Electronic Supplementary Material (ESI) for Soft Matter.




# Electronic supplementary information of the paper

## Measurement of the capillary interaction force between Janus colloidal particles trapped at a flat air/water interface

Virginia Carrasco-Fadanelli and Rolando Castillo*

Instituto de Física, Universidad Nacional Autónoma de México,
P.O. Box 20-364, México City, 01000, México.

* To whom correspondence must be addressed
e-mail: rolandoc@fisica.unam.mx

**Optical tweezers instrument**

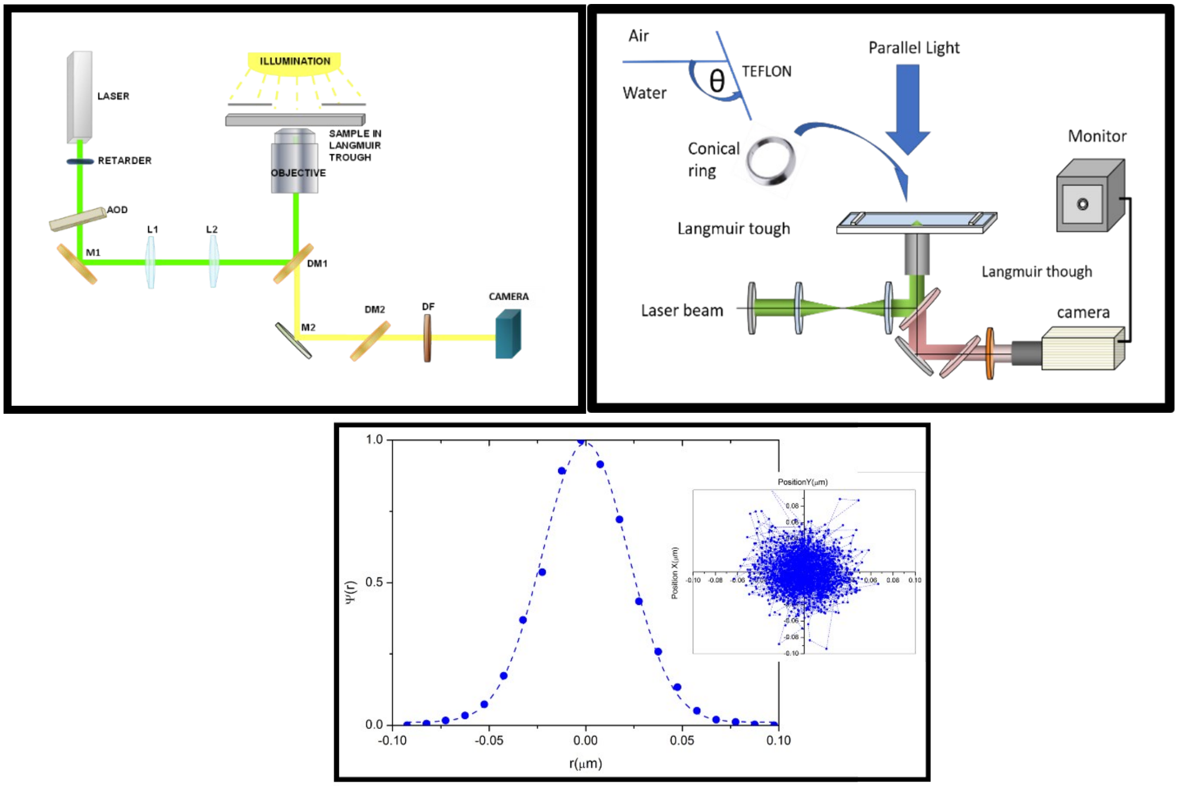


Figure ESI 1. Left panel: Sketch of the experimental setup for measuring the capillary interaction between Janus particles straddling at the A/W interface, using two beams of a time-sharing optical tweezer, as presented in V. Carrasco-Fadanelli, R. Castillo. *Soft Matter*, **15**, 5815 (2019), where M1 is a Gimbal mirror, L1 and L2 are the double telecentric lens, DM1 and DM2 are dichroic mirrors, M2 is a mirror, DF is a dichroic filter, and AOD is an acousto-optic deflector. Right panel: Schematic diagram of one part of our set-up: Langmuir trough where measurements are done at the A/W interface, which is a rectangular NIMA trough (601 M, Nima Technology Ltd., England) made of PTFE, with a working area starting at $84\ cm^2$. This trough is supplied with a sapphire UV-Visible transmission window for inverted microscopy where the laser beam that forms the tweezers enters with the aid of the high numerical aperture microscope objective. The focus of the tweezers is ~ *3 mm* above the window. To ensure that the A/W interface is horizontal, a 1-inch PTFE cylindrical cone was placed over the trough window. The slant angle of the cone was selected to allow that the W/ PTFE contact angle to be $\theta \sim 108\text{-}109^o$. Lower panel: An example of a particle probability density, $\Psi$, obtained from the positions of the geometrical center of one of the particles trapped with a tweezer, which also is in Brownian motion.

**Optical Tweezers.** Tweezers separation and swept-frequency are controlled with an acousto-optic deflector driver (ISOMET, USA). Particle motion is observed and detected with a video camera and a 100X objective. Particle tracking was made using standard software for tracking.[1] The position of the geometrical center, as well as the force constant of the tweezers, $k_i$, for each trapped particle, $i$, are determined. These parameters are obtained from the particle probability density, $\Psi(\boldsymbol{r},t)$, by solving the Smoluchowski equation for a particle in Brownian motion urged by the harmonic potential imposed by the optical tweezers. When $t >> \left(k/\xi\right)^{-1} \sim 0.7\,ms$, where $\xi$ is the friction constant, $\Psi(\boldsymbol{r},t)$ for each coordinate is given by:

$$\Psi(x) = \sqrt{k_i/2\pi k_B T}\,\exp\left\{-\frac{(x-x_o)^2}{2\left(k_B T/k_i\right)}\right\}$$

The first two moments, $\mu_1$ and $\mu_2$, of the probability distribution of the position fluctuations of the particle give the center position of the tweezer, $x_o = \mu_1$, and the tweezer force constant, $k_i = k_B T/\mu_2$.

**Measurement of force.** The pair interaction force is directly measured as the two straddling particles ($i = 1, 2$) at the interface that are optically trapped, come close to each other (Fig. ESI 2a). The force between them is obtained by determining the average displacement of the two trapped interacting particles at a distance $\boldsymbol{r}$, from their corresponding tweezer centers, $\delta \boldsymbol{x}_i$ (Fig. ESI 1a and ESI 1b) using a mechanical model (Fig. ESI 2b). The potential energy of the system is given by $U_T = U(r) + U_1(\delta x_1) + U_2(\delta x_2)$, where $U_i(\delta x_i) = \frac{1}{2} k_i \delta x_i^2$ represents the optical tweezer trapping potentials acting on each particle ($i = 1, 2$), and $U(r)$ represents the capillary interaction potential for fixed angle $\varphi_i$. The force of capillary origin is given by $F = -\nabla U(r) = -\sum_n \left(C_n/r^n\right)$; $C_n$ is a fixed constant, $n$′s are unknown exponent (in our case $n = 4, 5,$ and $6$), and $r = z - (\delta x_1 + \delta x_2)$; where see Fig. ESI 2b. When particles are forced to approach in a stationary way (quasi-static), *i.e.*, $\delta U_T/\delta(\delta x_i) = -\delta U/\delta r + k_i \delta x_i = 0$. From this last equation, we obtain: $k_1 \delta x_1 = C/(z - \beta \delta x_1)^n$, where $\beta = (1 + k_1/k_2)$. From that expression or $F/k_i = \delta x_i = -\frac{1}{k_i}\sum_n \left(C_n/r^n\right)$, the value of the constants of the potential can be determined by fitting the measured values of $\delta x_i$, and $r$.

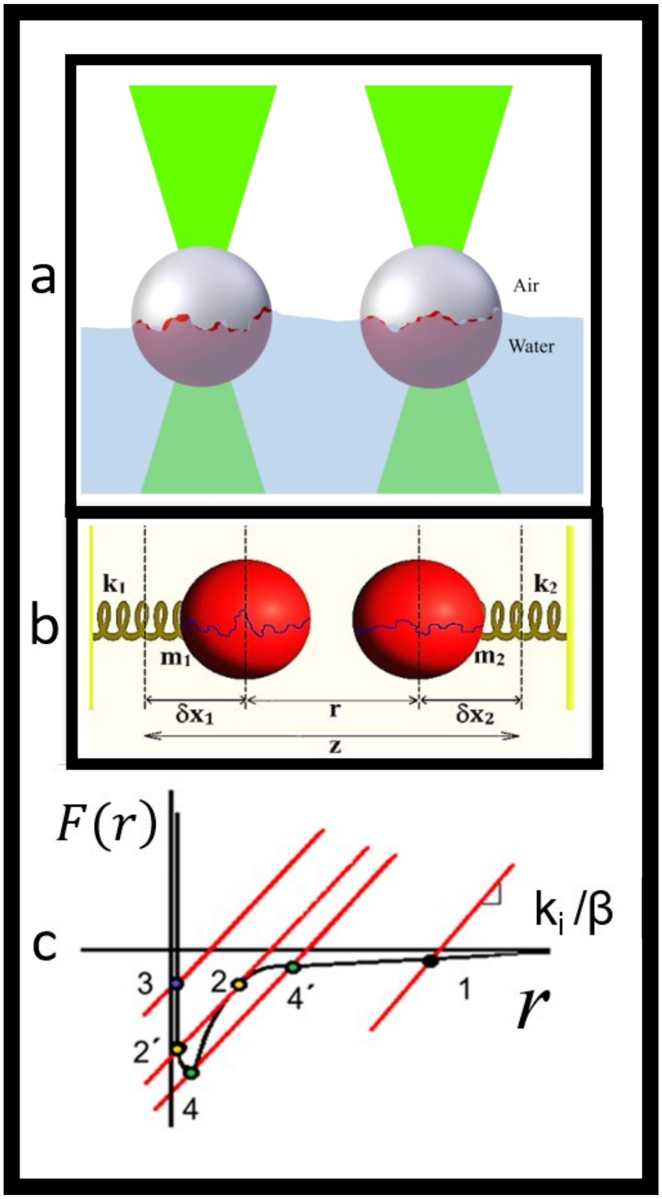


Figure ESI 2. a) Two Janus particles of mass $m_i$ adsorbed at the A/W interface, with a Bond number <<*1*, trapped with a time-sharing optical tweezer. The corrugation of the air/water/particle contact line and the corrugation of the hydrophilic and hydrophobic boundary line have been exaggerated. b) Mechanical model as given in Ref [2]: $\delta \boldsymbol{x}_i$ are displacements of particles interacting at distance $\boldsymbol{r}$ from the optical tweezer centers, and the $k_i$ are the force constants of each optical tweezer fixed by the laser power. c) Drawing of the force-displacement curve. Straight lines represent the effective constant and the black curve the interaction force with a harsh repulsion (contact). Colored dots are mechanical equilibrium points given by the intersection of the lines and the capillary force: 1, 2, 3, 2′, and 4′. When the force gradient is larger than the effective elastic constants, interacting particles become unstable, generating discontinuities from which hysteresis follows: The jump-to-contact (2–2′) in the approach curve and the jump-off-contact in the withdrawal curve (4–4′). When the particles make contact, it is not possible to separate them with the tweezers, because adhesion due to the van der Waals force is very strong at contact (Fig. ESI 2c). This figure is a modified version of Fig 1 in: V. Carrasco-Fadanelli, R. Castillo. *Soft Matter*, **15**, 5815 (2019).

The system is in stable equilibrium when: $\delta^2 U_T / \delta(\delta x_i)^2 > 0$, *i. e.*, $k_1/\beta > \partial F/\partial r$. Here, $k_1/\beta$ is an effective force constant. If the force gradient is larger than the effective constant, the system becomes unstable, and particles jump into contact (Fig. ESI 2c). This jump-to-contact discontinuity is equivalent to the jump-to-contact and the jump-off-contact instabilities found in AFM cantilevers. In AFM, it is difficult to measure force curves because the effective spring constant is fixed. In our case, by changing the power of the laser, we can access different values of the effective constant, making easier the measurement of the capillary force, and the value of *n*.

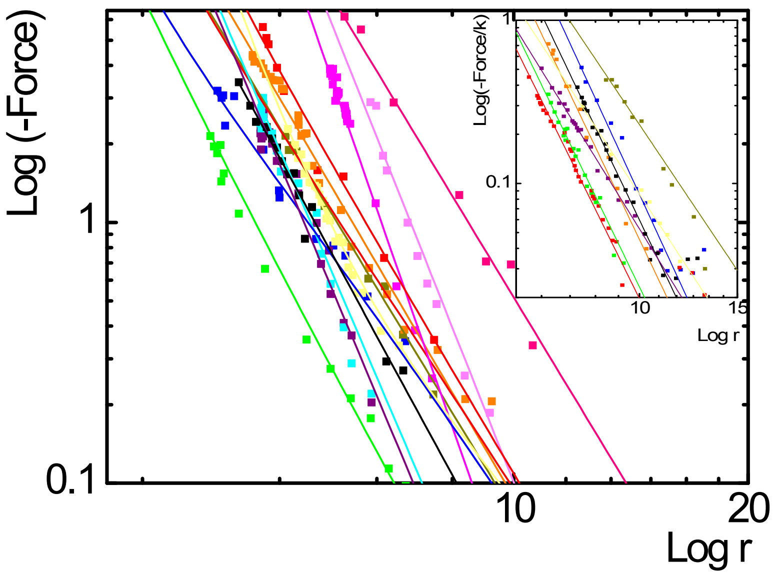


Figure ESI. 3. Figure complementary to Fig. 1, where we present the same data as there, but in logarithmic form: Log (-f) vs. log r, for the capillary interaction force between Janus colloidal particles adsorbed at the A/W interface of a diameter of 3μm. Inset b: *F/k* for particles of a diameter of 5 μm. Color denotes different experiments. Curves are linear fittings to data, and color code is the same as the main figure.

**Amplified Video Clips**

1] Fluctuating JP particles of 5 μm trapped with the time shearing optical tweezers and jump-to-contact

2] Clusters of 3 μm particles at the A/W interface.

1] S. V. Franklin, M. D. Shattuck in: Handbook of Granular Materials. (Chapter 2, Taylor & Francis, Boca Raton, 2016).

2] V. Carrasco-Fadanelli, R. Castillo. *Soft Matter*. **15**, 5815 (2019).