

# Wall Effects induced by Ceramic in Quiescent Liquids

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**Abstract:** At the liquid-solid interface, the energy of the liquid is different from the bulk resulting from surface tension due to the balance between the attraction between molecules to each other (cohesion) and the attraction to the surface (wetting). While capillary effects are well known and described at the air/liquid/solid interfaces, much less is known on the effects induced in the bulk close to the wall. The present experimental study reveals that non-negligible interfacial effects can be revealed in the bulk of the liquid using the high wetting power of ceramics. Close to the wall, thermal measurements reveal a progressive temperature drop in the liquid (about 0.15°C). This zone extends up to several millimeters, creates a non-equilibrium/equilibrium interface within the liquid and is balanced at larger distances by a temperature increase. This localized effect is highlighted with strong wetting metal oxide surfaces as ceramics.

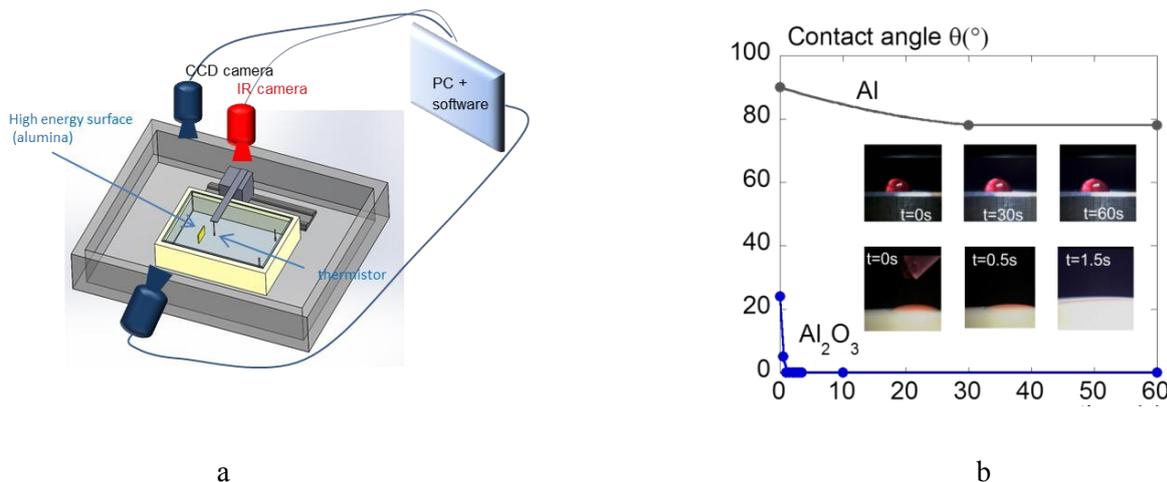
**Keywords:** ceramic, wetting, long range interactions, liquid/solid interface.

## 1. Introduction

In the bulk of the liquid, molecules are pulled in every direction by neighboring liquid molecules, resulting in a net force of zero. Close to a surface, the situation is different. The molecules at the boundary do not have other molecules on all sides of them and create some variation of internal pressure [1]. Thermal exchanges that take place in a liquid bulk close to an immersed wall or in between two walls are usually not explored, hardly modelled [2] and considered as restricted to very small length scales [3,4]. Recently a submillimetre scale thermal study of liquids under flow has revealed that shearing liquids may induce a cooling effect at low shear rates in ordinary Newtonian liquids as water or low viscous polymer melts [5]. The detailed analysis of this non-equilibrium endothermic process indicates that the cooling is firstly generated at the walls and propagates in the fluid giving rise to the establishment of a thermal shear banding regime along the flow axis [5]. We report here on the situation where no external force is exerted on the liquid; i.e. the quiescent state. We examine the influence of a solid wall strongly interacting (total wetting) with the molecules of liquids as water, glycerol or alkanes on the thermal equilibrium. The liquid is observed in its quiescent bulk away from the liquid-air interface. We report on the identification of a slight temperature fall observed at the vicinity of a wetting wall followed by a slight temperature rise at larger distance from the wall. This situation is particularly observable when the liquid is in strong interaction with the wall (total wetting condition). The attraction energy exercised by the wetting surface to the liquid produces a pressure variation, in correlation with a slowing down of the molecules at the wall and correlatively creates a different thermodynamic equilibrium. The cooling zone is compensated away from the surface by a zone slightly warmer than the average temperature. These wall effects are induced in various daily used liquids and are particularly observable using zero-porosity ceramic surfaces because of their high wetting ability. These results highlight the active role of strongly wetting surfaces as ceramics and reveal long range correlations in the liquid state.

## 2. Experimental

This pioneering approach is carried out by using two independent methods to measure the temperature within the liquid. A thermistor probe enables a localized probe of the temperature while Infrared absorption in real-time allows a 2D-mapping of the temperature. We use recent instrumental advances that enable the detection of absolute thermal variations as small as  $5.10^{-2}^{\circ}\text{C}$  for the 2D-infrared emission and as small as  $5.10^{-3}^{\circ}\text{C}$  (relative thermal accuracy) with the thermistor. All the measurements have been carried out at room temperature without forced convection (quiescent liquid equilibrated at least 4 hours before the measurement) in a box isolated from external thermal fluctuations (conduction and convection), in the darkness and in conditions as close as possible to the equilibrium state. The whole setup is equilibrated during several hours prior the experiment. A scheme of the experimental setup is given in Fig.1a.



**Figure 1.**

a) Scheme of the experimental setup: the ceramic surface is immersed in a bath filled with a liquid. The bath is itself placed in a thermally isolator container. Two optical cameras view the liquid from the side and the top of the liquid surface and an infrared CCD is positioned above the liquid surface (top view). The dimensions of the ceramic and Aluminum plates are about  $15 \times 20 \times 1 \text{ mm}^3$ . Three thermistors are immersed in the bath: one close to the plate and two others at fixed positions at 150mm away from the plate.

b) Measurement of the contact angle versus time for glycerol deposited at room temperature on an aluminum plate (grey circles) and on an alumina plate (blue circles). Similar stationary contact angles are found for liquid water.

*Local temperature measurements:* The temperatures are recorded using a  $10 \text{ k}\Omega$  (room temperature) calibrated thermistor of  $0.4 \text{ mm}$  diameter. The thermal probe is fixed to a deported arm that can slowly move the probe at different locations in the liquid. Two identical thermistors placed away from the probed surface serve assimultaneous references to renormalize the temperature from small random thermal fluctuations. Each thermistor is connected to a separated Keithley multimeter ( $5 \mu\text{A}$ ). The GPIB mode is used to enable the simultaneous recording of the temperatures. The relative reproducibility of the measurement is estimated at  $5.10^{-3}^{\circ}\text{C}$ .

*Micro-thermal 2D-Imaging:* The thermal mapping is based on the emissivity measurement; a medium radiates all the more that its temperature is high. The heat transfer by radiation can be expressed using the Stefan-Boltzmann law:  $E = em \cdot \sigma \cdot A \cdot (T^4 - T_c^4)$  where  $E$  the radiated energy,  $em$  the emissivity,  $A$  the radiating area,  $T$  the temperature of the sample and  $T_c$  the temperature of the surroundings.  $\sigma$  is the Stefan's constant. A high performance  $320 \times 240$  pixels B400 FLIR Infra-Red 2D-detector equipped with a close-up lens giving a spatial resolution of  $25 \mu\text{m}$  in a  $8 \times 6 \text{ mm}^2$  working area is placed at about  $50 \text{ mm}$  from the free surface of the sample filling the gap between two wetting substrates made of alumina [2]. The frame rate is  $30 \text{ Hz}$ . The resolution ellipsoid enables to probe a  $\pm 0.15 \text{ mm}$  depth of field. The spectral range goes from  $7.5 \mu\text{m}$  up to  $13 \mu\text{m}$  and the relative temperature accuracy is of  $\pm$

0.025°C. Finally, it is reminded that the emissivity of the liquid water is 1,000. This means that water is an absolute reference (the Wien law can be directly applied without emissivity correction).

*Surfaces:* Two surfaces are used in this experiment: a zero porosity alumina plate of 3 mm thickness and  $R_a = 1.6$  roughness providing a total wetting and an aluminum plate (AG3) of similar roughness providing a partially wetting (Fig.1b). We use practical Aluminum plates. Aluminum surfaces are naturally passivated by a thin oxidized aluminum film of alumina (gamma phase) [6]. The wetting degree is characterized by the contact angle method. The surfaces will be in contact with demineralized liquid water (preliminary degassed). The wetting ability is evaluated via the determination of the contact angle. It reaches zero when the wetting is total (alumina) and is around 75° in the case of the liquid water drop deposited on an aluminum substrate (partial wetting).

### 3. Results - discussion

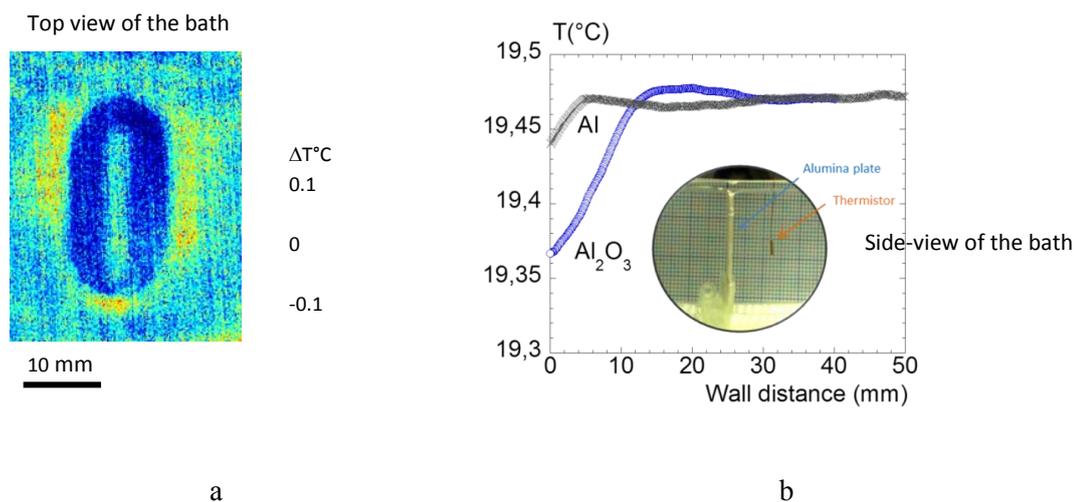
Two independent techniques are used to determine the thermal profile in the bulk of the liquid at the approach of an immersed wall. This wall is either by a highly wetting surface (ceramic) or by a partial wetting surface (aluminum). We illustrate here the results obtained at room temperature on liquid water in the quiescent state. These two techniques are complementary; Infrared measurement enables an instantaneous two-dimensional mapping of the temperature distribution viewed from the free surface of the water. The thermistor enables a punctual measurement with a higher accuracy in the liquid bulk.

Fig.2 (a) displays the infrared image corresponding to the thermal emission produced through the liquid surface (confocal configuration) of a bath filled with water at room temperature in which an alumina plate has been placed. The alumina plate is vertical and totally immersed in the water. The thermal mapping reveals that the plate is surrounded by two successive static thermal waves. Close to the plate, the interaction of the liquid to the plate produces a cooling zone. This zone is followed by a second wave of higher temperature than the medium and compensating the thermal loss corresponding to the first cooling zone. This thermal distribution is stable with time and suggests that the wall induces the coexistence of two different thermodynamic states in the quiescent liquid.

The temperature of a body is resulting from the dynamics at a molecular scale. This thermal excitation produces an infrared emission due to the vibration of molecules that continuously absorb and re-emit infrared photons. The observation in the liquid of a variation of infrared emission and of the correlated temperature variation close to the surface as illustrated in Fig.2a and 2b, indicates different vibration states. The interactions between molecules are modified and the motion is affected producing close to the solid wall a slowdown of the motion responsible of the reduced infrared emission. At larger distance from the wall, the subsequent increase of the infrared emission indicates an increase of energy.

The temperature cartography revealed by infrared emission is confirmed by the thermal sensor. This variation of the infra-red emission close to the wall is corroborated by the direct measurement of the temperature using an accurate thermistor placed at different positions in the bath. The thermistor enables to probe the temperature in the liquid bulk at various depths away from the liquid surface. Fig.2b displays the typical temperature profile recorded by the thermistor as a function of its distance from the plate. The profile shows that the temperature in the liquid decreases significantly close to the ceramic wall ( $\Delta T \cong 0.2^\circ\text{C}$ ) and much slightly in the case of Aluminum. At larger distance from the wall ( $d > 10\text{mm}$ ), the profile indicates a slight temperature increase.

The attraction of the wetting wall is such that the liquid exhibits close the wall, a slowing down of molecular dynamic (temperature decrease) and thus are lated lower pressure state. At distance away from the wall, the zone where the liquid exhibits a slightly higher temperature corresponds correlatively to a compressive zone. This effect that takes place within the liquid bulk can be interpreted similarly as typical pressure capillary effects usually described for air/liquid interfaces. A liquid/liquid interface is here produced by the induction of a lower pressure state close to the ceramic wall balanced by a higher pressure state away from the wall. The pressure difference between these two states creates locally an induced immiscibility in the liquid bulk. A capillary pressure separates the two states  $p_c = (p_{\text{low pressure}} - p_{\text{highpressure}}) < 0$  following the Young-Laplace equation, the pressure difference is proportional to the induced interfacial tension.



**Figure 2.**

a) Two-dimensional thermal cartography (top view) of the free surface of quiescent water below which a 3 mm thickness alumina plate (central vertical bar) has been immersed. The colors indicate different temperatures, the warmest corresponding to the highest temperatures while the cold ones (blue) indicate lower temperature regions. The experiment is carried out at room temperature in the quiescent state. These temperature variations are stable and persist in time during several days. Top view of the bath (recorded from the free liquid surface).

b) Temperature profile (average profile on 10 measurements of each 10min) recorded in the liquid water away from an alumina, aluminum surface respectively (at around 15mm depth) as a function of the distance from the plate. A similar profile is recorded at different depths away from the surface. Insert: photograph of the bath with the immersed plate (side-view of the bath) and of the thermistor at the approach of the plate.

Here the mechanism is complicated by the induction close to the wall of a convective motion due to the temperature gradient (Fig.3). The inductance of expansive and compressive states and of related thermal effects is also known during applied tensile strain for engineering materials in solids. Thermoelastic effects have been extensively studied in solids. Most of them describe effects in crystalline solids relating the dynamics of the molecular vibrations. Some studies report on thermoelastic effects in glasses [7, 8]. Finally, to our knowledge, no similar effect has been reported in the liquid state probably because these effects are usually very weak and academically not foreseen. However condensed matter can sustain negative pressures because of the attractive intermolecular interactions. The wetting the surface creates a local negative pressure. Moreover recent developments in stress dynamic measurements have shown that liquids as water, alkanes or polymer melts exhibit an elastic (solid-like) behavior in restricted geometry [9]. Sub-millimeter scale stress measurements highlight an intrinsic property supporting the hypothesis of a liquid formed by a weakly bound resilient self-assembly [10, 11]. The present observation of a temperature fall still active at nearly 10 mm from the wall is the firm indication that cohesive intermolecular forces are long range correlated in the liquid bulk. Correlatively the liquid state is easily modifiable, “stretchable” at the vicinity of a high energy surface as a wetting substrate.

#### 4. Conclusions

Though interfaces are known to crucially influence the behavior of physical, chemical, and biological systems, their contribution to the establishment of different coexisting thermodynamic states via contact is unknown or supposed negligible [3, 4]. While capillary pressure effects are well documented, much less is known concerning the possibility of modifying the thermodynamic equilibrium by wall interactions. The use of high energy surfaces as ceramic enables to highlight liquid/surface effects in the bulk that would have gone unnoticed. This experimental work evidences that the wall attraction induces the coexistence of slightly different thermodynamic states characterized by a weak, progressive and non-ambiguous temperature drop in the bulk of the liquid at

the approach of the wetting surface balanced by a succeeding temperature increase away from the wall. The negative temperature gradient is around several few tenths of a Celsius degree in liquid water. The greater attraction of molecules to the wetting surface (adhesion) than to each other (cohesion) produces surface attraction that forces the cohesive nature of the liquid to behave as a slightly stretched elastic state close to the wall. Similarly as capillary effects, this lower pressure state involves the liquid cohesion and modifies the intermolecular forces at the millimeter scale. This long range effect is incompatible with a description in terms of individual molecular dynamic or via a heat transfer process but involves the cohesion forces. The cohesive forces give rise to bulk and shear elasticity. The latter have been measured in the liquid state by different authors and methods [10-14]. Only scarce theoretical approaches consider the cohesive character of the liquid state, at the approach of a glass transition [15,16], close to the wall, at several molecular layers scale [17] or macroscopically, the strength of which depends on the network size [18]. Clearly the cohesive long range intermolecular correlations should play a key role in these giant (wall) effects. The identification of a wall induced gradient of temperature points out also many questions and requires more investigation to determine the relevant parameters: what is the mechanism that governs the interactions between liquid molecules and the surface atoms? What are the parameters of the surface and the characteristics of the liquid that define these effects? What are the consequences of the temperature gradient on the flow behavior, especially in solutions? How to overcome this thermal effect at the wall? In this challenge, a multiscale description should provide new insights in understanding the true nature of the liquid state involving a description of the interaction forces at play across the wall up to the macroscopic behavior. This puzzling wall-induced effect has profound fundamental origins that remain to be identified and various possible applications as for example a selective separation in solutes or solutions [19].

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