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## Dilational rheology of monolayers of nano- and micropaticles at the liquid-fluid interfaces

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Application of the methods of the dilational surface rheology to adsorbed and spread layers of nano- and microparticles at liquid – fluid interfaces gives insight in the structure and formation mechanism of the layers. This is especially important in view of the limited applicability of standard experimental methods of the interface science to heterogeneous surface layers. The literature in this field almost has doubled for the last few years and recent articles are discussed in this review. All the systems are divided into two groups of the layers of solid and soft particles depending on the influence of the particle deformability on surface properties. In the latter case the peculiarities of surface dilational rheological properties of adsorbed and spread layers of polylelctrolyte/surfactant aggregates, solid particles grafted by polymers, polymer microgels, and protein fibrils and microgelsare briefly discussed together with the merits and drawbacks of the existing experimental methods of the surface dilational theology.

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#### Introduction

A broad interest in emulsions and foams stabilized by nanoand microparticles for the last two decades is mainly caused by the possibility to create new materials on their basis  $[1-3]$ . The surface properties are of paramount importance in these systems because of the large area of liquid  $-$  fluid interfaces. Among a few experimental techniques used for the investigation of spread and adsorbed layers of particles, the methods of surface rheology attract special attention. Firstly, the surface rheological properties are a key factor in the stability of foams, emulsions and bijels (bicontinuous Pickering emulsions) [\[3,4](#page--1-0)',[5](#page--1-0)']. Secondly these properties are extremely sensitive to the interactions between particles in the surface layer and the kinetics of relaxation processes at the interface giving possibilities to study the mechanism of these processes and the layer structure  $[4^{\circ},5^{\circ},6]$  $[4^{\circ},5^{\circ},6]$  $[4^{\circ},5^{\circ},6]$  $[4^{\circ},5^{\circ},6]$  $[4^{\circ},5^{\circ},6]$  $[4^{\circ},5^{\circ},6]$  $[4^{\circ},5^{\circ},6]$ .

Any in-plane surface deformation can be decomposed into shear and dilational components. Therefore, one can distinguish between shear and dilational surface properties. The former properties are probably more sensitive to the interactions between the kinetic units in the system, while the latter ones lend themselves easier to theoretical description and thereby to quantitative interpretation  $[6-9]$ . Only the dilational surface properties are a subject of this review.

Dilational rheological properties of adsorbed and spread layers of nano- and microparticles have been widely studied during the last decades  $[3,4^{\circ},5^{\circ},6,10-13^{\circ}-21^{\circ}-32^{\circ}-36^{\circ}]$  $[3,4^{\circ},5^{\circ},6,10-13^{\circ}-21^{\circ}-32^{\circ}-36^{\circ}]$ [37](#page--1-0)<sup>•</sup>,[38\]](#page--1-0). The reviews [[4](#page--1-0)<sup>•</sup>,[5](#page--1-0)<sup>•</sup>] consider the articles published approximately before 2014. A very recent review [\[3](#page--1-0)] is devoted mainly to the shear surface properties, quasiequilibrium dilational properties calculated from the compression isotherms and to the problems of the oscillating drop method. Recent results on the dynamic dilational surface properties of the systems containing nano- and microparticles are under consideration below.

The next section discusses briefly the main concepts of the dilational surface rheology and the peculiarities of the application of surface rheological methods to particle adsorption layers.

The main part of the given work consists of two sections devoted to the dilational properties of the layers of solid and soft particles correspondingly. This discussion allows us finally to come to conclusions on the problems and perspectives of the dilational surface rheology of the layers of nano- and microparticles.

#### Dynamic elasticity of particle layers at the liquid-fluid interface

The system response to an infinitesimal compression or expansion of the liquid surface, the increment of surface tension  $\delta \gamma$ , depends in general case not only on the surface deformation (the change ofthe surface area δA) at time t but also on the deformations at any preceding times. This leads to an integral relation between the surface stress and the relative surface strain  $\delta A/A$  [[39](#page--1-0)]. In the case of an infinitesimal lsinusoidal surface deformations  $\delta A = (\delta A)_0 e^{i\omega t}$ , where  $(\delta A)_0$  is the amplitude of deformation and  $\omega$  is the angular frequency, the response is also sinusoidal  $\delta \gamma = (\delta \gamma)_0 e^{i \omega t}$ . The governing equation reduces to the following linear relation

$$
E = \frac{A\delta\gamma}{\delta A}
$$

where E is the complex dynamic dilational surface elasticity, also called the dilational modulus.

One can consider this relation as a definition of the dynamic surface elasticity for small harmonical oscillations of the surface area. In the case of a pure elastic system E becomes a real quantity and coincides with the static surface elasticity. In a more general case E depends not only on the amplitudes of the surface tension and the surface area oscillations but also on the phase shift between these two quantities and describes the viscoelastic behavior of the surface layer. The application of irreversible thermodynamics gives a possibility to connect E with kinetic coefficients of the relaxation processes in the surface layer and with its equilibrium parameters [\[9\]](#page--1-0). The theory of the surface elasticity of the layers of solid particles was developed by Lucassen [\[7](#page--1-0)] and later by Miller et al. on a different basis [\[40](#page--1-0)]. Pinaud et al. showed that the properties of the adsorption layer of soft polymer particles are determined by dangling chains of the particle shell [\[36](#page--1-0)<sup>••</sup>]. In this case one can apply the theory of the surface viscoelasticity of solutions of linear flexible polymers  $[8,9]$  $[8,9]$  to the particle layers at the interface.

A few methods have been proposed to measure the dilational surface rheological properties. The most popular one is probably the oscillating drop method based on the use of a commercial drop shape tensiometer [\[4](#page--1-0)\*[,24](#page--1-0),[32](#page--1-0)\*[,34](#page--1-0)-36\*\*[,38](#page--1-0)]. This method gives reliable results for solutions of conventional surfactants at low frequencies, <0.1 or 1 Hz depending on the equipment. At higher frequencies the equilibrium Young - Laplace equation does not describe the shape of a pending drop. At the same time, this method must be used with caution for dispersions of nano- and microparticles [\[3\]](#page--1-0). The deformations of the drop surface are not purely dilational and the local deformation can depend on the position on the drop surface. As a result shear stresses can influence the drop shape. This effect is usually negligible for solutions of conventional surfactants but can be increased for particle dispersions. The drop surface can be rigid at high surface concentrations of particles and the Young – Laplace equation needs modification in this case. Manga et al. showed that the particle sedimentation can result in their accumulation at the bottom of the drop leading to the distortion of the drop and thereby of the measured effective surface tension [[32](#page--1-0)°]. The curvature of the drop surface can have also other effects, for example, the ejections of some particles in the region of high curvature [\[41,42](#page--1-0)].

The oscillating barrier method is free from some complicating effects, which are connected with curved surface. In this case the liquid surface area in a Langmuir trough changes due to the motion of one or two hydrophobic barriers gliding back and forth along polished brims of the trough  $[4^{\circ},6,9]$  $[4^{\circ},6,9]$  $[4^{\circ},6,9]$  $[4^{\circ},6,9]$ . The corresponding oscillations of the effective surface tension are determined by the Wilhelmy plate method and in general case also have a contribution from surface shear stresses. This effect depends on the oscillation frequency and can be noticeable for high surface concentrations of the particles. The most adsorbed and spread layers of the particles are elastic, and the dynamic surface elasticity measured by the oscillating barrier method almost coincides with the quasistatic surface elasticity of the layer, which can be calculated from the surface pressure isotherm. Therefore some authors prefer to limit themselves only by the quasistatic measurements  $[3,37,43,44]$  $[3,37,43,44]$  $[3,37,43,44]$ . This is a reasonable approach at relatively low surface pressures but one can take into account that the dynamic surface elasticity can differ significantly from the quasistatic value at high surface pressures [[33\]](#page--1-0).

To get rid from the shear contribution to the effective surface elasticity and to measure pure dilational quantity, other experimental methods must be applied, for example, the oscillating ring method [[6](#page--1-0)]. In this case a glass ring partly immersed into the liquid oscillates along its axis, which is perpendicular to the liquid surface. The internal surface of the ring is roughened to improve wetting. The ring oscillations result in regular oscillations of the meniscus inside the ring and thereby of the surface area. The induced oscillations of the surface tension are also measured by the Wilhelmy plate. In this case the area deformations are more homogeneous and one can neglect the influence of shear surface properties.

#### Layers of solid particles at the liquid  $-$  fluid interfaces

#### Particle layers without surfactants

The first studies of the properties of particle monolayers at liquid - fluid interfaces are mainly based on the determination of surface pressure isotherms [[45,46\]](#page--1-0). To the best of our knowledge the first investigation of the dilational dynamic surface elasticity of a monolayer of polymer microparticles belongs to Kobayashi and Kawaguchi [\[47](#page--1-0)]. The dynamic surface elasticity of a monolayer of particles prepared by copolymerization of styrene and diacetone acrylamide changed

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