contribution of even harmonics. In this case the change of the strain direction can lead not only to the change of the stress sign but also of the stress absolute value. As a result the Lissajous plots become asymmetric loops and it is impossible to describe them by the Chebyshev polynomials. Recently Yu et al. proposed a more general approach to the stress decomposition taking into account both odd and even harmonics [47]. In this method the system response (the stress) is expanded into four components. Apart from pure elastic τ_1 and pure viscous τ_2 components the stress contains also two viscoelastic contributions τ_3 and τ_4.

$$\begin{aligned}
\tau_1 &= \frac{1}{4}(f(x,y) - f(-x,y) + f(x,-y) - f(-x,-y)) \\
\tau_2 &= \frac{1}{4}(f(x,y) + f(-x,y) - f(x,-y) - f(-x,-y)) \\
\tau_3 &= \frac{1}{4}(f(x,y) - f(-x,y) - f(x,-y) + f(-x,-y)) \\
\tau_4 &= \frac{1}{4}(f(x,y) + f(-x,y) + f(x,-y) + f(-x,-y))
\end{aligned} \qquad (12)$$

The difference between the two viscoelastic components is not obvious enough. τ_3 becomes more elastic at low strains and more viscous at the maximal strains. The opposite behavior is characteristic for τ_4. Therefore the physical interpretation is more difficult in this case. The appearance of even harmonics and the two viscoelastic components is connected with the asymmetry of the response in relation to the undeformed state. In its turn the asymmetric response is probably a consequence of the structural changes in the course of deformation. In the case of the dilational surface rheology it can be caused by the aggregate formation and destruction in the surface layer [50, 51, 52, 53, 54, 55, 56, 57, 58, 59].

The possibility of the analysis of a nonlinear signal with both odd and even harmonics allows the application of the method by Yu et al. to the interpretation of experimental data on the dilational surface viscoelasticity. The absolute values of the local viscoelastic moduli (the elastic component at minimum and maximum surface deformations, the viscous component at minimum and maximum deformation rates) in this case depend on the direction of the deformation. An example of the application of this method to the results for mixed PAA/DTAB solutions at pH 9.2 will be given in the next section.

3.4. *Comparison of mathematical tools*

The Fourier analysis gives overall information on frequency dependence (i.e., on the amplitude of the harmonics components) of the dynamic surface properties, while the main variable in the stress decomposition method is the deformation of the system in four sections of the oscillation cycle, retaining specific information about the nonlinear behaviour. As a result, these two approaches become complementary and the detailed analysis of experimental data requires application of the both of them.

The estimation of the THD parameter requires representation of the measured oscillations of the surface tension in a complex form and their expansion into the Fourier series according to the following algorithm [60]

$$\mathrm{Re}\{G(f_n)\} \approx \frac{2\Delta}{Z_{cycl}T}\sum_{k=0}^{N-1} g_k \cos(2\pi f_n t_k)$$

$$\mathrm{Im}\{G(f_n)\} \approx \frac{2\Delta}{Z_{cycl}T}\sum_{k=0}^{N-1} g_k \sin(2\pi f_n t_k) \qquad (13)$$

Here the summation is performed over all points of all whole cycles included in a selected temporal interval. $\mathrm{Re}\{G(f_n)\}$ and $\mathrm{Im}\{G(f_n)\}$ are the real and the imaginary parts of the complex transformed function, G, of frequency, f_n . g_k is the experimental value of surface tension (or of area) at time t_k , Δ is the time interval between two consecutive points, Z_{cycl} is the number of cycles in a selected temporal interval, $T/2$ is a half of the oscillation period.

After this operation, the amplitude of fundamental harmonic a_1 and amplitudes of higher harmonics $a_2, a_3, \ldots, a_n$ can be calculated according to the following equation

$$a_n = \left[\mathrm{Re}\{G(f_n)\}^2 + \mathrm{Im}\{G(f_n)\}^2\right]^{1/2}$$

The choice of the number n of higher harmonics depends on the system under examination. According to the most usual practice the THD-value is determined up to the fifth harmonic component (i.e., $n = 5$).

In the case of the stress decomposition method [44, 46] one has to generate the three new functions f(-x, y), f(x,-y) and f(-x,-y) from the set of experimental data on the surface strain x, the surface strain rate y and the surface stress Δγ(t)=f(x,y)). This allows calculation of τ_1, τ_2 , τ_3 and τ_4 according to equation (12). After this calculation, the coefficients of the polynomial fitting of τ_n can be used for the calculation of the local viscoelastic moduli [46].

4. **Experiments and results**

4.1. *Adsorption and spread layers of polymers, micro- and nanoparticles*

Aqueous solutions of various polymers usually display a linear response to the surface expansion/contraction in a rather broad interval of surface strains. For example, the amplitude of the surface tension oscillations of concentrated (2 wt. %) solutions of sodium polystyrene sulfonate was proportional to the corresponding amplitude of the surface area oscillations up to ΔA/A = ± 15 %, at least [60]. On the other hand, the nonlinear behaviour of insoluble polymer monolayers at relatively low strains is a more frequent phenomenon. Hilles et al. studied in detail the deviations from linear rheological behaviour for insoluble Langmuir monolayers of a few hydrophobic nonionic polymers [61]. These deviations at a given oscillation amplitude increased in the sequence: poly(vinyl acetate) (PVAc), poly(octadecyl acrylate), poly(vinyl stearate), when the quality of the water-air interface as a solvent decreased. In the semidilute regime of polymer monolayers the deviations from linear behaviour appeared at lower surface deformations if the surface concentration was higher. The slope of the dependence of the dilational surface modulus on the strain amplitude increased monotonically with the strain. In the concentrated regime one could observe some new phenomena. The slope of the dependence of the dilational surface modulus on the surface strain could decrease at the increase of the strain amplitude if this quantity and the surface concentration exceeded some critical values. Simultaneously the surface pressure decreased continuously in the course of surface oscillations. The observed “pseudo-plastic behaviour” was probably a consequence of the irreversible elongation of macromolecules in the direction perpendicular to interface at the surface compression. Alternatively, the “pseudo-plastic behaviour” may be attributed to anisotropy of the surface properties after the elongation of macromolecules. During the subsequent surface expansion the system was unable to recover its initial conformation and the surface pressure took a lower value due to a decrease of the number of polymer contacts with the interface. As a result the surface pressure was lower after a cycle of compression/expansion than before it [61].

Hilles et al. also measured the dynamic surface elasticity of a spread monolayer of latex microparticles at the water – n-octane interface [61]. At the high relative strain amplitude of 22 % the system was weakly nonlinear with the THD parameter a little higher than 10. The behavior of a monolayer of polystyrene (PS) latex particles at the surface of 0.01 M sodium chloride solution proved to be more complicated [62]. The surface pressure started to increase at the compression when the distance between the particle centers was about twofold their diameters. The surface elastic modulus increased at the further compression and one could observe a transition to a closed packed monolayer when the modulus approached about 50 mN m^{-1}. After that the modulus increased rather abruptly to the values higher than 500 mN m^{-1}, went through a maximum and decreased to almost zero at the monolayer collapse (at surface pressures close to 50 mN/m). In the range of surface particle concentrations below the elasticity maximum, the system displayed a linear response to the oscillations of the surface area with the amplitude of 2 %. At higher surface concentrations, the THD parameter increased strongly indicating the generation of higher harmonics. The observed nonlinearity was a consequence of the high surface elasticity. The surface pressure reached the critical value of the monolayer collapse even at small surface compressions in the region beyond the elasticity maximum and did not change after that until the monolayer expansion when it started to decrease again (Fig. 2). The constancy of the surface pressure at the monolayer collapse indicated that the rate of compression/expansion was much less than the collapse rate. The surface rheological data together with the results of optical methods allowed determination of the collapse mechanism of the monolayer of PS microparticles [62]. Unlike the case of a monolayer of silica nanoparticles, where one could observe the formation of multilayers beyond the critical collapse pressure [63], the collapse of the monolayer of PS microparticles was due to the monolayer buckling.

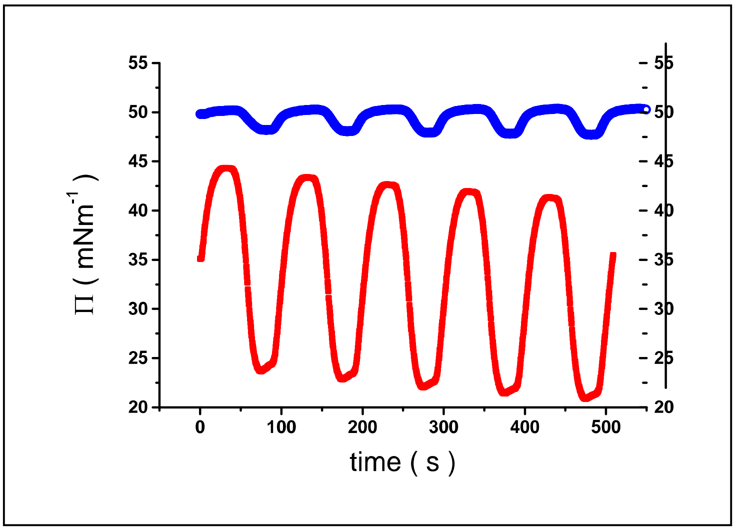

Fig. 2. Surface pressure oscillations for monolayers of PS particles on the surface of 0.01M NaCl solution at Π ≈ 32 mN/m (red closed squares) and at Π ≈ 49 mN/m (blue open circles).

In the case of spread and adsorbed monolayers of silica nanoparticles one can also observe a nonlinear response to surface area oscillations. Moreover, the addition of silica nanoparticles to insoluble lipid monolayers can enhance the nonlinearity of the system [64].

The negatively charged silica nanoparticles are hydrophilic but the adsorption of a cationic surfactant at their surface makes them amphiphilic and promotes their adsorption at the liquid-gas interface. The surface properties of the aqueous dispersion of 0.2 % in weight of monodisperse silica nanoparticles with the average diameter of 10 nm and with the addition of cetyltrimethylammonium bromide (CTAB) depend strongly on the surfactant concentration [63]. At the concentrations lower than 1 μM the surface elasticity is zero, the particles are hydrophilic and cannot be adsorbed at the liquid surface. In the surfactant concentration range from about 1.5 to 20 μM the surface dilational modulus almost does not depend on concentation and the system is characterized by linear rheological behavior at the changes of the surface area up to about 10 %. However, at the concentrations higher than 20 μM the behavior changes abruptly. The response to the oscillations of the surface area becomes nonlinear and the surface dilational modulus can reach extremely high values between 300–1000 mN m^{-1}, which depend strongly on the amplitude and duration of the surface oscillations. The surface tension after the oscillations was always lower than before them. When the oscillations stopped the surface tension started to increase and returned to its original value within a few hours. This means that the surface perturbations caused strong changes of the adsorption layer structure.

The observed nonlinear behavior has the following explanation. A dense rigid adsorption layer of nanoparticles forms at the surfactant concentrations higher than 20 µM. Even small surface compressions can cause the destruction of the layer and formation of some patches of almost incompressible multilayers. The subsequent expansion results in a splitting of the rigid layer (Fig. 3). New portions of nanoparticles from the subphase can fill in the empty space between the islands. The next compression leads to the formation of new aggregates and the process repeats again. The number of aggregates of high surface elasticity increases in the course of oscillations. The summation rule of Lucassen for a composite film containing incompressible aggregates shows that the film elasticity increases strongly with the increase of the surface area covered by the aggregates [65]. These ideas explain the extremely high surface elasticity and its strong dependence on the oscillation amplitude and the number of cycles of compression/expansion.

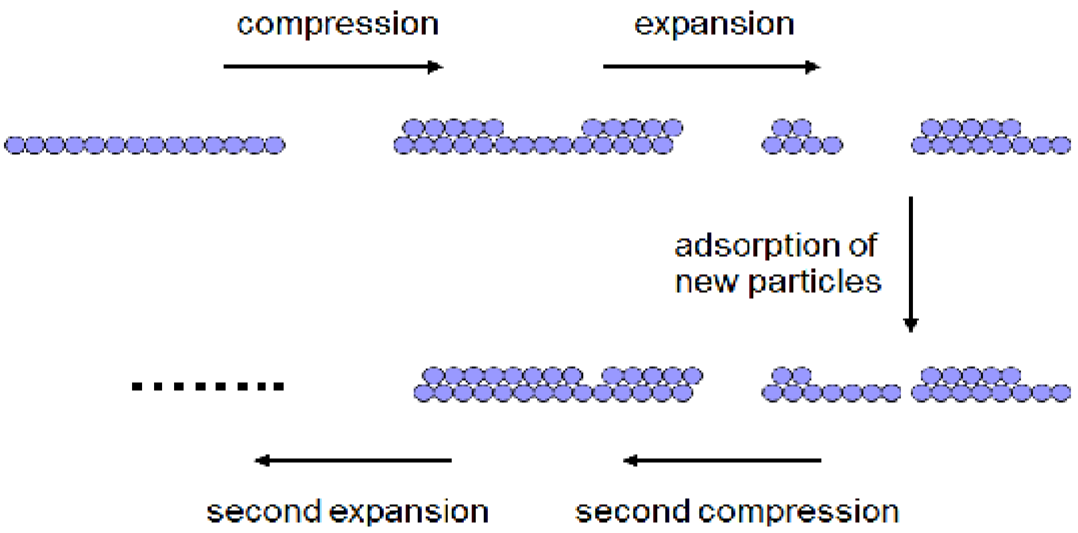

Fig. 3. A scheme of multilayer formation of silica nanoparticles in the course of oscillations of the surface area in the Langmuir trough.

The results of the Brewster angle microscopy agree with the conclusions from rheological measurements. At surfactant concentration below 20 µM, the adsorption layer is homogeneous and its morphology does not change during slight oscillations. Beyond this concentration the layer is also homogeneous in the system without external perturbations but after slight deformations one can see some surface aggregates. They are stable and do not change their position in the layer during a few hours. This observation indicates the high density of the adsorption layer. The regions between the multilayer aggregates are also filled by nanoparticles. The further periodical compressions and expansions of the surface result in a splitting of the aggregates. Their number increases and their size decreases. The morphology of the surface layer in this concentration range depends on the amplitude and duration of the surface oscillations leading to a nonlinear response to surface compression/expansion [63].

4.2. *Solutions of polyelectrolyte/surfactant complexes*

The mixed adsorption layers of polyelectrolytes and oppositely charged surfactants at the liquid-gas interface frequently display a nonlinear response to expansion and contraction. Ritacco et al. showed that this behaviour can be connected with the heterogeneity of the layer [53]. Even at slight compressions (< 10 %) the thickness of the layer of a copolymer of polyacrylamidopropane sulfonate with polyacrylamide and dodecyltrimethylammonium bromide (DTAB) became inhomogeneous at the macroscopic scale leading to poor reproducibility of the dynamic surface properties and the disagreement between the results of different methods. Similar behaviour was also observed for the layers of a copolymer of sodium 2-acrylamido-2-methyl-1-propansulfonate with N-isopropylacrylamide and DTAB [54].

Later on, a strong nonlinear response was discovered for the mixed solutions of poly(diallyldimethylammonium chloride) with sodium dodecyl sulfate (PDADMAC/SDS) in a narrow surfactant concentration range close to the concentration of polyelectrolyte monomers, where the THD parameter increased a few times [50]. In this range the surface tension increased during surface expansion but almost did not change upon compression. The authors assumed that the surface layer contained some three-dimensional microparticles (polyelectrolyte/surfactant aggregates) in this concentration range and the main relaxation process consisted in the matter exchange between these particles and the surrounding adsorption layer. The characteristic time of this process was less than the oscillation period when the surface tension approached a critical value of about 36.4 mN m^{-1} but the relaxation process was frozen at higher surface tensions probably due to the decrease of the number of aggregates.

Arriaga et al. used similar ideas to explain the nonlinear rheological behavior of lipid monolayers subjected to a dilational deformation [56]. The assumed matter exchange in this case was between an expanded continuous two-dimensional phase and condensed domains in it. A model based on the

Fick's law for surface diffusion gave a possibility to reproduce some features of the observed nonlinear effects.

The nonlinear rheological behavior of the mixed solutions of polyacrylic acid with alkyltrimethylammonium bromides [51, 52], polymethacrylic acid with DTAB [51] and polyethylenimine with SDS [57] was studied in more detail. It was shown that one can divide the whole concentration range of surfactant concentrations into four regions characterized by different kinetic dependencies of the dilational modulus. At low concentrations (region I) the kinetic dependencies were monotonical, the surface tension oscillations were sinusoidal and the surface elasticity reached high values at the approach to equilibrium. Beyond a certain critical concentration the behaviour changed abruptly (region II). The surface dilational modulus near equilibrium dropped abruptly and its kinetic dependencies became non-monotonical (Fig. 4). The surface elasticity reached high values in a short time but decreased strongly after that. Simultaneously one can observe a transition from pure harmonical oscillations to nonlinear behaviour (Fig. 5) with a strong increase of the THD (Fig. 4). The observed kinetic dependencies allow tracing the changes of the adsorption layer structure in the course of adsorption. The adsorption layer becomes heterogeneous if the surface pressure reaches a certain critical value leading to a new mechanism of the relaxation of surface stresses at the expense of matter exchange between the aggregates and surrounding monolayer. The gradual increase of the size and/or number of aggregates results in stronger deviations from linear behaviour, i.e. the increase of higher harmonics of the surface tension oscillations (Figs. 4, 5 and 6). The transparency of polyacid/DTAB solutions at concentrations corresponding to the nonlinear surface rheological behaviour excludes a possibility of the influence of any macroscopic aggregates from the bulk phase on the surface tension oscillations and the described effects have to be induced by microaggregates at the surface. Note that one can observe the aggregate formation in the adsorption layer of polyelectrolyte/surfactant complexes by the ellipsometry [50, 58] and atomic force microscopy at surfactant concentrations beyond the region of the abrupt drop of the dynamic surface elasticity [59].

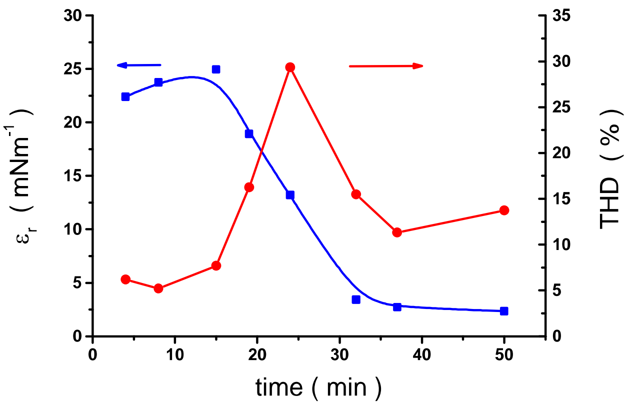

Fig. 4. The kinetic dependencies of the real part, ε_r , of the surface dilational modulus (blue squares) and total harmonic distortion, THD, (red circles) for PAA/DTAB solutions at PAA concentration of 0.005 wt % and DTAB concentration of 4×10^{-3} M.

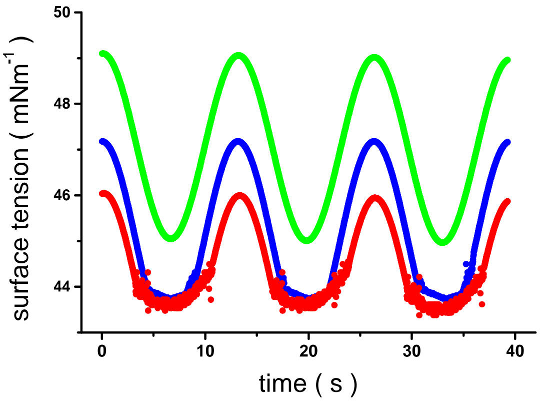

Fig. 5. Surface tension oscillations for PAA/DTAB solutions at a frequency of 0.075 Hz, PAA concentration of 0.005 wt % and DTAB concentration of 4×10^{-3} M after 15 (upper green curve), 19 (central blue curve), and 24 min (lower red curve).

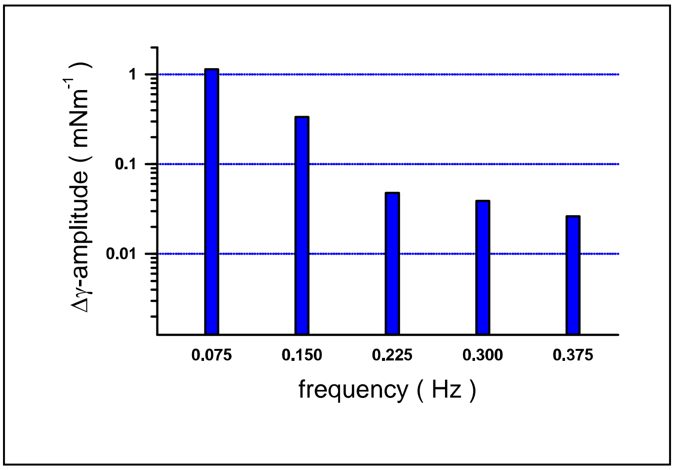

Fig. 6. Spectrum of the surface tension oscillations for PAA/DTAB solutions at a frequency of 0.075 Hz, PAA concentration of 0.005 wt % and DTAB concentration of 4 × 10^{-3} M after 24 min (lower red curve in Fig.5a). Total harmonic distortion THD% = 29.83 .

At higher surfactant concentrations (region III) the size and/or number of aggregates increases further in the course of adsorption. This leads to stronger interactions between the aggregates, the surface pressure increases and the surface elasticity starts to increase again [51, 52]. At a certain critical surface pressure some aggregates can be displaced from the surface into subphase. In this case the surface stresses can be relaxed at the expense of the matter exchange between the two layers of aggregates and the surface elasticity goes through the second local maximum (Fig. 7). At even higher concentrations (region IV) the surfactant forms micelles in the bulk phase and the polyelectrolyte is solubilized in them. The surface properties are determined by the adsorption of surfactant monomers and the surface tension oscillations become sinusoidal again.

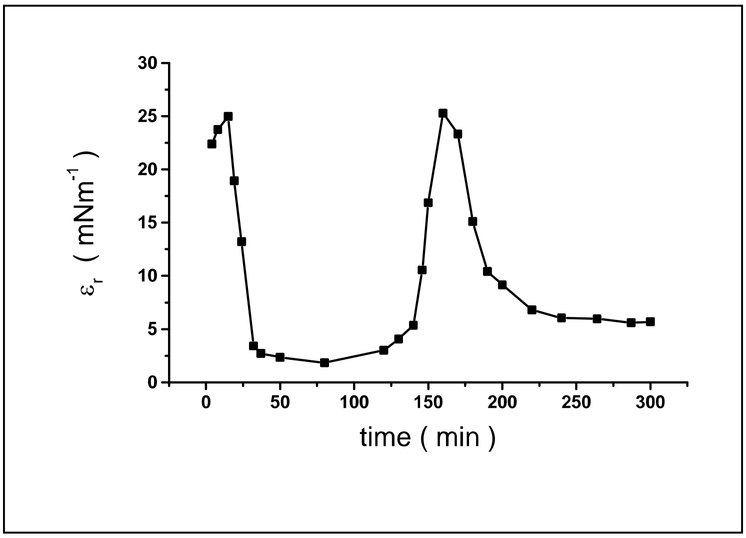

Fig. 7. The kinetic dependencies of the real part, ε_r , of the surface dilational modulus (squares) for PAA/DTAB solutions at PAA concentration of 0.005 wt % and DTAB concentration of 4×10^{-3} M.

The application of the stress decomposition method confirms the obtained conclusions. The expansion of the surface tension oscillations into four components allows calculation of the local surface elasticities, for example, for PAA/DTAB solutions at pH 9.2 (Fig. 8). The local surface elasticity at the maximal surface compression differs significantly from the value at the maximal expansion. In the latter case the adsorption layer is almost pure elastic. The real part of the surface dilational modulus is 24 mNm^{-1} and the imaginary part is 1 mNm^{-1}. These values are characteristic for the homogeneous adsorption layer at surface pressures just before the aggregate formation. At the same time, the layer at the maximal compression is viscoelastic with the real part of the dilational modulus of about 7 mNm^{-1} and the imaginary part of 6 mNm^{-1}. These data agree with the estimations from Fig. 1 and show that the analysis of the nonlinear system response to surface compression and expansion gives a possibility to obtain auxiliary information on the adsorption layer structure.

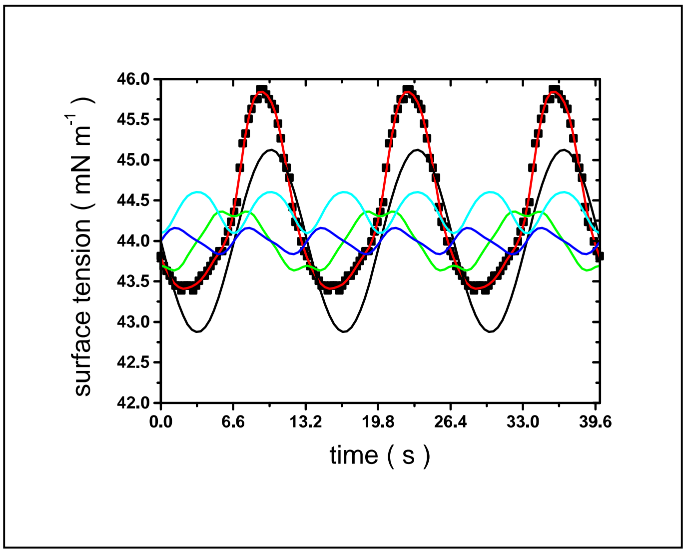

Fig. 8. The application of the stress decomposition method to surface tension oscillations for PAA/DTAB solutions at a frequency of 0.075 Hz, PAA concentration of 0.005 wt % and DTAB concentration of 4 × 10^{-3} M. The pure elastic τ_1, pure viscous τ_2, two viscoelastic τ_3 and τ_4 components are given in black, green, blue and cyan colors, respectively. The sum of all the components is a red line.

5. Conclusions

The interfacial adsorption layers exhibit a nonlinear dilational viscoelasticity, with memory, in dependence of the deformation amplitude.

Nonequilibrium thermodynamic formulations allow the phenomenology of interfacial viscoelasticity to be interpreted either for small and large area deformations, providing a powerful theoretical framework to investigate the dynamics of disperse multiphase systems.

A number of mathematical tools can be applied for quantifying the nonlinear interfacial viscoelastic behaviour, complementing the nonequilibrium thermodynamics. The Volterra series appears as a good mathematical modelling tool as it is a generalisation, including the memory effects, of the Taylor's series. Actually in principle the Volterra series extends the description of the interfacial viscoelastic properties to the nonlinear domain by *n*-th order frequency response functions (or *n*-th impulse response functions), in addition to the interfacial dilational modulus pertaining to the linear domain, however up-to-now no specific experimental procedure for determining the higher-order properties is devised in the surface-science field. In practice, Fourier-series analysis (together with the relevant THD-parameter) and the stress decomposition method appear useful complementary mathematical tools for a quantitative characterization of the nonlinear interfacial rheological behaviour.

The Fourier analysis gives a global (or intracycle) information on frequency dependence (i.e., on the amplitude of the harmonics components) of the dynamic surface properties, while the stress decomposition method analyzes the intercycle nonlinearities of the system in four sections of the oscillation cycle.

Adsorption and spread layers of polymers, polyelectrolyte/surfactant complexes and nanoparticles show notable nonlinear interfacial viscoelastic behaviour. The observed nonlinear findings reveal formation of complexes, patches, and other different interfacial structures.

Acknowledgements

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Figure captions

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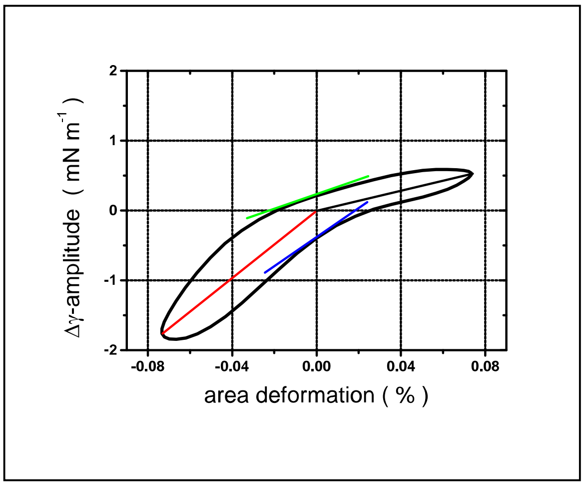
Figures



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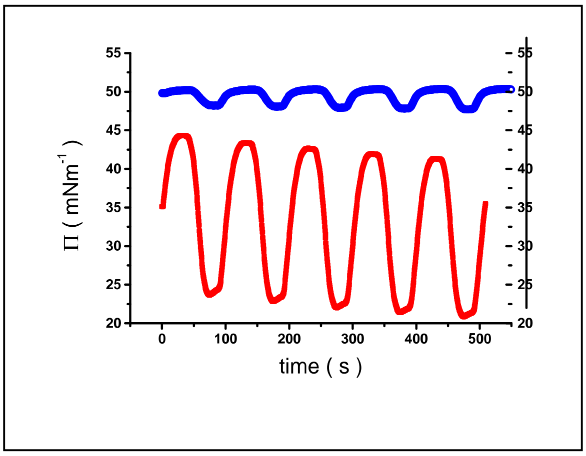

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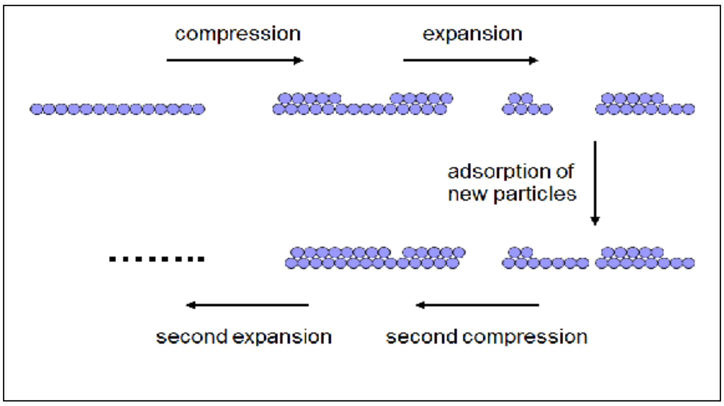


Fig. 3. A scheme of multilayer formation of silica nanoparticles in the course of oscillations of the surface area in the Langmuir trough.

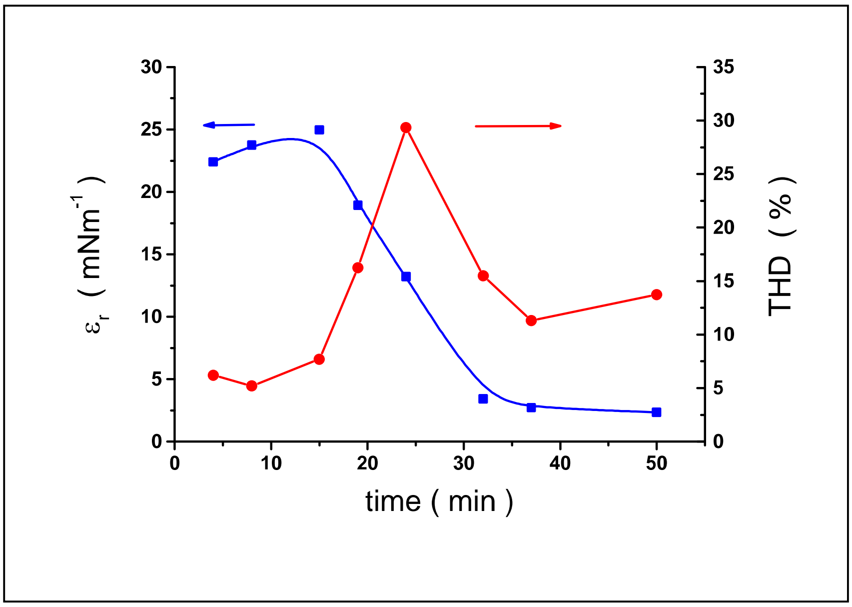


Fig. 4. The kinetic dependencies of the real part, ε_r , of the surface dilational modulus (blue squares) and total harmonic distortion, THD, (red circles) for PAA/DTAB solutions at PAA concentration of 0.005 wt % and DTAB concentration of 4×10^{-3} M.

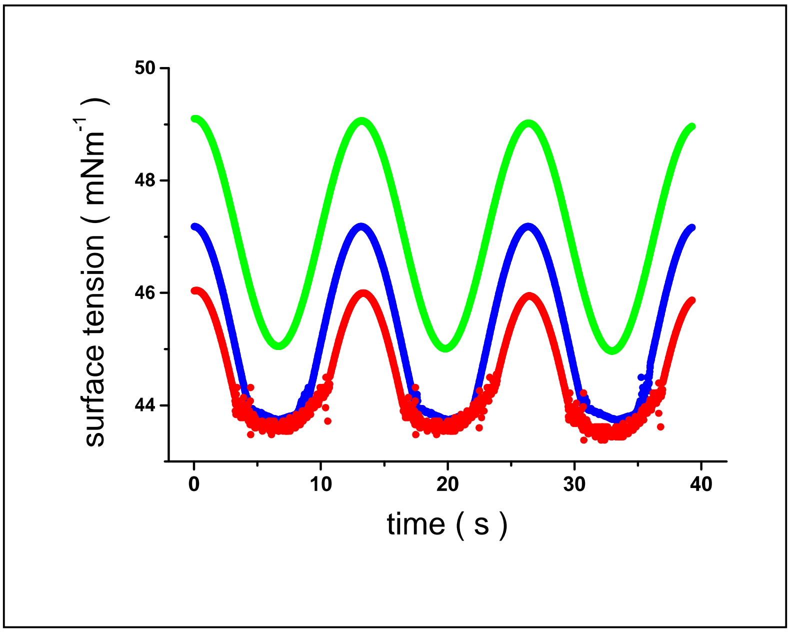


Fig. 5. Surface tension oscillations for PAA/DTAB solutions at a frequency of 0.075 Hz, PAA concentration of 0.005 wt % and DTAB concentration of 4 × 10^{-3} M after 15 (upper green curve), 19 (central blue curve), and 24 min (lower red curve).

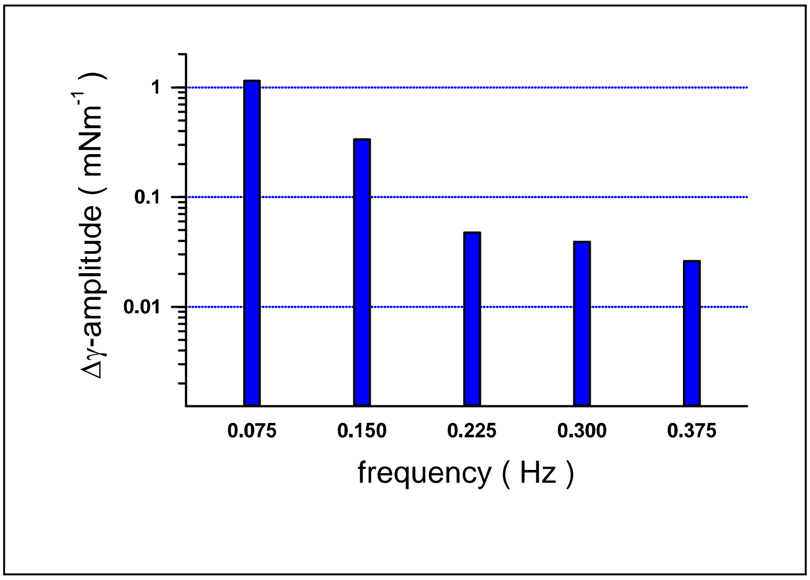


Fig. 6. Spectrum of the surface tension oscillations for PAA/DTAB solutions at a frequency of 0.075 Hz, PAA concentration of 0.005 wt % and DTAB concentration of 4 × 10^{-3} M after 24 min (lower red curve in Fig.5). Total harmonic distortion THD% = 29.83 .

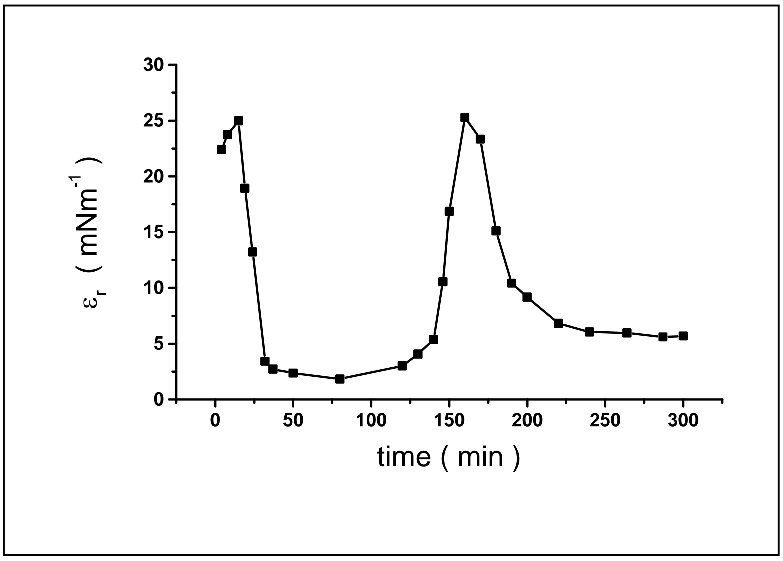


Fig. 7. The kinetic dependencies of the real part, ε_r , of the surface dilational modulus (squares) for PAA/DTAB solutions at PAA concentration of 0.005 wt % and DTAB concentration of 4 × 10^{-3} M.

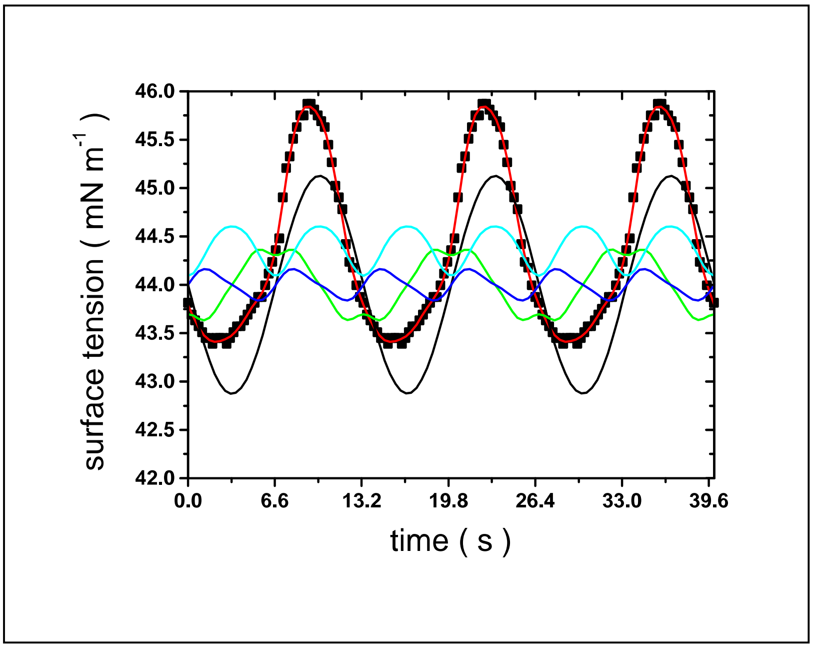


Fig. 8. The application of the stress decomposition method to surface tension oscillations for PAA/DTAB solutions at a frequency of 0.075 Hz, PAA concentration of 0.005 wt % and DTAB concentration of 4 × 10^{-3} M. The pure elastic τ_1, pure viscous τ_2, two viscoelastic τ_3 and τ_4 components are given in black, green, blue and cyan colors, respectively. The sum of all the components is a red line.

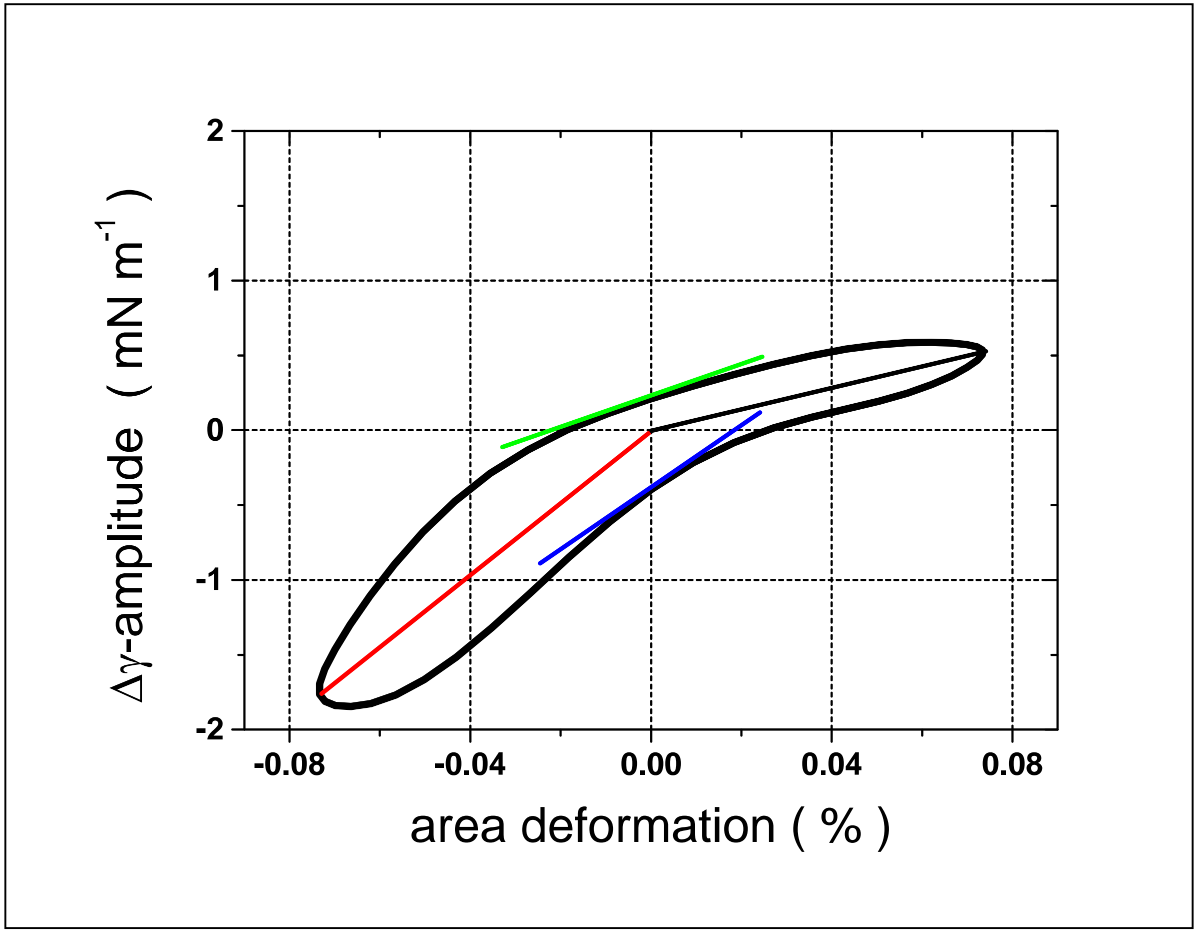
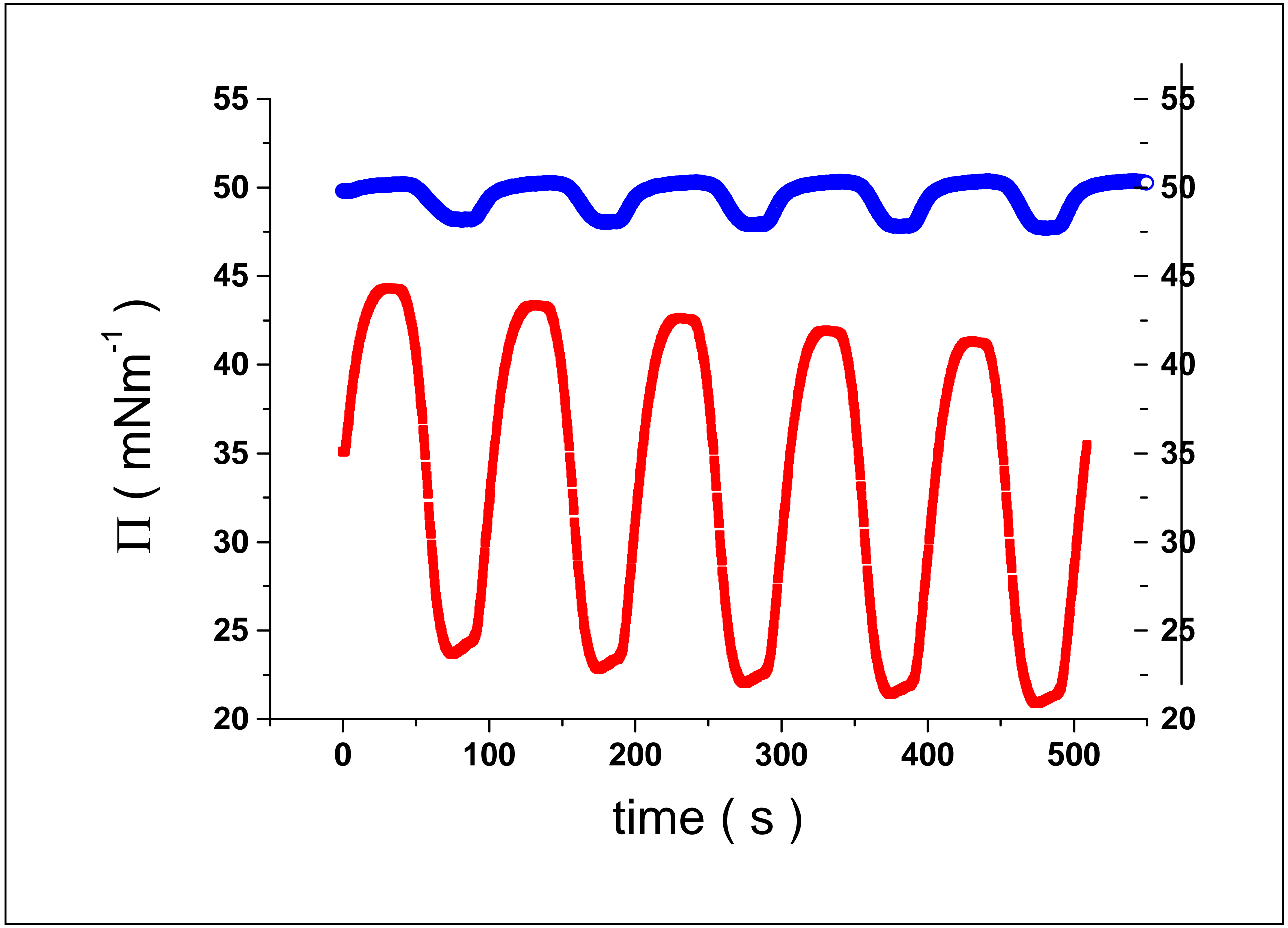


Fig. 1. The dependence of the change of surface tension on relative changes of the surface area (Lissajous plot) for mixed solutions of polyacrylic acid and dodecyltrimethyl ammonium bromide at pH 9.2. The tangent slope of the lines corresponds to the real part of the interfacial dilational modulus at maximal compression (black line), maximal expansion (red line), and at minimum strain in the course of compression (blue line), in the course of expansion (green line).

Figure(s)



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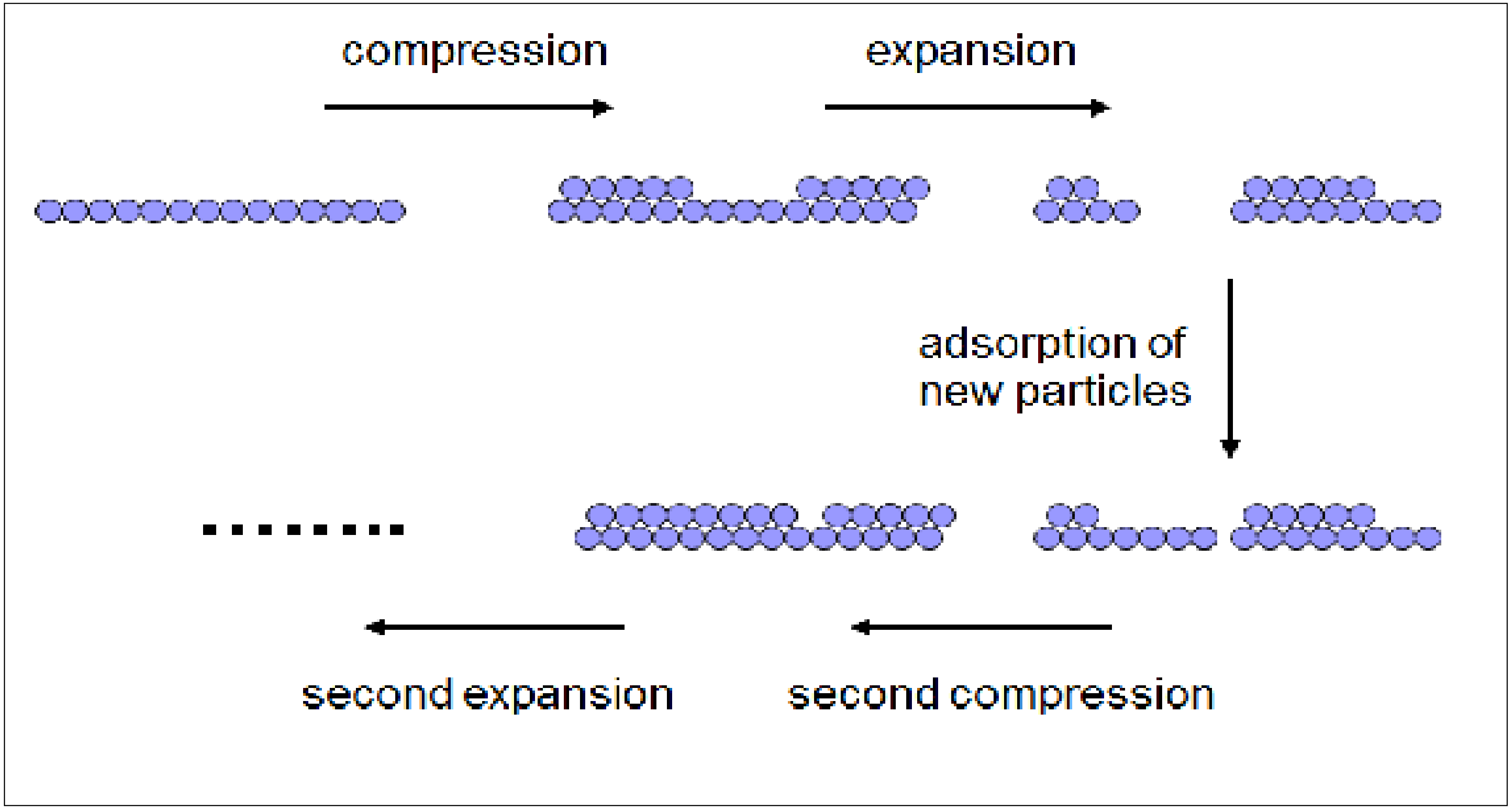

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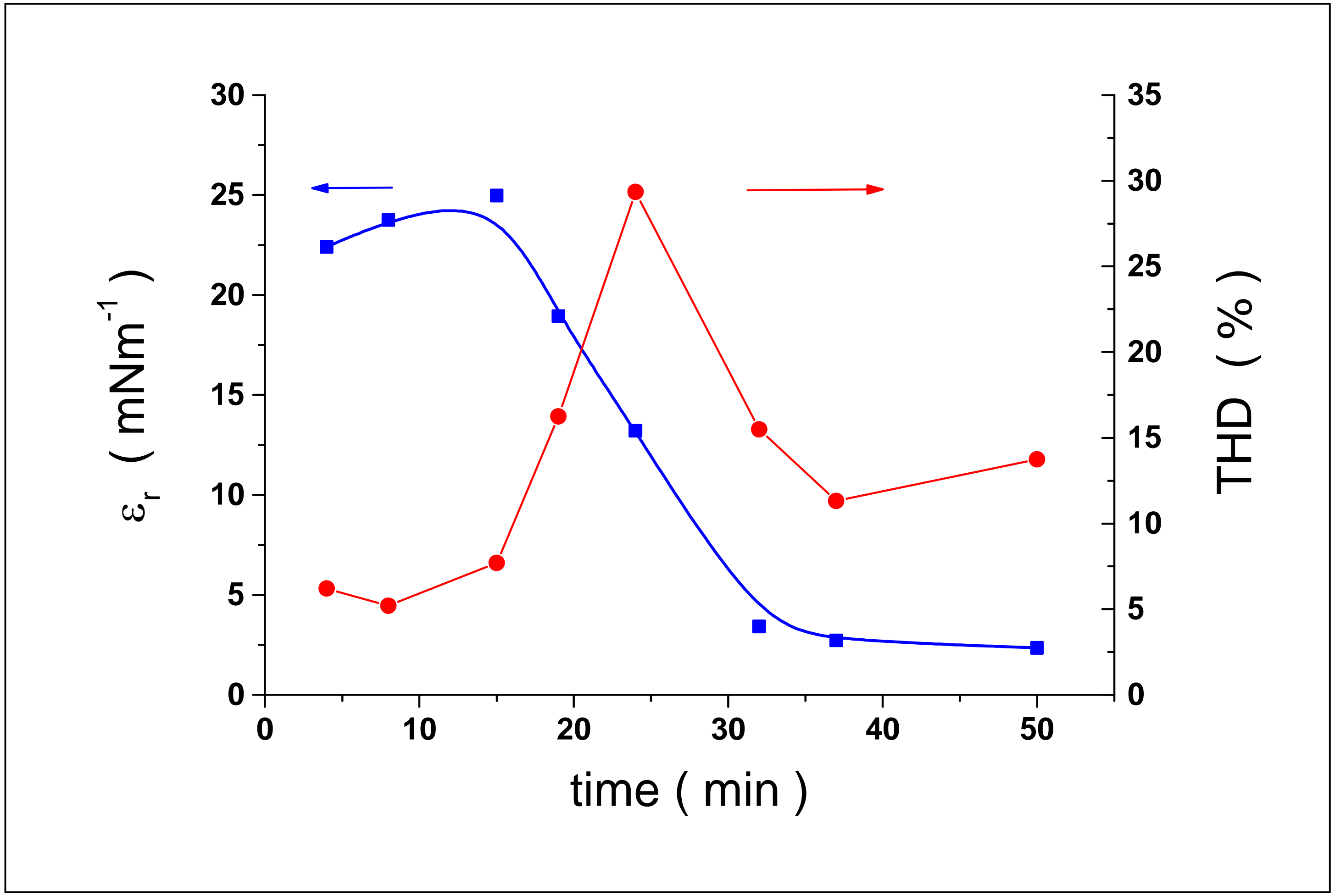

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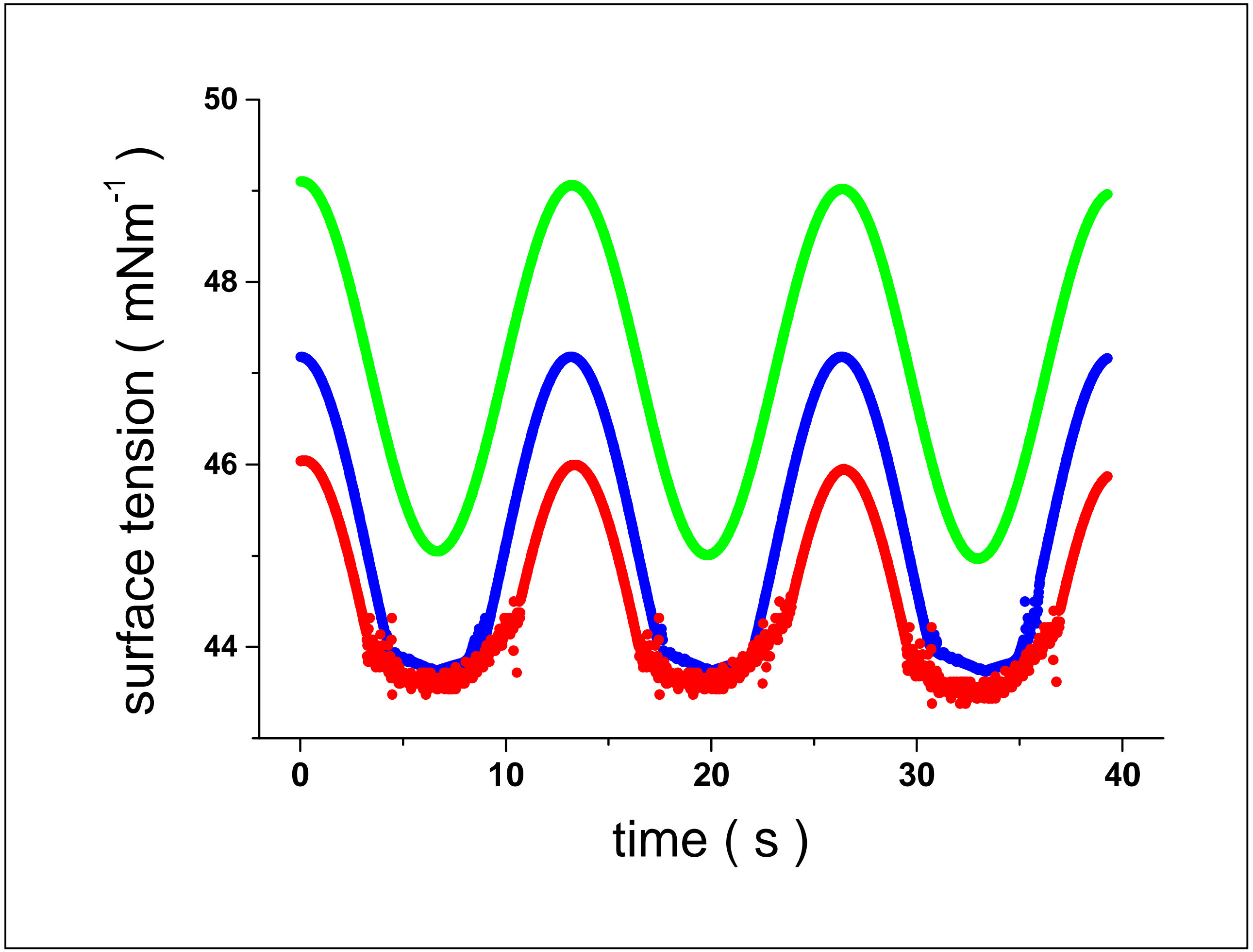

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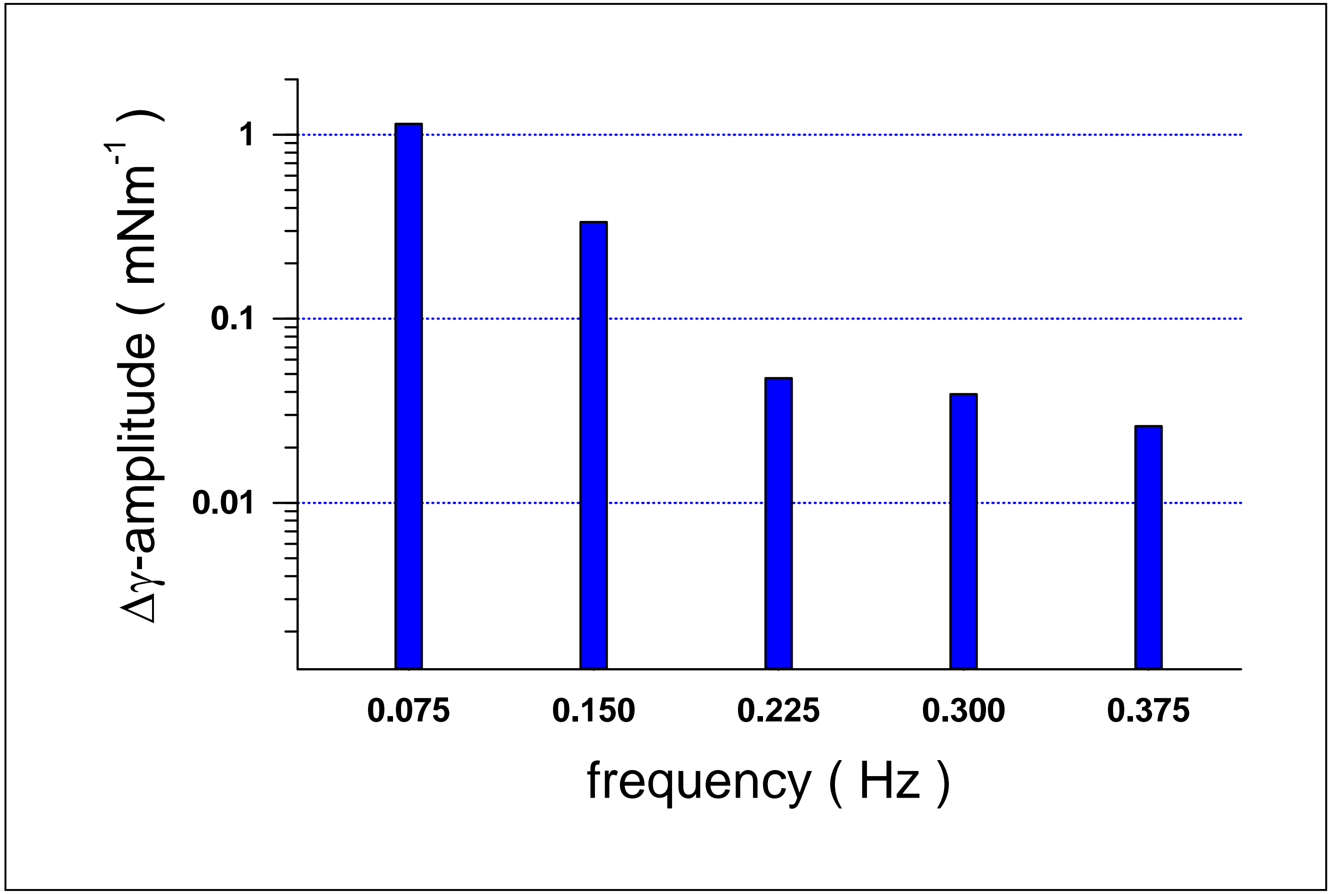

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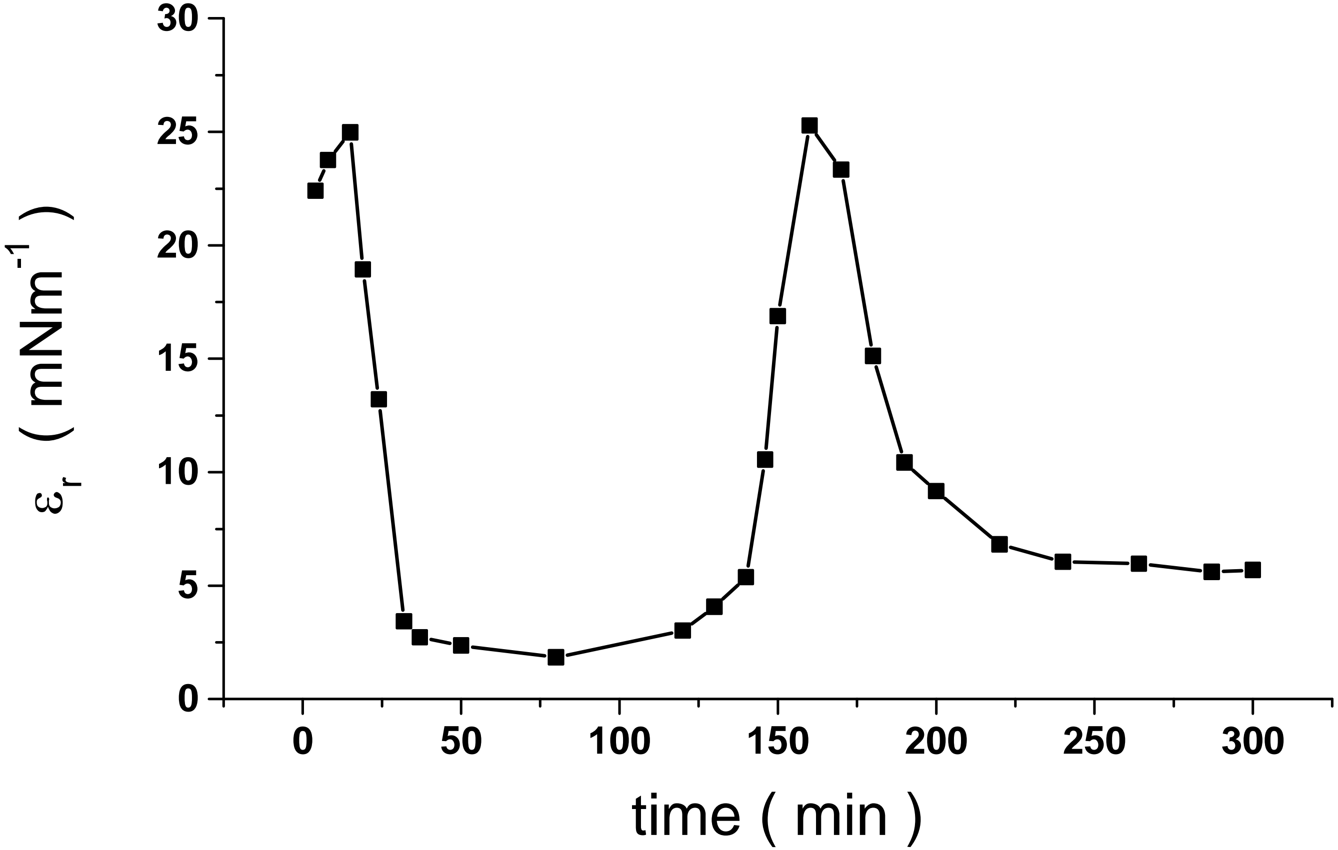

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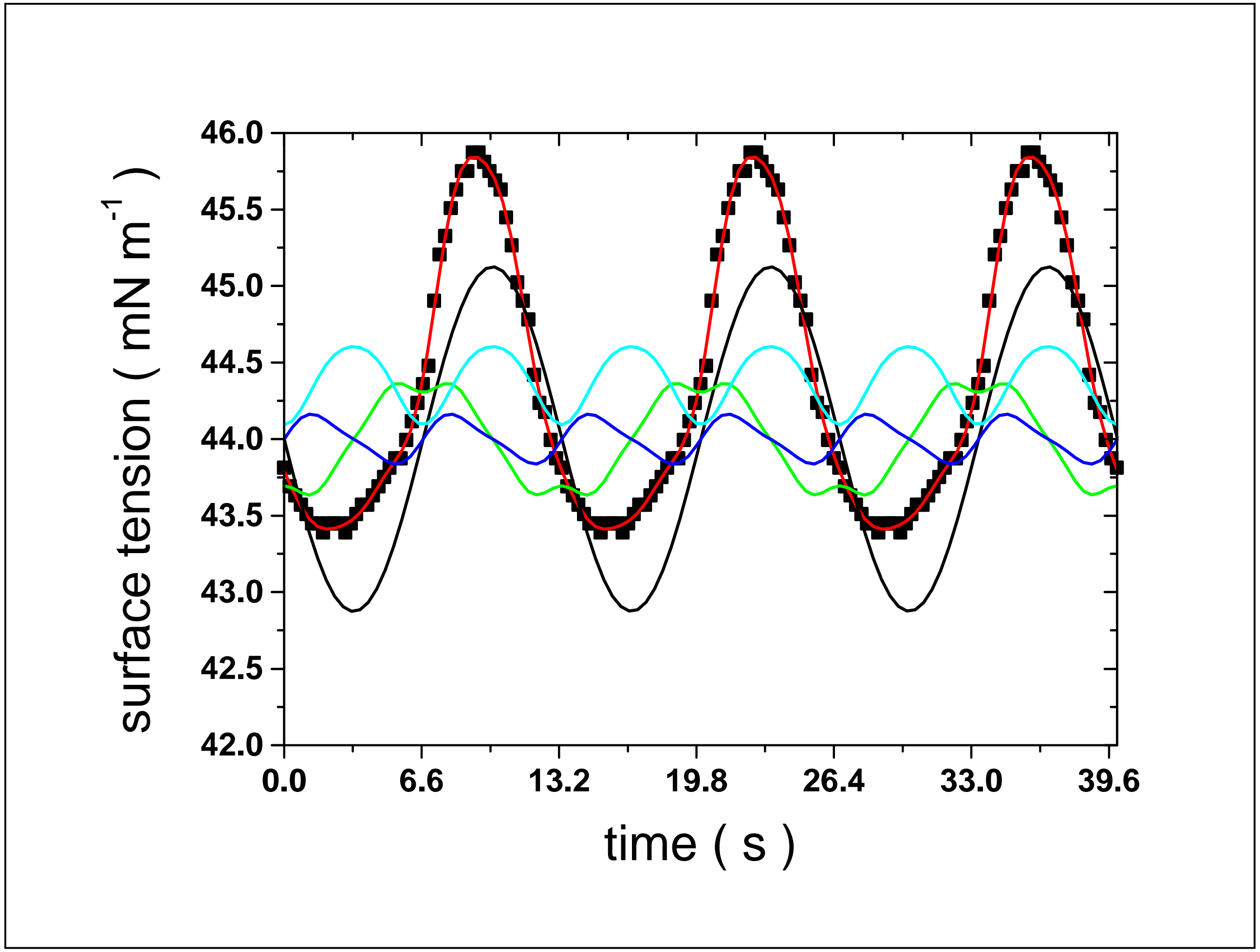

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