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# Generation of charges on a hydrophobic surface as a origin of stability of surface nanobubbles

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A new mechanism of stabilizing surface nanobubbles is proposed, based on the phenomenon of contact electrification — the generation of electrical energy when water moves relative to hydrophobic surfaces. Calculations carried out on the basis of the constructed model show that the phenomenon of contact electrification can slow down the process of diffusive dissolution of surface nanobubbles and increase their lifetime.

**Keywords:** surface nanobubble, contact electrification, hydrophobic surface, double layer.

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The number of published experimental and theoretical studies of surface nanobubbles (SNBs) has increased greatly in recent years, since such bubbles find application in various fields of science and technology. However, it still remains unclear why SNBs have long lifetimes and remain stable for extended periods of time (from several hours to several days) [1–5]. It was noted in [5] that pinning of the triple line (the boundary between liquid, solid, and gas phases) with oversaturation of a solution is a sufficient condition of SNB stability. The reason is fairly simple: the angle measured from the gas phase decreases gradually in the course of dissolution, and curvature radius $R$ increases accordingly (it is assumed that the interface between liquid and gas phases is spherical), reducing the Laplace pressure on gas. Since the SNB lifetime is proportional to this radius squared ($R^2$) [6], the end result is stabilization.

However, an SNB may be stable even without the triple line pinning [4]. It was demonstrated in [2,3] that a so-called wetting ridge emerges on the triple line if the substrate is soft (deformable) and has viscoelastic properties. This ridge absorbs mechanical energy, raises the dynamic contact angle (relative to the equilibrium value), and stabilizes an SNB against diffusion dissolution.

However, SNBs remain stable on both soft and hard hydrophobic surfaces. In the present study, a new physical mechanism of this phenomenon is proposed.

It is known that energy is generated in the course of motion of a water droplet along a tilted hard planar substrate coated with a polymer film: the droplet and the surface acquire opposite charges, thus converting mechanical energy into electrical one. This effect of contact electrification (CE) has been studied extensively (see [7–12] and references therein). According to the data from [12], $OH^-$ groups are transferred from a solution to a polymer surface at $pH > pH_{zch}$ ($pH_{zch}$ is the water acidity corresponding to the point of zero surface charge); water thus acquires a positive charge, and the polymer substrate becomes negatively charged. It is said that water is a Lewis base and the polymer material is a Lewis acid. At $pH < pH_{zch}$, $H^+$ groups leave water, which becomes negatively charged (Lewis acid); the polymer substrate then acquires a positive charge (Lewis base). According to the data reported in [10], CE is the most efficient for deionized water, and the addition of an electrolyte leads to a significant reduction in the amount of generated charge. It is known that CE is also observed at the interface between bulk nanobubbles in an aqueous solution [13]. Naturally, a double layer (DL) should also exist at the interface between an SNB and water. At $pH > pH_{zch}$, an SNB may be regarded as a hydrophobic surface that acquires a negative charge on contact with water.

Let us examine an SNB with base radius $r$ on a smooth hydrophobic surface (Fig. 1). The electrostatic energy of the substrate−aqueous solution DL increases in the process of dissolution, while the energy of the SNB−aqueous solution DL decreases. In the former case, CE interferes with the diffusion SNB dissolution; in the latter case, it contributes to dissolution. Let $\sigma_s$ be the density of the substrate surface charge at the interface with water. The DL thickness in a weak aqueous solution is approximately equal to the Debye length:

$$L_D = \sqrt{\frac{\varepsilon\varepsilon_0 k_B T}{2cN_A e^2}}, \qquad (1)$$

where $e$ is the elementary charge; $k_B$ and $N_A$ are the Boltzmann constant and the Avogadro number, respectively; $T$ is absolute temperature; $\varepsilon$ is the permittivity of water; $\varepsilon_0$ is the permittivity of vacuum; and $c$ is the molar concentration of ions [mol/m$^3$] (for simplicity, water is considered to be a symmetrical electrolyte with singly ionized ions).

Electrostatic energy $W_s$ of interaction of separated charges in water and the substrate may be presented in the form of capacitor energy

$$W_s = \frac{q_s^2}{2C}, \tag{2}$$

where $q_s = \sigma_s S$ is the charge per contact area $S$. Since the substrate is planar, the capacitor is also considered to be planar, and DL width $L_\mathrm{D}$ is a close approximation of the distance between plates. $C = \frac{\varepsilon_0 \varepsilon S}{L_\mathrm{D}}$ is the capacitance of the planar capacitor. The base radius of an SNB decreases by $dr$ in the course of its dissolution. The increment of electrical energy per unit length of the interface between three phases is then

$$\frac{1}{2\pi r}\frac{dW_s}{dt} = -\frac{\sigma_s^2 L_\mathrm{D}}{2\varepsilon\varepsilon_0}\frac{dr}{dt}. \tag{3}$$

Thus, the diffusion SNB dissolution and, consequently, a reduction in the thermodynamic Gibbs potential of the SNB–water system (it is assumed that the process proceeds under constant pressure and temperature) are accompanied by an increase in the electrostatic energy of the substrate–water system. The coefficient preceding triple line velocity $(-dr/dt)$

$$F_s = \frac{\sigma_s^2 L_\mathrm{D}}{2\varepsilon\varepsilon_0} \tag{4}$$

may then be regarded as a resistance force (per unit length) that is directed opposite to the triple line motion and interferes with the diffusion SNB dissolution.

Similar reasoning is applied to the SNB–water contact. According to the data from [14], potential drop $\Delta\Phi$ in the DL in the dipole approximation is $\Delta\Phi = D/\varepsilon\varepsilon_0$ (here, $D$ is the dipole moment of unit area). The thickness of the double layer is assumed to be equal to the Debye screening length. Then, $D = \sigma_g L_\mathrm{D}$ ($\sigma_g$ is the density of the SNB surface charge). If we take into account that the SNB–water contact area is $S_g = \frac{2\pi r^2}{1+\cos\theta}$, the following expression is obtained for the electrostatic energy of the double layer at the water–SNB interface: $W_g = \frac{\Delta\Phi\sigma_g S_g}{2} = \frac{2\pi r^2 L_\mathrm{D}\sigma_g^2}{2\varepsilon_0\varepsilon(1+\cos\theta)}$. Differentiating $\frac{1}{2\pi r}\frac{dW_g}{dt}$ (it is assumed that dynamic contact angle $\theta$ remains unchanged in the process of SNB dissolution), we find the final expression for the force per unit length:

$$F_g = \frac{\sigma_g^2 L_\mathrm{D}}{\varepsilon\varepsilon_0(1+\cos\theta)}. \tag{5}$$

Force $F_g$ facilitates the diffusion SNB dissolution (Fig. 1).

Let us assume for simplicity that dry and wet substrates have the same surface tension [2,3]. The equilibrium contact angle (calculated using the common Young's formula with no CE; i.e., at $\sigma_s = \sigma_g = 0$) is then a right one: $\theta_0 = 90°$, while the dynamic angle is calculated using the following relation ($\gamma$ is the surface tension of water):

$$\cos\theta = \frac{F_s}{F_g + \gamma}. \tag{6}$$

The results of calculation of dynamic contact angle $\theta$ performed in accordance with formulae (4)–(6) are shown in Figs. 2, 3. The growing charge density $\sigma_s$ on the hydrophobic surface and Debye length $L_\mathrm{D}$ contribute to an increase in resistance force $F_s$, thus reducing contact angle $\theta$ (Fig. 2). In contrast, the growth of surface charge density of an SNB $\sigma_g$ leads to an increase in contact angle $\theta$ and facilitates the diffusion SNB dissolution (Fig. 3).

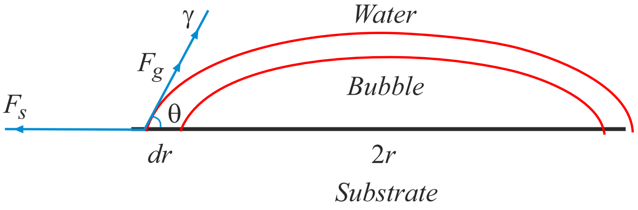

**Figure 1.** Schematic diagram of an SNB dissolving in water. The coefficients of interfacial tension at substrate–gas and substrate–water interfaces are assumed for simplicity to be equal, balance each other out, and are not shown in the figure.

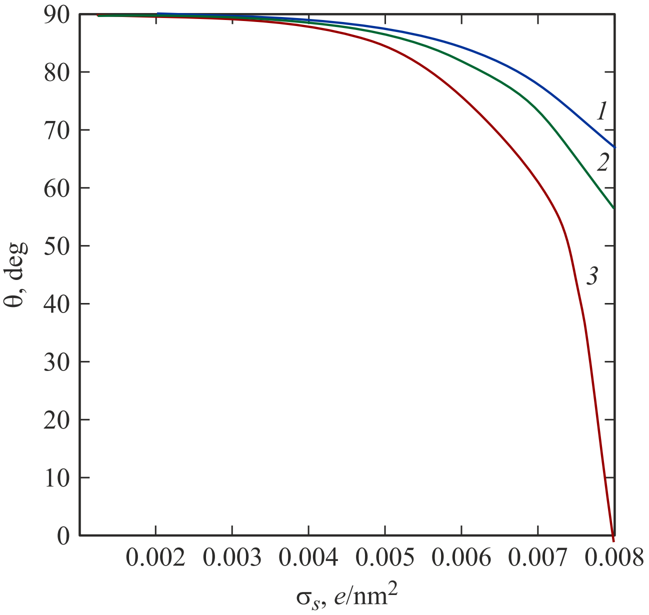

**Figure 2.** Dependence of dynamic contact angle $\theta$ on surface charge density $\sigma_s$ of the hydrophobic substrate at different molar concentrations $c$ of the electrolyte in water. Calculations were performed at room temperature, and the surface charge densities are measured in $e$/nm$^2$ (number of elementary charges per a square nanometer). $\gamma = 0.072\,\mathrm{N/m}$, $\sigma_g = 5\cdot 10^{-3}\,e/\mathrm{nm}^2$, and $\varepsilon = 80$. $c = 3\cdot 10^{-6}$ (*1*), $2\cdot 10^{-6}$ (*2*), and $10^{-6}$ M (*3*).

The obtained calculated data provide an opportunity to estimate the influence of CE on the SNB lifetime. As is known, it was not taken into account in classical study [6]. Let us denote the lifetimes and curvature radii of an SNB without and with account for charges as $\tau_0$, $R_0$ and $\tau$, $R$, respectively. As was already noted, $\tau_0 \propto R_0^2$ and $\tau \propto R^2$. If no great length of time has elapsed since the start of diffusion dissolution and base radius $r$ did not change much,

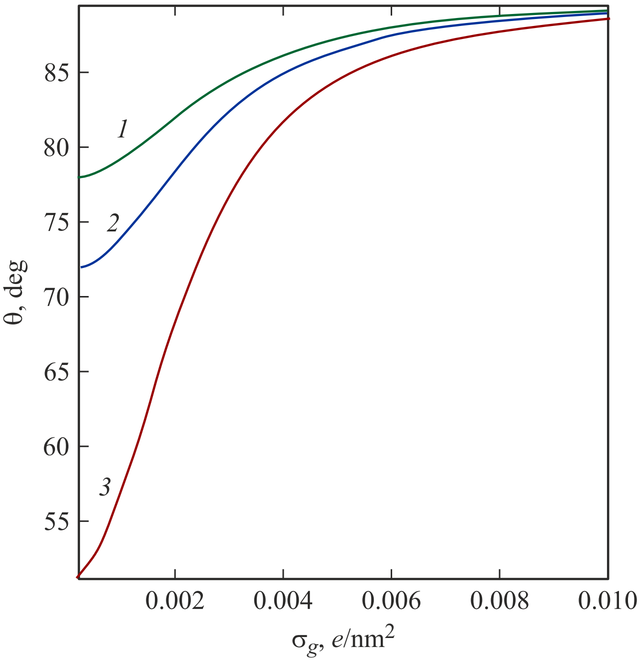

**Figure 3.** Dependence of dynamic contact angle $\theta$ on surface charge density of an SNB $\sigma_g$ at the interface with water at different molar concentrations $c$ of the electrolyte in water. $\sigma_s = 5 \cdot 10^{-3}\, e/\text{nm}^2$. $c = 3 \cdot 10^{-6}$ (*1*), $2 \cdot 10^{-6}$ (*2*), and $10^{-6}$ M (*3*).

condition $\frac{R}{R_0} \approx \frac{\sin\theta_0}{\sin\theta}$ is satisfied, and we obtain

$$\frac{\tau}{\tau_0} \approx \left(\frac{\sin\theta_0}{\sin\theta}\right)^2. \tag{7}$$

According to (7), if the dynamic angle is $\theta = 10°$, the lifetime increases by a factor of 33; at $\theta = 5°$ $\frac{\tau}{\tau_0} \approx 132$.

Thus, the following conclusions may be made.

1. Charges generated on a hydrophobic substrate and an SNB definitely affect the processes of diffusion SNB dissolution. According to the data reported in [7–12], surface charge density $\sigma_s$ varies within the $6.25 \cdot 10^{-5}$–$1.25 \cdot 10^{-3}\, e/\text{nm}^2$ range; however, no data on charge density $\sigma_g$ on an SNB are available. There is reason to believe that these charges are of approximately the same order of magnitude: $\sigma_g \approx \sigma_s$. Expressions (6), (7) obtained in the present study allow one to calculate contact angle $\theta$ and lifetime $\tau$. The results of calculation of $\theta$ are presented in Figs. 2, 3.

2. If charge density $\sigma_s$ is so low that inequality $F_s \ll \gamma$ is satisfied for the substrate resistance force, it follows from (6) that contact electrification cannot prevent the diffusion SNB dissolution.

## Conflict of interest

The author declares that he has no conflict of interest.

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