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WETTING & EVAPORATION OF SESSILE DROPS: SOME FUNDAMENTAL PARAMETERS

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Sessile drops are frequently used to characterise solid surfaces, using the measured contact angles of “probe” liquid drops, assuming them to be true, equilibrium values. By applying Young’s equation and one of various equations proposed to relate interfacial (solid/liquid) tension to the surface tensions of solid and liquid and their various components [e.g. 1-3], estimates of the surface properties can be obtained. Neglecting any possible doubts attached to the validity of the various interpretations, a serious problem is that of the measured contact angle itself. A simple force balance predicts an equilibrium value, but it is well-known that a range of values is usually accessible; giving rise to what is generally termed “wetting hysteresis”. This range may be very large, depending on the system. The causes are multiple, including solid surface roughness, solid deformation by capillary forces, local adsorption and chemical reactivity. However, a ubiquitous effect that has been largely overlooked till the mid 90s is that of concomitant evaporation [4]. Unless the drop is strictly at equilibrium with its vapour, which is highly unlikely, there will be liquid transfer, usually evaporation decreasing drop volume. How this occurs is far from trivial, and one of the first surprises was that due to Deegan *et al.* in their seminal work and others [5, 6], who convincingly showed that evaporation is exacerbated near the triple line (TL). If the TL is “pinned”, *i.e.* remains in its initial position during evaporation, liquid replenishment leads to an advective current, parallel to the solid surface. If it is not pinned, then a phenomenon of “stick-slip” can occur, in which contact angle decreases to a certain value, with the TL pinned, followed by a rapid TL jump to smaller contact radius and concomitant increase in contact angle [7].

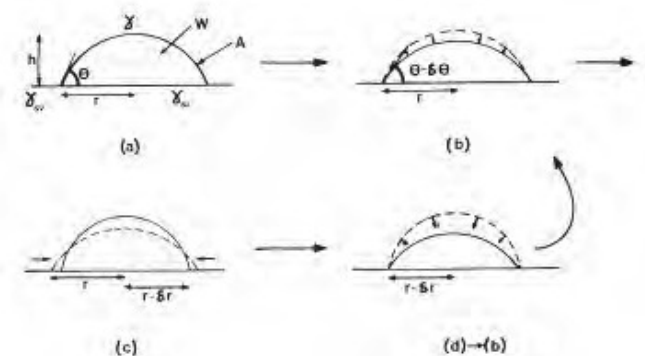


Fig. 1: Schematic representation of the “stick-slip” process in which evaporation at constant contact radius leads to an energy imbalance, finally depinning the triple line [7]. The play-off between evaporation and TL motion can

be quite complex, and we discuss various aspects here. For example, the tendency for a solid/liquid system to “opt” for either TL pinning or “stick-slip” motion is intrinsically related to the surface roughness of the solid; a rough solid allowing easier pinning. Less obvious, propensity for pinning is directly dependent on the initial value of contact angle. This can be related to hydrophobicity, depending on the liquid [8].

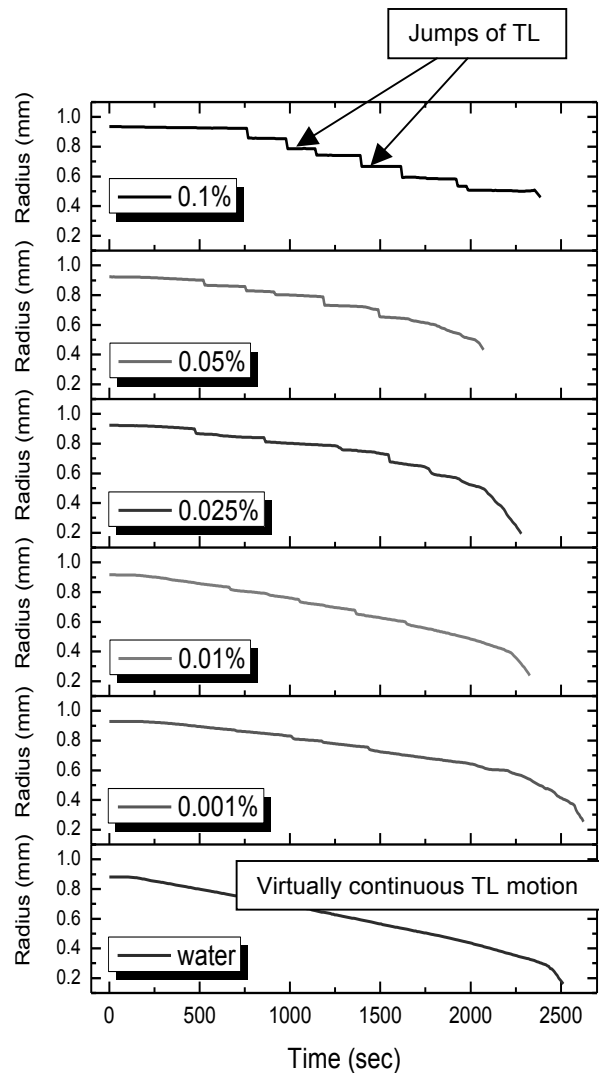


Fig. 2: Evolution of contact radius with time for droplets of nanofluids of different TiO₂ concentrations [9].

A pure liquid in general favours continuous motion of the TL. However, if the liquid is laden with (nano-)particles, “stick-slip” behaviour becomes predominant. For a nano-suspension, the relative particle content is important for determining the type of behavior expected [9]. During the “stick” phase the above-mentioned advective, replenishment current transports particles to the TL [5], and these form a deposit which effectively anchors the dewetting front. The form of these deposits is of considerable interest and, in certain cases, they can adopt a complex crystalline structure [10].

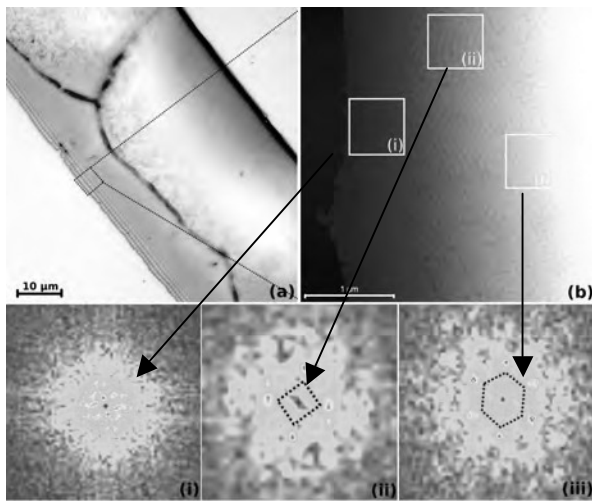


Fig. 3: (a) Optical micrograph showing particle ring stain. (b) topographic image with areas of interest. (i-iii) FFT analysis of these areas showing crystalline form [10].

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