Nanoparticles at the water/oil interface: emulsion stabilization and organization, Indo-French Workshop on Multifunctional Molecular and Hybrid Devices 6-10 October 2008, Saint-Aubin

Jean Daillant

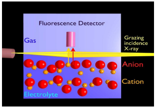
CEA,IRAMIS,LIONS

October 7, 2008

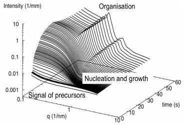
Nanochemistry

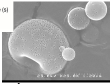
Interfaces, confined fluids and wetting

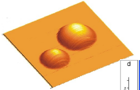
Charged systems

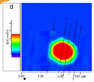


Nanoparticles, nucleation and growth, emulsions toxicity

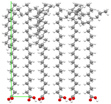




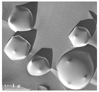


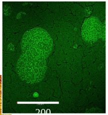


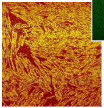
Wetting



Self-assembly, anionic+cationic surfactants



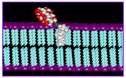




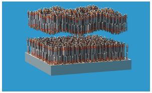
Bio-inspired mineralization

Interfacial films, amphiphiles, (charged polymers

Cage molecules



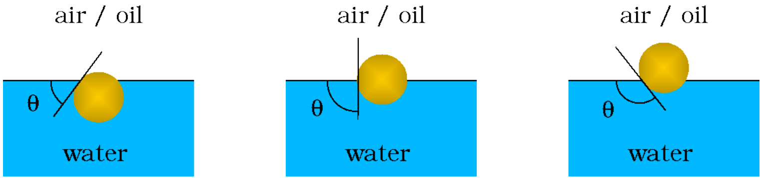
Biophysics



Outline

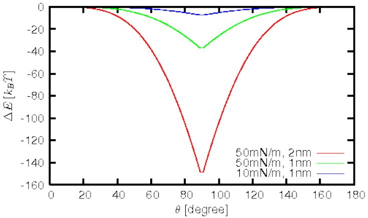
1. Interfacial Behavior
2. Monte-Carlo simulations
3. Emulsion stabilization

Nanoparticles as surfactants



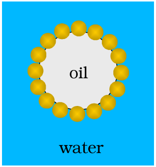
$$\gamma_{NPw} + \gamma_{ow} \cos\theta = \gamma_{NPo}$$

$$\Delta E = -\pi R^2 \gamma_{ow} (1 \pm \cos\theta)^2$$



- Large attachment energy; stability
- self-healing for nanoparticles?

Pickering emulsions



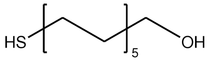
- $\theta < 90°$ oil in water
- $\theta > 90°$ water in oil
- Wettability can be tuned by chemically modifying the particle surface

- Stability
- Monodispersity (partial coalescence)
- Materials science aspects
- Importance of particle-particle interactions

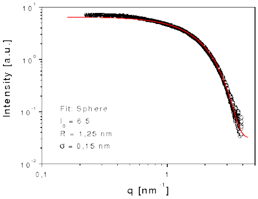
Synthesis and surface modification

Reduction of HAuCl4 in toluene by sodium borohydride in presence of alkanethiols (tetraoctylammonium bromide = tranfer agent)

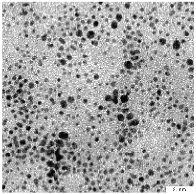
M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, *J. Chem. Soc., Chem. Commun.* 801 (1994)



SAXS



TEM

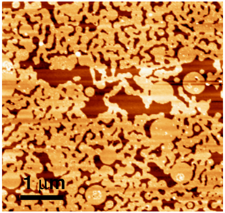


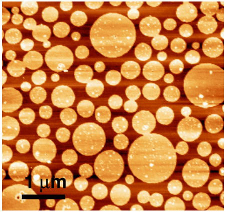
Ligand: hexanethiol partially exchanged with 11-mercapto-1-undecanol ratio 6:1 OH:CH_3 estimated by NMR

Radius $1.25 \pm 0.3 nm$

Particle-particle interactions

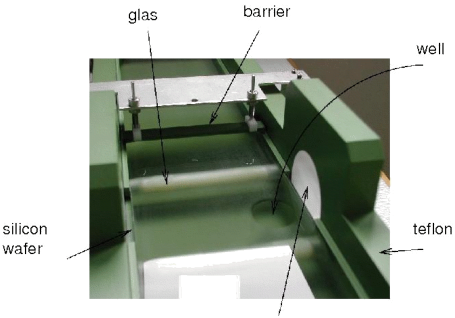
- Dispersion forces (attractive)
- Repulsion between ligand shells
- Coulombic (?)

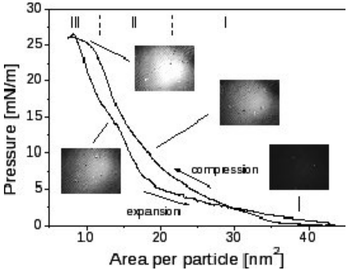




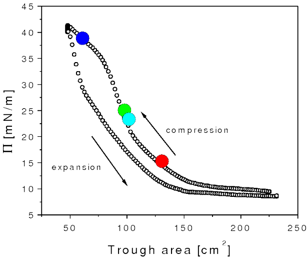
M.K. Bera et al., Europhys. Lett. **78** 56003 (2007)

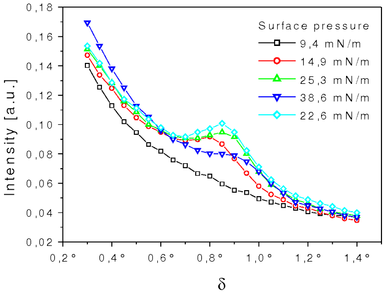
Compression isotherms and Brewster angle microscopy

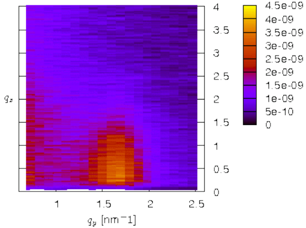


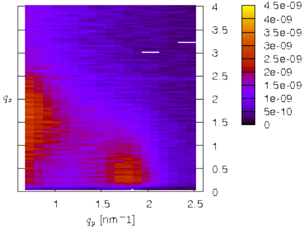


Grazing incidence diffraction and diffuse scattering







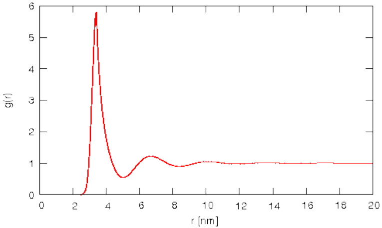


ESRF, ID10B, 21.9keV

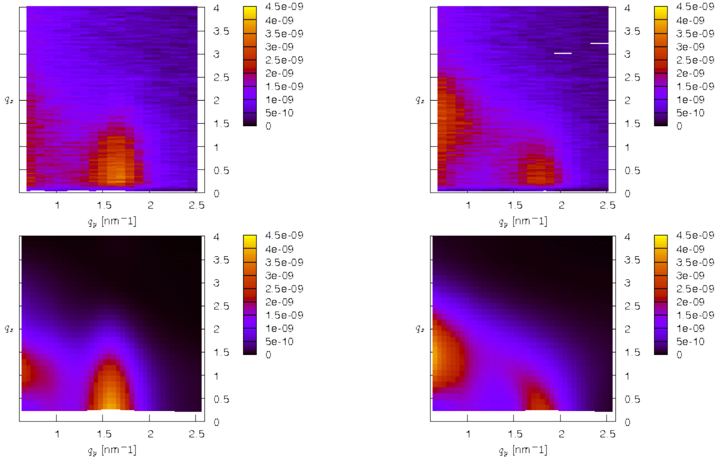
$$\frac{d\sigma}{d\Omega} = 4\pi^2 r_e \left|t_{in}\right|^2 \left|t_{sc}\right|^2 A(\widehat{\mathbf{e}}_{\rm in}.\widehat{\mathbf{e}}_{\rm sc})^2 \left|F(q)\right|^2 \rho \left[1 + 2\pi\rho \int (g(r_{\|}) - 1) J_0(q_{\|} r_{\|}) r_{\|} dr_{\|}\right]$$

$$F(q) = \frac{[\sin(qR) - qR\cos(qR)]}{qR^3}$$

+ Diffuse scattering



Grazing incidence diffraction

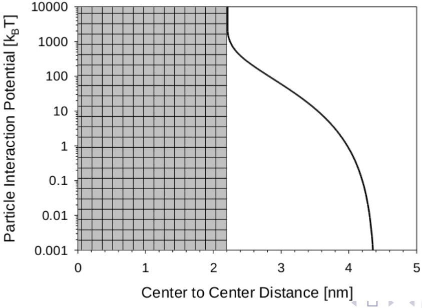


d=4.nm (about 8nm in the emulsions), ξ=20nm

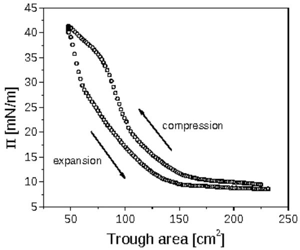
$$U_{\mathrm{Attach}}(z) = \pi\gamma(R+L)^2\left(\frac{z^2}{(R+L)^2} - 1\right) \qquad (\theta = 90\%)$$

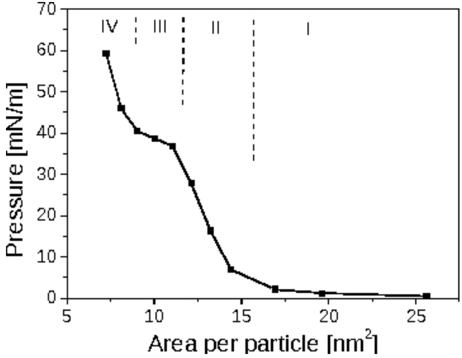
$$U_{NP-NP}(d) = -k_B T \frac{2\pi R_1 R_2}{s^3(R_1+R_2)}\left[-\frac{16}{5}\frac{(2L)^{9/4}}{(d-R_1-R_2)^{1/4}} + \frac{16}{77}\frac{(d-R_1-R_2)^{11/4}}{(2L)^{3/4}} - \frac{48}{35}(2L(d-R_1-R_2)) + \frac{48}{11}(2L)^2\right]$$

P.G. de Gennes, *Adv. Colloid Interf. Sci.* **27** 189 (1987).



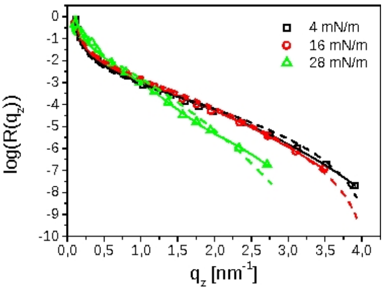
$$\Pi A = Nk_B T - \left\langle \frac{1}{3} \sum_i \sum_{j>i} r_{ij} \nabla_{r_{ij}} U(r_{ij}) \right\rangle$$

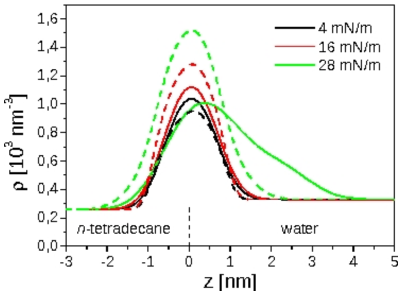




X-ray reflectivity

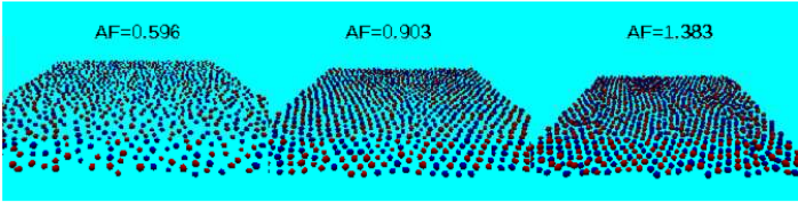
$$R(q_z) = R_F \left| \frac{1}{(\rho_w - \rho_o)} \int \left(\frac{\partial \rho}{\partial z} \right) e^{iq_z z} dz \right|^2 e^{-q_z^2 \sigma^2}$$

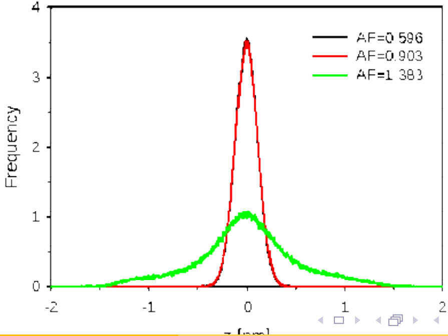




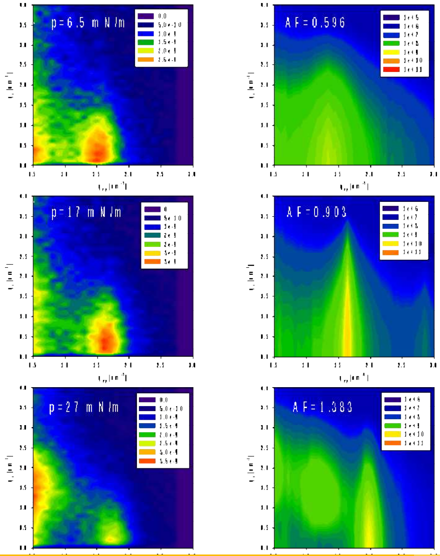
$$\sigma^2 = \frac{k_B T}{2\pi\gamma} log \frac{q_{\max}}{q_{\min}}$$ for q < simulation box size

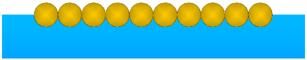
In-plane organization



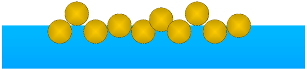


In-plane organization





$$I(\mathbf{q}) \propto \mathcal{A} \left| \sum_{j=1}^{N} V_j F_j(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r_j}} \right|^2$$



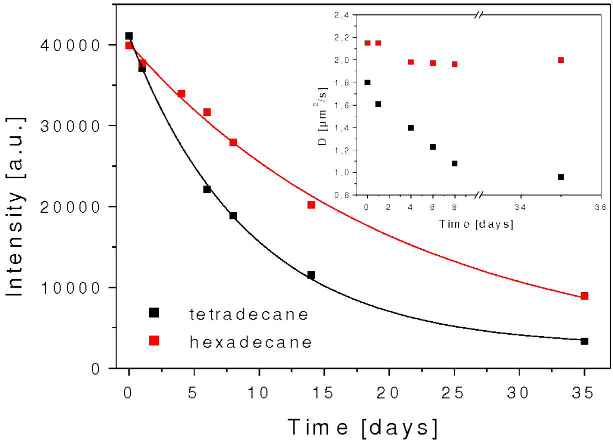
Emulsion preparation

Particles dispersed in isopropanol (2%-4%)

Addition of oil (tetra- or hexadecane) and emulsification by ultrasound

Removal of the excess oil and dialysis to remove the isopropanol

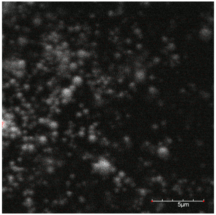
Dynamic light scattering I



Confocal microscopy and freeze fracture EM

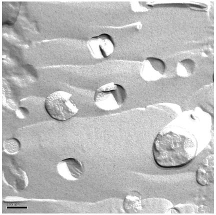
Confocal microscopy (tetradecane)

- Movement reduced by agarose
- Droplet size 400nm

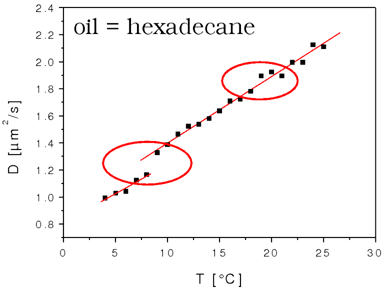


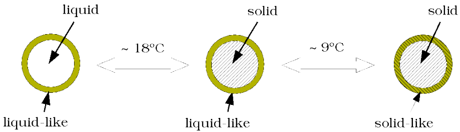
Freeze fracture (hexadecane)

- Droplet size 200nm
- J.-M. Verbavatz, CEA



Dynamical light scattering II

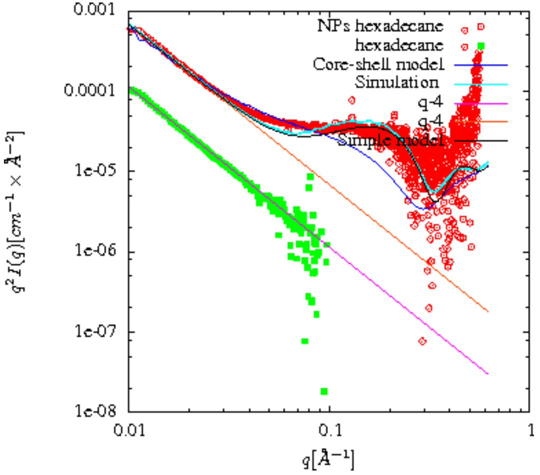




- Size and shape are not changing when the oil solidifies
- Pronounced change in diffusion when ligand shell solidifies
- Hexadecane emulsion is more stable than tetradecane
- Equilibrium hydrodynamic radius $R_H = 125nm$ in hexadecane and increases from $R_H = 140nm$ to $R_H = 250nm$ in tetradecane

SAXS measurements

SWING beamline, Soleil



Outlook

- 2nm nanoparticles can stabilize emulsions
- 2D films can be studied in detail at o/w interface
- Isotherms + Diffraction + MC simulations $\rightarrow$ NP-NP interactions
- Mechanism of emulsion stabilization?

- S. Kubowicz, M. Hartmann, M. Dubois
- Collaboration H. Möhwald (Potsdam)
- M.K. Sanyal (Calcutta)
- O. Konovalov, ESRF
- F. Meneau, J. Perez, O. Lyon, Soleil