Nanobubble “Snapshot” on a Polymer Matrix

Ex situ Imaging of Polymer Imprints of Gaseous Nanobubbles

The nanometer size of gaseous nanobubbles formed in liquids and their physical properties impose limitations to the selection of imaging techniques. The prospective ex situ imaging method is developed to utilize imprints, which nanobubbles form on immersed polymer surfaces. Polymer nanopattern represent a “snap-shot” record of the nanobubble existence, which can be imaged ex post by ex situ AFM. Thus, complicated imaging in liquids and nanobubble interaction with the AFM tip can be avoided.

Introduction

The existence of gaseous nanodomains at solid-liquid interface was at first indirectly elucidated by Phil Attard et al. [1] from the existence of unusual long-range (~100 nm) attractive forces between two adjacent hydrophobic plates immersed in water. Attard explained adhesive forces by bridging effects of what he called gaseous „nanobubbles”, adhering to water-immersed solid surfaces. The confirmation of presumed existence of such gaseous nano-objects came in 2001 from Tyrrel and Attard [2] by implementation of in situ AFM tapping technique, which allowed direct imaging of nanobubbles on water-immersed solid surfaces. Even then, however, a part of the scientific community considered nanobubble images as suspicious, possible artefacts, created by atomic force microscopy itself. The suspicion steamed out not only from the fact, that AFM was the only technique allowing nanobubble direct imaging, but also from seeming disobedience of some well-established physical principles, such as Young-Laplace Law stating that gaseous bubbles of nanometer size should burst and dissolve within a fraction of a second due to extremely high internal overpressure. Since then, further proofs supporting the existence of nanobubbles appeared together with attempts to explain their behavior [3], though plausible physical model fitting to all nanobubble properties is still missing.

Besides AFM-based semi-contact imaging, also noncontact, optical imaging techniques are emerging: Nonintrusive optical interference-enhanced reflection microscopy [4] and total internal reflection fluorescence (TIRF) microscopy [5] appear to be promising ways of optical resolution enhancement, though still, they
do not reach the high resolution of AFM.

Noncontact optical imaging represents also a step towards imaging of nanobubbles hovering in bulk. Unlike surface nanobubbles adhering to immersed solid surface, “bulk” nanobubbles freely moving in liquid, are inaccessible for imaging by atomic force microscopy, which requires just nanobubbles fixed on solid support – surface nanobubbles. “Bulk” nanobubbles are subject to Brownian motion, form aggregates and thus so far only indirect techniques like dynamic light scattering (DLS) are utilized for detection of nanobubbles in bulk.

On the other hand, AFM allows examination of nanobubble nanomechanical properties [6] which can be utilized for distinguishing nanobubbles from solid objects imaged as some kind of “material contrast” (fig. 1A, B).

Nanobubble-Assisted Nanopatterning
Interaction of nanobubbles with solid surface was recognized first by Wang, Bhushan et al. [7] who reported on rimmed nanoindents appearing stepwise on a water-immersed polystyrene film during hours-long in situ AFM scanning of locations occupied by surface nanobubbles. We have noticed a similar effect as nanobubble-assisted exfoliation of graphene planes of water-immersed highly ordered pyrolytic graphite (HOPG) [8]. Here, nanobubble interfacial forces were found to serve as cutting and stripping tools which rearranged HOPG basal planes at room temperature to graphene-composed nanoscrolled nanoparticles.

Based on previous findings, we have examined nanobubbles on a polystyrene surface, utilizing a novel ex situ approach with AFM analysis performed ex post - after exposition to nanobubbles and re-emersion from water. Unlike Bhushan’s findings, however, nanoprotrusions instead of nano-rims were formed on the polystyrene surface during short time of nanobubble exposition [9] as shown in figure 2.
Our discovery, that nanoprotrusions represent imprints of nanobubbles previously occupying a corresponding location on the polystyrene surface, led us to the suggestion to utilize nanobubble-assisted nanopatterning for *ex situ, ex post* identification of the nanobubble existence by their exposition on the surface of a polymeric matrix [9]. This technique allows making “snap-shots” of so subtle gaseous nanostructures like surface nano-foams (fig. 3A). The nanobubble imprint in the polymer matrix brings advantage of simple *ex situ* AFM analysis of solid surfaces utilized for gaseous nanobubbles. *Ex situ* imaging avoids a possible side-effect of *in situ* AFM imaging, caused by tip interaction with elastic compressible nanobubble.

Our research was further extended towards nanobubble-assisted nanopatterning of other hydrophobic surfaces differing by material parameters, i.e. besides HOPG and polystyrene also paraffin and polytetrafluorethylene (Teflon) [10]. Nanopatterning proceeds by short (~5 s) mild (~10 kPa) dynamic pressure drop applied on aqueous phase as a consequence of interfacial forces acting at pinned contact line perimeter of expanding nanobubbles (fig. 3B). Tension stress $\sigma = \frac{F_L}{\pi d_{NB} h_{layer}} \sim 10 \text{ MPa}$ induced in a polymer film its squeezing and lifting to form nanoprotrusions. Accordingly, the dimension of nanoprotrusions correlate well with polymer elastic moduli [10].

**Conclusion**
Gaseous nanodomains represent an important interfacial phenomenon, which is expected to influence significantly interfacial and membrane processes. Additionally, it can play the role of a surface nanostructuring tool and can be utilized to form imprints identifying nanobubble positions on a polymeric matrix by *ex situ* imaging.

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**References**


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