Limits of the Impact of Gravity on Self-Organizing Nanospheres

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To analyze the impact of gravity on the self-organization of nanospheres on substrates, drops of an aqueous suspension containing 60-nm polystyrene nanospheres were evaporated on different biomaterials. By reducing the speed of evaporation and by selecting different substrate positions, the interplay between gravitational force and pattern formation could be studied in detail. Results reveal limits for the gravitational force: for rings formed by nanosuspension droplets with diameters below 1 mm, the effect of normal gravitational force can be neglected.

Impact of Gravity

Rings formed from evaporation of droplets of nanosuspensions have attracted attention because of their relevance in the design of biomimicry patterns on biomaterial surfaces.[1] Similar rings can be found in polar regions, where they are formed by stones reaching the size of walnuts, self-organizing on the soil.[2] In explaining the mechanism of the pattern formation for the rings formed by stones, gravity is obviously an important factor. However, in interpreting the rings formed by nanoparticles, effects of gravity have been, until recently, largely neglected in the published literature. Gravity has been shown to possess a size-discriminative effect that could considerably affect both the formation dynamics and fine structure of ring patterns.[3] Figure 1 demonstrates the impact of gravity, exemplary for two representative rings. The rings were produced by droplets of equal volume of an aqueous suspension based on 60-nm polystyrene nanospheres, evaporating slowly in a closed Petri dish, on the surface of a mirror-polished titanium disk. The ring on the left was formed by a drop placed onto the surface of the disk and allowed to evaporate in the position indicated in the self-explanatory figure. The formation on the right was realized by turning the disk (fixed via double-sided adhesive tape to the bottom of the Petri dish) together with an attached drop, upside down. In this way, the effects of gravitational forces on particle deposition could be directly observed. One major difference that can be related to gravity is the amount of material deposited in the area enclosed by the rings. The difference can be seen more clearly in Figure 2, corresponding to a magnified representation of the situation shown in Figure 1. Interestingly, the organization of nanospheres collected here depended on the ring size, as can be verified by inspection of the central area of the small ring (3) in Figure 3, produced in the "upside-down mode", which was practically free of nanoclay. The large segments (1) and (2) in Figure 3 correspond to a different presentation of the segments contrasted in Figure 2. An analysis of the differences will reveal some characteristic details of the ring formation mechanism currently lacking in the published literature. Figure 4 shows the reproducibility of the phenomenon on a different substrate material. It is instructive to compare the proportions of the perfect ring in Figure 4 to those of the analogous ring in Figure 1: Apparently the material is more densely packed on

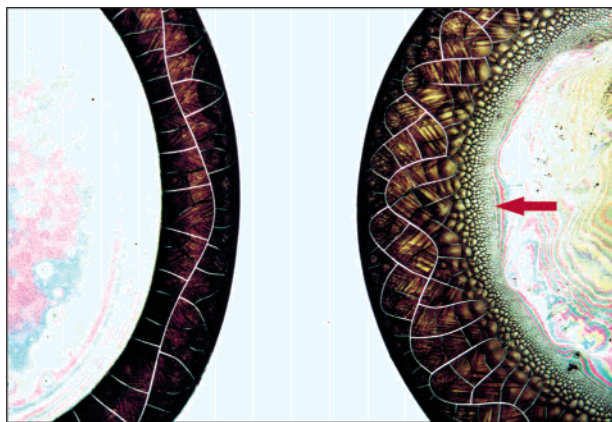* To whom correspondence may be addressed. E-mail: samoan@gmx.net.
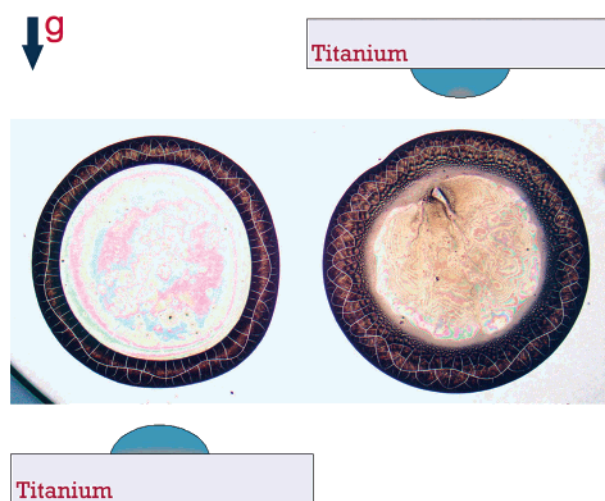
Figure 1. Representative light microscopy photograph of rings formed by slow evaporation of drops of an aqueous suspension containing 60-nm polystyrene nanospheres (Duke Scientific, Palo Alto, CA) on mirror-polished titanium disks (total surface roughness < 4 nm) in closed, 35-mm Petri dishes. Rings were formed as indicated by the related pictures. Ring diameter ≈ 4 mm.

the Petri dish than on the titanium disk. Such variations, probably caused by the interaction between nanoparticles and substrates, can indicate differences in the structure of nanoscopic water layers coating substrates, e.g., height and order, and their associated effect on both attachment and assembly of nanoparticles. The poor ring circularity (Figure 1) seems to indicate some contamination or a nonuniform substrate structure and is probably not primarily related to water layers.

Possible Impact of Water Layers

At room temperature and normal humidity, macroscopic substrates are coated with water layers. Scanning tunneling microscopy investigations have exposed layers exceeding 100 nm on titanium.[4] Nanoparticles seem also to be enveloped by substantial water layers: Measurements of solid nanoscopic combustion aerosols (petrol and diesel) indicated larger particles when the size determination was performed in air by atomic force microscopy compared to values obtained in a vacuum via scanning electron microscopy.[5] It appears reasonable to assume that nanoscopic water layers will have a greater influence on

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Figure 2. Central part of Figure 1 at higher magnification. Both rings show equal peripheral structures. In contrast to the segment on the left, with a sharp separation line between the ring and the enclosed area, the segment on the right reveals less-ordered structures with compact nanoclay bubbles, deposited from the hanging drop in the last phase of the evaporation process.
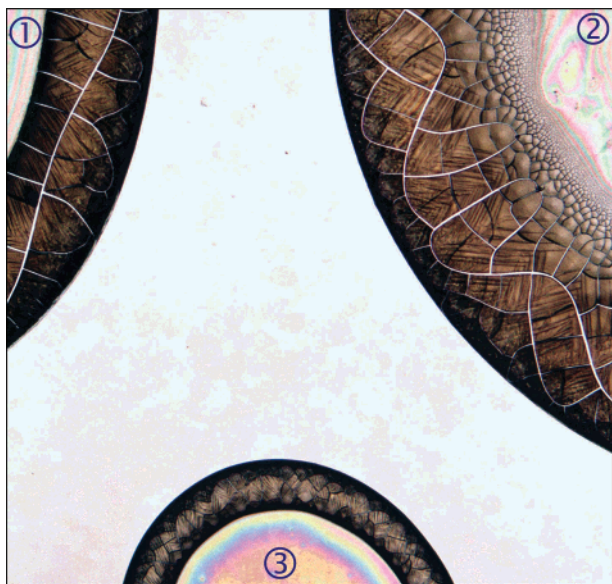
Figure 3. Ring segments (1) and (2) display representative structures of the rings shown in Figure 1, viewed at higher magnification. Segment (3) was produced as (2), in the "upside-down mode", but exhibits both the symmetrical ring-wall architecture and the proportions found in segment (1), produced in the "normal mode". Nanoclay is absent at the inner borderline of (3).
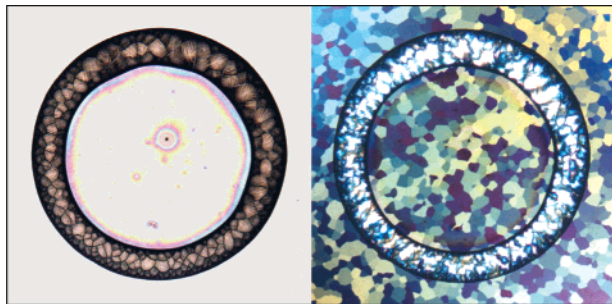

Figure 4. Light microscopy photographs of rings formed by drops of nanosphere suspension, slowly evaporating in covered, 35-mm Petri dishes (on side specified for cell cultures). Rings were formed as indicated by the order in Figure 1. Ring diameter ≈ 5 mm.

the interaction between nanoscale objects, or between nanoscale objects and macroscopic substrates, than they could have on the interaction between macroscopic objects. Moreover, water layers could be ordered,[6] presumably transferring the substrate's

molecular order to anything approaching it. This intuitive picture seems to be constructive for the theoretical modeling and the prediction of the behavior of biosystems contacting substrates. In particular, biomolecules and cells landing on a biomaterial surface in an aqueous milieu will probably first sense the presence of an organized layer of low mobility water molecules masking the surface. Prior to the establishment of an intimate contact (transient or durable) between a cell and a biomaterial, information on the nature of the biomaterial is transferred to the cell receptors in the form of viscosity gradients paralleling order or disorder as a blueprint of the underlying surface structures. It is believed that the first contact of a cell with a biomaterial surface is a crucial determinant for the cell's future development, in particular regarding durable attachment. Notably, titanium, one of the most prominent biomaterials, is suitable for the fabrication of implants, substituting considerable parts of body hard tissues. And titanium had the thickest water layer from a number of tested materials.[4] Anticipating that an order induced to the water layer by the substrate beneath will persist in an aqueous environment, it may be useful to extend the existing definitions of biocompatibility and arrive at a novel formula which includes, besides the traditional set of parameters surface roughness, toxicity, microstructure, nanostructure, and surface charge, the water layers and their molecular structures. Accurate determination of this structure is a serious challenge to both the theoretical and the experimental side.

Modeling the Effect of Gravity

The majority of the models describing formation of rings from drops of suspensions evaporating on surfaces is restricted to a consideration of the lateral evaporation route, which is the principal one, and is caused by a minimum in the surface tension along the liquid−solid−air contact line.[7−9] The vertical temperature gradient, causing suspended material to ascend from the liquid/solid interface to the evaporation-cooled drop surface, has been excluded from the majority of models accounting for evaporation-induced ring patterns. The gradient decreases with progressive evaporation due to a decreasing drop volume, transiently isolating the liquid/substrate interface from the drop apex. The impact of the vertical temperature gradient on formation of ring patterns has been recently explicity predicted.[1] Competition for space, particularly between dissimilar nanospheres, starts prior to surface contact. During this period, gravitational attraction and van der Waals interaction energies ($W = -AR/6D$, where A is the Hamaker constant, R the radius, and D the distance between particle and surface) are discriminating between different masses and chemically different nanoparticles, respectively. For nanospheres suspended in drops conforming to the position producing the ring on the left in Figure 1, the effect of the gravitational forces will be balanced to some extent by the vertical temperature gradient, causing nanospheres to fluctuate more up and down (parallel to the symmetry axis of the drop) than they would in the case of pure Brownian motion. In this way, the mean dwell time of a nanosphere in a drop (time passing until immobilization of a nanosphere) conforming to the situation on the left in Figure 1, will be in general longer compared to the mean dwell time in the corresponding configuration on the right in Figure 1. The difference is obvious from the parallel orientation of gravitational force to the temperature gradient in the second case, leading to a collection of nanospheres at the bottom of the hanging drop. Collected nanospheres will stay at the bottom until, with progressing evaporation, the nanoclay has reached the substrate level. However, since the carrier medium water

Figure 5. Light microscopy photographs of ring formed by a drop of nanosphere suspension, slowly evaporating in the "hanging mode" on mirror-polished titanium (commercial pure titanium). Left: approximately equal slope profile, inside the ring-wall and at the periphery. No accumulation of nanoclay inside the ring-wall. Right: validation via crossed polarizers (revealing the domain structure of the titanium beneath the nanostructured film enclosed by the ring, and also the crystalline structure of the ring). Ring diameter $\approx$ 1 mm.

continues to evaporate, the dense nanoclay in the middle of the ring has no chance of being incorporated into the ring and can only be swept to the side (arrow at ring margin in Figure 2). The small ring (3) in Figure 3, showing a similar ring−wall architecture as in the segment marked with (1), a magnified representation of the ring on the left in Figure 1, is the key permitting the validation of the model established here, allowing us to explain the structural differences in Figure 1. As mentioned above, the small ring was formed in the "upside-down mode". However, the field enclosed by the small ring shows virtually no nanoclay deposition, as can additionally be verified in Figure 5, showing a similar pattern. The structural discrepancy between the pattern formed by evaporation of the smaller (3) and the larger (2) "upside-down mode" drop in Figure 3 can be explained by assuming that the vertical temperature gradient acting on nanospheres suspended in the drops is reciprocal to the actual drop height. Indeed, from a reduced temperature gradient (now accelerating suspended material parallel to gravity), we could expect a relative prolongation of the mean dwell time of material suspended in the drop, with less attraction to the drop sink than in the case of the corresponding larger drop. Instead of sedimenting to form nanoclay, particles would be gradually integrated into the ring-wall. Integration receives additional support from a reduction of the distance between the circumference line and the symmetry axis of the drop. In drops with a smaller radius, suspended nanospheres will come faster into the range of the lateral force component, attracting material toward the minimal surface tension line at the periphery of the drop.

Conclusions

Small quantities of wetting liquid can dramatically change interaction processes in granular media, as has been demonstrated by analyzing conditions responsible for the stability of sandcastles.[10] Adhesion of water drops to substrates can be controlled by the surface structure (e.g., lotus effect) and by polarity. By understanding these parameters, water-repellent materials could be designed. Attachment of cells to biomaterials is more complicated and determined by several parameters. One key parameter could be the depth and the structure of the water layer present on surfaces at air. Methods permitting visualizing and predicting the interplay between water layers and the physical factors determining deposition of nanoparticles suspended in water onto substrates merit special attention. The selected experiments could provide some useful models, in particular for nanotechnological, biomedical, and biological applications.

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