

«Janus Beads»: Realization and Behaviour at Water/Oil Interfaces.

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Abstract. – We have prepared glass spherical particles, with one hemisphere hydrophilic, and the other one hydrophobic. These objects, named «Janus beads», may be considered as *amphiphilic solids*. We have studied the properties of such beads at oil/water interfaces and point out that they do behave differently from ordinary solid particles. These observations are interpreted semi-quantitatively and open up the way to further prospects and applications.

We present here novel objects, coined «Janus beads», purposely designed to exhibit special properties at liquid-liquid interfaces: the Janus bead (J-bead) is a spherical particle whose surface is half-hydrophilic, half-hydrophobic. These objects are unique in their combination of solid properties on the one hand, with dual surface affinity on the other: they may be considered as *amphiphilic solids*, by analogy with the well-known surfactant molecules [1]. In practice, J-beads are prepared from commercial glass spheres with diameters in the range of 50 to 90 μm and density ρ_s equal to 2.5 g/cm³. The key-idea of preparation is to protect one hemisphere with a cellulose varnish so that it remains hydrophilic, while the other hemisphere is chemically treated by octadecyltrichlorosilane ($\text{CH}_3-(\text{CH}_2)_{17}-\text{SiCl}_3$), leading to a uniform coverage of aliphatic chains that renders the surface hydrophobic. The detailed description of the process and the verification of its efficiency are given in ref. [2]. A schematic representation and a microphotography of a J-bead are presented in fig. 1: the limiting curve Δ separates its hydrophilic (P for polar) and hydrophobic (A for apolar) parts; the two parts of the beads are visualized on the photography by condensation patterns of water: the hydrophilic hemisphere is completely covered by a film of water, whereas the hydrophobic hemisphere is covered with small droplets.

Experimentally, the spheres are dispersed at a water/oil interface and individually observed under an optical microscope (magnification: $\times 500$). In table I, we give the values of densities and interfacial tensions with water for the different oils we have used. At this stage, it is worthwhile to point out that, in all the following experiments and theoretical

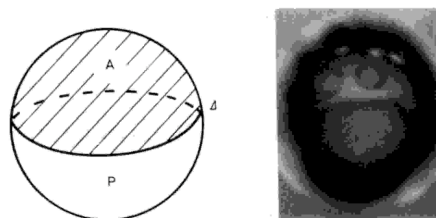


Fig. 1. – A schematic plot and a microphotography of a Janus bead. Δ is the separation line between the polar (P) and apolar (A) parts of the bead. This boundary is visualized on the photograph by breath-patterns («figures de souffle»): the water spreads on the hydrophilic part and makes a film, whereas on the hydrophobic part one observes small droplets as water does not wet completely.

TABLE I. – Values of densities, interfacial tension with water (measured by the pendent-drop method) and contact angles with different types of beads for the oils studied. The contact angles have been measured at oil/water interfaces for beads having a diameter of $60\ \mu\text{m}$, and being entirely polar (θ_P), entirely apolar (θ_A) and of Janus type (θ_J).

Oil	ρ_0 (g/cm^3)	$\gamma(\text{O}, \text{W})$ (dyn/cm)	θ_P	θ_A	θ_J
Hexadecane	0.77	39.4	$(112 \pm 4)^\circ$	$(27 \pm 2)^\circ$	90°
Polydimethylsiloxane (number units 90)	0.961	44	$(121 \pm 3)^\circ$	$(36 \pm 3)^\circ$	90°
Immersion oil (45% benzylbenzoate + 55% castor oil)	1.02	20	$(121 \pm 1)^\circ$	$(46 \pm 4)^\circ$	90°

discussion, we shall consider the liquid interface as flat: in the present experimental conditions, the capillary forces are indeed largely dominant over gravity and buoyancy effects—which may thus be neglected—because of the very small sizes of the spheres. This approximation is classically described as «low Bond number limit». More precisely, it may be shown [3] that the deviation from the «zero gravity» situation (*i.e.* flat interface) is, to the first order, proportional to the Bond number C defined as [4]: $C = ((\rho_0 - \rho_w)g/\gamma(\text{O}, \text{W}))R^2$ where ρ_0 and ρ_w are the densities of oil and water and $\gamma(\text{O}, \text{W})$ the interfacial tension between them. In the present experimental conditions, due to beads sizes, C is smaller than 10^{-4} (from table I), thus justifying the hypothesis of a nondisturbed interfacial profile.

In a preliminary step, we have studied the behaviour of homogeneous beads [5] (*i.e.* beads with totally hydrophilic or hydrophobic surfaces) of the same size and density as the J-beads: our purpose was to check the properties of glass surfaces, polar or apolar, that had undergone the same treatment as the two parts of a J-bead. When varying the focus under the microscope, one then observes successively two concentric circles, the larger corresponding to the equator (radius R) and the smaller to the intersection of the sphere with the liquid interface; the relative position of the two circles indicates in which of the two fluids the object is more immersed.

The experimental results obtained for polar and apolar beads are schematically drawn in fig. 2 and may be summarized as follows: for all the oils studied, the P-type beads are preferentially immersed in water and the A-type beads in oil. These results imply the

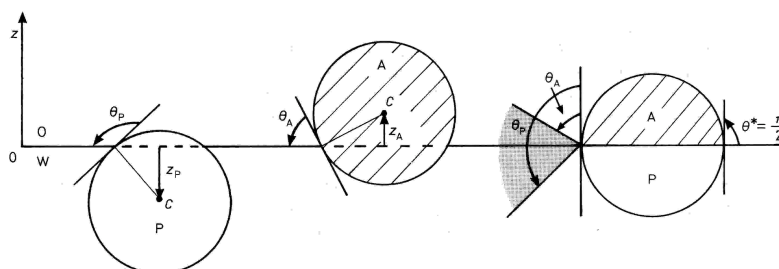


Fig. 2. - Schematic plot of the results observed experimentally at an oil/water interface for A, P and J-beads. θ is the contact angle between the solid surface and the two liquids.

following inequalities between the different interfacial tensions:

$$\begin{cases} \gamma(A, W) > \gamma(A, O) \\ \gamma(P, W) < \gamma(P, O) \end{cases} \quad (1)$$

where $\gamma(M_1, M_2)$ refers to the interfacial tension between two media M_1 and M_2 . As discussed further, the validity of conditions (1) is the relevant information needed for J-beads experiments and modellization.

Note that the corresponding contact angles θ_A or θ_P (fig. 2) may be deduced from the radii of the two circles observed under the microscope; their values are reported in table I. They are related to the different interfacial tensions of the system by the classical Young's equation

$$\cos \theta = \frac{\gamma(S, W) - \gamma(S, O)}{\gamma(W, O)} \quad (2)$$

(S standing for *solid*), where possible hysteretical effects have been ignored.

Turning now to Janus beads, we put into evidence a totally different behaviour: one observes a unique circle under the microscope, whatever the oil used. This observation means that a J-bead is always symmetrically positioned at the interface. Note that in this configuration the J-bead is anchored along the Δ line which delimits the A and P parts, and that the angle θ^* between the liquid interface and the solid is equal to $\pi/2$ (see fig. 2).

The difference between homogeneous and J-beads may be easily understood using the following energetical argument: the total energy of the system is the sum of two contributions: one corresponds to the interfacial energy between the solid and the liquids E_{SL} , and the other to the energy of the liquid-liquid interface E_{LL} . For a homogeneous bead, E_{SL} is minimized when the solid is entirely immersed in the «preferred» liquid, *i.e.* in the liquid with which it has the lowest interfacial energy. However, the existence of E_{LL} counterbalances this effect: the liquid-liquid interfacial energy is all the more decreased as the interface area is reduced, *i.e.* intercepted by the solid. The equilibrium position results from the minimization of these two antagonistic terms which lead either to a trapping of the bead at the interface or to a total immersion in one of the two liquids, depending on the relative values of the interfacial tensions implied in the system. The originality of a J-bead

lies in the fact that the two terms E_{LL} and E_{SL} are «agonistic», *i.e.* work together: for the symmetric configuration, E_{LL} is minimized as it realizes the smallest liquid area, and E_{SL} is at the same time minimized because each hemisphere of the bead «prefers» a different liquid, as expressed by conditions (1). It is important to underline that, in the previous symmetrical configuration, the A-P boundary Δ is a four-phase contact line, so that it is not possible to deduce the equilibrium angle by applying Young's equation; in such a situation, which is due to the discontinuity of the solid surface, the contact angle is in fact indeterminate within the limits defined by the canthotaxis angle [6]. An attempt of interpretation of this latter fact could be to consider that the boundary Δ is not a sharp discontinuity, but a transition zone whose surface energy varies continuously from the A value to the P value; the transition zone is thus able to accommodate any equilibrium angle, provided it is intermediary between θ_A , the Young angle for the A part, and θ_P , the Young angle for the P part. This fact is similar to what happens for a contact line pinned at a sharp solid edge [7, 8]. In the present experiment, since $\theta_A < \pi/2$ and $\theta_P > \pi/2$ (fig. 2), the value $\theta^* = \pi/2$ is indeed allowed. In fact, this is exactly equivalent to the pair of inequalities (1), which may thus be considered as a definition of a J-bead. Notice that this conceptual definition may be generalized [3] to any solids S_1 and S_2 and any liquids L_1 and L_2 as

$$\begin{cases} \gamma(S_1, L_1) < \gamma(S_1, L_2), \\ \gamma(S_2, L_1) > \gamma(S_2, L_2). \end{cases} \quad (3)$$

It is worthwhile noticing that the liquid-liquid interfacial tension does not intervene in this definition of a Janus behaviour.

With the above conditions (3), a bead with a composite S_1/S_2 surface that encounters the liquid interface will *always*, in its minimal energy configuration, be enched along its equatorial line at the interface. It is interesting to note that even if the homogeneous bead S_1 or S_2 is entirely immersed in one liquid (complete wetting), the corresponding J-bead will still be trapped at the interface, in a symmetric configuration. In particular, one may consider trapping at a chosen liquid/liquid interface, materials that would not stay in that situation otherwise.

When (3) is not verified, *i.e.* when both S_1 and S_2 solids «prefer» the same liquid, an S_1/S_2 bead is not expected to exhibit a Janus behaviour at a L_1/L_2 interface but is expected to behave like a homogeneous grain, obeying the classical contact angle equation.

One may next consider the case of nonsymmetrical J-beads. In this case, parts A and P still obey conditions (1), but they are not geometrically equal, *i.e.* the Δ line does not coincide with the equatorial diameter of the bead. We predict two different regimes: one of a Janus type and the other of a homogeneous type, depending on the relative position of the Δ line on the bead. Indeed, when the bead is continuously rendered more and more asymmetrical by shifting Δ , the anchoring position of the liquid/liquid interface varies to follow the boundary (it is easy to show that this is the minimum energy position), so that the equilibrium angle θ^* is altered too. But the equilibrium conditions (1) require that the angle θ^* is bounded between θ_A and θ_P , defining thus two limit lines beyond which the anchoring on Δ is no more possible. These two limit lines (Δ_P) and (Δ_A) are pictured in fig. 3. If Δ lies between Δ_A and Δ_P , the bead anchors on the Δ border line and has a Janus behaviour; outside this domain, *i.e.* for more asymmetrical beads, the anchoring on Δ is impossible and the bead behaves like a homogeneous A or P solid, when the dominant area is of type A or P, respectively. It will be interesting to check this prediction experimentally, since the realization of a perfectly symmetrical bead seems not necessary to obtain a Janus behaviour. In the extreme case, if each solid S_1 or S_2 is completely wetted by one of the two liquids, the bead is trapped at the

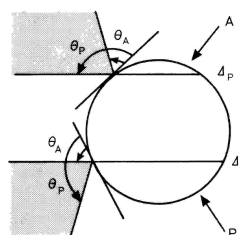


Fig. 3. – Case of an asymmetrical J-bead: the extreme separation lines (Δ_A) and (Δ_P) between the A and P parts correspond to the positions for which the equilibrium angle θ^* is equal either to θ_A (for Δ_A) or to θ_P (for Δ_P). Between them, the condition: $\theta_A < \theta < \theta_P$ is fulfilled, so that the bead anchors on the Δ line, leading to a Janus behaviour; outside the boundary lines, the anchoring on Δ is no more possible and the asymmetrical J-bead behaves like a homogeneous bead.

interface as soon as a very small part of the homogeneous bead is transformed into the other type. Experiments concerning the properties of asymmetrical J-beads are currently underway and the observation of the two anchoring regimes would be a conclusive verification of our model.

In conclusion, we may assert that the special properties of J-beads at liquid/liquid interfaces have clearly been demonstrated by the present experiments. Moreover, they suggest two promising directions for future developments and applications. The first refers to their amphiphilic nature which offers an advantage over homogeneous beads of comparable size and material with regards to emulsification processes: their manageability offers large possibilities of control and optimization of their efficiency. In a complementary way, the second advantage of J-beads lies in the fact that though amphiphilic, they are solid: their constitutive material may thus be altered easily in order to modulate their applications.

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