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Rheology of silver nanocluster solutions under confinement

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ABSTRACT

Drainage of solutions of silver (Ag) nano-clusters, pressed between the two apexes of a double-concaved drop situated in a capillary holder, was studied. The size of clusters was below 2 nm. The aqueous nano-suspension of Ag nano-clusters was stabilized by poly(methacrylic acid) (PMAA). The two tips of the double-concaved drop were pressed by a capillary pressure thus forming a foam nanofilm, the drainage kinetics of which was monitored by interferometry. For comparison, the drainage of foam films containing PMAA aqueous solutions with and without $AgNO_3$ was monitored as well. It was found that steric repulsion occurred between the two film surfaces due to the polymeric chains of PMAA. In addition, we observed also a significant change of this steric repulsion in nano-cluster suspensions, which is explained by changes of the polymer network in the film, affecting the entire drainage and stability of the suspension.

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1. Introduction

Nature operates with plethora of nano-machines: enzymes and ion channels in membranes [1], chemical nano-factories in autotrophic organisms [2], energy nano-factories in plants [3], centers for replication of DNA molecules [4], etc. Water is a universal medium participating actively in these processes via transportation of very small particles in confined micro- and nano-fluidic systems. Taking example from the Nature, biomimetics focused human efforts on creating of "labs-on-a-chip" [5–7], which are micro-fluidic systems with integrated chemical reactions. Further on, miniaturization led to development of nano-fluidic systems, whose length-scale [8] is comparable with the hydrodynamic slip length [9–11]. Thus nano-fluidics was also developed [12,13] describing the motion of very small volumes of fluids. Most of the studies in this area are focused on micro- and nano-flows of pure liquids and there is no experimental study on micro- and nano-fluidics of suspensions. At present, the theory of nano-fluidics described the motion of nano-confined molecular liquids, but not the behavior of nano-suspensions. The latter have own specific rheology, which has not been investigated by now in a confined state.

Nano-suspensions with typical size of particles below 10 nm exhibit new very interesting properties [14]. For example, semiconductor nano-particles of CdSe/CdS with typical size of 2–10 nm exhibit quantum confinement effects [15,16], expressed by variation of the wavelength of the light emitted by these particles when varying their size. Similar effect was found with gold (Au) nanoparticles [17]. Silver (Ag) nano-clusters with typical sizes of 1–2 nm exhibit fluorescence and electro-chemi-luminescence [14,18–21]. These and other properties of the nano-suspensions promote their application in optical systems [22], catalysis [23], biomedical technology [24], etc. Therefore, the study of the rheological behavior of nano-suspensions is particularly important.

Thin liquid films between bubbles or oil droplets are well known as a successful model for a liquid layer, squeezed by two fluid surfaces with certain capillary force [25,26]. Therefore, the thin layer drains to a certain final equilibrium thickness or the so-called critical thickness [26] at which the film ruptures or undergoes transition to long living black film. The drainage of thin films was studied for many years [27,28]. However, in most cases the films were stabilized by aqueous surfactant solutions with Newtonian rheology. The drainage of thin films stabilized by micellar solutions of surfactants was also studied [25,29]. It was found that oscillatory force at certain film thickness close to the sizes of the micelles [25]. However, solutions of micelles are not conventional suspensions due to the fact that the micelles are composed of surfactant molecules, which are in a dynamic equilibrium. The rheology of nano-suspension with particles exhibiting quantum confinement effects has not been studied till now. The present work investigates the drainage of thin liquid layers of silver nano-clusters squeezed by the two fluid surfaces and reports essential effects of the clusters on the rheology and stability of the layers.

2. Experimental

The procedure for producing of the silver nano-suspension is described in Ref. [14]. In short, to create Ag nano-clusters, a freshly prepared aqueous solution of silver nitrate was mixed with an

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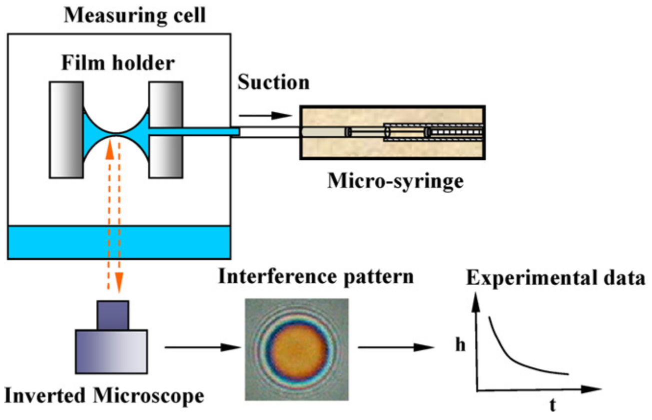

Fig. 1. Scheme of the interferometric setup for experiments on thin liquid films (not to scale).

aqueous solution of poly(methacrylic acid) (PMAA). The latter was used as stabilizer. At first, the solution was colorless and showed no absorption in the UV–vis spectrum. Subsequent exposure to visible light resulted in the partial conversion of silver ions into silver nano-clusters accompanied by a gradual color change to pink and the formation of a single broad UV–vis band that increased in intensity but did not show significant changes in shape or position as irradiation continued. In addition to the pink silver nano-cluster suspension, two blank samples were prepared, one by dissolving the same amount of PMAA in water, the other by dissolving the same amount of PMAA and $AgNO_3$ in water (without irradiation, colorless). The surface tensions and viscosity of the solutions were measured by Wilhelmy plate method and Ostwald viscometer, respectively. The solutions ionic strength was determined from electric conductivity data measured by a conductometer.

The full description of the experimental set-up was reported previously [30] and is not presented in details here. Briefly (see Fig. 1), the apparatus consists of a glass cell for producing horizontal foam films normal to gravity. The system was connected with thermostat to maintain constant temperature of 25 °C. First, a droplet of the solution was formed inside the film holder with radius 2.15 mm. Then it was left for achieving thermal equilibration for at least 30 min. After this an amount of liquid was pumped out by means of a gastight micro-syringe thus forming a microscopic thin foam film between the apexes of the double-concaved droplet. A metallurgical inverted microscope was used for illuminating and observing the film and its interference Newton fringes in reflected light of wavelength (= 546 nm. The latter was achieved by means of short-band green filter. A digital camera system connected with computer was used for storage of the data. The interferograms were processed offline using the "Image J" software for image processing delivering the pixel signal from a given small area. Thus the frames were extracted from the recorded movie. The film radii were measured in the series of sequent frames and the averaged film radius was derived with average deviation in the range of ±2 Πm. In addition only planar films were processed and hence their thickness was the same at each point of the film. At least 10 evolutions of foam films at each sample were recorded.

3. Results and discussion

Three solutions of PMAA, PMAA + $AgNO_3$ and PMAA + $AgNO_3$ + Ag nano-clusters, being set into the double concaved drop, were illuminated with a monochromatic green light with wavelength λ = 546 nm. The spectral properties of the silver cluster suspension are emission at λ ~ 630 nm and absorption at λ ~ 530 nm. Hence the Ag nano-clusters were continuously excited during the experiment, which lasted totally for about 40 min. The emitted light from the Ag nano-clusters (λ ~ 630 nm) was absorbed by the green filter of the microscope. The reddish color of the Ag nano-suspension remained the same during the whole time of the experiment, which is an indication that the nano-suspension was not degraded in the time.

The Reynolds drainage equation [25] was used to interpret theoretically the experimental drainage curves of the blank and nano-suspension samples

$$-\frac{dh}{dt}=\frac{2h^3(P_\sigma-\Pi)}{3\mu R_f^2}\equiv V_{Re} \tag{1}$$

where h and t are nanofilm thickness and time, μ is bulk viscosity and R_f is film radius. The capillary pressure $P_\sigma = 2\sigma/R_c$ was calculated from the surface tension σ and the radius R_c of the film holder, where the nanofilm is formed in. The total disjoining pressure Π is composed by electrostatic, van der Waals and other non-DLVO components [25].

The disjoining pressure in Eq. (1) is a sum of several components [31]. The electrostatic disjoining pressure Π_{EL} can be predicted by solving the Poisson-Boltzmann equation employing appropriate boundary conditions at the film surfaces. Under the condition of a constant surface potential, the exact numerical solution of the non-linear Poisson-Boltzmann equation can be semi-analytically represented as [31]

$$\Pi_{EL}=32ck_BT\tanh^2\left(\frac{y_0}{4}\right)\{[\cosh(\kappa h)+1]^{-1}$$
$$+f_0(y_0)\sinh^2\left(\frac{y_0}{4}\right)\exp[-f_0(y_0)\kappa h]\} \tag{2}$$

where c is the concentration of electrolytes in the solution and T is the absolute temperature. The Debye constant for a binary electrolyte of valence z is defined as $\kappa^2 = 2z^2e^2c/\varepsilon_0\varepsilon k_BT$, where ε_0 is the permittivity of the vacuum. The normalized surface potential is defined as $y_0 = ze\psi_s/k_BT$, where ψ_s is the surface potential. The function $f_0(y_0)$ is given by $f_0 = 2\cosh(0.332\,|y_0| - 0.779)$ for $|y_0| \le 7$. Under the condition of a constant surface charge density, the exact numerical solution to the Poisson-Boltzmann equation gives [30]

$$\Pi_{EL}=2ck_BTf_1/[\cosh(f_3\kappa h)-1]\sqrt{1+f_2^2\coth(f_3\kappa h/2)} \tag{3}$$

where f_1, f_2 and f_3 are functions of the surface potential at infinite separation (isolated surfaces) described for $|y_0| \le 5$ by the expressions $f_3 = 1 - 0.00848\,|y_0|$, $f_2 = 0.571\,|y_0|\exp\left(-0.095|y_0|^{1.857}\right)$ and $f_1 = f_2f_3\sinh\left(1.854\,|y_0| - 0.585|y_0|^2 + 0.1127|y_0|^3 - 0.00815|y_0|^4\right)$

The van der Waals disjoining pressure, Π_{vw}, as a function of the film thickness h is described in the form [32]

$$\Pi_{VW}=-\frac{A}{6\pi h^3}+\frac{1}{12\pi h^2}\frac{dA}{dh} \tag{4}$$

where $A(h,\kappa)$ is the Hamaker-Lifshitz constant, which is a weak function of the temperature T and the Debye constant κ, as well as of the film thickness h due to the electromagnetic retardation effect described by

$$A=\frac{3k_BT}{4}(1+2\kappa h)e^{-2\kappa h}\sum_{j=1}^{\infty}\frac{1}{j^3}\left(\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+\varepsilon_2}\right)^{2j}$$
$$+\frac{3\hbar\omega}{16\sqrt{2}}\frac{(n_1^2-n_2^2)^2}{(n_1^2+n_2^2)^{3/2}}\{1+(Kh)^q\}^{-1/q} \tag{5}$$

where Π_1 and Π_2 are the static dielectric permittivity of the dispersion phase (1 for air) and disperse medium (80 for water),

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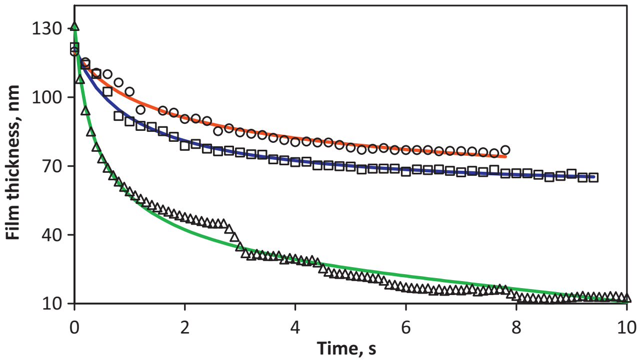

Fig. 2. Experimental and theoretical drainage curves *h* vs. *t* of foam films containing. PMAA sample (○, $B = 177$ Pa, $\lambda = 52$ nm), PMAA + $AgNO_3$ + Ag (□, $B = 240$ Pa, $\lambda = 33$ nm) and PMAA + $AgNO_3$ (△, $B = 34$ Pa, $\lambda = 50$ nm).

respectively, ω is the absorption frequency in the UV region typically for water around 2×10^{16} rad/s, n_1 and n_2 are the characteristic refractive indices of the dispersion phase and medium ($n_1^2 = 1$ for air, $n_2^2 = 1.887$ for water) and $q = 1.185$. The characteristic wave vector is defined as $K = \pi\omega n_2 \sqrt{(n_1^2 + n_2^2)/2}/2c$, where c is the speed of light. The total disjoining pressure includes non-DLVO contribution, which is described further in this section. Knowing the total disjoining pressure Π as a function of the film thickness, Eq. (1) is numerically integrated using the 4th order Runge-Kutta algorithm to obtain the transient film thickness. A program was written using VBA (Visual Basic for Application) programming language available in Microsoft Excel.

Some basic parameters (surface tension, conductivity, pH and viscosity) of the blank and Ag nano-suspension samples are presented in Table 1. It is worthy to note that the presence of $AgNO_3$ makes the sample less viscous, while Ag clusters have negligible effect. This indicates that $AgNO_3$ weaken the bulk 3D network of the PMAA chains, which is expected since PMAA is a polyelectrolyte. The decreased conductivity of the Ag nano-clusters should be due to the residual $AgNO_3$ after the reduction by means of a visible light.

Our qualitative analysis of the experimental data showed an existence of additional non-DLVO steric repulsion between the surfaces of the thin foam film. Such repulsion is expected in concentrated solutions of surfactants [33]. The corresponding steric disjoining pressure Π_{ST} was also derived [34]

$$\Pi_{ST} = B \exp\left(-\frac{h}{\lambda}\right)\left(\frac{h}{\lambda}\right) \qquad (6)$$

where h is film thickness, B is a constant and λ is the decay length of the repulsion force. The steric disjoining pressure from Eq. (2), related by the 3D network of polymer chains close to the film surfaces [33], was accounted for in Eq. (1) along with the electrostatic and van der Waals disjoining pressures $\Pi = \Pi_{EL} + \Pi_{VW} + \Pi_{ST}$. A fitting procedure with two matching parameters, B and λ, was conducted. The experimental and theoretical drainage curves of the foam films containing the blank and Ag nano-suspension samples are presented in Fig. 2. The concentration of electrolyte in all cases is high enough to decrease significantly the electrostatic repulsion between the film surfaces. Hence, without the steric repulsion the foam films should drain until reaching the critical thickness (*ca.* 30 nm). On the contrary, the experimental data shows that the foam films in both cases of PMAA and PMAA + $AgNO_3$ + Ag-nano-clusters reach equilibrium thicknesses about 76 nm for the blank sample and 66 nm for the nano-cluster suspension.

As being seen in Fig. 2 the addition of $AgNO_3$ to PMAA does not alter essentially the length λ but decreases significantly the magnitude B. This effect is expected, however, since the increased ionic strength reduces the electrostatic repulsion between the charged PMAA anions. As a result the steric repulsion diminishes and the films of PMAA + $AgNO_3$ drain to a very low thickness. By initiation of the photo-chemical reaction producing Ag-clusters the steric repulsion is restored. Our quantitative analysis showed that the presence of Ag nano-clusters reduces the value of the decay length λ of the steric disjoining pressure. This could be due to the change of the 3D network of the polymeric chains of the PMAA. Such an effect is supported also by the measured lower viscosity of the nano-suspension as compared to the blank sample containing only PMAA. It should be questioned here whether these effects are due to the Ag nano-clusters or the presence of $AgNO_3$. Using the experimental values of parameters B and λ one can calculate the lateral protrusion length via the relation $\delta = \sqrt{k_B T/\lambda B}$ [33]. It comes out that in films of PMAA sample the 3D structure is very anisotropic with $\delta/\lambda = 0.4$, which is probably due to strong electrostatics repulsion from the charged film surface. Addition of electrolyte suppresses the electrostatic interactions and, indeed, the surfactant structure becomes perfectly isotropic in PMAA + $AgNO_3$ with $\delta/\lambda = 1.0$. The presence of clusters in PMAA + $AgNO_3$ + Ag distorts again the isotropy of the 3D structure since $\delta/\lambda = 0.7$ in this case.

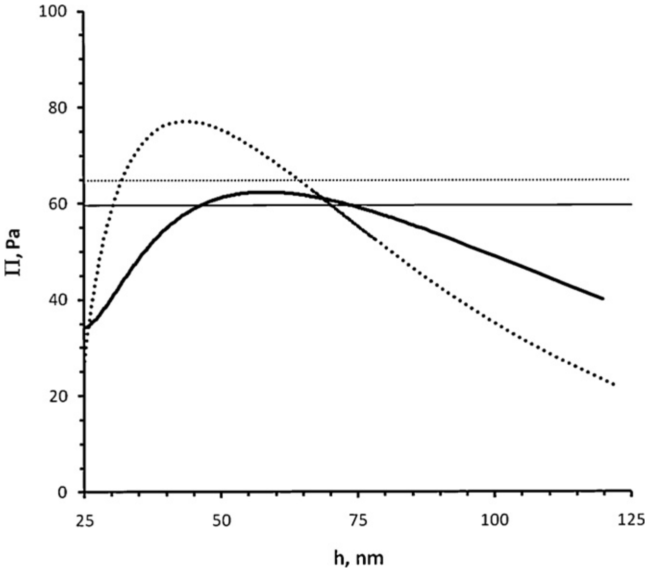

Fig. 3. Dependence of the total disjoining pressure on the film thickness for blank sample (solid line) and nano-suspension (dot line). The horizontal lines denote capilary pressures P_σ.

The photo-chemical reaction resulting in Ag nano-suspension involves obviously PMAA carboxylic groups. Thus PMAA transforms to a less charged coiled molecular architecture with a lower viscosity. Indeed, the bulk viscosity of the Ag suspension does not differ much from that of the blank sample. On the other hand, they are apparently different in respect to the steric repulsion since the coiled structure corresponds to lower λ. However, since the magnitude of repulsion is similar in the blank sample and Ag nano-suspension, the equilibrium film thickness of the foam films are commensurable. Anyway, the equilibrium thickness of the foam films with the Ag nano-suspension is evidently lower than that of the blank sample. Subsequently, the Ag nano-clusters have impact on the rheology of the nano-suspension in the foam films.

The disjoining pressure isotherms of the blank and suspension samples are presented in Fig. 3. As is seen, at thickness about 76 nm the blank sample is in equilibrium. Obviously, this state is not very stable since there is a small maximum dividing the equilibrium from critical thickness about 45 nm. Indeed, a blank sample film undergoes an abrupt transition to the lower critical thickness if it is disturbed and after some short lifetime there it ruptures (see Fig. 4).

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Table 1
Surface tension, conductivity, pH and viscosity of the solutions.

Solution	Surface tension (mN/m)	Conductivity (mS/cm)	Ionic strength (M)	pH	Viscosity cP
PMAA	64.1	0.7	0.006	3.0	1.27
PMAA + $AgNO_3$	67.9	12.5	0.116	3.2	1.03
PMAA + $AgNO_3$ + Ag clusters	69.7	12.4	–	3.4	1.04

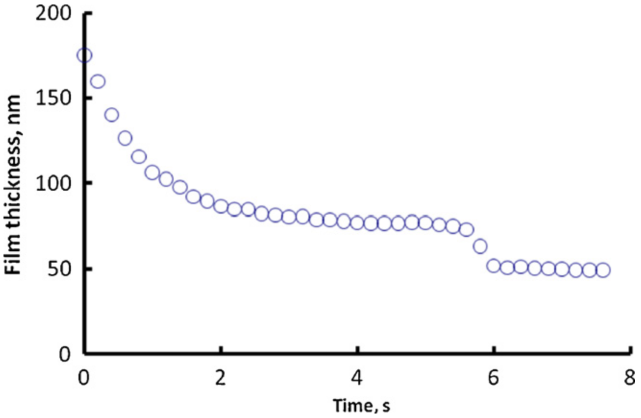

Fig. 4. Experimental thickness of foam film containing the blank sample.without preliminary equilibration.

On the contrary, if the double concaved drop containing the blank sample is equilibrated for about 30 min the foam film does not undergo any sudden transitions in the thickness as in Fig. 4. The equilibrium film with thickness about 66 nm from the Ag nanocluster suspension is, however, very stable due to the pronounced maximum in the disjoining pressure in Fig. 3. Hence, it is difficult to reach the critical thickness about 26 nm and our measurements show that the suspension films drain without complications even before preliminary equilibration. Hence, the Ag nano-clusters affect substantially the stability of nano-films as well.

4. Conclusions

The rheology and equilibrium of thin liquid layer of nanosuspension of quantum Ag nano-clusters were studied by means of interferometry. The sizes of the Ag nano-clusters were in the range of 1–2 nm and they were stabilized by poly(methacrylic acid) (PMAA). The theoretical analysis showed significant steric repulsion between the film surfaces in both cases of blank (PMAA) and nano-suspension (Ag nano-clusters, $AgNO_3$ and PMAA) samples. The presence of Ag clusters reduces the decay length of the steric repulsion, which is related also with a decrease of the value of the bulk viscosity. This effect stabilizes essentially the suspension equilibrium in a confined state such as nano-films.

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References

[1] K.B. Storey, Functional Metabolism: Regulation and Adaptation, John Wiley & Sons, Hoboken, N.J., 2004.
[2] R.A. Freitas, R.C. Merkle, Kinematic Self-Replicating Machines, Landes Bioscience/Eurekah.com, Georgetown, Texas, 2004.
[3] W.G. Hopkins, Photosynthesis and respiration, Chelsea House, New York, 2006.
[4] Z.A. Medvedev, The possible conservation of genetic information in repetitious sequences of DNA, Journal of Molecular Evolution 1 (1972) 270.
[5] J.M. MacInnes, Computation of reacting electrokinetic flow in microchannel geometries, Chemical Engineering Science 57 (2002) 4539–4558.
[6] H.A. Stone, A.D. Stroock, A. Ajdari, Engineering flows in small devices: microfluidics toward a lab-on-a-chip, Annual Review of Fluid Mechanics 36 (2004) 381–411.
[7] S. Mechkov, M. Rauscher, S. Dietrich, Stability of liquid ridges on chemical micro- and nanostripes, Physical Review E: Statistical, Nonlinear, Soft Matter Physics 77 (2008), 061605/061601-061605/061610.
[8] B.D. Ratner, S.J. Bryant, Biomaterials: where we have been and where we are going, Annual Review of Biomedical Engineering 6 (2004) 41–75.
[9] S. Granick, Y. Zhu, H. Lee, Slippery questions about complex fluids flowing past solids, Nature Materials 2 (2003) 221–228.
[10] M. Rauscher, S. Dietrich, Wetting phenomena in nanofluidics, Annual Review Materials 38 (2008) 143–172.
[11] A. Moosavi, M. Rauscher, S. Dietrich, Size dependent motion of nanodroplets on chemical steps, Journal of Chemical Physics 129 (2008), 044706/044701-044706/044705.
[12] T. Qian, X.-P. Wang, Hydrodynamic slip boundary condition at chemically patterned surfaces: a continuum deduction from molecular dynamics, Physical Review E: Statistical, Nonlinear, Soft Matter Physics 72 (2005) 022501.
[13] M.L. Kovarik, S.C. Jackobson, Attoliter-scale dispensing in nanofluidic channels, Analytical Chemistry 79 (2007) 1655.
[14] I. Diez, M. Pusa, S. Kulmala, H. Jiang, A. Walther, A.S. Goldmann, A.H.E. Muller, O. Ikkala, R.H.A. Ras, Color tunability and electrochemiluminescence of silver nanoclusters, Angewandte Chemie International Edition 48 (2009) 2122–2125.
[15] A.P. Alivasatos, Semiconductor clusters, nanocrystals, and quantum dots, Science 271 (1996) 933–937.
[16] A.D Yoffe, Low-dimensional systems: quantum size effects and electronic properties of semiconductor microcrystallites (zero-dimensional systems) and some quasi-two-dimensional systems, Advances in Physics 42 (1993) 173–262.
[17] Y.P. Bao, H.C. Yeh, C. Zhong, S.A. Ivanov, J.K. Sharma, M.L. Neidig, D.M. Vu, A.P. Shreve, R.B. Dyer, J.H. Werner, J.S. Martinez, Formation and stabilization of fluorescent gold nanoclusters using small molecules, The Journal of Physical Chemistry C 114 (2010) 15879–15882.
[18] I. Díez, H. Hahn, O. Ikkala, H.G. Börner, R.H.A. Ras, Soft Matter 6 (2010) 3160–3162.
[19] I. Díez, R.H.A. Ras, Advanced Fluorescence Reporters in Chemistry and Biology II, in: A.P. Demchenko (Ed.), Springer Series on Fluorescence, Springer, Berlin, 2010, pp. 307–332.
[20] I. Díez, H. Jiang, R.H.A. Ras, ChemPhysChem 11 (2010) 3100–3104.
[21] I. Diez, R.H.A. Ras, Fluorescent Silver Nanoclusters, Nanoscale 3 (2011) 1963–1970.
[22] C.L. Haynes, R.P. Van Duyne, Nanosphere lithography: a versatile nanofabrication tool for studies of size-dependent nanoparticle optics, The Journal of Physical Chemistry B 105 (2001) 5599–5611.
[23] D. Takagi, Y. Homma, H. Hibino, S. Suzuki, Y. Kobayashi, Single-walled carbon nanotube growth from highly activated metal nanoparticles, Nano Letters 6 (2006) 2642–2645.
[24] H. Kong, J. Jang, Antibacterial properties of novel poly(methyl methacrylate) nanofiber containing silver nanoparticles, Langmuir 24 (2008) 2051–2056.
[25] I.B. Ivanov (Ed.), Thin Liquid Films, Marcel Dekker, New York, 1988.
[26] D. Exerowa, P.M. Kruglyakov, Foam and foam films: theory, in: Experiment Application, Marcel Dekker, New York, 1998.
[27] A. Scheludko, Thin liquid films, Advances in Colloid Interface Science 1 (1967) 391–464.
[28] R. Tsekov, E. Evstatieva, A fractal classification of the drainage dynamics in thin liquid films, Progress in Colloid and Polymer Science 126 (2004) 93–96.
[29] E.D. Manev, S.V. Sazdanova, D.T. Wasan, Stratification in emulsion films, Journal of Dispersion Science and Technology 5 (1984) 111–117.
[30] S.I. Karakashev, A.V. Nguyen, Effect of sodium dodecyl sulphate and dodecanol mixtures on foam film drainage: Examining influence of surface rheology and intermolecular forces, Colloids Surfaces A 293 (2007) 229–240.
[31] A.V. Nguyen, G.M. Evans, G.J. Jameson, Approximate calculations of electrical double-layer interaction between spheres, in: A.T. Hubbard (Ed.), Encyclopedia of Surface and Colloid Science, Marcel Dekker, New York, 2002.
[32] A.V. Nguyen, H.J. Schulze, Colloidal Science of Flotation, Marcel Dekker, New York, 2004.
[33] R. Tsekov, Electric double layer in concentrated solutions of ionic surfactants, Annual of University of Sofia, Faculty of Chemistry 102 (2010), in press.
[34] J.N. Israelachvili, H. Wennerstrom, Entropic forces between amphiphilic surfaces in liquids, The Journal of Physical Chemistry 96 (1992) 520–531.