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Effect of energy dissipation on a viscoelastic substrate on the dissolution of surface nanobubbles

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Based on the analogy between the process of spreading a liquid droplet on a hydrophobic surface and the diffusion dissolution of surface nanobubbles (SNB), the shape of the wetting ridge, deformed by capillary forces of the substrate surface area adjacent to the contact line of the three phases, is calculated within the framework of linear elasticity theory. It is shown that the energy dissipation in viscoelastic substrates on the wetting ridge can cause the pinning of the triple line and the termination of the diffusion dissolution of the SNB.

Keywords: surface nanobubble, pinning, viscoelasticity.

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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 technological processes. SNBs play a prominent part in flotation, water purification and cleaning of contaminated surfaces, enhancement of slippage in microfluidic devices, inhibition of metal corrosion, transport of gases to membranes and cells, etc. [1].

Although their application range is rather wide, it still remain unclear why the lifetime of SNBs is so long (from several hours to several days). It was demonstrated in [2] that pinning of the contact line of three phases and oversaturation are sufficient conditions for SNB stability against diffusion dissolution. Molecular dynamics simulations performed in [3] suggested that the formation of surface nanobubbles on a „soft“ deformable (with a low shear modulus) substrate may provide the desired contact line pinning (the authors called this the self-pinning effect). The results of thermodynamic analysis in [4] revealed that the free energy has a local minimum, which corresponds to a stable state of the system, in the case of SNB formation on „soft“ substrates under self-pinning conditions.

Drawing on the wealth of published experimental and theoretical research into wetting (see [5–8] and references therein), we demonstrate in the present study that the lifetime of SNBs on a „soft“ viscoelastic substrate should be longer than the one corresponding to hard substrates.

The „classical“formula [9] for the lifetime of nanobubbles is

$$\tau = \frac{KR^2(0)}{3R_g TD}. \qquad (1)$$

Here, D is the coefficient of diffusion of gas molecules in water, K is the Henry's constant, T is absolute temperature, R_g is the universal gas constant, and $R(0)$ is the initial bubble radius. If pinning is lacking, the Young's formula holds true at the interface of three phases (gas, liquid, solid), which is also called the triple line. In the process of dissolution, this interface moves with a certain velocity at a constant equilibrium contact angle θ_{eq} (measured from the side of liquid). Formula (1) provides an estimate of the SNB lifetime that is several orders of magnitude lower than the actual value (for example, τ calculated using (1) for $R(0) = 100\,\text{nm}$ is on the order of a fraction of a millisecond).

Two factors ensure SNB stability [2].

(1) An aqueous solution is oversaturated with air (the authors examined air SNBs in water in contact with the atmosphere, although this theory may be applied to other gases and solvents); in other words, inequality $c_0 > c_s$ (c_s is the solubility of air in water (expressed in molar concentrations) that is related to atmospheric pressure p_a through the Henry's constant: $c_s = \frac{p_a}{K}$, while c_0 is the molar concentration of air in water away from an SNB) holds. This condition implies that, on the one hand, a substrate should not be immersed too deep into water (the hydrostatic pressure is negligible) and, on the other hand, the immersion depth should not be too shallow (the amount of water is sufficient for air not to diffuse into the atmosphere while an SNB is present).

(2) The triple line is pinned (stationary). The latter condition is very important. It follows from this condition that an obtuse contact angle (measured from the side of the liquid phase) increases in the process of dissolution; accordingly, curvature radius R grows, while the Laplace pressure decreases. In accordance with the Henry's law, a reduction in the gas pressure inside an SNB leads to a reduction in concentration $c(R)$ of dissolved gas at the water–SNB interface and to a corresponding moderation of the rate of diffusion dissolution. The process of dissolution stops when $c(R)$ becomes lower than c_0.

In the present study, we examine the influence of the triple-line velocity on the effects of energy dissipation on a

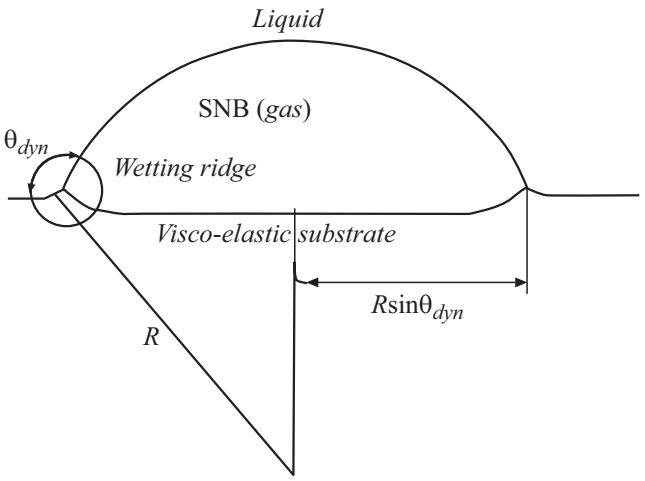

Figure 1. Schematic diagram of an SNB on a viscoelastic substrate. The substrate surface below the SNB bends under gas pressure, which is approximately equal to the Laplace pressure. An enlarged view of the wetting ridge (encircled) is presented in Fig. 2.

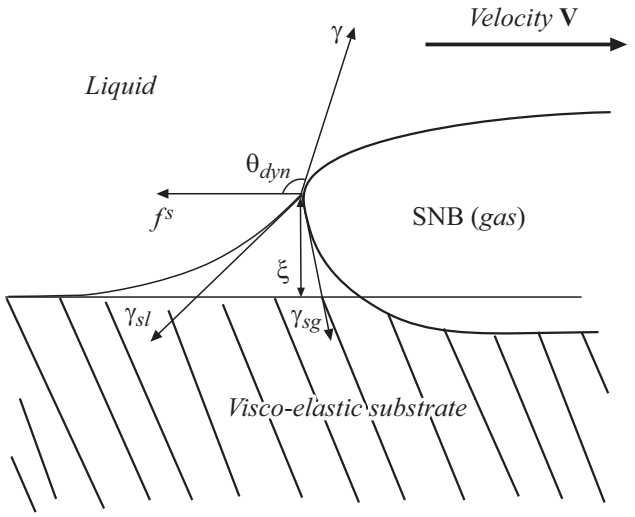

Figure 2. SNB on a „soft“ substrate. ξ — Wetting ridge height.

viscoelastic substrate. As is known, a so-called wetting ridge (Figs. 1 and 2), which absorbs mechanical energy, forms in the process of wetting (i.e., when a triple line moves with a certain velocity V along a „soft“ (deformable) viscoelastic surface). Its height is roughly equal to

$$\xi \approx \frac{\gamma}{\mu_0} \sin\theta_{dyn}.$$

Here, γ is the liquid–gas interfacial tension coefficient, μ_0 is the static shear modulus of the substrate material, and θ_{dyn} is the dynamic contact angle. According to [4–8], a substrate is „soft“ and inhibits the process of wetting if $\mu_0 \leqslant 10^4$ Pa. Having introduced viscoelastic force (per unit length of a triple line) f^s, one may write the condition of dynamic equilibrium for forces acting on an element of a triple line (when no external forces are present) in vector form

$$\mathbf{f}^s + \gamma + \gamma_{sl} + \gamma_{sg} = 0. \tag{2}$$

Here, γ_{sl} and γ_{sg} are the substrate–liquid and substrate–gas interfacial tension coefficients, respectively. Following [4–6], we assume for calculational simplicity that

$$\gamma_{sl} = \gamma_{sg} \equiv \gamma_s. \tag{3}$$

If condition (3) is satisfied, the following inequality holds:

$$\theta_{dyn} > \theta_{eq} = 90^\circ. \tag{4}$$

A phase difference between alternating shear stress with cyclic frequency ω and alternating strain emerges in viscoelastic materials. Consequently, shear modulus $\mu(\omega)$ of the material becomes complex:

$$\mu(\omega) = G_1(\omega) + iG_2(\omega), \tag{5}$$

where imaginary part $G_2(\omega)$ governs the energy dissipation. The following model of viscoelasticity was used in [5,6,8]:

$$\mu(\omega) = \mu_0\left[1 + (i\omega\tau)^m\right], \tag{6}$$

where τ and μ_0 are positive parameters characterizing the studied material. In the present case, frequency ω may be considered to be equal to the ratio of triple-line velocity V to the characteristic length of a wetting ridge γ_s/μ_0:

$$\omega = \frac{V\mu_0}{\gamma_s}. \tag{7}$$

According to(5)−(7), the heat loss modulus in the substrate increases monotonically with velocity:

$$G_2(\omega) \propto V^m. \tag{8}$$

The substrate thickness is usually much greater than characteristic length γ_s/μ_0 of a wetting ridge. Theory [5,6,8] then yields the following result:

$$\frac{\cos\theta_{eq} - \cos\theta_{dyn}}{\sin^2\theta_{dyn}} = aV^m, \tag{9}$$

where

$$a = \frac{\gamma}{\gamma_s}\left(\frac{2\tau\mu_0}{\gamma_s}\right)^m \frac{m}{\cos(m\pi/2)}. \tag{10}$$

Let us denote the initial radius of the SNB base as r. Since SNB curvature radius R in the non-equilibrium state (when it has just begun moving) and initial (equilibrium) SNB curvature radius $R(0)$ are given by (we assume that the spherical surface shape outside of the wetting ridge region is retained)

$$R = \frac{r}{\sin\theta_{dyn}}, \qquad R(0) = \frac{r}{\sin\theta_{eq}}, \tag{11}$$

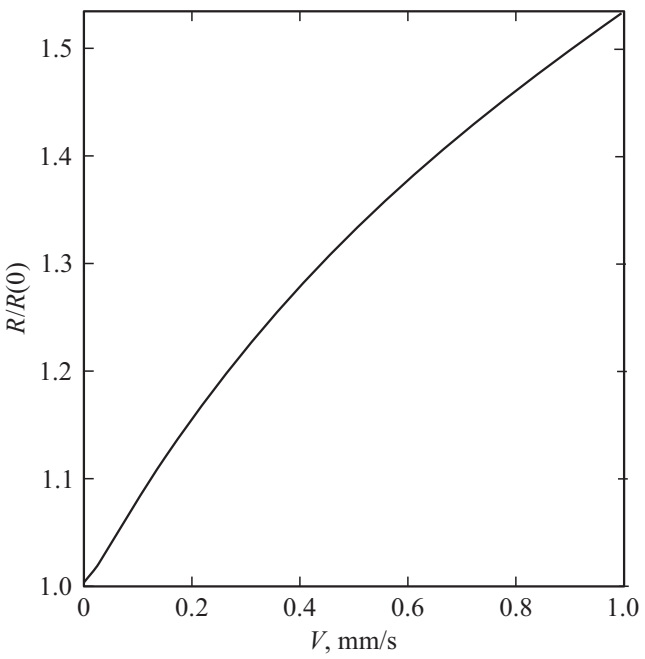

Figure 3. Dependence of ratio $R/R(0)$ of dynamic and initial (equilibrium) SNB curvature radii on triple-line velocity V. The calculation parameters correspond to those for soft viscoelastic silicon [5]: $\mu_0 = 1085\,\text{Pa}$, $\tau = 15.4\,\text{ms}$, $\gamma = 0.072\,\text{N}\cdot\text{m}^{-1}$, $\gamma_{sl} = \gamma_{sg} \equiv \gamma_s = 0.04\,\text{N}\cdot\text{m}^{-1}$, $\theta_{eq} = 90^\circ$.

Eqs. (4), (9)–(11) yield the following:

$$\frac{R}{R(0)} = \frac{1}{\sqrt{1 - \left(\frac{\sqrt{1+4a^2V^{2m}}-1}{2aV^m}\right)^2}}. \qquad (12)$$

The process of diffusion dissolution of an SNB is initiated immediately after its formation, and the triple line starts moving with a certain velocity V. Since the non-equilibrium curvature radius is greater than the equilibrium one ($R > R(0)$, see Fig. 3), the Laplace pressure decreases from its initial value, thus slowing down the dissolution process. Therefore, owing to dissipation, the rate of SNB dissolution on „soft“ viscoelastic substrates is significantly lower than the one corresponding to hard substrates. The issue of whether a viscoelastic substrate, as was argued in [3,4], provides pinning remains open; additional studies are needed to resolve it.

Note that the stabilizing effect of viscoelastic force f^s on SNBs is similar to the influence of negative linear tension [10].

Conflict of interest

The author declares that he has no conflict of interest.

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