Dynamics of bubbles in a lipid monolayer

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A dynamic analysis of the growth of a gas bubble system in a lipid monolayer is presented. The bubbles are separated by thin liquid films. The two-dimensional bubble pattern has, independently of the initial gas phase covering the surface, two different regimes of growth with time. Using simple arguments, we find a differential equation which links the radius of the bubble with the width of the liquid film. According to the mechanism of thinning this film, the model predicts two different power laws for the areal growth with time. If drainage is due to gravity, the power-growth exponent is $\alpha=\frac{1}{2}$ (the experimental value is $\alpha_{\text{expt}}=0.59\pm0.11$). When the film reaches the equilibrium thickness before rupture, the theoretical exponent $\alpha=1$ is in agreement with the experiment.

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INTRODUCTION

Here we present an explanation of a recent experimental study of the evolution of gas bubbles in a lipid monolayer [1]. In a plane interface of an argon-water system, after spreading a monolayer on it, the formation of gas bubbles in the liquid background was observed. The mean bubble size grows in time. When the initial gas coverage is 75%, the strongly packed gas bubbles are separated only by a thin liquid lamella. But if the initial coverage of bubbles is only 40%, the liquid separation between bubbles is of the order of their size. At the beginning, for both coverages, the mean area grows as a function of time, as in the case of soap froths [2], with a power law $\langle a \rangle \cong t^{\alpha}$ and an exponent $\alpha=0.59\pm0.11$. The bigger the bubbles the faster they evolve. The growth exponent α changes from 0.59 ± 0.11 to 1.0. Below we propose a model to explain these two different time behaviors.

THE LAWS OF BUBBLE GROWTH WITH TIME

Let us consider a two-dimensional bubble pattern in the liquid-gas region. The shapes of the bubbles change with time; the pressure in small bubbles is higher than in bigger ones. Smaller bubbles can disappear by dissolution in the system. The monolayer in contact with water will tend to settle at the free surface with the hydrophobic tail in contact with argon (gas) and the hydrophilic polar head in contact with water. The gas inside the bubbles is interchanged with the two bulk phases (argon and water) and also with the other bubbles via the liquid lamallae. The pressure in the two bulk phases remains nearly constant. The gas inside the bubbles will be first absorbed at the inner interface and then by diffusion through the liquid lamallae [3], will reach the upper argon-gas phase. A small part of gas, can by dissolution, reach larger bubbles or the water phase. The number of gas moles N per unit time adsorbed first and passing through the upper film later is proportional to the area of the film and to the difference in concentration Δc (number of moles per cm^{-3}) between the gas the the lamellae,

$$\frac{dN}{dt}=k4\pi r^2\Delta c \ , \tag{1}$$

where k is the permeability constant and r is the bubble's radius. If the gas bubble behaves as an ideal gas [$P(\frac{4}{3})r^3=NRT$, P being the pressure], the following relation holds:

$$\frac{dN}{dt}=\frac{4\pi r^2 P}{RT}\frac{dr}{dt} \ . \tag{2}$$

The change in the number of moles per unit volume in the lamellae is related to the excess pressure P_e on the lamellae surface by

$$\Delta c=\frac{P_e}{RT}=\frac{4\sigma}{rRT} \ , \tag{3}$$

σ is the surface tension. By substituting Eqs. (2) and (3) into (1) we obtain

$$Prdr=4k\sigma dt \ . \tag{4}$$

This equation, valid for any bubble of the system, is also valid for contiguous bubbles; then we have

$$rdr\cong 4k\frac{d\sigma}{dP}dt \ . \tag{5}$$

Using thermodynamic arguments, within the theory of film stability [4], it was shown that the film thickness h is simply

$$h=\frac{d\sigma}{dP} \ . \tag{6}$$

After substitution of Eq. (6) into (5) we obtain

$$rdr=4kh(t)dt \ . \tag{7}$$

This differential equation governs the bubble's area growth with time. In general, the thickness of the liquid

film changes with time. If we consider the film to be of such a thickness that the drainage would correspond to the flow of a viscous liquid between parallel plates, then the average velocity would be proportional to the square of the film thickness and finally the thickness will change with time as

$$h = C_1 t^{-1/2} , \tag{8}$$

where C_1 is a constant. In this derivation it was assumed that gravity is the driving force and the velocity is null at the surface of the film [5]. By introducing Eq. (8) into (7), after integrating we have

$$r^2 = r_0^2 + C_2 t^{1/2} , \tag{9}$$

where C_2 is a constant and r_0 corresponds with $t = 0$. As the film continues to drain, there will be a situation, if the film does not rupture spontaneously, where the concentration of gas at the surface remains constant. In such a situation the lamella thickness will be given by [6]

$$h = \frac{4\Gamma^2 RT}{EC} , \tag{10}$$

where E is the Gibbs elasticity of the film, C the bulk concentration of solute in moles/cm^3, and Γ the surface excess concentration of surfactant in moles/cm^2 at the interface. In this situation Eq. (7) becomes

$$r^2 = r_0^2 + C_3 t , \tag{11}$$

where C_3 is a constant. We can see from Eqs. (9) and (11) that the area growth depends strongly on the regime of flow of the lamella film.

CONCLUSIONS

The present dynamic model, for a two-dimensional bubble pattern in a liquid-gas interface, is able to predict two different power laws of the mean-bubble area growth with time. When drainage by gravity [7] is the thinning mechanism of the liquid lamellae, our model predicts a power exponent $\alpha = \frac{1}{2}$ while the experimental value is $\alpha_{\text{expt}} = 0.59 \pm 0.11$ [2]. As the bubbles approach each other along their centers, the lamellae surfaces deform and get thinner due to the drainage of the fluid by gravity. Long-range, both attractive and repulsive, forces and anomalous viscosity start to play an important role. Also when three or more gas bubbles meet, the curved lamellae called plateau border cause drainage because of the differences in the lamellae curvature [6,7]. In this situation the drainage process could end in the rupture of the film or could reach an equilibrium thickness [8,9]. If the film gets an equilibrium thickness, the area of the bubbles will grow linearly with time as is predicted by Eq. (11).

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