# Wetting of Emulsions Droplets: From Macroscopic to Colloidal Scale

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By using large oil-in-water droplets covered with ionic surfactant we measure contact angles to deduce the adhesive energy between macroscopic interfaces as a function of the temperature $T$ and the salt concentration $C$. A wetting transition takes place at a well defined temperature $T^*(C)$. At the colloidal scale, we have observed that submicron droplets covered by the same monolayers undergo a phases separation. We show that the phases diagram can be quantitatively predicted from the macroscopic contact angles. However, to describe the colloidal phase separation we have to account for both the entropy and the deformation induced by the wetting of the droplets. Finally, our results show how the macroscopic wetting transition can be shifted at the colloidal scale where droplets entropy plays an important role. [S0031-9007(97)04232-4]

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Various surfactants may adsorb on solid or liquid interfaces and govern surface interactions. Surface interactions are essential in controlling colloidal stability, fusion, or coalescence of liquid interfaces encountered in foams, emulsions, or biological membranes [1]. When brought into contact, surfactant monolayers may either repel each other or adhere. The adhesion between macroscopic drops or between a drop and a substrate is also known as wetting [2]. Repulsion is suitable for stabilizing colloidal dispersions, whereas adhesion or wetting is useful for sticking colloidal droplets or particles to get colloidal gels, or to coat surfaces. In this Letter, we measure the interaction between ionic charged monolayers adsorbed at the oil/water interfaces of oil-in-water drops which can become adhesive, and we show the consequences of this adhesion on colloidal stability.

Adhesion between two interfaces arises from the presence of attractive interactions which lower the tension of interfaces [3]. Dictated by mechanical equilibrium, a contact angle is formed at the junction between isolated and adhering interfaces which have a lower tension, as sketched in Fig. 1. The relation between the adhesive energy $\varepsilon$ and the resultant contact angle is known as the Young Dupré equation: $\varepsilon = 2\gamma[1 - \cos(\theta)]$ where $\gamma$ is the oil/water interfacial tension in the presence of surfactant and $\theta$, the contact angle. By measuring $\gamma$ and $\theta$, we show that charged monolayers may become strongly adhesive as previously observed [4], wetting between drops occurring above a well defined wetting transition. Such transition is in contrast with what is expected from mean field calculations for the electrostatic interactions between homogeneously charged surfaces (Poisson-Boltzmann) [5]. At the colloidal scale, we have observed that submicron droplets covered by the same monolayers undergo a phase separation. We show that the phase diagram of submicron suspensions can be quantitatively predicted from macroscopic contact angle measurements which allows quantification of the energy of adhesion as a function of temperature and electrolyte concentration. However, to describe the colloidal phase separation we have to account for both the entropy and the deformation induced by the wetting of the droplets. Because the adhesive interaction is supposed to be very short range, we consider the wetted droplets to be truncated spheres and therefore neglect the role of long range forces [6]. Our results show how the macroscopic wetting transition can be moved for droplets on the colloidal scale where droplet entropy plays an important role.

Oil droplets of several tens of microns in diameter are easily formed by slowly mixing 5% of hexadecane in a solution of an ionic surfactant, SDS (sodium dodecyl sulfate) at a concentration equal to $2 \times 10^{-4}$ mol/l, in the presence of salt (NaCl). We use these rather large droplets, which are nevertheless smaller than the capillary length (1 mm), to probe the adhesive properties of macroscopic interfaces. The possibility that oil-in-water droplets adhere in the presence of various salt and SDS surfactant has been previously reported [4,7]. The authors have clearly shown that the adhesion between droplets follows the same trends as the formation of the so-called

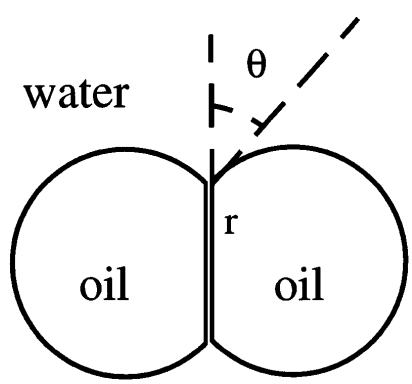


FIG. 1. Schematic representation of two adhesive droplets of radius $R$, forming a contact angle $\theta$ and a flat adhesive film of radius $r$.

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Newton black soap films [8,9]. The latter consists of closely contacting air/water interfaces covered with the same surfactant. The films associated with the oil droplets are also remarkably metastable when adhesive. In other words, they do not coalesce within the time scale of our experiment, which allows us to measure the contact angle by using an optical microscope. The interfacial tension $\gamma$ is measured by using the pendant drop technique. Figure 2 shows the evolution of $\varepsilon$ at various salt concentrations $C$ (from 0.4 to 0.8 mol/l) as a function of temperature. For each salt concentration $C$, there is a temperature threshold $T^*(C)$ below which the contact angle and therefore the adhesive energy becomes nonzero; $T^*(C)$ defines the wetting transition temperature at which the surface energy becomes temperature dependent. From these data we get an empirical form for the adhesive energy as a function of $T$ and $C$ (see inset of Fig. 2): $\varepsilon = 2.14 \times 10^{-4}\ C^{-3.42}\ (T + 12.5 - 100C)^2$ for $T < T^*(C)$, where $T^*(C)$ is given by $(100C - 12.5)$. $\varepsilon$ is expressed in mN/m, $C$ in mol/l, and $T$ or $T^*$ in degrees Celsius. This empirical expression yields a convenient function for the surface interaction which we use below. However, such an empirical quadratic equation suggests that the wetting transition is continuous. Since the film thickness (monolayer separation) is not changing continuously when the monolayers become adhesive, the transition is actually first order [2]. Indeed, as revealed by neutron scattering experiments [7], the equilibrium film thickness actually jumps to a constant value of about 30 Å at $T^*(C)$. This equilibrium thickness does not change with a decrease in temperature below $T^*(C)$ or with an increase in salt concentration, whereas the adhesive energy continues to increase (see Fig. 2). The same trends have been found for the transition between common black soap films and Newton black films [8,9].

We now consider the implications of this adhesion and of this wetting transition in determining the colloidal stability of submicron monodisperse droplets. When surfactant is adsorbed at the interfaces of such droplets their stability should also be related to their wetting properties.

By using the fractionated crystallization technique we produced monodisperse hexadecane-in-water droplets of various diameters (0.3, 0.5, 0.8 $\mu$m) from a crude polydisperse emulsion [10]. We used SDS to stabilize the droplets. By using a microscope and a thermostated cell we investigated the phase behavior when NaCl salt is added and the temperature is changed. At high temperature the droplets remain dispersed; at a well defined temperatures $T_g(C)$ a phase separation takes place between dense aggregates and a more dilute phase composed of Brownian droplets. The coexistence zone between aggregates and Brownian droplets extends over a rather small temperature range (less than 0.3 °C). At a temperature slightly below $T_g(C)$ (about 0.3° below), no Brownian droplets are left. We did not observe any hysteretic effects. Interestingly, the phase transition may exhibit trends of both colloidal aggregation and spinodal decomposition even though the dense phase is more analogous to a glass or gel [11]. In Fig. 3, we plot $T_g(C)$ for the three distinct droplet sizes. We also report the onset of adhesion (revealed by the existence of a nonzero contact angle) of macroscopic droplets stabilized with the same SDS surfactant. The distinction between $T^*(C)$ and $T_g(C)$ reflects the fact that colloidal droplets can remain dispersed, whereas large droplets under the same conditions are already exhibiting a measurable contact angle. We observed that the difference between $T^*$ and $T_g$ is increasing with decreasing the droplet diameter and with increasing salt concentration. $T_g(C)$ depends upon the salt concentration and droplet sizes, but is essentially independent of the droplet volume fraction $\phi$ when varied from 0.5% to 30%. When rapidly quenched 1° or 2° below

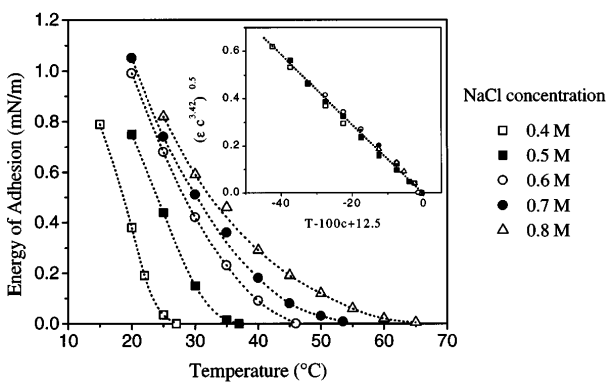


FIG. 2. Evolution of the energy of adhesion between oil-in-water droplets as a function of temperature for various NaCl concentrations (0.4, 0.5, 0.6, 0.7, and 0.8 mol/l). The inset shows a plot of an empirical expression of the adhesive energy as a function of $T$ and $C$ (see text).

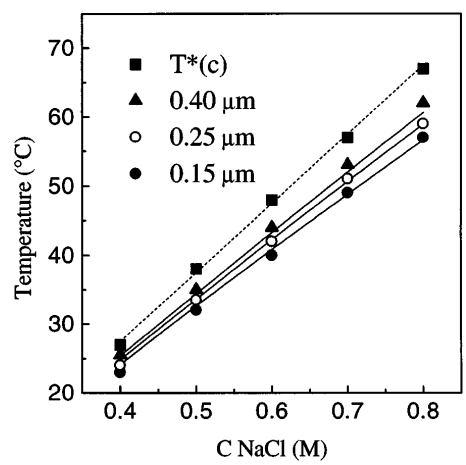


FIG. 3. Evolution of the wetting transition temperature $T^*(C)$ for macroscopic interfaces (black squares), $T_g(C)$ for emulsions of various droplet sizes. The solid lines are predictions of $T_g(C)$ (see text).

$T_g(C)$, the emulsion turns into a gel made out of connected nearly equally sized clusters [11].

From the determination of $\varepsilon(T, C)$ we attempt to predict the colloidal phase diagrams. In addition to the attractive interaction, obviously the role of entropy and the droplet deformation arising from adhesion should be introduced. The total pair contact interaction $U$ between droplets results from a combination of deformation and adhesive energies which have opposite signs. The energy due to deformation, $E_s$, for two adhesive droplets is $2\gamma\Delta s$ where $\Delta s$ is the surface difference between a sphere and a truncated sphere of equal volume (see Fig. 1); $\Delta s$ is a function of $R$, the droplet radius, and of the contact angle $\theta$ which is related to the radius $r$ of the flat thin adhesive film. The energy of adhesion $E_{\mathrm{ad}}$ for two droplets is $-\pi r^2\varepsilon$. $U$ is deduced from minimizing $E_s + E_{\mathrm{ad}}$ as a function of $r$, leading to $U = -\frac{\pi R^2\varepsilon^2}{2\gamma}(1 + \frac{\varepsilon}{4\gamma})$ [6]. Since the formation of flat adhesive films between droplets requires the formation of additional surface (from sphere to a constant volume truncated sphere) the resulting total attractive energy is less than (half) what is expected from two flat surfaces. We further assume that the pair interaction $U$ is the only enthalpic contribution to the colloidal phase transition and that the phase separation is liquid-solid-like. Taking into account that the fluid phase is fairly diluted ($\phi_{\mathrm{liq}} < 20\%$) and the solid phase mostly incompressible and compact (oil volume fraction fixed at random closed packing value $\phi_{\mathrm{sol}} = 64\%$), we can work out the following simple model [12]. The fluid free-energy density is taken to be the ideal-gas one,

$$f_{\mathrm{liq}} = \left(\frac{kT}{v}\right)[\phi \ln \phi + \phi(\mu^0_{\mathrm{liq}} - 1)],$$

where $v$ is the volume of an oil droplet, and $\mu^0_{\mathrm{liq}}$ the reference chemical potential of the liquid phase with $\mu^0_{\mathrm{liq}} = kT \ln(\frac{\lambda^3}{v})$, where $\lambda$ is the de Broglie length and $kT$ the thermal energy. The solid free-energy density is

$$f_{\mathrm{sol}} = \left(\frac{kT}{v}\right)\phi_{\mathrm{sol}}\left(\frac{zU}{2} + \mu^0_{\mathrm{sol}}\right),$$

where $\mu^0_{\mathrm{sol}}$ is the reference chemical potential of the solid phase and $z$ the nearest-neighbor number. $\phi_{\mathrm{liq}}$ at the coexistence point is a solution of the equation

$$f_{\mathrm{liq}} + (\phi_{\mathrm{sol}} - \phi_{\mathrm{liq}}) df_{\mathrm{liq}}/d\phi_{\mathrm{liq}} = f_{\mathrm{sol}}(\phi_{\mathrm{sol}}).$$

By introducing the expressions given above and neglecting the linear term we get $kT \ln \phi_{\mathrm{liq}} = \frac{zU}{2} + (\mu^0_{\mathrm{sol}} - \mu^0_{\mathrm{liq}})$. Therefore, this equation permits prediction of $\phi_{\mathrm{liq}}$ as a function of $T$ and $C$, provided $U$ is known. Here $U$ is varied very sharply with $T$, $\phi_{\mathrm{liq}}$ is weakly dependent on $T$: $\phi_{\mathrm{liq}}$ varies from a few tenths of a percent to 30% when the temperature decreases by about a tenth of a degree. Therefore, as observed experimentally, the coexistence zone is very narrow and $T_g(C)$ is essentially independent of $\phi$, once $\phi$ is greater than 0.1%. Therefore we can consider a unique temperature within a few tenths of a degree uncertainty at which the transition takes place. If we assume $\mu^0_{\mathrm{liq}} > \mu^0_{\mathrm{sol}}$ allowing us to neglect $\mu^0_{\mathrm{sol}}$ and taking $z = 12$, we directly compute $T_g(C)$ and compare it with experiments in Fig. 3 (see continuous lines). There is a clear agreement between this crude model and our experimental data for the three droplet sizes. Indeed, as observed experimentally we predict that $T_g(C)$ decreases with decreasing the droplet size. This effect is essentially due to the quadratic variation of $U$ as a function of $R$. Moreover, the difference between $T^*(C)$ and $T_g(C)$ is also predicted to increase with $C$ as a consequence of the $U$ versus $C$ dependency. We believe that, considering the many approximations involved in our calculations, the fairly good agreement that we observe is certainly due to the very sharp rise of $U$ with temperature which rapidly smooths out more subtle contributions. Therefore, $T_g(C)$ is quantitatively predicted, clearly demonstrating that the colloidal phase transition is mainly driven by the short range adhesive forces, droplet entropy, and deformability. This rules out the importance of some other contributions such as line tension effects including the role of long range forces.

As previously reported [7], neutron scattering experiments performed on the dense phase have revealed the presence of flat thin films in between colloidal droplets of about 0.2 $\mu$m in radius. The surface area of these flat films is increased by lowering the temperature or increasing salt concentration as found for macroscopic droplets according to their wetting transition. The experiments presented here nevertheless show that there is a temperature shift of the wetting transition when the droplet size reaches the colloidal scale. Our very simple model assumes that once colloidal droplets belong to the dense phase the contact angle is the same as the one observed at a macroscopic scale. Even though the agreement between this picture and our data is quite satisfying, there might exist a more subtle mechanism for the coupling between the wetting transition and the droplet entropy. However, we believe that the coupling is correctly accounted by our simple model because the adhesive interaction is very short range.

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