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Effect of particle geometry on triple line motion of nano-fluid drops and deposit nano-structuring

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ABSTRACT

We illustrate the importance of particle geometry on droplet contact line pinning, 'coffee-stain' formation and nano-structuring within the resulting rings. We present the fundamentals of pure liquid droplet evaporation and then discuss the effect of particles on the evaporation process. The resulting coffee-stain patterns and particle structuring within them are presented and discussed. In the second part, we turn our attention to the effect of particle geometry on the evaporation process. A wide range of particle shapes, categorised according to aspect ratio, from the simple shape of a sphere to the highly irregular shapes of platelets and tubes is discussed. Particle geometry effect on evaporation behaviour was quantified in terms of change in contact angle and contact radius for the stick-slip cases. Consequently the hysteretic energy barrier pinning the droplets was estimated, showing an increasing trend with particle aspect ratio. The three-phase contact line (TL) motion kinetics are complemented with analysis of the nano-structuring behaviour of each shape, leading to the identification of the two main parameters affecting nanoparticle self-assembly behaviour at the wedge. Flow velocity and wedge constraints were found to have antagonist effects on particle deposition, although these varied with particle shape. This description should help in understanding the drying behaviour of more complex fluids. Furthermore, knowing the fundamentals of this simple and inexpensive surface patterning technique should permit its tailoring to the needs of many potential applications.

Contents

1. Introduction

Nano-fluids are suspensions of nano-particles in a base solvent. The addition of these particles greatly enhances the properties of the base fluids. Potential applications of these novel fluids could be numerous

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in fields such as heat transfer, biology, chemistry and medicine, to name but a few [1]. As a result, scientific research into nano-fluids has been constantly growing over the past few decades. However, the evaporation of droplets of such fluids has only recently aroused the interest of the scientific community, especially since Deegan and co-workers reported on the mechanism governing the 'coffee-stain' formation [2]. Essentially, contact line pinning due to particulate accumulation at the triple phase line (TL) of solid–liquid-vapour of the droplet was the main reason for the formation of ring-stain deposits. Nonetheless, the exact mechanism is not yet fully understood as the interactions of the particles with the solid and the liquid at the constrained region of the TL near the edge of the droplet are rather complex. In this article we attempt to shed light on how the fundamental parameter of particle geometry affects the evaporation process. We shall present how particle geometry affects the contact line pinning mechanism and dictates both the evaporation behaviour of the droplet and also the self-assembly of the solute at the TL. The following section contains a comprehensive literature review on the area. The fundamental concepts of droplet evaporation, contact line pinning and structuring of ring-stains will be presented in order to act as a basis which will allow better understanding of the concept. Next, we discuss the influence of a wide range of particle geometries on TL motion kinetics and evaporation behaviour. Subsequently, the ring deposits are probed both at the macro- and the nano-scale. Extensive comparison of these data allows identification of differences and similarities in the self-assembly process of particles at the limited area of the droplet wedge. The combination of TL kinetics and self-assembly behaviour should allow the proposition of a plausible universal mechanism detailing how best to employ each particle shape, depending on the application.

1.1. Pure liquid sessile droplet evaporation

A drop of liquid deposited on a flat, smooth, solid surface (sessile drop) adopts the shape of a spherical cap, provided it is sufficiently small (less than the capillary length,$\kappa^{-1} = \gamma/\rho g$ where γ, ρ and g are respectively surface tension, density and gravitational acceleration). A schematic illustration of a sessile drop and the three phases acting on its interface is presented in Fig. 1.

The angle formed between the solid and the liquid tangent is called contact angle, θ. The interplay between the tensions of the three phases acting on the TL is responsible for the value of the contact angle and the shape of the droplet. At equilibrium, contact angle, θ, and the gas–liquid, γ_{GL}, liquid–solid, γ_{LS}, and gas–solid, γ_{GS}, surface tensions should obey Young's equation [3]:

$$\gamma_{GL}\cos\theta = \gamma_{GS} - \gamma_{LS}\,. \tag{1}$$

Ideally, if no wetting hysteresis is present and evaporation occurs quasi-statically, a pure liquid sessile droplet should evaporate with a continuously retracting TL, while its shape (ratio of height to contact radius) and hence its contact angle remain constant. However, the evaporation of such a droplet was found to proceed alternating between this mode and a second distinct one, that of constant radius and diminishing contact angle due to contact angle hysteresis [4]. A schematic illustration of this process is depicted in Fig. 2, where initially the TL of the droplet remains constant, "pinned", and the contact angle decreases, during the period (t_0–t_1). The TL then recedes with constant contact angle, period (t_1–t_4), and finally enters a second pinned mode until complete evaporation (t_4–t_5).

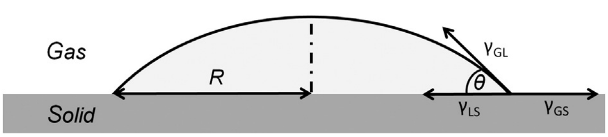

Fig. 1. Schematic representation of a sessile drop resting on a flat surface, illustrating the three surface tensions acting on the TL and the corresponding contact angle, θ, and radius, R.

This unexpected evaporation behaviour of pure liquid sessile droplets was thoroughly investigated both theoretically and experimentally by Picknett and Bexon [5]. Experimentally, they observed these two distinct modes. In addition, a third mode existed, which consisted of a combination of the characteristics of the afore-mentioned modes. They showed the dependency of evaporation rate on contact radius and angle. Consequently, they used the analogy between diffusion concentration field and electrostatic potential field, as both satisfy Laplace's equation, in order to develop a theoretical framework to account for each evaporation mode. The proposed framework allowed the prediction of the evaporation rate, half-life and lifetime of the droplet for each mode with very good accuracy compared to the experimental and other theoretical results [5].

Further light was shed onto the evaporation mechanism of sessile drops by Birdi et al. [6]. Initially, they focused their attention on the evaporation rate of such droplets by directly measuring the weight loss of a droplet over time [6]. The weight loss was found to be linear with time, which means that the evaporation rate of a water droplet is constant and hence the process is stationary. Additionally, the rate of evaporation of the droplet was found to be linearly proportional to the droplet radius and controlled by vapour diffusion as given by [6]:

$$I = 4\pi RD\left(C_{V,0} - C_{V,\infty}\right), \tag{2}$$

where R is the droplet radius, D is the diffusion coefficient and $C_{V,0}$, $C_{V,\infty}$ are the vapour concentration at equilibrium and at the vicinity and infinite distance from the TL respectively. Upon further experimentation with more pairs of substrates and liquids [7], a relation between evaporation rate and wetting properties of the liquid and the surface in question was found. Birdi et al. [7] reported that for wetting liquids with initial contact angles $\theta < 90°$, the evaporation rate remains linear whereas it became non-linear for non-wetting liquids with higher initial contact angles $\theta < 90°$. Although, vapour diffusion model is the theory most widely used to describe the evaporation of sessile droplets, another model which accounts for energy transfer phenomena has also been proposed [8,9]. However, we believe this model to be outside the scope of the present contribution, as most of the key concepts essential to the understanding of the main issue here were developed from the diffusion model. Still, the applicability of this new model merits investigation in the future.

Wetting or contact angle hysteresis is a phenomenon almost always present in cases where the evaporation of a sessile droplet deviates from ideal behaviour. Solid surfaces are seldom truly homogeneous and defects may be either geometrical [10–12] or chemical [13–15]. These defects, in turn, lead to TL pinning, and therefore the actual contact line of the system in question is rather difficult to determine. However, it is reasonable to assume that the actual contact angle, θ, lies somewhere in the range $\theta_a > \theta > \theta_y$, θ_a and θ_y being the advancing and

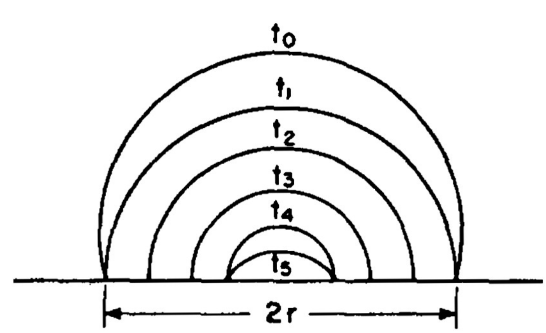

Fig. 2. Evaporation stages of a pure water drop resting on a smooth, flat surface. Image taken from [4].