

# Theoretical and experimental study of surface forces in disperse systems

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## *Teoretické a experimentálne štúdium povrchových síl v disperzných systémoch*

*V príspevku sú stručne zhodnotené výsledky priamych experimentálnych meraní povrchových síl medzi makroskopickými povrchmi so zvláštnym dôrazom na tzv. štrukturálny, resp. hydratačno-hydrofóbny typ povrchových síl. Súčasne sú analyzované povrchové sily medzi mikroskopickými časticami modelových disperzných systémov, a to nepriamo z ich agregáčnej kinetiky, a porovnané s uvedenými výsledkami priamych meraní povrchových síl. Prezentované sú aj dielčie výsledky meraní kinetiky homokoagulácie vodného sólu SiO<sub>2</sub>, pridaním koagulantov u ktorých sa predpokladá potlačujúci účinok na hydratačnú (KCl) a stimulačný účinok na hydrofóbnu (cetyltrimetylamónium bromid - CTAB) interakciu častíc uvedeného hydrosólu ako aj výsledky stanovenia heteroagregácie zo spektier elektroforetického rozptylu svetla binárneho sólu SiO<sub>2</sub>. Tieto merania zatiaľ nepotvrdili existenciu spomínaných krátkodosahových typov povrchových síl.*

**Key words:** surface forces, SFA, AFM, colloids, disperse systems, hydration force, hydrophobic force, DLVO theory

## Introduction

The surface forces (SF) manifest themselves between any surfaces or interfaces between solid, liquid, and gaseous phase, if they approach each other to the separation below a few hundreds nanometers. This universality of the existence of SF irrespective of the interface type intimates an immense importance of the study and knowledge of these forces as well as their role in many scientific fields. It is therefore difficult to briefly comprehend all areas where SF operate. Importantly, SF also arise between various particles of inorganic and organic origin (solid particles, droplets, bubbles, cells, bacteria, etc.) in disperse systems where various aggregation processes (coagulation, coalescence, flocculation, flotation, adhesion, ...) are induced thereby.

## Measurements of surface forces between macroscopic surfaces

An enormous attention is hence devoted to the SF by scientists from many fields, especially physicists, (colloid) chemists, chemical engineers and many others for over 60 years, i.e. from the time when the famous DLVO theory (Derjaguin, Landau, Verwey, Overbeek) was elaborated, predicting the existence of two independent types of SF, namely the van der Waals forces (vdW) and the electrostatic double layer forces (EDL) [1]. This theoretical step is in the area of colloid chemistry considered to be of the same importance as the Darwin's evolution theory in biology [2,3]. The argument is that the DLVO theory had been validated successfully soon after its introduction in ca. 1940 by direct SF measurements between some materials (glass filaments, gold foils, mica sheets) [4].

From that time, the experimental research of SFs progress by leaps and bounds, especially during last decades in connection with the development and wide availability of commercially produced equipments for the direct surface force measurements between macroscopic surfaces: Measurement and Analysis of Surface Interactions and Forces (MASIF), Surface Force Apparatus (SFA), Atomic Force Microscopy (AFM) and more recently other instruments [5]. The first SFA was constructed by J. N. Israelachvili and G. E. Adams in 1976 [6]. The SF are measured as a function of the separation between two surfaces of thin molecularly smooth muscovite mica sheets bend and stucked on glass cylinders (turned 90 degrees) from which the one (lower) is positioned on a spring to measure the interaction force and the other is fixed on the piezoelectric tube. The deflection of the spring (proportional to the interaction force) is determined from the difference between a chosen change of the piezo position and the corresponding change in the distance between the surfaces. This separation is determined interferometrically by using white light (FECO) passing through the mica sheets from inside and then entering the spectrophotometer. The whole system is immersed in an aqueous solution. The principle and appearance of the SFA instrument MARK IV is shown in Fig. 1.

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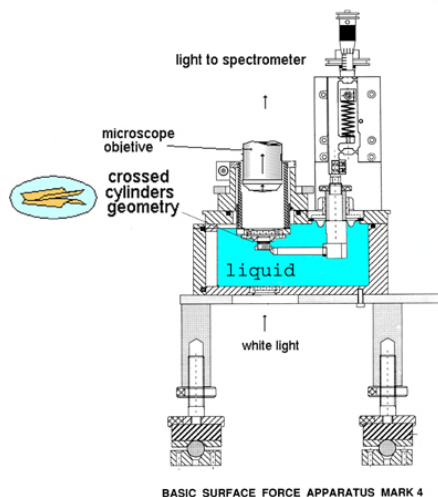


Fig. 1. The principle and appearance of the MARK IV Surface Force Apparatus

The utilization of AFM increases unprecedentedly in more and more fields, including biological sciences, where it allows e.g. to study biophysics of molecular interactions in such processes as the neuronal signal transmission in biological systems, etc.. AFM or SFM (Scanning Force Microscope) developed by G. Binnig, C. Gerber, and C. Quate in 1985 [7] (G. Binnig received the Nobel price in physics in 1986), utilizes an imaging technique in which the piezoelectric crystal scans horizontally together with a sample fixed on it. A sharp tip positioned on a stationary holder moves vertically, sliding on the surface features. The laser strikes upon the upper part of the tip holder and is reflected to the photodiode depending on the holder deflection. This optical method of the deflection evaluation differs AFM from the Scanning Tunneling Microscope (STM) where the tunneling current between the tip and the conductive surface is detected. In the so called calibration AFM regime, the interaction force between the tip and the imaged surface is measured. Here, the piezo with a sample is fixed in a horizontal position and is moved up and down, toward the tip and back, due to the applied voltage. Simultaneously, the deflection of the cantilever holding the tip is detected as a signal from the photodiode. The result is a dependence of this signal (proportional to the measured interaction force) on the applied piezo voltage. Since the geometry of the tip is unknown, the interaction force is difficult to calculate and a sphere is stuck on it, providing the sphere/flat interaction configuration (physically identical to the configuration of crossed cylinders in SFA), suitable for the mathematical treatment of the interaction force [8]. On the other hand, along with the interaction force measurement in the calibration regime, AFM can be used to image the surface features in the imaging (scanning) regime. The principle and appearance of AFM NanoScope is shown in Fig. 2. Both SFA and AFM can also be used to measure adhesion or the so-called pull-off force needed to overcome the adhesion forces between the measured surfaces in contact.

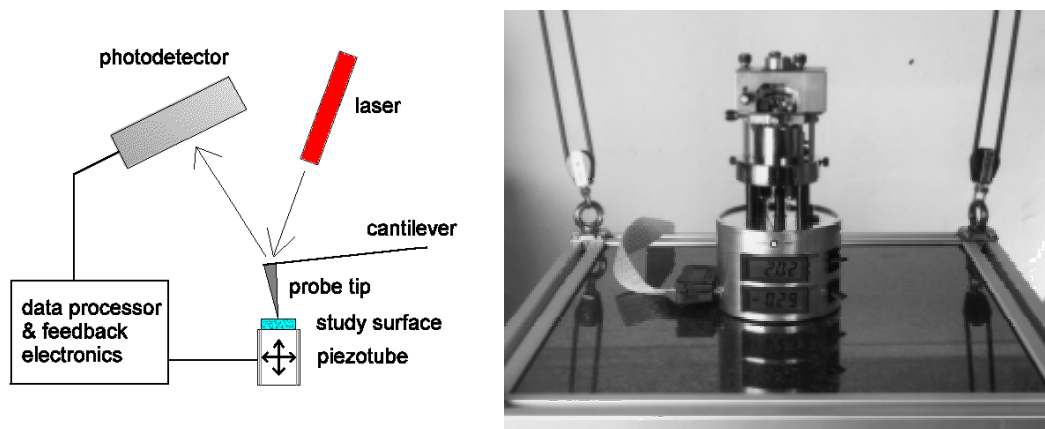


Fig. 2. The principle and appearance of the Atomic Force Microscope

In the direct measurements, aside from their unambiguous scientific contribution, however, many factors (previously not expected) have been noticed, complicating the evaluation and interpretation of surface

forces. Especially, it is the way of preparing and treating the surfaces, the deformation of the surfaces themselves due to their own SF, heterogeneity of the surfaces (roughness and chemical heterogeneity), the way and speed of approaching the surfaces, the way of measuring the SF and the intersurface distance, etc. These factors more or less caused that the SF measurements have not been extended to many materials and restricted almost exclusively to mica sheets with their molecularly smooth, homogeneous, easily cleavable, and well characterized surfaces. The recent rapid development of AFM experiments, where the interaction force curve between dissimilar materials (sphere/plate) is measured, extend the SF determinations to another materials but still suffer from similar and even more complicated and to a certain extent specific effects which must be considered in the analysis of SF.

### Measurements of hydration/hydrophobic force between macroscopic surfaces

The direct measurements not only contributed appreciably to the explanation of the above mentioned long-range vdW and EDL (DLVO) SF between ideal macroscopic substrates but revealed seemingly new, so-called non-DLVO types of surface forces, including short-range repulsive and attractive SFs occurring between hydrophilic and hydrophobic surfaces in aqueous solutions, respectively [9]. Since the measurement and evaluation of any short-range SF (detected at separations on the order of up to few tens of nanometers) is in principle more complicated by the above side factors, the results of the direct measurements of the above hydration/hydrophobic SFs in the SFA or AFM are shady and not explained so far (see [10] and references herein).

It is worth of mentioning that a serious attention has been devoted to the long-range „hydrophobic“ SF measurable between surfaces at their separations of several hundreds nanometers or so. However, it is recently shown that a pseudo-cavitation phenomenon is responsible for such a long-range attraction due to nano to microbubbles formed on the surfaces during the measurements (at approaching or separating the surfaces). A confirmation of the existence of such „bubbles“ is at the moment highly appealing but still remains controversial [11]. In this regard, it has been found that the way of hydrophobization (physical adsorption of surfactants, covalent silanation, Langmuir-Blodgett films, ...) of the surfaces as well as of their introduction into the solution plays an important role in this phenomenon [12]. The physical adsorption of cationic surfactants on the negatively charged surfaces of mica in the SFA appears to be the only way of hydrophobization allowing us to experimentally identify the „true“ hydrophobic force of its short decay.

Taking into account the above facts, the available SF curves between hydrophobic surfaces were reevaluated and, basing on the surface thermodynamics approach, it has been proposed that the hydration/hydrophobic SFs represent opposite regimes of a unique short-range SF of exponential decay and (possibly) structural origin [10].

### Measurements of surface forces between microscopic surfaces – aggregation experiments

Apart from the complications and limits accompanying the fundamental SFA or AFM experiments between fixed macroscopic surfaces, however, one of the basic goals of the research - the SF between surfaces of microscopic particles in disperse systems and their role in the aggregation phenomena - is apparently circumvented. It is true, however, that the direct measurements of DLVO SF helped us to explain many aspects of aggregation of disperse systems [13] and the mere detection of the structural hydration/hydrophobic forces is exceptionally important because such forces have been believed to explain a different character of lyophilic and lyophobic colloidal systems from the very beginning of colloid science as well as the origin of some aggregation processes (e.g. hydrophobic flocculation, shear flocculation, microflotation, etc.).

The determination of surface forces between particles of disperse systems is however not easier than in the SFA or AFM. The problem is that the surface forces between freely moving and mutually encountering particles with a kinetic energy must be experimentally evaluated from the aggregation process (which is, in fact, the consequence of the surface forces themselves) – i.e. indirectly in principle. Therefore, the quality of information about the SFs between particles from their spontaneous aggregation is given by the adequacy of the aggregation model adopted. Of course, a fitness of the model is markedly influenced by a character of a disperse system under study, i.e. its particles (generally, the more complicated disperse system, the more complex and less adequate is the aggregation model).

Experiments directed to the study of SF between particles in relatively diluted disperse systems (with the content of particles up to few %) can be preliminary divided into two limiting groups. Experiments aimed at detecting manifestations of aggregation such as the free settling and the height of sediment at a preset time or as a function of time (typical for micron-sized or coarser particles of unknown or undefined shape, size distribution, etc.). On one hand, these measurements are simple and widely spread due to their practical importance in evaluating SF and aggregation processes of real disperse systems in many industrial areas, but,

on the other hand, they cannot (owing to the incompleteness of pertinent theories of aggregation processes for such systems) provide the required (quantitative) information about individual types, especially the short-ranged surface forces [14].

On the other side, experiments aimed at observing and modeling the perikinetic aggregation of freely diffusing submicronal (colloidal) synthetic particles of spherical shape, minimum shape and size distribution, porosity, etc. can determine SF quantitatively. These experiments nevertheless differ in the method of determining the aggregation model parameters and so in the reliability of such parameters for evaluating the SF. Obviously, a coagulation aggregation process in well defined colloidal systems is monitored by the turbidity or absorbance development after adding a coagulant (electrolyte, polymer, polyelectrolyte or surfactant). (Anyway, the sole turbidity or absorbance after an elapsed time had been determined also for well defined colloidal systems [15]; these experiments can serve only to determine the so-called critical coagulation concentration of the coagulant, ccc, when the potential energy barrier between colloids vanishes).

Generally, SFs are evaluated by determining the so-called Fuchs stability ratio (a ratio of the rate constant of the so-called slow coagulation process hindered by the energy barrier, and that of the fast coagulation starting at the ccc, i.e. in absence of the barrier) [16], which relates theoretically the rate of the coagulation at the beginning of the coagulation and the SFs of spherical colloids. Obviously, the above (rather relative) rate constants of the dimer formation are determined by graphical constructing a tangent to the absorbance-time curve extrapolated into the beginning of the coagulation process [17]. A more precise way of determining the absolute rate constants seems to be the use of a model fitting the whole absorbance-time dependence and providing kinetic constants (being simply equal to the half of the dimer formation rate constants, by definition) of the whole coagulation process. Another, rather complicated experimental procedures are also usable, detecting the coagulation kinetics by static and dynamic light scattering [18]. In any case, despite of recent experiments determining the absolute coagulation rate constants for maximally ideal and well characterized colloidal spherical particles and entirely confirming the validity of the DLVO theory, the quantification of the short-ranged structural forces is still not available [19].

An original kinetic model of perikinetic coagulation of submicronal silica spheres of 75 nm diameter was successfully verified by the author [20]. The size of the silica colloids was selected to maintain the RGD light scattering regime. The software model, provided kindly by Dr. A. Puertas from the University of Granada allowed us to determine the absolute coagulation rate constants by fitting the whole time change in the absorbance of the colloidal system, induced by the addition of an electrolyte (KCl) or surfactant (cetyltrimethyl-ammonium bromide, CTAB). Interestingly, the kinetic constant, being identical to that determined by others for silica [21], was found to be same for both the electrolyte- (Fig. 3) as well as the surfactant-induced fast coagulation (Fig. 4), despite the fact that the wettability of the surface of silica particles was markedly influenced by the surfactant adsorption, as determined by their accumulation in hexadecane). This apparently confirms the validity of the DLVO theory (the fast coagulation occurred exactly at the isoelectric point in the presence of CTAB) and does not support the idea about the existence of the (even short-ranged) structural hydration/hydrophobic SF, at least for the studied colloidal silica particles under given conditions. Experiments on the coagulation kinetics of model silica spheres of different origin and size in the presence of various cationic surfactants are under way.

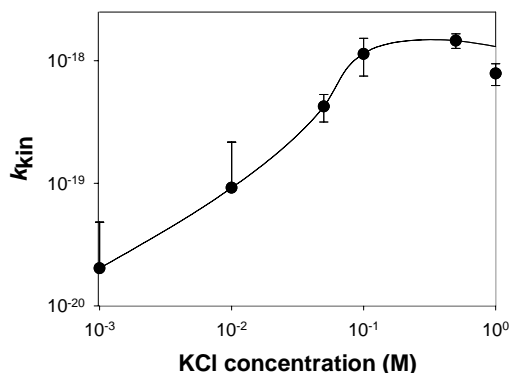


Fig. 3. Kinetic coagulation constant of silica colloids as a function of the KCl concentration. (from: Škvarla, J.: Surface forces between colloidal silica spheres in the presence of electrolytes and cationic surfactants determined from absolute coagulation rate constants, in preparation for submitting in Langmuir).

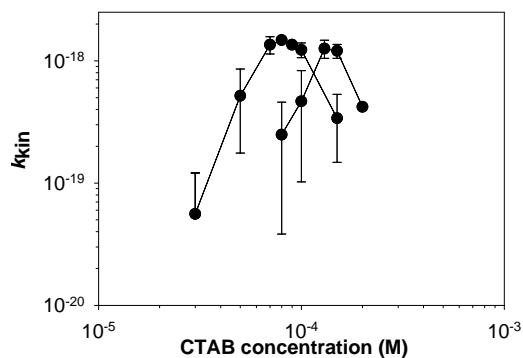
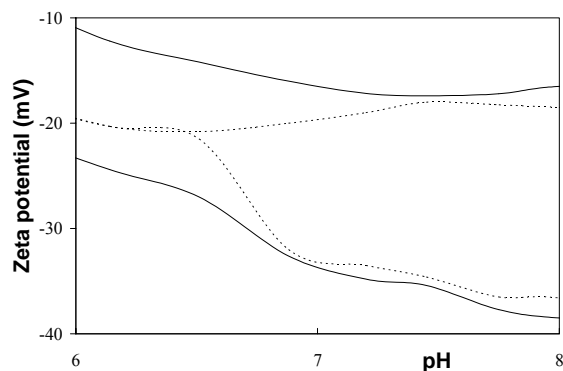


Fig. 4. Kinetic coagulation constant of silica colloids as a function of the CTAB concentration at pH 4 (left curve) and 5 (right curve). (from: Škvarla, J.: Surface forces between colloidal silica spheres in the presence of electrolytes and cationic surfactants determined from absolute coagulation rate constants, in preparation for submitting in Langmuir).

The second method of evaluating the SFs, this time between different particles, was also proposed by the author [22]. This method is based on the detection of heterocoagulation by analysing the electrophoretic light scattering (ELS) spectra of multicomponent mixtures of particles. This method was again verified for ideal colloidal particles of silica and (more hydrophobic) silica preliminary modified with aminopropyl. Fig.5 shows that the mean values of the monomodal zeta potential distribution of the silica and the silica/aminopropyl, as measured individually, differ from these of the bimodal zeta potential distributions of the silica-silica/ aminopropyl mixture at pH below ca. 6.6, indicating a heterocoagulation effect. It has been shown to be in agreement with theoretical calculations according to the DLVO theory, again not confirming the existence of the hydration/hydrophobic SF. In this case, however, for the combined hydrophilic/hydrophobic system, the surface thermodynamics itself predicts a very low interfacial energy and thus a very weak structural SF. Heterocoagulation experiments are presently made to study the role of surfactants in the interaction between different model particles in their mixtures.

Fig. 5. Mean value of the monomodal zeta-potential distribution of individual silica spheres (lower full line) and individual silica-aminopropyl spheres (upper full line), and the mean values of the bimodal zeta-potential distribution of their mixture (dotted lines) as a function of pH. (adapted from: Škvarla, J.: Electrokinetic properties of mineral mixtures, *Acta Montanistica Slovaca*, 2003, 8, 1-9).



## Conclusion

It follows from the above that, generally, in the study of SF operating in dispersions of particles, both direct experiments between macrosubstrates as well as indirect experiments between the particles have been utilizing. The possibility of getting a direct information about the surface forces from measurements between macroscopic surfaces is limited due to specific factors that influence such measurements and the inadequacy of the macroscopic surfaces themselves to the surface of particles in disperse systems by nature. From this point of view, straightforward studies of surface forces between particles in disperse systems should be preferred and/or paralleled with the direct measurements. In fact, there is not yet an agreement between the both kinds of experiments even for model colloidal systems. Moreover, since the surface forces between freely moving particles (being manifested through aggregation phenomena) are to be determined indirectly, a proper aggregation model has to be adopted. If such a model is applicable, the SFs can be determined immediately. The preliminary experiments on the coagulation kinetics of hydrophilic silica spheres with the diameter of 75 nm in the presence of a simple electrolyte and surfactant prove the DLVO theory and do not support the idea about the hydration/hydrophobic SF.

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