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Interfacial microrheology: Particle tracking and related techniques

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ABSTRACT

Microrheology offers several advantages over traditional macroscopic rheology: the use of very small samples, the possibility of studying heterogeneous samples and the broad range of frequency that can be explored. In this paper the study of the microrheology of fluid interfaces is reviewed, with special emphasis on particle tracking techniques. We comment the main results and the assumptions of the different approaches for describing the hydrodynamics of a particle trapped at a surfactant or polymer monolayer.

1. Introduction

Many of the diverse properties of soft materials (polymer solutions, gels, filamentous proteins in cells, etc.) stem from their complex structures and dynamics with multiple characteristic length and time scales. A wide variety of technologies, from paints to foods, from oil recovery to processing of plastics, all rely heavily on understanding the flow of complex fluids [1,2].

Rheological measurements on complex materials reveal viscoelastic responses which depend on the time scale at which the sample is probed. In order to characterize the rheological response one usually measures the shear or the Young modulus as a function of frequency by applying a small oscillatory strain; typically, commercial rheometers probe frequencies from mHz up to tens of Hz.

Although standard rheological measurements have been very useful in characterizing soft materials and complex fluids, they are not always well suited for all systems because they need sample volumes larger than a milliliter, thus precluding the study of rare or precious materials, including many biological samples that are difficult to obtain in large quantities. Moreover, conventional rheometers provide an average measurement of the bulk response, and do not allow for local measurements in inhomogeneous systems. To address these issues, a new class of rheology measurement technique has emerged, that probes the material response on micrometer length scales with microliter sample volumes. *Microrheology* is a term that does not describe one particular technique, but rather a number of approaches that attempt to overcome some limitations of traditional bulk rheology. Advantages over macrorheology include a significantly higher range of frequencies available without time–temperature superposition [2], the capability of measuring material inhomogeneities that are inaccessible to macrorheological methods, and rapid thermal and chemical homogenization that allow the transient rheology of evolving systems to be studied [3]. Microrheology methods typically use embedded micron-sized probes to locally deform the sample, permitting the use of very small volumes (~µl). Macro- and microrheology probe different aspects of the material: the former makes measurements over extremely long (macroscopic) length scales using a viscometric flow field, whereas the latter effectively measures material properties on the scale of the probe itself (since flow and deformation fields decay on this length scale). Detailed descriptions of the methods and applications of microrheology to the study of bulk systems have been given in review articles published in recent years [4–10].

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, etc. [11]. Particle-laden interfaces have attracted much attention in recent years. The tendency of colloidal particles to become (almost irreversibly) trapped at interfaces and their behavior once there, has lead to their use in a wide variety of systems including drug delivery, stabilization of foams and emulsions, froth, flotation, or ice cream production. The high trapping energy of particles at interfaces provides a route to use fluid interfaces as a substrate for the self-assembly of particles into materials of specific mechanical, optical or magnetic properties [12].

The interactions of the particles at interfaces are expected to be more complex than in the bulk [13,14••], indeed, the dynamic properties of particle-laden interfaces are strongly influenced by direct interparticle forces (capillary, steric, electrostatic, van der Waals, etc.) and complicated hydrodynamic interactions mediated by the surrounding fluids. In recent books overviews of particles at liquid interfaces have been published [13–17]. At macroscopic scales, the rheological properties of particle-laden fluid interfaces can be viewed

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as those of a liquid–liquid interface with some effective surface viscoelastic properties described by effective shear and compressional viscoelastic moduli. A significant fact is that for the simplest fluid–fluid interface, different dynamic modes have to be taken into account: the capillary (out of plane) mode, and the in-plane mode, which contains dilational (or extensional) and shear contributions. For more complex interfaces, such as thicker ones, other dynamic modes (bending, splaying) have to be considered [18*]. Moreover, the coupling of the abovementioned modes with adsorption/desorption kinetics may be very relevant for interfaces that contain soluble or partially soluble surfactants, polymers or proteins [19–21]. In recent years a number of experimental techniques have been developed for studying the dilational rheology in a broad range of frequencies (1 mHz–100 kHz), both in the linear and non-linear regimes [18,22,23]. In the case of surface shear rheology, most of the information available has been obtained using macroscopic interfacial rheometers which have a sensibility limit of about 10^{-6} N s m^{-1} [18,24–26], but many important systems have surface shear viscosities below this limit. Particle tracking techniques have been foreseen as a powerful method to study the dynamics of interfaces with shear viscosities as low as 10^{-10} N s m^{-1}. In spite that the measurement of diffusion coefficients of particles attached to interfaces is relatively straightforward with modern microrheological techniques, one has to rely on hydrodynamic models of the viscoelastic surroundings traced by the particles in order to obtain variables such as monolayer elasticity or shear viscosity. The more complex the structure of the interface the stronger are the assumptions of the model, thus resulting in more difficulties in checking their validity. In the present work we will briefly review the modern experimental techniques applied to interface dynamics. We will summarize the available theoretical models for calculating the shear microviscosity of fluid monolayers from particle tracking experiments. We will finally discuss the relatively few experimental results available of particle tracking at interfaces. We will highlight that we are far from understanding microrheology results, and we hope that this review will stimulate future works on this subject.

2. Experimental techniques

For studying the viscoelasticity of the probe environment there are two broad types of experimental methods: active methods, which involve probe manipulation, and passive methods, that relay on thermal fluctuations (Brownian motion). Passive techniques are typically more useful for measuring low values of predominantly viscous moduli, whereas active techniques can extend the measurable range to samples with significant elasticity modulus.

2.1. Microrheology techniques suitable for interface dynamics

In general, interface microrheology techniques are adaptations of bulk microrheology techniques. Among the bulk *active* techniques that can be used for interfaces probably the more promising and versatile one is optical tweezers. This technique uses a highly focused laser beam to trap a colloidal particle. A laser beam (usually in the IR range) is focused by a high-quality microscope (high numerical aperture objective) to a spot in the fluid plane. The basic principle behind optical tweezers is the momentum transfer associated with bending light. Light carries a momentum that is proportional to its energy and in the direction of propagation. Any change in the direction of light, by reflection or refraction, will result in a change of the momentum of the light. If an object bends the light, conservation momentum requires that the object must undergo an equal and opposite momentum change. This gives rise to a force acting on the particle in such a way that it is effectively trapped inside the light spot. A detailed description of the theoretical basis and of modern experimental setups has been given by Conroy [27]*. An advantage of this technique is that it can be used to characterize the interparticle interactions once the interface viscosity is known, or to measure the drag coefficient once the trap is calibrated [28]. Another *active* technique used is the Magnetic Nanowire Microrheology [3,29,30]. In this technique magnetic microrods are used as probes. By applying strong magnetic fields the probes can be moved at will and, by videomicroscopy, the response of the microrods can be followed as a function of the magnetic field applied or time. The principle is the same as the Fuller's macroscopic shear surface rheometer, but using a microscopic probe, thus corresponding to a higher Boussinesq number [25].

Some of the *passive* techniques suitable for interface microrheology are based on the light scattering phenomena: Thermal fluctuations of particles in transparent bulk systems can be studied by measuring the intensity correlation function from which the field correlation function $g_1(\tau)$ can be calculated, τ being the lag time. $g_1(\tau)$ is directly related to the average mean-squared displacement of the particles (MSD), $<\Delta r^2(\tau)>$ through

$$g_1(\tau) = \exp\left[-q^2 <\Delta r^2(\tau)> / 6\right] \tag{1}$$

q being the scattering wavevector [31**]. Once $<\Delta r^2(\tau)>$ is obtained, it is possible to calculate the real and imaginary components of the shear moduli, G' and G'' (see below). As far as we know, only in an old paper of Rice's group a setup was described to measure dynamic light scattering at interfaces on polymer monolayers using evanescent waves [32,33]. Further modifications were published by Sainov that improve the precision of the diffusion coefficient measurements [34]. Fluorescence correlation spectroscopy (FCS) can be considered a fluorescent counterpart of dynamic light scattering, and it is usually combined with optical microscopy. In this technique light is focused on a sample, and the fluorescence intensity fluctuations (in our case due to diffusion of labeled molecules or particles) can be measured in the form of a temporal correlation function from which the MSD is obtained. Recent problems to which FCS has been applied can be found in Refs. [35–38]. The use of microscopes makes FCS suitable for the study of the dynamics of particles at interfaces. Moreover, contrary to videomicroscopy particle tracking techniques, it is not necessary to "see" the particles, then interfaces with nanometer sized particles can be studied [39]. It is the same situation when particle tracking is combined with fluorescence detection as in a recent work by Dhar et al. [40] where they used 85 nm fluorescent nanoparticles to study the immersion depth of the nanoparticles from the drag coefficients obtained at the salt solution/air interface.

Particle tracking by videomicroscopy is also a *passive* bulk microrheology technique which was adapted to interfaces but we have chosen to treat it separately in a more extensive way in the next section because it is the most suitable, and simple (experimentally) technique for studying interface microrheology of all the techniques that we have mentioned till now.

2.2. Fundamentals of videomicroscopy particle tracking

The main idea in particle tracking is to follow the trajectories (Brownian motion) of probes introduced into (onto) the system by videomicroscopy. The trajectories of the particles, either in bulk or on surfaces, allow one to calculate the MSD, which is related to the diffusion coefficient, D, and the dimensions in which the translational motion takes place, d, by

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

where the brackets indicate the average over all the particles.

In case of diffusion in a purely viscous material (or interface), α is equal to 1, and the usual 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) or when the system is dominated by the probe particles interactions (being this particularly important at high particle surface coverage) Eq. (2) doesn't fully apply. The movement of nano- and microparticles in these solid-like interfaces cannot simply be interpreted assuming sub-diffusivity $\alpha<1$. In fact if we consider a Maxwell viscoelasticity model the mean square displacement adopts the form of

$$<\Delta r^2(\tau)> = \sigma / E + \sigma\tau / \eta \tag{3}$$

where σ is the stress, E is the elasticity modulus and η is 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) [41]. The diffusion coefficient is related to the friction coefficient, f, by the Einstein relation

$$D = \frac{k_B T}{f}. \tag{4}$$

In 3D f is given by Stokes law, $f = 6\pi\eta$, and for pure viscous fluids the shear viscosity can be directly obtained from the diffusion coefficient.

When the samples are heterogeneous at the scale of particle size (a situation rather frequent specially in biological systems [41–44]), single particle tracking gives erroneous results and the so-called "two-point" correlation method is recommended [45•]. 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 absolute time, t: Then the ensemble averaged tensor product of the vector displacements is calculated [9]:

$$\begin{aligned} D_{\alpha\beta}(r,\tau) &= \left\langle \Delta r^i_\alpha(r,\tau) \Delta r^j_\beta(r,\tau) \delta\left[r - R_{ij}(t)\right] \right\rangle_{i \neq j, t} \\ \Delta r^{i,j}_{\alpha,\beta}(r,\tau) &= r^{i,j}_{\alpha,\beta}(t+\tau) - r^{i,j}_{\alpha,\beta}(t) \end{aligned} \tag{5}$$

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. Two-point 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 [46].

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) [47,48••]:

$$\langle \Delta \tilde{r}^2(s) \rangle = \frac{2k_B T}{3\pi a s \tilde{G}(s)} \tag{6}$$

where $\tilde{G}(s)$ 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 [49]. Different methods have been devised to obtain $\tilde{G}(s)$ from the experimental MSD [49–53]. The GSE equation is valid under the following approximations: (a) the medium around the sphere may be treated as a continuum material, which requires that the size of the particle be larger than any structural length scale of the material; (b) no slip boundary conditions; (c) the fluid surrounding the sphere is incompressible; and (d) there are no inertial effects. 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 [54].

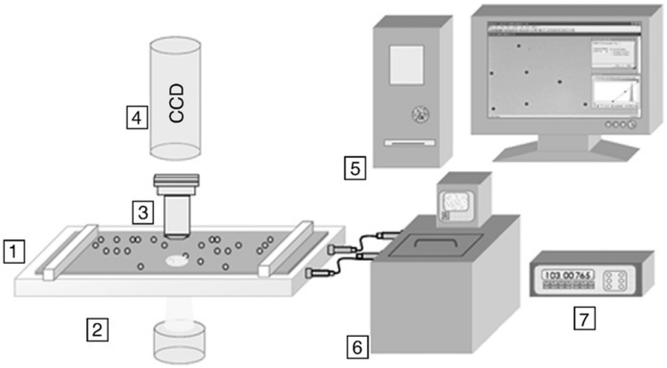

Fig. 1. Typical particle tracking setup for 2D microrheology experiments: 1: Langmuir trough; 2: illumination; 3: microscope objective; 4: CCD camera; 5: computer; 6: thermostat; 7: electronics for measuring the surface pressure.

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. [55] 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 [55–57]. So far, no comparison has been made between the surface shear viscosity calculated by hydrodynamic models and the GSE.

3. Dynamics of particles at interfaces

3.1. Experimental setup and diffusion coefficient of particles adsorbed at fluid interfaces

Fig. 1 shows a sketch of a typical setup for interface particle tracking experiments. A CCD camera (typically 30 fps) is connected to a microscope that permits to image the interface prepared onto a Langmuir Through. The series of images are transferred to a computer to be analyzed and to extract the trajectories of a set of particles. A common problem is that the Brownian motion of the particles is often

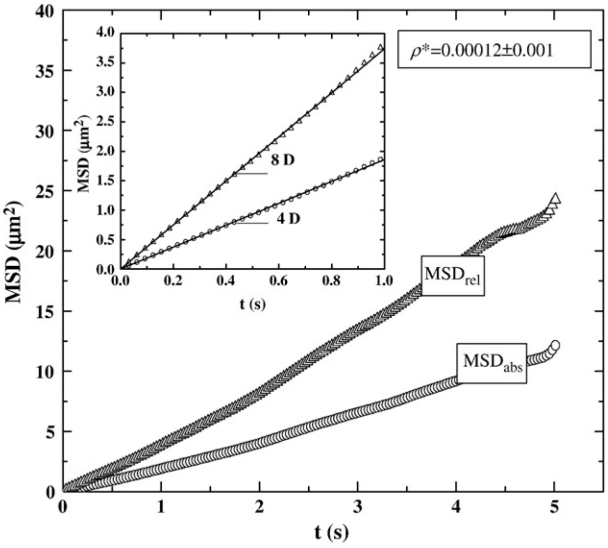

Fig. 2. Mean square displacements and relative square displacement for latex particles at the water/n-octane interface. Experimental details: set of 300 latex particles of 1 μm of diameter, surface charge density: $-5.8\,\mu C\,cm^{-2}$, and reduced surface density, $\rho^*=1.2 \cdot 10^{-3}$ ($\rho^*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

superimposed to a collective motion of the fluid arising from thermal gradients, and then the use of the relative mean square displacement of pairs of particles is useful as defined by

$$MSD_{\rm rel}\equiv\left\langle\Delta r^2_{\rm rel}(\tau)\right\rangle = \left\langle\left(\Delta\vec{r}_{ij}(t+\tau)-\Delta\vec{r}_{ij}(t)\right)^2\right\rangle = 8Dt. \qquad (7)$$

The above averages are taken over all the pairs of particles and initial times, *t*, of the system. In this way any collective motion is eliminated, or reduced.

Fig. 2 shows a typical set of results for the MSD of a system of latex particles (2 μm of diameter) spread at the water/n-octane interface. The analysis of MSD and $\mathrm{MSD_{rel}}$ in terms of Eqs. (2) and (6) 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. (2)). Therefore, only physically meaningful values of *D* can be obtained in the limit of short times, and this should be taken into account when extracting the surface microrheology parameters from *D*.

We want to mention here a problem which appears to be ignored in many papers when analyzing particle tracking at interfaces. As already mentioned, the motion of particles trapped at a fluid interface is strongly influenced by the presence of the other particles. Fig. 3 shows the behavior of *D* on a free surfactant interface as a function of particle surface coverage fraction, $\phi=\rho\pi a^2$, (ρ is surface concentration of particles and *a* the particle radius). Results for different particle radius and two surface charge densities are shown. The diffusion coefficient follows $D(\phi)=D_0-k\phi$, where D_0 is the diffusion coefficient at infinite dilution, and *k* is a parameter that depends on both thermodynamic and hydrodynamic interaction. Theories usually describe D_0, a value which cannot always be obtained because in many systems of biological or technological interest there is no way to modify ϕ in a controlled way.

3.2. Shear microrheology of monolayers at fluid interfaces — Models

For particles trapped at interfaces Einstein's equation, Eq. (4), 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 [58•].

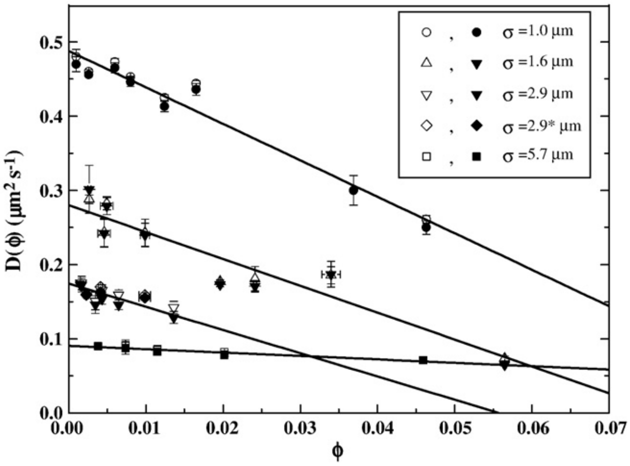

Fig. 3. Concentration dependence of the diffusion coefficient of latex particles at the n-octane–water interface. Symbols represent the experimental results for particles of different sizes. Empty symbols correspond to one-particle MSD, and full symbols for two-particle MSD. ϕ is the area fraction occupied by the particles. All the particles bear sulfate groups at the surface. The two types of particles of diameter $\sigma=2.9$ μm correspond to two different surface charge densities. The large difference between particles of $\sigma=1.0$ and 1.6 μm are related to big differences in their contact angles.

3.2.1. The Saffman–Delbrück equation

Saffman and Delbrück solved the hydrodynamic problem of a disk of radius *a* moving in a highly viscous membrane of thickness *h* [58•]. The membrane is considered of infinite size and both phases, above and below the membrane, to be infinite aqueous phases. The cylinder is allowed to move in the plane of the membrane and to rotate around the *z* axis. A non-slip boundary condition is assumed at the surface of the cylinder and membrane. The motion of the cylinder produces flow fields in both up and down phases in two ways: directly by the particle surface in contact with the fluid phases and by coupling to the 2D membrane flow fields (note that now the system is 3D avoiding the Stokes' paradox). They obtained the following expression for the translational mobility,

$$b_{\rm T}=\frac{1}{f}=\frac{1}{4\pi\eta_{\rm L}h}\left(\ln\left(\frac{\eta_{\rm L}h}{\eta_{\rm w}R}-\gamma\right)\right) \qquad (8)$$

been $\eta_{\rm L}$ and $\eta_{\rm w}$ the viscosities of membrane and liquids respectively, and γ the Euler constant. Note that there is no dependence on the cylinder height, because in the derivation it was assumed that $\eta_{\rm w}\lll\eta_{\rm L}$.

The Saffman and Delbrück model has been extended for a motion of a thin disk immersed in a membrane of arbitrary viscosity, $\eta_{\rm L}$ separating two phases of viscosities η_1 and η_2 [59]. The model assumes infinite phases surrounding the membrane. The case of a disk moving in an incompressible surfactant layer overlaying a sub phase of finite depths has been solved by Barentin et al. [24] on the basis of the assumption that the depth of the sublayer is small compared to the radius of the moving disk (lubrication approximation). Stone and Ajdari [60] have solved the problem for sublayers of an arbitrary depth. The solution is given in the form of a system of integral equations that must be solved numerically.

3.2.2. Danov's model for a sphere in a compressible surfactant layer

The above theories are limited to 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 [61–63] which were modeled as a *compressible* 2D-fluid characterized by two dimensionless parameters *K* and *E* defined as $E=\eta_{\rm sh}/(\eta a)$ and $K=\eta_{\rm d}/(\eta a)$, being $\eta_{\rm sh}$ and $\eta_{\rm d}$ the surface shear and dilational viscosity respectively. Danov et al. assumed that: 1) the movement implies low Reynolds number, thus they ignore any inertial term; 2) the moving particle is not affected by capillarity or electro-dipping; 3) the contact line does not move with respect to the particle surface, and 4) they considered $E=K$, i.e. the interface is compressible. 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 and of *E* (or *K*). They presented their results in graphical form, which are reproduced in Fig. 4.

These curves can be used to obtain the shear viscosity of compressible surfactant layer once one has obtained the diffusion coefficient by particle tracking experiments for a surfactant free interface, and in the presence of the surfactant layer.

3.2.3. Fischer's theory for a sphere in a compressible surfactant layer

Fischer, on the basis of that a Langmuir film cannot be considered as a compressible monolayer, has criticized Danov's theory [64,65]. In the presence of a surfactant, Marangoni forces (forces due to surface tension gradients) strongly suppress any motion at the surface that compress or expands the interface due to that any gradient in the surface pressure. Such gradients are instantly compensated by the fast

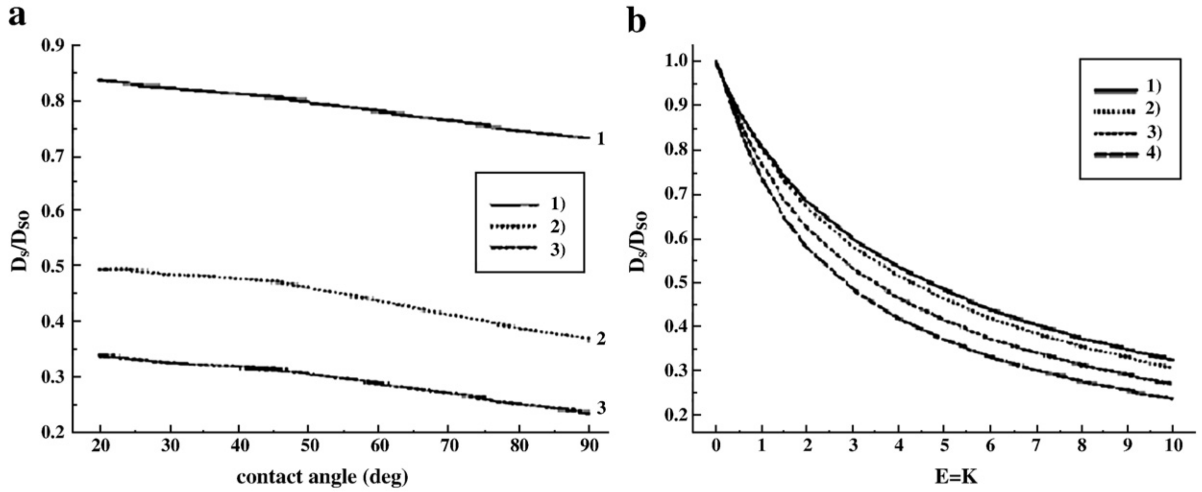

Fig. 4. Left: Effect of contact angle on the diffusion coefficient of a particle trapped at a fluid interface according to Danov's theory [61–63]. D_{s0} is the diffusion coefficient for the bare interface. The different lines correspond to the following values of E $(=K)$: 1) 0; 2) 1; 3) 5. Right: Effect of the surface to bulk shear viscosity on the diffusion coefficient. The different lines correspond to the following values of E $(=K)$: 1) 0; 2) 1; 3) 5; 4) 10.
Figures reproduced with permission from Ref. [63].

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 verified experimentally [66].

Fisher et al. have numerically solved the problem of a sphere trapped at an interface with a contact angle θ moving in an *incompressible* surface [64••]. They showed that contributions due to Marangoni forces account for a significant part of the total drag. This effect becomes most pronounced in the limit of vanishing surface compressibility. In this limit the Marangoni effects are simply incorporated to the model by approximating the surface as incompressible. They resolve the fluid dynamics equations for a 3D object moving in a monolayer of surface shear viscosity, η_s between two infinite viscous phases. The monolayer surface is assumed to be flat (no electrocapillary effects). Then the translational drag coefficient, k_T, was expressed as a series expansion of the Boussinesq number, $B=\eta_s/((\eta_1+\eta_2)\cdot a)$, a being the radius of spherical particle:

$$k_T = k_T^0 + Bk_T^1 + O\left(B^2\right). \tag{9}$$

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,

$$k_T^0 \approx 6\pi\sqrt{\tanh\left(32\left(\frac{d}{R}+2\right)\Big/\left(9\pi^2\right)\right)} \tag{10}$$

$$k_T^{(1)} \approx \begin{cases} -4\ln\left(\frac{2}{\pi}\arctan\left(\frac{2}{3}\right)\right)\left(\frac{a^{3/2}}{(d+3a)^{3/2}}\right) & (d/a>0) \\ -4\ln\left(\frac{2}{\pi}\arctan\left(\frac{d+2a}{3a}\right)\right) & (d/a<0) \end{cases} \tag{11}$$

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.

4. Particle tracking results

Sickert and Rondelez were the first to apply Danov's ideas to obtain the surface shear viscosity by particle tracking [67]. 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 $11\cdot10^{-10}$ 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 [68]. Video particle tracking together with Danov's theory were used by Hilles et al. [69] to study the glass transition in Langmuir films. Fig. 5 shows the results obtained for a monolayer of poly(4-hydroxystyrene) at an air–water interface. For all the monolayers reported in Refs. [68] and [69] the surface shear viscosity calculated from Danov's theory 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 [70]. These authors have later reanalyzed their original data [67] by combining the Danov and Fischer's theories [70]. They used the value determined by Danov's et al. [63] for the resistance coefficient of a sphere at a clean, compressible surface and at the contact angle of their experiments ($\theta=50°$), and the predictions of Fischer et al. [64] 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 $D_0/D_{\to0}$ (D_0 being the diffusion coefficient of the beads at a free compressible surface, and $D_{\to0}$ 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. [24] and Lee. et al. [3] for different systems. In spite of the apparent success of this Danov–Fischer theory, the surface viscosity

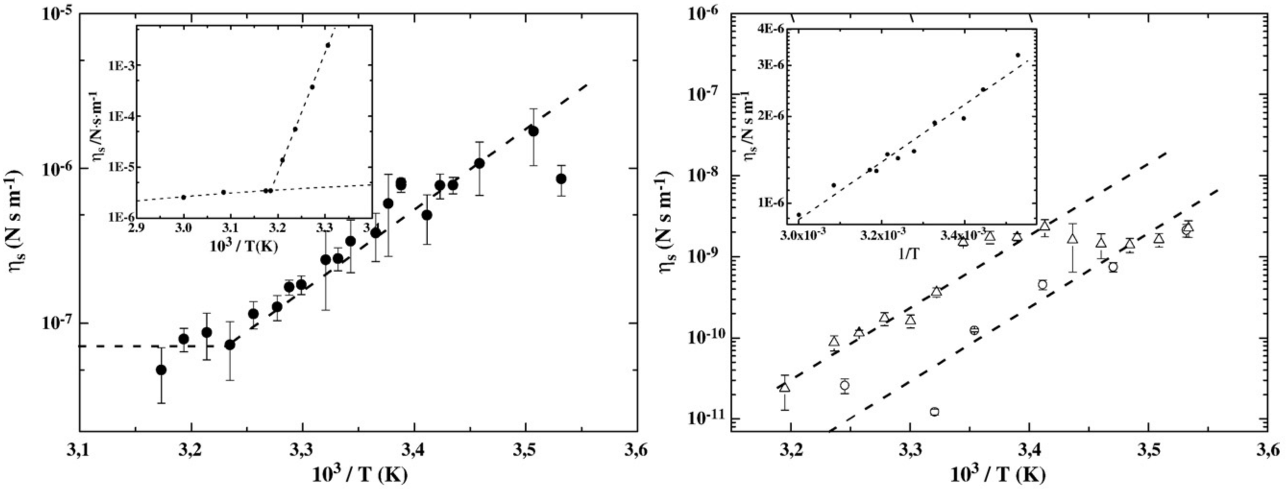

Fig. 5. Temperature dependence of the surface shear viscosity of a monolayer of poly(4-hydroxystyrene) at the air–water interface obtained by particle tracking (the insets show the corresponding values measured with a macroscopic canal viscometer). Left: experiments done at $\Pi = 8$ mN m^{-1}. Right: triangles correspond to $\Pi = 3$ mN m^{-1} and circles to $\Pi = 2$ mN m^{-1}. Notice that the results obtained by particle tracking are much smaller than those obtained with the canal viscometer.

values are rather low when compared to the results obtained by macrorheology methods (see below).

Fig. 6 shows the friction coefficient for 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 $f(\theta)_{\text{exp}}/f(\theta)_{\text{Fisher}} = 1.8 \pm 0.2$ 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 $f(\theta)_{\text{exp}}/f(\theta)_{\text{Fisher}} = 1.2 \pm 0.1$.

As abovementioned there is a quantitative inconsistency between macro and microrheology results. Fig. 7 shows clearly the large difference found between micro- and macrorheology for monolayers of poly(t-butyl acrylate) at the so-called Γ^{**} surface concentration [19]. The macrorheology results have been obtained using two different oscillatory rheometers [26].

The huge difference cannot be attributed to specific interactions between the particles and the monolayer. In effect, Fig. 8 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.

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 [43,44••]. 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 and Weeks have applied the two-particle correlation method (Eq. (5)) 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 [71]. 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 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

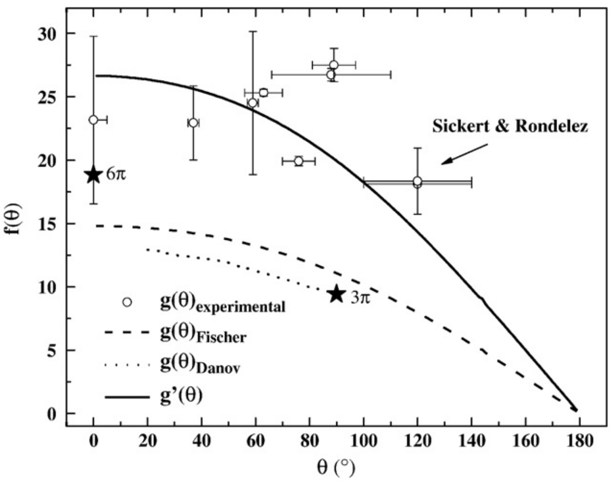

Fig. 6. Friction coefficients calculated from the experimental diffusion coefficients measured by particle tracking experiments (symbols), by Danov's theory (dotted line), by Fischer's theory (dashed line), and by the corrected Fischer's theory (continuous line).

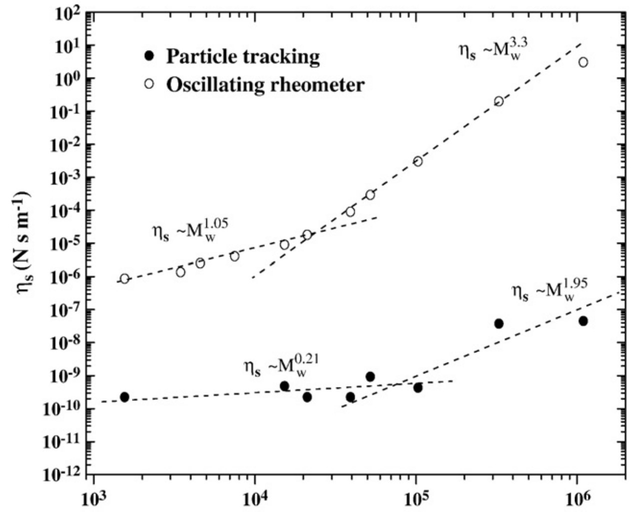

Fig. 7. Surface shear viscosity for monolayers of poly(t-butyl acrylate) as a function of the molecular weight and for a surface pressure of 16 mN m^{-1}. The lower curve corresponds to data obtained from particle tracking. The upper curve was obtained from conventional oscillatory rheometers.

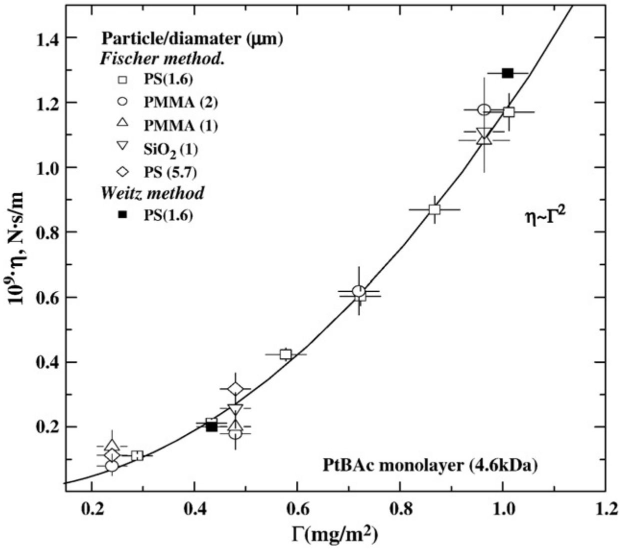

Fig. 8. Surface shear viscosity of a monolayer of poly(t-butyl acrylate) (molecular weight 4.6 kDa) measured by particle tracking. Different microparticles were used: poly(styrene) of 1.6 and 5.7 µm (stabilized by sulfonate groups); poly(methylmethacrylate) stabilized by Coulombic repulsions (PMMA1), 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.

results with macrorheology. In conclusion we need to be very careful when extracting surface viscosities in this kind of systems from single particle tracking, and whenever possible one should use two-particle correlated analysis.

However, the problem might be not only due to the length scale of the rheology but also because of the active or passive character of the technique used. In fact, Lee et al. [3] 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. 9). Both techniques are microrheology 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 et al. [72] have measured the surface viscosity of a commercial dishwasher surfactant (soluble) in a soap film by single and correlated particle tracking as a 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. 10 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.

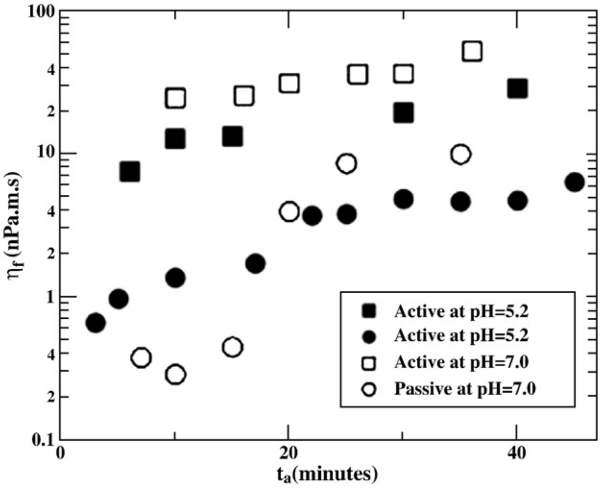

Fig. 9. Interfacial viscosities of β-lactoglobulin at the air–water interface as a function of adsorption time measured by an active microrheology technique (squares) and a passive one (circles).
Reproduce with permission from Ref. [3].

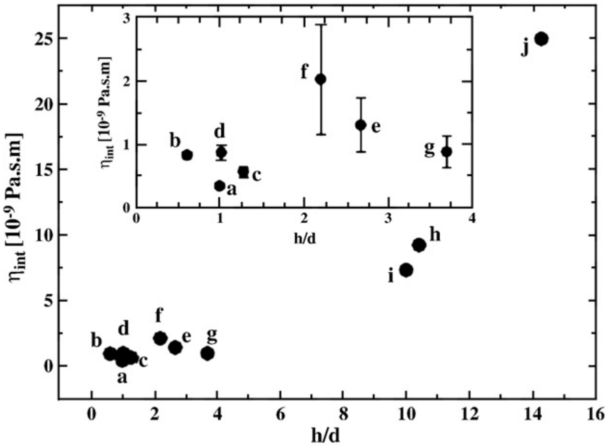

Fig. 10. Interfacial viscosity as a function of h/d. Note that for $h/d<4$ the viscosity is independent of h (points from a to g). A transition from 2D to 3D behavior occurs at $h/d\sim7$.
The figure was reproduced with permission from Ref. [72].

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 [3]. 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.

5. Conclusions

Microrheology techniques, and specially particle tracking, are probably the only suited techniques for the study of the rheology in many systems of interest as for example the dynamics inside cell membranes or in the expanded region of monolayers. However one must be very careful in interpreting the results obtained from single particle tracking and the available theories. When possible the correlated two-particle MSD should be used. It is clear from the results we just have shown that for fluid interfaces much more experimental and theoretical work is needed to explain why the shear surface microviscosity is much smaller than the one measured with conventional surface rheometers. Although all the problems mentioned, in our opinion it is worth continuing working on this microrheological techniques for its potentiality in the study of the dynamics of systems is of biological importance.

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