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Experimental studies on the detachment of multi-walled carbon nanotubes by a mobile liquid interface

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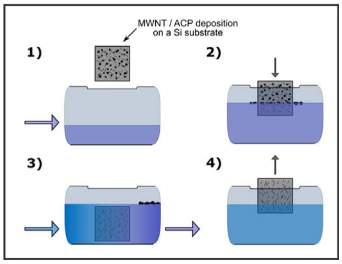
GRAPHICAL ABSTRACT



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ABSTRACT

Retention and detachment of colloidal particles from surfaces is often considered only in terms of spontaneous chemical dispersion when the surface is already fully submerged. Nevertheless, interfacial processes, where the particles are caught on a mobile liquid contact line by capillary effects are ubiquitous. Theoretical description of such interfacial processes exist for spherical microcolloids, while for anisotropic shapes the literature is limited. Arc-discharge synthesized multiwalled carbon nanotube (MWNT) material contains besides the very anisotropic tubes also irregular amorphous carbon particles (ACP) that both are strongly hydrophobic. As a water–air–solid contact line is swept over a deposition of MWNT material on a hydrophilic substrate, it causes selective detachment of the spherical ACPs over the one dimensional MWNTs. In this work we investigate the detachment process and the balance between the surface tension force and adhesive forces. Our results show that on hydrophilic substrates the surface tension force of the liquid interface dominates over adhesion, sweeping away most of the material. However, clean MWNTs oriented perpendicular to the contact line are able to resist detachment. On the other hand, on hydrophobic surfaces adhesive forces dominate, possibly via the hydrophobic interaction. We discuss these results with conventional models of capillarity and adhesion, including the van der Waals force and the electrostatic double layer interaction. However, a fully satisfactory analysis will require e.g. computational modelling of the problem.

1. Introduction

The detachment of nano- and microscale particles from solid surfaces to liquids is an intricate phenomenon when it occurs at the liquid–air–solid contact line [1,2], a.k.a. the wetting line. In certain conditions, the passing of the contact line over the solid surface may

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result in significant removal of particles by the surface tension of the liquid interface, i.e. capillary effects, rather than detaching when fully immersed in the liquid (surface-to-bulk liquid scenario). This phenomenon has been relevant in a few of the applied sciences. Examples are particle separation in mining industries [3], particle transport and trapping in environmental sciences [1], and in the cleaning processes of the microelectronics industry [4–6]. These conventional areas of technology are being complemented by the emerging field of nanotechnology, which brings forward new nanoscale particles whose interaction with capillary forces are an important topic as well [7,8].

The topic is also important as a complex scientific problem, in which the capillary forces, primarily influenced by the wetting of the particles, compete with particle-substrate adhesive forces. Fundamental studies of the problem have been few, since progress on the experimental side has largely been dependent on technical development in experimental nanoscience. Carbon nanotubes (CNT) offer in principle a magnificent test bed for experimental studies in this field, as they can be inert or functionalized, long or short, flexible or rigid. A few experimental works have been reported that involve in some way CNTs interacting with a liquid contact line [8–10], but in all of these the main goal has been something else than research on the issue of CNT interaction with the liquid interface.

In practice, synthesis and processing conditions impose severe limits on the kinds of experiments that currently are feasible, but future progress should widen these limits. Arc-discharge synthesized multiwalled carbon nanotube (MWNT) material has tubes of high quality [11], but also plenty of synthesis-born carbon debris, which consists of nano- and microscale amorphous carbon particles (ACP). In previous work, we have reported on the detachment of MWNTs and debris particles from spin coated depositions by surface tension forces at the propagating contact line of water [12]. Very interestingly, the detachment process, illustrated schematically in Fig. 1, was found to be selective between the MWNTs and the debris particles, tending to leave the former on the surface. This selectivity has been applied for on-chip purification of arc-discharge MWNT material [13], which is demonstrated in the inset of Fig. 1, that shows on a MWNT deposition an optical image of the boundary between purified and untreated regions.

Apart from our work, the detachment of CNTs in general has to our knowledge only been considered in the surface-to-bulk liquid scenario [14,15]. The standard description of detachment in that case involves the DLVO theory of particle adhesion, that combines the ever-present

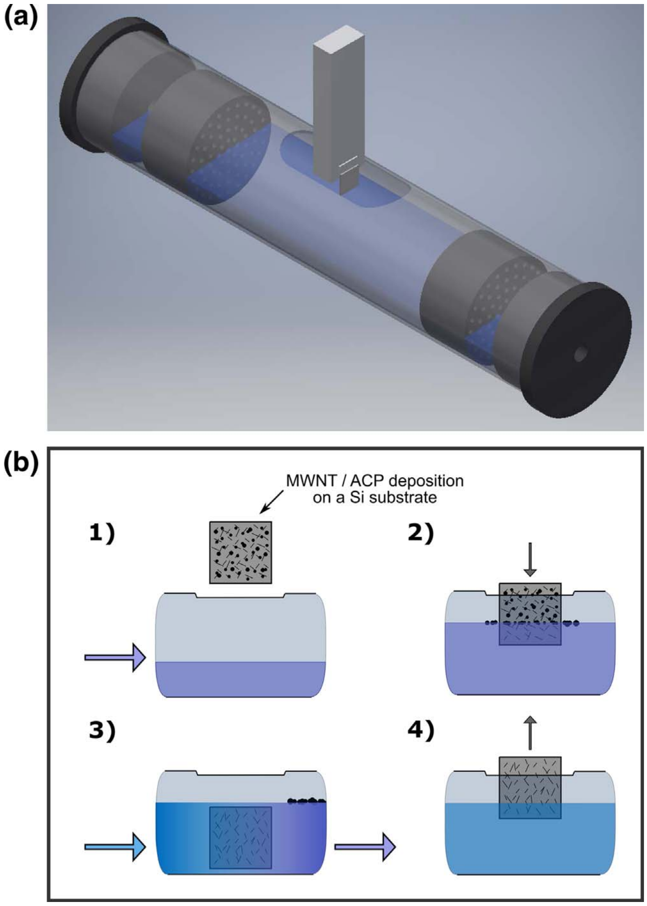

Fig. 2. Scheme of the procedure to sweep a water–air–solid interfacial contact line over a CNT deposit on a Si chip, illustrated in Fig. 1. (a) The flow chamber utilized in the experiments, with the Si chip and its support in the center. The left-hand end has an inlet that connects to separate reservoirs for immersion and rinsing liquids, while the outlet is at the right-hand end. (b) The immersion sequence: (1) filling the chamber with liquid; (2) the Si chip is immersed vertically; (3) with the chip fully submerged, the chamber is rinsed; (4) recovery of the sample.

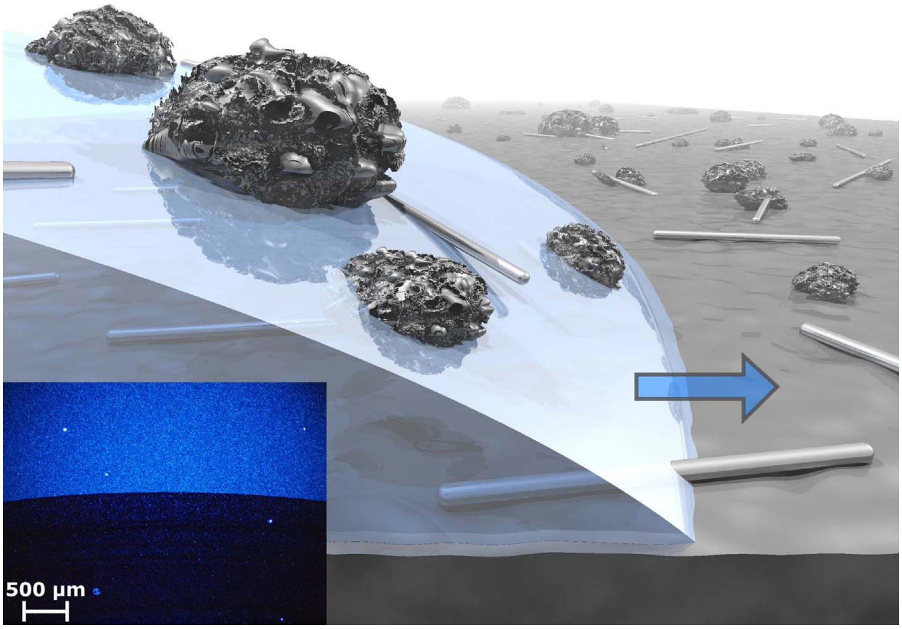

Fig. 1. Schematic illustration of a water interfacial contact line moving over a deposition consisting of clean MWNTs and ACPs (amorphous carbon particles) as well as MWNTs with ACPs solidly attached. The debris particles are captured by the surface tension and are suspended at the liquid surface, while some clean MWNTs are retained on the surface. Inset: dark-field optical micrograph demonstrating the effect on a MWNT deposition. The lower dark region corresponds to depopulation of coarse debris particles up to the dark/bright boundary where the contact line motion halted. The upper region is untouched and thus has debris particles that effectively scatter light and so appears bright.