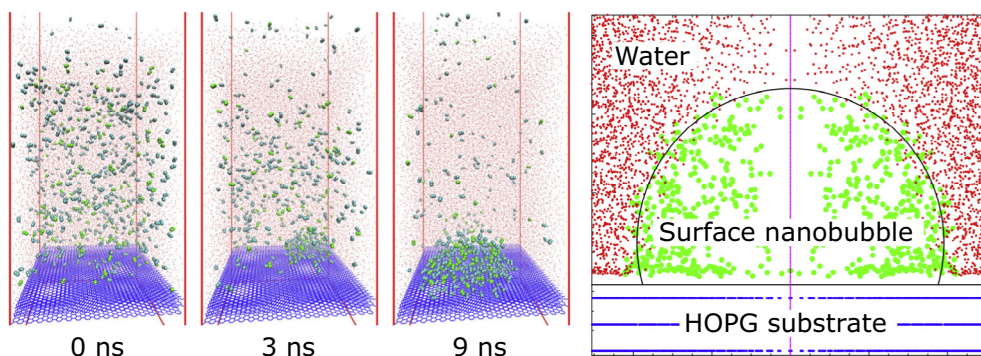


Regular Article

Formation, dissolution and properties of surface nanobubbles

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GRAPHICAL ABSTRACT



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ABSTRACT

Surface nanobubbles are stable gaseous phases in liquids that form on solid substrates. While their existence has been confirmed, there are many open questions related to their formation and dissolution processes along with their structures and properties, which are difficult to investigate experimentally. To address these issues, we carried out molecular dynamics simulations based on atomistic force fields for systems comprised of water, air (N_2 and O_2), and a Highly Oriented Pyrolytic Graphite (HOPG) substrate. Our results provide insights into the formation/dissolution mechanisms of nanobubbles and estimates for their density, contact angle, and surface tension. We found that the formation of nanobubbles is driven by an initial nucleation process of air molecules and the subsequent coalescence of the formed air clusters. The clusters form favorably on the substrate, which provides an enhanced stability to the clusters. In contrast, nanobubbles formed in the bulk either move randomly to the substrate and spread or move to the water–air surface and pop immediately. Moreover, nanobubbles consist of a condensed gaseous phase with a surface tension smaller than that of an equivalent system under atmospheric conditions, and contact angles larger than those in the equivalent nanodroplet case. We anticipate that this study will provide useful insights into the physics of nanobubbles and will stimulate further research in the field by using all-atom simulations.

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1. Introduction

Surface nanobubbles are gaseous phases that can form spontaneously at solid–liquid interfaces [1,2] (Fig. 1). They were observed

in experiments to typically have diameters of 50–100 nm and heights of 10–20 nm. Moreover, they are unexpectedly stable, namely they can exist for days without dissolving as, for example, in the case of a Highly Oriented Pyrolytic Graphite (HOPG) substrate immersed in water [1]. This is only one of the features that have motivated research on nanobubbles in various fields, including the relatively new field of plasmonic bubbles in the context of

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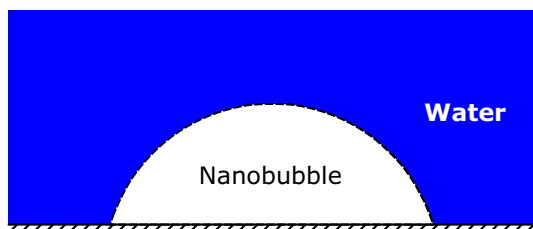


Fig. 1. Schematic illustration of a nanobubble (in white) surrounded by water (in blue) on a solid substrate (bottom).

energy conversion [3,4]. In addition, nanobubbles find important applications in nanomaterial engineering [5], transport in nanofluidics (e.g., autonomous motion of nanoparticles) [6], catalysis and electrolysis [7], cleaning [8], and flotation [9]. In the case of flotation, for example, nanobubbles attached to nanoparticles of certain sizes rise together due to buoyancy, in this way facilitating the separation of nanoparticles or even fine oil nanodroplets.

The existence of nanobubbles was speculated about twenty years ago [10], while the first atomic-force microscopy (AFM) image of nanobubbles was taken in the year 2000 [11,12]. Initially [13], researchers believed that the presence of nanobubbles on the image was an artifact, but the use of additional methods confirmed their existence [14–16]. However, the experimental characterization of these nano-objects still remains a difficult task despite significant efforts over the last decade. For example, the most popular method for studying nanobubbles, AFM [11,12,17], can only provide long time averages, preventing the study of nanobubble formation and dissolution [1]. In another example, surface plasmon resonance spectroscopy is sensitive to the chemical properties of interfaces [18]. As a result, it is difficult to isolate the properties of the nanobubbles from those of the interface. In addition, the control of the nanobubble size in experiments has to be involved, which is crucial for analyzing their size-dependent properties [11,19]. These are only a few of the reasons that many universal properties of nanobubbles still remain unexplored [1]. For example, nanobubbles are known to be stable for days, which contrasts with the expectation of their rapid dissolution within the diffusive time scale (microseconds) due to the high Laplace pressure inside nanobubbles [20]. Some studies suggest that contamination on the substrate may play a role in this stability [21], whereas other studies explain this phenomenon through the balance between gas influx and outflux [22,23], pinning [24–26], and gas oversaturation [27,28]. Recently, molecular dynamics (MD) simulations of a coarse-grained model suggested that nanobubbles dissolve within less than a microsecond, claiming that the experimental nanobubbles are stabilized by a nonequilibrium mechanism [29].

Hence, many fundamental questions are still open; even the proof that nanobubbles actually consist of a gaseous phase is under debate [1]. Clearly, we need systematic approaches to study the formation, dissolution and properties of nanobubbles targeting realistic systems. Understanding these phenomena requires the access to an atomistic/molecular-scale description of the phenomena, the absolute control of system parameters (e.g., thermodynamic conditions), and the ability to follow in detail the time evolution of the formation and dissolution processes of nanobubbles. To address these issues, we employed MD simulations based on atomistic force fields. In particular, we studied the spontaneous formation and dissolution mechanisms of air nanobubbles (N_2 and O_2 molecules) on an HOPG substrate immersed in water. This paper describes simulation results for this realistic situation and provides insights into morphological properties of nanobubbles, such as their size, density, contact angle, and interfacial tension.

2. Materials and methods

2.1. System configuration

The system consisted of an HOPG substrate at the bottom of a rectangular simulation box, air (N_2 and O_2) and water (H_2O) molecules, and a solid layer of silicon atoms on a square lattice at the top of the simulation box to regulate the pressure in the system and to prevent the air molecules from escaping from the simulation box (see Fig. 2). The top silicon layer and the bottom substrate were normal to the z direction and defined the size of the system in this direction, while periodic boundary conditions were applied in the x and y directions. The distance between the top surface and the water molecules was large enough to guarantee that these two components did not interact directly during the simulations. Moreover, the distance between the top surface and the liquid–vapor interface was large enough to capture the air molecules escaping from the liquid phase.

The amount of water used in experiments is beyond the reach of molecular-level simulations, which makes the simulation of the whole system almost impossible due to the high demand in CPU time. A test of different water volumes was performed and a largest possible system was selected to consider most features of the relevant processes with reasonable requirement in CPU time. Therefore, the escape rate of the air molecules was inevitably much higher than in experiments. However, it is believed that this does not affect significantly the understanding of the formation and the properties of nanobubbles [29]. The HOPG substrate is one of the most well-studied cases in the context of nanobubbles in experiments [30–32], hence our choice in this study. Here, the HOPG substrate is an ideal form of synthetic graphite (without contamination or defects) consisting of several layers of carbon atoms in a hexagonal arrangement (see Fig. 2).

2.2. MD simulation method

The study was performed by using MD simulations of atomistic force fields [33–35]. Simulations were carried out in the NVT

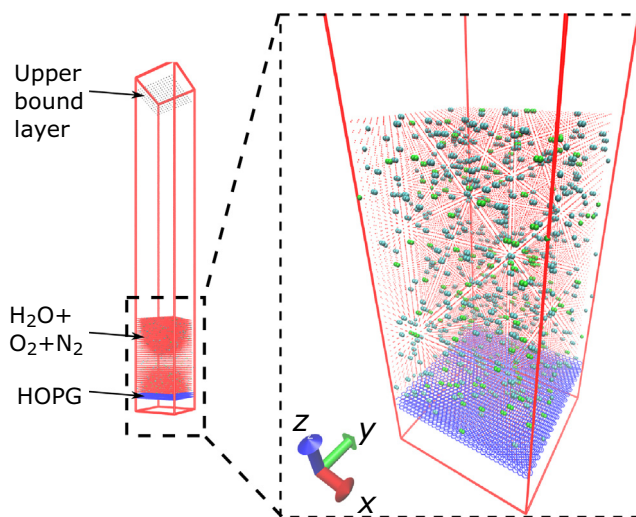


Fig. 2. Perspective view of an initial configuration of the system used in a simulation to investigate the subsequent formation of surface nanobubbles on an HOPG substrate in water. The magnified region highlights the gas molecules (cyan color for N_2 and green color for O_2) dispersed randomly within the aqueous medium (in red). The HOPG substrate (in blue) at the bottom of the simulation box consists of three layers of carbon atoms arranged on a hexagonal lattice. The red straight lines indicate the boundaries of the simulation box with periodic boundary conditions applied in the x and y directions. The top of the simulation box is bound by a silicon wall (in black).

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