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## LETTER TO THE EDITOR

# Pressure effects on the shearing of a colloidal thin film

Jean-Marie Georges and Denis Mazuyer

Laboratoire de Technologie des Surfaces, Unité Associé au CNRS 855,  
Ecole Centrale de Lyon, 69131 Ecully, France

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**Abstract.** The pressure effect in the frictional behaviour of a colloidal suspension of overbased calcium carbonate stabilized in pure dodecane has been investigated. With a surface force apparatus, we have observed the squeeze effect and the frictional resistance of the suspension using sphere- and plane-geometry on a nanometric scale and for low contact pressure ( $10^4$  to  $10^6$  Pa). With tribometers, which can support heavy loading, we have analysed the high pressure domain ( $10^4$  to  $10^9$  Pa). After a critical pressure, evaluated at  $10^6$  Pa, the colloidal film does not flow in the contact of the solids, but forms a compacted 'mattress' sliding on the plane surface, and squeezing a hydrocarbon layer. The mean shear strength of the interface,  $\tau$ , can then be expressed by a relation of the form  $\tau = \tau_0 + \alpha p$ , where  $p$  is the mean contact pressure. The meaning of  $\tau_0$  and  $\alpha$  is discussed.

If we consider the macroscopic contact of two solids rubbing together, the real nature of the solid surfaces in contact, and of the lubricant, is very often colloidal [1]. Both the solids and the lubricant consists of assemblies of particles [2]. The size of each isolated particle is larger than that of common molecules, being greater than 1 nm, but it is smaller than 1  $\mu\text{m}$ , which is small in comparison with the size of the contact. Mineral oils and greases contain such colloids, especially in the form of additives. For instance, a dispersion of overbased calcium salts is widely used as an anti-wear agent in diesel engines [3].

The frictional force between two sliding solids lubricated with a very thin film usually results from three phenomena [4]: the ploughing of the surfaces by asperities; the adhesion at the many small areas of intimate (or real) contact; and the shear of the interfacial film. If the surface roughness is very small, then the shear properties of the thin film are dominant. Bowden and Tabor [5] established the relation giving the friction coefficient,  $\mu$ , for the situation where the surfaces in their contact region are separated by a thin solid film. The critical shear stress of the film,  $\tau$ , is less than that of the bulk material of the two solids in contact:

$$\mu = T/F = \tau/p \quad (1)$$

where  $T$  and  $F$  are the tangential and the normal forces and  $p$  is the mean pressure in the contact. Bowers and Zisman [6] clearly show that the shear strength of the film depends on the real applied pressure. Consequently they write:

$$\mu = \tau(p)/p. \quad (2)$$

It is in fact difficult to find in the literature the shear-strength value of the material for a

**Table 1.** Tribometers and materials used in the experiments.  $\Phi$  is the volume fraction of calcium carbonate particles diluted in pure dodecane.

Tribometers	Normal load (N)	Sliding speed	Materials	$E$ (GPa)	Lubricant $\Phi$
Surface forces	$10^{-6}$ – $10^{-3}$	$1 \text{ nm s}^{-1}$	Steel 52 100	210	Solution ( $\varphi = 10^{-4}$ ) adsorbed film
Ball on flat (alternative)	$10^{-2}$ – $10$	$10 \mu\text{m s}^{-1}$	Sapphire	420	Dry film ( $\varphi = 0.5$ )
Ball on flat (rotative)	400	$1 \text{ cm s}^{-1}$	Steel 52 100	210	Solution ( $\varphi = 0.1$ )

given pressure. Nevertheless, some authors [7, 8] prefer writing the pressure dependences in the following form:

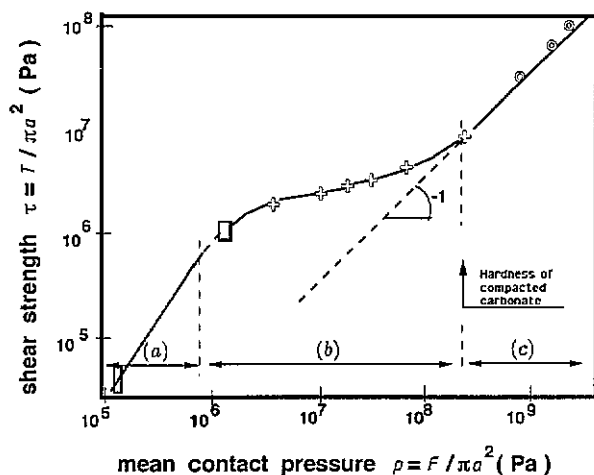
$$\tau = \tau_0 + \alpha p. \quad (3)$$

If this expression appears to be quite general for thin solid films, then the question is if the quantity  $\tau$  is a true measure of the shear strength of the film material or a measure of the shear strength of the interface between the solid and the film material. According to Briscoe and Tabor [7],  $\tau$  is a true measure of the shear strength of the film material, which is less than the critical shear stress of the bulk material.

In this letter, we report the frictional behaviour of a thin colloidal film. Using three tribometers, we analyse the shear behaviour for a large range of pressure. We show that for such a film  $\tau$  measures the shear strength of the interface.

Three series of experiments are carried out with three different tribometers using a large range of normal load as reported in table 1. The colloid system chosen consisted of spherical calcium carbonate particles suspended in *n*-dodecane. The *n*-dodecane, obtained from Merck-Schuchart (> 90%), is used as received. The particles were stabilized by an adsorbed monolayer of calcium didodecyl benzene sulphonate surfactant and prepared by Elf Co. [9]. The particles have been well characterized. Their external diameter, measured by light scattering and electronic microscopy, is  $9.5 \pm 0.5 \text{ nm}$  [10]. The calcium carbonate of the core has an amorphous structure and is surrounded by a monolayer of surfactant of thickness  $1.7 \text{ nm}$  [11]. Liquids were stored over  $\text{P}_2\text{O}_5$  prior to use in order to scavenge any trace of water.

(i) Using a surface force apparatus, we first observed the squeeze effect of the colloidal solution between a rigid sphere and a plane. Secondly, we studied the effects of the sliding. The data, already published, are summarized [12, 13]. The specimens are made with heat-treated steel 52 100. Their surfaces are very highly polished with an asperity height of less than  $5 \text{ nm}$ . The measurements of the static force as a function of the sphere-plane distance  $D$  and the mechanical transfer function of the interface (stiffness and damping) permitted us to describe the interface, as already reported in the literature [14]. Due to the adsorption process and a slight flocculation phenomenon, the surfaces are covered by a solid layer of agglomerated colloids [15]. So, with a solution of  $5 \times 10^{-4}$  after 10 h of adsorption, each surface is covered by a  $3.5 \text{ nm}$  thick layer. During the indentation process, the colloidal layer is compacted and an averaged value of the volume fraction,  $\Phi$ , of colloids in the interface can be evaluated. The sliding process is conducted for two distances,  $D$ . For a distance  $D = 3 \text{ nm}$ , which corresponds to a mean volume fraction of the interface  $\Phi = 0.3$ , the extra normal pressure is  $1.4 \times 10^4 \text{ Pa}$  (absolute mean pressure  $p = 1.14 \times 10^5 \text{ Pa}$ ). In this condition, the initial mean sliding shear stress is  $\tau = 1.4 \times 10^4 \text{ Pa}$ , but increases rapidly during the sliding. The layer flow



**Figure 1.** Pressure dependence of the shear strength of a film of colloidal carbonate at 20 °C. Sliding speeds of the order of  $1 \text{ nm s}^{-1}$  to  $1 \text{ cm s}^{-1}$ . The experiments are conducted with three different tribometers. (a) For the low range of the contact pressure, a surface force apparatus is used (data are represented by rectangles). (b) For the medium range of the pressure, a sapphire sphere is loaded against a glass plane. (c) For the high range of pressure, high polished steel surfaces are used. If for the first situation, (a), the flow of the colloidal solution can be homogeneous, for the cases (b) and (c), a compacted film of colloids adheres to the sphere, and the sliding takes place between the film and the plane.

in the interface leads to a consolidated film. For a distance  $D = 2 \text{ nm}$ , the indented layer is more compacted ( $\Phi = 0.5$ ). The mean contact pressure and the mean shear stress are

$$p = 2 \times 10^6 \text{ Pa} \quad (4)$$

and

$$\tau = 1.2 \times 10^6 \text{ Pa} \quad (5)$$

respectively. We note that the tangential stiffness is not stable, indicating that the flow is not continuous in the interface.

(ii) With a second tribometer, a smooth sphere of radius  $R = 4.75 \text{ mm}$ , is loaded against a smooth plane upon which a colloidal film is deposited, the volume fraction of which is about 0.5. The film is about  $0.1 \mu\text{m}$  thick. In these experiments, the specimens used are made of sapphire and have a low surface roughness (asperity height is close to  $3.5 \text{ nm}$ ). The transparency of the plane permits us to observe the contact interface with an optical microscope. Using Newton's interference rings, it is possible to measure the contact area. The plane then describes a motion with an amplitude of  $100 \mu\text{m}$ . Optical observations of the contact zone during the sliding process give an evaluation of the contact radius. The contact pressure for a smooth sphere and plane loaded below the elastic limit can be calculated as the mean 'Hertzian' pressure when the interfacial film has a negligible effect on the contact area. The contact radius,  $a_h$ , is related to the normal load,  $F$ , by the Hertz's relation [17]:

$$F = (a_h^3/1.3)E_s/R \quad (6)$$

where  $E_s$  is the composite elastic modulus of the samples and  $R$  is the radius of the sphere. We found that the experimental data agree with this law for  $F > 2 \text{ N}$ . At this load, the contact pressure corresponds to the hardness of a compact colloidal film

( $H = 2 \times 10^8$  Pa). When the contact pressure value is lower, the two solids are not elastically deformed; they are rigid. They elastically deform the thin film [16], the elastic modulus of which is  $E_f$ . The contact radius,  $a$ , of the rigid sphere indenting the film is given by the elastic foundation model [17]:

$$F = (\pi/4)E_f(a^4/Rt) \quad (7)$$

where  $t$  is the film thickness before indentation. The elasticity of the film varies with its compaction, and then with the contact pressure. Experimentally, we have found the following law [18]:

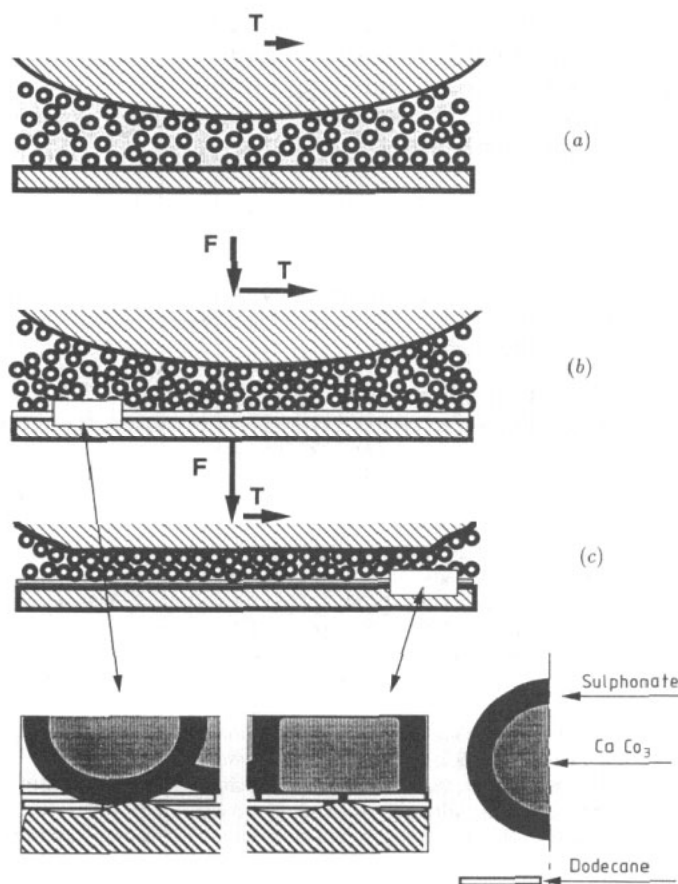
$$E_f = 562 p^{0.75} \text{ Pa.} \quad (8)$$

Taking in account the relations (7) and (8), we found that, for low load,  $a$  is proportional to  $F^{1/10}$ , in agreement with experimental data.

(iii) For the high pressure experiments, we used the same type of contact with 52 100 steel specimens. The roughness is now in the range of 150 nm (peak to valley). The lubricant is a solution of colloids in *n*-dodecane ( $\Phi = 0.1$ ). The sphere describes a circular track on the plane with a sliding speed of the order of  $1 \text{ cm s}^{-1}$ . The contact pressure is less than the elastic limit of the contact (2 GPa). The stabilized friction force is obtained after a few revolutions. The optical observation carried out after the test clearly shows a thin white deposit on the contact zone, the size of which corresponds exactly to the computed Hertzian area of contact.

Figure 1 indicates the evolution of the mean shear stress as a function of the computed averaged pressure for the three series of experiments. For the high pressure region (figure 1(c)), the pressure,  $p$ , is higher than the compacted film hardness. A dry film (deposit of colloidal calcium carbonate subsequently dried) has a hardness value of  $H_f = 1.5\text{--}1.7 \times 10^8$  Pa. We assume that this value corresponds to the hardness of the core which is amorphous calcium carbonate [10]. In this pressure region, the two solids in contact are elastically deformed and the mean shear stress  $\tau$  is almost proportional to the pressure  $p$ , so that  $\tau = \alpha p$ . We found  $\alpha = 0.04$  for  $p = 3 \times 10^8$  Pa and  $\alpha = 0.055$  for  $p = 3 \times 10^9$  Pa. These values, which are the same as those obtained by Bridgeman [22] for paraffins, can correspond to the shear of dodecane molecules aligned on the surface. At this pressure, the dodecane is a solid (the solidification pressure at  $20^\circ\text{C}$  is  $1.8 \times 10^8$  Pa [21]). The slip would occur involving  $\text{CH}_2\text{:CH}_2$  interactions as described by the 'crankshaft' (or wrinkle) model proposed by Tabor [19]. In these experiments the slip takes place between the steel (or sapphire) plane and the compacted film adherent to the sphere. We note that at this pressure, the surrounding shell of a sulphonate is probably removed as shown, recently, by electron energy loss spectroscopy (EELS) [23]. The frictional force does not depend here on the nature of the substrate, as already found for  $\text{MoS}_2$  thin coatings [8].

For the medium range of pressure (figure 1(b)),  $\tau$  is almost independent of the pressure ( $\tau = \tau_0 \sim 3 \times 10^6$  Pa). We note that, in this situation, a slab of compacted film governs the pressure. The mean shear strength,  $\tau_b$ , of the compacted material, which constitutes the film, can be evaluated as  $\tau_b = H/6$  (i.e.  $\tau_b = 3 \times 10^7$  Pa); therefore  $\tau_b/\tau_0 = 10$ . Briscoe [7] mentions such a ratio value for the polymers. We conclude that  $\tau_0$  does not correspond to the strength of the carbonate film, but of the shear stress of the carbonate film-plane interface. This interface is constituted by dodecane molecules and the surfactant of the colloid (diododecyl benzene sulphonate), which presents a



**Figure 2.** Schematic representations of the sphere–plane interfaces lubricated with the colloidal solution, for different pressures. (a) The sphere–plane distance is kept constant during the sliding and the normal pressure ( $10^5$ – $10^6$  Pa) has a low value. The colloidal solution can flow continuously in the interface. (b) The colloidal film is compacted and the sliding takes place between the plane and the film. (c) For a pressure higher than  $2 \times 10^8$  Pa, the sphere–plane contact is elastically deformed, as, also, is the colloid itself. The shell of sulphonates surrounding the colloid is destroyed and the sliding involves dodecane molecules.

$\text{CH}_3$  head. A value of  $\tau_0 = 3 \times 10^6$  Pa is given in the literature for the sliding of  $\text{CH}_3$  against  $\text{CH}_3$  at low contact pressure [7, 20].

For the low range of pressure (figure 1(a)), we have observed, by mechanical measurement, the consolidation of an adsorbed layer of colloidal particles on solid surfaces during the normal approach of the substrates. Hence we have shown that the frictional resistance is strongly dependent upon the consolidation, leading to instabilities for a critical volume fraction of colloids in the interface. This corresponds to a pressure of  $2 \times 10^6$  Pa, where the sliding takes place between the plane and compacted film (figure 2).

In conclusion, the common feature of the experiments is that, after a critical pressure

evaluated as  $10^5$  Pa, the colloidal film does not flow in the interface of solids in contact, but forms a compacted 'mattress' between the two surfaces. Sliding takes place between the 'mattress' and the plane surface, squeezing a hydrocarbon layer. The mean shear strength of the interface can then be expressed by a relation of the form  $\tau = \tau_0 + \alpha p$ , where  $p$  is the mean contact pressure.

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