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Particle laden fluid interfaces: Dynamics and interfacial rheology



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ABSTRACT

We review the dynamics of particle laden interfaces, both particle monolayers and particle + surfactant monolayers. We also discuss the use of the Brownian motion of microparticles trapped at fluid interfaces for measuring the shear rheology of surfactant and polymer monolayers. We describe the basic concepts of interfacial rheology and the different experimental methods for measuring both dilational and shear surface complex moduli over a broad range of frequencies, with emphasis in the micro-rheology methods. In the case of particles trapped at interfaces the calculation of the diffusion coefficient from the Brownian trajectories of the particles is calculated as a function of particle surface concentration. We describe in detail the calculation in the case of subdiffusive particle dynamics. A comprehensive review of dilational and shear rheology of particle monolayers and particle + surfactant monolayers is presented. Finally the advantages and current open problems of the use of the Brownian motion of microparticles for calculating the shear complex modulus of monolayers are described in detail.

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1. Introduction

Interfaces play a dominant role in the behavior of many complex fluids. Interfacial rheology has been found to be a key factor in the stability of foams and emulsions, compatibilization of polymer blends, flotation technology, fusion of vesicles, mass transport through interfaces, drug delivery from micro- and nanocapsules, etc. [1,2]. Interfaces are also of fundamental importance to understand living organisms, in which many of processes involve membranes and the transport of matter through them as well as soft solid surfaces and the adsorption of molecules onto them [3]. In most cases the stability of interfaces is controlled by surfactants, either natural or synthetic. In the case of industrial processes, the environmental regulations in the EU are becoming stricter, and conventional synthetic surfactants have to be substituted by environmentally friendly chemicals. A very interesting possibility is to stabilize the interfaces using natural or biocompatible synthetic micro- or nanoparticles trapped at the interfaces. Indeed, particle laden interfaces have already been studied in very different systems, including drug delivery, nanocapsule stabilization, ice cream production, froth, or, as already mentioned, stabilization of foams and emulsions [1]. In spite of their interest, these systems pose many academic challenges, and current knowledge is still far from being appropriate for the correct design of technological processes. In part, one may expect that particles at interfaces have rather different characteristics depending on their size. For instance, diffusion in and out the fluid interface is very effective in the case of nanoparticles, including globular proteins. However, microparticles may be trapped almost irreversibly, depending on the interface/particle contact angle. For the sake of example, for particle of 1 µm diameter, and contact angle $\theta = 70^{\circ}$ (the value of silica particles at the water/n-octane interface, the trapping Gibbs energy is higher than $10^6 \cdot k_B T$ [4]. In this case the diffusion of the particles in and out the interface is suppressed even for long experimental times unless convection exists. As a consequence, the system very frequently is in a non-equilibrium state. Moreover, while for small systems the surface tension, γ , concept is a well-defined thermodynamic variable, for microparticles y must be understood as an adsorption Gibbs energy [4]. However, other physical effects may be involved in such adsorption Gibbs energy, e.g. interactions of particles with surfactants, and therefore hereinafter we will refer to the surface tension, which is the quantity experimentally measured [5]. A further complication in particles trapped at fluid interfaces is that the interaction between them is more complex than in bulk. This is because in addition of direct forces (capillary, steric, electrostatic, magnetic, van der Waals, etc.), hydrodynamic interactions mediated by the surrounding fluid are involved [6,7]. Both the structure and the dynamics of the particles at the interface have been found to determine their ability for stabilizing foams and emulsions, and to control the transfer of matter through the interface [8]. Obviously the structure and the dynamics are controlled by the interaction between particles.

The situation is more complicated when the interface contains mixtures of surfactants and particles, a rather frequent situation in real technological processes and in biological systems [9]. In this case, understanding the interfacial rheology over a broad range of frequency, and of the adsorption/desorption kinetics is absolutely necessary. For instance, the Ostwald-ripening mechanism of emulsion destabilization [10], or the draining mechanism of foam destabilization [11], are coupled to the interface viscosity and to the adsorption/desorption kinetics of particles and surfactants at the interface, and of the surfactants at the particle surface.

Even for a fluid interface at least two dynamic modes exist: a capillary (out of plane) mode, and the in-plane mode, which contains dilational (or extensional) and shear contributions. For more complex interfaces, such as thick interfaces, other dynamic modes (bending, splaying) have to be taken into account [12,13]. This may be especially important in particle laden interfaces, where the thickness and the interaction range may be larger than for interfaces of simple fluid interfaces.

In recent years several books and reviews have overviewed the behavior of particles at interfaces. The interaction potentials have been studied by Bresme and Oëtel [6] and by Kralchevsky et al. [7]. The phase diagram of particles and of mixtures of particles at interfaces has been discussed by Bonales et al. [14], showing that the surface density determines the fluid-like or crystalline structure of the particle monolayer, and therefore the interfacial rigidity. Moreover, in the case of polydisperse particles, the monolayers have glassy or crystalline structures depending on the size ratio, and on the volume fraction of small particles [15,16]. The dynamics of particles trapped at interfaces has been described by in terms of Brownian dynamics for highly dilute monolayers, or of constrained Brownian dynamics for higher surface densities within the 2-D fluid state [17,18]. In mixed particle + surfactant monolayers the analysis of the motion of particles allows one to obtain the complex shear modulus of the monolayer [19,20]. However, the use of particles as probes for micro-rheology measurements is restricted to low particle densities, and does not measure the shear viscosity and elasticity of the particle + surfactant monolayer at high particle densities. In this case, oscillatory disk or ring interface rheometers [21], or magnetic-needle rheometers have been used [22], though systematic studies have been reported so far. Microrheology experiments have been restricted to microparticles; macrorheometers can also be used in the case of nanoparticles. An unsolved problem is whether micro- and macro-rheological techniques do really measure the same physical variable, since strong discrepancies have been reported for some monolayers [23]. The dilational rheology of particle laden interfaces has received the attention of several groups in the last five years. Both particle monolayers, and mixed particle + surfactant monolayers have been studied using Langmuir balances, pendant drop or bubble tensiometers, as well as a capillary wave technique [24,25].

In this work we will give a short review of the experimental techniques used for the study of the dynamics of particles trapped at fluid interfaces, and of the complex shear and dilational rheology of particle laden interfaces. We will also review the results published in the last few years.

2. Background of interfacial rheology and experimental methods

It is well known that many surface active substances, polymers with hydrophilic groups among them, are able to adsorb at water interfaces. They can form either Gibbs monolayers, when adsorbed from a bulk polymer solution, or Langmuir films, when insoluble polymers are formed by spreading at the interface. From the equilibrium point of view, the surface tension, γ , is in both cases decreased with respect to the bare interface γ_0 . The adsorbed film is characterized by the surface pressure, Π , that represents the decrease of surface free energy per unit area, resulting of the spontaneous adsorption of the film. However, in most practical applications the interfaces are subject to external mechanical perturbations such as the change of shape or size. The response of the interface to a change of size at constant shape is characterized by the dilational elasticity and viscosity, whereas the response of the interface to a shape deformation at constant size is characterized by the shear elasticity and viscosity [26].

The storage (G') and loss moduli(G") are phenomenological parameters directly obtained from the rheological the experiments. In order to properly account for the surface elasticity and viscosity, both shear and dilational, one must assume a given viscoelastic model. The simpler viscoelastic models commonly used are the Kelvin–Voigt that assume additive stresses and the Maxwell model that assume additive rate of strains [27].

2.1. Dilational rheology

Let us consider an infinitesimal change of the interfacial area, $\delta A(t)$. The area perturbation induces a change in the state of the film leading to a change in the surface pressure $\delta \Pi(t)$. If the interface is purely elastic, the surface pressure, $\Pi(t)$ follows immediately the area change, A(t), without any phase delay. However, and depending on the relative rates of the area change and the rate of the relaxation process (or processes) within the interfacial layer, a phase delay could exist given place to a dissipation term and a dilational viscosity, $\zeta(t)$. The response can then be written as [1,28],

$$-d\Pi(t) = \left[\mathbb{E}(t) + \zeta(t) \frac{\partial}{\partial t} \right] \cdot u(t) = \widetilde{\mathbb{E}}(t) \cdot u(t).$$
(1)

Being $u(t) = \delta A(t)/A_0$ the relative change in area; E(t) the elastic dilational modulus and $\tilde{E}(t)$ the visco-elastic modulus which is defined as [1,28]

$$\widetilde{E}(t) = -\left(\frac{\partial \Pi}{(\partial A/A)}\right)_{T}.$$
(2)

Note that in Eq. (1) the dissipation term is taken proportional to the dilation rate.

For a small-amplitude oscillatory motion $[\delta A(t) \sim e^{i\omega t}]$ of frequency ω , the modulus, $\widetilde{E}(t)$ is a complex quantity. The constitutive viscoelastic parameters $E(\omega)$ and $\omega\zeta(\omega)$ obtained as a function of ω contain the time-dependent response of the system subject to a small disturbance, and allow probing the surface dynamics of the adsorbed film.

For insoluble films at equilibrium, or when the film is disturbed along a *quasi*-static path ($\omega \rightarrow 0$), the surface dilation causes an instantaneous change in surface concentration, $\delta A / A = -\delta \Gamma / \Gamma$. In this case, the elasticity modulus equals the compression modulus, which can be obtained as the relative slope of the equilibrium isotherm [29]

$$\mathbf{E}(\boldsymbol{\omega} \to \mathbf{0}) = \mathbf{E}_{\mathbf{0}} = \Gamma\left(\frac{\partial \boldsymbol{\prod}}{\partial \boldsymbol{\Gamma}}\right)_{\mathrm{T}}$$
(3)

and the dilational viscosity equals its frequency-independent Newtonian limit

$$\zeta(\omega \to 0) = \kappa_0. \tag{4}$$

As an illustration of the described behavior, Fig. 1 summarizes the material response expected for a viscoelastic polymer film exhibiting a relaxation process due to chain diffusion.

In the preceding paragraphs only small deviation from equilibrium was considered because only in that case the conditions of linearity are generally observed. For many systems, even for small stress perturbation,



Fig. 1. Typical frequency dependence of the elasticity, loss modulus and viscosity of a visco-elastic material undergoing a dynamic process.

the interfacial response is non-linear, for example for some mixtures of polymer/surfactants, polymer or microparticle Langmuir monolayers [30–34], in those cases the previous analysis are not applicable. Additionally, the real situations, where the surface rheological parameters of the systems are of relevance, occur far from equilibrium where the interfacial response is no longer linear. Theoretical efforts are being made, in particular using irreversible thermodynamic formalism (rational and extended irreversible thermodynamics) [35] for developing a non-linear theory of interfacial dynamics. However, the derived equations have no analytical solutions and the numerical solutions find difficulties to handle the equations accurately, which makes the use of these equations difficult to apply in the analysis of experimental results.

Non-linear behavior on dilational rheology experiments in several systems with small-molecule surfactants, lipids, polymers and particles adsorbed and under a sinusoidal deformation has been analyzed by means of a Fourier expansion of the surface stress response, $\sigma(t) = \Pi(t) - \Pi_0$, of the form [32],

$$\sigma(t) = \sigma_0 e^{i\omega t} + \sigma_1 e^{2i\omega t} + \sigma_2 e^{3i\omega t} + \dots$$
(5)

where, σ_0 is the amplitude of the stress response, measured with respect to the initial surface pressure Π_0 and where σ_1 , σ_2 , and σ_3 , are the amplitudes of the harmonic components of the non-linear response. This analysis, usually called Fourier-transform rheology, is easily applicable; however the departures from linearity that can be modeled is rather limited because in fact it represents an expansion of the stress around the zero interface deformation rate, which is valid in general for small deviations from linearity. It is worth noticing that in the case of shear rheology only odd terms are expected in Eq. (5) because of the time-symmetry of the stress tensor. However, this is not the case for dilational rheology because, for a given value of the strain, the system explores different states during the compression and the expansion cycles.

2.1.1. Mechanical relaxation experiments

The majority of the experimental methods of surface dilational rheology are based on mechanical perturbation of the surface area and the measurement of the system response. In what follows we give a brief description of these techniques.

2.1.1.1. Stress relaxation. Relaxation experiments are performed when the equilibrium state has been reached by suddenly perturbing it by a small change in area, surface concentration or other parameters; then relaxations start to re-establish the equilibrium state [36].

Experiments of mechanical rheology can be easily performed in commercial Langmuir troughs and pendant drop or sessile bubble devices [37]. Particularly, the stress relaxation $\gamma(t)$ [or $\Pi(t)$] can be recorded as a function of time, t, after a sudden compression (or expansion) of the interface. As a consequence of the surface compression the surface pressure deviates from the equilibrium value, and a surface pressure change $\Delta\Pi$ is induced, the so-named dilational stress, and acts as restoring force for recovering the initial state of the film when strain ceases. A typical experimental record is plotted in Fig. 2A.

2.1.1.2. Creep experiments. Creep experiments are typically made on a Langmuir trough [38]. Once the equilibrium surface pressure, Π_0 , is reached the interface is suddenly (and as faster as possible) compressed till a desired surface pressure, $\Pi = \Pi_0 + \sigma$ is attained; then in order to maintain that pressure constant, the movement of the balance barriers is allowed under computer control. Then, the surface film tries to adjust the excess pressure by relaxing the area A(t), see Fig. 2B. In these experiments the creep compliance is defined as,

$$J(t) = \frac{u(t)}{\sigma} = \frac{-\delta A/A_0}{\Pi - \Pi_0}.$$
 (6)



Fig. 2. Behavior of the time-dependence of the area and of the surface pressure. (a) A typical step-relaxation experiment, and (b) a typical dilational creep experiment.

This function J(t) can be described by phenomenological functions [39] and gives information on how the structure of the film responds to resist stress [38].

2.1.1.3. Oscillatory area experiments. In this case, the interface area is subjected to a sinusoidal perturbation at a constant frequency ω , which can be expressed as $u(t) = \delta A(t)/A_0 = (u_0/2) \exp(i\omega t)$. In principle, for the drop and bubble geometry, at frequencies low enough, the sinusoidal changes in area produce only compression and expansion. However for films strained in a Langmuir trough by a uniaxial in-plane compression, both the applied strain u and the response stress σ have dilational (xx) and in-plane shear (xy) components. This is also true for relaxation and creep experiments on a Langmuir trough (Note: A modified version of balance barriers using rubber bands avoid (or reduce) the shear by producing an isotropic deformation [40].). In terms of a generalized stress function, the dilational response function (Eq. (1)) involves a modulus containing two components coupled together, the dilational (K) and the shear (S) components: $\tilde{E} = E_{K} + E_{S}$; being in general both E_K and E_S complex numbers [1,28]. For fluid films the shear component is generally small [1].

In the linear regime the response closely follows the sinusoidal shape of frequency ω imposed by the strain:

$$\Pi(t) = \Pi_0 + \sigma(t)$$

$$\sigma(t) = \frac{\sigma_0}{2} e^{i(\omega t + \phi_\sigma)}.$$
(7)

Here, ϕ_{σ} is a phase factor accounting for the viscous delay in the response. In the linear regime, the elasticity modulus E and the dilational viscosity ζ can be obtained as

$$\mathbf{E} = |\mathbf{E}| \cos\phi_{\sigma}; \quad \boldsymbol{\omega}\zeta = |\mathbf{E}| \sin\phi_{\sigma}; \quad |\mathbf{E}| = \frac{\sigma_0}{u_0}. \tag{8}$$

When the visco-elastic response becomes non-linear, the sinusoidal model in Eq. (8) does not hold. In that case the use of direct Fourier-transform rheology and Eq. (6) is possible [32].

2.1.1.4. Surface wave experiments. There are two kinds of surface wave experiments for surface rheology, one involves "natural" thermal fluctuations of the surface position, which is a consequence of the second law of thermodynamics, and the other "artificial" produced surface waves by means of electrical or mechanical perturbation. In both cases the features of the fluctuations (amplitude, frequency, damping, etc) are related to surface rheological properties of the interface [13,41].

2.1.1.4.1. Surface quasi-elastic light scattering (SQELS). This technique is based on the light scattered by the transverse surface waves, and measures the dynamics of the thermal roughness of the interface

[13,41,42]. SQELS probes the surface dynamics at equilibrium because it relies on observing the dynamics of thermal fluctuations around the equilibrium state being the amplitude of the thermal fluctuations very small (a few Angstroms), it probes the rheology in the linear regime. In SQELS experiments one obtains either the heterodyne autocorrelation function or its Fourier transform, the power spectrum of scattered light $P(\omega)$ [41],

$$P(q,\omega) = \frac{k_B T}{\pi \omega} \left[\frac{i\omega \eta (m+q) + \tilde{E} q^2}{D(\omega)} \right]$$
(9)

 η is the subphase viscosity, q is the wave-vector, \tilde{E} the complex dilational modulus (compression + shear), and D(ω) the surface wave dispersion relation given by [41],

$$\begin{split} D(q,\omega) &= \left[\widetilde{E}\,q^2 + i\omega\,(q+m)\,\right] \left[\gamma q^2 + i\omega\,(q+m) - \frac{\rho\omega^2}{q}\right] - \left[i\omega\eta\,(q-m)\right]^2 \end{split} (10) \\ m &= \sqrt[4]{q^2 + \frac{i\omega}{\eta}} \end{split}$$

being ρ the subphase density and γ the surface tension. By measuring the P(ω) and the surface tension independently the dilational elasticity and viscosity can be obtained from Eqs. (9) and (10). The frequency range of the SQELS technique is 1 kHz $\leq \omega \leq 2$ MHz.

2.1.1.4.2. Electrocapilary waves (ECW). In this case an external excitation, electrical or mechanical, is used to produce surface waves with amplitudes well above those of SQELS (\sim 1µm) [43]. Electrical excitation is better than mechanical because its non-invasive character and its experimental design are simpler. EWC measures the spatial profile of the generated capillary wave by scanning the liquid surface using laser reflectometry. The spatial profile is then fitted using a damped wave function,

$$A = \exp(-\beta x) \cos\left(\frac{2\pi x}{\lambda} + \phi\right).$$
(11)

Here λ is the capillary wavelength, β is the spatial damping constant of the capillary wave oscillations, and φ is a phase term obtained as a function of the excitation frequency. Measurements at different frequencies allow one to obtain the group velocity, and to transform the results from the space to the time domain. Then, the frequency, the independently measured surface tension and the parameters λ and β obtained in the fitting are used to resolve numerically the dispersion equation for each frequency to give the dilational elasticity and viscosity of the interface. The frequency range of the ECW technique is $20 \text{ Hz} \le \omega \le 1.5 \text{ kHz}.$

2.2. Shear rheology

The study of the response of interfacial layers against shear deformations has been in general less developed than the dilational studies, and it is only in recent years when a noticeable interest has been paid to the shear properties of interface due to its recognized importance in a wide range of technical aspects with technological relevance such as mass transfer process, foaming, emulsification, oil recovery processes and coating fabrication [44,45]. The evaluation of the shear properties of interfacial layers applies the rheological concepts developed for three-dimensional systems. However, the special characteristics of the interface introduce some notable limitations. (a) The drag forces make that the interfacial shear properties depend on the geometry of the apparatus that provokes the necessity to consider the effect of the coupling with the subphase in the data interpretation. (b) It is necessary that no radial flow is induced by the deformation at constant area [21,46].

The hydrodynamic equations point out the decoupling between the shear modes and the capillary and compression ones: both their amplitude and time evolution are independent [41]. This allows one to define the interfacial shear elasticity G for a 2D deformation in the x-y plane as a proportionally factor between the applied strain (u_{xy}) and the stress response of the monolayer (σ_{xy}). Solid like films present a mainly elastic behavior described by: $\sigma_{xy} = Gu_{xy}$. In the opposite side, the totally fluid films present a viscous behavior characterized by a strong dependence of the shear response on the strain rate: $\sigma_{xy} = \eta_S du_{xy} / dt = \eta_S \dot{u}_{xy}$, being \dot{u}_{xy} the strain rate and η_S the shear viscosity of the interface.

The existence of attractive interactions between the different components of the layers (e.g. segments of adsorbed and/or spread polymer, surfactant molecules, etc.) increases G and η_s due to the energy dissipation necessary to overcome these interactions that leads to the stress relaxation by the surface elements flows. However, the most part of the interfacial layers present viscoelastic behavior that allows defining the response to periodic shear deformations of frequency ω by a complex shear modulus G^{*}, in a similar way that for bulk rheology,

$$G^{*}(\boldsymbol{\omega}) = G^{'}(\boldsymbol{\omega}) + iG^{''}(\boldsymbol{\omega})$$
(12)

where G' and G" are the storage and loss components of the viscoelastic modulus, respectively. For small amplitude of oscillatory deformation of frequency ω ($u \sim u_0 e^{i\omega t}$) it is possible to correlate the loss modulus and the viscous friction $G'' = \omega \eta_s$.

From an experimental point of view, the shear measurements are performed under conditions where the interfacial flows are generated by the movement of solid boundaries within the interface or by the application of surface pressure gradients. A wide variety of experimental techniques allows evaluating the shear response of monolayers. The most commonly used techniques have been channel viscosimeters for insoluble monolayers, and oscillating disk and bi-cone surface rheometers for both soluble and insoluble monolayers [44]. More recently, new rheological methodologies have been developed, the socalled microrheological techniques [17,20,47]. The main advantage of the microrheology is the possibility to test the material response on the micrometer scale with small sample volumes. The main difference between both types of techniques is related to the types of probes used. Whereas the macrorheological techniques deform the interface by macroscopic probes [44], in microrheology the probes are microparticles embedded at the interface that strain the interface [17,20]. In all the cases the accurate determination of the interfacial shear properties requires a decoupling between the purely interfacial effects and those due to the adjacent bulk liquid [48]. This is defined by the Boussinesq number, B₀, which reflects the relative contributions of the interfacial stress in relation to those generated with the subphase

$$B_0 = \frac{\eta_S}{\eta L}$$
(13)

where η_{s} and η are the viscosities of the interface and the bulk, respectively, and L is a length scale linked to the dimension of the used probe. For liquid–liquid interfaces the viscosity of both phase must be considered and the B₀ must be expressed as,

$$\mathsf{B}_0 = \frac{\eta_{\mathsf{S}}}{(\eta_1 + \eta_2)\mathsf{L}} \tag{14}$$

where η_1 and η_2 are the viscosities of the up and bottom phases, respectively. When B_0 is much larger than 1, the drag experimented by the measuring probe is dominant, whereas in the opposite case for B_0 much smaller than 1, the properties of the surrounding medium are measured. The Boussinesq number plays a key role in the establishment of the most adequate probe for the determination of the interfacial shear properties. In order to obtain accurate results, it is necessary the dominance of the interfacial contribution in the rheological response that makes necessary the minimization of the velocity gradients in the surrounding fluid. This can be accomplished by the minimization of the characteristic length scale of the probe L [22,49].

An extension to viscoelastic interfaces considers the existence of a dependence on the Boussinesq number of both the real and imaginary components of the viscoelastic surface moduli [50]. In this case, the Boussineq number presents a frequency dependent, ω , complex form,

$$B_{0}(\omega) = \frac{G'(\omega) - iG'(\omega)}{\omega \eta L}.$$
(15)

2.2.1. Macrorheology techniques

The different bidimensional shear rheometers developed in the last few years can be considered as an extension of the classical ones used for the rheological characterization of bulk solutions and dispersions that takes into account the special requirements of the rheological characterization of interfaces. In the following, the main features of the most commonly used macrorheometers will be described.

2.2.1.1. Channel surface viscometers. The channel surface viscometers can be considered as a capillary viscometer for interfacial studies [51]. This technique allows the determination of the interfacial shear viscosity, η_s , by the evaluation of the flow rate, Q, of the monolayer through a narrow channel when a gradient of surface pressure, $\Delta \Pi$, is created by compressing the monolayer at one side of the channel. The shear surface viscosity is given by

$$\eta_{\rm S} = \frac{\Delta \Pi W^3}{12 {\rm LQ}} - \frac{W \eta}{\pi} \tag{16}$$

where W and L are the width and length of the channel, respectively, and Q is the flow of material toward the part of the trough where Π is smaller. It is worth to mention that this technique is limited to the study of insoluble monolayers at the air–liquid interface. The channel viscometer technique together with the microrheological techniques is usually considered as an indirect interfacial shear rheometer [52]. This technique requires channels with smooth walls, the absence of slip in the walls, Newtonian flows and the existence of dilational motion at the end of the channel.

2.2.1.2. Oscillatory shear rheometers. The oscillatory shear tests are considered as direct measurements where a direct measurement of the torque on a probe located at the interface to deform it is measured [52]. The oscillatory approach defines the dynamic surface modulus as a proportional factor between the stress and the strain [22],

$$\sigma = S^* u \tag{17}$$

where $u = u_0 e^{i\omega t}$ is the applied strain of fixed frequency ω , and amplitude u_0 . $\sigma = \sigma_0 e^{i(\omega t + \delta)}$ is the resultant stress at the experimental

frequency, being σ_0 and δ the stress amplitude and the phase shift relative to the strain, respectively. Rearranging the terms, it is possible to define the surface shear modulus as,

$$\mathbf{S}^{*} = \sigma_0 \mathbf{u}_0^{-1} \mathbf{e}^{\mathbf{i}\delta(\boldsymbol{\omega})} = \mathbf{G}^{'}(\boldsymbol{\omega}) + \mathbf{i}\mathbf{G}^{''}(\boldsymbol{\omega}).$$
(18)

Finally each single measurement allows one to obtain G' and G"

$$G' = \frac{\sigma_0}{u_0} \cos\delta \tag{19}$$

$$G^{''} = \frac{\sigma_0}{u_0} \sin\delta \tag{20}$$

where $\tan \delta = G''/G'$. The interfacial shear experiments using oscillatory deformations are probably the most widely used in literature [52–55]. The classical measurement device consists in a probe placed at the interface. This probe is forced to rotate or oscillate within the interface by a motor that detects simultaneously the torque and the displacement, in order to facilitate the calculation of the mechanical properties of the interface [21]. The oscillatory rheometers can be considered as a 2D Couette geometry and the interfacial shear viscosity can be calculated from the torque [52].

Depending on the type of used probes, generally defined by the probe geometry, the rheometers adopt different names: knife-edge viscometer, blunt-knife surface viscometer, plate surface viscometer, bicone surface viscometer or double wall-ring surface viscometer.

2.2.1.3. Magnetic needle rheometer (ISR). This type of rheometer was developed by the group of Fuller [22,56] and consists of a magnetic needle placed at the interface in the center of a channel and subject to a magnetic field gradient that governs its motion. Under operation conditions, a known force F is applied to the needle due to the application of a magnetic field gradient; the motion of the needle induces a shear deformation of the interface. The surface stress, σ , can be obtained from the ratio of the applied force and the perimeter of the needle L_N [22], and the strain, u, can be evaluated by tracking the needle position, and it can be considered equal to the needle oscillation amplitude X divided by the distance between the needle and the boundaries of the shear cell W. The stress–strain relationship allows one to determine the surface viscosity as well as the storage and loss moduli from the following expression [56],

$$G(\omega) = \frac{\sigma(\omega)}{u_0(\omega)} = \frac{W}{L_N} \frac{F}{X} e^{i\phi}$$
(21)

where ϕ is the phase shift between the strain and the stress. For films with low values of G, the measurements can be strongly affected by drag forces due to the subphase. Another limitation is found for very rigid films where the high force needed to move the needle may induce non-linear effects in the measurements.

2.2.2. Microrheology

2.2.2.1. Videomicroscopy particle tracking. The main idea in particle tracking is to follow the trajectories of probes introduced into (onto) the system by videomicroscopy. The trajectories of the particles allow one to calculate the mean square displacement, MSD, which is related to the diffusion coefficient, D, and the dimensions in which the translational motion takes place, d, by

$$\left\langle \Delta r^{2}(\tau) \right\rangle = 2 \mathrm{dD} \tau^{\alpha}$$
 (22)

where the brackets indicate the average over all the initial times in single particle tracking (SPT), and initial times and all particles in multiple tracking (MPT).

In case of diffusion in a purely viscous material (or interface), α is equal to 1, and the usual Einstein's linear relation is obtained between the MSD and the lag time τ . For highly viscous materials or interfaces (like condensed surfactant or lipid monolayers and dense polymer monolayers) the movement is sub-diffusive, $\alpha < 1$. For nano- and micro-particles in solid-like interfaces Eq. (23) does not apply. In fact if we consider the limits $\tau \rightarrow 0$ and $\tau \rightarrow \infty$ of the Maxwell viscoelasticity model, the mean square displacement can be expressed as

$$\left\langle \Delta r^{2}(\tau) \right\rangle = \sigma/E + \sigma \tau/\eta$$
 (23)

where σ is the stress, E is the elasticity modulus and η the viscosity coefficient and all of them refer to pure shear deformations. The characteristic Maxwell time is given by $\tau_c = \eta / E$. Anomalous diffusion $\alpha < 1$ has been invoked in many systems of biological interest where the Brownian motion of the particles is hindered by obstacles, or even constrained to defined regions (corralled motion) [57].

The diffusion coefficient is related to the friction coefficient, f, by the Einstein relation

$$D = \frac{k_B T}{f}.$$
 (24)

In 3D f is given by Stokes law, $f = 6\pi\eta R$, and for pure viscous fluids the shear viscosity can be directly obtained from the diffusion coefficient. However Stokes law does not apply to interfaces.

Fig. 3 shows a typical set of results for the MSD of a system of latex particles (1 µm of radius) spread at the water/n-octane interface at low particle surface densities (gas-like phase) [14]. The analysis of MSD in terms of Eq. (22) and in the linear range allows one to obtain D. However, it must be taken into account that for laden interfaces, even below the threshold of aggregation or fluid–solid phase transitions, the MSD shows a sub-diffusive behavior ($\alpha < 1$ in Eq. (22)) and a more complex method has to be used for calculating D (see below).

When the samples are heterogeneous at the scale of particle size (a situation rather frequent, especially in biological systems [57–60]), single particle tracking gives erroneous results and the so-called "two-point" correlation method is recommended [61]. In this method the fluctuations of pairs of particles at a distance R_{ij} are measured for all the possible values of R_{ij} within the system. Vector displacements of individual particles are calculated as a function of lag time, τ , and initial

Fig. 3. Mean square displacements and relative square displacement for latex particles at the water/n-octane interface. Experimental details: set of 300 latex particles of 1 μ m of diameter, surface charge density: $-5.8 \ \mu$ C cm⁻², and reduced surface density, $\rho^* = 1.2 \cdot 10^{-3} \ (\rho^* = \rho a^2), 25 \ ^{\circ}$ C.



absolute time, t: Then the ensemble averaged tensor product of the vector displacements is calculated [62]:

$$D_{\alpha\beta}(\mathbf{r},\tau) = \left\langle \Delta \mathbf{r}_{\alpha}^{i}(\mathbf{r},\tau) \Delta \mathbf{r}_{\beta}^{j}(\mathbf{r},\tau) \delta \left[\mathbf{r} - \mathbf{R}_{ij}(\mathbf{t})\right] \right\rangle_{i \neq j,t}$$

$$\Delta \mathbf{r}_{\alpha\beta}^{i,j}(\mathbf{r},\tau) = \mathbf{r}_{\alpha\beta}^{i,j}(\mathbf{t}+\tau) - \mathbf{r}_{\alpha\beta}^{i,j}(\mathbf{t})$$
(25)

where i and j label two particles, α and β are coordinate axes and R_{ij} is the distance between particles i and j. The average corresponding to i = j represents the one-particle mean-squared displacement. Twopoint microrheology probes dynamics at different lengths from distances much larger than the particle radius down to the particle size which reflects extrapolation of long-wavelength thermal fluctuations of the medium to the particle size [63].

For the case in which the particles are embedded in a viscoelastic fluid, particle tracking experiments allow one to obtain the viscoelastic moduli of the fluids. Manson and Weitz first in an ad-hoc way, and later Levine and Lubensky in a more rigorous way, proposed a generalization of the Stokes–Einstein equation (GSE) [64,65]:

$$\left\langle \Delta \widetilde{r}^{2}(s) \right\rangle = \frac{2k_{B}T}{3\pi as\widetilde{G}(s)}$$
(26)

where $\widetilde{G}(s)$ is the Laplace transform of the stress relaxation modulus, s is the Laplace frequency, and a is the radius of the particles. An alternative expression for the GSE equation can be written in the Fourier domain [66]. Different methods have been devised to obtain $\widetilde{G}(s)$ from the experimental MSD [66–70]. Very recently, Felderhof has presented an alternative method for calculating the shear complex modulus from the velocity autocorrelation function that can be calculated from the particle trajectories [71].

For interfaces the situation is more complex, and the calculation of the surface shear viscosity has relied on the use of hydrodynamic models of the interface (see below). Only very recently Song et al. [72] have performed computer simulations that indicate that the GSE can be applied to fluid interfaces. Furthermore, the same group has applied the GSE to the study of interfaces in oil–water emulsions [72–74]. So far, no comparison has been made between the surface shear viscosity calculated by hydrodynamic calculations and the GSE equation.

Optical tweezers can also be used for tracking the trajectory of microparticles at interfaces. In this case there is no free-Brownian motion because the particles are subject to the trap potential, and as a consequence sub-diffusive motion is observed [75]. A similar behavior is found in the case of the solid-like states of particles monolayers.

3. Dynamics of particles at interfaces

The dynamics of colloids is determined not only by direct interparticle forces, but also by long-range solvent-mediated interactions. Consequently, we have to consider the hydrodynamic properties of the surrounding solvent in order to understand the motion of colloids. These interactions determine the relevant timescales governing the evolution of the particle-laden interfaces: [76,77]

- a) The shortest time-scale t_s is that on which the solvent behaves as a compressible fluid. A moving sphere of radius "a" generates a density fluctuation which propagates away as a sound wave. The characteristic time associated to this phenomena is $t_s = a / c_s$, where c_s is the velocity of sound. Usually it is of the order of $t_s = O(10^{-10} \text{ s})$, non measurable with the more common experimental techniques and extremely short as compared with the rest of the characteristic time-scales of the system. Hence, this time-scale is usually not even considered.
- b) The next time-scale is associated with the propagation of hydrodynamic interactions, t_H. A colloid in motion acts as a source of transverse momentum that diffuses away from the particle. Through this velocity field, one particle exerts a drag force on another particle. This is the so-called hydrodynamic interaction (HI). In 3D these interactions are positive, i.e. particles drag one another in the same direction, and decays with the interparticle distance r as 1/r. The time-scale of these interactions is determined by the time that takes the transverse momentum to diffuse a typical interparticle distance comparable to the diameter of the colloids. Hence, this is $t_H = 0 (a^2/v)$, typically of the order of 10^{-8} s, being v the diffusion coefficient for transverse momentum. As we will discuss later on, the confinement of the particles has the strong effect on the pair hydrodynamic interaction between colloid particles.
- c) Next, we get the time-scale for the decay of the initial velocity of a colloid. For a typical colloidal particle, the velocity correlation function decays algebraically with a power that depends on the dimensionality d of the system as $t^{-d/2}$. These "long-time tails" are due to the effect on the particle of time-dependent velocity fields set up in the fluid by the particle motion itself. The time scale is controlled by the diffusion coefficient for transverse momentum of the fluid and is on the same order of t_H.
- d) The colloids move diffusively, and the diffusion constant is related to the Stokes friction constant f by $D = k_BT / f$. The time it takes to observe displacements of the colloidal particles in the interface over a distance comparable to its own radius is of the order of milliseconds to seconds. Clearly, there is a wide time-scale separation between the diffusive time and the other times. Hence we could be attempted to assume that at long times, those comparable to the diffusive time-



Fig. 4. Time dependence of the mean square displacements of latex microparticles at the octane/water interface, obtained by videomicroscopy particle tracking at three different reduced particle surface densities, $\rho^* = \rho d^2$, where *d* is the particle diameter. These densities correspond to a gas-, fluid- and solid like states, respectively. The continuous lines are the fits to a Langevin equation of a Brownian particle bound in a harmonic potential, Eq.(27), in the overdamped limit ($f^2 > 4$ km). All the results were taken at 25 °C. [LJ. Bonales, Ph.D. Thesis, Complutense University, Madrid 2009].

scale, the colloids perform uncorrelated Brownian motion. However, the direct and the hydrodynamic interactions make that the effective diffusion constant of every colloid depends on the instantaneous configuration of its neighbors. This is one of the reasons why the dynamics of the particles adsorbed in an interface is not simple.

Many of the diverse properties of the particle-laden interfaces originate from this additional complexity in structures and dynamics, which span a wide range of time and length scales. We cannot cover all this extent of phenomenology in a few pages, so we will focus on two aspects of colloid dynamics that clearly illustrate the time-lengthscales problem. The first is self diffusion of particles in diluted and concentrated conditions. The second goal of this section addresses the dynamical aspects of collective evolution.

3.1. Diffusion coefficient of particles adsorbed at fluid interfaces

In the case of particle monolayers of very low surface concentration (gas-like states) the plot of MSD vs. t is linear and D can be easily obtained from Eq. (22). However, for slightly denser fluid-like states MSD exhibits two different linear time dependencies at short and long times. At short times the particles explore the environment made up by the surrounding

neighbors, and a short-time self-diffusion coefficient, $D_{\rm S}=\lim_{t\to 0}\frac{\langle\Delta r^2\rangle}{4t},$ is

obtained. The interaction with other particles lead to a decrease of D_s as the particle density, Γ , increases $D_s = \alpha D_0 (1 - \mu \Gamma)$, where μ depends on the interactions. Several authors have found that μ decreases with increasing the particle radius though so far there is no analytical theory for explaining the size dependence of μ [78].

At longer times a few particles start to move collectively making some hopping between different cages formed by the neighboring

particles, which allows one to define a long time diffusion coefficient D_m

 $=\lim_{t\to\infty}\frac{\langle\Delta r^2\rangle}{4t}$. This is a process that recalls the so-called α -relaxation, and has been studied recently by Mazover et al. [79]

Once the system is completely dominated by the particle repulsions at higher Γ s, the particles seem to be arrested within the experimental time window. At this high density conditions no exact analytic results exist. To provide some quantitative results the simplest model is the harmonically bound independent Brownian oscillator (BHO) [80]. In this model particles obey the Langevin equation including an elastic force [18]:

$$m\frac{dv}{dt} = -f \cdot v + F(t) - k \cdot x \tag{27}$$

where m is the mass of the particle, v its velocity, f the friction coefficient, k the characteristic force constant of the elastic force acting on the particle, and F(t) is the random force, so that time average $\langle F(t) \rangle = 0$. Even though the particle–particle interaction potential is not strictly parabolic, it is a very good approximation for particles in a laser trap for laser intensities such that the particles are trapped relatively deep inside the potential well, or for particle interactions in liquid-like states [14], and for particles immersed in an entangled medium. A similar equation is used to analyze DLS [81] and DWS [82] results of probe particles in 3D entangled media like gels. The solution of Eq. (27) neglecting inertia and in the overdamped limit, ($\zeta^2 > 4 \text{ km}$), the so called BHO model [79], gives

$$\left\langle \Delta r^{2}(\tau) \right\rangle = 2 \mathrm{d}\delta^{2} \left[1 - \mathrm{e}^{-D_{0}\tau/\delta^{2}} \right]$$
(28)

where d is dimensionality, $\delta^2 = k_B T / k$, being k the force constant of the oscillator, and the short time diffusion coefficient is $D_0 = k_B T / f$. The characteristic time is given by $\tau_{BHO} = \delta^2 / D_0 = f / k$.

This equation has been corrected by different authors in an ad hoc manner to account for the dynamics of interacting Brownian particles, and with the dynamics of particles embedded in solutions of viscoelastic giant micelles. Bellour et al. introduced a more complete equation [83]

$$\left\langle \Delta r^{2}(\tau) \right\rangle = 2 d\delta^{2} \left[1 - e^{-\left(D_{0}\tau/_{\delta^{2}} \right)^{c}} \right]^{1/c} \left(1 + \frac{D_{m}}{\delta^{2}} \tau \right).$$
⁽²⁹⁾

The new equation includes modifications one that account for nonexponential character of the decay, which include a power c in a similar fashion of the stretched exponential commonly used in DLS, and a term that accounts for the long-term escape of the cages recovering the linear dependence with time.

In Eq. (29) c < 1 is a fitting parameter that accounts for the width of the relaxation time spectrum [83]. The same equation was used by Galvan-Miyoshi et al. [84]. In both cases the model was able to describe precisely the experimental results. Fig. 4 shows that the extended BHO model also fits very well the data for dense fluid monolayers. An important point is that the fits allow one to obtain the diffusion coefficient at infinite dilution, D_0 .

For monolayers in solid-like states the oscillators can no longer be considered as independent. Keim et al. have shown that the Overdamped Bead-Spring (OBS) model was able to describe properly their experimental results for colloidal crystals [85]. The OBS model regards the colloidal crystal as a classical beadspring lattice immersed in viscous media, and the Langevin equation takes the form [86]

$$m\frac{dv_{i}}{dt} = -fv_{i}(t) + F_{i}(t) - k\sum_{j}^{nn} \left[u_{j}(t) - u_{i}(t)\right]$$

$$(30)$$

where k is the force constant common to all the springs, $u_i(t)$ represents the displacement of the particle i at time t, and nn is the number of nearest neighbors of particle i. Notice that at densities where the monolayer is in a solid state the particle cannot escape from its cage, thus no linear increase of MSD is expected at long times. The solution of Eq. (30) leads to

$$\left\langle \Delta r^{2}(\tau) \right\rangle = \frac{2dk_{B}T}{kN} \sum_{b} \frac{1}{L(q_{b})} \left\{ 1 - \exp\left[-\frac{kL(q_{b})}{b}t\right] \right\}$$
(31)

Eq. (31) includes only the nearest-neighbor interactions. The lattice factor is given by $L(q_b) = \sum_j^{nn} \Bigl[1 - cos \Bigl(q_k \cdot n_j \Bigr) \Bigr]$, where q_b is the b^{th} wave vector of the relaxation mode q, and n_j is a vector pointing from the lattice point i towards the nearest neighbor j. The sum is done over all the allowed values of q_b except $q_b = 0$.

The initial slope of MSD is the same as that of the BHO model, and reaches an asymptotic value given by

$$\lim_{\to\infty} \left\langle \Delta r^{2}(\tau) \right\rangle(\tau \to \infty) = \frac{2dk_{\rm B}T}{kN} \sum_{\rm b} \frac{1}{L(q_{\rm b})}$$
(32)

which depends both on the strength of the harmonic force and on the lattice factor. The experimental results of Keim et al. [85] are well described by this model.

4. Rheology of particle monolayers

4.1. Dilational rheology

The studies of dilational rheology allow one to obtain important information related to dynamic exchanges and relaxations that lead to the particle-laden interfaces to their equilibrium state [87]. This interest in the dilational shear properties of particle layers has stimulated a strong development of the theoretical [88] and experimental [24] aspects of this topic. In this section we will review the most recent advancements in the study of the dilational rheology of particle-laden interfaces.

Despite the potential technological interest that have evidenced the layers formed exclusively by nanoparticles due to their good performance as stabilizing agent of foams [11,89], the number of studies present in literature is quite low. Furthermore, most part of these studies are exclusively devoted of the dilational properties of interfacial layers of fumed silica nanoparticles (dendritic aggregates – 200 nm of primary particles) with different hydrophobicity degree [25,90,91], and to latex particles [32].

To the best of our knowledge, the first authors that proposed the problematic of the dilational rheology of particle-laden interfaces were Miller et al. [88]. These authors developed a theoretical model to explain the dilational response of particles and particles + surfactant layers considering exclusively equilibrium aspects. This model is analogous to the previously developed one to explain proteins and proteins + surfactant systems [92], introducing as additional parameter the cohesion between the particles at the layer. This important parameter is strongly dependent on the wettability properties of the particles. However, this model has not been applied to experimental results.

The effects of the hydrophobicity on the dilational rheology of fumed silica nanoparticles monolayers at the air–water interface were investigated by Safouane et al. using a capillary wave technique in the frequency range of 200–990 Hz [90]. However, no studies in function of the frequency are presented. The results point out that both the equilibrium, rheological and structural characteristic of the layers are strongly dependent on the hydrophobicity of the particles. E' > E'' was found independently of the nanoparticle hydrophobicity degree and surface coverage. An increase of the real part of the elasticity modulus was found with the increase of the nanoparticle hydrophobicity due to the larger affinity of the nanoparticles for incorporation at the interface; similar dependence was found for the static compression modulus. The values of the loss modulus do not evidence any clear dependence on the particle hydrophobicity or surface coverage.

More recently, Zang et al. [25] have revisited the interfacial dilational rheology of silica particle layers and by means of a multitechnique approach (continuous compression, oscillatory barrier and step compression experiments) have scanned the frequency dependence of the dilational response of this systems. The main characteristic of these systems is their high values of elasticity, almost one order of magnitude higher than those reported by Safouane et al. [90] for higher frequencies of measurements, and their long range of linear dilational response. The authors found a good agreement between the results of the different techniques in the range of overlapping frequencies. The authors evidenced the absence of dependence on the frequency of the dilational response in the studied range by the oscillatory barrier (in the range 0.016-0.1 Hz). However, an extension of the rheological data including the results obtained by techniques that allows one to obtain information about slower frequencies shows the existence of a dynamic process with characteristic frequency around 10⁻³ Hz which is related to the interfacial reorganization of the particle layer. It is also significant that the increase of the dilational modulus with the increase of the packing degree of the film is expected for a more dense film.

Zang et al. [91] have also evaluated the effect of the contact angle of the particles in the dilational response of silica layers at the air–water interface and found a strong dependence of the elasticity modulus in the contact angle, being the particles with intermediate hydrophobicity (around 34% of the silanol groups silanized) those with the higher elasticity. This higher elasticity correlates with better characteristics for the stabilization of foams [11]. Furthermore, the elasticity of layers with same nanoparticles density obtained by compression and by spreading was studied. The results evidence the higher elasticity of the layers obtained by compression that is ascribed to non-equilibrium conformation with slow relaxation processes associated. The measurements of dilational interfacial rheology of particle-laden have been also used to evaluate the stability of foams stabilized by nanoparticles as in the works by Stocco et al. [11] and Cervantes-Martinez et al. [89]. These authors defined the stability of the foams by the ratio between the elasticity of the layers and the surface tension of the particle-laden interface, using the so-called Gibbs criteria.

It has been shown that charged microparticles tend to form dense monolayers even at relatively low surface coverage [14]. As a consequence the linear regime is relatively small, and the experiments have to be performed using small strains and low frequencies. Fig. 5 shows an example of the non-linear oscillatory behavior of a monolayer of latex microparticles at the water/n-octane interface [32]. Fig. 5B shows the Fourier spectrum of the system's response to the sinusoidal strain, in this case only odd harmonics are observed. Notice that the strain amplitude is similar to the ones observed in emulsion droplets, while the frequency is very low.

4.2. Shear rheology

The study of the shear response of particle layers started to be developed before than the studies of dilational rheology. Furthermore, the shear properties of both nano- and micro-particles layers have been studied, in contrast to the studies of the dilational rheology focused mostly on the study of nano-sized particles.

Cicuta et al. [93] studied the dependence of the shear rheology of polystyrene particles (order of $3 \mu m$) on the coverage fraction of the interface. The colloidal spheres at the interface present a mainly



Fig. 5. Oscillatory experiment corresponding to a monolayer of latex particles on the water/n-octane interface at 297.15 K. The initial surface pressure was 12.9 mN m^{-1} , the strain amplitude was 22% and a frequency of 17 mHz. The symbols are experimental data, while the curves correspond to the Fourier spectrum of the system's response. Reprinted from Ref. [32], Copyright (2006), with permission from Elsevier.

viscous behavior (G'' > G') that contrasts with the behavior observed for monolayers of the globular protein β -lactoglobulin, whose behavior is mainly elastic in a broad concentration range. Furthermore, the viscoelasticity modulus of the layers of particles increases with the concentration whereas that of the protein layers tends to an asymptotic value beyond a concentration threshold. These differences were explained considering that particles behave as a hard disk whereas the proteins have behavior of deformed and compressible disk, which determines the formation of different types of 2D glasses.

Madivala et al. [94] demonstrated the potential interest of selfassembling of particles in the control of mechanical properties of the interfaces. They studied the mechanical properties under shear of rodlike polystyrene particles (order of 10 µm) at the water-air and water-oil interfaces. They found that the layers of these ellipsoidal particles present a high elasticity, even at low surface coverage. This contrasts with the results found by Cicuta et al. [93] for spherical particle layers, where the elasticity was only significant for interfacial coverage over a critical threshold value (around 66% of the surface area). This different mechanical behavior was explained by the trend of the ellipsoidal particle to self-organize forming very stable ramified particle networks in contrast with the formation of aggregate networks for spherical particles of similar size and surface properties. The formation of this self-assembled structure is governed by an intricate balance between electrostatic interactions and shape-induced capillary ones. These results are in agreement with the effect observed by Basavaraj et al. [95]. Furthermore, buckling transitions were observed for the rod-like particles above a threshold value of the interfacial coverage. The results point out that the structural transitions in monolayers of ellipsoid particles are more complex than for spherical particles, and lead to a more complex rheological behavior.

The special characteristics of ellipsoidal particles were later used for the fabrication of ultra-stable emulsions [96], both water-in-oil and oilin-water. The results pointed out that the high interfacial shear modulus of these monolayers, together with its particular packing effects, lead to the formation of emulsion with stability higher than those stabilized by spherical particles. Cui pointed out that the particles under shear flows suffer reorientation processes at the interface [97]. These are governed by the geometry of the particles that provoked the generation of different structural patterns at the interface.

Recently, Reynaert et al. [98] studied the interfacial jamming phenomenon of charged polystyrene spheres at the water–oil and at the water–air interface. They pointed out the important role of the interfacial structure of the monolayer in the rheological response. The aggregated 2D layer showed a rheological behavior analogous to threedimensional aggregated particles dispersion, characterized by an elastic response with a low linearity range. Furthermore, the elastic response follows a power law on the surface coverage, and shows dependence on the strength of the particle interactions which was controlled by the addition of the anionic surfactant sodium dodecylsulfate (SDS) and sodium chloride.

The above discussion corresponds so far to the interfacial shear viscoelasticity of microparticle laden interfaces, which corresponds to a typical soft glass-like material analogous to their 3D counterparts. It is well known that the reduction of the size of the particles has strong effects on the phase diagram of particle laden monolayers. More specifically, in the case of monolayers of charged particles (mainly repulsive interactions), they have a disordered (fluid-like and hexatic) state that extends over a larger density range, before entering the hexagonal solid structure, as the size decreases [99]. Therefore, it can be expected that the response against shear will be also affected by the particle size.

Krishnaswamy et al. [100] studied the response against steady and oscillatory shear of silver nanoparticles (10–50 nm of diameter) at the toluene–water interface. These authors followed the formation of the particle layers by means of shear rheology, and found that the densification of the layers lead to an increase of both the storage and

the loss moduli till they reached the equilibrium state. The increases of G' and G" were attributed to the increase of nanoparticle concentration with time. Moreover, they found a frequency independent elastic character of the film, G' > G'', over the low frequency range. This together with the negative slope observed for G" in this region allowed the authors to conclude that the monolayers were a 2D soft glassy material with long relaxation times. Furthermore, as it is expected for this type of materials, the dynamic relaxations present a strong dependence on the strain rate amplitude. Strain sweep measurements revealed a shear thinning phenomena in the loss modulus at large strain amplitudes. In contrast, the storage modulus is almost independent of the strain amplitudes till the shear thinning. The shear thinning of G' and G" follows a power law decay with a 2:1 ratio between the exponents. Steady shear measurements revealed the presence of a finite yield stress in the limit of low shear ratios. For shear rates bigger than 1 Hz, a gradual increase in the shear stress was observed. These results together with the significant deviation from the Cox-Merz rule were considered additional evidences of the formation of a 2D glassy system.

In contrast to the glassy like state observed for silver nanoparticles at the toluene–water interface, Orsi et al. [101] have recently reported that gold nanoparticles at the air–water interface present a gel-like behavior characterized by a strain-softening phenomena with a mechanical response constant until a threshold strain (around 0.1%), followed by a significant drop of G'. These gel-like materials present a rheological response dominated by the elasticity. Furthermore, the viscoelasticity moduli of these particle-laden interfaces increase with the interfacial coverage following a power law with exponent 0.65, that the authors correlated to percolation phenomena as for bulk systems. The storage modulus does not depend on the perturbation frequency whereas the loss modulus increases at the highest frequencies.

Safoaune et al. [90] studied the effect of the particle's hydrophobicity in the shear rheological behavior of silica particles layers. They performed studies at fixed layer density and found that the values of shear moduli were small but almost two orders of magnitude bigger than those of dense layers of surfactants (around 10^{-3} mN/m⁻¹). They also observed a strong dependence of the shear moduli on the particle wettability, G' and G" increasing with hydrophobicity. The layers obtained at low hydrophobicity degrees present negligible values of the shear moduli whereas at larger hydrophobicity G' > G'', probably due to the hydrophobic interactions between the nanoparticles. The particles of intermediate hydrophobicities present values of G' = G''. This crossover is defined by the authors as a gel point. More recently Zang et al. have extended the work by studying the dependence of the shear modulus on the strain amplitude [25,91,102]. They found that for low strain amplitude the storage modulus is higher than the loss modulus (almost two orders of magnitude) and quite independent on the strain amplitude. However, above a threshold amplitude the monolayer melts and G" reaches a maximum value while G' drops significantly above this yield amplitude. The authors also reported that at fixed strain, G'' > G' at low frequencies, whereas a crossover was observed at high frequencies. They proposed that this behavior is related to the decrease of the structural relaxation time with increasing the strain-rate amplitude in analogy of the typical scenario of 3D softsolids [103]. Furthermore, this work has demonstrated the validity of the strain-rate-frequency superposition principle developed by Wyss for interfacial shear measurements in 3D solids [103]. This idea consists of maintaining the strain-rate constant as the frequency is varied. Following this principle the authors isolated the component of the response due to structural relaxation, even though they can occur at frequencies too low to be accessible with standard techniques. Furthermore, the authors found that dependence of both G' and G" on the frequency defines a master curve G'/a and G''/a vs. b, being a and b parameters that depend exclusively on the shear rate. The authors found that the relaxation time depends approximately linearly with the shear-rate, as in the three dimensional systems. Another important point of this work was the self-healing character of the particle-laden

interface when the stress is released. This self-healing character of the layers is strongly correlated to the layer coverage and wettability properties of the particles. The same authors [91] point out that both the yield stress and the melting stress of these particle layers are dependent on the wettability properties with maximum values for particles with intermediate hydrophobicity.

A more sophisticated system was studied by Vandebril et al. [104] These authors evaluated the shear modulus of hematite nanoparticles at the interface between two fluid polymers. They pointed out that the stabilization mechanism against the coalescence of the two liquid phases is due to the modification of the rheological properties of the interface by a mechanism similar to that occurring in the Pickering emulsions. Furthermore, they found a dependence of the shear modulus on the strain analogous to that found for Zang et al. for silica nanoparticles at the air–water interface [25]. It is worth mentioning that the hematite nanoparticles form a strong gel-like behavior at the polymer–polymer interface.

The most recent studies related to the shear properties of particleladen interfaces have been performed by Keim and Arratia [105]. These authors studied jammed monolayers of a particle mixture of two different sizes ($4.1 \,\mu$ m and $5.6 \,\mu$ m), and pointed out the existence of a threshold strain amplitude that separates two different regimes. For low strain amplitudes, the interfacial structure remains at long times whereas over the threshold strain value the particles rearrange continuously. This threshold value is identified as the yield strain.

5. Monolayers with particles and surfactants

5.1. Dilational rheology

More intriguing than the study of layers formed exclusively by nanoparticles is the study of the dilational response of mixed layers formed by nanoparticles + surfactant [24]. Ravera et al. [106] studied the effect of hydrophilic silica nanoparticles (diameter around 30 nm) in the adsorption properties and the dilational rheological in the low frequency range (0.005-0.2 Hz) properties of CTAB at both air-water and hexane water-interface. They pointed out the formation of complexes between the surfactant molecules and the nanoparticles that change the hydrophobicity of the silica nanoparticles, thus fostering their adsorption at the interface. However, this process does not present any synergic effect as in the case of polyelectrolyte + surfactant complexes [107]. The values of the elasticity modulus for the mixed layers were higher than those of the surfactant layers of the same concentration, and it was frequency dependent. These effects were found to be stronger for the hexane-water interface than for the water-air one. In a latter work the previous studied were extended to the high frequency range [108], which allowed the authors to two different dynamic relaxations with different frequencies. The lowfrequency dynamics was related to the diffusion of the particles towards the interface, and the high-frequency one was related to the exchange between the interface and the bulk. The theoretical analysis performed for the layers of silica + CTAB at the water + hexane interface showed that the adsorption mechanism shift from a mainly diffusion controlled one for the less hydrophobic nanoparticles to a mixed mechanism for more hydrophobic ones.

Further refinements in the study of the above mentioned system at the air–water interface were made by Liggieri et al. [24]. They performed a broad-frequency range study of the interfacial dilational response (from 10^{-3} to 102 Hz), and obtained qualitative and quantitative information about the kinetics and structure of this type of system by the application of the model developed by Ravera et al. [108]. Fig. 6 shows a typical example for the frequency dependence of the real and imaginary parts of the viscoelastic modulus for an interfacial layer of silica + CTAB and the corresponding fittings to the model proposed by Ravera et al. [108].

This series of works related to the study of silica nanoparticles + CTAB layers have pointed out that the behavior of such systems is governed by an intricate balance between CTAB depletion, the particles hydrophobization by the electrostatic adsorption of the surfactant molecules, and the different interactions established between the particles in the bulk and the interface [109,110]. Wang et al. [111] confirmed the above behavior for larger silica particles.

Ravera et al. [108] and Yazghur et al. [112] have studied the effect of the aging of the interfacial layers of silica + CTAB at the hexane–water and air–water interfaces, respectively. They found a significant effect of aging of the particle layer interface without appreciable variation of the interfacial tension. The elasticity of the interfacial increases strongly during aging, and the particle-laden interface becomes a solid-like insoluble monolayer with high elasticity modulus values, similar to those found for spread monolayers of fumed silica [25]. These aging processes are associated to a significant densification of the interfacial layer as evidenced by the BAM images obtained by Yazghur et al. [112]. The existence of aging processes is a confirmation of the irreversible attachment of the nanoparticle to the interface.

Santini et al. [113,114] and Zabiegaj et al. [115] have studied the dilational rheology of adsorption layers formed by carbonaceous nanoparticles of different nature and two different surfactants: CTAB and sodium 1-decanesulfonate. The same problem has been studied by Arriaga et al. [116] for a system formed by silica nanoparticles and short chain amino based surfactants. More recently Santini et al. have studied the system that has been the one formed by palmitic acid and silica nanoparticles [117]. This system shows a dilational response quite dependent on the hydrophobization degree of the nanoparticles and for nanoparticles with highly hydrophobic it leads to the formation of solid-like films as evidenced by the BAM images with high values of the elasticity modulus.

In the last few years the toxicity effects of nanoparticles in the lungsurfactant system have been studied by dilational rheology. Guzman et al. have studied several mixed systems formed by silica nanoparticles and different lipids (DPPC [118,119], DPPC + Palmitic acid [34], DPPC + DOPC [120] and DPPC + Cholesterol [121]). The results showed an important frequency dependence of the dilational interfacial modulus, and a significant slowing down of the dynamic response as compared with the monolayers of the pure lipids. Furthermore, new dynamic processes were reported for systems containing lipids that can form hydrogen bonds (palmitic acid and cholesterol) with nondissociated silanol groups at the silica surface. These processes were related to the exchange of lipid molecules between the interface and



Fig. 6. Real (top panel) and imaginary (bottom panel) parts of the dilational viscolasticities of the 1 wt.% silica dispersion with contents of CTAB $c_{CTAB} = 5 \times 10^{-5}$ M. The results in the different range of frequency were obtained by drop shape tensiometer (OD-DS), capillary pressure tensiometer (OB-CPT) and electro-capillary waves (ECW). Reproduced from Ref. [24] with permission from The Royal Society of Chemistry.

the surface of the nanoparticles. A typical example of this type of processes is shown in Fig. 7.

The existing results show that shear rheology is a powerful tool for understanding of the 2D glass like systems.

5.2. Shear rheology

Very few studies have been devoted to the response of particle + surfactant layer against shear deformation. One of the first studies that explores the shear rheology of particles + surfactant systems was the one by Maas et al. [122] who studied the shear of monolayers of different lipids and silica nanoparticles of two different hydrophobicity at the water/oil interface. In their experiments the lipids were dissolved in the oil phase and interacted with the nanoparticles exclusively at the interface. The film formation was monitored in situ by shear rheology. The results evidenced a two-stage kinetic of formation of the interfacial layer. The first step presents a duration approximate of 1 h where the moduli experiment a fast increase till the formation of a cohesive and mainly elastic layer (G' > G''). During the second step (much slower), the moduli grow more slowly as particles and lipid molecules accumulate in the proximity of the interface until the equilibrium exchange between the bulk phases and the interface is reached. At the end of the formation process of the interfacial layer, the values of both G' and G" are much higher than for normal surfactant monolayers in analogy with the results by Safouane et al. [90] for monolayers of silica at the air-water interface. The authors also observed that at fixed particle concentration (5% in the case of Ludox HS-30 silica nanoparticles) it is possible to define a concentration threshold above which the shear modulus remains constant. This threshold concentration coincides with the formation of a close packed lipid film. In an analogous way, fixing the lipid concentration (1 mM of stearic acid), the modulus remains constant above a particle concentration of 10%. The authors concluded that the nanoparticle-lipid films are mainly elastic and that their linear viscoelasticity region is small. Similar conclusions were reached by Degen et al. for monolayers of maghemite nanoparticles $(\gamma$ -Fe₂O₃) and different surfactants (SDS, CTAB, and Brij 35) [123].

5.3. Microrheology

5.3.1. Friction factor of particles at interfaces

For particles trapped at interfaces Einstein's equation, Eq. (23), is still valid. However, one cannot calculate the friction coefficient using Stokes equation and directly substituting the interfacial shear viscosity. Instead, f is a function of the viscosities of the phases (η s), the geometry of the particle (e.g., the radius "a" for spheres), the contact angle between the probe particle and the interface (θ), etc. There is no solution for the slow viscous flow equations for steady translational motion of a sphere in an ideal 2D fluid (Stokes paradox). This problem was first solved by Saffman and Delbrück [124], and then Barentin [125] and Stone and Ajdari [126] solved the same problem but relaxing some of the assumptions made in Ref. [124].

The above authors only treated non protruding particles (or high membrane viscosities); however, in particle tracking experiments the spherical particles used as probes are partially immersed in both fluid phases separating the interface. Danov et al. have calculated the hydrodynamic drag force and the torque acting on a micro spherical particle trapped at different interfaces [127–129] which were modeled as a *compressible* 2D-fluid. With these assumptions they solved numerically the Navier–Stokes equation to obtain the values of the drag coefficient f as a function the contact angle, θ , the dilational elastic modulus, E, and the shear modulus, K. However, they presented their results only in graphical form for given values of θ , E and K, which make it difficult for other researchers to use. Hence we will only briefly review the theory of Fischer [130–132].

Fischer considered that a Langmuir film cannot be considered as a compressible monolayer. In the presence of a surfactant, Marangoni forces (forces due to surface tension gradients) strongly suppress any motion at the surface that compresses or expands the interface due to that any gradient in the surface pressure. Such gradients are instantly



Fig. 7. Modulus of the dilational viscoelasticity vs. frequency by oscillatory barrier experiments for DPPC + Palmitic acid monolayers spread on water (upper) and on silica nanoparticle aqueous dispersion (below), at different values of surface pressure. Reproduced from Ref. [34] with permission from the PCCP Owner Societies.

compensated by the fast motion of the surfactant at the interface, thus leading to a constant surface pressure, and then behaving as an incompressible monolayer (Fischer assumes that the velocity of the 2D surfactant diffusion is faster than the motion of the beads). The fact that the drag on a disk in a monolayer is that of an incompressible surface has been compared with experiments in Ref. [132].

Fischer et al. have numerically solved the problem of a sphere trapped at an interface with a contact angle θ moving in an *incompressible* surface [132]. They solved the fluid dynamic equations for a 3D object moving in a monolayer of surface shear viscosity, η_s between two infinite viscous phases. Then the translational drag coefficient, k_T , was expressed as a series expansion of the Boussinesq number, $B = \eta_{\rm S}/((\eta_1 + \eta_2) \cdot a)$, "a" being the radius of spherical particle:

$$k_{\rm T} = k_{\rm T}^0 + B k_{\rm T}^1 + O\left(B^2\right). \tag{33}$$

For B = 0, and for an air–water interface $(\eta_1, \eta_2 = 0)$, the numerical results for $k_T^{(0)}$ and $k_T^{(1)}$ are fitted with an accuracy of 3% by the formulas,

$$k_{\rm T}^0 \approx 6\pi \sqrt{\tanh\left(32\left(\frac{\rm d}{\rm R}+2\right)/(9\pi^2)\right)} \tag{34}$$

$$k_{\rm T}^{(1)} \approx \begin{cases} -4\ln\left(\frac{2}{\pi}\arctan\left(\frac{2}{3}\right)\right) \left(\frac{a^{3/2}}{(d+3a)^{3/2}}\right) & (d/a>0) \\ -4\ln\left(\frac{2}{\pi}\arctan\left(\frac{d+2a}{3a}\right)\right) & (d/a<0) \end{cases}$$
(35)

where d is the distance from the apex of the bead to the plane of the interface (which defines the contact angle). Note that if d goes to infinity, $k_T^0 = 6\pi$, which is the correct theoretical value for a sphere in bulk (Stokes law). They found that, even in the absence of any appreciable surface viscosity, the drag coefficient of an incompressible monolayer is higher than that of a free interface, and the MSD data cannot be used to extract the surface shear viscosity using Danov's theory especially in the limit of low surface viscosities.

5.3.2. Experimental results

Sickert and Rondelez were the first to apply Danov's ideas to obtain the surface shear viscosity by particle tracking [133]. They used spherical microparticles trapped at the air–water interface, which was covered with different Langmuir films. They have measured the surface viscosity of three monolayers formed by pentadecanoic acid (PDA), L- α -dipalmitoylphosphatidylcholine (DPPC) and N-palmitoyl-6-n-penicillanic acid (PPA), respectively. The values of the shear viscosities for PDA, DPPC and PPA reported were in the range of 1 to 11.10^{-10} N s m⁻¹ in the liquid expanded region of the monolayer. These values are beyond the range that can be reached by macroscopic mechanical methods, that usually have a lower limit in the range of 10^{-7} N s m⁻¹.

Bonales et al. have calculated the shear viscosity of two polymer Langmuir films using Danov's theory, and compared these values with those obtained by canal viscosimetry [134]. Video particle tracking together with Danov's theory were used by Maestro et al. [135] to study the glass transition in Langmuir films. Fig. 8 shows the results obtained for a monolayer of poly(4-hydroxystyrene) at an air-water interface. For all the monolayers reported in Ref. [23] the surface shear viscosity calculated from Danov's theory and Fischer's theories using the D values obtained from single particle tracking was lower than that measured with the macroscopic canal surface viscometer. Similar qualitative conclusions were reached at by Sickert et al. for their monolayers [136]. These authors have later reanalyzed their original data [133] by combining the Danov's et al. [127] for the resistance coefficient of a sphere at a clean, compressible surface and at the contact angle of their experiments (θ = 50°), and the predictions of Fischer et al. [130] for a sphere in a surfactant monolayer (incompressible) with the contact angle corrected by the change in the surface tension. By combining the two theories in this way, they found that the relation $D_0 / D_{\rightarrow 0}$ (D_0 being the diffusion coefficient of the beads at a free compressible surface, and $D_{\rightarrow 0}$ the value of an incompressible monolayer which surface concentration is tending to zero) is, theoretically, not equal to 1 but to about 0.8, which is confirmed by their experiment, and also confirms the observations of Barentin et al. [125] and Lee et al. [137] for different systems. In spite of the apparent success of this Danov–Fisher theory, the surface viscosity values are rather low when compared to the results obtained by macrorheology methods (see below).

Fig. 9 shows the friction coefficient of latex particles at the water–air interface obtained from single particle tracking for polystyrene latex particles. It also shows the values calculated from Danov's and from Fischer's theories (notice that for the bare interface E = B = 0). The figure clearly shows that both theories underestimate the experimental values over the whole θ range. An empirical factor of $f(\theta)_{exp}/f(\theta)_{Fisher} = 1.8 \pm 0.2$ brings the values calculated with Fischer's theory in good agreement with the experiments at all the contact angle values. A similar situation was found for the water–n-octane interface with a smaller correction factor $f(\theta)_{exp}/f(\theta)_{Fisher} = 1.2 \pm 0.1$.

The huge difference cannot be attributed to specific interactions between the particles and the monolayer. In effect, Fig. 10 shows that the values obtained are the same for particles of rather different surface characteristics and sizes. Moreover, the values calculated from the modified-Fisher's theory or by direct application of the GSE equation lead to almost indistinguishable surface shear viscosities [23].

This discrepancy between micro- and macrorheology in the study of monolayers seems to be a rather frequent situation and no clear theoretical answer has been found so far for this fact. This type of disagreement has been also found in 3D systems, where in some cases the origin of the problem has been identified to be the inhomogeneity of the system [138,139]. In the analysis of the particle tracking at interfaces shown above, it has been assumed that systems are homogeneous, which might not be the case. Prasad et al. have applied the two-particle correlation method (Eq. (26)) to the motion of particles trapped to the air–water interface covered with a Langmuir monolayer of human serum albumin (HSA) as a function of surface concentration [140]. They found that for high surface concentrations the one and two particle (correlated) measurements give different values of the viscosity. They explained this by suggesting that the



Fig. 8. Temperature dependence of the surface shear viscosity of a monolayer of poly(4-hydroxystyrene) at the air-water interface obtained by particle tracking (the insets show the corresponding values measured with a macroscopic canal viscometer). Left: experiments done at $\Pi = 8 \text{ mN m}^{-1}$. Right: triangles correspond to $\Pi = 3 \text{ mN m}^{-1}$ and circles to $\Pi = 2 \text{ mN m}^{-1}$.



Fig. 9. Friction coefficients calculated from the experimental diffusion coefficients measured by particle tracking experiments (symbols), by Danov's theory (dotted line), by Fischer's theory (dashed line), and by the corrected Fischer's theory (continuous line).

monolayer is inhomogeneous. Both methods agree when the particle size is of the same order than the scale of the inhomogeneities of the system. However, the authors did not compare particle tracking results with macrorheology.

However, the problem might be not only due to the length scale of the rheology but also because the active or passive character of the technique used. In fact, Lee et al. [137] combined active and passive microrheology methods to study protein (β -lactoglobulin) layers at the air–water interface. They used *magnetic nanowire microrheology* and *particle tracking* with correlated analysis as a function of adsorption time, and found that the surface viscosity obtained is about one order of magnitude larger when measured with the active technique (see Fig. 11). Both techniques are micro-rheology methods but give quite different values for the surface viscosity.

It is also needed to bear in mind that ideal 2D systems do not exist, the interface is a region of certain thickness which makes the interpretation of the results quite slippery. For example, Prasad and Weeks [141] have measured the surface viscosity of a commercial dishwasher surfactant (soluble) in a soap film by single and correlated particle tracking as a



Fig. 10. Surface shear viscosity of a monolayer of poly(t-butyl acrylate) (molecular weight 4.6 kDa) measured by particle tracking. Different microparticles were used: poly(styrene) of 1.6 and 5.7 µm (stabilized by sulfonate groups); poly(methylmethacrylate) stabilized by Coulombic repulsions (PMMA1), or by steric repulsions (PMMA2); silica particles stabilized by Coulombic repulsions. Empty symbols: the viscosities were calculated using Fischer theory. Full symbols: calculated by the GSE equation.

function of the film thickness. They found unphysical values for the surface viscosity using the Saffman equation when the thickness of the film is larger than a certain value. Above this critical thickness, single particle tracking gives negative values for the surface viscosity, and two-particle correlated MSD gives large positive values compared to the values found in thin films. Fig. 12 shows their results.

It would be possible to extend this idea to thick monolayers (for example, for some polymer monolayers), and consider that the motion of the beads does not take place in a 2D environment but in a 3D one. This would make quite tricky the interpretation of the particle tracking results obtained using the theories outlined in the previous paragraphs.

It was also shown that sometimes for very dense layers of polymers, the probes move faster than they do in layers formed at lower surface concentrations of the same polymer. In these cases we can imagine that the particle probes could be expelled out of the interface and keep under (or on) the layer given erroneous values of the diffusion coefficient and for the surface viscosity when calculated from the MSD of those particles and the mentioned theories.

6. Conclusions

A relatively large number of well understood experimental techniques are available for measuring the dilational rheology of fluid interfaces, including particle laden ones. The measurements can be performed in frequency range spanning from 1 mHz to a few MHz, though above 1 kHz some of the surface-wave techniques can only be applied for interfaces for which the ratio of elastic modulus to the surface tension is small. In the case of surface shear rheology the high frequency range can only be reached using micro-rheological techniques.

For particle laden interfaces, in the absence of surfactants, the diffusion coefficient of the particles is strongly affected by interparticle interactions, and their dynamics is found to be subdiffusive except for very low particle concentrations. Nevertheless, in most cases the dynamics of the particles can be analyzed with reasonable accuracy using the Langevin equation for particles bound by an elastic force. The infinite dilution diffusion coefficient obtained using this method agrees well with that obtained from the analysis of Brownian dynamics of highly diluted particle monolayers. This is important because in most real cases the particle concentration at the interfaces is relatively high. The dilational rheology experiments carried out with different techniques have pointed out that the elastic modulus strongly depends on the contact angle of the particles at the fluid interface. The concentration and frequency behavior of the elastic modulus have been satisfactorily modeled with the same model used for protein monolayers. An important issue is that the linear viscoelastic regime



Fig. 11. Interfacial viscosities of β -lactoglobulin at the air–water interface as a function of adsorption time measured by an active microrheology technique (squares) and a passive one (circles). Reprinted with permission from Ref. [137]. Copyright (2010) American Chemical Society.



Fig. 12. Interfacial viscosity as a function of h/d. Note that for h/d < 4 the viscosity is independent of h (points from a to g). A transition from 2D to 3D behavior occurs at $h/d \sim 7$. Adapted with permission from Ref. [141]. Copyright (2009) by The American Physical Society.

of particle monolayers is small, which is a strong problem because in real systems the mechanical perturbations usually have large amplitudes. The shear rheology of spherical particles trapped at interfaces has pointed out that the loss modulus is much higher than the elastic one. However, this is no longer true at high particle concentrations, where the system can even form a soft-glass. It has been found that for these systems the strain-frequency superposition principle holds. The situation is different for ellipsoidal particles, where the elastic modulus is large due to the formation of selfaggregates that associate to form ramified networks.

The rheology of monolayers containing both surfactants and particles has received much attention because both components are usually present in emulsions and foams. In most cases soluble nanoparticles and soluble or insoluble surfactants have been used. In general surfactants adsorb on the particle surface, thus changing its hydrophobicity. In general the elasticity modulus of the mixed layers was higher than that of the surfactant monolayer, and shows a complex frequency dependence. The later was modeled with the same theory than the protein + surfactant monolayers. The behavior of these systems is governed by an intricate balance between surfactant depletion, particle hydrophobization, and the interactions between particles at the interface and in the bulk. Contrary to dilational rheology, only a few studies exist on the shear surface rheology of the composite monolayers, thus clearly more work is necessary to understand the behavior of these systems.

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References

- [1] Miller R, Liggieri L, editors. Interfacial rheology. Leiden: Brill; 2009.
- [2] Dynamics and rheology of complex fluid-fluid interfaces. In: Vermant J, Fuller GG, editors. Special Issue. Soft Matter, 7; 2011.
- [3] Volkov AG, Deamer DW, Tanelian DL, Markin VS. Liquid interfaces in chemistry and biology. New York: John Wiley & Sons; 1998.
- [4] Binks BP, Horozov TS. Colloidal particles at liquid interfaces. Cambridge: Cambridge University Press; 2006.
- [5] Binks BP. Particles as surfactants similarities and differences. Curr Opin Colloid Interface Sci 2002;7:21–41.
- [6] Bresme F, Oëttel M. Nanoparticles at fluid interfaces. J Phys Condens Matter 2007;19:413101.
- [7] Kralchevsky P, Nagayama K. Particles at fluid interfaces, attachment of colloid particles and proteins to interfaces and formation of two-dimensional arrays. In: Möbius D, Miller R, editors. Studies in interfacial science, vol. 10. Amsterdam: Elsevier; 2001.

- [8] Whitby CP, Fornasiero D, Ralston J, Liggieri L, Ravera F. Properties of fatty aminesilica nanoparticle interfacial layers at the hexane–water interface. J Phys Chem C 2012;116:3050–8.
- [9] Maestro A, Kotsmar C, Javadi A, Miller R, Ortega F, Rubio RG. Adsorption of βcasein-surfactant mixed layers at the air-water interface evaluated by interfacial rheology. J Phys Chem B 2012;116:4898–907.
- [10] Meinders MBJ, van Vliet T. The role of interfacial rheological properties on Ostwald ripening in emulsions. Adv Colloid Interface Sci 2004;108–109:119–26.
- [11] Stocco A, Rio E, Binks BP, Langevin D. Aqueous foams stabilized solely by particles. Soft Matter 2011;7:1260–7.
- [12] Muñoz MG, Monroy F, Hernández P, Ortega F, Rubio RG, Langevin D. Anomalous damping of the capillary waves at the air–water interface of a soluble triblock copolymer. Langmuir 2003;19:2147–54.
- [13] Monroy F, Ortega F, Rubio RG, Velarde MG. Surface rheology, equilibrium and dynamic features at interfaces, with emphasis on efficient tools for probing polymer dynamics at interfaces. Adv Colloid Interface Sci 2007;134–135:175–89.
- [14] Bonales LJ, Rubio JEF, Ritacco H, Vega C, Rubio RG, Ortega F. Freezing transition and interaction potential in monolayers of microparticles at fluid interfaces. Langmuir 2011;27:3391–400.
- [15] Bonales LJ, Martínez-Pedrero F, Rubio MA, Rubio RG, Ortega F. Phase behavior of dense colloidal binary monolayers. Langmuir 2012;28:16555–66.
- [16] Law AD, Buzza DM, Hozorov TS. Two-dimensional colloidal alloys. Phys Rev Lett 2011;106:128302.
- [17] Cicuta P, Donald A. Microrheology: a review of the method and applications. Soft Matter 2007;3:1449–95.
- [18] Morse DC. Theory of constrained Brownian motion. In: Rice SA, editor. Advances in chemical physics. Hoboken, NJ: John Wiley & Sons; 2004.
- [19] Moschakis Th. Microrheology and particle tracking in food gels and emulsions. Curr Opin Colloid Interface Sci 2013;18:311–23.
- [20] Ortega F, Ritacco H, Rubio RG. Interfacial rheology: particle tracking and related techniques. Curr Opin Colloid Interface Sci 2010;15:237–45.
- [21] Krägel J, Derkatch SR, Miller R. Interfacial shear rheology of protein-surfactant layers. Adv Colloid Interface Sci 2008;144:38–53.
- [22] Brooks CF, Fuller GG, Frank CW, Robertson CR. An interfacial stress rheometer to study rheological transitions in monolayers at the air-water interface. Langmuir 1999;15:2450–9.
- [23] Maestro A, Bonales LJ, Ritacco H, Fischer TM, Rubio RG, Ortega F. Surface rheology: macro- and microrheology of poly(t-butyl acrylate) monolayers. Soft Matter 2011;7:7761–71.
- [24] Liggieri L, Santini E, Guzmán E, Maestro A, Ravera F. Wide-frequency dilational rheology investigation of mixed silica nanoparticle – CTAB interfacial layers. Soft Matter 2011;7:6699–7709.
- [25] Kobayashi T, Kawaguchi M. Surface dilational moduli of latex-particle monolayers spread at air-water interface. J Colloid Interface Sci 2013;390:147–50.
- [26] Krotov VV. Basics of interfacial rheology. In: Miller R, Liggieri L, editors. Interfacial rheologyLeiden: Brill; 2009. p. 1.
- [27] Danov KD, Radulova GM, Kralchevsky PA, Golemanov K, Stoyanov SD. Surface shear rheology of hydrophobin adsorption layer: laws of viscoelastic behavior with applications to long-term foam stability. Faraday Discuss 2012;158:195–221.
- [28] Joos P. Dynamic surface phenomena. Utrecht: VSP; 1999.
- [29] Lyklema J. Fundamentals of interface and colloid science, vol. III. San Diego: Academic Press; 2000.
- [30] Ritacco H, Cagna A, Langevin D. Oscillatory bubble measurements of the compression viscoelasticity of mixed surfactant-polyelectrolyte surface layers. Colloids Surf A 2006;282–283:203–9.
- [31] Hiles H, Maestro A, Monroy F, Ortega F, Rubio RG. Polymer monolayers with a small viscoelastic linear regime: equilibrium and rheology of poly(octadecyl acrylate) and poly(vinyl stearate). J Chem Phys 2007;126:124904.
- [32] Hiles H, Monroy F, Bonales LJ, Ortega F, Rubio RG. Fourier-transform rheology of polymer Langmuir monolayers: analysis of the non-linear and plastic behaviors. Adv Colloid Interface Sci 2006;122:67–77.
- [33] Catapano ER, Arriaga LR, Espinosa G, Monroy F, Langevin D, López-Montero I. Solid character of membrane ceramides: a surface rheology study of their mixtures with sphingomyelin. Biophys J 2011;101:2721–30.
- [34] Guzmán E, Liggieri L, Santini E, Ferrari M, Ravera F. Influence of silica nanoparticles on dilational rheology of DPPC-palmitic acid Langmuir monolayers. Soft Matter 2012;8:3938–48.
- [35] Sagis L. Dynamic properties of interfaces in soft matter: experiments and theory. Rev Mod Phys 2011;83:1367–402.
- [36] Monroy F, Ortega F, Rubio RG. Dilational rheology of insoluble polymer monolayers: poly(vinylacetate). Phys Rev E 1998;58:7629–41.
- [37] Alexandrov NA, Marinova KG, Gurkov TD, Danov KD, Kralchevsky PA, Stoyanov SD, et al. Interfacial layers from the protein HFBII hydrophobin: dynamic surface tension, dilatational elasticity and relaxation times. J Colloid Interface Sci 2012;376:296–306.
- [38] Hilles HM, Monroy F. Dilational creep compliance in Langmuir polymer films. Soft Matter 2011;7:7240–6.
- [39] Findley WN, Lai JS, Onaran K. Creep and relaxation of nonlinear viscoelastic materials. New York: Dover Pubs.; 1976.
- [40] Benjamins J, Lucassen-Reynders EH. Surface dilational rheology of proteins adsorbed at air/water and oil/water interfaces. In: Moebius D, Miller R, editors. Proteins at liquid interfaces. Philadelphia: Elsevier Science; 1998.
- [41] Langevin D. Light scattering by liquid surfaces and complementary techniques. New York: Marcel Dekker; 1991.

- [42] Cicuta P, Hopkinson I. Recent developments of surface light scattering as a tool for optical-rheology of polymer monolayers. Colloids Surf A 2004;233:97–107.
- [43] Grigoriev D, Stubenrauch C. Surface elasticities of aqueous dodecyl-p-maltoside solutions: a capillary wave study. Colloids Surf A 2007;296:67–75.
- [44] Krägel J, Derkatch SR. Interfacial shear rheology. Curr Opin Colloid Interface Sci 2010;15:246–55.
- [45] Fuller GG, Vermant J. Complex fluid-fluid interfaces: rheology and structure. Annu Rev Chem Biomol Eng 2012;3:519–43.
- [46] van den Tempel M, Lucassen-Reynders E. Relaxation processes at fluid interfaces. Adv Colloid Interface Sci 1983;18:281–301.
- [47] Choi SQ, Steltenkamp S, Zasadzinski JA, Squires TM. Active microrheology and simultaneous visualization of sheared phospholipid monolayers. Nat Commun 2011;2:312.
- [48] Fuller GG. Rheology of mobile interfaces. Rheol Rev 2003;1:77-123.
- [49] Vandebril S, Franck A, Fuller GG, Moldenaers P, Vermant J. A double wall-ring geometry for interfacial shear rheometry. Rheol Acta 2010;49:131–44.
- [50] Verwijlen T, Modenaers P, Stone HA, Vermant J. Study of the flow field in the magnetic rod interfacial stress rheometer. Langmuir 2011;27:9345–58.
- [51] Hilles HM, Ritacco H, Monroy F, Ortega F, Rubio RG. Temperature and concentration effects on the equilibrium and dynamic behavior of a Langmuir monolayer: from fluid to gel-like behavior. Langmuir 2009;25:11528–32.
- [52] Masschaele K, Vanderbril S, Vermant J, Maldivala B. Interfacial rheology. In: Gallegos C, editor. Rheology, vol. 1. Paris: EOLSS; 2010.
- [53] Pelipenki J, Kristl J, Rosic R, Baumgartner S, Kocbek P. Interfacial rheology: an overview of measuring techniques and its role in dispersions and electrospining. Acta Pharm 2012;62:123–40.
- [54] Maestro A, Hilles HM, Ortega F, Rubio RG, Langevin D, Monroy F. Reptation in Langmuir polymer monolayers. Soft Matter 2010;6:4407–12.
- [55] Maestro A, Ortega F, Rubio RG, Rubio MA, Krägel J, Miller R. Rheology of poly(methyl methacrylate) Langmuir monolayers: percolation transition to a soft glasslike system. J Chem Phys 2011;134:104704.
- [56] Reynaert S, Brooks CF, Moldenaers P, Fuller GG, Vermant J. Analysis of the magnetic rod interfacial stress rheometer. J Rheol 2008;52:261–85.
- [57] Saxton MJ, Jacobson K. Single-particle tracking: applications to membrane dynamics. Annu Rev Biophys Biomol Struct 1997;26:373–99.
- [58] Konopka MC, Weisshaar JC. Heterogeneous motion of secretory vesicles in the actin cortex of live cells: 3D tracking to 5-nm accuracy. J Phys Chem A 2004;108:9814–26.
- [59] Vilaseca E, Isvoran A, Madurga S, Pastor I, Garces JL, Mas F. New insights into diffusion in 3D crowded media by Monte Carlo simulations: effect of size, mobility and spatial distribution of obstacles. Phys Chem Chem Phys 2011;13:7396–407.
- [60] Louit G, Asahi T, Tanaka G, Uwada T, Masuhara H. Spectral and 3-dimensional tracking of single gold nanoparticles in living cells studied by Rayleigh light scattering microscopy. J Phys Chem C 2009;113:11766–72.
- [61] Chen DT, Weeks ER, Crocker JC, Islam MF, Verma R, Gruber J, et al. Phys Rev Lett 2003;90:108301.
- [62] Gardel ML, Valentine MT, Weitz DA. Microrheology. In: Brauer K, editor. Microscale diagnostic techniques. Berlin: Springer; 2005.
- [63] Liu J, Gardel ML, Kroy K, Frey E, Hoffman BD, Crocker JC, et al. Microrheology probes length scale dependent rheology. Phys Rev Lett 2006;96:118104.
- [64] Mason TG, Weitz DA. Optical measurements of frequency-dependent linear viscoelastic moduli of complex fluids. Phys Rev Lett 1995;74:1250–3.
- [65] Levine AJ, Lubensky TC. One- and two-particle microrheology. Phys Rev Lett 2000;85:1774–7.
- [66] Bhattacharya R, Basu JK. Microscopic dynamics of nanoparticle monolayers at airwater interface. J Colloid Interface Sci 2013;396:69–74.
- [67] Dasgupta BR, Tee SY, Crocker JC, Frisken BJ, Weitz DA. Microrheology of polyethylene oxide using diffusion wave spectroscopy and single scattering. Phys Rev E 2002;65:051505.
- [68] Evans RM, Tassieri M, Auhl D, Waigh ThA. Direct conversion of rheological compliance measurements into storage and loss moduli. Phys Rev E 2009;80:012501.
- [69] Mason ThG. Estimating the viscoelastic moduli of complex fluids using the generalized Stokes–Einstein equation. Rheol Acta 2000;39:371–8.
- [70] Wu J, Dai LL. One-particle microrheology at liquid–liquid interfaces. Appl Phys Lett 2006;89:094107.
- [71] Felderhof BU. Estimating the viscoelastic moduli of a complex fluid from observation of Brownian motion. J Chem Phys 2009;131:164904.
- [72] Song Y, Luo M, Dai LL. Understanding nanoparticles diffusion and exploring interfacial nanorheology using molecular dynamics simulations. Langmuir 2009;26:5–9.
- [73] Wu Ch-Y, Tarimala S, Dai LL. Dynamics of charged microparticles at oil-water interfaces. Langmuir 2006;22:2112–6.
- [74] Wu Ch-Y, Song Y, Dai LL. Two-particle microrheology at oil-water interfaces. Appl Phys Lett 2009;95:144104.
- [75] Ou-Yang HD, Wei MT. Complex fluids: probing mechanical properties of biological systems with optical tweezers. Ann Rev Phys Chem 2010;61:421–40.
- [76] Frenkel D. Soft condensed matter. Phys A 2002;313:1-31.
- [77] Dhont JKG. An introduction to dynamics of colloids. Amsterdam: Elsevier; 1996.
- [78] Peng Y, Chen W, Fischer Th M, Weitz DA, Tong P. Short-time self-diffusion of nearly hard spheres at an oil-water interface. J Fluid Mech 2009;618:243–61.
 [79] Mazoyer S, Ebert F, Maret G, Keim P. Eur Phys Lett 2009;88:66004.
- Mazoyer S, Ebert F, Maret G, Keim P. Eur Phys Lett 2009;88:060 Mazoyer S, Ebert F, Maret G, Keim P. Eur Phys J E 2009;34:101.
- [80] Pusey PN, van Megen W. Dynamic light scattering by non-ergodic media. Phys A 1989;157:705.
- [81] Krall AH, Weitz DA. Internal dynamics and elasticity of fractal colloidal gels. Phys Rev Lett 1998;80:778–81.
- [82] Romers S, Scheffold F, Schurtenberger P. Sol-gel transition of concentrated colloidal suspensions. Phys Rev Lett 2000;85:4980–3.

- [83] Bellour M, Skouri M, Munch J-P, Hébraud P. Brownian motion of particles embedded in a solution of giant micelles. Eur Phys J E 2002;8:431–6.
- [84] Galvan-Miyoshi J, Delgado J, Castillo R. Diffusing wave spectroscopy in Maxwellian fluids. Eur Phys J E 2008;26:369–77.
 [85] Keim P, Maret G, Herz U, von Grünberg HH. Harmonic lattice behavior of two-
- dimersional colloidal crystals. Phys Rev Lett 2004;21:215504. [86] Ohshima YN, Nishio I. Colloidal crystal: bead-spring lattice immersed in viscous
- media. J Chem Phys 2001;114:8649–58. [87] Liggieri L, Miller R. Relaxation of surfactants adsorption layers at liquid interfaces.
- Curr Opin Colloid Interface Sci 2010;15:256–63.
- [88] Miller R, Feinerman VB, Kovalchuk VI, Grigoriev DO, Leser ME, Michel M. Composite interfacial layers containing micro-size and nano-size particles. Adv Colloid Interface Sci 2006;128–130:17–26.
- [89] Cervantes-Martinez A, Rio E, Delon G, Saint-James A, Langevin D, Binks BP. On the origin of the remarkable stability of aqueous foams stabilized by nanoparticles: link with microscopic surface properties. Soft Matter 2008;4:1531–5.
- [90] Safouane M, Langevin D, Binks BP. Effect of particle hydrophobicity on the properties of silica particle layers at the air-water interface. Langmuir 2007;23:11546–53.
- [91] Zang DY, Rio E, Delon G, Langevin D, Wei B, Binks BP. Influence of the contact angle of silica nanoparticles at the air-water interface on the mechanical properties of the layers composed of these particles. Mol Phys 2011;109:1057–66.
- [92] Miller R, Fainerman VB, Makievski AV, Krägel J, Grigoriev DO, Kazakov VN, et al. Dynamics of protein and mixed protein/surfactant adsorption layers at the water/fluid interface. Adv Colloid Interface Sci 2000;86:39–82.
- [93] Cicuta P, Stancik EJ, Fuller GG. Shearing or compressing a soft glass in 2D: timeconcentration superposition. Phys Rev Lett 2003;90:236101.
- [94] Madivala B, Fransaer J, Vermant J. Self-assembly and rheology of ellipsoidal particles at interfaces. Langmuir 2009;25:2718–28.
- [95] Basavaraj MG, Fuller GG, Fransaer J, Vermant J. Packing, flipping, and buckling transitions in compressed monolayers of ellipsoidal latex particles. Langmuir 2006;22:6605–12.
- [96] Madivala B, Vandebril S, Fransaer J, Vermant J. Exploiting particle shape in solid stabilized emulsions. Soft Matter 2009;5:1717–27.
- [97] Cui Z. Weakly sheared active suspensions: hydrodynamics, stability, and rheology. Phys Rev E 2011;83:031911.
- [98] Reynaert S, Moldenaers P, Vermant J. Interfacial rheology of stable and weakly aggregated two-dimensional suspensions. Phys Chem Chem Phys 2007;9:6463–75.
- [99] Mendoza A. Unpublished results.
- [100] Krishnaswamy R, Majumdar S, Ganapathy R, Agarwal VV, Sood AK, Rao CNR. Interfacial rheology of an ultrathin nanocrystalline film formed at the liquid/liquid interface. Langmuir 2007;23:3084–7.
- [101] Orsi D, Baldi G, Cicuta P, Cristofolini L. On the relation between hierarchical morphology and mechanical properties of a colloidal 2D gel system. Colloids Surf A 2012;413:71–7.
- [102] Zang DY, Rio E, Langevin D, Wei B, Binks BP. Viscoelastic properties of silica nanoparticle monolayers at the air-water interface. Eur Phys J E 2010;31:125–34.
- [103] Wyss HM, Miyazaki K, Mattsson J, Hu Z, Reichman DR, Weitz DA. Strain-rate frequency superposition: a rheological probe of structural relaxation in soft materials. Phys Rev Lett 2007;98:238303.
- [104] Vandebril S, Vermant J, Moldenaers P. Efficiently suppressing coalescence in polymer blends using nanoparticles: role of interfacial rheology. Soft Matter 2010;6:3353–62.
- [105] Keim NC, Arratia PE. Yielding and microstructure in a 2D jammed material under shear deformation. Soft Matter 2013;9:6222–5.
- [106] Ravera F, Santini E, Loglio G, Ferrari M, Liggieri L. Effect of nanoparticles on the interfacial properties of liquid/liquid and liquid/air surface layers. J Phys Chem B 2006;110:19543–51.
- [107] Bain CD, Claesson PM, Langevin D, Meszaros R, Nylander T, Stubenrauch C, et al. Complexes of surfactants with oppositely charged polymers at surfaces and in bulk. Adv Colloid Interface Sci 2010;155:32–49.
- [108] Ravera F, Ferrari M, Liggieri L, Loglio G, Santini E, Zanobini A. Liquid–liquid interfacial properties of mixed nanoparticle-surfactant systems. Colloids Surf A 2008;323:99–108.
- [109] Santini E, Krägel J, Ravera F, Liggieri L, Miller R. Study of the monolayer structure and wettability properties of silica nanoparticles and CTAB using the Langmuir trough technique. Colloids Surf A 2011;382:186–91.
- [110] Maestro A, Guzmán E, Santini E, Ravera F, Liggieri L, Ortega F, et al. Wettability of silica nanoparticle surfactant nano-composite interfacial layers. Soft Matter 2012;8:837–43.
- [111] Wang H, Gong Y, Lu W, Chen B. Influence of nano-SiO₂ on dilational viscoelasticity of liquid/air interface of cetyltrimethyl ammonium bromide. Appl Surf Sci 2008;254:3380–4.
- [112] Yazhgur PA, Noskov BA, Liggieri L, Lin S-Y, Loglio G, Miller R, et al. Dynamic properties of mixed nanoparticle/surfactant adsorption layers. Soft Matter 2013;9:3305–14.
- [113] Santini E, Ravera F, Ferrari M, Alfè M, Ciajolo A, Liggieri L. Interfacial properties of carbon particulate laden liquid interfaces and stability of related foams and emulsions. Colloids Surf A 2010;265:189–98.
- [114] Santini E, Guzmán E, Ravera F, Ciajolo A, Alfè M, Liggieri L, et al. Soot particles at the aqueous interface and effects on foams stability. Colloids Surf A 2012;413:216–23.
- [115] Zabiegaj D, Santini E, Guzmán E, Ferrari M, Liggieri L, Buscaglia V, et al. Nanoparticle laden interfacial layers and application to foams and solid foams. Colloids Surf A 2013. <u>http://dx.doi.org/10.1016/j.colsurfa.2013.02.046</u>.
 [116] Arriaga LR, Dreckham W, Salonen A, Rodrigues JA, Iñiguez-Palomares R, Rio E, et al.
- [116] Arriaga LR, Dreckham W, Salonen A, Rodrigues JA, Iñiguez-Palomares R, Rio E, et al. On the long-term stability of foams stabilised by mixtures of nanoparticles and oppositely charged sort-chain surfactants. Soft Matter 2012;8:11085–97.
- [117] Santini E, Guzmán E, Ravera F, Ferrari M, Liggieri L. Properties and structure of interfacial layers formed by hydrophilic silica dispersions and palmitic acid. Phys Chem Chem Phys 2012;14:607–15.

- [118] Guzmán E, Liggieri L, Santini E, Ferrari M, Ravera F. Influence of silica nanoparticles on phase behavior and structural properties of DPPC–palmitic acid Langmuir monolayers. Colloids Surf A 2012;413:280–7.
- [119] Guzmán E, Liggieri L, Santini E, Ferrari M, Ravera F. Effect of hydrophilic and hydrophobic nanoparticles on the surface pressure response of DPPC monolayers. Phys Chem C 2011;115:21715–22.
- [120] Guzmán E, Liggieri L, Santini E, Ferrari M, Ravera F. DPPC–DOPC Langmuir monolayers modified by hydrophilic silica nanoparticles: phase behavior, structure and rheology. Colloids Surf A 2012;413:174–83.
- [121] Guzmán E, Liggieri L, Santini E, Ferrari M, Ravera F. Mixed DPPC-cholesterol Langmuir monolayers in presence of hydrophilic silica nanoparticles. Colloids Surf B 2013;105:284–93.
- [122] Maas M, Ooi CC, Fuller GG. Thin film formation of silica nanoparticle/lipid composite films at the fluid-fluid interface. Langmuir 2010;26:17867–73.
- [123] Degen P, Wieland DCF, Leick S, Paulus M, Rehage H, Tolan M. Effect of magnetic nanoparticles on the surface rheology of surfactant films at the water surface. Soft Matter 2011;7:7655–62.
- [124] Saffman P-G. Delbrück Brownian motion in biological membranes. Proc Natl Acad Sci U S A 1975;72:3111–3.
- [125] Barentin C, Muller P, Ybert C, Joanny J-F, di Meglio J-M. Shear viscosity of polymer and surfactant monolayers. Eur Phys J E 2000;2:153–9.
- [126] Stone H, Adjari A. Hydrodynamics of particles embedded in a flat surfactant layer overlying a subphase of finite depth. J Fluid Mech 1998;369:151–73.
- [127] Danov K, Aust R, Durst F, Lange U. Influence of the surface viscosity on the hydrodynamic resistance and surface diffusivity of a large Brownian particle. J Colloid Interface Sci 1995;175:36–45.
- [128] Danov K, Dimova R, Pouligny B. Viscous drag of a solid sphere stradding a spherical or flat surface. Phys Fluids 2000;12:2711–22.

- [129] Dimova R, Danov K, Pouligny B, Ivanov IB. Drag of a solid particle trapped in a thin film or at an interface: influence of surface viscosity and elasticity. J Colloid Interface Sci 2000;226:35–43.
- [130] Fischer ThM, Dhar P, Heinig P. The viscous drag of spheres and filaments moving in membrane monolayers. J Fluid Mech 2006;558:451–75.
- [131] Dhar P, Prasad V, Weeks ER, Bohlein Th, Fischer ThM. Immersion of charged nanoparticles in a salt solution/air interface. J Phys Chem B 2008;32:9565–7.
- [132] Fischer ThM. Comment on "Shear viscosity of Langmuir monolayers in the low density limit". Phys Rev Lett 2004;92:139603.
- [133] Sickert M, Rondelez F. Shear viscosity of Langmuir monolayers in the low density limit. Phys Rev Lett 2003;90:126104.
- [134] Bonales LJ, Rubio JEF, Rubio RG, Monroy F, Ortega F. Dynamics in ultrathin films: particle tracking microrheology. Open J Phys Chem 2007;1:25–32.
- [135] Maestro A, Guzmán E, Chuliá R, Ortega F, Rubio RG, Miller R. Fluid to soft-glass transition in a quasi-2D system: thermodynamic and rheological evidences for a Langmuir monolayer. Phys Chem Chem Phys 2011;13:9534–9.
- [136] Sickert M, Rondelez F, Stone HA. Single-particle Brownian dynamics for characterizing the rheology of fluid Langmuir monolayers. Eur Phys Lett 2007;24:66005.
- [137] Lee MH, Reich DH, Steebe KJ, Leheny R. Combined passive and active microrheology study of protein-layer formation at the air-water interface. Langmuir 2009;25:2476-82.
- [138] Alexander M, Dalgleish DG. Diffusing wave spectroscopy of aggregating and gelling systems. Curr Opin Colloid Interface Sci 2007;12:124–86.
- [139] Hasnain I, Donald AM. Microrheology characterization of anisotropic materials. Phys Rev E 2006;73:031901.
- [140] Prasad V, Koehler SA, Weeks ER. Two-particle microrheology of quasi-2D viscous systems. Phys Rev Lett 2006;97:176001.
- [141] Prasad V, Weeks ER. Two-dimensional to three dimensional transition in soap films demonstrated by microrheology. Phys Rev Lett 2009;102:178302.